Introduction to Fats and Oils Technology

Second Edition

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To be a forum for the exchange of ideas, information, and experience among those with a professional interest in the science and technology of fats, oils, and related substances in ways that promote personal excellence and provide high standards of quality.

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Preface

The first edition of Introduction to Fats and Oils Technology, organized from the lectures of a processing short course, was very well received. Since the first edition was introduced, the fats and oils industry has undergone a number of changes and challenges that have prompted the development of new and revised products, technologies, and processing techniques. With the generous inputs from the invited authors, the second edition provides a more complete coverage of the pertinent subjects in fats and oils technology. At the same time, the second edition follows the original objective, i.e., to provide an overview of the fats and oils industry and serve as a starting point for new fats and oils scientists and engineers. It introduces all of the essential components of fats and oils technology, properties, and relevant engineering principals. It starts with the raw material sources and continues through processing, quality management, applications, packaging and delivery to the consumers.

The second edition has been expanded from 19 to 29 chapters and subdivided into five sections, covering raw materials, processing, quality, applications, and new developments. The material covered in the 16 chapters retained from the first edition has been updated to include the advances in technology and practice. Thirteen new chapters that pertain to new areas of fats and oils technology were added to supplement the original material. In the processing section, the hydrogenation chapter was updated to address nutritional issues regarding trans-isomers and saturates. A new chapter covering interesterification was added to the processing section as a result of renewed interest in this processing technology to produce more nutritionally acceptable basestocks and products. In addition, the fractionation chapter was expanded to include all aspects of this processing technology rather than simply the winterization technique. A new chapter covering packaging was also added to this section to discuss this often overlooked product preservation technology. One additional chapter was added to discuss workplace, environmental, food safety, and other regulations that apply to oilseed processors and oil refiners. The quality section was expanded to three chapters instead of only one in the first edition. New chapters on flavor, the most important quality indicator, and process quality were added to supplement the updated quality management chapter. Application chapters covering liquid oils and specialty products were added to the expanded shortening, margarine, emulsifier, and by-product chapters from the first edition. Finally, a completely new section, entitled new developments, was considered necessary to fulfill the objective of the monograph to cover the processing technologies and current practices of the edible fats and oils industry. This section contains two chapters, dealing with genetically engineered and identity-preserved oils and the somewhat controversial subject of strategies for the replacement of fats and oils in food products.

We hope that the objectives of this monograph to provide new professionals or managers with a fresh reference and a thorough overview of the fats and oils industry were achieved. We also hope that this material will serve as a starting point for scientists and engineers to stimulate their efforts in the development of new and improved products and processes.

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Fats and Oils: An Overview

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Introduction

Mankind has been familiar with fats and oils and some of their properties since prehistoric times. For centuries, humans have used fats and oils for food and a variety of other uses. Evidence has been found that early civilizations utilized fats and oils as food, medicine, cosmetics, sources of illumination, paints, lubricants, soaps, and other uses in times that predate the First Dynasty. The physical properties that made one fat or oil product perform better in a specific application were identified long before the knowledge of the chemical nature of the different fats and oils was developed. The use of fats and oils for some foods was probably instinctive; other applications, however, most likely resulted from observations of the properties and behavior of fats and oils under different environmental conditions, i.e., the beginning of fats and oils technology.

Before the beginning of the 19th century, the use of fats and oils was based on empirical knowledge accumulated over many centuries, whereas today's uses stem largely from a knowledge of composition, structure, properties, and reactions of the component fatty acids obtained through the application of scientific research. A thorough understanding of the functions of the chemical and physical properties of the edible fats and oils is a basic key to formulation of food products with the desired performance attributes. Similarly, the chemical and physical properties of the raw materials used for nonfood products have a decided bearing on the composition, performance, and the quality of the product that can be produced from them.

Sources of Fats and Oils

Humans have survived as hunters and gatherers for a majority of their known existence on earth. It was only during the last 10,000 years that they learned to domesticate plants and animals. During this period, the evolution of cultivated plants was shaped to the needs of modern man. Today's agricultural crops are mankind's creation. Humans cannot survive without them, nor can the crops that have been developed survive without their care. The combined largest source of vegetable oils are the seeds of annual plants grown in relatively temperate climates. Most of these annual plants are not only cultivated as a source of oil but are also utilized as protein-rich foods.

A second source of vegetable oil is the oil-bearing trees. Olive, coconut, and palm oils are extracted from the fruit pulp rather than the seed of the fruit. Palm also has seeds, which provide palm kernel oil. All of the oil-bearing tree fruits require a relatively warm climate, i.e., tropical for coconut and palm, and a warm climate for olive trees. Most of the oil-bearing tree fruits and kernels provide the highest oil yields. Oilseeds are annual plants that must be replanted each year, whereas the fruit oils are harvested from trees with long life spans. Olive trees are the most hardy and can become several hundred years old. Coconut trees start to bear fruit after 5–6 y; their life expectancy is as long as 60 y. Palm trees start to bear fruit after 4–5 y and continue for another 20 y.

Edible meat fats are supplied almost entirely by three kinds of domesticated animals, i.e., lard from pigs, tallow from cattle and sheep, and milk fat or butter from cows. These animals are raised in the greatest quantities, where they thrive the best, in temperate climates. Animal husbandry has evolved to the stage that these domestic animals require not only a temperate climate but also intensive agriculture to provide a plentiful supply of foodstuffs to produce the desired quality and quantity.

Vegetable Oil Yields

Fats and oils are renewable resources. The achievements of agriculture and plant cultivation have made it possible to exceed the demand resulting from world population growth. The major vegetable oilseeds and fruits utilized for edible purposes are listed in Table 1.1 with their typical oil contents, yield per acre of land, and major producing areas (1–5). Palm is unparalleled in oil yield. The palm tree yield of 2670–4450 pounds per acre for palm oil also produces 267–445 pounds per acre of palm kernel oil from the same fruit bunch. This yield is almost 10 times the soybean oil yield per acre of land. Most of the vegetable oils from oilseeds are annual crops and the harvest is seasonal; however, palm oil is a perennial crop producing two crops per year. Coconut, also with a high oil content and yield, requires 9–12 mo to mature, but fruit is available each month of the year. Olives mature annually and are the most delicate fruit; extraction must be performed as soon as possible to obtain a quality oil. Olives also have the lowest yield of all the tree oils evaluated and surpass only the oil content of corn oil of all the vegetable oils listed in Table 1.1 To produce one quart of olive oil requires 1300–2000 olives.

Three of the four tree oils have the highest oil contents but soybean, an annual oilseed crop with a low oil content, still provides the largest vegetable oil production in the world. Corn has the lowest oil content but has provided large enough quantities to be the third most utilized vegetable oil in the United States. Canola, an annual oilseed crop developed and grown for its oil composition, has moved from a virtual unknown to second only in oil utilization to soybean oil. Canola seed has the second highest oil content and oil yield per acre of all the annual plants presented in Table 1.1; it is surpassed only by peanut or groundnut oil content and yield.

TABLE 1.1 Vegetable Oils: Oil Content, Yield, and Producing Areas

	Vegetable oils		
	Oil content (%)	Oil yield (lbs/acre)	Producing areas
Annual plants			
Canola	40–45	525–590	Canada, China, India, France, Austria, United Kingdom, Germany, Poland, Denmark, Czechoslovakia
Corn	3.1–5.7	215–390	USA, Mexico, Canada, Japan, China, Brazil, South Africa, Argentina, Russia, Commonwealth of Independent States (CIS), Belgium, France, Italy, Germany, Spain, United Kingdom
Cottonseed	18–20	185–210	China, Russia, USA, India, Pakistan, Commonwealth of Independent States (CIS), Brazil, Egypt, Turkey
Peanut	45–50	1120–1245	China, India, Nigeria, USA, Senegal, South Africa, Argentina
Safflower	30–35	545–635	China, USA, Spain, Portugal
Soybean	18–20	400–450	USA, Brazil, Argentina, China, India, Paraguay, Bolivia
Sunflower	35–45	460–590	Russia, Argentina, Commonwealth of Independent States (CIS), Austria, France, Italy, Germany, Spain, United Kingdom
Trees			
Coconut	65–68	650–870	Philippines, Indonesia, India, Mexico, Sri Lanka, Thailand, Malaysia, Vietnam, Mozambique, Papua New Guinea, Ivory Coast
Olive	15–35	90–260	Spain, Italy, Greece, Tunisia, Turkey, Morocco, Portugal, Syria, Algiers, Yugoslavia, Cyprus, Egypt, Israel, Libya, Jordan, Lebanon, Argentina, Chile, Mexico, Peru, USA, Australia
Palm	45–50	2670–4450	Malaysia, Indonesia, China, Philippines, Pakistan, Mexico, Bangladesh, Colombia, Nigeria, Ivory Coast
Palm kernel	44–53	267–445	Malaysia, Indonesia, China, Philippines, Pakistan, Mexico, Bangladesh, Colombia, Nigeria, Ivory Coast

Availability of Fats and Oils

The availability of fats and oils has a significant effect upon pricing. In the case of vegetable oils, availability depends not only on yield per acre but on the number of acres involved. For example, a hurricane in Malaysia can cause availability to decrease with a corresponding price increase; alternatively, a good soybean crop in the United States, with shrinking world demands, means increased availability, thus depressing the price. Shrinking world demands depend upon many factors, such as the Russian sunflower crop, African peanuts, South American soybean oil, and/or cottonseed oil yields and so forth. This is a one world market in which variable inputs affect availability, which in turn controls price structure.

Another important contributor to pricing is that most of the fats and oils production is controlled by factors other than demand. Corn and cottonseed oils are clearly by-products, whereas soybeans are crushed to meet the demands for meal. Sunflower, canola, and peanut plantings are subsidized and controlled by the governments of the major producing countries. Palm kernel oil production is dependent upon palm oil requirements because it is grown in the same fruit bunch. Olive, coconut, palm, and tung oils are all produced from the fruit of trees that have long productive life spans; therefore, their production cannot be adjusted to demand changes from year to year. Animal fats are dependent upon meat consumption, and butter output is subject to milk production. Even the industrial oils are by-products; linseed oil is a by-product of fiber flax, tall oil is a by-product of wood pulp, and part of the castor oil supply is obtained from castor beans harvested from perennial plants. Thus, fats and oils availability is not geared to their demand.

Edible Fats and Oils Utilization in the United States

Climate and availability certainly influenced the eating habits of our ancestors. Inhabitants of central and northern Europe obtained their edible fats from animals, whereas people in southern Europe, Asia, and Africa acquired their edible oils from vegetable sources. The food products developed in these different regions used the available fats and oils products. Consequently, the cuisine of central and northern European countries developed around the use of solid fats such as butter, lard, and tallow for breads, pastries, and many other baked products. Similarly, the diets of inhabitants from the warmer climates were developed around liquid oils for food products such as sauces or dressings (6). These trends appear to continue to be the preference of their descendants.

Immigrants to the United States brought their food preferences with them and introduced them to others from different regions of the world. Fats and oils technology has further increased the varied and rich American diet by the improvement of existing products and development of new food products. The North American eating habits that resulted have made the United States a consumer of almost every available fat and oil but with a different rank order than that of the world production. Table 1.2 (2) compares U.S. fats and oils consumption with world production. The American consumer is offered these fats and oils as a liquid oil, margarine, shortening, or when used as an ingredient in a prepared food product. The fourteen major U.S. fats and oils sources are listed in Table 1.3, which reviews the annual usage of both animal and vegetable oils over the past 47 years (2,7–9).

Per Capita Consumption of Fats and Oils

Fats and oils consumption has been categorized into visible and invisible sources. Visible fats and oils are those isolated from animal tissues, oilseeds, or oil fruits and used for food preparation as shortening, margarine, or salad oil. Invisible fats and oils are consumed as part of meats, poultry, eggs, dairy products, fish, fruits,

TABLE 1.2 World Vegetable and Marine Oil Production and United States Usage Compansion

Rank order	1997 Oils (million pounds) U.S. usage		World production		% U.S. usage
1	Soybean	15159	Soybean	50248	30.17
2	Canola	1290	Palm	37334	0.74
3	Corn	1260	Rapeseed	25630	5 03
4	Coconut	1195	Sunflower	18612	1.16
5	Cottonseed	985	Peanut	9262	2.33
6	Olive	360	Cottonseed	8338	11.81
7	Palm kernel	322	Coconut	7480	15 98
8	Palm	276	Olive	5170	6.96
9	Peanut	216	Palm kernel	4994	6.45
10	Sunflower	215	Fish	1958	0.00
	Total	21278	Total	169026	12.59

or vegetables and account for ~60% of fat consumption. The pounds per person values reported on Table 1.3 are those from visible sources only. Visible fats and oils usage has more than tripled in the United States over the past 47 years, not only as a result of population increases but also from increased consumption. Average per person consumption has increased by almost 50% during this period.

TABLE 1.3 Edible Fats and Oils Usage in the United States

	Year (millions of pounds) 1950	1960	1970	1980	1990	1997
Canola					577	1290
Coconut	129	172	788	1032	897	1195
Corn	223	310	445	673	1149	1260
Cottonseed	1445	1225	891	523	851	985
Olive	79	51	67	58	213	360
Palm		1	182	299	256	276
Palm kernel	26	53	94	nr[a]	362	322
Peanut	103	62	193	112	197	216
Safflower			100		58	73
Soybean	1446	3011	6253	9114	12164	15159
Sunflower				64	200	215
Lard	2050	1889	1645	1023	807	917
Tallow	156	328	518	995	955	1275
Butter oil	1327	1113	1075	1017	1095	1114
Total	6984	8215	12251	14910	19781	24657
Pounds per person	45.9	45.5	52.5	60.3	65.2	68.2

[a] nr, not recorded.

Edible Fats and Oils Usage

The fats and oils usage data on Table 1.3 reflect some distinct trends, including the following: (i) a move away from animal fats to vegetable oils; (ii) replacement of previously established fats and oils with different source oils; (iii) introduction of new vegetable oils; (iv) a rise and fall of some individual source oils; (v) source oil changes reflecting the results of medical studies; and (vi) introduction of new oilseed varieties.

Soybean Oil. Raw material selection by the U.S. edible oil processors has definitely been influenced by availability, technology, nutritional studies, consumer acceptance, religious preference, and economics. All of these considerations helped soybean oil to become the leading edible oil utilized in the U.S., but technology played a very important role. Initially, product developers had a problem identifying a use for soybean oil. It is high in polyunsaturates, which led to its classification as a semidrying oil; however, as a paint oil, it dried slowly and developed "after tack," whereas as an edible oil, it tasted like paint. The use of soybean oil in foods was limited because of a flavor reversion problem that had to be solved before it would be accepted by the food industry (10). During World War II, German edible oil processors developed a formula or process to cure soybean oil reversion; the process included the addition of citric acid to the deodorized oil, which complexed trace prooxidant metals. Upon release of this technology, edible oil processors almost immediately adopted metal deactivators; of these, citric acid remains the most popular chelating agent. Other edible fats and oils can tolerate copper and iron in the parts per million (ppm) range, whereas soybean oil flavor is compromised by as little as 0.5 ppm iron and 0.01 ppm cooper. This discovery promoted the removal of brass valves and the conversion of cold, rolled-steel deodorizers to stainless steel for processing. Another effective precaution was to blanket oils with an inert gas, usually nitrogen, at all critical high-temperature processing steps and with packaging.

At this point in time, investigations still had not identified the cause of the off flavor development with soybean oil, but circumstantial evidence pointed to the 7–8% linolenic fatty acid content. A classic experiment interesterified 9% linolenic fatty acid into cottonseed oil, which typically contains <1% of the $C_{18:3}$ fatty acid. Flavor panels identified this modified product as soybean oil. This result presented the following three alternatives for improving the flavor stability of soybean oil: (i) breed out the linolenic fatty acid, (ii) extract the linolenic fatty acid with fractionation, or (iii) selectively hydrogenate the linolenic fatty acid to a more stable fatty acid. Hydrogenation to reduce the linolenic fatty acid content was chosen as the most practical short-term approach (11). Soybean salad oil with the linolenic fatty acid reduced to 3–4% was introduced into the U.S. market in the late 1950s. This product was lightly hydrogenated and subsequently winterized to remove the hard fractions that developed during hydrogenation. This soybean salad oil was quickly accepted by the retail salad oil consumers and industrially as a component of salad dressings, mayonnaise, margarines, and shortenings (12). In the late 1970s, improvements in soybean oil processing produced a Refined Bleached and Deodorized (RBD) oil that was more acceptable for industrial users and was eventually introduced to the retail market. This RBD soybean oil, promoted as all natural and light, was introduced to the retail market in the late 1980s and rapidly replaced the hydrogenated, winterized, and deodorized salad oil.

Canola Oil. Canola oil has experienced a strong U.S. demand as a result of its low saturated fatty acid content and pricing at a discount to sunflower oil. Canola oil has moved from a virtually unknown vegetable oil to the second most utilized oil in the United States. Initially, the U.S. canola oil requirements were imported, but the consumers favorable response after the name change from low erucic acid rapeseed to canola was approved, has encouraged U.S. plantings to produce a portion of the requirements. Canola oil typically has a higher level of linolenic fatty acid than soybean oil but has not had the flavor stability problems. The relatively high α-tocopherol content of 19 mg/100 g, protection of the linolenic fatty acids by its attachment to the triglyceride in the 2-position, the 37 mg/100 g brassicasterol content, and the remaining trace amounts of erucic fatty acid are all believed to improve the keeping qualities of canola vs. soybean oil in spite of similar to higher linolenic fatty acid levels (13).

Corn Oil. Corn oil is third in vegetable oil volume in the United States despite the fact that a corn kernel contains only 3.1–5.7% oil and is usually priced at a premium compared with soybean oil. Corn oil production is dependent upon the demand for corn sweeteners, starch, meal, and ethanol. It has wide consumer acceptance due primarily to flavor, quality, and a healthy image. Promotion of the polyunsaturated oils for nutritional purposes during the 1950s and 1960s led to an explosion in corn oil acceptance. The distinctive musty flavor and odor have helped corn oil to retain a popular acceptance both for home use and for prepared food products; consumption is mainly as consumer bottled oil, salad dressing preparation, snack frying, and margarine production.

Coconut Oil. In the United States, over two thirds of the coconut oil consumption is for industrial products and one third for food use. Coconut oil is used in food products for its taste, stability, shelf life, and functionality. It has a sharp melting point at 23–26°C with lauric as the major fatty acid. Coconut oil has application as a frying oil, in nondairy products, coffee whiteners, candy centers, compound coatings, margarine, popping popcorn, and as a spray oil for biscuits, crackers, croutons, and breakfast cereals. Due to its high medium-chain triglyceride (MCT) content, coconut oil is used in tailor-made medicinal foods for people who require the energy from fat but cannot absorb the long-chain fatty acids. It is also used in infant formulas for the MCT (C_6–C_{10}) content (4). Coconut oil demand in the United States suffered losses in volume due to a campaign against tropical oils in the late 1980s; it was claimed that its saturated fatty acid content raised serum cholesterol levels. Subsequently, world coconut production decreased 8% in 1995/1996, which increased its cost to users and caused them to substitute with less expensive palm kernel oil.

Cottonseed Oil. Cottonseed oil dominated the U.S. and world vegetable oil markets until just before World War II when soybean oil became the leading vegetable oil source. Thereafter, U.S. domestic usage of cottonseed oil decreased steadily until the mid-1980s when it started to regain market share. Cottonseed oil is stable in the β-prime crystal form and imparts this property to fats and oils blends at levels as low as 5–10% of the composition. The β-prime crystal form is desirable for most solidified products because it promotes plasticity. The renewed popularity of cottonseed oil was most likely at the expense of tallow and palm oil, i.e., both of these oils are also β-prime formers that lost consumer appeal as a result of unfavorable publicity highlighting nutritional concerns with saturated fatty acids and/or cholesterol. The supply of cottonseed in the United States responds primarily to the demand for cotton lint and is heavily influenced by provisions of the U.S. Government cotton program. The cotton acreage planted is determined largely by the USDA on the basis of the expected lint requirements.

Olive Oil. Olive oil has had a fantastic increase in U.S. consumption; usage in 1990 was almost four times that of 1980. U.S. supermarket sales of vegetable oils for all fats and oils categories have declined since 1986, but olive oil sales have almost tripled. This increased usage of olive oil during that decade was due in part to the promotion of the health benefits and the gourmet image. Of the fatty acids in olive oil, 10–12% are saturated, largely palmitic ($C_{16:0}$), and 88–90% are unsaturated, largely oleic ($C_{18:1}$). Olive oil is a very stable oil with a distinctive flavor; it is used widely as a table and cooking oil; however, it is generally too expensive to use in shortening- and margarine-type products.

Palm Kernel Oil. Palm kernel oil is a co-product of palm oil, which is the primary commodity derived from the oil palm. Generally, palm kernel oil production is estimated at 10–12% of palm oil output. Palm kernel oil does not possess the physical or chemical characteristics of palm oil; it is high in lauric fatty acid with a sharp melting point, whereas palm oil contains only trace amounts of lauric fatty acid and has a broad range between its melting and softening point. Like coconut oil, palm kernel oil has a relatively sharp melting point at 24–26°C because the saturated fatty acids that make up ~85% of the composition have a relatively small difference between their melting points, i.e., only ~20°C, whereas palm oil can have a >70°C difference between fatty acid melting points. A sharp melting point is an advantage when formulating food products that are expected to melt quickly in the mouth, e.g., candy coatings, candy centers, icings, and other confections. Palm kernel oil more than tripled its consumption in the United States between 1970 and 1990; some of this volume likely replaced coconut oil usage.

Palm Oil. Palm oil is characterized by its high palmitic fatty acid content ($C_{16:0}$), combined with a rather low level of unsaturated fatty acids to result in an elevated melting point and a flat solid fat index. It has physical characteristics somewhat similar to those of beef tallow or a hydrogenated vegetable oil base stock used for the production of shortenings for baking and frying. For these reasons, palm oil threatened to become a major source oil for U.S. shortenings in the mid-1970s. It grew from a inconsequential level in 1960 to >16% of the total shortening raw material requirement in 1975, primarily at the expense of cottonseed oil and tallow. Unfavorable publicity highlighting nutritional concerns with the effect of saturated fatty acid on atherosclerosis decreased palm oils usage by >50% between 1985 and 1989 to a level that it has maintained since that time.

Peanut Oil. Peanut acreage in the United States has been static to lower since 1965; however, production has increased nearly 1.5 times due to higher yields. Peanut oil has excellent oxidative stability and is considered a premium cooking and frying oil. However, the United States consumes more than half of its peanut crop as whole-nut products, and only small amounts are crushed for oil and meal. In general, peanuts in the United States are crushed only for the following reasons: (i) oversupply, (ii) immature seeds, (iii) less than premium quality, and (iv) aflatoxin contamination. Fortunately, alkali refining and bleaching eliminate aflatoxin from the oil so that it can be used for edible purposes.

Sunflower Oil. Although native to North America, sunflower oil has gained more acceptance in other countries; it ranks fourth in world production but has a rank of 13 in U.S. consumption. Two general varieties of sunflower oil are marketed, i.e., normal or high oleic. The normal sunflower oil variety is rich in linoleic fatty acid, has a high vitamin E activity, and <15% saturated fatty acids, all of which have helped it gain acceptance as a healthy oil. The high-oleic variety has a higher oxidative stability with an even lower saturated fatty acid content, making it attractive to food processors. Sunflower oil exports have accounted for as much as 80% of the entire production, leaving the United States with consumption at <1.0% of the total fats and oils requirement.

Safflower Oil. Most of the regular safflower oil used is purchased because it has the highest level of polyunsaturates available; those who require its particular fatty acid structure are willing to pay a premium over other oils. High-oleic safflower is a mutation that produces an oil in which the normal ratio of 77% linoleic/15% oleic fatty acids is reversed. This change produces an oil that is much more stable than the normal safflower oil because it is monounsaturated instead of polyunsaturated. This safflower variety is used primarily in the production of baby formulas, for special snack frying, and in blends with other oils (14). Safflower oil is a minor oilseed crop; it has maintained about the same planted acreage for the last 10 years to produce oil volumes averaging 48 million pounds per year.

Animal Fats

Aside from butter, animal fat supply is driven by red meat consumption and varies according to the animal population rather than the need that may exist for these products. Availability varies by market price, feed supply, and animal health. Typically, lard and tallow have had a significant price advantage over vegetable oils. Fats and oils demand around the world as well as in the United States has shifted from lard and tallow to vegetable oils, and from butter to margarine. The high saturated fatty acid and cholesterol content has made them lose popularity for use in consumer products. Health concerns over the ingestion of cholesterol and saturated fat (plus religious preferences) have decreased the use of lard and tallow for human foods since the mid-1980s.

Butter Oil. Traditionally, milk fat or butter has always had the highest economic value of any of the milk constituents; this places it at an economic disadvantage to other edible fats and oils products. The actual and potential flavors are among the most important attributes of butter oil. Butter oil opportunities for edible fats and oils processors are limited because most processing would destroy the flavor attributes. As a tablespread, the aim is to retain the mild delicate flavor; however, in baking, cooking, and many processed foods applications, the object is to generate a buttery, caramel-like flavor. Because butter is more expensive than most other fats and oils, its use is restricted to those products in which the distinctive flavor makes a significant contribution.

Tallow. The United Nations Codex Standard for Edible Fats and Oils describes edible tallow as the product obtained by rendering clean, sound, fatty tissues, attendant muscles, and bones of bovine animals and/or sheep in good health at the time of slaughter and fit for human consumption as determined by a competent authority recognized in national legislation (15). In the United States, most tallow is obtained from beef cattle, with a lesser amount from sheep. Tallow, like lard, is essentially ready for food use as is; however, it is deodorized when the distinctive beef flavor is not acceptable. Undeodorized tallow was a preferred frying fat for french fries because of its flavor-enhancing characteristics until the health issues regarding saturated fat and cholesterol practically mandated changes to cholesterol-free vegetable oil products. Nevertheless, edible tallow use in the United States continues to increase slowly.

Lard. The Codex Standards for lard are that it be a fat rendered from fresh, clean, sound fatty tissues from swine in good health at the time of slaughter, and fit for human consumption as determined by a competent authority recognized in national legislation. The tissues do not include bones, detached skin, head skin, ears, tails, organs, windpipes, large blood vessels, scrap fat, skimming, settlings, pressings and the like and are reasonably free from muscle tissues and blood (15). For many generations, lard was the fat of choice for baking because it had sufficient plasticity to cream with sugar and eggs. Originally, vegetable oil shortenings were lard substitutes, developed during supply shortages as low cost alternatives; these eventually exceeded lard's performance capabilities in bakery products. Table 1.2 indicates that edible lard has experienced a steady decline in usage in the United States since 1950.

The decline was related initially to lower product costs for the vegetable shortenings, then to lower costs for tallow-based products, and finally because of nutritional concerns regarding cholesterol and saturated fatty acids.

Industrial Fats and Oils Utilization in the United States

Fats and oils serve a vital function in the United States and world economics for both food and nonfood applications. Natural fats and oils and their derivatives such as fatty acids or fatty alcohols consist of compounds that differ in chain length and saturation and that have industrial application. Vegetable oil and animal fats are utilized to produce nonfood products such as soaps, detergents, paints, varnish, animal feeds, resins, plastics, lubricants, fatty acids, and other products as well as food products. Interestingly, many of the raw materials important for industrial purposes enjoy a special status as by-products of oil and fat processing for food use. Industrial use has accounted for 25–35% of the agriculturally derived fats and oils used in the United States since 1935. Total U.S. fats and oils consumption has varied from 20.3 to 22.1 billion pounds over the 6-y period from 1991 through 1996 with an average of 28.6% of this consumption or 5.7–6.7 billion pounds used for industrial purposes. End use comparisons for these years are presented in Table 1.4 (2,8,16–18).

TABLE 1.4 Industrial Fats and Oils Usage in the United States

Million pounds			Percentage	
Food use	Industrial		Food use	Industrial
		Period		
		1935–1939	67.2	32.8
7236	3883	1950–1959	65.1	34.9
9108	4903	1960–1969	65.0	35.0
11492	5458	1970–1979	67.8	32.2
15245	5533	1980–1989	73.4	26.6
18009	5996	1990–1997	75.0	25.0
		Fats and oils sources[a]		
None	54.5	Castor oil	None	100.0
198.7	592.3	Coconut oil	25.1	74.9
326.3	110.5	Lard	74.7	25.3
None	122.1	Linseed oil	None	100.0
33.6	1852.4[b]	Rapeseed oil	1.8	98.2
11341.6	297.3	Soybean oil	97.4	2.6
None	1109.2	Tall oil	None	100.0
1139.0	3128.1	Tallow	26.7	73.3
None	11.5	Tung oil	None	100.0

[a] Average for 1989–1996.
[b] Estimated.

Some fats and oils can be interchangeable for many industrial applications, which makes the choice of raw material depend upon price and availability. For example, hydrogenated soybean oil fatty acids can be used in place of tallow as a source of stearic fatty acid, the main fatty acid of commerce (9). In other cases, a particular source oil or fat is required for the application, e.g., rapeseed oil for separation of erucic fatty acid for use as an additive to lubricants. Rapeseed is the most available and economical source of erucic fatty acid.

Oleochemicals for industrial use are produced by splitting and further reactions of oils and fats. Some of the oleochemicals can be produced from petroleum; therefore, the agriculturally produced fats and oils must compete with the petrochemicals as raw materials for the organic chemical industry. Manufacture of synthetic fatty acids from petroleum and natural gas has become a large industry worldwide for products that initially required natural fatty acids.

Industrial Fats and Oils

Fats and oils that are important for industrial purposes include both edible and inedible agriculture products. Oils and fats used in nonfood products originate from a variety of sources. Most of the fats and oils used for food preparations have application for industrial use as well; however, some fats and oils are available exclusively for technical uses due to their special compositions. Castor oil, linseed oil, tall oil, and tung oil are of vegetable origin and are produced especially for industrial uses. The major fats and oils used for food and nonfood use are coconut, lard, regular rapeseed oil, soybean oil, and tallow. The ratios of industrial to food use for these fats and oils products are shown in Table 1.4, and the industrial uses for these agricultural raw materials are shown in Table 1.5 (8).

TABLE 1.5 Fats and Oils Industrial Applications in the United States

Industrial usage	Raw material	Soap	Varnish and paint	Animal feed	Resin and plastic	Lubricant	Fatty acid	Other
				(%)				
1.0	Castor oil	10.4[a]	7.2[a]	0.0	2.2	3.4	0.0	78.5
7.4	Coconut oil	18.2	0.7[a]	0.0	0.6	1.1	67.8[a]	11.6[a]
54.6	Tallow	7.5	0.0	68.5	0.0	2.7	19.1	2.2
2.3	Lard	0.0	0.0	0.0	0.0	12.2	0.0	87.8
1.6	Linseed oil	0.0	18.6	0.0	48.1	0.0	1.0[a]	32.3[a]
8.0	Rapeseed oil	0.0	0.0	0.0	0.0	0.0	100.0	0.0
5.1	Soybean oil	0.7[a]	16.5	8.0[a]	39.7	0.0	3.0[a]	32.1
19.6	Tall oil	3.7[a]	13.7[a]	0.0	1.6	0.6	78.9	1.5[a]
0.4	Tung oil	0.0	0.0	0.0	76.8[a]	0.0	0.0	11.0[a]
100.0	Category total	7.8	1.4	40.4	3.4	2.1	31.9	13.0

[a] Estimated.

Coconut Oil. The industrial uses for coconut oil in soap, fatty acid, and other industrial areas far outweigh its food uses; the industrial applications averaged 76.2% of the consumption for 1991 through 1996. The popularity of coconut oil for industrial applications can be traced to the high content of medium-chain fatty acids. Because of the low molecular weight of these fatty acids, coconut oil possess a distinctive combination of a very low degree of unsaturation and a relatively low melting point. In addition, because its unsaturation is low, coconut oil is extremely resistant to oxidation and polymerization. The major uses for coconut or lauric oil fatty acids are as nitrogen derivatives in detergents, in soaps, in the conversion into alcohol, surfactants, textiles, and cosmetics (19).

Inedible Tallow. Inedible tallow, also known as industrial or technical tallow, includes tallow and greases and often contains fats derived mainly from cattle but also from hogs, sheep, and poultry. The distinction between edible and inedible classifications is based on hygienic and regulatory considerations rather than chemical differences. Edible tallow must be derived from clean, sound tissues from animals in good health at the time of slaughter. Further, edible tallow must be produced under hygienic conditions and regulatory supervision. Inedible tallow is traded in various grades in which a minimum melting point, 40°C titer, and maximum color, free fatty acid content, moisture, insoluble, and unsaponifiables are specified rather than origin. An inedible tallow classification is mandatory when the fat is rendered from inedible materials but may also arise from esthetic considerations. Tallow is a preferred fat source for feeds, soaps, and fatty acids because of its ratio of saturated and unsaturated fatty acids, which provides a desirable oxidative stability, solubility, and hardness. Tallow contains high quantities of the fatty acids in demand for industrial applications, i.e., 40–45% saturated palmitic and stearic fatty acids and 40–45% monounsaturated oleic fatty acid. Another reason that tallow is a preferred fat source is its relatively low price and ready availability as a by-product of the meat processing industry.

Lard. Industrial-use lard may also be identified as white or yellow grease. An inedible classification may arise from esthetic considerations, an oversupply of edible product, or the product may have a dark color and/or high free fatty acid content; however, it must have a titer below 40°C. Its principal industrial applications have been in soaps and fatty acids, but lubricants and other applications are identified as the current principal uses by the USDA Economic Research Service.

Rapeseed Oil. Regular rapeseed oil has a high erucic acid content ($C_{22:1}$), which is converted to behenic fatty acid ($C_{22:0}$) with hydrogenation. In the United States, it is used almost entirely for inedible purposes to produce erucic and behenic fatty acids used as lubricant additives and for various other industrial purposes. Food use of rapeseed is limited by the U.S. FDA regulations because oils high in erucic fatty acid have been shown to cause heart muscle lesions followed by other cardiac problems in laboratory animals. Only hydrogenated rapeseed oil is permitted in foods at restricted levels. The major food use is as a peanut butter stabilizer.

Soybean Oil. Originally, soybean oil was used predominately for industrial products in the United States but was converted to predominately a food oil with technological developments. Currently, only 2.5% of U.S. soybean oil consumption is in industrial products. Soybean oil had been regarded as too viscous and reactive to atmospheric oxygen to be used for fuels, cosmetics, lubricants, and chemical additives, but not reactive enough for most paints and coating applications. However, more stringent environmental standards, rising costs for petroleum-derived products, and processing to tailor soybean oil for improved performance and more cost-effective conversion processes are favoring soybean oil as an ingredient for industrial products. Even though soybean oil typically contains only 8–12% linolenic fatty acid compared with 50–60% for linseed oil, the $C_{18:3}$ amount is high enough for it to be classified as a "semidrying" oil. Therefore, soybean oil can be added to a drying oil like linseed oil, at levels up to 25%, as an extender in periods of drying oil shortages, or to reduce costs. Further, a "blown oil" process, which initiates oxidation and polymerization, has improved the performance properties of soybean oil in replacing linseed oil in paints, printing inks, as a binder in foundry cores, and as a plasticization agent for rubber (20).

Castor Oil. Castor oil is different in many respects from any other oil because it consists largely (up to 90%) of an unusual fatty acid, ricinoleic. Castor oil and ricinoleic fatty acid find many uses in the textile, petroleum, and lubrication fields because they exhibit certain viscosity behavior and surface-acting properties not found in other oils and fatty acids. Physically, castor oil differs from other oils by its high hydroxyl value, high specific gravity, greater viscosity, and ability to hydrogenate to an unusually high melting point, i.e., 86–88°C. Castor oil is noted for its ability to carry high concentrations of dyes and pigments used in cosmetics, plastics, and rubber applications as well as many other specialty uses, including use as an ingredient for protective coatings, plasticizers, or lubricants, an oil for sulfonation, or a fluid for hydraulic systems.

Linseed Oil. Linseed oil is obtained from flaxseed. It has an very high linolenic fatty acid content (35–60%), thus qualifying as a "drying oil" for the manufacture of paint, varnish, linoleum, oilcloth, printing inks, and other industrial products. The value of the drying oils as a raw material for protective coatings is their ability to polymerize after application to a surface to form a tough, adherent, impervious, and abrasion-resistant film. Therefore, the quality of linseed oil for technical purposes depends upon its degree of unsaturation. Because this quality is somewhat variable, it is necessary to blend lots of oils from different sources to obtain a consistent level of unsaturation.

Tall Oil. Tall oil is a by-product of the Kraft process for producing wood pulp from pine wood. Crude tall oil is acid refined and separated by fractionation into rosin and fatty acids. The term tall oil is a misnomer because it is not an oil. Good quality tall oil typically contains 97.1% fatty acids, 0.9% rosin acids, and 2% unsaponifiables. The fatty acid composition is typically 3% palmitic and stearic, 48% oleic, 46% linoleic, and 3% miscellaneous fatty acids. The absence of linolenic fatty acid in tall oil is an advantage in alkyd resins for color retention and nonyellowing of interior finishes. Tall oil fatty acids have become an important raw material for paints and varnish but are also used in soaps, detergents, industrial lubricants, plastics, hot melt adhesives, polyester resins, rust prevention products, corrosion inhibitors, vinyl, cosmetics, and various intermediate chemicals (21).

Tung Oil. Tung oil is obtained from the kernels of the fruit of the tung tree. The oil qualifies as a "drying oil" because of its polymerization properties caused by a high content (77–86%) of eleostearic fatty acid, which is a conjugated isomer of linolenic fatty acid. Oils containing conjugated fatty acids polymerize much more rapidly than oils containing nonconjugated fatty acids. In the past, it was used in quick-drying enamels and varnishes and in combination with other drying oils to improve overall characteristics. However, synthetic resins have replaced the natural oils to a great extent; its current use is predominately in resins and plastics (22).

Industrial Fats and Oils Applications

Since World War II, major changes have occurred in the industrial markets for fats and oils. There has been an increased use of plastics and synthetic resins, drying oils use has declined, the use of detergents has increased with a consequential decline in the fats and oils used in soap making, and new markets have developed for animal feeds and fatty acids. Table 1.5 identifies the major industrial fats and oils used in the United States and their applications for 1996 (8).

Animal Feeds. The largest U.S. market for industrial fats and oils is animal feeds. Fats and oils are added to various types of feeds at different levels from 0.5 to 10% for a number of reasons including the following: (i) for caloric or energy value, (ii) as a growth factor, (iii) to increase feed efficiency, (iv) to increase palatability, (v) to reduce dustiness, (vi) to allow easier handling, (vii) to reduce wear on machinery for handling, mixing, pelleting, and other processes, (viii) to aid in homogenizing and stabilizing the mixture of fine-particled feed additives, and (ix) to give feed a better appearance. This market has been dominated by tallow and soybean oil as indicated by Table 1.5.

Fatty Acids. Fat splitting, fatty acid distillation, and glycerine water evaporation are production techniques used to produce oleochemicals or fatty acids. These processes resemble the fat splitting of fatty glycerides or the hydrolysis process by which fat is metabolized by humans and animals. The oils used to produce fatty acids are selected for their dominant fatty acid contents. Table 1.6 (23) identifies the natural fat and oil sources for the commercially desirable fatty acids. The saturated fatty acids, stearic and palmitic, are used to make products that include soap, detergents, cosmetics, candles, waxes, chemical intermediates, and synthetic rubber. The

TABLE 1.6 Agrichemical Fatty Acids

Fatty Acid	Type	Natural fat and oil sources
Caprylic, capric	Saturated	Coconut oil, palm kernel oil, babassu oil
Lauric	Saturated	Coconut oil, palm kernel oil, babassu oil
Palmitic and lauric	Saturated	Coconut oil, palm kernel oil, babassu oil, tallow, palm oil
Palmitic	Saturated	Tallow, palm oil
Stearic	Saturated	Tallow, hydrogenated soybean oil, palm oil
Oleic	Unsaturated	Tallow, tall oil, high-oleic sunflower, high-oleic safflower
Oleic-linoleic	Unsaturated	Tall oil
Linoleic, linolenic	Unsaturated	Soybean oil, tall oil, safflower oil, linseed oil
Erucic	Unsaturated	Rapeseed oil
Behenic	Saturated	Hydrogenated rapeseed oil

unsaturated fatty acids, oleic and linoleic, are used in paints, printing inks, metallic driers, soaps, detergents, flotation agents, cutting oils, lubricating oils, linoleum, and chemical intermediates. Some of the fats and oils are split for more specific fatty acids, for example, rapeseed for erucic and behenic fatty acids and coconut oil for lauric and the short- and medium-chain fatty acids. The principal raw materials for fatty acids in descending order of preference are tall oil, tallow, rapeseed oil, coconut oil, soybean oil, and linseed oil as identified by the USDA for 1996 and listed in Table 1.5.

Soap Manufacture. Soap has been one of the largest industrial markets for fats and oils, declining from 2.3 billion pounds usage in 1947 to 567 million pounds in 1997, a 75% decline. Detergents now command a major share of the home and commercial laundry market. However, the toilet bar or hand bar soap is still a viable product because detergent bars are more expensive, have a tendency to crumble, and dissolve more oil out of the user's skin, leaving a dirty feeling. The most important fats and oils used in the manufacture of soaps are tallow, coconut oil, and tall oil. Castor oil has been used to produce a special bar soap. The principal consideration for selecting a mixture of fats and oils for making soap is that it contain the proper ratio of saturated and unsaturated, and long-, medium-, and short-chain fatty acids to result in the desired qualities of stability, solubility, ease of lathering, hardness, and cleaning ability in the finished soap.

Resins and Plastics. The number of oleochemicals used in resins and plastics is large, and the products are varied. Some of the primary functions are as follows (24):

- Slip agents used in resins for plastic film allow one surface to slide horizontally across another. The main feedstocks used for the primary amide slip agents are oleic and erucic fatty acids.
- Plasticizers are incorporated into plastics or rubber-like materials to increase flexibility, workability, distensibility, and toughness. Many plastics are hard

materials with limited usefulness unless properly plasticized. Epoxidized fats and oils are used extensively to plasticize plastic resins. The principal oils used for this industrial application are linseed, soybean, tall, and tung oils.

- Internal and external lubricants are used in a variety of resins. The external lubricants effect the release of polymer melts from the metal surfaces of the processing equipment, whereas internal lubricants promote polymer flow. Lubricants and mold-release agents for these purposes include fatty amides, metallic stearates, fatty acid esters, and fatty ketones, which utilize fatty acids with 18–22 carbon atoms, i.e., stearic, oleic, and erucic fatty acids.
- Plastics are nonconductive materials that allow a build-up of static charges on the surface. This causes problems, including sparking and accumulations of dust and dirt on the surface. This phenomenon can be alleviated by treating the resin with a fat-derived antistatic agent. Ethoxylated glycerol esters of fatty acids are used as both internal and external antistats. Glycerol monstearate or monooleate are also used as internal antistats. The ethoxylated and glycerol monoproducts are usually produced with a tallow feedstock.

Lubricants. Natural fats and oils were once widely used for lubrication fluids, but petroleum-derived mineral oils have replaced most of this usage. The principal advantage of the natural fats and oils is their superior clinging to metal surfaces in very thin films. The disadvantages are that under extreme conditions, the natural fats and oils can hydrolyze to become acidic and corrosive. Today, most of the fats and oils used for lubricating oils and greases are animal fats, castor oil, coconut oil, and/or tall oil.

Varnish and Paint. Paints are coatings used to cover surfaces and must dry quickly. Varnishes are similar, except that no pigment is used to hide the surface. Once applied to a surface, the solvent evaporates, leaving a film of pigment and resin on the surface, and the film polymerizes through oxidation of the double bonds in the unsaturated fatty acids. Oxidation or polymerization is accelerated by using oils high in polyunsaturated fatty acids or more conjugated unsaturation, or by air blowing the oil.

The development of synthetic resins and the popularity of water-emulsion latex paints has caused a decline in vegetable oil use for drying applications. Vegetable oil use in drying oil applications peaked around 1950 and has declined from over a billion pounds per year to 0.47 billion pounds since then, with an average of 2.0% annually. The USDA has determined that the vegetable oils currently used for drying applications are linseed, soybean, tall, and castor oils.

Other Industrial Applications. Animal fats and vegetable oils have many diverse applications; they are essential to cosmetics, pharmaceuticals, textiles, adhesives, inks, food emulsification, and other applications in addition to those previously identified. Some specific examples of other applications include the following:

- Cosmetics: Ethylene glycol mono- and diesters are surfactants used in preparation of cosmetics.
- Textiles: Polyamide nylon 11 is made from undecenaoic acid obtained from castor oil (18).
- Printing: Biodegradable printing inks produced with soybean oil provide superior print qualities, brighter colors, less rub-off, more print mileage, and cleaner press runs than petroleum-based inks (20).
- Building Industry: Sealing, caulking, or glazing compounds utilize vegetable oils to produce rubber-like properties.
- Pharmaceuticals: Vegetable oils act as antifoaming agents in production of penicillin, streptomycin, tetracycline and other aerated fermentation–based pharmaceuticals (20).
- Food Emulsifiers: Natural glycerine derived from soap making and fatty acid industries is utilized to produce mono- and diglycerides, the most dominant food emulsifier.

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Chapter 2

Properties of Fats and Oils

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Introduction

Natural fats, which are solid at ambient temperature, and oils, which are liquid under room temperature conditions, have many properties that differentiate them from the other two major food components, i.e., proteins and carbohydrates. The most obvious difference is that fats and oils are hydrophobic and immiscible with water. In addition, their caloric value (9 kcal/g) is twice as high as that of proteins and carbohydrates. The molecular weights of fats and oils, from several hundred to >1000, are generally smaller than those of proteins and carbohydrates. They serve as a heating medium and are frequently used to cook and preserve foods. Their reversible solid-to-liquid phase transition properties allow them to function as pastry fats, frying shortenings, and confectionery applications. Their ability to dissolve color and flavor, and to provide lubricity plays an important role in making food palatable and desirable.

Fats and oils are common and easily obtained from various sources. They were used long before systematic terminology and characterization were applied to these materials. Therefore, many common or trivial terms were developed and continue to be used in industry and business. Many oils are produced in a given geographical region and thus carry much local culture. Initially, fat and oil products were produced and consumed locally, but as our society evolved and civilization expanded, fats and oils were shipped to and traded in places far away from where they were produced. To ensure that the quality of these fats is acceptable, their properties have to be defined and tested. In the last 40 years, due to unpredictable climate, supply or nutritional concerns, much research have been devoted to the development of fat substitutes for targeted performances, such as cocoa butter substitutes, frying shortening to replace tallow for French fries, fat substitutes using microcrystalline cellulose and sucrose polyesters. To accomplish this, one has to compare selected chemical and physical properties of the conventional fat and substitutes to ensure their functional equivalency.

This chapter describes the physical and chemical properties of fats and oils that are used frequently in the oil industry and business. Readers will be directed to other references (1–10) for detailed testing procedures or equipment required in determining these properties.

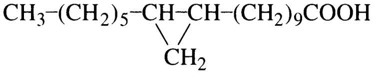
Nomenclature and Structure

Lipid Classes

Lipids can be classified according to their chemical structure, solubilities, and rate of turnover (1). On the basis of their chemical structure, lipids can be classified into hydrocarbons, aliphatic alcohols, aliphatic acids, waxes, glycerol-containing lipids, sphingosine (*trans*-D-erythro-1,3-dihydroxy-2-amino-4-octadecene)–containing lipids, phospholipids, sterols, and miscellaneous lipids. For the purpose of this monograph, we will discuss aliphatic acids, glycerol-containing lipids, and several minor lipids.

Aliphatic Acids

Aliphatic acids are normally called fatty acids. They have various carbon chain lengths terminated with a carboxylic acid (–COOH), which is the Δ-terminal, and a methyl group (–CH_3), which is often given the symbol n or ω. Fatty acids are either saturated or unsaturated. Those with one or more double bonds along the carbon chain are unsaturated; saturated fatty acids do not have any double bonds. They also exist as hydroxy acids; for example, 12-hydroxy oleic acid (or ricinoleic acid) is found in castor seed, and cyclic acids, e.g., cyclopropanoic acids,



$$CH_3\text{–}(CH_2)_5\text{–}\underset{\diagdown\ \diagup\atop CH_2}{CH\text{–}CH}\text{–}(CH_2)_9COOH$$

are present in trace amounts in cottonseed oil.

Saturated Fatty Acids

Most of the natural saturated (alkanoic) acids have an unbranched structure with an even number of carbon atoms. Acids from C_2 to longer than C_{30} have been reported, but the most common and the most important fatty acids fall in the range from C_{12} to C_{22}. These are designated by a numerical structural symbol, e.g., 18:0, or a systematic name, octadecanoic acid, or a common name, stearic acid. These names along with their common sources are shown in Table 2.1 (2,7).

Unsaturated Fatty Acids

Unsaturated fatty acids can be monoene (alkenoic) or methylene-interrupted polyene acids (–CH=CH–CH_2–CH=CH-) as shown in Tables 2.2 and 2.3, respectively (3). In nature, the double bonds are oriented with both hydrogen atoms on the same side of the double bond (*cis*- form). However, hydrogen atoms on opposite sides of the double bond (*trans*-form) are thermodynamically more stable. Fatty acids with *trans*-double bonds melt at a higher temperature than their *cis* counterparts. When there is enough chemical energy, such as through oxidation or hydrogenation, the *cis*-double

TABLE 2.1 Names and Selected Physical Properties of Alkanoic Acids

Structural symbol	Systematic name	Common name	mp (°C)	bp[a] (°C)	d[b] (g/mL)	ΔH_f (kJ/mol)	Molecular weight
4:0	Tetranoic	Butyric	-5.3	164	0.9583	—	88.10
6:0	Hexanoic	Caproic	-3.2	206	0.9276	16.1	116.16
8:0	Octanoic	Caprylic	16.5	240	0.9105	21.4	144.21
10:0	Decanoic	Capric	31.6	271	0.8858	28.0	172.26
12:0	Dodecanoic	Lauric	44.8	130[a]	0.8477	36.6	200.31
14:0	Tetradecanoic	Myristic	54.4	149[a]	0.8439	44.8	228.36
16:0	Hexadecanoic	Palmitic	62.9	167[a]	0.8414	54.4	256.42
18:0	Octadecanoic	Stearic	70.1	156[a]	0.8390	63.2	284.47
20:0	Eicosanoic	Arachidic	76.1	204[a]	—	—	312.52
22:0	Docosanoic	Behenic	80.0	—	—	—	340.57
24:0	Tetracosanoic	Lignoceric	84.2	—	—	—	368.62

[a] Boiling point (bp) at 1 mm Hg pressure instead of 760 mm Hg.
[b] Measured at 20°C.

bonds may be isomerized to form *trans*-double bonds, which are often accompanied by positional shifts of the double bond on the aliphatic carbon chain. Thus, the *trans* acids may exist in numerous positional isomers, and their presence in the oil usually implies that oxidation or chemical modification has occurred. To simplify the structural representation of fatty acids, a numerical symbol is often used, e.g., 18:1 or 18:1(9) or 9*c*-18:1 for oleic acid, instead of the systematic name, 9*c*-octadecenoic acid. The number before the colon indicates the total number of carbon atoms. The first number after the colon stands for the number of double bonds; the next number in the parenthesis shows the location of the double bond counting from the Δ terminal or numerically marked in front of the total carbon number to indicate that the double bond occurs between the 9th and 10th carbon in a *cis* form (e.g., 9*c*). Another convention to indicate the position of a double bond on a fatty acid carbon chain is to count the carbon atom from the ω- or n-terminal.

TABLE 2.2 Structural Symbol, Systematic, Common Names, and Melting Points (mp) of Some Monoenoic Acids

Structural symbol	Systematic name	Common name[a]	mp (°C) cis	*trans*	Molecular weight
14:1 (9)	9*c*-Tetradecenoic	Myristoleic	–4	18.5	226.34
16:1 (9)	9*c*-Hexdecenoic	Palmitoleic	0.5	32	254.40
18:1 (9)	9*c*-Octadecenoic	Oleic	16	45	282.45
20:1 (9)	9*c*-Eicosenoic	Gaddeic	—	—	310.50
22:1 (13)	13*c*-Docosenoic	Erucic	34	60	338.56

[a] Name of *cis* form.

TABLE 2.3 Structural Symbol, Systematic and Common Names of Methylene-Interrupted Polyunsaturated Acids

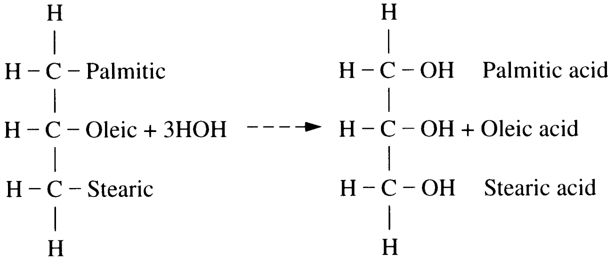
Structural symbol	Systematic name	Common name	Molecular weight
18:2 (9,12)	9*c*,12*c*-Octadecdienoic	Linoleic	280.44
18:3 (6,9,12)	6*c*,9*c*,12*c*-Octadectrienoic	γ-Linolenic	278.42
18:3 (9,12,15)	9*c*,12*c*,15*c*-Octadectrienoic	α-Linolenic[a]	278.42
20:4 (5,8,11,14)	5*c*,8*c*,11*c*,14*c*-Eicosatetraenoic	Arachidonic	304.46
20:5 (5,8,11,14,17)	5*c*,8*c*,11*c*,14*c*,17*c*-Eicosapentaenoic	Eicosapentaenoic (EPA)[a]	302.46
22:6 (4,7,10,13,16,19)	4*c*,7*c*,10*c*,13*c*,16*c*,19*c*-Docosahexaenoic	Docosahexaenoic (DHA)[a]	328.46

[a] These are ω-3 or n-3 polyunsaturated fatty acids. Others in the table are ω-6 or n-6 acids.

Glycerol-Containing Lipids

Fatty acids can exist alone as free fatty acid or in a combined form of esters. A majority of the combined forms are esters with glycerol (propane-1,2,3-triol). They are called triacylglycerols or triglycerides. Upon hydrolysis, each triglyceride molecule can release three fatty acids and one glycerol as shown in Figure 2.1. Other glycerol-containing lipids may contain sugar and phosphate residues, which are called glycolipids and phospholipids (or phosphatides), respectively. When glycerol is represented as the Fischer projection, the three carbon atoms are numbered 1,2,3 from top to bottom. They can also be designated as α, β and α′, which should not be confused with the fat crystallinity notation discussed later in this chapter.

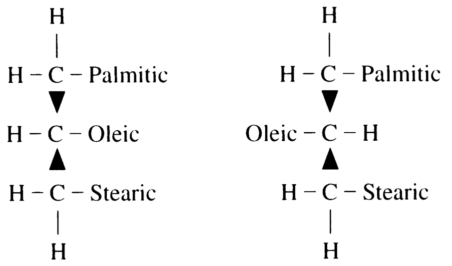
When triglycerides have three identical fatty acids, they are called simple or monoacid triglycerides. When triglycerides contain more than one type of fatty acid,



$$\begin{array}{lcll}
\mathrm{H} & & \mathrm{H} & \\
| & & | & \\
\mathrm{H-C-Palmitic} & & \mathrm{H-C-OH} & \text{Palmitic acid} \\
| & & | & \\
\mathrm{H-C-Oleic + 3HOH} & \dashrightarrow & \mathrm{H-C-OH} & +\ \text{Oleic acid} \\
| & & | & \\
\mathrm{H-C-Stearic} & & \mathrm{H-C-OH} & \text{Stearic acid} \\
| & & | & \\
\mathrm{H} & & \mathrm{H} &
\end{array}$$

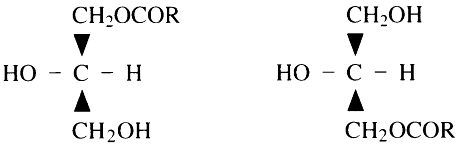
β-oleopalmitostearin
or
1-palmito, 2-oleo, 3-stearin
or
α-palmito, β-oleo, α'-stearin

Fig. 2.1. Graphical representation of triglycerides and their hydrolyzed components.



(R-form) (L-form)

β-oleopalmitostearin

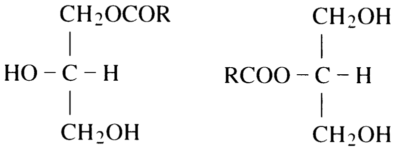


1-acyl-*sn*-glycerol (*L*-Form)

3-acyl-*sn*-glycerol (*R*-Form)

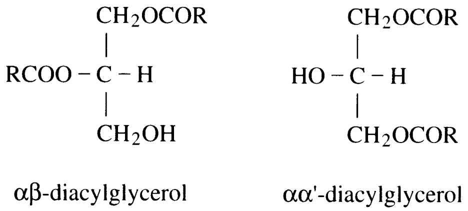
Fig. 2.2. Racemic isomers of β-oleopalmitostearin and a monoglyceride.

they are called complex or mixed triglycerides. Triglycerides with different fatty acids (see Fig. 2.1) can be isomers due to the possible arrangement of the three fatty acids on the glycerol molecule. Should all three fatty acids be different, each of the three triglyceride molecules can also have two enantiomeric (or racemic) forms and are denoted as D or L (Dextrorotating or Levorotating) or *R* or *S* notation. The D or *R* designation indicates an optical isomer that can rotate the plane of incident polarized light to the right (clockwise direction). The second carbon or β-carbon of the glycerol backbone is the chiral center. When the Fischer projection system is used, the symbol *sn* (stereospecific numbering) is used to indicate the existence of racemic isomers as shown in Figure 2.2. Other common glycerol-containing lipids are monoacylglycerols (monoglycerides) and diacylglycerols (diglycerides). Monoacylglycerols exist as 1-acyl or 2-acyl isomers which may also be designated as α- and β-monoglycerides as shown in Figure 2.3. The 1- and 3-acyl *sn* isomers are enantiomers, which together comprise the racemic mixture of α-monoglycerides.



1-acylglycerol 2-acylglycerol

Fig. 2.3. Graphic representation of monoglycerides.



$$\begin{array}{c} CH_2OCOR \\ | \\ RCOO-C-H \\ | \\ CH_2OH \end{array} \qquad \begin{array}{c} CH_2OCOR \\ | \\ HO-C-H \\ | \\ CH_2OCOR \end{array}$$

Fig. 2.4. Graphic representation of diacylglycerols or diglycerides.

Diacylglycerols exist as α-β and β-α′ or (1,2- and 2,3)-diacyl esters and α-α′ or (1,3)-diacyl esters as displayed in Figure 2.4.

Natural oils and fats are mainly triacylglycerols. This is the most significant class of storage lipids in plants and in most animals with the exception of some marine lipids in which ether lipids are frequently found.

Composition of Fats and Oils

Most of the refined oils contain at least 98% triglycerides. The remainder is composed of <0.5% diglycerides, 0.1% free fatty acids, 0.3% sterols, 0.1% tocopherols and ppm levels of phospholipids and various pigments.

Tocopherols are known by their properties as oil-soluble antioxidants and vitamin E. The effectiveness of the four isomers of tocopherols as vitamin E and antioxidants are $\alpha \gg \beta$, γ, and δ; and $\delta \gg \beta > \gamma > \alpha$, respectively. The contents of tocopherols in some common oils are shown in Tables 2–4 (6). Sterols are crystalline, neutral, unsaponifiable alcohols; they have high melting points with properties resembling those of cholesterol. The sterols comprise the bulk of the unsaponifiable matter in many fats and oils. They are ordinarily of little concern to the oil technologist and do not appear to contribute to any important property of the oil. They are useful by-products derived from the deodorizer distillate and are used for the synthesis of sex hormones and vitamin D. The sterol contents in some common fats and oils are shown in Table 2.5 (6).

TABLE 2.4 Typical Tocopherol Contents in Some Refined Oils

	Tocopherols (ppm)			
Oil	α	γ	δ	Total
Corn	90	810	—	900
Cottonseed	600–710	240–270	—	870–950
Lard	23	—	—	27
Palm	300–500	—	—	560
Palm kernel	240	240	—	480
Peanut	200	200	—	420
Rice bran	580	330	—	910
Soybean				
Crude	200	980	500	1680
Refined	200	740–780	—	940–990

TABLE 2.5 Typical Sterol Contents of Some Fats and Oils[a]

Fats and oils	Sterols (%)
Beef tallow	0.08–0.14
Butterfat	0.24–0.50
Cocoa butter	0.17–0.20
Coconut	0.06–0.08
Corn	0.58–1.00
Cottonseed	0.26–0.31
Lard	0.11–0.12
Olive	0.23–0.31
Palm	0.03
Palm kernel	0.06–0.12
Peanut	0.19–0.25
Rapeseed	0.35–0.50
Rice bran	0.75
Soybean	0.15–0.38

[a] *Source:* Ref. 6.

Free Fatty Acids

Nonesterified fatty acids are often referred to as free fatty acids (FFA). FFA are generated by hydrolysis in the oil-bearing materials throughout harvesting, handling and processing. FFA in extracted crude oils are usually removed as soap by caustic refining. A high FFA concentration in crude oil means higher refining loss. After refining, any residual FFA can be removed by deodorization. Deodorized oils should not contain >0.05% FFA. Undeodorized meat fat should contain <1% FFA. The FFA content in oil can be determined conveniently by titrating the oil in isopropanol and hexane (85:15) against NaOH (AOCS Method Ca 5a-40). The result is reported as the weight percentage of free oleic acid. FFA composition and content can also be determined by silylation and gas chromatography (GC) (11). Acidity of oil is sometimes measured as acid value or neutralization number, which is defined as the milligrams of potassium hydroxide (KOH) required to neutralize the FFA in 1 g of fat. Each unit of acid value is equivalent to 0.503% FFA, i.e., the acid value or acid number of a fat is normally about twice its FFA concentration.

Fatty Acid Composition (FAC) or Distribution (FAD)

The reliability of GC has made it a routine assay for the FAC of fats and oils. The AOCS method Ce 1-62 describes the procedure used. It involves the hydrolysis of fats or oils into FFA followed by methylation to form fatty acid methyl esters (FAME). Each component fatty acid is identified by its retention time in the GC column and reported as the percentage of total amount of fatty acid detected. The quantitative estimation can be calibrated by adding a known quantity of internal standard such as margaric (heptadecanoic, C_{17}) acid in the oil sample to be analyzed or by

TABLE 2.6 Fatty Acid Compositions of Selected Oils

Structural symbol	Common name	Soybean	Corn	Cottonseed	Sunflower	Peanut	Olive	Low-erucic rapeseed	Rapeseed	Palm
14:0	Myristic	0.4	<0.1	0.4–2.0	<0.5	<0.4	0.05	<0.2	<1.0	0.5–5.9
16:0	Palmitic	7–14	8–19	17–31	3–10	6.0–16	7.5–20	2.5–6.0	1.5–6.4	32–59
9*c*16:1	Palmitoleic	<0.5	<0.5	0.5–2.0	<1.0	<1.0	0.3–3.5	<0.6	<3.0	<0.6
18:0	Stearic	1.4–5.5	0.5–4.0	1.0–4.0	1.0–10	1.3–6.5	0.5–3.5	0.9–2.1	0.5–3.1	1.5–8.0
9*c*-18:1	Oleic	19–30	19–50	13–44	14–65	35–72	56–83	50–66	8–45	27–52
9*c*,12*c*-18:2	Linoleic	44–62	34–62	33–59	20–75	13–45	3.5–20	18–30	11–29	5.0–14
9*c*,12*c*,15*c*-18:3	α-Linolenic	4.0–11	<2.0	0.1–2.1	<0.7	<1.0	<1.5	6.0–14	5–16	<1.5
20:0	Arachidic	<1.0	<1.0	<0.7	<1.5	1.0–3.0		0.1–1.2	<3.0	<1.0
9*c*-20:1	Eicosenoic	<1.0	<0.5	<0.5	<0.5	0.5–2.1		0.1–4.3	3–15	
22:0	Behenic		<0.5	<0.5	<1.0	1.0–5.0		<0.5	<2.0	
13*c*-22:1	Erucic			<0.5	<0.5	<2.0		<0.5	5–60	
24:0	Lignoceric		<0.5	<0.5	<0.5	0.5–3.0		<0.2	<2.0	
15*c*-24:1	Nervonic				<0.5					

Symbol	Common name	Cocoabutter	Palm	Palm kernel	Coconut	Butter	Lard (pork)	Beef tallow	Goat	Red deer
4:0	Butyric					3.6				
6:0	Caproic			<0.5	<1.2	2.2				
8:0	Caprylic			2.4–6.2	3.4–15	1.2				
10:0	Capric			2.6–7.0	3.2–15	2.8				
12:0	Lauric		<1.2	41–55	41–56	2.8			3.5	0.3
14:0	Myristic	0.1	0.5–5.9	14–20	13–23	10.1	2.0	2.5	2.1	5.7
9*c*-14:1	Myristoleic							3.0		0.4
16:0	Palmitic	26.0	32–59	6.5–11	4.2–12	25.0	27.1	27.0	25.5	30.9
9*c*-16:1	Palmitoleic	0.3	<0.6	1.3–3.5	1.0–4.7	2.6	4.0	10.8		2.0
18:0	Stearic	34.4	1.5–8.0	10–23	3.4–12	12.1	11.0	7.4	28.1	35.7
18:1	Oleic	34.8	27–52	0.7–54	0.9–3.7	27.1	44.4	47.5	38.4	15.4
9*c*,12*c*-18:2	Linoleic	3.0	5.0–14			2.4	11.4	1.7		1.1
9*c*,12*c*,15*c*-18:3	α-Linolenic	0.2	<1.5			2.1		1.1		
20:0	Arachidic	1.0	<1.0						2.4	
2:0	Behenic	0.2								

using a known mixture of fatty acid standards. This method is precise to the first decimal of a percentage. Typical FAD data of several common oils and fats are listed in Table 2.6.

Triglyceride Distribution

The most extensive chemical composition data of fats and oils one can obtain are their triglyceride distribution with the amount of individual fatty acid and its position on the glycerol backbone identified. This is accomplished by using an enzymatic 2-position fatty acid assay and GC analysis. An oil sample is first hydrolyzed by the 1,3 specific lipase. The hydrolyzed fatty acids and β-monoglycerides are then

TABLE 2.7 Triglyceride Composition of Some Natural Fats (Percentage of Fatty Acids in Specific Positions on the Glyceride Molecules)[a]

		Fatty acids						
Fat	Position	14:0	16:0	18:0	18:1	18:2	18:3	Other acids[b]
Soybean	1		14	6	23	8	9	
	2		1	tr	22	70	7	
	3		13	6	28	45	8	
Cocoa butter	1		34	50	12	1		
	2		2	2	87	9		20:0 (1,0,2)
	3		37	53	9	tr		
Rapeseed	1		4	2	23	11	6	20:1 (16,2,17)
	2		1	0	37	36	20	22:1 (35,4,51)
	3		4	3	17	4	3	
Human	1	4	39	10	33	3		
	2	11	10	2	50	9		16:1 (5,11,4)
	3	1	25	9	51	5		
Pig	1	2	16	21	44	12		
	2	4	59	3	17	8		16:1 (3,4,3)
	3	tr	2	10	65	24		
Ox	1	4	41	17	20	4		
	2	9	17	9	41	5		16:1 (6,6,6)
	3	1	22	24	37	5		
Chicken	1		25	6	33	14		
	2		15	4	43	23		16:1 (12,7,12)
	3		24	6	35	14		
Cow's milk	1	11	36	15	21	1		4:0 (5,3,43)
	2	20	33	6	14	3		6:0 (3,5,11)
	3	7	10	4	15	0		8:0 (1,2,2)
								10:0 (3,6,4)
								12:0 (3,6,4)
								16:1 (3,2,1)

[a] *Source:* Ref. 2.

[b] The three figures in parentheses indicate the percentage of the acid at the 1-, 2-, and 3-positions, respectively.

separated and analyzed for FAC by GC. With the 2-position fatty acids and total fatty acid distribution known, one can assign all of the available fatty acids to their corresponding positions on the glycerol molecules. This assumes that the fatty acids are distributed equally between the 1- and 3-positions of glycerol. To obtain specific fatty acid distributions at all three positions, several extra steps have to be taken (2). Obviously, it is rather time consuming to obtain this type of information. For a less specific triglyceride composition, one can use capillary GC to determine the triglycerides by their total carbon numbers.

If cost is not a critical concern, these types of data should provide a good correlation with the oil functionality and properties, thus providing the necessary insight for tailoring desired fats and oils for targeted purposes. Triglyceride compositions of several natural fats are given in Table 2.7 (2).

Chemical Properties and Reactions

Fats and oils undergo several types of chemical reactions during the various handling and processing steps. They are hydrolysis, saponification, esterification, interesterification, hydrogenation, and oxidation. Hydrogenation and interesterification will be discussed in more detail in **Chapters 10** and **12**, respectively. Esterification and interesterification reactions, as applied to the production of emulsifiers, will be treated in **Chapter 26**.

Hydrolysis and FFA

Hydrolysis of glycerides with water is catalyzed by enzyme, acid, or metals to yield FFA and glycerol products.

$$\underset{\text{Fat}}{C_3H_5(OOCR)_3} + \underset{\text{Water}}{3HOH} \rightleftarrows \underset{\text{Glycerol}}{C_3H_5(OH)_3} + \underset{\text{Fatty acids}}{3HOOCR}$$

This reaction proceeds in stages and will reach equilibrium if products or reactants are not removed. In practice, fat is hydrolyzed or split under high temperature and pressure. More complete hydrolysis can be accomplished with a large amount of excess water and periodic removal of the glycerol-rich water phase. Hydrolysis is normally catalyzed by acids. Lipolytic enzymes or lipases, which have received much attention in recent years, can catalyze the hydrolysis at near ambient temperatures (40–50°C). However, the high cost of lipases makes the enzyme hydrolysis possible only for specialty applications.

Hydrolysis of oils in oilseed can take place in the preharvest and postharvest handling and storage, during oil extraction, crude oil storage, and shipping. The result is an elevation of the concentration of FFA in the crude oil. Great attention should be given during the various steps of the process to minimize the amount of FFA in the starting or finished oil products. High FFA in crude oil will cause greater refining loss. High FFA in finished oil will cause smoke and shorter shelf life.

Esterification

Esterification can be considered simply as reversing the hydrolysis reaction by combining fatty acids with alcohols, glycols, and polyfunctional materials such as propylene glycol, sugar, and polyglycerols. In addition to the esters, water is also a product of esterification. The removal of water can lead to a more complete reaction. Either acid or alkali can be used to promote the esterification. Esterification and interesterification are practiced to produce emulsifiers, such as monoglycerides, propylene glycol mono- and diesters, and sucrose esters. Tailored triglycerides for unique applications and sucrose polyesters as fat substitutes such as olestra have been commercialized in recent years.

Interesterification

Interesterification can be done by any one of the following methods with the use of an alkaline catalyst: (i) the reaction between fat and alcohols is called alcoholysis and produces simple esters of fatty acids or wax esters of long-chain alcohol and fatty acid; (ii) the reaction between fat and glycerol is termed glycerolysis and is often used to produce mono- and diglycerides; and (iii) the interchange of fatty acids between two triglycerides is called either interesterification or randomization and yields a fat with different melting characteristics than those of its original component fats. Recent nutritional concerns about the *trans* fatty acid isomers generated by the hydrogenation process have prompted renewed interest in both chemical and enzymatic interesterification processes.

Saponification and Iodine Value

The saponification value (AOCS Method Cd 3-25) is determined by reacting a known amount of fat with a known quantity of excess ethanolic KOH. Unreacted KOH is determined by titration with standard HCl in the presence of an indicator. The saponification value is calculated as the milligrams of KOH required to saponify 1 g of fat. The average molecular weight of a fat is in inverse proportion to its saponification value.

In principle, one can derive molecular weight and degree of unsaturation of a fat from FAC or triglyceride composition data. However, due to the simplicity of these assay procedures, saponification value and iodine value continue to be used to estimate the average molecular weight of fatty acids and the amount of unsaturated fatty acids present in the oil.

Iodine value (AOCS Method Cd 1-25 or Wijs Method) is obtained by reacting fat with a known amount of excess halogen, iodine, or iodine chloride. The reduction of the excess halogen with KOH and titration with standard sodium thiosulfate using starch solution as an indicator of free iodine determines the amount of iodine consumed by the fat. The final iodine value is expressed as the centigrams of iodine per gram of fat (or % iodine absorbed). A higher iodine number means a higher degree of unsaturated fatty acids present. Saponification and iodine values for several oils are given in Table 2.8 (2).

Oxidative Stability

Oxidation is a primary cause of oil deterioration. When the oxidation of oil releases undesirable oxidized odor, it is considered as oxidative rancidity. In addition to the time-consuming and costly sensory evaluation, quality control professionals often rely on the measurement of hydroperoxides and conjugated dienes or the amount of carbonyls (aldehydes and ketones), which are secondary oxidation products of oils, as indicators of oxidative stability of an oil. GC and GC-mass spectrometry (MS) have also been used frequently to determine the oxidized volatile compounds. This subject is discussed in **Chapter 18** and was thoroughly presented in a monograph by Frankel (12).

Peroxide Value (PV). When an oil becomes oxidized, it first develops hydroperoxides. The extent of oxidation is measured by the amount of free iodine the oxidized fat can liberate from potassium iodide (KI). The results are expressed as peroxide value (PV) in milliequivalents of iodine formed per kilogram of fat (AOCS Method Cd 8-53). Freshly deodorized oil should have a PV of 0. Cooking oil with PV much higher than 10 is considered unusable.

Conjugated Diene (CD). Polyunsaturated fatty acids (PUFA) are likely to be oxidized first. As peroxides form, one of the methylene-interrupted double bonds of a linoleic acid is shifted to form CD. The amount of CD in oil is determined by dispersing the oil in octane and measuring the absorbance at 233 nm as described in the AOCS method Ti 1a-64 (5). CD correlates well with PV for a given oil and is a simpler method than that for PV. CD can be accumulated and measured at elevated

TABLE 2.8 Fatty Acid Composition (%), Saponification Number (SN) and Iodine Value (IV) of Some Common Fats and Oils[a]

	Saturated acids			Unsaturated acids				
Source	14:0	16:0	18:0	16:1	C_{18}	C_{20}	SN	IV
Coconut oil[b]	18	9	1	—	9	—	250	9
Butter fat[c]	8	22	15	—	38	4	230	30
Lard	1	26	12	2	66	3	198	55
Mutton tallow	5	25	0	—	40	—	193	40
Cottonseed oil	2	20	3	—	75	—	193	110
Sardine oil[d]	6	10	2	13	24	26	191	185

[a] *Source:* Ref. 2.

[b] Also contains 46% 12:0 and 17% saturated acids below 12:0.

[c] Also contains 13% saturated acids below 14:0.

[d] Also contains 19% C_{22} unsaturated.

temperatures. However, CD is highly dependent on the fatty acid composition (FAC). CD values cannot be compared easily among oils with different FAC (13).

Anisidine Value (AV). Peroxides are unstable. They tend to decompose and form aldehydes and ketones. The content of aldehyde, principally 2-alkenal, in the oil can be measured to further assess its degree of oxidation. This is called the anisidine value; it is measured by determining the absorbance of the sample in isooctane at 350 nm (8). This is a simple method like CD, but it is not very sensitive and cannot be used to compare the quality of different types of oil. Like CD, AV may be used to track the quality of the same oil (13).

Oil Stability Test. Traditionally, the oxidative stability of a fat or oil is assessed by the Active Oxygen Method (AOM) (AOCS Method Cd 12-57), which determines the number of hours required for an oil sample to reach a PV of 100 mEq/kg under a specified aeration condition and 97.8°C. This method is time consuming and can vary by as much as 25% among laboratories. To minimize the variability of the AOM, oxidative stability can be determined automatically by commercial equipment, Rancimat (Brinkmann Instrument, Westbury, NY) or Oxidative Stability Instrument (Omnion, Rockland, MA). Both instruments use a principle similar to that of AOM and continuously monitor the amount of volatile acidic components from the heated and aerated oil samples that are trapped in deionized water within a conductivity cell. When the conductivity of the deionized water takes a sharp rise, an induction period in terms of minutes or hours can be determined. This induction time of the oil under the specified temperature is the Oil Stability Index (OSI). This procedure has now been adopted by the American Oil Chemists' Society as an official method (AOCS Cd 12-92) (5).Other accelerated procedures for oil oxidative stability determination are also available, such as oxygen bomb and Oxidograph (Mikrob Aarhus, Denmark) (14). Both of these methods determine the induction points at which the oil sample consumes oxygen at a rapid rate.

Protection of Oil from Oxidation. All oils should be handled with care to prevent exposure to air, heat or light. Oil temperature should be kept at a minimum, blanketed with a nitrogen head space, and packaged in containers with good moisture and air barriers. For vegetable oil, it is also common to add an antioxidant such as tertiary butyl hydroquinone (TBHQ) to slow the rate of oxidation. For animal fats, butylated hydroxyanisole (BHA) or butylated hydroxytoluene (BHT) are the most effective antioxidants. Mixed tocopherols and rosemary extracts are also available commercially as natural antioxidants. Their cost effectiveness should always be assessed for each targeted application.

Flavor

Although there are sophisticated analytical methods being used to study the flavor quality of oil, such as GC-MS, sensory evaluation by a trained expert taste panel is still the most reliable method. Usually, the oil sample is kept near or slightly above body temperature. After tasting, the panel is asked to score the oil according to its bland or neutral flavor from 1 to 10. The most bland taste is rated as 10 and the most rancid or oxidized oil taste is rated as 1. Usually an oil with a sensory score >6 is considered acceptable. Another asset of the flavor panel is to identify and quantify the desirable (nutty and buttery) and undesirable (beany, grassy, burnt, tart, or hydrogenated) flavor characteristics of an oil. Sometimes, sensory evaluation is also used to study the influence of storage conditions on oil flavor stability. Many accelerated storage conditions have been devised according to the way an oil is handled and used. Some investigators have reported that the Schaal Oven Test results correlate well with shelf-life and some have found the Schaal Oven Test to offer only a rough guideline for the determination of the shelf-life of fats and oils at 29°C (85°F) (4). This is an old test condition with many modifications. The storage temperature of the oil sample is usually 60°C (140°F) but can be higher or lower according to the individual situation. A sample is removed periodically from the oven for sensory evaluation until rancidity is detected.

Physical Properties

Crystal Structure of Fats

The functional performance and textural quality of fats, and fat-containing products are determined mainly by the balance between the solid and liquid phases and the crystal structures of the solid fats. Fats can crystallize in different forms in a phenomenon called polymorphism. It is known that polymorphism of fat greatly affects the consistency, plasticity, graininess and other physical properties of many products such as butter, lard, margarine, hydrogenated vegetable shortenings, and cocoa butter. During storage, there is a tendency for the fat to be transformed into the most stable crystal form, which may or may not be desirable. Therefore, much effort is given to designing the processing, tempering, or storage conditions so as to achieve and maintain the desirable crystal forms.

Generally, fats in the α-form are characterized as waxy; fats in the β'-form are characterized as fine-grained with smooth texture; the β-form crystals are termed coarse and grainy. In the production of margarine, one strives to maximize the crystallization in the β'-form and minimize the β-form. Because β-crystals can easily grow in size, they tend to give an unacceptable grainy or sandy mouthfeel to margarine.

When a melted monoacid triglyceride is cooled rapidly, it will first crystallize in the α-form. These α-form crystals and the melted liquid state comprise a thermodynamically reversible phenomenon. This α-form is then transformed irreversibly to a more stable form β', which is finally transformed to the most stable form, β.

Several methods have been used to study fat polymorphism. The most widely used include calorimetry, dilatometry, infrared spectroscopy, and X-ray diffraction. Among these methods, differential scanning calorimetry (DSC) is considered the

TABLE 2.9 The Melting Points (mp) and Long Spacings of Monoacid Triglycerides

Acid chain length	mp (°C)			Long spacing (nm)		
	α	β′	β	α	β′	β
10	-10.5	17.0	32.0	3.02	2.72	2.65
12	15.0	34.5	46.5	3.56	3.29	3.12
14	33.0	46.0	58.0	4.10	3.73	3.57
16	45.0	56.5	66.0	4.58	4.25	4.08
18	54.7	64.0	73.3	5.06	4.70	4.51
20	62.0	69.0	78.0	5.58	5.07	4.95

most versatile. It can provide qualitative, quantitative and kinetic properties of the fat crystals. Due to the complexity of the triglycerides, it can be difficult to correlate all of these data. X-ray data indicate that the unit cell for long-chain compounds is a prism with two short spacings and one longer one. The melting points and long spacing data for α, β′, and β forms of some monoacid crystalline triglycerides are shown in Table 2.9 (2).

Melted fat has a tendency to remember the structure from the crystals present before melting. To ensure that this memory is erased completely, the melt has to be heated for several minutes to at least 30°C above the melting point of the fat. The chains of melted triglycerides are in gauche-conformation, and they will reach a stretched zig-zag form or transconfiguration during crystallization. In the β′-form, the chains are still in a highly disordered state so that they can either oscillate or rotate in a hexagonal packing, and the hydrocarbon chains are vertical in relation to the plane through the molecular bilayer.

During cooling of the α-form, the mobility of the chains is reduced. The chains arrange into a new packing in which every second plane is perpendicular to the others. This packing, which is called β′, is more densely packed and has more even end-group planes. A further stability of the crystal packing is obtained by having all chain planes parallel to each other and the end planes even more regular. This is the most stable β-form.

The above-described polymorphic transitions are for simple or monoacid triglycerides. All natural fats show principally the same polymorphic pattern, but the rate of transformations among α, β′, and β varies extensively. The practical reasons for stabilizing the β′ crystals are as follows: (i) to stabilize the orthorhombic chain packing by adding 1,2 diglycerides instead of 1,3 diglycerides and so on and (ii) to delay the β′→ β transition by disturbing the crystal lattice through varying the chain length of triglycerides.

The degree of heterogeneity of fatty acid profiles of natural fats determines their preferred crystal forms. Crystal forms of several fully hydrogenated fats are listed in Table 2.10 (4). The differentiation of these fully hydrogenated fats lies in the rate of their polymorphic transition to the most stable form.

TABLE 2.10 Crystal Structures of Fully Hydrogenated Fats in Their Most Stable States[a]

β′-Tending	β-Tending
Cottonseed	Soybean
Palm	Sunflower
Rapeseed	Peanut
Herring	Corn
Menhaden	Olive
Tallow	Coconut
Butter	Palm kernel
	Lard
	Cocoa butter

[a] *Source:* Ref. 4.

Thermal Properties

Melting Point

Fats and fatty acids can solidify in several crystal forms; therefore, they may melt at several distinctly different temperatures or over a wide range of temperatures. For these reasons, softening points (AOCS Method Cc3-25) and congeal points (AOCS Method Cc 14-59) for fats are sometimes reported. In general, the melting points of fatty acids increase with increasing chain length and decrease as the acids become more unsaturated. Melting points of the most stable (highest-melting) forms of different saturated fatty acids and their glycerides are given in Table 2.11 (6).

Heat of Combustion

The heat of combustion of the saturated fatty acids increases as the chain length increases, varying from ~5900 cal/g for butyric acid (4:0) to 9600 cal/g for stearic acid (18:0) and 9800 cal/g for behenic acid (22:0). Values for oleic (18:1) and linoleic (18:2) acids were reported to be 9450 and 9350 cal/g, respectively. Triglycerides

TABLE 2.11 Melting Points (°C) of Fatty Acids and Their Glycerides[a]

Structural symbol	Common name	Acid	1-Mono-glyceride	1,3-Di-glyceride	Triglyceride
10:0	Capric	31.6	53	44.5	31.5
12:0	Lauric	44.8	63	57.8	46.4
14:0	Myristic	54.4	70.5	66.8	57.0
16:0	Palmitic	62.9	77	76.3	63.5
18:0	Stearic	70.1	81.5	79.4	73.1
20:0	Arachidic	76.1	84	—	—

[a] *Source:* Ref. 6.

have essentially the same heats of combustion as the fatty acids of which they are composed; hence the heat of combustion of common fats, such as lard and tallow, is ~9500 cal/g. The heat of combustion of a variety of fatty oils is expressed closely by the following equation (6):

$$\text{Heat of combustion} = 1080 - (\text{Iodine Value}) - 9.15(\text{Saponification Value})$$

Calculated values range from 9020 for coconut oil to 9680 for rapeseed oil.

Specific Heat and Heat of Fusion

Specific heat, c_p, is defined as the amount of heat required to raise the temperature of 1 g of material by 1°C. Fats or simple derivatives such as fatty acids or methyl esters at temperatures just above their melting points have specific heats of ~0.5 cal/g or somewhat higher. Their solid forms, on the other hand, have a specific heat that is generally <0.5 cal/g. Specific heat of a given material usually increases with increasing temperature. Specific heat data for saturated fatty acid and their corresponding simple triglycerides are given in Table 2.12 (6).

The heat of fusion (H_f) of a fatty material includes the amount of energy required to melt a gram of material and the heat of crystal transition. Heat (with a negative sign) is released when a fat crystal is transformed from a less stable form to a more stable form. Heat of fusion data for several monoacid triglycerides are given in Table 2.13 (6).

TABLE 2.12 Specific Heat (c_p) of Fatty Acids and Their Corresponding Simple Triglycerides[a,b]

Carbon number	Common name	c_p [cal/(g·°C)] (Fatty acids)		c_p [cal/(g·°C)] (Simple triglycerides)	
		Solid	Liquid	Liquid	Solid
10:0	Caprylic	0.5009 (0–24)	0.4989 (35–65)	—	—
12:0	Lauric	0.5116 (19–39)	0.5146 (48–78)	0.510 (66)	
14:0	Myristic	0.5209 (24–43)	0.5157 (40–84)	0.518 (65.3)	
16:0	Palmitic	0.4920 (22–53)	0.5416 (50–68)	0.519 (65.7)	
18:0	Stearic	—	—	0.530	0.310 (–30.3, β) 0.346 (–36.5, α)
20:0	Arachidic	0.4597 (20–56)	0.5663 (50–100)	— —	

[a] *Source:* Ref. 6.

[b] Numbers in parentheses indicate the temperature or temperature range in °C.

TABLE 2.13 Heat of Fusion (ΔH_f) and Transition of Some Fatty Acids and Their Corresponding Simple Triglycerides[a]

Carbon number	ΔH_f (cal/g)	Simple triglyceride		Temperature (°C)	ΔH_f (cal/g)
		Name	Transition		
10:0	38.9	Tricaprin			
12:0	43.7	Trilaurin	$\beta \rightarrow$ Liq	46.3	46.2
14:0	47.1	Trimyristin	$\beta \rightarrow$ Liq	57.0	50.3
			$\alpha \rightarrow$ Liq	32.3	34.6
			$\alpha \rightarrow \beta$	32.3	−12.6
16:0	50.6	Tripalmitin	$\beta \rightarrow$ Liq	65.7	53.1
			$\alpha \rightarrow$ Liq	44.7	37.4
			$\alpha \rightarrow \beta$	44.7	−13.3
18:0		Tristearin	$\beta \rightarrow$ Liq	72.5	54.5
			$\alpha \rightarrow$ Liq	54.0	38.9
			$\alpha \rightarrow \beta$	54.0	−13.7

[a] *Source:* Ref. 6.

Vapor Pressure and Boiling Point

Triglycerides of long-chain fatty acids have extremely low vapor pressures and can be distilled satisfactorily only by molecular or short-path distillation. Therefore, their boiling points can be observed only under very high vacuum condition. Some of these data are shown in Tables 2.14 and 2.15 (6).

Monoglycerides have much higher vapor pressures than those of triglycerides and can be distilled under appropriate conditions. However, high-vacuum, short-path distillation is preferred to keep the temperature as low as possible to avoid any undesirable reactions including interesterification. Fatty acids are more volatile than the corresponding mono- and triglycerides and can be distilled readily under reduced pressure.

TABLE 2.14 Vapor Pressure of Simple Triglycerides and Oils[a]

Material	Temperature (°C)	
	0.05 mm Hg	0.001 mm Hg
Tricaprin	213	159
Trilaurin	244	188
Trimyristin	275	266
Tripalmitin	298	239
Tristearin	313	253
Soy oil	308	254
Olive oil	308	253

[a] *Source:* Ref. 6.

TABLE 2.15 Boiling Points of Saturated Fatty Acids (°C)[a]

Pressure (mm Hg)	Carbon number of saturated fatty acid				
	10	12	14	16	18
1	110.3	130.2	149.2	167.4	183.6
4	132.7	154.1	173.9	192.2	209.2
8	145.5	167.4	187.6	206.1	224.1
760	270.0	298.9	326.2	351.5	376.1

[a] *Source:* Ref. 6.

Smoke, Flash, and Fire Points

The smoke, flash, and fire points of fatty materials are measures of thermal stabilities of fats and oils when heated in the presence of air. These indices are often used as a quick quality control means for a critical process step such as deodorization. Lower than normal smoke, flash, or fire points indicate the presence of an excess of residual nontriglyceride impurities, such as FFA, monoglycerides, and other volatiles, which should be largely removed during steam deodorization.

Smoke point is the temperature at which smoking is first detected in a laboratory apparatus protected from drafts and provided with special illumination (AOCS Method Cc 9a-48). Flash point is the temperature at which volatile products are evolved at such a rate that they are capable of being ignited but do not support combustion. The fire point is the temperature at which the volatile products will support continuous combustion. Values of the smoke, flash, and fire points of corn oil, cottonseed oil, or peanut oil and FFA are given in Table 2.16. Frying shortening and all-purpose household shortening usually have a smoke point of ~218°C (425°F) and 190°C (375°F), respectively.

Density

Liquid oils have a density between 0.91 and 0.92 g/mL at room temperature. Oil density generally increases with lower molecular weight and higher unsaturation of

TABLE 2.16 Smoke, Flash, and Fire Points (%F) for Oils Containing 0.01% Free Fatty Acids (FFA) and Pure FFA

Point (°F)	Oil (0.01% FFA)	100% FFA
Smoke point	450	200
Flash point	625	380
Fire point	685	430

TABLE 2.17 Densities of Solid Tristearin and Lard

Fat	Temperature (°C)	Density (g/mL)
Tristearin, α	–38.0	1.014
Tristearin, β′	–38.0	1.017
Tristearin, β	–38.6	1.043
Lard, highest melting form	–38.6	1.005

the fatty acids. As approximate expression for the specific gravity of liquid oil at 15°C compared with that of water is as follows (6):

Specific Gravity = 0.8475 + 0.00030(Saponification Value) + 0.00014(Iodine Value)

The densities of solid fats are generally higher than those of their liquid states. But the various types of crystal forms, α, β′, and β, melting at progressively higher temperatures, also show increasing densities (Table 2.17).

Dilatometry and Solid Fat Index (SFI)

Due to thermal expansion, the density of either solid fat or liquid oil generally decreases with increasing temperature. These density or volumetric changes of fat and oil at various temperatures can be measured precisely by using a dilatometer. A dilatometer is essentially a specially designed pycnometer capable of measuring small volume changes due to thermal expansion or contraction of the liquid oil and solid fat and their mixtures. This technique is known as dilatometry. In the edible oil industry, this method is used to estimate the solid fat content at several selected temperatures for a fat used to make shortening or margarine. The specific volumes (mL/g)

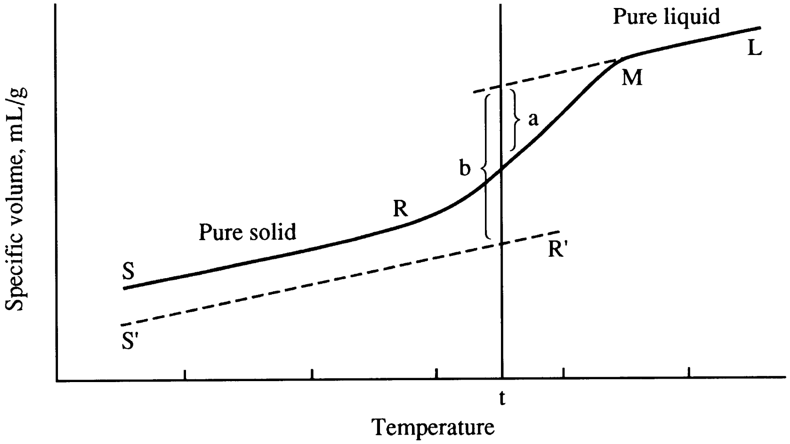


Fig. 2.5. Dilatometric curve of a typical fat.

of liquid oil and liquid/solid mixtures at selected temperatures can be measured accurately with a dilatometer. This can be expressed as in Figure 2.5. However, the specific volumes of pure solid fat at various temperatures are difficult to measure. Therefore, a hypothetical line for pure solid fat, R′S′, is constructed at 0.100 specific volume units below but parallel to that of the liquid line, LM.

The ratio of *a*/*b* will be the estimate of solid fat content of the fat sample at temperature *t*, which is called solid fat index (SFI). Details of the procedure can be found in the AOCS Method Cd 10-57. The values of SFI at 50,70,80, 92, 100, and 104°F or only several of these temperatures are measured for a fat product that contains a large fraction of liquid oil. Certain SFI values of a finished fat blend are critical for its intended functional application. SFI of some natural fats and margarine oils are shown in Table 2.18.

The dilatometry method is accurate but requires >5 h to analyze at five temperatures. The SFI assay often becomes the bottleneck in determining the release of a batch of product for shipment. The desire for a faster method to replace the traditional SFI method has led to the wide-line nuclear magnetic resonance (NMR) method. The NMR method for SFI is gaining popularity in the edible oil industry and is described later in this chapter.

Consistency

Consistency of a fat or shortening is the textural quality generally described by its firmness, softness, and spreadability. Although other devices and procedures exist, the most frequently used instrument to assess the consistency of fat is the manual or automated penetrometer. The penetrometer measures the depth of penetration of a

TABLE 2.18 Solid Fat Index (SFI) of Natural Fats and Margarine Oils

	Melting point		SFI value				
Fat	°C	°F	10.0°C 50°F	21.1°C 70°F	26.7°C 80°F	33.3°C 92°F	37.8°C 100°F
Cocoa butter	29	85	62	48	8	0	0
Coconut oil	26	79	55	27	0	0	0
Palm kernel oil	29	84	49	33	13	0	0
Palm oil	39	103	34	12	9	6	4
Tallow	48	118	39	30	28	23	18
Lard	43	110	25	20	12	4	2
Butter	36	97	32	12	9	3	0
Margarine stick	—	—	28	16	12	2–3	0
Soft stick	—	—	15	11	9	5	2
Tub	—	—	13	8	6	2	0
Baker's	—	—	27	17	16	12	8
Puff pastry	—	—	25	24	23	22	21

fat at a specified temperature and time interval by a metal cone of known geometry and weight (AOCS Method Cc 16-60). The temperatures of 85 and 50°F are commonly used for shortening and margarine, respectively. The spreadability or machinability of puff pastry fat is sometimes assessed by penetration tests on preconditioned fat samples at several selected temperatures for 48 h.

Viscosity

Viscosity or dynamic viscosity is a measure of internal friction of a liquid to resist flow. It is usually denoted by η, and defined in the following equation:

$$\eta = \sigma/\dot{\gamma}\ [\text{dyne}/(\text{cm}^2\cdot\text{s})]$$

where σ = shear stress = force per unit area (dyne/cm^2)

$\dot{\gamma}$ = shear rate = velocity gradient (1/s) between the moving and stationary plates

The viscosity, η, carries a dimension of dyne/(cm^2·s) or poise (P). Most liquids have values <1 P; for example, water has a value of 1 centipoise (cP) at 20°C. The viscosities of oils are much higher than that of water, which can be attributed primarily to the intermolecular attractions of the long-chain fatty acids of their glycerides. This is one of the reasons why the oil exhibits its unique oily characteristics and lubricity.

Because most oils behave like Newtonian fluids (i.e., shear stress increases linearly with increasing shear rate), oil viscosity can be measured by a low shear rheometer or by the relative time required to flow through a special cup or tube over a standard fluid. The viscosities of saturated fatty acids C_{12}–C_{18} at 70 and 90°C (6) are presented in Table 2.19.

The experimental data of viscosities of simple triglycerides were found to fit the following equation:

$$\log(\log\eta) = C - DT$$

where T is the temperature in °C, between the melting point and 95°C. The values of the constants C and D are tabulated along with their viscosities at several

TABLE 2.19 Viscosities of Saturated Fatty Acids

	Dynamic viscosity (cP)	
Carbon number	70°C	90°C
12:0	4.415	2.982
14:0	5.984	3.906
16:0	7.682	4.885
18:0	9.583	6.294

TABLE 2.20 Viscosity Constants and Viscosities of Some Simple Triglycerides[a]

Simple triglyceride	Constants		Viscosities (cP)			
	C	D	60°C	70°C	75°C	80°C
Trilaurin	0.3414	0.00505	13.59	10.30	9.11	8.09
Trimyristin	0.3649	0.00468	17.71	13.42	11.70	10.35
Tripalmitin	0.3894	0.00447	—	16.79	14.67	12.92
Tristearin	0.3972	0.00419	—	—	18.50	16.21

[a] *Sources:* Refs. 5 and 6.

temperatures (5,6) in Table 2.20. From these viscosity data of fatty acids and their simple triglycerides, it is obvious that the viscosity of oil increases moderately with the chain length of the fatty acid but decreases drastically with increased temperature.

Surface and Interfacial Tension

Surface tension at the air and oil surface is defined as the force (dyne) required to pull the oil film with a known width (cm). The surface tension of water is 72 dyne/cm at 25°C. At 20°C, oleic acid is reported to have a surface tension of 32.50 dyne/cm and an interfacial tension against water of 15.59 dyne/cm. The surface tensions (dyne/cm) of cottonseed and coconut oils are shown in Table 2.21. The values of the surface tension of saturated fatty acids and their interfacial tension against water at 75°C are shown in Table 2.22 (6).

The presence of monoglycerides and lecithin can dramatically lower the interfacial tension between oil and water from 30 to <10 dyne/cm. This reduction of interfacial tension will lower the energy required to homogenize the oil/water mixture, thus making possible the fine oil-in-water or water-in-oil dispersions.

TABLE 2.21 Surface Tension of Oils

Temperature (°C)	Cottonseed	Coconut
20	35.4	33.4
80	31.3	28.4
100	27.5	24.0

TABLE 2.22 Surface and Interfacial Tensions of Saturated Fatty Acids at 75°C[a]

Fatty acid	Surface tension (dyne/cm)	Interfacial tension against water (dyne/cm)
Caproic	23.0	2.1
Caprylic	24.2	5.8
Capric	25.1	8.0
Lauric	25.9	8.7
Myristic	26.8	9.2
Palmitic	27.3	9.2
Stearic	27.7	9.5

[a] *Source:* Ref. 6.

Solubility of Gases and Water in Oils

Some selected solubility data of N_2, O_2, H_2, and CO_2 are shown in the Table 2.23 (6). With the exception of CO_2, the solubilities of these gases in oil increase with temperature. The mutual solubility of oil and water is relatively low. Some of the values are given in Table 2.24 (6).

TABLE 2.23 Solubility of Gases in Oils (mL gas/mL oil)[a]

Oils	Temperature (°C)	N_2	H_2	O_2	CO_2
Cottonseed oil (IV = 104.3)	49.6	0.0779	0.0540	—	—
	147.8	0.1183	0.1024	—	—
Lard (IV = 70.1)	41.5	0.0765	0.0521	—	—
	147.3	0.1206	0.1035	—	—
Hydrogenated lard (IV = l)	64.3	—	—	—	0.920
	67.0	0.0844	—	0.1450	—
	88.0	—	—	—	0.790
	139.4	0.1168	0.0979	—	0.619
Soybean oil					
Crude oil	22.5	—	—	0.032	—
Refined oil	22.5	—	—	0.013	—
Sunflower oil					
Crude oil	22.5	—	—	0.029	—
Refined oil	22.5	—	—	0.019	—

[a] *Source:* Ref. 6.
[b] Abbreviation: IV, iodine value

TABLE 2.24 Mutual Solubility of Water and Fatty Acids[a]

Fatty acid and oils	% Water in fatty acid	Fatty acid (g/100 mL water) at 20°C
Caproic (6:0)	9.7 (46°C)	0.968
Caprylic (8:0)	3.88 (14.4°C)	0.068
Capric (10:0)	3.12 (29.4°C)	0.015
Lauric (12:0)	2.35 (43°C)	0.0055
Myristic (14:0)	1.7 (53°C)	0.0020
Palmitic (16:0)	1.25 (62°C)	0.00072
Stearic (18:0)	0.92 (69°C)	0.00029
Coconut fatty acids	20 (230°C) Completely miscible (290°C)	—
Tallow fatty acids	9 (230°C) Completely miscible (320°C)	—

[a] *Source:* Ref. 9.

Optical and Spectroscopic Properties

Refractive Index. The refractive index is defined as the speed of light in vacuum divided by the speed of light in a known medium. It is also defined as the ratio of the sine of the incident angle of light from vacuum and the sine of the refractive angle in the medium. It is a simple method and requires only a few liquid drops for the measurement. The refractive index data can be obtained quickly and precisely and is correlated easily with the structure and composition of the sample. Therefore, it is used frequently to examine the purity and concentration

TABLE 2.25 Refractive Indices (n) of Fatty Acids, Simple Triglycerides, and Natural Oils[a]

Fatty acid	n 75°C	Simple triglyceride	n 60°C	Oils	n 40°C
Butyric	1.3758			Butter	1.4548
Caproic	1.3944			Cocoa butter	1.4568
Caprylic	1.4069		—	Coconut	1.4493
Capric	1.4149	Tricaprin	1.4370	Corn	1.4735
Lauric	1.4208	Trilaurin	1.4402	Cottonseed	1.4782
Myristic	1.4251	Trimyristin	1.4428	Olive	1.467
Palmitic	1.4288	Tripalmitin	1.4452	Palm	1.4578
Stearic	1.4318	Tristearin	1.4471	Palm kernel	1.4569
Oleic	1.4487	Triolein (50°C)	1.4548	Rapeseed	1.4706
Linoleic	1.4583	Trilinolein (50°C)	1.4645	Soybean	1.4729
Linolenic	1.4678	Trilinolenin (50°C)	1.4741	Cod liver	1.4810

[a] *Source:* Ref. 6.

of a liquid sample, and to control the progress of reactions, e.g., hydrogenation and isomerization. For lipids, the refractive index normally increases with the hydrocarbon chain length and with the number of double bonds and conjugation. The refractive indices of some common fatty acids, triglycerides, and oils are given in Table 2.25 (6).

Color

Pure fats, fatty acids, and esters are colorless and essentially transparent to visible light. Natural fats and oils, however, often contain pigments that partially absorb transmitted light. Most of these pigments are removed from fats and oils by the refining and bleaching processes. The color of oils and fats is the initial indicator of quality. Most oils have their specific color due to the type and amount of natural pigments present, i.e., chlorophyll in soybean oil and gossypol and flavonoids in cottonseed oil. Some oils, therefore, are naturally darker than others.

Lightly colored oils and white shortenings are preferred by consumers and food processors. However, due to a poor grade of crude or improper processing and handling, the oils and fats can be darker than usual or even have a pinkish cast. Insufficient refining may leave residual phospholipid gums (lecithin), which will darken the oil during deodorization. Vegetable oils and shortenings will darken after being stored for a long time or at elevated temperatures due to the oxidation of tocopherols to tocoquinones. During frying, oil darkening is further complicated by polymerization of oil and interaction between the oil and other components of the food being fried. Further discussion on this subject will be covered by a separate chapter in this monograph.

The color of an oil is usually measured by the Lovibond tintometer (AOCS Method Cc 13b-45). This is done by comparing the color of the oil in a glass tube at a standard depth with the color of several glass standards. The colored glasses are graduated in three series, i.e., yellow, red, and blue. Most oils require only a combination of yellow and red glasses. The analyst selects the closest red glass, which is the easiest color to match and then selects a yellow glass with 10 times the color value. The color of the measured oil is customarily reported as Red Index/Yellow Index. Normal soybean oil has a Lovibond color of Red 1.0/Yellow 10.0.

Chlorophyll, a green plant pigment, is difficult to remove during refining. Its concentration in oil can be determined by absorption spectra at 630, 670, and 710 nm. The results are expressed as ppm chlorophyll (AOCS Method Cc 13d-55). The Lovibond blue number has also been used because yellow and blue combine to make green. Automated colorimeters have recently become available and a new method (AOCS Method Cc 13j-97) has been established for oil color, which will minimize the operator error often encountered in the visual color determinations. Colors of shortenings are often examined or compared visually. Various color reflectance meters are available and can provide more objective and reproducible data. These are used for peanut butter, margarine, and mayonnaise (4).

Ultraviolet Spectroscopy

Monoene and methylene-interrupted polyene acids absorb ultraviolet light at wavelengths too low for convenient study. However, ultraviolet spectroscopy is valuable for detecting fatty acids with conjugated double bonds. Conjugated dienes show a single absorption peak at 230–235 nm, whereas conjugated trienes show three peaks at ~260, 270, and 280 nm. In the edible oil industry, the amounts of conjugated dienes in the finished fats and oils are estimated spectrophotometrically at 233 nm (AOCS Method Ti 1a-64).

Infrared Spectroscopy

The infrared spectra provide useful information about polymorphism, crystal structure, conformation, and chain length. The most frequent use of infrared spectroscopy is in the recognition of *trans* isomers. The *trans*-double bond produces characteristic absorption at 968 cm^{-1}. The procedure used to estimate the percentage of *trans* of the total amount of double bonds is described in the AOCS Method Cd 14-61.

Nuclear Magnetic Resonance (NMR) Spectroscopy

Proton or ^{13}C NMR can provide structural information concerning saturated and unsaturated esters. The NMR technique can also differentiate *cis*- and *trans*-alkenoic acids by the various chemical shifts and coupling constants of hydrogen atoms. In recent years, the application of NMR for determining the solid fat content (SFC) or solid fat index (SFI) of fats and shortenings has gained popularity.

Currently, SFC is measured by wide-line NMR or pulsed NMR. Both of these techniques distinguish hydrogen atoms in liquid and solid environments. In wide-line NMR, the sample signal, which measures hydrogen in a liquid environment, is compared with the signal from a totally liquid sample at the same temperature. In pulsed NMR, a measurement related to the total number of hydrogen atoms is followed by a second measurement 70 μs later, which measures only those hydrogen atoms in a liquid environment. This determination depends on the fact that the transversal magnetization of hydrogen in a solid environment decays much more quickly (~10 s) than that of hydrogen in a liquid environment (~100 s). For oilseed breeders, the NMR method is often used to estimate the oil content of oilseeds in a nondestructive manner.

Application of Some Analytical Data

Fat and oil properties are measured routinely to ensure expected functional performance, to achieve targeted quality or process improvements, and to establish agreeable specifications for suppliers and users. A few typical specifications are given in Table 2.26. Should some performance problems unexpectedly arise, one can examine the various properties selectively as described in the specification.

TABLE 2.26 Sample Specifications of Oil and Shortenings

Typical analysis	Peanut oil	Liquid frying shortening	Frying shortening for donuts
Melting point (Wiley°F)[a]	—	106 ± 2	115 ± 2
AOM stability (h)	15	35	60
Smoke points ('F min)	440	440	440
Free fatty acids (% max.)	0.05	0.05	0.05
Peroxide value (mEq, max.)	0.5	0.5	1.0
Iodine value	90–110	102 – 2	76–79
Lovibond color (red, max.)	2.0	2.0	2.0
Odor and flavor	Slightly nutty	Bland	Bland
Solid fat index		(%)	
50°F	—	4–6	30 ± 2
70°F	—	3–4	21 ± 2
80°F	—	—	18 ± 2
92°F	—	2–3	13 ± 2
104°F	—	1–2	9 ± 2

[a] Wiley Melting Points Method is described in the AOCS Method Cc 2-38.

Future Challenges

Although an ideal, all-purpose fat may be definable in the foreseeable future, at present, we still have to deal with the best fat for each application at a reasonable cost. Therefore, for the professionals in the edible oil industry, the immediate concerns are the following: (i) to continue improving the selected analytical method for better accuracy, sensitivity, and reproducibility at reduced turn-around time; (ii) to search for reliable and sensitive on-line sensors to determine FFA contents for refining processes and refractive index for hydrogenation and interesterification control; (iii) to develop innovative processes that will minimize quality loss, improve productivity, and provide value-added products; and (iv) to look for new oil sources through conventional breeding or genetic engineering programs to provide desired nutritional and/or functional properties. The first three areas are generally guided by the current needs of manufacturers and end users. Therefore, their objectives can be defined clearly. New oil sources or new varieties of oilseeds, however, are often difficult to define or differentiate adequately from the existing ones. The simple reason for this ambiguity is that the selected benefit, i.e., to reduce the linolenic acid (18:3) content in soybean oil below 3% or reduce the total saturates, is not easily justified on the basis of its potential return. Other confusions arise from the rapidly generated nutritional data on lipids. The ideal fat for good health and superior functionality remains a moving target at the moment. Nevertheless, it is clear that technology in general, the understanding of the function-structure relationship, and nutritional requirements of oils are advancing rapidly.

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Chapter 3

Sources of Fats and Oils

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Commercial Sources of Fats and Oils

The edible vegetable and animal fats and oils important in world commerce are shown in Tables 3.1 and 3.2, respectively, along with their typical fatty acid compositions. Table 3.3 lists the composition of several important fats and oils used in industrial products. The typical values given in Table 3.1 are subject to considerable variation, and many of the references cited give information about the range of variation that may be encountered. Vegetable fats and oils may vary as a result of environmental conditions and their genetic make-up (1). They often vary with the location in which they are produced because of climate, weather, and the varieties favored in particular regions. Table 3.4 lists the fatty acid composition of some genetic variants of common fats and oils. Animal fats may vary in composition from place to place depending on the carcass and the animal's diet (1). Table 3.2 gives the range of variation in composition that has been reported.

By-Product Fats and Oils

The fats and oils listed in Tables 3.1–3.3 are in production for a variety of reasons. Several fats and oils are by-products, and the amount produced (Table 3.5) depends on the demand for some other product. Thus, cottonseed oil production is limited by the market for cotton. Corn oil production is tied to the corn milling industry because it is profitable to extract oil only after the corn germ is separated from the endosperm. Palm kernel oil is a by-product of palm oil production. Tallow and lard production depend on animal slaughter and the demand for meat products. Fish oil production depends on the size of the fish catch and the resources devoted to fishing. Butter's position has changed over the years from that of being the primary product of some dairy regions to more of a by-product status. The amounts of milk fat diverted into butter can vary with the demand for other dairy products and the nature of government support programs. Tall oil, a source of free fatty acids for industrial use, is a by-product of paper manufacture.

TABLE 3.1 The Typical Fatty Acid Composition of Some Edible Plant Fats and Oils

Fatty acid	Canola	Cocoa butter	Coconut	Corn	Cotton-seed	Olive	Palm	Palm kernel	Peanut	Safflower	Sesame	Soybean	Sunflower
Reference	(31)	(2)	(32)	(33)	(34)	(6)	(10)	(8,35)	(36,37)	(38)	(13)	(29)	(40)
6:0	—	—	0.4	—	—	—	—	—	—	—	—	—	—
8:0	—	—	8.2	—	—	—	—	4.0	—	—	—	—	—
10:0	—	—	5.6	—	—	—	—	4.0	—	—	—	—	—
12:0	—	—	47.1	—	—	—	0.2	48.0	—	—	—	—	—
14:0	—	0.7	19.4	—	0.8	—	1.1	16.0	—	—	—	—	—
16:0	3.9	25.2	7.8	11.5	22.2	12.9	44.0	9.0	11.4	5.9	9.7	11.4	5.9
18:0	1.8	35.5	4.3	2.0	2.5	2.8	4.5	2.0	4.0	1.5	4.8	3.7	4.1
20:0	—	—	1.0	0.2	—	0.4	0.4	—	1.7	—	—	—	—
22:0	—	—	—	—	—	0.1	—	—	3.7	—	—	—	—
24:0	—	—	—	—	—	0.3	—	—	1.5	—	—	—	—
16:1	—	—	—	—	0.8	—	0.1	—	0.1	—	—	—	—
18:1	60.3	35.2	4.3	24.1	17.8	72.2	39.2	15.0	41.5	8.8	41.2	22.9	21.5
18:2	23.9	3.2	1.8	62.5	55.2	10.5	10.2	2.0	34.9	83.8	44.4	53.6	67.5
18:3	9.6	0.2	—	1.8	—	0.7	0.4	—	0.2	—	—	8.4	0.2
20:1	—	—	—	—	—	0.2	—	—	1.0	—	—	—	—
22:1	—	—	—	—	—	—	—	—	—	—	—	—	—

TABLE 3.2 Range of Fatty Acid Composition of Some Animal Fats and Oils

Fatty acid	Herring[a]	Menhaden[a]	Lard[b]	Tallow[b]	Milkfat[c]
4:0	—	—	—	—	7–14
6:0	—	—	—	—	2–7
8:0	—	—	—	—	1–3.5
10:0	—	—	—	—	1.5–5
12:0	—	—	—	—	2.5–7
14:0	6.0–16.3	5.6–7.7	1–4	2–8	8–15
16:0	19.6–24.0	11.8–18.6	20–28	24–37	20–32
18:0	11.2–17.9	6.2–8.0	5–14	14–29	6–13
20:0	2.4–3.4	1.1–2.0	—	—	0.3
22:0	—	11.7–25.2	—	—	0.1
10:1	—	0.1–0.6	—	—	0.3
12:1	—	—	—	—	0.1
14:1	—	—	—	—	0.8
16:1	—	—	—	—	1.5
18:1	10.7–23.4	11.7–25.2	41–51	40–50	13–28
18:2	0.9–1.7	0.1–0.6	2–15	1–5	1–4
18:3	0.4–3.7	—	0–0.1	—	0.4–2
18:4	0.8–3.6	1.1–2.8	—	—	0.1
20:1	1.1–2.7	7.3–19.1	—	—	—
20:2	—	—	—	—	0.1
20:3	—	—	—	—	0.1
20:4	0.6–2.3	0.3–0.8	0.3–1.0	—	0.1
20:5	10.2–14.1	11.4–15.2	—	—	—
22:1	0.2–1.0	6.9–15.2	—	—	—
22:4	—	—	—	—	0.1
22:5	1.1–2.5	0.3–1.0	—	—	0.1
22:6	3.8–10.6	4.8–7.8	—	—	—
24:1	—	0.6–1.3	—	—	—

[a] Source: Ref. 41.
[b] Source: Ref. 11.
[c] Source: Ref. 42.

Edible Fats and Oils with Special Properties

Melting Behavior. Many fats and oils are produced and valued because of their particular properties such as melting behavior, flavor, flavor stability, nutritional advantage, or particular industrial use. Cocoa butter, for example, is valued because its fairly sharp melting point (near human body temperature) makes it ideal in the manufacture of various confections. This melting behavior depends not only on the fatty acid composition of cocoa butter but also on its glyceride structure. Its relatively high price has led to numerous attempts to duplicate its properties with less expensive raw materials (1,2).

TABLE 3.3 Typical Fatty Acid Composition of Some Plant Industrial Oils

Fatty acid	Castor	Crambe	Linseed	Rapeseed	Tall	Tung
Reference	(43)	(44)	(45)	(38)	(46)	(47)
14:0						
16:0	1.3	8	6.0	3.0	6.5	3.1
18:0	1.0		4.0	0.8	2.0	2.1
16:1	—	—	—	—	1.0	
18:1	4.2	17	19.7	13.1	40.0	11.2
18:2	4.5	9	15.3	14.1	39.0	14.6
18:3	0.6	6	55.0	9.7	0.5	
18:1 OH	88.3					
18:3 conj						69.0
20:1		5		7.4		
22:1		55		50.7		

Cottonseed oil is valued in some hydrogenated fats because of its palmitate content, which is ~20%. The major unsaturated fatty acids in most other vegetable oils have chain lengths of 18 carbons. This can lead to the undesirable β-crystal form in hydrogenated products. Cottonseed, with its relatively high palmitate content, gives rise to the more desirable β′-crystal form in hydrogenated products (3).

TABLE 3.4 Fatty Acid Composition of Some Oils Variations Produced by Breeding

	16:0	18:0	18:1	18:2	18:3	Reference
Soybean						
Lo Sat	3.8	3.2	29.2	54.3	9.5	(48)
Lo 18:3	11.2	6.4	37.6	42.2	1.9	(49)
High 16:0	30.4	5.2	10.1	42.6	11.7	(50)
High 18:0	8.3	29.9	21.9	34.9	5.1	(51)
High Sat	23.6	24.1	8.0	37.4	6.9	(51)
Canola						
Low 18:3	3.9	2.1	63.0	25.0	1.6	(52)
High 18:1	3.7	2.3	74.8	13.0	2.4	(52)
Sunflower						
High 18:1	3.4	4.3	83.2	6.4	—	(53)
Safflower						
High 18:1	4.3	1.4	74.1	19.7	—	(38)
Linseed						
Low 18:3	6.2	3.6	13.9	73.0	2.0	(52)
Corn						
High 18:1	12.6		64.5	22.1	0.6	(54)
Peanut						
High 18:1[a]	15.4		49.3	2.9	—	(55)

[a] Contains <2% of several other long-chain acids.

TABLE 3.5 Disappearance of Various Fats and Oils in the World[a]

	Year					
	93/94	94/95	95/96	96/97	97/98	
	(10^6 metric ton)					Major Producing Areas
Butter[b]	5.88	5.80	5.64	5.75	5.84	EU-15,[c] FSU,[c] India
Castor	0.46	0.47	0.48	0.49	0.49	India, Brazil, China, FSU
Coconut	3.06	3.39	3.16	3.20	3.33	Philippines, Indonesia, India
Corn	1.69	1.76	1.87	1.88	1.94	U.S.A., EU-15
Cottonseed	3.50	3.77	4.05	4.04	3.96	China, U.S.A, FSU, India, Pakistan
Fish	1.26	1.41	1.41	1.32	1.10	Peru, Chile, EU-15, Japan
Lard	5.56	5.77	5.99	6.13	6.38	China, EU-15, FSU
Linseed	0.62	0.67	0.66	0.67	0.67	EU-15, Argentina, India, U.S.A.
Olive	2.04	2.00	1.84	2.21	2.37	EU-15, Tunisia, Turkey
Palm	14.47	14.68	15.52	17.14	17.88	Malaysia, Indonesia, Nigeria
Palm kernel	1.92	1.88	1.99	2.12	2.20	Malaysia, Indonesia, Nigeria
Peanut	4.22	4.32	4.24	4.29	4.10	India, China, U.S.A., Senegal
Rapeseed	9.54	10.34	11.68	11.51	12.13	EU-15, China, India Canada, Japan
Sesame	0.68	0.70	0.75	0.76	0.78	China, India, Sudan, Japan
Soybean	18.43	19.20	19.99	21.13	22.58	U.S.A., Brazil, EU-15, Argentina, China
Sunflower	7.48	8.28	8.97	9.51	9.07	EU-15, Argentina, FSU, India, Turkey
Tallow	7.47	7.44	7.53	7.38	7.50	U.S.A., EU-15, FSU, Australia
Tung	0.03	0.05	0.04	0.03	0.04	China

[a] Source: Ref. 56.
[b] Fat basis, butter is 80% fat
[c] Abbreviations: EU-15, European Union; FSU, Former Soviet Union

Of the animal fats, lard is valued because its unusual glyceride structure gives it an advantage in certain shortening uses (4). Butter also is valued for its melting behavior, although many consider it too hard when used as a spread; however, its melting properties are the basis for a number of baked products. The unique flavor of butter is likely more responsible for its popularity than its melting behavior. This flavor is complex, but it is caused in part by the presence of short-chain acyl groups and also by small amounts of hydroxy- and keto-esters, which can give rise to lactones and methyl ketones (5).

Flavor. Oils that are prized for their flavor properties include olive (6), peanut (7), coconut, palm kernel (8), and sesame. The flavors of these oils often are important in the dishes that are native to their producing regions. Olive, peanut, and sesame have unique flavors that reflect the plants from which they arise. They often are sold with minimal processing to preserve these flavors. Coconut and palm kernel both contain short-chain acyl groups that are flavorful when present as free fatty acids.

Stability. The flavor stability of fats and oils also is an important consideration in their utilization. Unsaturated fatty acids are subject to oxidation, which can give rise to flavor compounds. In general, the more double bonds a fatty acid has, the more prone it is to oxidation (9). Although these oxidized flavors are important in some foods, many fats and oils are particularly valued for their stability. Thus, coconut and palm kernel are valuable because they are quite stable to oxidation and yet are fluid at room temperature (8). They owe their stability to their composition, i.e., they are composed mainly of saturates and have relatively few acyl groups with multiple double bonds. They are able to maintain their fluidity in spite of this high degree of saturation because many of the saturates have short chains. For these reasons, these oils are often used in foods that require a long shelf life.

Fats with large amounts of long-chain saturates and relatively little unsaturate content such as tallow, lard, and palm oil (10) are also quite stable, but their high melting point and texture may limit them in various uses. They often are valued particularly as heat-transfer media in frying operations (11). Unsaturated oils can be hydrogenated to increase their stability and make them comparable to the more saturated fats.

Olive oil also is valued for its stability, which is caused by its relatively small amount of polyunsaturates (6,12). Its fluidity is due to its high percentage of monounsaturated oleate. It is not subject to the off-flavors on hydrolysis that may cause trouble with coconut and palm kernel oil with their short-chain acyl groups. The value of olive oil has led to attempts to reproduce its stability in other oilseeds by varieties that are rich in oleate (Table 3.4).

Corn, sunflower, peanut, cottonseed, and safflower oils contain significant amounts of linoleate and are regarded as being less stable than olive and other high-oleate oils. Most of these high-linoleate oils require extensive processing and protection from further oxidation while in trade channels. Sesame oil, which falls into the same category on the basis of its fatty acid composition, is considered extraordinarily stable because of a unique natural antioxidant that it contains, namely, sesaminol (13).

Oils such as soybean and low-erucic rapeseed oil that contain appreciable amounts of linolenate are regarded as significantly less stable than those that contain little linolenate (14,15). Sometimes these oils have been hydrogenated selectively in an attempt to reduce the amount of linolenate that they contain. Linseed oil, which contains large amounts of linolenate, is usually not regarded as an edible oil because of its flavor instability, although low-linolenate varieties are now available (Table 3.4). Fish oils that contain appreciable amounts of acyl groups with four, five and six double bonds are particularly unstable and subject to the development of off-flavors (16).

Nutritive Value. Nutritional considerations have played an important role in determining the value and utilization of fats and oils in recent years. The erucic acid found in rapeseed oil was shown to have deleterious consequences when used as a major constituent of the diets of animals, and several countries require that rapeseed oil for human consumption have a low concentration of erucic acid (17,18).

The consumption of large amounts of saturated fatty acids and cholesterol-containing animal fats has been regarded as predisposing many people to artery disease; numerous pronouncements by health authorities have counseled against the consumption of large amounts of these fats. The public also has been advised to decrease the proportion of total energy coming from fat to reduce risks from cancer as well as artery disease (19,20). This advice has depressed the utilization of tallow, lard, milk fat, palm oil, coconut oil, palm kernel oil, and hydrogenated oils in many products. However, this advice also has depressed the price of these fats and oils, thus making them more likely to be used in prepared foods and items that the public is less likely to monitor for saturated fatty acids and cholesterol.

Peanut oil was identified as especially atherogenic (21), but recently this has been attributed to incomplete removal of lectins in the oil (22). The negative claims about peanut oil seemed not to have affected its consumption and price to any great degree, possibly because the general public never became very aware of these claims.

When animals consume linoleate and linolenate, they convert them into longer-chain fatty acids with additional double bonds. Animals can introduce additional double bonds near the carboxyl end of the fatty acid chain, but they cannot alter the configuration near the methyl end of the chain. Thus, linoleate and linolenate give rise to two separate families of fatty acids in animals. Some of these polyunsaturated fatty acids are converted to the prostaglandin hormones; the hormones arising from the two families of fatty acids have different physiologic effects. This new understanding, in combined with dietary analyses, has somewhat revived the economic fortunes of oils containing linolenate acid and eicosapentaenoate (23). The latter, which is chiefly available to humans through fish, suffers from such flavor instability that its incorporation into food with appealing flavor is a formidable technological problem. It is less clear to what extent linolenic acid–containing oils such as soy and low-erucic rapeseed will serve to meet these needs or what levels of consumption of these oils will be most advantageous.

The consumption of fats and oils tends to rise with national income up to a point, but among the relatively rich nations, there is a great variation in the amounts of fats and oils consumed (19). In the United States, per capita consumption of fats and oils, which has been rising for many years, appears to have been declining since 1993 (Fig. 3.1). This may be a result of the nutritional advice to which Americans have been subjected. There also has been a proliferation of foods with minimally hydrogenated fat and reduced fat content. There has been increased interest in the production of foods with reduced-calorie and fat substitutes (24,25).

Industrial Uses of Fats and Oils

Some fats and oils are valued for their properties in nonfood products. Linseed oil is used as a drying oil in paints and protective coatings (26). Its high content of linolenic acid makes it dry quickly and form a tough, flexible film. Safflower also makes an excellent drying oil. Castor oil contains large amounts of ricinoleate,

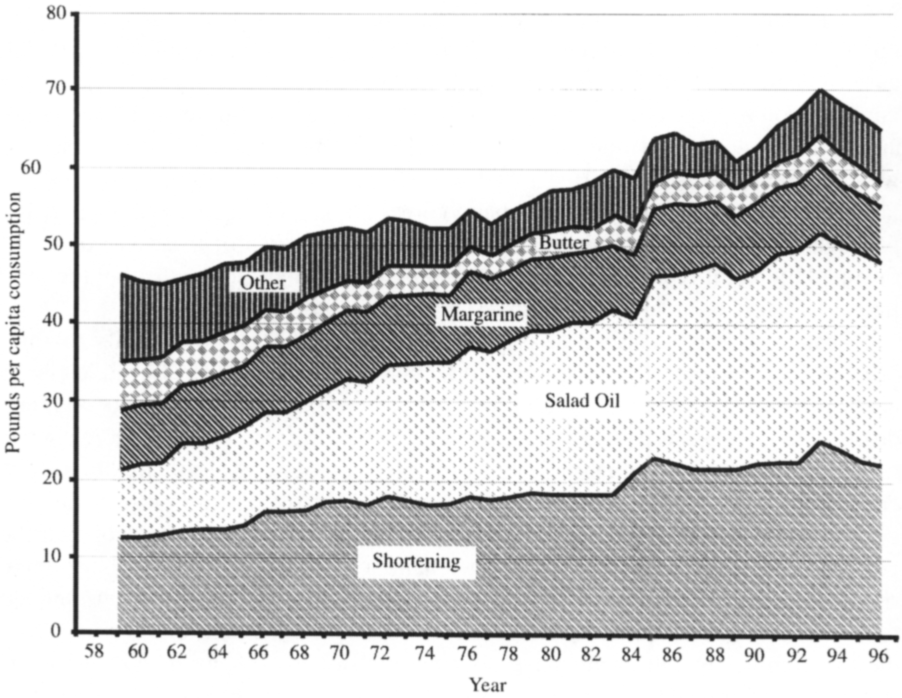

Fig. 3.1. Per capita consumption by year of various fats and oils products in the United States. *Source*: Ref. 27.

which contains a hydroxy group. The well-known use of castor oil as a laxative is a very minor use; most of it goes into drying oils. Ricinoleate can be dehydrated to form a conjugated diene that has desirable drying properties for special uses. Ricinoleic acid also is a raw material in the production of heptanal and undecylenic acid. Tung oil has a unique fatty acid, the conjugated triene eleostearate, which has special uses in drying oils. Castor and tung oils are relatively expensive because of high production costs (Table 3.6). The castor bean contains allergens and toxic components that make its production especially difficult. Tung oil is produced from trees with a rather restricted growth range. High-erucic rapeseed oil has special uses in lubricants (26). Erucic acid can be oxidized at its double bond to produce a dicarboxylic acid, brassylic acid, which can be made into a type of nylon that is particularly tough and suitable for making gears.

Oils such as coconut and palm kernel with their short-chain fatty acids have special uses in the detergent and surfactant fields, especially because of the foaming properties of these fatty acids (26). Aside from the special fats and oils that go into industrial uses, there is a more general demand for fats and oils in the feed, protective coating, and detergent industries (26). Considerable amounts of fats and oils are converted to free fatty acids to meet a multitude of industrial needs. In the United

TABLE 3.6 Approximate Prices of Several Fats and Oils in \$/Metric Ton[a]

	1992	1993	1994	1995	1996	1997	Average 1992–1997
Butter[b]	1830	1631	1477	1675	2205	—	1764
Castor	776	820	972	992	919	915	899
Coconut	688	556	670	794	940	899	758
Corn	529	481	602	586	584	547	555
Cottonseed	472	573	597	591	571	584	564
Fish oil	373	362	325	457	445	548	427
Lard	505	456	552	642	580	575	561
Linseed	677	699	716	772	818	799	747
Palm	478	467	619	728	586	601	580
Palm kernel	571	437	629	677	728	915	899
Peanut	803	1090	955	908	960	990	951
Rapeseed	420	466	616	614	555	565	563
Safflower	1322	1543	1301	1301	1301	1301	1344
Soybean	425	500	615	591	525	513	528
Sunflower	505	591	686	637	544	517	580
Tallow	317	328	384	423	443	457	392
Tung	2355	2612	1678	1300	1396	2238	1560

[a] Source: Ref. 27.
[b] Butter is 80% fat.

States, the amount of fats and oils used in feed and industrial products has ranged from 25 to 30% of total use in recent years (27). These needs tend to be met by the least expensive fat or oil that will produce the properties required. The least expensive sources for free fatty acids are tall oil, a by-product of the paper industry, and those resulting from the alkali refining of edible fats and oils.

Generalized Demand for Fats and Oils

Palm, soybean, sunflower, and rapeseed oils, which are the products of the tropic (palm), temperate (soybean and sunflower), and high latitudes (rapeseed) tend to be the crops that meet generalized demands for oils, taking up whatever market is left from the specialty and by-product fats and oils. The increasing per capita consumption of fats and oils (19) has caused a massive increase in the production of these oils in recent years (Fig. 3.2). Each of these oils has particular advantages. Palm oil is produced with great efficiency in yield per acre compared with other oilseed crops (28). In addition to oil, soybeans produce an equally valuable high-protein meal. The animal feed industry of the world has provided an almost limitless sink for this meal. Other vegetable oils produce meals of some value in animal feeds, but none comes close to rivaling soybean meal in protein quantity and nutritive value. Rape and sunflower are among the most valuable crops that can be produced in particular geographic regions.

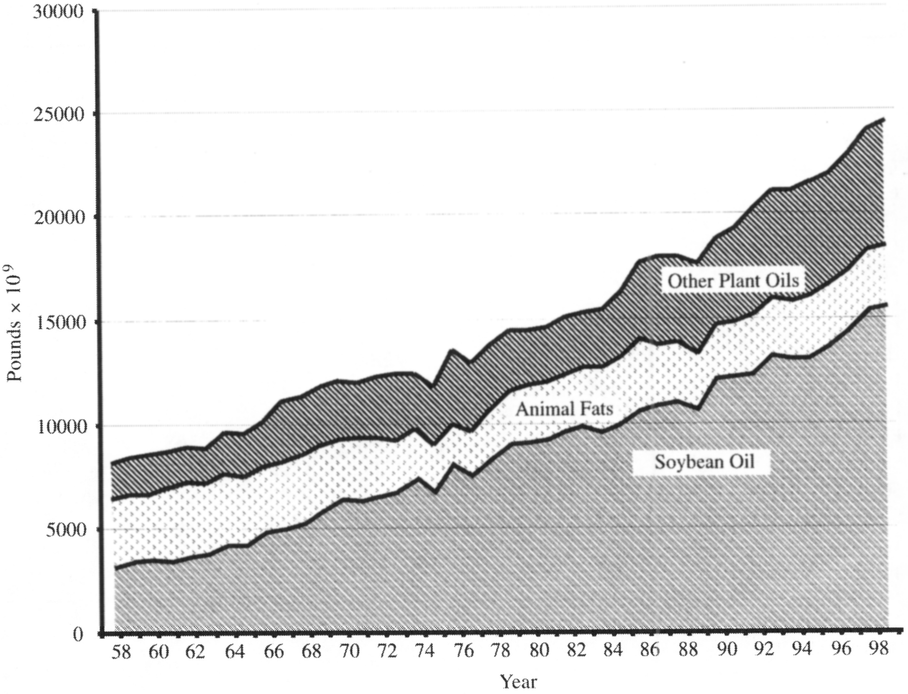

Fig. 3.2. Consumption by year of various fats and oils in the United States. *Source*: Ref. 27.

It is significant that palm oil is the product of a tree, whereas soybean, sunflower, and rapeseed are annual plants. Oil palms take several years of growth to come into good production; once producing, they keep producing for several years regardless of what happens to the price of fats and oils. Growers of soybeans and rape can respond more readily to short-term trends and predictions about oil markets. Other tree crops such as olive, tung, and cocoa also have the same inability to alter production volume rapidly.

Typical Prices of Fats and Oils

The prices of fats and oils (Table 3.6) reflect the advantages and disadvantages in utilization that have been discussed. The price of palm, soybean, and rape varies with the general world oil supply. Sunflower, corn, peanut, and cottonseed are slightly more expensive than soybean because of their increased stability and special advantages in flavor and in hydrogenated products. Coconut and palm kernel are more valuable than soybean oil because of their special stability and industrial uses.

Of the animal fats, butter is the most valued for its special flavor properties. Lard is more valuable than tallow because of its use as a shortening. The values of all of these animal fats are depressed because of their content of saturated fatty acids and cholesterol. Fish oil is the cheapest oil because of its flavor instability.

Consumption Trends in the United States

Per capita consumption of fats and oils in the United States increased during the last 50 years until 1993. Since then, the per capita consumption has shown a modest decline (Fig. 3.1). Soybean oil has met most of the increasing generalized demand for oil (Fig. 3.2) and, in the form of hydrogenated soybean oil, has met much of the demand for shortening and margarine as well. The consumption of animal fats has been fairly steady during this period, and the consumption of vegetable oils other than soybean has increase slightly during the last 15 years. The dominance of soybean oil is being challenged by palm and low-erucic rapeseed oil, but in the United States, soybean oil has maintained its position to date. The trend to consume more of our total fats and oils in the form of unsaturated salad and cooking oils was well established long before public bodies began to urge us to eat less saturated fat in 1977 (19,20).

Alternative Fats and Oils

There are numerous oilseed plants that might be used to meet the world demand for edible fats and oils as well as demands of special industrial uses (29). In addition, plant breeders have demonstrated that the fatty acid composition of many fats and oils can be varied over wide ranges, although sometimes with detriment to the seed or oil yield (Table 3.4). Fatty acids foreign to an oilseed species have been introduced by molecular genetics (30), but achieving significant percentages of such exotic fatty acids in the oil has often been quite difficult.

There are not many examples of the successful introduction of new vegetable oils in recent years except for that of low-erucic rapeseed oil. This was accomplished for nutritional reasons by governmental fiat rather than for economic reasons. If we were to go back to the beginning of the 20th century, however, we would find that corn, cottonseed, palm, peanut, soybean, and sunflower oils either were introduced, or their geographical range and volume of consumption expanded greatly in the intervening years. The introduction of a new species is difficult today because oil production requires considerable scale for efficiency. Markets must be developed at the same time that processing plants are built, and large areas of land must be devoted to a new crop. Before this, a number of years of variety development usually are required for a wild species to hope to compete with an established crop, and harvesting machinery might have to be adapted. The simultaneous accomplishment of all these things creates a formidable barrier to the introduction of new oilseed varieties. It was easier to introduce new oil seeds commercially earlier in the century when smaller-scale processing was competitive, and a smaller array of competitive fats and oils was available.

The prospects are more promising for the alteration of the oil composition of already established crops or conversion of established crop species to oilseed crops. Thus, we have the development of the varieties of Table 3.4, some of which are in commercial production. Corn and oat varieties with high oil contents have been identified (1). The marketing of even established crops that have altered oil compositions or oil percentages presents difficulties. The marketing channels and processing plants usually are designed for handling only one variety of an oilseed commodity. For a special variety of a crop to be an economic success, it must have enough additional value to bear the costs of encouraging its production and keeping it segregated in trade channels. Often the economic advantage that will accrue from the change is difficult to measure exactly; thus, someone must be willing to bear the risk of introducing a new variety on a scale that is sufficient to test the market.

Thus, we can see why various fats and oils are in production, what factors determine their relative value, and the barriers to the introduction of rival sources.

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Chapter 4

Nutritional and Health Aspects of Dietary Lipids

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Introduction

Cardiovascular disease and cancer are presently the two leading causes of death in the United States. Although the incidence of coronary heart disease (CHD) has decreased consistently for many years, it still accounts for the majority of deaths in the United States. During this same time period, the incidence of cancer has been increasing. Both CHD and cancer have been classified as multifactorial diseases. Coronary heart disease has traditionally been shown to be affected by smoking, hypertension, and abnormal lipid metabolism. Common advice to CHD patients has been to stop smoking, control blood pressure, and consume foods that contain less cholesterol and saturated fat. Cancer has also been associated traditionally with a variety of factors, including smoking and dietary fat intake. During the past three decades, a great deal of new information has been gained about the causes of these diseases; therefore, many professionals in the field have radically modified dietary advice.

Dietary Lipids and Coronary Heart Disease

Early emphasis regarding diet and CHD was placed on the role dietary cholesterol and saturated fatty acids played in lesion formation; however, this focus has shifted to other mechanisms over the past 25 years. More recent theories about the causes of CHD have emphasized alternative approaches to lesion formation that involve oxidized cholesterol, as well as other oxidative by-products and abnormal serum homocysteine concentrations. Interaction between damaged cardiovascular tissue and platelets as well as between damaged endothelial cells and cardiovascular musculature have also been proposed to play a key role in CHD. During the past decade, the migration of bacteria (*Chlamydia pneumoniae*, *Helicobacter pylori* and *Porphyromonas gingivalis*), and viruses (Cytomegalovirus) into the coronary arteries from other parts of the body has been identified as a possible cause of CHD (1). Cancer has also been scrutinized and reevaluated to elucidate the effect of diet on its initiation, promotion, and progression.

Dietary lipids have frequently been analyzed to determine their role in disease development. The lipids most often mentioned in this regard include sterols (i.e., cholesterol) and fatty acids (saturated and unsaturated). Although a certain amount of cholesterol and fatty acids are important for maintenance of good health, controversy surrounds these compounds because it has been difficult to determine proper levels of intake and, in the case of fatty acids, the types that can be consumed safely. Current research emphasis has been placed on specific fatty acid families (n-3 and n-6 fatty acids, n-9 fatty acids, conjugated n-6 fatty acids, and *trans* fatty acids) as well as cholesterol and fatty acid containing lipoproteins [i.e., lipoprotein (a)] to establish which dietary lipids induce disease and which prevent disease.

Cholesterol

Until the mid 1970s, it was thought that both patients suffering from CHD and the American population as a whole would benefit from The Prudent Diet, i.e., a diet low in cholesterol and saturated fatty acids with increased amounts of polyunsaturated fatty acids (PUFA). This type of diet had been shown to decrease cholesterol concentrations in the blood and was therefore thought to play a role in decreasing the initiation, development, and progression of cardiovascular lesions. Two fundamental problems have been shown to exist with the hypothesis that the Prudent Diet can help prevent or cure CHD. First, the American Heart Association (AHA) National Health and Examination surveys indicate that there has been a steady decline in CHD-related deaths in America since 1965, despite relatively stable serum cholesterol values during the same time frame (2). Second, data from the National Health and Nutrition Examination Survey (NHANES) have indicated the existence of an inverse relationship between intake of dairy products that contain significant amounts of cholesterol (e.g., whole milk or cheese) and CHD (3). Longitudinal studies of Seventh-Day Adventists also showed no difference in relative risk of CHD when subjects consumed cheese and dairy products with either high or low frequency (4–6). A number of studies have also indicated that alterations in the amounts of dietary cholesterol cause only marginal changes in serum cholesterol concentrations and have little, if any effect on mortality when associated variables are taken into consideration (7,8). Other studies (9,10) have shown that substantial genetic variability exists regarding individual responsiveness to the lowering of serum cholesterol *via* dietary intervention.

Clearly, a great deal of confusion remains concerning exactly how dietary cholesterol affects serum cholesterol and CHD in most Americans. Taylor *et al.* (11) analyzed the benefits of dietary cholesterol reduction programs and concluded "for persons aged 20–60 y who are at low risk, we calculate a gain in life expectancy of 3 d to 3 mo from a lifelong program of cholesterol reduction. For persons who are at high risk, the calculated gain ranges from 18 d to 12 mo." Most recently, however, a meta-analysis of Step I and II diets indicated that lipoproteins and lipid profiles may be improved with dietary intervention, although the degree of improvement should be balanced against dietary compliance (12).

Cholesterol Oxidation Products (COP)

Cholesterol oxidation products (COP) are found in dietary ingredients and can be produced in the body. Food products contain varying levels of these compounds, depending on processing temperature, heating time, and storage conditions.

Concentrations of prooxidants and reactive oxygen as well as the PUFA content can also alter both the type and quantities of COP found in food (13).

Research has shown that not all COP have the same atherogenicity. Oxidized low-density lipoprotein (LDL) cholesterol, a metabolic COP, has been proposed to have its negative effect primarily in this oxidized form. Oxidized LDL cholesterol has been shown to be atherogenic in both experimental animals and humans (14–17). Macrophages have been shown to ingest oxidized LDL cholesterol which can then affect cell membrane properties as well as levels of free intracellular calcium. These macrophages will eventually develop into foam cells, which in turn play a key role in the development of cardiovascular lesions by inducing inappropriate cell replication (18). Other cholesterol oxidation by-products (i.e., 7β-hydroxycholesterol) have also been shown to play a major role in the progression of atherosclerosis. Cholesterol oxidation products have a more powerful negative effect than either smoking or lipid oxidation (as indicated by the formation of LDL thiobarbituric acid-reactive substances) (19). Ghee, a clarified butter product consumed by immigrants from India, has been shown to be high in COP and to be correlated with the development of atherosclerotic lesions (20).

Treatment of problems related to cholesterol oxidation includes the use of antioxidants. Animal studies have shown that butylated hydroxytoluene (BHT) and other antioxidants such as probucol (a fat replacement product) lower both plasma and aortic COP concentrations. Human studies (21) indicate that α-tocopherol and carotenoids decrease LDL oxidation. Human arterial cells, however, do not seem to be protected by vitamin E from COP-induced toxicity (22).

In general, antioxidant nutrients (e.g. vitamin C, β-carotene, and vitamin E) seem to prevent LDL cholesterol oxidation and the formation of COP. Epidemiologic studies indicate that diets that are high in fruits, vegetables, or antioxidant vitamins decrease both mortality and morbidity (23). At present, the AHA recommends that people obtain antioxidants from foods so as to decrease any risk from high doses of vitamins.

Lipoproteins

At present, a significant portion of the cholesterol-related CHD research has focused on the methods of cholesterol transport in the body. It has been shown that cholesterol in peripheral tissues is bound and transported to the liver for possible metabolism and removal by high-density lipoproteins (HDL), whereas LDL carry cholesterol to the peripheral tissues. Increased concentrations of LDL cholesterol have been associated with increased mortality from CHD (24). Those subjects who have LDL of greater density (pattern A) have increased CHD compared with those who have LDL that is less dense (pattern B). In contrast, higher concentrations of HDL cholesterol have been associated with a reduction in CHD (25). Some confusion remains concerning the role of serum lipoproteins in the development of CHD.

Lipoprotein (a). Plasma lipoprotein [Lp(a)] concentrations are determined primarily by genetic factors that regulate its production by the liver. Lp(a) is a modified form of LDL cholesterol that binds to the endothelium, resulting in cholesterol accumulation. Berg *et al.* (26) reported in early work that people with CHD had a much higher frequency of increased concentrations of Lp(a), and more recent studies have confirmed this observation. For all races, subjects with CHD have higher concentrations of Lp(a) than those with little on no CHD. Patients with severe CHD have Lp(a) concentrations that are twice as high as concentrations found in normal subjects (27). In general, serum Lp(a) concentrations are thought to be insensitive to dietary change; however, research conducted by Herrmann *et al.* (28) has indicated that dietary n-3 fatty acids may have a lowering effect on the compound. Some studies have shown that *trans* fatty acids can raise Lp(a), whereas other saturated fats may lower Lp(a) (29,30). Other studies (31) have shown that estrogen also lowers Lp(a) by as much as 50% in postmenopausal women. The effect of dietary phytoestrogens on Lp(a) has not been studied to date. Specific therapy to lower the level of Lp(a) may be indicated for patients with CHD; however, new drugs that have potent effects on Lp(a) concentrations will have to be developed.

Unsaturated Fatty Acids

Classification and Sources

Unsaturated fatty acids are often classified on the basis of the position of the first double bond in relation to the methyl (CH_3) end that is also termed the omega (ω) end. Those fatty acids in which the first double bond occurs between the third and fourth carbon atoms are termed n-3 fatty acids, whereas those fatty acids that have a double bond between the sixth and seventh carbon atoms are termed n-6 fatty acids. The naming sequence can be extended to include the n-9 fatty acids, which have a double bond between the ninth and tenth carbon atoms. Table 4.1 provides the classification and dietary sources of these families of unsaturated fatty acids.

The n-3 and n-6 Polyunsaturated Fats

Early epidemiologic studies in the 1960s, 1970s, and 1980s involving low cholesterol/high PUFA diets and CHD were inconclusive (32). Recent efforts have involved the study of specific dietary fats, which are not normally consumed in large quantities by Americans. A particular family of PUFA, which has drawn attention, is the n-3 family. Fatty acids in this family are found in chloroplasts; consequently, they are obtained *via* the ingestion of chloroplast-containing plant products or tissue from animals that eat these chloroplasts (e.g., certain fish, other marine life, or deer). Populations that consume increased amounts of these fats have been shown to have a much lower incidence of CHD than do Western populations that consume primarily n-6 fatty acids. A number of recent studies have shown inverse associations between fish intake and CHD.

Greenland Eskimos eat large quantities of marine life and have lower concentrations of LDL and very-low-density lipoprotein (VLDL) cholesterol, and higher

TABLE 4.1 Dietary Sources of Unsaturated Fatty Acids

Family	Fatty acid	Number of carbon atoms	Number of double bonds	Food source
n-3	Linolenic (18:3 3)[a]	18	3	Linseed oil, canola oil, and soybean oil
	Eicosapentaenoic (20:5 3)	20	5	Fish oils, some animal tissue fats
	Docosahexaenoic (22:6 3)	22	6	Fish oils, some animal tissue fats
n-6	Linoleic (18:2 6)	18	2	Safflower oil, sunflower oil, cottonseed oil, corn oil, many seed oils
	Arachidonic (20:4 6)	20	4	Peanut oil, animal tissue fat
n-9	Oleic (18:1 9)	18	1	Olive oil, some animal fats, and plant oils

[a] (18:3 3) means 18 carbon atoms, 3 double bonds, the first of which is located 3 carbons from the omega end.

concentrations of HDL cholesterol than Europeans. These Eskimos also have a lower incidence of atherosclerosis (33,34). Shahar *et al.* (35) showed that even limited fish intake can have a beneficial effect on plasma triglycerides, platelets, blood viscosity, and inflammation. Numerous other researchers (36,37) have confirmed these clinically significant results. For this reason, numerous studies have been conducted to determine the effect of marine fatty acids on cardiovascular health. Phillipson *et al.* (38) fed a diet containing fish oil to hyperlipidemic patients. This diet was shown to lead to a 40% reduction in total blood cholesterol. Other studies (39) have indicated that fish oils may minimize the possible cholesterol-raising effect of dietary cholesterol. Several studies (40,41) have also shown that dietary fish oil can also help reduce VLDL and LDL concentrations. This change, however, seems to be concentration dependent, with low concentrations of fish oil leading to LDL increases and higher concentrations leading to LDL decreases. Sanders *et al.* (42) proposed that moderate intakes of fish oil are not useful for treatment of hypercholesterolemia, but can be used as an effective treatment for hypertriglyceridemia resulting from increased VLDL synthesis. Studies of fish oil effects on HDL cholesterol concentrations are inconsistent. Some studies show that HDL cholesterol concentrations do not change with fish oil consumption, whereas others show that they increase (38).

The n-3 fatty acids may play a significant role in LDL particle size. Sorensen *et al.* (43) fed healthy volunteers sunflower oil margarine for 3 wk followed by 4 wk of sunflower/fish oil/vitamin E margarine. Little effect was noted on serum lipoprotein and lipid profiles, but a significant change occurred after fish oil consumption. There was an increase in cholesterol and cholesterol ester constituents of LDL, making the particles larger and less dense. This is of significance because the smallest LDL particles are more susceptible to oxidation and have been associated with an increase in myocardial infarction (44–46).

Dietary fish oil also seems to have an influence on CHD *via* its effect on thrombus formation. The involvement of thrombosis in the initiation of CHD was a neglected topic for many years. In a study in which mackerel was fed to seven men for a 6-d period, the fatty acid composition of their blood became very similar to that found in Greenland Eskimos, and both platelet aggregation and thromboxane synthesis were reduced (47). Because thromboxanes cause platelets to aggregate, whereas prostacyclins have the reverse effect, it has been proposed that diet may cause a shift in the ratio of thromboxane to prostacyclin production and that these changes can increase or lessen the likelihood of developing thrombosis. Renaud *et al.* (48) reported on human studies in which dietary linolenic acid reduced platelet aggregation, clotting, and thrombus formation. In a recent review by Simopoulos (49), it was pointed out that the risk of thrombosis increases as dietary saturated fat increases.

The n-3 fatty acids affect other cardiovascular hemodynamic properties. For example, the dietary intake of n-3 fats has been shown to decrease blood pressure and thereby affect CHD (50,51). A recent meta-analysis study (52) concluded that marine oils in relatively high doses decreased blood pressure in subjects with cardiovascular disease or hypertension. It has been proposed that this effect is caused by an increase in the activity of the renin-angiotensin system (53). Normotensive subjects do not seem to have a blood pressure change with increased intake of n-3 fat. Grimsgaard *et al.* (54) showed that dietary docosahexaenoic acid (DHA) and eicosapentaenoic acid (EPA) influenced cardiovascular hemodynamics *via* their effect on heart rate, and subsequent effect on left ventricular function, thereby providing cumulative cardioprotective effects.

Specific unsaturated n-3 fatty acids that are commonly found in plant products (i.e., α-linolenic acid) have proven to be protective against ischemic heart disease (55). α-Linolenic acid is a precursor to long-chain n-3 fatty acids and has been used as a substitute for fish oils. Dietary linoleic acid affects both the action and metabolism of α-linolenic acid (56).

Dietary n-6 fatty acids, including both linoleic and arachidonic acids, have been of interest for many years, primarily because of their ability to lower serum cholesterol concentration compared with saturated fats (57). More recently, attitudes about these fatty acids have been in flux in relation to CHD because linoleic acid has been shown to lower LDL cholesterol and, unfortunately, HDL cholesterol (58,59). These effects seem to be the strongest when the intake of PUFA exceeds 20% of the energy in the diet (60). Other studies have shown that most populations with low CHD rates consume relatively low levels of linoleic acid. At present, there is considerable interest in the scientific community regarding a possible antagonistic effect between the n-3 and n-6 families of fats and their roles in CHD.

Monounsaturated Fats

Early work on dietary fats and disease has indicated that certain populations seemed to consume rather large quantities of fat and yet do not exhibit elevated rates of CHD

(61). Middle-aged men in Crete exhibit a low incidence of CHD, considering their serum cholesterol concentrations. Analysis of the effects of risk factors such as smoking and high blood pressure could not account for this difference. It was proposed that high intakes of monounsaturated fats may have been the causative factor in this anomaly. A variety of studies have supported this hypothesis. Early work by a variety of researchers has suggested that monounsaturated fats (e.g., oleic acid) lower serum cholesterol concentrations. This finding was confirmed in a study by Mattson *et al.* (62) in which diets containing monounsaturated fats (safflower oil high in oleic acid), polyunsaturated fats (safflower oil high in linoleic acid), or saturated fats (palm oil high in palmitic acid) were provided to 20 normotriglyceridemic subjects. Dietary fat provided 40% of the total energy intake on a daily basis. Normotriglyceridemic patients consuming the diet containing either monounsaturated fats or polyunsaturated fats exhibited significant decreases in plasma LDL cholesterol concentrations. Subjects consuming the polyunsaturated fat diet also showed a decrease in HDL cholesterol compared with those fed the monounsaturated fat diet. Grundy *et al.* (63) provided additional support for the hypothesis that dietary monounsaturated fatty acids can effectively reduce LDL cholesterol. In a metabolic study, liquid formula diets containing high concentrations of monounsaturated-rich safflower oil or high levels of carbohydrates in the form of glucose were provided to 11 hypercholesterolemic subjects. It was concluded that diets high in monounsaturated fat were as effective in lowering plasma cholesterol as low-fat, high-carbohydrate diets. The population given low-fat, high-carbohydrate diets, unfortunately, exhibited decreased concentrations of HDL cholesterol and increased triglyceride concentrations, whereas the group receiving monounsaturated fats exhibited no change in concentrations of triglyceride or HDL cholesterol.

Baggio *et al.* (64) investigated the effect of olive oil–rich diets on serum lipoproteins. Eleven volunteers were involved in this metabolic study. A significant decrease occurred in the concentrations of serum cholesterol (–9.5%), LDL cholesterol (–12.2%), and total triglycerides (–25.5%) in subjects fed this diet. Total HDL cholesterol and HDL cholesterol subfractions remained unchanged. It was concluded that olive oil was a natural fat that could be used as a valid dietary alternative to PUFA for the control of plasma and LDL cholesterol concentrations.

Not all studies have shown dietary monounsaturated fat in such a positive light with respect to cardiovascular disease. Becker *et al.* (65) fed normolipidemic men cholesterol-free diets containing monounsaturated fats, n-6 polyunsaturated fats, or saturated fats. The group of subjects who received the unsaturated fat diets exhibited decreased concentrations of LDL cholesterol. No change in HDL cholesterol concentration was noted in any dietary group.

The mechanisms underlying the action of n-9 fatty acids on the cardiovascular system are unknown. However, Spady *et al.* (66) suggested that these dietary fatty acids modulate LDL receptor activity and may decrease cholesterol concentrations *via* an enhanced receptor-mediated LDL catabolism.

Conjugated Linoleic Acid

Conjugated linoleic acids (CLA) are naturally occurring isomers of linoleic acid (18:2) that have conjugated double bonds at positions 9 and 11 or 10 and 12 and present themselves in both the *cis* and *trans* configurations (67). CLA is found in the fat products of ruminating animals. The quantities of CLA found in dairy products, such as milk, can be manipulated *via* animal feed (68). Studies done in animal models have shown mixed results concerning CLA and atherosclerosis development. In both rabbit and hamster models, CLA-supplemented diets led to marked decreases in LDL cholesterol and triglycerides (69,70). Physical dissection of aortas in both models also revealed less atherosclerotic lesion development compared with control groups fed a diet unsupplemented with CLA. Recently, Munday *et al.* (71) refuted this association of CLA supplementation and decreased atherosclerotic events. In their study, three groups of 20 mice were fed diets containing CLA, CLA + linoleic, or linoleic acid only. Serum lipid concentrations did not change significantly when the CLA-supplemented diet was fed compared with the unsupplemented diet. In addition, the CLA-supplemented diet increased the development of aortic fatty streaks compared with controls. In conclusion, the role played by CLA in atherosclerotic disease remains controversial.

Trans Fatty Acids

The major sources of *trans* fatty acids (elaidic acid) in the diet are products containing hydrogenated vegetable oils. *Trans* fatty acids (TFA) are formed during the process of partial hydrogenation in which liquid vegetable oils are converted to margarine and vegetable shortening. The highest levels of TFA are found in french fries, doughnuts, Danish pastries, and corn chips. Margarines are also important contributors to TFA intake. Research has shown that TFA raise concentrations of total serum cholesterol, triglycerides, LDL cholesterol, and Lp(a) and may lower HDL cholesterol (72,73). Zock and Katan (74) conducted a meta-analysis of studies comparing the effects of butter and margarine on blood lipids and concluded that replacement of butter by low-TFA soft margarine had a favorable effect on the blood lipoprotein profile. High-TFA margarine did not seem to confer any benefit over butter. In a recent study by Judd *et al.* (77), butter was compared with TFA-free margarine. In that study, the lipoprotein profile improved. Noakes and Clifton (78) compared their findings to those of Judd *et al.* (75) with respect to TFA effect on lipid profiles. They concluded that when TFA-free margarine is compared with butter, the TFA-free margarine may be equal to or more effective than butter in lowering LDL cholesterol, and that this could have a substantial effect on coronary artery disease reduction. Dietary TFA have been shown to have multiple unfavorable effects on lipoprotein concentrations, thus increasing the risk of CHD. On the basis of the known relation of blood lipid concentrations to risk of coronary artery disease, Ascherio and Willett (73) estimated that 30,000 premature deaths each year in the United Sstates are attributable to consumption of TFA. When reviewing epidemiologic studies, Thomas *et al.* (77) reported that values for TFA were higher in the adipose tissue of patients who died from ischemic heart disease. This study, among others, also showed a positive association between TFA and CHD.

Dietary Lipids and Cancer

Dietary lipids have also been criticized for their possible involvement in the initiation and/or development of cancer (78). High-fat diets have been associated with cancer for many years (79). Epidemiologic work has suggested a direct correlation between total fat consumption and certain cancers. Several epidemiologic studies have suggested a link between dietary fat and cancer in migrating populations who move from regions with low-fat diets to areas with high-fat diets. Other research has shown possible links between fat consumption and specific cancers, such as colon and prostate cancer (80–83). Controversy today centers on whether certain types of dietary fats are more likely to cause cancers than other types. Human and animal research seems to be in disagreement in this regard. Reddy (84), as well as other researchers, reported that the type of dietary fat is a significant factor in the development of cancer (85).

Cholesterol

In many of the studies that have associated dietary vegetable fats and cancer, low concentrations of serum cholesterol have been reported (86). Data from the Framingham study indicated that low serum cholesterol concentrations are associated with an increased incidence of death from cancer, particularly colon cancer (87). In several studies in which serum cholesterol concentrations were lowered by either clofibrate treatment or diet modification, there were increased incidences of cancer associated with decreased concentrations of serum cholesterol (88,89). In a study involving a 10,000-man cohort of Swedish residents of Malmo, 86 deaths were noted over a 5-y period (90). When the population was divided into quintiles, by serum cholesterol concentration, most of the cardiovascular deaths aggregated in the upper two quintiles, but these were more than offset by an aggregation of deaths in the lower quintiles resulting from malignancy and nonneoplastic diseases, the latter predominantly related to alcoholism. In one of the largest health-related studies to date (MRFIT Study) men (n = 361,662) were screened, and a significant excess of cancer was found in those in the lowest decile with respect to serum cholesterol values (<168 mg %) (89). A possible mechanism for the association between low concentrations of serum cholesterol and cancer has been proposed by Cruse *et al.* (91) who suggested that unabsorbed cholesterol may act as a co-carcinogen in the colon. Others have reported that cancer patients develop lymphocytes that cannot produce cholesterol and have a diminished ability to locate and kill tumor cells (92,93). In a report from the National Academy of Science (Committee on Diet, Nutrition and Cancer) it was stated that many studies relating to serum cholesterol concentrations and cancer mortality in human populations have demonstrated an inverse correlation with colon cancer among men, but the evidence is not conclusive (94). This report also states that the relationship between dietary cholesterol and cancer remains unclear. In a recent review of cholesterol and cancer, it was suggested that a "possible" link exists between dietary cholesterol and lung and pancreatic cancer (95).

Cholesterol Oxidation Products

Cholesterol oxidation products (COP) may be associated with cancer. Epidemiologic studies have linked COP to colon cancer and past work has also shown that oxidative products such as cholesterol-α-epoxide, (α-CE) have been linked to breast and prostate cancer (96–98). Preliminary work by Abplanalp *et al.* (99) indicates that oxidized LDL may interfere with estrogen conversion, thereby decreasing inactivation of active estrogen. Elevated plasma estrogen concentrations are linked to the pathogenesis of breast cancer. Cholesterol oxidation products and their link to cancer continue to be an active area of research.

Fatty Acids

Unsaturated and Saturated Fatty Acids

Controversy today centers on whether certain types of dietary fats are more likely to cause cancers than other types. A number of studies (100,101) have suggested that correlations exist between cancer incidence and various types of dietary lipids. Carroll and Khor (101) reported that increased dietary PUFA enhance the development of mammary tumors to a greater extent than saturated fat. In an animal study by Reddy *et al.* (102), colon cancer was induced by the feeding of a carcinogen. The feeding of both animal and vegetable fat enhanced tumor formation; however, vegetable oils were more potent promoters of cancer development. The report presented by the NRC (94) concluded that when intake of total fat was low, PUFA appeared to be more effective than saturated fats in enhancing tumorigenesis. With certain types of tumors (i.e., prostate), diets that are rich in saturated fatty acids have been positively correlated with tumor growth (82). In a recent study involving subjects from both North America and Europe, cancer mortality data were correlated with the consumption of animal fat (103).

The n-3 and n-6 Fatty Acids

Research has also been done in which the effects of n-3 and n-6 fatty acids on cancer formation have been investigated. Animal studies seem to indicate that n-3 fatty acids have antitumor effects (104,105), whereas n-6 fatty acids potentiate tumorigenic effects (106,107). Excess dietary linoleic acid has been proposed to be a tumor promoter (108). It has been hypothesized that excessive consumption of linoleic acid may lead to excessive levels of arachidonic acid, which in turn may encourage cancer *via* imbalances in biologically active eicosanoids. Studies have shown that n-6 fatty acids, compared with n-3 fatty acids, increase cyclooxygenase activity in colonic mucosa and tumors, and this in turn promotes tumor growth (109,110). Studies by Caygill *et al.* (111) indicate that consumption of fish and fish oil is inversely correlated with colon cancer. Dayton *et al.* (100) studied heart patients who were being treated with a diet high in PUFA and found that cancer mortality increased by 82% in male patients. The patients showed successful reductions in both serum cholesterol concentrations and fatal cardiovascular complications. However, this mortality drop was countered by an increased occurrence of both respiratory and gastrointestinal malignant neoplasms. Polyunsaturated fat may be prone to oxidation, which may play a role in carcinogenesis and increase the susceptibility of LDL particles to oxidative modification. Very recent research by Zock and Katan (74) disagrees with these studies and suggests that a high dietary intake of linoleic acid does not substantially raise the risk of breast, colorectal, or prostate cancer.

Monounsaturated Fatty Acids (n-9)

Recently, there has been renewed interest in the consumption of monounsaturated fats because people in Mediterranean countries consume significant amounts of fat (monounsaturated) and yet have relatively low cancer rates (112). Dietary sources of monounsaturated fatty acids are varied. Palmitoleic acid is found in animal and vegetable fats but is more abundant in fish and some nuts. Oleic acid is a major monounsaturated fatty acid that is readily available in olive oil and is also a major component of many animal fats and select vegetable oils.

Simonsen *et al.* (113) showed that consumption of oleic acid had a stronger inverse correlation with breast cancer than any other monounsaturated fatty acid. This finding is consistent with evidence from several recent studies in Mediterranean populations, suggesting that olive oil consumption may protect against breast cancer. However, they did not show a consistently protective effect of monounsaturated fatty acids with postmenopausal breast cancer patients.

Trans Fatty Acids

Isomerized fats have been studied to determine whether they are associated with the development of cancer (114). It has been hypothesized that TFA may alter cell membrane permeability to carcinogens and thereby induce tumor formation (115). One of the few studies performed in this area showed a correlation between TFA and cancer of the breast and pancreas (116). This study was based upon mathematical correlations; thus it is open to criticism. Reddy *et al.* (117) found no correlation between tumorigenesis and *trans* fatty acid intake. At this time, no definite statements can be made regarding the effects of isomerized fats on tumorigenesis.

Conjugated Linoleic Acid

The role played by CLA in cancer has been studied to a limited degree using rats as an animal model. Conjugated linoleic acid was effective in preventing the growth of mammary tumors (118). Cell culture studies showed that CLA inhibited the proliferation of colorectal cancer cells (119). When CLA was provided in the diet of rats, the number of abnormal crypt foci was decreased (120).

Summary

At present, definitive advice cannot be given concerning which types of dietary fats provide maximum health benefits. Current research indicates that the "traditional" dietary approach to the treatment of coronary heart disease (i.e., a low-cholesterol diet that emphasizes polyunsaturated fats) may not be as beneficial as was once assumed. Dietary lipid components that have recently come to the forefront with respect to the prevention of both CHD and cancer include n-3 and n-9 fatty acids as well as conjugated linoleic acid.

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Chapter 5

Oil Trading

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Introduction

Trading plays a key role in the fats and oils industry. It serves as the major method of price discovery; it facilitates price risk management and the transformation of oils and fats from places, times, and forms of plentiful supply to places, times, and forms of poor supply.

Agricultural products such as oils and fats represent commodities that approximate most closely behavior consistent with pure competition as it is understood in economic theory. Especially when taken in the international context, there are a large number of participants who as individual companies do not produce or consume a quantity sufficient to affect the price of these commodities to any measurable extent. Therefore, the fundamental relationships of supply and demand are much more responsible for changes in price than in many other industries. What this means for anyone involved in the fats and oils industry is that price volatility is a major issue because the market value changes by the day, hour, or minute. As the marketplace perceives a change in the relationship of supply to demand on the basis of constantly changing information such as weather, prices of competing crops, economic conditions, government policy or exchange rates, so too does the price of the oil in the marketplace change. For anyone involved in the producer-processor-consumer chain of oils and fats, price volatility translates into a major risk factor in doing business because the magnitude of value added at each step can be appreciably less than the market price swings during the time in which a commodity is being held. A farmer who makes planting decisions in February that are based on a perceived market price obtainable in October may be very disappointed when October finally comes. The management of these price risks and the tools used in this management are generally the most confusing aspect of commodity trading to a newcomer to the field.

Purpose

Price Discovery

The trading of oils and fats provides the essential function of determining prices for various grades of vegetable oil and animal fat at any point in time. This allows the participants to make decisions on the type of fat to buy or sell, the shipment or delivery period in which to sell or buy, and the correct time to enter the marketplace to make transactions. The process of price discovery occurs through many participants making offers of quantities and qualities of oil that they would like to sell and others making bids for what they would like to buy. It is not unheard of for the same participant to have an offer and a bid in the market at the same time, the former higher than the latter, of course.

It is important for participants to know the relative values of different fats and oils at various places around the world so that they can make both short-term and strategically efficient decisions for their companies. For example, if a producer of bottled vegetable oils for retail sale is selling a blended vegetable oil, he will be looking at the relative price of soy, sunflower, and canola oil to determine how to make the product at "least cost" without changing his retail price.

Risk Management

With the increasing globalization of the fats and oils trade, the volatility of prices has increased immensely. Weather conditions in the corn belt of the United States during the growing season are no longer the prime variable in the marketplace; other factors such as palm oil production, Indian demand, Chinese crushing economics, and South American weather have been added to the equation. The role of managing risk has become much more important. Different players in the industry have different levels of risk, depending on the part of the chain in which they are involved. The producer carries an enormous amount of risk, given that the price of what he sells has very little correlation to the price of his inputs; therefore, how high he is able to sell will have a direct effect on his income. Processors generally have a high degree of correlation between the prices of what they buy and what they sell; however, they have risk between the time that they take delivery of their raw material and the time at which they sell their finished goods. Consumers, in general, experience a minimal relationship between the price of the ingredients they buy and the goods and services that they sell. For example, even though the prime ingredients of French fries are potatoes and vegetable oil, a restaurant chain will very rarely change the price of fries when the price of oil changes. Therefore, how low they are able to buy will have a large effect on the profitability of the restaurant business.

Transformation

The other important function of trading is the movement or transformation of oils and fats from places, times, and forms of surplus to places, times, and forms of shortage.

Place. There are many more soybeans crushed in Iowa that there are people to consume them. At the same time, there is much more oil consumed in New York State than there is oil produced. Thus, the price of oil is higher in New York than in Des Moines, and it is the function of the trader to move the oil from the lower-priced market to the higher-priced market in the most efficient manner possible to make a profit.

Time. Annual crops such as soybeans, sunflowers, and canola have only one harvest per year. The crops are most plentiful in the months after harvest and are scarce in the months leading up to harvest. Demand for those crops, however, is relatively constant throughout the year. It is the function of the trader to buy commodities when they are cheapest during harvest and store them until they are needed, in the most efficient manner possible to make a profit.

Form. The palm plantations of Malaysia and Indonesia produce large amounts of crude palm oil. The margarine manufacturers and biscuit makers of Europe consume a large amount of palm oil–based shortenings, whereas consumers in India use a large amount of cooking oil. The palm oil refiners in both the Far East and Europe buy the crude from the plantations; through refining and fractionation, they turn it into cooking oil and shortening in the most efficient manner possible to make a margin. It is the trader, through the diligent purchase of crude oil and the sale of olein and stearin, who ensures that the refining business operates at a margin.

Participants

Producers

The farmer plays a large role in the commodity-trading picture because the decision to plant or not plant one commodity vs. another has a major effect on the perceived supply of a given commodity and, therefore, the price. In recent times, the plantations of the Far East, which have 20-year production cycles, have also played an increasingly important role in the behavior of prices. The producers' willingness or reluctance to sell at any given time can have a major effect on either the basis or the futures price or both. The producer also carries a great deal of risk, which must be managed to remain competitive.

Processor

Processors include flour millers, corn millers, oil refiners, oilseed crushers, or others who are buying essentially raw agricultural products and producing value-added products sold as food ingredients. Processors generally buy from country elevators on the basis of the futures market and sell products in the same way.

Brokers

Brokers can insert themselves into any step of the chain and provide the service of putting together a buyer and a seller. They do not take positions in any goods, but are paid a fee, generally by the seller, for each unit of product for which they arrange a sale. Brokers provide the service of keeping small customers apprised of markets and act as industry clearing houses for information.

Dealers/Shippers

Unlike brokers, dealers actually take title to goods and also positions in the market. They are particularly active in flat-price traded commodities such as tallow, palm, or coconut oil. Dealers provide a measure of liquidity to markets that otherwise would require a small number of producers or processors getting together with a small number of consumers whose timing of trading may not coincide.

Consumers

At the end of the chain is a group who is buying a raw commodity or a processed commodity for use directly, or as an ingredient, in a food product. Consumers have the common characteristic of being very concerned with the flat price of the commodity with which they are dealing. A consumer can be a country, a food company, or an individual.

Others

Many other participants can enter into the process of commodity trading, including shipping lines, freight brokers, export brokers, commission houses, surveyors, tank terminal operators, banks, and expediters. A discussion of the roles played by these participants is far beyond the scope of this chapter, but they are mentioned in order to give some further insight into the complexity of many commodity trades and an appreciation of the skills required of an experienced trader.

Tools of Trading

Trading Rules

The first area for any aspiring trader to study is the relevant trading rules for the commodity in which they will be dealing. These not only outline the rules for weights, payment terms, invoicing, shipment periods, and so on, but they also stipulate the quality characteristics, which are of prime importance.

Many organizations participate in the setting of trading rules for commodities. In the United States, the government sets the rules for corn, wheat, and soybeans, and the NIOP (National Istitute of Oilseed Products), NCPA (National Cottonseed Products Association), AFOA (American Fats and Oils Association), and NOPA (National Oilseed Processors Association) for other oilseeds and oil- and meal-related products. International bodies such as FOSFA (Federation of Oilseed Seeds and Fats Association), PORAM (Palm Oil Refiners Association of Malaysia), AVOC (Asian Vegetable Oil Clubs), PCOPA (Philippine Coconut Oil Producers Association) and ANEC also have rules for the trading of fats and oils. Although these organizations have standard quality definitions and quality characteristics, these and other contract terms are subject to modification by the buyer and seller.

Trading rules, as they relate to the quality aspects of products, become less and less important as agricultural products are more and more processed; they become differentiable on the basis of their particular attributes related to performance. Trading rules are not perfect, but they are necessary to ensure that some standards that will protect both buyer and seller are in place. They are also extremely important in expediting contract negotiations because a number of terms can be agreed upon quickly by referencing a certain set of trading rules.

Futures Markets

The futures market, as typified by the Chicago Board of Trade, is the single most important tool for managing the price risk involved in commodity trading. The concept of a futures market goes back many years and evolved from the necessity for farmers and interior elevators to be able to store crops through the winter (when frozen water ways prevented delivery) and sell them in the spring with some certainty of their selling price. In this transaction, the two sides of the futures market become apparent, i.e, one is the farmer who is minimizing price risk by selling his crops for a known price; the other is the merchant or processor who wishes to source raw materials to operate his facilities through the summer months before the next crop becomes available. This started with forward contracts in the 1850s and later evolved into what is now known as the futures market. However, the real facilitator of the modern day futures market are the speculators. They are participants who have no interest in either making or taking delivery of the physical commodity, but are betting that they are better at forecasting future prices than the rest of the market. It is important to recognize this principle of risk transference, which is a very important function of the futures market, whereby those involved in the physical handling of commodities (producers, transporters, processors, consumers) can transfer their price risk to speculative participants. These participants have no intention of actually being involved with physical commodities, but instead are gambling that the market will go either up or down from the price at which they have bought or sold.

Another function that the futures market provides is liquidity. An active futures market used by many buyers and sellers means that buying and selling can always be accomplished. In a nonliquid market, it is sometimes difficult to find a buyer when someone wants to sell (or *vice versa*), if the buyers and sellers are scattered all over the world.

Hedging

Although the terms of a futures contract specify quantity, quality, and specific deliverable locations, it is seldom that any one in the producer-processor-consumer chain ever intends to deliver or take delivery under the terms of a futures contract. The futures market is used instead as a paper transaction to offset an actual physical commodity transaction or "cash" trade.

For example, in March, a farmer wants to lock in a price for beans to be harvested in November. He does this by selling November bean futures at the market price of $6.00/bushel. When November comes and the beans are harvested, the beans are not delivered on the futures market according to the terms of the futures contract. They are sold instead to the local elevator at a price, which is based on the current futures market. The farmer receives a check from the elevator for his beans and immediately buys back the futures, which were sold in March. The money that was made or lost on the futures position is offset by an opposite gain or loss in the cash transaction.

The analysis of this transaction in trading terms is as follows:

- In March, the farmer wants to sell his November beans, in other words he is long cash November beans.
- He sells November futures so that he is now short futures and long cash or a net even.
- In November, he sells cash beans to the elevator so that he is now even cash, but short futures and immediately buys the futures to become even in all positions.
- Two things must be remembered, i.e., (i) the farmer receives $6.00/bushel no matter what the market does between March and November, and (ii) the rules of hedging are as follows: "Buy the cash, sell the futures; sell the cash, buy the futures."

Because the concept of hedging is so important in understanding commodity trading, another example is appropriate. In this case, assume that a soybean oil refiner is involved and that this refiner requires $0.04 over crude oil cost to cover refining and profit. In this case, also assume that crude oil has to be bought 2 mo in advance in order to be at the refinery when it is actually needed to produce finished oil. Crude oil is purchased on the basis of the futures market price, and refined oil is sold on the basis of the futures market price.

Step 1. Assume that crude oil is required for July, and a deal is struck between a refiner and a crude producer for July oil with a futures price of $0.2200 lb. At the time this price is agreed upon, the refiner immediately sells futures at the same level to offset the cash purchase. (Because the crude oil producer is also operating in a hedged fashion, he or she buys futures to offset the cash sale. This process can be short-circuited by a direct transfer of futures from the refiner's account to the crusher's account at an agreed upon futures price level.) At this point, the refiner is long July cash oil and short July futures or net even.

Step 2. It is now July and the refiner sells refined oil to a customer at $0.04 plus the July futures price, which has dropped to $0.1700/lb. or $0.2100 for the refined oil. At the time of the sale of refined oil, July futures are bought at $0.1700 so that the position is *even* cash and even futures. In this case, oil was bought at $0.2200 and sold for $0.2100, yet the refiner still received the $0.04 required to run the refinery.

The transaction works as follows:

- In the *cash transaction*, the refiner bought crude oil at $0.22/lb. The refiner sold refined oil at $0.21/lb. The "cash" gain or loss = $0.01/lb loss.
- In the *futures transaction*, the refiner sold futures at $0.22/lb and bought futures at $0.17/lb. The "futures" gain or loss = $0.05/lb gain; the net transaction = $0.04/lb gain.

The concept of hedging is so basic to commodity trading that it is simply automatically assumed to be functioning in trades between various links in the processing chain. Everything is done "basis" the futures market, which leads to the way trading is actually done or "basis trading."

Basis Trading

In the examples shown above, the "cash" price and the "futures" price were assumed to be the same. This is virtually never the case; although the futures market determines the value of a commodity on a macrobasis, the actual value of a given commodity in a single location is determined by microeconomic factors in a given area. Freight considerations, supply factors, and alternatives to a given commodity in a given market all contribute to a cash market, which is different from the futures price. For example, soybean oil may have a cash value (in basis terms) of 200 over FOB Gulf, 440 under FOB South America, 40 under FOB Illinois, 80 under in Western Iowa, or 20 over in Georgia. The "overs" and "unders" refer to the Chicago Board of Trade futures price for the time period under discussion.

Commodity handlers and processors practice basis trading to such an extent that values of commodities are virtually never discussed in terms of basis plus futures (flat price) but are discussed in the basis terms only. The basis is extremely important to processors because it is the basis that reflects any efficiencies or competitive advantages of one processor vs. another.

Flat Price. Flat price is largely irrelevant to the middlemen in the chain linking producer to consumer because it can be managed in large part by hedging (although basis risks need to be similarly managed); nevertheless, flat price is extremely important to producers (farmers) who ultimately receive a check for the flat price of their commodities, to consumers who ultimately have to factor in a flat price as an ingredient cost, and to traders who deal in commodities for which a futures market does not exist (e.g., palm oil, coconut oil, peanut oil, tallow, lard, and others). A flat price commodity trader has a much more difficult time from both a hedging and liquidity standpoint. It is the flat price that also determines the relative competitiveness of commodities on a worldwide perspective.

Supply and Demand Analysis

In this chapter, we have mentioned many aspects of trading that rely on traders making the correct decisions concerning when and at what levels to buy and sell. Essential to making those decisions is a good understanding of current supply and demand trends and their effect on future prices. A number of companies invest significant amounts of time and money in this endeavor. The large trading houses have several economists who collect data, create models, and attempt to predict the future; they use this for their own profit. Futures commission houses also exert a similar amount of effort, sharing the results of their efforts with their clients. There are also independent research houses that sell their information and analysis for a fee. In addition to these, the government also expends large amounts of effort through the U.S. Department of Agriculture to forecast supply and demand trends; this is available to the public through monthly updates. No matter how a trader receives his information and analysis, it is important that he understand the implications of market-moving events on the level of supply that will be available to the market and the corresponding demand for those products. This chapter is not the place to list all of the variables that can affect supply and demand (hence prices); however, they include such factors as weather, planting intentions, yields, soybean meal demand, storage capacity, railroad performance, overseas demand, overseas crop production, and consumer preferences.

Government Policy

No discussion of commodity trading and pricing mechanisms can ignore the role of government in agriculture around the world. Government subsidies and the mechanisms whereby these subsidies are given play major roles in determining relative competitive advantage of one country vs. another in world markets. Because world prices of commodities are a function of complex subsidy interaction, any change in agricultural policy can have major implications for commodity prices. At times, U.S. government policy acts as a floor for commodity prices; at other times, it acts much like a ceiling. For a commodity trader, forecasting the actions of governments in agricultural policies can become as important as forecasting supply and demand factors in price prediction.

Suggested Readings

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Chapter 6

Fats and Oils Processing

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Introduction

Edible fats and oils can vary from pleasant-smelling products that contain few impurities to very offensive-smelling products with impurities that impair performance. Fortunately, researchers have developed technologies for modifying the fats and oils products to make them more useful for foods and other applications. Processing technologies have been developed to make them flavorless and odorless, remove or reduce color, modify the melting behavior, rearrange the molecular structure, and facilitate other changes to make them more desirable for the intended application. Developments in lipid processing technology this century have been instrumental in the development of many of the currently available food products that meet the functional and nutritional requirements of discerning and better-informed consumers.

Almost all of the edible fats and oils used for food purposes are processed in some manner. The first step in processing is the separation or extraction of the fat or oil from the seed, nut, or tissues in a manner that will maximize yield and produce a good quality lipid product. After extraction, a variety of procedures including both chemical reactions and physical separations may be involved in the conversion of the separated fats and oils to edible products. Care must be exercised during all processing stages to keep oxidation and hydrolysis to a minimum because both are detrimental to the fats and oils quality. Oxidation, which produces flavor, odor, and flavor stability problems, is caused by exposure to oxygen and accelerated with heat. Hydrolysis occurs whenever water is mixed with fats and oils to cause free fatty acid development. The important reactions for most vegetable oils are hydration of the phospholipids in degumming, neutralization of the fatty acids with alkali and/or removal with steam distillation, physical adsorption to remove color pigments, and chemisorption to remove peroxides and secondary oxidation products. Animal fats are essentially ready for use after rendering except for clarification to remove proteinaceous materials. All fats and oils products can be deodorized to remove flavors and odors, reduce the fatty acid content, remove peroxides, and provide incidental heat bleaching.

Nonglyceride Components

Of primary importance in the processing of any fat or oil is its composition. Although most fatty materials can be converted to edible products by similar procedures, the composition of the particular crude fat or oil is a determining factor for the processes utilized, conditions, and treatment materials. The primary constituents in crude fats and oils are the triglycerides, but they also contain varying amounts of nonglyceride impurities. Not all of the nonglyceride impurities are undesirable. Therefore, the objective in all of fats and oils processing is to remove the objectionable impurities with the least possible damage to the desirable constituents.

The extracted or rendered fats and oils are purified or processed for use as edible fats and oils. Ideally, the purification process or processes remove only the materials detrimental to the application of the processed fats and oils product. In most cases, free fatty acids, phospholipids, moisture, color pigments, oxidation products, waxes, trace meals, proteins, pesticides, trace metals, dirt, and other gross impurities are the materials that must be removed. Most vegetable oils contain tocopherols, which are natural antioxidants that protect the oils from oxidation and should be retained. For some products, either the pigments or waxes are not detrimental and need not be removed. The major concerns are usually with free fatty acids, phospholipids, oxidation products, pesticides, proteins, and trace metals, i.e., all materials that affect the odor, flavor, and flavor stability of edible fats and oils products. In the United States, the color of fats and oils is usually a major concern from a cosmetic point of view, leading to the inclusion of pigment adsorption to remove such impurities, especially for products marketed directly to consumers.

Free Fatty Acid

Free fatty acid is the result of hydration of the fat or oil with moisture; the process is accelerated with heat and pressure. This reaction occurs in crude oils and may be elevated during storage, handling, and certain processes. Some crude fats and oils have higher initial fatty acid contents as a result of enzymatic hydrolysis or abuse during harvesting, transportation, or storage. Therefore, free fatty acid is a good measure of the oil quality as crude, during processing, and in the finished products. The level of the free fatty acid in the fat or oil at any point in processing will determine the required treatment for neutralization to produce the desired product flavor. Higher free fatty acid levels naturally require more severe treatments, which affect processing losses adversely.

Phosphatides

Phosphatides occur to varying degrees in animal fats and vegetable oils, with the oils containing by far the greater amount. The phosphatide levels in animal fats is very low. Phosphatides consist of polyhydric alcohols esterified with fatty acids and phosphoric acid, combined with a nitrogen-containing compound. Lecithin and cephalin are two common phosphatides that occur in vegetable oils. Soybean, corn, cottonseed, and canola oils all contain significant quantities of phosphatides. The phosphatides can either be recovered for their by-product value through degumming or treated as impurities and removed from the vegetable oils during caustic neutralization. For processing, the position of the phosphoric acid radical is important. When it is attached to an outer carbon link with the glycerol molecule, it is termed an α-lipoid and is hydratable. β-Lipoid compounds, with the phosphoric acid radical in the center position, and divalent metal phosphatides are not hydratable. The hydratable phosphatides can be removed with a typical degumming process. Pretreatment of crude oils with phosphoric acid before caustic refining is successful in removing nonhydratable and hydratable phosphatides.

Moisture

Moisture can come in contact with a fat or oil in many different ways, e.g., condensation, broken coils in a vessel, an intentional or unintentional addition during processing, or other events, causing hydrolysis. The reaction of water with a triglyceride to break it down into a diglyceride and a fatty acid is called hydrolysis. The free fatty acid liberated from this reaction has an objectionable stringent acidic flavor, which is usually described as rancid. Moisture is removed during processing by vacuum systems that are utilized with many of the processes.

Waxes

Most vegetable oils are solvent extracted with the seed and hull together for operational efficiency. The seed hulls can contain waxes that are soluble in oil. Waxes are high-melting esters of fatty alcohols and fatty acids with low solubility in oils. These waxes solidify after a period of time to give the oil a cloudy appearance, an unsightly thread, or a layer of solidified material. The quantity of wax in the various vegetable oils can vary from a few hundred parts per million to >2000 ppm. The wax content in an oil must be reduced to <10 ppm to ensure that the oil will not cloud or develop a wisp. Corn, sunflower, safflower, and canola oils contain waxes that are usually removed so that the bottled oils will maintain clarity on the retail store shelf and in the consumer's pantry or refrigerator. The classic dewaxing process is a separation or fraction technique, which involves cooling of the oil to solidify the waxes for removal by filtration.

Oxidation

The unsaturated fatty acids in fats and oils are subject to oxidation, a chemical reaction that occurs with exposure to air and leads to the development of an objectionable flavor and odor. The double bonds contained in the unsaturated fatty acids are the site of this chemical activity. The oxidation rate is roughly proportional to the degree of unsaturation; for example, linolenic fatty acid ($C_{18:3}$) with three double bonds is more susceptible to oxidation than linoleic ($C_{18:2}$) with only two double bonds, but it is twice as susceptible as oleic ($C_{18:1}$) with only one double bond. Oxidative deterioration results in the formation of hydroperoxides, which decompose into carbonyls, dimers, and polymerized gums. It is accelerated by temperature, oxygen pressure, earlier oxidation, metal ions, lipoxidases, hematin compounds, antioxidant reductions, absence of metal deactivators, time, and ultraviolet or visible light. Extensive oxidation will eventually destroy the beneficial components contained in many fats and oils such as the carotenoids (vitamin A), the essential fatty acids (linolenic and linoleic) and the tocopherols (vitamin E). Prevention of oxidation is a major factor that must be designed into all edible fats and oils processes.

Fats and oils oxidative reactions are related directly to the fatty acid composition or more specifically to the unsaturation type and amount. Oxidative stability estimates can be made from the iodine value measurement, calculated iodine value, or an oxidative stability formula. These oxidative stability estimates were calculated for the major edible fats and oils and presented in Table 6.1 (1). The formula for the oxidative stability rating (2) is as follows: Multiply the decimal fraction of each unsaturated fatty acid present by its relative oxidation rate and then sum these to obtain the expected oxidative stability rating. Comparisons of the calculated inherent oxidative stability with the double bond total or the calculated iodine value in Table 6.1 indicate that all estimates provide the same result. The oxidative stability for each fat and oil is different and must be a consideration during all processing to identify which oils are more susceptible and require extra protection from heat, oxygen, and light along with more stringent processing controls.

Oxidation Products

Peroxides formed by the reaction between oxygen and the unsaturated fatty acids are the primary products of oxidation. Peroxides have no flavor or odor but break down to form aldehydes, which have a strong, disagreeable flavor and odor. Deodorization

TABLE 6.1 Fats and Oils Oxidative Stability Estimates

Rating	Fat and oil source	Inherent oxidative stability	Total double bonds	Calculated iodine value
Worst	Safflower	9.546	168.8	146.1
	Soybean	8.579	153.7	133.1
	Sunflower	8.489	156.3	135.3
	Corn	7.708	148.4	128.4
	Cottonseed	6.895	130.1	112.6
	Canola	5.349	131.3	113.3
	Peanut	4.326	112.6	97.1
	Lard	2.426	68.5	59.3
	High-oleic sunflower	1.894	99.4	85.6
	Olive	1.740	95.6	82.4
	Palm	1.724	60.8	81.8
	High-oleic safflower	1.710	96.8	83.3
	Tallow	1.267	55.6	48.4
	Palm kernel	0.430	20.1	17.2
Best	Coconut	0.360	11.0	9.6

destroys peroxides with high temperatures but the oxygen compounds or secondary oxidation products that are the precursors of flavor reversion can be removed only by the bleaching process (3).

Color Pigments

The color bodies in fats and oils include the carotenes, which impart yellow and red colors to the oil, chlorophylls, which give it a greenish cast, degraded proteins and/or carbohydrates, which have a brownish cast, gossypol, which provides the yellowish color to cottonseed oil, and some others still not completely identified such as the blue color observed occasionally in lard. The carotenes, which are widely distributed in fats and oils, are heat sensitive and readily adsorbed by bleaching earths. Carotene concentrations are low in most fats and oils with palm oil having the highest content, 0.05–0.2% (4). With heat and oxidation, gossypol pigments form color compounds that are difficult to remove from cottonseed oils except with caustic refining. Soybean oil, canola oil, rapeseed oil, olive oil, and some tallows have green colors from chlorophyll or related compounds. The green color from chlorophyll is more prominent when the red and yellow colors are reduced by heat bleaching. Chlorophyll pigments are more easily removed in the bleaching process before the color is heat set. Proteinaceous materials in animal fats that will turn black when exposed to high temperatures can be eliminated with clarification by filtration or water washing.

Trace Metals

Metals can be encountered throughout fats and oils processing; these are harmful to product quality, human health, and reduce the efficiency of the process. Trace quantities of copper, iron, manganese, and nickel substantially reduce the oxidative stability of oils, whereas calcium, sodium, and magnesium reduce the efficiency of the refining, degumming, bleaching, and hydrogenation systems. The effects of the metals can be diminished by the use of chelating agents at various process points to sequester the trace metals (5). The most widely used chelating agents are citric and phosphoric acids.

Tocopherols

Vegetable oils contain tocopherols, which are natural antioxidants that protect fats and oils from oxidation. Nature's fat-soluble antioxidants exist in four forms: α-, β-, δ-, and γ- tocopherol. α-Tocopherol, also known as vitamin E, is widely used as a nutritional supplement. β-Tocopherol exists in concentrations too low to have any practical significance. Both δ- and γ-tocopherols are known for their antioxidant properties. The tocopherol content decreases during each stage of processing, with the highest reductions occurring during chemical refining and deodorization. Caustic refining can remove as much as 10–20% of the tocopherols, but 30–60% of the remaining natural antioxidants can be lost during deodorization.

Sterols

Sterols are minor components of all natural fats and oils and comprise most of the unsaponifiable matter; the remainder consists essentially of hydrocarbons. The sterols are colorless, heat stable, and relatively inert; thus they do not contribute any important property to a fat or oil. Chemical refining removes a portion of the sterols, but more effective removal requires fractional crystallization, molecular distillation, or high-temperature steam refining. The most extensively investigated animal sterol is cholesterol. The vegetable sterols are known collectively as phytosterols (6).

Pesticides

Pesticides have been used for increased agriculture production throughout the world. Studies have shown that the majority of the pesticides applied eventually reach the soil surface where they gradually spread, translocate to other environments, or eventually degrade. Translocation to oil-bearing plant seeds has also been demonstrated. Processing studies have shown that neither solvent extraction nor bleaching affects the pesticide levels in vegetable oils. However, it was found that pesticides were removed by volatilization during hydrogenation and/or deodorization (7–9). U.S. government agencies have recognized that the insecticides are distilled from edible oils during the deodorization process and have forbidden the use of deodorizer distillates in animal feeds.

Triglyceride Functionality

The physical properties of natural fats and oils vary widely, even though these substances are composed of the same or similar fatty acids. The proportion of the fatty acids and the structure of the individual triglycerides are the reasons for the differences. Among the factors that affect the fatty acid composition of the vegetable oils are climate, soil type, growing season, plant maturity, plant health, microbiological factors, seed location within the flower, and the genetic variation of plant. Fatty acid compositions for the animal fats vary according to the animal species, diet, health, fat location on the carcass, and maturity.

Structurally, fats and oils are a combination of glycerin and fatty acids. The glycerin molecule has three separate points at which a fatty acid molecule can be attached, hence the common reference to fats and oils as triglycerides. The difference between a fat and an oil is the physical state at ambient temperature, i.e., a fat is a solid and an oil is a liquid. The different properties are determined by the fatty acid composition and their position on the glycerin molecule. Generally, solid fats are indicated by a dominance of saturated fatty acids, and liquids by a high level of unsaturated fatty acids. This generalization is complicated by the type and position of the fatty acid on the glycerin molecule. For a detailed explanation of triglyceride distributions, see Chapter 2 of this volume.

TABLE 6.2 Triglyceride Functional Relationships[a]

		Triglyceride description		Melting point		
Triglyceride category	Liquidity zone	Fatty acid composition	Symbol	(°F)	(°C)	Functionality
Trisaturated	Heated	Stearic-stearic-stearic	GS3	149	65.0	Structure
		Stearic-stearic-palmitic	GS3	142	61.1	Moisture barrier
		Stearic-palmitic-palmitic	GS3	140	60.0	Lubricity
		Palmitic-palmitic-palmitic	GS3	133	56.1	
Disaturated Monounsaturated	Body temperature	Stearic-stearic-oleic	GS2U	107	41.7	
		Stearic-palmitic-oleic	GS2U	100	37.8	Structure
		Palmitic-palmitic-oleic	GS2U	95	35.0	Aeration
		Stearic-stearic-linoleic	GS2U	91	32.8	Moisture barrier
		Stearic-palmitic linoleic	GS2U	86	30.0	Lubricity
		Palmitic-palmitic-linoleic	GS2U	81	27.2	
Monosaturated Diunsaturated and Tniunsaturated	Intermediate temperature	Stearic-oleic-oleic	GSU2	73	22.8	
		Oleic-oleic-palmitic	GSU2	60	15.6	Lubricity
		Stearic-oleic-palmitic	GS2U	43	6.1	Clarity
		Oleic-oleic-oleic	GU3	42	5.6	
	Refrigerator temperature	Stearic-linoleic-linoleic	GSU2	34	−1.1	
		Oleic-oleic-linoleic	GU3	30	−1.1	Clarity
		Palmitic-linoleic-oleic	GSU2	27	−2.8	Nutrition
		Palmitic-linoleic-linoleic	GSU2	22	−5.6	Lubricity
		Oleic-linoleic-linoleic	GU3	20	−6.7	
		Linoleic-linoleic-linoleic	GU3	8	−13.3	

[a] Abbreviations: GS3, trisaturated; GS2U, disaturated, monounsaturated; GSU2, monosaturated, diunsaturated; GU3, triunsaturated.

Therefore, fats and oils are triglyceride structures, and their functionality relates directly to their individual triglyceride compositions. The relationship of triglyceride composition to functionality is illustrated in Table 6.2 (1,10,11). All triglycerides fit into one of the following four categories: Trisaturated (GS3), disaturated monounsaturated (GS2U), monosaturated diunsaturated (GSU2), and triunsaturated (GU3). The trisaturates are high-melting triglycerides that function as stabilizers, moisture barriers, and lubricants. Disaturated monounsaturated triglycerides melt near body temperature and provide structure, aeration, moisture barrier, and lubricity properties. The intermediate-melting triglycerides, made up primarily of monosaturated diunsaturated triglycerides with some triunsaturates, will remain liquid only if held at room temperature or above. At refrigerator temperatures, the triunsaturated and some monosaturated diunsaturated triglycerides remain liquid. The triunsaturated and monosaturated diunsaturated triglyceride groups provide lubricity only and contribute softening or fluidity to the structure of a food product. The triunsaturated triglycerides provide clarity at refrigerator temperatures, which is an important characteristic for the functionality and appearance of salad oil.

Processing Flow Sequence

Fats and oils processing involves a series of processes in which both physical and chemical changes are made to the raw material. Figure 6.1 illustrates the flow sequence of most of the potential processing steps taken to produce the various fats and oils products. The choice of processing equipment and techniques depends on the following: (i) fats and oils source, (ii) raw materials quality, (iii) labor situation, (iv) maintenance capabilities, (v) processed oil requirements, (vi) financial resources, (vii) crude fats and oils proximity, (viii) marketing philosophy, and (ix) other considerations.

The processing of fats and oils is initiated by an extraction or rendering process to remove the fat or oil from the seed, bean, nut, fruit, or fatty tissue. The processing of vegetable oil after extraction almost always includes neutralization or refining, bleaching, and deodorization; the major differences are the choice of equipment and techniques used. Rendered animal fats are normally clarified to remove impurities, bleached and deodorized, again with alternative equipment and techniques providing the major differences. Clarification, neutralization, bleaching, and deodorization are all processes that affect the flavor, flavor stability, and appearance of the fat or oil product. Generally, the flavor of a processed fat or oil product should be completely bland to enhance a processed food product's flavor. Bleaching, both by adsorption and heat treatment, removes color pigments to lighten the color or appearance of most processed oils.

Vegetable oils and animal fats are natural products with variable characteristics contributed by nature. The selection of fats and oils products for a particular application must be made on the basis of functionality. As discussed earlier, fats and oils functionality is dependent upon the triglyceride composition. Therefore, the performance characteristics desired can be obtained from the following: (i) selection of a fat or oil with the desirable triglyceride composition, (ii) blending of fats and oils from different sources to achieve the desired triglyceride composition, or (iii) modification of the fats and oils by processing to provide the desired triglyceride composition. The processes capable of modifying the triglyceride composition of a fat or oil product are as follows: (i) hydrogenation, which saturates the unsaturated fatty acids; (ii) fractionation, which separates hard and soft fractions; and (iii) interesterification, which interchanges the fatty acids among triglycerides. Further, the products of these processes and/or natural products can be blended to change the melting profiles, solidification points, crystal tendencies, and other physical characteristics of the fats and oils ingredients.

Fats and oils processing is discussed in detail in the following chapters on the entire range of processing operations; however, a brief explanation of each unit operation is presented here.

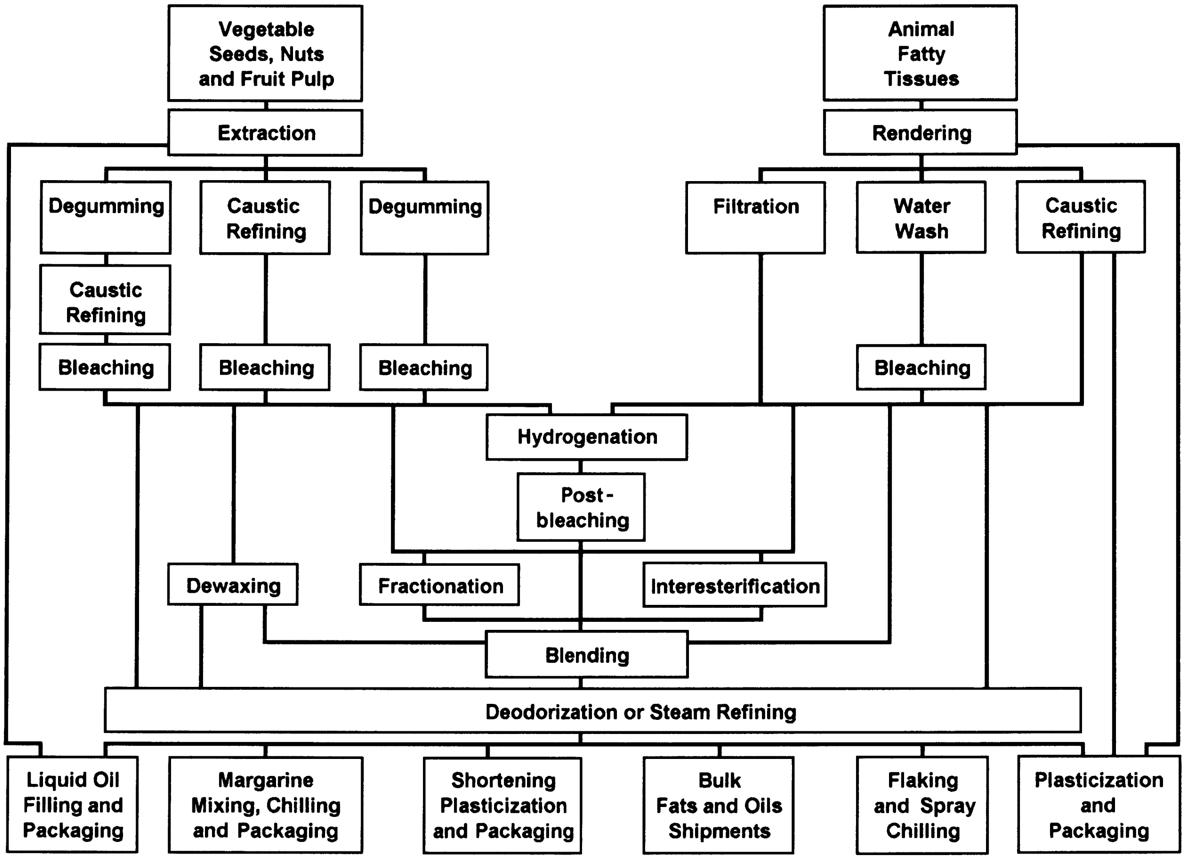

Fig. 6.1. Flow sequence of fats and oils processing.

Extraction

Extraction of oil from materials of plant origin is usually done either by pressing with the use of a continuous screw press or by extraction with volatile solvents. Before 1940, mechanical pressing was the primary method used. Mechanical pressing had limits because the oil recovery was poorer than with solvent extraction and the high temperatures generated damaged both the oil and the meal. Solvent allows a more complete oil extraction at lower temperatures. Solvent extraction plants can be either batch or continuous. The continuous extraction plants can be percolation, immersion, or direct extraction plants. Generally, the oilseeds may be divided by oil content, i.e., above and below 20% oil content. In most cases, oilseeds with a low oil content are subjected to both continuous and batch solvent extraction. Seeds with a high oil content are normally extracted in two stages, first pressing and then solvent extraction; however, many single-step continuous direct solvent extraction systems are in current use.

Rendering

The fatty tissue from meat animals that is not a part of the carcass or that has been trimmed from the carcass in preparation for sale constitutes the raw material from which lard and tallow are obtained. Separation of fat from the fatty tissues of animals is called rendering. The rendering process consists of two basic steps. First, the meat by-product is heated to evaporate the moisture, melt the fat present, and condition the animal fibrous tissue. Two alternative cooking temperatures are used, fat temperatures <120°F and fat temperatures >180°F. A more complete separation of the fat and protein is accomplished with the higher-temperature processing, but a better quality protein is obtained with the lower-temperature processing. Normally, the value of the protein dictates the use of the lower-temperature, poorer separation technique; this likely leaves trace quantities of protein in the rendered lard or tallow. After cooking, the fat is separated from the solid proteinaceous material. In batch rendering, the cooked material is allowed to separate and the fat to drain followed by filtration to complete the separation. Continuous rendering, introduced to replace the batch systems, normally consists of a continuous cooker, which requires less cooking time and is more energy efficient with better quality control (12).

Refining Systems

Processors have the option of approaching edible oil purification in two ways, i.e., either chemical or physical refining. The two systems utilize very similar processes; the major difference is the method used for free fatty acid removal. Chemical refining, the conventional method used for removal of the nonglyceride impurities from edible fats and oils, consists of optional degumming, caustic neutralization, bleaching, and deodorization. The alkali refining process produces good quality oil; its flexibility allows it to treat different oils and different qualities of individual oils. However, caustic refining has three major drawbacks as follows: (i) the soap produced promotes a tendency for emulsion formation, which will occlude neutral oil to increase oil losses; (ii) oil losses are particularly high when processing oils with free fatty acids >3.0%; and (iii) disposal of the soapstock produced has become more difficult.

The second process, which has become known as physical refining, consists of removing the fatty acids from the oil by steam distillation under vacuum after the phosphatides have been removed by a degumming process followed by a pretreatment process before bleaching. The major advantages of physical refining are the elimination of soapstock, lower capital costs, and fewer processes to operate and maintain. The objective of the initial processing step in either refining method is the removal of phosphatides, color bodies, and trace metals. Removal of these nontriglyceride impurities is crucial to ensure good product quality. Herein lies the major drawback for the physical refining system, i.e., complete phosphatide removal with degumming and bleaching is very difficult. Other problems with physical refining systems include the following: (i) additional bleaching earth is usually required; (ii) pesticides are codistilled with the fatty acids during steam refining; (iii) phosphoric acid treatment may darken the gums produced, and incomplete removal can produce off flavors in the oil after deodorization; (iv) steam distillation or deodorizer units must be designed to handle higher concentrations of free fatty acids; (v) cottonseed oil cannot be refined physically because the gossypol pigment must be removed with alkali refining; and (vi) it may be necessary to steam refine before hydrogenation or other processing to adjust melting characteristics, and then deodorize again after these processes. Physical refining is favored for processing high free acidity oils with low phosphatide contents; it has been demonstrated to produce good quality product from coconut, palm kernel, palm, lard, tallow, and some of the seed oils (13).

Degumming

Degumming is the treatment of crude vegetable oils with water, salt solutions, or dilute acids such as phosphoric, citric, or maleic to remove phosphatides, waxes, and other impurities. Degumming converts the phosphatides to hydrated gums, which are insoluble in oil, for separation as a sludge by settling, filtering, or centrifugal action. Phosphatide removal is the first process for the physical refining system; this may also be true for chemical refining. However, with chemical refining, the processor has the option of removing the phosphatides for their by-product value as lecithin or treating them as impurities to be removed along with free fatty acids during caustic neutralization.

Caustic Neutralization

The conventional caustic neutralization process is the most widely used and best-known purification system. The addition of an alkali solution to a crude oil brings about a number of chemical and physical reactions including the following: (i) the alkali combines with the free fatty acid present to form soaps; (ii) the phosphatides absorb alkali and are coagulated through hydration; (iii) pigments are degraded, absorbed by the gums, or made water soluble by the alkali; and (iv) the insoluble matter is entrained with the other coagulable material. Efficient separation of the soapstock from the neutralized oil, which is usually accomplished with centrifugal separators, is a significant factor in caustic neutralization. The conventional caustic soda neutralization systems have the flexibility to refine efficiently all of the crude oils presently utilized for food products (1).

Caustic neutralization is ordinarily accomplished by treating the fat or oil with diluted sodium hydroxide. This treatment forms soapstock with the free fatty acids, phosphatides, trace metals, pigments, and other nonglyceride impurities that can be separated by settling or centrifugal force from the neutralized oil. The neutral oil is usually water washed and again separated by settling or centrifuged to remove trace impurities and residual soaps from the neutralization and separation processes. After it is water washed, the oil is either dried with a vacuum dryer or immediately bleached to remove the trace quantities of water remaining.

Bleaching

Bleaching of edible fats and oils is popularly and correctly regarded as the partial or complete removal of color; however, bleaching is also an integral process in both the chemical and physical refining systems. Bleaching is relied upon to clean up the traces of soap and phosphatides remaining after caustic neutralization and water washing for the chemical refining system. The technical feasibility of physical refining depends upon bleaching as a pretreatment to remove phosphatides, trace metals, waxes, and the color pigments. Another very important function of bleaching in both refining systems is the removal of peroxides and secondary oxidation products.

The usual method of bleaching is by adsorption of the pigments and other nonglyceride impurities on bleaching earth. In a typical process, the bleaching materials are added to the oil in an agitated vessel either at atmospheric pressure or under vacuum. The oil is heated to bleaching temperature and held, to allow contact time with the bleaching earth. After the adsorbent has captured the impurities, it is removed from the oil with a filtration system.

Animal Fat Purification Systems

Traditionally, the method used to purify meat fats has been a form of physical refining. The two main impurities in meat fats are proteins carried over from the rendering process and free fatty acids. The pretreatment phase for meat fats is the removal of the proteinaceous materials. Typically, this is accomplished easily by adding small amounts of diatomaceous earth and/or bleaching earth followed by filtration. An alternative clarification or pretreatment method is to water wash the fat to remove the proteins. This method also requires bleaching or at least drying to remove the moisture remaining in the oil after water washing. A third method for meat fat clarification is caustic refining. Chemical refining is usually reserved for poor-quality animal fats or for specialty products used undeodorized to preserve the characteristic meat fat flavor. The caustic refining system consists of caustic neutralization, water washing, and vacuum drying.

Hydrogenation

The hydrogenation process is an important tool for the edible fats and oils processor. With hydrogenation, liquid oils can be converted into plastic or hard fats that are more suitable for a particular food product. The two reasons to hydrogenate a fat or oil are to change the physical form for product functionality improvement and to improve oxidative stability. Hydrogenation involves the chemical addition of hydrogen to the double bonds in the unsaturated fatty acids. The reaction is carried out by mixing heated oil and hydrogen gas in the presence of a catalyst.

Most hydrogenations are preformed in batch reactors due to the variation in raw materials and the desired end products. Normally, batch hydrogenation is performed in an agitated tank reactor with heating and cooling capabilities designed to withstand pressures of 7–10 bar. First, the catalyst is suspended in the oil. Then, hydrogen gas, dispersed as bubbles, must be dissolved in the oil to reach the surface of the catalyst. The three reaction variables, pressure, temperature, and rate of agitation, are controlled to reduce batch-to-batch variation for preparation of the desired hydrogenated product or base stock. The typical analytical evaluations used for endpoint control are refractive index, iodine value, and various melting points; these help measure consistency.

Postbleaching

A separate bleaching operation, which occurs immediately after the hydrogenation process, has the following three purposes: (i) to ensure that all traces of the prooxidant hydrogenation catalyst that escaped the filtration system after hydrogenation have been removed, (ii) to remove undesirable colors, generally of a greenish hue, that have accentuated during hydrogenation by heat bleaching of the red and yellow pigments, and (iii) to remove peroxide and secondary oxidation products. Postbleach systems are usually batch systems for the same reasons as those given for hydrogenation systems, i.e., production of a wide variety of hydrogenated base stocks.

Fractionation

Edible fats and oils are fractionated to provide new materials that are more useful than the natural product. Fractionation may be practiced to remove an undesirable component, which is the case with dewaxing and winterization, or to provide two or more functional products from the same original fat or oil, as is the case with cocoa butter equivalents or substitutes and high-stability oils.

The three fractionation process types practiced commercially to produce the value-added products are dry fractionation, solvent fractionation, and aqueous detergent fractionation. Dry fractionation, which includes winterization, dewaxing, hydraulic pressing, and crystal fractionation processes, is probably the most widely practiced. Solvent or aqueous detergent fractionation processes provide better separation of specific fractions for the more sophisticated fats and oils products. All of these fractionation process practice the following three successive stages of fractionation: (i) cooling the oil to supersaturation to form the nuclei for crystallization, (ii) progressive growth of the crystalline and liquid phases, and (iii) separation of the crystalline and liquid fractions.

Interesterification

The interesterification process can alter the original order of distribution of the fatty acids in the triglyceride-producing products, leading to melting and crystallization characteristics different from the original oil or fat. Unlike hydrogenation, interesterification neither affects the degree of saturation nor causes isomerization of the fatty acid double bond. It does not change the fatty acid composition of the starting material but rearranges the fatty acids on the glycerol molecule. The process of interesterification can be considered as the removal, shuffling, and then replacement of fatty acids on the glyceride molecules at random. This change in the distribution of the fatty acids affects the structural properties and melting behavior of the fats and oils. Commercially, the interesterification process has been utilized for the production of confectionery fats, margarine oils, cooking oils, frying fats, shortenings, and other special application fats and oils products.

Two types of chemical interesterification process are practiced, namely, random or directed. Random rearrangement of fats and oils can be accomplished using either a batch or continuous process. Both random interesterification processes perform the three important rearrangement steps, i.e., pretreatment of the oil, reaction with the catalyst, and deactivation of the catalyst. In the directed rearrangement process, one or more of the triglyceride products of the interesterification reaction are selectively removed from the ongoing reaction. Continuous processes are normally used for directed rearrangements for better control. Trisaturated glycerides are crystallized and separated from the reaction, which upsets the reaction equilibrium so that more trisaturated glycerides are produced.

Blending

Different stocks are blended to produce the specified composition, consistency, and stability requirements for the various fats and oils products, such as shortenings, frying fats, margarine oils, specialty products, and even some salad or cooking oils. The base stocks may be composed of hydrogenated fats and oils, interesterified products, refined and bleached vegetable oils, purified animal fats, and/or fractions from winterization, dewaxing, or another form of fractionation. The products are blended to meet both the composition and analytical consistency controls identified by the product developers and quality assurance. The consistency controls frequently include analytical testing for solid fat index, iodine value, various melting points, fatty acid composition, and other evaluations designed to ensure compliance with customer requirements. The blending process requires scale tanks and meters to proportion the base stocks accurately for each different product. The blend tanks should be equipped with agitators and heating to ensure a uniform blend for consistency control (1).

Deodorization

Most of the major edible fats and oils retain certain undesirable odors and flavors after extraction or rendering and purification, and other flavors are obtained during processing. Normal bleaching imparts an "earthy" flavor and odor, whereas hydrogenation adds an odor and flavor that can be described only as typical and certainly undesirable. To provide the bland flavor and odor that consumers in most countries have been conditioned to accept, these undesirable impurities must be removed by deodorization or steam distillation. Deodorization is primarily a high-temperature, high-vacuum, steam distillation process to remove volatile, odoriferous materials present in edible fats and oils. It is the last major processing step through which the flavor and odor and many of the stability qualities of a fat or oil can be controlled. From this point forward, efforts must be directed toward retaining the quality that has been built into the fat and oil product with all of the preceding processes (1).

The odoriferous substances in fats and oils are generally considered to be free fatty acids, peroxides, aldehydes, ketones, alcohols, and other organic compounds. Experience has shown that fats and oils flavor and odor removal correlates well with the reduction of free fatty acids. Therefore, all commercial deodorization consists of steam stripping the oil for free fatty acid removal. Currently, batch, semicontinuous, and continuous systems of various designs are utilized by edible fats and oils processors to produce deodorized oil. All of the systems utilize steam stripping with four interrelated operating variables, i.e., vacuum, temperature, stripping steam rate, and holding time.

Liquid Oil Filling and Packaging

Most salad and cooking oils are packaged shortly after deodorization in containers for home, restaurant, or large food processor use. The processing necessary for most oils includes oxidative stability preservation measures such as nitrogen protection, temperature control, light avoidance, and the addition of any additives required by the individual products.

Shortening Plasticization and Packaging

Plasticized shortening products can be defined as fats with a consistency that can be readily spread, mixed, or worked. Considerably more is involved in the plasticization of shortening and margarine than merely lowering the temperature to cause solidification. Slow cooling of these products produces a grainy, pasty, nonuniform mushy product that lacks the appearance, texture, and functional characteristics associated with plasticized products. The development of these characteristics is a function of controlled crystallization or plasticization. The final consistency of a shortening is the culmination of all of the factors influencing crystallization and plasticization, i.e., chilling, working, tempering, pressure, and gas incorporation.

The plasticization process involves the rapid chilling and homogenization of the shortening mixture. Most shortenings are quick-chilled in closed, thin-film, scraped-wall heat exchangers with extrusion valves to deliver a smooth homogeneous product to the package at 17–27 atm pressure. Nitrogen is injected at 13 ± 1% into most shortenings to increase the product's workability and provide a white, creamy appearance. After packaging, many processors temper shortenings at temperatures slightly above the packaging temperature to allow the crystal structure of the hard fraction to reach equilibrium and form a stable matrix. After tempering, shortenings are usually stored and shipped at controlled temperatures of 70–80°F (21.1–26.7°C) to avoid crystal change and loss of the plastic properties (14).

Margarine Mixing, Chilling, and Packaging

Margarine was developed as and continues to be a butter substitute. It is a flavored food product containing 80% fat, made by blending selected fats and oils with other ingredients, such as milk, salt, color and fortification with vitamin A to produce a table, cooking, or baking fat product that serves the purpose of dairy butter but is different in composition and can be varied for different applications. Today, spreads have been developed as margarine substitutes. The major difference between spreads and margarine is that spreads are not required to contain a minimum of 80% fat.

Processing for margarines and spreads begins with the preparation of an emulsion of the ingredients. Emulsions are prepared by adding the oil-soluble ingredients to a heated margarine oil formulation in an agitated emulsion tank. Concurrently, a pasteurized aqueous phase is prepared by mixing all of the water-soluble ingredients together in another vat. The water phase is then added to the oil phase to make the emulsion. The emulsion is chilled rapidly with scraped-wall heat exchangers similar to those used for shortening products. The plasticized products are then formed into prints, or filled into the various containers for consumer, restaurant, or food processor use. Most margarine and spread products are stored at refrigerator temperatures immediately after packaging, except for some specialized baking products (1).

Flaking and Spray Chilling

Fat flakes describe the higher melting fat and oil products solidified in a thin flake form for ease of handling, quick remelting, or for a specific function in a food product. Chill rolls and processed oil formulations have been adapted to produce several different flaked products that can provide distinctive performance characteristics in specialty formulated foods. The flaked products, produced almost exclusively for the restaurant and food processor consumers, are hard fats or stearines, shortening chips, icing stabilizers, confectioners fats, hard emulsifiers, and other customer-specific products.

Flakes are solidified on a chill roll, which has been described as an endless moving chilling surface held at a temperature below the crystallization point of the applied fat or oil product to form a congealed film on the outer surface. Specifically, chill rolls are usually 4-ft diameter hollow metal cylinders, in various lengths, with a machined and ground smooth surface, internally refrigerated, that revolve slowly on longitudinal and horizontal axes, with several options for feeding the melted oil onto the surface. After application, a thin film of liquid fat is carried over the roll, and as the revolution of the roll continues, the fat is partially solidified. The solidified fat is scraped from the roll by a doctor blade positioned ahead of the feeding mechanism with all of the chill roll designs. Flakes are packaged in kraft bags, corrugated cartons with vinyl liners, or other containers suitable for storage and shipment (15).

Spray-chilled or powdered fats are specialized products developed for ease of incorporation, handling, melting efficiency, uniform delivery with addition systems, encapsulation, and other special purpose uses. The spray-chilling process consists of atomizing a molten fat in a crystallization zone or tower, maintained under temperature conditions in which a very fine mist of the melted fat is contacted with cooled air or gas to cause crystallization without marked supercooling (1).

Undeodorized Fats and Oils Packaging

Most vegetable oils are deodorized to obtain a bland flavor; however, some liquid oils are consumed as undeodorized product. Olive oil is almost always marketed throughout the world in the undeodorized form; the natural flavor is an important asset that would be destroyed by deodorization. Soybean, peanut, sunflower, sesame, and some other vegetable oils are generally consumed in their crude form as extracted in Central Asia, India, and China. The undeodorized oils are usually packaged in the same type of containers as the deodorized oils.

Animal fats are marketed undeodorized for both economic and flavor retention reasons. There was a case in which tallow was caustic refined and used undeodorized for frying french fries to obtain the characteristic tallowy flavor. Additionally, lard used in operations in which the flavor is desirable, such as for pie doughs and ethnic foods, is often only filtered, with no further processing before packaging and use. These products are normally plasticized like the shortening products discussed earlier for handling convenience and better functionality in some cases.

Bulk Fats and Oils Shipments

Food processors that use fats and oils in large quantities generally have the facilities to handle this ingredient liquid in bulk. All of the products packaged for shipment and use can be provided to the customers in tank cars or tank trucks, except for the margarine and spread mixes, which contain milk and salt. The customers for these bulk products must have fats and oils bulk handling systems to receive, store, and handle the liquid products.

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Chapter 7

Recovery of Fats and Oils from Plant and Animal Sources

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Introduction

Fats and oils have been recovered for thousands of years from oil-bearing seeds and fruits, and fatty animal tissues. Fats and oils have been and continue to be important sources of food, cosmetics, lubricants, and chemicals. Soybeans in Asia, and sesame seed and olives in the Middle East were the earliest sources of edible oils. Nine crops now provide most of the edible oils in the U.S. market, i.e., soybeans, palm fruit, corn (germs from wet and dry milling), canola seed, cottonseed, sunflower seed, peanuts, safflower seed, and coconut, whereas, flax seed, rapeseed, crambe seed, and castor beans are important sources of industrial oils. Tallow and milk fat from cattle, lard from swine, tallow from sheep, and oil from fish are important animal sources. Historically, whale oil has also been important, but international treaties that prevented the hunting of whales have now eliminated whale oil as a commercial product.

Despite the wide diversity of today's sources, the purpose of all recovery processes is to obtain triglycerides in high yield and purity, and to produce coproducts (usually high in protein content) of maximum value. Oilseeds are processed by one of three types of processes, namely, hard pressing, prepress solvent extraction, and direct solvent extraction. The seed extraction process that is preferred depends upon how much oil is present in the material, how much unextracted oil can remain in the meal without affecting its market value, how much protein denaturation is allowed in the meal, how much investment capital is available, and how restrictive local environmental laws are concerning emissions of volatile organic compounds (VOC).

Fatty fruits, such as palm fruit, coconuts, olives, and avocados, also provide large quantities of edible fats and oils. Palm fruit is unusual in that the fleshy tissue surrounding the seed provides liquid oil, whereas the seed (kernel) is also a source of fat, which is particularly useful in confectionery products (as a cocoa butter substitute). Oil-bearing fruits are pressed to obtain oil, sometimes after drying (as with coconut copra) or sterilizing (as with palm fruit); at other times, no heat is used (as with virgin olive oil).

Terrestrial and marine animals also are important sources of edible and industrial fats and oils such as lard, tallow, and fish oil. Both wet- and dry-rendering processes can be used to recover fats or oils. In both processes, heat plays an important role in freeing triglycerides from the tissue. Meat and bone meal, coproducts from rendered tissues that are unmarketable as food, are important protein ingredients in livestock feed. Fishmeal is particularly valuable in poultry and fish diets because of its ideal amino acid balance and unidentified growth promoters.

Recovery of oil from one example each of oilseeds (soybeans), oil-bearing fruits (oil palm) and fatty animal tissues (lard) will be described in detail. Recovery of oil from most other sources will be similar to one of these three examples; specific processing details for other oilseeds are available from Bockisch (1). Additional information on processing these crude oils into edible products is described in the following chapters and by Johnson (2).

Processing Seeds

General Methods

Hard pressing is the oldest method to process oilseeds; it is completely mechanical and requires the least amount of capital investment and attention to safety. In this process, the oil is squeezed or pressed from the solids known as "cake," usually after cooking and/or drying to enhance oil recovery (Fig. 7.1). In the early years, batch systems incorporating lever presses and screw-operated presses powered by work animals were used. During the 19th century, batch hydraulic presses (similar to today's cider press) were used. By the turn of the 20th century, continuous screw

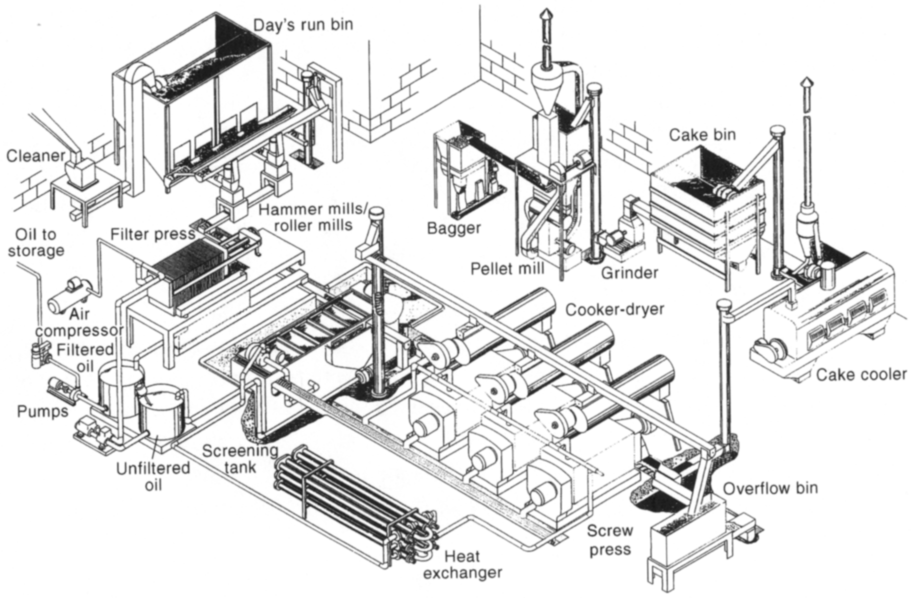


Fig. 7.1. Depiction of hard screw pressing (provided by Anderson International, Cleveland, OH).

presses connected to line shafts driven by steam engines were used. Today, electric motor–powered, continuous screw presses, sometimes referred to in the industry as "expellers," are used for high oil–content seeds. The term "crushing" to denote oil recovery originates from the days when pressing was the only method available to process oilseeds.

Normally seeds containing >30% oil have required pressing, either hard pressing or prepressing before solvent extraction (so that the material is sufficiently dense to withstand solvent extraction and not produce fine particles, which adversely affects various operations). Hard pressing involves squeezing out as much oil as possible. In prepressing, only the easily extractable oil is squeezed out before subjecting the partially de-oiled material to more complete extraction with solvent. Sunflower seed, safflower seed, wet-milled corn germ, rapeseed, and sesame seed are usually prepressed, followed by solvent extraction. However, the recent adoption of the expander (an extruder-like device) has allowed some high oil–content seeds to be solvent extracted without prepressing (Fig. 7.2). Although hard pressing soybeans was common before WWII, direct solvent extraction (without prepressing) is now the most widely practiced method for soybeans. Oil is more completely recovered when solvent extraction is employed (typically <1% residual oil content for solvent extraction vs. >6% for hard pressing).

As a simplification, one can describe solvent extraction of oilseeds as being like cleaning a paint brush. To clean the brush thoroughly, the solvent must have good contact and penetration into the brush bristles, enough clean solvent to remove all of the paint, sufficient heat to do the cleaning quickly, and enough time. Although many solvents have been tried over the years, mixtures of hexanes are used today. Most hexane mixtures used contain about two thirds *n*-hexane; the remainder is mostly other isomers of hexane.

Direct solvent extraction is usually preferred for soybeans; soybean plants capable of processing as much as 10,000 ton/d have been constructed (3000 ton/d would be common). Both prepress solvent extraction and direct solvent extraction are depicted in Figure 7.3.

Recovery of Oil from Soybeans

Soybeans constitute an important source of edible oil; many have argued, however, that it is actually a "protein crop" because ~70% of the returns in processing soybeans is due to the sale of meal. Thus, the processes used to extract oil are designed to maximize meal quality. The flow diagram for processing soybeans is shown in Figure 7.4, and aerial and interior photographs of soybean plants are shown in Figure 7.5. Erickson (3) provides an excellent reference for more detailed information on soybean processing.

Seed Handling. Soybean tissue is composed of many cells containing oil, protein, and metabolites; these supply energy, nitrogen storage reserves, and other important compounds, respectively, to support germination of new plants. The triglycerides are

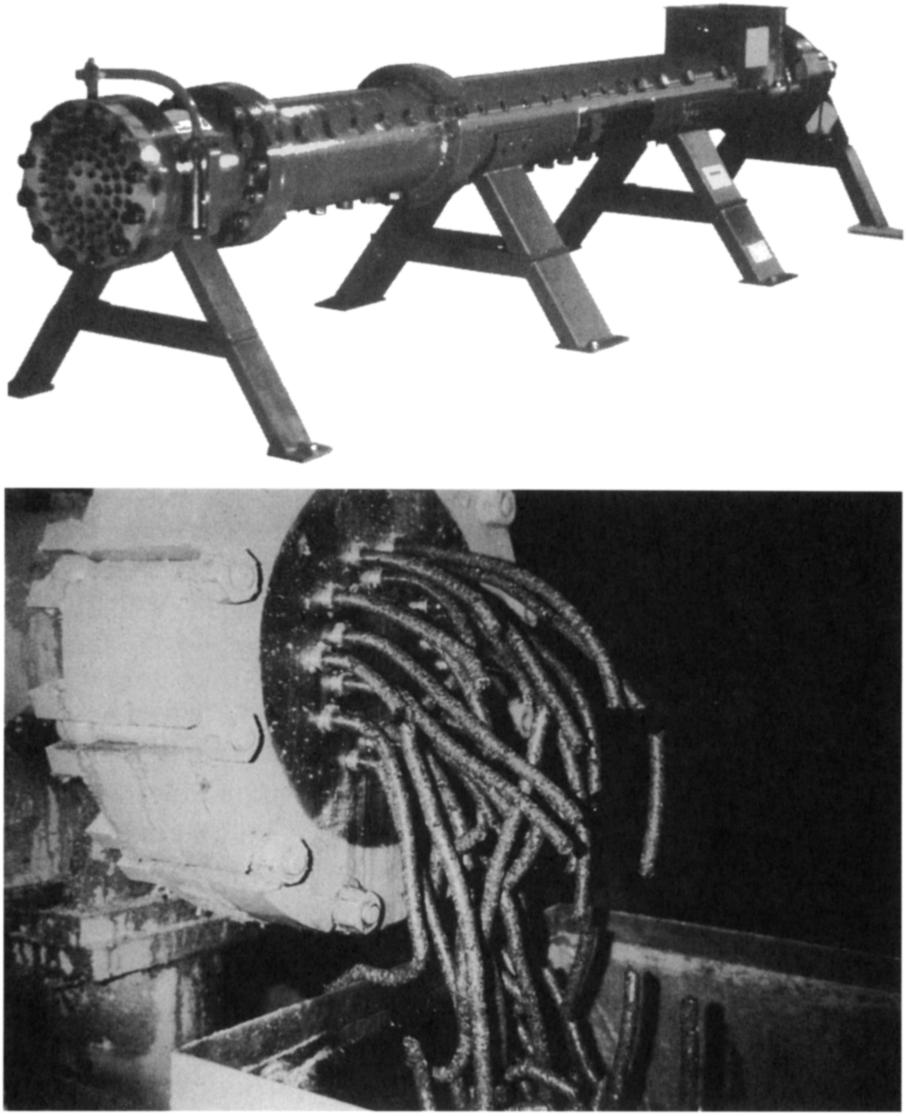


Fig. 7.2. Photograph of an operating expander (provided by Anderson International, Cleveland, OH).

stored in discrete bodies called "oil bodies" or "spherozomes." The preponderance of the protein is storage protein, which is concentrated in other discrete bodies known as "protein bodies." Most of the phospholipids are associated with membranes around the protein bodies and spherozomes. However, catabolic enzymes (enzymes responsible for hydrolysis of lipids and proteins) and cellular metabolites

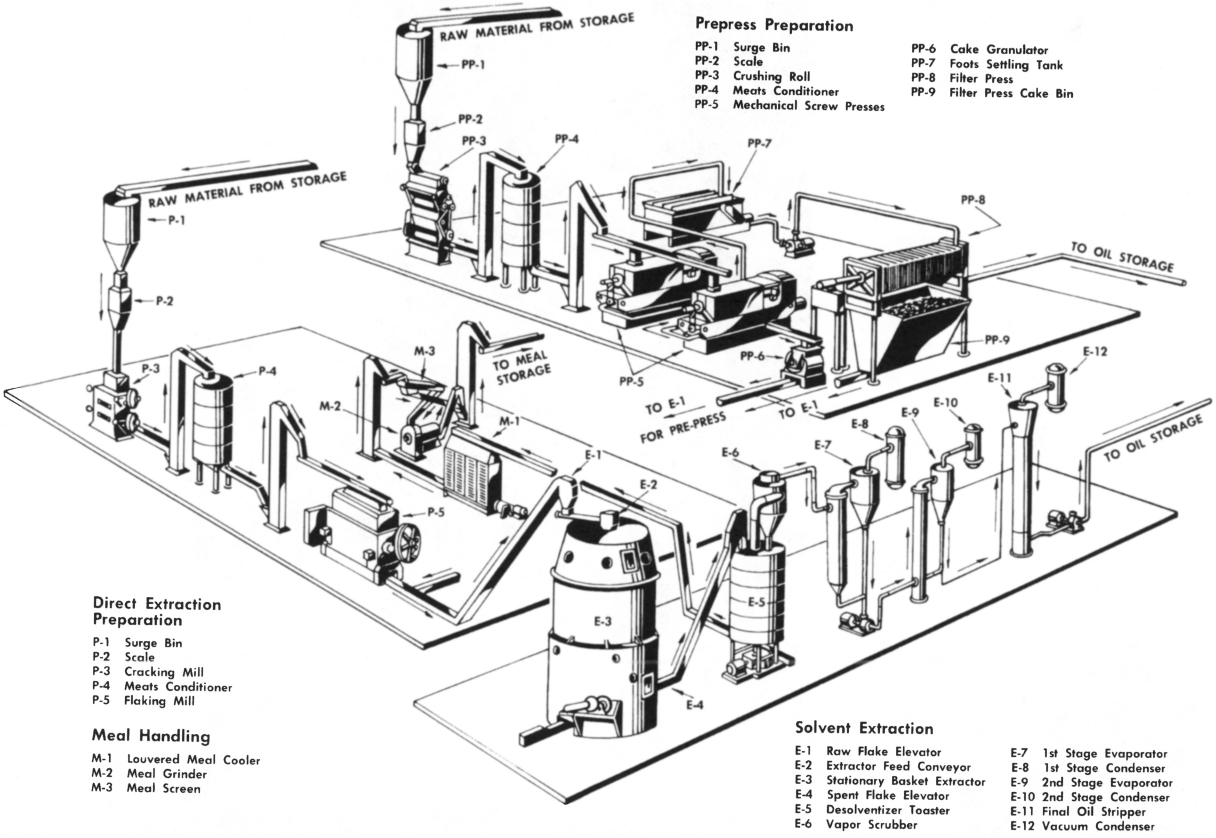


Fig. 7.3. Depiction of prepress solvent extraction and direct solvent extraction (provided by French Oil Mill Machinery Co., Piqua, OH).

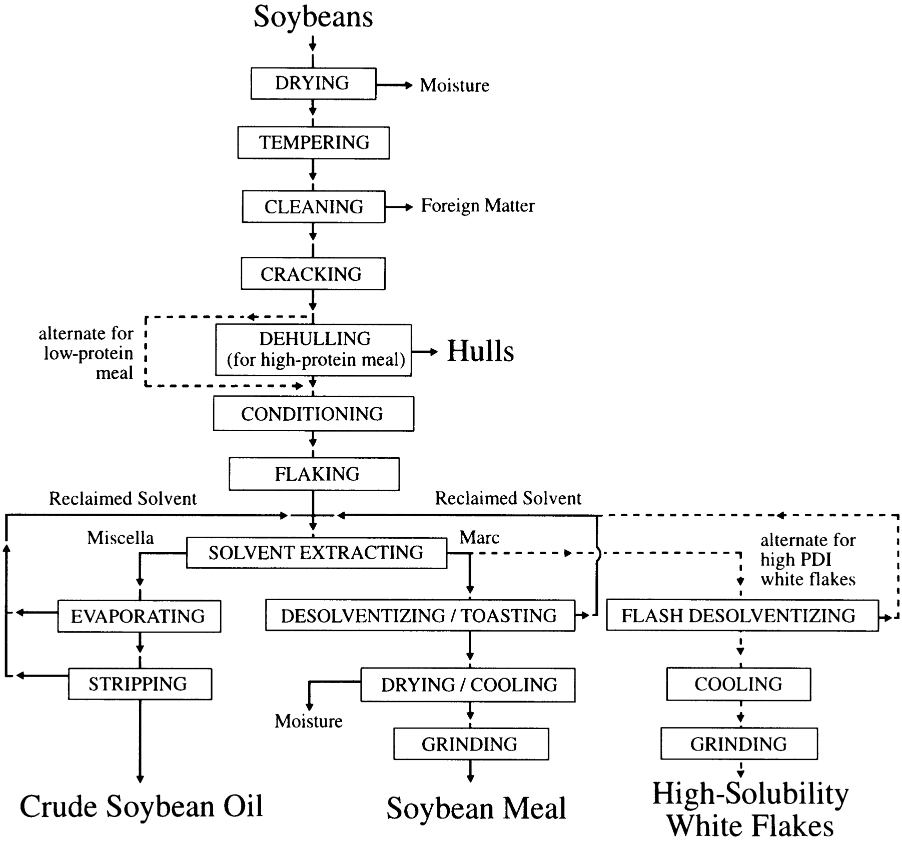


Fig. 7.4. Flow diagram for processing soybeans.

are present in the cytoplasm. This separation of enzymes and substrates is important to long-term storage because its breakdown, such as by bruising when hitting a hard surface, leads to enzymatic deterioration of oil quality.

Lipase is an enzyme that catalyzes triglyceride hydrolysis, thus increasing the free fatty acid content that must be removed by refining (lipase action is not usually a problem in soybeans, but is quite important in cottonseed storage and palm fruit processing). The class of enzymes known as phospholipases may catalyze the conversion of phospholipids to a nonhydratable form that is very difficult to remove from the oil by today's refining procedures. Still another class of enzymes in soybeans known as the "lipoxygenases" (three known isoenzymes) oxidizes linoleic and linolenic acids, causing beany flavors. Anyone who has chewed soybeans knows the consequences of lipoxygenase activity, i.e., rapid production of obnoxious flavors.

The quality of soybeans is highest just before harvesting in a year with ideal weather. If cell walls and membranes become ruptured, oil and deteriorative enzymes come into contact with one another. As temperature, moisture content, and

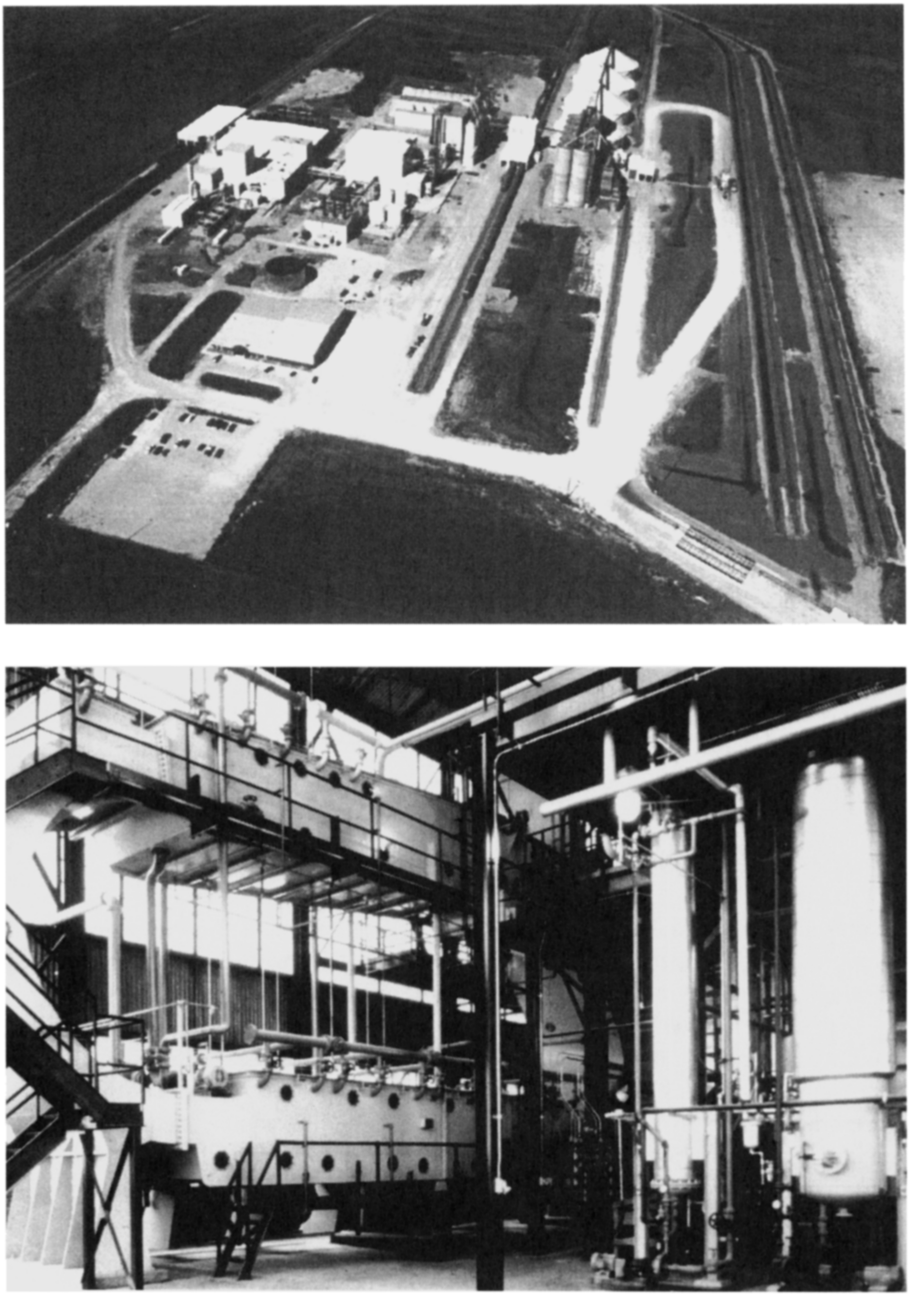


Fig. 7.5. Aerial and interior photographs of a soybean processing plant (aerial photograph provided by Bunge Corporation, St. Louis, MO; interior photograph provided by Crown Iron Works, Minneapolis, MN).

extent of damage increase, so do the rates of enzyme-catalyzed reactions. Some physical damage to seed is inevitable during harvesting and shipping, but it must be minimized. Similarly, once seed processing begins, it must be done quickly to produce oil of maximum quality.

Soybean Drying. Usually soybeans are allowed to dry in the field to ~13% moisture before harvesting; that amount of moisture is considered safe for long-term storage. When the moisture content exceeds this critical value, the beans must be dried, which is usually done with open-flame grain dryers. Seed temperature should not exceed 76°C during drying to prevent seed and oil discoloration and protein denaturation.

Soybean Storage. Farmers often store soybeans on the farm in metal bins or at local elevators in concrete silos. Higher prices are usually paid later in the crop year. Storage for extended periods at moisture contents >13% also reduces the recoveries of oil and protein in addition to affecting the quality of the oil adversely.

When soybeans are harvested, they are alive and respiring; that is, they are still actively breaking down seed mass to CO_2 and other metabolites. The respiration rate is low when either the temperature is low (e.g., 5°C) or the moisture content is <13%. Oilseeds with higher oil contents than soybeans (20% oil) have lower critical moisture values for safe storage. When soybeans contain >13% moisture, respiration increases; soybeans may even germinate or be attacked by fungi. As soybeans respire, heat is produced, and the increased temperature further accelerates respiration. In worst-case conditions, the soybeans may become heat damaged and scorched. Modern storage facilities employ temperature-monitoring systems to alert operators when seed temperatures exceed set points. Soybeans that are heating are moved to another bin to disperse hot spots, or ambient air is blown through the beans to provide cooling. The amount of heat-damaged beans is a factor in the U.S. grades and standards for soybeans. Heat-damaged beans have a high free fatty acid content, and the oil color darkens, thereby increasing refining loss.

Overdrying also has consequences. The soybean cotyledon is prone to breaking into halves, called "splits," when the hull becomes separated from the cotyledon during conveying and transporting. Seed breakage becomes worse when the beans are overdried. Splits are difficult to separate from foreign matter, and their oil deteriorates at a faster rate. Catabolic enzymes are activated in splits, increasing the contents of free fatty acids, phosphatides, iron, and peroxides in the oil. In addition, oils from field- and storage-damaged soybeans usually have poor flavors. As a consequence, the contents of damaged kernels and splits are recognized as contributing to U.S. grades and standards for soybeans.

When soybeans are received at the crushing plant, they are sampled to analyze moisture, foreign matter, splits, and damaged seed contents. Sometimes oil and protein contents are also determined (only test weight, total damaged kernels, heat-damaged kernels, foreign matter, splits, and soybeans of other colors are considered in U.S. grading standards), and prices paid may be based upon the values obtained.

Soybeans with excessive foreign matter are transferred to scalping operations for removal of the foreign matter, which usually contains more moisture than the beans. The foreign matter tends to become concentrated under discharge spouts during placement into storage bins; consequently, this area of the bin is prone to heating. Removing foreign matter reduces the moisture content, improves storability of the beans, and improves oil quality.

Inside storage systems, primarily concrete silos and metal bins, are used for storing soybeans at elevators and plant sites. Unlike storing cottonseed in dry locations (e.g., west Texas), soybeans are rarely and for only very short periods stored on concrete pads without protection against the weather.

Cleaning. Stems, pods, leaves, broken grain, dirt, sand, small stones, and extraneous seeds are typical components of foreign matter. Cleaning is usually the first step in processing soybeans. Foreign matter reduces oil and protein contents, adversely affects oil quality (especially color), and increases wear and damage to expensive processing equipment. Vibrating and/or shaker screens, sometimes with aspiration, remove foreign materials. Shaker screens are used to separate particles on the basis of size, whereas aspiration separates on the basis of density and buoyancy in a stream of air. Tramp iron, extraneous metal acquired during harvesting, transporting, or upstream processing steps, must be removed to prevent damage to equipment by the placement of magnets in chutes just ahead of vulnerable processing equipment.

Dehulling. It is desirable to remove the hull (seed coat) that covers the soybean cotyledon or "meat." The meats contain much more oil and protein than do the hulls. Soybean hulls account for ~8% of the bean dry matter but contain <1% lipid. Removing the hull reduces the amount of material that must be further processed, thus increasing downstream plant capacity and reducing energy consumption per unit processed. However, removing the hull is usually done to raise the protein level of the meal. The protein content of soybean meal increases by ~4% when the hull is removed (44% protein meal is produced when not employing dehulling vs. ~48% with dehulling). Hulls can be helpful at times because they allow easier hard pressing and enhance solvent drainage. However, the majority of soybeans today are dehulled because the feed industry prefers high-protein soybean meal.

Decortication, the freeing of the hull (pericarp) from the cotyledon, becomes easier after further drying of the beans to ~10% moisture (from 13% for safe storage). The beans are sometimes tempered for 24 h to allow the moisture content to equilibrate throughout the bean before decorticating. Decorticating is accomplished by cracking the bean into 6–8 pieces with corrugated roller mills. Cracking must be done carefully so that the cotyledon is not broken into fine particles that would be difficult to separate from the hull. Also, crushing the meats during dehulling causes oil cells to rupture, freeing the oil. This damage should be minimized to prevent absorption of liberated oil by hulls. Both problems increase the oil content of the hulls and reduce oil yield.

Shaker screens, aspirators and/or gravity tables may be used to separate hulls from meats. Hulls should be larger in size, lower in density, and more buoyant in an air stream than the oil-rich meat. The hulls may be heat treated to inactivate antinutritional factors before being sold for feed. Hulls may be blended back with meal to control protein level or sold as a separate coproduct for cattle roughage.

Hot dehulling systems have been developed recently; these eliminate the need for tempering. Cleaned beans are heated to 60°C over a 20- to 30-min period to allow moisture to migrate to the surface. Then they are heated quickly to 85°C to dry the beans 1~3%. This helps decortication. The beans are split into halves; the hulls are further loosened by friction or impact and removed by aspiration. Hot dehulling is more energy efficient than conventional dehulling; it provides more complete hull removal, which is becoming more important so that higher protein levels can be made with lower protein beans.

To minimize oil loss, complete hull removal is not desired when marketing the protein as meal for livestock feeding. On the other hand, when making edible flours or "white flakes" (untoasted soybean meal) for protein extraction, nearly complete removal of hulls is required. Over 90% of the hulls from soybeans must be removed to meet the minimum specification of 50% protein. Hulls also adversely affect the appearance, functionality, and performance characteristics of soy protein ingredients. Livestock feeders are also moving toward higher protein–containing meals. It is becoming increasingly difficult to produce soybean meal with high protein content because increasing soybean yields on the farm are depressing protein content. This trend is leading to increased acceptance of hot dehulling.

Hard Screw Pressing. In the United States, hard screw pressing is limited largely to the minor oilseeds or locations in which oilseed supplies are not sufficient for large-scale solvent plants (e.g., peanuts, rapeseed, and some cottonseed). There is growing interest in hard pressing oilseeds to produce organic, specialty (unique fatty acid composition), and vegetable oils that are not genetically modified. In some locations, such as California, local laws prevent construction of new solvent plants, and hard pressing is the only option for local processing. A small amount of soybeans is hard pressed in cases in which the meal has particularly high value (e.g., high rumen by-pass protein and high metabolizable energy for dairy cattle feed) or identity-preserved processing is desired (Fig. 7.6). The few remaining hard press plants crushing soybeans tend to be small scale, with the exception of one Iowa plant that processes >1000 ton/d. Hard pressing is used widely for processing copra, peanuts, sesame, and cocoa beans.

Before hard pressing, soybeans are heated (Fig. 7.1). The heated and dried beans are then conveyed to screw presses. By employing proper cooking methods and using a well-maintained, modern screw press, cake oil contents as low as 3–4% can be achieved. Using more and more pressure becomes self-defeating, because pressure and heat cause capillaries to be reduced in volume, sheared, and eventually sealed by coagulation of protein. However, most hard press plants have not invested sufficient capital to prepare beans optimally before screw pressing; thus, as much as 6–10% oil often remains in the solids.

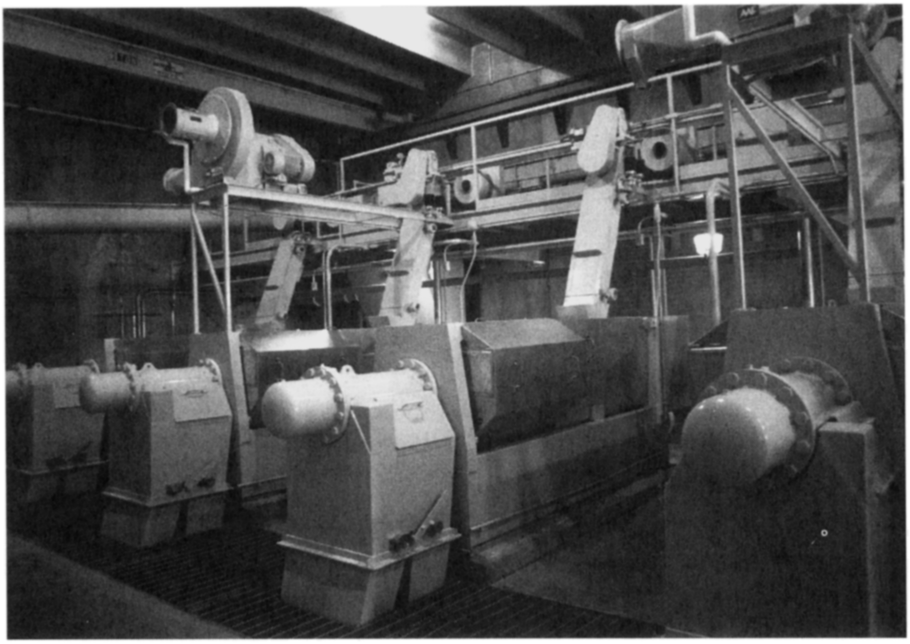


Fig. 7.6. Photograph of a screw-press plant.

A screw press is a continuous screw auger designed to subject the oil-rich material to increasing pressure as it is conveyed through the barrel. The barrel forms a cage of bars surrounding the screw in a parallel fashion. The bars of the cage are separated by spacers that decrease in size, thus allowing the oil to drain from the cage while the solids are conveyed down the barrel towards higher pressure. The discharge opening for the solids and, thus, the back pressure, is controlled by a choking device. A plug of compressed oil-lean solids, termed "cake," forms at the discharge. The pressure increases down the length of the barrel by increasing the root diameter of the screw, decreasing the pitch of the screw flights, and controlling the cake discharge opening by means of a choking device. The feed is rammed against the plug, causing the oil to be squeezed out through the bars of the cage. In hard pressing, screw presses are choked to achieve maximum pressure within the barrel while maintaining cake discharge and an acceptable amount of "foots" (cellular debris) in the oil.

The considerable frictional heat that is generated must be removed to achieve low residual oil and prevent damage to the cake and oil. Some screw presses recycle cooled pressed oil over the cage to remove the heat, whereas others use water-cooled shafts and bar cages.

The oil is pumped or flows by gravity to a sedimentation basin to facilitate settling of the foots. The settled foots are recycled to the press to reclaim entrained oil. The oil is filtered and placed into storage tanks. The cake is then ground into meal.

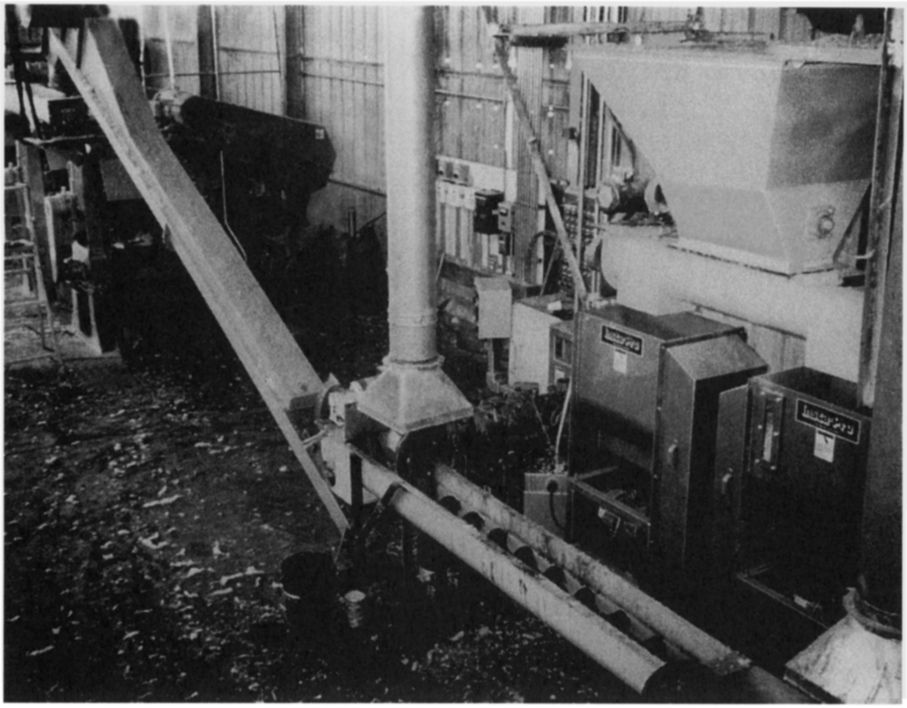


Fig. 7.7. Photograph of an extruder-screw press soybean plant.

In recent years, extruding and then hard pressing soybeans (Fig. 7.7) has become popular, especially where there is a local dairy cattle feeding industry to utilize the higher fat–containing meals. Unfortunately, there are few markets for the oil—one major food company and a few companies producing lubricants and other industrial products. There is growing interest among these small soybean plants to process specialty oils whose market does not justify larger plants. Some of these extrusion-pressing plants seek to develop low-cost refining techniques so that they can also bottle edible oils for niche markets. Some of the niche markets for specialty soybean oils include the following: oil high in oleic acid for health and stability reasons; oil low in saturated fat for health advantages; oil high in saturated fat to eliminate the need for hydrogenation; oil low in linolenic acid for better shelf life; organically produced oil; and oil certified to be free of transgenetic modification (such as those tolerant to herbicides).

Prepress Solvent Extraction. Only when soybeans are processed in plants designed for other oilseeds (e.g., cottonseed or sunflower seed) are they subjected to prepress solvent extraction. Soybeans do not contain sufficient oil to justify or require prepressing. In prepress solvent extraction, part of the oil, that which is easily removed, is pressed out, generally as described for hard pressing. In prepressing, the press is choked so that less pressure develops than in hard pressing; therefore, less press oil is recovered and the capacity of the screw press is increased. The oil content of prepress cake is typically 15–18%, and the partially de-oiled cake is then extracted with solvent. The cake may be broken into pieces and even flaked to increase bulk density and extractor capacity, and to speed solvent extraction. The remaining steps are the same as those for direct solvent extraction, which is described in the next section. Usually pressed and solvent extracted oils are mixed before transporting to a refinery.

Direct Solvent Extraction. Although hard pressing was used extensively before World War II to process soybeans, probably >97% of the soybeans crushed in the United States are now processed by direct solvent extraction. Solvent extraction of soybeans is a mass transfer unit operation. The walls of soybean cells are impermeable to oil and nearly so to extraction solvents; consequently, they must be distorted (ruptured) before extraction. This requires reducing the size of soybean meats and flaking. In addition to cell distortion, the rate of oil extraction also depends upon flake thickness. Oilseeds are conditioned (heated without drying) before flaking by using vertical stack cookers or rotary tube conditioners to heat the seed to 60–70°C over a 20- to 30- min period while maintaining 10.5–11.5% moisture (slight injection of steam is required). Small pieces transfer heat and moisture more readily during conditioning; however, excessive size reduction reduces mechanical distortion during flaking. This treatment makes the meats pliable so that they can be flaked with smooth-surfaced roller mills to ~0.25-mm (0.010–0.012 in) thickness without producing excessive fines, which adversely affect other operations. Proper plastic texture is necessary to produce thin, nonfragile flakes with minimum fines and maximum cell rupture.

Flaking is carried out by passing the cracked conditioned meats through smooth-surfaced roller mills. Flaking larger particles causes more cell rupture than flaking smaller particles. The flaked material must have a tenacious, thin structure with porosity that allows transport of the oil or "miscella" (solvent-oil mixture).

Moisture content of the flakes is yet another factor affecting rate of solvent extraction. In most cases, 9–11% moisture is ideal. Hexane and water are immiscible, and higher moisture contents interfere with the penetration of hexane. Lower moisture levels reduce the structural strength of the flakes and produce more fines.

Solvent temperature also has a large effect on extraction rate; thus the solvent is heated close to the boiling point. Solvent boiling must be avoided because extraction vessels are not designed for pressurization change; solvent losses increase and safety is compromised. The solvent used today is hexane, but other solvents have been tried (ethanol, isopropanol, acetone, isopentane, isohexane, trichlorethylene). Alternative extraction solvents have been reviewed extensively by Johnson (4). The disadvantages of hexane include its flammability, a price structure that is tied to petroleum prices, and increasing regulatory pressures on emissions; its advantages include high oil solubility, ease of evaporation, abundant availability, and historically low price.

In actual practice, soybean extraction does not follow the single mechanism of leaching as described in the overly simplified brush-cleaning analogy. Instead,

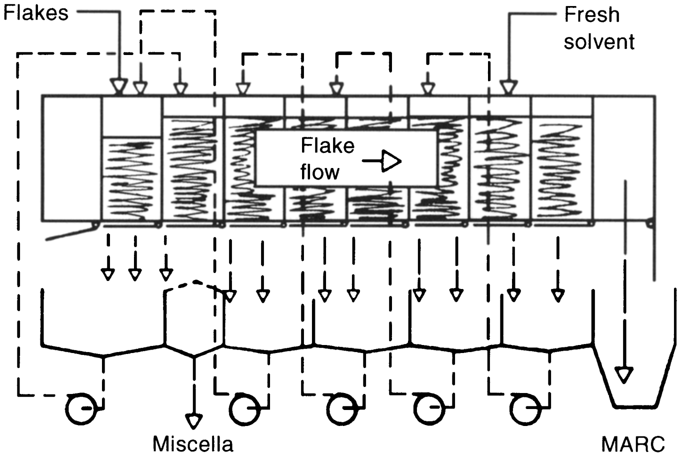


Fig. 7.8. Depiction of countercurrent extraction principles (redrawn from Ref. 3).

soybean extraction involves a combination of leaching, diffusion, and dialysis. This combination of mechanisms leads to an ever-decreasing rate of extraction as the relative importance of each mechanism changes during the course of extraction. For flakes, the larger proportion of readily extractable oil originates with ruptured cells, especially those near the flake surface. The transfer of oil from ruptured interior cells is governed by capillary flow, and the rate of oil transfer is dependent in part on the viscosity of the miscella. A portion of the slowly extracted oil is contained within intact unruptured cells and must be transferred by osmosis, which is a very slow process. Presumably, the process of extruding flaked meats, known as "expanding," shifts the relative importance toward leaching because nearly all of the cells are ruptured and the collet (extrudate) is quite porous.

The best quality oil, low in phosphatides, free fatty acids, nonsaponifiables, and pigments, is extracted first, whereas poorer quality lipids are extracted with more exhaustive extraction. However, the industry strives for the most complete extraction possible. Typically, residual oil contents of solvent-extracted soybean meal range from 0.5 to 1.0%.

The flow of solvent relative to the flakes is countercurrent to reduce the amount of solvent used (Fig. 7.8). In countercurrent systems, the freshest flakes contact the oldest solvent and progress through the process until nearly oil-free flakes contact fresh solvent. The extractor is a vessel enclosed to contain solvent vapors and designed to wash, extract, drain, and transport flakes. Because hexane is highly flammable, controlling solvent vapor loss to an absolute minimum is critical for safety.

Two principal types of extractors have been employed, i.e., "immersion extractors" and "percolation extractors" (Fig. 7.9). In the former, materials are immersed and soaked in solvent (the Soxhlet extractor is a laboratory example). Immersion extractors require more solvent usage and have material conveyance

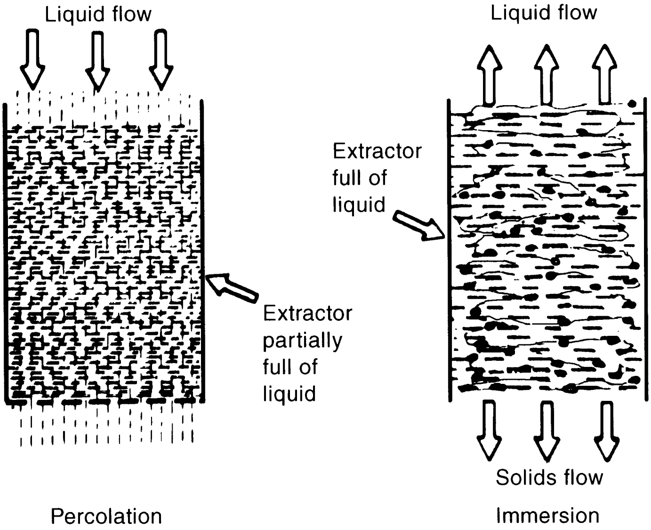


Fig. 7.9. Depiction of immersion extraction and percolation extraction principles (redrawn from Ref. 3).

problems; therefore, percolation extractors predominate almost exclusively in the industry today. A percolation extractor uses gravity to percolate the solvent downward through a bed of material (the Goldfisch apparatus is a laboratory example of a percolation extractor). As the solvent percolates downward through the flake bed, the solvent flows over the flakes and diffuses through them. Miscella flows in successive passes through the flake bed while the solvent sprays the bed as it moves in a direction opposite to the solvent flow. The oil concentration increases as the number of passes increases (usually 5–6 passes).

The extraction principles employed by most percolation extractors are the same, but the method by which each achieves countercurrent flow of solvent to flakes is different. The shallow-bed, chain extractor (Fig. 7.10), which resembles a full-loop conveyor, is one of today's popular extractors. Flakes are fed into an inlet hopper and are conveyed down the first leg of the loop where they are washed with moderately dilute miscella to extract surface oil and penetrate the cells. As the flake bed moves into the bottom horizontal section, full miscella is recycled through the bed for filtering, and then to a liquid cyclone for final removal of fines. The clarified full miscella goes to the evaporation system. Flakes are conveyed counterclockwise, through progressively more dilute miscella washes. A final wash with fresh solvent is used in the top horizontal section of the loop. The latter half of the top loop is for drainage, after which the "marc" (solvent-laden spent flakes) is conveyed to the meal desolventizer. The chain extractor uses relatively shallow bed depths (generally <3 ft); this promotes drainage and, consequently, low solvent carryover to the meal desolventizer.

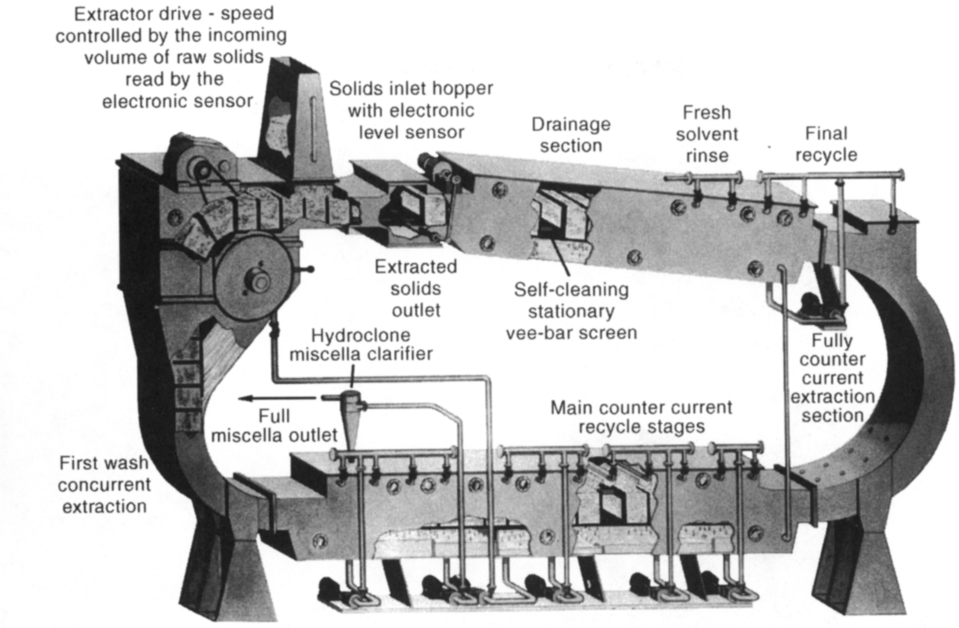


Fig. 7.10. Depiction of a shallow-bed, chain-type extractor (provided by Crown Iron Works, Minneapolis, MN).

Another popular extractor is the stationary basket extractor (Fig. 7.11). Unlike other extractors, the solids do not move. Countercurrent solvent to flake flow is accomplished by rotating the flake inlet, the solvent and miscella sprays, the miscella collection cells, and the marc discharge. The bed is divided into cells or baskets to prevent back mixing of oil-lean miscella with oil-rich miscella. Typically, the bed depths used in this extractor are much deeper than those of the chain extractor. The drained marc discharges when an opening in the bottom screen and discharge hopper rotate into appropriate positions.

A third popular technique is the belt-type extractor (Fig. 7.12). In this type of extractor, the flakes are conveyed through a series of solvent sprays by means of a belt. Fresh solvent is introduced at the discharge end and is circulated in a manner countercurrent to the flow of flakes by a series of stage pumps. There are no dividers in the belt, but the belt is inclined to ensure countercurrent flow of solvent to solids. The drained marc discharges the extraction belt by means of rotary paddles.

A fourth type of extractor is the deep-bed, rotary-basket extractor (Fig. 7.13). Countercurrent solvent to flake flow is accomplished by rotating the baskets of flaked material while the solvent and miscella sprays, the miscella collection cells, and the marc discharge remain stationary. The bed is divided into cells or baskets to prevent back mixing of oil-lean miscella with oil-rich miscella. The drained marc discharges when the basket rotates to the position above the discharge hopper.

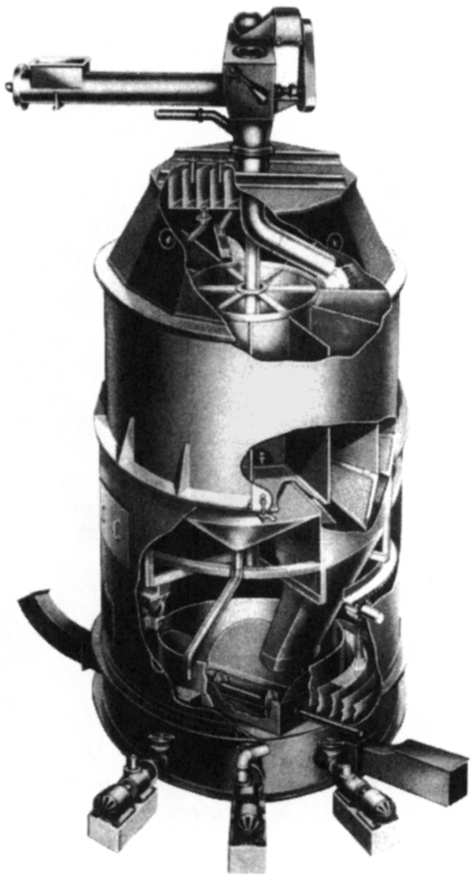


Fig. 7.11. Depiction of a deep-bed, stationary basket extractor (provided by French Oil Mill Machinery Co., Piqua, OH, rights now owned by De Smet Process and Technology, Marietta, GA).

Soybean flakes are extracted for 30–60 min depending on type of extractor used to achieve <1% residual oil in the extracted material. In soybean extraction, less than one part of hexane is used for each part of soybean flake extracted, and industry continually strives to reduce the amount of hexane used and the amount of energy consumed in evaporating. The full miscella contains 22–30% oil and is sent to evaporation and stripping columns to separate the oil from hexane. The full miscella is heated under vacuum to evaporate the solvent in two stages of evaporators. The first-stage evaporator concentrates the oil to 65–80% using reclaimed heat from heated solvent vapors produced in desolventizing the meal. The second-stage evaporator uses steam to concentrate the oil to 93–97%. The concentrated oil is sent to a disc-and-donut stripping column in which heat, vacuum, and sparging with live steam are used to remove most of the remaining hexane. The hexane is recycled to the extractor to be used again. After the stripping column, the crude oil contains <0.15% moisture and hexane. The stripped oil then goes to an oil dryer to remove any condensed moisture. Normally, the oil exiting the oil dryer contains <200 ppm of hexane. The oil must have a flash point

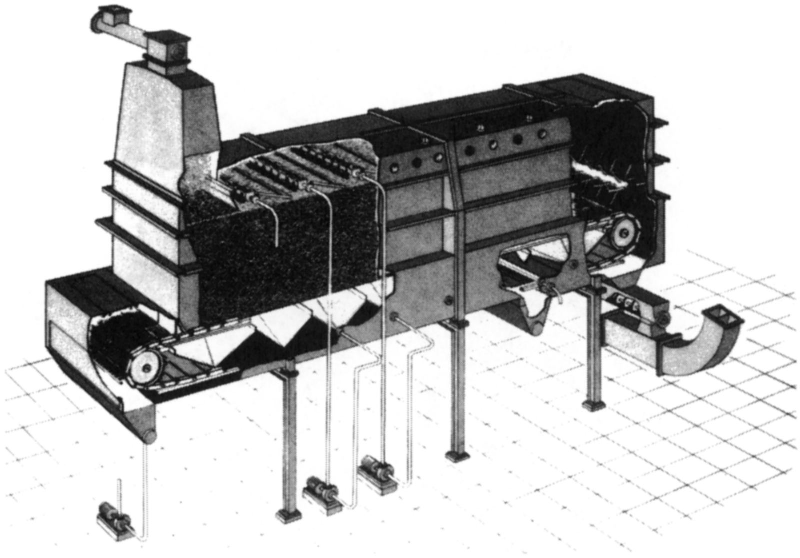


Fig. 7.12. Depiction of a deep-bed, belt-type extractor (provided by De Smet Process and Technology, Marietta, GA).

>250°F, which is equivalent to <800 ppm of hexane. The remaining hexane is removed during deodorization at the oil refinery.

The marc generally contains 30–32% hexane (known as "solvent hold-up"), which also must be recovered and recycled to the extractor. Heat must be used to evaporate the hexane from the meal. Live steam is also injected to aid heat transfer and provide moisture vapor to strip the solvent. The extracted flakes, known as "spent flakes," must be drained of solvent as much as possible to reduce the amount of energy required to desolventize the meal.

Because >97% of the available soybean meal is used for feed, extensive heat treatment is necessary to maximize feed conversion efficiency by livestock. Toasting denatures protease inhibitors (trypsin and chymotrypsin inhibitors, in particular) and the enzyme urease, and improves protein digestibility. None of these objectives can be obtained without the protein being denatured and losing water solubility. However, depending on the method used, meals with great differences in protein solubilities or dispersibilities can be produced. The optimum amount of heat treatment in toasting soybean meal continues to be debated among animal nutritionists.

A conventional desolventizer/toaster (DT) is a vessel composed of about six stacked trays, all with indirect heating. The first two also have provisions for injecting live steam through nozzles within the sweep arms. The meal advances down through the trays, evaporating more and more solvent. The lower four trays are essentially toasting/drying sections where the meal is held at a minimum temperature of 100°C, and the meal is partially dried before going to the meal dryer.

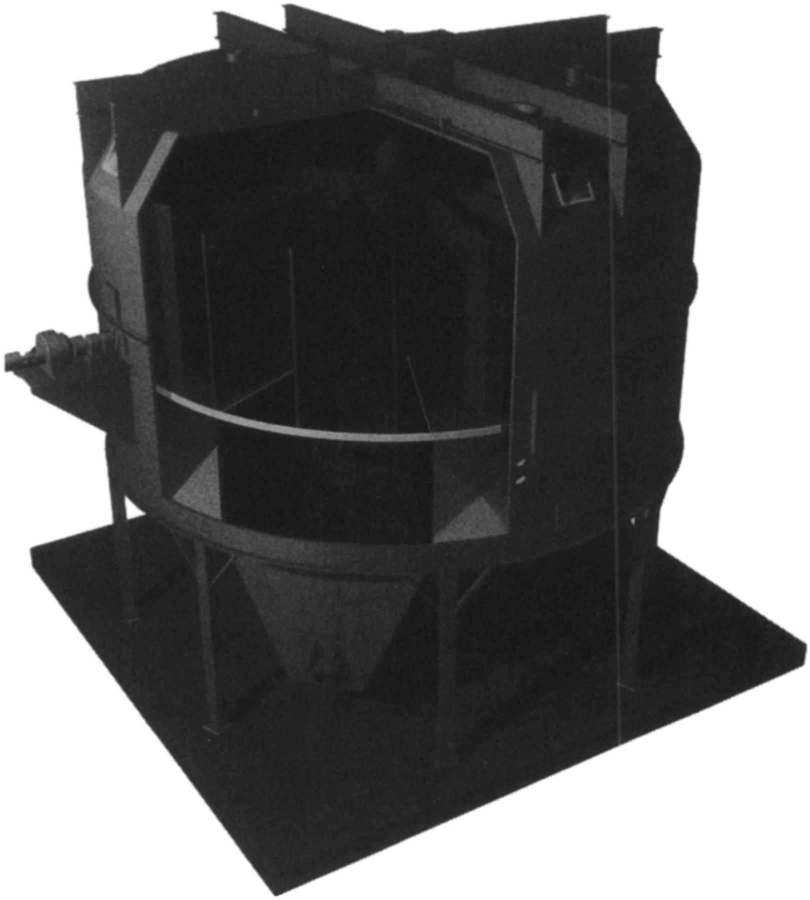


Fig. 7.13. Depiction of a deep-bed, rotary basket extractor (provided by French Oil Mill Machinery Co., Piqua, OH, rights now owned by De Smet Process and Technology, Marietta, GA).

The Schumacher-type Desolventizer/Toaster/Dryer/Cooler is a relatively recent development; it was designed to reduce energy use and has become widely accepted (Fig. 7.14). This device consists of multiple trays as follows: the top one or two trays are for predesolventizing; the second set of one or two trays is for desolventizing-toasting with injection of steam through perforated bottoms (achieving countercurrent use of steam relative to solvent evaporation); the third set of one tray is for sparging steam; the fourth set of one or more trays is for drying with hot air blown through perforated bottoms; and the fifth set of one or more trays is for cooling by blowing cold air through perforated bottoms.

About 3% of the available soybean meal is processed into edible flours and protein concentrates (>65% protein) and isolates (>90% protein). The "flash desolventizer"

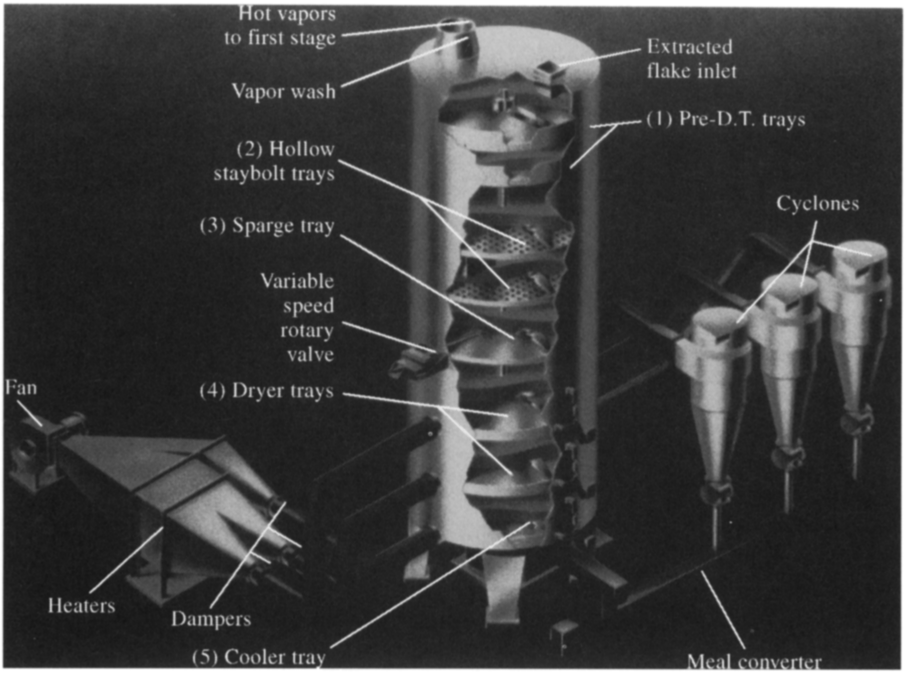


Fig. 7.14. Depiction of the Schumacher-type Desolventizer/Toaster/Dryer/Cooler (provided by Crown Iron Works, Minneapolis, MN).

was developed to reduce protein denaturation and to produce highly soluble protein food ingredients from soybeans (Fig. 7.15). Integrating these systems with cooking systems produces edible protein flours with a broad spectrum of protein dispersibility characteristics. The system includes a desolventizing tube, a flake separator, a circulating blower, and a vapor heater. These units are arranged in a closed loop in which hexane vapor is superheated under pressure and continuously circulated. Solvent-laden flakes, usually from dehulled soybeans, are fed into the system and conveyed by the high-velocity circulating vapor stream. The turbulent superheated vapor flow (160°C) elevates the temperature of the flakes to 77–88°C over a period of <3 s, well above the boiling point of hexane (65°C). As the flakes travel through the tube to the cyclone separator, the greatest portion of the entrained hexane is evaporated. Because the flakes enter the flash desolventizer at low moisture for a very short period and no steam is injected into the vapor stream, little protein denaturation occurs. At the exit point, the protein dispersibility index (PDI) of the protein will be as high as 90. The substantially desolventized flakes, known as "white flakes," are removed from the system through a cyclone with a vapor-tight, rotary airlock and go to deodorizers and then to cookers if moderate protein solubilities are desired.

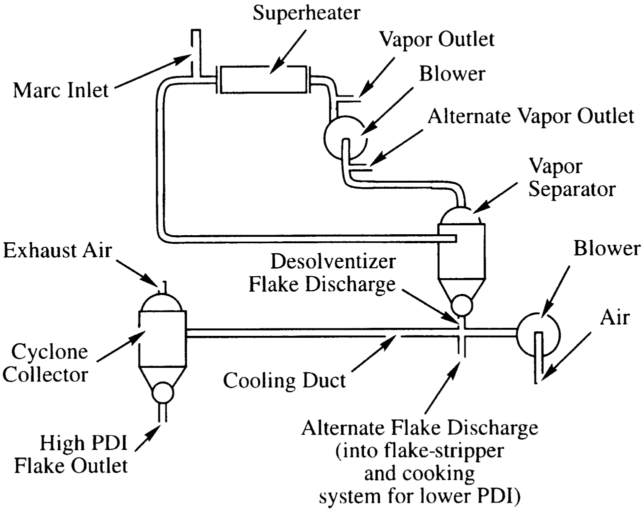


Fig. 7.15. Depiction of a flash desolventizing system.

Meal Grinding. Desolventized meal is ground with a hammer mill so that 95% passes through a U.S. 10-mesh screen and a maximum of 3–6% passes through a U.S. 80-mesh screen. Excessive meal grinding causes dust problems during feed handling. Meal for edible purposes is ground, sized, and sold as grits in a wide variety of sizes and flour (<U.S. 100-mesh). Edible flours may have refined oil or lecithin added or be texturized by using extruders. When white flakes are used for manufacturing soy protein concentrates or isolates, the meal is not usually ground because protein purification is easier with flaked material.

Oil and Meal Storage. Both oil and meal must be cooled before placing in storage because high temperatures accelerate degradation reactions. Neither should be stored any longer than necessary. Oil degrades through oxidation, and reducing contact with air is important. Crude oil is more stable to oxidation than refined oil because crude oil contains natural antioxidants that are removed in the refining steps. It is also important to prevent oil from contacting water so that hydrolysis, which increases refining losses, does not occur. Thus, protection against water, heat, and air is important for maintaining oil quality.

Processing Oil-Bearing Fruits

Palm oil production has grown very rapidly in recent years and is approaching the level of world soybean oil production. Palm fruit provides two distinctly different triglycerides. The fruit flesh provides an oil, and the seed kernels provide a solid fat. The palm oil is often fractionated into two fractions with very different melting points, olein (lower melting point) and stearin (higher melting point). A complete discussion of palm oil products is provided by Basiron (5).

Palm Oil Recovery

Oil palm trees are grown on plantations, particularly in Malaysia and Indonesia. It takes 3 y before the plantings mature and bear fruit. They produce for ~25 y. Palm fruits are hand harvested and immediately transported to the mill where they are "sterilized." Fruits are processed within hours after harvesting because the oil begins to degrade immediately after harvesting.

The process flow diagram for palm oil is shown in Figure 7.16, and plant photos are shown in Figure 7.17. The fruits are sterilized by heating with steam (130–145°C)

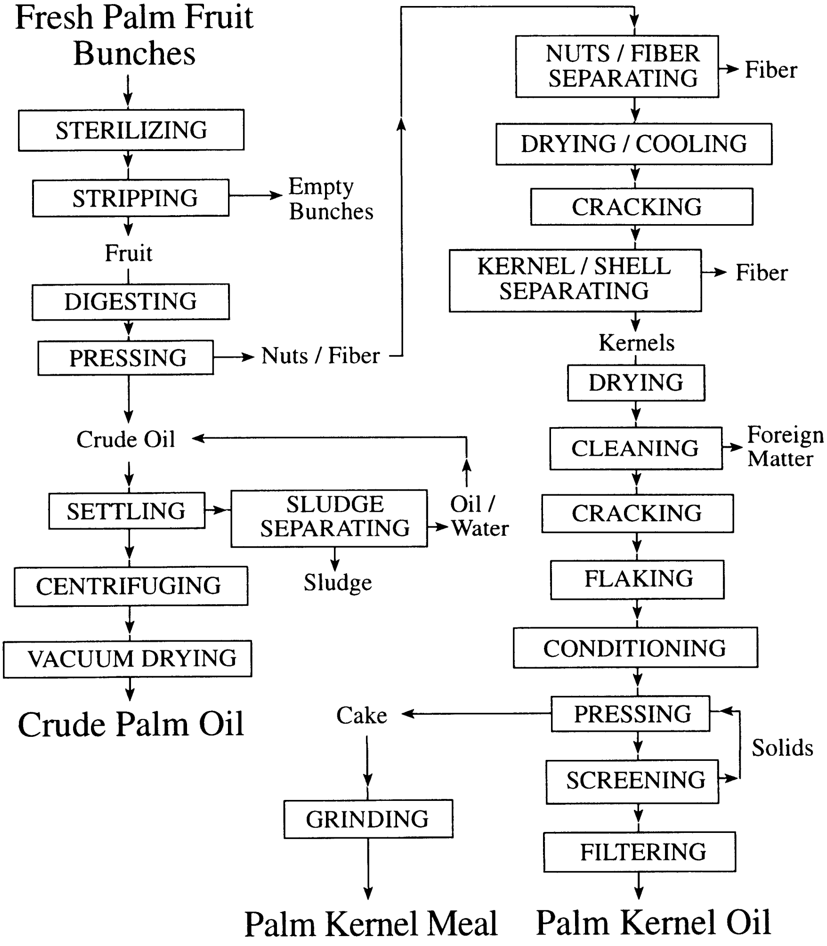
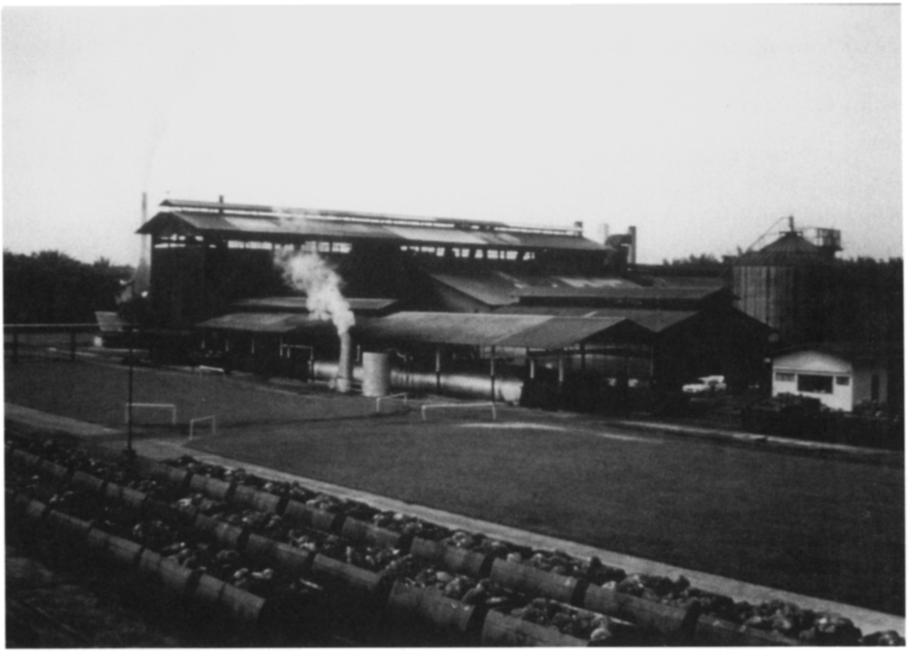


Fig. 7.16. Flow diagram for processing palm fruit.



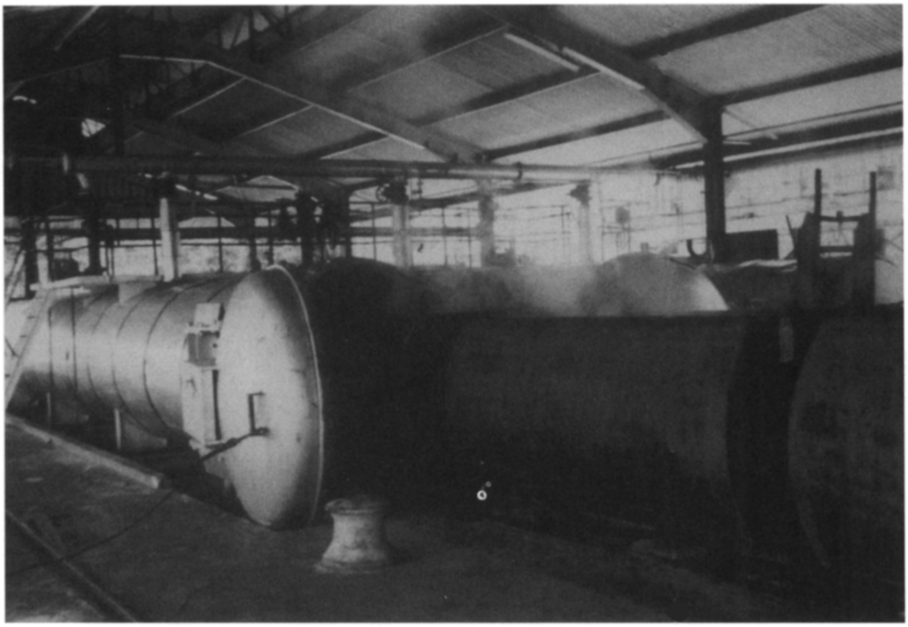


Fig. 7.17. Interior and exterior photographs of a palm oil processing plant (provided by the Palm Oil Research Institute of Malaysia, Kuala Lumpur, Malaysia).

for ~1 h to inactivate lipase that otherwise would quickly hydrolyze the oil and increase refining loss. Sterilization also aids in stripping the fruit from bunch stalks and preconditions the material for subsequent steps. The sterilized fruits are stripped from bunch stalks by vigorous shaking and beating using drum-type strippers. The material is then sent to a digester where it is reheated (95–100°C for 20-30 min) to loosen the pericarp from the nuts and to break the oil cells. The material is conveyed to continuous screw presses, similar to those used for oilseeds, to extract oil from the fruit flesh, but not the kernel. The liquid extract, "press liquor," from the screw press contains ~65% oil, 25% water and 10% solids. Water is added to facilitate settling of the solids, an operation referred to as clarification. The diluted press liquor is screened to remove any fiber, and the slurry is allowed to settle, separating into oil and sludge. Oil is skimmed off the top and passed to a centrifuge (clarifier) and then to a vacuum dryer. The crude oil is cooled and placed in storage.

The cake from the presses contains fruit flesh fiber and nuts. The press cake is conveyed by means of a breaking conveyor to an aspirator (a vertical air column) in which the nuts fall to a rotating polishing drum at the bottom, and the fruit fiber is blown to a cyclone where it is separated from discharge air. The fiber is used to fuel the boiler to generate process steam.

Palm Kernel Fat Recovery

The process flow diagram for processing palm kernels is also shown in Figure 7.15. Usually, the plant processing the nuts is different from that processing palm oil and receives nuts from several palm oil plants. The nuts typically contain ~22% fat. The nuts are conditioned by drying to loosen the kernels from the shell and cooling the nuts to harden the shell. With proper conditioning, the shell will crack into two or more pieces, freeing the kernel. The nuts are cracked with an impact mill, ripple mill, or hammer mill. The kernels and shells differ in specific gravity (1.07 vs. 1.17, respectively) and are separated with winnowing columns and by hydrocloning or clay bathing. All three of these operations separate shells from kernels on the basis of density differences. A hydroclone is a cyclone (centrifugal) separator using water instead of air. A clay bath is a mixture of clay and water to achieve a specific gravity of 1.12 so that the kernels float and the shells sink. The separated shells may be used as fuel. The kernels are dried quickly to minimize lipase activity. They are screw pressed or solvent extracted to produce palm kernel oil and meal. One ton of palm kernel oil is produced for every 10 ton of palm oil.

Processing Animal and Marine Sources

Animal fats and marine oils are extracted from fatty tissues by cooking processes known as "rendering" (Fig. 7.18). Many fatty animal tissues contain 70–90% fat when separated from bone; the remainder is mostly protein and moisture. Although both edible and inedible fats are produced, inedible tallow and grease constitute the majority and are often used in livestock feeds as an energy source. Raw materials include

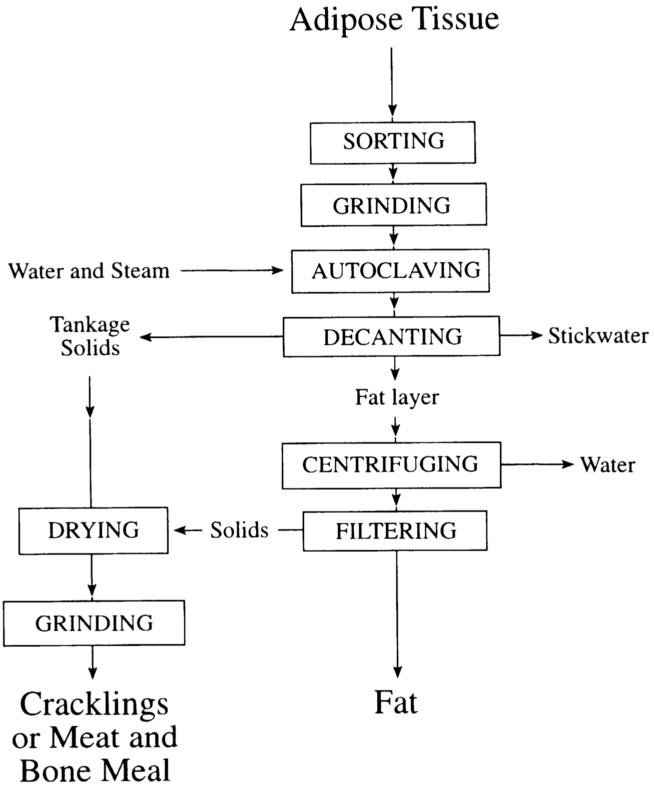


Fig. 7.18. Flow diagram for wet rendering.

animal offal, bones, and trimmings from meat processing, fish species considered undesirable for human consumption, other fish products (menhaden, pilchard, or herring), and fish cannery wastes. Whole carcasses of dead animals unsuitable for food as meat may be rendered to recover inedible fat and meal.

Edible tallow and lard were once used in large quantities for deep frying in fast-food restaurants; however, consumer concerns over cholesterol and saturated fats have led to declines in consumption in these markets. Instead, greater proportions are now being shifted into margarine and bakery shortenings (2). Excellent quality protein obtained from defatted solid material after rendering can be sold for use in livestock feeds as "meat and bone meal" (45–54% protein), "meat meal" (52–60% protein), "poultry by-product meal" (58–62% protein), and "fish meal" (60–65% protein). Fish meal is highly valued in poultry and fish diets which is reflected in the high prices that fish meal brings.

There are four methods of rendering, i.e., wet rendering, dry rendering, slurry rendering, and digestive rendering. Wet (Fig. 7.19) and dry rendering processes predominate in lard production, and discussion of rendering will be limited to these two

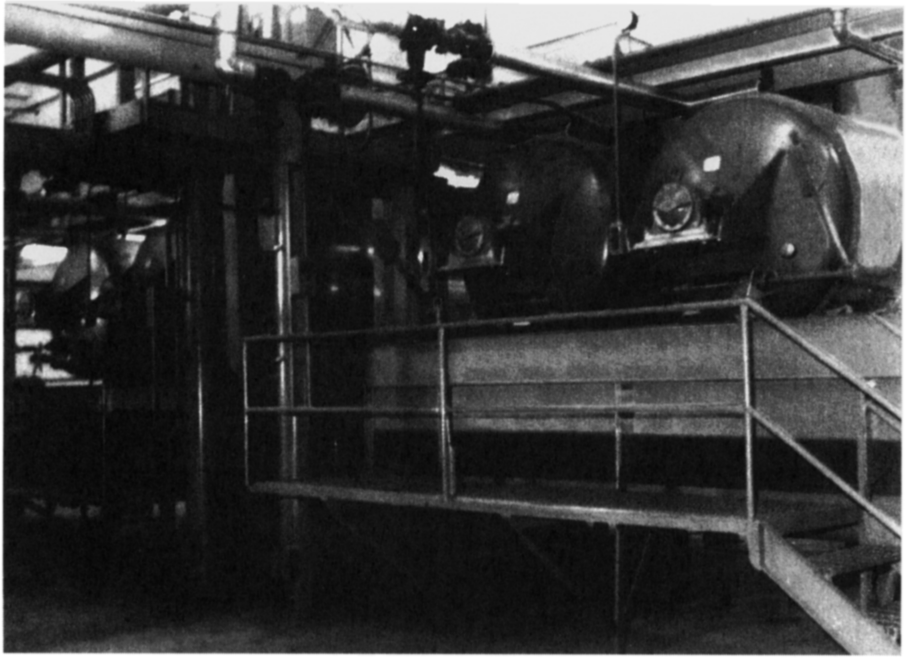


Fig. 7.19. Interior photograph of a rendering plant showing the autoclaves (provided by Anderson International, Cleveland, OH).

methods. Additional information on rendering is provided by Williams and Hron (6) and Laisney (7). Regardless of process employed, cell walls and membranes of adipose tissue must be broken to recover the fat; each method involves four steps, i.e., breaking cell walls and membranes by grinding and cooking, solid-liquid separation, water-fat separation, and drying the solids.

Lard Production

Leaf fat from pork-packing plants contains extraordinarily high amounts of fat (90–95%) whereas backfat and other trimmings contain 80–85% fat, and bonestock only 10–15% fat. Both "wet rendering" and "dry rendering" methods are used in semicontinuous and continuous designs. Wet rendering is preferred when color and flavor are important and when the amount of material to be rendered is not too great. Wet rendering does use a considerable amount of water.

Regardless of the process used, the material from the meat-packing plant to be rendered is dumped into a conveyor and moves to a crusher or prebreaker to break the material into small pieces (2–5 cm). The broken material is conveyed to either batch or continuous cookers where heating and grinding evaporate the moisture, break down the fat cells, and release the fat. The basic steps in all rendering processes involve disintegration, heating and separation—only the method of heating differs.

Wet Rendering. Wet processes are the oldest method of rendering, and two types of processes are practiced. One method is to use hot water below the boiling point, and the other is to use steam in pressure vessels. The latter is called "steam rendering" and involves cooking the material by steam under pressure 172–516 kPa (25-75 psi) for 2-6 h using autoclaves usually with conical bottoms to separate water from the fat. This process is used to produce "prime steam lard." The fatty material is placed into the autoclave along with a small amount of water. Steam is allowed to enter the vessel and boils the water; steam also displaces air, which could oxidize the fat. The cooking time varies with the selected temperature and the fatty material being rendered. At the high temperature, the fatty tissues disintegrate. The water, denatured protein, and other solids settle to the bottom, whereas the fat, which is less dense, floats on top of the liquid. The fat is drawn off after settling or centrifuging to remove water and solids; finally, the oil is filtered. The water, known as "stick water," is drained, and the remaining solids, "tankage," are dried. The dried tankage may contain >70% protein and ~10% fat; the stick water solids contain as much as 90% protein and ~2% fat. Any bones are largely disintegrated by the process. Because autoclaves are usually batch devices, a semicontinuous process is achieved by alternating the discharge from two or more autoclaves. Steam rendering is slower and consumes more energy than alternative rendering methods.

Dry Rendering. Dry rendering is similar to frying bacon. Heat breaks cell walls of fatty tissues and frees the melted fat. Dry rendering involves cooking the material in its own fat (115–120°C) in agitated, steam-jacketed vessels until the moisture has evaporated (1.5–4 h). Unlike wet rendering, no steam or water is added to the materials being rendered. The free fat is allowed to drain away from the cooked material as the rendered materials pass across a screen. The remaining drained tankage is sent to a press. Presses may be either the hydraulic batch type or continuous screw presses similar to those used in the oilseeds industry and described previously. The high-protein solids, much of it from connective tissue, are known as "cracklings" and typically contain 6–10% residual fat. The cracklings are ground with a hammer mill and screened with oversized particles being recycled to the mill, thus producing "meal." The fat discharged from the press is combined with the drained fat and is centrifuged and/or filtered.

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Chapter 8

Refining of Fats and Oils

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Introduction

Crude oils and fats obtained with extraction or rendering processes contain non-triglyceride components most of which must be removed before shelf-stable, pleasant-tasting products can be created. Refining involves the removal of phospholipids, color, trace metals, and free fatty acids (FFA). The goal is to produce a high-quality refined oil with the highest yield of purified triglycerides. Refining has been identified as by far the most important step in processing. An improperly refined oil will present problems throughout the remainder of the fats and oils process.

Terminology

In Europe, the term refining encompasses all of the refining and purification processes an oil goes through, i.e., degumming (if applicable), neutralization, bleaching, and deodorization, to produce finished products. Another terminology used in Europe is that hydrogenation, fractionation, and interesterification all come under the category of "modification." In the United States, the term refining is not as well identified. Refining could mean the chemical refining process only, or it could mean all of the refining processes to which the oil is subjected to produce finished products. In addition, when the word "modification" is used in the United States, it usually refers to the interesterification process only. A brief review of basic fats and oils processes that are referred to as refining in Europe and sometimes in the United States may be helpful, particularly to demonstrate how the chemical refining process (or neutralization) fits into the overall scheme of "oil refining."

Degumming

Oils such as soybean, canola, and rice bran have relatively high levels of impurities, including phosphatides, and proteinaceous and mucilaginous substances. Although these substances can be removed simultaneously with the FFA in chemical refining, operating efficiency, yield, and quality are enhanced when degumming is performed as a separate unit operation before chemical refining. In the case of soybean oil, high-quality, food-grade lecithin can be produced. It should be obvious that producing lecithin, as a marketable product, is better than producing large quantities of soapstock that has no market value. In addition, degumming makes a major contribution to reducing wastewater treatment costs.

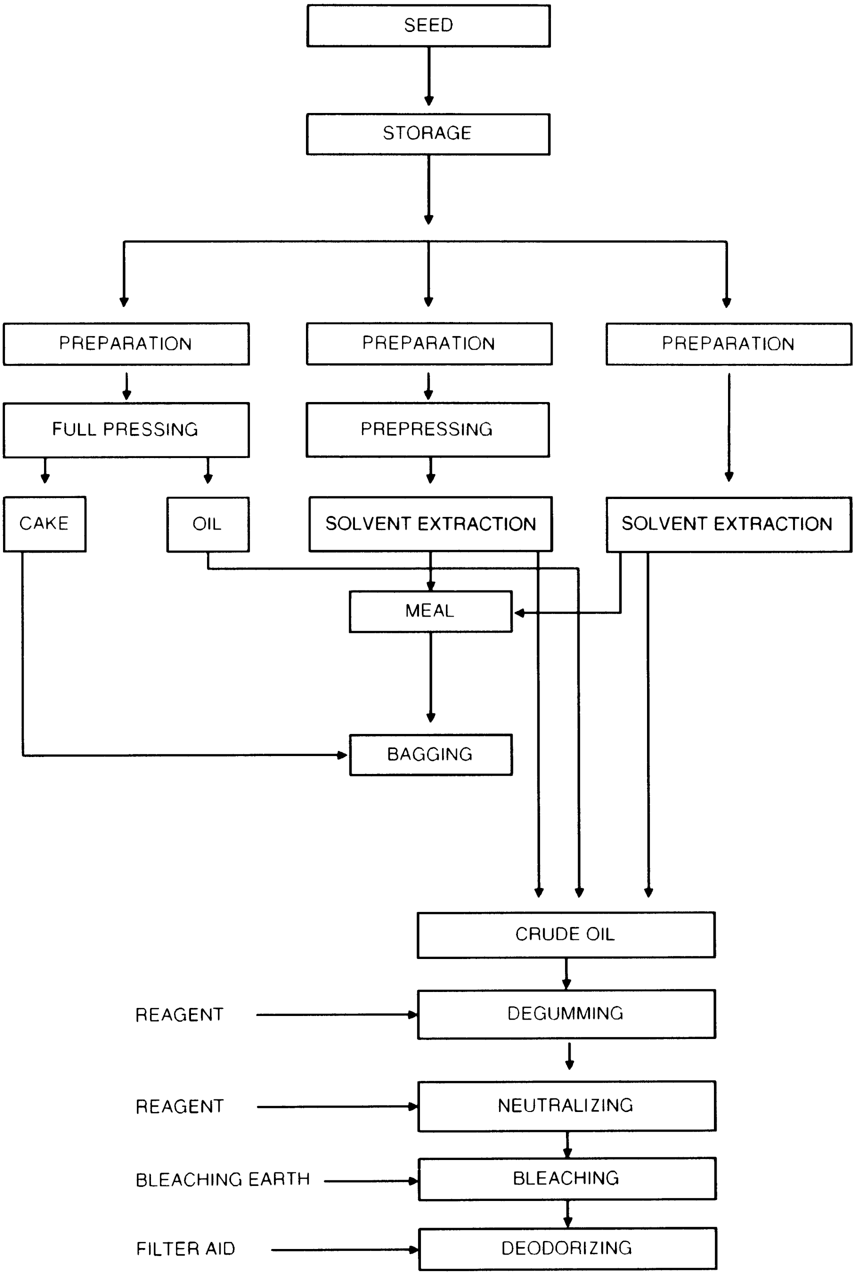

Fig. 8.1. The crude oil refining process.

Refining

The process of chemical refining is performed to neutralize the FFA content, remove the phosphatides (if degumming was not performed as a prerequisite), lighten the color, and remove other trace elements that may be part of the nonhydratable phosphatides (NHP). Soluble soaps formed by alkali solution (caustic) are typically removed by water washing.

Bleaching

The chemically refined oil is next subjected to the process called bleaching. The oil is mixed with acid-activated bleaching clay at elevated temperature and under vacuum to remove trace impurities, soap, color pigments, and chlorophyll. Naturally light colored oils such as soybean, safflower, sunflower, and peanut will be heat bleached in the deodorizer and little red color removal is required in bleaching. The main purpose for bleaching of these oils is to remove chlorophyll, the source of the green color, and secondary oxidation products.

Deodorization

Deodorization removes volatile substances that have objectionable odor and taste. The modern consumer is very particular and expects the oil to be odorless and tasteless; it must not contribute either odor or taste to the foods prepared. Deodorization is a steam distillation process conducted under precise conditions of temperature, vacuum, and stripping steam. The stripping steam serves are a carrier for volatile substances. Deodorization is the most unforgiving of all the refining processes. If not conducted properly, the oil will not be perfect, and only perfect is acceptable! It should be emphasized that deodorization cannot correct mistakes made in the upstream processes, such as refining, bleaching, and hydrogenation. All of these processes must be operated with good process control so that the deodorizer can deliver the designed quality. All of the vegetable oil processes, from the seed to the finished product, are depicted in Figure 8.1.

Introduction to the Chemical Refining Process

Throughout the world, two types of chemical refining processes are used. In Europe, the high-temperature/short-mix process predominates. In the United States, the low-temperature/long-mix process is favored. In other parts of the world, the process utilized is a function of which group had the greater influence, the Europeans or the Americans. Both groups are highly opinionated, and it is unlikely that actual research will change these opinions. This author has had the opportunity to test both techniques around the world with most oil types and prefers the low-temperature/long-mix process. Therefore, this presentation will deal with the low-temperature/long-mix process only. An important requirement for the success of either process is that sufficient attention to detail is exercised to provide the operating techniques that optimize both refining yield and

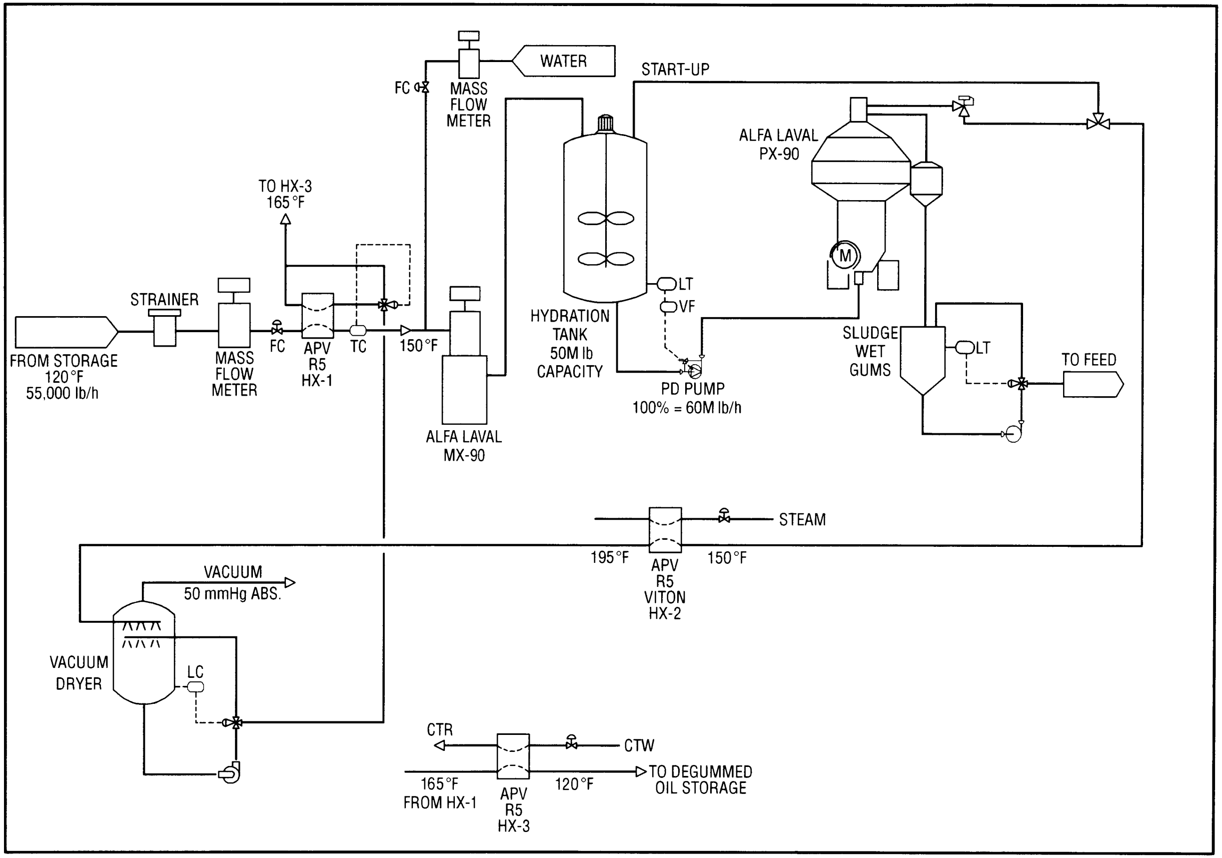

Fig. 8.2. A modern water degumming plant.

quality. Those new to the industry who learn and practice these techniques can operate a world-class refinery with respect to yield, quality, and profitability.

The four main areas that this chapter will cover include the following: (i) conventional chemical refining process with water washing; (ii) chemical refining with silica purification and the possible elimination of water washing; (iii) new refining techniques, including physical refining of soybean oil; and (iv) new refining techniques that may be commercialized over the next few years. First, the refining of soybean oil will be examined in detail. Then, the treatment of other oils and how it differs from the treatment of soybean oil will be reviewed.

Degumming of Soybean Oil

As stated in the introduction, it is preferable to degum soybean oil before caustic refining for many reasons. A modern water degumming plant is depicted in Figure 8.2. In this process, the proper ratio of water is injected into the incoming oil stream; the oil then passes through a high-speed mixer and finally to the hydration tank. The hydration tank is sized to allow up to 45 min retention time. The hydration temperature is 145–155°F (62.8–68.3°C). The oil with hydrated gums then passes to the automatic self-cleaning centrifuge. The wet gums exiting the centrifuge may be added to animal feed, or they may pass to a wiped film evaporator to become soybean oil lecithin. The degummed oil exiting the centrifuge passes to a vacuum dryer to dehydrate the oil. If degumming is close-coupled to the refining process, vacuum drying is not necessary. However, true direct close-coupling of degumming to refining is not recommended because the success of the refining system is dependent upon a uniform and consistent feedstock.

Table 8.1 gives the phosphatide level in common vegetable oils that require degumming. The proper dosage of water for degumming can be computed as follows:

$$\text{Water treatment} = (P_{\text{ppm}} \times 31.7 \times 10^{-4})0.7$$

Example: If the phosphorus content in the crude oil is 800 ppm,

TABLE 8.1 Phosphatide Level in Common Vegetable Oils[a]

Type of oil	Phosphatide level (%)	As phosphorus (ppm)
Soybean	1.0–3.0	311–940
Corn	0.7–0.9	220–280
Safflower	0.4–0.6	130–290
Sunflower	0.5–0.9	160–280
Peanut	0.3–0.4	95–190
Canola (superdegummed)	0.16	50
Canola (crude)	1.0–3.0	311–940

[a] The amount of phosphorus is calculated as follows: [Phosphatide (%) × 10^4]/31.7 = phosphorus (ppm).

$$\text{Water treatment} = (800 \times 31.7 \times 10^{-4})0.7 = 1.8\%$$

Special degumming, for soybean oils that are high in NHP, or for pretreatment for physical refining, is discussed later.

Continuous Chemical Refining Process

The objective in refining vegetable oils is to obtain a minimum refining loss, or a maximum refined oil yield, while producing acceptable refined oil quality. The minimum amount of excess caustic must be used, while maintaining acceptable quality, to reduce saponification of neutral oil. Therefore, very close process control of refined oil is important to minimize losses. The type and amount of mixing, temperatures, and the type and condition of the centrifuges become very significant. Improper mixing and soap conditioning can increase neutral oil losses to the soapstock. The centrifuges are the heart of a refining system; the condition and operation of these centrifuges, more than any other single factor, affect the refining efficiency.

Vegetable oils are refined by the reaction of alkali, usually caustic soda (sodium hydroxide), with the crude oils. Upon intimate mixing of the caustic solution with the crude oil, the FFA are neutralized. A predetermined amount of excess caustic is added to ensure proper removal of other impurities such as phosphatides and color bodies. The caustic solution strength varies from 20–50°Be for cottonseed oil, and 16–24°Be is common for soybean, sunflower, safflower, peanut, and corn oil. The continuous refining process is depicted in block diagram form and in flow diagram form in Figures 8.3 and 8.4, respectively.

The critical components that make up the refining process are the following:

1. Acid pretreatment system
2. Caustic addition system
3. Caustic/oil mixer
4. Retention mixers
5. Primary centrifuge
6. Wash water treatment system
7. Water wash centrifuge
8. Vacuum dryer for refined oil

Each of these components will be examined and their importance emphasized.

Acid Pretreatment of Crude Oil

For the last 30 years, acid pretreatment was performed by adding an acid, typically phosphoric acid, to day tanks. Day tanks were sized such that they would provide a uniform supply of crude oil to the refinery for one full day, or 24 h. For large refineries, these tanks may be $\geq 1.5 \times 10^6$ lb. Proper dispersion of the acid in tanks this large is difficult. Even when a minimum holding time of 24 h is practiced, there remains a concern that

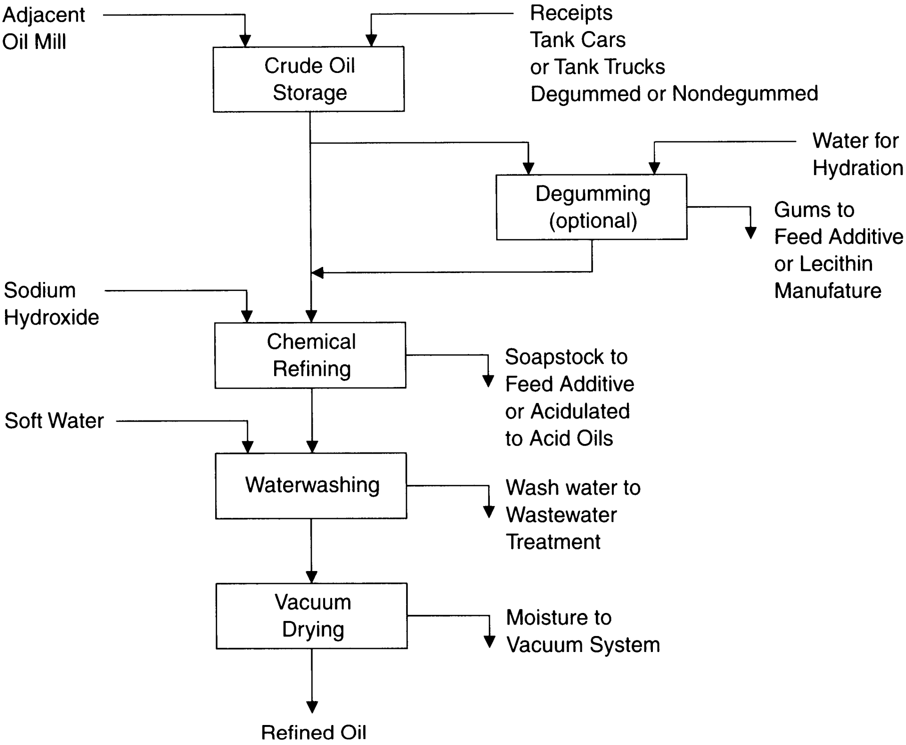

Fig. 8.3. Continuous refining of vegetable oils (block diagram form).

proper dispersion is not being achieved. Proper dispersion of the acid is mandatory for the acid to convert the NHP to hydratable phosphatides (HP). It is amazing that many fats and oils processors have added acid for pretreatment for years without knowing why; however, they did know that acid pretreatment was advantageous for refining.

A weakness in the method of acid pretreating vegetable oils was recognized ~10 years ago. Instead of adding acid in the larger day tank, it was added *via* a high-shear mixer; then the acid/oil mixture was transferred to a small day tank, providing ~4 h retention time. This combination of high-shear mixing followed by a shorter retention time has been proven to provide the maximum conversion of NHP to HP.

The proper dosage of acid is critical as well. An underdose of acid will not make the proper conversion of NHP to HP; an overdose offers no advantage and can actually increase refining loss. The proper dosage of phosphoric acid can be estimated with the following simplified formula:

$$H_3PO_4 = (Ca + Mg)/2 \times 10$$

where H_3PO_4 is the amount of phosphoric acid added in ppm, Ca is calcium in ppm in the crude oil and Mg is magnesium in ppm in the crude oil.

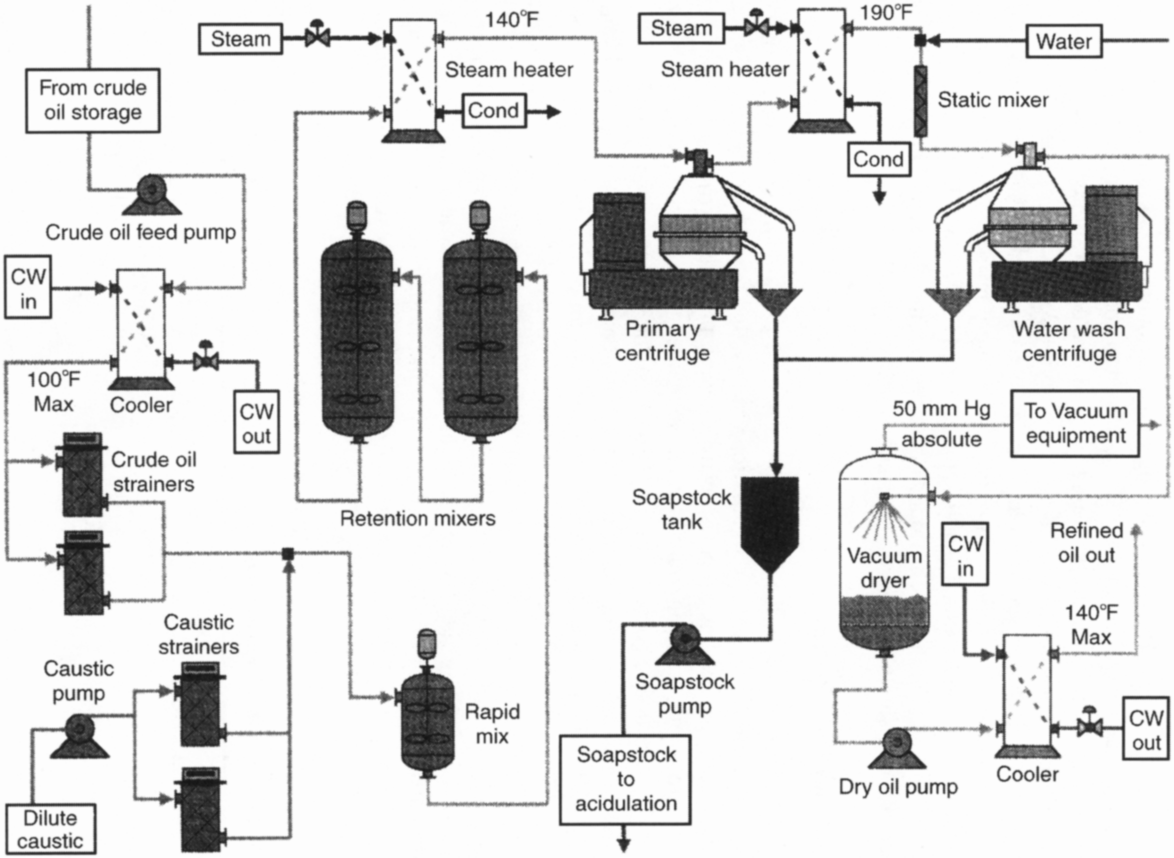

Fig. 8.4. Continuous refining of vegetable oils (flow diagram form).

Example: If Ca = 80 ppm and Mg = 70 ppm,

$$H_3PO_4 \text{ (ppm)} = (80 + 70)/2 \times 10 = 750 \text{ ppm}$$

Note that phosphorus (P) has no bearing on the amount of acid required, only the calcium and magnesium. Heavy metals, such as iron and copper, can have a bearing on the acid level, but if the proper dosage of acid is added to split calcium and magnesium from the phosphatide radical, these metals are deactivated as well. Of course, to use the formula, processors must have the capability of analyzing the crude oil for trace elements. It is the author's firm belief that every refinery must have an ICP-type instrument for trace metal analysis, operating 24 h/d, 7 d/wk. These instruments are expensive and demand well-trained operators, but the return will be evident in a matter of months with improved yields and improved quality.

Caustic Addition System

Control of caustic flow to the refining process is of paramount importance to optimize quality and refining yield. In addition to the actual flow of caustic, the caustic concentration, the amount of excess caustic above the neutralizing dose, and the temperature are all very important. It is recommended that any modern-day refinery should have automatic controls for the ratio of caustic flow to oil flow.

The typical caustic excesses required for many common vegetable oils are listed in Table 8.2. The formula for determination of amount of caustic treat is given in Table 8.3. Table 8.4 lists the densities and concentrations of caustic soda solutions.

In the last few years, very accurate and reliable caustic metering systems have evolved. Usually, the pump is a progressive cavity pump with variable frequency control. The mass flow meter is very accurate with a wide turn-down, and preferably has the capability of displaying specific gravity. In computerized systems, the operator must enter only the FFA and the desired percentage of excess caustic for the computer to determine the proper caustic flow at that particular density.

TABLE 8.2 Typical Caustic Excess Required for Common Vegetable Oils[a]

Oil type	% Excess	Remark
Degummed soybean	0.01–0.05	Minimum amount for residual phosphorus level <2 ppm
Nondegummed soybean	0.15–0.25	"
Safflower	0.01–0.05	"
Sunflower	0.05–0.15	"
Cottonseed oil	0.15–0.40	Minimum amount required to obtain acceptable laboratory bleach color

[a] If excess caustic levels >0.40% are required for cottonseed oil to meet target laboratory bleach color, it is generally preferable with respect to refining yield to accept a higher laboratory bleach color, with anticipation of re-refining the oil at a later time. Re-refining losses run ~1.0%.

TABLE 8.3 Determination of Amount of Caustic Treat

% Treat = [(Factor × % FFA[a]) + (% Excess)/% NaOH] × 100
where Factor = 0.142

Example: FFA = 1.30%
Caustic strength = 20°Be
Caustic % by weight for 20°Be = 14.33%
% Excess = 0.18%

% Treat = [(0.142 × 1.30 + 0.18)/14.33] × 100
= [(0.185 + 0.18)/14.33] × 100
= 2.55%

If crude oil flow is 20,000 lb/h, then caustic flow would be 20,000 lb/h × 0.0255 = 510 lb/h

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% Excess can be calculated as follows:
Example: FFA = 1.30%
Caustic strength = 20°Be = 14.33%

If caustic flow = 510 lb/h and oil flow = 20,000 lb/h, then

% Treat = 510/20,000 × 100 = 2.55%

2.55% = [(0.142 × 1.3 + % Excess)/14.33] × 100

% Excess = (2.55 × 0.1433) – (0.142 × 1.3)
= 0.365 – 0.185
= 0.18%

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[a] Abbreviation: FFA, free fatty acids.

Caustic/Oil Mixer

Proper dispersion and reaction of caustic with the oil is important. Caustic reacts with FFA almost immediately, and this takes place in a very short time. Previously, this was accomplished *via* pipe-line mixers, but these mixers were troublesome and required excessive maintenance. The trend was to use motionless (static) mixers, but static mixers are efficient at a finite flow rate. If the refining flow rate is reduced by 50%, mixing conditions can be quite different. A series of rapid mixers was introduced a few years ago, which appears to be ideal for this service. These mixers must be sized for each incremental refining flow rate.

Retention Mixers

In the low-temperature/long-mix process, the contact time takes place in the retention mixers. Alfa-Laval USA is the only known manufacturer of this type of mixer. As mentioned above, FFA are neutralized immediately, but in the low-temperature process, extended retention time is required for a proper reaction with the phospholipids, color bodies, and other impurities. Currently available AL retention mixers with their capacity (in U.S. gallons) include the following: RM 110, 110 gal; RM 250, 250 gal; RM 350, 350 gal; and RM 500, 500 gal. The approximate retention times for the

TABLE 8.4 Densities and Concentrations of Caustic Soda Solutions at 60°F (1)

°Be	°Twaddell	sp gr	Weight of 1 gal (lb)	Caustic soda (NaOH)[a] (wt%)	Caustic soda (NaOH)[a] (g/L)	Caustic soda (NaOH)[a] (lb/gal)	Each gallon H_2O requires lb NaOH	Each gallon H_2O forms gallons solution
1.0	1.4	1.007	8.40	0.60	6.04	0.05	0.05	0.999
1.7	2.3	1.012	8.44	1.00	10.10	0.08	0.08	0.998
2.0	2.8	1.014	8.45	1.22	12.35	0.10	0.10	0.998
3.0	4.2	1.021	8.51	1.86	18.97	0.16	0.16	0.998
3.3	4.6	1.023	8.53	2.00	20.43	0.17	0.17	0.998
4.0	5.6	1.028	8.57	2.50	25.68	0.21	0.21	0.998
4.8	6.8	1.034	8.62	3.00	30.99	0.26	0.26	0.997
5.0	7.2	1.036	8.64	3.15	32.61	0.27	0.27	0.997
6.0	8.6	1.043	8.70	3.81	39.70	0.33	0.33	0.997
6.2	9.0	1.045	8.71	4.00	41.77	0.35	0.35	0.997
7.0	10.2	1.051	8.76	4.50	47.25	0.39	0.39	0.997
7.7	11.3	1.056	8.80	5.00	52.77	0.44	0.44	0.997
8.0	11.6	1.058	8.82	5.18	54.75	0.46	0.46	0.997
9.0	13.2	1.066	8.89	5.88	62.62	0.52	0.52	0.997
9.1	13.5	1.067	8.90	6.00	63.99	0.53	0.53	0.997
10.0	14.8	1.074	8.95	6.60	70.82	0.59	0.59	0.997
10.6	15.7	1.079	9.00	7.00	75.43	0.63	0.63	0.997
11.0	16.4	1.082	9.02	7.31	79.02	0.66	0.66	0.997
11.9	17.9	1.089	9.08	8.00	87.09	0.73	0.73	0.998
12.0	18.0	1.090	9.09	8.05	87.67	0.73	0.73	0.998
13.0	19.6	1.099	9.15	8.79	96.43	0.80	0.80	0.998
13.3	20.2	1.101	9.18	9.00	98.99	0.83	0.83	0.998
14.0	21.4	1.107	9.23	9.54	105.51	0.88	0.88	0.999
14.6	22.4	1.112	9.27	10.00	111.10	0.93	0.93	0.999
15.0	23.0	1.115	9.30	10.30	114.74	0.96	0.96	1.000
15.9	24.6	1.123	9.36	11.00	123.43	1.03	1.03	1.001
16.0	24.8	1.124	9.37	11.09	124.54	1.04	1.04	1.001
17.0	26.6	1.133	9.45	11.88	134.48	1.12	1.12	1.002
17.1	26.8	1.134	9.45	12.00	135.97	1.13	1.14	1.002
18.0	28.4	1.142	9.52	12.69	144.79	1.21	1.21	1.003
18.4	29.0	1.145	9.55	13.00	148.75	1.24	1.24	1.004
19.0	30.2	1.151	9.60	13.51	155.36	1.30	1.30	1.005
19.6	31.3	1.156	9.64	14.00	161.74	1.35	1.36	1.006
20.0	32.0	1.160	9.67	14.33	166.08	1.39	1.39	1.007
20.8	33.5	1.167	9.73	15.00	174.96	1.46	1.47	1.008
21.0	33.8	1.169	9.75	15.17	177.17	1.48	1.49	1.008
21.9	35.7	1.178	9.82	16.00	188.3	1.57	1.59	1.010
22.0	35.8	1.179	9.83	16.02	188.70	1.57	1.59	1.010
23.0	37.8	1.189	9.91	16.89	200.64	1.67	1.69	1.012
23.2	37.9	1.190	9.92	17.00	202.05	1.69	1.71	1.012
24.0	39.6	1.198	9.99	17.78	212.81	1.78	1.80	1.015
24.3	40.1	1.201	10.01	18.00	215.91	1.80	1.83	1.015
25.0	41.6	1.208	10.07	18.68	225.45	1.88	1.91	1.018
25.4	42.3	1.212	10.10	19.00	230.01	1.92	1.95	1.019

TABLE 8.4 *(continued)*

			Weight of 1 gal (lb)	Caustic soda (NaOH)[a]			Each gallon H_2O	
°Be	°Twaddell	sp gr		(wt%)	(g/L)	(lb/gal)	requires lb NaOH	forms gallons solution
26.0	43.6	1.219	10.15	19.61	238.63	1.99	2.03	1.021
26.4	44.6	1.223	10.20	20.00	244.33	2.04	2.08	1.022
27.0	45.8	1.229	10.25	20.55	252.33	2.11	2.15	1.024
27.5	46.8	1.234	10.29	21.00	258.85	2.16	2.21	1.026
28.0	47.8	1.239	10.33	21.50	266.15	2.22	2.28	1.028
28.5	49.0	1.245	10.38	22.00	273.60	2.28	2.35	1.030
29.0	50.0	1.250	10.42	22.47	280.62	2.34	2.41	1.032
29.6	51.1	1.256	10.47	23.00	288.56	2.41	2.49	1.034
30.0	52.2	1.261	10.51	23.46	295.57	2.47	2.55	1.036
30.6	53.3	1.267	10.56	24.00	303.74	2.53	2.63	1.039
31.0	54.4	1.272	10.61	24.46	310.84	2.59	2.70	1.041
31.5	55.5	1.278	10.66	25.00	319.13	2.66	2.78	1.043
32.0	56.6	1.283	10.70	25.50	326.87	2.73	2.85	1.046
32.5	57.7	1.289	10.75	26.00	334.73	2.79	2.93	1.048
33.0	59.0	1.295	10.80	26.52	343.13	2.86	3.01	1.051
33.5	59.9	1.300	10.84	27.00	350.55	2.93	3.08	1.054
34.0	61.2	1.306	10.89	27.61	360.26	3.01	3.18	1.058
34.3	62.1	1.310	10.92	28.00	366.58	3.06	3.24	1.060
35.0	63.6	1.318	10.99	28.71	378.06	3.15	3.35	1.064
35.2	64.2	1.321	11.01	29.00	382.79	3.19	3.40	1.066
36.0	66.0	1.330	11.09	29.86	396.78	3.31	3.55	1.072
36.1	66.4	1.332	11.11	30.00	399.21	3.33	3.57	1.073
37.0	68.5	1.343	11.19	31.00	415.78	3.47	3.74	1:080
37.8	70.6	1.353	11.28	32.00	432.57	3.61	3.92	1.087
38.0	71.0	1.355	11.30	32.21	436.05	3.64	3.96	1.089
38.6	72.7	1.363	11.36	33.00	449.51	3.75	4.10	1.095
39.0	73.6	1.368	11.41	33.42	456.78	3.81	4.18	1.098
39.5	74.8	1.374	11.46	34.00	466.67	3.89	4.29	1.103
40.0	76.2	1.381	11.51	34.67	478.36	3.99	4.42	1.108
40.2	76.8	1.384	11.54	35.00	483.98	4.04	4.48	1.112
41.0	78.9	1.394	11.62	36.00	501.50	4.19	4.69	1.121
41.7	80.9	1.404	11.71	37.00	519.17	4.33	4.89	1.131
42.0	81.6	1.408	11.74	37.31	524.85	4.38	4.96	1.133
42.5	82.9	1.415	11.80	38.00	537.06	4.48	5.10	1.140
43.0	84.4	1.422	11.86	38.70	549.81	4.59	5.26	1.147
43.3	84.9	1.425	11.88	39.00	555.03	4.63	5.32	1.150
44.0	86.9	1.436	11.96	40.00	573.28	4.78	5.55	1.161
44.6	88.9	1.444	12.04	41.00	591.61	4.94	5.79	1.174
45.0	90.0	1.450	12.09	41.61	602.80	5.03	5.93	1.181
45.3	90.8	1.454	12.12	42.00	610.13	5.09	6.03	1.186
46.0	92.7	1.465	12.21	43.00	628.76	5.25	6.28	1.198
46.6	94.6	1.473	12.28	44.00	647.57	5.40	6.54	1.212
47.0	96.0	1.480	12.34	44.68	660.66	5.51	6.73	1.221
47.2	96.5	1.483	12.36	45.00	666.59	5.56	6.81	1.226

TABLE 8.4 *(continued)*

°Be	°Twaddell	sp gr	Weight of 1 gal (lb)	Caustic soda (NaOH)[a]			Each gallon H_2O	
				(wt%)	(g/L)	(lb/gal)	requires lb NaOH	forms gallons solution
47.8	98.4	1.492	12.44	46.00	685.79	5.72	7.09	1.241
48.0	99.0	1.495	12.46	46.27	691.11	5.77	7 17	1.245
48.5	100.3	1.502	12.52	47.00	705.16	5.88	7.39	1.256
49.0	102.2	1.510	12.60	48.00	724.72	6.05	7.69	1.273
49.7	104.1	1.521	12.68	49.00	744.45	6.21	8.00	1.289
50.0	105.2	1.526	12.72	49.60	756.21	6.31	8.20	1.300
50.2	106.0	1.530	12.76	50.00	764.36	6.38	8.33	1..307
50.8	107.9	1.540	12.84	51.00	784.45	6.55	8.67	1.325
51.0	108.6	1.543	12.86	51.32	791.14	6.60	8.78	1.331
51.4	109.8	1.549	12.91	52.00	804.77	6.72	9.02	1.345
51.9	111.6	1.558	12.99	53.00	825.10	6.89	9.39	1.366
52.0	111.8	1.559	13:00	53.10	827.08	6.90	9.43	1.368

[a] To convert NaOH to equivalent Na_2O, multiply by 0.7748.

common vegetable oils are as follows: corn and peanut oils, 4 min; soybean, sunflower, safflower and canola oils, 6 min; and cottonseed oil, 9 min.

The size and number of retention mixers required for a particular oil (example: Soybean oil at 70,000 lb/h) can be calculated as follows:

$$70{,}000 \text{ lb/h} \times 1 \text{ gal/7.5 lb} \times 1 \text{ h/60 min} = 155 \text{ gal/min}$$

To achieve a 6-min retention time for soybean oil, 155 gal/min × 6 = 930 gal. Thus, for this size refinery, two 500-gal mixers would be required. In another example, for a refinery with a design capacity of 45,000 lb/h, the choice could be made between two 250-gal mixers or two 350-gal mixers; the latter choice would be preferable because it would be better to have extra retention time instead of less.

Primary Centrifuge

The most critical component in the whole refining process is the primary centrifuge. This machine must have preventive maintenance as required and be kept in excellent working order to maintain consistent quality and to optimize refining yield. In the case of manually cleaned machines, the quality of the oil exiting the centrifuge must be monitored closely to determine when the machine must be shut down for cleaning.

Probably, the greatest single development for refining edible oil over the last 20 years was the development of the automatic self-cleaning centrifuge. Later models, introduced ~10 years ago, have been equipped with fine-tuning devices, allowing the zone of separation to be "fine-tuned" while the centrifuge was on-line. The main advantage of the self-cleaning centrifuge is that it does not have to be stopped for cleaning. Because the manual cleaning of a centrifuge is such a difficult, menial job, operators will tend to run the machine long after cleaning is required, and oil yield and quality can suffer.

In addition to the development of the automatic self-cleaning centrifuge, these machines are becoming larger and larger. In year 2000, Alfa-Laval and Westfalia introduced centrifuges capable of 100,000 lb/h. These machines are currently being tested at rates as high as 120,000 lb/h but it will be a few years before their ability to operate at such capacities is proven. The centrifuges currently available (year 2000) from GEA Westfalia and Alfa-Laval are listed in Table 8.3. It is likely that we have approached the limit in centrifuge capacity. For example, if a refinery is built for 150,000 lb/h, it would be better to use two 75,000 lb/h centrifuges instead of trying to build yet another higher-capacity centrifuge.

Water Wash Treatment System

The usual amount of water added for water washing is 15% wt/wt of the oil flow. The range could be 12-15%. Only soft water should be used, and recycling of waste water streams should not be attempted. Double water washing, which was practiced in the past, is no longer required with the improved centrifuges available today.

Oil exiting the primary centrifuge (~150°F or 65.6°C) is heated to~190°F (87.8°C) for water washing. The water can be preheated to 190°F (87.8°C) before injection into the oil line, or the water and the oil can be heated simultaneously. In the past, the manner in which the water was added to the oil was haphazard at best. Water was sprayed into the oil in a small mixing tank, agitated, and the mixture was pumped to the water wash centrifuge. Later, static mixers were used, but they were not very effective. About 25 years ago, the author introduced the use of the water wash holding tank. By allowing ~0.5 h retention time in an agitated tank, the soap in the oil was transferred more efficiently to the water phase. Residual soap in this water-washed oil was <20 ppm. Then it was found that by adding a small amount of phosphoric acid to this retention tank, the residual soap was lowered to 0 ppm. Bleaching clay efficiency was greatly enhanced, as a result of the 0 ppm soap level. In recent years, this process has been streamlined by the utilizing of retention mixers to give the proper contact time with water.

Vacuum Dryer for Refined Oil

When the water washed oil is to be stored for any period of time it must be vacuum dried. This is usually accomplished with a continuous spray dryer, operating at 50 mm Hg absolute pressure. Because the oil was already heated to 190°F (87.8°C) for water washing, no additional elevation of temperature is required. When the refined washed oil is coupled directly to silica purification and/or bleaching, the vacuum drying step is not required.

TABLE 8.5 GEA Westfalia Separators Nominal Capacities (lb/h)

	Westfalia model	Water degumming	Acid degumming	Neutralization	Water washing	Miscella refining	Winterization	Cold refining
Current models								
Solid bowl	RTB 45	5500	4584	5500	9150	NA	4585	2750
	RTA 50	6875	6875	6875	13750	6875	5500	4585
	RTC 150	27500	27500	27500	38500	18350	13750	11000
Self-Cleaning	RSA 60	13750	11000	13750	13750	9150	5500	4585
	RSE 70	18350	18350	18350	18350	13750	9150	9150
	RSE 110	27500	27500	27500	27500	18350	13750	11000
	RSE 150	38500	38500	38500	38500	22000	18350	16500
	RSE 200	73350	66000	73350	73350	27500	27500	22000
	RSE 300	91650	73330	91650	91650	NA	33000	27500

Alfa-Laval Separators Nominal Capacities (lb/h)

Type of Separator	Water degumming	Acid degumming	Neutralization (maximum 3% free fatty acids)	Re-refining	Water wash (hot)	Winterization (dewaxing) (cold wash)	Cold refining (or cold degree)	Miscella refining
SRG 610	9190	—	9190	13,780	13,780	4600	3680	—
SSG214	18,370	—	—	—	32,150	—	—	—
SRG214	—	—	18,370	22,960	22,960	13,780	9190	—
PX30	4600	3680	4600	4600	4600	2300	1380	—
PX60	13,780	11,020	13,780	13,780	13,780	6890	4600	—
PX70	27550	22960	27550	27550	27550	18370	13780	—
PX80	41330	36740	41330	41330	41330	—	—	—
PX90	73470	64290	73470	73470	91840	36740	27550	—
PX100	91840	73470	91840	91840	11020	41330	32150	—
MIS600	—	—	—	—	—	—	—	18,730

Chemical Refining of Other Fats and Oils

Up to this point, this chapter has dealt with the chemical refining of soybean oil. Because soybean oil is considered the most difficult oil to refine, any system well-suited for soybean oil, should be well-suited for most other oils. Oils that could be refined through the low-temperature/long-mix system for soybean oil include sunflower, safflower, and canola oils. Corn and peanut oils also refine well in a soybean system. The only difference is that the shorter retention time during caustic mixing may prove advantageous. Thus, multiple retention mixers would be an advantage over one single larger retention mixer.

Animal fats, such as beef tallow, lard, and chicken fat are quick breaking with caustic refining and require very little retention time. In this case, part or all of the retention mixers may be by-passed.

Lauric oils, such as palm, palm kernel, and coconut, must be refined by the high-temperature/short-mix process. In a system designed for soybean oil, the incoming oil will be heated to ~160°F (71.1°C), caustic added, and all of the retention mixers will be by-passed. If these lauric oils have reasonable FFA (<5.0%), then they will be chemically pretreated, purified with silica and bleaching clay, and physically refined. In physical refining, the FFA are removed by steam distillation, a process similar to deodorization.

The most unique vegetable oil, with respect to refining, is cottonseed oil. When crude cottonseed oil is chemically refined, it is mandatory to use the low-temperature/long-mix process, and the system designed for soybean oil is ideally suited. However, a longer retention time is usually required to achieve an acceptable color. As mentioned earlier, cottonseed oil may require up to 9 min retention time. A soybean oil refinery that runs cottonseed oil occasionally may have to add another retention mixer to achieve this longer retention time.

In the author's opinion, all cottonseed oil should be miscella refined at the oil mill. The oil mill would market only the PBSY (prime bleach, summer yellow) grade of cottonseed oil. By refining in the miscella, yields are dramatically higher and the quality or color is much better. The key to successful miscella refining of cottonseed oil rests with the fact that oil is refined before the final evaporation stage for solvent removal. This provides a much lighter red color with a dramatically lower caustic dosage. Conventional crude refining of cottonseed oil is probably doomed for economic reasons.

Recent Technological Developments in Soybean Oil Refining

Close-Coupling of Refining and Bleaching

In recent years in the United States, it has become customary to close-couple the refining and bleaching processes. The advantages for this system include the following: (i) energy savings; (ii) quality improvement; and (iii) improved oil stability and/or shelf life. Therefore, any discussions about chemical refining must include the bleaching process. Some novel techniques for operation of the bleaching filters have been developed. Typically, two bleach filters are used so that a new filter can be put on line as soon as the previous filter is spent. Thus, the flow of bleached oil is not interrupted, which is a requirement when bleaching is close-coupled to a continuous refining process.

The first innovation was operating the bleach filters in the packed-bed mode. That is, all of the bleaching clay for the entire filter cycle is packed (precoated) on the filter before start-up. This filter will stay on line until the filtered oil is found out of specification in respect to chlorophyll. At that point, the second filter, which has been precoated previously, goes on line to produce a packed bed.

The second innovation was operating the filters in the lead-trim approach. In this method, when the second or new filter goes on line, the oil continues to flow through the first filter. This is done because the bleaching clay (the packed bed) continues to display a great deal of activity, thereby reducing the use of bleaching clay. The packed bed approach and the lead-trim approach have been found to be considerably more effective when the refined oil is purified with silica before entering the bleaching process.

Modified Caustic Refining or Silica Refining

A modified caustic refining process is depicted in Figure 8.5. In this process, silica hydrogels are used to remove residual soap and other trace metals from the refined oil, eliminating the water washing step. The environmental effect of the oil refining process is greatly reduced by the elimination of water washing, better quality oil is provided, and the amount of bleaching clay required to remove chlorophyll and other impurities is greatly reduced (2).

More recent systems are designed around the concept of silica addition and removal with a dedicated filter for silica filtration before bleaching, as depicted in Figure 8.5. The three new large refineries installed in the United States between 1995 and 2000 were designed around this concept. In addition, the one new large U.S. refinery being built for start-up 2000–2001 is designed around this concept. Silica refining or silica purification may be the greatest improvement in the oil refining process over the last 10 years, and more specifically over the last 5 years. The advantages of this concept are numerous and include the following:

1. Capital and operating cost savings by eliminating the water wash centrifuge.
2. Operating simplification with the use of only one large high-capacity primary centrifuge instead of multiple machines. This change gives the refining operator has more time to optimize the whole process.
3. "Greening" of the complete refining complex. Elimination of water washing has a major effect on the environment. This change reduces the refinery wastewater discharge by >50%, and the remaining waste water discharge is lower in biochemical oxygen demand, fats, oils, and greases, thus providing a stream that can be treated very economically. Fats and oils processing plants can make a major contribution to water conservation by eliminating the water wash step.

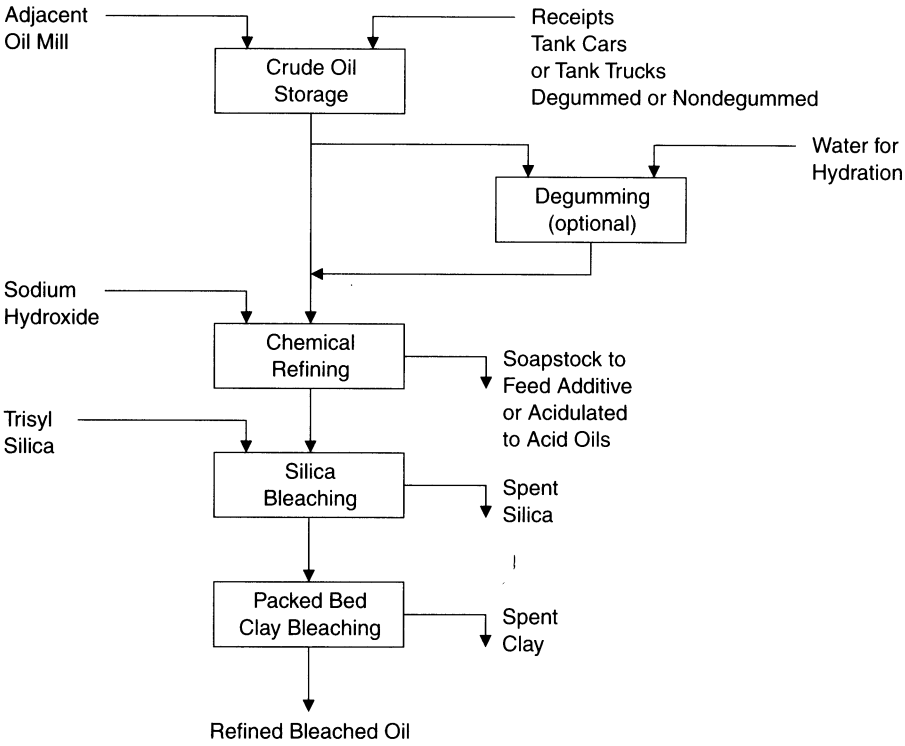

Fig. 8.5. The modern caustic refining process with silica purification.

4. Silica purification cleanses the oil much more efficiently than water washing. All of the trace impurities, soap and trace metals are reduced to 0 ppm. Thus, the efficiency of bleaching clay is greatly enhanced because it has to remove only chlorophyll and secondary oxidation products. Bleaching clay usage has been reduced in some plants by 50–75%.

Sodium Silicate Refining

Several years ago, refining trials were made using sodium silicate in place of sodium hydroxide in chemical refining. The assumed advantages were improved yield, improved quality, and more efficient removal of soap and trace metals, either with water washing or silica purification. These plant trials were complete failures because the automatic self-cleaning centrifuge "plugged up" in less than an hour. Silicate bonded to the discs in the disc stack and stopped the centrifuge from functioning. It was a disaster because several days were lost in cleaning the centrifuge disc stacks by hand.

Texas A&M University has advanced this technology by removing the sodium silicate soaps by filtration instead of a centrifuge. For reasons not totally understood at this moment, sodium silicate soaps are filterable, whereas sodium hydroxide soaps are not at all filterable. A logical theory lies in the fact that sodium silicate reacts with FFA, forming silica hydrogel. If this is true, it explains the filterability.

Texas A&M University has licensed this technology to Oxychem Corporation, a manufacturer of sodium silicate. De Smet Process and Technology is currently installing a small refinery designed to utilize sodium silicate refining. This small plant is actually a large semiworks plant in capacity, which should be an excellent location in which to prove or disprove the process with respect to operating efficiencies and quality.

It is known already that sodium silicate refining may not be applicable at all locations. Additionally, degumming of the crude soybean oil is a prerequisite, and it may be necessary to combine this process with this author's ultra-degumming process to capture synergy. Plant trials utilizing this concept will begin in late 2000.

Membrane Refining

Considerable research has been performed over the last eight years developing the process of degumming and refining soybean and other oils in miscella using membrane separation. The separation takes place in miscella to capture quality advantages for both the oil and the lecithin; the lower viscosity offered by solvent in miscella is a requirement for membrane separation.

The first years were devoted to identifying membranes that were compatible with oil and solvent, that could be easily cleaned with the same solvent, and that would offer a reasonable flux or flow rate. It turned out that a new membrane system had to be designed for this particular application. After several years of laboratory and plant trials with a portable pilot plant, the next step would be to build a semiworks plant to be located in a solvent extraction plant, operating in parallel with the existing plant. Most likely, the plant will have to operate for at least one year before a full-size commercial plant can be designed.

All the work currently centers around simultaneous degumming and refining in a single step to produce a filtered oil with a phosphorous level of <2.0 ppm. Thus the oil must be bleached only to remove chlorophyll and secondary oxidation products, followed by physical refining. A pleasant surprise has been that the chlorophyll in the membrane-separated oil is less than one half that of conventionally processed oil. If this technology is proven and if it can be operated in a cost-effective manner, it may be one of the greatest developments in oil processing during the 20th and 21st centuries.

Organic Refining Process

Recently, AGP, Omaha, NE was granted a U.S. Patent for a new refining technology. The developers plan to introduce this technology at the World Conference of Oilseed Processing in Cancun, Mexico, November 12–17, 2000. Not enough is known about this technology at present for an opinion as to its viability. It is mentioned here only to include it as an emerging technology.

Physical Refining of Soybean Oil

Development of a successful operating system for the physical refining of soybean oil has not taken place, although it has been an industry goal worldwide over the last 25 years. The few companies that are practicing physical refining around the world are doing it out of necessity because of a lack of an outlet for soapstock and refining wash water; they have been able to accept a quality that is less than U.S. standards. With the globalization of the fats and oils industry, substandard quality will no longer be acceptable. As a result, almost all of the refineries that practiced physical refining of soybean oil have had to modify their systems to more conventional refining techniques.

Physical refining of soybean oil has been an elusive process due to the relatively high level of NHP. Acid pretreatment, coupled with special mixing, cannot convert a high enough level of NHP to HP, that is, not to the extent that cost-effective physical refining can be offered. The author installed the first plant of commercial size in the U.S. in 1996 to physically refine soybean oil. The system performed quite well, delivering oil quality even better than caustic-refined oil when the crude soybean oil contained a low level of NHP. Due to the low FFA in the special degummed oil, the tocopherol level in the deodorizer distillate remained the same, not diluted with higher FFA. However, the process did not deliver the projected savings when the NHP were high. This process has evolved into what is now termed "semiphysical refining." The addition of caustic at a level less than the typical neutralizing dose and reasonable silica, as low as 0.02%, has enabled the plant with this system to continue operations. This plant is currently producing high-quality soybean oil with low operating costs.

The concept of semiphysical refining has been further refined. In this system, the crude oil is analyzed for trace metals, phosphorus, calcium, and magnesium, before start-up. The amount of NHP is proportional to the calcium and magnesium level. Then, the refining process that is chosen by the operator is the one that best suits that level of NHP. This concept is depicted in Figure 8.6.

Originally, the refining process was chosen on the basis of the calcium and magnesium level, but as stated above, the NHP content is proportional only to the calcium and magnesium level; however, this does not apply to all soybean oils. The author's current theory is that elemental calcium and magnesium may be present in the crude oil and not necessarily reacted with or bonded to the phospholipid radical. If calcium and magnesium are not totally reacted, then degummability cannot be predicted by the calcium and magnesium level alone. Because necessity is the mother of invention, a laboratory test was developed to determine the degumming efficiency of a crude soybean oil. This laboratory test procedure is depicted in Table 8.6.

In summary, the operator of the multi-purpose refining process will choose the process that is best-suited for that particular oil, on the basis of the degumming efficiency. It is estimated that in a plant producing its own crude oil in a proper manner and of the of proper quality, the physical refining process could be used 90%

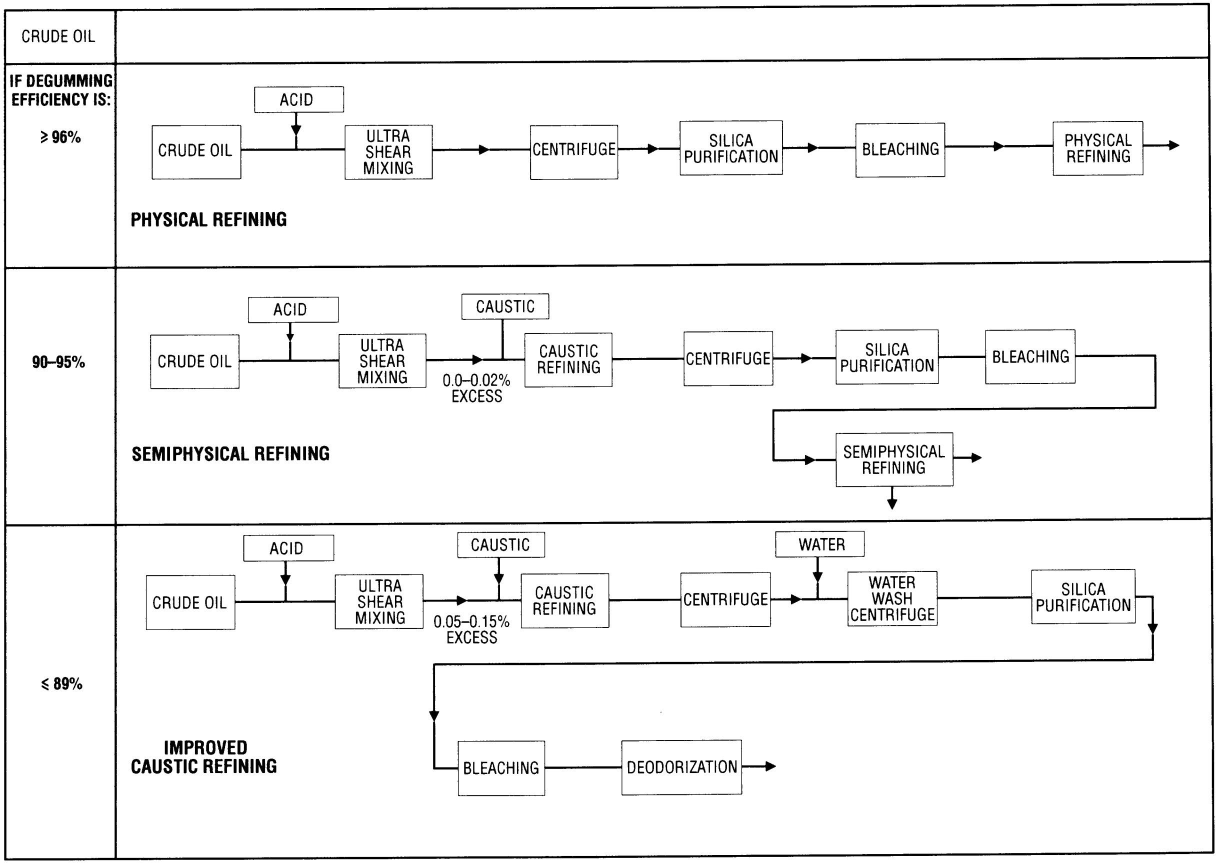

Fig. 8.6. Multi-Purpose Refinery (3).

TABLE 8.6 Degummability Test for Soybean Oil[a]

Analyze the crude oil for P, Ca, and Mg.

Add 400 g crude oil to a 800-mL beaker.
Place on stirrer/hot plate with stirrer bar set at medium speed.
Heat to 130°F (do not overheat).
Slowly add water (deionized water preferred).
Water treat = $(P_{ppm} \times 31.7 \times 10^{-4})0.7$.
Example: If P = 800 ppm → $(800 \times 31.7 \times 10^{-4})0.7 = 1.78\%$.
400 g oil × 1.78% = 7.1 g water.
Agitate at slow speed for 20 min without additional heat.
Turn off agitator and let sit idle for 5 min.
Filter through filter paper by gravity.
Analyze filtrate for P, Ca, and Mg.

Compute degumming efficiency

Degumming efficiency = $[(P_{ppm}\text{ crude oil} - P_{ppm}\text{ degummed oil})/P_{ppm}\text{ crude oil}] \times 100$
Example: If $P_{\text{crude oil}} = 800$ ppm and $P_{\text{degummed oil}} = 35$ ppm,
then degumming efficiency = $[(800 - 35)/800] \times 100 = 95.6\%$

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[a] To determine how well a crude oil will degum or refine and which refining process is best-suited for a particular oil.

of the year, resulting in lower operating costs and offering a major contribution toward improvement of the environment.

Conclusion

The refining process and downstream processing are very interesting and almost totally absorbing; fortunately, however, refinery managers, researchers, and refining operators are never satisfied and feel there must be a better way. It is fortunate for the industry that this attitude exists because without that perspective and commitment to excellence, very few in the industry would have survived past the year 2005, and many would become extinct before then. With overproduction of soybeans, coupled with overcapacity in crushing and refining, the survivors will be those who implement the latest technologies to improve yields, reduce operating costs, reduce energy costs, reduce environmental costs, all while improving quality, training, and motivation of the employees.

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Chapter 9

Bleaching

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Introduction

Bleaching is an important process used to remove impurities from edible fats and oils. It usually follows neutralization, but it may also follow the degumming process in the case of physical refining. Bleaching is an old process; it is rather complicated and not easily understood. Although degumming and neutralization are strictly chemical processes and deodorization a physical process, bleaching is a combination of the two. An understanding of the bleaching process requires a knowledge of the properties of the bleaching clay as well as the types of impurities present in the fats and oils. This chapter has the following goals: (i) to identify the typical impurities and their sources; (ii) to determine which impurities can be removed with bleaching; (iii) to explain the effects of certain impurities on bleaching earths; (iv) to discuss the most important bleaching parameters such as temperature, time, vacuum, type, and amount of bleaching earth; and (v) to review the possible uses for spent bleaching clay.

Bleaching Earth Structure and Properties

Bleaching earth is made from naturally occurring minerals such as palygorskite, which is also known as attapulgite, sepiolite, bentonite, and other minerals that all belong to the aluminum silicate family. Bleaching earth, often called "fuller's earth," has been known and used for many years (1). The use of fuller's earth for filtration and color improvement of oils was identified and developed by W.B. Albright and H. Eckstein for N.K. Fairbanks & Company, Chicago, IL. Initially, in 1880, they developed a process to bleach cottonseed oil with fuller's earth (2). Bleaching earths consist of natural clays, which have "bleaching activity," and others that become active only after a specific treatment. The first activated bleaching earths were developed by Pfirschinger Mineralwerke, Kitzingen in 1907 and by Erdwerke Kronwinkl, Franz Schmidt & Co. in 1909 (3,4).

An understanding of the activity during the oil treatment with bleaching clay requires a review of the physical and chemical properties of the untreated mineral. First, the bleaching clays must exhibit a certain cation exchange capacity. The other important parameters for natural bleaching clays are a high absorption capacity, a certain porosity, and large surface area. Natural bleaching clays can be slightly acidic to slightly basic. For most of the bentonites, the necessary surface area and porosity have to be created. This is usually accomplished by a treatment with acids.

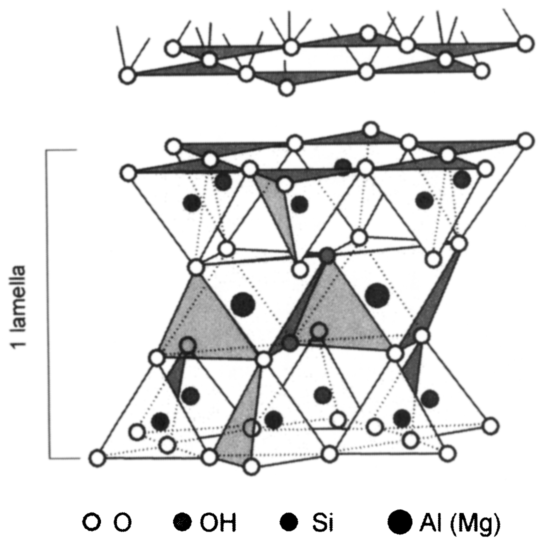


Fig. 9.1. Crystal structure of montmorillonite.

Better activity for certain reactions is obtained by mixing with organic or inorganic acids, or acidification by other methods.

The activation step for montmorillonite, the main component of bentonite, is explained in detail to illustrate the changes in the structure of the lattice and the other reactions during clay treatment.

Activation of Montmorillonite

Montmorillonite is a layer silicate as shown in Figure 9.1 (5). Each layer consists of two silicon layers surrounded by oxygen tetrahedras and an aluminum layer surrounded by oxygen octahedras. Due to the replacement of some of the aluminum ions by Mg^{2+}- and Fe^{2+}-ions, the aluminum silicate layer obtains a negative charge. This negative charge is neutralized by cations, normally alkali or earth-alkali ions, which are in between the negative layers, thus connecting the layers. One crystal contains ~15 layers. Looking at the crystal, it is understandable why montmorillonite has swelling capacity, i.e, the alkali ions, and to a lesser degree the earth-alkali ions, are hydrated, thus expanding the different aluminum silicate layers.

When montmorillonite is treated with an acid such as sulfuric acid, all of the cations located in between the negatively charged aluminum silicate layers are exchanged. With more vigorous treatment, the mineral acid attacks the lattice and dissolves Al-, Fe-, and Mg-ions and destroys the crystal from the edges as shown in Figure 9.2. Without entering into the particulars, it can be concluded that the acid treatment enlarges the surface and pore volume of the montmorillonite to form acid centers. Eventually, with continued treatment, the montmorillonite crystal completely dissolves to form pure silica. Figure 9.3 charts the surface area and activity to show "bleaching activity" with increasing levels of hydrochloric acid (6).

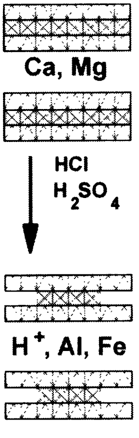


Fig. 9.2. Acid-activated bentonite. The characteristics include exchange of protons, acidic surface, high surface area, and high pore volume.

Obviously, an optimum acid treatment must be determined for the desired activity, depending on the type of acid, its concentration, time, and temperature of the treatment, and last but not least, the crude clay quality.

During activation, the density of the bentonite is reduced. The density reduction is caused by a disorientation of the layers due to the formation of flexible silica tails. This change is illustrated in Figure 9.4.

Another important characteristics of the final product is particle size. It is influenced by the processing steps that follow acid activation. First, the remaining solids from the acid treatment are filtered from the excess acid and the dissolved metal ions.

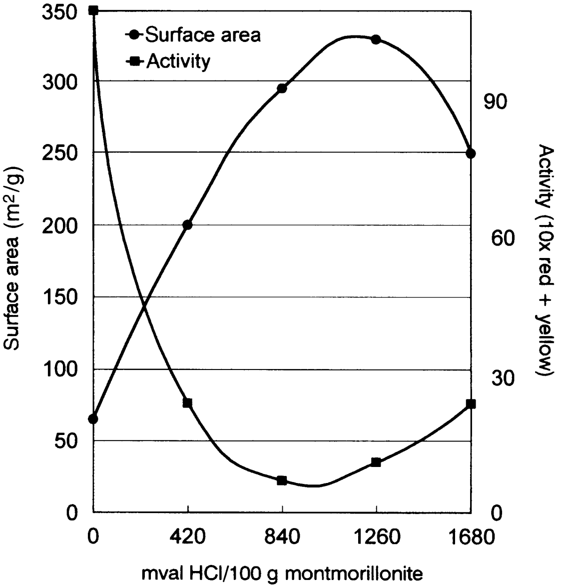


Fig. 9.3. Activation of montmorillonite.

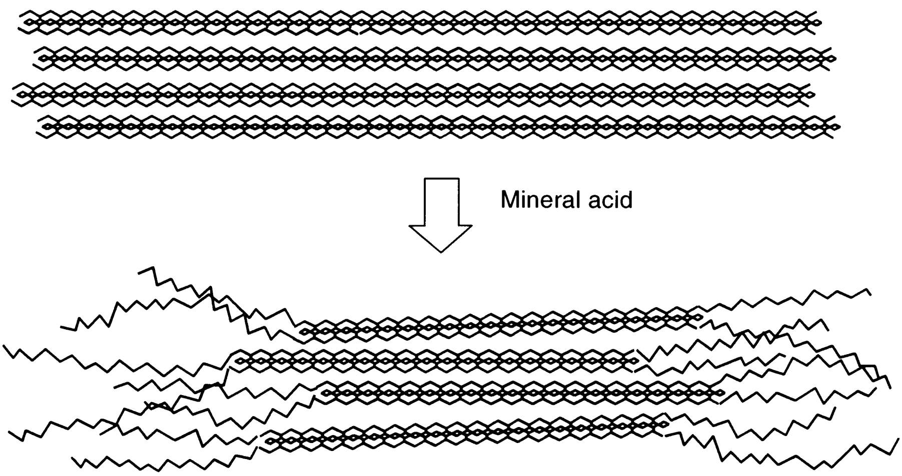


Fig. 9.4. Formation of amorphous silicic acid at the edges of the silicate laminae during acid activation.

The activated clay is then washed to remove the excess acid. The resultant wet clay, which contains ~40% solids, is then dried to evaporate most of the water. The final moisture content depends upon on the type of raw material and the mineral acid used for activation. The moisture content influences the particle size distribution. Optimum filtration properties are obtained with moisture contents ranging from 7 to 15%. Agglomerates of the primary bleaching earth particles are formed during drying; these affect the particle size distribution, which in turn affects filtration and activity. Particle size must be closely controlled because activity increases with particle size reduction; unfortunately, however, filtration decreases as the particle size is reduced (6).

The advantages for an activated bleaching earth include the following: (i) the surface area of the starting material has increased by several hundred percent which results in a high adsorption capacity; (ii) acid activation has provided the clay with some acid centers by formation of silanol groups and by replacing the Ca-ions between the layers with protons and Al-ions, both of which give the clay catalytic properties; (iii) a third important parameter is related to the ion exchange capacity and is strongly related to the ion exchange capacity of the starting clay material.

Activated Bleaching Earth Properties

As discussed previously, the efficiency of a bleaching earth is influenced by the following five characteristics (7): Adsorption capacity, acid properties, catalytic properties, ion exchange capacity, and particle size distribution. On the basis of these characteristics, it is clear that "activated bleaching earth" does much more than simply remove color. The same is partially true for natural bleaching clays, but nature provides some limitations that are eliminated with acid activation. It should also be clear that producers of bleaching earths can optimize a certain product for a specific oil type. For example, a certain bleaching earth may be particularly suited for palm oil but not necessarily effective for another type of oil.

Oil Quality

Fats and oils processing includes a number of processes in which the material is treated chemically or physically. The quality of the crude oil determines whether each process is required and the extent to which it is required. A classic example is olive oil, which has several grades that are recognized by most consumers. The highest quality olive oil is cold pressed only. It has no further processing to preserve the unique flavor and typical color that command a high cost. Conversely, the lowest grade of olive oil is almost inedible, requiring processing to become acceptable for human consumption. Here, quality is affected by the type and amount of impurities contained in the oil.

Impurities in vegetable oils have various sources. They can be minor ingredients naturally contained in the oil or degradation products produced with abuse of the seed, fruit, or extracted oil. Technically, some of the impurities are compounds produced by the oil plant and should be called by-products rather than impurities. Some detrimental impurities develop due to degradation processes in the oil fruit or seed; some develop downstream during processing. The chemicals added during processing are another source for impurities in edible fats and oils. Table 9.1 lists most of the common impurities and by-products contained in edible fats and oils. Table 9.2 defines and classifies the impurities by origin.

Quality oil products require decisions regarding the retention or removal by further processing of certain impurities or by-products. This difficult decision depends upon many variables, including further processing requirements, usage of the oil, or consumer habits. Further, this decision also depends upon the type and amount of the impurities in the oil.

TABLE 9.1 Impurities or By-Products

Meal
Phosphatides
Unsaponifiables
Sterols
Tocopherols
Hydrocarbons
Trace metals
Sulfur
Halogens
Color bodies (e.g., gossypol, carotene, chlorophyll)
Alcohol
Ester
Ether
Soap
Free fatty acid
Conjuenes
Peroxides
Ketones
Aldehydes
Trans fatty acids
Polycyclic aromatic hydrocarbons (PAH)
Solvents
Pesticides
Thermal degradation products
Diglycerides
Polymers
Acids (phosphoric, citric)
Water

TABLE 9.2 Definition of Impurities in Fats and Oils

Definition of by-products	Typical examples
Primary by-products Oil-soluble compounds from the oil-bearing organism (vegetable or animal)	Proteins, phospholipids, unsaponifiables (e.g., sterols, tocopherols, hydrocarbons), color bodies (e.g., chlorophyll, carotene, gossypol), metal complexes, sulfur and halogen compounds, alcohol, ether, ester
Secondary by-products Degradation compounds, which develop in the seed or during storage of the oil (crude or refined)	(Impurities) Free fatty acids, peroxides, conjuenes, ketones, aldehydes, *trans* fatty acids, metal and sulfur compounds, color bodies, nonhydratable phospholipids
Tertiary by-products Remaining chemicals added during growing and processing, degradation compounds and derivatives of those chemicals, contaminants from the equipment, from high temperature and from other oils	(Impurities) Pesticides, solvents, polycyclic aromatic hydrocarbons (PAH), metal traces, soaps, acids (e.g., free fatty acid, phosphoric acid, citric acid), *trans* and conjugated fatty acids, dimers, polymers

The fats and oils industry has established refining processes for the removal of impurities. Table 9.3 compares the two most popular refining sequences used, i. e., alkali or chemical vs. physical or steam distillation refining. Other processes are also employed for the removal of specific impurities to produce an oil with characteristics more suited for the intended finished product. For example, dewaxing and winterization are processes designed to remove hard fractions to obtain a clear liquid oil. Other processes create impurities while performing the intended function. Hydrogenation and interesterification change the physical and/or chemical properties of an oil product but also create and/or impart impurities that have to be removed from the product.

TABLE 9.3 Refining: Alkali vs. Physical

Alkali	Physical
Degumming	Degumming
Neutralization	Bleaching
Bleaching	Deacidification
Deodorization	

This chapter deals predominately with the bleaching process. Bleaching is regarded by many fats and oils processors as the most important step in the refining process. However, it must be stated that all of the processing steps must be treated with equal importance to produce a quality product at the least cost.

Effect of Bleaching Clay on Triglycerides and Minor Constituents

The aim of the bleaching process is to to remove the unwanted impurities listed in Table 9.1 without changing the triglyceride molecule. During bleaching, the oil is treated with a chemical and an adsorptive material to remove all of the undesirable impurities present except for those captured by the deodorization process. The five characteristics of activated bleaching earth outlined earlier make bleaching a versatile and highly effective tool to remove most of the undesirable impurities. However, the bleaching process must be controlled to prevent the development of other undesirable impurities.

Acidic Properties Effects

It is important to distinguish between the various types of acid centers in bleaching earths. For example, some of the acid from the activation process remains after washing. Bleaching earths activated with hydrochloric acid contain <0.1% mineral acid, whereas bleaching earths activated with hydrochloric acid normally contain between 0.1 and 1.0% mineral acid. Additionally, in special cases, an acid is added to bleaching earth after washing. This acid content does not influence the formation of free fatty acids during the bleaching process as shown in Figure 9.5.

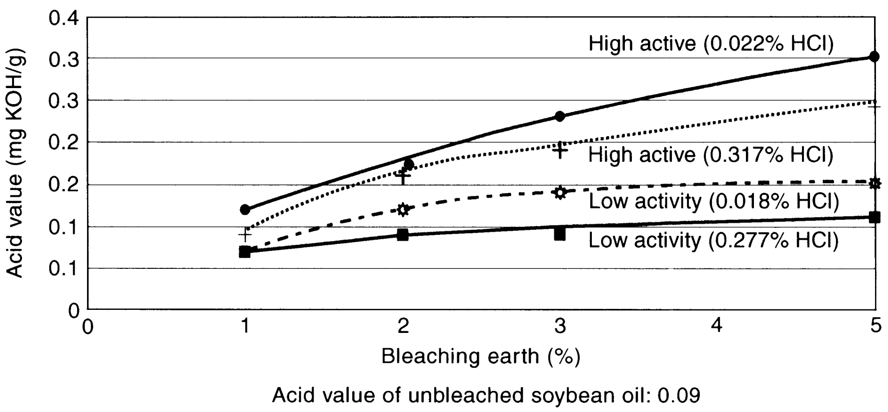


Fig. 9.5. Influence of acidity and amount of bleaching earth. The acid value of unbleached soybean oil is 0.09.

Apart from the remaining mineral acid, activated bleaching earth has further acidic properties. These properties are due to the protons and hydrated aluminum ions, which balance the negative charge of acid-activated montmorillonite, known as activated bleaching earth. In addition the silanol groups of the silicic acid on the edges of activated montmorillonite also have acidic properties. The acidic properties are responsible for a number of desirable reactions but also present some that are undesirable. A desirable reaction is the splitting of soap according to the formalized equation shown below:

$$\text{H-bentonite} + \text{Na-soap} = \text{Na bentonite} + \text{fatty acid}$$

An undesirable reaction is the splitting of the triglyceride according to the formalized equation shown below:

$$\text{triglyceride} + \text{water} = \text{diglyceride} + \text{fatty acid}$$

To control the free fatty acid (FFA) increase caused by hydrolysis during bleaching, it is necessary for the fats and oils processor to remove the soap remaining after the alkali refining process with water washing or by other convenient methods before bleaching. Also, vacuum bleaching will evaporate and remove excess moisture in the oil or that adsorbed on the bleaching earth. In physical refining, a moisture content improves the removal of nonhydratable phospholipids during bleaching. Wet bleaching is important for soybean, sunflower, or rapeseed oils that have been physically refined. Activated bleaching earth can be regarded as solid acid with a good cation exchange capacity. In the presence of moisture, activated bleaching earths act like phosphoric or citric acids to chelate trace metals (8). In both cases, either with bleaching earth or the chelating acids, the "nonhydratable" calcium and magnesium salts of the phosphatidic acid are split and become water soluble for removal either with the water phase or by absorption on the bleaching earth. The conditions for wet bleaching are shown in Table 9.4. Vacuum bleaching is recommended for

TABLE 9.4 Wet Bleaching: Laboratory Conditions

Wet bleaching	Fill in oil at room temperature Add 0.3%/0.9% water Stir at room temperature for 2 min Addition of bleaching earth Temperature: 55°C Time: 15 min Pressure: 900 mbar
Dry bleaching	Temperature: 100°C Time: 30 min Pressure: 50 mbar
Filtration	Cool to 80°C Purge with Ar Filter

wet bleaching to facilitate removal of the excess moisture for good filtration. Wet bleaching is not a new discovery; it has been practiced for quite some time (3). Table 9.5 compares wet and dry bleaching of a water-degummed canola oil for the removal of chlorophyll and phosphatides with 1.0, 2.0, and 3.0% bleaching earth. In all cases, wet bleaching was more effective than dry bleaching.

Catalytic Behavior

The acidic and catalytic properties of activated bleaching earth are difficult to separate. Nevertheless, some reactions during bleaching can be explained by the catalytic behavior of activated bleaching earth. The best known and by far the most important reaction is the decomposition of hydroperoxides. Figure 9.6 charts the decomposition of peroxides with activated bleaching earth at 0.5 and 3.0% treatment levels. A higher catalytic activity is equated with a lower peroxide value after bleaching. A number of secondary oxidation products such as aldehydes and ketones may form when the hydroperoxides decompose. Additionally, conjugated fatty acids may develop; these are much more sensitive to oxygen than nonconjugated unsaturated oils. Therefore, it is very important that contact with air be avoided during bleaching with the use of a vacuum and with nitrogen protection during filtering and storage (8,9).

Adsorptive Power

The best known property of bleaching earth is its adsorption of color bodies such as carotene and chlorophyll. When the adsorption is due to van der Waal's forces, it is called physical adsorption. When chemical reactions are involved, it is called chemisorption. The important criterion for physical adsorption is the ability of the adsorbent to adsorb a certain substance, or adsorbate, at a defined temperature.

The surface properties of the bleaching earths are also important for adsorption behavior. Some bleaching earths adsorb certain compounds better than others. Compounds with cationic properties or compounds that are polar are more easily adsorbed (10). This is also true for compounds that are polarized in the presence of

TABLE 9.5 Bleaching of Canola Oil: Dry vs. Wet[a]

Bleaching earth	Amount (%)	Chlorophyll (ppm)		Phosphatides (ppm P)	
		dry	wet	dry	wet
Untreated		5.63	5.63	34.6	34.6
Tonsil Opt.210 FF	1	0.21	0.08	24.5	3.1
Tonsil Opt.210 FF	2	0.02		18.6	1.5
Tonsil Opt.210 FF	3			9.2	1.5

[a] Pretreatment (wet): 1% water, 80°C, 20 min, 700 mm Hg. Bleaching: 1–3% bleaching earth, 90°C, 30 min, 50 mm Hg.

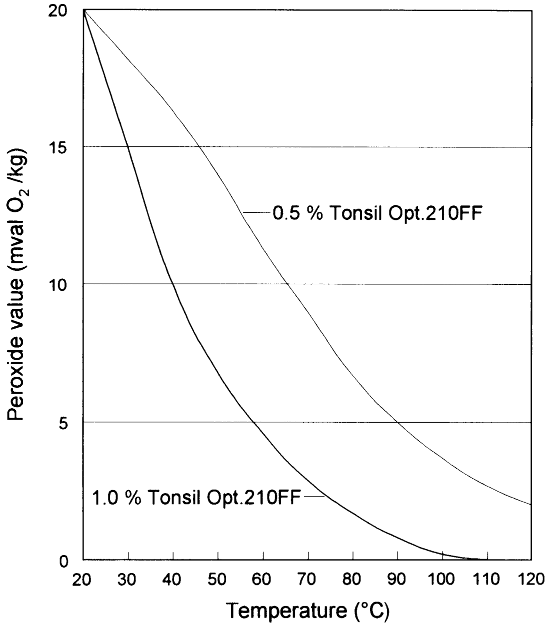


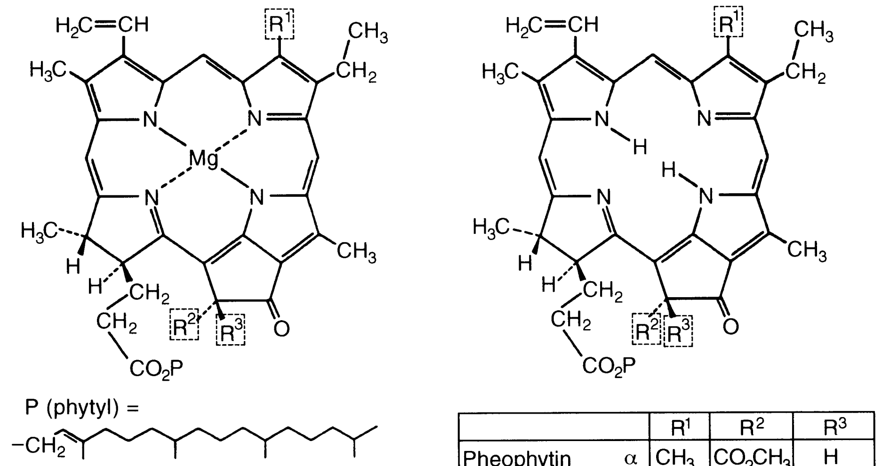
Fig. 9.6. Decomposition of peroxides with highly activated bleaching earth. Solid line: 1.0% Tonsil Opt.210FF; dotted line: 0.5% Tonsil Opt.210FF.

acids. This behavior is due to the negative charge of the bleaching earth lattice. This also explains why certain compounds such as the slightly acidic gossypol or the nonpolar polyacyclic aromatic hydrocarbons (PAH) are not adsorbed by bleaching earth. Activated carbon, which has a nonpolar surface, must be used to adsorb heavy PAH (11). Light PAH are removed during deodorization (12).

Ion Exchange Capacity

During acid activation of montmorillonite, the cation exchange capacity (CEC) decreases. High-quality bentonite has a CEC of 80–100 aVal/100 g. Activated bleaching earth has a reduced CEC of 30–60 mVal/100 g, depending upon the degree of activation. During activation, the porosity of bleaching earth increases, which in turn increases the speed of adsorption. Furthermore, the silanol groups formed during activation also react with the metal ions. These properties explain why wet bleaching is more effective than dry bleaching for the removal of nonhydratable phospholipids. The acidic properties alone are not sufficient to split the Ca-, Mg-, or Fe-salts. The cations must be removed to shift the equilibrium, which is possible in the presence of water as a reaction medium.

A similar mechanism can be postulated for adsorption of chlorophyll or hemin. Figure 9.7 shows the structure of chlorophyll derivatives (13). The acidic cation exchanger exchanges the central magnesium or iron ion (14). The metal free porphyrin is then protonated and absorbed on the surface of the negatively charged bleaching earth crystal.



		R^1	R^2	R^3
Chlorophyll	α	CH_3	CO_2CH_3	H
	α'	CH_3	H	CO_2CH_3
	β	CHO	CO_2CH_3	H
	β'	CHO	H	CO_2CH_3

		R^1	R^2	R^3
Pheophytin	α	CH_3	CO_2CH_3	H
	α'	CH_3	H	CO_2CH_3
	β	CHO	CO_2CH_3	H
	β'	CHO	H	CO_2CH_3
Pyropheophytin	α	CH_3	H	H
	β	CHO	H	H

Fig. 9.7. Structure of chlorophyll derivatives.

The cation exchange capacity is also important for the removal of heavy trace metals from oils, especially iron and copper, which are strong prooxidants. Hydrogenated fats and oils will contain small amounts of nickel. The cation exchange capacity of the bleaching earth guarantees the removal of the trace nickel by post-bleaching with 0.3–0.5% bleaching earth, depending upon its capacity and the amount of nickel in the hydrogenated fat or oil. Some suppliers offer activated bleaching earths that have been optimized especially for the removal of trace metals. For soap removal, the ion exchange capacity is not essential; the acidity of the acid-activated bleaching earth is sufficient for this purpose. Table 9.6 summarizes the influence of the bleaching clay's characteristics on the various impurities present in fats and oils.

TABLE 9.6 Influence of Bleaching Clay on Impurities and By-Products

Characteristic	Influence on
Acidic	Phosphatides, chlorophyll, free fatty acid, soap
Catalytic	Conjuenes, carotene, color bodies, peroxides, ketones, aldehydes, *trans* fatty acids, free fatty acids, dimers, polymers, hydrocarbons
Ion exchange	Phosphatides, chlorophyll, free fatty acids, soap, trace metals
Adsorption	Phosphatides, chlorophyll, carotene, phosphoric acid, free fatty acids dimers, polymers, hydrocarbons

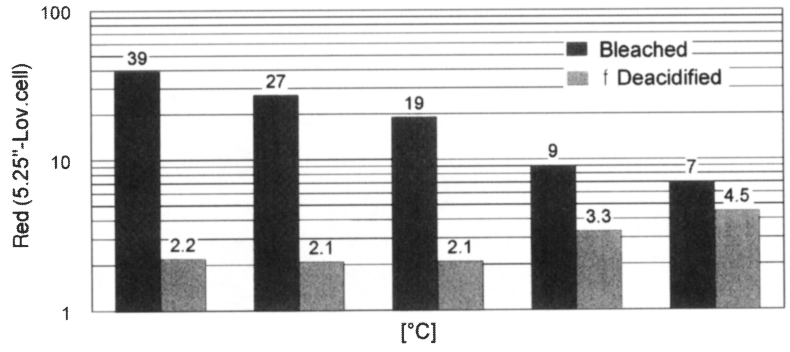
Influence of Temperature, Time, Pressure, and Bleaching Earth Quantity on Bleaching Earth Quality

Color reduction and the removal of other undesirable impurities are strongly influenced by the reaction conditions. At higher temperatures, exposure to oxygen will cause color fixation and a drastically reduced oil stability, which is even more pronounced with the use of a highly activated bleaching earth. This explains why natural bleaching earths apparently have better color reduction with atmospheric conditions than do activated bleaching earths (15). Conversely, with vacuum bleaching conditions, activated bleaching earths provided better color reduction than did the natural bleaching earths.

Influence of Temperature

If bleaching earths were simply adsorbents, the best color reduction would be expected at low temperatures. The adsorption equilibrium would be expected to shift toward desorption with high temperatures, and some of the adsorbed molecules would dissolve back into the oil. However, this is not observed. Decoloration improves as the temperature is increased, which indicates that bleaching earth is more than simply an adsorbent. Chemical reactions take place on the surface of the bleaching earth. According to the rule of van't Hoff, the speed of reaction doubles with each temperature increase of 10°C. This rule is valid for all reactions, both the wanted and the unwanted. Consequently, there must be an optimum temperature. This optimum temperature depends upon the type of oil, the by-products, and the impurities. Figure 9.8 shows the influence of temperature on the color of bleached and deodorized palm oil. It can be observed that when the optimum temperature is exceeded, color fixation occurs.

As a practical rule of thumb, oils should be bleached at the lowest reasonable temperature. This temperature must be high enough to provide a low oil viscosity. It must be low enough to avoid undesirable side reactions, which would damage the oil and reduce the quality and shelf life. Most oils are bleached at temperatures be-



1.5% Tonsil Supr.110FF, oil deacidified at 240°C

Fig. 9.8. Color of bleached and deacidified palm oil as dependent on temperature. Conditions: 1.5% Tonsil Supr.110FF, oil deacidified at 240°C.

tween 90 and 100°C (194–212°F). Difficult-to-bleach oils may require a temperature as high as 120°C (248°F). It has also been found that less active bleaching earths require somewhat higher temperatures.

Influence of Time

The time necessary for maximum color removal depends on the quality of the bleaching earth and the bleaching temperature. Rich (15) proved that soybean and cottonseed bleached at 80°C (176°F), most likely under atmospheric conditions, experienced decolorization improvements with increased time. Further, optimum decolorization at 105°C (221°F) was attained after 35 min, and optimum bleaching time was decreased to 5 min with a temperature increase to 120°C (248°F). Color removal increases as the temperature and/or time is increased; however, longer oil contact time with a bleaching earth can cause color reversion, which also increases as the temperature increases. State-of-the-art bleaching time for most oils is in the range of 20–30 min at a temperature of 90–100°C (194–212°F). Shorter times are recommended when higher bleaching temperatures are utilized. Long exposure times with bleaching earth and high temperatures damage the oxidative stability or quality of edible fats and oils.

Influence of Pressure

In the early days of fats and oils processing, bleaching was generally performed under atmospheric conditions. However, the detrimental effect of oxygen on the quality or oxidative stability has been recognized since at least 1929 (3). Eicke (16) reported on the differences experienced with atmospheric and vacuum bleaching of beef tallow at the DGF conference in Regensburg. Table 9.7 shows that atmospheric bleaching of tallow at 90°C (194°F) provided a lower color than vacuum bleaching. However, a high increase in peroxide value (PV) was observed with atmospheric bleaching conditions, whereas the vacuum bleaching conditions had considerably lower PV increases. These results confirm that hydroperoxides decompose at least partially to conjugated fatty acids, which are more sensitive to oxidation.

TABLE 9.7 Bleaching of Tallow: Atmospheric vs. Vacuum[a,b]

Temperature (°C)	Pressure (mm Hg)	FAC-color	PV
90	atm	175	16
90	50	225	2
110	atm	225	14
110	50	15	2
130	atm	225	24
130	50	75	1

[a] Conditions: 5% Tonsil Standard 310 FF; time, 30 min.

[b] Abbreviations: FAC, Fats Analysis Committee of AOCS; PV, peroxide value.

Atmospheric bleaching provides ideal conditions for oxidation, i.e., exposure to oxygen at high temperatures. Obviously, vacuum bleaching offers better protection from oxidation than atmospheric bleaching. In general, fats and oils must be protected from exposure to oxygen during processing to maintain a bland or pleasing flavor with good stability or shelf life.

Bleaching Earth Quantity and Quality

According to the equation of Freundlich, the removal of impurities improves with increasing amounts of adsorbent. However, it is difficult to calculate the minimum amount of bleaching earth necessary for efficient bleaching. This is due to the fact that oils contain varying amounts of impurities, which react differently with bleaching earths. The impurities may be soaps or phospholipids in the case of alkali-refined oils or phospholipids and other gums in the case of physically refined oils. Soaps deactivate the active centers of the bleaching earth, and phospholipids block the surface. Soaps and gums also cause the bleaching earth particles to clog together, which results in a pressure drop during filtration. Therefore, the presence of these impurities requires either a higher bleaching earth consumption or a more active bleaching earth to remove the color bodies adequately and decompose the hydroperoxides. For more detailed information on the influence of impurities on the rate of filtration, please refer to Ref. 6. As filtration of the bleached oil proceeds, the color will become lighter. This is the so-called press effect, which is due to the high concentration of bleaching earth on the filter screens or leaves. This higher concentration results in a further purification of the oil or fat (12).

Oil Quality Requirements

For the refined oil to meet the requirements for bleaching through either alkali or physical processes, it is necessary that crude oils maintain a certain quality. We recommend that the crude oil specifications require specific limits for free fatty acid, color, phosphatides, peroxide value, anisidine value, iron, and cooper. In addition, extinction values for conjugated dienes and trienes should be determined because these evaluations are better descriptors of the oxidative history of fats and oils than are peroxide or anisidine values only.

Oil to Bleaching Quality

The effect of the bleaching earth on an oil has been described; conversely, quality requirements for the oil to be bleached also exist. Relaxation of these requirements results in increased demand for bleaching clay and, in some cases, all of the impurities are not removed from the oil. Therefore, specification limits for the unbleached oil should be determined. The following values are recommended for neutralized or alkali refined oils (13): <5 mg/kg phosphorus and <50 mg/kg soap. The oil should not be heat damaged and should have a low degree of oxidation. Poor quality oils that do

TABLE 9.8 Characteristics Desired in Bleaching Oil

Ingredient	Amount
Phosphorous	<5 mg/kg
Soap	<10 mg/kg
Bleaching earth	<5 mg/kg
Free fatty acid	<0.5%[a]
Moisture	<0.1%
Copper	<0.1 mg/kg
Iron	<0.1 mg/kg
Nickel	<0.1 mg/kg[b]

[a] For physically refined oils.
[b] For hydrogenated fats.

conform to these limits will result in poor color removal and oxidative stability. Physically refined oils do not contain high amounts of phosho- and glycolipids. Our laboratory has achieved good bleachability with phosphorus levels as high as 30 mg/kg.

Bleach Oil Quality

Bleached oil is the most sensitive oil with regard to oxidation. It is therefore highly recommended that precautions be taken to protect it from contact with air. This starts with vacuum bleaching, blowing the filter with nitrogen or steam, and storage of the bleached oil under an inert atmosphere. Table 9.8 lists the characteristics desired in bleached oil (12). In addition to the specification limits shown in the table, the peroxide value should be zero. Conformance to these limits indicates that bleaching was performed properly and guarantees a high-quality oil after deodorization. Obviously, bleached oil quality is dependent upon a number of criteria including the following: Type of clay; concentration of clay; FFA. soap content; PV, anisidine value, conjuenes; phosphatide content; color; pressure; agitation; time; temperature; and filtration.

Bleaching Practice

Laboratory Bleaching Tests

Laboratory bleaching tests are recommended to determine suitable parameters for oils of unknown quality (13). This evaluation is performed in a round-bottomed three-neck flasks equipped with a stirrer, a contact thermometer, and a three-way valve as shown in Figure 9.9.(13)]. The desired temperature is chosen *via* the contact thermometer. The three-way valve is used to apply or break the vacuum with nitrogen. After the oil is bleached, the bleaching clay is removed by filtration, and the color plus the other parameters of the filtrate are measured. This method allows the laboratory to simulate plant conditions to determine bleaching earth and activated carbon dosage necessary to achieve the desired bleached oil parameters.

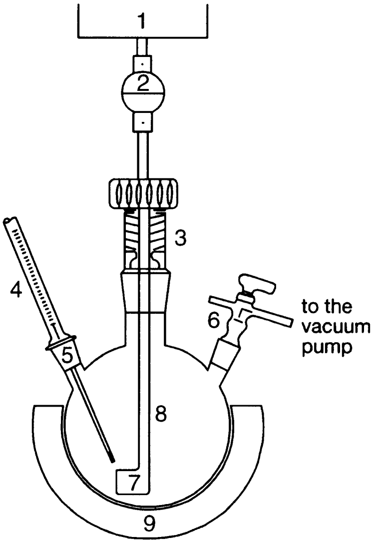


Fig. 9.9. Vacuum bleaching equipment. The parts are as follows: 1, stirrer, infinitely variable (0–600 U/min) with tension lining; 2, flexible coupling; 3, vacuum stirring plug, grinding N/S 29/32; 4, electronic contact thermometer with range from –50 to +300°C; 5, variable conical grinding with contact thermometer NS 14.5/23; 6, evacuation attachment with vent hole NS 14/23; 7, blade stirrer; 8, round-bottomed three-neck flask holding 250 mL, medium neck NS 29/32, side necks NS 14/23; 9, heating mantle for 250-mL round-bottomed flask with carrying grip.

Bleaching Conditions in Practice

Because of the danger of color reversion at elevated temperatures, the contact time between an oil and the bleaching earth should not be too long. The recommended contact time is ≤20 min at 100°C (212°F) as reviewed earlier. State-of-the-art bleaching requires that no oxygen should contact the oil during bleaching, which makes vacuum bleaching preferred. Bleaching earth dosage requirements vary depending upon the type and quality of the oil and its pretreatment steps; the variance covers a wide range (typically 0.1–2.0%), but can increase up to 5.0% in some special cases. Physically refined oils usually require a higher bleaching earth dosage than fats and oils that are alkali refined. All oils should be treated with some bleaching earth; even bright oils, which do not need color reduction, should be treated because of the other beneficial effects (17). The use of activated carbon is recommended only for the removal of heavy polycyclic aromatic hydrocarbons (PAH) (11). Light PAH are removed during deodorization (12) as discussed earlier. A blend of activated carbon and bleaching earth is also used occasionally to treat badly oxidized oils; the ratio used is usually limited to 5 or 10 parts carbon to 95 or 90 parts bleaching earth. The in-process evaluations normally used to control the bleaching process are color, phosphorus, and trace metals.

Spent Bleaching Clay

The task of a bleaching earth is to remove undesirable by-products from the triglycerides, thus improving the appearance, flavor, taste, and stability of the final product. If other processes follow bleaching, such as hydrogenation, bleaching also facilitates those processes by adsorbing catalyst poisons (18).

Oil Retention

Activated bleaching earth has a high adsorption capacity. It not only adsorbs undesirable by-products but also a certain amount of triglycerides. This property is called oil retention. A typical range for oil retention is 35–40%. This value can be reduced to 20–30% by suitable procedures, such as blowing through the cake in the filter with nitrogen or steam after filtration. Oil retention is calculated according to the following equation:

$$\text{oil retention } (\%) = W_{\text{filter cake}} - (WBE - W_{\text{water content}}) \times 100\ W_{\text{filter cake}}$$

where W is the weight in grams and BE is the fresh bleaching earth. This means that for each 100 kg of fresh bleaching earth, ~25–45 kg of oil is lost. Therefore, for each ton of bleaching earth added to the bleaching process, the processor has to dispose of 1.25–1.5 ton of spent bleaching earth.

Composition and Properties of Spent Bleaching Earth

After its use, bleaching earth is loaded with a number of different impurities adsorbed from the oil, depending upon the type and condition of the oil bleached. Further utilization of the spent bleaching earth will depend upon the type of by-products adsorbed with consideration of ecological as well as economical aspects. The important parameters that help to determine the further use of a spent bleaching earth are as follows: Oil content, moisture content, biological decomposition of organic substances, soluble heavy metals content, nonbentonitic material content (activated carbon, filter aid), and self-ignition.

Spent Bleaching Earth Self-Combustion and/or Self-Heating

Self-combustion or self-ignition of spent bleaching earth is a very important consideration for storage and transportation. The potential for self-ignition depends upon the type of oil that has been bleached, the amount of oil retained, and the type of bleaching earth used. The danger of self-ignition rises as the unsaturation level of the fatty acids increases in the retained oil. Therefore, spent bleaching earths containing fish or linseed oils, high in unsaturates, have a relatively high risk of self-initiation, whereas the risk of self-ignition is lower with spent bleaching earths that contain more saturated fats such as hard fats, tallow, or palm oil.

Spent bleaching earths with a tendency to self-heat have to be classified as hazardous material according to class 4.2, number 5c, Rand number 2431 as stated in the rules for transport of hazardous waste of the European Commission for Economy. If there is no risk of self-heating, according to the prescribed testing, such used clays must be classified in class 4.1 number 6. The corresponding United Nations numbers are 1325 for class 4.1 and 1386 for class 4.2. Depending upon the degree of potential for self-ignition, used bleaching earth must be classified to letter "b" (self-ignition possible) or to letter "c" (low degree of self-ignition). This affects road transportation because transport in bulk is allowed only for materials classified under "c." However, it has been proven that safe transportation of loose bulk is feasible, provided that certain precautions are observed. This issue will be discussed more completely in the following paragraphs.

Recommendations for Storage and Transportation

Precautions During Storage. Oil containing bleaching earth contacts air for the first time when the filters are emptied. At this point, spent bleaching earth has a temperature of ~80–120°C (176–248°F). The exact temperature depends on the bleaching temperature and the type and duration of blowing of the filter. Self-ignition or self-combustion is possible only if the spent earth can react with a sufficient amount of oxygen. For this reason, care must be taken to ensure the least possible contact between air and spent bleaching earth that contains oil. The used bleaching earth must be protected from drafts and, if possible, covered by a protective gas atmosphere. Sprinkling with water has proven to be the most effective and economic method to avoid self-initiation because water cools down the bleaching earth cake. With this method, the rising steam also acts as a protective gas, thus reducing the oxygen partial pressure. As the bleaching earth cake cools down slowly, the stored spent bleaching earth must be watched carefully. Additionally, the used bleaching earth should be protected from direct exposure to sunlight.

Precautions During Transportation. Only full containers should be transported because this will minimize the air volume above the oil-containing spent bleaching earth. Drafts must be avoided, making closed containers preferable; however, the use of containers with a good tarpaulin cover should be adequate. As a further precaution, after the container has been filled, the load should be sprinkled with water, ~5–10 L/m^2, to make the entry of air more difficult. Again, a protective gas atmosphere is created by the evaporating water, which also serves as a cooling agent.

Potential Uses of Spent Bleaching Earth

In most cases, spent bleaching earth is discarded in a land fill. However, investigations have been underway for quite some time evaluating the possible use of the energy or oil portion of spent bleaching earth as well as the inorganic component. Considering the high energetic value of the oil-containing spent bleaching earth, which is equivalent to that of lignite, this utilization seems to have the most potential. The possibility of using spent bleaching earth depends on the following four main criteria: (i) type of impurities or by-products in the spent material; (ii) economical aspects, i.e., most of the potential uses for spent bleaching earth are relatively cost efficient when the logistics are favorable; (iii) logistics, i.e., utilization of the spent bleaching earth must be decentralized to minimize freight costs; and (iv) ecological aspects, i.e., in any potential use of the spent bleaching earth, a high priority must be given to finding environmentally friendly ways of utilization. All of the disposal methods must create the least possible harm to humans or to the ecology.

A number of possibilities and processes for utilization of the spent bleaching earth have been evaluated; these include incineration, use in cement production, use in brick manufacture, soil improvement, oil extraction, regeneration, use in bio-gas digesters, use in waste water treatment plants for dentrification, addition to animal feeds, and addition to bitumen products.

Oil Extraction. Deoiling of used bleaching earth salvages a portion of the oil and facilitates dumping of the spent bleaching clay. It has been projected that future regulations may require a reduction of the oil portion of the spent bleaching earth before dumping in a land fill. The following four methods for extracting the oil from the spent bleaching earth were presented at the AOCS World Conference in Amsterdam (19,20): (i) extraction with hexane in the bleaching filter; (ii) extraction with a polar or nonpolar solvent as a separate process; (iii) mixing spent bleaching earth with oil seeds before extraction; and (iv) extraction with hot water in the presence of a surface active agent.

Addition to Animal Feed. Spent bleaching earth, whether used in the edible oil industry or for nonedible oils, contains on the basis of its triglycerides, predominately biologically degradable compounds with a high energy value. Accordingly, there are many possibilities for further utilization. Tests with pigs, poultry, and cattle showed that 3% spent bleaching earth may be added to the feed without any problem (21). Even at these high concentrations, neither vitamin A deficiency nor deficiencies in mineral requirements were observed (22,23). When adding the spent bleach earth to animal feeds, precautions are necessary to avoid contact with atmospheric oxygen to preclude oxidation or even self-ignition.

Use in Biogas Plants. The fine distribution of the fats or oils on the surface of the bleaching earth guarantees a fast decomposition and a high degree of utilization for its biological application. Utilization of spent bleaching earth in biogas facilities is environmentally friendly when certain rules are observed. Essentially, the entire organic content is converted to biogas, thus reducing the increase of CO_2 in the earth's atmosphere as well as improving soils. Soil improvement is also an important consideration. When the sludge of fermented sewage obtained from anaerobic fermentation of fat is spread on agricultural fields, bleaching clay contributes to an improvement of the soil. Bentonite, the natural mineral used to produce bleaching earths, is present in all fertile soils and gives them good water adsorption and water retention capacity. In addition, due to its natural ion exchange capacity, bentonite retains trace elements in the soil, thus improving its fertility. A further benefit was identified by studies in Sweden in the early 1980s, which showed that bleaching clay also helps to reduce the nitrate level in ground water, i.e., surplus organic material helps to reduce the nitrate anion. When used in biogas plants, even small amounts of nickel adsorbed from hydrogenated fats do not reduce anaerobic decomposition. This is not surprising because the methane-producing enzymes do contain nickel. Nevertheless, biogas facilities do not use spent bleaching earth containing nickel because of a fear that over a long period of time, this might lead to an excessive nickel concentration in the soil in which the fermented sludge is used as a fertilizer (24).

Cement or Brick Production. Another potential application for spent bleaching earth is its use in the production of cement in which the organic compound serves as an energy source. As mentioned earlier, used bleaching earth has an energy content that corresponds to lignite or coal. The inorganic residue is an aluminum silicate, and thus a raw material in cement production. In this application, traces of heavy metal, such as nickel, are not a concern because they are immobilized at the high temperatures in the cementation furnace. The same is true for the use of spent bleaching earth in the production of bricks. These applications are the most environmentally friendly means of utilizing spent bleaching earth because the whole material is used, either as an energy source or as mass in the finished product. In this application, it is of no importance whether the used bleaching earth contains heavy metals, activated carbon, edible oil, or mineral acid.

Regeneration. Finally, another possibility for recycling bleaching earth is the regeneration of used bleaching earth; several patents have been issued in the United States and Europe for bleaching earth regeneration (25–31). Under ideal conditions, regenerated material with an activity of 90–95% of the original bleaching earth can be produced. The spent bleaching earth to be regenerated must not contain any filter aids, activated carbon, phosphorus compounds, or alkali. Unfortunately, all of the currently known procedures are so expensive that fresh bleaching earth is more cost effective.

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Chapter 10

Hydrogenation

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Introduction

All edible oils and fats, whether of vegetable, meat, or marine origin, are composed of triglyceride molecules. Triglycerides have a glycerol backbone to which three fatty esters are attached. Although the three fatty esters, represented by R, R′ and R″ in Figure 10.1, could all be the same, they usually are not. They ordinarily contain from 12 to 22 carbon atoms and are connected by 0–3 double bonds. Multiple double bonds are unconjugated. The most prevalent ester (Fig. 10.2) contains 18 carbon atoms and has a maximum of three double bonds in any given chain, or radical, as they are usually referred to by organic chemists. If there are three double bonds, they are located in the 9-10, 12-13, and 15-16 positions. The common name of this ester is linolenic; its Geneva System name is 9,12,15-octadecatrienoic. If there are two double bonds, they are in the 9-10 and 12-13 positions. The common name of this ester is linoleic. If there is only one double bond, it is in the 9-10 position and is commonly called oleic. In the case of complete saturation (no double bonds), the C_{18} ester is named stearic.

Figure 10.3 is a pictorial representation of a triglyceride (1). Note the three carbon atoms, the oxygen to which each is linked, and its linkage to the first carbon

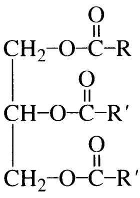

Fig. 10.1. Triglyceride molecule.

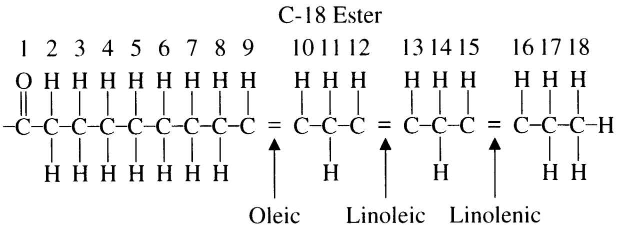

Fig. 10.2. Configuration of C_{18} fatty esters.

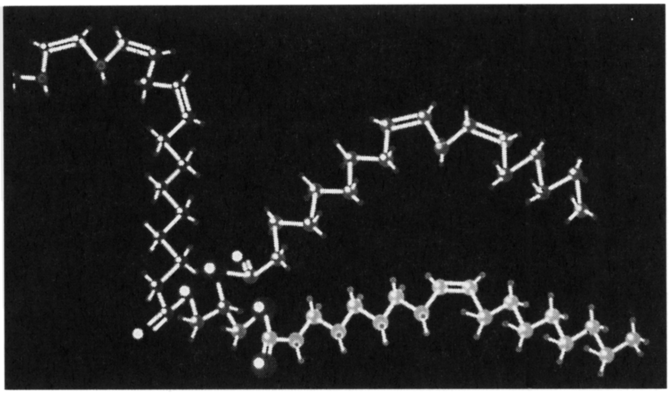

Fig. 10.3. Configuration of a triglyceride.

atom in a continuing chain. The lower horizontal chain is an oleic ester; its one double bond is in the 9-10 position, as expected. The middle ester is a linoleic and on the left is a linolenic.

Hydrogenation has two purposes. The first is to impart oxidative stability to the oil so as to maintain its organoleptic acceptability as a human food for an extended time after deodorization. The second is to convert naturally occurring fats and oils into physical forms having melting and handling characteristics that are either required for functionality reasons or desired for acceptability. An example of functionality is in the manufacture of shortenings suitable for mixing into dough for bread or batter for cakes. Acceptability is exemplified by margarine for edible consumption as a butter alternative.

The number of double bonds in a fatty ester chain significantly affects both its own physical and chemical properties as well as those of the triglyceride to which it is attached. For example, linolenic esters are quite unstable to oxidation, and their presence facilitates the development of undesirable flavors or odors. This problem can be reduced significantly by hydrogenating the linolenic ester to a linoleic. The relative rates of oxidation of common fatty acids (2) are stearic, 1; oleic, 10; linoleic, 100; and linolenic, 150. However, odor and flavor instabilities are complex subjects, and hydrogenation to reduce unsaturation should not be considered a panacea.

Esters with different saturation also have significantly different melting points. For example, linolenic melts at –13°C, linoleic at –7°C, oleic at 16°C and stearic at 70°C.

Very light (brush) hydrogenation is sometimes employed to convert oxidatively unstable liquid oils to more stable liquid oils. Further hydrogenation converts liquid oil to visually appearing solid fat. Selective hydrogenation is the tool by which partial hydrogenation can be accomplished in a controlled manner. There are two types of selectivity, i.e., preferential and *trans*-isomer. Preferential selectivity is the saturation with hydrogen of a double bond in a more unsaturated radical in "preference" to a double bond in a less unsaturated radical. Perfect preferential selectivity would

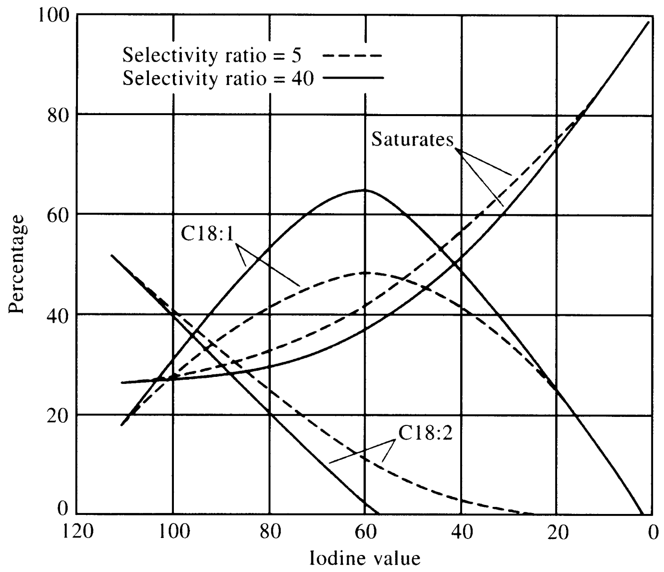

Fig. 10.4. Hydrogenation of cottonseed oil.

first convert all linolenic esters to linoleic, then all linoleic to oleic, and without the formation of any stearic. This is not possible because several esters are present in the oil and all of the reactions are occurring simultaneously, to a greater or lesser degree.

There are two natural factors favoring selectivity. The first is the law of probability. For example, one of the three double bonds in linolenic will have arithmetically 1.5 times as much likelihood of becoming attached to a hydrogen molecule as one of the two double bonds in a linoleic, and three times as much as the single bond in an oleic. Similarly, one of the two double bonds in a linoleic will have twice the probability of the single bond in an oleic. The second factor favoring selectivity is that linolenic has been shown experimentally (3) to be twice as reactive as linoleic, and linoleic is 20 times as reactive as oleic. This natural phenomenon is no doubt due to relative distances of the double bonds from the core of the organic molecule.

Gas–liquid chromatography (GLC) gives processors a tool for measuring the actual fatty ester constituents in partially hydrogenated oil. A picture of the course of the hydrogenation reaction can be obtained by catching a series of samples as the iodine value is reduced, determining their ester contents by GLC, and then graphing the results. Figure 10.4 is an example of such a picture. Here the technique is used to illustrate preferential selectivity differences when a variable is inserted into a hydrogenation—in this case, two different catalysts. The selectivity ratios listed on the graph were calculated using a formula devised by Albright (4). Figure 10.5 is a simplified version of Albright's technique for measuring preferential selectivity.

Isomerization at the double bond linkage in the ester chain is the other very important phenomenon that occurs during partial hydrogenation. As can be noted in an

$$\text{Linolenic } K_{1\rightarrow} \quad \text{Linoleic } K_{2\rightarrow} \quad \text{Oleic } K_{3\rightarrow} \quad \text{Stearic}$$
$$\text{C18:3} \qquad\qquad \text{C18:2} \qquad\qquad \text{C18:1} \qquad\qquad \text{C18:0}$$

$$\text{Linolenic selectivity ratio} = \frac{K_1}{K_2}$$

$$\text{Linoleic selectivity ratio} = \frac{K_2}{K_3}$$

Fig. 10.5. Preferential selectivity.

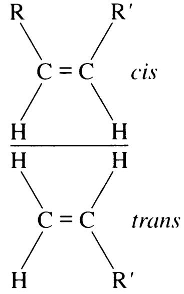

Fig. 10.6. Geometric isomers.

examination of Figures 10.6 and 10.7, where a *cis* double bond exists, the fatty ester chain bends in what has been described as an "elbow" linkage. With a *trans* double bond, there is no bending, and the straight radical looks very much like a stearic ester. This probably accounts for its having a 44°C melting point rather than the 16°C of the *cis*-isomer. The 44°C melting point of *trans*-oleic (elaidic), along with its rapid melting point, makes it of great importance in the formulation of commercial edible oil products such as margarine, shortenings, and confectionery fats. On the other hand, the similarity of its straight chain shape to saturate configuration has

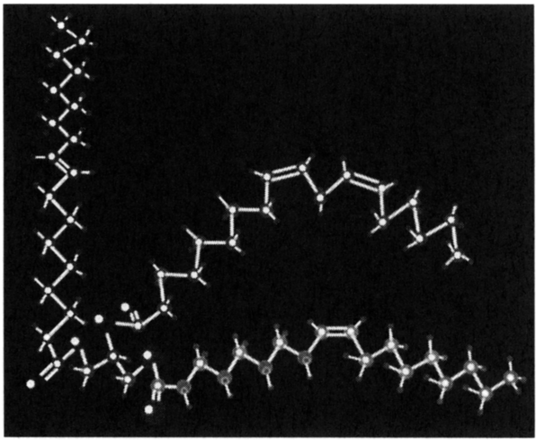

Fig. 10.7. Glyceride structure with *trans* double bond.

brought it under suspicion from a health standpoint. Product formulation and health concerns will be discussed later in the chapter.

The edible oil hydrogenation reaction takes place on the active surface of a metal catalyst by the addition of a hydrogen molecule to the double bond (unsaturation point) in the ester linkage of a triglyceride. Only hydrogen, which has been dissolved in the oil, is available for the reaction. The catalyst performs in a classic manner. It facilitates (in fact, is essential for) the reaction to take place but is not consumed by it. Factors affecting the rate and selectivity of the hydrogenation reaction are reactor design, hydrogen purity, feedstock quality, operating conditions, and catalyst performance characteristics.

Reactor Design

At present, two different reactor design approaches are being utilized commercially for partial hydrogenation of triglycerides. They are stirred/slurry/batch and loop/slurry/batch. The first, which is the overwhelming favorite, is depicted in Figure 10.8 (5). There are several variations of this design, which are effective in

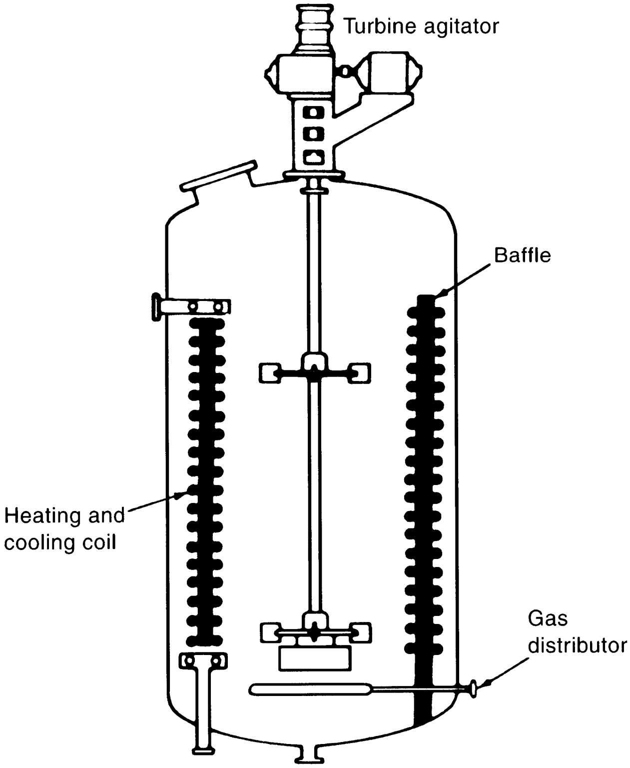

Fig. 10.8. Hydrogenation converter.

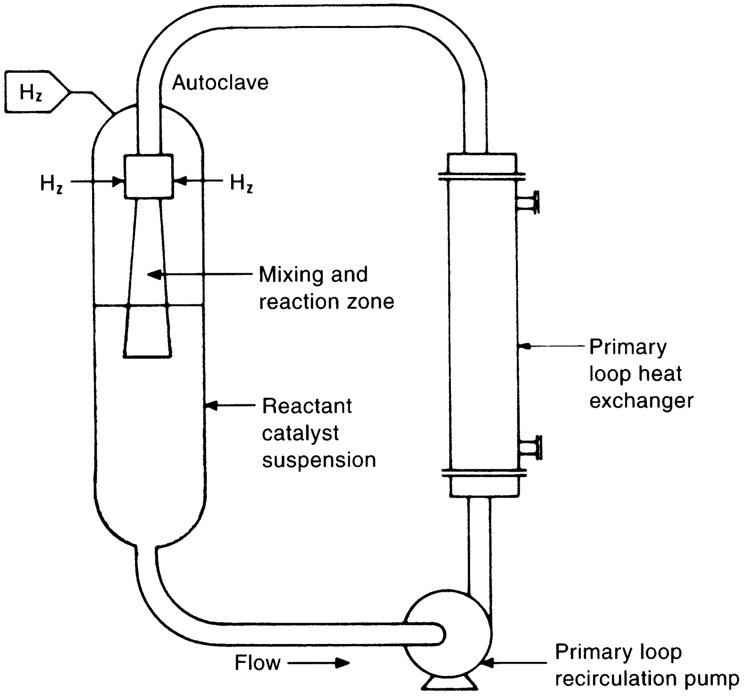

Fig. 10.9. Loop hydrogenation reactor.

reincorporating hydrogen accumulated in the headspace back into the body of the oil (6,7). Gas reincorporation increases reaction rate significantly and also results in better product uniformity. By its design, the loop/slurry/batch reactor, as depicted in Figure 10.9 (8), naturally has excellent liquid/gas mixing.

For the processor, the reactor (converter) performs one step in a series of operations that constitute the hydrogenation process. Collectively, they are usually referred to as a "hardening plant." Figure 10.10 (9) is a flowsheet for a typical hardening plant. The converter receives feedstock from upstream refining and purification operations. Hydrogen is supplied under pressure, either from on-site generation or as purchased from a commercial supplier. Catalyst is added to the converter, either as a liquid by pumping or by utilizing the converter's vacuum system for dry aspiration. A single-stage steam ejector is capable of providing sufficient vacuum for the hardening plant operations of aspirating catalyst, drying the feedstock, and evacuating air from the headspace. Electricity is provided to the motors, which drive the agitators and pump oil through the system. Although low-pressure steam is ordinarily available, it is not needed in energy-efficient plants except for startup. Most of the heat generated by the hydrogenation exotherm is exchanged with incoming feedstock, bringing it to reaction temperature. As can be seen in Figure 10.10, it is held in a measuring (hot oil) tank for charging to the converter. Plants are often designed so that the excess heat,

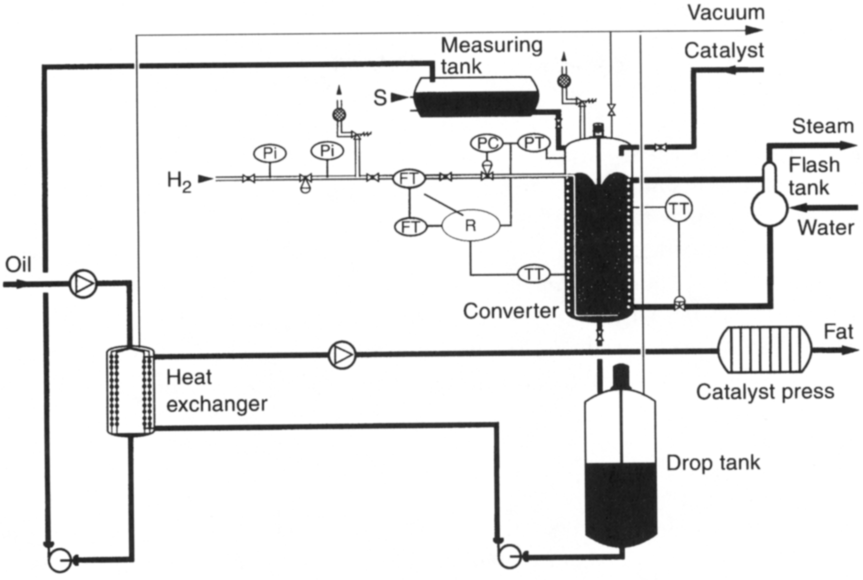

Fig. 10.10. Hardening plant.

in the form of steam generated from the vaporization of converter cooling water, can be used for other refinery operations.

Hardening plants usually process from 4 to 8 converter batches per day. However, with a design, such as that in Figure 10.10, this can be increased to 12–15 batches, or even more. To achieve rapid cycling, it is necessary to maximize the use of the converter as a hydrogenation reactor. This means minimizing its use as a heating, cooling, and storage tank. This is accomplished by having a heat exchange system with vessels, piping, pumps, and a catalyst filter press designed to operate at a cycle time equivalent to converter batch time. It also requires an adequate, available hydrogen supply with appropriately sized piping.

In addition to appropriate design capabilities, other requirements facilitating high converter turnover include the following: (i) feedstock of high and consistent purity; (ii) catalyst with uniform and predictable performance characteristics; (iii) a reliable computer-controlled batch cycling program; and (iv) a means to determine the batch end point without stopping the reaction.

Historically. the most difficult to achieve of the above capabilities has been end point determination. The base stock system, in which several batches of the same stock are made in succession with a small number of analyses being performed "on the run," has been of considerable help. Meter measurement of hydrogen consumption has also been developed to good reliability.

Fixed bed systems for partial hydrogenation may become feasible and attractive in the future, particularly if precious metal catalysts are utilized. Although the fixed bed is excellent for continuous operation, as exemplified by its widespread use in the petrochemical industry, it presents significant contamination problems for product changes.

Hydrogen Purity

Catalyst poisons, such as carbon monoxide, were at one time of serious concern to edible oil processors utilizing hydrogen produced from reformed hydrocarbons. The same was sometimes true of diluents, such as nitrogen. However, the addition of pressure swing adsorbers to reforming plants has essentially eliminated these problems. Electrolytic plants have never had any comparably serious poison or diluent problems. Therefore, whether produced from the reforming of hydrocarbons or by electrolysis, 99.99+% pure hydrogen is now readily available. The normal specifications of commercially purchased hydrogen, whether gaseous or liquid, also guarantee very high purity.

Feedstock Purity

There are constituents in all naturally occurring fats and oils, whether of meat, marine or vegetable origin, that either inhibit hydrogenation or affect the selectivity of the reaction by poisoning or inactivating the catalyst. These vary widely among feedstocks. For example, phosphorous is present in soybean and rapeseed, sulfur is found in rapeseed and marine oil, and protenaceous material is common in meat fats and marine oils. Variations within a vegetable oil source are caused by seed variety, weather, or handling. Meat and marine impurities are always due to handling. Whatever their cause or source, a principal function of the processing steps before hydrogenation is to reduce or eliminate these impurities. Processors have learned that the costs of purification are almost always less than the preventable downstream costs of higher catalyst usage, lower yields, and inferior quality products. The availability of improved processing controls, combined with better analytical techniques and instruments, has enabled processors to measure and control impurity levels more accurately during the refining and bleaching steps. Utilization of coupled plasma spectrophotometry, for instance, has permitted processors to improve significantly the measurement and control of phosphorous levels in soybean and canola oils.

Operating Conditions

Pressure, temperature, catalyst loading level, and degree of agitation all have an effect on activity and on preferential and *trans*-isomer selectivities. To a considerable extent, all are under the control of the hydrogenator.

Temperature. Figure 10.11 (11) contains GLC curves depicting the partial hydrogenation of canola oil at a relatively high pressure (3 atm–44 psig) with 0.02% catalyst as nickel, and at two very different temperatures, i.e., 200°C (392°F) and 140°C (284°F). From the lesser amount of saturates formed at the higher temperature, along with the faster disappearance and correspondingly greater formation of

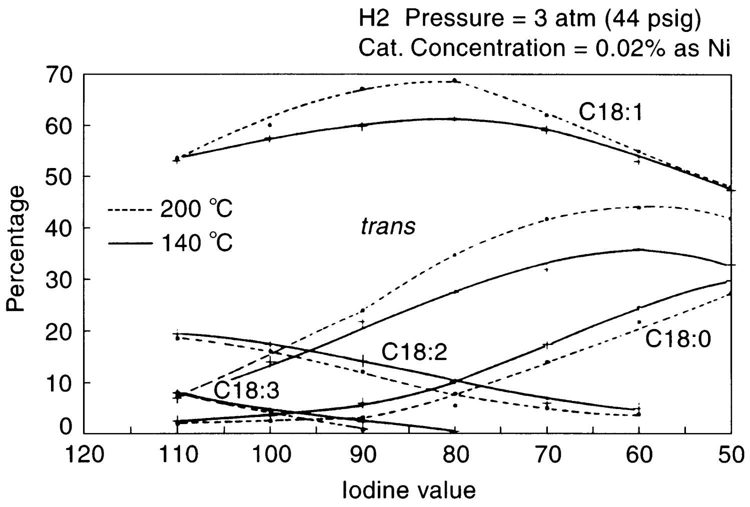

Fig. 10.11. Effect of temperature on selectivity in hydrogenation of canola oil.

oleic, it is obvious that increasing temperature increases preferential selectivity. The *trans* plot shows that it also increases *trans*-isomer formation. As expected, the rate of reaction (not shown) is greater at the higher temperature. The effect of the GLC results depicted in Figure 10.11 are strikingly confirmed in the solid fat melting curves of Figure 10.12 (11).

Pressure. Figure 10.13 (11) contains GLC and *trans*-isomer curves depicting ester analyses when the hydrogenation temperature and catalyst concentration are held

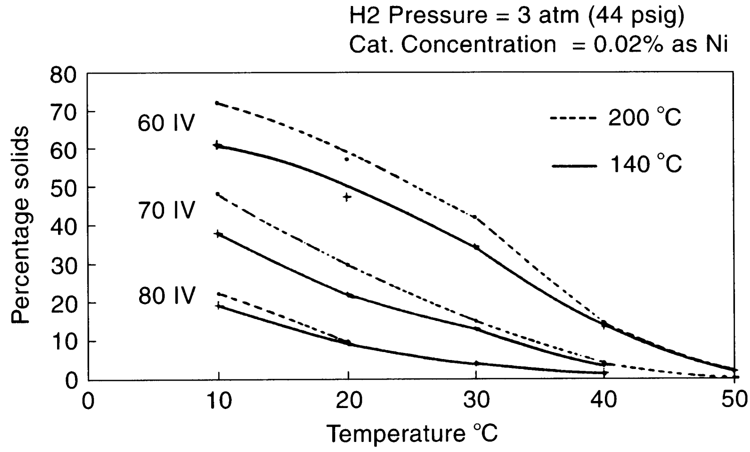

Fig. 10.12. Effect of temperature on solid fat content in hydrogenation of canola oil.

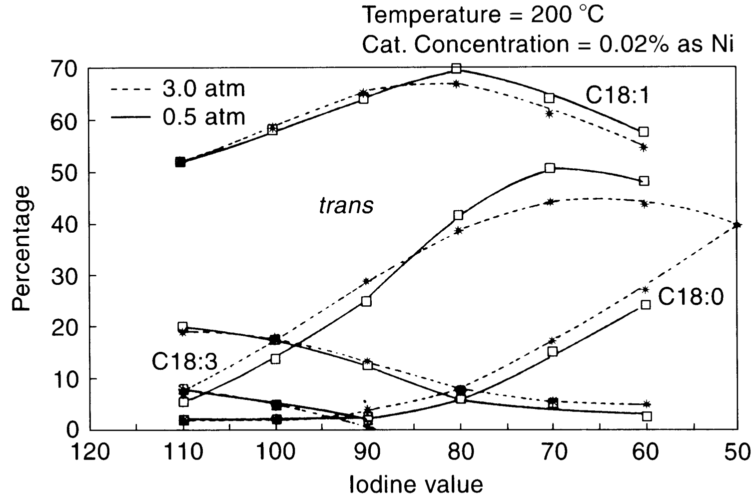

Fig. 10.13. Effect of pressure on selectivity in hydrogenation of canola oil.

constant and the pressure is varied. The results illustrate that increasing pressure decreases preferential selectivity and also decreases *trans*-isomer formation. Again, as expected (not shown), the rate of reaction is greater at the higher pressure. The solid fat melting curves depicted in Figure 10.14 (11) are flatter at the higher pressure, as anticipated.

Hydrogenating the same canola oil within the same parameters as above, the cumulative effect of varying both temperature and pressure is shown at iodine values of 60 and at 80 in the melting curves of Figure 10.15 (11). The gross differences between

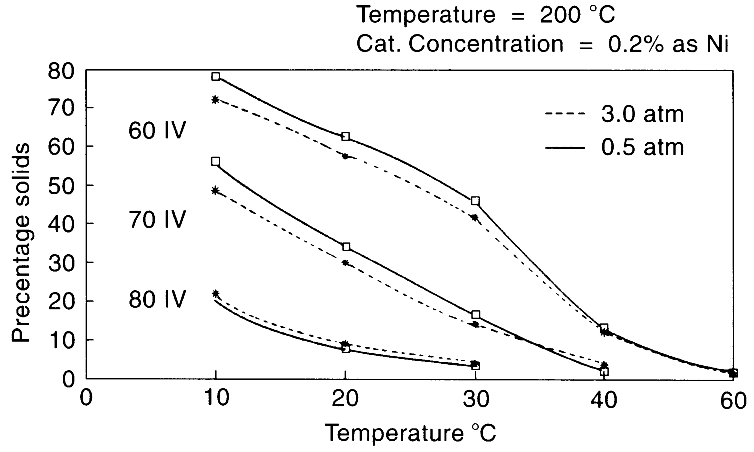

Fig. 10.14. Effect of pressure on solid fat content in hydrogenation of canola oil.

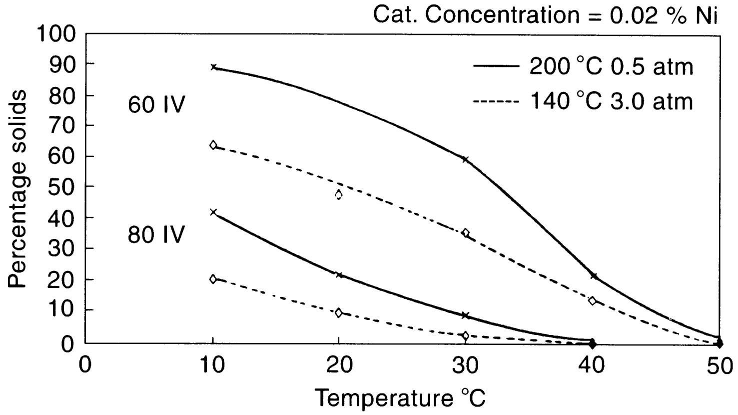

Fig. 10.15. Combined effect on solid fat content of varying both temperature and pressure.

the two sets of melting curves, at both iodine values, are especially meaningful because the hydrogenator can, and does vary both temperature and pressure simultaneously. The highly preferentially selective and *trans*-isomer–forming (high temperature/low pressure) conditions are normal for a margarine base in which a fast melting but room temperature solid-appearing product is desired. Conversely, low temperature/high pressure conditions are normal for shortening for which a slow melting fat is desirable for batter preparation over a wide range of mixing temperatures.

Catalyst Loading Level. The effects of catalyst concentration and agitation on selectivity are depicted in Figure 10.16 (12). In this case, soybean oil was the feedstock. As the graph indicates, the linoleic selectivity ratio (SR) is increased with higher catalyst concentration. Although it is interesting to be aware of this phenomenon, the cost of obtaining greater selectivity by increasing catalyst usage is not a viable economic option for the manufacture of most products. On the other hand, for certain specialty products, such as confectionery fats, it can be sensible when considering their cost compared with preparation from substantially more expensive raw materials.

Better mixing, as depicted by agitator rpm in Figure 10.16, decreases selectivity somewhat. Commercially, this is a price the processor is usually willing to pay to gain the greater activity and product uniformity that result from better mixing.

Nutrition

Beginning in the 1950s, the subject of nutrition began to attract attention. It was brought about by the increasingly high incidence of heart disease–related deaths in the United States and Northern Europe. Saturated fats in the diet, brought about by the hydrogenation of vegetable oils, was suspected as being a contributor because they are converted to cholesterol in the body. The threat to the industry reached a crescendo in

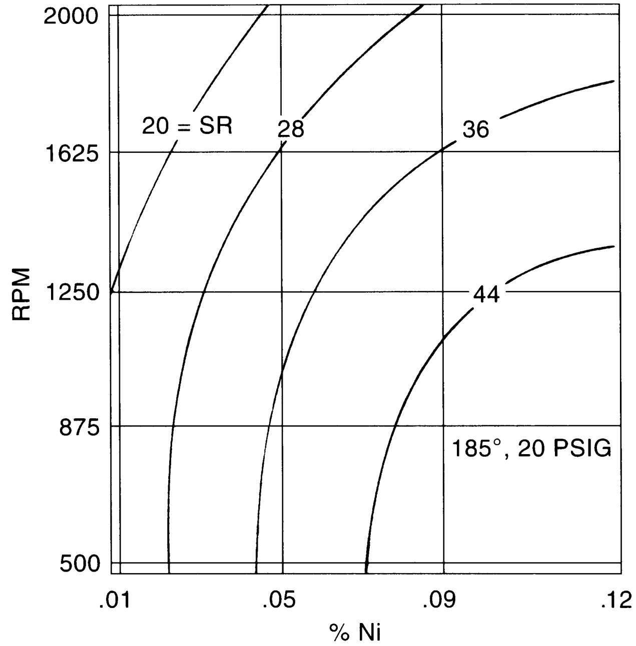

Fig. 10.16. Effects of agitation and catalyst concentration on selectivity ratios (SR).

the early 1960s. Edible oil processors responded by converting their margarine and shortening formulations to a base stock system (13). This technique permitted the amount of saturates in the formulations to be reduced and the amount of unsaturated oils to be increased. In the United States, the system utilized several partially hydrogenated soybean oils, whose melting curves are depicted in Figure 10.17 (14), plus a high palmitic–containing stearine, such as palm or cottonseed oil, and nonhydrogenated soybean oil.

To some extent, the lower saturates in base stock formulations were replaced by *trans*-isomers. The 44°C melting point of elaidic acid facilitated this action. Utilization of these techniques, when combined with factors such as a more balanced diet, more exercise, and less smoking, resulted in a reduction of nearly 50% in mortality from heart disease in the United States in the 25 years between 1960 and 1985, a stupendous achievement.

More recently, *trans*-isomers have also come under attack as likely contributors (but to a lesser degree) to the formation of cholesterol in the body in a way similar to saturates. As a result, governments are either considering or implementing regulations that either allow or mandate the presence of *trans*-isomers to be quantified on package labels, particularly of margarine.

Because fats and oils are an essential part of the human diet, it is neither physiologically sensible nor practical to eliminate them. Instead, research efforts are focused on development of margarine and shortening formulations and processing

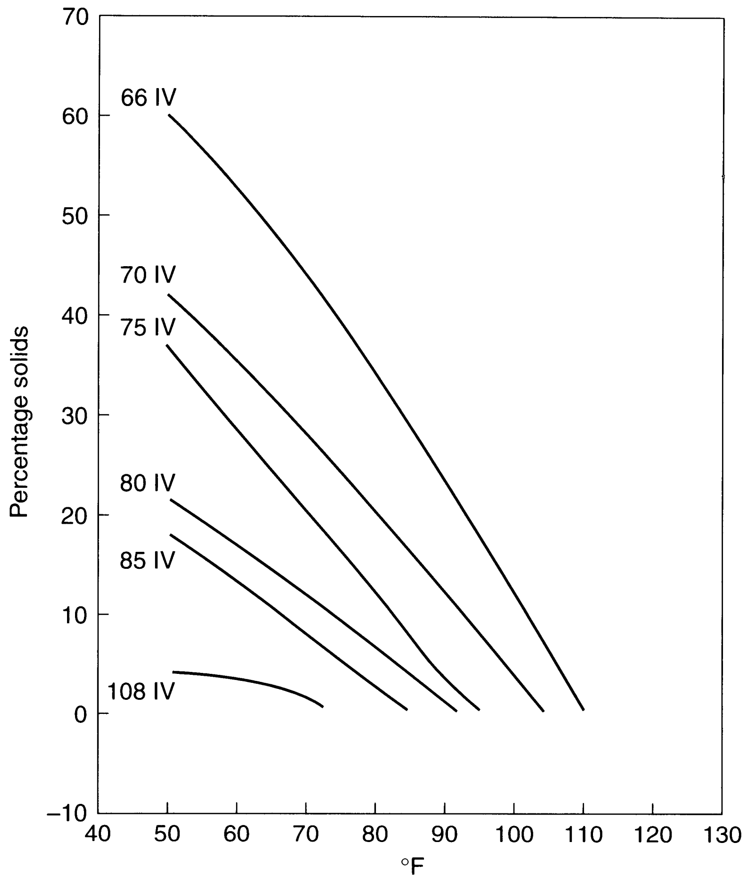

Fig. 10.17. Soybean oil base stocks.

techniques that continue their use but with lower saturate and/or *trans*-isomer content. The challenge is to retain satisfactory functionality along with acceptable appearance and taste. For example, industrial shortenings vary greatly in functionality requirements. Each is designed to be optimal for making a particular product, such as bread, pastry, layer cake, pound cake, or other. Table margarine, in addition to having a familiar appearance, is expected to spread easily on bread and not oil out at room temperature, while melting rapidly in the mouth.

There are several ways in which hydrogenation can be used as a tool (15,16) to reduce or eliminate saturates and/or *trans*-isomers in edible oil products. One is through manipulation of the operating conditions (temperature and pressure) employed in the partial hydrogenation of relatively unsaturated vegetable oils, such as soybean and canola. This was discussed above and is illustrated in Figures 10.11, 10.13 and 10.15. Functionality is the challenge. Consumers expect products to look, taste, and perform as they have traditionally. Eating habits change very slowly.

Another approach is to harden an oil to a very low iodine value and then interesterify it with an unhydrogenated oil (17). Although this method eliminates *trans*-isomers completely, a correspondingly higher amount of saturates is formed. The additional interesterification processing step also adds significantly to cost.

Technical developments, particularly as they relate to the relative importance consumers place on nutrition/health/longevity, may play an important role in the future of hydrogenation. For example, the use of precious metal catalysts, having performance characteristics quite different from those of nickel, might become common, probably in a fixed bed mode (18). Long term, the development of genetic variations of vegetable oils could radically alter the availability of "designer" oils and fats (18), which require more, less, or simply different hydrogenation.

Edible oil hydrogenation became a commercial process 100 years ago. During the 20th century, it has undergone many changes in thrust. Most have been brought on by feedstock availability and/or advances in technology. The emphasis on nutrition/health/longevity in recent years will very likely continue to spur progress in these two areas so as to continue adaptation of the tool of hydrogenation in its second century of use.

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Chapter 11

Fractionation

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Introduction

Among the various modification processes used in the oils and fats industry, fractionation has gained increasing interest over the last years as a widespread, proven, and clean technology. More than other processes, the fractionation process, and more specifically dry fractionation, offers interesting perspectives on a whole variety of fatty materials because it is a purely physical and reversible process.

Growing demands for products with very specific physical properties have led to new technological developments. Multifunctionality and flexibility have become very important as more and more fatty materials of different origin are being fractionated. Today, a whole variety of food products, from salad and frying oils to margarines, shortenings and confectionery products, are prepared with fractionated fats and oils. In addition to its edible applications, fractionation is also used to split fatty acids, mono- and diglycerides, and other oil derivatives, to produce fractions with well-defined properties for soap manufacturing or for the oleochemical and pharmaceutical industries.

Initially, fractionation was used primarily to improve the cold stability of a liquid oil by removing small amounts of solid impurities (better known as winterizing), whereas today it is being applied more for separating oils or fats into liquid and solid fractions, both with distinct physical properties (1,2).

Winterization is a narrow form of fractionation. From a technological point of view, the process is less sophisticated than fractionation (Fig. 11.1). The oil is usually cooled very slowly in large crystallizer tanks and kept at a low temperature (5–10°C) for a long time (12–24 h) to allow rather small quantities of waxes or saturated glycerides to crystallize (0.01–2 %). After maturation and stabilization, and before filtration, the oil temperature is normally increased to allow an easier filtration (3). Filter aid (0.1–0.5%) is often added during crystallization and/or before filtration to improve filterability and thus reduce oil losses.

Winterization is used for sunflower and corn oil to reduce waxes to <50 ppm (Table 11.1) or for cottonseed oil to remove saturated glycerides, which render the oil cloudy and even partially solid upon storage at cold temperatures. Winterized oils must withstand a cold test at 0°C usually for at least 5.5 h, and in many cases, as long as 24 or even 48 h (4).

One of the main differences between fractionation and winterization is the distinct change in physicochemical properties of both the liquid and solid fractions produced

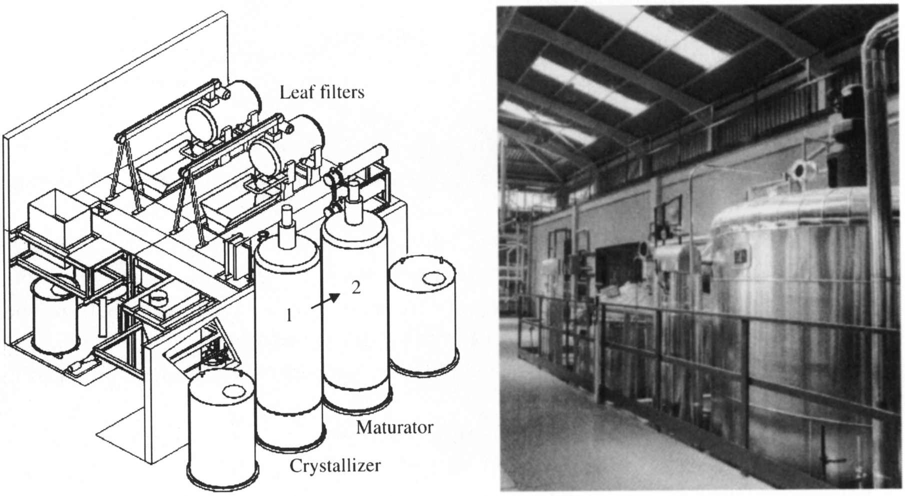


Fig. 11.1. A three-dimensional view of a winterizing plant for sunflower, corn, and cottonseed oil (De Smet).

by fractionation, whereas after winterization, the oil remains chemically and physically the same. Because much larger amounts of solids are crystallized during fractionation (up to 50% of the total mass in the case of fractionation vs. 0.1–2% during winterization), control of crystallization is more critical and filtration more elaborate.

TABLE 11.1 Effect of Wax Content on Cold Stability of Sunflower Oil[a]

Wax content	Cold test	Storage time at 0°C (d)				
(ppm)	5.5 h 0°C	1	2	3	4	8
6	–	–	–	–	–	–
8	–	–	–	–	–	+
10	–	–	–	–	+	++
20	–	–	–	–	++	++
30	–	–	+	++	++	++
40	–	–	+	++	++	++
50	–	–	+	++	++	++
60	–	–	+	++	++	++
70	–	+	+	++	++	++
80	+	+	+	++	++	++
100	+	++	→ settling at bottom			
150	+	++				
200	+++	++				

[a] – clear oil; + visible turbidity; ++ more pronounced turbidity.

Principles of Fractionation

Fractionation is basically a two-stage process. First, the oil is crystallized by cooling the mixture in a controlled manner to the required temperature in specifically designed crystallizers.

The oil is then sent to a filter, or in some cases a centrifuge, where the remaining liquid is separated from the solid fraction by means a vacuum filter or membrane filter press (Fig. 11.2).

The first fractionation technologies were basically modified winterization processes. Over the years, several fractionation systems have been developed. There are generally three different principles, i.e., dry fractionation, solvent fractionation, and detergent fractionation. The first system implies that no additives are used, whereas the other systems involve the use of a solvent or a detergent to improve separation efficiency.

Solvent fractionation is by far the most efficient fractionation process. Crystallization is performed in the presence of a solvent, usually acetone, at a ratio of between 3 and 5 to 1 (solvent to oil). Separation is usually performed on a vacuum belt filter. The main advantages of solvent fractionation are the high separation efficiency and subsequent improvement in purity and yield of the solid fraction. However, high investment and operating costs, have rendered the process less attractive for commodity oils. Today, the process is used mainly for the production of high-added-value fats such as confectionery fats. A typical example is given in Figure 11.3.

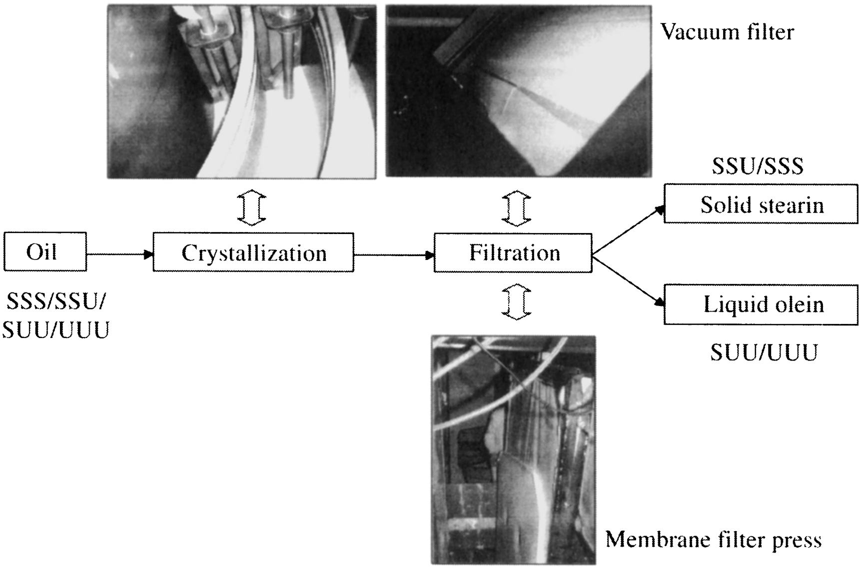


Fig. 11.2. Principle of dry fractionation.

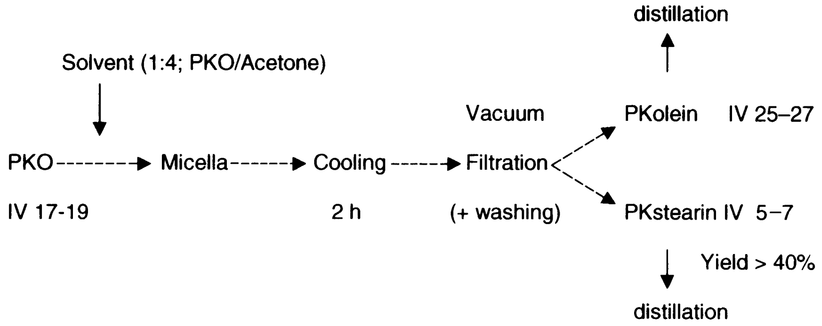


Fig. 11.3. Principle of solvent fractionation; example, palm kernel oil (PKO); IV, iodine value.

In a *detergent fractionation* process, a wetting agent, usually sodium lauryl sulfate, in combination with an electrolyte, usually magnesium sulfate, is added to the crystallizing fat or oil to allow the crystals to be suspended easily in the aqueous phase. The water phase with the crystals is separated from the liquid phase by means of a centrifuge. After separation, the stearin and olein fractions are heated, washed, and dried to remove the additives. Although the detergent solution is recycled, there are always losses of the oil and washing waters.

Apart from some specific applications, mainly in the nonfood industry (e.g., fatty acid industry), interest in this technique has declined due to the high operating cost and contamination of the end products (Fig. 11.4). Furthermore, the ongoing improvements in the efficiency of dry fractionation allow the production of similar and even better products than can be achieved with detergent fractionation.

Dry fractionation is by far the simplest and cheapest fractionation technique because no additives or supplementary post-treatment of the end products is involved. The ongoing process and product developments have made the technology more and more efficient and versatile. For example, a whole variety of products normally pro-

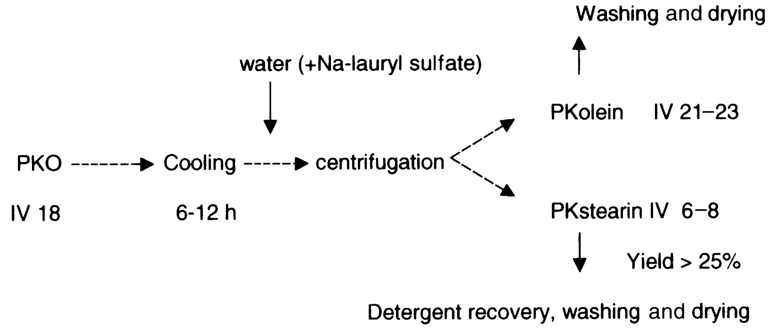


Fig. 11.4. Principle of detergent fractionation; example palm kernel oil (PKO); IV, iodine value.

duced by solvent fractionation can now be processed by dry fractionation. Another dry fractionation process that is still in use is the block crystallization process, better known as the panning and pressing process. In this process, the fat or oil is poured into metal pans and stored in cold rooms to crystallize. After hard setting, the cakes are wrapped in filter cloths (usually cotton), stacked between perforated plates in hydraulic presses, and pressed (up to 200 bar). Results are not as good as those from solvent fractionation, but very good quality stearins can be obtained at a reasonable yield. Compared with solvent fractionation, the capital cost of such a process is much lower. However, the operation is very labor intensive and quite dirty.

To overcome these disadvantages, the process has undergone several technical improvements. The use of a continuous belt instead of pans in the cold room and the introduction of automated high-pressure membrane filter presses instead of the manual hydraulic presses have led to a considerable reduction in manual operation and interventions. Results from these modified plants are comparable to those from traditional panning and pressing (Fig. 11.5).

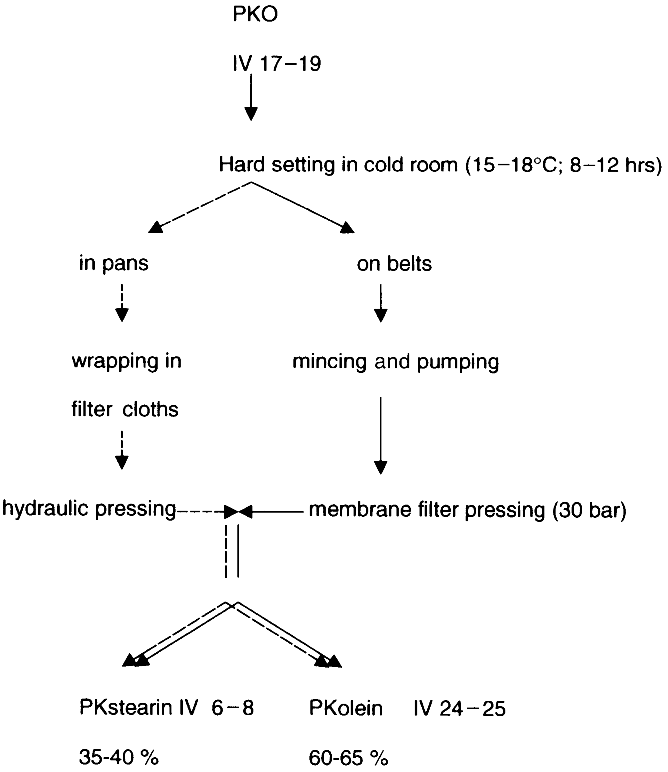


Fig. 11.5. Block crystallization process (panning and pressing); example, palm kernel oil (PKO); IV, iodine value.

Fractionation Technology

Solvent and detergent fractionation plants are usually continuous operations, whereas most of the industrial dry fractionation plants are semicontinuous systems. Among them, the De Smet and Tirtiaux process are the best known (3,5). Other similar systems have been commercialized by other companies such as Oiltek and Krupp. Figure 11.6 represents a three-dimensional view of a dry fractionation system. The main components in the design are the crystallizer and the filter press, which largely determine the plant performance.

Crystallization

Crystallization is usually performed semicontinuously. There are three successive steps, i.e., supercooling of the melt, nucleation, and crystal growth. The crystals do not always remain single but tend to agglomerate. Both crystal shape and crystal size distribution are determined by the way the lipid material is cooled and agitated. Crystallization is an exothermic process, that is, ~200 kJ of heat per kilogram of crystallized fatty matter is released during solidification; this is much higher than the heat released during cooling (~2 kJ/kg). Because oils are very poor heat conductors, heat transfer during crystallization is determined largely by mass transfer to and from the cooling surface. Crystallization increases viscosity, which in turn affects mass transfer and hence, heat exchange. The agitator as well as the cooling surface

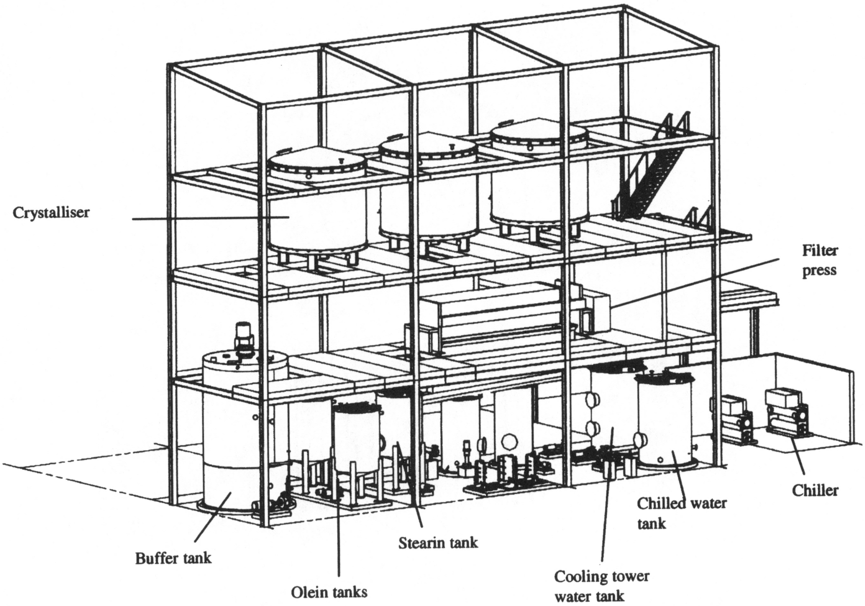


Fig. 11.6. Three-dimensional view of a dry fractionation plant (De Smet).

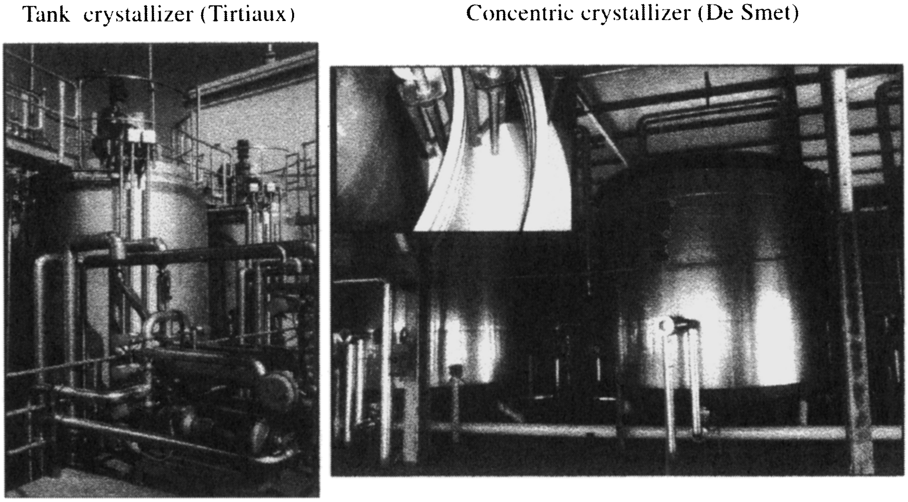


Fig. 11.7. Crystallizer types used in edible oil fractionation.

design of the crystallizer vessel are therefore of the utmost importance to guarantee a perfect mass transfer and accurate control of crystallization. In Figure 11.7, some crystallizer types used in dry fractionation are represented. Depending upon the design, a fast or slow crystallization is allowed by the controls. Both the cooling surface and the agitation geometry determine the heat exchange capacities of a crystallizer. Cooling surfaces may range from only a few square meters up to >15 m^2/ton of oil.

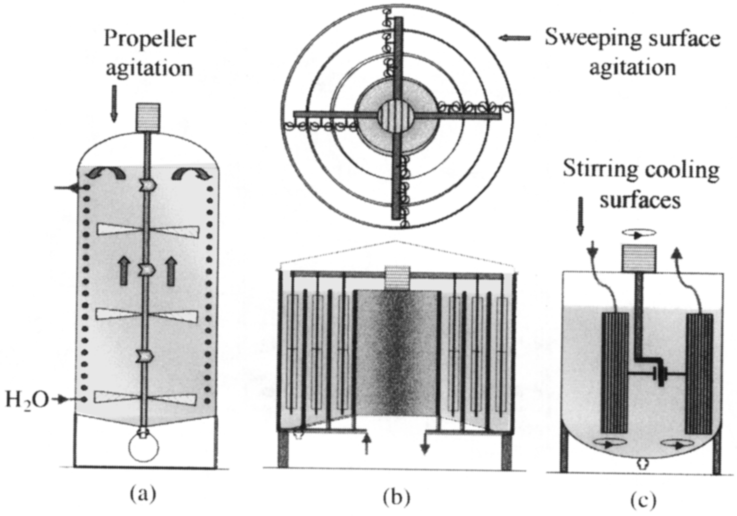
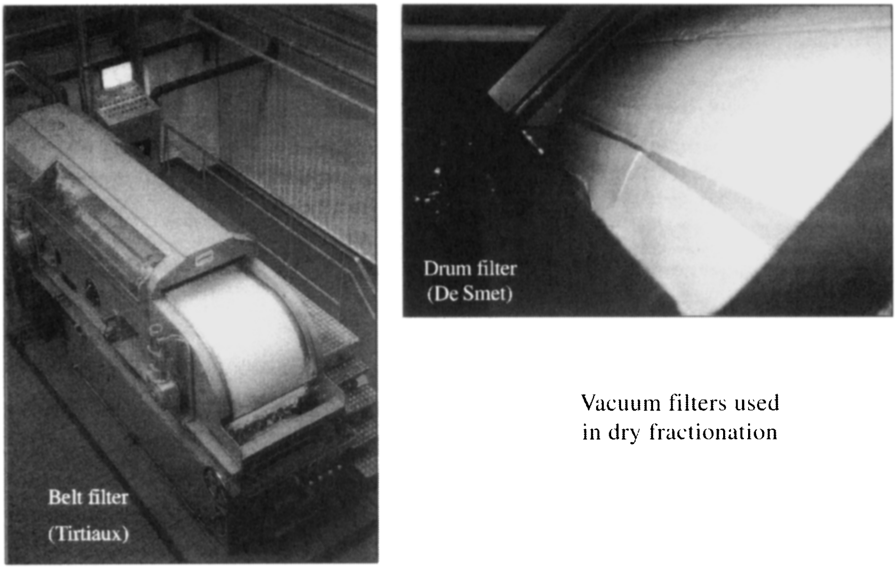


Fig. 11.8. Agitation types used in edible oil fractionation: (a) Tirtiaux, (b) De Smet, (c) Krupp.

However, it should be mentioned that cooling surface alone does not determine the crystallization time required to achieve the proper or desired crystal formation. The latter is determined in large part by the polymorphic behavior and intersolubility of the composing triglycerides in the oil or fat. Some oils require a long and slow crystallization (e.g., cottonseed oil), whereas other oils (e.g., partially hydrogenated soybean oil) allow a much faster crystallization.

The agitator design affects the mass transfer and hence heat transfer from the crystallizing oil to the cooling surface. Some crystallizers apply propeller type agitators, and some use complicated stirring cooling surfaces or agitators that sweep the cooling walls (Fig. 11.8) (3,6). Crystallization control is accomplished by controlling the oil temperature. This can be done either by applying a differential temperature profile between oil and water, or by a predetermined water temperature profile. It is



Vacuum filters used
in dry fractionation

Membrane filter presses used in dry fractionation

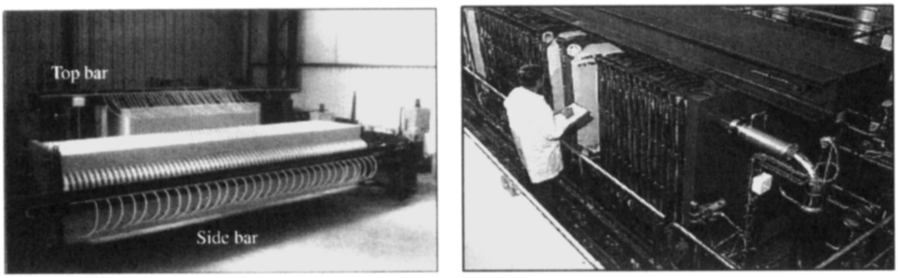


Fig. 11.9. Filter types used in edible oil fractionation.

TABLE 11.2 Effect of Filtration Pressure on the Separation Efficiency and Quality of Soybean Oil Fractions[a]

Analysis	Feedstock PHSBO	Vacuum filtration	Membrane filtration 5 bar	15 bar	25 bar
SFC_{slurry} (%)		22.3		22.5	
SFC_{cake} (%)		51	58	67.5	73
Olein fraction					
Yield (%)		55.5	64.6	69.9	72
IV		92.2	92.5	92.7	92.7
CP(°C)		-7.0	-7.2	-7.4	-7.3
SFC (%)					
0°C		7.3	7.0	6.8	7.1
10°C		4.8	5.1	5	5.4
20°C		—	—	—	—
Stearin fraction					
Yield (%)		44.5	35.4	30.1	28
IV	86	77.8	74.5	71.2	69.6
MP (°C)	32.8	36.5	39.0	39.9	40.4
CP(°C)	13.0				
SFC (%)					
0°C	49.6	66.2	72.7	79.1	84.2
10°C	39.1	60.7	66.4	74.5	80
20°C	16.3	37.9	49.9	59	63.5
30°C	2.5	11.2	21.2	27.3	29.2
40°C	—	—	—	—	1.2

[a] PHSBO, partially hydrogenated soybean oil; SFC, solid fat content; IV, iodine value, CP, cloud point, MP, melting point.

difficult to determine which approach provides the best results with respect to the quality of end products because both have proven their efficiency.

Separation

The efficiency of dry fractionation is determined not only by the crystallization behavior during the cooling sequence, but also by the conditions of separation. Today, most modern dry fractionation installations operate with a membrane filter press, although there are still a number of plants that use a vacuum filter (Fig. 11.9). A standard membrane filter press normally operates at a pressure of 5-6 bar, which, in most cases, is more than sufficient.

Over the last years, high-pressure membrane filter presses have been developed to operate at pressures up to 30 bar (7). Higher pressures are necessary to meet the required specifications, especially in cases in which the solid fraction is the premium product. The advantage of using higher pressures is translated into a higher overall yield in liquid and, consequently, in a lower residual amount of unsaturates in the stearic fraction. This in turn has a positive effect on the quality of the stearic fraction, i.e., a lower iodine value, a higher melting point, and a steeper solid fat content profile (Table 11.2).

The olein is normally not affected by the filtration pressure, unless stearin passes through the filter cloths. Depending on their firmness and size, crystals can resist a high mechanical stress. However, this is not always the case. Some oils, such as cottonseed oil, produce rather weak crystals, which tend to break down and partially fluidize once a high pressure is applied. The technology of membrane press filtration has undergone extensive development in recent years. In addition to an increase in operating pressure, special devices have been designed to facilitate cake discharge and to control filtration temperature in a precise manner. In addition, special antistatic filter cloths and filter plates have been developed to prevent build-up of electrostatic energy during filtration. Today, modern fractionation plants can operate in a fully automatic manner, reducing manual intervention and energy consumption to a minimum.

Fractionated Products

At present. a whole variety of vegetable oils and animal fats are already being fractionated on an industrial scale (Table 11.3) (3). The capacity of the plants in operation ranges from only a few tons up to 3000 ton/d. The best known are palm oil (Southeast Asia), hydrogenated soybean oil (United States), and milk fat (Europe). Other fats such as tallow, fish oil, and cottonseed oil are also fractionated industrially. Most of the fractions are used in commodity products such as salad and cooking oils, margarines, or shortenings. In addition, some are used in the oleochemical and soap industries as a raw material for fatty acids and fatty acid derivatives.

A group of fats that requires special fractionation techniques are the confectionery or speciality fats (8,9). These speciality fats are applied in a whole range of special food products in which specific physical properties are required They are used in combination with other ingredients such as cocoa powder, milk products, sugar, flavors, and a whole range of other additives.

Many of the speciality fats are intended to be added to cocoa butter (CB) or to replace it, partially or even totally. A steep melting behavior in the mouth is very crucial for a good CB replacement fat, to give a cooling effect with no greasy impression. To obtain this, the fat must be solid at room temperature, have a desirable snap, with a smooth and rapid melting in the mouth.

CB has a very high solid fat content at room temperature, which gives the fat its typical hard and brittle character. Between 25 and 35°C, it melts quickly and completely, leaving a cooling sensation in the mouth together with a sudden flavor release. The main components in CB responsible for this specific physical behavior are the symmetrical monounsaturated triglycerides POP, POS, and SOS (65–80%). CB replacement fats are mainly of vegetable origin, although some are made from animal fats, e.g., tallow. They can be categorized into three main groups, according

TABLE 11.3 Fractionation of Vegetable Oils and Animal Fats: Some Examples[a]

Feedstock				Oleins		Stearins		Yield	Stages[b]
Palm	IV	CP(°C)	MP(°C)	IV	CP(°C)	IV	MP(°C)	Olein (%)	
Palm oil	52	21	41	56	9	32	54	82	Single
"	"	"	"	60	4	38	51	63	Single
"	"	"	"	63	2.5	41	47	50	Single
Palm olein	56	10	24	65	1.0	45	30	55	Double
Palm olein	63	2.5		69	−1	58	13	45	Double
	IV		MP(°C)	IV	MP(°C)	IV	MP(°C)	Olein (%)	
Palm stearin	41		47	49	27	22	57	70	Double
PMF	45		32	53	19	36	34.5	53	Triple
Palm kernel	IV		DP(°C)	IV	DP(°C)	IV	DP(°C)	Olein (%)	
Palm kernel oil	18		28	25	24	7	32	62	Single
Soybean	IV	CP(°C)		IV	CP(°C)	IV	DP(°C)	Olein (%)	
Partially hydrogenated	115	2		119	−11	98	33.5	81	Single
"	109	6.5		114	−10	92	34.5	77	Single
"	97	12		104	−9	84	35.5	65	Single
"	85	15.5		94	−7	75	36.5	53	Single
"	75	20.5		84	−5	68	37	44	Single
Cotton	IV	CP(°C)	MP(°C)	IV	CP(°C)	IV	MP(°C)	Olein (%)	
Cotton oil	109	−3	10	115	−6	79	24	83	Single
Butter	IV		DP(°C)	IV	DP(°C)	IV	DP(°C)	Olein (%)	
Milk fat	35		33	38	18	29	42	65	Single
MF olein	38		18	43	13	30	24	60	Double
MFol-ol	43		13	47	7	37	19	60	Triple
MF stearin	29		42	32	33	22	47	70	Double
MFol-st	30		24	35	17	23	31	60	Triple
Tallow	IV		DP(°C)	IV	DP(°C)	IV	DP(°C)	Olein (%)	
Tallow	47		47	54	31	36	52	60	Single
Tallow stearin	36		52	48	34	25	58	50	Double
Tallow olein	54		31	60	18	48	34	50	Double
Lard	IV		DP(°C)	IV	DP(°C)	IV	DP(°C)	Olein (%)	
Esterified lard	62		33	69	24	47	48	70	Single
"	63		32	75	15	51	44	50	Single
Fish	IV		CP(°C)	IV	CP(°C)	IV	CP(°C)	Olein (%)	
Crude fish oil	198		2	208	−8	160	14	80	Single
"	146		5	156	−5	119	19	70	Single
Hydrogenated	IV		DP(°C)	IV	CP(°C)	IV	DP(°C)	Olein (%)	
"	124		28	135	−4	105	34	65	Single
	115		31	129	−2	84	37	70	Single

[a] IV, iodine value; CP, cloud point; MP, melting point; DP, dropping point; PMF, palm mid-fraction; MF, milk fat.

[b] Number of stages starting from initial feedstock material.

TABLE 11.4 Cocoa Butter (CB) Replacement Fats

CB Substitutes:	Lauric oils rich in C_{36}–C_{40} (LLL, LLM, LMM,...) Palm kernel stearin fraction (solvent, dry fractionated) → Not compatible with CB in solid state
CB Equivalents:	Nonlauric-based oils rich in SUS (POP, POS, SOS) Cocoa butter, Illipe (natural fats) Palm oil fraction (hard palm mid-fraction, solvent, dry fractionated) Sal fat, shea butter (stearin fractions, usually solvent fractionated or traditionally panned and pressed) → Highly compatible with CB in solid state
CB Replacers:	Nonlauric oils rich in *trans*-monounsaturated fatty acids (SEE. PEE,...) Partially hydrogenated oils (oils rich in SUU triglycerides such as soybean, sunflower, rapeseed, cottonseed, safflower oil) → Partially compatible with CB in solid state

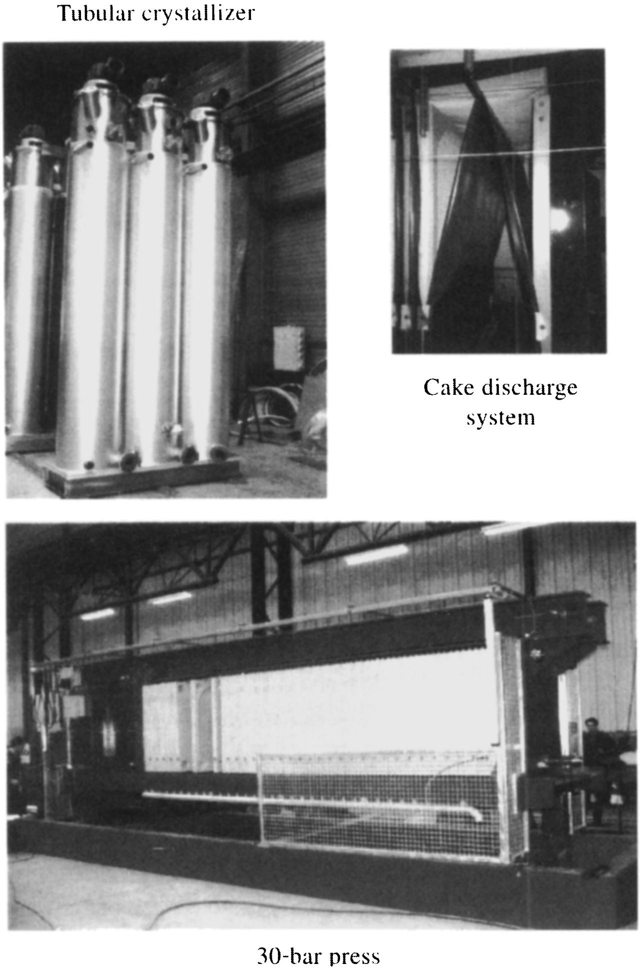
to their origin and degree of compatibility in the solid state with cocoa butter as presented in Table 11.4.

Most fractionated speciality fats used in the confectionery industry today are produced traditionally by the labor-intensive panning and pressing method or by micella fractionation, using acetone as a solvent. Recent developments in dry fractionation technology have created new alternatives for the production of a whole range of confectionery products. With the introduction of reliable high-pressure membrane filter presses and high-viscosity resistant crystallizers, high-quality speciality fats can now be produced in a more cost-effective way (Fig. 11.10) (10).

Some typical examples are given in Table 11.5. It should be mentioned, however, that not all products produced with solvent fractionation can be produced with dry fractionation. One important advantage of solvent fractionation, which cannot yet be overcome by dry fractionation, is the ability to wash out entrained olein in a more efficient way as well as to retain certain unwanted components in the solvent, e.g., mono- and diglycerides or other more polar components. A typical example is shea butter; the fat may contain up to 4% of a polyisoprenoid hydrocarbon, a gum-like material, which disturbs the functionality when left behind in the stearin fraction. With solvent fractionation, this major impurity is removed with the solvent phase during fractionation, leaving behind a very hard and gum-free stearin fraction.

Conclusion

Fractionation technology has undergone some important improvements over the last years. The development of new and more efficient types of crystallizers and reliable high-pressure membrane filter presses has made the technology accessible for a whole variety of fatty materials. From a technological point of view, the dry



Tubular crystallizer

Cake discharge system

30-bar press

Fig. 11.10. Crystallizer and filter press used in speciality fats fractionation.

fractionation technology offers a good alternative not only to other more costly fractionation technologies such as solvent fractionation, but also to other modification technologies such as hydrogenation and interesterification. However, a major weak point remains, namely, insufficient experience and knowledge of the dry fractionation process. The process is often a black box for many users and operators, i.e., what actually happens during the processes of crystallization and separation remains a great mystery to many. To explore and exploit the capabilities of dry fractionation, more process research and product development are required, creating a challenge to everyone attracted by this exiting technology.

TABLE 11.5 Production of Speciality Fats by Dry Fractionation: Some Examples[a]

Feedstock			Oleins		Stearins		Yield	Stages[b]
Palm kernel	IV	MP(°C)	IV	MP(°C)	IV	MP(°C)	Olein (%)	
RBD	18	27.5	24.8	23	7	32.5	38	Single
Palm	IV	MP(°C)	IV	MP(°C)	IV	MP(°C)	Olein (%)	
Mid-fraction	45.7	31	55.2	18	35.7	34	50	Triple
Soybean	IV	MP(°C)	IV	MP(°C)	IV	MP(°C)	Olein (%)	
(partially hydrogenated)	81	31.5	88	18	73	35	55	Double
Cocoa butter	IV	MP(°C)	IV	MP(°C)	IV	MP(°C)	Olein (%)	
Soft CB	35	31	37	29	33	34.5	50	Single

[a] IV, iodine value; MP, melting point; RBD, refined, bleached, deodorized; CB, cocoa butter.
[b] Number of stages starting from initial feedstock material.

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Chapter 12

Processes and Products of Interesterification

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Introduction

Interesterification (INES) is a general term used for a number of reactions; it describes the technology to rearrange fatty acids for different melting and physical characteristics. These include acidolysis, alcoholysis, glycerolysis, and ester interchange or transesterification, which can be random, directed, or enzymatic. Interesterification, also often referred to as "rearrangement," is a relatively simple process that has been used for many years. The equipment is readily available and, unlike hydrogenation, the process requires no explosive gases. The costs are similar to those of hydrogenation, but until now, INES has been practiced sparingly.

INES is used to modify physical, chemical and/or functional characteristics of the materials undergoing this process. For a number of specialty applications, INES is an important process for the fats and oils industry. In the future, the use of INES may increase due to nutritional concerns, especially for the reduction of *trans* fatty acids formed during partial hydrogenation. In many cases, total saturate plus *trans* would be lower than either tropical or partially hydrogenated fats and oils, when used in food applications in which a liquid oil will not function. Saturated fatty acid content for such products, however, will often increase, compared with partially hydrogenated alternatives.

If solids are required for a shortening or margarine type product, the only two sources, at least at this time, are saturates and *trans* fatty acids. Products using INES, especially margarines and spreads that are very low in *trans* isomers, are available currently in Canada, Europe, and to a lesser extent, the United States. The technology has existed for quite some time because a patent on such products was granted to Unilever in 1961 (1).

The ability to modify the melting point and functional crystallization characteristics without changing the fatty acid composition makes INES a process with a number of interesting possibilities. Early work involved functionality and was not directed at nutritional issues. A number of patents exist for functionality improvement for shortenings and cocoa butter substitutes (2–5). The improvements include stabilization of crystal structure in the preferred (in this case, β' form) and lowering of melting point.

Improvements in raw material quality and processing efficiency, especially the potential ability to monitor chemical INES on-line (6), should also reduce the overall costs of this process. This will be discussed later, in greater detail.

Types of Interesterification

Although the primary focus of this chapter will be transesterification, including random, directed, and enzymatic variations, we will begin with a brief overview of acidolysis, alcoholysis and glycerolysis, including simple chemical equations for the specific reactions (7).

Acidolysis is the exchange reaction between a fat/oil and free fatty acids. This is the least used INES process.

$$R_1COOR_2 + R_3COOH = > R_3COOR_2 + R_1COOH$$

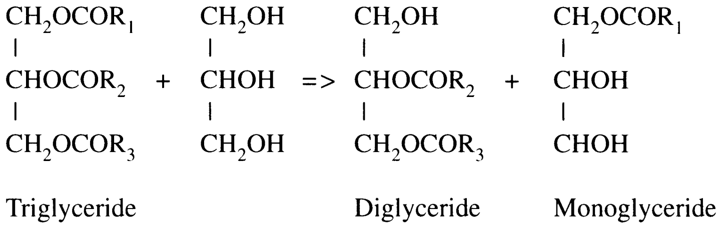
The reaction results in less selectivity; it is relatively time consuming and requires high temperatures. The finished product composition is also difficult to duplicate because the interchange of both free fatty acids and fatty acids available in the fat/oil is random.

Alcoholysis refers to the reaction of an alcohol with a fat/oil. The basic reaction is similar to that of acidolysis.

$$RCOOR_1 + R_2OH = > RCOOR_2 + R_1OH$$

As an example, by methanolysis (methyl alcohol), fats and oils are converted to fatty acid methyl esters (FAME) for fatty acid determination using gas–liquid chromatography (GLC). Another potentially important use for this reaction is in the production of FAME for use as fuels. For this application, refining soapstocks and used frying oil are several possible starting materials, due to their low cost.

Glycerolysis is an important reaction that is used for the production of mono- and diglycerides. During glycerolysis, a triglyceride is reacted with excess glycerol and mono- and diglycerides are produced.



$$\begin{array}{lclclcl}
CH_2OCOR_1 & & CH_2OH & & CH_2OH & & CH_2OCOR_1 \\
| & & | & & | & & | \\
CHOCOR_2 & + & CHOH & => & CHOCOR_2 & + & CHOH \\
| & & | & & | & & | \\
CH_2OCOR_3 & & CH_2OH & & CH_2OCOR_3 & & CHOH \\
\text{Triglyceride} & & & & \text{Diglyceride} & & \text{Monoglyceride}
\end{array}$$

The use of mono- and diglycerides in both food and industrial applications is widespread. Glycerol can react with various fatty acids or fats/oils to produce these extremely functional compounds. Some of the more common uses are as emulsifiers, wetting agents, starch complexing agents, aeration/foaming agents, crystal modifiers, lubricants, and agglomerating agents.

There are also a wide variety of mono- and diglyceride products on the market. Functionality and price are controlled by the types of fat and oils used to make these products. Common raw materials include cottonseed and palm oil for specific crystal promotion, soybean oil and hydrogenated variations for intermediate cost and functionality, tallow and lard for low cost, and liquid oils such as sunflower for low-melting, easy to handle options. Standard mono- and diglycerides contain 40–45% monoglycerides. These can be increased to ~53% without the need for distillation. Distilled monoglycerides usually contain at least 90% α-monoglycerides. For specific applications, these can also be acetylated or ethoxylated.

Even fat replacers can be synthesized using INES, in this case with the use of *sucrosolysis*. The product line resulting from the INES of sucrose with primarily long-chain fatty acid methyl esters, is sucrose polyester. Procter & Gamble (Cincinnati, OH) has patented the use of a range of sucrose polyesters, commercially known as Olean.

Olean is currently allowed in ready-to-eat savory snacks as a no-calorie fat replacer.

Chemical Interesterification

One of the most important types of interesterification with respect to fats and oils applications is chemically catalyzed random ester interchange (transesterification or ester-ester interchange). Natural fats and oils have specific fatty acid distributions and positional arrangements. In large part, this determines their specific physical and functional characteristics such as melting point, oxidative stability, and nutritional make-up.

After catalyst addition to an oil or blend at slightly elevated temperatures under agitation, the triglyceride ester bonds are broken. The resulting fatty acids mix together and eventually reattach. If there is only one fat/oil or the fatty acids reattach to the same glycerol molecules, the specific reaction is sometimes called "intraesterification." If the fatty acid attaches to a different glycerol molecule, it is termed interesterification. If the reaction is allowed to continue long enough, the fatty acids will reach a random equilibrium arrangement. The specifics of this reaction were identified almost 200 years ago. Initial process conditions were too severe, i.e., very long reaction times at very high temperatures without the aid of catalysts (8).

It was not until over a century later that both the process and specific products were commercialized. One of the first successful applications for this reaction was with edible lard. It was found that by the use of intraesterification, the crystallization characteristics of lard could be changed. Lard's typical fatty acid distribution consists of ~27% disaturated glycerides, most of which are oleopalmitostearin (OPS). Randomization reduces the proportion of palmitic fatty acid in the middle position from ~64 to 24%, which lowers the melting point. In this case, the stable crystal form went from β to β′, which is preferred for most bakery applications (9).

For INES, starting materials can be quite varied; they include alcohol esters, glycol esters, and numerous forms of glycerides. This reaction is used in both food and industrial applications. The primary benefits are modification of physical properties such as melting point, solid fat index/content at various temperatures, and modification of the tendencies of the stable crystal form. To one degree or another, similar types of modifications are possible by hydrogenation or physically, by the use of fractionation. Both of these processes, however, do change the fatty acid distribution of the final product(s).

In the case of both intra- and interesterification of fats and oils, the simple fatty acid distribution and iodine value (IV) of the combined starting materials are virtually the same as those of the end product. They are rearranged at random for chemical INES.

> "Because fats or fat mixtures often have some degree of organization—produced either naturally or artificially— with respect to the distribution of their component fatty acids, profound changes in composition will often result from a random molecular rearrangement.
>
> Some vegetable seed oils, for example, cottonseed oil, peanut oil, cocoa butter, tend (more or less) to have each fatty acid distributed evenly, insofar as that is possible, among the different glyceride molecules. Hence trisaturated glycerides generally do not occur in quantity in these oils unless the content of saturated fatty acids exceeds about two-thirds of the total. On the other hand, with random distribution of all acid radicals, a fat containing two-thirds saturated fatty acids will contain nearly 30% fully saturated glycerides, and even a fat containing as little as one-third saturated acids will have 3.7% fully saturated glycerides. Since the plastic range, and particularly the melting point, of a fat is highly dependent on the trisaturated glyceride content, it follows that random rearrangement of a seed oil will usually change the consistency considerably and raise the melting point. A mixture of two radically different fats is always very far from a random distribution of fatty acids and hence will respond to this type of interchange. In particular, a mixture of highly saturated fat with a liquid oil or an oil of the coconut type will be greatly lowered in melting point by random rearrangement because the acids of the saturated fat become more widely distributed" (10).

Table 12.1 (10) illustrates the effects of randomization on a number of fats, oils, and blends. These data were taken from a number of published articles and patents that can be found in Ref. 10. With INES, the most noticeable effects occur when the fat/oil is a seed oil or a mixture of fats/oils differing widely in melting point. The melting points of palm oil, lard, and tallow are less affected (10).

For oils such as soybean and cottonseed, fatty acids are naturally nonrandom. The saturated fatty acids are usually in the *sn*-1 or -3 positions and the -2 position is usually unsaturated. For soybean oil, linoleate is often found in the *sn*-2 position, and oleate and linolenate show no particular preference. Although soybean oil contains >15% saturates (at the time of this writing), there are no trisaturates. This is also true for cottonseed oil which has ~28% saturates (11).

During intraesterification, some fully saturated triglycerides are formed, evidenced by the higher melting points in those fats/oils. There is also some concern

TABLE 12.1 Effect of Random Molecular Rearrangement on Melting Point of Various Fats and Fat Mixtures[a]

	Melting point (°F)		
Fat	Before	After	Reference
Soybean oil	19.4	41.9	214
Cottonseed oil	50.9	93.2	214
Oleo stock (beef fat)	121.1	120.2	214
Prime steam lard	109.4	109.4	214
Palm oil	103.7	116.6	215
Tallow (beef fat)	115.2	112.3	213
Coconut oil	78.8	82.8	215
Kokum butter	94	126	215[b]
Butterfat	68.4[b]	78.2[b]	216
10% Highly hydrogenated cottonseed oil + 60% coconut oil	136	106	217
25% Tristearin + 75% soybean oil	140	90	218
50% Highly hydrog. lard + 50% lard	135	106	219
15% Highly hydrog. lard + 85% lard	140	90	219
25% Highly hydrog. palm oil + 75% highly hydrog. palm kernel oil	122.3	104.5	220

[a] *Source:* Ref. 10.
[b] Setting point (°F).

that through INES, there is a formation of triglycerides not found in nature, specifically, those with saturates in the center position. To date, studies on the effects of consumption of such triglycerides have not shown any significant differences.

Using Table 12.1 as a general guide, it is possible to select the appropriate starting materials for specific formulations more accurately. For example, one can raise the melting point of soybean oil by intraesterification without the use of hydrogenation.

To create a fat blend that has a very low *trans* fatty acids level and acceptable melting points and/or solids profiles, liquid oil can be interesterified with fully hydrogenated soybean, cottonseed, palm, palm kernel, and coconut oils. Palm, palm kernel, or coconut oils and their stearin fractions can provide solids without hydrogenation.

Interesterification affects the melting curve [differential scanning calorimetry (DSC), solid fat index (SFI), and/or solid fat content (SFC), for example], without affecting the fatty acid distribution (FAD).

Figure 12.1 illustrates the complete randomization of fatty acids in a typical triglyceride having a stearic, oleic, and linoleic fatty acid attached, in that order. Technically, this is an example of intraesterification. All possibilities are shown. As can be seen, with INES, this monosaturated, diunsaturated molecule becomes a mixture of monounsaturated (disaturated), diunsaturated (monosaturated), triunsaturated, and

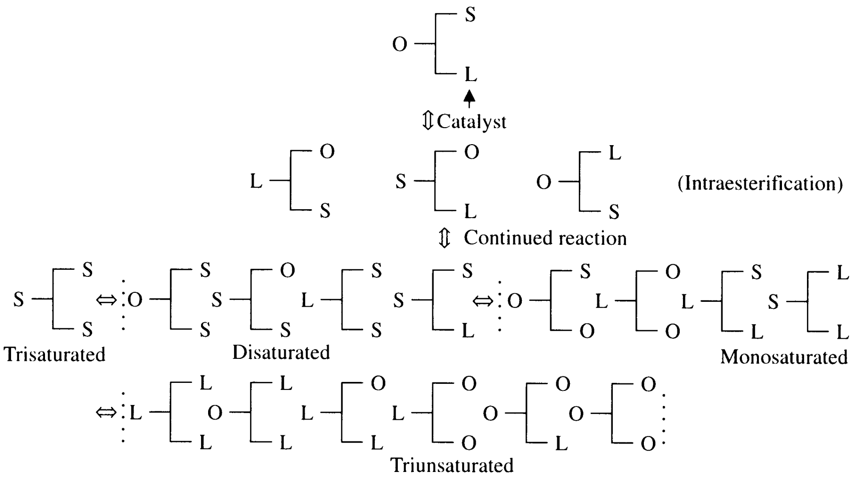


Fig. 12.1. Interesterification equilibrium mixture. *Source:* Ref. 10.

trisaturated components. Because each component has a different melting point, the final interesterified product is quite different from the starting material.

One can mathematically predict the percentages of each isomer on the basis of the laws of probability (10). The relevant equations can be found in the reference. The final percentages of the example shown above are as follows:

S-O-L = 22.2% (Starting material)

S-S-S = 3.7%
S-S-0 = 11.1%
S-S-L = 11.1%

O-O-O = 3.7%
O-O-L = 11.1%
O-O-S = 11.1%

L-L-L = 3.7%
L-L-O = 11.1%
L-L-S = 11.1%

Figure 12.2 is a simplified overview of what occurs during chemical interesterification of a liquid oil (triunsaturate) and a solid trisaturate. The starting materials are quite different and continue to behave independently after physical mixing. The final randomized mix, however, has been moderated because most of the combinations have intermediate melting characteristics. During randomization, by chance, some triglycerides that are identical to the starting components are formed.

By distributing the saturated fatty acids randomly, the melting profile and melting point are lowered considerably because trisaturates have extremely high melting points compared with unsaturates, monosaturates, and disaturates. Tristearin, for example, has a capillary melting point of ~66°C.

This process generally promotes the β′ crystal structure by increasing the number of different fatty acid combinations attached to the glycerol backbones. In this case, the blend would have 50% saturates and 50% unsaturates. These ratios could be easily modified for specific requirements. If the unsaturates are *cis*, all blends would also be virtually free of *trans*.

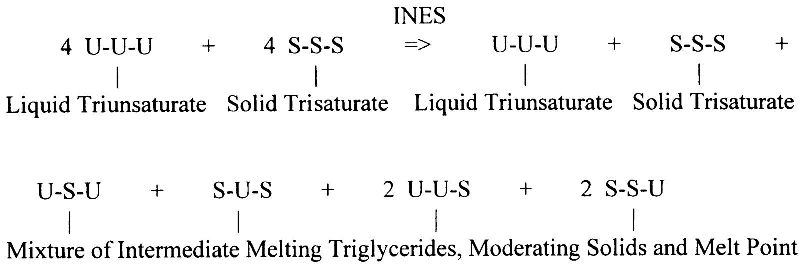


Fig. 12.2. Chemical interesterification (INES) of a liquid triunsaturate and solid triunsaturate and the resulting mixture of triglycerides with various melting points.

There are a number of reasons why one should consider INES (12), including melting point modification, solid fat curve modification, crystallization modification, improvement of plasticity, and the combination of properties of different fats and oils, especially with respect to nutrition. INES does not affect the following: (i) the IV of the fat, oil, or blend; (ii) the overall fatty acid composition of the fat, oil, or blend; (iii) the saponification value of the fat, oil, or blend; or (iv) the *trans* fatty acid content of the fat, oil, or blend.

Proposed Mechanisms for Chemical Interesterification

There are two published variations of catalytic reaction mechanisms proposed for this reaction. The first (13) suggests that the reaction begins when the catalyst attacks the α-hydrogen of an acyl group to form an enolate ion. This enolate ion then reacts with another ester to form a β-ketoester. This is also referred to as the Claisen mechanism. A reddish brown color forms with the addition of "catalyst," which is often used as an indication that INES has begun. This is believed to be a result of the formation of a complex of oil and the "catalyst," which might in fact be the active catalyst.

The second hypothesis (14) proposes that the methoxide ion attacks the carbonyl group directly to form a diglyceride anion. This anion functions as the real catalyst and transfers acyl groups around the glyceride backbones. Diglyceride ions are formed *via* both mechanisms. The basic difference between the two proposals is that in the first, both β-keto- and acylesters are the donors for acyl INES, and in the second, only acylesters are the donors. In neither case is the formation of the reddish brown color explained adequately.

Types of Chemical Interesterification

There are two basic types of chemical INES, i.e., random and directed. Both involve the use of transition metals such as sodium or, more commonly, derivatives such as sodium methoxide. In general, the differences in these two reactions have been quantified (Kellens, unpublished data) and are shown in Table 12.2.

TABLE 12.2 Chemical Interesterification

Random	Directed
	Controlled cooling during interesterification
Single temperature (90–140°C)	Low temperature (20–60°C)
Short reaction time (13–30 min)	Long reaction time (6–24h)
Low catalyst consumption (0.05–0.1%)	Higher catalyst consumption (0.1–0.3%)
=>Nonselective (law of probability)	=>Selective segregation determined by crystallization, eventually followed by filtration

Random Interesterification. This is the most common type of chemical INES. If one knows the fatty acid composition of the initial component(s), the final triacylglyceride composition (TAG analysis) can be predicted accurately, as shown earlier. The reaction normally reaches equilibrium within 30–60 min of catalyst addition.

The reaction process of partially hydrogenated palm kernel oil was monitored by Mettler dropping point (MDP) and solid fat content (SFC) and is shown in Table 12.3 (Wainwright, unpublished data). Clearly, an "induction period" followed by fatty acid reshuffling with subsequent formation of new TAG species (as evidenced by alterations of melting properties) is demonstrated (Wainwright, unpublished data):

Directed Interesterification. This is a modification of random interesterification. The reaction is directed, in that the natural equilibrium is interrupted. This is usually accomplished by temperature, in most cases, a low temperature. During randomization,

TABLE 12.3 Reaction Progress of Partially Hydrogenated Palm Kernel Oil[a]

	Solid fat content (%)		
Reaction time (min)	MDP(°C)	33.3(°C)	37.8(°C)
0	42.7	14.2	6.3
5	42.4	13.8	6.3
10	42.7	14.1	5.9
15	42.5	13.8	5.6
20	40.9	12.8	4.4
25	41.5	12.9	4.3
30	40.2	12.0	2.5
35	37.0	9.4	0
40	36.3	8.3	0
45	35.5	7.4	0
50	35.5	7.6	0
60	35.8	7.6	0
65	35.8	7.6	0
75	35.7	7.0	0

[a] Abbreviation: MDP, Mettler dropping point.

trisaturates are formed. If the reaction temperature is lowered below the melting point of these specific trisaturates formed, they will crystallize and no longer be a part of the reaction. The remaining fatty acids will then attempt to randomize fully, resulting in the formation of more trisaturates, which again crystallize at lowered temperature. If the diagram of complete randomization shown earlier is used as the model, the following percentages of specific triglycerides will result (in the case of the triglyceride SOL previously used to illustrate INES)(15):

Solids	Stearic-stearic-stearic	33.33 mol%
Liquids	Oleic-oleic-oleic	8.33 mol%
	Linoleic-linoleic-linoleic	8.33 mol%
	Oleic-oleic-linoleic	24.99 mol%
	Oleic-linoleic-linoleic	24.99 mol%

This could greatly reduce the saturates from an oil, if this mix were fractionated after INES. If filtration is not performed, the melting point of the final product would be significantly higher, which may be of benefit in some bakery applications.

As already shown, directed INES normally takes considerably longer because the temperature of this type of INES is much lower than that for a standard randomization. Figure 12.3 (16) illustrates the differences caused by random and directed INES on the solid fat curve for palm oil. As can be seen in this figure, the solids and melting point of an oil or fat (palm in this example) can be altered radically by intraesterification, without changing the fatty acid composition. The effect of the increase in trisaturates formed during directed INES is most noticeable.

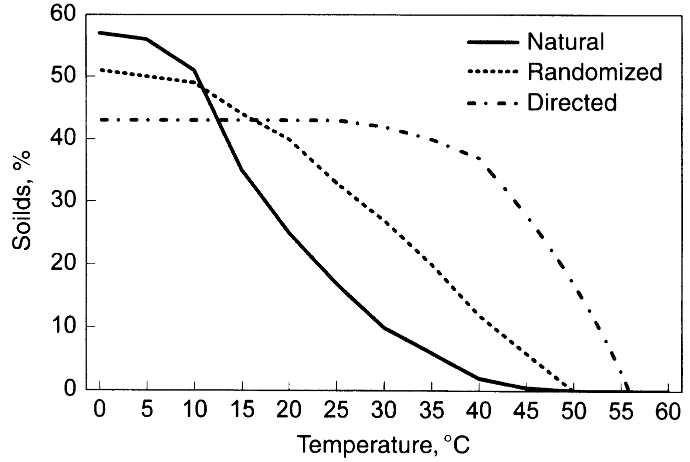


Fig. 12.3. Example of the effect of random and directed chemical interesterification on the solid fat behavior of palm oil.

Enzymatic INES

The primary reason for the use of enzymes over chemical catalysts for INES is to obtain positional specificity of the resulting interesterified product. Some enzymes can be selective with respect to where fatty acids can be cleaved and reattached. To date, this is primarily in the *sn*-1 and -3 acyl chains of triglycerides. This is quite useful, if not essential for specific applications such as the functional match for cocoa butter or nutritional match for human milk fat. This reaction is still random for the *sn*-1 and -3 positions.

Enzyme catalysts are expensive, and the reaction times are generally much longer than those for chemically catalyzed INES because the reaction temperature is close to ambient. Processing conditions must be more closely controlled (e.g., temperature, pH, or moisture content) and impurities in the starting material must be as low as possible to prevent inactivity of the enzyme catalyst. This process, like chemical INES, can be carried out in batch systems or as a continuous process. In either case, there is a substantial premium paid in terms of cost for the products produced in this manner, relative to chemical INES. Several examples of enzymatic applications will be given later in this chapter.

The Chemical Interesterification Process

Although random and directed chemical transesterification can occur without catalyst at temperatures >250°C, in practice, catalysts are typically used and the reaction temperature range is usually 80–110°C. The catalyst can be an acid, alkaline, or metal. Alkali metal alkoxides such as sodium methoxide are often the preferred choice because they are the most efficient. Table 12.4 lists the catalysts that have been used for this type of reaction.

TABLE 12.4 Common Types of Chemical Interesterification Catalysts[a]

Type of catalyst	Concentration (%)	Temperature (°C)	Time (min)
Alkali metals Na, K, Na-K alloys	0.1–1	25–270	1–120
Alkoxides CH_3ONa, C_2H_5ONa	0.1–2	50–120	5–120
Alkali hydroxides NaOH, KOH	0.5–2	150–250	90
Mixture NaOH + glycerol	0.5–0.1 +0.1–0.2	60–160	30–45
Metal soaps Sodium stearate	0.5–1	250	60
Metal hydrides NaH, $NaNH_2$	0.2–2	170	3–120

[a] *Source:* Ref. 16.

TABLE 12.5 Inactivation of Catalysts by Poisons

Poison		Catalyst inactivated (kg/ton oil)		
Type	Level	Na	CH_3ONa	NaOH
Water	0.01%	0.13	0.3	—
Fatty acid	0.05%	0.04	0.1	0.07
Peroxide	1.0%	0.023	0.054	0.04
Total catalyst inactivated		0.193	0.454	0.11

The oil and catalyst must be completely dry because moisture, even in very small amounts, will deactivate the catalyst and can cause soap formation. The oil quality is also critical to the success and economics of INES. As is the case of water, free fatty acids (FFA) and peroxides will also poison the catalyst; thus, they must be reduced to very low levels, as shown in Table 12.5 (16). These impurities not only inactivate the catalyst, but also form additional unwanted compounds such as methanol, FAME, and soaps, reducing the yield of finished product. Therefore, refined oil is customarily used rather than crude. Drying normally at 110–130°C, under vacuum, and neutralization are also required before INES, as is a prebleaching step for starting materials that have high peroxide values.

The oil is then cooled to 70–90°C and the catalyst is added as a dry powder or suspended in the dry oil. The catalyst concentration is routinely between 0.05 and 0.15%, and the average reaction time is 30 min. The reaction is often allowed to continue for 15–30 additional minutes to ensure complete randomization.

Theoretical losses can also be calculated. These occur in postrefining (postbleaching and postdeodorizing) (Crown Ironworks, unpublished data). In the case of postbleaching, for every kilogram of bleaching earth added to the oil, there is a loss of 30–35% of oil adhering to the earth. Between 0.5 and 1.0% bleaching earth is typical, resulting in a 0.15–0.30% loss. Loss through deodorization is caused by the formation of FFA, FAME, and mono- and diglycerides during INES.

Losses from FFA plus FAME are equal to~10 times the catalyst consumption. In a normal reaction, the consumption is 0.1%, producing losses of 1.0% from both FFA and FAME (Crown Ironworks, unpublished data). Total losses are typically in the neighborhood of 1.5–2.0%, including the formation of mono- and diglycerides.

In a typical batch process, the reaction is carried out under agitation. Various designs are available, ranging from batch to semicontinuous to continuous. There are pros and cons for each type of system. In a simple batch reaction, as described in Figure 12.4 (adapted from Figure 1.11, ref. 1), the reactor is normally capable of heat, vacuum, and agitation. Even today, this is the most common type of processing system. There are semicontinuous and continuous processes available as well. These are generally more efficient for large volumes of a relatively few different products.

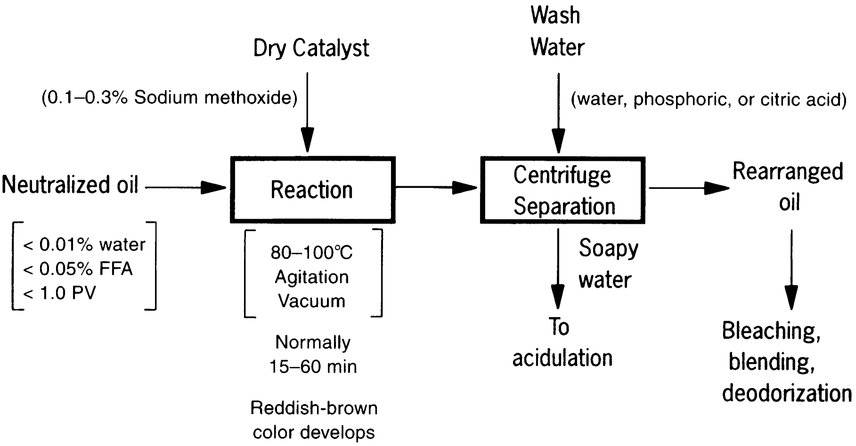


Fig. 12.4. Typical chemical interesterification process. Abbreviations: FFA, free fatty acids; PV, peroxide value.

For continuous systems, the catalyst is often metallic sodium. The catalyst is mixed with the dry oil at very low levels (0.05%) under shear agitation. The reactor is generally tubular in design allowing for accurate control of reaction time. Deactivation with steam is followed by a water-wash and centrifugation (17). A deaerator/dryer vessel is normally used for a continuous system before the oil enters the continuous postbleacher. Changeover, however, is more difficult.

During INES, a reddish-brown color develops, which has been used for many years as an indication that the reaction is proceeding as expected. The higher the quality of the ingredients and catalyst, the less loss there will be during the reaction. Minimization of required catalyst also improves the yield.

Once it has been determined that the reaction is complete, the batch is normally transferred to a postbleacher, where the catalyst is inactivated and the process stopped by the addition of water or acid (citric or phosphoric) solution. In the bleacher, the inactivated catalyst or soaps are absorbed by the bleaching earth. The oil is dried and deaerated. After bleaching, the oil/earth mixture is pumped through a filtration system and then to either blending or deodorization.

Tests to Ensure Complete Randomization.

To date, all methods for end-point determination are off-line; these somewhat time- and labor-consuming methods are discussed in the following.

Melting Point. Depending upon the effect of INES, melting point can be used. In most cases, the melting point does change as was shown in Table 12.1. This test is relatively quick, simple, and reliable; it has been used for many years. Extra time is given before taking a sample, however, to ensure complete randomization.

Solid Fat Measurement. This can be done *via* SFI, SFC or DSC. Although extremely accurate, all are time-consuming and somewhat labor intensive.

Sterol Content. In most oils, there is a detectable level of free sterols. During INES, these sterols are also esterified. The sterol content can be measured in a sample. Complete randomization has been assumed when the free sterol content drops below detectable levels.

Glyceride Compositional Analysis. INES changes the specific fatty acid order in triglycerides. Methods such as thin-layer chromatography (TLC) and GLC with mass spectrometry (MS) have been used on production applications (10).

On-Line Specrometric Monitoring. Recently, it has been discovered (6) that chemical INES can be monitored by ultraviolet (UV)/visible spectrometry, at least on a bench scale. There is a direct correlation between the absorbance at 350–400 nm to the reaction itself. It has been shown in laboratory experiments using a variety of oils that INES begins with an absorbance of ~0.4 at a wavelength of 374 nm (in the upper range of the UV spectrum) as shown in Figure 12.5 (6) This chart illustrates absorbance measurements from 0.4 to 0.8, indicating that complete randomization did not occur.

Randomization is complete at an absorbance of ~1.0. If this new technology can be validated for commercial production, a number of advantages become apparent.

1. Catalyst levels can be minimized to reduce cost and improve yield.
2. The total time to INES can be minimized to increase capacity and improve finished product quality; i.e., less color formation, improved oxidative stability, due to reduced tocopherol inactivation. This is due primarily to the potental elimination of off-line analytical testing.
3. Equipment design can be improved to increase efficiency and reduce the cost of this process.

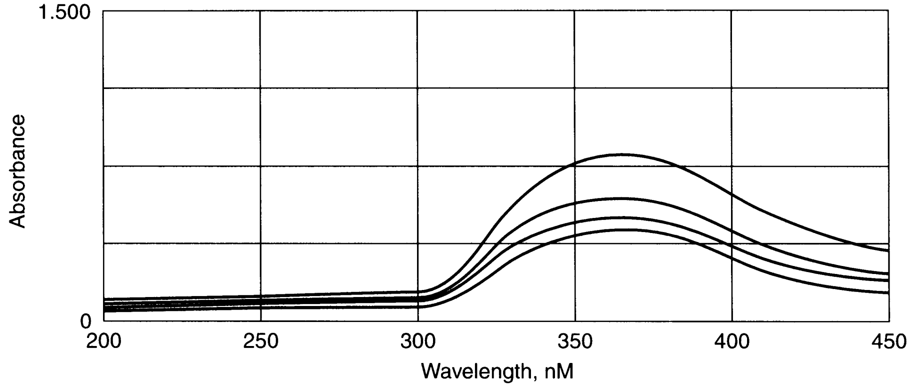


Fig. 12.5. Spectrometric chart of the absorbance change at 374 nm during a bench-scale interesterification reaction.

4. The potential exists for reproducible partial INES for the formulation of unique products.

Partial INES of a liquid oil and hard fat results in a flatter solids slope with a higher melting point, without any increase in saturated fat content (6). This will be shown in greater detail in the section on applications.

Stability

Whether stability (oxidative and/or flavor) is affected by INES is not clear. There are a number of variables that can affect fat and oil stability, including fatty acid position on the glycerol backbone and effect on tocopherols. It has been shown in a number of studies that the stability of interesterified fats and oils decreases compared with the natural starting materials (11,17–19). It appears that the position of the unsaturated fatty acids on the triglyceride molecule may affect stability. In nature, as mentioned before, most of the middle *sn*-2 positions are unsaturated.

During complete randomization, some saturates move to this position. Concurrently, unsaturates move from this center position to the *sn*-1 and -3 positions. This effect is consistent with both intra- and interesterified blends, when the stability was compared before and after INES. In addition, another study (20) indicates that stability cannot be predicted simply by knowing the total content of unsaturated fatty acids. That study showed that triglycerides having the same acyl groups at the α-positions and a different fatty acid in the center were more stable than triglycerides with the same fatty acid composition, but having the same fatty acids at the *sn*-1 and -2 positions and the odd at the third position.

In yet another study (21), partial effects have been indicated. Conjugated diene content was measured on a number of natural oils before and after INES. No statistical differences were seen at 55°C in any of the oil sets. At 28°C, however, canola, corn, and soybean oils had lower stability after INES, whereas linseed and sunflower oils remained the same.

Flavor was examined in a project involving a physical mix of 90% soybean oil and 10% fully hydrogenated soybean stearine before and after INES (11). In this case, the flavor of the physical blend was slightly worse and thought to be due to the soy stearine portion. The authors also found that the INES blend with added antioxidants had a stability similar to that of commercially available partially hydrogenated margarine oil.

As a final example of experimentation in this area, improved stability was found from the INES of sardine oil (22). This fish oil, with long-chain n-3 fatty acids, was interesterified with fully hydrogenated soybean oil at a ratio of 40:60. This blend was evaluated before and after INES for flavor and peroxide value. The INES blend was much more stable.

From these studies, it is apparent that we are learning about the effects of INES in bits and pieces and that the issue of stability is quite complex. Tocopherol degradation during INES is also an issue. The longer a reaction takes and/or the higher the level of catalyst required for oils such as soybean, which contain substantial amounts of tocopherols, the lower the tocopherol content in the final product and the lower the oxidative stability (6).

Applications

Margarines/Spreads

All or part of margarine/spread fat blends can be produced using INES. The primary purposes in using randomized base stocks are to minimize *trans* fatty acid and/or saturate plus *trans* fatty acid content, in both tub and print products or, to a lesser extent, improve the crystallization characteristics with the promotion of β′ in β-tending fat blends. Soybean oil, which contains almost 90% 18-carbon fatty acids tends to crystallize in the β form. It has been demonstrated (11) that due to randomization of these fatty acids, an interesterified blend of liquid soybean oil and fully hydrogenated soybean oil crystallizes in the more preferred β′ form.

As is the case with conventional fats and oils, cottonseed stearine, palm oil, or palm stearine further stabilize most fat blends in the β′ form. A patent was issued to Procter & Gamble in 1967 (23) for the INES of blends such as hydrogenated rapeseed oil, palm oil, and coconut oil purely on the basis of exceptional eating qualities, improved heat resistance, and also because they melted quickly in the mouth. For the first time, stick margarines that could incorporate liquid oils such as soybean in the finished blends were formulated.

Common base stocks include liquid vegetable oils and fully hydrogenated vegetable oils for the United States and liquid vegetable oils, palm oil and fractions, palm kernel oil and fractions, and coconut oil, with or without complete hydrogenation, for Europe and Canada.

As can be seen in Table 12.6, *trans* fatty acid content has been greatly reduced

TABLE 12.6 Examples of Margarine/Spread Blends with and Without Interesterified Base Stocks

		Saturates	*Trans*	Solid fat index		
	Margarine/Spread blend	(%)		50°F	70°F	92°F
	Tub					
#1	Standard commercial blend[a]	18.0	10.0	10.0	5.5	2.5
#2	INES blend[b]	24.0	1.0	9.5	6.0	3.5
	Print					
#3	Standard commercial blend[c]	19.5	22.0	22.0	13.5	2.5
#4	INES blend[d]	22.0	9.5	19.5	13.0	4.0

[a] 80% soybean oil/20% partially hydrogenated soybean oil.

[b] 32.5% canola oil/67.5% interesterification (INES) (70% canola oil/30% fully hydrogenated soybean oil).

[c] 50% soybean oil/50% partially hydrogenated soybean oil.

[d] 50% canola oil/30% INES (60% soybean oil/40% fully hydrogenated soybean oil)/20% partially hydrogenated soybean oil.

and saturates have increased substantially. Also, the solids curve of the interesterified blends is flatter, the solids at 50°F are slightly lower, and the solids at 92°F are higher. This is common for all blends in which *trans* solids are replaced with longer-chain (C_{16} and to a greater extent C_{18}) saturates.

Two options to increase the solid fat slope include the limited use of partially hydrogenated base stock s, as shown in formulation #4 in Table 12.6, or shorter-chain saturate base stocks (primarily lauric fats) in the blends. *Trans* fatty acids and lauric saturates have lower melting points and therefore lower solids at higher temperatures; however, they also have higher solids at lower temperatures, especially at 50°F (10°C). The Palm Oil Research Institute of Malaysia (PORIM) (24) gives several examples of *trans* free margarine blends. These are listed in Table 12.7.

Table 12.8 (25) illustrates several options that can be used as is or more likely in blends with liquid oils, for specific margarine and shortening applications. All are very low in trans fatty acids (<2%). Hydrogenated palm oil contains 46% palmitic fatty acid and 51% stearic; hydrogenated rapeseed oil (canola) contains 93% stearic fatty acid.

Most noticeable are the differences in solids at the higher temperatures before and after INES and the comparison of blends with high percentages of laurics vs. the high percentage of fully hydrogenated rapeseed oil. The blend with 80% fully hydrogenated rapeseed oil has very high solids even after INES because of the large amount of high-melting stearic acid.

Another possible option is the use of high-saturate domestic oils such as high-stearic soybean oil (26). As can be seen in Table 12.9, three different varieties of high-stearic soybean oil were interesterified. The solids curves and melting points were significantly different before and after INES.

Supporting the data provided in Table 12.1, one of the most significant reasons that the melting points and solids at higher temperatures increase after INES is the relative increase in di- and trisaturates formed during INES that were not present in the natural state. As mentioned earlier, the primary reason for the changes seen is the shift of positioning of some of the saturates from the *sn*-1 and -3 positions in the natural compositions to the *sn*-2 position during INES.

TABLE 12.7 Examples of *Trans*-Free Margarine Blends with Interesterification (INES)[a,b]

Formulation	Application
30% INES (87.5% PO/12.5% PKO) /70% SBO	Table margarine
30% INES (75% POo/25% PKOo) /70% SBO	Table margarine
55% INES (60% PO/20% PKOo/20% SFO)/45% SFO	Table margarine
50% INES (60% POs/40% PKO)/50% RSO	Tub margarine
60% INES (70% POs/30% PKOo)/40% RSO	Packet margarine
85% INES (70% POs/30% PKO)/15% POo	Pastry margarine

[a] *Source:* Ref. 23.

[b] Abbreviations: PO, palm oil; POo, palm olein; POs, palm stearine; PKO, palm kernel oil; PKOo, palm kernel olein; RSO, rapeseed oil; SBO, soybean oil; SFO, sunflower oil.

TABLE 12.8 Effects of Random Interesterification on the Solid Fat Content (SFC) of Blends Containing Fully Hydrogenated Oils[a]

Temperature (°C)	SFC profile (%)	
	Before	After
60% fully hydrogenated palm/ 40% coconut		
10	90	93
20	77	83
30	66	58
35	59	40
40	53	20
30% fully hydrogenated palm/ 70% palm kernel		
10	80	87
20	62	61
30	33	24
35	28	6
40	22	0
80% fully hydrogenated rapeseed oil/ 20% coconut oil		
10	92	94
20	87	92
30	80	85
35	78	77
40	75	63

[a] Values were obtained by pulsed nuclear magnetic resonance.

TABLE 12.9 Effect of Interesterification (INES) on Physical Properties and Component Glycerides of Genetically Modified Soybeans That Are High in Stearic Acid

Sample state	Stearic acid (%)	Solid fat index			
		10.0 (°C)	21.1 (°C)	33.3 (°C)	MDP[a]
A Natural	23.9	11.2	0.0	0.0	19.7
INES	23.9	6.8	3.3	1.5	23.2
B Natural	27.1	22.8	12.1	0.0	18.7
INES	27.1	13.7	4.5	2.6	38.2
C Natural	33.0	18.7	7.9	0.0	19.9
INES	33.0	13.5	5.5	3.5	36.4

[a] Abbreviation: MDP, Mettler dropping point.

Shortenings

As previously mentioned, one of the first commercial applications for INES was to stabilize lard in the β′ form by randomizing palmitic fatty acid, which is found predominantly in the 2-position of its disaturated (S_2U) triglycerides (9). This improves the functionality for most shortening applications.

Today, the applications for INES in shortenings are basically the same as those for margarines/spreads. Fats and oils with high levels of $C_{16:0}$, palmitic acid, such as palm and cottonseed oils, are used to ensure that conventional shortenings used in the bakery industry maintain a β′ crystal structure. By randomizing the fatty acids, many shortenings can now be formulated to be β′ stable without these fats and oils.

As shown in Table 12.10, when fatty acids solids are replaced with saturate content, the solids content at 50 and 70°F is considerably lower and that of saturates is much higher. The total saturates plus *trans* content, however, is lower. In Table 12.10, INES blend #4 is much closer in solids to standard all-purpose shortening and will work for this and many pastry applications. The saturates plus *trans* content is higher than for INES blend #2; in addition, the cost is higher because the entire blend is interesterified. Despite the solids content being lower for blend #2, its functionality has been shown to be similar to that of standard all-purpose shortening for many applications in laboratory tests.

After the success in monitoring INES in the laboratory, controlled partial INES was attempted. The key here is control, i.e., the ability to make the same product every time. Historically, it has not been possible to reproduce partial INES because each reaction has too many variables, e.g., catalyst activity, feedstock purity, temperature, agitation considerations, etc. Even with the best control, the finished product was quite variable. Tests such as melting point and solid fat content are much too slow to be used to control a partial reaction. As shown in Table 12.11, with partial INES, in this case using soy stearine as a base stock, a higher percentage of di- and tristearine remains in the final product. This increases the solids and melting point, without increasing the total

TABLE 12.10 Examples of Shortening Blends with and Without Interesterified Base Stocks

	Saturates	*Trans*	Solid fat index				Melting point
Shortening	(%)		50°F	70°F	92°F	104°F	(°F)
#1 All purpose[a]	23.5	32.0	28.0	20.0	14.0	9.0	116
#2 INES blend[b]	34.0	2.0	20.0	13.0	10.0	8.0	114
#3 P-INES blend[c]	32.0	2.0	22.0	16.5	14.0	12.0	117
#4 INES blend[d]	45.0	2.0	27.5	20.0	16.0	11.0	122

[a] 90% partially hydrogenated soybean oil/10% fully hydrogenated cottonseed oil.

[b] 30% high-oleic canola oil/70% interesterification (INES) (55% high-oleic canola oil/45% fully hydrogenated soybean oil.

[c] Partially INES (70% high-oleic canola oil/30% fully hydrogenated soybean oil).

[d] INES (55% high-oleic canola oil/45% fully hydrogenated soybean oil).

TABLE 12.11 Examples of Partial Interesterification (INES) and How They Compare to Fully Randomized Counterparts[a,b]

Product	Total saturates (%)	Total *trans*	Solid fat content (SFC) *via* NMR 50°C	70°F	92°F	104°F	MDP (°F)
Randomized 70% HO canola/ 30% Soy stearine	35	1.5	22.7	16.7	4.8	2.3	104
Partial INES I 70% HO canola/ 30% Soy stearine	35	1.5	27.9	19.1	5.4	2.9	107
Partial INES II 70% HO canola/ 30% Soy stearine	35	1.5	31.0	22.5	8.3	4.4	114
Randomized 65% HO canola/ 35% Soy stearine	39.5	1.5	33.3	19.9	11.9	7.2	118
Partial INES III 70% HO canola/ 30% Soy stearine	35	1.5	37.3	29.6	17.6	13.0	126

[a] *Source:* Ref. 6.

[b] Abbreviations: NMR, nuclear magnetic resonance; MDP, Mettler dropping point; HO, high oleic.

saturates and *trans* content. This could be significant in the future to further optimize healthier margarine/spreads and shortenings. The absorbance ranged from 0.52 for partial INES I (Table 12.11) to 1.0 for the completely randomized products.

With the ability of on-line tracking *via* spectrometry, which allows a reaction to be stopped at a specific absorbance, reproducibility has been achieved, again at least on a bench scale. It is not known at this time whether a commercial reaction can be stopped at a specific absorbance value. As is the case for margarines, shortenings can also be made almost *trans* free with palm oil and palm fractions (24). Several examples are given in Table 12.12.

TABLE 12.12 Shortening Formulations Based on Interesterified Palm Products and Liquid Oils[a]

Formulation	Solid fat content (%) 10°C	20°C	30°C	35°C	40°C
60% POs/40% INES RSO	36.8	23.3	14.0	10.1	7.4
INES (70% POs/30% SBO)	44.5	26.8	14.8	13.7	9.6
INES (100% POo)	49.9	28.9	12.8	10.6	6.8

[a] Abbreviations: POs, palm stearine; INES, interesterification; RSO, rapeseed oil; SBO, soybean oil; POo, palm olein.

Confectionery Fats

Cocoa Butter Alternatives. Cocoa butter is expensive, and supply is sometimes problematic. To reduce costs in some applications, cocoa butter alternatives were developed and have become popular for confections and coating fats. They are often referred to as "hard butters" and are composed primarily of palm, palm kernel, and coconut oils. To simulate the melting profile of cocoa butter more closely, these oils can be interesterified.

For lauric fats, this is most effective when the oil is fully hydrogenated before INES. Without INES, a fully hydrogenated oil, such as palm kernel shown in Table 12.13, has very high solids at mouth temperature. With the use of INES, the solids remain high at lower temperatures and drop off sharply by 33.3°C (92°F) (Wainwright, unpublished). This fully hydrogenated and interesterified cocoa butter substitute can be used as is or blended with other lauric or nonlauric fats and oils to further modify the solids curve, the melting point, and/or other functional properties such as bloom resistance, gloss, or snap that are required for quality confections and coatings. These products are not compatible with cocoa butter.

The functional properties of palm (PO)/palm kernel (PKO) blends (PO/PKO ratios of 100/0, 80/20. 60/40, 50/50, 40/60, 20/80, and 0/100) before and after INES have been examined (Grimaldi, unpublished). It was shown that after INES, improvements were seen in solids curves, consistency, and crystal structure. The general conclusions were as follows: (i) the plasticity of the fractions was improved after INES; (ii) INES decreased eutectic effects seen in the physical mixes; (iii) after INES, PKO demonstrated β' crystal tendencies; (iv) improvement in compatibility of PO and PKO was proven mathematically; and (v) specific blends (PO/PKO at 80/20 and 60/40) were shown to be preferred as bases for formulations.

Cocoa Butter Equivalents (CBE). These are not the same as cocoa butter alternatives. They are compatible with cocoa butter in all proportions without altering the

TABLE 12.13 Changes in Melting Profile and Melting Point of Fully Hydrogenated Palm Kernel Oil After Interesterification

	Saturated palm kernel	Saturated and interesterified palm kernel
Iodine value	0.8	0.8
Mettler dropping point (°C)	44.6	35.7
Solid fat content at 10.0°C	95.6	93.4
21.1°C	85.0	77.3
26.7°C	54.1	47.9
33.3°C	17.4	10.7
37.8°C	9.7	0.0

physical characteristics of cocoa butter, such as melting point and solids profile. Cocoa butter typically contains 80% symmetrical 2-oleo disaturated triglycerides such as POP, SOP and SOS.

As one might imagine, oils, such as high-oleic sunflower and safflower, are very good feedstocks to provide oleic fatty acid in the *sn*-2 position for CBE products. Saturated fatty acids, in the form of fully hydrogenated domestic or tropical oils, allow their introduction at the 1,3-position by the use of lypase enzymes (27).

> "This group of enzymes catalyses the hydrolysis of triglcyerides; the reaction is reversible and thus lipases will also encourage the formation of aclyglycerols from fatty acids and glycerol. Enzymatic modification permits the production of pure and specific products under mild conditions thereby severely limiting the extent of side reactions. A regiospecific lipase, for example, 3A from fermentation of a selected strain of *Mucor miehei* fungus, will confine the exchange of fatty acid groups to the α positions on the triglyceride. The process can be made continuous by immobilization of the enzyme; this also provides the opportunity to reuse the lipase.
>
> Macrae has described one such example that involves the directed interesterification of palm midfraction (rich in POP) with either stearic acid or tristearin to produce the following new triglycerides: POSt, StOSt, PStP, and PStSt. Fractionation typically follows to further tailor the triglyceride families to mirror the distribution characteristics of cocoa butter" (28).

Nutritional Blends

Reduced Calorie Fats and Oils. Another application for INES, especially chemical transesterification, is in the production of reduced calorie fats and oils. These products generally have calorie contents ranging from 3 to 6 kcal/g. Two products that have become recognized for this type of technology are Salatrim and Caprenin.

Conventional fats and oils contain 9 kcal/g. The concept of Salatrim is based on the premise that saturated fatty acids with carbon chain lengths ≥18 are poorly absorbed from the digestive system. Only the fatty acids in the 1- and 3-positions of a triglyceride are hydrolyzed by pancreatic lipase. This leaves a monoglyceride with a fatty acid in the 2-position, which is readily absorbed regardless of fatty acid structure. Therefore, a designed fat having long-chain saturates on the *sn*-1 and -3 positions should be lower in calories (29).

Such triglycerides, however, would have relatively high melting points. In an attempt to remedy this situation and further reduce the total energy content of these triglycerides, very short-chain fatty acids can be placed in the 2-position. These fatty acids, such as acetic, propionic, and butyric are thought to result in a caloric energy of ~4 kcal/g, similar to that of carbohydrates, due to a different metabolic route taken during digestion. This would lower both the melting point and total energy content of the resulting tailor-made triglycerides.

By proper selection of fatty acid combinations, fats and oils with varying melting points and energy densities can be achieved. A few of the vast possibilities are as follows:

S-A-S, S-P-S, S-B-S, B-A-B, B-A-S, B-P-B, B-P-S, ...

where A is acetic acid, B^1 is bytyric, B^2 is behenic acid, P is propionic acid, and S is stearic acid. Each combination has its own specific characteristics, e.g., melting point or energy content. If and when the components are mixed together, the total composite also behaves differently, depending upon those components. The more varied the combinations, the greater the tendency towards β′ crystallization and the harder it is for the mixed triglycerides to pack, which lowers the resulting melting point to some degree.

By using this technique, it is possible to design reduced-calorie oils and fats with a variety of functional characteristics, from salad oils to confectionery coating fats. In general, the energy content for this group of lipids is 5/9 that of normal fats and oils. The basic process to make these types of products is through the INES of fully hydrogenated fats with short-chain triglycerides such as triacetin, tripropionin, and/or tributryin. The amounts of each component are selected to provide the desired functionality with the highest degree of energy reduction possible for that particular end use. Because most, if not all fatty acids are saturated, there is very little, if any *trans* fatty acids present. Complete saturation also improves resistance to oxidation. Most of these products are quite stable.

A study involving the use of enzymes in the synthesis of similarly structured tryglycerides indicated that they lead to further enhancement of the nutritional aspects of these types of products (30). The best performance was with *Rhizomucor miehei*. By the use of enzymes, the *sn*-2 position became predominantly oleic and the *sn*-1 and -3 positions, short-chain fatty acids including butyrate and caproate. Oleic is believed to reduce low-density lipoprotein (LDL) serum cholesterol and if located in the *sn*-2 position, absorption is believed to be improved. Calorie reduction is reduced, however, due to the use of oleic fatty acid.

Another area of potential importance is the incorporation into fats and oils of "nutritional" oils or fatty acids such as high n-3 and/or n-6 fatty acids from fish oils, medium-chain fatty acids, or oils modified especially to be high in conjugated linoleic fatty acids (CLA). One of the earliest examples of this was the use of INES to produce low *trans* blends high in essential fatty acids (31).

INES with caprylic and capric fatty acids (medium-chain triglycerides often referred to as MCT) can be useful for several reasons. Energy content is reduced compared with normal fats and oils and they have relatively low melting solids. Caprenin (32) is a randomization of MCT and tribehenin. The long-chain saturated behenic fatty acid, like stearic acid, is poorly absorbed; thus the total energy content of this material is reduced to ~6 kcal/g. One of the possible applications of this material is in confections. In one study, Caprenin did tend to elevate LDL serum cholesterol, whereas Salatrim had no such effect (33).

MCT are easily digested, taking a different digestive route than longer-chain fatty acids (34,35). They are therefore of benefit and interest to adults with specific digestive difficulties, anoretics, AIDS and cancer patients, burn victims, and infants, especially preterm babies. Products have been developed for these applications.

INES of MCT with oils such as soybean and canola is available commercially. The blends are specific for each medical area. The MCT by themselves are not nutritionally balanced; for example, they contain no essential fatty acids, which are prevalent in soybean and canola oils (36). MCT are quickly digested in the body and longer chains also provide a source of longer-term energy.

Infant Formulations

There are a number of approaches and compositions for these types of products. These range from relatively simple blends of fats and oils to more closely approximate the overall fatty acid composition of human milk to enzymatic INES, which also closely matches the position of the fatty acids on the glycerol backbone. As the sophistication increases, so does the cost.

To match more closely the composition and nutritional value of human milk, INES has been used successfully (37). Human milk contains ~23% palmitic fatty acid, and a high percentage of this is found in the *sn*-2 position. Domestic oils such as soybean, canola, corn, and sunflower have relatively low levels of palmitic fatty acid, and what is present is not in the -2 position. This is even true for cottonseed oil, which has ~25% palmitic acid content.

By complete INES of palm oil, roughly one third of the palmitic can be transferred to the 2-position. As mentioned previously, in this position, during digestion, the *sn*-1 and -3 fatty acids cleave, leaving a monoglyceride with the fatty acid in the center. Long-chain fatty acids such as palmitic, in this position, are better absorbed in this form. This work has lead to a number of patents relating to interesterified compositions for both full term and preterm infant formulations such as the one just cited for Tomarelli (37). These were shown to be nutritionally superior to physical blends. Several consisted of blends of randomized palm olein, coconut oil, high-oleic safflower oil, soybean oil, and medium-chain triglycerides.

Unlike adults, infants use 25% of their energy intake for growth (38). They therefore require concentrated sources of energy. Fat and especially MCT are one way to provide that energy, especially for preterm or low-birth-weight infants. They can be toxic at high concentrations, however, and this must be taken into account for infant formulations.

As we uncover more and more specifics about how fats and oils affect human nutrition, INES will likely be used to customize specific blends for both total fatty acid content and positional requirements.

Economics

Formulation Considerations

INES adds cost to formulations, in terms of both ingredients and processing. Complete hydrogenation of base stocks and the interesterification process add to the cost compared with partially hydrogenated blends. There is always a competition between these types of products and simpler, somewhat less expensive "tropical" blends, which use palm oil, palm kernel oil, coconut oil, and their fractions. Even interesterified tropical blends could be somewhat less expensive. Successful blends have been prepared; one such example comes from List *et al.* (11).

A blend of 75–80% palm oil interesterified with 20–25% soybean or cottonseed stearine (fully hydrogenated) produced a functional base stock. This could be blended at a ratio of 65% base stock and 35% additional soybean oil to produce a shortening with functionality similar to that of standard all-purpose shortening.

Because generic soybean oil is relatively unstable for ambient and/or elevated temperature applications, more stable liquid oils, such as high-oleic and/or low-linolenic oils and/or added antioxidants can be used to further improve shelf-life capabilities. In addition to this cost, the major difference is of course the chain length of the saturates involved. Domestic oils have C_{18} as the predominant chain length. Tropical oils have shorter chains, primarily in the C_{12}–C_{16} area. Differences between the two relate to functionality, i.e., the longer the chain length, the higher the corresponding melting point and possibly health issues.

Processing Considerations

Naturally, there are costs involved in the interesterification process. As mentioned previously, heat and vacuum equipment is required; often centrifuges are used after the reaction is complete; there is a catalyst used, by-products formed, and losses. It has been calculated (Kellens, unpublished) that the cost of this process is usually between $25 and $40/ton. As a reference, it was also estimated that hydrogenation costs range from $30 to $70/ton, depending upon the degree of hydrogenation.

This cost is above and beyond any additional costs for special starting materials such as high-oleic oils, medium-chain triglycerides, or special fractions. For no/low *trans* shortenings, for example, there would be a cost for the high-oleic oil portion, a cost for complete hydrogenation of the fully hardened portion, and the cost of interesterification. Losses from INES and by-product streams must also be taken into account. The products made *via* INES must have real value to cover these costs.

For a greenfield plant sized at 100 metric tons/d, the current total production cost per ton, including investment payoff, has been calculated to be between $31 (for a continuous system) and $35 for a batch operation. A semicontinuous plant would fall in the middle of this range. This is based on a cost of ~$1.5 to $2.0 million for the plant, building, utilities, and installation/engineering. The facility would operate 330 d/y; the bottom-line cost also includes manpower, maintenance, ingredient costs (sodium methoxide, citric acid, bleaching earth), steam, cooling water, oil losses, and electricity (Crown Ironworks, unpublished). For specialty products, including but not limited to health/nutrition and functionality, interesterification can help to create solutions. Costs are a concern, but for many applications, interest is increasing.

Conclusions

There are many types of reactions included in the broad category of interesterification (INES). Most are specific to desired end product functionality and/or nutrition. Chemical INES is the most common type; its use may increase in the future, thus addressing the issue of lowering *trans* (actually *trans* plus saturates) in fats and oils. For specific high-value products such as human milkfat replacer and cocoa butter equivalents, enzymatic INES is a preferred alternative.

With this process, the position of rearrangement of fatty acids is controlled for functional improvements. The actual process of INES is relatively well understood, although the exact mechanism(s) of catalyst function are not completely understood. Batch, semicontinuous, and continuous systems are available, and quality and efficiency (including yield improvements) are being improved continually. Examples of products made *via* INES include the following:

- Low/no-*trans* margarines and shortenings
- Cocoa butter substitutes, alternatives, and equivalents
- Low- and no-calorie fats and oils (Salatrim, Caprenin, Olestra/Olean)
- Nutritionally designed fats and oils (e.g., low-saturate, medium-chain, n-3, or n-6 fortified)

The cost of INES is generally comparable to the cost of hydrogenation, but in some cases, some of the starting materials have relatively high costs, i.e., specialty oils and fully hydrogenated oils. For the functional and nutritional benefits possible, and the continuing trend to reduce fat/oil in foods, the overall value is improving.

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Chapter 13

Deodorization

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Introduction

All crude oils and fats, obtained after rendering, crushing or solvent extraction, inevitably contain variable amounts of nonglyceridic co-constituents, such as fatty acids, partial glycerides (mono- and diacylglycerols), phosphatides, sterols, tocopherols, hydrocarbons, pigments (gossypol, chlorophyll), vitamins (carotene), sterol glucosides, glycolipids, protein fragments as well as resinous and mucilaginous materials, traces of pesticides, and "heavy" metals.

Some of these co-constituents have a positive effect on the oil quality. Tocopherols, for example, protect the oil from oxidation, performing a role that is vitally necessary. Thus, they are considered to be highly useful constituents. Phosphatides, on the other hand, although they offer protection from oxidation in the crude oil, must be removed because they interfere with further processing, more specifically, deodorization. Most of the other components are objectionable because they darken the oil, cause it to foam, smoke, or precipitate. The objective of refining is to remove the objectionable co-constituents in the oil with the least possible damage to the glycerides and minimal loss of desirable constituents (Table 13.1).

The ongoing objectives of improving oil quality and reducing processing costs are forcing process equipment manufacturers to improve their technology beyond its present stage. In the past, oil quality was defined mainly by organoleptic parameters such as taste, odor, and color. Because of possible nutritional aspects, more emphasis is placed currently on the minor components (*trans* fatty acids, tocopherols, polymeric and oxidized triacylglycerols). Industrially, process technology and conditions have

TABLE 13.1 Stages in Edible Oil Refining

Refining step		Components removed/created
Degumming		Phosphatides, proteins, glycolipids, gums
Neutralization		Free fatty acids, residual phospholipids, oxidation by-products, metallic compounds, gossypol (cotton), aflatoxin (peanut)
Bleaching		Pigments, peroxides, soaps, metals, polycyclic-aromatic hydrocarbons
Winterization		Waxes, saturated triacylglycerols
Deodorization	+	Odors, flavors, pigments (heat bleach), free fatty acids, pesticides, aldehydes, ketones, degradation by-products
	–	Tocopherols, sterols, *trans* fatty acids, polymers

been adapted to reach these new product standards. Deodorization technology, in particular, has undergone some considerable changes because this final, major processing step in refining determines the ultimate organoleptic and nutritional quality of the oil or fat.

Chemical vs. Physical Refining

There are two major processing methods, known as "chemical" and "physical" refining. In chemical refining, free fatty acids (FFA), most of the phosphatides, and other impurities are removed during the neutralization with an alkaline solution (e.g., NaOH). In physical refining, the FFA are removed by distillation during deodorization (Fig. 13.1).

The physical refining process can offer important advantages to the refiner, including a higher overall oil yield, the use of fewer chemicals (e.g., phosphoric acid, sulfuric acid, or caustic soda), and, above all, a much lower effluent (by-product) production. This last advantage has become very important due to the increasingly stringent limits on the quality and quantity of waste water discharged from the refineries. Physical refining, however, is a quite delicate process that is not applicable to all crude oils.

The quality of the crude oil is a very important factor. Although physical refining can be applied to almost any crude oil, the process is less adapted to crude oils of low quality than chemical refining because a wide range of undesirable products are much more easily removed by an alkali treatment than by an advanced degumming. Some oils, such as cottonseed oil, cannot be refined physically; it requires an alkali treatment to remove the gossypol. For lauric oils and palm oil, on the other hand, physical refining is preferred in terms of both operating costs and refining losses. In

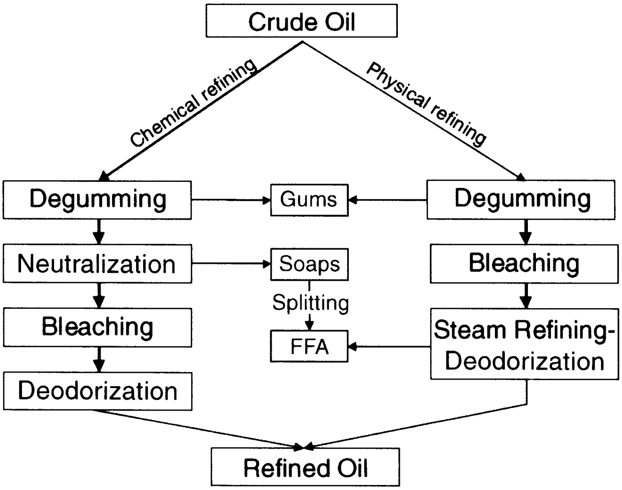


Fig. 13.1. General overview of a physical and chemical refining line. FFA, free fatty acids.

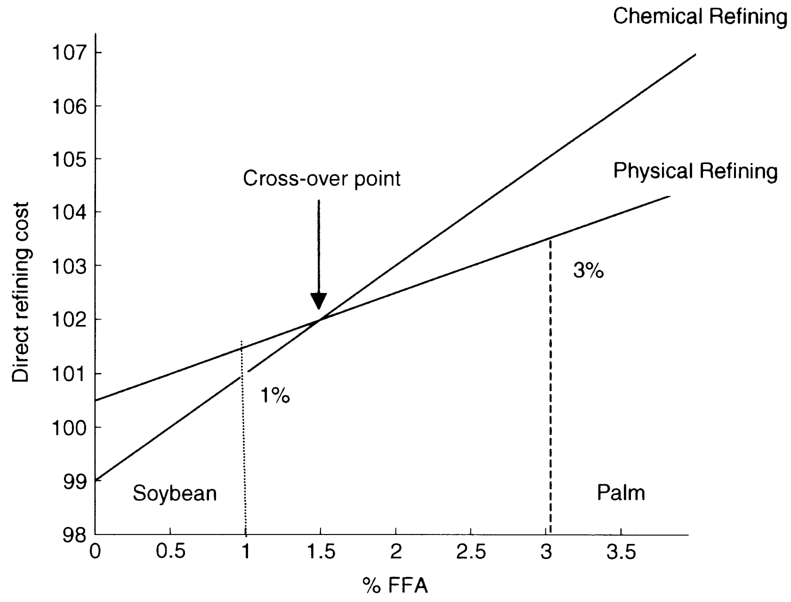


Fig. 13.2. Influence of initial free fatty acid (FFA) content on the direct refining cost.

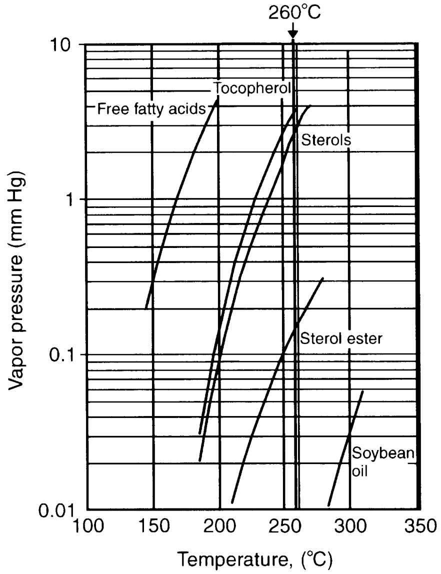
the case of soybean and rapeseed oil, physical refining is suitable only for crude oils of a good quality, i.e., with a low level of oxidation and a sufficiently low phosphatide content after degumming (<15 ppm). If this is not the case, chemical refining will yield better results.

Another important factor is the FFA content of the crude oil. In general, physical refining becomes interesting only when the acidity of the crude oil is sufficiently high as illustrated in Figure 13.2. For relatively cheap oils such as soybean oil, the higher oil yield of physical refining is less important than the higher consumption of bleaching earth, thus shifting the crossover point of the two curves to higher FFA. For other unsaturated oils with a higher value, such as peanut oil and sunflower oil, the crossover point will shift to lower FFA. Consequently, physical refining of these oils will be more attractive because it is less difficult.

The decision to use chemical or physical refining has a direct effect on the deodorizer design and performance. Chemically refined oils usually require less stripping steam and a shorter residence time; they can be deodorized at a higher pressure and lower temperature than a physically refined oil (see Table 13.2).

Principles of Deodorization

Deodorization is basically a vacuum-steam distillation at elevated temperature during which FFA and volatile odiferous components are removed to obtain a bland and odorless oil. Additionally, certain carotenoid pigments are destroyed, resulting in a



Component	Mol. Weight	Relat. volatility
Fatty acid	**280**	**2.5**
Squalene	**411**	**5**
Tocopherol	***415***	***1***
Sterol	**410**	**0.6**
Sterol ester	**675**	**0.04**
Oil	**885**	**<small>**

Fig. 13.3. Vapor pressure-temperature relationship for different components in vegetable oil.

heat-bleaching effect. These undesirable components are present in the oil in relatively low concentrations (usually between 0.1 and 1%). An efficient removal of these volatile substances depends mainly upon their vapor pressure and their concentration in the oil. The vapor pressure for a given constituent is a function of the temperature and increases with increasing temperature (Fig. 13.3). The lower the vapor pressure, the lower the volatility, and the more difficult it is to remove the constituent from the oil (1).

To achieve a proper deodorization, an optimal deodorizing temperature, operating pressure, and amount of stripping gas are required. These are determined not only by the type and state of the oil (chemically or physically refined), but also by the deodorizer design. In Table 13.2, some typical deodorizer conditions for soft oils are represented. As observed, physical refining imposes more severe conditions than does chemical refining. The major reason for this is the distillative removal of the FFA; this is more critical in physical refining because the levels are considerably higher, between 1 and 3% for most soft oils compared with between 0.03 and 0.1% for chemically refined soft oils.

To obtain the required final FFA content of 0.03–0.05% for physically refined oils, it is necessary to modify the operating conditions. The easiest way is to increase the deodorization temperature (for example, to 250°C), but this results in a higher production of *trans* fatty acids as well as in a greater loss of tocopherols. Higher temperatures can be avoided by lowering the deodorizer pressure and increasing the amount of stripping steam, but this in turn raises the overall cost of production. In addition, a high temperature is beneficial for a good heat bleaching. Shortening the

TABLE 13.2 Typical Deodorizer Operating Conditions for Vegetable Oils (Soybean, Rapeseed, Sunflower, Corn, Palm)

Conditions	Chemical U.S.	Chemical Europe	Physical Europe
Temperature (°C)	250–260	230–240	240–250
Pressure (mbar)	3–4	2–3	2
Sparge steam (%)	0.5–2[a]	0.5–1	1–2
Deodorizing time (min)	20–40	40–60	60–90
Final acidity (% free fatty acid)	←	0.03–0.05	→
Trans fatty acids (%)	←	0.5–1	→
Tocopherol losses (%)[b]	up to 60	max 25	max 25

[a] To remove tocopherols, a higher amount of steam is required.

[b] For example, for soybean oil in the United States, the minimum is 500 ppm; in Europe, it is 900 ppm.

overall residence time is also an alternative. But experience has shown that certain reactions within the oil itself, unrelated to FFA removal, are necessary to provide a stable oil. These reactions and the heat bleaching are time and temperature dependent. Therefore, commercial deodorizers should provide a retention period at the deodorizing temperature to allow these reactions to occur.

Today, most deodorizers used in the refining of soft oils operate at temperatures between 230 and 260°C, a pressure of 3 mbar or even lower, with a stripping steam consumption of ~10 kg/ton of processed oil. All three parameters have a direct effect on the design of the vacuum unit. For a given amount of stripping steam, the volume of the gas phase to be removed by the vacuum production unit increases considerably when the working pressure is reduced (Table 13.3). The gas volume also increases with increasing temperature, but the effect is less dramatic. In a conventional vacuum production unit with steam-jet ejectors (boosters), more motive steam per kilogram of stripping steam is therefore required to remove the gas phase (Table 13.4). Consequently, the deodorization stage in physical refining is more expensive than in chemical refining.

TABLE 13.3 Effect of Pressure and Temperature on Sparge Steam Volume[a]

Pressure (mbar)	Volume (m^3/kg steam) 230°C	Volume (m^3/kg steam) 240°C	Volume (m^3/kg steam) 250°C
4	581	592	604
3	774	790	805
2	1162	1185	1208

[a] Volume of steam (m^3/kg) = $4.6189 \cdot (273.15 + X)/Y$ (from equation $PV = nRT$) where X = temperature (°C) and Y = pressure (mbar).

TABLE 13.4 Effect of Deodorizer Pressure on Steam and Fuel Consumption[a]

Pressure		Stripping steam (kg/ton oil)	Booster steam (kg/ton oil)	Fuel (kg)
Booster	Deodorizer			
(Chemical refining)				
2.5	3 mbar	10	45	4.23
(Physical refining)				↕
1.5	2 mbar	15	93	8.31

[a] Conditions: Barometric condenser water inlet temperature, 24°C; outlet temperature, 30°C; assumed total pressure drop of 0.5 mbar in fatty acid scrubber; assumed fuel consumption of 1 kg for each 13 kg of steam produced.

Theory of Steam Distillation

The mathematical principles and theoretical background of the steam distillation process have been described in many publications (2–4). All calculations start from the basic laws of Raoult and Dalton, which are established for ideal mixtures. However, in practice, the mixture of a fatty acid and a vegetable oil has a "nonideal" behavior. Consequently, Raoult's law may be written as follows:

$$P_{L,i} = \alpha \cdot x_i \cdot p_i^{\circ} \qquad [1]$$

where $P_{L,i}$ is the partial pressure of a given fatty acid in the liquid phase, α is the activity coefficient, x_i is the molar fraction of a given fatty acid in the liquid phase, and p_i° is the vapor pressure of a given fatty acid.

According to Dalton's law,

$$P_{V,i} = y_i \cdot P_t \qquad [2]$$

where $P_{V,i}$ is the partial pressure of the volatile component in the gas phase, P_t is the total pressure of the gas phase, and y_i is the molar fraction of the volatile component in the gas phase. In the case of an ideal mixing between the stripping steam and the oil, $P_{L,i} = P_{V,i}$. However, in practice, an ideal mixing cannot be achieved and therefore:

$$P_{V,I} = E \cdot P_{L,i} \qquad [3]$$

where E is the vaporization efficiency.

The vaporization efficiency, E, has to be considered as a measure of the completeness with which the steam bubbles become saturated with volatile substances during their passage through the oil (2). In practice, the vaporization efficiency can be influenced by the depth of the oil layer and the steam injection geometry. The shallower the oil layer, the higher the risk that the steam will leave the oil surface without being saturated. At the other extreme, for deep oil layers, the contact time is longer, but then problems will arise with respect to the agitation, leading to an insufficient renewal of the upper oil layer and a nonuniformly treated oil mass.

The importance of the equipment design was illustrated by Deffense (5) who conducted some steam consumption experiments on a laboratory scale. An elimination of reflux and radiation losses combined with an optimization of the steam distributor reduced the necessary steam consumption significantly and resulted in a final overall vaporization efficiency of 0.93. Industrial deodorizers, however, have a lower efficiency because they usually operate under conditions that are less ideal than those of a laboratory deodorizer.

In general, the steam distillation of unwanted compounds is described by the following mathematical equation:

$$S = \frac{P_t}{E \cdot p_i^0} \cdot \ln \frac{V_a}{V_0} + \left(\frac{P_t}{E \cdot p_i^0} - 1 \right) \cdot (V_a - V_0) \qquad [4]$$

where S is the total moles of steam, V_a is the initial molar concentration of the volatile component in the oil, and V_0 is the final molar concentration of the volatile component in the oil.

When the initial FFA content is low, as in the case of a classical deodorization, $(V_a - V_0)$ becomes so small that the equation can be simplified as follows:

$$S = \frac{P_t}{E \cdot p_i^0} \cdot \ln \frac{V_a}{V_0} \qquad [5]$$

In any case, from both equations, it can be derived that the amount of steam required for deodorization is directly proportional to the amount of oil and the absolute pressure in the deodorizer and inversely proportional to the vapor pressure of the pure volatile component at the process temperature and the overall vaporization efficiency E.

Definition of Refined Oil Quality

In the past, refined oil quality was defined mainly by organoleptic parameters such as taste, odor, and color. Because of their possible nutritional aspects, more emphasis is currently placed on the minor components (*trans* fatty acids, tocopherols, polymeric and oxidized triacylglycerols). Table 13.5 shows typical characteristics of some major refined vegetable oils.

Free Fatty Acids (FFA)

The efficiency of deodorization is usually quantified by the disappearance of FFA during deodorization. Experience has shown that, in most cases, flavor and odor removal correlates well with the reduction in FFA. Because FFA have a relative low volatility, their efficient removal usually indicates good removal of other more volatile components, although there are some differences among the different oils. Soybean oil, for example, requires less steam than rapeseed (0.6–0.8 vs. 0.8–1.2%), due to the typical rapeseed odor, which is more difficult to remove and the crude oil

TABLE 13.5 Characteristics of Fully Refined Oils and Fats (Target Figures)[a]

Oils and Fats		Rapeseed/ Soybean	Corn/ Sunflower	Palm	Coconut/ Palm kernel
FFA (%)	max	0.05	0.05	0.05	0.05
Trans (%)	max	1	0.5	0.5	—
Moisture (%)	max	0.05	0.05	0.05	0.05
Impurities (%)	max	0	0	0	0
POV (meq O_2/kg)	max	0.5	0.5	0.5	0.5
Phosphorous (ppm)	max	1	1	1	1
Tocopherols (ppm)	min	500	750	—	—
Total metal (ppm)	max	0.1	0.1	0.1	0.1
PAH (ppb)	max	25	25	25	25
Color (5¼-in cell)	max	1.5R–15Y	2.0R–20Y	2.5R–30Y	1.5R–15Y
Cold test (0°C)	min	48 h	48 h	—	—
Smoke point (°C)	min	220	220	220	—

[a] Abbreviations:FFA, free fatty acids; POV, peroxide value; PAH, polycyclic-aromatic hydrocarbons.

quality of rapeseed oil, which is less consistent. Corn oil usually requires a higher temperature and/or longer residence time to achieve more heat bleaching. In addition, chemically refined oils are easier to deodorize than physically refined oils, not only because of the lower acidity before deodorization (0.1% for chemically vs. 1–3% for physically refined oils) but also as a consequence of a better removal during chemical neutralization of a whole range of polar minor components, oxidation products, and pigments.

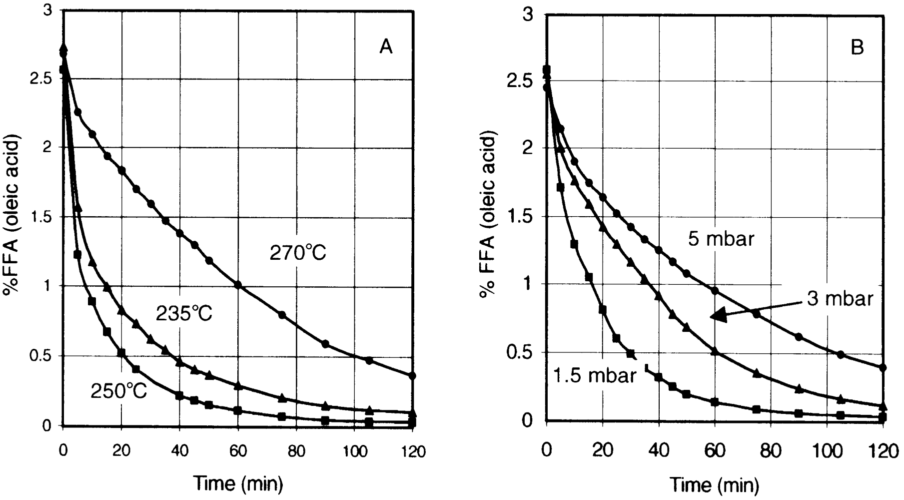
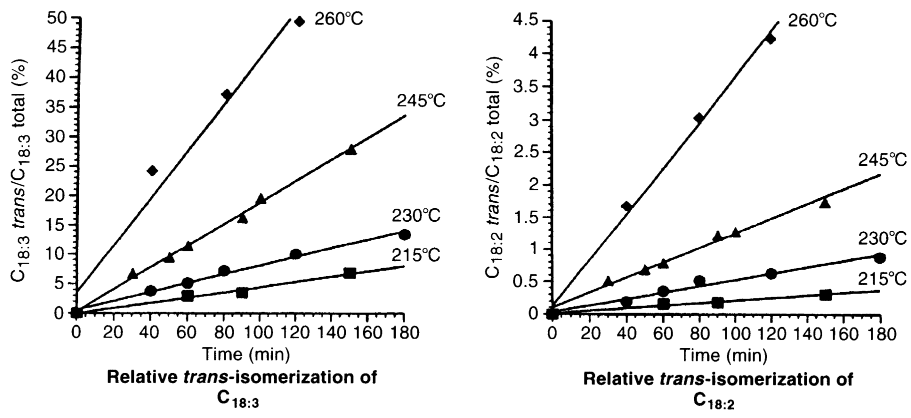


Fig. 13.4. Effect of (a) temperature and (b) pressure on free fatty acid (FFA) removal during deodorization/deacidification of soybean oil. Conditions: (a) 3 mbar, 0.5 sparge steam/h, varying temperature; (b) 230°C, 0.5 sparge steam/h varying pressure.



Relative *trans*-isomerization of $C_{18:3}$

Relative *trans*-isomerization of $C_{18:2}$

Fig. 13.5. Effect of temperature and time on *trans*-isomerization of linolenic acid ($C_{18:3}$) and linoleic acid ($C_{18:2}$).

For most oils, a residual FFA of 0.03–0.05% is targeted. In Figure 13.4, the effect of pressure and temperature on FFA stripping is represented for C_{18}-rich oils The figures are only approximations for C_{18}-rich oils deacidified in cross-flow type deodorizers. With packed columns, stripping steam consumption is somewhat lower (~30%) due to the countercurrent effect.

Trans *Fatty Acids (TFA)*

TFA are mono- or polyunsaturated fatty acids with one or more double bonds in the *trans* configuration. In crude vegetable oils, double bonds are nearly always in the *cis* configuration, with the hydrogen atoms sterically located on the same side of the double bond. Because of the low activation energy (125 kJ/mol), TFA are formed relatively easily at elevated temperatures (e.g., during deodorization or hydrogenation).

TFA have a structure comparable to that of saturated fatty acids. Consequently, they have a higher melting point than the corresponding *cis*-isomers. Highly polyunsaturated oils, such as soybean and rapeseed oil, are particularly sensitive to *trans*-isomerization during deodorization. The isomerization rate is the highest for linolenic acid and the lowest for oleic acid. The relative isomerization rate can be expressed as follows: $C_{18:3}$ (100) >> $C_{18:2}$ (10) >> $C_{18:1}$ (6).

Trans fatty acid formation during deodorization is influenced only by time and temperature. Generally, *trans* formation is negligible below 220°C; it becomes significant between 220 and 240°C, and nearly exponential above 240°C (Fig. 13.5). Today, *trans* fatty acid levels <1% (for rapeseed and soybean oil) and <0.5% (for other oils, e.g., sunflower oil and corn oil) are required.

Tocopherols

The main components of nonsaponifiables in vegetable oils are tocopherols and sterols, although the amounts vary in different oils. Tocopherols are the most important

TABLE 13.6 Tocopherol Content of Some Crude Vegetable Oils

Oil type	Tocopherols (ppm)	Iodine value	Unsaponifiables (%)
Soybean	900–2000	120–143	0.6–1.6
Rapeseed oil			
Low erucic	700–1200	110–126	0.5–1.2
High erucic	700–1000	94–120	0.5–1.2
Corn oil	1000–1500	127–133	0.4–1.2
Sunflower	600–800	110–144	0.3–1.3
Olive oil	100–200[a]	75–94	0.4–1.1
Palm oil	400–800[b]	50–55	0.3–0.9
Palm kernel	3–10	13–23	0.3–0.5
Coconut oil	30–80	7–12	0.2–0.5

[a] High squalene content, 1000–7000 ppm.
[b] Predominantly tocotrienols.

natural antioxidants occurring in vegetable oils. At the same time, they have an important vitamin E activity.

$$\text{Vitamin E} = \alpha\text{-toco} + 0.25\ \beta/\gamma\text{-toco} + 0.01\ \delta\text{-toco} \qquad [6]$$

Their level is governed by the level of unsaturated acids, i.e., the higher the unsaturation, the higher the amount of tocopherols present in the oil (Table 13.6). Tocopherols are present in different homologues, α-,β-, γ-, and δ-tocopherol. The α-isomer is the most active biologically, whereas the γ-tocopherol is perceived as the best antioxidant. During deodorization, part of the tocopherols are lost as a result of distillative removal and as a consequence of thermal degradation. The major factors affecting distillative losses are deodorizing temperature, pressure, and stripping steam (Fig. 13.6).

Thermal degradation, on the other hand, depends more on time and temperature and becomes significant only at elevated temperatures (>260°C). Under nor-

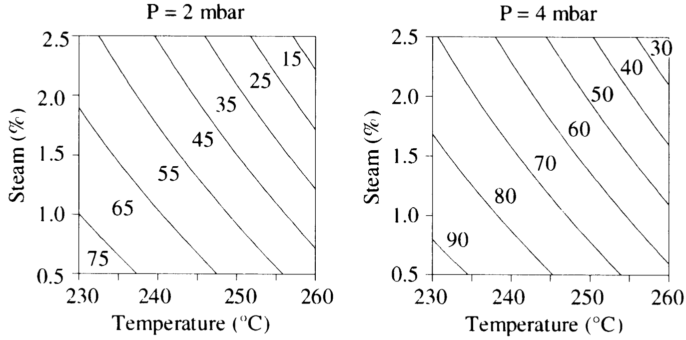


Fig. 13.6. Relative total tocopherol retention during the physical refining of soybean oil.

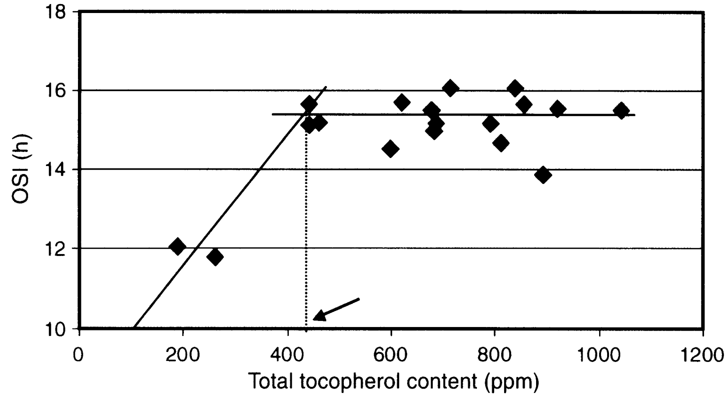


Fig. 13.7. Oxidative stability (OSI) of refined soybean oils as a function of the total tocopherol content.

mal deodorization conditions, most of the tocopherols are lost by distillation. The issue of a minimum required tocopherol level in deodorized soft oils is quite different in Europe and the United States.

In the United States, most soft oils are chemically refined, and tocopherol removal during deodorization is maximized. A level of 500 ppm for soybean oil, for example, is considered more than sufficient to protect the oil from oxidation (Fig. 13.7). The excess tocopherols are collected in the fatty acid distillate (FAD), which is then sold as a high-added-value by-product. Tocopherol levels in the FAD may range from a few percent up to 20%. For soybean FAD, in particular, prices are determined primarily by the tocopherol concentration, i.e., the higher the content, the higher the price per pound of tocopherol.

In Europe, where physical refining is more popular, tocopherol retention in the refined oil is maximized. In terms of the levels of tocopherol required in deodorized oils, for example, a good quality deodorized corn oil should have a tocopherol content of at least 800, preferably 1000 ppm.

Polymeric and Oxidized Triacylglycerols

Other substances, such as the polymeric and oxidized triacylglycerols, are also formed during edible oil refining. The increasing evidence that these compounds may be detrimental to health means that their presence must be restricted to the lowest possible levels. The main factors affecting polymerization are the presence of oxygen and temperature. In contrast to *trans*-isomerization, polymerization has already taken place during crushing, pretreatment, and final deodorization. Table 13.7 shows the *trans* fatty acid content and dimeric triglyceride content of some fully refined vegetable oils.

Polymerization and dimerization, in particular, may be of thermal or oxidative origin. Oxidized triacylglycerols formed during earlier treatments are assumed to act

TABLE 13.7 *Trans* Fatty Acid and Dimer Concentrations of Some Random Commercial Samples of Fully Refined Vegetable Oils[a]

Oil type	*Trans* fatty acid (%)	Dimeric triacylglycerols (%)
Soybean oil	0.9–3.5	0.6–1.3
Sunflower oil	0.3–1.3	0.7–1.2
Rapeseed oil	0.9–1.5	1.2–1.5
Corn oil	0.6–4.1	1.0–1.5
Peanut oil	0.1–0.3	0.5–1.3
Deep fried oil	—	>10

[a] *Source:* Ref. 6.

as catalysts for dimerization and polymerization. The level of oxidized triacylglycerols should therefore be kept to a minimum by restricting oil-oxygen contact as much as possible in the different refining stages.

Deodorizer Distillate

Deodorizer distillate is the material collected from the steam distillation of edible oils. The use and value of deodorizer distillate depend on its composition. This composition is not only oil dependent but is also determined by the refining technique applied (physical or chemical) and the operating conditions during deodorization. In the case of physical refining, the distillate consists mainly of FFA (>80%) with only small amounts of unsaponifiable components (Table 13.8). If these distillates contain low amounts of pesticides, they can have some value for use in the feed industry. Otherwise, they are sold as a source of industrial fatty acids. Deodorizer distillates from chemical refining have clearly higher values. Due to their higher tocopherol content, they are an attractive feedstock for the production of vitamin E. End users of these tocopherol rich distillates apply different chemical and physical techniques to

TABLE 13.8 Typical Composition of a Deodorizer Distillate from a Physical and Chemical Refining Plant

Composition	Chemical refining (%)	Physical refining (%)
Neutral oil	25–33	5–10
Fatty acids	33–50	80–85
Unsaponifiable matter[a]	25–33	5–10
~Tocopherols	6–15	2–5

[a] Note: unsaponifiable matter includes sterols and tocopherols.

purify the tocopherols. Due to the increasing interest in natural antioxidants, such as tocopherols and the use of phytosterols in the food and pharmaceutical industry, the importance of the distillate will certainly increase.

Deodorizer Technology

Deodorization can be considered as a multistep process comprising the deaeration, heating, deodorization-deacidification, and cooling of the oil.

Deaeration

In this first step, the oil is deaerated before heating to avoid excessive oxidation and hence risk of polymerization. Information on the solubility of gases in oils is rather limited (1). Soft oils dissolve readily between 4 and 10% of their own volume of air and other gases at ordinary temperature. All gases, with the exception of carbon dioxide, increase in solubility with increasing temperature. The relation between solubility (*S*) and temperature (*t*) can be expressed by the following linear equations:

For nitrogen $S(N_2) = 0.0590 + 0.000400 \times t$ [7]

For oxygen $S(O_2) = 0.1157 + 0.000443 \times t$ [8]

with *S* expressed in volume of gas/volume of oil at atmospheric pressure and *t* in °Celsius.

To achieve a proper deaeration, the bleached oil is sprayed into a tank under reduced pressure before entering the heating section. The lower the pressure applied, the lower the residual oxygen in the oil. Usually the oil is heated to at least 80°C and sprayed into a tank, which is kept at a pressure of <50 mbar. Some refiners even use the low pressure of the deodorizer or add some sparge steam in the spraying tank to improve deaeration.

Heating

The subsequent heating of the oil is usually accomplished in two stages. In the first stage, the incoming oil is heated countercurrently in an oil-oil heat exchanger (economizer), with the finished oil leaving the deodorizer. Finally, the oil is heated under reduced pressure to deodorizing temperature with a high temperature source such as high pressure steam, heat transfer fluids or, in rare cases, by electrical heating. Thermal oil heaters were used quite commonly in the past to heat the edible oils, but due to the potential risk of contamination, the technology has been abandoned. Today nearly all deodorizers operate with high-pressure steam boilers (Fig. 13.8, Table 13.9).

The net heating energy required for a deodorizing system can be calculated as follows:

$$H = [O \cdot c \cdot (T2 - T1)] \cdot f_L \cdot f_R \qquad [9]$$

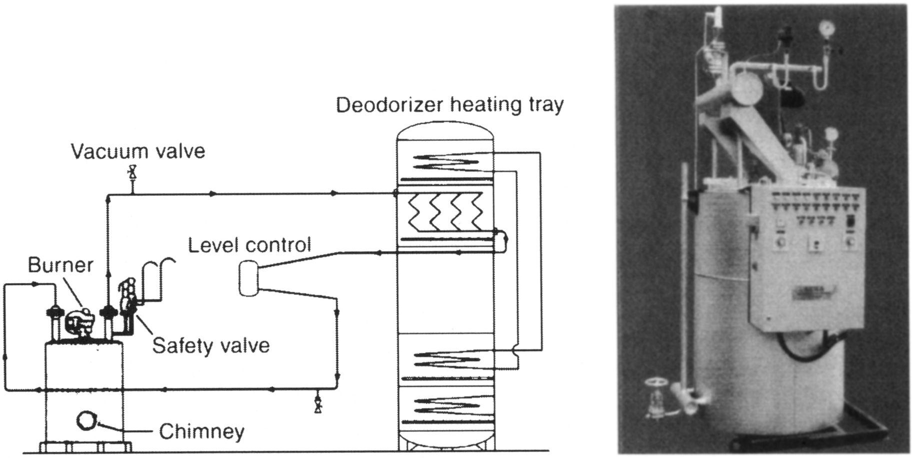


Fig. 13.8. High-pressure steam boiler used in deodorization (Geka).

where *O* is the amount of oil (kg), *T*1 and *T*2 are the incoming and final temperature of the oil (°C), *c* is the average specific heat capacity of vegetable oils [typically 2.2–2.4 kJ/(kg·°C)], f_L is the heat loss factor from radiation (typically 1.05–1.15), and f_R is the heat recovery factor [1 – (%heat recovery/100)].

In industrial practice, heat recovery has become an important factor because it minimizes the cost for the additional heating of the oil to the deodorization temperature. In recent years, there has been a very fast evolution in the manufacture of heat exchangers for heat recovery. Generally speaking, they can be divided into external and internal heat exchangers (Fig. 13.9).

External heat exchangers usually result in high recovery and provide easier access for cleaning. On the other hand, internal heat exchangers allow energy recov-

TABLE 13.9 Steam Temperature vs. Pressure

Pressure (bar)	Steam temperature (°C)	Latent heat (kJ/kg)	Specific volume (m^3/kg)
1	99.6	2258	1.694
2	120.2	2202	0.8853
3	133.5	2163	0.6056
5	151.8	2108	0.3747
7	164.9	2065	0.2762
10	179.9	2014	0.1943
15	198.3	1945	0.1316
20	212.4	1889	0.09952
30	233.8	1794	0.06663
40	250.3	1713	0.04975
50	263.9	1640	0.03943

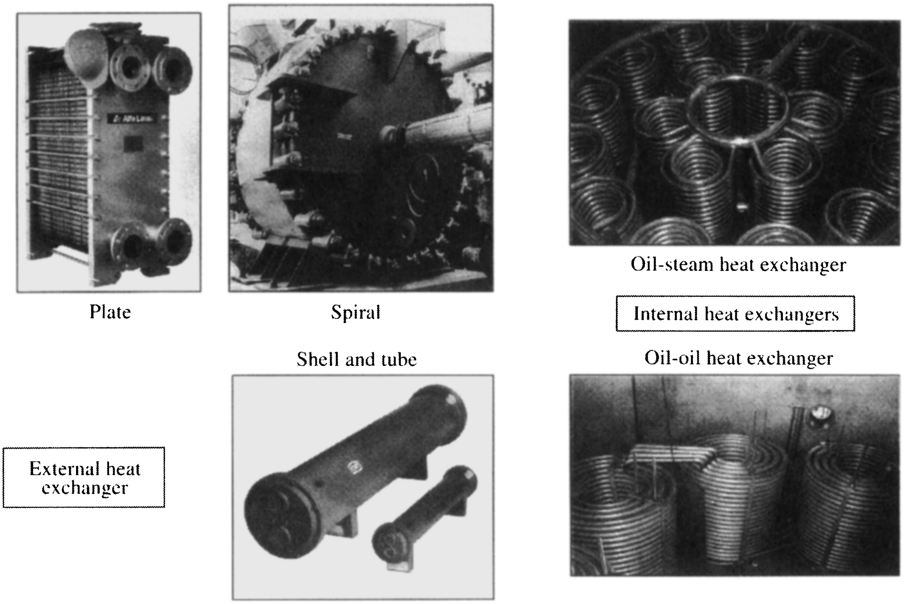


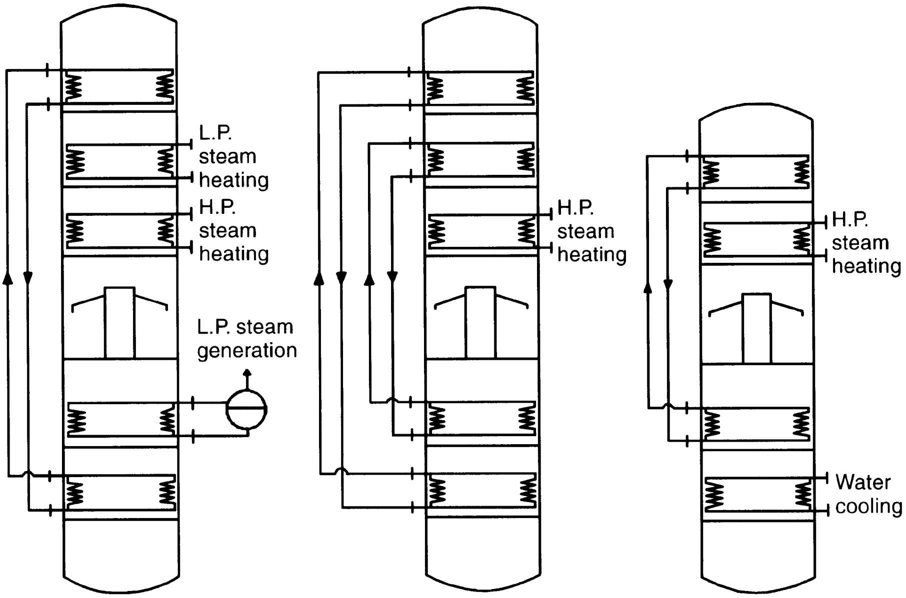
Fig. 13.9. Examples of external and internal heat exchangers used in edible oil deodorization (Alfa Laval, Ciat, De Smet).

ery under vacuum and ensure less product intermixing and less risk of fouling. The final choice for a heat exchange system is based not only on its thermal performance but also must comply with other criteria such as easy maintenance, low risk of fouling, low level of intermixing, no adverse effect on the product quality, and an acceptable installation cost compared with the expected energy recovery.

Heat recovery can be achieved directly by the exchange of heat between two oil streams at different temperatures (e.g., bleached vs. deodorized oil), flowing in a countercurrent direction through the exchangers, or indirectly by the production of steam. The direct heat recovery system is the most efficient, i.e., up to 85% of the heat can be recovered. It is usually applied in continuous deodorizers, whereas the indirect heat recovery system is used preferentially in semicontinuous deodorizers with frequent feedstock changes. The efficiency of the indirect heat recovery depends strongly upon the type and design of the system (Fig. 13.10). A special indirect heat recovery device is the thermosyphon system; the steam produced in the oil-cooling section is sent in a closed loop to the oil-heating section, and the condensed water is returned back to the cooling section.

Steam Stripping

The final deodorization and deacidification are usually conducted at a temperature between 230 and 260°C, at a pressure between 2 and 4 mbar and under injection of 0.5–2% sparging steam. From a thermodynamic point of view, the stripping agent



L.P steam generation and thermosyphon heat recovery 75%

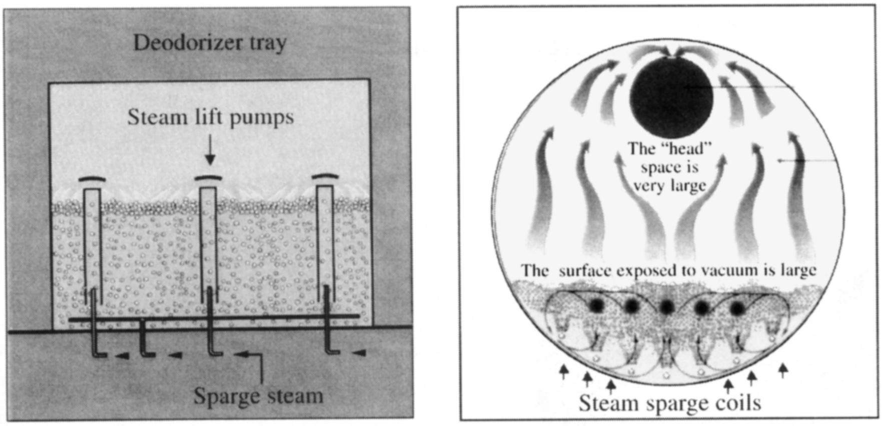
Double thermosyphon heart recovery 67%

Single thermosyphon heat recovery 45%

Fig. 13.10. Indirect heat recovery systems used in semicontinuous deodorizers (thermosyphon systems) (De Smet). LP, low-pressure steam; HP, high-pressure steam.

takes over the part of the total pressure equal to its partial pressure. As a consequence, the vapor-liquid equilibrium is reached at a lower molar fraction, x_i, resulting in the removal of significantly more volatile substances than would be possible without the use of a stripping agent. The amount of stripping agent required is directly proportional to its molecular weight. Therefore, stripping agents with the lowest possible molecular weights are selected. In most cases, steam is the best solution, but sometimes nitrogen is preferred. Because nitrogen is an inert, noncondensable gas, its use will result in lower losses (no hydrolysis) and a higher quality of the distillate. Although it is possible to work with nitrogen under the commonly applied process conditions, experiments have shown that the profitability is very uncertain, depending on the existing installations in the factory and the nitrogen supply. In any case, the stripping agent must be "dry" and free of oxygen. Superheating will ensure that the stripping agent is "dry" and that no cooling of the oil occurs. Apart from the stripping agent, all different deodorizer designs attempt to provide the best contact between the gas phase and the oil phase by creating large contact surfaces and/or thin oil films, together with an optimal sparge steam distribution. In this way, the optimum level of vaporization efficiency can be reached.

The sparge steam is introduced into the oil through special steam distributors. These can be sparge coils with very fine holes (between 0.5 and 2.5 mm) or even



Deep bed deodorizer

Shallow bed deodorizer

Fig. 13.11. Sparge steam injection systems used in deodorizers (De Smet, Tirtiaux).

sintered metal pipes. In some cases, steam lift pumps are introduced; however, their main function is to improve agitation and overall deodorization efficiency by continuously refreshing the oil in the top layer (Fig. 13.11). Deodorization occurs mainly at the vapor-liquid contact zone where the lowest operating pressure exists.

Another way to improve the evaporation efficiency is to increase the contact surface between steam and oil by means of a packed column. Packed columns have been applied in edible oil deodorization for decades. Their main function is to provide a large intimate contact between the vapor and the oil at low pressure by creating a continuous thin film of oil flowing over the packing material. Both random and structured packings are used, but the structured packing is preferred for its lower pressure drop and higher efficiency. Because stripping steam is introduced into the column in a countercurrent way, packed columns require less steam than tray deodorizers, which work according to the cross-flow principle (Fig. 13.12). Due to the very short hold-up time in a packed column, however, stripping of certain volatile components such as FFA may be sufficient, but deodorization is incomplete. Therefore, a retention vessel is usually placed after a packed column to deodorize the oil properly. The steam introduced into the retention vessel can be reused as stripping vapor for the packed column, which reduces overall steam consumption. The reuse of this "dirty" steam, however, may have a negative effect on the final oil quality.

For chemically refined soft oils, for example, a stripping steam consumption of 0.5–0.7% is reported as being sufficient for packed columns, compared with 1–1.2% for tray deodorizers, although modern tray deodorizers operate with even less steam (as low as 0.7–0.9%). In Table 13.10, a mathematical calculation demonstrates the effect of deacidification under defined conditions on the residual FFA in C_{18} oils for a conventional tray deodorizer and a packed column. As can be seen, the stripping efficiency of a deodorizer can be improved either by integrating a packed column or

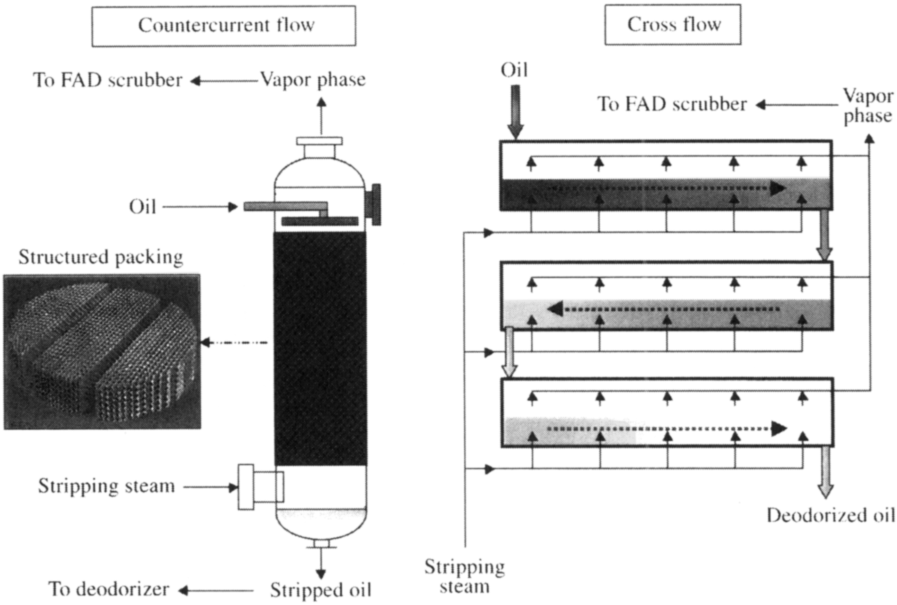


Fig. 13.12. Principle of countercurrent and cross-flow stripping. FAD, fatty acid distillate.

by reducing the operating pressure of the deodorizer. The best solution, of course, is a combination of both, but this results in a relatively expensive deodorizer technology.

In reality, deacidification is far from ideal because other factors, such as hydrolysis, pressure drop, or fouling, reduce the stripping efficiency. In addition, removal of FFA alone does not result automatically in a good oil quality because residence time, heat bleaching, and other factors determine the final quality of a deodorized oil.

TABLE 13.10 Mathematical Calculation of Residual Free Fatty Acid (FFA) Content in a C_{18} Oil Under Ideal Conditions (Efficiency $E = 1$)

Conditions	Cross-flow deodorizer			Packed column		
Theoretical trays		5			5	
Steam (kg/ton)		6			6	
FFA in (%) (chem. ref.)		0.3			0.3	
Temperature (°C)	230	245	260	230	245	260
Pressure (mbar)		3			3–4	
FFA out (%)	0.14	0.08	0.032	0.09	0.023	0.003
Pressure (mbar)		2				
FFA out (%)	0.097	0.043	0.014			
Pressure (mbar)		1.5				
FFA out (%)	0.07	0.026	0.008			

TABLE 13.11 Steam Flow Rates for Orifices of Different Size at Different Steam Pressures

Pressure (bar)	0.5	0.7	0.9	1.1	1.3	1.5	1.7	1.9
Orifice size (mm)	Steam flow rate (kg/h)							
1	0.15	0.21	0.27	0.33	0.39	0.45	0.51	0.67
1.5	0.34	0.48	0.61	0.75	0.88	1.02	1.16	1.29
2	0.61	0.86	1.09	1.33	1.37	1.82	2.06	2.30
2.5	0.95	1.32	1.70	2.08	2.46	2.84	3.21	3.59
3	1.36	1.90	2.45	2.99	3.54	4.08	4.62	5.17
4	2.42	3.38	4.35	5.31	6.28	7.25	8.21	9.18
5	2.78	5.29	6.80	8.31	9.82	11.53	12.84	14.35

A convenient way of controlling the flow of stripping steam through the steam distributors is to maintain a fixed pressure behind an orifice plate of known size. Because the pressure always falls to a low value beyond the orifice, the flow of steam will be proportional to the absolute pressure on the high side. In Table 13.11, steam flow rates are given for orifice plates of different size at different steam working pressures. Orifice plates are usually placed on each steam sparge coil to allow a consistent distribution of the stripping steam. Steam from the main low-pressure sparge steam line (3–5 bar) is distributed to the different deodorizer compartments. Before entering into the sparge steam coils, the steam pressure is reduced to the required pressure by means of a pressure-reducing valve. Usually, there is one pressure reducer per compartment to allow variable steam injection rates over the different deodorizer trays.

Vacuum Systems

The required low absolute pressure, usually between 2 and 4 mbar, is commonly generated by vacuum systems consisting of a combination of steam-jet ejectors (boosters), vapor condensers, and mechanical (liquid ring) vacuum pumps (Fig. 13.13). Liquid ring pumps are used in the final stage of the vacuum system to remove the noncondensable gases. Due to high vapor volumes to be removed, motive steam consumption in such steam-jet ejectors is quite high and may account for up to 75% of the steam consumed in a deodorizer.

A way to reduce motive steam consumption in a steam-jet ejector system with barometric condensers is to lower the temperature of the water recirculating in the barometric condensers (Table 13.12). The benefit of the lower motive steam consumption, however, must be weighted against the extra chilling capacity and consequent electrical energy to cool the barometric condenser water. Another benefit from using a lower barometric condenser water temperature is a better condensation of volatile odiferous material, which in turn reduces the odor emission problem.

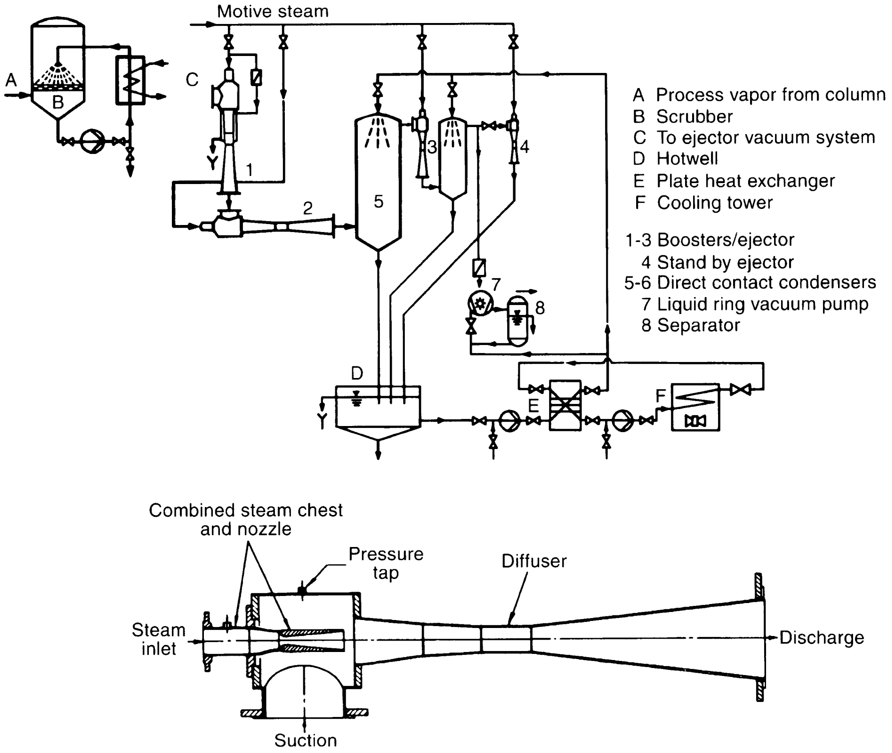


Fig. 13.13. Vacuum steam ejector system with barometric condensers used in edible oil deodorization (Korting).

Together with the condensed steam and highly volatile material, a small amount of fatty matter is usually found back in the condenser water, ~1% of the stripping steam. This fatty matter may decant partially and separate from the water. The rest of the water is usually sent to a water effluent treatment plant where it is mixed with other effluent streams from the refinery.

TABLE 13.12 Effect of Barometric Condenser Water Temperature on Motive Steam Consumption in Steam-Jet Ejector System

Pressure		Motive steam/Strippng steam	
Booster	Deodorizer	(kg/kg)	
(mbar)		30°C[a]	10°C[b]
2.5	3	4.5	1.6
1.5	2	6.2	2.5

[a] Barometric condenser water inlet temperature, 24°C; outlet temperature, 30°C.

[b] Barometric condenser water inlet temperature, 5°C; outlet temperature, 10°C.

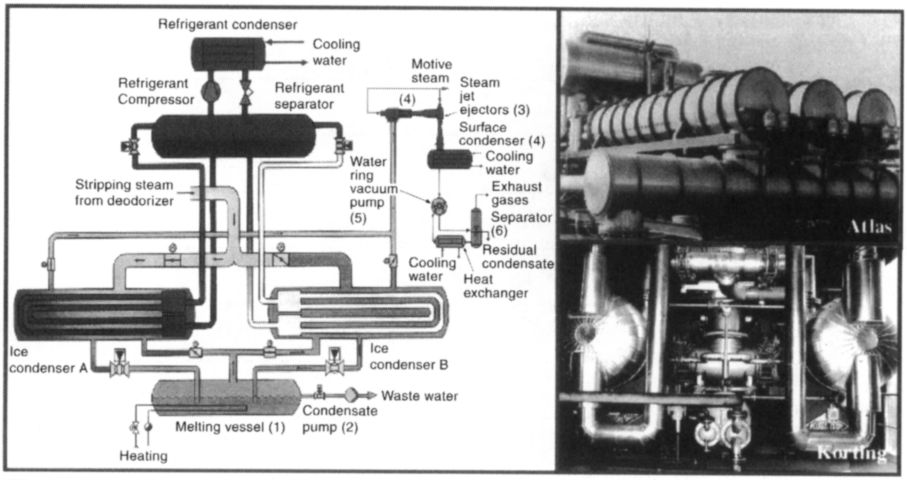


Fig. 13.14. Vacuum system with cold condensers used in edible oil deodorization (Korting, Atlas).

Special vacuum production units have been developed to reach lower pressures and operating costs and, at the same time, reduce emissions by a more efficient condensation of the volatiles. The dry condensing system (Fig. 13.14) is becoming more and more the standard in new refining plants. In this system, the sparge steam is condensed on surface condensers working alternately.

The remaining noncondensables are removed by mechanical pumps or roots blowers in series with a liquid ring pump or by a vacuum steam ejector system (booster). The dry condensation system reduces the motive steam consumption but requires extra electrical energy (Table 13.13).

Due to the relatively high capital cost for a dry condensing system, the return of investment (ROI) may take several years. The length of time depends upon the ratio

TABLE 13.13 Cost Comparison Between Classical Vacuum Plant with Steam Ejectors and a Dry Condensing Plant (Europe, 1996)[a]

Vacuum system	Capital cost (US$)	Operating cost (US$[b])	Effluent (m^3/y)	Pay back (y)
Conventional plant with boosters	80,000	222,500	20,500	—
Ice condensing plant	670,000	86,500	2100	4.3

[a] Note: The basis for comparison is the semicontinuous deodorization of oils. The costing is based on 8000 h/y continuous operation.

Deodorizer capacity (500 ton/d)	21 ton/h	Air (300 ppm)	7 kg/h
Stripping steam (12 kg/ton)	250 kg/h	Free fatty acids passing scrubber	3 kg/h
Deodorizer pressure	2 mbar	Cost of steam	20 US$/ton
Suction pressure at vacuum plant	1 mbar	Cost of electricity	0.06 US$/kwh
Vapor temperature	70 °C		

[b] Excludes cost of effluent treatment.

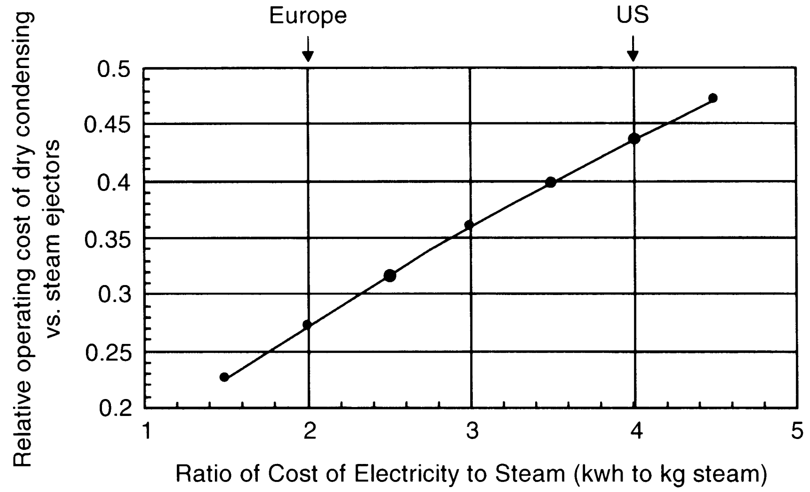


Fig. 13.15. Cost comparison between classical vacuum plant with steam ejectors and a dry condensing plant (De Smet).

between the cost of steam and electricity (Fig. 13.15). In Europe, with higher fuel costs, the production cost of steam is higher, which reduces the ROI of a dry condensing system compared with a classical vacuum system. More important than the ROI, however, is the much lower environmental effect, because much lower quantities of effluents are generated by dry condensing (Table 13.13). Condensing the stripping steam before gas exhaust by the vacuum unit largely reduces the total gas volume to be removed by the vacuum unit. To allow stripping steam to condense at such low pressures, special stripping steam condensers operating at extremely low temperatures (–30°C) are required.

Due to pressure losses caused by the oil demisters, the fatty matter scrubbers, and other equipment, the pressure in the deodorizer is always higher than at the suction side of the vacuum unit, usually between 0.5 and 1.5 mbar. To reach a deodorizing pressure of 2 mbar, a pressure of not more than 1.5 mbar at the suction side is required, which makes steam condensing more difficult than it appears (Table 13.14).

Pressure drops should therefore be minimized as much as possible through optimization of the overall deodorizer design. An overall pressure drop of <1, preferrably 0.5 mbar is achievable for a tray deodorizer. For packed columns, however, pressure drops are significantly higher because this is related directly to the packing type and size as well as the vapor and liquid load of the column. Modern deodorizers with packed columns operate with a pressure drop of 1.5–2 mbar.

Vapor Scrubbing Systems

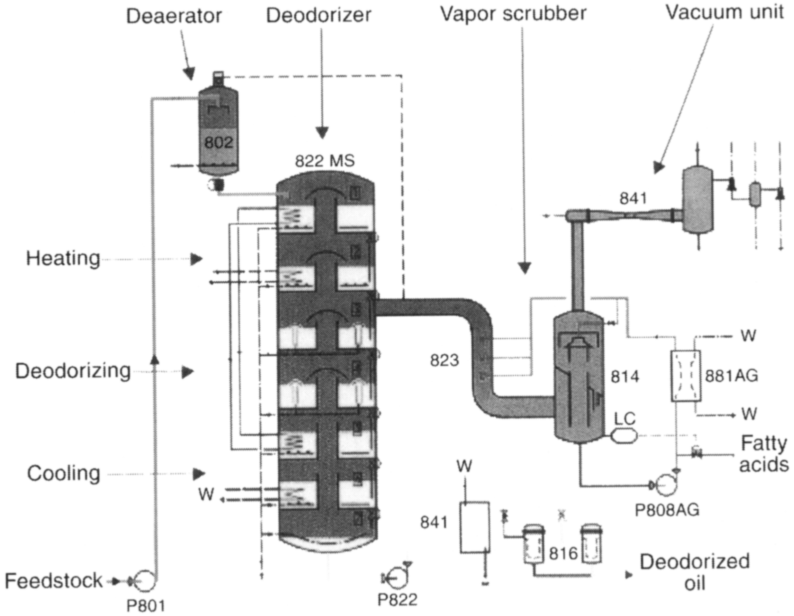
The volatile components, distilled during deodorization, are condensed and usually recovered in a direct condenser or vapor scrubber for the fatty substances (Fig.

TABLE 13.14 Effect of Suction Pressure on Condensation Point of Stripping Steam

Pressure at condenser side (mbar)	Condensation point of steam (°C)
0.5	-27.3
1	-20.3
2	-12.9
3	-8.4
5	-2.4
10	7
20	17.5
30	24.1

13.16). The vapor from the deodorizer is cooled and the volatiles condensed by creating an intimate contact between the vapor and the fatty acid distillate recirculating in the scrubber. This is done either by a series of sprayers built into the ducts or through a packed bed (random or structured packing) in the scrubber vessel. The distillate is usually kept at the lowest possible temperature (just above the melting point) to ensure the lowest possible vapor temperature leaving the scrubber.

A demister is sometimes installed at the top of the scrubber, ahead of the vacuum unit, to reduce liquid carryover of small oil droplets, which would otherwise



De Smet "Multistock" deodorizing

Fig. 13.16. Flowsheet of a stock change deodorizer (De Smet).

end up in the water from the barometric condenser or in the condensate from the cold condensers.

Apart from an efficient cooling of the vapor and condensing of the fatty matters, the pressure drop in the scrubber should be kept as low as possible because it directly affects the operating pressure of the main deodorizer. The pressure drop should be <1 mbar, preferrably <0.5 mbar.

Final cooling of the oil is usually done under reduced pressure by first pumping the oil through a heat economizer to reach a temperature of ~120–130°C, and further through a final cooler. The necessity of conducting cooling under vacuum while maintaining steam injection has always been a matter of discussion. The intent is to eliminate degradation by-products, which could appear during cooling. Due to the technological complexity and cost of this principle, cooling under vacuum is usually applied in large-capacity deodorizers, Small-capacity plants often make use of external oil-oil heat exchanging devices. Whether the difference in deodorized oil quality is noticeable remains a point of discussion yet to be resolved.

Commercial Deodorizer Systems

Deodorization can be conducted in different ways (continuous, semicontinuous, or batch). The selection of the most appropriate deodorizer technology depends on many factors such as the number of feedstock changes, heat recovery, investment, and operating costs.

Batch Deodorization

Batch deodorization is especially suitable for small capacities [<50 ton/d (TPD)], irregular production, or in processing small batches of different oils that demand minimum intermixing. Batch deodorizers consist mainly of a single-shell welded vertical cylindrical vessel (Fig. 13.17). Their major advantages are a very simple construction and a low capital cost. Low capacities, high operating costs (high steam consumption, very low heat recovery), and relatively long processing times (sometimes up to 8 h) have made batch deodorization less attractive in today's oil refining industry.

Continuous Deodorization

Continuous deodorizers are most preferred by high-capacity plants with few stock changes. The main advantages are the moderate investment costs, the possible high heat recovery, and the easy maintenance. There are several configurations of continuous deodorizers. One type is based on a series of horizontal single-shell cylindrical vessels, with agitation steam injected by multiple pipe distributors running the length of the vessel (e.g., Tirtiaux; Fig. 13.18). Heating, deodorization, and cooling/heat recovery are performed in separate horizontal vessels. The deodorizing vessels have an upper and lower deck with oil flowing from one side to the other in a shallow bed. Collection of the vapors from the different vessels is done in a separate

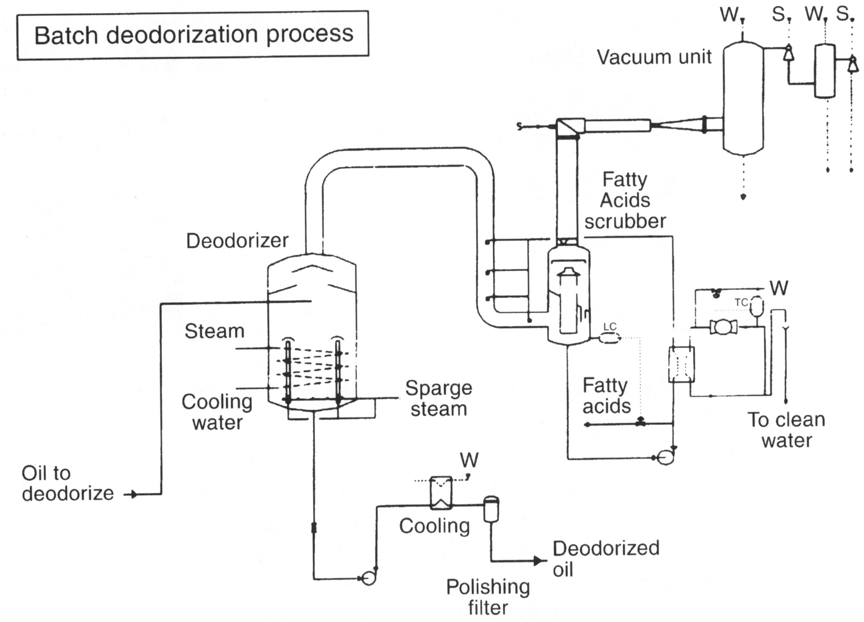


Fig. 13.17. Flowsheet of a batch deodorization process (De Smet).

vertical manifold. Scrubbing is performed in a combined spray and packed-tower-type fatty acid condenser.

Another very popular type is based on a series of trays or compartments stacked vertically in a cylindrical shell, with each tray designed to do its specific task (e.g., De Smet; Fig. 13.19). All operations, heating, deodorization, and cooling/heat recovery,

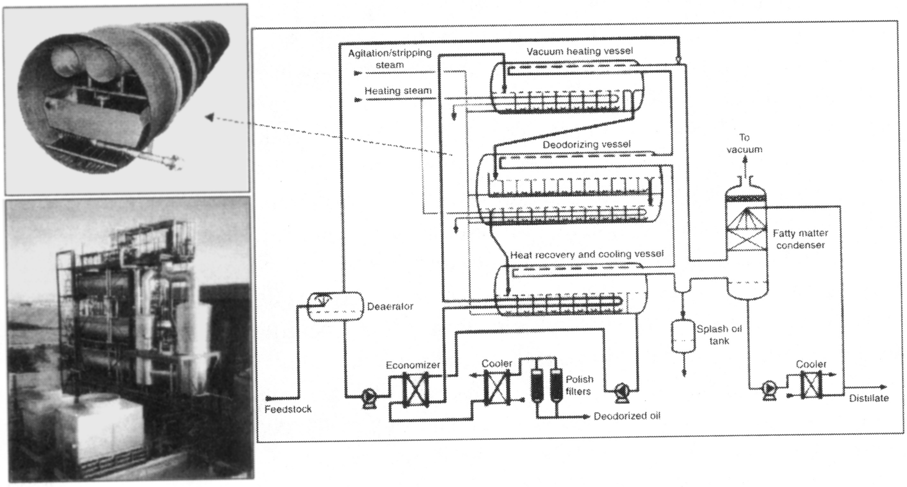


Fig. 13.18. Continuous multivessel horizontal deodorizer (Tirtiaux).

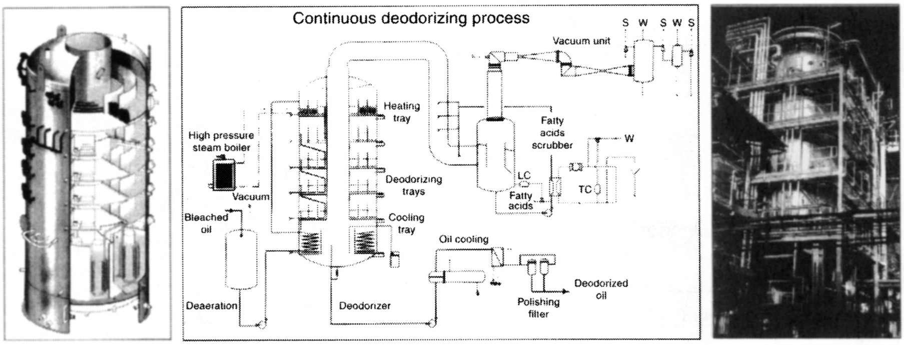


Fig. 13.19. Continuous vertical deodorizer (De Smet).

are combined in a single vessel. Steam is injected through multiple coils, sometimes in combination with gas lift pumps to ensure perfect agitation. The oil flows in a concentric path from the inner to the outer ring, ensuring a nearly perfect plug flow. The vapors from the different compartments are collected in a central chimney and sent to a separate vapor scrubber with a sprayer system. In some cases, an extra structured packing is installed in the scrubber to improve condensation and to reduce fatty matter carry over to the barometric water condenser system.

Heating and cooling are performed best under reduced pressure. Heating under vacuum reduces the flash effect, whereas cooling under vacuum allows removal of flavors, formed during cooling. The single vessel concept allows an easy installation and maintenance as well as reducing the risk of air leakages.

The packed column deodorizer provides a maximum surface-to-volume ratio during thin-film processing. This is achieved by the use of a structured packing over which deaerated and fully heated oil flows while stripping steam is added countercurrently (e.g., Alfa Laval; Fig. 13.20). A structured-type packing with a surface of ~250 m^2/m^3 is used most commonly. Packed columns typically have a bed height of 4–8 m and a capacity of ~10 ton/(h·m^2 cross section) at a pressure drop of 0.2–0.5 mbar/m packing. Although this system provides excellent fatty acid stripping with a minimum of steam, due to the relatively short retention time, it does not provide a great deal of heat bleaching and effective deodorization. To overcome this, a retention vessel is provided as part of the system, before or after the thin film device.

Packed columns are often installed to increase the capacity of existing deodorizers. Their main function is to reduce the vapor load of the deodorizer vessel by pre-stripping the main part of the volatile material. The deacidified oil is then sent to the deodorizer for the final deodorization. In the palm oil industry, for example, the FFA level is reduced from 3–5% to <0.5%, before the oil enters the deodorizer vessel. This has led in some cases to a doubling of the capacity of the deodorizing plant. Overall steam consumption for a given final acidity is lowered at the same time. However, the oil is often found to be somewhat lower in quality, probably as a consequence of an insufficient residence time or a too low consumption of stripping steam.

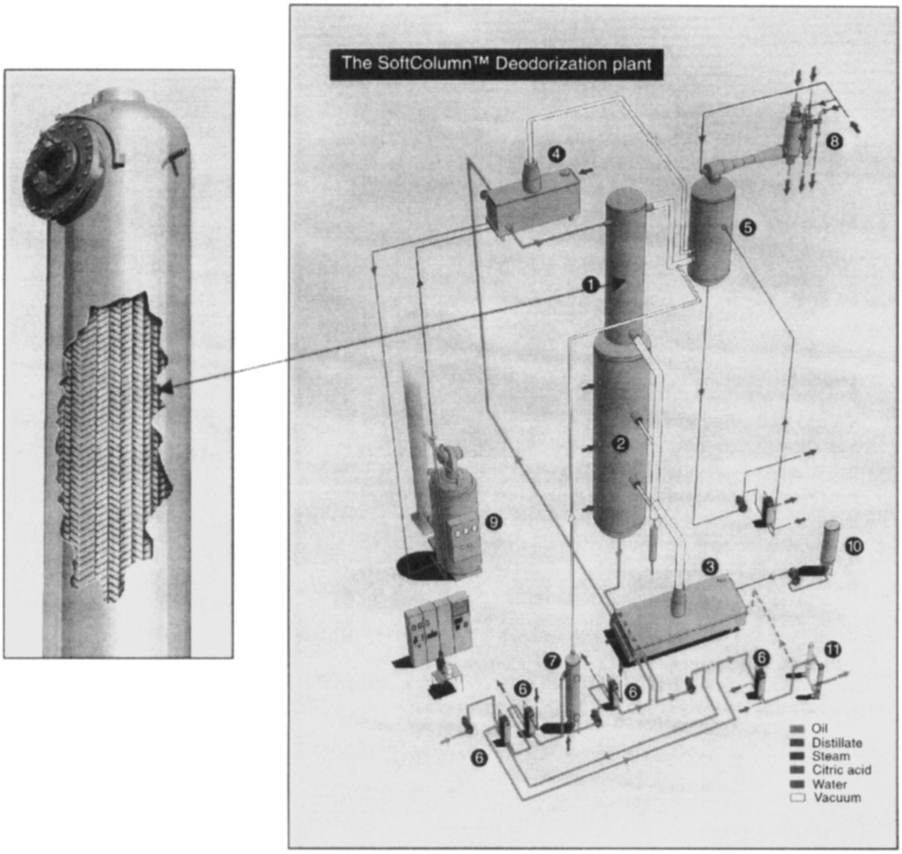


Fig. 13.20. Packed column deodorizer (Alfa Laval).

Due to the very high oil-metal contact surface in packed columns, the risk of fouling is higher. A more frequent cleaning of the packed column is therefore required to secure a consistent oil quality and at the same time prolong the useful life of the structured packing. The frequency of cleaning as well as the efficiency of the structured packing material in packed columns is strongly determined by the type of oil processed, the frequency of plant shutdowns, and feedstock changes, as well as by the purity of the feedstock and the air tightness of the deodorizer equipment. Packed columns running on physically refined oils, for example, require more frequent cleaning (once every 6–10 mo), and their structured packings are replaced more frequently (every 2–3 y) than when processing chemically refined oils (cleaning once every year and a lifetime of 3–4 y).

For other specific cases, packed columns provide an excellent solution. The increasing interest in tocopherol recovery from vegetable oil fatty acid distillates, for example, requires a very efficient distillation device. Due to the low volatility

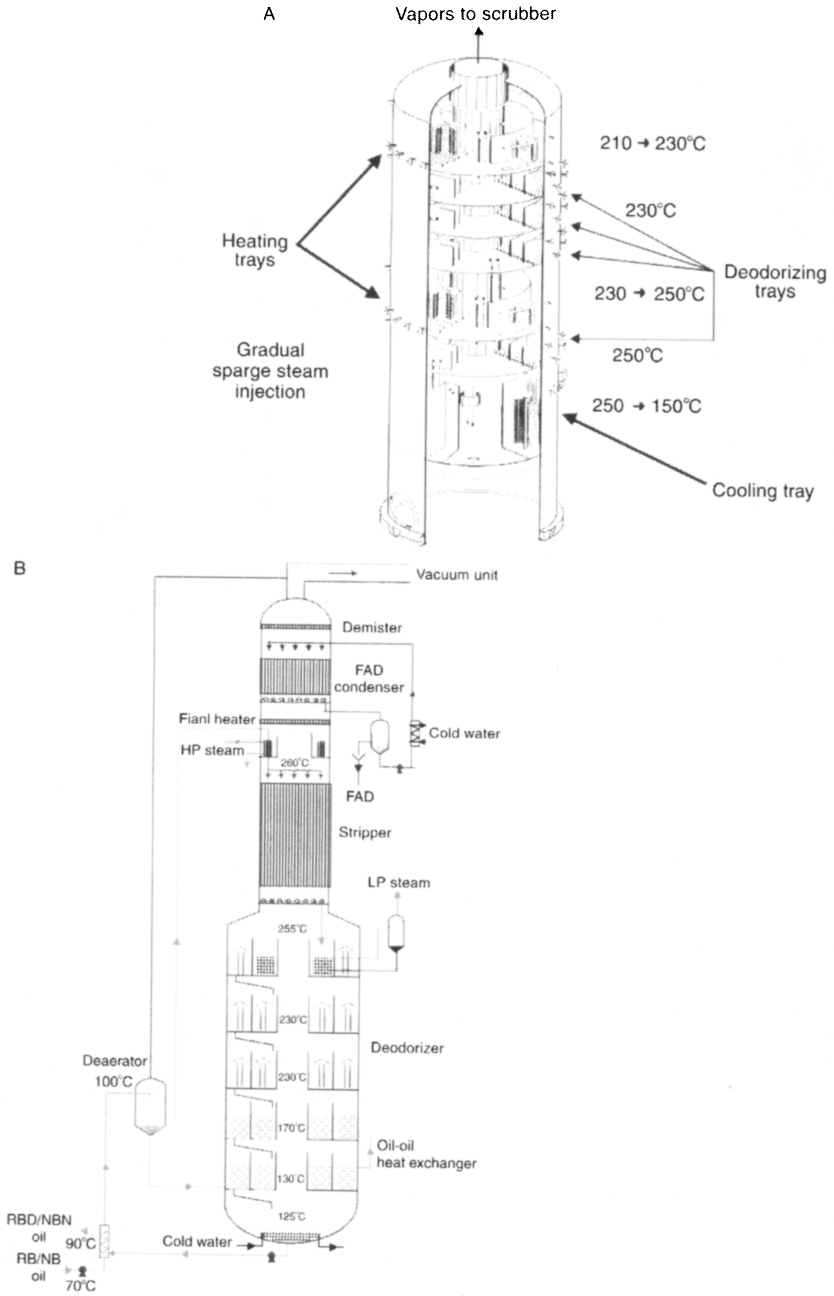


Fig. 13.21. (a) Dual Temp L/H continuous deodorizer (De Smet); (b) Dual Temp H/L deodorizer with packed column. FAD, fatty acid distillate; HP, high pressure; LP, low pressure; RBD, refined, bleached deodorized.

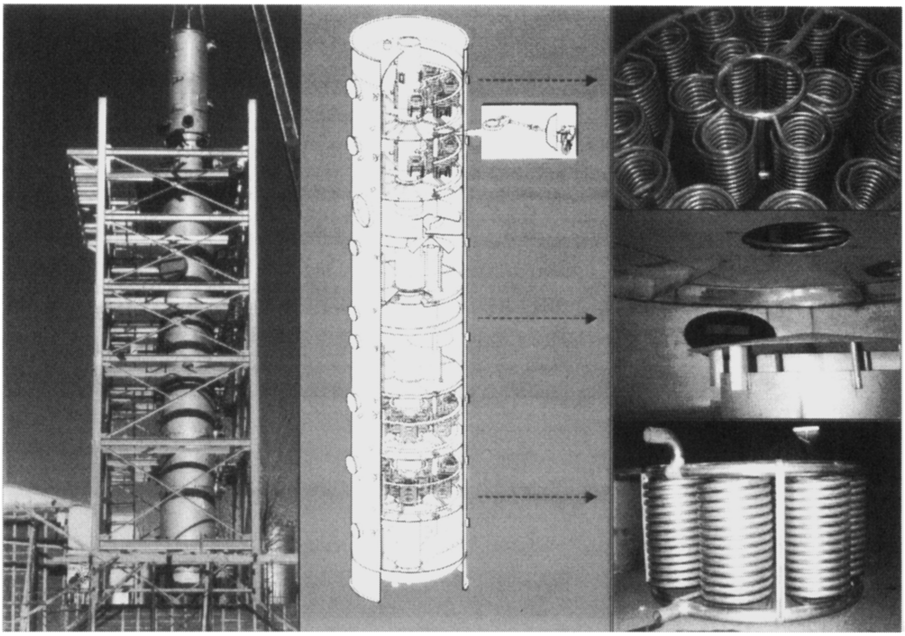


Fig. 13.22. Multistock semicontinuous deodorizer for frequent stock changes (De Smet).

of tocopherols, (see Fig. 13.2) and low concentrations (0.12–0.15% in soybean oil, for example), a high temperature (260°C) and high stripping steam consumption (2–2.5%) are required in a conventional tray deodorizer. However, this may induce other unwanted side reactions, such as the formation of *trans* fatty acids or more oil carry over.

A packed column may be a good solution in this case because the residence time at high temperature is very short (a few minutes) and steam consumption is lower (~1.5%). Special processes have been developed to respond to such special cases. A recent development is based on a dual-temperature concept in which a packed column operating at high temperature is combined with a deodorizer operating at a lower temperature; the latter is placed behind or in front of the packed column stripper (Fig. 13.21).

Semicontinuous Deodorization

Semicontinuous deodorizers are basically batch systems designed for larger capacities. Their main application is in plants with frequent feedstock changes of oils sensitive to intermixing. In most designs, a batch of oil is transferred into the system and then sent by gravity in a time sequence through a number of vertically stacked compartments or trays (Figs. 13.16 and 13.22). The semicontinuous design allows a more efficient heat recovery than a batch system. Heat recovery is performed by means of indirect economizers (see Fig. 13.10). Steam produced in the bottom deodorized oil cooling section is sent in a closed thermosyphon loop to the top bleached oil heating section to heat the incoming oil. A single thermosyphon system has a recovery efficiency of ~50%. With a double system, coupled with a low pressure steam production device, up to 75% of heat can be recovered.

Today, even for small capacity plants (10–50 TPD), semicontinuous deodorizers are clearly more suitable than conventional batch deodorizers. The shorter hold-up time in a semicontinuous deodorizer is a good argument in its favor, even in cases in which small capacities with very frequent feedstock changes are required. Compared with continuous systems, the main advantages of semicontinuous deodorizing are its shorter time for feedstock change and its much lower intermixing. Heat recovery is less efficient, however, than in continuous operation, e.g., 10–20% more sparge steam is also required.

Losses During Deodorization

In addition to the inevitable losses such as FFA, secondary oxidation and hydrolysis products, tocopherols, sterols, and other volatile products, a relative amount of refined oil is entrained in the vapor and lost as such in the distillate. The amount of this "neutral oil" is related to the initial acidity and composition of the oil.

Furthermore, the losses increase with higher deodorizing temperature, lower pressure, and larger amount of stripping steam. Part of the mechanically distilled oil droplets can be recovered by installing baffles and demisters in the vapor chimneys. In some cases, part of the neutral oil lost during deodorization is a consequence of an effective evaporation of glyceridic components. In coconut oil, for example, short-chain mono- and even diacylglycerols are distilled during deacidification (Table 13.15). They should be counted as distillation losses, but are usually considered as part of the neutral oil loss (NOL).

Oil losses during deodorization are usually higher for physically refined oils than for chemically refined oils. This is mainly a consequence of the higher acidity before deodorization, but also of the presence of volatile components and impurities in physically refined oils which, in the case of chemically refined oil, were already removed during neutralization (e.g., monoglycerides). Therefore, when comparing chemical and physical refining, one should consider the overall refining loss rather than only the NOL during deodorization. That loss can be approximated from the initial and final acidity of the oil and the acidity of the fatty acid distillate (FAD) as follows:

$$\text{FAD flow (\%)} = (\text{FFA}_{\text{OIL IN}} - \text{FFA}_{\text{OIL OUT}})/(\text{FFA}_{\text{FAD}} - \text{FFA}_{\text{OIL OUT}})\cdot 100 \qquad [10]$$

$$\text{NOL (\%)} = \text{FAD flow}\cdot(100 - \text{FFA}_{\text{FAD}})/100 \qquad [11]$$

Example:
Physical refining: $\text{FFA}_{\text{OIL IN}} = 2\%$, $\text{FFA}_{\text{OIL OUT}} = 0.03\%$, $\text{FFA}_{\text{FAD}} = 80\%$

$$\text{NOL (\%)} = 0.49\%$$

TABLE 13.15 Melting and Boiling Points of Some Fatty Acids and Glyceridic Components

Component Chain length	Fatty acid	Monoglyceride	Diglyceride	Triglyceride
	Melting point (°C)			
C_6	-3.4	19.4	—	-25
C_8	16.7	—	—	8.3
C_{10}	31.6	53	44.5	31.5
C_{12}	44.2	63	57.8	46.4
C_{14}	54.4	70.5	66.8	57.0
C_{16}	62.9	77	76.3	63.5
C_{18}	69.6	81.5	79.4	73.1
$C_{18:1}$	16.3	35.2	21.5	5.5

Component Chain length	Fatty acid	Monoglyceride	Diglyceride	Triglyceride 0.05 mm Hg
	Boiling point (°C) at 1 mm Hg			
C_6	61.7	—	—	135
C_8	87.5	—	—	179
C_{10}	110.3	175	—	213
C_{12}	130.2	186	—	244
C_{14}	149.2	199	—	275
C_{16}	167.4	211	—	298
C_{18}	183.6	190 (0.2 mm Hg)	313	
$C_{18:1}$	—	186 (0.2 mm Hg)	308[a]	

[a] For olive oil.

Chemical refining: $\text{FFA}_{\text{OIL IN}} = 0.1\%$, $\text{FFA}_{\text{OIL OUT}} = 0.03\%$, $\text{FFA}_{\text{FAD}} = 30\%$

$\text{NOL}\ (\%) = 0.16\%$

In practice, NOL are usually higher as a result of side reactions (e.g., hydrolysis, polymerization) occurring during deodorization; these are more difficult to quantify.

Deodorized Oil Handling and Storage

Deodorized oils require particular handling and storage conditions to avoid oxidation or other processes that may reduce the quality. Flavor deterioration, in particular, and, to a lesser extent, color reversion may appear if the oil is not properly protected. Nitrogen blanketing and storage at low temperature in stainless steel tanks protect the oil against oxidation when stored in bulk for extended periods. Modern processing plants are usually equipped with an inert gas blanketing system through the different refining stages. All parts in contact with the oil are best made of stainless steel (minimum SS 304) to avoid migration of metal to the oil. Furthermore, the storage temperature is kept as low as possible because the autoxidation rate increases with increasing temperature. In general, the rate of oxidation doubles with each 15°C increase. It has become common practice to add a small amount of citric acid to the oil after deodorization because it improves the flavor stability and at the same time acts as a metal scavenger. Usually between 20 and 50 ppm of citric acid is added. Some refiners even add expensive antioxidants such as tocopherols, which were removed during deodorization, back to the oil. It seems more logical to prevent the oil from losing too many natural antioxidants during deodorization by using less severe conditions.

In a modern refining operation, end product storage is minimized because oil is shipped in bulk or bottled as soon as possible. Furthermore, there is an increasing tendency to integrate the refinery with the finishing lines in the crushing plant to reduce intermediate and final oil storage. Despite careful measures taken during bulk handling and shipment to industrial customers, a large part of the refined oil is redeodorized before its final use. This redeodorization serves to remove small off-flavors formed during transport and storage. Redeodorization normally requires less severe conditions, i.e., a lower temperature (180–230°C), a higher pressure (3–5 mbar), a small amount of steam (0.5–0.7%), and a shorter residence time (20–30 min) are applied.

Bottled oils, on the other hand, are well protected against oxidation, but are often filled in transparent plastic bottles for the retail market. Light deterioration, however, is an important factor in storage stability. Direct sunlight, in particular, and large temperature drops during storage strongly reduce the shelf life of the oil and should therefore be avoided as much as possible.

Future Challenges

With the ongoing investigations to define more properly the nutritional quality of oils, the deodorization concept is changing continuously. In the past, deodorization was focused mainly on achieving the best organoleptic quality (i.e., a bland taste, no odor, and a light color) and a high stability (long shelf life, long oxidative and cold stability), whereas more attention is given now to the real parameters of nutritional quality. The lowest possible levels of *trans* fatty acids, degradation, and polymerization products are required with maximum preservation of the natural antioxidants and vitamins. New deodorizers must reply to a whole range of requirements. They should be able to run under a range of conditions and permit easy feedstock change with minimum contamination, highest heat recovery, and lowest operating cost.

To do so, new vacuum systems have been developed to reach lower operating pressures, as low as 1 mbar in the deodorizer section. New dual-temperature deodorizers operate at different temperatures to reach the best compromise between residence time for deodorizing (at low temperature) and heat bleaching and final stripping at high temperature (for a short period). In some cases, packed columns are integrated to improve stripping efficiency, when needed. New heat exchangers are being developed to improve heat recovery, and more efficient sparge steam distributor systems have been designed to reduce steam consumption.

The increasing environmental pressure to limit pollution coming from refineries and crushing plants as much as possible makes further improvement of the air cleaning systems and effluent treatment plants necessary. Some exciting challenges in the oil refining industry exist for the future. The introduction of completely new technologies, such as ultra- and microfiltration for oil purification, will without doubt affect future refining and deodorization operation in particular.

Suppliers for Oil Deodorizing Processes

In addition to the equipment suppliers already mentioned in this chapter, there are a number of other suppliers of commercial deodorizer systems for oils and fats. It is not possible to describe in detail the features of every commercial deodorizer design available today. Table 13.16 lists the primary international suppliers and the main characteristics of their deodorizer products.

In addition to the deodorizer types described here, there are also other designs, including one custom-designed for a specific company. Generally, deodorizers are purchased as a unit on the basis of performance guarantees, utility requirements, and

TABLE 13.16 Main International Suppliers for Oil Deodorizing Processes

Supplier	Country	Main products	Typical characteristics
Alfa Laval	Sweden	Soft column	Vertical single-shell thin film deodorizer (packed column)
Andreotti	Italy		Multivessel vertical deodorizer
Campro	Canada		Horizontal multisectional tray-in-shell deodorizer
CMB	Italy		Vertical multitray deodorizer (with optional packed column prestipper)
Crown	U.S.	Diflow	Vertical shallow bed cascade deodorizer with sintered sparge steam pipes
De Smet	Belgium	Unistock	Vertical all-in-one single-shell continuous cross-flow deodorizer
		Multistock	Vertical multitray stock change deodorizer with thermosyphon heat recovery
		Dual Temp	Vertical two-temperature deodorizer with optional packed column
H.L.S.	Israel		Vertical deodorizer design with multiple trays in single shell
Kirchfeld	Germany		Horizontal multivessel shallow bed (Lau type)
Krupp	Germany		Vertical single-shell cross-flow continuous deodorizer with spiral trays
Lurgi	Germany		Vertical multistage single-shell deodorizing column
Oiltek	Malaysia		Vertical deodorizer with sectioned baffle trays (with separate prestripper)
Sket	Germany		Packed column vertical deodorizer
Tirtiaux	Belgium		Horizontal multivessel shallow bed deodorizer (Lau type)

quality of finished oil. Furthermore, the engineering competence and technical support of the supplier, as well as the after sales service and financial credibility, are becoming more and more important factors in the final decision.

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Chapter 14

Packaging and Bulk Handling of Edible Fats and Oils

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Introduction

The final step in the processing of edible fats and oils is packaging. A package holds the contained product inside, protects it from external attacks, and identifies the contents. Processed fats and oils are packaged after deodorization in containers designed for home, restaurant, or food processor use. Package selection requires serious consideration because the product quality and cost of the finished products are dramatically affected by the container. The edible fats and oils package contains and protects the products until used by the consumer. A product that has been processed carefully to obtain optimum palatability, performance, and nutrition can be maintained or lost by the selection of its packaging material. Therefore, an effective package is one that delivers a satisfactory product to the user at the least cost (1).

The last step in edible fats and oils process in which the properties are intentionally altered is deodorization. When the conditions of the preceding processes and the quality of the raw materials have been satisfactory, the result is a tasteless, odorless, light-colored product, free of hydroperoxides and contamination. The packaging, handling, and storage methods for these finished products must be directed toward protection of the achieved quality. Primarily, the products must be protected against oxidation deterioration, contamination by water, dirt, and other foreign materials, absorption of foreign odors and flavors, thermal decomposition, microbiological contamination, hydrolysis, and the packaging materials themselves. With this objective, the principles for packaging are quite general for all fats and oils products intended for human consumption, e.g., liquid oils, shortenings, margarines, flakes, emulsifiers, and other specialty products (2).

It is not customary for fat and oil processors to store large quantities of finished products; common practice is to package the edible oil products and ship them to the customer as soon as possible after deodorization. Deodorized oil is at its peak of quality as it exits the deodorizer, and quality decreases subsequently over time (3). The packaging materials and the practices employed for edible oils determine the product protection that delays quality deterioration. A package contains and protects the product from oxidation and other contaminants starting at the processor and continuing through usage by the consumer. An ideal container provides the following four important attributes: (i) product protection; (ii) cost effectiveness; (iii) end use application; and (iv) appealing appearance. Preservation practices and measures that may be employed for fats and oils are nitrogen protection, temperature control, light avoidance, and the addition of protective additives approved by product or customer specification, e.g., antioxidants, chelating agents, or antifoaming agents.

Packaging Development

Packaging in some form has been used since prehistoric times. Nature provided packages before humans were able to develop technologies to produce packaging. Animal skins and bladders were used as pouches. Leaves and tree bark were wrappers. Gourds and hollow tree trunks served as containers for liquids and powders. The first man-made package was probably a pot fashioned from wet clay with subsequent firing for functionality and durability. Broken jars have been found in Egypt with oil residues dated back to the 6th century B.C. The oil residue has been identified as a mixture of beef tallow and coniferous oils.

Containers reflective of today's usage began to appear during the industrial revolution when the world started to change from a rural economy to an urban-technological economy. Paper containers probably originated in Germany during the 16th century when paper workers used some of their own by-product to wrap their writing paper. Andreas Bernhart produced the earliest known form of printed wrapper at his paper mill on the Ocker in 1550. In 1657, a marked bottle was used for wine. Packaging requirements in the 1700s allowed one at a time, handmade, and hand-lettered bottles to meet the demand. Apparently, the demand for packaging materials increased in the 18th century to provide the impetus for Nicolas-Louis Robert to invent a paper-making machine in 1798. Alois Senefelder invented the principle of lithography in the same year. Shortly thereafter, American firms combined the two technologies to produce a more complete package. Rapid developments of machinery to replace hand labor occurred during the industrial revolution of the 19th century. The increased productivity affected products and packaging alike; one significant packaging development of this era was the tin can and the machinery for its manufacture (1).

Tin containers of various shapes and sizes became the preferred package for many of the major fats and oils products. This package preference continued well into the 20th century because these containers provided most of the following attributes of a perfect fats and oils package: (i) tin plate is not a strong catalyst to accelerate oxidation like many other metals; (ii) the product is kept in the dark, which protects it from oxidation catalyzed by light; (iii) airtight to protect the product from oxygen and foreign odors; (iv) practically unbreakable and provides good protection from dirt, moisture and other contaminants; (v) tamperproof capabilities; (vi) user friendly, easy to handle, and reusable by the consumer; (vii) light weight; (viii) cost effective; and (ix) appealing appearance.

Another traditional container for edible fat and oil products was glass blown of flint glass. Flint glass is a clear, uncolored glass that is produced by melting and fusing silica and an alkali such as soda ash or lime. Glass has most of the attributes listed for tin cans with the obvious exceptions that it is breakable, moderately heavy, and usually transparent. This transparency has been shown to be both an advantage and a disadvantage. It allows the customer to view the product before purchase but at the same time it allows light to attack the product. Amber glass was found to nullify the influence of light on the product's flavor and odor (4); however, retail consumers rejected this package in favor of clear glass bottles (5).

Paper products can also be classified as traditional packages for fats and oils products. During World War II, paper containers were adopted for a number of fats and oils products when metal was disallowed for civilian food products (6). Parchment and paper foil laminate have been the packaging materials of choice for butter and margarine prints for many years. The prints were encased in a wax-coated or foil-laminated carton. Most of the primary fats and oils packages for margarine, butter, shortening, and liquid oil containers were also encased in a corrugated fiberboard shipping container. Before the widespread adoption of plastic packaging materials, the traditional packaging material in the United States for the various fats and oils products had evolved as described in Table 14.1.

Plastics have replaced many of the traditional metal and glass fats and oils packaging materials over the past few decades by providing a more user friendly product. The different plastic resins can be shaped into containers resembling those traditionally accepted or into new improved packages with many advantages. Plastic containers have all of the attributes listed for tin and glass with the following additional qualities: (i) lighter weight, which saves on shipping expense; (ii) uniform weight, which gives improved weight control; (iii) almost unbreakable; (iv) clear or opaque, as required; and (v) lower cost.

Packaging represents the second most significant portion of the total cost of finished fats and oils product after raw materials. These costs and other advantages have encouraged many large fats and oils users to install facilities to handle these

TABLE 14.1 Evolution of Packaging Materials in the United States

Fats and oils products	Traditional container
Liquid oils	
Retail	Flint glass bottles
Foodservice	5-gal metal cans
Food processor	55-gal closed-head metal drum
Shortenings	
Retail	3-lb metal can
Foodservice	50- and 110-lb round metal can with replaceable lid
Food processor	55-gal open-head metal drum
Margarines	
Retail	Parchment or foil laminate–wrapped prints in a wax-coated fiber board or foil laminate carton
Foodservice	Parchment-wrapped 1/4- or 1-lb prints
Food processor	50- and 110-lb round metal can with replaceable lid

ingredients in bulk. First, large industrial users of cooking and salad oils that could be maintained at ambient temperatures installed bulk handling facilities. These installations were followed by fats and oils handling that required additional equipment, i.e., more complex unloading facilities, temperature-controlled storage, and chilling and plasticization capabilities for shortening and margarine-type products. All of the fats and oils products packaged for shipment can be delivered to the customers in tank cars or trucks with the exception of margarine emulsions, which contain moisture and salt. Bulk handling of the fats and oils products substantially reduces the product cost to the food processor by eliminating packaging materials, labor to package and unpackage, and the disposal costs of the used packaging supplies. The bulk handler does have increased costs for quality and labor to handle the bulk ingredients in addition to the capital expenditures for the handling equipment.

Liquid Oil Packaging

Before the 1970s, oils for the retail and industrial markets were traditionally packaged in glass bottles, tin-plated cans, and steel drums. Although these materials are still in use today, plastics have taken control of this market mainly as a result of consumer preferences and reduced costs. Today, glass and metal containers are used for gourmet or specialty oils, such as olive oil, to signify a premium product. Consumer liquid oils in the United States are currently packaged in 8-, 16-, 24-, 32-, 38-, 48-, and 64-oz rectangular-shaped, clear, plastic containers, as well as 1-gal opaque plastic containers. The liquid oils produced for the food service and food processor markets are packaged in larger containers designed for their requirements.

Consumer Liquid Oil Packaging Materials

Glass bottles, which replaced tin-plated cans in Europe and the United States for liquid oils packaged for the household consumer, were well established as the efficient package for retail consumer oils until the mid-1980s. Then, plastic replaced glass as a result of consumer preference for lightweight, unbreakable, and easily handled containers with added benefits of improved economics effected by lower package costs, reduced transportation costs, and equivalent product protection. Initially, extrusion-blown polyvinylchloride (PVC) bottles were used for the smaller sizes to provide the required oxygen barrier needed for oils, and high-density polyethylene (HDPE) was used as a lower-cost alternative for the larger sizes with smaller surface-area-to-volume ratios. Polyethylene tetraphthalate (PET) bottles captured significant market shares in Europe, Japan, and the United States in the later 1980s due primarily to clarity. Today, most consumer oils are bottled in stretch-blown PET, which orients the molecular chains, improving strength and other physical properties. The resulting lightweight containers offer excellent strength, toughness, and clarity compared with the other plastic resins, while providing adequate protection from oxygen permeation to achieve acceptable shelf life for the oils (7). The plastic bottles are typically the same volumetric size as their original glass counterparts but smaller in exterior dimensions and in weight because the plastic bottle has a thinner wall and is lighter. A major concern with plastic containers is the possibility of either off-flavor or flavor scalping. Off-flavor can occur when the product takes on an odor from the bottle. Flavor scalping occurs when the plastic in the bottle takes some of the flavor note from the product; this is not a common occurrence with the bland liquid oils but can occur with specialty flavored oils.

Industrial Liquid Oil Packaging Materials

Plastic containers replaced tin plate for the larger industrial-sized containers long before consumer packaging was converted to these materials. The HDPE opaque plastic containers were much less of a change, except for lower material costs, from the traditional 1- and 5-gal can containers than were the glass containers used for consumer oils. Liquid oils for foodservice customers are currently packed in 5-qt, 1-, 2 1/2-, and 5-gal reclosable, reusable, opaque plastic containers. Liquid oils are also packed in 55-gal closed-head steel or plastic drums for the larger foodservice and food processor customers.

Liquid Oil Filling Equipment

Oil is typically filled into a container using a liquid filler that fills from the bottom up. This simply means that the filler nozzle is inserted into the bottom of the bottle before the product begins to flow. As the filler nozzle is elevated, the product flows into the bottle displaying an "onion" like appearance as it flows to the outer wall. This is done to minimize the entrapment of air within the oil during filling. Any entrapped air will eventually rise to the surface of the bottle creating excessive headspace, which can result in a bottle with a lower fill level (called a short-fill). Consumers will reject short-filled bottles as under weight even if the weight exceeds the labeled amount. Because filling is the critical component of a packaging line, it is important that the bottle be filled as quickly as possible with a minimum of entrapped air. Numerous filler nozzle designs have been developed and are in use to accomplish this task.

Modified-Atmosphere Packaging

The purpose of modified-atmosphere packaging (MAP) for liquid oil packaging is to eliminate oxygen from the bottle, thus reducing oxidation to prolong the shelf life of the liquid oil. Two methods are available to achieve MAP. The first is to flood the bottle with an inert gas such as nitrogen before filling. The gas is heavier than air and will settle in the bottle. As the liquid enters the bottle, the gas simply overflows from the neck of the bottle leaving only inert gas in the headspace. The second method is to flood the headspace with the inert gas after filling. Both methods are being used successfully.

Hermetically Sealed Containers

After the bottle is filled, it is important to seal the bottle to retain the inert gas atmosphere to ensure the intended shelf life of the product. Hermetic seals are airtight to prevent the transmission of the interior gas from the package to the outside or *vice versa*. A hermetic seal is typically achieved by one of two methods. One method is the application of a membrane to the neck of the bottle before application of the cap. The membrane must be positioned and sealed to the neck of the bottle using a conductive sealing system and the cap immediately applied to the bottle. The second method is to have the manufacturer preinsert a membrane into the cap. After the cap is applied to the bottle, the membrane is sealed to the bottle neck using an inductive sealing system. The first method requires additional capital to provide a separate process for placing the membrane on the bottle; however, the material costs are lower with this alternative. The second methods requires a lower initial expenditure for equipment but the material costs are higher.

Leakers

Liquid oil containers that allow the oil to escape due to a misapplied cap, a missing seal, a pin hole, high-altitude rupture, or some other cause are called leakers. This is a major problem with consumer packaging because one leaking bottle within a pallet of product can damage the entire pallet. Some of the preventative measures to control the occurrence of leakers are as follows: (i) adequate quality control by the bottle supplier; (ii) proper sealing of the bottles on the filling line; (iii) control of the headspace within the bottle to minimize internal pressure; and (iv) careful handling of the packages during distribution.

High-Altitude Shipment

It is important to minimize the amount of headspace in bottles that may be shipped through high altitudes. Air trapped in the headspace expands as the altitude increases to create a higher pressure within the container. If severe enough, this internal pressure can cause ruptures at the seal or at a weak region of the container to create a leaker. Typically, the greater the headspace in a bottle, the higher the possibility of bottle damage during high-altitude shipment. Damage during high-altitude shipment increased dramatically after the change from glass to plastic because plastic is not as strong as glass and the manufacturers' effort to lightweight the containers to save on plastic costs.

Shortening Packaging

Shortenings appear to be solid materials, but in reality are predominately fluids. A household shortening with a plastic-like consistency consists of ~25% crystalline solid triglycerides suspended in liquid triglycerides. All fats and oils are polymorphic, which means that with cooling, a series of increasingly organized crystal changes occur until a final crystal form is achieved. This crystallization process is initiated during the chilling process just before packaging, and the crystal structure is developed and stabilized during the tempering process immediately after packaging. Creaming gas is incorporated into shortenings at 13 ± 1% for texture improvement, providing a white creamy appearance and a satin-like surface sheen with improved handling characteristics. Therefore, shortening packaging materials must have the ability to contain the supercooled, semifluid product filled at relatively high pressures. During tempering, usually at 85 ± 5°F (29.4 ± 2.8°C) for 48 h, the heat of transformation must be dissipated as rapidly as possible. If the shortening is allowed to retain this heat by virtue of the product or package thermal-insulating capacity, an appreciable portion of the crystal might be melted and subsequently transform the product into an undesirable consistency. After tempering, the package must protect the shortening from the handling and temperature variations encountered in distribution.

Household Shortening Packaging Materials

The tin-plated, cylindrically shaped, metal can with a key opening tear strip and a captive lid was the standard U.S. household shortening container for many years. These 1- and 3-lb containers were filled carefully so that the shortening surface was smooth, had a satiny sheen, and a curlicue on the top, just barely touching the center of the lid. Shortening cans were filled and allowed to solidify on a slow-moving time-delay conveyor before the lid was seamed on and the label applied to avoid sloshing the shortening to one side of the container and presenting an unsightly appearance to the homemaker.

The standard metal can has undergone several cost reduction changes since the 1960s. First, the expensive tear strip and key were eliminated and replaced with a plastic overcap to reclose the can after the lid was removed with a standard can opener. Next, the tin plate in the body of the can was replaced by a fiber-wound composite material. The composite material was made of a laminate of dissimilar materials, commonly polyethylene, polypropylene paper, and foil. The barrier properties of these various materials provide the necessary protection from the elements as do the various plastics used in the manufacture of plastic bottles. Household shortenings are also packaged in opaque HDPE plastic containers, but the composite containers are the most prevalent because they cost the least. Both the composite and plastic cans are hermetically sealed to provide the necessary product protection. Initially, the lid and bottom of the composite and plastic cans remained tin plate, requiring the homemaker to open them with a can opener. Now, the metal lid has been replaced with a peelable membrane that has a plastic overcap for reclosure between uses. The easy peelable opening feature solved the major consumer complaint with the metal-seamed can end package of "impossible to open with an electric can opener." The peelable opening also provided two other advantages, i.e., safety because there were no sharp edges to cut the consumer's fingers and lower costs. One constant throughout all of these changes has been the cylindrical shape (and general appearance) of the container.

Household shortenings have also been packaged in glass jars, cellophane bags, parchment-lined cartons, and metal or plastic pails with pressure closure lids. Many of these shortening packages, with the exception of the glass jars, are still used for shortening products, at least on a regional basis. The most recent shortening package introduction for consumer shortenings was the shortening stick. Packaging for this product has changed from a parchment-wrapped 1/4 lb stick similar to the margarine print formed on Morpak equipment, to a parchment-wrapped stick in a foil container. The focus of this packaging concept was to offer a convenient package to smaller households where all of the members have full-time employment away from the home (8).

Consumer Shortening Filling Equipment

The commonly used filling machines are rotary-positive displacement volumetric machines. This type of filler employs a rotating table onto which the empty can is fed. A feed hopper rotates above it. The shortening feed is delivered to this hopper at ~300–400 psig; it is discharged at substantially atmospheric pressure through an extrusion valve. Measuring cylinders are located in the bottom of the periphery of the hopper and deliver an exact volume product through the operation of a cam-actuated piston. In operation, the can is positioned in its station on the table and a cam raises it under the filling spout and opens the filling valve. The piston displaces the shortening into the can; as it is being filled, it lowers back to the table surface. Gentle oscillation of the can by the driving cam can be used to tamp the product down as it is being filled. This oscillation motion accounts in part for the smooth top surface configuration of concentric rings. Product weight control with this type of equipment depends upon control of the creaming gas content within tolerances no greater than ±1% (9).

The development of the closed plasticization units, commonly known as Votators, made it possible to exclude air from shortening products. The previous chilling and plasticization systems were exposed to the atmosphere, and air was incorporated during the chilling and working processes. It was also found desirable to fill the free space between the surface of the shortening and the lid with inert gas. This practice has become even more beneficial because the shortening formulations have been changed to have as high a unsaturated fat content as possible. The simplest blanketing procedure is to wash the surface of the shortening, just before capping and seaming, with nitrogen. Nitrogen in the headspace protects the shortening from oxidation of the unsaturated fatty acids until the consumer opens the container.

Foodservice and Food Processor Shortening Packaging Materials

The once popular 50- and 110-lb tins and the 375-lb open-head steel drums of shortening have almost disappeared from the U.S. markets, like the wooden tierces before them. The 50-lb cube is the dominant shortening package for both foodservice and food processor customers. Shortening cube cases are corrugated paper boxes measuring ~1 ft in height, width, and depth. Some shortening suppliers use other dimensions, but their volume must still approximate 1 ft^3. The corrugated cases are plastic lined to keep the shortening from leaking through the container. The plastic used for the liner generally is a 2-mil, low-density blue-colored polyethylene bag formed from a continuous-tube extrusion with a seal at the bottom edge. The blue color of the plastic liner has two applications, namely, a blue background intensifies the white color of the shortening and also distinguishes it from the product in case the film is torn during removal. After filling, the extended top portion of the liner is folded over the contents. This package type is applicable only to relatively stable shortening products requiring a moderate shelf life. The quick product turnover by the food service and food processor customers makes a 6-mo shelf life more than adequate for these products.

Batch size packaging is also offered to the foodservice and food processor customers by fats and oils processors. The shortening chub package consists of a quantity of premeasured shortening, encased in a low-density blue-colored continuous extruded polyethylene tube, individually sealed at each end with metal clips. This package provides a relatively good oxygen barrier and protection from moisture and other foreign materials up to the point of use. The metal clips used for closure on this package gave rise to a safety concern that the metal clips might accidentally find their way into the finished product. Alternative packaging available for this same concept consists of parchment wrapped blocks of shortening, which do not offer the oxygen barrier, protection from foreign materials, nor adequate product containment but do satisfy the metal clip safety concern.

Foodservice and Food Processor Shortening Packaging Equipment

Most foodservice and food processor shortenings are filled into plastic-lined corrugated cases or metal cans utilizing a reciprocating filling nozzle with the package on weight cells that activate the valves to the filling nozzles. Molten liquid shortening that has been injected with nitrogen is supercooled in a scraped-wall heat exchanger, passes through the worker unit to an extrusion valve, and is delivered to the filler at ~300–400 psig in minutes. At the filler, the shortening passes through another extrusion valve into the package. After filling, the case is sealed, labeled, and coded with the appropriate nomenclature for identification and retrieval should it become necessary.

Chub packaging is accomplished with shortening that has been supercooled; it is similar to the process for cube cases. It is introduced to the chub polyethylene tube by a variable-speed, positive-displacement metering pump that controls the flow rate of the product. Control of product flow and tube formation rates maintains accurate weight and package length. The polyethylene tube containing the product is propelled by drive wheels to voider rolls that are timed to void the product from the tube. Closure plates then gather the voided tube and install the top closure clip on one package and the lower clip on the following package. Simultaneously, a knife cuts the plastic tube midway between the two clips. The lower chub is then complete and slides down the exit chute to the corrugated case station (1).

Parchment-wrapped, portion-controlled shortenings are supercooled but do not have creaming gas injected and are not worked similarly to the shortenings filled in cube cases or chubs. In this operation, the molten shortening is supercooled, passed through a quiescent aging tube, formed, wrapped in parchment, and packaged in corrugated cases.

Margarine Packaging

Margarine is a flavored food product containing 80% fat, made by blending selected fats and oils with other ingredients and fortified with vitamin A to produce a table, cooking, or baking fat product that serves the same purpose as dairy butter; however, it is different in composition and can be varied for different applications (10). Margarine, which was developed as a substitute for butter, now also has a substitute. Spreads that have the appearance and consistency of margarine and are prepared in the same manner have been developed, but they do not contain the fat content required by the U.S. Standards of Identity to be called margarine. There are >10 different margarine and spread product types produced today; these include prints, soft tub, whipped tub and stick, liquid, diet, no-fat, restaurant, bakers, and other specialty types. Most of these margarine types may be packaged in several different containers.

Margarine and spreads are emulsions prepared with a two-phase system; all of the oil-soluble ingredients and the pasteurized aqueous phase composed of the water-soluble ingredients are mixed together in separate vats. The two phases are then combined to produce a water-in-oil emulsion. After the formation of the emulsion, the essential steps for processing margarines and spreads are somewhat similar to those for shortening except that all of the equipment must be stainless steel because of the water and salt contained in margarine products. Considerable care must be exercised during packaging of margarine to avoid contamination of the product with microorganisms. Typically, margarines are refrigerated after packaging because of the low melting point and to retard spoilage. i.e., potential microbial growth due to the moisture content and oxidation of the unsaturated fatty acids in oil.

Consumer Margarine and Spreads Packaging Materials

Margarine sales in the United States were restricted by legislation enacted in 1886 and amended in 1902, 1930, and 1931. The Federal Margarine Act of 1950 abolished the structure of taxes and licensing administered by the Internal Revenue Service (IRS) and placed the regulation of margarine under the Federal Food and Drug Administration (FDA). The Standard of Identity established in 1941 for margarine regulates ingredients, labeling, and packaging. With the 1950 legislation, margarine manufactures realized the following two immediate benefits: (i) colored margarine was allowed, and (ii) the tax savings reduced product costs. National legalization of colored margarine opened up the consumer market for new developments.

Consumer margarine packaging before the legalization of precolored product was predominately 1-lb prints wrapped in parchment and placed in heavy, waxed cartons similar to those used for butter. Just before 1950, when precolored product was allowed by the federal government, the following two margarine packaging innovations representing departures from previous practices were introduced: (i) a plastic bag with a color capsule, and (ii) the 1/4 lb print. The plastic bag packaging concept was an instant success but had a short life. This package with the coloring material contained within the bag made the problem of coloring margarine in the home less onerous. This innovative idea was doomed by two factors; first, both the cost of the bag and filling labor costs were considerably higher than the parchment and carton package, and second, the federal taxes on colored margarine were repealed (9). The 1/4 lb print, a seemingly less innovative package, is still available in grocery stores today. Probably, the largest change in this package has been the introduction of foil-laminated wrap and cartons whose use has remained limited to the more premium products.

Soft margarine, spreadable from the refrigerator, was introduced in 1962. This major change in margarine consistency necessitated a new package concept. The product required a better oxygen barrier than that afforded by parchment or foil laminates due to the high level of polyunsaturates in the formulation; in addition, the product was too soft to be printed. The initial containers for this soft product were thermoformed high-density polyethylene (HDPE), which were changed to acrylonitrile-butadiene-styrene (ABS) later due to quality problems. Concern about packages constructed of ABS, because of available acrylonitrile contained in some packages, led to the next change, which was to injection-molded polyethylene containers (1). The soft margarine packages consisted of two 8-oz tubs in a fiber board sleeve or one 16-oz package. Soft whipped margarine was introduced later; it was essentially the same product as the original soft tub margarine with more creaming gas incorporated before chilling. Approximately 8% nitrogen was injected into the original soft tub margarine, whereas the whipped products contain ~33% nitrogen by volume. This product necessitated a larger volume tub to contain the greater volume at the same product weight. Liquid margarines in squeezeable plastic dispensers, introduced in 1963, have never achieved significant consumer acceptance.

Consumer Margarine Packaging Equipment

Margarine packaging begins when the margarine emulsion is pumped from the supply tank to the internal chiller. The temperature of the emulsion entering the scraped-wall heat exchanger is usually controlled at 10°F (5.6°C) above the melting point of the oil portion of the product to prevent precrystallization. Consumer margarine emulsions are normally chilled to a temperature of 45–50°F (7.2–10°C) in < 30 s. From this point on, the process depends upon the margarine type to be produced. Two basic types of equipment are used in the United States to produce 1/4 and 1-lb margarine prints, i.e., molded print and formed print equipment. Most molded print systems pump the product from the chiller into a crystallization chamber, which fills the mold block cavity by line pressure. The formed print is discharged into the parchment paper wrapping chamber and then to the cartoning chamber. The filled print system accepts margarine with a semifluid consistency from the quiescent tube. It is filled into a cavity that is prelined with parchment or foil interwrap. The interwrap is then folded before ejection from the mold into the cartoning equipment. The cartoned prints are combined into corrugated cases and tempered at 45 ± 5°F (7.2 ± 2.8°C).

The margarine oil blends for soft tub margarines are formulated with higher levels of liquid oils than the stick margarine products so as to produce a product that is spreadable directly from the refrigerator or freezer. The crystallization technique also contributes to the desirable soft consistency of these margarines, which are packaged in plastic tubs with snap-on lids for product protection and to adequately contain the product. Plasticization of these margarines is similar to that of shortening so as to achieve the desired consistency. The emulsion is pumped to the chilling unit at 95–105°F (35– 40.6°C) with a high-pressure pump to the scraped-surface heat exchanger or chilling unit with nitrogen gas at 8% by volume injected into the oil stream. The product is rapidly chilled to 50 ± 2°F (10 ± 1.8°C) before passing through a worker unit to dissipate the heat of crystallization. This product is then delivered to the filler where it is forced through an extrusion valve at pressures in the range of 300–400 psig. Either a rotary or a straight-line filler may be used to fill the tubs with margarine. After filling, the tubs have lids applied, are inserted into sleeves if used, and then cartoned, before tempering at 45 ± 5°F (7.2 ± 2.8°C).

Liquid margarines can be prepared using the same equipment to chill and work the product as that used for the soft tub margarines. Improved resistance to product separation is claimed when the oil blend is subjected to a crystallization period before addition of the aqueous phase to prepare the emulsion. The emulsion can then be chilled, crystallized, and filled into the plastic squeeze bottles with a liquid filler (11).

Processing and packaging for spreads is similar to that of the corresponding margarine products except that the lower-fat content products have more critical manufacturing tolerances as a result of instability. These products are more sensitive to line pressures, air incorporation, temperature variations, agitation rates, or cooling rates.

Foodservice and Food Processor Margarine Packaging Materials

Foodservice and food processor margarines may be either duplicates of the retail products or designed for a specific use, which may be product or process related. The most popular foodservice product is the consumer stick margarine formulation packaged in 1-lb solids for use in food preparations. Individual-serving margarines are also large-volume products for the foodservice market. These products have evolved from "pats" or 1/4 oz margarine triangle-shaped pieces separated in a 72-count carton by parchment paper, to reddies, which were 1/4 oz squares on a white fiberboard square with a parchment topper also packed in 72-count cartons, to the individually sealed 1/4 oz cups of spread or margarine product available today. Foodservice and food processor customers also utilize margarines packaged in corrugated cases that resemble the shortening case. However, these cases have a smaller volume requirement because margarines normally do not have creaming gas additions.

Foodservice and Food Processor Margarine Filling Equipment

The equipment used to prepare the 1-lb solid margarines is the same as that used for the consumer print margarines. The major difference is the cavity size used in the forming block and parchment wrap adjustments. The industrial filling and packaging equipment utilized for 50-lb cases of margarines is almost an exact duplicate of the equipment used for the food processor and foodservice shortenings. One major difference is that all of the equipment, transfer lines, and pumps must be resistant to corrosion to withstand the moisture and salt in margarine products. The fillers used for the individual-serving food service margarines are manufactured to fill plasticized soft margarine or spread product.

Specialty Product Packaging

Flakes, chips, emulsifiers, stabilizers, and hard butters are all highly saturated fats and oils products with high melting points that may be considered specialty products. These are predominately food processor products; they are usually flaked or spray-powdered to facilitate handling. The flake form is produced on chill rolls, which are hollow metal cylinders with a smooth surface that is internally refrigerated and turns slowly on longitudinal and horizontal axes. Melted product is fed to the chill roll to form a thin film of liquid material, which is carried over the roll and solidifies as the roll revolves. The solidified fat is scraped from the roll and is usually gravity fed into the package.

Three different methods are practiced in the United States to produce powdered fats and oils, i.e., spray cooling, grinding flaked products, and spray flaking and grinding. The major difference among the three products is the shape of the granule. The spray-cooled products, which are atomized into a tower and cooled while descending to the bottom, have a smooth spherical shape. The ground flakes and the spray-flaked products have granular shapes. It is claimed that the granular powders can be metered at more uniform rates and resist stratification or separation in mixes with other granular materials.

Specialty Products Packaging Materials

The flaked and powdered products are more resistant to oxidation than most of the other fats and oil products due to their low level of unsaturated fatty acids. Therefore, the packaging materials emphasis is concentrated on durability to withstand handling during storage and transportation, ease of handling by the user, and costs. The three package types used for these products are described in Table 14.2. All of these materials are usually gravity fed into the container, the weight is manually adjusted to net, and the package is then closed, sealed, sewn, or has a lid applied.

TABLE 14.2 Packaging for Specialty Products

Product	Package description
Low iodine value flakes and emulsifiers	Multiwall, 3-ply, kraft, plain brown bag, 50-lb capacity
Chips, stabilizers, beads, hard butters, and powders	RSC[a] style, 200-lb test, corrugated box, RSC glued inside joint with a blue, tubular, 2.25 ± 5 mil film gauge polyethylene bag, sized for the case
Powders and beads	Fiber open-top drum with clear polyethylene bag sized for the drum

[a] Abbreviation: RSC, Regular Slotted Container. All of the flaps of an RSC style case are the same length and the lengthwise outer flaps meet at the center of the box.

Bulk Handling

Many large-volume users of processed fats and oils products purchase their requirements in bulk because of the cost savings. Among the savings are elimination of container costs, reduced shipping costs, and lower labor requirements due to more efficient unloading and handling of the product for the user's plant. Other advantages include reductions in product waste and sanitary problems associated with small containers. Bulk handling may also reduce the amount of storage space required to handle the product.

A major drawback to handling finished fats and oils in bulk quantities is the sizable investment for the purchase and installation of an unloading station, tanks, pumps, lines, filters, nitrogen protection, and the other essential equipment. Operation of a bulk handling system requires the attention of more skilled and trained personnel than the unloading and warehousing of packaged product. A further disadvantage is that the product may deteriorate before use. This problem is more acute with shortenings that must held at elevated temperatures. Heated products are considerably more susceptible to deterioration than packaged products as well as bulk products, which can be maintained at ambient temperatures (12). For example, the oxidation rate for fats and oils increases by a factor of 3 for each 20°F (11.1°C). For a bulk handling system to be cost efficient, the minimum delivery must be used before the product deteriorates to the point that the quality of the product produced suffers. The minimum bulk shipment for truck deliveries is 40,000–50,000 lb and 80,000 lb for rail cars. The storage life of the different shortening products depends upon the formulation and the handling conditions within the user's plant. From the point of view of formulation, the degree of unsaturation is roughly proportional to the degree of oxidation, i.e., the higher the unsaturated fatty acid level, the faster the rate of oxidation. From the point of view of the facility, oxidation is accelerated by temperature increase, oxygen pressure increase, concentrations of oxidized materials, metals, absence of antioxidants and/or metal deactivators, and light. More simply, the storage life of a bulk shortening depends on the product formulation and the protection that the facility has available to prevent oxidation.

Bulk Handling Precautionary Measures

Bulk handling systems for fats and oils products must be designed and operated with the following three primary considerations for the maintenance of quality: (i) avoid contamination, (ii) avoid overheating, and (iii) minimize exposure to air (8,12). We will examine these individually.

Contamination. A contaminant is any undesirable material that may taint, infect, corrupt, modify, or degrade by contact or association. The contaminants most likely to affect bulk handled fats and oils are as follows:

1. Moisture. Precautions must be taken to protect the fat and oil products from hydrolysis and the development of free fatty acids. Moisture sources may be wet delivery tanks, steamed lines, ruptured coils, leaking coolers, condensation, rain during loading or unloading, and others.
2. Metals. Metallic contamination cannot be overstressed. Copper and iron are strong prooxidants for oils and are capable of lowering the flavor and oxidative stability at levels of 0.01 and 0.1 ppm, respectively. Cooper or copper-containing alloys should never be used in equipment involved in handling or storing fats and oils products. Iron exposure is more difficult to avoid because it is used for construction of tanks, pumps, and lines. However, through proper treatment and cleaning of the black iron equipment, contamination can be kept to a minimum.
3. Impurities. Foreign material contamination in bulk products is usually caused by a malfunction in the in-line unloading filter, inadequate tank cleaning or rinsing, open hatch covers, or other similar occurrences.
4. Commingling. Inadvertent mixing of two different fat and oil products is a serious contamination. Each fat and oil product has its own specific properties; depending upon its field of application, the tolerance toward admixture of other fats is usually very low. Product mixing is usually the result of a mispumping, unloading fresh product into a tank with a sizable heel remaining, or a malfunctioning valve.

Overheating. Localized overheating is detrimental to fat quality and should be avoided. Products received in a solid or semisolid state should be heated and agitated slowly until liquid and homogenous before pumping. Heating should start at a time calculated to provide the required temperature without exceeding the maximum rate of 10°F (5.6°C)/24 h.

Tank car overheating can occur with high-pressure steam usage or even with low-pressure steam handled improperly. When steam is used, the steam pressure should not exceed 1.5 kg/cm^2 to prevent localized overheating. All storage tanks with heating devices should be equipped with a mechanical agitator. Power agitation will not only minimize product damage from localized overheating but will save time and heating costs as well.

Air Exposure. Oxidation results when fats and oils are exposed to air to produce offensive flavors. Air can be almost completely excluded by maintaining a nitrogen atmosphere in the bulk handling system. Nitrogen sparging into the stream of oil as it is unloaded will saturate the oil plus provide an excess. This excess is released when the oil is pumped into the storage tank to displace the air in the headspace. This practice requires ~5 ft^3 nitrogen/1000 lb oil.

The unloading lines should discharge near the bottom of the storage tank to minimize aeration of the product. Allowing heated fats and oils to cascade or fall through the air into a tank permits the product to splash and aerate. Pumps and lines must be maintained routinely to avoid sucking of air into the suction side of the pumps or lines caused by faulty seals or fittings. Creation of whirlpools or vortexes, which whip air into a product through improper agitation, must be avoided. Lines should be blown with nitrogen to evacuate them. Air use brings oxygen in contact with a large product surface area and it will bubble through the product in the storage tank.

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Chapter 15

Environmental Considerations in Fats and Oils Technologies

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Introduction

The extraction, refining and processing of edible oils produce a variety of waste products. In no other industry are the proper control and handling of these wastes as dependent on the understanding and control of the processes themselves. Several other presentations in this monograph allude to the control of effluent strength and volume through process control and modification and explore in depth the major processes involved in fats and oils handling.

This chapter presents a brief review of the major processes and facilities, particularly as they relate to waste generation and control. The chapter starts from the position of defining wastes from a well-run facility. This is followed by an analysis of those processes that are the largest potential waste generators. In addition, those factors that affect process control as it relates to waste generation are reviewed.

This is followed by a review of abatement technologies for air, water and solid waste streams. The chapter stresses wastewater and solid waste with less emphasis on air emission controls, primarily due to the author's areas of expertise. In addition, the current emphasis on water recycling is addressed.

The chapter is directed mainly at conventional caustic refining and related downstream processes, in which the increasing use of physical refining has an effect. However, one must not lose sight of the fact that oil losses occur in physical refining and will manifest themselves as waste in one form or another.

Process Components and Major Waste Sources

Figure 15.1 is a conceptual flow diagram showing major processes of a typical oil processing facility. The following processes were considered:

- milling and extraction
- caustic refining
- further processing and handling (e.g., bleaching and winterization)
- deodorization
- acidulation
- tank car washing
- packaging
- margarine production
- salad dressing/mayonnaise production

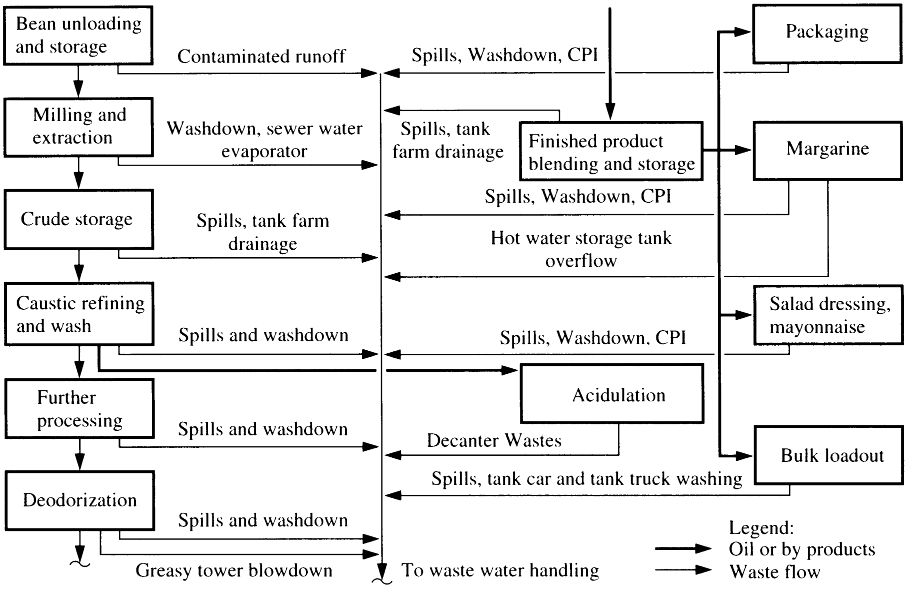

Fig. 15.1. Flow diagram of edible oil handling facilities.

This section describes the major waste sources from these various processes relative to wastewater, air emissions, and solid waste.

Wastewater Loadings

Primary Parameters. Table 15.1 lists these processes and associated waste loadings. Separate subtotals are presented with and without salad dressing and mayonnaise, because these processes are often absent, and portions of this chapter do not consider them. (See Reference 1 for clarification of terms and test methods.)

Note that only fats, oils, and grease (FOG) and 5-d biochemical oxygen demand (BOD) are listed. Numerous other parameters are often discussed, monitored, and interpreted, but except in rare circumstances, treatment and control strategies can be reduced ultimately to these two items. Loadings are presented as average and maximums; however, the variable operations of a fats and oil facility are such that a true average is less relevant than an operating range. Maximums are reasonable upper figures, with higher loadings possible in spillage situations.

Control of wastewater pH is important; ultimately, however, it becomes a byproduct of controlling FOG and BOD. Chemical oxygen demand (COD) can usually be estimated predictably at 1.4 to 1.6 times BOD. As a result, measurement of COD is a useful tool with which to determine BOD values indirectly.

Many effluent permit limitations also include total suspended solids (TSS). The test procedure for TSS also measures oil and grease that is removed in the filter paper used in the test process. Experience has shown that non-oil–suspended solids

TABLE 15.1 Fats and Oils Processes and Wastewater Loads[a]

Process	Flow (g/d avg)	Waste load BOD, (b/d) (avg)	(max)	FOG (avg)	(lb/d max)
Milling and extraction	60,000	370	600	10	25
Caustic refining	11,000	220	1000	115	400
Deodorization/Hydrogenation	8000	800	1200	100	200
Acidulation	22,000	3200	5000	25	800
Tank car washing	8000	250	1500	125	250
Packaging	10,000	250	1000	125	500
Subtotal	119,000	5090	10,300	500	2175
Margarine production	70,000	600	1000	300	500
Salad dressing/mayonnaise	50,000	2000	3500	1000	1700
Total	239,000	7690	14,800	1800	4375

[a] Abbreviations: BOD, biochemical oxygen demand; FOG, fats, oils, and grease.

are normally quite low in wastes from edible oil handling. Therefore, the parameter is not really of use in most applications. There are some exceptions, such as wastes from milling and extraction areas, along with salad dressing and mayonnaise.

Process Loading. The data in Table 15.1 are developed around the following criteria:

1. Milling and extraction, 2000 tons of seeds processed per day.
2. Caustic refining with single-stage water wash, 60,000 lb/h, nondegummed soybean oil, finished oil capacity.
3. Continuous deodorization with scrub cooler, surface condenser with atmospheric noncontact cooling tower.
4. Acidulation of soap stock and wash water with 90–95% recovery efficiency.
5. Bottling line and/or other extensive liquid oil packaging.
6. Margarine, mayonnaise, and salad dressing production and packaging.
7. Tank car washing of finished oil cars only (no crude oil cars).

Clearly, operations of different size, and lacking some of the processes, will have different waste loads. The effects of process control and its effect on wastewater loading are outlined in the next section.

These loadings represent a reasonably well run operation from a process loss control standpoint. Loadings will vary for better or more poorly run plants. In addition, the figures in Table 15.1 assume that all of the waste streams have been subjected to at least a modest degree of gravity separation for removal of gross quantities of floatable oils and solids.

A final source of wastewater is potentially contaminated rainfall runoff from truck and rail loadout areas, tank farm drainage, and related operations. This runoff can contribute the equivalent of 5–10 gal/min to the total daily average flow during rainy periods, and affect peak flows to a much greater extent.

Other Significant Parameters. Two other parameters are of particular interest, nickel and phosphorus. Nickel may enter the wastewater stream from cleanup and minor losses in the hydrogenation process areas due to nickel catalysts. Caustic cleaning of filter screens from the catalyst is a particularly significant source. Quite often this can be controlled at the source.

Crude oils, particularly soybean oil, contain significant quantities of organic phosphorus in the form of phosphatides. These compounds are removed to a large extent from the oil phase in the caustic refining and wash processes. If refinery wash waters and soap stock are acidulated, the phosphorus is carried into the water phase. There are other sources of phosphorus in an edible oil operation, but the majority result from the mechanism described above.

Facilities that use activated silica filtration in place of refinery water wash, and do not acidulate soap stock, can largely avoid phosphorus management in wastewater. The facilities described for this presentation can generate between 500 and 1000 lb of phosphorus per day in the total waste stream. This will depend on the type of crude, the geographic area, and other factors relating to the amount of phosphorus contained in the oilseed.

Air Emissions

Major sources of air emissions considered for this presentation include the following: dust particulates from grain and meal handling, hexane from solvent extraction, odors from meal cooling and deodorization, along with particulate emissions and nitrous oxides (NO_2) from coal-fired boilers.

There are a number of reference sources for each of the individual sources; however, an excellent overview of the subject in general, and one relied upon heavily by the author of this chapter is a paper by Henricks (2) that was presented at an AOCS Environmental Short course.

Grain Dust. This arises from a variety of sources throughout the handling and milling of oilseeds. Elevator losses as a whole are usually assumed to be 2–3%. This loss figure is a combination of moisture reduction, spilled whole seeds and meal, along with dust. The dust portion comprises a smaller absolute number. However, it can create substantial problems when measured as particulate air emissions. As a result, dust collectors in the form of cyclones, bag houses, and related filters are in use universally to control these emissions. These materials are often recycled to the hull processing systems.

Solvent Extraction. The paper by Henricks (2) discusses the subject in great detail. However, the generally accepted limit is 0.2 gal of hexane per ton of soybeans crushed, for the entire operation. Attainment of this figure requires a well-run mineral oil absorber on the tail end of the process and computerized process controls that minimize solvent loss during start-up/shutdown and other nonnormal process conditions. Sources include handling losses, and meal dryer and cooler exhausts.

Odors from Meal Dryer and Oil Deodorization. Odor is a qualitative parameter from the standpoint of both measurement and control. Motivation for abatement usually arises from citizen complaints. The author's first work at a soybean operation many years ago was in a plant located next door to one of the largest pulp and paper mills in the world. Therefore, it was some time before it was realized that oilseed operations actually had odor problems.

Nevertheless, the industry has its share of odor control challenges—although not on the same scale as those of pulp and paper. The main sources of odor are meal dryers and refined oil deodorization. Acidulation has been an odor producer in some isolated instances. However, this is more likely the result of poor basic design and operation and is usually found in batch, open-topped kettles. Modern well-designed acidulation systems will not have odor problems.

Both of the other two processes (meal drying and deodorization) are inherent producers of odors by their very nature. They subject meal and oil to high temperatures to drive off volatile fractions. In the case of deodorization, this is done specifically to strip odor-causing compounds from the oil. As will be discussed later, exerting this control has become an integral part of the processes. Control of odors in extraction has been greatly enhanced by the development of the stacked DT/DC, which have replaced many of the rotary kiln dryers.

Coal-Fired Boiler. Increases in energy cost have driven a number of processors to install coal-fired boilers, primarily for steam. Particularly in Midwestern states, the development of tax incentives has encouraged intrastate use of coal suppliers. This subject is also addressed well by Henricks (2), and there is a large body of other literature due to the widespread use of coal-fired boilers.

Primary concerns with boilers revolve around ash particulate emissions and associated visual plumes. Boilers installed before 1972 are equipped with mechanical collectors; however, newer units employ a variety of fluidized bed technologies to maximize efficiency and reduce emissions. This is coupled with emission controls to meet current emission levels, which vary locally. Particulate emissions from coal-fired boilers can be 0.03–0.05 lb/MM BTU input.

Solid and Hazardous Waste

The generation and handling of solid and hazardous waste has not been a major problem in this industry compared with wastewater and air emissions. However, there are a number of significant sources, which are of concern. These are discussed below and potential control technologies are presented.

Refinery Bleach. Various bleaching clays are used to purify and remove color bodies from refined oils. These spent bleaching clays contain 25–35% oil. The characteristics of these wastes are such that they will combust spontaneously. This has created a problem for disposal in sanitary landfills. However, it can be overcome by several methods. The model refinery discussed will generate ~5600 lb/d of waste earth, of which ~1250 lb is oil.

The material is not considered hazardous by any existing criterion (other than spontaneous combustion). However, some local landfills are reluctant to accept it due to combustion and/or oil content. Technologies are available to recover this oil; however, the overall economics of this are not favorable and the practice is not widespread.

Spent Hydrogenation Catalyst. Nickel catalyst is used in the hydrogenation of oil. Depending on the process facility, catalyst may be recycled a number of times. Therefore, waste generation rates differ. The model refinery will generate ~220 lb/d of spent catalyst. In the past, this material has either been recycled or disposed of in sanitary landfills (or onsite). The recycling for nickel recovery has been spotty and not well organized in the past, but has improved greatly in recent years, and virtually all spent catalyst is now recycled for nickel recovery. Although nickel has not yet been designated as hazardous by the Federal Environmental Protection Agency, several states have classified nickel as hazardous and it is generally treated in that manner by most processors.

Waste Grain Solids. The milling and extraction end of the process, and associated feed mill operations, generate substantial volumes of spilled grain solids. This varies greatly with the operation, from day to day, ranging from little or nothing to several bushels per day. This does not reflect those handling losses that are routinely collected and recycled back into the process. Meal and grain solid losses may amount to 1–10 lb/1000 bu of crush. These wastes are not considered hazardous and can be disposed of in a sanitary landfill. It is extremely important, in any event, that these solids be kept out of the sewers because they will exert a very substantial wastewater loading.

Process Factors Affecting Waste Generation and Characteristics

The modern design of oilseed processing and oil refining and processing facilities has been focused on increased loss efficiency and reduced energy consumption. These factors inevitably result in lower wastewater generation and lower BOD and FOG levels in the waste waters. New processes are evolving that will affect this even further. The use of enhanced silica bleaching has eliminated the water wash step in some process plants. Other fundamentally new processes and equipment are expected to develop. The use of a reboiler on effluent discharges from extraction facilities virtually eliminates this wastewater source. The same process improvement evaluation is occurring and producing similar effects for air and solid waste emissions.

Wastewater

Soapstock Handling. The largest single factor affecting wastewater loading is handling of refinery soap stock. The following four methods are employed routinely: (i) acidulate soap stock for fatty acid or animal feed fat value; (ii) sell as raw soap stock on the open market; (iii) spray on meal as a fat additive (if an oilseed operation is present); and (iv) partially neutralize and dewater soap stock.

Acidulation is probably the most misunderstood and maligned process in the entire fats and oils industry. Few people are content with their acidulation techniques and tend to think that someone else must have a better method. This chapter focuses on how the designing process affects process loss and waste load rather than on the process itself. The easiest part of an acidulation design is the production of an oil with an acceptable acid quality. The challenge is the minimization of the middle phase and generally creating an oil-free wastewater. This implies that the facility be properly designed from the standpoint of reaction kinetics as well as the mechanical aspects of acid/soap stock mixing, decanting, and middle phase recovery.

Methods (ii) and (iii) mentioned above do not produce any wastes other than from handling losses; however, they are usually not the most economical methods of dealing with soap stock. The fourth method is a recent innovation developed to reduce water content of soap stock sold for acidulation elsewhere. The water phase generated in the decant can have an equal or greater waste load compared with that generated from a well-run acidulation plant. Figure 15.2 shows a relationship devel-

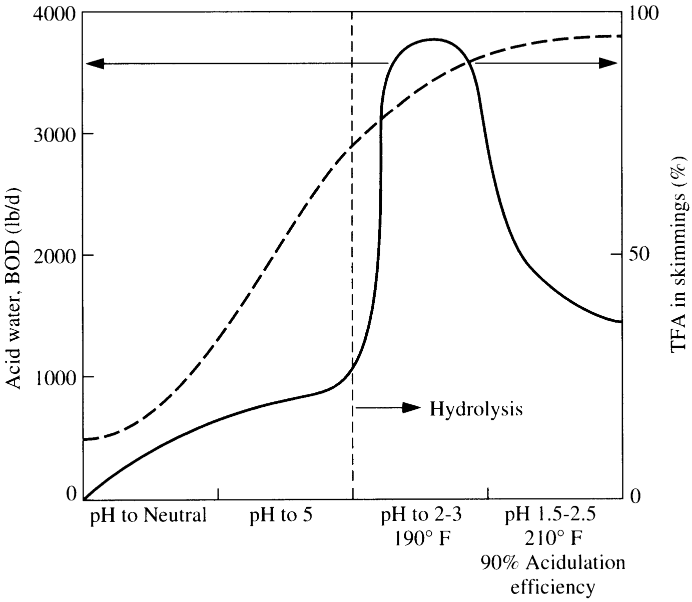

Fig. 15.2. Wastewater and TFA vs. acidulation efficiency. Abbreviations: BOD, biochemical oxygen demand; TFA, total fatty acids.

oped from one such operation. Note that some gain is realized by a moderate pH reduction; however, in later phases, the operation essentially becomes an inefficient acidulation process. The economic advantage of freight cost gained should be weighed against additional waste handling costs.

Deodorization. This process should be a minor contributor; however, it can produce significant waste loads if the deodorizer does not have a well-operated scrub cooler. If a barometric recycling system is used, the return flow should have its own oil separator in operation on blow-down skimming. In certain instances, an indirect heat exchange system is used to reduce odor problems arising from the greasy water tower. In any event, the waste load should be no greater than the deodorizer steam load with ~500 mg/L FOG, the soluble oil fraction at steady-state recycle. Several suppliers are using polymer addition to enhance this effect. The current tendency in deodorizer design is a surface condenser with an indirect heat exchanger. These systems employ a dilute caustic wash to maintain a clean surface in the condenser. This caustic wash has a high pH and is high in BOD and FOG. The net result from a waste load standpoint is about the same as that involved in a well-run direct cooling barometric system.

One final note on deodorizers. About once a year, these units are boiled out with caustic soda and citric acid as a maintenance operation. This boil-out water is an extremely high waste load and must be stored for regulated release into the sewer system.

Refining. The water wash centrifuge stage is susceptible at times to oil breakover due to back pressure control. Few plants have a method to monitor or control such an occurrence other than doing so visually. This can represent substantial quantities of oil. A secondary gravity separator should be used in-line on the wash water stream to recycle the floatable refined oil directly rather than allowing it to downgrade as acidulated material.

Cleanup, Handling Losses. There is no end to the potential to create (and eliminate) waste load and water flow through in-house control in this area. This is primarily a matter of employee training and attitude. However, there are physical aspects to consider. For example, water from the vacuum pump seal can make up a large percentage of total water flow if not recycled or otherwise minimized. To address this issue properly, a plant-wide study of oil loss and wastewater generation points should be conducted and evaluated. Using that information, a cost-effectiveness analysis of potential operational and physical remedial measures can be conducted. There are few plants in which such study has not produced an array of opportunities for loss reduction and money savings.

Air Emissions

Grain Dust. This is generated primarily from mechanical handling of grain and meal solids. Good maintenance of transfer and handling facilities is essential to dust minimization. Also, as it relates to internal elevator dust formation, control and cleanup are essential to prevent fire and explosions.

Odor Control. Facilities to control odor have become essentially a part of the process themselves. Therefore, this topic will be discussed here and not addressed under the next section on abatement technologies. Deodorization of fats and oils is a necessary process for removing disagreeable flavor and odors that are present naturally or created during processing. The deodorization of soybean oil produces odors that have been the greatest challenge historically to the industry for odor control.

Three steps are used to eliminate these odor problems. The first is a distillate recovery system, which recovers most of the fatty acid and many of the odors in the deodorizer vapor discharge. The second is a closed-loop cooling system, which keeps the water from the fat-laden hot well out of the cooling tower. The third is a vapor scrubbing or oxidation system to eliminate volatile organic compounds that are not removed in the two previous steps.

A typical distillate recovery system consists of a scrub cooler located at some point in the deodorizer vacuum system. The deodorizer vapor effluent is stripped of ~95% of the condensable organic material by direct contact in the cooler. The circulating distillate is cooled to remove the heat of condensation before being returned to the stripping tower. Several equipment companies offer design/equipment packages that perform this task.

The remaining deodorizer vapors and the stripping steam are condensed in either barometric condensers or shell-and-tube condensers. In areas in which additional odor control is not required, the liquid discharge of both condensers and the air discharge of the last ejector are discharged to a hot well. From the hot well, the cooling water then passes to a cooling tower before recirculation to the condensers. This system is the source of "normal" soybean processing odor. The second item is not featured in the surface condenser approach.

This system normally uses a condenser discharge directly to a hot well and then to a cooling tower, often by gravity. The cooling tower overflow and blow down are discharged to a water treatment or pretreatment facility as part of the plant's oily wastewater handling needs.

If odors from the cooling tower require further control, the cooling water from the hot well is pumped through plate heat exchangers, allowing for indirect cooling. However, due to fouling problems, an extra heat exchanger must be provided to enable off-line heat exchanger cleaning. Either steam or water and detergent are used for the cleaning. One benefit of using steam is that the fatty material is reclaimed more easily. The closed-loop system is more expensive to install (more equipment) and has higher energy costs for pumping water and motive steam in the vacuum system.

The third portion of the odor control system, if necessary, is to pass the air from the last ejector stage to either a Dowtherm or Therminol boiler. As a portion of the combustion air, the vapor is almost completely oxidized. Other less desirable alternatives are jet Venturi scrubbers, packed towers, or carbon bed absorbers.

Solid Wastes

Bleaching Earth. The quantity of earth used is primarily a function of crude oil quality and press efficiency. In both cases, there is already a high degree of problem recognition due to the process and economic implications. Therefore, there will generally not be substantial opportunities to reduce waste earth through process control simply for environmental purposes. Certain brands and types of filter media are better for various crude mixtures and presses. However, this is also dictated by necessary process conditions. There is a tendency to use excess clays to ensure final product quality. Proper dosage should be maintained.

Spent Catalyst. Opportunities may exist to reduce the volume of waste catalyst by reusing the catalyst through several hydrogeneration batches. However, experts disagree on the efficacy of this procedure. Hydrogeneration efficiency serves as the final measurement of the value of reusing catalyst.

Grain and Meal Solids. This is the area in which the greatest improvements in solid waste can be made through loss control. Transport of these materials is highly mechanical, involving equipment such as conveyors, elevators, or pneumatic systems. Losses tend to occur at transfer points along the entire conveyance system as well as at loading and unloading points (e.g., barge, rail car, or truck). In addition, building dust collectors, cyclones, and similar air emission control devices are a constant source of grain and meal solids losses due to plugging and overflowing. An important factor is that many of these points are located on building roofs; therefore, the losses may go unnoticed and undetected.

A program of good maintenance and repair is essential to minimizing these losses. Again, there are physical measures that can be installed on a cost-effective basis. These include load-back bins at loss points to allow material to be recovered as product rather than waste. Closed chutes and other conveyance devices, particularly at discharge points into rail cars, for example, will add greatly to loss control.

Waste Treatment Processes and Technologies

Wastewater

This section describes briefly the various treatment/chemical systems encountered in fats and oils applications along with their capabilities relative to the parameters of interest. The processes listed are generally consistent with the order in which they might appear in a treatment facility.

Gravity Oil Separation. This process can be considered as an in-plant process control item, or as a wastewater treatment process. In either case, it is essential that adequate gravity separation be provided at every fats and oils handling facility. This subject is addressed in some detail because poorly conceived gravity separation facilities are a major problem.

In one instance, at a new, grass-roots edible oil refining and processing plant, the waste collection and in-plant controls were being designed by the refinery engineering team. When questioned why no gravity oil separation facilities were provided or desired, the new plant manager noted that this was to be a state-of-the-art refinery and would experience no oil spills, due to excellent process operations control. Therefore, no gravity separation facilities were required. Needless to say, some months after the facility started up, some very expensive retrofitting was required to provide in-plant gravity separation capabilities.

Where is the best place to locate gravity separation facilities in an edible oil operation? The answer is as many places as possible and as close to the source as possible. This is not always practical or efficient, of course. The main considerations are as follows:

1. Prevent cross contamination of a higher-quality recoverable product with a lower-quality material whenever possible, i.e., do not combine packaging area drainage with deodorizer cooling water flow, which may contain pesticide residue.
2. Place gravity separators wherever wastewater gravity flow ends and pumping begins. If there is any kind of a wet pit involved in the pumping, the oil will float to the surface despite all attempts to keep it in solution. Take advantage of this and construct a gravity separation section as part of or adjacent to the wet pit, where practical.
3. All waste streams must receive oil separation of some sort before any further treatment.

Every fats and oils processing plant requires facilities for the capture of floatable fats and oils resulting from both day-to-day losses and larger spill situations. Gravity oil separators for these applications should be designed for rise rate loadings to accommodate peak flows if practical. Experience dictates rise rates in the range of 0.25–0.5 $g/(d{\cdot}ft^2)$ of effective separator surface area. The second criterion for sizing gravity separators is the capability to contain a certain sized spill. In almost all cases in oilseeds processing, the spill containment criterion will govern.

The rise rate concept is applicable to the design of continuous flow separation devices. Many designers use retention time for separator sizing. This is acceptable if desirable separator geometry dimensions are maintained (e.g., length to width ratios). The concept of retention time may be applied directly for design of batch settling vessels.

Skimming of oil and grease from the surface of separation vessels can be performed on a manual or continuous basis. However, the viscosity of many oils used in edible oil processing at ambient temperature is such that surface contact skimming devices (e.g., belts or ropes) are not particularly effective in some cases. In cases in which these devises are used, a wide screen is essential to prevent localized spillage. Chain and scrapper type skimmers are effective but not physically adaptable to every skimming situation. Shop-fabricated, manually operated, decant devices have been quite effective.

A portion of the flow to a separator often originates in rainfall from affected runoff areas with oil and grease. This may result in flow rates too high to handle practically at desirable rise rates. This often dictates a need to handle process waste flows and contaminated runoff in separate systems.

Equalization. The variance in process conditions, rainfall contributions, and related flow makes equalization facilities for stabilization of waste flow and strength essential. The volume of equalization required will depend on the variation of incoming flows and strength over a reasonable period of time. The volume of equalization required for flow and strength for the typical edible oil operation defined in the previous section will be about the same. The only stream from that operation not requiring equalization is the effluent from the milling and extraction operation. This stream is composed primarily of the sewer water evaporator steam condensate and is usually without much variation.

The volume of equalization required can be determined in a straightforward manner using a volumetric influent hydrograph approach. The required volume can be determined graphically to the level of accuracy required. A check of influent and resulting effluent strength variation can be made to confirm the suitability of the volumetric design for a specific application. Figure 15.3 is an idealized sample hydrograph. In general, the equalization surge volume required will vary between 30 and 50% of the daily average flow, but this can differ for each application.

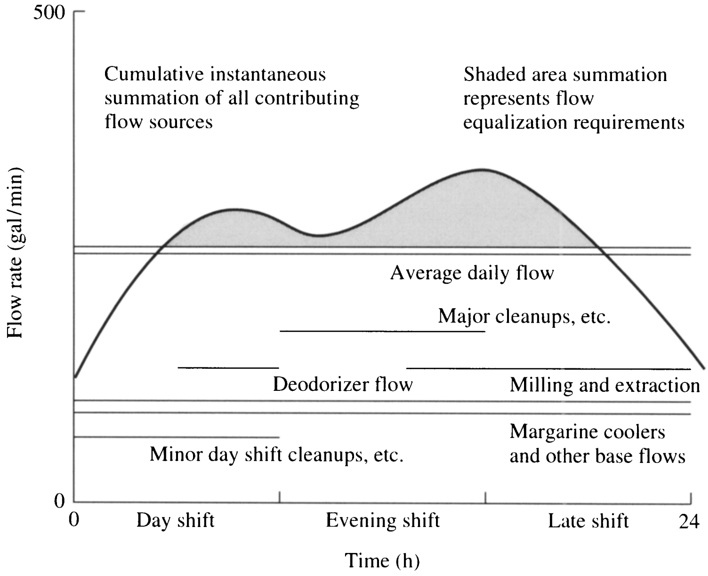

Fig. 15.3. Wastewater inflow hydrograph.

TABLE 15.2 Treatment Process Efficiencies

Process	Effluent Oil and grease (mg/L)
Well-designed gravity separation (neutral pH range)	100–500
Dissolved air flotation, chemically assisted	30–100
Pressure diatomaceous	50–150
Acid hydrolysis	50–150

Dissolved Air Flotation. Dissolved air flotation (DAF) is a technique that utilizes minute air bubbles to enhance the flotation of oils and suspended materials not removable in reasonably sized gravity separation. The bubbles are formed by pressurizing all or part of the waste flow and introducing air into a pressurization cell. Subsequent depressurization allows the bubbles to form, according to Henry's law. This process is enhanced by the addition of polymers, lime, alum, or other flocculants. This chemical addition provides for coagulation and flocculation of colloidal oils and solids into larger particles, which can be removed easily.

In fats and oils applicators, this technique has been shown to be very effective in removing FOG and BOD; however, significant quantities of waste sludge are generated. Table 15.2 shows the removal rates that can be expected for various processes discussed in this presentation.

The selection of a chemical flocculant must consider pH conditions as well as the removals desired. In the application of DAF in a fully integrated oilseeds extraction and refinery, aluminum sulfate and polymers are effective. An alternate approach is to use sodium hydroxide, the most commonly used refinery waste neutralizing agent, to bring pH up to a range of ~5.0; then lime can be used as a pH trimmer chemical. The resulting insoluble sludge will perform the same function as alum at less cost. The lime sludge may settle better than it floats, however, and DAF should be evaluated against settling.

DAF is not an effective process for primary separation of oil and grease. DAF has been applied effectively as a process after the use of other treatment facilities for FOG removal that require a 100 mg/L FOG limit or lower. This can sometimes be accomplished using food-grade approved polymers. In that event, the recovered material can be sold as a low-grade feed fat rather than disposed of as a waste sludge; however, without further dewatering of the recovered oil, the moisture value will depress the sale price.

Filtration. In-line filtration using diatomaceous earth is an effective device for reducing FOG and associated insoluble BOD to very low levels. It will not remove soluble BOD components due to acidulation wastes. This process has not found extensive use in fats and oils applications.

Acid Hydrolysis. An alternative approach, which has been used successfully at several fats and oils handling facilities, employees a low-pH, high-temperature hydrolysis effect to recover oils and grease (Fig. 15.4).

If the process facility acidulates soap stock and/or wash water, the resulting acidulation waste will contain sufficient residual heat and acidity to adjust the entire waste stream pH and temperature. This obviously assumes an alkali refining process rather than physical refining. This will produce an acidulation effect on residual oils. These oils can then be readily removed in a gravity separation process. If no acidulation takes place onsite, the chemical costs for artificial pH reduction and subsequent readjustment are usually not significant; however, the process will not be effective in refining wash water if this material is not acidulated.

The acid hydrolysis process offers the following advantages:

1. Process control is relatively easy. If the waste stream pH remains ≤3.5 at a temperature of ≥100°F, relatively constant effluent results can be obtained. The exception to this is carryover of excess middle phase from an inefficiently operated acidulation system. This material will not separate by gravity phase and will actually inhibit the process effectiveness for other plant waste streams.

   Under proper conditions, the effluent BOD strength in the separator underflow will be equal to the soluble BOD load from acidulation plus a small additional contribution from the residual oil and grease in the separator effluent.
2. The material recovered in the separator will contain relatively low moisture and high total fatty acids (TFA); thus the material can usually be sold for ~$0.03–0.06/lb less than acid oil.

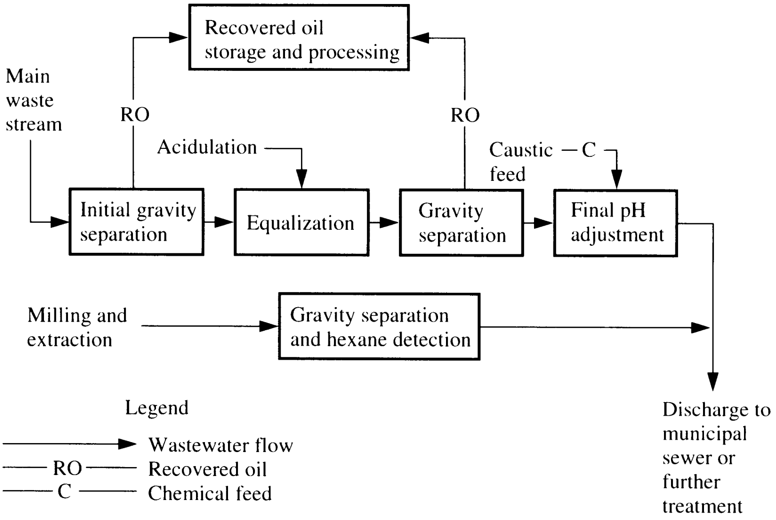

Fig. 15.4. Acid/hydrolysis process.

3. If the facilities can be constructed near acidulation facilities, the existing acid handling, steam, and recovered oil storage tanks can be utilized for both purposes.

The primary disadvantage is the need to use construction materials that will withstand high temperature and low pH conditions.

A wide variety of tankage, process controls, and related equipment can be used in designing these treatment facilities, depending on refinery size and processes, individual preferences, existing equipment to be used, and other related factors.

Neutralization of the separator effluent is usually accomplished with NaOH. However, lime or ammonia are occasionally used in special situations. A two-stage system using well-mixed tanks of suitable size is recommended. The neutralization invariably occurs on the steep part of the titration curve in these applications. Any inappropriate design, such as an excessively remote pH readout, will result in a nonfunctional system. As a result, it is highly recommended that an individual experienced in designing pH control systems review the final design.

Other Processes. Other treatment processes that have had only marginal success in these wastewater applications are presented briefly. Various membrane technologies have been tried on these wastes. Although the removal levels of pollutants are good in some applications, membrane life and regeneration have presented problems. As a result, operating costs for periodic membrane replacement are quite high.

At least one attempt has been made to use activated carbon to remove residual organics. The nature of the soluble components in the acidulation stream (the primary source of solubles) is such that they cannot be removed effectively by activated carbon.

Attempts have been made to apply inclined-plate and other packaged media separator systems for primary oil and grease separation. These have not functioned well in edible oil applications. This is also due to the viscous oils coating the separator media.

Biological Treatment. Wastes from fats and oils operations have been treated successfully using biological treatment in any number of circumstances. Pretreated effluents have been treated in combination with domestic waste in publicly owned pretreatment works (POTW). In addition, a number of biological systems are in place that treat waste onsite, either as pretreatment or for direct discharge. Figure 15.5 shows relative rates of biodegradation for a variety of oils. Clearly it can be seen that oils of animal and vegetable origin are highly biodegradable and compatible with municipal domestic waste.

Good gravity separation of floatable oils is mandatory before further treatment in a biological facility. Additional oil removal pretreatment may be required for oil value, prevention of sewer line blockage problems, or merely to reduce the size of the biological facilities.

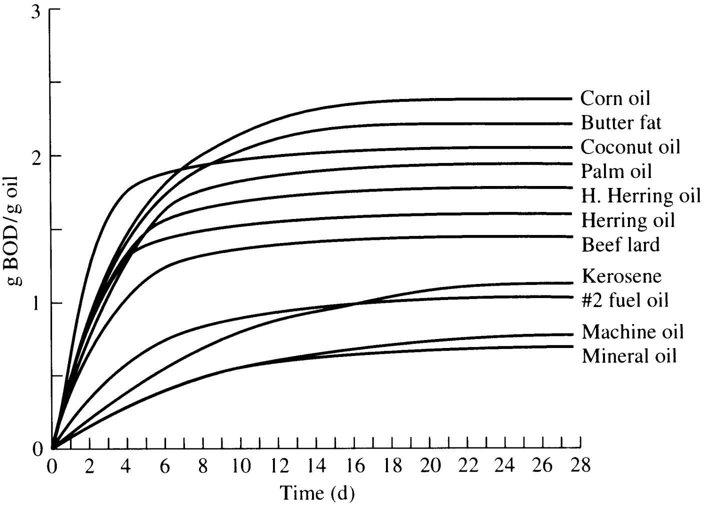

Fig. 15.5. Biochemical oxygen demand (BOD) curves for edible and petroleum oils.

Tertiary Treatment and Recycling Potential

Significant potential exists to recycle process waters within an oilseed and oil processing facility. This applies to both internal waters and the recycling of treated effluents. The figures in Table 15.1 assume a reasonably well-managed facility with a limited amount of internal water recycling.

There are several sources of water that can be reused to meet lower-quality demands. These sources include vacuum pump seal water, condensates, and noncontact cooling water. These flows can be used for air emission scrubbers, the make-up of floor wash-down water, and related uses.

Several processors in North America are currently recycling portions of treated effluent. Facilities that have direct surface water discharges virtually must have tertiary filtration of effluents from biological treatment facilities to meet discharge limits consistently. This filtered effluent is suitable for cooling tower make-up. Between 30 and 50% of this filtered water can be recycled without concern for the build-up of dissolved solids (TDS). Each application must have a TDS mass balance analysis to determine the appropriate level. Additional facilities require chlorination or some sort of disinfecting, along with storage, pumping, and distribution facilities.

Filtered effluents can also be used for boiler feed water. In these applications, a goal of 70–80% recycled effluent is possible, with the use of reverse osmosis (RO) The remaining 20–30% will be in the form of RO rejects. Other creative systems capture and store storm water for fire prevention.

Water recycling opportunities are virtually always subject to the same short-term financial acceptability tests as other plant discretionary spending. Trends in environmental regulation and management are clearly in the direction of more rather than less control. This means that projects that are only marginally desirable from a financial standpoint today will be the clear winners tomorrow. The resulting recommendation is to view these projects with the future in mind rather than strictly on the basis of short-term financial analysis.

Air Emissions

This subject has not been covered in great detail in this presentation. By and large, controls are highly integrated with the process. In some areas separate emission control technologies are used. These include cyclones, bag houses, and filters for grain solids, scrub coolers for odors, and a variety of devices for boiler flue gas control. Air emission control technology is not as highly industry specific as are solutions to wastewater handling in the fats and oils area. As a result, a much broader range of reference material is available. The interested reader can start with the paper by Henricks (2) and expand from that point.

Solid Wastes

Bleaching Earth. Several techniques have been used successfully in the past to remove and recover oil from spent clays. The most popular of these uses soda ash. Several commercial suppliers have accepted waste earths in the past. However, the increasing costs of disposing of this material as a waste may make this an economically viable trade again in the near future.

Spent Catalyst. Increasing regulation of spent nickel catalyst as a hazardous waste has created a new industry. A number of companies are beginning to accept waste catalyst and recycling it for the nickel value. Some of these are the actual catalyst manufacturers and some are independent processors. The whole area still lacks stability, but it is improving as waste handling costs continue to rise.

Grain and Meal Solids. These materials often result in contamination of storm water runoff from plant ground area surfaces. This contamination can be significant, amounting to the addition of 1000 lb of BOD and suspended solids per day to the waste load.

References

1. *Standard Methods for Water and Wastewater Analysis*
2. Henricks, R.L., Air Pollution Issues Associated with Soybean Process Facilities, from Environmental Short Course, Dallas, TX, 1984.

Chapter 16

Regulatory Considerations for Oilseed Processors and Oil Refiners

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Introduction

Many workplace, environmental, food safety, and other regulations (see Tables 16.1 and 16.2 for summary information on U.S. laws and regulations) apply to oilseed processors and oil refiners (1). Most of the environmental and workplace legislation came about in the 1970s in response to increased general public awareness, concern, and desire for a cleaner environment, safer workplace, and safer food supply. This has led to an increasing number of regulations, and it is expected that there will continue to be more and stricter regulation in the future.

This chapter discusses some of the regulations required in the United States. Many other countries have similar requirements, but if they do not, it would be prudent for oilseed solvent extraction operations and vegetable oil refiners to consider

TABLE 16.1 U.S. Worker Health and Safety Laws and Regulations

- Laws
    - Occupational Safety and Health Act of 1970 (OSH Act) (PL 91-596 as amended by PL 101 552; 29 U.S. Code 651 *et seq.*)
- OSHA Health Standards
    - Air Contaminants Rule, 29 CFR 1910.1000
    - Hazard Communication Standard, 29 CFR 1910.1200
    - Occupational Exposure to Hazardous Chemicals in Laboratories, 29 CFR 1910.1450
- OSHA Safety Standards
    - Process Safety Management, 29 CFR 1910.119
    - Emergency Action Plan, 29 CFR 1910.38(a)(1)
    - Fire Prevention Plan, 29 CFR 1910.38(b)(1)
    - Fire Brigades, 29 CFR 1910.156
    - Permit-Required Confined Space, 29 CFR 1910.146
    - Lockout-Tagout, 29 CFR 1910.147
    - Occupational Noise Exposure, 29 CFR 1910.95 and Hearing Conservation Program, 29 CFR 1910.95(c)
    - Personal Protection Equipment:
    - General Requirements, 29 CFR 1910.132
    - Eye and Face Protection, 29 CFR 1910.133
    - Respiratory Protection, 29 CFR 1910.134
    - Head Protection, 29 CFR 1910.135
    - Foot Protection, 29 CFR 1910.136

TABLE 16.2 U.S. Environmental Laws and Regulations[a]

Law or Regulation	Purpose
Environmental Protection Agency (EPA) (established 1970)	To protect human health and welfare and the environment.
Clean Air Act (CAA) (42 U.S. Code 7401 *et seq.*)	To protect the public health and welfare. Provides EPA with the authority to set NAAQS, to control emissions from new stationary sources, and to control HAP.
Federal Water Pollution Control Act (known as the Clean Water Act) (CWA) (33 U.S. Code 1251 *et seq.*)	The major law protecting the "chemical, physical and biological integrity of the nation's waters." Allows the EPA to establish federal limits on the amounts of specific pollutants that can be released by municipal and industrial facilities.
Toxic Substances Control Act (TSCA) (15 U.S. Code 2601 *et seq.*)	Provides a system for identifying and evaluating the environmental and health effects of new chemicals and chemicals already in commerce.
Resource Conservation and Recovery Act (RCRA) (42 U.S. Code 6901 *et seq.*)	A system for handling and disposal of nonhazardous and hazardous waste.
Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) (42 U.S. Code 9601 *et seq.*)	(Known as "Superfund"), gives the EPA power to recover costs for containment, other response actions, and cleanup of hazardous waste disposal sites and other hazardous substance releases.
Emergency Planning and Community Right-to-Know Act (EPCRA; also "SARA 313") (42 U.S. Code 1101 *et seq.*)	(Part of Superfund) Provides authority for communities to devise plans for preventing and responding to chemical spills and release into the environment; requires public notification of the types of hazardous substances handled or released by facilities; requires state and local emergency plans.

[a] Abbreviations: NAAQS, National Ambient Air Quality Standard; HAP, Hazardous Air Pollutant.

meeting these regulations and for these industries to have environmental, health and safety, and quality management programs (2,3). Other chapters in this book discuss process controls, and Boyer (Chapter 15) reviews processes related to waste generation and control abatement technologies for air, water, and waste streams directed mainly at conventional caustic refining and related downstream processes. A glossary of terms/abbreviations is given in the Appendix.

Workplace Regulations (OSHA)

Workplace regulations (Table 16.1) are promulgated and enforced in the United States by the Occupational Safety and Health Administration (OSHA), which is part of the U.S. Department of Labor. The purpose of OSHA is to ensure that employers maintain a safe and healthful workplace. OSHA general industry standards [29 Code of Federal Regulations (CFR) 1910] apply to oilseed extraction and oil refining, and several of these workplace standards are discussed. Many other health and safety standards that cover all industries (e.g., bloodborne pathogens, noise, and lockout/tagout) also apply (4). In addition, even if there is not a specific standard, OSHA can site a facility under the "general duty clause" [Sec. 5(a)(1) of the OSH Act] because the OSH Act requires the employer to maintain a safe and healthful workplace.

Air Contaminants Standard (29 CFR 1910.1000)

The purpose of the air contaminants standards is to reduce risk of occupational illness for workers by reducing permissible exposure limits (PELs) for chemicals. Table 16.3 lists the PELs for *n*-hexane, hexane isomers, and some other solvents and chemicals. PEL are 8-h time-weighted average (TWA) exposures. To achieve compliance with the PELs, administrative or engineering controls must first be determined and implemented, whenever feasible. When such controls are not feasible to achieve full compliance, personal protective equipment, work practices, or any other protective measures are to be used to keep employee exposure below the PEL.

In the case of a mixture of contaminants, an employer has to compute the equivalent exposure when the components in the mixture pose a synergistic threat (i.e., toxic effect on the same target organ) to worker health (5,6). The mixture calculation is expressed as follows:

$$E_{\mathrm{m}} = (C_1/L_1 + C_2/L_2) + \ldots + (C_{\mathrm{n}}/L_{\mathrm{n}}) \qquad [1]$$

where E_{m} is the equivalent exposure for the mixture (E_{m} should be ≤ 1 for compliance), C is the concentration of a particular substance, and L is PEL (the exposure limit for that substance specified in 29 CFR 1910).

Hazard Communication Standard (HCS) (29 CFR 1910.1200)

The HCS requires all employers to provide information to their employees on the hazardous chemicals to which they are exposed through hazard communication programs, labels and other forms of warning, material safety data sheets (MSDS), and training programs. A written hazard communications program and recordkeeping are also required.

A substance is a "hazardous chemical" if it is a "physical hazard" or a "health hazard" [29 CFR 1910.1200 (c)]. A flammable or explosive liquid is a "physical hazard." A flammable liquid means "any liquid having a flashpoint below 110°F (37.8°C), except any mixture having components with flashpoints of 100°F (37.8°C) or higher, the total of which make up 99% or more of the total volume of the mixture." "Health hazard" means "a chemical for which there is statistically significant evidence based on at least one valid study that acute or chronic health effects may

TABLE 16.3 U.S. Workplace Regulations: Air Contaminants[a,b]

Chemical name (CAS no.)	Permissible Exposure Limit (PEL) [Health risk: basis for the PEL]
n-Hexane (110-54-3)	500 ppm/1800 mg/m^3; new PEL was 50 ppm/ 180 mg/m^3, same as ACGIH (TLV); [neuropathy]
Commercial hexane[c] (none)	Same as *n*-hexane
n-Heptane (142-82-5)	500 ppm/200 mg/m^3; new PEL was 400 ppm/1640 mg/m^3, (500 ppm STEL), same as ACGIH (TLV); [narcosis]
Cyclohexane (110-82-7)	300 ppm/1050 mg/m^3; ACGIH (TLV) 300 ppm/1030 mg/m^3; [sensory irritation]
Cyclopentane (287-92-3)	None; new PEL was 600 ppm, same as ACGIH (TLV); [narcosis]
Hexane isomers	None; new PEL was 500 ppm/1760 mg/m^3 (1000 ppm STEL), same as ACGIH (TLV); [narosis]
Commercial isohexane[d] (none)	(Same as hexane isomer)
2-Methyl pentane (isohexane)(2-MP) (107-83-5)	(Same as hexane isomer)
3-Methyl pentane (3-MP) (96-14-0)	(Same as hexane isomer)
Methyl cyclopentane (MCP) (96-37-7)	(Same as hexane isomer)
2,2 Dimethyl butane (neohexane) (2,2-DMB) (75-83-2)	(Same as hexane isomer)
2,3 Dimethyl butane (2,3-DMB) (79-29-8)	(Same as hexane isomer)
Methyl cyclohexane (108-87-2)	500 ppm; new PEL was 400 ppm/1610 mg/m^3, same as ACGIH (TLV); [narcosis]
Isopropyl alcohol (2-propanol)(IPA) (67-17-5)	400 ppm/980 mg/m^3; ACGIH (TLV) same plus 500 ppm/1230 mg/m^3 STEL; [sensory irritation]
Ethyl alcohol (ethanol) (64-17-5)	1000 ppm/1880 mg/m^3; ACGIH (TLV) same; [narcosis, irritation]
Acetone (67-64-1)	1000 ppm/2400 mg/m^3; ACGIH (TLV) 750 ppm (1000 ppm STEL); [sensory irritation]
Particulate not otherwise regulated (PNOR)	
Total dust	15 mg/m^3
Respirable dust	5 mg/m^3 ; [physical irritation]
Phosphoric acid (7664-36-2)	1 mg/m^3; [sensory irritation]
Sodium hydroxide (1310-73-2)	2 mg/m^3; [sensory irritation]
Sulfuric acid (7664-93-9)	1 mg/m^3; [sensory irritation]

[a] CAS no. is the Chemical Abstracts Service Registry Number; PEL is from 29 CFR 1910.1000, Table Z-1; American Conference on Governmental Industrial Hygienists (ACGIH), threshold limit value (TLV); under the HCS, a Material Safety Data Sheet is required for all of the compounds (physical and/or chemical hazard); all of the solvents are flammable liquids or gases, under the OSHA definition, and are regulated under the Process Safety Management Standard.

[b] Abbreviations: STEL, 15 min. short term exposure limit; DMB, dimethylbutane; IPA, isopropyl alcohol.

[c] Commercial hexane as used in the U.S. is usually ~65% *n*-hexane; the rest is hexane isomers [e.g., methyl cyclopentane (MCP), 2-methyl pentane (2-MP), and 3-methyl pentane (3-MP)], and contains <10 ppm benzene.

[d] Mixture of 2-MP (45-50%), 3-MP, 2,2-DMB, and 2,3-DMB. *Source*: Ref. 30.

occur in exposed employees." Hexane requires a MSDS because all flammable liquids (physical hazard) as defined by OSHA and/or possible health hazards that have an U.S. OSHA PEL require an MSDS. *n*-Hexane isomers (e.g., isohexane) do not have an OSHA PEL but do have an American Conference of Industrial Hygienist (ACGIH) threshold limit value (TLV) (7), which some states and countries enforce as a mandatory standard.

Chemical manufacturers and importers are required to review the available scientific evidence concerning the hazards of chemicals they produce or import, and to report the information to manufacturing employers who use their products [29 CFR 1910.1200(b)]. If a chemical mixture has not been tested as a whole to determine whether the mixture is a hazardous chemical, the mixture is assumed to present the same hazards as do the components that comprise ≥1% of the mixture or a carcinogenic hazard if it contains a component in concentration of ≥0.1% that is a carcinogen [29 CFR 1910.1200(a)(5)]. Commercial hexane, containing 52% *n*-hexane, has been tested and found not to be neurotoxic, unlike pure *n*-hexane (8–10). Thus, mixtures with <52% *n*-hexane should not be considered to be neurotoxic, although *n*-hexane would have to be listed on the MSDS, if in greater quantity than 1% of the mixture.

Process Safety Management (PSM) Standard (29 CFR 1910.119)

PSM is for the prevention or minimization of the consequences of catastrophic releases of toxic, reactive, flammable, or explosive chemicals. This regulation applies to all processes that involve one or more of 137 listed chemicals (29 CFR 1910.119, Appendix A) above their threshold quantities or have ≥10,000 lb of a flammable liquid or gas, as defined by the U.S. OSHA HCS [29 CFR 1910.1200(c)]. This includes *n*-hexane, hexane isomers, and the other solvents listed in Table 16.3. The requirements for meeting this regulation are described in more detail by Lajeunesse (11) and Strube (12).

In addition to the PSM standard, U.S. OSHA has been enforcing two other regulations for operations/processes with flammable liquids. First, under Personal Protective Equipment-General Requirements (29 CFR 1910.132), OSHA has cited or obtained voluntary agreement from organizations relative to flame-resistant (FR) clothing. Operators and other employees working in the area of a flammable process are required to wear FR-work clothing. For facilities that use commercial hexane and other flammable solvents, it would be prudent to require FR-clothing for all personnel working in areas in which there is an exposure to a flammable liquid. Second, OSHA has cited organizations for failure to meet related safety regulations under Fire Brigades (29 CFR 1910.156), specifically for standards such as the following: (i) training, both initial and annual refresher training; (ii) protective equipment availability and testing; and (iii) fitness for duty including periodic physicals. If an onsite fire brigade is part of the site's Emergency Response Plan (29 CFR 1910.38), then these requirements must also be met. In addition, the requirement of the PSM standard for an Emergency Response Plan triggers the requirements of Emergency Action Plan [29 CFR 1910.38(a)].

Environmental Regulations (EPA)

The U.S. Environmental Protection Agency (EPA) administers all regulations affecting the environment and chemicals in commerce. The purpose of the EPA is to protect human health and welfare and the environment. The individual states and state environmental regulatory control boards implement and enforce most of the regulations. The legislation that serves as the basis for the regulations can be divided into the following statute areas:

1. Statutes that are media-specific [Clean Air Act (CAA) and Clean Water Act (CWA)].
2. Statutes that manage solid and hazardous waste [Resources Conservation and Recovery Act (RCRA) and Comprehensive Environmental Response, Compensation and Liability Act (CERCLA; "Superfund")].
3. Statutes that directly limit the production rather than the release of chemical substance [Toxic Substances Control Act (TSCA) and Federal Insecticide, Fungicide and Rodenicide Act (FIFRA)]. (See Table 16.2 for a summary of the information on environmental laws and regulations, Table 16.4 for an overview of environmental requirements for air and water, Table 16.5 for a summary of air threshold emissions, and Table 16.6 for an overview of environmental requirements for waste.)

Clean Air Act (CAA; 42 U.S. Code 7401 et seq.)

The purpose of the CAA is to protect the public health and welfare. To satisfy the CAA requirements, states and state air control boards are required to implement regulations and develop state implementation plans (SIP) (13,14). Criteria pollutants [e.g., ozone (O_3), particulate matter (PM), nitrogen oxides (NO_x), sulfur oxides (SO_x), carbon monoxide (CO), and lead (Pb)] are regulated with National Ambient Air Quality Standards (NAAQS); hazardous air pollutants (HAP), such as *n*-hexane, are regulated with National Emissions Standards for Hazardous Air Pollutants (NESHAP). The 1990 CAA expanded the list of HAP to 188, including *n*-hexane, and regulates nonattainment areas more strictly for criteria pollutants such as O_3, PM, CO, and NO_x.

Hazardous Air Pollutants (HAP) or Air Toxics (40 CFR 61). If a facility is a major emitter of any of the chemicals on the CAA list of HAP (presently 188), EPA requires sources to meet national emissions standards (13,15,16). *n*-Hexane is on the HAP list, but isohexane, acetone, and other solvents listed in Table 16.4 are not.

The air toxic requirements of the CAA for establishing control measures for source categories are technology-based emission standards (not health based) established for major sources (10 ton/y of one HAP or 25 ton/y of total HAP) that require the maximum degree of reduction emissions, taking into account costs, other health and environmental effects, and energy requirements. Standards are set on the basis of known or anticipated effects of pollutants on the public health and the environment, the quantity emitted, and the location of emissions. Compliance with a NESHAP involves the installation of Maximum Achievable Control Technology

TABLE 16.4 U.S. Environmental Regulations: Air and Water[a]

Chemical name (CAS no.)	VOC	HAP	CWA[b]
n-Hexane (110-54-3)	Yes	Yes	Yes
Commercial hexane (none)	Yes		
n-Heptane (148-82-5)	Yes	No	Yes
Cyclohexane (110-82-7)	Yes	No	Yes
Cyclopentane (287-92-3)	Yes	No	Yes
Hexane isomers (none)	Yes	No	Yes
Commercial isohexane (same as hexane isomers) (none)		No	Yes
2-Methyl pentane (a hexane isomer) (also called isohexane) (107-83-5)	Yes	No	Yes
3-Methyl pentane (a hexane isomer) (96-14-0)	Yes	No	Yes
Methyl cyclopentane (a hexane isomer) (96-37-7)	Yes	No	Yes
2,2 Dimethyl butane (a hexane isomer) (neohexane) (75-83-2)	Yes	No	Yes
2,3 Dimethyl butane (a hexane isomer) (79-29-8)	Yes	No	Yes
Methyl cyclohexane (108-87-2)	Yes	No	Yes
Isopropyl alcohol (2-propanol) (67-17-5)	Yes	No	Yes
Ethyl alcohol (ethanol) (64-17-5)		No	Yes
Acetone Misc. (67-64-1)	No[c]	No	Yes

[a] Abbreviations: CAS no., Chemical Abstracts Service Registry number; VOC, volatile organic chemical; HAP, hazardous air pollutant; CWA, Clean Water Act.

[b] Under the CWA, there could be stormwater and National Pollution Discharge Elimination System permit requirements; none of the solvents are listed as priority toxic pollutants in 40 Code of Federal Regulations 401.15.

[c] Acetone is considered by the U.S. EPA not be a VOC (60 Federal Register 31643; June 16, 1995).

(MACT); MACT essentially is maximum achievable emission reduction. For new sources, MACT standards must be no less stringent than the emission control achieved in practice by the best controlled similar source.

On May 26, 2000 [65 Federal Register (FR) 34252], the U.S. EPA published the proposed NESHAP for solvent extraction for vegetable oil production. EPA considers

TABLE 16.5 Summary of Threshold Emission Levels

Regulation	Threshold emission level	Requirement[a]
Major source (40 FR 70)	≥ 100 ton criteria pollutant or 10/25 ton HAP/y	Title V permit (Federal operating permit)
Hazardous Air Pollutants (HAP)	10 ton of one HAP/ 25 ton total HAP/y	NESHAP/MACT standard
NAAQS:O_3 (VOC)[c]	10–100 tons (depending on degree of severity of nonattainment)	RACT/BACT standard
Particulate matter	70 tons nonattainment; 100 ton attainment	RACM/BACM standard
NSR:PSD[d]	250 ton	Preconstruction/building permit, BACT; much paperwork
Nonattainment NSR	100 ton/y	Preconstruction permit, LAER, emission offsets
Toxic Release Inventory (TRI)	10,000–25,000 lb/y (Hexane is covered/ hexane isomers not covered)	Annual reporting (Form R);112(r)[e]
PSM[f]	>10,000 pounds in one tank (All flammable solvents including hexane/hexane isomers are covered)	Written plan, controls, training

[a] See Appendix: Glossary of Terms for NESHAP, MACT, RACM, BACM, RACT, BACT, and LAER.

[b] For example, threshold can range from 10 to 100 ton depending on degree of severity of ozone (O_3) nonattainment.

[c] Ground level ozone (O_3) is not emitted directly into the air, but is formed when sunlight reacts with nitrogen oxides (NO_x) and volatile organic compounds (VOC) such as hexane.

[d] PSD is Prevention of significant deterioration, a requirement of New Source Review (NSR) in attainment area.

[e] Section 112(r) of the Clean Air Act [40 Code of Federal Regulations (CFR) 68] is for prevention of chemical accidents. Hexane/hexane isomers not covered by 112(r).

[f] PSM is Process Safety Management (29 CFR 1910.119), Occupational Safety and Health Administration standard to prevent or minimize the consequences of catastrophic releases.

solvent extraction for vegetable oil production processes as major sources of the HAP *n*-hexane. Figure 16.1 shows a general flow diagram of a typical vegetable oil production facility, identifying the most common emission sources of hexane (31). Hexane emissions occur from ten general sources: 1) the main vent; 2) meal dryer vent; 3) meal cooler vent; 4) crude meal; 5) crude oil; 6) equipment leaks; 7) solvent storage tanks; 8) process wastewater collections; 9) facility startup/shutdowns; and 10) operational upsets. Facilities covered are those that produce crude vegetable oil and meal products by removing crude oil from listed oilseeds (corn germ, cottonseed, flax, peanuts, rapeseed, safflower, soybeans, and sunflower) through direct contact with solvent. The rule will require all existing and new solvent extraction processes that are major sources (potential to emit ≥10 ton/y of *n*-hexane) to meet these HAP emission standards, as a 12-mo rolling average based on a 64% *n*-hexane content. HAP emission standards vary for each oilseed (Table 16.7) and reflect the

TABLE 16.6 U.S. Environmental Regulations: Waste

Chemical name (CAS no.)	(RCRA) Sec. 304 RCRA Code[b]	CERCLA (RQ)	(EPCRA/SARA Title III)[a] Sec.311/312	Sec.313 (TRI)
n-hexane (110-54-3)		5000[c]	Yes	Yes
Commercial hexane (none)				Yes[d]
n-Heptane (142-82-5)			Yes	No
Cyclohexane (110-87-7)	U056	1000	Yes	Yes
Cyclopentane (287-92-3)			Yes	No
Hexane isomers (none)			Yes	No[e]
Commercial isohexane (none)				No[e]
2-Methyl pentane (also called isohexane) (107-83-5)			Yes	No[e]
3-Methyl pentane (96-14-0)			Yes	No[e]
Methyl cyclopentane (96-37-7)			Yes	No[e]
2,2 Dimethyl butane (neohexane) (75-83-2)			Yes	No[e]
2,3 Dimethyl butane (79-29-8)			Yes	No[e]
Methyl cyclohexane (108-87-2)			Yes	No
Isopropyl alcohol (2-propanol) (67-63-0)			Yes	No[f]
Ethyl alcohol (64-17-5)			Yes	No
Acetone (67-64-1)	U002	5000	Yes	No

[a] From Title III Lists of Lists, U.S. EPA, EPA 740-R-95-001 (April 1995); 40 Code of Federal Regulations (CFR) 52-99; [59 Federal Register (FR) 4478; January 31, 1994] hexane added to Toxic Release Inventory (TRI) list; (60 FR 31633; June 16, 1995) acetone removed from TRI list.

[b] 40 CFR 261.33, listed hazardous waste–EPA Resource Conservation and Recovery Act (RCRA) Hazardous waste number. All of the solvents that are on the RCRA list are listed because of Section 3001 of RCRA (part for identification and listing of hazardous waste) except hexane which is on because of Clean Air Act Section 112 (hazardous air pollutant).

[c] Reportable quantity (RQ) in pounds for hexane finalized June 12, 1995 (60 FR 30939).

[d] Only the amount of commercial hexane that is *n*-hexane has to be reported (e.g., if the commercial hexane is 62% *n*-hexane, only 62% of the emissions have to be reported for TRI).

[e] The EPA clarified that the listing for hexane was only for *n*-hexane; other isomers of hexane are not included (59 FR 61457; Nov. 30, 1994).

[f] The EPA has indicated (62 FR 22318, April 25, 1997) that isopropyl alcohol (IPA) itself does not meet the criteria for listing on the TRI list. The EPA will remove IPA from the TRI list.

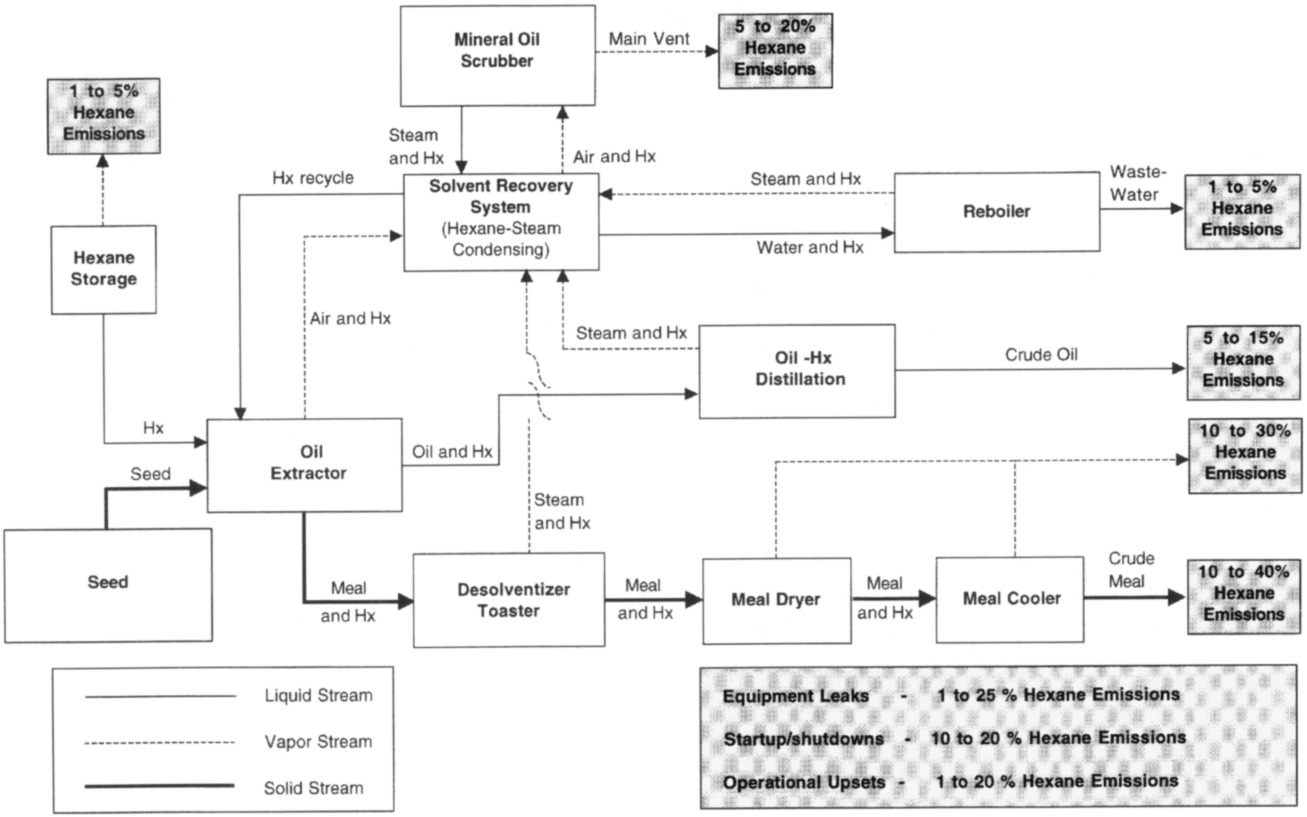

Fig. 16.1. Overview of process operations at a typical vegetable oil production facility and identification of common emission sources (31).

TABLE 16.7 U.S. Oilseed Solvent Loss Factors for Allowable Hazardous Air Pollutant (HAP) Loss (12-mo Rolling Average)

		Oilseed solvent loss factor (gal/ton)	
Type of oilseed process	Description of process	Existing sources	New sources
Corn germ, wet milling	Processes corn germ that has been separated from other corn components using a wet process of centrifuging a slurry steeped in a dilute sulfurous acid solution.	0.4	0.3
Corn germ, dry milling	Processes corn germ that has been separated from the other corn components using a dry process of mechanical chafing and air sifting.	0.7	0.7
Cottonseed, large	Processes ≥120,000 tons of a combination of cottonseed and other listed oilseeds during all normal operating periods in a 12-mo operational period.	0.5	0.4
Cottonseed, small	Processes <120,000 ton of a combination of cottonseed and other listed oilseeds during all normal operating periods in a 12-mo operational period.	0.7	0.4
Flax	Processes flax.	0.6	0.6
Peanuts	Processes peanuts.	1.2	0.7
Rapeseed	Processes rapeseed.	0.7	0.3
Safflower	Processes safflower.	0.7	0.7
Soybean, conventional	Uses a conventional style desolventizer to produce crude soybean oil products and soybean animal feed products.	0.2	0.2
Soybean, specialty	Uses a special style desolventizer to produce soybean meal products for human and animal consumption.	1.7	1.5
Soybean, small combination plant	Processes soybeans in both specialty and conventional desolventizers and the quantity of soybeans processed in specialty desolventizers during normal operating periods is <3.3% of total soybeans processed during all normal operating periods in a 12-mo operational period. The corresponding solvent loss factor is an overall value and applies to the total quantity of soybeans processed.	0.25	0.25
Sunflower	Processes sunflower.	0.4	0.3

application of MACT (65FR34252; May 26, 2000). The final rule is expected in early 2001, and the solvent loss factors are expected to be those listed in Table 16.7. Industry will have 3 y after the standard is finalized to become compliant. Because the emission loss factor values are 12-mo rolling averages, the first compliance report would be due 48 mo after the standard is promulgated. The requirements cover normal operations and start-up, shutdown, and malfunction.

There are also variable emission requirements depending on the oilseed for allowable emissions for vegetable oil processing in Europe (Table 16.8) (17). The EEC directive for Europe is to be fully implemented by all member states by Oct. 30, 2004 for new plants and Oct. 30, 2007 for old plants. However, there are some intermediate targets before full compliance, i.e., starting Oct. 30, 2001 for new plants and Oct.30, 2005 for old plants, the target solvent consumption is 1.5 times the final level. The EEC counts the total input of solvent into a plant per calendar year or any 12-mo period and also requires a solvent management plan that is to be updated yearly and contains the following requirements: (i) verification of compliance to the ECC regulation through a mass balance; (ii) identification of future reduction options; and (iii) development of a waste minimization plan.

In the United States, a health-based standard would be for a boundary-line level of a solvent (e.g., *n*-hexane) based on the inhalation reference concentration (RfC) (18). The current RfC for hexane is 200 μg/m^3. Recent research suggests that the RfC for hexane should be at least 10 times higher (>2000 μg/m^3).

NAAQS. The NAAQS are set at levels sufficient to protect public health, including the health of sensitive populations (primary air quality standards) and public welfare (secondary air quality standards; "welfare effects" include protection against

TABLE 16.8 European Maximum Solvent Loss Factors (EEC Directive for Vegetable Oil Extraction)(17)

	Maximum volatile organic compound (VOC) usage/(ton seed/y) per year	
	kg/ton	gal/ton
Oilseed		
Olives	2.5	1.0
Castor	3.0	1.2
Rapeseed	1.0	0.4
Sunflower	1.0	0.4
Soybeans	0.8	0.3
Soy flash	1.2	0.5
Other seeds	3.0	1.2
Oil refining and fractionation		
Fractionation without degumming	1.5	0.6
Degumming plant	4.0	1.6

decreased visibility, damage to wildlife, crops, vegetation, and buildings, and effects on personal comfort and well-being) from any known or anticipated adverse effect of the pollutant with an adequate (appropriate) margin of safety.

Volatile organic compounds (VOC) are essentially the same as the criteria pollutant ozone (14–16). Ground level ozone is not emitted directly into the air, but is formed when sunlight acts on emissions of NO_x and VOC. VOC are very broadly defined by the U.S. EPA (40 CFR 51.100) as follows: Any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, that participates in atmospheric photochemical reactions. This includes any organic compound other than those specifically listed as having been determined to have negligible photochemical reactivity. Reactive VOC are essentially all those judged to be clearly more reactive than ethane, the most reactive member of the "negligibly reactive" class. C_4–C_6 paraffins are of relatively low kinetic reactivity but produce NO_2, and potentially ozone (19). *n*-Hexane, hexane isomers, and the other solvents discussed, except acetone, would be considered VOC (Table 16.4) that can undergo photochemical oxidation in the atmosphere to form ozone. In the United States, acetone was added to the list of compounds excluded from the definition of VOC in 1995 because it was determined to have negligible photochemical reactivity (2).

Most U.S. vegetable oil extracting facilities would be major sources of VOC and would be covered by the requirements for ozone emissions and attainment, unless they used a solvent that was not classified as a VOC. (The definition of "major source" changes as the severity of the ozone nonattainment area increases. Plants in marginal and moderate areas are considered major sources if they emit 100 ton VOC/y; in serious areas, 50 ton/y; in severe areas, 25 ton/y; and in extreme areas 10 ton/y). All facilities in ozone nonattainment areas could be required to reduce emissions through implementation of Reasonable Available Control Technology (RACT) standards or Best Available Control Technology (BACT).

Most vegetable oil production facilities are major sources of PM. Depending on the oilseed processed, PM emissions can be 0.1-0.3 lb of total suspended particulate, which is ~50% PM10 and <3% PM2.5, per ton of seed processed. PM controls (Table 16.5) would also have to be part of a facility's federal and state permits. Vegetable oil production facilities probably also have to include NO_x, SO_x, and CO emissions in their federal and state permits.

Any new or significantly modified facility would have to comply with the new source review (NSR) requirements. NSR is a preconstruction permission program. If new construction or making a major modification will increase emissions by an amount large enough to trigger NSR requirements (Table 16.5), then the source must obtain a permit before it can begin construction. Permits for sources in attainment areas are prevention of significant deterioration (PSD) permits and those in nonattainment areas are nonattainment NSR permits. For a PSD permit, a source must apply BACT and for nonattainment NSR, Lowest Achievable Emission Rate (LAER) is required.

Odor. There are no specific federal regulations for odor. States can, however, regulate odor if they choose to. For example, Colorado requires hog lagoons to be covered because of a state referendum vote. Also odor can generate complaints that cause states to require more stringent emission controls. Boyer (Chapter 15) discusses methods for odor control.

Federal Permits (40 CFR 70). All major sources of regulated solvents are required to have federally enforceable operating permits (13,14) (also referred to as Title V permits).

State Permits. Most states require state permits for facilities that emit listed air pollutants (13,14). In some states, federal permits and state permits are combined, whereas in other states, facilities are required to have both a state or county (air district) permit and a federal permit. As part of annual emission inventory reporting requirements, many states already require reporting of HAP and VOC because of their SIP.

Clean Water Act (CWA; 33 U.S. Code 1251 et seq.)

The CWA is the major law protecting the "chemical, physical and biological integrity of the nation's waters." Under the act, the U.S. EPA establishes water quality criteria used to develop water quality standards, technology-based effluent limitation guidelines, and pretreatment standards; it has also established a national permit program [National Pollution Discharge Elimination System (NPDES) permits; 40 CFR 122] to regulate the discharge of pollutants. The states have responsibility to develop water quality management programs. Oilseed processing and oil refining are covered by the following: (i) basic discharge effluent limitations (40 CFR 122); (ii) stormwater regulations (40 CFR 122 and 123); and (iii) oil spill prevention and response plans (40 CFR 112) (14).

Basic Discharge and Stormwater. Vegetable oil extracting facilities and oil refining are covered by basic discharge effluent limitations [direct discharges to receiving waters or indirect discharges to publicly owned treatment works (POTW)], and stormwater regulations (14). The amount of solvent in effluent discharges and in stormwater (for those covered) has to be determined and possibly monitored as part of an NPDES permit and as part of the visual examination or testing of stormwater quality. None of the solvents normally used in oilseed extraction and refining are listed as priority toxic pollutants (40 CFR 401.15).

Oil and Hazardous Substances Spills and Response Plans. Under Oil Pollution Prevention and Response (40 CFR 112), there are requirements for oilseed extraction and refining for storage and transportation of vegetable oil. Spill Prevention Control and Countermeasure Plans (SPCC) (i.e., prevention plans) are required for on-site storage and are intended to prevent spills of oil (of any kind) by nontransportation-related onshore and offshore facilities into the waters of the United States or adjoining shorelines. The requirements for preparation and implementation of SPCC plans (14) state that if a facility discharges, or could reasonably be expected to discharge oil in harmful quantities [a discharge of oil that can cause a sheen (iridescent appearance) on the surface of water; 40 CFR 110.3] into navigable waters of the United States or adjoining shoreline, a SPCC plan is required. The regulations apply to facilities with total above ground storage capacity >1320 gal, or total underground storage capacity >42,000 gal.

Pursuant to the Oil Pollution Act of 1990 (OPA-90) (Public Law 101-380), the EPA amended the Oil Pollution Prevention regulations by adding response plan requirements for nontransportation-related onshore facilities that handle, store, or transport oil. Facilities that could cause substantial harm to the environment are required to prepare and submit response plans to the EPA. The "flowchart of criteria for substantial harm" (14) was published in the Federal Register on July 1, 1994 (59 FR 34104); if the facility transfers oil over water to or from vessels and has a total oil storage capacity ≥42,000 gal or the facility has a total storage capacity ≥1 million gal, a response plan is required. In 2000 (65FR40776; June 30, 2000) EPA amended this rule to provide more specific guidance for operators that handle, store, or transport vegetable oils.

Under OPA-90, comprehensive oil spill response plans are also required for transportation of non-petroleum oils (i.e., vegetable oil) by rail and road in amounts ≥42,000 gal [regulated by Research and Special Programs Administration (RSPA), Department of Transportation (DOT); Final Rule, 61 FR 30533 (June 17, 1996)] and for marine transportation-related facilities [regulated by the DOT, Coast Guard; Final Rule, 65 FR 40820 (June 30, 2000)].

Resource Conservation and Recovery Act (RCRA; 42 U.S. Code 6901 et seq.)

RCRA subtitle C (40 CFR 261) is a federal "cradle-to-grave" system to manage hazardous waste (including provisions for cleaning up releases and setting statutory and regulatory requirements). Subtitle D covers nonhazardous wastes. Materials or items are hazardous wastes if and when they are discarded or intended to be discarded. The act requires generators, transporters, and disposers to maintain written records of waste transfers, and requires the U.S. EPA to establish standards, procedures, and permit requirements for disposal. The act also requires states to have solid-waste management plans, prohibits open dumping, and requires the EPA to establish criteria for sanitary landfills. EPA under RCRA also regulates underground storage tanks that store or have stored petroleum or hazardous substances.

Hazardous wastes are either listed wastes (40 CFR 261.30-.33) or characteristic wastes (40 CFR 261.21-.24). The U.S. EPA defines the following four characteristics for hazardous waste: (i) ignitability (40 CFR 260.21); (ii) corrosivity (40 CFR 260.22); (iii) reactivity (40 CFR 260.23); and (iv) toxicity (40 CFR 260.24). Any waste that exhibits one or more of these characteristics is classified as hazardous under RCRA. The ignitability definition includes a liquid that has a flash point <60°C (140°F); the EPA included ignitability to identify wastes that could cause fires during transport, storage, or disposal (e.g., used solvents). All of the solvents in Table 16.6 have flash points <60°C, thus all could be a RCRA ignitability waste.

Spent bleaching clay is not a RCRA hazardous waste (40 CFR 302). It is usually disposed of by taking it to a regular landfill. A spontaneous combustion (oxidation of unsaturated fatty acids in the retained oil causing self-heating leading to combustion) problem can exist when it is taken to the landfill. The potential for spontaneous combustion in bleaching earth depends on the type and amount of oil retained and rises with increasing unsaturation of the fatty acids in the retained oil. U.S. DOT classifies materials liable to spontaneous combustion as Class 4.2 hazardous materials [49 CFR 173.124 (b) and Appendix E 3]. Spent bleaching clay can be finely ground and put in small quantities into the animal meal in operations that do oil extraction. With the increased concern about dioxin in food and feed product by the U.S. Food and Drug Administration (FDA) and EPA, this is discouraged since some clays can contain measurable amounts of dioxin. Zachau (Ref. 20 and Chapter 9 this book) describes other ways to utilize spent bleaching clay, including those that are environmentally friendly.

Spent nickel catalyst does not have a RCRA waste number and is not considered a RCRA hazardous waste (40 CFR Table 302.4). No reporting of release of this substance is required if the diameter of the solid metal released is ≥100 μm. The reportable quantity (RQ) for particles >100 μm is 100 lb. Most, if not all, spent nickel catalyst is recycled.

Comprehensive Environmental Response, Compensation and Liability Act (CERLA, "Superfund"; 42 U.S. Code 9601 et seq.)

"Superfund" is the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) of 1980; it gives the U.S. EPA authority to force those responsible for hazardous waste sites or other releases of hazardous substances, pollutants, and contaminants to conduct cleanup or other effective response actions.

Section 103 of CERLA requires the person in charge of a facility to immediately report any release of a hazardous substance in an amount equal to or greater than its RQ to the National Response Center (NRC) [also see discussion below on Emergency Planning and Community Right-to-Know Act (EPCRA) Section 304]. *n*-Hexane, acetone, and other chemicals in Table 16.6 as well as NO_x (RQ = 10 lb/24 h), hydrogen sulfide, and ammonia (for both, RQ-100 lb/24 h) are CERLA hazardous substances and have a CERLA RQ for releases. CERLA and EPCRA, however, do not require notification to the NRC, the State Emergency Response Commissions (SERC), and the Local Emergency Planning Committees (LEPC) of "federally permitted releases" of hazardous air releases/emissions as defined in CERLA Section 101 (10) (H), i.e., any emission into the air subject to a permit or control regulation under Section 111, Section 112, Title I part C, Title I part D, or state implementation plans in accordance with Section 110 of the CAA.

Emergency Planning and Community Right-to-Know Act (EPCRA; 42 U.S. Code 11001 et seq.)

Enacted as Title III of the 1986 Superfund Amendments and Reauthorization Act (SARA), the Act mandates the EPA to monitor and protect communities regarding releases of chemicals into the environment. It requires states to establish emergency planning districts with local committees to devise plans for preventing and responding to chemical spills and releases.

Section 304 (40 CFR 355.40). Section 304 of EPCRA requires the owner or operator of a facility to immediately notify the SERC and LEPC committees of any accidental releases (that are not "federal permitted"), in quantities equal to or greater than their RQ, of an EPCRA designated extremely hazardous substances or a CERCLA hazardous substances (40 CFR 302, Table 302.4) and provide written follow-up notice as soon as practicable thereafter (also see discussion on CERLA Section 103). *n*-Hexane, cyclohexane, acetone, and some of the other solvents discussed are CERCLA hazardous substances and have CERCLA RQ for air releases (Table 16.6).

Section 311, 312 (40 CFR 370.20-.21). For chemicals that are required to have an MSDS, businesses must make them available to state and local officials. Because all of the solvents discussed require MSDS under the OSHA HCS, all are covered by these requirements.

Section 313 (40 CFR 372), Toxic Release Inventory (TRI). Businesses are required to file annual reports with federal and state authorities of releases to air, water, and land above a certain threshold for chemicals on the TRI/Section 313 list (40 CFR 372.65) by July 1 each year for the previous year's releases (21). TRI requirements are triggered if a facility with 10 or more full-time employees manufactures, processes, or otherwise uses one or more listed substance(s) in a quantity above the statutory reporting threshold of 25,000 lb/y (manufactured or processed) or 10,000 lb/y (otherwise used). Beginning with the 1991 reporting year, such facilities also must report pollution prevention and recycling data for such chemicals pursuant to Section 6607 of the Pollution Prevention Act (42 U.S. Code 13106).

n-Hexane was added to the TRI list in 1994 with reporting for 1995 emissions (2,21). The other solvents discussed are not on the TRI list. The EPA can add new chemicals to or delete chemicals from the TRI list as deemed necessary, and any person may petition the EPA to add chemicals or delete chemicals from the list as occurred for acetone (2) in 1995 (60 Fr 31643; June 16, 1995) and phosphoric acid in 2000 (65 Fr 39552; June 27, 2000); thus, they no longer require reporting under TRI.

Toxic Substances Control Act (TSCA; 15 U.S. Code 2600 et seq.)

If a chemical's manufacture, processing, distribution, use, or disposal would create unreasonable risks, the U.S. EPA, under the TSCA (40 CFR Section 700, *et seq.*), can regulate it, ban it, or require additional testing.

Section 4(a). Under Section 4(a) of TSCA, the U.S. EPA can require testing (referred to as a "Section 4 test rule") of a chemical substance or mixture to develop data relevant to an assessment of the risks to health and the environment.

Section 5(a)(1). This section of TSCA (40 CFR 720) mandates the U.S. EPA to monitor and control the use of toxic substances by requiring the Agency to review the health and environmental effects of new chemicals (referred to as "Premanufacturing Notice" or "PMN") and chemicals already in commerce. The U.S. EPA also has Significant New Use Rules (SNUR) under Section 5(a)(2) of TSCA (40 CFR 721), which provides a way for the U.S. EPA to restrict uses of chemical substances already in commerce, when they are proposed for new uses. *n*-Hexane, hexane isomers, acetone, and the other solvents discussed are already commercially available, thus a PMN would not apply. However, some of the solvents other than *n*-hexane could be subject to a SNUR (40 CFR 721, subpart A) because they are not presently being used as extraction solvents in large quantities.

Section 8: Reporting and Retention of Information. Section 8(d) of TSCA (Health and Safety Data Reporting; 40 CFR 716) requires that lists of health and safety studies conducted or initiated with respect to a substance or mixture be submitted to the U.S. EPA. Section 8(e) of TSCA (no 40 CFR Reference) requires that all new toxicological data of the effects of a chemical not previously mentioned must be reported immediately, if the data reasonably support the conclusion that such substance or mixture presents a substantial risk of injury to health or the environment. Testing (Section 4 test rule) was required for several of the solvents earlier [e.g., commercial hexane for which new toxicological information was reported to the U.S. EPA since 1992 (22)], and any new toxicological information will have to be reported to the U.S. EPA under Section 8(e) and 8(d).

Inventory Update Rule (IUR) (40 CFR 710). The IUR was established in 1986 to require manufacturers and importers of chemicals listed on the master TCSA Inventory to report current data every 4 y on the production volume of chemicals imported or produced. Food and feed products produced from natural agricultural product, such as oilseeds, are not required to be reported, but the rule applies to all oil and meal products obtained by solvent extraction that is sold for uses other than food or feed (e.g., oils as chemical raw materials and meal as fertilizer). This list from 1990 was used to determine the High Production Volume (HPV) chemicals (>1 million lb/y) that are part of the HPV testing program. Vegetable oils are listed as a category 1, which does not require toxicity testing at this time.

Food Safety (FDA)

In the United States, the U.S. FDA regulates all aspects of food, including food ingredients and labeling. To be used legally in the United States, oilseed extraction solvents and food processing substances must have been subject to an approval by the

U.S. FDA or the U.S. Department of Agriculture (USDA) during 1938–1958 for this use ("prior sanction"), be generally recognized as safe (GRAS) for this use, or be used in accordance with food additive regulations promulgated by the U.S. FDA.

Many prior sanctions and GRAS determinations are not codified in the U.S. FDA regulations. However, extracting solvents used in food manufacturing, such as *n*-hexane, have been labeled as food additives, solvents, defoaming agents, components of a secondary food and color additives, minor constituents, or incidental additives (i.e., "additives that are present in a food at significant levels and do not have any technical or functional effect in that food"), depending on the application. Incidental additives can be "processing aids," (i.e., "substances that are added to a food during processing but removed from the food before it is packaged"). Most food-processing substances, including solvents, can be regarded as "incidental additives" and thus are exempt from label declaration in the finished food product. Even if exempt from label declaration, all extraction solvents must be used in accordance with the U.S. FDA good manufacturing practices (GMP; 21 CFR 100).

Commercial hexane, containing ~50–85% *n*-hexane, has been in major use since the 1940s as an oilseed-extraction solvent on the determination that it is GRAS, and it may also be subject to a prior sanction. Like many other food-processing substances, there is no U.S. FDA regulation specifically listing *n*-hexane as GRAS or having prior sanction. However, under FDA regulations hexane has been cleared as a solvent (residue not >5 ppm) in the manufacture of the food additive, fish protein isolate (21 CFR 172.340); a solvent for use in manufacturing modified hop extract used in beer brewing (residue not more than 25 ppm) (21 CFR 172.560); an extraction solvent (residue not >25 ppm) for the color additives; targets (Aztec marigold) meal and extract (21 CFR 73.295); carrot oil (73.300), color endosperm oil (73.315), paprika oleoresin (73.345), annatto extract (73.30); a component of resinous and polymeric coatings (21 CFR 175.320) and of adhesives for food packaging (21 CFR 175.105); and a defoaming agent for use in coatings that are used in producing, packaging, processing, preparing, treating, transporting, or holding foods (21 CFR 176.200). The FDA set a tolerance of 60 ppm (21 CFR 172.894) for *n*-hexane residues for food additive–modified cottonseed products ("defatted cottonseed flour"); for secondary direct food additives, FDA allows 25 ppm as *n*-hexane residue in the extraction of spice oleoresins and a residue not to exceed 2.2 wt% *n*-hexane in hops extract [21 CFR 173.270 (a) and (b)]. In addition, hexane has been cleared as a minor constituent (not >5 ppm) of a cocoa butter substitute, a direct food additive that has been affirmed by FDA as GRAS for food use (52 FR 47918, December 17, 1987; 21 CFR 184.1259).

Since 1958, the Flavor and Extract Manufacturers' Association (FEMA) has conducted a program that uses a panel of expert pharmacologists and toxicologists to determine substances that are GRAS. This panel uses all available data, including experience based on common uses in food. This safety assessment program ("FEMA GRAS") is widely accepted and considered an industry/government partnership with the U.S. FDA (23). A number of papers published in Food Technology since 1961

(24,25) list the substances that the panel has determined to be GRAS and the average maximum levels in parts per million (ppm) at which each has been reported to be GRAS for different categories of food. The U.S. FDA has not incorporated these substances into their regulations but does recognize the findings of the Expert Panel of FEMA as GRAS substances.

Because vegetable oil and other human food-grade oils undergo deodorization (steam distillation) and other purification processes (i.e., refining and bleaching) as part of the manufacturing process before being used as a food product, they should not contain any of the extraction solvent, if proper manufacturing practices are followed. Refining removes nonglyceride materials (e.g., phospholipids, color, and trace metals) and free fatty acids; bleaching with acid-activated bleaching earth or clay (e.g., bentonite) removes color-producing substances; and deodorization, the last major processing step in edible oils refining removes volatile compounds (undesirable ingredients occurring in natural oils and those that may be imparted by prior unit processes or even storage, many of which are associated with undesirable flavors and odors) (24,25). Most commercial deodorizers operate at a temperature of 245–275°C (475–525°F) under a negative pressure of 2–10 mm Hg (26,27). It has been reported that no *n*-hexane residue remains in the finished oil after processing due to its high volatility (28). In addition, animal-feeding studies with expeller and solvent-extracted meals have not indicated any adverse health affects related to the extraction solvent (29).

GRAS status may be determined by a company ("GRAS self-determination"), an industry, an independent scientific organization (e.g., FEMA GRAS), or the U.S. FDA. The Federal Food, Drug and Cosmetic Act (21 U.S. Code 321 *et seq.*) does not provide for the U.S. FDA to approve all ingredients used in food, and the U.S. FDA explicitly recognizes that its published GRAS list is not meant to be a complete listing of all substances that are in fact GRAS food substances. Although there is no requirement to inform the U.S. FDA of a GRAS self-determination or to request FDA review or approval on the matter, the U.S. FDA has established a voluntary GRAS affirmation program under which such advice will be provided by the agency. Solvents that do not have prior sanction, a GRAS determination, or a tolerance set probably should be evaluated for compliance under food safety requirements, if a facility is considering changing its extracting solvent or using a solvent for the extraction of the various biological materials for specialty markets.

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Appendix: Glossary of Terms

ACGIH, American Conference of Industrial Hygienists, an independent standards setting organization.

BACM, Best Available Control Measures.

BACT, Best Available Control Technology.

CAA, Clean Air Act, 42 U.S. Code 1251 *et seq.*

CERCLA (Superfund), Comprehensive Environmental Response, Compensation, and Liability Act, 42 U.S. Code 9601 *et seq.*

CFR, Code of Federal Regulations. U.S. federal regulations are codified here after promulgation. The preceding number is the Title, the succeeding number (after CFR) is the Part of Section (e.g., 29 CFR 1910 is Title 29 Code of Federal Regulations at Part 1910).

CWA, Clean Water Act (Federal Water Pollution Control Act), 33 U.S. Code 1251 *et seq.*

DOT, Department of Transportation.

EPA, Environmental Protection Agency, 42 U.S. Code 4321 *et seq.*

EPCRA, Emergency Planning and Community Right-to-Know Act.

FDA, U.S. Food and Drug Administration.

FEMA, Flavor and Extract Manufacturers' Association.

FR, Federal Register. Regulatory announcements and new rules and their justification are published here. The preceding number is the volume, the succeeding number (after FR) is the page, usually followed by the date when it appeared (e.g., 51 FR 27956 is Volume 51 Federal Register, page 27956).

GRAS, Generally Recognized As Safe.

HAP, Hazardous air pollutant, 40 CFR 61.

HCS, Hazard Communication Standard, 29 CFR 1910.1200.

HPV, High production volume.

IUR, Inventory Update Rule, 40 CFR 710.

LAER, Lowest Achievable Emission Rate.

LEPC, Local Emergency Planning Committees.

MACT, Maximum Achievable Control Technology.

MSDS, Material safety data sheet, required under OSHA HCS

NAAQS, National Ambient Air Quality Standard, 40 CFR 50.

NESHAP, National Emission Standard for Hazardous Air Pollutants under the CAA.

Nonattainment, Areas that are not meeting NAAQS, 40 CFR 51.100 *et seq.*

NO_x, Nitrogen oxides.

NPDES, National Pollution Discharge Elimination System. The national permit program under the CW, 40 CFR 122.

NRC, National Response Center.

NSR, New Source Review.

OPA–90, Oil Pollution Act of 1990.

OSHA, Occupational Safety and Health Administration (part of the Department of Labor), 29 U.S. Code 651 *et seq.*

Ozone (O_3), One of the compounds on the NAAQS list that is formed through chemical reaction in the atmosphere involving VOC, NO_x, and sunlight; also a primary constituent of smog.

PEL, Permissible Exposure Limit for an air contaminant under OSHA standards.

PM, Particulate Matter. One of the NAAQS; denotes the amount of solid or liquid matter suspended in the atmosphere. The EPA regulates PM as PM10 ("coarse" particulate ≤ 10 µm) and PM2.5 ("fine" particulate ≤ 2.5 µm).

POTW, Publicly owned treatment works, for indirect wastewater discharge.

PSD, Prevention of significant deterioration, a requirement of NSR.

PSM, Process Safety Management standard.

RACM, Reasonably Achievable Control Measures.

RACT, Reasonably Available Control Technology.

RCRA, Resource Conservation and Recovery Act, 42 U.S. Code 6901 *et seq.*

RCRA-Characteristic Wastes, Hazardous wastes that are ignitable, corrosive, reactive, or toxic, 40 CFR 260.64.

RCRA-Listed Wastes, Specially listed hazardous wastes in 40 CFR 261.30–33.

RfC, Inhalation reference concentration.

RQ, Reportable quantity.

SARA, Superfund Amendments and Reauthorization Act.

SERC, State Emergency Response Commissions.

SIP, State implementation plan.

SNUR, Significant New Use Rules.

TCLP, Toxic characteristic leaching potential under RCRA, 40 CFR 261.24.

Title V, The part of the Clean Air Act that deals with federal permits, 40 CFR 70.

TLV, Threshold limit value for an air contaminant under ACGIH regulations.

TRI, Toxic Release Inventory, under Section 313 of EPCRA.

TSCA, Toxic Substances Control Act.

TWA, Time-weighted average.

U.S. Code, The United States Code in which legislation, including health, safety, and environmental legislation, is codified once enacted by Congress (e.g., 42 U.S. Code 7401 is Title 42 U.S. Code at paragraph 7401).

VOC, Volatile organic compounds. A group of chemicals that react in the atmosphere with nitrogen oxides (NO_x) in the presence of heat and sunlight to form ozone; does not include compounds determined by EPA to have negligible photochemical reactivity.

Chapter 17

Economics of Fats and Oils Plants

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Profits

The fundamental objective of a company in the fats and oils industry is to make a profit. Sound economic practices are required to ensure that profit trends move in the right direction. For example, Table 17.1 illustrates the profit trend for a fictitious company. During y 1 of the example, the gross profit was $27.9 million from a net sales of $205.8 million. During y 2 and 3, profits shrank to a level of $12.8 million from net sales of $265.9 million. For y 4, a plan was implemented to correct the downward trend in profits by increasing sales to $316.2 million, while reducing the rate of growth of the cost of sales.

Such a turnabout can be achieved by setting up specific programs and objectives for both sales and costs. For example, net sales can be improved by a hard-nosed evaluation of product lines and eliminating the losers and low-profit items, while emphasizing the sales of the high-profit items. Cost of sales can be improved by a determined effort to analyze all important costs of the organization and establishing cost reduction programs to eliminate or reduce expense items.

Table 17.2 illustrates a portion of a cost reduction plan by a fictitious company. In this example, the company has experienced a continuing increase in investment over y 1–3. This was due primarily to an increase in money invested in inventories from $25 million in y 1 to $56 million in y 3. Over the same period, there was only a slight increase in fixed assets, from $24 million to $31 million. Because of this experience, the company initiated an "inventory control program" as well as a "cost reduction program," which required a major investment in new equipment to reduce costs and improve quality. Year four indicates that the company achieved a major turnabout in the total investments in the business by these two programs.

TABLE 17.1 Plant Economics Make a Satisfactory Profit

	(MM$)			
Year	1 Actual	2 Actual	3 Actual	4 Planned
Net sales	205.8	223.6	265.9	316.2
Cost of sales	177.9	201.7	253.1	283.5
Gross profit	27.9	21.9	12.8	32.7

TABLE 17.2 Investment

Year	(MM$) 1	2	3	4
Inventory	25	40	56	28
Net fixed assets	24	29	31	43
	—	—	—	—
Total	49	69	87	71

Operating Functions

In the typical company, as shown in Fig. 17.1, operations are comprised of the following: (i) raw materials acquisition, such as seed or oil; (ii) processing or manufacturing; and (iii) marketing/distribution. In an oil refinery plant, the "acquisition group" buys crude oil for the refineries "processing group." Resultant refined oil is turned over to the "marketing/distribution group" for packaging and delivery to end users. Industrial tank oils are delivered to end-users. The processing operation itself is seldom highly profitable and can easily lose money if sufficient attention is not given to raw materials, process control, and markets. Profits may be increased more by skilled buying and selling than by improved process efficiency; however, the latter must not be ignored. Costs and expenses allocations to these operations are illustrated in Fig. 17.2.

The purchased cost of raw materials is the responsibility of the seed/oil acquisition group. In most organizations, the yield/loss value of the processing of these raw materials is the responsibility of the processing group. It is important for the company to have a system of controlling the quality/cost of purchased oils because poor quality raw materials will result in increased processing loss, hence poor cost performance in the process operation. Thus, the seed/oil acquisition group is responsible for acquiring oilseeds for the oilseed operation and crude oil for the refineries, at the right quality and within the budgeted forecast cost. The processing group is responsible for processing and selling industrial bulk oil, either directly to end-users as "industrial tank"

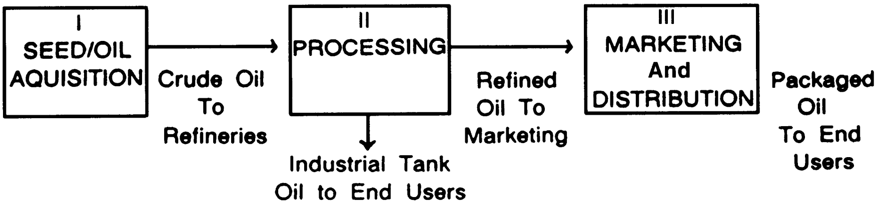


Fig. 17.1. Plant operations.

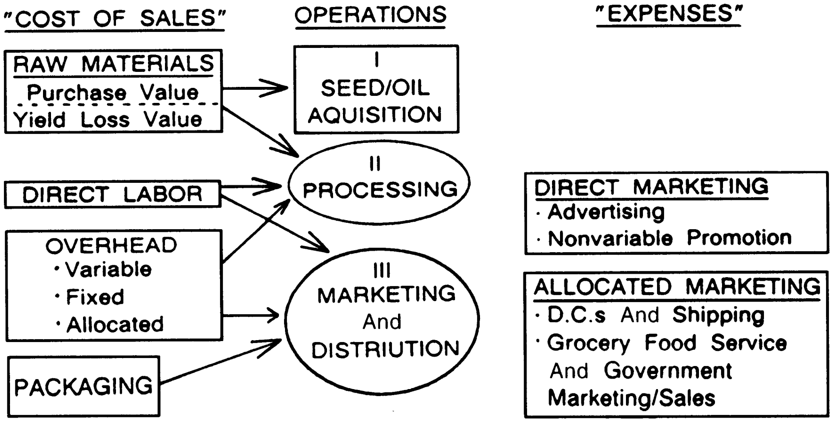


Fig. 17.2. Costs and expenses.

or to the marketing and distribution group for packaging, within quality specifications and budgeted processing costs. The marketing and distribution group is responsible for the profitable packaging, selling and distribution of packaged products in food service, grocery, government, and other end-use markets.

Within our industry, we have companies that range from a one-plant operation up to a multiplant operation with various manufacturing facilities around the world. In a multiplant operation, it is important to track the economics from plant to plant, first to compare performance and then determine the specific reasons for variation in performance. Table 17.3 illustrates cost variables for an example six-plant organization. In total, the processing costs (losses, variable, fixed costs) are greater than the "margin over crude." This is the term for acquisition profits generated by purchasing oils at prices lower than those forecast for the budget. Plant B shows a large loss and is the major cause of the negative total gross profit for the corporation. Obviously, economic evaluations should be performed to decide a plan of corrective action.

TABLE 17.3 Plant to Plant Comparison

	(M$)						
	A	B	C	D	E	F	Total
Margin over crude	1997	5674	4788	7567	6841	6,210	33,077
Yield loss	(222)	(1665)	(1554)	(2886)	(2553)	(2222)	(11,102)
Variable cost	(121)	(896)	(596)	(889)	(903)	(958)	(4,363)
Fixed cost	(1503)	(5233)	(2207)	(3596)	(2913)	(3075)	(18,527)
Gross profit	151	(2120)	431	196	472	(45)	(915)

TABLE 17.4 Policy Factors Affecting Plant Economics

- Technological factors
- Type of oil purchased
  - —Color
  - —Degummed/nondegummed
  - —Blend
- Loose oil inventory levels
- Amount of oil reprocessed
  - —Due to normal downgrading
  - —Due to rejection of off-specification production
- Scheduling procedures
- Qualifications of plant management
- Organization

TABLE 17.5 Technological Factors

Equipment	Key performance variables
Refining	Yield
Standard refining (centrifugal)	
DeLaval (modified?)	
Other	
Steam refining	Quality
Solvent (miscella)	Throughput
Bleaching	
Batch	Yield
Atmosphere	
Vacuum	(in clay)
Continuous	Quality
Atmosphere	
Vacuum	Throughput
Hydrogenation	
Batch	Flexibility
Dead-end	Quality
Gas recirculation	
Blending	
Soda fountain	Flexibility
Tanks	Quality
Winterization	
Batch	Yield
Continuous	Throughput
Solvent	Quality
Deodorizing	
Batch	Throughput
Semicontinuous (tray)	Quality
Continuous (tray)	

Economic Performance

An important tool for economic evaluation and control is the plant budget. For each unit operation in the plant, "best estimates" are established for each unit operation. For example, the refining step should have estimates for direct and indirect costs, such as raw material, utilities, labor, packaging, maintenance, insurance, and miscellaneous charges. Estimates for each unit operation are combined to form the total plant budget. Each month, unit operation costs are compared with the budget forecast and variances are calculated. Budgets and variances can then be used to identify operations with unsatisfactory cost performance, in order to develop programs of corrective action.

Some of the major policy factors that affect plant economic performance are shown in Table 17.4. These policies, which can vary from company to company and plant to plant, will affect both equipment and personnel performances. Table 17.5 provides examples of technological factors or gaps, which can have a profound effect on the key performance variables in a plant. Gaps in equipment or operating technology will affect yield, quality, throughput, and flexibility of the operation.

If materials cannot be properly processed to meet quality specifications the first time, then considerable reprocessing costs must be absorbed by the organization. Figure 17.3 illustrates what can happen when poor quality performance results in reprocessing requirements getting out of hand. In this example, "out of specification" product has increased from 2.0 to 21.2% over the period 1980–1984. Obviously, reprocessing costs of ~$7 million/y can have a serious negative effect on

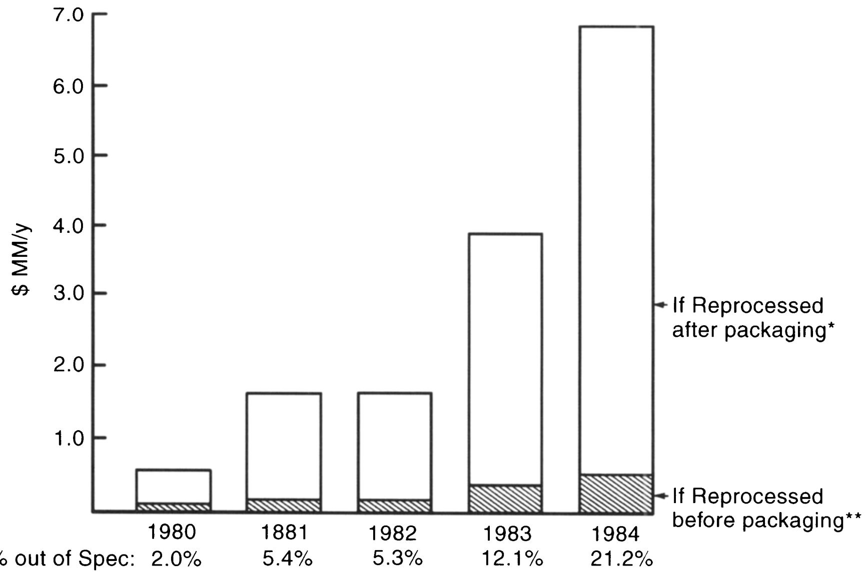


Fig. 17.3. Out of specification reprocessing costs. *Assumes that packaging materials are discarded. **Assumes that loss in total plant throughput is equal to 60% of volume reprocessed.

the economics of an operation. The amount of oil requiring reprocessing is related directly to the type and quality of oil purchased.

Performance Factors

Several key refinery cost-performance factors are outline in Table 17.6. It is important that the quality parameters of crude oil purchased be controlled as carefully as the price of the materials purchased. There have been many examples of oil acquisition groups purchasing raw materials at the lowest possible price. On this basis, the acquisition group will perform much better than the budget forecast for their department, but such a purchase may cost the organization many more dollars lost in additional reprocessing costs to bring poor quality crude oil up to the company's quality standards for finished oils.

In addition, the amount of oil requiring reprocessing can be minimized by doing the job right the first time. Poor performance in the plant and in the laboratories will increase losses and the quantities of oil that must be rejected eventually for out of specification reasons. Unfortunately, it is human nature to pass off problems from one department onto the next downstream department. It is very important to educate supervisory and operating personnel that products should not leave a department until it meets the quality specifications.

Care must be taken to control loose oil inventory levels to a practical minimum. Unnecessarily high inventories can tie up corporate cash, which could be generating interest when properly invested. In addition, some companies borrow money to cover inventory costs. Large quantities of oil held in inventory have a detrimental effect on product quality and reprocessing costs.

Inefficient plant scheduling practices will adversely affect yield performance. For example, a major cause of poor refining performance is the frequent start-up and shutdown of the continuous system. Each organization must also develop a reasonable balance between customer service and plant performance economics. The sales department is motivated to deliver product to the customer of the type and at the time that is required by the customer. Unless the plant obtains an agreement that schedules cannot be changed within a certain time frame, plant inefficiencies and operating frustrations will result.

A properly educated and trained operating and management staff is important for the successful control of plant economics. Operators must be trained to be fully

TABLE 17.6 Refinery Cost Performance Factors

- Crude oil quality
- Staff attitudes for cost and quality
- Staff education and training
- Loose oil inventory levels
- Plant scheduling practices
- Incentive plans

aware of the effects of their operations on the total performance of the plant. They must be carefully schooled in start-up and shutdown procedures that will minimize losses, as well as the proper in-process operating procedures to ensure manufacture of "inspecification" products. Promptly and properly recorded log books and quality control statistical charts are required for a professional operation. Management should be expert in personnel relations and all technical factors related to equipment and systems necessary for the modern plant.

Organizational structures and attitudes should be designed to ensure that all employees are working in the same direction as company goals. Incentive plans that allow everyone in the company to participate and work together as a team should be established, with the goal of achieving satisfactory customer service, product quality, and budget guidelines.

These factors are important to the development of a satisfactory "cash flow." This is the term for revenues minus operating costs minus capital costs. Figure 17.4

	Year															
Cash flow	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Operating Costs																
Raw materials																
Seed or Oil																
Chemicals																
Utilities																
Fuel																
Electricity																
Water																
Wages and salaries																
Maintenance and repairs																
Packing																
Administration etc.																
Total																
Capital																
Fixed																
Working																
Revenue																
Crude oil																
Refined oil																
Meal																
Hulls																
Acid oil																
Total																
Cash flow (= Revenue minus operting costs minus capital)																
Cumulative cash flow																

Fig. 17.4. Cash flow.

TABLE 17.7 Cash Flow Development (M$)

	Year							
Item	0	1	2	3	4	5	6	7→21
Operating costs	—	—	30,938.8	30,938.8	30,938.8	30,938.8	30,938.8	30,938.8→30,938.8
Raw materials								
Seed	—	—	25,140.0	—	—	—	—	—
Chemicals	—	—	251.3	—	—	—	—	—
Utilities	—	—	1189.0	—	—	—	—	—
Labor	—	—	1843.0	—	—	—	—	—
Maintenance and spares	—	—	775.0	—	—	—	—	—
Insurance	—	—	44.9	—	—	—	—	—
Packaging	—	—	1445.6	—	—	—	—	—
Administration	—	—	250.0	—	—	—	—	—
Investment	12,352.0	24,406.1	—	—	—	—	—	—
Fixed capital	12,352.0	12,351.5	—	—	—	—	—	—
Working capital	—	12,054.0	—	—	—	—	—	—
Revenue	—	—	43,462.9	43,462.9	43,462.9	43,462.9	43,462.9	43,462.9→43,462.9
Refined oil	—	—	31,701.3	—	—	—	—	—
Meal	—	—	11,323.6	—	—	—	—	—
Acid oil	—	—	438.0	—	—	—	—	—
Cash flow	(12,352.0)	(24,406.6)	12,524.1	12,524.1	12,524.1	12,524.1	12,524.1	12, 524.1→12,524.1
Cumulative cash flow	(12,352.0)	(36,758.6)	(24,234.5)	(11,710.4)	813.7	13,337.8	25,861.9	38,386.0→213,723.4

illustrates a cash flow system for either a crushing or refining operation. Operating costs include raw materials, utilities, wages and salaries, maintenance and repairs, packaging, and administration costs. Capital costs are the combination of fixed and working capital costs. Revenues include the value return from sales of crude oils, refined oils, meal, hulls, or acid oil.

The "cumulative cash flow" is the combination of the cash flows from each year of operation. When major equipment installations are considered for eliminating the technological gaps, the cumulative cash flow is an important factor in determining whether an investment should be made. In most cases, the first few years or so will

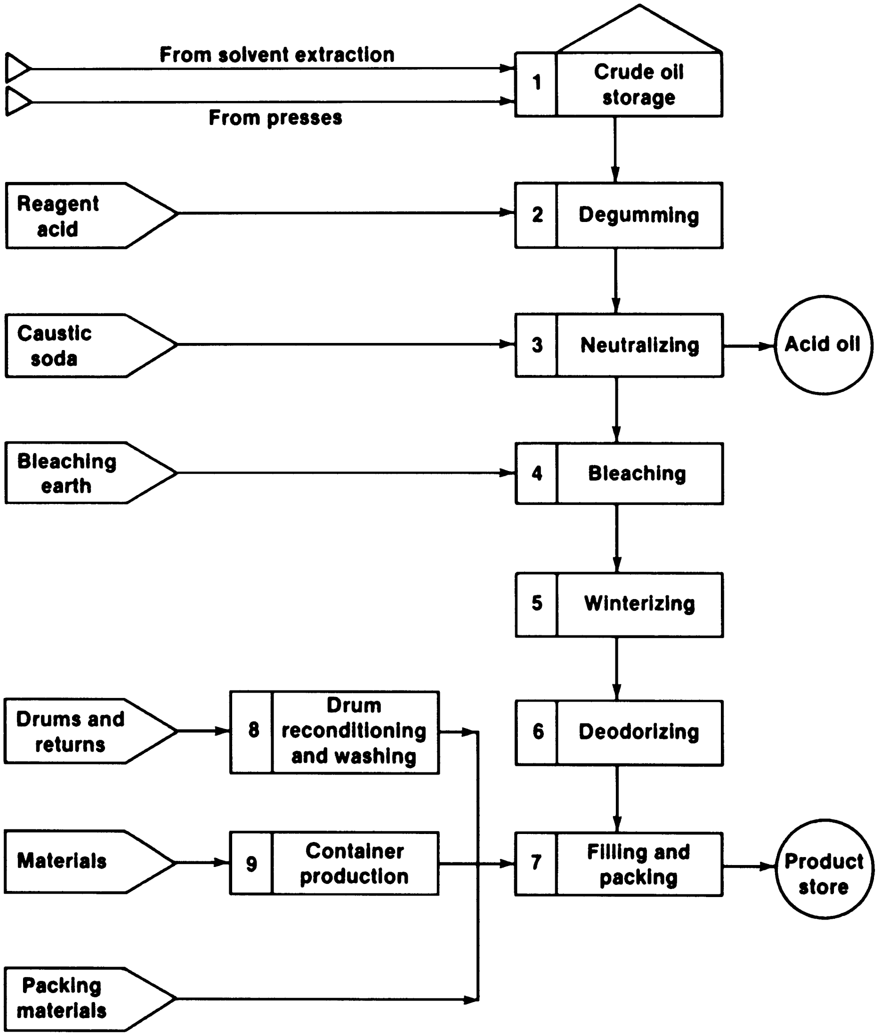


Fig. 17.5. Refined oil production.

TABLE 17.8 Soybean Plant

Plant capacity (t/d)	Estimated equipment costs (MM$)
500	2.0
800	2.5
1200	3.1
1500	3.6

have a major negative cash flow because of the high level of fixed costs required for the installation plus start-up costs. Improved volumes, operating costs, or sales profits should result for subsequent years if the project objectives are achieved. Eventually, the cumulative cash flow should become positive. The "pay-back" is the number of years required for the cumulative sum of the cash flows to equal the initial investment.

The cash flow method is appealing because of its simplicity, but it fails to fully measure profitability in the longer term because no account is taken of cash flows beyond the pay-back period. Highly profitable projects could, therefore, be rejected on the grounds of slow pay back. Under such screening, investment in oilseed processing plants could possibly be rejected.

The rate of return, shown in the following equation, provides an average return on investments over the life of a project:

$$\%\ \text{rate of return} = (\text{sum of annual cash flows} \times 100)/(\text{number of years of operation} \times \text{investment outlay})$$

TABLE 17.9 Estimated Construction Costs (M$)

	Refining,bleaching, deodorization only	Including hydrogenation-winterization
Land and site preparation	102	168
Yard work	144	156
Buildings and structures	290	434
Utilities	168	192
Purchased equipment	1452	2616
Purchased equipment installation	653	1177
Piping	523	942
Instrumentation	290	523
Process wiring and electrical	218	392
Insulation	363	654
Painting	73	131
Freight charges	116	209
Engineering and construction	794	1367
Contractor fee	182	314
Contingency	599	1031
Total fixed capital	5987	10,308

The investment outlays include investment in plant and machinery, plus working capital requirements. Although this method is more satisfactory than the pay-back method, it is not completely ideal because it does not take into account the timing of cash flows. More sophisticated programs are available from accounting experts. However, cash flow and rate of return approaches are satisfactory for the purposes of this presentation. Table 17.7 provides an example of a project that develops a positive cash flow during y 4 of the project. Such a system can be used for deciding new equipment installations or the value of building a completely new plant as shown in Fig. 17.5.

TABLE 17.10 Operating Cost (Plant Size: 360,000 lb/d)

	$0.01/lb	
	Refining,bleaching, deodorization only	Including hydrogenation-winterization
Factory manufacturing costs		
Direction production costs		
Raw materials	0.28	0.44
Packaging materials	0.00	0.00
Operating labor	0.48	0.58
Indirect labor	0.19	0.23
Maintenance	0.23	0.41
Operating supplies	0.05	0.06
Utilities	0.52	0.91
Total	1.75	2.63
Fixed charges		
Insurance	0.11	0.20
Taxes	0.14	0.24
Depreciation	0.04	0.77
Rent	0.00	0.00
Total	0.29	1.21
Plant overhead costs		
Nonwage payments	0.13	0.17
Laboratories	0.06	0.07
Miscellaneous factory expense	0.04	0.05
Total	0.23	0.29
Total factory manufacturing expense	2.27	4.13
General expense		
Interest on working capital	0.14	0.23
Research and development	0.10	0.17
Administration and general	0.82	1.31
Total general expense	1.06	1.71
Cost to make	3.33	5.84

TABLE 17.11 Estimated Yields and Operating Cost Data Per Bushel of Soybeans

Yield of products per bushel crushed	
Oil (lb)	11.2
Meal (lb)	48.0
Total	59.2
Manufacturing costs ($/bu)	
Wages, payroll taxes	0.10
Insurance	0.02
Property taxes	0.02
Power	0.06
Fuel, water	0.12
Plant supplies	0.02
Repairs	0.06
Depreciation	0.06
Miscellaneous	0.02
Total	0.48
General and administrative expenses ($/bu)	0.08
Financial expenses ($/bu)	
Total	0.07
Total costs and expenses ($/bu)	0.63

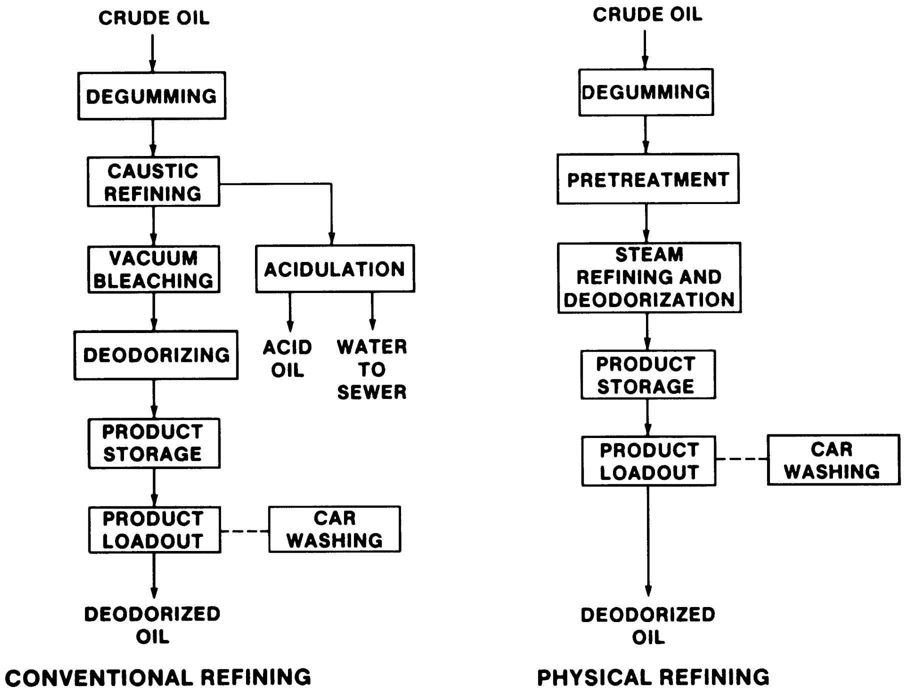
Capital and Operating Costs

In a review of some specific examples for capital and operating costs for plants and processes, Table 17.8 provides estimated equipment costs for various soybean plant capacities. Table 17.9 provides estimated construction costs for two different types of plants. Estimated operating costs for a 180 ton/d soybean plant are provided by Table 17.10. Table 17.11 estimates the yields and operating costs per bushel of soybeans.

With regard to technology improvements, some refiners consider that steam or physical refining has advantages over chemical refining, as compared in Table 17.12. Figure 17.6 indicates that there are both construction and operating cost savings for the physical refining system. Table 17.13 estimates the installed costs for a soybean oil refinery, either conventional or physical, for crude oil rates of 15,000 and 30,000 lb/h. In addition to major installations, considerations should be given to

TABLE 17.12 Steam Refining vs. Chemical Refining

Installed cost	22%lower
Steam usage	28% lower
Cooling water	7% lower
Process makeup water	85%lower
Waste water treatment	63%lower
Electrical power	62%lower
Refining loss	60%lower



CONVENTIONAL REFINING

PHYSICAL REFINING

Fig. 17.6. Refined systems.

TABLE 17.13 Estimated Installed Costs for Soybean Oil Refinery: $US (1988)

	Case			
	A	B	C	D
Crude oil rate (1b/h)	30,000	30,000	15,000	15,000
(t/h)	13.61	13.61	6.80	6.80
Refining method	Conventional	Physical	Conventional	Physical
Equipment and engineering[a]	4,329,600	3,595,200	2,929,600	2,344,000
Construction[b]	5,592,000	4,544,000	4,952,000	3,702,400
Total	9,921,600	8,139,200	6,632,000	5,296,000

[a] Includes all processing equipment and all engineering drawings including those for foundations and new buildings.

[b] Includes installation of new equipment, piping, electrical, erection of new building, and site preparation, but not new sanitary sewer lines and facilities, rail sidings, new water treatment, and supply or installation of new utilities as may be required.

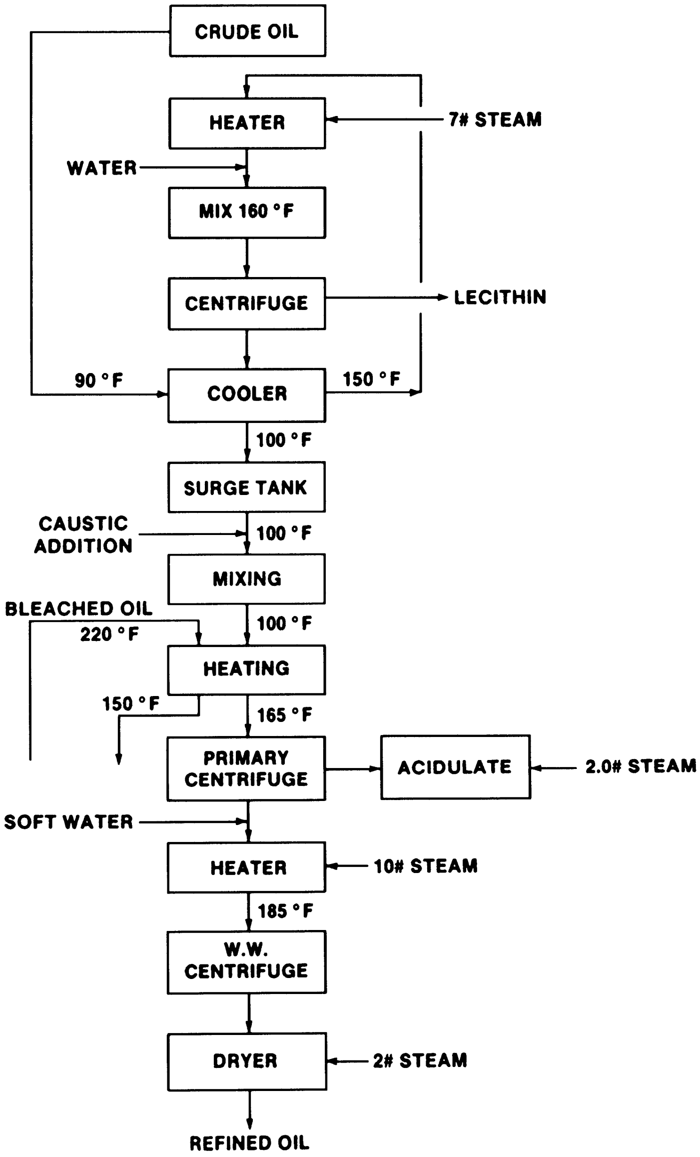


Fig. 17.7. Caustic refining with degumming and heat recovery (per 1000 lb oil).

relatively minor operating improvements that will reduce operating costs, such as the utilization of heat recovery equipment as shown in Fig. 17.7. Estimates of potential heat recovery savings are shown in Table 17.14.

In most plants, operating budgets are broken down by the major unit operations, such as caustic refining, bleaching, hydrogenation and postbleach, deodorization, fill and pack, and winterization. Table 17.15 provides processing cost estimates for each unit operation in $0.01/lb and $0.01/kg. Totals are shown for refined/bleached/deodorized (RBD) soybean oil and hydrogenated/winterized (LHW) soybean oil.

TABLE 17.14 Heat Recovery Savings (1984)[a]

	No heat recovery	Heat recovery
	($)	
Steam	150,000	37,500
Electricity	57,000	57,000
Total	187,000	94,500

[a] Utilities cost (steam $7.5/1000 lb, electricity $0.06/kwh, 30,000 lb/h).

TABLE 17.15 Processing Cost Estimates

	$0.01/lb	$0.01/kg
Caustic refining	1.3	2.9
Bleaching	0.5	1.1
Hydrogenation and postbleach	2.0	4.3
Deodorization	0.8	1.7
Fill and pack	2.0	4.3
Winterization	1.3	2.9
RBD soybean oil[a]	2.6	5.7
LHW soybean oil[a]	5.9	12.9

[a] Without packaging cost.

Chapter 18

Flavor Quality of Fats and Oils

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Introduction

The flavor quality of the fats and oils we consume is vitally important to the flavor impact of the foods that contain them. The lipids contribute undesirable as well as desirable flavors. In addition, fats and oils are excellent solvents for many of the good-tasting components in foods and provide the desirable "flavor release" and "mouthfeel" that are lacking in foods with reduced or no fat. The positive flavor contribution of fats and oils is particularly apparent in fried foods, not only because of the numerous reactions that occur between fat and food components such as proteins and carbohydrates, often *via* Maillard browning reactions, but also because of breakdown products from the oil itself. These reactions produce the good flavors we associate with fried foods. Aged cheeses also derive some of their good flavors from lipid oxidation. In general, however, lipids are more commonly associated with the negative aspects of food flavor. They are responsible for off-flavors associated with hydrolytic or oxidative rancidity as compounds resulting from the beginning stages of hydrolysis or oxidation, from interaction of these compounds with other food components, or from inherent materials in the native fat. The flavor impact of lipid oxidation often is termed "rancidity." The objective of this chapter is to describe the many factors affecting fat and oil quality, especially in relation to sensory aspects in foods.

Fats and oils are considered to be the glycerol esters of fatty acids, termed triacylglycerols, and contribute up to 99% of the lipids of plant and animal origin. The distinction between a fat or oil has merely to do with its physical state at room temperature, solid or liquid; thus the terms may be used interchangeably.

Formation of Flavors and Off-Flavors in Fats and Oils

Hydrolytic Rancidity

Cleavage of the fatty acids from the glycerol backbone of a triacylglycerol may occur with the application of heat and moisture or by enzyme action (1). The resulting free fatty acids may produce good flavors or poor off-flavors. For example, release of the free fatty acids in milk fat is particularly noteworthy for two reasons. First, nearly 400 different fatty acids moieties have been reported to exist in butterfat; ~21–25% of the fatty acids are short-chained (4–12 carbons in length) (2). The short-chained fatty acids produce strong, usually undesirable rancid flavors when cleaved from the glycerol backbone (3), but the wide array of different fatty acids and arrangements within the triacylglycerols likely contributes to the unique positive flavor of butterfat (4). Second, enzymes naturally present in raw milk typically cause this reaction. These native milk lipases, or microbial lipases added to a cheese culture, cause hydrolysis of the fatty acids, yielding desirable cheese flavors (5–7). High amounts of free fatty acids in cheese caused by excessive lipolysis, however, produce undesirable rancid off-flavors (6). The amounts of free fatty acids present in typical fresh milk probably are not important because the flavor threshold levels of these compounds are much greater than the concentrations found (3). Milk fat also contains small amounts of β-keto acids and hydroxy acids, known precursors of the highly flavored compounds, methyl ketones and lactones, respectively (8).

Furthermore, free fatty acids in any fat can catalyze additional reactions that lead to flavor changes by acting as prooxidants (1), apparently by the action of the carboxylic molecular group, which accelerates the rate of decomposition of hydroperoxides (9). Indeed, the prooxidant effect of the carboxylic group was confirmed by noting that the conversion of a free fatty acid to a methyl ester eliminated its oxidative effect (1).

Storage fats from live animals are generally devoid of free fatty acids, but enzymes become active after an animal is slaughtered. Thus, inactivation of the enzymes during rendering of animal fat is important to preserve its quality. The occurrence of hydrolytic rancidity in oils derived from plant sources varies greatly, depending on the presence and activity of native lipase enzymes and on the condition of the plant material during harvest. Most vegetable oils are neutralized after extraction with sodium hydroxide to remove small amounts of free fatty acids that might have formed. The activity of native lipase enzymes in coconut is particularly high (10), creating many problems in the production of its oils. In fact, in improperly processed coconut oils, >50% of the triacylglycerols may be broken down into their free fatty acids and glycerol. Even if such an oil is neutralized and the free fatty acids removed, the reduced yield of this product limits its economic potential. Like milk fat, coconut oil contains many short-chain fatty acids that may be particularly poor tasting when present as free fatty acids because of their volatility and solubility. A soapy flavor may arise. Palm kernel oil also contains short-chain fatty acids, resulting in some of these same flavor problems.

Food applications of oats also are diminished by fat-related problems (11). The oat has a greater level of lipase activity than most other cereals (12), even before germination (13,14). As a result, oat oil contains a measurable portion of free fatty acids even with storage under optimal conditions (15). Cell damage in the oat, caused by kernel damage during harvesting or processing by grinding or flaking, liberates the endogenous lipase enzymes, further enhancing hydrolytic rancidity and production of bitter-tasting off-flavors (16,17). Consequently, processing of oat generally involves some type of heat inactivation of the lipases. The wheat grain is subject to some of these same flavor concerns, although the problem is more pronounced in oat.

Finally, hydrolytic rancidity occurs typically during deep-fat frying of foods, enhanced by the high temperatures and accumulation of moisture from the food being fried. The presence of free fatty acids in a frying fat lowers the smoke point of the oil, enhances oil absorption into the food, and lowers the quality of the resulting fried food. As previously noted, however, the interaction of the free fatty acids with other food components to form Maillard browning reaction products produces some desirable flavors we typically associate with fried food flavor.

Oxidation Reactions and Volatile Compound Formation

Generalized Scheme for Lipid Autoxidation. Lipid oxidation causes chemical changes in fats and oils that lead to flavor deterioration and food spoilage. These changes can occur regardless of the oil source, but are more pronounced in more polyunsaturated oils (18). The more polyunsaturated the oil, the greater the free radical formation and subsequent uptake of oxygen by the lipid. Thus, traditional vegetable oils from such sources as canola, rapeseed, and soybean are particularly susceptible to oxidation and flavor changes. Human consumption of oxidized lipids, and especially the resulting free radicals formed during oxidation, has been suggested as a possible cause of cancer development. Thus, eliminating or reducing the amount of oxidation is desirable from a health standpoint, as well as for flavor quality.

A brief overview of lipid oxidation is presented in Figure 18.1. The fat or oil is depicted by the formula RH in the upper left-hand corner, where R represents a triacylglycerol molecule, or more specifically, one of its fatty acids and H represents a hydrogen atom that may be readily removed during oxidation. A "quantum" of energy from several possible sources, such as light or heat, catalyzes removal of the H during the first step of oxidation. The resulting free radical, R•, may readily react with oxygen in its singlet or triplet state, forming peroxy free radicals, ROO•, which can break down to form aldehydes and ketones (key off-flavor components). Alternatively, the ROO• may continue the catalytic reaction by securing a H atom from another RH molecule to form a hydroperoxide (ROOH). The reactive ROOH continues its deterioration process by forming RO• (middle of Fig. 18.1), a precursor to the formation of many different aldehydes, ketones, and alcohols, which contribute off-flavors and off-odors. The hydroperoxides are primary oxidation products, indicative of the first mechanistic steps in lipid oxidation. The carbonyl compounds (aldehydes, ketones, and alcohols) are referred to as secondary oxidation products because they are formed from secondary reactions during the oxidation process. The secondary oxidation products are important to study because, as noted, these components are responsible for the actual flavors and odors associated with oxidized fats and oils.

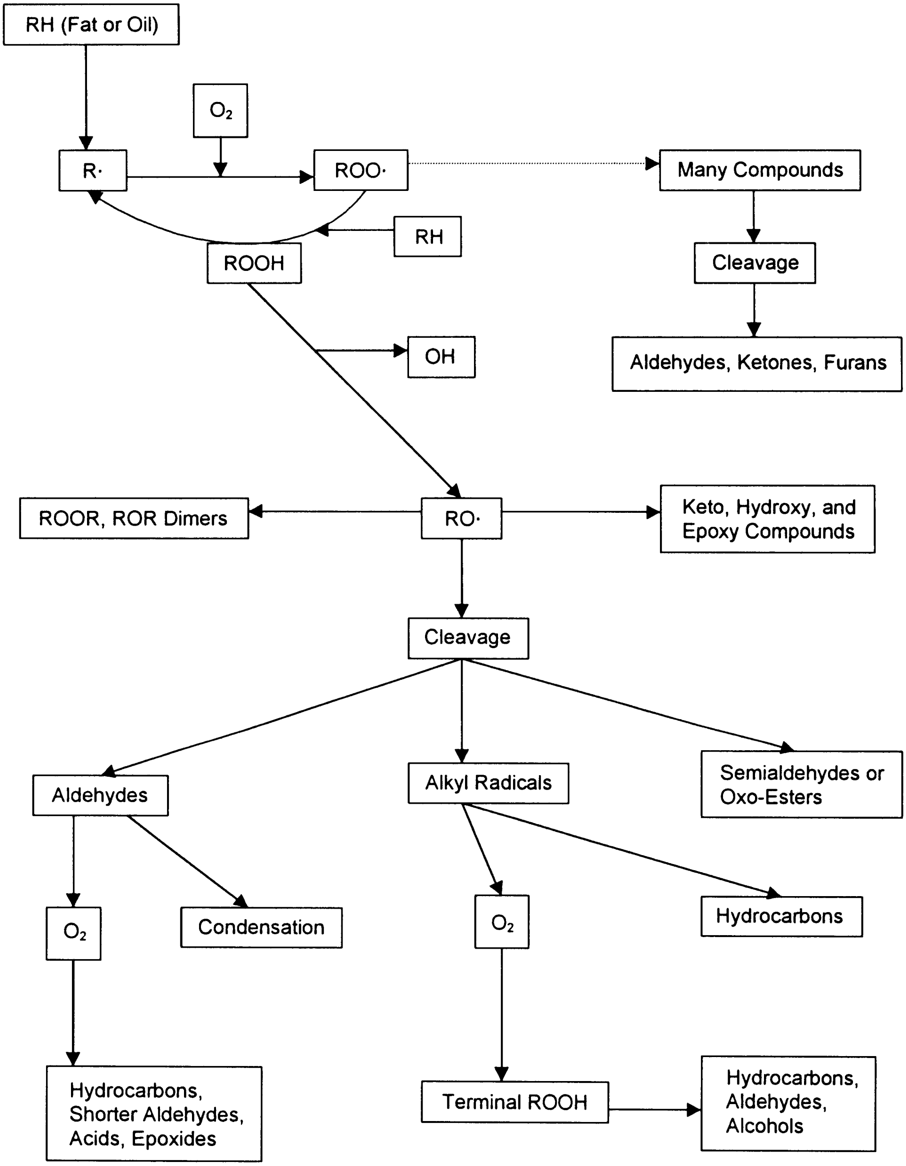


Fig. 18.1. Generalized scheme for lipid oxidation. *Source*: Ref. 106.

Autoxidation. The chemistry of alkene autoxidation was first reported over 50 years ago (19). The reaction of unsaturated fatty acids with oxygen to form hydroperoxides *via* a free-radical reaction is commonly depicted by the following scheme:

Initiation:

$$\mathrm{RH} \xrightarrow{\text{Initiator}} \mathrm{RH\bullet} + \mathrm{H\bullet}$$

Propagation:

$$\mathrm{R\bullet} + \mathrm{O_2} \longrightarrow \mathrm{ROO\bullet}$$
$$\mathrm{ROO\bullet} + \mathrm{RH} \longrightarrow \mathrm{ROOH} + \mathrm{R\bullet}$$

Termination:

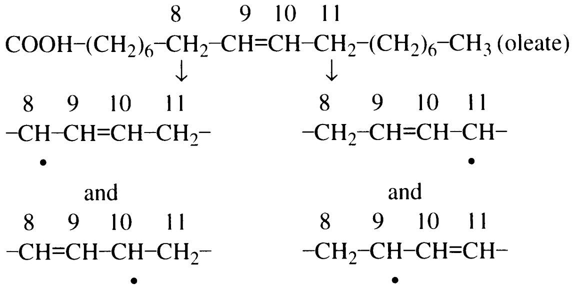
$$\mathrm{R\bullet} + \mathrm{R\bullet} \longrightarrow \mathrm{2R}$$
$$\mathrm{R\bullet} + \mathrm{ROO\bullet} \longrightarrow \mathrm{ROOR}$$
$$\mathrm{ROO\bullet} + \mathrm{ROO\bullet} \longrightarrow \mathrm{ROOR} + \mathrm{O_2}$$

During initiation, the unsaturated fat (RH) loses hydrogen (H) at the carbon atom adjacent to a double bond, where the dissociation energy for the H abstraction is fairly low (20). The initiator may be from any number of factors, as previously noted (and will be discussed later). Once a free radical (R•) has formed, the overall reaction propagates quickly when R• reacts with O_2 to create a peroxy free radical (ROO•). The ROO• abstracts H more slowly from another RH, thus creating a chain reaction that may be repeated thousands of times. The latter step is rate determining. Termination occurs when nonradical products are formed from the free radicals, as shown, but this stage of oxidation does not become important until late in the process unless oxygen becomes limiting.

The actual rate at which autoxidation proceeds is dictated primarily by the fatty acid composition, although many other factors may influence this process. The oxidative stability of unsaturated lipids generally decreases with increased degree of unsaturation (9,21). Thus, polyunsaturated fatty acids, because of their great abundance in many oils and susceptibility to oxidation, are among the most important precursors of undesirable flavor compounds (18). The relative rates of autoxidation of the purified esters of oleic acid (18:1):linoleic acid (18:2):linolenic acid (18:3) were reported to be 1:12:25 on the basis of peroxide or conjugated diene development in systems containing only the individual ester (225). The relative autoxidation rates of these same unsaturated esters in a mixed system were 1:10.3:21.6 (23). The ease of removal of the H is influenced by the presence of allylic methylene groups (24). In oleate, the single allylic methylene, -CH=CH-$\boldsymbol{CH_2}$-CH_2-CH_2-, has a bond strength estimated at 77 kcal/mol, compared with 52 kcal/mol in the doubly allylic methylene in linoleate, -CH=CH-$\boldsymbol{CH_2}$-CH=CH-, also referred to as the 1,4-pentadiene structure. Linolenate has two doubly allylic methylene groups, -CH=CH-$\boldsymbol{CH_2}$-CH=CH-$\boldsymbol{CH_2}$-CH=CH-, doubling its autoxidation rate over that of linoleate, but not influencing the bond strength of each methylene group.

The exact hydroperoxides formed during autoxidation vary, depending upon the fatty acid ester involved in the reaction. For oleate, the electrons are delocalized over three carbon atoms, and for linoleate or linolenate, over five carbon atoms (25). Thus, the O_2 may attach to any number of different carbon atoms, resulting in the formation of a variety of isomeric hydroperoxides, as reviewed by Frankel (24). In oleate, the H is initially abstracted from the carbons, 8 or 11, but the double bonds may shift, ultimately producing 8-, 9-, 10-, or 11-hydroperoxides, as follows:

Formation of free radicals:



$$\mathrm{COOH{-}(CH_2)_6{-}\overset{8}{C}H_2{-}\overset{9}{C}H{=}\overset{10}{C}H{-}\overset{11}{C}H_2{-}(CH_2)_6{-}CH_3}\ \text{(oleate)}$$

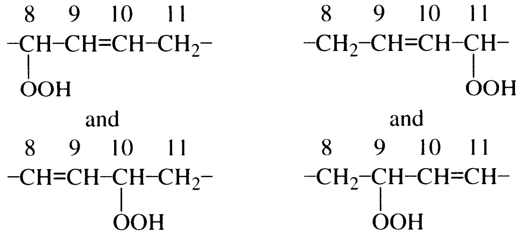
$$\downarrow \qquad\qquad \downarrow$$

$$\mathrm{{-}\underset{\bullet}{\overset{8}{C}H}{-}\overset{9}{C}H{=}\overset{10}{C}H{-}\overset{11}{C}H_2{-}} \qquad \mathrm{{-}\overset{8}{C}H_2{-}\overset{9}{C}H{=}\overset{10}{C}H{-}\underset{\bullet}{\overset{11}{C}H}{-}}$$

$$\text{and} \qquad\qquad \text{and}$$

$$\mathrm{{-}\overset{8}{C}H{=}\overset{9}{C}H{-}\underset{\bullet}{\overset{10}{C}H}{-}\overset{11}{C}H_2{-}} \qquad \mathrm{{-}\overset{8}{C}H_2{-}\underset{\bullet}{\overset{9}{C}H}{-}\overset{10}{C}H{=}\overset{11}{C}H{-}}$$

Formation of four isomeric hydroperoxides from the free radicals:

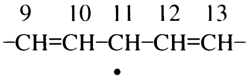


$$\mathrm{{-}\underset{\underset{OOH}{|}}{\overset{8}{C}H}{-}\overset{9}{C}H{=}\overset{10}{C}H{-}\overset{11}{C}H_2{-}} \qquad \mathrm{{-}\overset{8}{C}H_2{-}\overset{9}{C}H{=}\overset{10}{C}H{-}\underset{\underset{OOH}{|}}{\overset{11}{C}H}{-}}$$

$$\text{and} \qquad\qquad \text{and}$$

$$\mathrm{{-}\overset{8}{C}H{=}\overset{9}{C}H{-}\underset{\underset{OOH}{|}}{\overset{10}{C}H}{-}\overset{11}{C}H_2{-}} \qquad \mathrm{{-}\overset{8}{C}H_2{-}\underset{\underset{OOH}{|}}{\overset{9}{C}H}{-}\overset{10}{C}H{=}\overset{11}{C}H{-}}$$

The formation of hydroperoxides from linoleate takes place in a fashion similar to that just shown for oleate, except hydrogen abstraction from the methylene group at carbon 11 produces a pentadienyl radical intermediate:



$$\mathrm{{-}\overset{9}{C}H{=}\overset{10}{C}H{-}\underset{\bullet}{\overset{11}{C}H}{-}\overset{12}{C}H{=}\overset{13}{C}H{-}}$$

The pentadienyl radical intermediate reacts with O_2 to form conjugated 9- and 13-hydroperoxides (25). Linolenate contains two 1,4-pentadiene structures that overlap at the double bond between carbons 12 and 13, promoting H abstraction at carbons 11 and 14. The resulting isomeric hydroperoxides include 9-, 12-, 13-, and 16-hydroperoxides. Double bonds in all of the hydroperoxides have the possibility of shifting to the *trans* form from the *cis* form; thus, additional hydroperoxide isomers may be present in an oxidized oil mixture.

Photosensitized Oxidation. As noted in the last section, the major mechanism for oxidation of unsaturated fatty acids is through autoxidation. One frustration in making this assumption, however, has been explaining the origin of the initial free radicals. As shown in Figure 18.1, the initiation source is described as a "quantum" of energy. This energy source may arise *via* two types of photosensitization, a topic reviewed by Min *et al.* (26). Briefly, oxygen in the presence of light and a suitable sensitizer, such as riboflavin, can promote autoxidation through what is referred to as type I photosensitized oxidation. In this type of oxidation, the sensitizer reacts with a fatty acid substrate (RH) to produce radicals by transfer of the H, or radical ions by electron transfer. The radicals produced react with the oxygen to produce the same hydroperoxide isomers formed *via* autoxidation.

Other sensitizers, such as chlorophyll and heme compounds, convert oxygen to its more reactive state, singlet oxygen, thus promoting type II photosensitization. In addition, chemical, enzymatic, and physical methods may initiate singlet oxygen formation (type II photosensitization), also promoting the photoxidation. Results from a recent study supported the assumption of singlet oxygen as a promoter of the first steps of oxidation (27). The hydroperoxides formed by singlet oxygen (type II photosensitization) differ from those formed by autoxidation, because singlet oxygen can attach directly to one of the unsaturated carbon atoms at the site of a double bond by a non-radical mechanism. Thus, the isomeric hydroperoxides formed *via* singlet oxidation are as follows: for oleate, 9- and 10-hydroperoxides; for linoleate, 9-, 10-, 12-, and 13-hydroperoxides; and for linolenate, 9-, 10-, 12-, 13-, 15-, and 16-hydroperoxides (28,29). There is additional evidence for differences in the mechanisms of oxidation *via* singlet oxidation and autoxidation. The relative photosensitized oxidation rates for purified oleate, linoleate, and linolenate were in the ratio of 1:1.7:2.3, close to the number of double bonds in these esters, and were seemingly unaffected by the presence of a methylene group as with autoxidation (30).

Photosensitized oxidation also is thought to give rise to the phenomenon referred to as flavor reversion, characterized by the development of offensive odors and flavors occurring at very low levels of oxidation. This flavor deterioration, occurring in soybean oil and other linolenate-containing oils, is described as beany and grassy at the early stages and as fishy or painty at the more advanced stages. Many different compounds have been suggested to contribute to reversion, as discussed in the section on decomposition of hydroperoxides.

Enzymatic Oxidation. Enzymes native to plants and animals can initiate oxidation reactions contributing to flavor in foods (31). The most important of these enzymes is lipoxygenase, the name given to a widely occurring group of enzymes found in most plants and animals. In particular, the activity of three soybean lipoxygenase isozymes is greatly associated with the development of off-flavors, especially green-beany flavors, in soybean products. Lipoxygenase-1 has optimum activity at pH 9, whereas lipoxygenase-2 and -3 have optimum activity at pH 6.5–7.0 (32), and all of the isozymes require a substrate that contains a *cis, cis*-1,4- pentadiene system, such as that present in linoleate and linolenate. The hydroperoxides formed from lipoxygenase activity are the same isomers as those formed during autoxidation of linoeate and linolenate. For example, from linoleate, lipoxygenase-1 produces mainly the 13-hydroperoxide; lipoxygenase-2 and -3 produce both 13- and 9-hydroperoxides, although in different relative amounts (33).

Although lipoxygenase has been shown to promote the formation of hydroperoxides, the actual effect of the isozymes on the overall oxidation and flavor quality of refined, bleached, and deodorized (standard edible-oil treatments) soybean oil is questionable. Endo *et al.* (34) concluded that the lipoxygenases did not contribute to flavor reversion in soybean oils stored under light irradiation at 30°C. Also, storage at 60°C resulted in no significant differences in flavor scores between oils from traditional soybeans and from soybeans lacking lipoxygenase-1 (35). In another study, the absence of lipoxygenase-2 or of both lipoxygenase-2 and -3 had little effect on flavor during storage at 50–60°C in the dark or at 35°C in the light, and was not as important to oil quality as was the linolenate content (36). Similar findings resulted from deep-fat frying followed by storage at 60°C in the dark (37). Finally, a lack of all three soybean isozymes did not significantly improve the oil flavor over that from traditional soybeans during storage at 60°C in the dark or at 35°C in the light (38). All soybeans were harvested, stored, and processed under ideal conditions. Once again, minor differences in the polyunsaturated fatty acid composition had more effect on flavor quality than did the presence of lipoxygenase isozymes. Perhaps the amount of oxidation promoted by lipoxygenases in properly processed beans is so minor compared with that promoted by autoxidation and photoxidation that the overall effect is negligible. It is possible that an improvement in oil quality of the oils from beans lacking the enzymes over that of oil from normal beans might be noted if soybean storage and/or oil processing conditions were unfavorable.

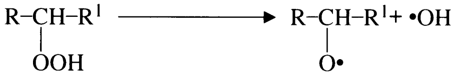
Function of Antioxidants. Antioxidants, whether native to a lipid or food system or added, are widely used to control lipid oxidation. Antioxidants are effective because they interfere with the chain reaction of autoxidation, by either removing or deactivating the free radicals that are formed before they can catalyze the formation of more free radicals. The reaction is commonly depicted by the following scheme:

$$R\bullet + AH \longrightarrow RH + A\bullet$$

in which R• is a fatty free radical and AH is an antioxidant. Even though the end products include a free radical, the resultant A• is a "stable resonance hybrid," meaning that it will not initiate or propagate further oxidation. Most antioxidants are phenolic compounds containing at least one hydroxy (OH) group, which allows resonance of the free radical around the benzene ring, with ultimate removal of the hydrogen from a hydroxy group. The remaining oxygen can form a double bond with the carbon of the benzene ring, thus avoiding free radical formation. Compounds such as citric acid also enhance oil stability but are not true antioxidants. Citric and other specific acids chelate metals, thus removing them from potential reactivity in the oil. Metal chelators have a strong effect on oil quality and stability. The topic of specific natural and synthetic antioxidants is discussed later in this chapter.

Decomposition of Hydroperoxides. As noted earlier, hydroperoxides are the primary products formed during oxidation. Although they are flavorless and odorless, the hydroperoxides are important to overall flavor because they are very unstable and break down into a wide variety of shorter-chained volatile and nonvolatile products, many of which contribute to flavors in oils and lipid-containing foods. Some of the volatile compounds have extremely low flavor thresholds and thus are detected at very low concentrations (39). A wide body of literature exists on the decomposition of hydroperoxides and formation of the resulting products and is the topic of several chapters and reviews (24,25,39–42).

In general, hydroperoxide decomposition involves homolytic cleavage of the –OOH group to form an alkoxy radical and a hydroxy radical as shown:



$$\mathrm{R{-}\underset{\underset{\displaystyle OOH}{|}}{C}H{-}R^1} \longrightarrow \mathrm{R{-}\underset{\underset{\displaystyle O\bullet}{|}}{C}H{-}R^1 + \bullet OH}$$

The alkoxy radical may further decompose to form aldehydes by way of β-scission on the C-C bond on either side of the carbon bearing the oxygen:

$$\mathrm{R{-}\underset{\underset{\displaystyle O\bullet}{|}}{C}H{-}R^1} \longrightarrow \mathrm{R{-}CHO + R^1\bullet}$$

The reaction products from this hypothetical alkoxy radical may include two types of aldeyhydes, an olefin, and an alkyl radical (24). The β-scission reaction is the most important pathway by which free radical formation is promoted and flavorful aldehydes are created, leading to rapid flavor deterioration in fats and oils. Additional aldehydes, as well as ketones, alcohols, hydrocarbons, hydroperoxides, and other products, will result from further breakdown of these compounds. There is evidence of greater ease of decomposition of the linolenate hydroperoxides than of the linoleate hydroperoxides (43). The original hydroperoxide isomer (e.g., 9- or 10-hydroperoxide) dictates the exact compounds formed. Thus, oxidation products may be traced to the type of oxidation (autoxidation or photoxidation) and the fatty ester (oleate, linoleate, or linolenate) from which it was formed.

Flavor Impact of Aldehydes. Keppler (44) reported the flavor (taste and odor) thresholds of 19 aldehydes, most ranging in chain length from 5 to 11 carbons and with one or two *cis* or *trans* double bonds in various positions, in an effort to establish a correlation between molecular structure and flavor of the compounds. Stronger flavors resulted from the presence of the following: (i) a n-3 double bond (derived from linolenic acid); (ii) an isolated double bond; (iii) mono- or diunsaturation; and (iv) three or more double bonds in chains with >12 carbon atoms. No consistent pattern between molecular structure and flavor could be concluded. Odor thresholds ranged from 0.002 to 34 mg/kg, whereas taste thresholds ranged from 0.00055 to 5.5 mg/kg, but the medium in which the aldehydes were carried was not noted. The carbonyl, 4-*cis*-hexenal, had the lowest odor and taste thresholds and 2-*trans*-decenal had the greatest odor and taste thresholds. Seven of the aldehydes had taste thresholds <0.1 mg/kg, including 2-*trans*,4-*trans*-hexadienal (green, banana); 2-*trans*,4-*cis*-heptadienal (rotten apples); 2-*trans*,6-*trans*-nonadienal (tallowy, green); 2-*trans*,6-*cis*-nonadienal (cucumber-like); 4-pentenal (creamy, burned milk, methional-like); 4-*cis*-hexenal (green, creamy, methional-like); and 5-*cis*-hexenal (green, potato peel-like). Some of these compounds have been detected in oxidized oils, especially soybean oil.

Frankel (39) reported various ranges of flavor (taste) thresholds for classes of aldehydes and other volatile compounds; these are listed in Table 18.1. Hydrocarbons had extremely high flavor thresholds, whereas vinyl ketones were the most sensitive to detection. Specific aldehydes with low flavor threshold values included 6-*trans*-nonenal (45) and 4-*cis*-heptenal (46). Seals and Hammond (47) noted that 4-*cis*-heptenal contributed a fishy odor to soybean and linseed oils and another aldehyde, 2,4-pentadienal, produced a potato-like odor. One of these compounds, 4-*cis*-heptenal, along with heptanal, was identified as the chief odor contributor in good-flavored freshly deodorized soybean oil, illustrating the complex nature of these aldehydes in contributing to both positive and negative flavor profiles (48). Furthermore, diacetyl was positively identified in soybean oil during early stages of oxidation, and its addition to fresh soybean oil reproduced the buttery flavor typical of slightly oxidized oil (49). Other volatile compounds found in fresh soybean, corn, and olive oils included 2-*trans*-heptenal, hexanal (a dominant oxidation product of linoleate), and nonanal, whereas the major compounds in fresh canola oil were the 2,4-*cis*,*trans* and

TABLE 18.1 Flavor Threshold Values of Classes of Volatile Compounds[a]

Class of compound	Threshold value (mg/kg)
Hydrocarbons	90–2150
Substituted furans	2–27
Vinyl alcohols	0.5–3
1-Alkenes	0.02–9
2-Alkenals	0.04–2.5
Alkanals	0.04–1.0
trans,trans-2,4-Alkadienals	0.04–0.3
Isolated alkadienals	0.002–0.3
Isolated *cis*-alkenals	0.0003–0.1
trans,cis-2,4-Alkadienals	0.002–0.006
Vinyl ketones	0.00002–0.007

[a] *Source:* Ref. 39.

trans,trans-heptadienals (50). Aged canola oil odor was dominated by 2,4-*cis,trans* and *trans,trans*-decadienals. The grassy flavor component observed in autoxidized milk fat was identified as 2,6-*trans,cis*-nonadienal (51). The aldehydes, 3-*cis*-hexenal, octanal, nonanal, 2-*trans*- and 2-*cis*-nonenal, 3-*cis*-nonenal, and 2,6-*trans,cis*-nonadienal were predominant odor components thought to contribute to the reversion flavor in oxidizing soybean oil (52).

Dixon and Hammond (53) measured flavor thresholds of various carbonyl compounds in oil and water emulsion systems. Mixtures of carbonyls in quantities found typically in oxidized soybean oil had flavor intensities similar to those predicted from adding the intensities of the individual carbonyls. Thus, a synergistic effect of the compounds on flavor was not suggested.

Flavor Impact of Ketones. Other carbonyl compounds resulting from the breakdown of fats and oils that contribute important flavors are the ketones. Hammond and Hill (51) noted that oct-1-en-3-one accounted for the metallic flavor of autoxidized milk fat. The compound is also present in aged canola oils (50). Cadwallader *et al.* (54) identified the same compound in alligator tail meat and described its odor as metallic and mushroom-like. The mushroom-like odor, however, may actually be an artifact of oct-1-en-3-one synthesis (55). Other researchers also identified this ketone as a predominant contributor to reverted flavor in soybean oil, along with 1,5-*cis*-octadien-3-one (52). As noted in Table 18.1, the vinyl ketones have particularly low threshold values (39). A mixture of vinylethyl ketone and pentanal gave a flavor to freshly deodorized soybean oil similar to the flavor of oil in the early stages of autoxidation (56). In other work, these researchers were able to reproduce the dominant flavor characteristics of autoxidized milk fat with a combination of vinylamyl ketone, 2,4-decadienal, and 2,4-*trans,cis*-nonadienal (51). Seals and Hammond (47) also noted the contribution of 2,3-pentanedione, along with diacetyl, to the buttery flavor of soybean oil.

The flavor threshold of C_6–C_{10} methyl ketones, compounds particularly important to the flavor of some cheeses, is ~0.2–2 mg/kg (0.2–2 ppm) in water and ~10-fold higher in oil (53). The threshold is lowest for 2-octanone. The threshold values for this class of ketones are comparable to those of volatile compounds having relatively low potency (Table 18.1). Dixon and Hammond (53) noted that the flavor intensities of 2-ketones tended to rise at significantly greater rates with increasing concentration than did those of several aldehyde series. Therefore, reported thresholds of ketones may underestimate their flavor impact.

Flavor Impact of Furans. A well-known singlet oxidation product of linoleic acid, and thus of many vegetable oils, is 2-pentylfuran (57). Its formation may also arise from linolenate *via* singlet oxidation (39). In particular, 2-pentylfuran may contribute to the reversion flavor of soybean oil (58). More recently, other fatty acids containing a furan ring (also known as furanoid fatty acids) were reported to cause flavor problems in soybean oil. Guth and Grosch (59) identified three furanoid acids in soybean oil, two of which could be photoxidized easily to produce a strong-flavored compound, 3-methylnonane-2,4-dione, which they believed to be important in the flavor of photoxidized (reverted) soybean oil. They found moderate amounts of these furanoid fatty acids in wheat germ oil and minor amounts in rapeseed and corn oils, but none in olive and sunflower oils. The compound, 3-methylnonane-2,4-dione, was previously reported to have a very low odor threshold of 0.01 ng/L air and was characterized as "lard-like, strawy and fruity" (60). In a effort to direct breeding of soybean varieties with fewer furanoid fatty acids, Wu *et al.* (61) determined that both growth environment and variety caused significant differences in the furanoid content of 56 soybean varieties.

Impact of Other Components. The cleavage of lipid hydroperoxides also produces alcohols, alkanes, alkenes, and alkynes, but most of these compounds have very high flavor thresholds; thus, they are not considered important to the flavors of fats and oils and lipid-containing foods. Coconut oil is unique among vegetable oils in the great amount of γ- and δ-lactones present, which contribute positively to its flavor and aroma (62). Milk fat also contains some desirable lactones.

Inherent Factors Affecting Fat and Oil Flavor Quality

Fats and oils are composed primarily of triacylglycerols, with a variety of possible fatty acids attached to the glycerol backbone in an array of possible combinations, depending upon the plant or animal source. As just discussed, the fatty acids differ in their susceptibility to oxidation; thus fatty acid make-up of an oil has a major effect on its stability. The position of these fatty acids on the glycerol backbone also may influence oxidation rate. Finally, the presence of minor constituents that make up <1% of the oil can alter oxidation dynamics. All of these inherent features of an oil can greatly affect its flavor quality.

Triglyceride Structure

Some researchers have suggested that concentration of unsaturated fatty acids at the *sn-2* position of the triacylglycerol stabilizes a fat against autoxidation, although other theories also have been considered. Most plants naturally synthesize oils with unsaturated fatty acids concentrated on the *sn*-2 position. Raghuveer and Hammond (63) randomized (redistributed fatty acids on the glycerol backbones) mixtures of triunsaturated glycerides with tridecanoin and studied the rate of autoxidation of the products. Less oxidation occurred when the unsaturated fatty acids were present on the *sn*-2 position. Similar effects of randomization were observed with corn oil (64) and lard (65). Konishi *et al.* (66) also observed that normal soybean oil randomly interesterified with stearate was far less stable than when stearate was placed selectively on the *sn*-1 and *sn*-3 positions. Hoffman *et al.* (65), however, suggested that oxidative stability was not determined solely by position of the unsaturated fatty acids, and was affected by potential asymmetry of the triacylglycerol structure.

Synthetic triacylglycerols with the same fatty acids on the *sn*-1 and *sn*-3 positions to create balance and a different fatty acid on the *sn*-2 position were more stable than the corresponding isomers with the same fatty acid on the *sn*-2 and either the *sn*-1 or *sn*-3 position. In later work, Hoffmann obtained conflicting information on the theory of asymmetry and lipid oxidation (personal communication, 1990). Synthetic triacylglycerol blends with balanced fatty ester arrangements were not always more oxidatively stable than those that were unbalanced. Hoffmann suggested that steric hindrance caused by the presence of the bulky linolenate group on the *sn*-2 position decreased the oxidative stability of the triacylglycerol, whereas oleate and linoleate were protected from oxidation when on this position. Fatemi and Hammond (23) measured the effect of fatty acid asymmetry on oxidation of natural and randomized olive and soybean oils and could find no evidence of such an effect. They also calculated the potential effect of asymmetry of fatty acid group distribution in these oils and concluded that any possible effect on oxidation would be minimal. It was also proposed that the method of randomization itself may decrease oxidative stability of an oil (67).

Although the answers are not definitive, most experts now agree that the placement of fatty acids within the triacylglycerol does have an effect on oxidation. The reasons for the effect are less understood but may have to do with a critical concentration of autoxidatively sensitive triacylglycerols (i.e., those with more polyunsaturated fatty acids) (68). Thus, whether randomization of an oil increases or decreases oxidative stability would depend on its original concentration of the sensitive triacylglycerols. The implications to the fats and oils industry are that is it is possible to alter (increase or decrease) the oxidative stability of a native oil by randomization, thus expanding the options for new product development. Control of the randomization process may be a key to forming a more stable product.

Presence of Free Fatty Acids, Mono- and Diglycerides, and Phospholipids

Free fatty acids oxidize slightly more quickly than when esterified to the glycerol backbone. In addition, the presence of free fatty acids in a bulk oil can catalyze the oxidation of the entire system. Catalytic trace metals from oil processing and storage equipment can be attached to the free fatty acids, also accelerating oxidation of the system. Thus, removal of free fatty acids from commercially refined oils with citric acid is commonly practiced to enhance overall quality and to extend the shelf life. As previously noted, fatty acids may be cleaved from the glycerol backbone by action of enzymes native to the plant or animal from which the oil is removed.

The presence of mono- and/or diglycerides also reduces the oxidative stability of an oil. Normal, fresh soybean oil contains ~0.1% monoglycerides and 1.2% diglycerides (69). Mistry and Min (70) studied the effects of monolinolein on the oxidative stability of soybean oil during storage at 55°C and determined that volatile compound generation and peroxide values of the oils increased with increased level of the monoglyceride from 0 to 1.0%, indicating a decrease in oxidative stability. In a similar fashion, they noted decreased oxidative stability of soybean oil with the addition of monostearin, distearin, monolinolein, or dilinolein, with the oxidative effect increasing as the levels of the mono- and diglycerides in the oil increased from 0 to 0.5% (71).

Phospholipids, present in crude soybean oil at ~1.5%, have been reported as anti- and prooxidants, depending upon a number of factors (72). In the presence of iron and other minerals, phospholipids act as antioxidants because they chelate the mineral, thus making it unavailable to catalyze oxidation. In the absence of iron, however, the phospholipids may act as prooxidants. Presumably, the presence of both hydrophilic and hydrophobic groups within the same molecule enhances the introduction of oxygen into an oil, thus increasing the prooxidant activity of phospholipids, as well as free fatty acids and mono- and diglycerides (73). These components are nearly completely removed from most crude vegetable oils during refining, bleaching, and deodorization to produce a stable processed product.

Presence of Native Phenolic Components as Antioxidants

Phenolic compounds are widely distributed in cereals and legumes and are important to controlling oxidative processes in both the plants and in their extracted oils. Phenolic compounds include tocols, flavonoids, and phenols, phenolic acids, and their derivatives. These antioxidants inhibit lipid oxidation in foods and biological systems by stabilizing hydroperoxy and other free radicals (74), and their presence has a major effect on oil flavor quality. Tocols, abundant and ubiquitous natural antioxidants found in plant-based oils, include four tocopherol and four tocotrienol isomers, each designated as α, β, γ, or δ on the basis of methylation of the chromanol ring. The tocopherols have a saturated side chain, whereas the tocotrienols have an unsaturated side chain. Flavonoids are characterized by having the carbon skeleton C_6-C_3-C_6, whose basic structure consists of two aromatic rings linked by a three-carbon aliphatic chain. Compounds in the flavonoid group, including flavones, flavonols, isoflavones, catechins, flavanones, and chalones, demonstrate primary antioxidant activity as free-radical acceptors and as chain breakers (75). Flavonoids also may scavenge radicals such as superoxide anions (76,77), quench singlet oxygen (78,79), and chelate metals (80,81). The most common phenolic compounds found in cereals include ferulic, caffeic, protocatechuic, *p*-hydroxybenzoic, vanillic, syringic, and *p*-coumeric acids (82); in legumes, these compounds include chlorogenic, isochlorogenic, caffeic, ferulic, *p*-coumaric, syringic, vanillic, and *p*-hydroxybenzoic acids (83).

A recent survey showed total tocopherol concentrations in crude oils ranging from 534 to 1858 μg/g in sunflower, 504–687 μg/g in canola, 1205–2195 μg/g in soybean, and 1947–4082 μg/g in wheat germ oils (84). The ranges are similar to values reported in the literature, except for the upper limits found in sunflower and wheat germ oils, which exceeded previous values (85). The concentrations of the different isomers vary considerably, depending on the plant source. For example, α-tocopherol is the only tocopherol found in useful levels in sunflower oil, whereas γ-tocopherol is the most abundant isomer in canola, soybean, and generally wheat germ oils. Soybean oil is unique in having the only appreciable concentration of δ-tocopherol. In soybeans, it was also noted that the greater the growing temperature, the greater was the total tocopherol content of the crude oil from the beans (86). Furthermore, low-linolenic varieties of soybeans produced oils with higher α-tocopherol and lower γ-tocopherol concentrations than did normal soybeans, illustrating the effect of both temperature and genetics on oil composition of these minor constituents (86).

The stability of many vegetable oils has been credited to the presence of these native tocopherols and other phenolic compounds; however, the presence of too many tocopherols (>1500 µg/g, i.e., 0.15%) was shown to enhance oxidation of linoleic acid in an aqueous medium (87). In purified soybean oil, the concentrations of α-, γ-, and δ-tocopherols offering optimum oxidative stability were 100, 250, and 500 µg/g, respectively, at 55°C in the dark (88). Significant prooxidant effects were noted at greater concentrations. With corn oil as the medium, α-tocopherol showed maximum antioxidant activity at 250–500 µg/g in bulk oil, but no significant difference was observed between 250 and 1000 µg/g in emulsions (89). α-Tocopherol had a slight initial prooxidant effect at ≥250 µg/g concentrations in bulk oil and at ≥500 µg/g concentrations in emulsions, whereas γ-tocopherol showed no prooxidant activity in either system. γ-Tocopherol had less antioxidant activity than did α-tocopherol at 100 µg/g, but greater antioxidant activity at greater concentrations in both systems (89). At concentrations normally found in the refined oils, γ-tocopherol was a more effective antioxidant than α-tocopherol in soybean and sunflower oils (90). In general, the relative antioxidant activity of the various tocopherols depends on temperature, lipid composition, physical state (bulk oil phase or emulsion), and tocopherol concentrations (88,89,91,92).

Lard has long been considered to be oxidatively unstable because of its lack of natural phenolic components, especially tocopherols. Consequently, to enhance its oxidative stability, most lard in the United States is sold containing the maximum allowable quantity of an added synthetic antioxidant (93), butylated hydroxytoluene, of 0.02%. Lard would benefit from having a greater concentration of native antioxidants as shown by Marinova and Yanishlieva (94), who studied the antioxidant activity of 20–2000 µg/g (0.2–2.0 g/kg) of α-tocopherol on purified lard triacylglycerols at 25, 50, 75 and 100°C. The optimal antioxidant effect was observed with 200 µg/g (200 mg/kg) α-tocopherol. The researchers also compared the antioxidant properties of the phenols, benzoic and cinnamic acid derivatives, in the concentration range from 200 to 2000 µg/g (0.02–0.2 wt%) during autoxidation at 100°C of lard and sunflower oil methyl esters. In both systems, the derivatives of benzoic acid had weaker inhibiting properties than did the corresponding analogs of cinnamic acid.

The antioxidant activity of flavonoids may vary with the test medium. Myricetin showed strong antioxidant activity in sunflower oil stored at 30 and 60°C and in oil-in-water emulsions stored at 30°C with or without the presence of tocopherols or citric acid (95). Quercetin was similar to myricetin in stripped sunflower oil, but was not effective in oils that contained tocopherols and citric acid. With the addition of some, but not all copper and iron salts, a prooxidant effect was observed. Evidently, flavonols may exert a prooxidant effect in the presence of metal salts, but the nature of the metal salt may alter the effect. The overall effect of the flavonoids on quality of oils or of oil-containing foods may be substantial.

Thus, the issue of how much antioxidant is ideal for a particular oil or system is highly dependent upon a number of factors. It is perhaps sufficient to note that the presence of tocopherols, flavonoids, and other phenolic antioxidants is important to overall oxidative stability of oils and oil-containing foods, but that each system should be optimized for the exact amount needed.

Presence of Other Minor Constituents

Endo *et al.* (96) suggested the contribution to flavor reversion in soybean oil of unusual triglycerides consisting of 10-oxo-8-octadecenoate and 10- and 9-hydroxy octadecanoate, although no flavor threshold studies were conducted on these components to determine their potential effect. These minor constituents are likely oxidative products produced during the early stages of oil oxidation.

Two fat-soluble pigments, chlorophyll and carotenoids, frequently found in fats and oils may act as a pro- or antioxidants depending upon the conditions and circumstances. In the dark and at low temperature, chlorophyll and pheophytin (a water-soluble derivative of chlorophyll) prevented oxidative deterioration of a vegetable oil (97). But in purified virgin olive oil, chlorophyll acted as a photosensitizer for singlet oxygen formation under light (98). The carotenoids, β-carotene and lycopene, are particularly effective at quenching singlet oxygen, especially at the low oxygen pressures found in biological systems (99). At low levels (5–20 μg/g), β-carotene significantly protected soybean oil against light deterioration, presumably by acting synergistically with δ-tocopherol (100). In the dark, however, β-carotene had a prooxidant effect in soybean oil. The presence of chlorophyll in canola and soybean oils, a common problem in immature seed, is generally agreed to reduce oxidative stability during storage. Thus, growing conditions and harvest time can affect the quality of canola and other vegetable oils. In general, oil processors bleach vegetable oils to effectively remove both chlorophyll and carotenoids. Remaining concentrations of ≤50 ppb of the chlorophyll compounds were required to avoid rapid oxidation of oil in the presence of light (101).

The sterols, lipid-soluble components extracted with the triacylglycerols, are not effective as traditional antioxidants; however, some specific sterols have remarkable antipolymerization activity in heated oils. The unsaponifiable fraction that contains sterols was isolated from olive, corn, wheat, and *Vernonia anthelmintica* oils and found effective at protecting safflower oil from oxidative polymerization during heating at frying temperature (102). δ^5-Avenasterol and fucosterol reduced polymerization at 180°C in a triacylglycerol mixture similar in composition to olive oil (103). The addition of oat-sterol fractions containing δ^5-avenasterol reduced the deterioration of soybean oil at 180°C (104). The antipolymerization activity of the effective sterols was shown to reside in the side chain, which contains an ethylidene group (105). Thus, retaining some of these effective sterols in a processed oil would be desirable for oil quality.

External Factors Affecting Flavor Quality of Fats and Oils

In addition to factors inherent in the composition of an oil, a topic noted earlier in this chapter, external components may affect oil quality. The presence of light, oxygen, and any prooxidants has a detrimental effect on oil quality, with the effect generally increasing with increasing concentration (106). At high oxygen concentrations, the rate of oxidation is independent of oxygen concentration. At very low concentrations, the rate is somewhat proportional to concentration. An oxygen concentration ≤2% was shown to reduce oxidation effectively in a vegetable oil (107). Displacement of oxygen to a concentration of 1.2% by liquid nitrogen and 0.3% by solid carbon dioxide reduced lipid oxidation dramatically in freeze-dried carrots (108). Early research demonstrated some reversion flavor development in soybean oil aged under inert gases, presumably because of small amounts of dissolved oxygen in the system (109). The exact rate of oxidation also depends on other factors such as temperature and surface area. Oil stability is generally greater at lower temperatures. Also, oxidation increases with an increase in the surface area of the fat or oil that is exposed to air. Oxidation of an oil-in-water emulsion is governed by the diffusion rate of oxygen into the system.

The effect of moisture on lipid oxidation is strongly dependent upon the water activity (a_w) of a food system. Very low a_w values of <0.1, typical in dried food products, greatly enhance oxidation. An a_w value of ~0.3 generally results in a minimum rate of oxidation, presumably because the water slows access of oxygen to the lipid or reduces the catalytic activity of metal catalysts by quenching free radicals. When the a_w value of a food system becomes considerably greater (a_w = 0.55–0.85), the oxidation rate again increases, perhaps because of increased mobilization of catalysts and oxygen. The oxidative stability of a pure edible oil is generally greatest at extremely low water activities, where hydrolysis of the fatty acids from the glycerol backbone is unlikely. By keeping these factors in mind, a number of steps can be taken to protect oil quality of pure oils and of foods containing lipids. For example, packaging pure oils in dark bottles or potato chips in light-proof packages prevents light-induced damage. Saturating a package with an inert gas, such as nitrogen, inside an oxygen-impermeable package reduces oxidation of the food or oil. Moisture-proof packaging allows a product to maintain its initial a_w, presumably at a targeted optimum level.

The presence of prooxidants in lipid-containing foods and oils can dramatically increase oxidation. The prooxidants are generally transition metals, particularly those possessing two or more valency states. Oxidation catalyzed by copper and iron is probably the most important from a practical point of view, but other metals, such as manganese, chromium, nickel, vanadium, zinc, cobalt, and aluminum can also promote oxidation. Trace amounts of metals found in fats and oils typically arise from metallic equipment used in processing or storage, as well as from the soil in which an oil-bearing plant was grown or within animal tissues. Metals are also present within the fluids of biological materials, such as eggs, milk, and fruits. Thus, it is extremely difficult to remove trace metals completely from fats and oils. For this reason, metal chelators, especially citric acid, are typically added to fats and oils during processing. These chelators bind minor amounts of metals, thus "removing" them from the lipid system and resulting in a reduction of oxidation. Citric acid decomposes at 150°C; thus it is typically added to an oil during the cooling stage of deodorization. The timing of the addition is fairly important because if the citric acid is added too late, it is minimally effective; if too early, it also may act as a prooxidant. Ascorbic, phosphoric, and tartaric acids, as well as phospholipids, may also act as chelators in some foods.

Antioxidants, in addition to those naturally present, are typically added to fats and oils to reduce and slow the rate of oxidation (110). Typical synthetic antioxidants used in food-grade products include butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), monotertiary butylhydroquinone (TBHQ), and propyl gallate (PG). Others, such as ethoxyquin (EQ), are effective antioxidants, but are approved only for use in animal feeds. Other researchers have reviewed the history and use of these and other synthetic antioxidants in fats and oils (111). Nearly all of the native phenolic antioxidants discussed earlier in this chapter also may be extracted from various sources and added to fats and oils and lipid-containing foods to enhance oxidative stability and shelf life. The tocopherols are probably the most common "natural" antioxidants used today.

Methods to Measure Flavor Quality of Fats and Oils

Any method used for evaluating lipid oxidation in foods and edible oils should relate directly to the actual flavor of the oxidizing product because the flavor is ultimately what is important. Therefore, the measurement of compounds specifically involved in flavor development is important. The more exact the measurement, the better. Also, minimizing artifact production during measurement is vital. An overall assessment of lipid oxidation should involve evaluation by several different types of measurements and storage of the oil/food under at least two different conditions of oxidation. Measurement types include chemical, volatile, and sensory; conditions might vary according to light exposure (under fluorescent light or in the dark), or temperature (35 or 60°C), or a combination of these and other conditions. Some of the most common methods of evaluation are described in this chapter, but many more procedures are available.

Chemical Methods of Analysis

Peroxide Value. Assessment of the peroxide value (PV) of an oil during oxidative storage is quite common, and fairly useful. The PV measures hydroperoxides, formed by the reaction of unsaturated oils with triplet or singlet oxygen, and one of the preliminary oxidation steps noted in Figure 18.1. Hydroperoxides are primary products of lipid oxidation and intermediate to the formation of volatile carbonyl compounds responsible for flavors associated with oxidation. The PV, expressed as milliequivalents of peroxide per kilogram of oil, is said to be an index to the oxidative state of an oil. The most common method for measuring PV is by one of several titrametric procedures. Official and Tentative Methods of the American Oil Chemists' Society (112) method Cd 18-53 uses acetic acid and chloroform in which to disperse the oil for titration. A newer procedure, Cd 8b-90, replaces the chloroform with isooctane, a less harmful solvent that is thought to be noncarcinogenic. The International Union of Pure and Applied Chemistry (113) method 2.501 describes a procedure similar to that of AOCS Cd 18-53. Other methods for measuring PV involve colorimetric reactions among other techniques.

Advantages to using the titrametric PV procedure are speed, simplicity, and the lack of need for expensive equipment. If done under consistent conditions, the PV is fairly accurate, resulting in coefficients of variation of <1%. Disadvantages include several procedural problems. The PV is highly empirical in that altering time and/or temperature of the various steps would result in erratic results. Thus, a single operator should handle all evaluations within a test. Also, the preferred solvent, isooctane, is flammable, requiring care in handling. Rapid mechanical stirring is needed to completely mix the isooctane with the aqueous medium to prevent phase separation. Finally, iodine may be liberated from potassium iodide during the reaction by any oxygen present in the solution, resulting in an overestimation of PV.

To interpret the results of PV tests, one must remember that peroxides are unstable and transitory components formed during oxidation. In fact, they are intermediate products leading to the true products of rancidity (oxidation) that actually cause off-flavors, such as volatile carbonyl compounds. As a result of this process, the PV passes through a maximum value at some point during excessive oxidation, when the rate of hydroperoxide formation is similar to the rate of decomposition. After that, the PV will decline gradually. Thus, periodic measurement of PV during lipid oxidation allows recognition of these various stages of peroxide formation and decomposition. In addition, peroxides are particularly sensitive to breakdown at elevated temperatures and decompose rapidly at frying temperatures (~180°C). Thus, PV should *not* be used to monitor changes in oils during frying.

Theoretically, a freshly deodorized oil should have a PV of 0.0 mEq/kg oil, although tiny amounts of peroxides begin forming in an oil almost immediately after deodorization. To be considered "fresh," an oil should have a PV of <1.0 mEq/kg oil (114). For soybean oil, an oil is considered to have low oxidation with a PV of 1.0–5.0 mEq/kg oil, moderate oxidation at a PV of 5.0–10.0 mEq/kg oil, high oxidation at a PV >10.0 mEq/kg oil, and to have poor flavor quality at a PV >20.0 mEq/kg oil. These quality estimates, however, are oil specific and higher PV may be acceptable in other oils such as corn and peanut oils. Although the PV measurement cannot predict the flavor quality of an oil completely, good correlation values (R^2) of 0.80 and 0.97 have been reported for PV and sensory evaluation scores (115).

Other Chemical Methods of Analysis. There are many other methods for measuring lipid oxidation by chemical means. A few of the best-known procedures are mentioned here. The conjugated dienoic acid test captures the chemical shift of double bonds that accompanies peroxide formation, as shown in Figure 18.1. Two official procedures are equally effective at this measurement, i.e., method Ti la-64 (112) and method 2.505 (113). These methods measure primary products of oxidation, similar to the PV method. Another indication of lipid oxidation is the formation of carbonyl compounds, as noted in Figure 18.1. The carbonyl value (CV) is an official procedure of the Japan Oil Chemists' Society (116), method 2.4. 22-73, and is based on research by Henick *et al.* (117). Although this procedure measures secondary products that contribute to flavor, it does not differentiate between volatile and nonvolatile carbonyls. Thus, all carbonyls are measured, regardless of whether they produce flavor. A well-refined oil should have a CV of 0.5–2.0 mmol/kg oil.

The *p*-anisidine value (AV), official method Ed 18-90 (112) and method 2.504 (113), measures light absorbance at 350 nm of aldehydes, primarily 2-alkenals, and 2,4 dienals. The method is not entirely specific, however, because the color intensity developed during the analysis depends on the actual aldehyde structure. Also, as noted earlier, not all 2-alkenals and 2,4-dienals contribute to oxidation off-flavor.

Finally, headspace oxygen analysis also is common for measuring lipid oxidation. As fats and oils oxidize, they absorb oxygen that is incorporated into the material, as shown in Figure 18.1. Oxygen present in the headspace of a closed container decreases over time, and its disappearance can be an effective measure of lipid oxidation, if done carefully.

Volatile Compound Analysis by Gas Chromatography

Figure 18.1 shows the route for formation of many carbonyl compounds. As noted earlier in this chapter, the volatile carbonyl compounds in fats and oils are major contributors to off-flavor development during oxidation. Aldehydes and ketones tend to have lower flavor thresholds than do the alcohols, hydrocarbons, and short-chain fatty acids; thus, efforts at identification and quantification are generally focused on the former compounds. Analysis of volatile compounds in oils and in oil-containing foods is difficult because the compounds are soluble in lipids and present in small concentrations. Oil is quite viscous, making it difficult to remove the volatile compounds. Also, measurement of flavor intensity of the aldehydes and ketones can be confusing because the compounds have a higher flavor threshold when placed in oil rather than in water. Researchers find it easier to measure the sensory perception of flavors mixed in water than in oil because oil often has its own background flavors and is difficult to remove from the mouth during tasting. Further difficulties in measuring carbonyl compounds in oils arise from the widespread contamination by carbonyls in solvents, glassware, and other materials used in the laboratory. Thus, identifying carbonyl compounds from the oil alone can be complicated. These features are further confused by the fact that hundreds of volatile compounds may be formed in fats and oils during oxidation. Their identification and quantification require the use of efficient gas chromatography columns and proper means of identification.

Three basic gas chromatographic procedures are generally employed for measuring volatile compounds related to the flavor quality and oxidative stability of fats and oils. The procedures, described with method Cg 4-94 (112), include static headspace, dynamic headspace, and direct injection. Static headspace is the classical headspace analysis, involving equilibration of gases from the area above a liquid sample. The equilibration step may take several hours but is absolutely necessary for accurate results. A set volume of the headspace gas from the sample is then injected directly into the gas chromatograph (GC) for separation and quantification. Automated static headspace systems have simplified the procedure, often employing multiple sample injections to improve the accuracy of measurement. The dynamic headspace method, also known as purge and trap, employs a sorbent to collect volatile compounds from the fat, oil, or fat-containing food. Volatile compounds are swept from a heated sample with nitrogen and trapped on a sorbent, such as Tenax GC, Chromosorb, or Porapak Q. Low heating temperatures (≤60°C) result in the collection of compounds that are representative of components present in the original sample. Volatile trapping may take several hours and is affected by concentration of the volatiles present. After trapping, the sorbent may be extracted with solvent, or transferred directly to the GC, and cryofocused at –50°C. The static headspace method is selective toward the low-molecular-weight compounds, such as pentane, whereas the dynamic headspace method is selective toward medium- and higher-molecular-weight compounds, such as 2-4-decadienal.

Finally, volatile compound analysis by direct injection into the GC also may be used. The entire range of low- to high-molecular-weight compounds can be detected by direct injection. The sample may be pretreated by three possible procedures. The first treatment involves an external purging system in which volatiles are transferred from the sample to a temperature-controlled unit external to the GC. The sample is then injected directly into the GC. In a second treatment, the oil, fat, or food is placed in the injector insert and positioned in the injection port of the GC. The volatile compounds are transferred directly to the GC column by cryofocusing onto a capillary column. Alternatively, an oil sample may be injected directly into the port of the GC through a silanized glass wool plug. A disadvantage of direct injection techniques is that they are highly dependent upon the sampling conditions. Also, the technique requires relatively high temperatures of 150–190°C, which can cause artifact formation if the actual oil sample is present.

Interpretation of the chromatograms obtained from the GC can be somewhat difficult because many peaks are obtained. Generally, the best results can be obtained by selecting a subset of several peaks from the chromatogram. An example of a typical chromatogram resulting from soybean oil is shown in Figure 18.2. The areas from ~1–2 peaks to 12 peaks have been used to obtain good correlations with flavor analyses. Volatile compounds frequently used to correlate with flavor include propanal, pentane, pentenal, pentanol, hexanal, 2-pentenol, 3-hexenal, 2-heptenal,

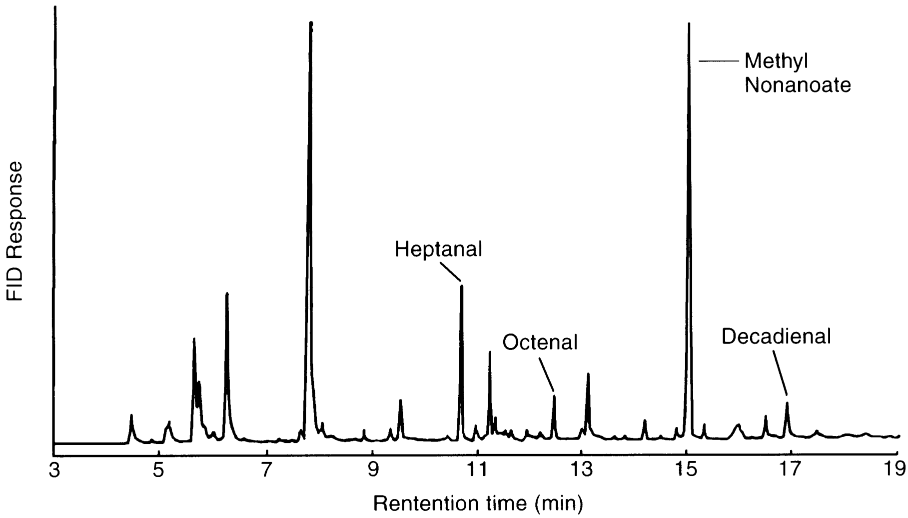


Fig. 18.2. Typical gas chromatogram of volatile compounds from soybean oil used for correlating with flavor scores.

octen-3-ol, 2,4-heptadienal, nonanal, and 2,4-decadienal, listed in order of increasing retention time on a nonpolar column. The exact volatile compounds created from a sample vary according to the oil type, as described previously in this chapter.

Sensory Methods of Analysis

The ultimate method to assess oil quality and stability is sensory analysis. No chemical or instrumental methods can replace sensory evaluation, although some methods can correlate fairly well with this overall evaluation. Sensory evaluation was recently defined as "a scientific discipline used to evoke, measure, analyze, and interpret reactions to food and material characteristics as they are perceived by senses of sight, smell, taste, touch and hearing" (114). Sensory testing of oil samples is best done by a panel of experts as described in method Cg 2-83 (112). Briefly, the oil samples are evaluated first for odor intensity by swirling a covered container holding the oil, removing the cover, and sniffing. The samples can then be tasted in approximate order of increasing intensity, thus allowing stronger tasting samples to be evaluated last to avoid carryover of strong flavors to mild-flavored oils. To determine oil taste, 5–10 mL of oil is taken into the mouth, thoroughly swished throughout the mouth with air drawn over the top, and expectorated into a waste cup. Carbon-filtered tap water, heated to 38°C, is used to rinse the mouth of any oily residue between samples.

Several advantages exist for using sensory analysis of fats, oils, and fat-containing foods. The oils are evaluated "as is," i.e., with no chemical modifications or potential alterations in the components. Flavor perception is what determines flavor quality in

TABLE 18.2 Sensory Evaluation Score Sheet to Be Used for Oil Intensity[a]

Score	Intensity level	Characteristic
10	Bland	No flavor detected
9	Trace	Detectable. too weak to identify
8	Faint	Typical of freshly deodorized oils
7	Slight	Typical of most commercialized oils
6	Mild	Typical of oils with peroxide value (PV) <5
5	Moderate	
4	Definite	Typical of oils with PV >5
3	Strong	
2	Very strong	Typical of oils with PV >10
1	Extreme	

[a] For Use with AOCS Method Cg 2-83. *Source:* Ref. 112

the end. Many features define overall flavor of foods and oils; thus, no one or even two chemical or instrumental methods can fully characterize its quality. Thus, human perception is still the best overall method of analysis. Even so, there are a few disadvantages to using sensory panels. Panelists are not reliable as instruments, great differences among humans may exist in their flavor perceptions, and organizing and training sensory panels is time consuming. Statisticians generally recommend averaging scores from an entire "expert" sensory panel of 10–12 members to obtain a single evaluation score. A replicate value should be obtained by repeating the entire evaluation of the panel and averaging the scores to obtain a second replicate score.

Tables 18.2 and 18.3 give examples of score sheets recommended in AOCS method Cg 2-83 to be used for sensory evaluation of fat and oil samples and their characteristics at various stages of oxidation (114). The oil intensity scale shown in

TABLE 18.3 Sensory Evaluation Score Sheet to Be Used for Oil Quality[a]

Score	Quality level	Characteristic
10	Excellent	
9	Good	
8		Typical of good-quality oil; weak characteristic flavors; no off-flavors
7	Fair	Weak off-flavor or some loss of characteristic flavor
6		
5	Poor	Moderate off-flavors
4		
3	Very poor	Strong off-flavors
2		
1	Bad	

[a] For Use with AOCS Method Cg 2-83. *Source:* Ref. 112.

Table 18.2 is appropriate for use with bland oils, such as soybean, canola, and sunflower oils, whereas the oil quality score shown in Table 18.3 should be used for oils with distinctive flavors, such as corn, peanut, olive, and sesame oils.

Procedures other than those just mentioned may be used to successfully obtain similar types of information. Most important to the usefulness of the analyses, is to use several methods that measure compounds directly related to the flavors in oxidized oil samples, to employ two or more storage conditions in the experimental design, and to repeat the entire testing protocol.

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Chapter 19

Oil Quality Improvement Through Processing

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Introduction

Vegetable oils are refined to remove the impurities that are present in the crude oil. Some of these impurities occur naturally in the seeds or oil-bearing fruits. A great majority of these impurities are also formed during harvesting and storage of the seeds and fruits, or during extraction of crude oil and, subsequently, during refining.

Oil refining processes for vegetable oils are designed to remove these impurities from the oil or reduce them to a level at which their deleterious effects on oil stability are minimal. An oil processor should be familiar with the characteristics of these impurities, how they are formed in the oil, and how to minimize their formation during oil processing.

Modes of Oil Breakdown

Vegetable oil begins to undergo degradation almost immediately after the seed is crushed. The oil becomes more prone to oxidation as it is processed further from the crude to the finished stage. Deodorized oil has the highest tendency toward oxidation. The oil begins to show signs of primary oxidation as measured by its peroxide value (PV) (1). Under certain circumstances, the oil may develop a darker color or higher free fatty acids (Anderson Clayton Co., unpublished data) and eventually an unpleasant flavor (2–5). Obviously, all of these reactions require certain catalysts that are very specific for these reactions. The presence of oxygen, moisture, and high temperatures accelerates the reaction process. The three principal modes in which a vegetable oil undergoes degradation are as follows: (i) oxidation, which encompasses autoxidation and photooxidation; (ii) hydrolysis; and (iii) thermal decomposition, which includes oxidative polymerization and thermal polymerization.

Oxidation

Oils oxidize in two different ways, i.e., autoxidation and photooxidation; the latter includes photochemical reaction and photosensitized reaction. Autoxidation and photochemical reactions are somewhat similar in nature. Each reaction starts with the help of an initiator. In the case of autoxidation, the initiator is a metal (6). In the photochemical reaction, the initiator is ultraviolet (UV) light (7,8). The reaction is propagated in both cases by a group of catalysts, termed free radicals (6), which are formed from the unsaturated fatty acids in the oil in the presence of the initiators.

Autoxidation. As mentioned above, autoxidation of the oil is initiated by a metal ion that produces a free radical from a molecule of unsaturated fatty acid. This occurs when the oil is subjected to high temperatures, and especially in the presence of metal ions such as iron, nickel, or aluminum; it is called the "initiation" phase of the reaction. Unsaturated fatty acids break down to form peroxy radicals, which are also free radicals. Each peroxy radical then reacts with another unsaturated fatty acid molecule, forming a hydroperoxide and another free radical, which continues to catalyze the reaction. This is known as the "propagation" phase. The reaction proceeds very rapidly in the presence of oxygen or air.

During the reaction, the PV in the oil increases, reaches a peak, and then begins to decrease because hydroperoxide molecules decompose readily due to their fragile nature (9). The hydroperoxide molecules break down to produce a whole host of secondary and tertiary oxidation products, such as aldehydes, ketones, acids, alcohol, epoxides, or polymers. The reaction continues until all unsaturated fatty acids are reacted, or there is no more oxygen available to form peroxides, or all free radicals have reacted with each other forming dimers, trimers, or polymers. The last step of reaction is referred to as the "termination" phase. The oil becomes inedible, long before this state is reached. Figure 19.1 shows the reaction sequence in the autoxidation process. This process can occur in the oilseeds and fruit palm even before the oil is extracted; it can also occur during extraction as well as during the subsequent steps of oil processing.

Sources of Free Radicals. Free radicals are formed in the oilseeds, palm fruits, and their oils at various stages of the production as a result of the following conditions: (i) poor quality oilseeds; (ii) improper handling and storage of oilseeds; (iii) improper conditions during crushing; (iv) poor handling and storage of the crude oil; (v) overheating the oil during processing; (vi) undue exposure of the oil to oxygen during processing; (vii) atmospheric bleaching; (viii) deodorization under poor vacuum; and (ix) storage and handling of the finished oil without nitrogen.

Unsaturated fatty acid (RH) + initiator = R* (free radical) + H*—Initiation
R* + O_2 = ROO* (peroxy radical)—Propagation
ROO* + RH = ROOH (hydroperoxide) + R*—Propagation
R* + R* = RR (dimer••)—Termination
R* + ROO* = ROOR—Termination
ROO* + ROO* = ROOOOR—Termination

Fig. 19.1. Reactions during autoxidation of oil. ••Indicates oxidative dimers and polymers.

Poor-quality oilseeds, which are field damaged or damaged due to drought or excessive rainfall, are known to have poor stability (10–12). Poor-quality oilseeds require excess caustic treatment and extra bleaching (13). This also produces higher than normal level of free radicals in the oil. When the soybeans are stored at temperatures >45°C and at a moisture content ≥14%, lipase and lipoxygenase in the beans are activated, resulting in free radical formation (14,15). In addition, another enzyme, known as phospholipase-D, increases the level of nonhydratable phospholipids in the crude oil (16). This requires extra caustic treatment in refining; however, as mentioned earlier, this can increase the formation of free radicals in the crude oil. Like the oilseeds, fruit palm also shows an increase in free fatty acid content if it is damaged during harvest or not processed within 24 h after harvest.

Therefore, one must be aware of the source of free radicals in the crude oil as it is received. The degree of oxidation in the crude oil must be monitored. PV indicates the state of primary oxidation of the oil. However, hydroperoxides are very unstable. These compounds break down to produce secondary oxidation products, such as aldehydes and ketones. Some of these secondary oxidation compounds can be measured by analyzing the oil for *para*-anisidine value (pAV), commonly termed anisidine value.

To extract oil from soybean, the beans are cracked, heated (tempered) in horizontal or vertical cookers, flaked, and then the oil is extracted with hexane. This process allows ample opportunity for the free radicals to be formed because the cracked seeds are heated in the presence of air. The cracked pieces of soybean go through a temperature range in which the enzymes are most active. This creates an opportune environment for the formation of free radicals in the oil while it is still in the cracked seeds.

Normally, the cracked seeds are heated faster in a horizontal cooker than in a vertical cooker, offering some advantage for the former over the latter. Another method used in the seed extraction process is known as the expander process. Expanders are extruders, in which the soybean flakes are subjected to extrusion in the presence of live steam. The feed reaches a high temperature very rapidly, aiding in the process of enzyme deactivation. The author has experienced a reduced level of nonhydratable phospholipids in the crude soybean oil obtained from the expander process. In addition, the crude oil from the expander process, after degumming to <5 ppm phosphorus, produced soybean oil that had flavor stability superior to that of the oil obtained from the standard process (17). This offers indirect evidence of the fact that reduced enzyme activity during crushing can produce improved oil stability due to reduced free radical activity in the crude oil.

For fruit palm, the fruit bunches are autoclaved with steam at a pressure of 45–50 lb/in^2. Fruit bunches are placed in the cages of roughly 1- to 1.5-ton capacity. The cages are rolled into an autoclave and live steam is injected into the autoclave. After 15–20 min of heating, the steam from the autoclave is vented to remove the air from the inside of the autoclave. The autoclave is repressurized with steam, and the fruits are heated for another 60–75 min. The mode of operation of the autoclave makes the conditions conducive to the formation of free radicals and free fatty acids. The fruits go through a heating process in which they are in contact with the air but are not heated rapidly enough to deactivate the enzymes and prevent enzymatic reaction.

Crude oil produced from oilseeds or fruit palm must be protected against exposure to oxygen. It is common knowledge that the PV in the oil is reduced to zero when an oil with a high PV is bleached and deodorized. This does not necessarily indicate that the quality of the finished oil is improved as the PV drops to zero. When the peroxide is reduced to zero, the anisidine value (AV) in the oil goes up. AV measures the level of secondary oxidation products in the oil, which contain free radicals that can propagate autoxidation in the oil. In addition, peroxide formation can occur while the fatty acid is still attached to the glycerol molecule. In the deodorization process, 90% of these molecules remain in the oil (18). These partial molecules are free radicals. They can continue to break down the unsaturated fatty acids while the finished oil is in storage (19). Researchers (18) have demonstrated that when crude soybean oil is heavily preoxidized, the freshly deodorized oil may show good flavor; however, it develops an oxidized flavor and becomes rancid very rapidly. Overheating the oil during processing (20) or undue exposure to oxygen increases the formation of peroxides, which lead to poor oil stability.

Recommendation. It is recommended that the degree of oxidation in the incoming crude oil be monitored at the time of receipt and during its storage, before refining. PV alone does not provide the true picture of the state of oxidation in the crude oil. In addition to PV, one must also measure the AV in the crude oil. These analyses must also be conducted while the crude oil is in storage, waiting to be refined. The goal should be to keep both of these values as low as possible. The crude oil must be refined immediately, if these values begin to rise.

Many processors of oils do not cool the crude oil before it is stored, i.e., many soybean crushers send the crude soybean oil into the storage tank at 158°F (70°C) after the oil leaves the stripper. In most cases, crude palm oil is stored at 167–194°F (75–90°C) by the fruit palm crushers. This practice is highly damaging to the oil.

Recommendation. It is recommended that an oil cooler be installed for both seed oils and palm oil processes to cool the oil to <105°F (40°C) before the crude oil is sent to storage.

In many Third-World countries, oil is bleached under atmospheric conditions. The oil is heated to 230–248°F (110–120°C), bleaching clay is added, the oil is agitated for 30–45 min and then filtered. This is an ideal situation for the oil to react with oxygen. Generally, the PV in freshly bleached oil would be very low or zero, but the AV of the bleached oil from the atmospheric bleaching process is always high. This is because the oil produces hydroperoxides during bleaching. Hydroperoxides break down in the process soon after they are formed. Therefore, determination of only PV in the bleached oil is not sufficient to establish the state of oxidation in the oil.

Recommendation. It is recommended that AV also be determined in the bleached oil along with the PV to establish the exact state of oxidation in the oil. Bleached oil must be analyzed for the trace impurities such as phosphorus, calcium, magnesium, iron, soap, chlorophylls, and Lovibond Red color. To minimize the formation of excess free radicals in the bleaching process, one must avoid using the atmospheric process and adopt the vacuum bleaching method. In addition, use of hydrogel silica, such as Trisyl, can reduce soap, trace metals, phospholipids, and free radicals that are present in the oil and improve its stability.

The final step in oil processing is deodorization. In this process, the bleached oil is steam-distilled under vacuum. The object is to remove the volatile impurities from the oil. The red color of the oil is also reduced due to heat bleaching of the carotenes.

In the deodorization process, it is necessary that the absolute pressure in the deodorizer system be maintained as specified by the manufacturer. In the United States and around the world, the author has noted that the production personnel as well as the management in an oil processing operation tend to operate the deodorizers improperly in the following ways: (i) using a throughput far beyond the designed limit; (ii) maintaining an absolute pressure in the deodorizer much higher than the designed operating limit; and (iii) deodorizing oils at a temperature that is too high in order to compensate for poor vacuum in the deodorizer and/or higher deodorizer throughput. All of these practices produce either incompletely deodorized oil or damage the oil in the deodorization process.

A higher than designed pressure in the deodorizer vacuum system generally indicates the presence of air. At a deodorizer temperature of 468–500°F (242–260°C), the oil can undergo very rapid oxidation and polymerization if the system is not maintained at the designed operating pressure. Researchers (18) have shown that as the dimer content in the deodorized oil goes up, the flavor acceptability in freshly deodorized oil goes down. At the same time, the oil containing higher levels of dimers demonstrates poor flavor stability. Poor vacuum in the deodorizer can produce high amounts of oxidative polymers in the oil. Some of these polymers contain as much as nine times the amount of oxygen present in a triglyceride molecule. These compounds break down in the absence of light, oxygen, and even at very low temperatures, releasing more free radicals that cause flavor degradation in the oil in storage or in the food processed with this oil (21). This is known as hidden oxidation in the oil. Standard analytical tools that are normally used to measure oil oxidation, such as PV, cannot explain this phenomenon.

Recommendation. The oil in the deodorizer must be cooled down to ≤302°F (150°C) before it is taken out of the deodorizer for external cooling. The addition of citric acid is critical to chelate the metals that can cause autoxidation of the oil in storage. Citric acid must be added at a temperature no greater than 145°C to prevent its decomposition. The oil leaving the deodorizer must be cooled down to a temperature no greater than 9°F (5°C) above its melt point before it is stored. The liquid oils must be cooled down to <105°F (40°C). It is highly recommended that all deodorized oils be saturated with nitrogen as they leave the deodorizer. The oils must be stored under a nitrogen atmosphere with a maximum oxygen content of 0.5% in the tank headspace. Oils stored under these conditions have shown no rise in the PV for 6-8 wk (M.K. Gupta, unpublished data), without the use of antioxidants.

Photooxidation. It was mentioned earlier that there are two types of photooxidation reactions. The first type is photochemical reaction. This reaction is initiated by UV light. Unsaturated fatty acids form free radicals in the presence of the UV light. The rest of the reaction proceeds in the same manner as the autoxidation process. Photochemical reaction proceeds at the same rate as autoxidation. The second type, photosensitized reaction, occurs when the oil is exposed to visible light in presence of a photosensitizer such as chlorophyll (22). This reaction proceeds 1500 times more quickly than autoxidation or photochemical reaction.

Chlorophylls, naturally present in soybean and canola oils, are photosensitizers. For this reason, excess chlorophylls present in these oils must be removed to reduce photosensitivity of these oils during the following applications: (i) when the oils are packaged and stored in clear bottles; and (ii) when processed foods are prepared with these oils and packaged in clear bags or containers. Chlorophylls (A and B) are reduced in the bleaching process. Acid-activated clay is used to remove chlorophylls from vegetable oils. In the United States and Canada, the chlorophyll content is maintained at <30 ppb in both soybean and canola oils.

It has been found (23–25) that chlorophylls undergo decomposition under acidic conditions and in presence of oxygen. The breakdown products of chlorophylls are known as pheophytins, pheophorbides, and pyropheophorbides. These compounds are 10 times stronger photosensitizers than their parent compounds. Therefore, measurement of only chlorophylls in the bleached oil may not provide all of the information regarding its photosensitivity. It has also been demonstrated that chlorophyll B and its decomposition products are stronger photosensitizers (24) compared with chlorophyll A. Therefore it is important to measure the breakdown products of chlorophylls in the bleached oil to establish its photosensitivity. An atmospheric bleaching process provides an ideal opportunity for the chlorophylls to break down and make the oil more prone to photooxidation.

Silica treatment of oil in both the conventional and modified chemical refining processes (26) has led to improved oil stability. This is because silica is a very good adsorbent for soap, trace impurities, and free radicals to improve the autoxidative stability of the oil. In addition, silica can reduce the dosage of bleaching clay required to achieve the desired green color in soybean and canola oils. This may also reduce chlorophyll breakdown during bleaching and provide improved photooxidative stability of the oil.

Recommendations.

1. The vacuum bleaching process is a preferred option for oil bleaching because an atmospheric bleaching process is damaging to the oil.
2. Silica pretreatment, before the acid-activated clay treatment of the oil, is recommended for bleaching all types of vegetable oils.

3. In addition to chlorophyll measurement, it is prudent to check for chlorophyll breakdown compounds in soybean and canola oils. This can provide a better indication of the photoxidative stability of the oil.

Hydrolysis

When a molecule of water reacts with a molecule of triglyceride, the resulting products are diglyceride and fatty acid (commonly termed free fatty acid). As more water molecules react with the oil, more free fatty acids are formed, together with diglycerides and monoglycerides. Eventually, the reaction products are glycerol and fatty acids. This reaction can occur only when the oil and water are in perfect solution (27). Oil and water do not form a solution under normal processing conditions, because both temperature and pressure are insufficient to create a solution. However, the presence of a small amount of surfactant in the oil increases intersolubility between the two liquids and promotes hydrolysis of the oil during processing. This occurs because the surfactant reduces the interfacial tension between oil and water.

In commercial fat-splitting reactors, a small amount of caustic is used to produce soap through the reaction between the oil and caustic. The soap thus produced acts as a surfactant for the reaction. Crude oils contains natural surfactants, such as phospholipids. The other sources of surfactants include the following: (i) soap left in the oil from the caustic refining process or from neutralized (unbleached) oil; (ii) some products of oil oxidation have a surface-active property and can promote hydrolysis in the oil (28); (iii) mono- and diglycerides produced in the oil due to overrefining of the crude oil (29), or excess caustic treat needed for refining poor quality crude oil (12).

In the chemical refining process of seed oils, the recommendation for the final phosphorus content in the oil is <1 ppm. It has been experienced by the author that when the phosphorus content in the vegetable oil is ≥3 ppm, the free fatty acid in the finished oil begins to rise while the oil is in storage. This is experienced commonly in physically refined palm oil or palmolein because the oil has to be purchased in large quantities and stored for months at a time due to the distance between the source of the oil and the end-users. In many instances, the oil has to be redeodorized to reduce the increased free fatty acids produced during storage. Physically refined palm oil or palmolein contains 3–5 ppm phosphorus in the finished oil. This is believed to be one of the major drivers for the rise of free fatty acid in these oils during storage.

High phosphorus in the oil can cause some hidden losses in oil yield; it can poison the nickel catalyst in hydrogenation. This increases the consumption of catalyst. Additional diatomaceous earth is required to remove the extra nickel catalyst. Hydrogenated oil, produced with poisoned catalyst, tends to contain a high level of colloidal nickel. This is removed from the oil in the postbleaching process in which the hydrogenated oil is treated with acid-activated bleaching clay together with citric or phosphoric acid under vacuum. The postbleaching process always increases the free fatty acid content in hydrogenated oil, which increases oil loss in the deodorization process. A higher free fatty acid content in deodorizer feed reduces the rate of deodorization. This means reduced productivity due to slower deodorizer throughput.

Although the excess free fatty acids are removed in the deodorizer, there is always some additional loss of neutral oil in the distillate when the deodorizer feed contains a high concentration of free fatty acids.

If the phosphorus content is high in the deodorizer feed, the oil can undergo hydrolysis during deodorization. This can be verified by measuring the diglyceride content of the feed to the deodorizer and the deodorized oil. The additional diglycerides formed in the deodorized oil do not undergo distillation and can be analyzed. There is a tendency to deodorize physically refined palmolein at a temperature of 500–509°F (260–265°C). This is generally done to reduce deodorization time and increase throughput. However, at this higher temperature, the oil can undergo hydrolysis, creating a condition in which reduction of the free fatty acid to <0.05% becomes difficult. One must also recognize that surfactants, such as phospholipids, reduce interfacial tension between the oil and air. Therefore, given a poor vacuum and a high level of phosphorus, there is an opportunity for the oxygen to react with the oil in the deodorizer to form free radicals that lead to the formation of oxidative dimers and polymers.

Soap can be left in the refined oil as a result of inadequate bleaching. This can produce a reaction similar to that with phospholipids in the oil. Some cottonseed oil processors believe that Prime Bleach Summer Yellow (PBSY) cottonseed oil does not require bleaching because of the low color of the oil. This is not correct because PBSY cottonseed oil contains some residual soap that must be removed from the oil to prevent hydrolysis and oxidation of the oil in subsequent processing and handling. Neutralized oils also suffer from the same risk as the PBSY cottonseed oil because they contains soap.

Crude palm oil may contain soap. This normally results from improperly cleaned shipping vessels. Even a small amount of soap content must be eliminated from the oil before it is deodorized. Some unscrupulous palm oil processors have also delivered crude palm oil that has been partially neutralized in order to meet the 5% limit on the free fatty acid, set forth by the Palm Oil Research Institute of Malaysia (PORIM). This practice causes long-term instability in the oil.

Recommendation. It is recommended that the soap content in palm oil and all types of partially neutralized oil receipts be measured and that the oil be bleached to remove the soap before the oil is processed further. The oil can be treated with either silica or bleaching clay to accomplish this. Table 19.1 shows the recommended oil analytical parameters for crude, refined, water-washed, and bleached oils for best performance.

Thermal Decomposition

Vegetable oils undergo decomposition when they are subjected to high heat. When the oil is heated to 302°F (150°C) in air, even the saturated fatty acids break down to produce compounds, such as the homologous series of carboxylic acid, 2-alkanones, 2-alkanals, lactones, *n*-alkanes, and *n*-alkenes (30). When triglycerides containing even-numbered fatty acids, ranging from 6 to 16 carbon atoms, were heated

TABLE 19.1 Maximum Recommended Values for Oil Quality Parameters for Seed Oils

Analysis	Crude oil	Refined oil	Water washed oil	Bleached oil
% FFA	—	0.01–0.03	0.02–0.05	0.04–0.1
Soap, ppm	—	<500, never >1000	<50, never >100	0
PV, maximum	4[a]	4	4	0
p-Anisidine value	4	4	4	6
Phosphorus, ppm	—	3	3	<1
Calcium, ppm	—	—	—	<0.2
Magnesium, ppm	—	—	—	<0.2
Iron, ppm	—	—	—	<0.2

[a] At a peroxide value (PV) >8, seed oil may produce unacceptable flavor stability.

in air to 356–482°F (180–250°C) for 1 h, they all produced homologous hydrocarbons, aldehydes, ketones, and lactones (31–33).

Thermolytic nonoxidative products from saturated fatty acids can be detected even when the oil is heated to 356°F (180°C) under vacuum (30). Volatile compounds detected under these conditions include normal alkanes, fatty acid, oxypropyl ester, propene, propanediol esterdiglycerol, and acrolein.

In the case of unsaturated fatty acids, formations of dimeric and cyclic compounds appear to be the predominant thermolytic breakdown products (33). The degree of complexity of these compounds increases with the degree of unsaturation of the fatty acids present. Heat treatment also leads to the formation of several aromatic compounds (34–36). Thermal dimers and cyclicmonomers have been isolated from several types of heated vegetable oils (37,38).

It can be seen from the above discussions that exposure of oil to high heat can lead to both oxidative and thermolytic degradation of the oil. All types of vegetable oils degrade through the following processes: (i) the autoxidative process; (ii) the photooxidative process, which includes the photochemical reaction process and the photosensitized reaction process; (iii) the hydrolytic process; and (iv) the thermolytic process. All of these reaction processes can be greatly reduced by following certain operating guidelines at each and every step of the process as mentioned earlier.

Conclusions

High stability in processed vegetable oils is of paramount importance. Today, the oil is used not simply for cooking in homes and restaurants. It is used to manufacture shelf-stable prepared foods, including fried snacks. These applications require oils that are low in trace impurities and free radicals. As the underdeveloped nations become more affluent, the consumers in those countries will demand higher-quality prepared foods, including snack products. The oils used in these applications must have high stability.

The oil processors must become aware of the conditions that are essential to improve stability of the vegetable oils using proper processing guidelines. Referring to

TABLE 19.2 Recommended Analyses for Deodorized Vegetable Oils[a]

Analysis	Target	Maximum	Remarks
% FFA	<0.03	0.05 max	Higher FFA may indicate lower shelf life stability
PV	0	0.5 max	As loaded in trucks
		1.0 max	As received by customer
AV	2	4	Never to exceed 6
% Dimers	<0.2	0.4 max	Never to exceed 0.5%
% Polymers	<1	2 max	Higher polymers may impart bitter flavor in prepared foods
Chlorophyll, ppb	—	30 max	Increases photosensitivity in the oil
Phosphorus, ppm	<0.5	1.0 max	Baking shortening and margarine can tolerate higher phosphorus level
Calcium, ppm	—	0.2 max	A value >0.5 ppm implies poor quality oil
Iron, ppm	—	0.2 max.	A value >0.5 ppm implies poor quality oil
Magnesium, ppm	—	0.2 max.	A value >0.5 ppm implies poor quality oil
Lovibond Red color	<1.0, for Soybean oil Canola oil Sunflower oil	1.5 max. for Soybean oil Canola oil Sunflower oil	>1.5 Lovibond Red color implies poor quality crude or poor oil processing
% Triglycerides	98 minimum	—	A lower value implies poor quality crude in case of seed oils
% Monoglyceride[b]	—	0.3	A lower value implies poor quality crude or over refining in case of seed oils
% Diglyceride[c]	—	0.6	A lower value implies poor quality crude or over refining in case of seed oils

[a] Abbreviations: FFA, free fatty acids; PV, peroxide value; AV, anisidine value.
[b] Typical values in commercial palm oil and palmolein: 0.5–1 % monoglycerides.
[c] Typical values in commercial palm oil and palmolein: 3–11 % diglycerides.

the discussions presented in this article, an oil processor should be able to identify the areas of opportunity in the operation. It is interesting to note that through proper scrutiny and analysis of the operation, one might discover opportunities that are simply procedural. This will require proper training of the personnel to develop a sound understanding of the finer points in vegetable oil processing.

Recommendations. The recommended analytical parameters for deodorized seed oils are listed in Table 19.2. The general information provided in this table is applicable to all types of seed oils and palm oil (palmolein). It must be noted that Lovibond Red color is different for different oils, and mono- and diglyceride contents in palm oil and palmolein are always higher than in the seed oils.

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Chapter 20

Managing Oil Quality

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Introduction

The edible oil processing industry has entered an era of rapidly changing technology. Understanding of the physical and chemical properties of oils and the methods for their refining treatment has advanced significantly in recent years. Now, more than ever before, there is a need for highly skilled plant technicians and laboratory personnel to monitor the processes to deliver high-quality edible oils at a low cost. This requires all-round training for operators and quality control personnel.

Unfortunately, quality control is viewed as an unnecessary overhead by many top-level managers, rather than as a contributor to the corporation's profit. As a result, these corporations have trimmed the quality control departments and have implemented rather ineffective procedures to manage quality.

On the other hand, several companies in the United States have gone to the extent of training their operators to use sophisticated analytical instruments, such as ICP (Inductive Coupled Argon Plasma Emission Spectrophotometer) for controlling the refined oil quality. These companies also maintain quality control laboratories with the latest analytical instruments and trained analysts to support the production department.

In reality, the principles behind oil quality management are no different than those used in managing any function or activity in an organization. Managing quality control requires the following:

1. A list of well-defined objectives.
2. Identification of the focal points.
3. Setting priorities.
4. Defining strategy or action steps.
5. Establishing procedures and facilitating implementation.
6. An organization to carry out the task.
7. Defining the channel for communications within the company.
8. Establishing the criteria for measuring progress and the procedure for the appraisal.
9. A follow-up procedure to measure progress.

Define Objectives

For successful quality control, there must be well-defined objectives or targets. These must be clear, measurable, and realistic; they must produce positive results for the bottom line of the corporation's annual profit. These targets must be for specific quality standards for the finished products, packaging materials, or customer service. A few examples of such targets are the following: (i) 100% compliance with the finished product standards; (ii) 100% compliance with the process operating standards; (iii) zero defects on all shipments of products; (iv) zero customer refusal for noncompliance of quality; and (v) reprocessing of products must be <2% of the total production.

Identify Focal Points

Once the objectives are clearly defined, it is time to identify the areas that require attention and set priorities for establishing the strategy or the action steps required for meeting the desired objectives. Before launching any activity, it is necessary to identify the areas of operation that require the most attention and also determine whether these issues are related to the following factors: (i) noncompliance to process standards; (ii) defective raw materials; (iii) defects in the processing material; (iv) defective packaging materials; (v) inadequately defined product standards; (vi) inadequately defined process standards; (vii) faulty equipment; and (viii) lack of personnel training.

Setting Priorities

After identifying the areas that require attention, one must evaluate carefully the overall situation and identify the areas that require immediate attention. A list is prepared outlining the issues. The underlying causes must be identified, using the above list as a guideline. Issues requiring a minimum amount of effort for the correction must be addressed immediately. The remaining issues must be evaluated on the basis of their effect on the business. It is generally recommended that the issues that most affect the business be addressed first. Priority for solving the quality issues can be set by using Pareto's Law of Mal Distribution. According to Pareto, most of the economic and quality effects in a company are caused by a very small number of issues. Therefore, one can effectively determine the cause, identify the source, determine its effect on the business, and then set the priorities.

Strategy or Action Steps

Once the priorities have been established, it becomes important to define a strategy to address each of the identified areas for improvement. This requires the following steps: (i) a thorough evaluation of the specific areas to work on; (ii) identification of the specific issues and factors responsible for the underlying causes behind these issues; (iii) definition of the corrective steps needed to achieve the desired goal; (iv) identification of available internal resources required to address the issues and develop solutions; (v) determining whether external resources are required to complete the job; and (vi) development of a time line to complete the job.

Procedure for Implementation, an Organization to Carry Out the Tasks, and Establishing the Lines of Communication

All of these tasks are interrelated. To take these tasks any further, there must be a quality control organization that has the right organizational structure, available personnel with the required training or qualifications to perform the duties, and well-defined lines of communication within the various segments of the company. Unfortunately, most companies use the quality control department for policing purposes. This causes animosity between this department and the production departments. Sometimes, the hard feelings are extended to the warehousing and shipping department. This is counterproductive.

On the other hand, the quality control department can become a valuable entity in the company if it offers assistance to the rest of the plant operation in the following areas:

- Provide the necessary knowledge to the plant personnel on product quality, significance of all quality standards, and the relationship between the process conditions and the product quality.
- Provide assistance to the operating departments to solve their quality issues, instead of merely pointing out their shortcomings. This requires a change in the traditional concept of a quality control department.

Therefore, a successful quality control department requires the following: (i) well-qualified personnel; (ii) a thorough understanding of the products and the process; (iii) a proactive, not a policing organization; (iv) capability of looking beyond the day-to-day issues to the future needs for the company in the areas of product quality and process control; (v) provision of the necessary technical training for the operating personnel so that they can deliver the right product; (vi) a view of quality control as a corporate responsibility; (vii) established quality assurance function at every plant and the corporate office; (viii) define accountability for the individual members of the quality control organization; (ix) separate the quality control function from production; (x) have a well-established and on-going training program in place to train all plant personnel so that they understand fully the product standards, process control, and the consequence of deviation from the standards, in terms of product performance and cost; (xi) also provide adequate training to the plant personnel for trouble-shooting the process issues or product defects.

Quality Control: A Corporate Responsibility

Quality control must be viewed as a corporate responsibility. It is essential that a corporation appoint a high-ranking officer to be in charge of quality control. This will demonstrate the commitment of high management to quality. A central quality control department, in the corporate office, must have staff responsible for investigating and implementing the most appropriate quality control methods for the company. This includes areas, such as all of manufacturing, including warehousing, product shipping, regulatory compliance, and customer complaints. Quality control managers at every plant must have direct-line accountability to the plant manager and a dotted-line responsibility to an individual at the central quality control department, assigned to work with the plant quality control managers. In a smaller corporation or at a single plant operation, the quality control personnel at the plants must fulfill the role of the central staff in a large corporation. The quality control manager must report to the plant manager with a direct reporting responsibility to the production manager. In a manufacturing plant, the production manager can easily influence the decision of the quality control manager. Sometimes, this can result into making wrong decisions. Therefore, it is desirable to have the quality control manager report directly to the plant manager.

Figure 20.1 shows a model for a daily communication network between the operating and plant quality control personnel. The quality control analyst has an important function with the following responsibilities: (i) to analyze all process control samples; (ii) to compare the results against the standards; (iii) to report back the results to the operator; (iv) to make a note on the report if the quality standards are not met; (v) to analyze finished products before they are packaged; (vi) to report all results to the operator; and (vii) to report unsatisfactory product analyses to the quality control manager.

It is essential that the process operator and the quality control laboratory analyst communicate with each other regarding the results of analysis on every sample submitted to the laboratory. It must be remembered that off-quality oil is not to be transferred over to the next processing step at any time. This can result into serious quality issues in the subsequent processing steps and finished products.

The process operator also has an important function. Using the guidelines provided by the quality control manager, the operator performs the following tasks under the direct management of the production foreman: (i) resamples oil at any time the analysis is out of limit; (ii) if the repeat analysis confirms the previous result, the oil is held in the department and not transferred to the next processing step; and (iii) requests disposition from the process foreman for the off-quality material, unless a clear guideline is available.

The process foreman advises the operator on specific procedures for the disposition of any off-quality stock. He also informs the process manager and the production manager of the deviations and seeks advice for disposition, if it is not clearly defined. The quality control manager informs the production manager of any off-quality finished product. If the existing guidelines for the disposition do not apply, the two managers discuss and agree on a method for the disposition of the off-quality product.

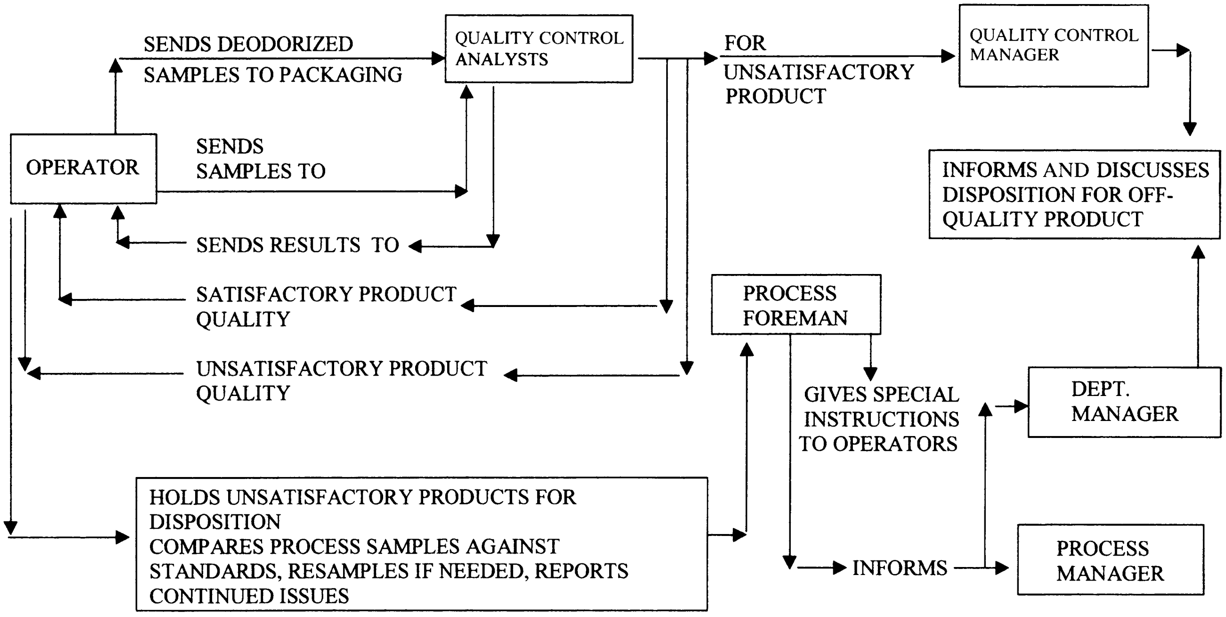

Fig. 20.1. Daily information network.

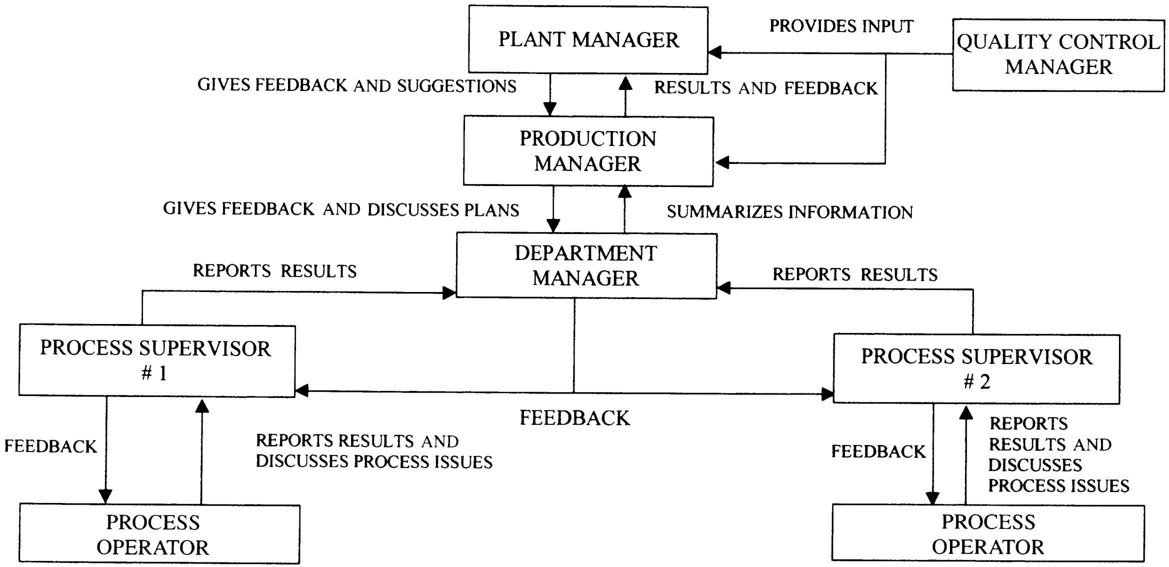

Fig. 20.2. Quality control feedback network.

Figure 20.2 shows an example of a quality control feedback network. The responsibilities of the general manager or officer in charge of the overall function of quality control in the company include the following:

1. To establish corporate guidelines for quality control procedures and standards.
2. To assign specific individuals to the development and implementation of appropriate quality control techniques at the manufacturing plants as well as at the central corporate laboratory.
3. To assist the central corporate laboratory personnel in their search for more reliable analytical methods or instruments. The instruments must be rugged, user friendly, and must be suitable for the plant quality control environment.
4. To keep abreast of the latest regulatory rules and disseminate the information immediately throughout the organization along with procedures for compliance.
5. To establish a quality review procedure that allows the monitoring of day-to-day quality performance and long-term goals.
6. To review quality progress reports with the plant managers, provide necessary input, and critique progress.
7. To express appreciation for good performance.
8. To provide the necessary guidance to improve performance for the future.

The plant manager should be accountable for the quality performance of his plant. It is always a good idea to make "quality" an integral part of all intermediate and senior managers' performance and compensation, including those for the plant managers.

Periodic Review of Quality Performance

The plant manager must set quality objectives for his plant and devise a plan with his managers for periodic review of the following areas: (i) the corporate, individual plant, and each manager's objectives; (ii) the completed and unfinished items on the list; (iii) action steps required for follow-up; (iv) revised time schedules for completion of the unfinished items; (v) the periodic performance of the plant (with the general manager or senior officer) to receive feedback; (vi) the general manager's feedback with his staff; (vii) any new goals or strategies that might have been generated from discussion with the general manager.

Personnel Training

Successful quality control also requires an on-going program of personnel training. Plant personnel, whether working in the production department or in the quality control department, must be familiar with the product quality standards in order to produce and deliver high-quality products. This requires a comprehensive training program.

There has been a great deal of interest in ISO 9000. Many oil processors, primarily outside of the United States, have received ISO 9000 certification. This is a very good program that teaches the management and workers how to track data and make decisions on corrective action for maintaining good product quality. However, oil processing is an area that is not governed by the standards, such as ASME (American Society of Mechanical Engineers) or ASTM (American Society for Testing Materials). The quality of the oil must be monitored and controlled from crude to finished product. Sometimes, the quality standards depend on the oil type. There are no universal standards for oil quality that could be compared with the ASME or ASTM standard. The NIOP (National Institute of Oilseed Products), NOPA (National Oil Producers Association), and Palm Oil Research Institute of Malaysia (PORIM), all specify certain oil quality standards. Although these are satisfactory for trading purposes, most oil refiners use their own standards, based on the performance of their products and customer's needs.

Therefore, it is necessary to train all operating and quality control personnel to be familiar with the following: (i) the internal oil quality standards set by the company's quality control department; (ii) established process control parameters; (iii) critical sampling points for good process and quality control; (iv) sampling frequency; and (v) troubleshooting guidelines.

As one can see, it would be rather difficult to apply the ISO 9000 program without knowing the fundamentals of oil processing and the quality targets. This is because ISO 9000 can teach the procedure to measure and monitor product quality. However, this program cannot identify the desired targets without the knowledge of oil processing. Therefore, in the current discussion, the author will concentrate on the basic requirements for good oil quality management. One could take the recommended guidelines, presented in this paper, to determine how to apply ISO 9000. It is the opinion of the author that if correct quality targets are chosen and proper process control techniques are used, the ISO 9000 program adds no additional value to the overall oil quality control program or the quality of the oil produced by an oil refiner.

Oil Processing

A schematic diagram for oil processing is shown in Figure 20.3. Crude oil is received, unloaded, and stored in the crude oil storage tank. Crude oil is degummed and then refined. Water degumming of crude soybean oil is conducted to recover the hydrated phospholipids to produce lecithin. Acid degumming is done to reduce further the nonhydratable phospholipids in the crude oil. Phospholipids recovered from the acid degumming process cannot be used for producing lecithin.

In most oil refineries, the crude oil undergoes acid pretreatment instead of acid degumming before refining. In this process, the crude oil is treated with phosphoric acid to hydrate the nonhydratable phospholipids so that they can be removed from the crude oil more effectively during refining. Unlike acid degumming, in an acid pretreatment process, the gums are not separated from the oil by centrifuging.

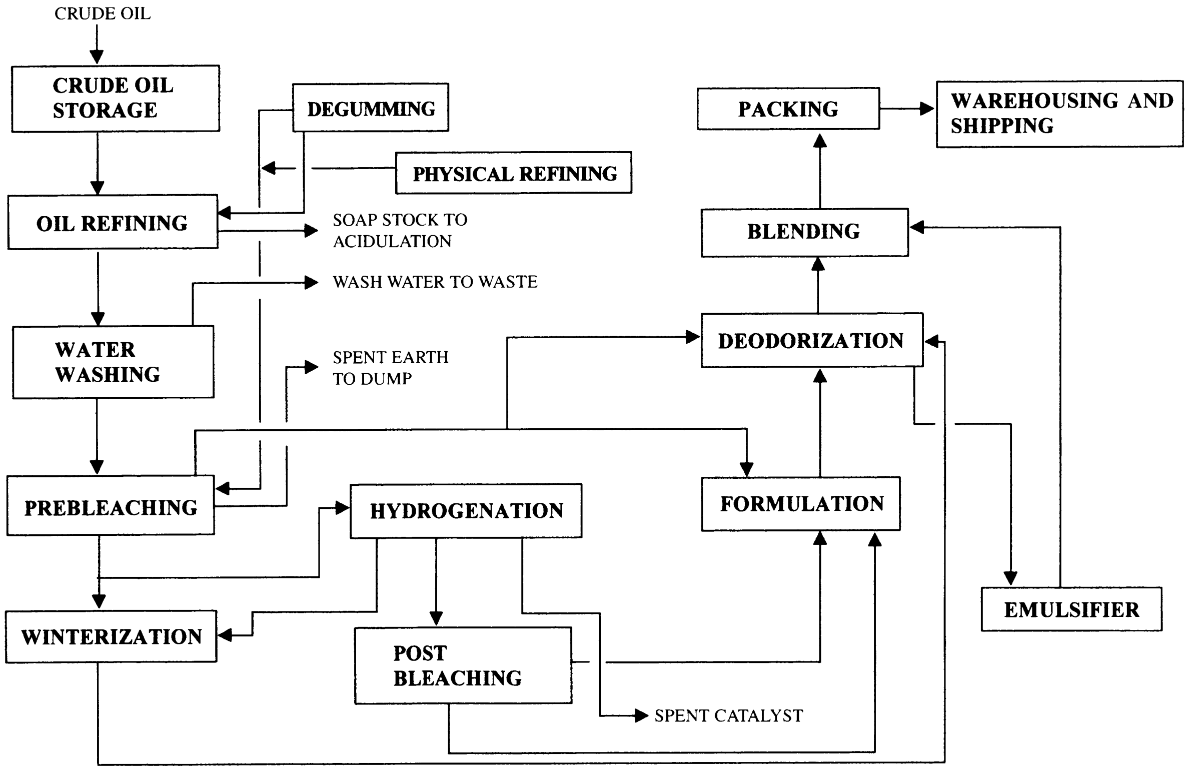

Fig. 20.3. Sequence of oil flow in chemical refining process.

In chemical refining, the crude oil is treated with sodium hydroxide (caustic) to react with the free fatty acids. Along with the free fatty acids, the caustic reacts with the nonhydratable phospholipids and other impurities. The caustic and crude oil mixture is heated and then centrifuged to separate the soap from the oil. The soap is then either acidulated to make fatty acid, commonly known as acid oil, or it is used in animal feed. In many Third World countries, the soap stock is used for manufacturing laundry soaps. A schematic diagram for oil refining is shown in Figure 20.4A.

The refined oil is mixed with soft water and centrifuged to remove more soap from the oil. Typically, the amount of wash water is 10–15% of the refined oil flow. A schematic diagram for water washing is shown in Figure 20.4B. Water washed oil is prebleached to reduce the trace impurities in the oil, such as phospholipids, iron, calcium, magnesium and other trace metals, and the residual soap. This process also reduces chlorophyll, carotene, and other color bodies. Prebleaching is preferably carried out under vacuum, using acid-activated clay, with or without hydrated silica. A typical schematic for the process is shown in Figure 20.4C.

After prebleaching, the oil is sent to winterization, hydrogenation, or to deodorization, depending on the type of oil or product. Typically, sunflower, corn, or

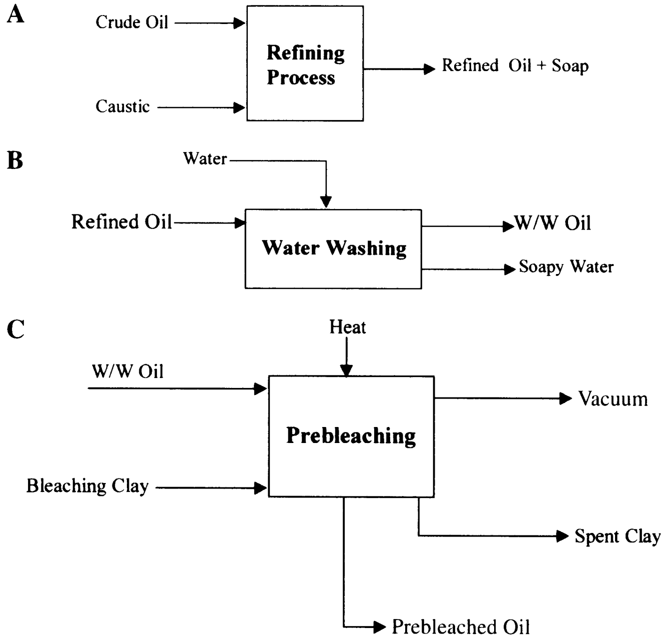

Fig. 20.4. (A) Schematic for chemical refining. Conditions: Free fatty acids (FFA), 0.01–0.02%. (B) Schematic for water washing. Conditions: FFA, 0.02–0.05%. (C) Schematic for prebleaching. Conditions: Absolute pressure of 50 mm of Hg. column, maximum; soap = 0 ppm; P < 1 ppm; Fe < 0.3 ppm; Ca < 0.2 ppm; Mg < 0.2 ppm; chlorophyll for soybean or canola oil < 20 ppb.

canola oil is winterized for dewaxing. Cottonseed oil is winterized to remove the stearine, only if the oil is to be used as salad oil. Sometimes, partially hydrogenated soybean oil is winterized to produce an olein fraction, used as high-stability salad oil. This process has become somewhat obsolete in the United States. If the prebleached oil is not processed to the quality as mentioned above, the winterization process produces poor separation of the solids from the oil, causes premature blinding of the filter screens, and slows down the filtration process.

Physical refining is another method for oil refining that is used primarily for palm oil, lauric oils, and to some degree with sunflower oil. The phospholipid content in the crude oil is reduced by either acid degumming or special degumming to a low level. The oil is then prebleached with a higher dosage of bleaching clay to remove the trace metals, color bodies, and the remaining phospholipids. The oil is then processed through the remaining steps. The nature of the deodorizer is different from that used for chemically refined oils because the oil in the physical refining process contains all of the free fatty acids originally present in the crude oil. This process reduces the plant effluent, thus causing less pollution of the environment compared with the chemical refining process. There are pros and cons for both the physical and chemical refining processes; these will not be discussed in this chapter.

Hydrogenation is a process in which the refined and prebleached oil is reacted with pure hydrogen gas in the presence of a nickel catalyst. The purpose is to reduce the unsaturated fatty acids in the oil. This improves oxidative stability of the oil, increases the solid content, melt point, and the amount of *trans* fatty acids in the oil. As in prebleaching, the quality of the incoming oil is critical for this step. The prebleached oil must meet the quality standards as listed above. If the impurities are not removed adequately, the nickel catalyst is poisoned. This reduces productivity, increases catalyst usage, and increases the amount of colloidal nickel in the hydrogenated oil. The colloidal nickel in the hydrogenated oil is removed *via* postbleaching, in which the oil is treated with acid-activated clay, citric or phosphoric acid under vacuum and elevated temperature, and then filtered. During postbleaching, the free fatty acid content of the oil can slow down the deodorizer, requiring a longer residence time for proper removal of the free fatty acids from the oil. Therefore, it is of utmost importance that the oil meet the quality standard at each and every step of oil processing before it is sent to the next processing step in order to avoid quality and productivity issues. A schematic diagram for the batch hydrogenation process is shown in Figure 20.5.

Product formulation is based on the finished product standards. Every product application is different and requires shortening or oil of different solids content, melt point, or color. The specifications for commonly used shortenings, such as heavy-duty frying shortening or all-purpose shortening, are more or less standardized. However, most shortening used by food processors for baking, prepared frozen meals, or prepared cake mixes can vary widely.

In the deodorizer, the oil is steam-distilled under very low pressure and at a high temperature to distill the fatty acids, the odor-bearing compounds and reduce the red

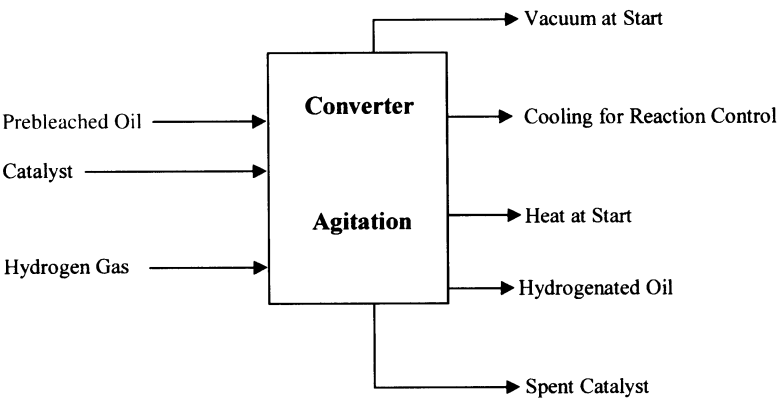

Fig. 20.5. Schematic for hydrogenation.

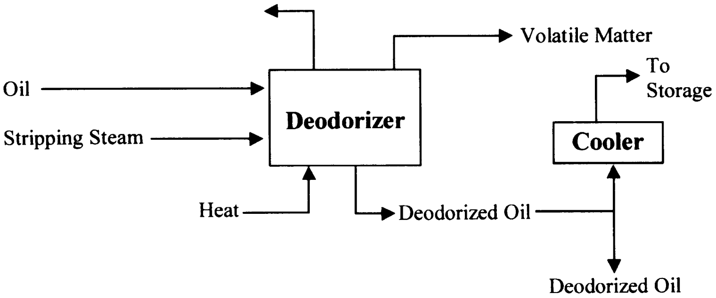

Fig. 20.6. Schematic for the deodorizer. Conditions: < 3 mm HG absolute pressure; P = 1.0 ppm, maximum; Fe < 0.3 ppm; Ca < 0.2 ppm; Mg < 0.2 ppm. Conditions for deodorized oil quality: Free fatty acids < 0.04%; flavor, bland; Lovibond Red color, meet standard; filter grade, 8 minimum.

color. This is the final step in the oil refining process. The oil is cooled and stored under nitrogen. The finished oil is packaged in bottles, cans, cubes, 5-gal pails, 55-gal drums, trucks, or rail cars. The schematic diagram for the deodorizer is shown in Figure 20.6.

Critical Control Locations for Oil Quality Management

On the basis of these discussions, it can be seen that managing oil quality begins from the time the crude oil is produced, continues throughout the process, and extends through distribution and usage. The critical areas for oil quality management are as follows: Incoming crude oil, unloading procedure, crude oil storage, degumming, refining, prebleaching. hydrogenation, postbleaching, winterization, formulation, deodorization, deodorized oil storage, warehousing/distribution, and responding to customer complaints. The guidelines for oil quality management are discussed in detail below.

Incoming Crude Oil

1. Check the cleanliness certificate for the truck, previous load carried, when cleaned, and by whom.
2. Inspect car or truck seals (and numbers) to make sure they are not broken. Do not accept oil if the seals are broken.
3. The number on the seal must match that on the shipping documents. If not, do not unload and notify purchasing to contact the supplier for a resolution.
4. Inspect the vessel for cleanliness. Do not unload oil if the vessel exterior is dirty.
5. Open the hatch and inspect the top interior of the vessel for cleanliness. Follow the previous guidelines.
6. Collect a sample of the oil and check it for color, odor, appearance, and presence of any foreign matter. Identify the type of oil in the vessel and verify against the documents. Check flash point and refractive index (RI). A hand-held refractometer is generally satisfactory for identifying most crude oils.
7. Do not unload the oil if the quality checks are not satisfactory.

Unloading Oil

1. Collect a sample from the vessel for analysis using AOCS procedure.
2. If the vessel must be heated, use low-pressure steam with thermodynamic steam traps at the discharge of the heating coils to avoid scorching of the oil.
3. Preshipment samples and oil analyses from the supplier must be available when the shipping vessel arrives.
4. Oil must be analyzed for free fatty acids (FFA), color, moisture, sediments, and refining loss.
5. It is recommended that the shipper use vessels that are dedicated for shipping only food products.
6. Do not use steam to clear the unloading line. This practice can hydrate the gums and increase the refining loss.

Crude Oil Storage

1. Crude oil storage tanks must have a mechanical agitator, with a low-level cut-off switch. Nonagitated tanks allow the gums, meals, and moisture to settle to the tank bottom, increasing the refining loss.
2. Maintain crude oil tanks at ambient temperature.
3. In cold weather, the oil must be heated with care to avoid overheating.
4. Check tank temperature daily.
5. Refine on first in/first out basis.
6. Never leave the hatch open at the top of the tank.
7. The agitator must be left on at all times.
8. The tanks must be emptied and cleaned once every 6 mo, and at least every 12 mo.
9. The sludge from the tank bottom must not be added back to crude oil for refining.

Oil Refining

1. Check the crude oil for FFA and laboratory refining loss, before start.
2. Conduct laboratory bleach color test on the laboratory refined oil. Calculate the amount of caustic needed for neutralizing the FFA and add some excess. This is for hydrating the nonhydratable phospholipids in the crude oil. Use the following formula to determine the amount of caustic required:

$$\text{Amount of caustic needed} = \frac{(0.142 \times \% \text{ FFA}) + \text{excess}}{\% \text{ NaOH in solution}/100}$$

An example for calculating caustic dosage is given below. The assumptions are as follows:

Crude oil flow rate = 50,000 lb/h; % FFA in crude oil = 1.0; % excess caustic = 0.15; and caustic strength = 10°Be (6.6%, NaOH)

The calculations are as follows:

Caustic needed to neutralize the FFA = 0.142 × 1.0 = 0.142%
Excess caustic = 0.15%
Total caustic needed at 10°Be (6.6% NaOH) = 0.292%
= 0.292/0.066
= 4.42 lb of solution/100 lb of oil
Crude oil flow rate = 50,000 lb/h
Total caustic solution needed = 4.42 × 50,000/100
= 2210 lb/h

3. Using the table on caustic solution (°Be vs.% NaOH), determine the amount of caustic needed before start.
4. Check % FFA and ppm phosphorus in the refined oil (except sunflower or safflower oil).
5. Readjust the caustic flow as needed to obtain complete refining.
6. Sample the oil at the exit of the primary separator and the water wash separator as shown in Table 20.1.

Checking oil quality at a certain frequency and analyzing the samples for the critical analyses are important for achieving good oil quality. This is true for every step of oil processing. Table 20.2 shows the recommended analyses for the oil in the refining step. These quality standards are critical. Oil processing in the subsequent processing steps can have serious quality issues resulting from the impurities in the refined oil; this increases the cost of oil processing.

Refined and water-washed oil is prebleached. In this process, the oil is treated with acid-activated clay, sometimes together with hydrated silica. The bleaching

TABLE 20.1 Oil Sampling During Refining[a]

Sample location	Frequency of analysis	Free fatty acids (%)	Lovibond Red	Soap (ppm)	Moisture (%)	Laboratory bleach color (Lovibond Red)	Phosphorus (ppm)
Crude oil	Once/Shift	X	—	—	X	—	X
Exit, primary separator							
At start	Once/15 min		—	X	—	—	X
At steady state	Once/2 h	X	—	X	—	—	X
Exit W/W separator							
At start	Once/15 min	X	—	X	—	—	X
At steady state	Once/2 h	X	—	X	—	—	X
Exit vacuum dryer	Once/4 h	—		X	X	X	X

[a] Abbreviation: W/W, water washed.

clay is removed from the oil *via* filtration. The filter can be of the plate and frame or the pressure-leaf type. In any case, it is very important that the oil quality is checked to ensure that it meets all of the quality standards before it is released either to a bleached oil storage tank or to hydrogenation, winterization, or deodorization. The oil at the exit of the filter must be checked at a predetermined frequency to ensure that the desired oil quality is met. Table 20.3 shows the sampling frequency and Table 20.4 shows the oil quality standards recommended for prebleaching.

With proper quality control in prebleaching, the oil is made suitable for hydrogenation and winterization. In hydrogenation, high moisture and or trace impurity content causes catalyst poisoning, resulting in poor oil quality, increased catalyst usage, and reduced productivity. In hydrogenation, the quality of hydrogen gas is also important for obtaining proper reaction, oil quality, and productivity. Hydrogen gas must be dry and free of any carbon monoxide, sulfur compounds, and moisture. High moisture and phosphorus in the oil reduce the filtration rate in the winterization process. Phosphorus can also interfere with the crystallization process, causing

TABLE 20.2 Recommended Oil Quality Standards at Refining[a]

Sample location	FFA (%)	Soap (ppm)	Phosphorus (ppm)
Exit primary separator	0.01–0.03	<500	<3
Exit W/W separator	0.02–0.05	50 maximum	<3

[a] Abbreviations: FFA, free fatty acids; W/W, water washed.

TABLE 20.3 Steady-State Sampling at Filter Exit in Prebleaching[a]

Analysis	Soybean oil	Cottonseed oil	Palm oil
Soap (ppm)	X	X	X
Lovibond Red color	X	X	X
Absorbance at 450 nm	—	—	X
Filter grade	X	X	X
Chlorophyll (ppb)	X	X	X
Trace metals (ppm)	X	X	X
Phosphorus (ppm)	X	X	X

[a] This sampling should take place every 4 h, minimum; however, at start up, it should occur every 15 min until the standards are met. Sampling frequency should be increased if quality deviation occurs.

poor separation of the solid and the liquid fractions and produce an unacceptable oil quality. Table 20.5 shows the recommended traits for hydrogenated oil.

Products are formulated according to the specifications set by the quality control department. There must be formal written documents with clearly defined oil and product specifications. The recommended guidelines for product formulation are as follows:

- Specifies type of oil to be used.
- Defines the degree of hydrogenation required for each type of oil, by providing either iodine value or solid fat index.
- Target amounts with approximate tolerance limits for each type of oil to be blended.
- Solid fat index targets and ranges for the blends are specified for each product formulation.

TABLE 20.4 Recommended Oil Quality Standards in Prebleaching[a]

Analysis	Recommended standard
FFA, %	<0.1[b]
Soap, ppm	0
Moisture, %	<0.05 %[c]
Filter grade	7, minimum
Color limit	Must meet standards
Chlorophyll	Must meet standards
Trace metals, ppm	<0.5
Phosphorus, ppm	<1

>[a] Abbreviation: FFA, free fatty acids.

[b] Poor quality crude oil requires overrefining, i.e., extra caustic treatment, which generates more soap in the refined oil that cannot be separated easily by the primary separator. This also leaves high soap levels in the water washed oil. Free fatty acid is increased in the prebleached oil due to hydrolysis of the excess soap in the water washed oil.

[c] Must not exceed 0.1%.

TABLE 20.5 Recommended Oil Quality Standards for Hydrogenated Oil

Quality trait	Recommended standard
Iodine value	Must meet standard
Melt point	Must meet standard
Solid fat index	Must meet standard
Filter grade	7, minimum
Colloidal nickel	<0.1 ppm

The product must not be released to the deodorizer unless it meets all specified standards according to the individual product specifications.

Once the product is ready, it is deodorized. This is the final step in oil processing. After deodorization, the product is stored in tanks, packaged for warehousing and distribution, or loaded into trucks or rail cars for customers. In the deodorization process, the oil is subjected to steam distillation under a very low absolute pressure and high temperature. Steam is bubbled through the oil. Under these conditions, the free fatty acids and other volatile compounds that are generally odiferous are removed from the oil. The oil becomes odorless and lighter in color. Deodorized oil must be cooled rapidly, either internally or externally, before storage. Citric acid is added to the oil to chelate any metal ions to improve its autoxidative stability. The oil should be stored under nitrogen to protect it from oxidation. Table 20.6 shows the recommended standards for deodorized oil. The table also includes the recommended procedures for oil storage and daily monitoring.

Deodorized product should be checked for quality standard before it is sent to packaging or loaded into trucks or rail cars. No product should be released for packaging or truck loading unless all finished product standards are met. Procedure for the disposition of any off-quality product must be clearly specified by the quality control department.

Warehousing is required to store packaged products before shipment. Quality control measures are required in several areas in the warehouse to provide proper product protection and to maintain product quality. The warehouse personnel must be provided with clear guidelines regarding product storage temperature, humidity, length of product storage period, disposition of old and damaged products, procedure for handling trade-returns, and truck inspection before loading. There must be a comprehensive sanitation program that includes a pest control program, which also includes fumigation, cleaning procedure and frequency, warehouse inspection procedure, and the accountabilities of the warehouse and the quality control managers.

Plant quality control and process personnel must be familiar with the most common process and quality issues. They must also know the procedures for correcting the problems. Table 20.7 lists the most commonly experienced plant issues.

TABLE 20.6 Recommended Standards for Deodorized Oil[a]

Analysis	Recommended standard
Free fatty acids (FFA), %	0.03%, not >0.05%
Flavor	Bland
Lovibond Red color	Must meet standards
Filter grade	8 minimum
Smoke point	238°C minimum (without added emulsifier)
Trace impurities (ppm)	
P	< 0.5, not >1
Fe	< 0.3, not >0.5
Ni	< 0.1, not >0.3
Ca	< 0.2, not >0.5
Mg	< 0.2, not >0.5
Melt point	Must meet standard
AOM	Must meet standards
OSI	
Rancimat	
Storage conditions	
Temperature	5°C above melt point, maximum
Headspace (nitrogen blanket)	Oxygen in headspace 0.5%, maximum
Agitation	Required for all hydrogenated products
Daily monitoring	Peroxide value Flavor FFA Lovibond red color Headspace oxygen level Temperature Filter grade before packing or shipment

[a] Abbreviations: AOM, active oxygen method; OSI, oil stability instrument.

This information has been compiled after many years of personal experience in oil processing.

Thus, one can see that oil processing is a complex operation. It has many variables and control points that are critical for the delivery of good quality oil. This cannot be achieved without good process training and a good quality control system in place. Plant personnel have to understand each and every step of oil processing, the significance of every process standard, raw material quality, process material quality, and the finished product standards. The common thread throughout the process is "understand your operation, quality control, and do not move the product to the next operation unless it fully meets the specified oil quality standards." Plant personnel can troubleshoot quality issues only when they are adequately trained and there is strong, and proactive support from the quality control department.

In conclusion, managing oil quality starts with a set of well-defined quality objectives. A top-level corporate executive must be assigned the accountability for the company's quality control function. The quality control department requires

TABLE 20.7 Typical Quality Issues

Process issue	Effect on the process or oil quality
Incompletely refined oil	High in phosphorus Possibly high in soap High in trace metals This can result in poor prebleaching, catalyst poisoning, high colloidal nickel in hydrogenated oil, or high laboratory bleach color
Incomplete prebleaching	High soap High phosphorus High trace metals Can poison the catalyst, produce high colloidal nickel, darker color, and poor oil stability High colloidal nickel requires postbleaching, raising free fatty acids, which reduces deodorizer rate and increases oil loss
Incomplete filtration in prebleaching	Presence of bleaching clay causes oil oxidation and darkens the oil Increased oxidation poisons the catalyst
Poor quality hydrogen	Poisons the catalyst Increases colloidal nickel Requires postbleaching Increases free fatty acids and deodorization time Reduces oil stability
Incomplete filtration in hydrogenation	Presence of particulate nickel produces dark-colored deodorized oil Reduces autoxidative stability of the product in storage and application Can cause color reversion for the product in storage

well-qualified and trained personnel who can be proactive and prime movers for quality control and the training functions for the operating personnel. The quality control department must complement the plant operating departments.

Finally, the most important message in oil quality management is as follows: Do not send the product to the next processing department if all of the product standards are not satisfactory.

Chapter 21

Utilization of Fats and Oils

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Introduction

Before the beginning of the 19th century, the use of fats and oils was based on practical knowledge that had been accumulated slowly over many centuries. Today, fats and oils products are developed, and the subsequent production is controlled with a knowledge of their composition, structural and functional properties, and the expected reactions obtained through the application of appropriate physical, chemical, and performance technologies. Utilization of fats and oils for the production of useful products depends on a thorough knowledge of the characteristics of the raw materials, the changes effected by each process, and the requirements of the individual prepared food products. Physical, chemical, and performance analysis are tools available to the fats and oils processors for the purchase of raw materials, development of new products, and evaluation of the products produced.

Fats and oils are key functional ingredients for a variety of food products. They have particular physical properties of importance in the processing and final use of natural and formulated foods. Most of the world's favorite foods could not be prepared without fats and oils. This would include pan- and deep-fried foods, baked products, spoonable and pourable salad dressings, nondairy products, whipped toppings, confectionery products, pastries, peanut butter, table spreads, sauces, and gravies. All of these products possess desirable properties attributable to the fats and oils ingredients in their formulation. Fats and oils affect the structure, stability, flavor, storage quality, eating characteristics, and appearance of foods. To accomplish the desired performance, developers must recognize that most applications require a fat or oil product with different physical and organoleptic properties.

The development of a fat and oil product for a food application depends upon many interwoven factors. These factors may differ from customer to customer, depending on the equipment used, processing limitations, product preference, customer base, and many other facets. Tailored fats and oils products are now being designed to satisfy these individual specific requirements, and other products are designed with a broad general appeal. The design criteria for a general purpose product must be of a broader nature than those for a specific product and process. The important attributes of a formulated fat or oil in a food product vary considerably. In some food items, the flavor contribution of the fats and oils ingredient is of minor importance; however, it does contribute a beneficial effect to the eating quality of the finished product. In many products, such as cakes, pie crusts, icings, cookies, and certain pastries, processed fats and oils are major contributors to the characteristic structure and eating character, while providing other significant effects on the quality of the finished product. (1)

Functional Properties of Fats and Oils

Fats and oils are very versatile raw materials; processing methods have been developed to make them even more useful to the food industry, whereas analytical chemists have devised methods to qualify the product produced. Satisfactory fats and oils product performance depends on several important elements that determine suitability. Fats and oils formulators must identify the important attributes and utilize the different functional properties of the available processed fats and oils effectively to satisfy the prepared foods requirements. Successful production of these products relies on the manipulation of the fat blend to produce suitable physical properties and to prevent undesirable changes during and after processing. Important fats and oils performance characteristics that must be considered for any product formulation are discussed below (1).

Flavor. Generally, the flavor of a processed fat and oil product should be completely bland to enhance the food product's flavor rather than contribute a flavor. In some specific cases, a typical fats and oils flavor such as lard or butter is desirable for a particular application. However, the reverted or oxidized flavors and odors of most fats and oils are offensive.

Flavor Stability. The fat and oil ingredient must possess the identified degree of resistance to both oxidative and lipolytic flavor degradation to maintain a bland or typical flavor throughout the shelf and use life of the prepared food product.

Physical Characteristics. Each fat and oil has a characteristic fatty acid composition and triglyceride distribution. The physical, functional, and organoleptic properties of fats and oils are determined in part by the fatty acid composition, but are affected also by the fatty acid distribution in the triglyceride that comprises the raw materials. Consistency, plasticity, emulsification, creaming properties, or spreadability of fats and oils products and the prepared foods produced are determined by the unsaturation and saturation of the fatty acids and their position in the triglyceride, which control melting rate and range.

Crystal Habit. Fats and oils are polymorphic, which means that, with cooling, a series of increasingly organized crystal changes occur until a final stable crystal form is achieved. Fats can exist in three crystal forms, i.e., α, β', and β. The crystal types formed define the textural and functional characteristics of most fat-based products. Many prepared foods are mixtures of ingredients held in a matrix of solid fat. The fat is the major functional ingredient, binding the other ingredients together; at the same time, it imparts texture and mouth feel to the product and affects flavor release and dispersion in the mouth at a controlled rate. Large β crystals can produce products with a sandy, brittle consistency; the result is poor baking performance in which creaming properties are important. The small, uniform tightly knit β′ crystals produce products with good plasticity, heat resistance, and creaming properties. The large β crystals are desirable for applications such as frying, pie crusts, and as a stabilizer for opaque liquid shortenings or margarines. Crystal habit can be controlled by the source oils selected and the plasticization, tempering, and storage conditions employed.

Nutritional Concerns. Fats and oils are recognized as important nutrients for both humans and animals because they provide a concentrated source of energy, contain essential fatty acids, and serve as carriers for fat-soluble vitamins. However, research studies have indicated a possible relationship between fats and the incidence of coronary heart disease. Diet modifications, including reductions in fat consumption, saturated fats, cholesterol, and *trans* isomers, have been proposed.

Additives. In addition to emulsifiers, a number of other chemical compounds provide a specific function for edible fats and oils products. The additive categories include antioxidants, antifoamers, metal inactivators, colorants, flavors, crystal inhibitors, preservatives, and emulsifiers.

Current chemical and physical processing techniques provide the processor with the capability of modifying one or more of the fats and oils properties. It is possible to change the functionality of the fats and oils products to provide the ability to formulate "tailor-made" products to suit a particular product or process. Further, the processing techniques provide the processor with a wider range of alternative raw material sources to improve commercial viability. Some of the objectives for applying the available modification or processing techniques are as follows (1):

1. Produce a fat and oil product to meet certain performance characteristic not possible with natural source fat and oil products.
2. Potential utilization of a more economic feedstock to duplicate the functionality of a more expensive alternative.
3. Improvement in oxidative stability through elimination of the reaction sites.
4. Improvement of palatability.
5. Modification of the crystallization behavior.
6. Provide more nutritionally acceptable products, i.e., reduce saturates and *trans* fatty acids while increasing polyunsaturates.

Edible Fats and Oils Consumption

Fats and oils are the raw materials for margarine, shortening, liquid oil, and other specialty or tailored products that become essential ingredients in food products prepared in the home, restaurants, and by food processors. Butter, lard, and tallow are

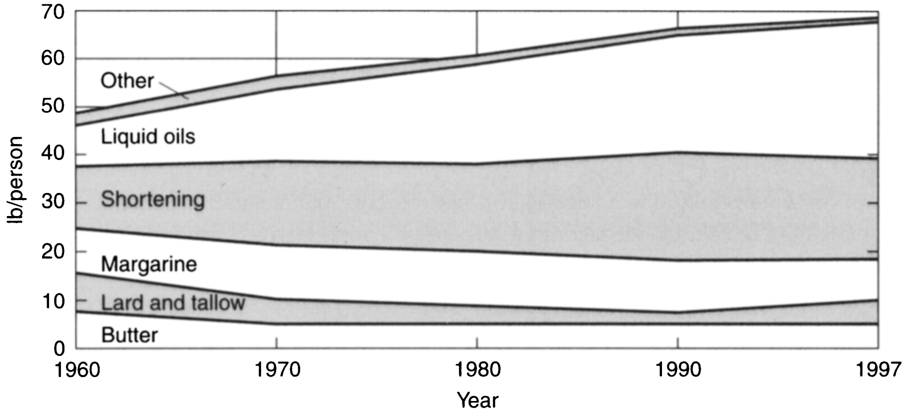

Fig. 21.1. U.S. fats and oils consumption in foods.

fats that are used as raw materials for margarines or shortenings as well as direct use with little or no processing. The direct usage of animal fats has decreased considerably since 1960 as shown in Figure 21.1 (2,3). Butter usage decreased 44% from 1960 to 1997. Lard and tallow direct use also had a substantial decrease (68%) through 1990 but rebounded for only a 38% overall decrease from 1960 to 1997. Margarine, developed as a butter substitute, also experienced a decrease (24%) in popularity since 1980. Shortening usage increased steadily until after 1990; it experienced a 6% decline in demand between 1990 and 1997. The usage rate for liquid oils has more than tripled since 1960 to absorb all of the other fats and oils product losses and then some. In summary, these fats and oils usage data show that the individual fats and oils consumption rate has increased 1.5 times since 1960 with a move toward liquid oils. The increased popularity of liquid oils is more than likely due to the following: (i) diet modifications to reduce saturated fats, *trans* isomers, and cholesterol; (ii) awareness of the high polyunsaturated or essential fatty acid content of liquid oils; (iii) more convenient handling of the liquid oils than solid fats; (iv) improved product formulations and processes to accommodate liquid oils; and (v) reduced dependence on the crystalline properties of solid fats for functionality through the use of emulsifiers.

Shortening Products

Originally, shortening was the term used to describe the function performed by naturally occurring solid fats such as lard and butter in baked products. These fats contributed a "short" or tenderizing quality to baked products by preventing the cohesion of the flour gluten during mixing and baking. Shortening later became the product identification used by all-vegetable oils processors in the United States to abandon the lard substitute concept; hence, shortening was an American invention. As the shortening product category developed, the limited application also expanded to include all baked products. Today, in the United States, shortening has become virtually synonymous with fat to include many other types of edible fats designed for applications other than baking. In most cases, products identified as shortening will be 100% fat; however, there are exceptions such as puff pastry and roll-in shortenings, which may contain moisture. Generally, a fat product containing at least 80% fat and the required vitamin A content, is margarine. Products that do not meet these criteria are identified as shortening because they do not have a U.S. Standard of Identity. Currently, a description for shortening would be as follows: processed fats and oils products that affect the stability, flavor, storage quality, eating characteristics, and the eye appeal of prepared foods by providing emulsification, lubricity, structure, aeration, a moisture barrier, a flavor medium, or heat transfer (1).

Most shortenings are identified and formulated according to usage. The packaged shortening forms that have emerged to satisfy the requirements of the consumers and the food industry are plasticized, pumpable liquid, flakes, powders, chips, and beads. Almost all of these shortening products can also be shipped to large customers in liquid bulk quantities. A brief description of each of the shortening forms is given below (4).

Plasticized Shortenings. General-purpose plasticized shortenings are still identified as all-purpose, unemulsified, emulsified, animal-vegetable blends, all-vegetable, or the like, whereas the trend is to formulate food service and food processor shortenings to perform a specific function for the intended food product. These shortenings are also identified by their intended usage, i.e., a baking application such as cakes, icings, puff paste roll in, and others, frying applications, specific dairy analog products, household use, and so on.

Liquid Shortenings. The pumpable liquid shortening designation covers all fluid suspensions that consist of a hard fat, usually β tending, and/or a high-melting emulsifier dispersed in a liquid oil. This shortening type was developed to pour or pump at room temperature for volumetric measurement or metering for either packaged or bulk-handled products.

Flakes. Hard fat, hard butter, hard emulsifier, and stabilizer flakes are high-melting fat- and oil-based products solidified into thin flake form for ease in handling and quick melting; they are used to perform many different functions in food products.

Chips. Shortening chips are thicker and larger than flakes for incorporation into baked products to provide a flaky product similar to Danish pastry without the labor-intensive roll-in process.

Powders. The higher-melting fats and oils products can be spray chilled to produce powders. Most of the flaked products can also be powdered for ease in handling or encapsulation of a food product for protection and/or delayed release in a finished food product.

Beads. Shortening beads have irregular granular shapes that can be metered at more uniform rates with vibratory or screw feeders; they resist stratification or separation in mixtures with other granular materials.

Bakery Shortening Applications

Baking applies not only to the production of bread but to all food products in which flour is the basic material and to which heat is applied directly. Bakery products also include the toppings, filling, frostings, and others additions that are used to finish the baked products. Shortenings are very important ingredients for the baker because they make up from 10 to 50% of most baked products. Shortening contributions to baked products include the following: (i) flavor; (ii) eating characteristics; (iii) aeration; (iv) grain and texture enhancement; (v) flakiness; (vi) lubrication; (vii) moisture retention; (viii) structure; and (ix) shelf life improvement.

Bakery shortenings are designed to satisfy individual specific requirements, as well as offering products with a broad general appeal. The design criteria for a general purpose product must be of a broader nature than those of a shortening for a specific product or process; therefore, all-purpose shortenings are formulated to perform adequately in many different applications within a category and are likely not superior in any of them. Formulation for specific application allows the developer to adapt the shortening more specifically to the product requirements, processing conditions, and any other limitations or requirements. The types of shortening products available to the food service and food processor bakers for general and specific applications are reviewed below (1).

All-Purpose Shortenings

These "compromise" shortenings are designed for performance in all types of baked products as well as deep-fat frying. Most all-purpose shortenings are formulated to have a wide plastic or working range, that is, not too firm at 50°F (10°C) and not too soft at 90°F (32.2°C). Normally, a cottonseed, tallow, or palm oil hard fat is added to a softer base stock to produce the desired plastic range, heat tolerance, and a β' crystal habit.

All-Purpose Emulsified Shortenings

Mono- and diglyceride emulsifiers are added to an all-purpose nonemulsified shortening base to produce this product. This additive improves the quality of cakes, icings, fillings, yeast-raised and other baked products by improving the emulsion stability to provide better creaming properties, aeration, starch complexing, moisture retention, and handling properties. Functionality improvements over the unemulsified all-purpose shortening are attained in every area with the exception of frying. Emulsified shortenings darken rapidly, smoke excessively, and foam when heated to frying temperature.

Cake Mix Shortenings

The requirements for a cake mix shortening are different from those of a bakery cake shortening. Cake mix shortening requirements include a plasticity to meet the demands of the mix manufacture's compounding equipment, emulsification capable of batter aeration with a high moisture content, and oxidative stability for an extended shelf life before preparation, as well as producing a tender, moist, high-volume, appetizing cake under many different handling conditions. Propylene glycol monoester (PGME)-emulsified shortenings have provided the best fat dispersion and air incorporation for prepared cake mixes. The hardest shortening base that can be distributed evenly by the mix equipment provides the best baking performance and oxidative stability. Therefore, cake mix shortenings are normally formulated specifically for each manufacturer and sometimes specifically for a type of cake.

Liquid Cake Shortenings

Pumpable cake shortenings combine the functional characteristics of plastic shortenings with the bulk handling characteristics of liquid oils. Liquid opaque cake shortenings are dependent upon the emulsifiers suspended in a liquid oil, with or without a hard fat stabilizer, to provide the functionality necessary for cake production. The liquid shortenings depend on both the formulation and processing technique for a stabilized suspension of the solid fat products in the liquid oil base for viscosity control. Most liquid cake shortenings are composed of a soft partially hydrogenated vegetable oil base stock, a β-tending hard fat and emulsifier systems containing mono-and diglycerides with either glycerol lactoester and/or propylene glycol monoesters.

Icing and Filling Shortenings

Both butter creme icings and creme fillings are sugar-based confections that depend on shortening for aeration, eating characteristics, body, and heat stability. Icings are low-moisture coatings for cakes, whereas fillings are aerated higher-moisture confections used inside of cakes. These shortenings are formulated somewhat like the all-purpose shortenings with a hydrogenated base stock and a hard fat, with an emulsifier system designed to provide aeration, good eating characteristics or "get away," and emulsion stability. Many of the icing and filling shortenings use synergistic emulsifier systems composed of mono-and diglycerides, lecithin, and a hydrophilic emulsifier such as polyglycerol ester or a polysorbate.

Icing Stabilizers

Flat icings and glazes for yeast raised sweet rolls, breads, Danish, donuts, and other baked products consist principally of powdered sugar with enough water to provide the consistency desired. These icings can become dull, brittle, stick to the wrapper, retain finger prints, and flake off the baked product easily. Low additions of flaked icing stabilizers melted and added to the icing mixture provide elasticity to combat brittleness and provide antisticking properties and more rapid setting to refuse fingerprints. The icing stabilizers are usually hydrogenated cottonseed and/or soybean oils with melting points slightly higher than body temperature, i.e., 113, 117, and 125°F (45, 47, and 52°C). Small amounts of lecithin, up to 0.5%, may be added to increase fluidity of the icing. A flat solid fat index (SFI) slope is important for the hydrogenated base stock to provide maximum solids while maintaining the melting point for the desired eating and handling characteristics.

Plasticized Bread Shortenings

Shortening is a minor ingredient in white bread; functionally, however, it is one of the more important ingredients because of its influence on dough mixing, handling, proofing, volume, eating characteristics, and freshness. Most all-purpose shortening with and without emulsifiers and supplemental softeners and/or conditioners may be used effectively for conventional bread production. The continuous bread process requires three fats and oils components that can be provided as one product or added separately by the baker, i.e., (i) a soft partially hydrogenated base shortening for lubrication; (ii) hard fat to provide solids and structure during proofing; and (iii) hard mono- and diglycerides for shelf life, dough strength, and texture. Additionally, one or more of the softeners and/or dough conditioners may be utilized in the shortening formulation or separately by the baker.

Liquid Bread Shortenings

Pumpable or liquid bread shortenings are stable dispersions of crystalline solids in a liquid oil matrix that is fluid at room temperature like other opaque liquid shortening products. These liquid shortenings must utilize the same components as the plasticized-type shortening but are processed similarly to the liquid cake shortening for suspension stability and viscosity control to maintain liquidity in the baker's storage tanks without heating.

Yeast-Raised Sweet Dough Shortenings

Sweet doughs are distinguished from breads by a sweeter taste and a richer eating sensation. These baked products are formulated with more shortening, milk, and sugar than breads, and usually contain eggs. Hard mono- and diglycerides, at 8.0 to 9.0% α-monoglyceride levels, are usually blended with either animal or vegetable soft shortening bases for the yeast-raised shortenings. The hard mono- and diglycerides provide softer, moister, longer keeping sweet rolls.

Cookie Shortenings

Shortening is an essential ingredient in most cookie formulations, ranging from 10 to 20%, depending upon the cookie variety to provide tenderness, keeping qualities, grain, texture, and richness. All-purpose type shortenings with a wide plastic range, β′ crystal habit, and good heat stability are usually adequate for soft cookie production. Emulsified all-purpose shortenings produce a soft cookie with a gummy bite preferred by some cookie bakers. Selectively hydrogenated shortenings with a narrow plastic range and good oxidative stability are suitable for hard cookies, which usually require only lubrication.

Cookie Filler Shortenings

Filler is a description of the filling between two cookie pieces to form a sandwich cookie. Cookie fillers are made up almost entirely of sugar and shortening. This high level of shortening requires specific functionalities to perform properly including (i) quick "get-away" in the mouth, (ii) up to a year's oxidative stability, (iii) high aeration potential, and (iv) the ability to produce a nontacky, smooth, heat-stable filler consistency. Cookie filler shortenings are composed usually either of lauric oils or are specially hydrogenated to prepare a shortening with a steep SFI slope, a melting point at or near body temperature, and a high Active Oxygen Method (AOM) stability.

Biscuit Shortenings

American biscuits are usually made with baking powder in combination with buttermilk or another acid ingredient for leavening and a high shortening content for flakiness. Firm, high-stability shortenings are preferred by most biscuit manufactures to produce a flaky consistency.

Danish Roll-In Shortenings

Danish pastry is a rich, yeast-leavened sweet dough with interleaving of the dough sheets and layers of shortening that separate when baked to form an open network of crisp and flaky layers. The most important features of a roll-in shortening for Danish pastry are plasticity and firmness. The shortening should be slightly firmer than an all-purpose shortening but possess the ability to be spread repeatedly in unison with the dough and remain in unbroken layers during the dough preparation. Danish roll-in shortenings are usually formulated to achieve a flat SFI with a β′ crystal habit for plasticity. Plasticization conditions are especially important for roll-in shortenings to initiate and develop the β′ crystal desired for a plastic consistency.

Puff Paste Roll-In Shortenings

The make-up of puff pastry is similar to that of Danish pastry but with a different dough formulation. Danish pastry is yeast-leavened, whereas puff pastry dough leavening is provided completely by the interlayering of dough and fat. The fat layers melt and expand during baking to create lift and a flaky texture. The roll-in shortening properties necessary to produce puff pastry with excellent volume and flaky layers resembling pages in a book are as follows: (i) plasticity over a wide range of temperatures,

(ii) firm, waxy but not brittle consistency, (iii) β' crystal habit, (iv) melting point slightly higher than body temperature, and (v) an extremely flat SFI.

Shortening Chips

Thicker fat flakes developed to provide a flaky baked product similar to Danish pastry with the traditional roll-in process are called shortening chips. Many other uses have been identified, including biscuits, pizza doughs, breads, croissants, dinner rolls, cookies, pie crusts, and various dry mix products. Shortening chips are incorporated into a dough or batter just before mixing is complete to distribute them throughout while retaining chip integrity. When baked, the shortening chips melt, causing small pockets that simulate the flakiness of laminated doughs. Flavors, colors, spices, and other materials can be encapsulated in the shortening chips for distribution into the product. Shortening chips are usually formulated to have a steep SFI with a melting point as low as possible to allow the chip to maintain form in the package until use. Shortening chips are flaked on chill rolls that solidify the oils into the thick flakes.

Cracker Shortenings

Crackers doughs contain moderately high levels of shortening with a low moisture content. The main function of the shortening is lubrication; therefore, the chief emphasis in the selection of a cracker shortening is a bland or mild flavor with a good oxidative stability for shelf life.

Frying Shortenings

Frying, a centuries old cooking method, has become one of the most important methods of food preparation. It is used extensively in the home as well as restaurants, institutions, bakeries, and snack food industries to prepare foods. Frying is a fast and convenient food preparation technique, and frying fats have unique properties that add to the flavor and mouth feel of the foods prepared. Frying consists simply of immersing the food into heated frying fat for the time required to cook the product. The frying fat is an effective heat transfer medium that becomes a part of the food. This deceptively simple process is one of the most complex and least understood fats and oils applications (5).

Fats and oils undergo many reactions during frying; these include hydrolysis, oxidation, polymerization, steam distillation, flavor changes, and darkening. Some of the changes are desirable, others are detrimental, and some qualify as both desirable and undesirable. Fats and oils deteriorate with heat, and exposure to high frying temperature accelerates all of the breakdown reactions. Heating alone without any food preparation will cause a frying shortening to deteriorate, rendering it unacceptable for further use. The oxygen in air reacts with the unsaturated double bonds in the triglycerides to oxidize and form offensive odors and flavors, which promote polymerization and gum formation. Moisture in the food causes hydrolysis, which splits the triglycerides into their component parts, i.e., mono- and diglycerides, free glycerine, and free fatty acids. These component parts have lower smoke points, objectionable flavors, and cause increased fat absorption into the foods prepared. Moisture in the food also contributes to a steam distillation process to strip oxidation products during frying to delay the deterioration process. Contamination is another enemy of the frying medium that accelerates deterioration. The food fried is a contaminant, as well as soap or detergents, burnt food particles, polymerized gums, trace metals, and other materials that can cause fat deterioration. The extent of the frying shortenings exposure to these enemies determines the degree of product deterioration (1).

A wide range of fat and oil products are used for frying ranging from heavy duty shortenings to refined, bleached, and deodorized oils. The selection criteria for frying shortening are the same as those for food service and food processor operations; that is, the frying media must be matched to the performance requirements of the product fried, limitations of the frying equipment, and the demands of the operation. However, the product that satisfies each individual operation's demands will be quite different. Identification of the ideal frying media to satisfy these demands must include careful consideration of the following three requirements: (i) the product characteristics required of the fried food, including palatability, appearance, and texture, (ii) the degree of exposure to adverse conditions to help determine the required frying fat stability to achieve the frying life requirements, and (iii) the product shelf life required after frying.

Food Service Deep-fat Frying Shortenings

Because each food service operation is unique in regard to its menu, product mix, equipment, and operation, many different shortenings have been formulated to meet the different performance expectations. In restaurant and institutional deep-fat frying, the rate of fat absorption into the fried food, called turnover, varies considerably with an average usage rate in the 20–35% range. This low turnover rate is due to the fact that frying is not continuous but frying to order, which results in peak and slack periods of use. Four general types of plasticized and liquid deep-fat frying shortenings that are available to the food service operator in addition to the specialized or tailor-made products for specific customers are discussed below (6).

All-Purpose Shortenings. General or all-purpose shortenings are compromise products designed for performance in baking and frying. These products were the first shortenings formulated with frying capabilities as a criterion; consequently, they have better frying stability than most oil products but less than the other shortenings formulated especially for frying. The all-purpose functionality of these shortenings appeals to operations with limited inventory capabilities.

Animal-Vegetable Blended Frying Shortenings. Animal fats alone or blended with hydrogenated vegetable oils have been used as frying shortenings for many years. Animal fat shortenings have been attractive to the food service operator due to their usually low initial cost, good frying stability, and the potential meaty flavor enhancement of some foods. Tallow, alone or in combination with a hydrogenation vegetable oil, has exceptionally good frying stability.

Heavy-Duty All-Vegetable Frying Shortenings. These were the first specialty shortenings formulated for a definite function. These solid shortenings were developed for maximum frying stability through the reduction of unsaturates *via* hydrogenation.

Liquid Frying Shortenings. Liquid opaque frying shortenings were introduced to the food service industry and quickly became very successful for the following two reasons: (i) the shortening could be poured into the fryer instead of packing the fryer with solid shortening and (ii) it offered a longer frying stability. The secret to the liquid product's frying stability was the addition of an antifoamer additive, i.e., dimethylpolysiloxane. The addition of this substance in parts per million quantities increased the frying stability of a fat and oil product dramatically, sometimes >5 times that of the original fat or oil product. Consequently, fats and oils processors added the antifoamer agent to all of the frying shortening products as soon as possible.

Food Service Pan and Grill Shortenings

Pan and grill frying are major methods of food preparation for breakfast items; ~75–80% of all breakfast menu items are prepared on the grill or in a frying pan. The fats and oils products used for pan frying and griddle food preparation include butter, margarine, and cooking oils; however, the specialty pan and grill shortenings have become the favorite products. Two types of pan and grill shortenings are generally available to the food service operator: (i) products that are solid at room temperature usually containing 10–25% lauric oils for a sharp melt, and (ii) fluid vegetable shortenings that pour at room temperature. Most of these products contain butter flavor, yellow color, an antifoaming agent for gum control, antioxidants for oxidative stability, and lecithin as an antisticking agent. Additionally, some of these products are available with salt for flavor enhancement (7).

Bakery Frying Shortenings

Bakery deep-fat fried products consist of several hundred varieties but can be classified into the following three general classifications: (i) yeast raised, (ii) cake or chemically leavened, and (iii) fried pies. The frying methods utilized for these classifications are either surface frying, which requires turning the product halfway through the frying process, or submerging the product beneath the surface of the frying fat until done. Many of the bakery products also have various types of coatings, toppings, or fillings applied. Therefore, bakery frying shortenings have three functions rather than the usual two for other deep-fat frying applications, namely, heat transfer, ingredient in fried product, and binder for the toppings or coatings. This third requirement, incorporates a need to control the crystallization of the shortening after frying to comply with the solidification time restraints of the sugar, glaze, or other toppings. Additionally, bakery frying shortenings usually do not contain antifoaming agents because glaze and sugar problems have been attributed to their use. Conveniently, bakery fried products almost always have a high absorption rate, which provides a high turnover rate for the shortening, thus precluding the need for the antifoamers (1).

Snack Frying Shortenings

Frying shortenings are a crucial element in the quality of snacks, which are estimated to use >10% of the fats and oils available in the United States. Two basic types of snack foods are deep-fat fried, i.e., savory snacks, such as potato chips, corn chips, tortilla chips, pork skins, or puffed snacks, and nut meats. Savory snack frying shortenings are not abused as much as restaurant or bakery frying media due to the extremely high turnover rate, continuous frying, and the controls exercised. The choice of savory frying shortening is influenced by flavor, mouth feel, texture, product appearance, and the snack itself. Generally, vegetable oils, selectively hydrogenated to increase the oxidative stability, with a melting point maintained well below body temperature, are the most attractive snack frying oil from a quality and economic view. However, a typical savory snack frying shortening probably does not exist. Most snack food processors have specific frying shortenings for their products that have been developed independently or with their supplier's assistance.

Shortenings for nut roasting have different requirements than those for savory snacks. Nut meats have relatively low moisture contents with high oil contents. As a result, the fat absorption rates of fried nuts are very low to produce a very low turnover rate. Therefore, frying stability is a paramount attribute for nut roasting shortenings. Coconut oil, selectively hydrogenated vegetable oils, and liquid oils with low unsaturate levels are the frying media most acceptable to the nut roasting industry (1).

Dairy Analog Shortenings

A shortage of dairy products during World War II led to the development of dairy analogs. Dairy analog products are basically emulsions of fats and oil products in water with varying quantities of protein, sugar, stabilizers, emulsifiers, flavors, colors, and buffer salts with the appearance and eating characteristics of natural dairy products. Acceptance of these products was caused by the technical advances in fats, oils, improved emulsion technologies, and product formulation achievements. These technologies enabled the food processors to simulate dairy products with improved performances such as the following: Ease of handling, extended shelf life, tolerance to temperature abuse, tolerance to bacteria spoilage, nutritional value control, source oil selection, and economic advantage.

Fat is the most important ingredient used in the dairy-like products. It establishes eating properties, physical appearance, and stability of the finished dairy analog. A shortening that performs in one dairy analog application may not be satisfactory for another. Therefore, it is necessary to match the performance characteristics of the shortening with the finished product requirements of the individual dairy analog. Shortening requirements for various dairy analogs are discussed below (1).

Nondairy Creamers. These products are not imitation creams but formulated systems similar in functionality to the natural dairy product with advantages of longer shelf life, more convenient product forms, more uniform quality, and consistent performance. The nondairy creamer product form has a significant effect on the shortening requirements.

Liquid coffee whiteners, both refrigerated and frozen, require a shortening with a relatively low melting point and a steep SFI; it may be composed of coconut oil, palm kernel oil, or selectively hydrogenated vegetable oils.

Spray dried coffee creamers are free-flowing dry powders that require fat systems tailored to meet the performance requirements of the different powder types and the abuse experienced during processing. In most cases, these products require higher melting points, typically 106–112°F (41.1–44.4°C), for free flow, dispersion, whitening, and oxidative stability.

Whipped Toppings. Nondairy whipped toppings are more functional than whipped cream due to the shortening's SFI and the complementary emulsifier systems. Whipped topping shortenings are characterized by a steep SFI with sufficient solids at whipping temperature to provide rigidity and a melting point target close to body temperature for rapid "get away" in the mouth. Typically these products are vegetable oils that have been specially hydrogenated, interesterified, or fractionated to provide the desired characteristics.

Cheese Analogs. A nondairy cheese replacement requires the use of a shortening or fat source other than butter, a protein other than milk solids, and a flavor system that duplicates natural cheese as closely as possible. The shortening requirements are a relatively steep SFI, good oxidative stability, and a bland flavor. Shortenings that simulate the SFI of butter fat have performed more than adequately in cheese analogs.

Mellorine or Frozen Dessert. Mellorine is the name adopted by several states as the official generic name for imitation ice cream made with fats other than butter fat. The shortenings used in cheese analogs will also function in mellorine products.

Sour Cream Analogs. Imitation sour creams are used extensively for party dips, salad dressing, potato toppings, sauce enrichments, cold soups, and many other applications. These dairy analogs are usually produced with lower fat levels, are more resistant to wheying off, have a longer shelf life, and are usually less expensive than natural sour cream. Specially hydrogenated, or hydrogenated fractionated vegetable oils with a steep SFI and a melting point slightly higher than body temperature provide the stable consistency desired for the sour cream analogs.

Fluid Milk Analogs. For liquid milk analog products, the butter fat is replaced with a vegetable fat. Shortenings that have been used successfully are composed of lauric oils or are hydrogenated domestic vegetable oils; the most advantageous replacement, however, would probably be the liquid shortening products that offer a high polyunsaturate to saturate level.

Household Shortenings

Shortenings produced for use in the home have not become tailored products for specific applications like the products produced for the food service and food processor industries. Household shortenings marketed in the United States are still all-purpose shortenings. These shortenings are designed for frying, cooking, baking, candy making, and all other home food preparation. The two basic types of household shortenings available at retail grocery stores are differentiated by composition, i.e., all-vegetable or animal-vegetable blends. Very little change has been implemented in the animal-vegetable blends, but the all-vegetable products have been reformulated over the years to increase the polyunsaturate to saturate ratio. The other major changes have been with packaging. The familiar 3-lb can has evolved from a metal can with a key opening tear strip and captive lid to a fiber-wound composite can with a foil tear-off top and a plastic overcap for reclosing after opening.

Margarine and Spreads

Margarine is a prepared food product developed because of a butter shortage in France. Its evolution to a highly accepted table spread and ingredient for cooking, baking, and prepared foods is an prime example of fats and oils technology. Margarine has evolved from an imitation of dairy butter to a nutritive food, which provides a concentrated source of energy, a uniform supplement of vitamin A, a source of essential fatty acids, satiety, a universally accepted flavor, and serves as a complement to other foods (8). The U.S. Food and Drug Administration (FDA) and USDA regulations define margarine as a plastic or liquid emulsion food product containing not <80% fat and 15,000 IU/lb of vitamin A; it may contain optional ingredients with specific functions. The usual optional ingredients are water, milk or milk products, emulsifiers, flavoring materials, salt and other preservatives, and colorants.

Low-fat spreads, originally introduced in the 1960s as diet margarines, are available with a multitude of fat levels between 20 and 70%. Low-calorie and low-fat marketing created a consumer interest in spreads after the diet margarines had been rejected by consumers for poor melting and eating characteristics. Functionally, the spread products are intended to be used as a tablespread or for cooking, and most packages have a statement that the spread is not intended for baking or frying (9).

Consumer Margarines and Spreads

Margarine prints generally in quarter and 1-lb solids were the basic margarine products available until soft margarines were introduced in 1962. The soft margarines with higher unsaturated fatty acid levels were packaged in plastic tubs in both regular and whipped versions. The whipped margarines were easier to spread and provided fewer calories per serving due to the 30% nitrogen content. The nutritional appeal of the soft margarines was carried even further with the introduction of spreads that began to capture market share in the 1970s; the market share of spreads increased from <5% in 1976 to >74% in 1995.

The major uses for consumer margarines and spreads continue to be as a tablespread, cooking ingredient, and seasoning agent. The consumer-directed functional aspects of the margarine and spread products are spreadability, oiliness, and melting properties. Spreadability continues to be one of the most highly regarded attributes of consumer margarine products, second only to flavor. Oil-off is the most serious for print products because the inner wrappers become oil soaked and oil may even leak from the outer package. The melting properties of the margarine oil ingredient, the emulsion tightness, and the processing, tempering, and storage conditions that help determine crystal development and stability have a direct effect on the mouth feel and release of the flavoring materials as well as the consistency.

Scratch baking in the home declined considerably with the introduction of prepared mixes and frozen ready-to-eat products with good quality. Nevertheless, for any baking, the U.S. homemaker will usually choose shortening or a print margarine. Measurement of soft margarine requires a different scale than stick products because of the creaming gas content, i.e., 5% in regular and 30–35% in whipped soft margarines. In addition, spreads have exceptionally poor baking functionality due to the high-moisture/low-fat content.

Industrial Margarine and Spreads

Food service and food processor margarine and spreads are usually considered industrial products. The most popular food service margarine is the consumer stick margarine formulation packaged in 1-lb solids that are used for cooking and seasoning. Individual serving or portion control spread products are also popular food service dining room products. Additionally, a baker's margarine formulated with an all-purpose shortening base is used by many food service kitchens for their baking requirements.

Food processor margarine and spread products are formulated for more specific uses than those of either the food service or consumer products. The stick margarine formulations are packaged in 50-lb cube cases for use in prepared foods. Margarines are also formulated and plasticized with Danish pastry roll-in capabilities, such as the shortening products discussed in the section on bakery shortening, to take advantage of the flavor, color, and moisture incorporated into the emulsion. Spread-type products were used by food processors before the consumer had accepted them, but for different applications. One of the applications is for self-basting of meat and poultry products during baking. Another is a biscuit topping with special dairy flavor notes and buttermilk curd. Others employ different flavors, spices, or other special ingredients for specific applications, product, or process.

Liquid Oils

A liquid oil is usually identified by its physical state at ambient temperature regardless of whether the source material is animal, vegetable, or marine. Some source oils appear to disagree with this designation until the mean temperature at the place of origin is considered. For example, oil products from palm and coconut trees are a solid at ambient temperatures in cool climates but a liquid at the prevailing temperatures in the tropical climates in which these plants grow. Therefore, the definition of a liquid oil would be "any oil that is a clear liquid without heating."

Liquid oils are further classified by their functionality traits, i.e., cooking, salad, and high stability. The definition for each of these classifications is as follows:

Cooking Oil. An edible oil that is liquid and clear at room temperature or 75°F (23.9°C) that may be used for cooking. Cooking oils are typically used for pan frying, deep-fat frying, sauces, gravies, marinades, and other nonrefrigerated food preparations in which a clear liquid oil has application. Cooking oils usually congeal or solidify at refrigerator temperatures.

Salad Oil. An edible oil that is suitable for the production of a mayonnaise or salad dressing emulsion that is stable at low temperatures. This requirement has been refined to require that an oil sample remain clear without clouding for at least 5 h while submerged in an ice bath to qualify as a salad oil.

High-Stability Oil. An edible oil that possesses an exceptional oxidative or flavor stability and is a clear liquid at room temperature . The measure of oxidative stability used for high-stability oils is the AOM (AOCS Method Cd 12-57). High-stability oils will withstand the AOM abuse for periods >75 h and some longer than 300 h compared with the 8–20 AOM hours for cooking and salad oils.

Consumer Liquid Oils

Cooking and salad oils available for home use are bottled and marketed through grocery stores and other retail outlets. The source oils available to the retail consumer are canola, corn, cottonseed, olive, peanut, safflower, soybean, sunflower, blends of these source oils, and some other specialty oils. Most of the oils are only refined, bleached, and deodorized with the exception of those that require dewaxing or winterization to remain clear liquids on the grocery store shelves (canola, corn, cottonseed, and sunflower).

A steady growth in the consumption of cooking and salad oils is evident from the USDA Economic Research Service statistics (3). In fact, salad and cooking oils were the sole fats and oils growth area for the year 1997. The trend away from solid fats to liquid oils indicates that the U.S. consumer is reacting to the cautions of the medical profession regarding fats and oils and coronary disease. As a result, consumers have replaced solid shortenings and margarines with liquid oils.

Industrial Cooking Oil Applications

Cooking oils are utilized wherever liquidity is permissible or important, and the application does not require a clear liquid oil at cool temperatures. Cooking oils may be used for pan frying, deep-fat frying, gravies, and other applications. Cottonseed oil has a unique flavor property that makes it a desirable frying oil for snack foods. Corn oil is regarded as exceptional in flavor and quality with a healthy image for incorporation into processed foods and also for frying of snack foods. Peanut oil maintains a respectable cooking oil market for snack frying and food service frying operations, especially for fish and chips. Some of the other applications for cooking oils are in packing canned meats and fish products, pan release products, bread, buns, and sweet doughs.

Industrial Salad Oil Applications

Salad oils are required in most dressing products, sauces, and other food products prepared or stored at cool temperatures. Salad oils were developed for use in mayonnaise and are a necessity for the preparation of other salad dressings, sauces, and food products that are emulsions prepared at cool temperatures or that must withstand clouding or congealing at refrigerator temperatures after preparation. Most of these products require high quantities of oil in the formulation (30–80%) to provide the eating characteristics and consistency desired.

High-Stability Oils

The primary prerequisites of a high-stability oil are liquidity at ambient temperatures and resistance to oxidation. Most oils that are liquid at room temperature contain high levels of unsaturated fatty acids, which are most susceptible to oxidation; this limits their application to products in which an extended shelf life is not a requirement. Technology has identified two techniques to enhance the stability of liquid oils, i.e., hydrogenation and fractionation to separate the hard fraction from the liquid oil fraction which retains a high stability and the use of plant bleeding techniques to produce liquid oils with very high monounsaturated fatty acid levels. The applications established for the high-stability oils are described below (1).

Deep-Fat Frying. The high-stability oils have substantially increased frying stability by limiting the opportunities for oxidation due to the absence of polyunsaturates. Frying stability for the high-stability oils is near the performance for heavy-duty frying shortenings with the convenience and fried food appearance of a liquid oil.

Protective Barrier. Surface application to food products with the high-stability oils provides protection from moisture and oxygen invasion, prevents clumping, and imparts a glossy appearance. Specific applications include raisins and other fruits, breakfast cereals, nut meats, snacks, croutons, bread crumbs, spices, and seasonings.

Carrier. Colors, spices, flavors, and other additives may be blended into the high-stability oils to preserve the flavor, color, and activity without development of off-oil flavors for long periods.

Pan Release Agents. High-stability oils can serve as a major ingredient in the preparation of oxidative stable spray or brushing lubricants for baking pans, confectionery products, and other materials.

Food-Grade Lubricants. The high-stability oils are food-grade alternatives to the mineral oil products for lubrication of equipment that contacts food products.

Compatibility. Unlike solid fats, the high-stability oils are compatible with all types of fats and oils because the crystal type is not a concern.

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Chapter 22

Shortening Technology

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Introduction

Shortening is an American invention, developed for cottonseed oil utilization and perfected for soybean oil. Shortening was originally a baking term that described the function of a solid fat to give a "short" or tenderizing effect to baked products. The water-insoluble shortening agents prevent cohesion of flour gluten during mixing and baking to produce tender products. Shortening later became the product identification used by vegetable oil processors to abandon a lard substitute concept. As the shortening product category developed, a limited application expanded to include all baked products. Today, the term shortening has become virtually synonymous with fat and includes many other edible fats or oils products designed for all prepared foods, not simply baking.

The term "fat" is usually understood to refer to a lipid that appears to be a solid and the term "oil" to a lipid that is liquid at ordinary temperatures. Fat products are very seldom a complete solid; rather, they are intimate mixtures of a liquid phase and a solid phase, which are made up of microscopic triglyceride crystals. The plasticity of a fat and the other characteristics that distinguish it from an oil depend on the varying proportions of the two phases with changes in temperature. Initially, shortenings or compounds were produced to resemble the consistency and plasticity of lard. For many generations, lard was the fat of choice in preparing doughs and batters because it had sufficient plasticity at room temperature to cream with sugar and mix with eggs. Now, shortenings are designed to satisfy individual specific requirements for all of the food industry as well as offering products with broad general appeal. With this broader application, the consistency of shortening varies from wide workable ranges to brittle products with sharp melting characteristics, from very firm consistencies to liquid or pumpable products, or from creamy, smooth textures to grainy structures, depending on the requirements of the application.

In most cases, products identified as shortening are 100% fat; however, there are exceptions, such as the roll-in shortenings, which may contain moisture. In some cases, a fat or oil system may be identified as a shortening to distinguish it from a margarine product. Generally, in the United States, if a fat product contains ≥80% fat and has the required vitamin A content, it is a margarine. Products that resemble margarine but contain <80% and not > 40% fat are required to be labeled as spreads. Products that do not meet these criteria have been identified as shortening because it does not have identity standards. Currently, a description for shortening would be as follows: Processed edible fats and oils that affect flavor, oxidative stability, shelf life quality, eating characteristics, nutrition, and the eye appeal of prepared foods by providing emulsification, lubricity, structure, aeration, moisture barrier, flavor medium, and/or heat transfer (1,2).

Shortening Development

Climate and availability were major influences on the eating habits of our ancestors. Inhabitants of central and northern Europe obtained their edible fats almost exclusively from wild animals and later domesticated animals. Consequently, their foods developed around the use of solid fats such as butter, lard, and tallow. In the more heavily populated areas of Asia, southern Europe, and Africa, where it was impractical to dedicate land to livestock grazing, diets developed with liquid vegetable oils as the major fat source. North American's preference for solid fats was influenced by the early immigrants from northern Europe who adapted large sections of the country to raising domestic animals (3).

Vegetable shortening with all of the physical characteristics of a plastic animal fat was an American invention. It was created by the cotton-raising industry and perfected for soybean oil utilization. Increased cotton production, influenced by Eli Whitney's cotton gin, after the American Civil War made available large quantities of cottonseed oil. Its use as an inexpensive substitute for whale oil used in lamps for illumination disappeared with the development of petroleum industry in 1859. For two decades after the Civil War, cottonseed oil was used in the manufacture of laundry soap or exported to Europe for use in animal feeds or to be mixed with olive oil. Adulteration of olive oil led to tariffs on U.S. cottonseed oil, which discouraged cottonseed oil imports. At home, the hog supply could not keep up with the demand for lard, the edible fat of choice for baking and frying. It had become common practice to mix beef fat or tallow with lard; thus, adulteration with cottonseed oil was a natural step for the use of the inexpensive oil. After public exposure of widespread lard adulteration with cottonseed oil, the U.S. Congress mandated that these mixtures must be identified as "lard compounds." Thereafter, technology developments with vegetable oil processing improved the substitute product to the point that it was superior to the original product in both price and performance. Vegetable oil processors had the foresight at this point to abandon the lard substitute concept to market their products as a food ingredient that has become known as shortening.

Several major technology improvements in oil processing had to take place before substantial quantities of vegetable oils could replace lard as the preferred fat for baking and frying. The first process to be employed concerned hard fat production. It involved a fractionation technique in which stearine was separated by slow cooling followed by straining and draining. This method was attributed to Blondeau in 1761. Initially, cottonseed oil was blended with lard and tallow to produce the adulterated lard; later, however, the lard compounds were formulated with relatively small portions of oleostearine or other hard fats derived from animal fats with the use of a fractionation technique.

Alkali refining procedures were developed in Europe around 1840, but were not employed in the United States until the 1880s. Vegetable oils were alkali refined in open kettles; the foots were separated by gravitation until continuous systems utilizing centrifuges were introduced (4–6). Refining with caustic soda reduced both free fatty acid content and a large portion of the red-yellow color pigment gossypol in cottonseed oils. Caustic-refined cottonseed oils were found acceptable for packing sardines and marginally acceptable for mixing with lard when lard was scarce and expensive. Neutralized cottonseed oil (after caustic refining) retained an acrid flavor and somewhat unpleasant odor, which limited consumer acceptance.

Further color removal from cottonseed oil was necessary to make the oil more acceptable. Initially, bleaching was accomplished by using a palm oil technique that exposed the cottonseed oil to sunlight in large shallow tanks on factory roofs for up to 18 mo. This procedure reduced color but also tied up capital for long periods and damaged the oil flavor and stability. Carbon, the first adsorbent agent used for bleaching, was replaced with bleaching earths. The use of bleaching earths was an American achievement. In 1880, Alexander Winters obtained a U.S. patent for purifying animal and vegetable fats by treatment with pulverized fuller's earth. Six years later, William B. Allbright secured a patent for fuller's earth applied with steam to facilitate removal of oil from the used earth.

Although refining removed free fatty acids and other impurities, and bleaching with fuller's earth solved the color problem, the unpleasant flavor contributed by the vegetable oil portion was so strong that lard substitutes or compounds continued to experience very limited acceptance. The unpleasant flavor and odor limited the amount of bleached cottonseed oil that could be used in lard compounds. Attempts to remove the offensive flavor chemically or mask them with spices or flavors were unsuccessful. Deodorization by blowing live steam through the oil at elevated temperatures was introduced around 1891 and was quickly adopted by most American processors. David Wesson later perfected the deodorization process by exposing the oil to superheated steam in a vacuum to produce a bland-flavored oil with improved oxidative stability. Deodorization enabled the processors to increase the amount of cottonseed oil in lard compounds to ≥80% (7–10) .

Introduction of the catalytic hydrogenation process around 1910 gave the vegetable shortening processor independence from the meat packing industry and initiated a new era for all edible fats and oils, particularly shortening agents. In 1909, the American rights to Normann's British patent for liquid-phase hydrogenation of fatty oils were acquired by the Procter & Gamble Company. Crisco, short for crystallized cottonseed oil, was introduced two years later. The success of the hydrogenated shortening inclined other manufactures to litigation actions, which led to a U.S. Supreme Court decision invalidating Procter & Gamble's exclusive use of the Normann patent and cleared the way for all processors to employ the hydrogenation process. Thereafter, shortening development followed two divergent courses, i.e., all-hydrogenated or compound formulation.

The hydrogenation process gave vegetable oil shortenings a definite advantage over the compound shortenings offered by the meat packers. This key process permitted the processors to change the composition of the inherently liquid oils to increase their oxidative stability. The superior neutrality, oxidative stability, and uniformity of the hydrogenation vegetable oil shortenings found favor with commercial bakers and homemakers alike at the expense of the meat fat products. This was confirmed by the willingness of consumers to consistently pay higher prices for the hydrogenated vegetable oil shortenings. Subsequent formulation technology advancements have enabled processors to interchange source fats and oils controlled by hydrogenation and blending of unhydrogenated, partially hydrogenated, and fully hydrogenated base stocks to provide a range of shortening products varying in state through a continuum of plasticity from a pumpable liquid to a sharp melting solid (11).

Solidification of smooth, plastic shortening agents containing beef fat and lard or hydrogenated cottonseed oil posed other challenges as well. Pure lard contains relatively little high-melting fractions; therefore, slow cooling was a satisfactory procedure for production of a smooth, plastic product. Agitation of the shortening products in chilled tanks, which had been the usual practice for lard, resulted in grainy products with the compounds and the hydrogenated shortenings. The internally refrigerated chill roll, developed for crystallizing shortening products, was patented by O.G. Burnham in 1883. The chill roll consisted of a revolving hollow metal cylinder chilled by circulating cold water or chilled brine water through its interior. The melted compound or hydrogenated shortening was allowed to run in a thin film over the revolving cylinder, leading to almost instant chilling. The thin layer of solidified fat was then scraped off automatically and dropped into a trough or picker pan where crystallization continued; a shaft with a number of paddles incorporated air into the product to provide a creamy white appearance. After picking, the shortening was forced through a small orifice or slot at high pressure to complete the homogenization of air and oil and to minimize graininess. This processing allowed the use of a higher portion of oil with a lower hard fat level for the adulteration of lard and later compound formulations. The chill roll proved particularly effective because at this same time, the ammonia refrigeration machine came into use, making possible the employment of very cold brine to chill the rolls.

In the early 1930s, the development of improved heat-transfer equipment for freezing ice cream led to the perfection of a closed continuous internal chilling unit, which replaced chill rolls as shortening plasticization units. The liquid fat to be chilled was pumped into a relatively small annular space between the outer jacket, through which the refrigerant passes, and the large intermutator shaft. As the oil contacts the cold jacket wall, it congeals and is instantly scraped off by floating scraper blades attached to the rapidly turning mutator. This repeated high-speed congealing/scraping sequence provided extremely high heat-transfer rates and a homogeneous product. Normally, air or nitrogen was introduced into the melted oil entering the chilling unit, and a worker unit was positioned after the closed internal chilling unit to simulate the effect of the picker pan with the chill roll process (12). Versions of these closed internal chilling systems are still employed to plasticize shortenings.

In 1933, the introduction of superglycerinated shortening brought about significant changes for the baker and the shortening industry. These shortenings contained mono- and diglycerides, which contributed to a finer dispersion of fat particles into cake batters, causing a greater number of smaller-sized fat globules, which strengthened the batters. Emulsified shortenings allowed bakers to produce cakes with additional liquids that permitted higher sugar levels. Additionally, the surface-active agents improved aerating or creaming properties, which allowed less reliance upon specific crystalline and solids properties for functionality. This improvement also allowed a reduction of shortening levels in some bakery cake formulations without sacrificing aeration and tenderness qualities. Altogether, the superglycerinated shortenings produced moister, higher-volume cakes with a fine grain, an even texture, and extended shelf life. As a bonus, it was determined that lighter icings and fillings with higher moisture levels could be produced with emulsified shortenings and that the shelf life of yeast-raised products was extended (13). Performance improvements were also found in many other food products in which aeration, moisture retention, starch complexing, and the other benefits of emulsification helped to improve the functionality of shortenings.

Development of emulsified shortenings added a new dimension to the fats and oils industry; it ushered in the era of tailor-made shortenings. New shortenings specifically designed for special applications such as layer cake, pound cake, cake mixes, breads, sweet doughs, icings, creme fillings, whipped toppings, laminated pastries, and other bakery products were developed and introduced rapidly after World War II (14). Specialty shortening development fostered further improvements in all aspects of the fats and oils industry and expanded shortenings beyond the baking industry. New food products and concepts developed as dairy analogs, for confectionery, food service, and other areas, were successful in many cases due to the development of functional specialty shortening products.

Increased automation promoted by inflation and labor costs caused food processors to investigate new handling methods for all ingredients in the late 1950s. Processors using large quantities of packaged shortenings began investigating and converting to bulk handling of these products. In many cases, these systems required the food processor to install plasticization equipment in addition to storage and unloading facilities for handling heated shortenings. These bulk-handling requirements encouraged the development of liquid shortenings. Through unique processing procedures, these products consisting of suspended hard fats, emulsifiers, or other additives in a liquid oil, that remained fluid or pumpable at room temperature. It is possible to pump, meter, and bulk store these shortenings without heating. Liquid shortenings are dependent upon emulsifiers or other additives to provide the functionality required for specific product applications, typically cakes, frying, bread, or dairy analogs. Liquid shortenings have not eliminated plasticized packaged or bulk-handled shortenings; they have created another shortening type.

Shortening products have been developed for a specific food product and in many cases for a particular process to prepare that product. Shortenings include a wide range of products that may be used to provide exterior gloss and moisture resistance for some baked items, as well as emulsification, creaming, and lubrication. In frying applications, shortenings allow quick, even heat transfer for cooking and aid in formation of a moisture barrier. Shortenings have been classified in several different ways as follows:

1. Composition: (i) animal or vegetable; (ii) compound or all hydrogenated; and (iii) emulsified or unemulsified.
2. Physical form: (i) plastic; (ii) pumpable or liquid; (iii) flake or chip; and (iv) powdered or bead.
3. Functionality: (i) baking shortening, usually for a specific baking function such as all-purpose or specifically for cakes, icings, fillings, donuts, roll-in, sweet doughs, breads, biscuits, or cookies, for example; (ii) frying shortenings, also for specific applications such as heavy-duty, hotel, restaurant, and institution, snack frying, or donut frying; (iii) dairy analog shortenings, formulated and identified for specific dairy analog products and applications; (iv) household shortenings, the all-purpose shortenings formulated for use in the home kitchen for baking, frying, and cooking; and (v) customer specific, shortenings designed for a specific product and/or process.

Technology advances have increased the storehouse of fats and oils knowledge, allowing the introduction of more advanced products for all aspects of the food industry. Specialty shortenings have helped create entirely new food products and improved product extensions for the retail consumer and the food service industry. The word shortening no longer identifies the function performed by a fat or oil product nor does it indicate the type or consistency of the fats and oils product. Shortening products are now produced in solid plastic, liquid, flake, and powdered forms for a diverse application range, including bakery products, dairy analogs, snack foods, nutritional supplements, confections, and other prepared foods (2).

Raw Material Utilization

Natural fats and oils are mixtures of mixed triglycerides. Their functional properties and quality characteristics are related directly to the type of triglycerides in the fat system. The types of triglycerides are determined by the fatty acid composition of the triglycerides and the distribution of the fatty acids on the individual triglyceride molecules. Distribution of the fatty acids on the individual triglyceride molecule and the quantity of each triglyceride species depend on the proportions of the individual fatty acids, the fat or oil source, and its processing history.

Most vegetable oils have no inherent structural characteristics, that is, they do not contain any significant quantity of triglycerides made up of two or three saturated fatty acids. However, these structural characteristics can be built in by the use of hydrogenation, interesterification, and/or fractionation processes. These processing techniques are sufficiently flexible to provide a wide variety of compositional

TABLE 21.1 Raw Materials Usage in U.S. Shortening[a]

	1940	1950	1960	1970	1980	1990	1997
	Million Pounds						
Coconut oil	18	20	10	45	103	34[b]	120[c]
Corn oil	1	1	4	12	18	270	74
Cottonseed oil	823	549	365	276	189	252	256
Palm oil	NR	NR	NR	90	188	98[c]	128[b]
Peanut oil	23	12	2	16	W	W	W
Soybean oil	212	841	1169	2182	2651	4004	4517
Lard	17	177	481	430	378	264	272
Tallow	58	31	267	546	673	637	312
Unidentified	44	96	3	2		125	
Total	1196	1727	2302	3599	4200	5684	5679

[a] NR, not reported; W, withheld.
[b] Estimated.
[c] Total edible.

structures. In this manner, the ratio of the structural triglycerides can be manipulated to form the desired solid fat indices (SFI) curves to produce the components for blending or complete shortenings. These factors have allowed shortenings to develop into unique food ingredients with a high degree of interchangeability among the available raw materials. Table 21.1 tracks the changes in the source oil utilization for U.S. shortenings from 1940 through 1997 (3,15–17). These data indicate that the shifts in raw materials used to produce shortenings can be attributed to technological improvements, economics, and nutritional concerns.

Lard usage as a shortening agent decreased to a low point in 1940 when cottonseed oil became the dominant source oil for shortenings. Soybean oil was beginning to challenge cottonseed oil for the vegetable oil position at this early date with 18% of the shortening volume. Hydrogenation of the shortening components reduced the unsaturated fatty acids that caused much of the offensive reverted flavors of soybean. The next decade, influenced by World War II, brought some dramatic changes in the source oil utilization of shortenings. A comparison of the 1940 and 1950 usage data shows that soybean oil replaced cottonseed oil as the dominant vegetable oil, and lard regained favor with the introduction of crystal-modified lard. Interesterification modified the triglyceride structure of lard to provide consistency, appearance, and creaming properties comparable to those of all-vegetable shortenings.

The shortage of vegetable oils during World War II had brought soybean oil from a minor, little known, problem-related oil before 1940 to a volume exceeding the vegetable oil of choice, cottonseed. After the war, these volume gains were in jeopardy unless technology could be developed to improve the flavor stability of soybean oil products. Fortunately, Germany had developed a cure for soybean oil reversion, i.e., treatment with citric acid to chelate prooxidant metals. This change, along with other processing improvements and controls, helped soybean oil reach a dominant position as a source oil for shortening in 1960, providing a little over 50% of requirements for this oil category. This dominance has been maintained and grown to almost 80% of the oil requirements for shortening in 1997.

Palm oil threatened to become a major raw material for U.S. shortenings in the mid-1970. It grew from a level too small to report in 1960 to >16% of the shortening requirement in 1975. Very attractive costs had forced fats and oils processors to investigate palm oil use wherever possible. Palm oil was found to be an excellent plasticization agent to force the crystal habit of shortenings to β'; it could be used to replace a portion of the hydrogenated base stocks, and it was an excellent frying shortening for some high-volume foods. The use of palm oil for shortening manufacture was primarily at the expense of cottonseed oil and tallow with a small threat to soybean oil. Unfavorable publicity severely decreased the use of palm oil in the U.S. by highlighting nutritional concerns with the effects of saturated fatty acids on atherosclerosis. Palm oil usage in shortening decreased steadily from 16% of the requirements in 1975 to 4.5% in 1980 and <1.5% in 1995. The U.S. usage level appears to be maintaining a range between 1.5 and 2.0% since 1990.

Both lard and tallow regained popularity as shortening raw materials in the mid-1950 era. Two major reasons for the improved status of these meat fats were that the major fast-food concerns were promoting the beefy flavor imparted to french fries by tallow frying shortenings, and interesterification of lard gave it performance characteristics equivalent to those of the hydrogenated vegetable oil shortenings. Later, in the 1970s, technology was developed to replace crystal-modified lard with tallow and vegetable oil blends, which had more attractive product costs. Meat fat usage in shortenings continued to grow as a result of attractive initial costs and a lower processing expense until concerns about cholesterol intake brought pressure on the major end users to provide food products that had better nutritional images. The share of meat fat usage in shortenings had dropped to the 20% range with the tallow/vegetable substitutions for crystal-modified lard and then dropped to about a 10% share with the cholesterol concerns. This level has been maintained since the beginning of the 1990s.

Coconut oil and the other lauric oils are not among the more desirable oils for most shortening products because of their short plastic range, tendency to foam when blended with other oils during frying, and the soapy flavor that develops with hydrolysis. However, the sharp melting characteristics are advantageous for cookie fillers, dairy analogs, candy fillings, and other products that require a rapid "get away" in the mouth. The lauric oils also have excellent frying stability when isolated from other oils due to their high saturated fatty acid content. Coconut oil also suffered from nutritional concerns regarding the saturated fatty acid content, which caused fast food restaurants to change to frying shortenings with a healthier image (2).

Corn oil has traditionally been a premium-priced oil but had some high usage years as a shortening ingredient, i.e., the period from 1989 to 1994. This was probably due to an increased availability resulting from the demand for high-fructose corn syrup. Corn oil can be hydrogenated to make an excellent frying shortening or base stock component for other shortenings to replace soybean oil base stocks. As a frying shortening, corn oil has the advantage that it reverts to a desirable musty flavor instead of the offensive flavors of some other vegetable oils.

Peanut oil is a premium-priced oil in the United States due to the fact that peanuts are grown for edible use and the existence of government price supports. The usage of peanut oil in shortenings is <1.0% of the total consumption. However, in the rest of the world, where peanuts are produced for oil and protein content, its usage for shortening-like products is much higher.

Shortening Consumption

Per capita shortening consumption is shown in Figure 21.1, comparing the changes in source fats and oils to the combined total (16,18). These data confirm that personal consumption of shortenings more than doubled between 1950 and 1985 and that vegetable oils are the dominant raw material. The increased popularity of shortening during this period reflects the changing eating habits of Americans in place, time, and frequency. Eating outside the home and convenience and snack foods experienced a sharp rise in popularity during this period. It has been estimated that >45% of the U.S. consumer's food budget is consumed away from home. These changes have affected the type and quantities of shortening required to meet the food service and food processor industry demands for specialty shortenings, while household shortenings experienced a decline. Shortening consumption slipped only slightly during the decade between 1985 and 1995 and then a sharper decline was experienced. Lard and tallow absorbed all of the losses until 1995 when vegetable oil shortening consumption was also affected. This 9% decline in shortening consumption is likely due to the following: (i) diet modifications to reduce saturated fats, *trans* isomers, and cholesterol; (ii) development of finished product formulations and processes to accommodate liquid oils; (iii) palatability improvement of fat-free products; (iv) reduced dependence on the crystalline properties of solid fats for functionality through the use of emulsifiers.

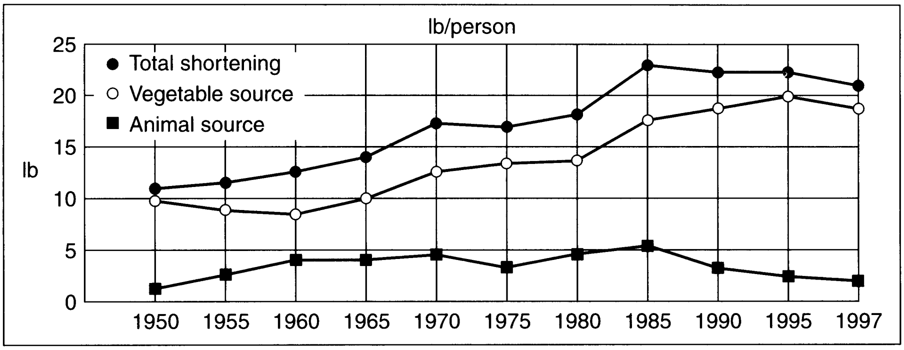

Fig. 21.1. Changes in source oil utilization for U.S. shortenings (1940–1997).

Shortening Attributes

Shortenings are functional ingredients that contribute heavily to the success of the food product prepared. Shortenings can be tailor-made for a specific food product and process or designed as a general-purpose product that must perform in varying conditions, product types, processes, and formulations. Adequate performance of a shortening for a food application depends on a number of factors. These requirements differ for each customers and/or application depending on the product formulation, equipment, processing, preferences, and other considerations. Therefore, performance is dependent upon the interwoven elements that determine acceptability.

Flavor

Generally, the flavor of a shortening should be completely bland, so that it can enhance the flavor of the food product rather than contribute a flavor. Bleaching and deodorization of the shortenings remove primary and secondary oxidation products. In some cases, shortening is the carrier for a flavor desired in the finished product. Flavor additives to shortening products are usually butter-like flavors, e.g., the butter flavor incorporated into most pan and grill shortenings. Also, the flavor of the source oil may be desired for a specific food preparation, e.g., a lardy flavor for pie crusts, a peanut flavor for English fried fish, or a musty corn flavor for corn-based snacks.

Flavor Stability

The bland, typical, or formulated flavor must remain stable throughout the shelf and use life of the prepared food product. Reverted or oxidized and hydrolyzed flavors and odors of most fats and oils are objectionable. Shortenings must possess the identified degree of resistance to both oxidative and lipolytic flavor degradation. Flavor stability is built into shortenings by selection of saturated or monounsaturated components, or processing to decrease the unsaturated fatty acid content. The processes that influence flavor stability are hydrogenation, fractionation, or interesterification. Flavor stability can be preserved after it has been established with the use of antioxidants.

Physical Characteristics

Shortenings are pictured as solid materials, but in reality are predominantly fluids. A plastic shortening consists of approximately one-quarter crystalline solid triglycerides suspended in liquid triglycerides. The ratio of these two phases determines the consistency of a shortening as it relates to firmness, softness, and spreadability. Fats and oils processors change the consistency of a shortening by manipulating the solids to liquid ratio over a range of temperatures. Three processes capable of altering the consistency of a shortening component are hydrogenation, fractionation, and interesterification. Fractionation processes make physical separations of the hard and soft fractions. Interesterification rearranges the position of the fatty acids in the triglycerides to affect melting characteristics. Hydrogenation, the most popular process for

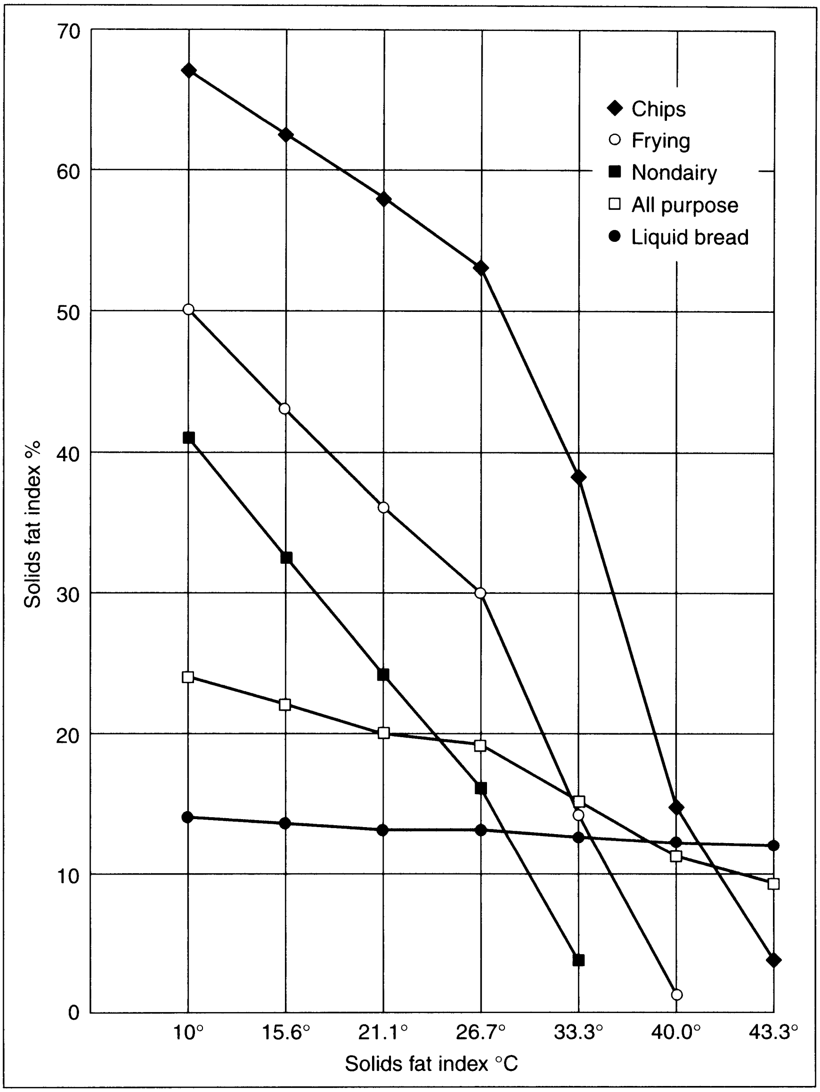

Fig. 21.2. Solid fat index (SFI) curves for five shortenings with different applications.

modifying solid/liquid ratios, saturates the unsaturated fatty acids to affect melting characteristics. The solid/liquid proportions of the shortening components can be altered somewhat selectively with these procedures to provide the physical characteristics most suited to the desired functionality. Figure 21.2 compares the SFI curves for five shortenings designed for different applications to illustrate changes in physical characteristics that can be effected for shortenings. The SFI analysis is an empirical determination of the moment at which a fat passes from a solid to a liquid at the measurement temperatures. A plot of the results produces a curve that illustrates the changes in solid and/or liquid content, which indicate the following:

- Consistency. The factor influencing the consistency of a shortening most directly is the proportion of the product in the solid phase. The consistency of a shortening at use, preparation, and storage temperature conditions materially affects the performance of the prepared food product. SFI curves characterize the firmness of the shortening over a range of temperatures and liquidity at mouth temperature, for development, selection, and control purposes.
- Plastic Range. Shortenings are normally plastic and workable for SFI values between 15 and 25. At an SFI value >25, shortenings start to become brittle; at <15, they become too fluid. The range of temperatures at which the SFI values remain within the 15–25% solids is usually referred to as the plastic range.
- Flat Solids Curves. SFI values that provide east-to-west directional slopes generally have a better plasticity because the product is maintained at the ideal consistency over a greater temperature range. This same attribute contributes a slower "get away" in the mouth due to melting points above body temperature caused by higher SFI contents over a greater temperature span.
- Steep Solids Curves. Poor plasticity but good mouth feel and oxidative stability are usually indicated by a north-to-south directional SFI slope. A narrower span of temperatures for the higher solids values provides sharper melting tendencies for better palatability and good oxidative stability. The preferred bland flavor is retained longer due to a lower unsaturated fatty acid content. However, steep SFI curves from hydrogenated products usually indicate a higher *trans* fatty acid content.

Crystal Habit

Fats and oils are polymorphic, which means that, with cooling, a series of increasingly organized crystal changes occur until a final crystal form is achieved. Each fat and oil has an inherent crystallization tendency, either β or β′. The tiny, uniform, tightly knit, needle-like β′ crystals produce smooth-textured shortenings with good plasticity, heat resistance, and good creaming properties. The large, high-melting, self-occluding, coarse, stable β crystals produce visibly grainy, sandy, brittle shortenings, which can experience separation of the liquid oil portion. Both of these crystal habits provide physical conditions desirable for particular functionalities; for example, β′ is ideal for cake and icings shortenings requiring good creaming and/or air entrapment capabilities, whereas β is preferred for pie crust shortenings in which a grainy consistency helps provide a flaky texture. Crystal habit can be controlled by source oil selection and complemented by the plasticization conditions employed; these include chilling, which initiates the crystallization process, and tempering, in which the desirable crystal nuclei are developed and stabilized.

Appearance

Appearance is one of the collective results of all of the following processes used to convert crude edible fats and oils into shortening: i) refining, bleaching, and deodorization are all involved in the removal of the color pigments; ii) hydrogenation, fractionation, or interesterification affect the SFI content which helps determine product consistency; iii) formulation determines crystal structure and SFI content for texture and consistency control; iv) chilling and tempering initiate, develop, and stabilize the crystal nuclei; and v) storage and transportation under proper conditions prevent product damage.

Nearly all plasticized shortenings contain 12–14% nitrogen by volume, added during the chilling process. The gas is finely dispersed to enhance creaming properties, control texture, and improve the appearance of the shortening. Shortenings containing creaming gas are creamy white in contrast to a yellow or green cast characteristic of Vaseline when no nitrogen is present.

Emulsification

The emulsifying properties of shortening are achieved by adjustment of the fat structure and/or the addition of surface-active agents such as mono- and diglycerides. Food emulsifiers supplement and improve the functionality of a properly developed shortening to act as a lubricant, emulsify fat in batters, build structure, aerate, improve eating qualities, extend shelf life, modify crystal development, act as an agent for antisticking, dispersal, and moisture retention, and more. Obviously, no single surfactant can perform all of these different functions. Emulsifier selection requires the same attention to functionality that is used to identify the other components for shortenings.

Antioxidants

The oxidation rate for a shortening depends primarily on the number of double bonds and their arrangement in the triglyceride. However, the oxidation process can be slowed down with the preservation of the natural antioxidants or the addition of synthetic antioxidants. Antioxidants are chemical compounds that delay the onset of oxidation. They function by inhibiting or interrupting the free radical mechanism of autoxidation; they function as a free radical acceptor, thereby terminating oxidation at the initial step. Tocopherols are the natural antioxidants contained in most vegetable oils. Phenolic compounds that provide antioxidant activities include butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), and tert-butylhydroquinone (TBHQ). Much of the success of the antioxidants depends on their being in chemical contact with the product they are protecting; therefore, various combinations of different antioxidants and chelating agents are generally combined for use. These combinations provide a synergistic effect to increase the effectiveness of the antioxidants and allow the incorporation of a chelating agent to sequester prooxidant trace metals.

Trace Metals

Vegetable oils pick up metals from the soil in which the plants are grown and later from contact during crushing, processing, and storage. Meat fats have similar metal contents obtained from feeds, during rendering, processing, and storage. Many of these metals promote oxidation, which results in off flavors and odors accompanied by color development. Studies have identified copper as the most harmful followed by nickel, manganese, chromium, and iron. Metal scavengers, added at low levels during processing before filtration, facilitate removal of the harmful metals. The most widely used chelating agent is citric acid, normally added at a rate of 50–100 parts per million (ppm).

Foaming

Polymerization occurs during frying to produce three-dimensional polymers, which result in an increased frying shortening viscosity. Foam develops on the surface when the frying shortening will no longer release moisture but keeps it trapped as steam vapor. Polymerization can be inhibited with the use of dimethylpolysiloxane, which has been labeled as an antifoamer. Dimethylpolysiloxane may be safely used in processed foods at levels not exceeding 10 ppm. The effective usage range to inhibit foaming for frying shortening has been identified as 0.5–2.0 ppm, which must be controlled strictly because concentrations >10 ppm will promote foaming. Additional control is also necessary to segregate the use of these additives to frying shortenings only; unintentional additions to bakery shortenings can lead to cake and icing failures, glazes that do not adhere to donuts, and snack foods that lack crispness.

Nutrition

Fats and oils are recognized as important nutrients for both humans and animals because they provide a concentrated source of energy, contain essential fatty acids, and serve as carriers for fat-soluble vitamins. Research studies have also indicated a relationship between saturated fats, cholesterol, and *trans* isomers and the incidence of coronary heart disease. In many cases, shortening functionality can be maintained with formulations limiting cholesterol, the identified saturated fatty acids, and *trans* isomers. Shortening formulation can also aid in reducing fat consumption by development of more effective products to reduce the levels required to produce the desired functionality.

Shortening Formulation

A myriad of food products exist that require shortening in their formulation. The word shortening no longer identifies a bakery function performed; it has emerged as a functional ingredient to satisfy the requirements of the entire food industry. Technology advancements have allowed the introduction of functional shortening products for all of the food industry. Specialty shortenings have helped improve existing food products and create entirely new food products for all areas of the food industry. Shortening products with desirable physical and functional end properties can be achieved by manipulating the melting and crystallization habits of edible fats and oils with processing and blending of different base oils. Shortening processors can produce a different hydrogenated, fractionated, or interesterified base oil for each different product or they can utilize a base stock blending system.

Base Stock Blending

The development of a base stock utilization program can be a definite asset for a fats and oils processor to provide production efficiency, product quality control, and cost containment. Production efficiencies result from the ability to prepare many different functional products from a few base stocks. For example, a hydrogenated base stock with a steep SFI and a melting point of 35°C can be used to make margarine, blended with another base stock to make a frying shortening, used for nondairy applications, function as a base for mono- and diglycerides, and as an application in many other blends to produce the desired SFI slope and melting point. This same aspect is true for the other components that make up a base stock system.

Efficiencies can also be realized through improved scheduling by maintaining a base stock inventory instead of reacting to customer orders. Production can also react to product orders more efficiently by the use of already prepared base stocks. Base stock blending enhances the quality of finished products by the ability to average the results of several batches and producing the same hydrogenated product more often; it eliminates the need for the processor to utilize heels from previous products that may not meet the SFI requirements or have experienced deterioration before use.

Base stock requirements will vary, depending on the product mix of the individual processing plant. A wide variety of fats and oils raw materials are available and used for shortenings as previously identified above. The processor must first narrow these choices by product performance, customer specifications, cost, religious prohibition, traditional preferences, legislation, transportation, and any other factor that affects functionality, expense, and above all, customer satisfaction. Most U.S. fats and oils processors probably have base stock systems dominated by soybean oil, with other fats and oils included for a specific function or preparation of a specialty product. The SFI curves for six hydrogenated soybean oil base stocks are plotted in Figure 21.3. Utilization of a system containing similar base stocks with the addition of a cottonseed or palm oil and a soybean oil hard stock, should enable a processor to meet most fats and oils product requirements by blending two or more base stocks, except for some specialty products that can be made only with special hydrogenation conditions and catalyst.

When formulating shortening blends it is necessary to consider the crystal habit of the base stocks available and their effect on the final crystal form of the shortening. When a fat is chilled rapidly from the liquid phase, the first crystals formed are in the α form. This form is unstable, and the crystals change their form to β'. The third polymorphic form is known as β, which is more stable than β' for many fats and oils.

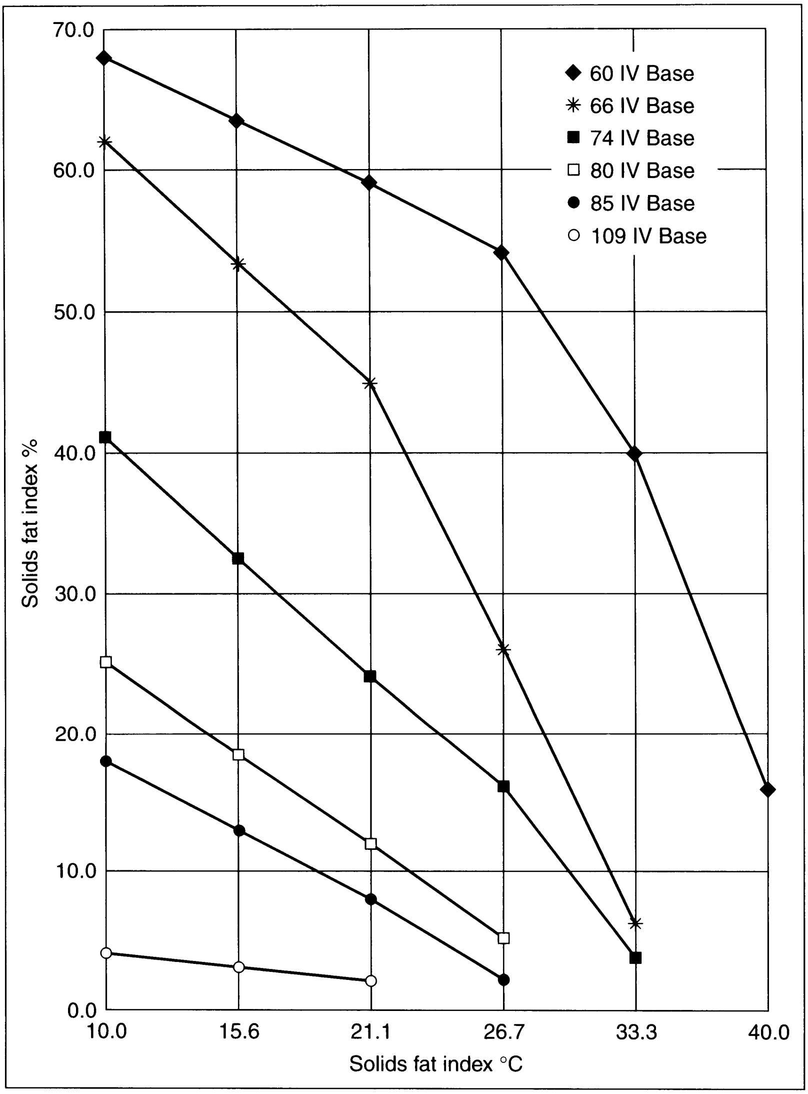

Fig. 21.3. Solid fat index (SFI) curves for six hydrogenated soybean oil (H-SBO) base stocks.

The crystal habit of hydrogenated oils and fats that could be used to prepare shortenings are shown in Table 21.2. β' is the desired crystal form for most shortenings because of the smooth texture it imparts to the product, and the enhanced creaming properties. For blending purposes, the ratio of β to β' crystal formers helps to determine the dominant crystal habit, but the higher melting triglyceride portions usually force the blend to assume that crystal form. In practice, shortening blends with

TABLE 21.2 Crystal Habit of Hydrogenated Oils and Fats

β Type	β′ Type
Canola	Butter fat
Cocoa butter	Cottonseed
Coconut	Herring
Corn	Menhaden
Lard	Modified lard
Olive	Palm
Palm kernel	Rapeseed
Peanut	Rice bran
Safflower	Tallow
Sesame	
Soybean	
Sunflower	

5–20% hydrogenated β′ oils can force the blend to crystallize in the β′ form. The dominant hydrogenated oil component must have a higher melting point than the other components for the entire product to crystallize in the stable β′ form (2,19).

Shortening Categories

Most shortenings are identified and formulated according to usage or performance. The SFI profile gives each shortening particular functional properties. Figure 21.2 illustrates the diverse SFI or melting point relationships among five shortenings formulated for different applications. All-purpose and other bakery shortenings require wide plastic ranges for use, handling, and spreadability at elevated as well as cool room temperatures. Steep solids curves provide the frying stability and eating characteristics ideal for frying shortenings and the sharp melting character for the palatability required for nondairy applications. Flat curves with low solids values provide the fluidity and crystallization seed for the opaque pumpable shortenings popular for their convenient handling characteristics. Finally, the steep high-solids curve for shortening chips provides resistance to incorporation during mixing but still has a satisfactory "get away" in the mouth for eating characteristics. These shortening products illustrate an approach to formulation development that requires identification of the key functional attributes that the shortening is expected to provide to the food product.

Wide Plastic Range Shortenings. The ultimate plastic range is produced with a blend of liquid oil and hard fat. Compound shortening formulation has always produced shortenings with a wide plastic range but poor oxidative stability due to the unsaturated liquid oil component. Replacement of the liquid oil with a partially hydrogenated base stock improves the oxidative stability of the shortening with a slight sacrifice in plastic range. A shortening with a wide plastic range could be formulated with ~90% of the 85 iodine value (IV) soybean oil base stock shown in Figure 21.3 and 10% cottonseed oil hard stock. A formulation with ~92% of the 80 IV soybean base stock and 8% soybean oil hard fat would provide an improved oxidative stability with a similar but slightly softer SFI profile, and the heat stability or resistance to high temperatures would be poorer. Utilization of a base stock firmer than the 80 IV hydrogenated soybean oil (H-SBO) can reduce the plastic range considerably.

The hard stock utilized for shortenings with a wide plastic range could be hydrogenated palm oil or tallow instead of the cottonseed oil hard stock mentioned earlier; all three have high palmitic fatty acid ($C_{16:0}$) content and crystallize in the β' crystal form. The amount of hard stock required to provide comparable SFI values varies, depending on the IV of the hard stock and the titer or solidification point. Vegetable oils, such as soybean, peanut, and corn, can be hardened to considerably higher titers than tallow or cottonseed and palm oils, but these hard stocks are not usually used for wide plastic range shortening formulation because they solidify in the undesirable β polymorphic form. This tendency and the high titer value are caused by a predominance of 18-carbon fatty acids (C_{18}), which forms tristearin triglycerides when hydrogenated. Tallow, cottonseed oil, and palm oil contain sufficient proportions of fatty acids with higher and lower carbon chains to ensure that little tristearin will be formed and a lower titer value will be obtained at the same degree of saturation as measured by IV.

The technique of blending a partially hydrogenated base stock with a hard stock to produce a wide plastic range has led to the existence of a whole family of shortenings for the baking industry. Figure 21.4 shows the progression of bakery shortening development from a compound all-purpose shortening to the specialty shortenings utilized for cakes, icings, fillings, roll-in products, mixes, or fillers (1,19). These developments have proceeded in the following two directions: i) base stock manipulation for performance or ii) the addition of an emulsifier or emulsifier system for functionality. Of course, a third and logical direction is a combination of these two development techniques.

Narrow Plastic Range Shortenings. Plasticity has a minor importance and can be a detriment for shortenings requiring a relatively quick melt at mouth temperature with a high oxidative stability. Shortenings designed for most frying situations, dairy analogs, cookie fillers, crackers, and confections require a flavor stability and eating characteristics not possible with blends of moderately hydrogenated base stocks and hard fats. These shortening products require a lower IV for oxidative stability, a steep SFI slope, and a complete melt at lower than mouth temperature to prevent a greasy or waxy sensation on the palate that can mask the characteristic flavor of the food product. The frying and nondairy shortenings plotted in Figure 21.1 are characteristic of steep SFI slopes for these applications.

Restaurant frying shortenings must meet the industry requirements of a stable heat-transfer medium, which becomes a part of the food to supply texture, palatability, and enhancement of the food flavor. Heavy-duty frying shortenings are usually composed of a single selectively hydrogenated oil or a blend of two selectively hydrogenated base stocks to produce high solids, which decrease rapidly to a melting

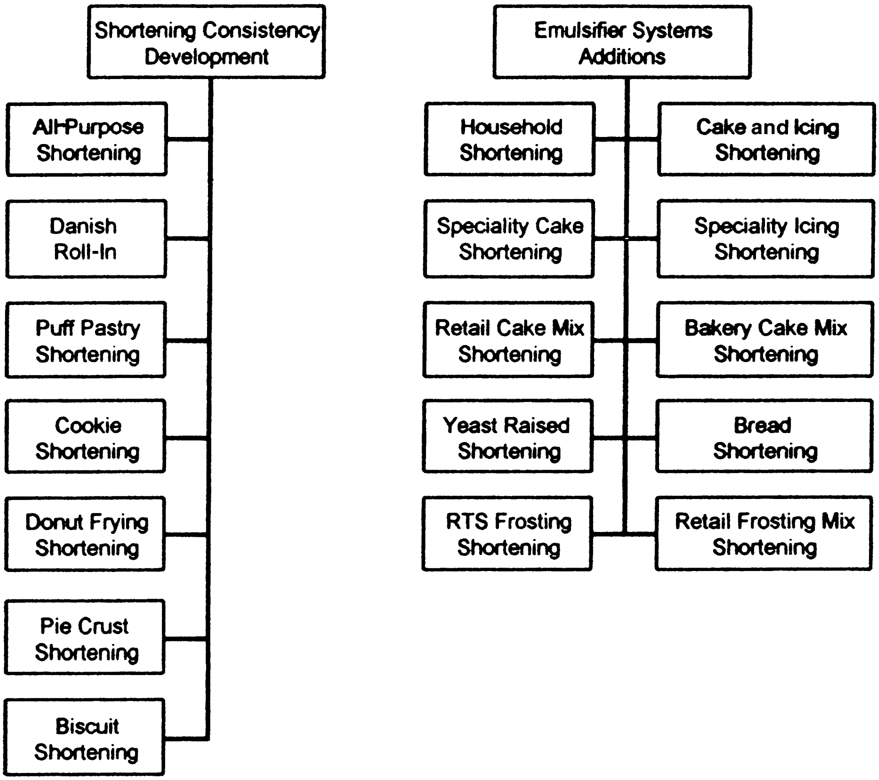

Fig. 21.4. Development of a bakery shortening from all-purpose to specialty use.

point just slightly above body temperature for the desired mouth feel. Selective hydrogenation provides the sharp melting characteristics with increased oxidative stability, which also relates to frying stability. The frying shortening plotted in Figure 21.1 is approximately a 40:60 blend of the 66 and 74 IV base stocks.

Shortenings for nondairy and confectionery applications require a steep SFI slope and a short melting range, which ensure a quick melt for a pleasant mouth feel and excellent oxidative stability. The nondairy shortening depicted in Figure 21.1 is prepared with the 74 IV soybean oil base stock illustrated in Figure 21.2. This selectively hydrogenated soybean oil has a solids slope and melting point similar to those of butter fat, which is the fat source for natural dairy products and many confection applications.

Liquid Opaque or Pumpable Shortenings. Before the introduction of emulsifiers, antioxidants, and antifoamers, shortenings relied on fatty acid composition, crystal habit, plasticization, and tempering to provide functionality. The aeration function of plastic shortenings was correlated with the polymorphic form of the triglyceride, whereas shelf life and frying stability were attained by the level of saturation to resist oxidation. Plastic shortenings that exist in the small β′ crystal form aerate batters much more thoroughly than those in the large β form, and saturation of the unsaturated fatty acids eliminates a reaction site for oxygen, thus extending flavor and frying stability. These rules are still applicable, but emulsifiers, antioxidants, and antifoamers have significantly reduced the dependence on the plastic consistency for functionality. This reduced dependence has allowed the development of liquid shortenings that combine the functional characteristics of plastic shortenings with the bulk handling characteristics of a liquid oil.

A liquid shortening is a stable dispersion of solids with the proper polymorphic form in a continuous oil phase that is both flowable and pumpable over a temperature range of 60–90°F or 15.6–32.2°C. The solids are derived from either hard fats or emulsifiers, and sometimes both. For some applications, the primary function of the liquid shortening is as a delivery system for emulsifiers that alter the characteristics of the food product. The liquid oil choice is governed by the specific end-use application. Finished products with short shelf life requirements can utilize unhardened oils, whereas those with shelf life requirements >7–10 d are formulated with a partially hydrogenated base stock for flavor stability. Oxidative stability is improved with the use of a lightly hydrogenated base stock, plus the addition of antioxidants and antifoamers, but it cannot approach the stability of a plastic shortening with these same additives.

The type and level of solids are important considerations for the development of a stable fluid suspension. In contrast to plastic shortenings, it is desirable to formulate β-stable blends, whose large crystals tend to form a stable dispersion. Normally, a low IV, β-forming hard fat is used to seed crystallization for liquid shortenings. The hard stock levels can vary from as low as 1.0% to higher levels, as required to produce the required viscosity, usually no higher than 10%. The ease with which β-forming hard fats convert to the stable β crystal form makes them ideal for liquid shortening crystallization. The β crystals do not intertwine to form a matrix that can enmesh the liquid phase and form a thick product as found with β′ hard fats. The liquid opaque shortening SFI slope plotted in Figure 21.1 is typical of a liquid bread shortening formulated with 10% soybean hard fat crystallized in 90% unhardened soybean oil.

Shortening Flakes and Chips. Another shortening form is represented by flakes and chips, i.e., solidified thin flakes and thicker chips. These shortening products utilize both the steep and flat SFI slopes produced with selective and nonselective hydrogenation techniques, depending on application. Shortening chips are designed to resist incorporation into doughs and batters during mixing and still have a palatable mouth feel. Steep SFI base stocks with high solids contents at 50–80°F (10–26.7°C) and declining rapidly thereafter provide this functionality. The shortening chip profile in Figure 21.2 was made with a 90:10 blend of 60 and 66 IV H-soybean oil base stocks. Nonselectively hydrogenated oils are used to formulate stabilizer shortenings. An icing stabilizer's performance requires a flat SFI slope to maintain a soft consistency with solids contents high enough to facilitate a rapid set. The rapid set allows the icing to resist finger printing when handled, whereas the flat SFI slope allows the icing to retain an elasticity to prevent product brittleness and flaking.

Plastic Shortening Crystallization

The following three processes influence the functionality of solidified edible oil products: (i) formulation, consisting of the source fats and oils choice and the hydrogenation, fractionation, or interesterification techniques used to prepare the base stocks; (ii) chilling, which initiates the crystallization process; and (iii) tempering, during which the desirable crystal nuclei are developed and stabilized. Formulation, the first requirement has been reviewed in the preceding section. Chilling and tempering which develop, mature, and stabilize the desired crystal structure introduced by the product composition are reviewed in this section.

Shortening plasticity and consistency depend on the amount of the solid materials at particular temperatures, as well as on the development of the crystal nuclei capable of surviving high-temperature abuse to serve as starting points for new desirable crystal growth. The mechanical factors influencing crystallization and plasticity are chilling, working, creaming gas, pressure, and tempering. Each of these is individually and collectively important; shortening performance can be adversely affected if any of these processes do not conform to the standards established for each individual shortening. Table 21.3 summarizes the effects of the crystallization processes on shortening consistency (20), which is discussed in greater detail in the following sections.

Chilling

The body and functionality of a plastic shortening are influenced significantly by the size of the crystals formed during the solidification process. A shortening becomes progressively firmer as the average size of the crystals decreases, and softer as the crystal size increases. A shortening that has been melted and allowed to crystallize slowly under static conditions will contain many large crystals plainly visible to the eye. Crystals formed in the same shortening by rapid chilling methods will be microscopic in size. Quickly chilled product with very small crystals will be firmer and

TABLE 21.3 Influence of Crystallization Process Variables on Shortening Consistency

Plastic	Process	Brittle
13 ± 1%	Gas incorporation	None
Cold	Chilling	Warm
More	Mechanical working	Less
High	Pressure	Low
85 ± 5°F	Tempering	Cold

will have a plastic range much wider than that of a slowly crystallized fat. The slowly crystallized product will also be softer than the rapidly chilled shortening.

A very critical and complicating factor in plasticization of shortenings is the supercooling property of triglycerides. A fat can remain liquid when chilled below its melting point. Due to this fact and because fats are polymorphic and can crystallize in two or more forms, the solidification and plasticization process requires careful control. The degree of supercooling and the temperature at which the supercooled product is allowed to reach equilibrium are related directly to the temperature range over which the product will be workable. In practice, the temperature to which the product is supercooled, worked, and packaged is controlled to produce the widest plastic range for the individual product formulation. Additionally, the extent to which the shortening is supercooled can affect not only the consistency, but also the melting point of the solidified product.

Mechanical Working

Solidification of a supercooled shortening without working or agitation will produce a firm consistency and a narrow plastic range. The product will also lack smoothness of texture and have a nonuniform appearance. Solidification without working allows the fat crystals to grow together to form a crystal lattice with greater strength than that of the same product with the crystals broken into smaller discrete particles. Therefore, for optimum plasticity, the supercooled shortening must be mechanically worked during this crystal formation period until substantially all of the latent heat of crystallization has been dissipated. The degree of work applied to shortenings differs due to the finished product consistency desired. A semifluid condition is preferred at the package filling station.

Gas Incorporation

Creaming gas, preferably an inert gas such as nitrogen instead of air, is incorporated into most plasticized shortenings at 13 ± 1%. The reasons for the addition of creaming gas to these products are as follows: (i) white creamy appearance; (ii) bright surface sheen; (iii) easier handling; (iv) texture improvements; (v) homogeneity; and (vi) increased volume. The correct gas content is important for shortening appearance and stability. Shortenings without creaming gas develop a Vaseline-like appearance, and too low a gas content gives a yellowish greasy appearance. High creaming gas levels cause a dead-white chalky appearance with a lifeless-looking surface and often large air pockets within the product, which give a puffy feel or consistency. Nonuniform gas dispersion gives an unattractive streaked appearance.

Tempering

Tempering is performed to control the consistency and plasticity of the shortening; it involves a relationship between temperature and time. During the tempering period, the heat of transformation must be dissipated as rapidly as possible. If the shortening is allowed to retain this heat by virtue of its normal thermal-insulating capacity, an appreciable portion of the crystal might be melted, and the subsequent gradual cooling under normal storage conditions will tend to promote transformation of the remaining crystal to the undesirable β form.

Tempering usually consists of holding the packaged product in a quiescent state at a temperature slightly above the fill temperature for ≥40 h. During tempering, the crystals transform to the polymorphic form in which they normally exist under ordinary conditions. In practice, a tempering holding temperature of ~85°F for 24–72 h or until a stable crystal form is reached is used by several shortening processors. The primary purpose of tempering is to condition the solidified shortening so that it will withstand wide temperature variations in subsequent storage and still have a uniform consistency when brought back to use temperature, normally 70–75°F or 21.1–23.9°C. Slow crystallization during tempering favors crystal growth, which extends plasticity for improved creaming properties and baking performance.

Plasticization Equipment

One of the early mechanical means of solidifying shortenings was with a chill roll, which was refrigerated internally by circulating chilled brine water. Melted shortening was fed into a trough from which a thin film of fat was picked up as the roll revolved and crystallized into a semisolid state during each revolution. A doctor blade removed the solidified fat film, which fell into a trough equipped with a rotating shaft with metal fingers, called a picker box; the picker box worked or mixed the product to make it homogeneous and to incorporate air. After working, the shortening was transferred to filling machines and packaged. Chill rolls are still used to flake hard fats, shortening chips, stabilizers, and other specialty products. For plasticized shortenings, however, the chill roll system had many inherent defects such as moisture condensation on the roll surface, lack of product uniformity, and poor thermal efficiency.

The chill roll deficiencies were overcome by the introduction of closed chilling machines, which incorporated the use of scraped-wall heat-transfer units. Development work aimed at equipment for freezing ice cream led to the perfection of a continuous internal chilling machine that was soon applied to the plasticization of shortenings. The Votator system was the first such process and remains a popular installation. The sequence of operation for a Votator system in the solidification of a shortening is described below (1).

> From holding tanks, the melted shortening is fed to a small float-controlled supply tank, from which it is picked up by a gear pump and forced first under pressure through a coil-type cooler, where its temperature is reduced to no less than 10°F or 5.6°C above the product melting point. Nitrogen to be dispersed in the product is admitted in controlled flow into the suction of the pump, and then the product passes through one or more of the chilling cylinders called "A" units. Inside each Votator "A" unit, a mutator shaft, equipped with float-

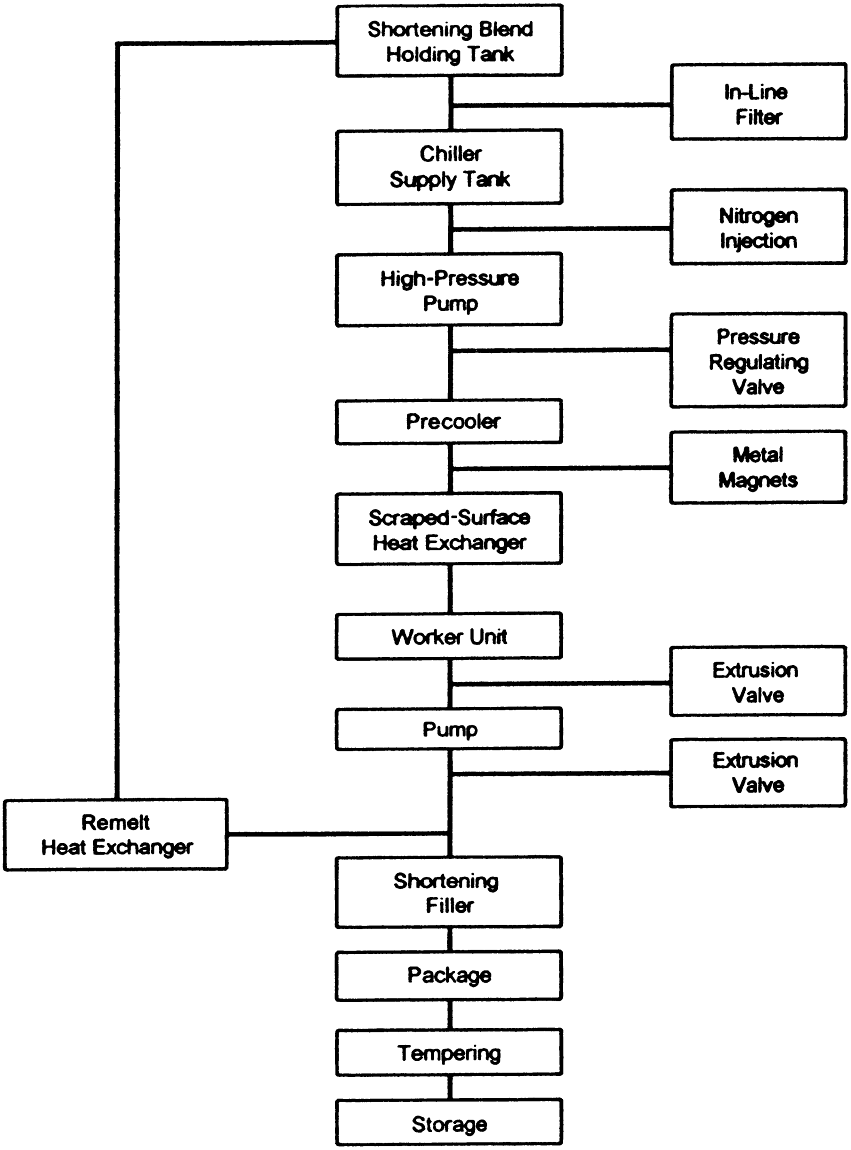

Fig. 21.5. Typical process flow of shortening plasticization in the United States.

ing blades, rotates to continuously scrape the product film from the cylinder wall. The product passes through an annulus formed by the shaft and heat-transfer tube. Heating and cooling media flow in an insulated jacket to minimize energy loss and protect personnel. Within a period of 9–18 s, the shortening is chilled to the previously identified desired temperature, probably in the range of

> 60–70°F or 15.6–21.1°C. It leaves the chilling cylinders in a supercooled and highly fluid condition, but with nuclei established for the formation of a very fine crystal structure. Crystallization is substantially completed in closed cylinders, known as "B" units, which are somewhat larger than the chilling units and equipped with rotating shafts set with projecting fingers. These fingers are placed on the shaft in a spiral manner, to produce a helical movement of the shortening through the cylinder, and they intermesh with similar stationary fingers projecting from the cylinder wall. The "B" unit is not jacketed or cooled; its function is merely to maintain the fat in a state of uniform agitation while crystallization proceeds. If shortening is filled directly into containers from the chilling cylinders, and allowed to crystallize therein in a static condition, it will be of poor texture and excessively hard. In the "B" unit, the temperature of the shortening rises several degrees through liberation of its heat of crystallization. A second pump takes the fat from the "B" unit and forces it at 250–400 psig through a homogenizing valve and thence to the package filling equipment.

In addition to the Votator process, there are at least two other systems that employ scraped-wall heat exchangers. The Gerstenberg and Agger system is manufactured in Denmark and the "Kombinator" apparatus is manufactured by Schroeder and Co., Germany. All three systems operate in a somewhat similar fashion. Figure 21.5 (2) depicts a typical shortening plasticization process flowsheet in the United States, beginning when the deodorized shortening blend has been transferred to the chilling unit supply tank and all of the specified additives have been incorporated.

Liquid Shortening Crystallization

The crystallization process for liquid shortenings shares equal importance with the product formulation to provide a β crystal matrix in a concentration that will maintain a viscosity low enough for pumping or pouring but high enough for a prolonged stable suspension. Fluid shortenings are suspensions of hard fats, emulsifiers, and/or additives, in liquid oils formulated and processed to be pourable or pumpable at room temperature and stable in storage over a range of temperatures. Liquid shortening processing involves controlled crystallization of the product before filling or shipping to provide the desired consistency. A liquid shortening is a stable dispersion of solids with the proper polymorphic form in a continuous oil phase that is both flowable and pumpable over a temperature range of 60–90°F or 15.6–32.2°C. Almost all liquid shortenings are milky-white in appearance due to the dispersion of hard fats in the form of microcrystallization particles, which do not settle out because of the crystallization process.

Most fluid shortenings are composed of components that are stable in the β crystalline form. Stearic fatty acid esters readily crystallize out of the liquid oil and form a stable crystalline matrix. A stable fluid system in the β crystalline form will not increase in viscosity or gel once it is properly crystallized. The rate at which a fat transforms into its stable form is important in liquid shortening processing

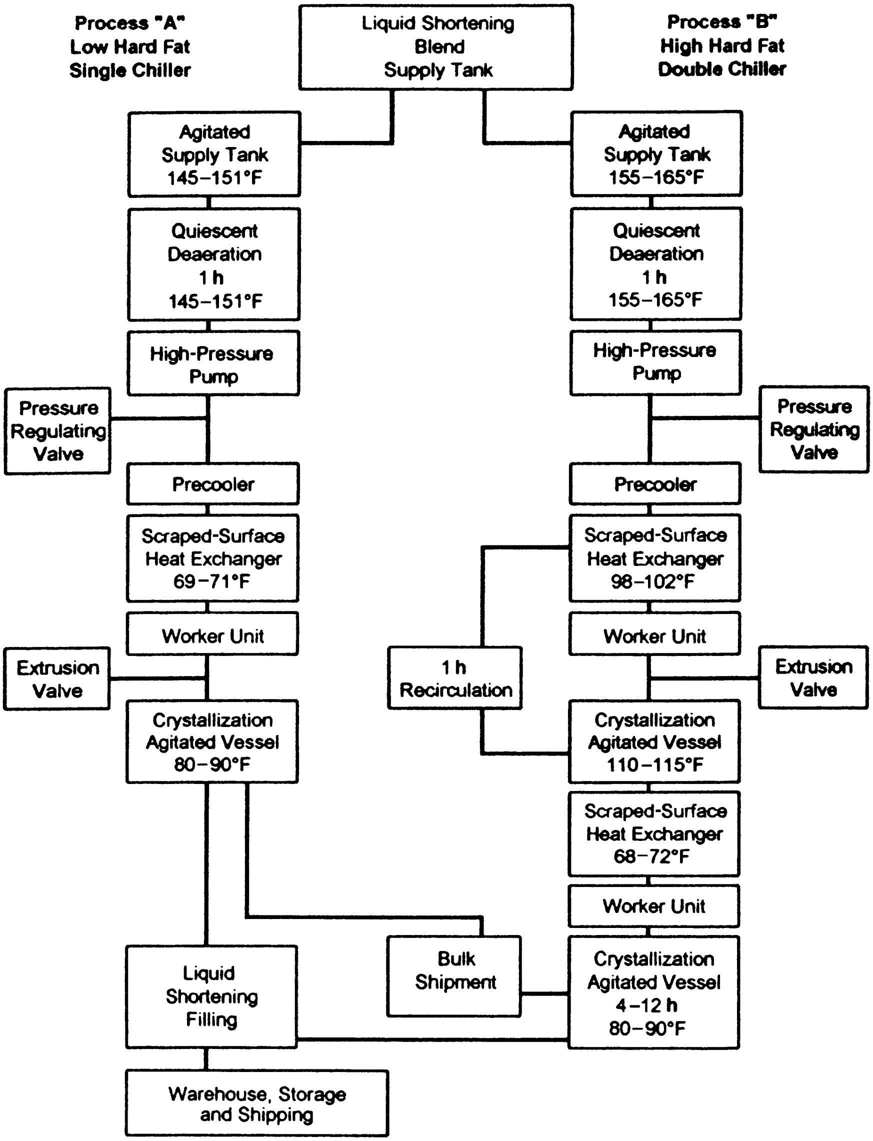

Fig. 21.6. Examples of two liquid shortening processing procedures.

because it must be in the stable form before packaging to avoid solidification in the package. Therefore, transformation to a stable crystal form must be accomplished in the shortest time possible. The quickest transformation of a liquid shortening blend into its stable crystal form can be attained by the following procedure:

1. Heat the liquid shortening blend until completely melted.
2. Rapidly cool the blend to just below the α crystal melting point. Theoretically, the α melting point is very near the lower limit to which fatty materials can be cooled without forming crystals. This point may be identified with the use of AOCS Method Cc 6-25 (21), which determines the temperature at which a cloud is induced in a fat caused by the first stage of crystallization.
3. Heat the blend to just above the β′ crystal melting point but below the β crystal melting point. The β crystal melting point or the highest melting form may be estimated with AOCS Method Cc 1-25 (21) for capillary melting point.

Many different processes have been proposed and patented for preparing liquid shortenings. Most of the processes require rapid chilling of the product with a scraped-surface heat exchanger followed by a crystallization period in an agitated vessel; these processes are in agreement on several points as follows: (i) all are dispersions of solid and liquid fractions; (ii) β-forming hard fats are the preferred solid fraction to seed crystallization; (iii) the heat of crystallization must be dissipated before a stable product is achieved; and (iv) aeration of the product must be avoided before, during, and after crystallization for viscosity control and to prevent separation. Two liquid shortening processing procedures are diagrammed in Figure 21.6. Process "A" is proposed for liquid shortenings with hard-fat levels <5% and Process "B", which requires more process time, is proposed for products with >5% hard fat or emulsifier additions (2).

Flake and Chip Crystallization

Shortening flakes and chips describe the higher melting edible oil products solidified into a thin flake form for ease of handling, quicker remelting, or for a specific function in a food product. Chill rolls, utilized for the chilling of shortening and margarine before the introduction of scraped-wall heat exchangers, are still used to crystallize fat flakes. The product formulations have been adapted to produce several different flaked products with distinctive performance characteristics in formulated foods. One of the distinguishing differences among the flaked products produced are the melting points as shown in Table 21.4.

TABLE 21.4 Melting Points Ranges of Various Flaked Products

	Melting point	
Product	Range (°F)	Range (°C)
Hard fats or stearines	125–150	51.7–65.6
Shortening chips	110–115	43.3–46.1
Icing stabilizers	110–130	43.3–54.4
Confectioners fats	97–112	36.1–44.4
Hard emulsifiers	140–150	60.0–65.6

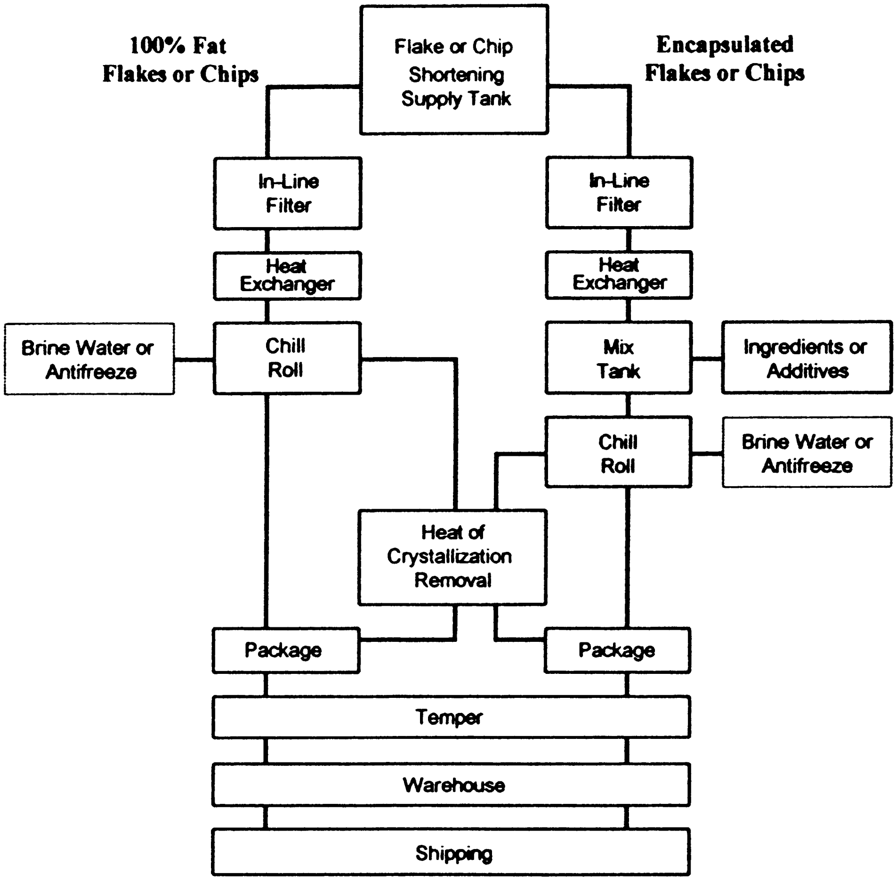

Fig. 21.7. Process flow diagram for flake and chip production.

All of the flake and chip products can be produced as 100% fat products or to encapsulate other ingredients. The purpose of encapsulating other ingredients in fat flakes or chips is to provide a specialize performance trait, such as the following: (i) separate reactive components within a mixture; (ii) mask objectionable flavors, colors, or aromas; (iii) protect unstable components from the environment; (iv) provide a controlled release and release rate; (v) reduce hygroscopicity; (vi) improve particle flow; or (vii) reduce dustiness. A process flow diagram for flake and chip production is presented in Figure 21.7, which shows flow diagrams for 100% fat and encapsulated flake products.

Chill Roll Description

A chill roll has been described as an endless, moving chilling surface, held at a temperature below the crystallization point of the applied fat or oil product to form a congealed film on the outer surface. After solidification, the product is scraped from the drum by a doctor blade, conveyed to a filling station, and filled into a suitable container for shipment. Chill rolls were used for crystallizing shortening and margarine before the introduction of the scraped-wall heat exchanger, which provided a more effective and efficient method of plasticizing those products. Chill rolls continued to be used for the production of hard fat or stearine flakes and were later adapted to produce specialty flake and chip products.

Chill rolls are available in different sizes, configurations, surface treatments, feeding mechanisms, but those used for edible fat products are usually hollow metal cylinders, 4 ft in diameter and either 9 or 12 ft in length, with a surface machined and ground smooth to true cylindrical form. The chill rolls are refrigerated internally with either flooded or spray systems, and turn slowly on longitudinal and horizontal axes. Several options exist for feeding the melted oil products to chill rolls, i.e., (i) a trough positioned at the center of the roll; (ii) a trough arrangement positioned at varying locations on the top quarter section of the roll; (iii) a dip pan at the bottom of the roll; and (iv) a header feeding product to a space between the chill roll and a smaller applicator roll. After application, a thin film of liquid fat is carried over the roll, and as the revolution of the roll continues, the fat is partially solidified. In all of the chill roll designs, the solidified fat flake is scraped from the roll by a doctor blade positioned ahead of the feeding mechanism.

Crystallization of Flake and Chip Shortenings

During fat crystallization, two types of heat must be removed, i.e., sensible heat and heat of crystallization. The heat removed to cool the fat to just above the melting point is sensible heat. This identification has been applied because the temperature decrease during this period can be sensed or measured. When crystallization begins at the solidification point, heat is generated; therefore, this process is called heat of crystallization. During flaking, sensible heat is removed quickly, and the product is supercooled sufficiently to initiate rapid crystallization. The sensible heat and heat of crystallization generated while the product is on the chill roll surface are absorbed by the cooling medium inside the chill roll.

The coolant in the chill roll must absorb 0.5 cal/g/°C of heat during the sensible heat removal; this period starts when the liquid fat is picked up by the chilled surface and lasts until solidification begins. The heat generated and released during crystal development is considerably more than the sensible heat. The degree of heat generated by crystallization is determined by the triglyceride composition. Peter Wan lists the heat of transition or crystallization for several different triglycerides and specific or sensible heat in Chapter 2 of this volume. In all cases, heat removal requirements during crystallization are 100 times greater than those during cooling to solidification for sensible heat removal.

Crystallization of the flake continues after it is removed from the chill roll, and more heat is generated. The heat generated after removal from the chilled surface causes a temperature rise in the package unless it is dissipated by further cooling before filling. The product temperature can increase enough to initiate partial melting of the flake, causing it to fuse together and produce lumps. Several different methods of removing the heat generated by crystallization have been evaluated. Successful procedures absorb or remove the heat generated to prevent a temperature rise high enough to cause crystal reversion to the α and liquid forms.

Flaking Conditions

Chill roll operations have four different controls for shortening flake and chip production. Each product type and some individual products within a product type will require different operating conditions to produce the desired product. The controls and their effects on the finished flake or chip are discussed below.

Oil Temperature. The oil temperature to the roll must be above the melting point of the product to avoid precrystallization but not too hot to prevent flavor and color degradation. Product thickness and solidification time can be controlled somewhat with feed oil temperature adjustment. Product viscosity decreases as the temperature increases to produce a thinner flake, whereas lower temperatures increase viscosity to produce a thicker flake. Lower temperatures speed up the solidification process, and higher oil temperatures increase the time period before solidification occurs.

Oil Level. The product level in the feed mechanism controls the amount of product available to the chilling surface for thicker or thinner flakes, which also affects heat removal.

Coolant Temperature. The type of coolant used and the coolant flow rate can be adjusted to control the chill roll's surface temperature. The coolant temperature must provide sufficient cooling to solidify the flake as completely as possible before removal but must not be so cold that it causes the solidified film to pull or pop away from the chilled surface to discontinue heat absorption from the flake.

Chill Roll Speed. Increased roll speeds produce thinner flakes, reduce solidification time, and increase production rates; decreased roll speeds produce thicker flakes, increase solidification time, and decrease the production rate.

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Chapter 23

Margarine Types and Preparation Technology[a]

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Introduction

Margarine is a semisolid fatty food emulsion designed to resemble butter. The physical characteristics of margarine, including appearance, color, texture, aroma, flavor, and energy content are equivalent to those of butter. Margarine is a French invention, born of economic necessity for a reasonably priced alternative to butter. In 1869, Napoleon III of France offered a prize to anyone who could invent an inexpensive substitute for butter. The Industrial Revolution caused large numbers of people to leave farms to work in factories in the cities, and the rising population of the cities created a demand for butter that could not be met in sufficient quantities; thus, butter prices soared. The situation was particularly bad in France, then in the throes of a severe depression. Most of its citizens simply could not afford to pay the high price farmers asked for butter. Moreover, the Army desired a butter substitute for use because war with Prussia threatened and then materialized the following year. Napoleon therefore called for a new, less expensive, and more readily available high-energy food fat. A chemist named Hippolyte Mege-Mouries came through with an idea that won the imperial prize the same year it was offered. He named his brainchild Margarine after the Greek word for "pearl-like" because the new product had a pearly luster when crystallized. It was made principally from oleo oil, an oil derived from beef fat, which Mege-Mouries churned with butter and flavored with salt. His margarine was primitive compared with present-day standards and actually bears only a historical relationship to margarine. It was very firm when cold and was approximately equivalent to butter in nutritional value. It was an outstanding achievement for its time (1).

During the next decade, it gained increasing favor throughout Europe; as early as 1874, it was manufactured in the United States, but from oleo oil. The first primitive refining techniques did not make large-scale production and distribution of "artificial butter" (as one early U.S. patent referred to margarine) economically feasible, but as techniques improved,the volume of sale, though still relatively small, was sufficient to attract political attention. Against the background of general discontent among the dairy farmers of the United States, laws that required either prohibition of margarine or imposition of a tax on it were proposed.

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[a] Richard J. Bell, author of Chapter 11, Shortening and Margarine Products, in the first edition of this book, died on April 1, 2000. This revision is dedicated to his memory. Many of his words are incorporated here.

In 1886, Congress passed the first of a series of antimargarine laws, which were to last for 64 years. The Oleomargarine Act of 1886, together with some subsequent amendments in 1902 and 1930, imposed taxes on white, and then on yellow margarine. It also required that the new table fats be labeled oleomargarine; for this reason we still hear the term "oleo." Despite restrictive legislation by both Congress and the states, there was a slow but steady growth in margarine sales as manufacturers began experimenting with the use of other fats and oils. It was not until 1954 that margarine sales equaled those of butter in the United States (2).

Historical Milestones

The history of margarine in the United States is a series of changes in process and composition, all directed to economic advantage. A brief outline follows.

1890	Bacterially cultured milk was used to provide flavors.
1917	Animal fats were replaced by coconut oil.
1923	Vitamin A was added to margarines.
1934	Hydrogenated vegetable oils replaced coconut oil.
1941	Margarine composition was defined by Federal Standard of Identity.
1947	Coal tar–based colorants were replaced by β-carotene.
1950	Margarine Act passed by U.S.Congress, abolishing federal taxes on the product.
1952	The first soft spreading margarines appeared.
1956	Margarine blends of vegetable oil and butter fat were marketed.
1957	Margarine overtook butter in U.S. per capita consumption.
1957	Whipped stick margarine was marketed.
1964	Soft margarine was distributed nationally as a mainstream grocery item.
1966	Diet margarine (40% fat) was introduced.
1967	Fluid, pourable margarine was developed and introduced.
1975	Lower-fat spreads (typically 60% fat) were introduced.
1981	Butter/margarine blends were introduced to the national market.
1981–1997	Lower-fat spreads proliferated.
1991	U.S. Nutritional Labeling and Education Act was passed by U.S. Congress.
1991	No-fat margarines appeared.
1998	Cholesterol-reducing spreads were introduced.

Types of Products

Margarines and spreads are best classified by physical form:

- Solid products are bulk cubes of 50 lb or 25 kg (55 lb), packed for institutional food processor or food service consumption.These products are typically formulated specifically for the intended use, and generally are of more firm structure and higher solid fat content than retail margarine. Typical use is in general baking, with additional usage in layered pastries. Other types of solid margarine are brick and stick, packaged conveniently for consumer use. Solid margarine is packaged also in individual servings of 5–14 g, distributed *via* food service operators.

- Brick margarine is typically 1 lb net weight, paper- or foil laminate–wrapped, and packed 24–36 lb/case. Customary uses are in general cooking, pan-frying, basting, and the like. The products are similar to retail formulations in texture, flavor, and consistency.
- Stick margarines are made for household kitchen and table use; they are typically packaged 4 sticks/lb. These products are wrapped in paper or laminated foil, then packaged in a carton of paperboard and packed in cases of 12–36 lb. The lower-weight cases are recent developments to address inventory management programs among grocers, who count case turnover rather than actual poundage. It may be of interest that in the United States, two styles of stick margarine are found. The Eastern stick is marketed east of the Rocky Mountains and is packed either in flat units or in "two over two" cartons. The Western style product is shorter in length, but larger in width and breadth. The two styles arose from availability of packaging equipment in the respective market areas.
- Soft products are generally intended for direct use for spreading on breads. Retail products are packed in twin cups of 8 oz net weight, sleeved two per pound, or in 16-oz tubs.
- Whipped products are soft or stick products into which nitrogen is injected at manufacture, with the primary intent of expanding the volume for economy of serving. Typical volume expansion is ~50%, yielding 6 sticks/lb, or 24 fluid oz at net weight of 16 oz.
- Liquid margarines are typically formulated to be resistant to solidification at refrigerated temperatures while maintaining structure of the emulsion. Typical uses are as a topping for hot vegetables, waffles, pancakes, or popcorn.

Margarine conforming to the U.S. Standard of Identity may not be sold in packages >1 lb at retail. Many lower-fat spreads are packaged for retail sale in units of 2 or 3 lb or more. Soft products for food service use include portion control cups of 5, 7, 10 or 14 g. Soft product is occasionally seen in single-serving pouches.

The Regulatory Identity of Margarine (3)

Title 21, Section 166 of the Code of Federal Regulations (21 CFR 166) defines margarine labeling and composition. The labeling provision of this section requires that the word "margarine" or "oleomargarine" must appear on the principal display panel in type or size at least as large as any other type or lettering. Other regulations require listing of ingredients in the product, with the exception that proprietary flavorant substances may be identified as "artificial flavor." The composition provision of the 21 CFR 166 (4) requires the following:

1. Margarine must contain at least 80% fat, and be made from edible fats and/or oils or mixtures whose origin is vegetable, rendered animal carcass fats, or any form of oil from a marine species that has been affirmed as generally regarded as safe (GRAS) or listed as a food additive.
2. Margarine must contain water and/or milk and/or milk products or suitable edible protein. These materials must be pasteurized.
3. Vitamin A at a concentration ≥15,000 IU/lb is also required.
4. All other ingredients in margarine are optional, including vitamin D, salt, nutritive carbohydrate sweeteners, emulsifiers, preservatives, color additives, flavorings, acidulants, or alkalizers.

Margarine Fat

The triglycerides provide structure, lubricity, energy density, and satiety to the product. Physical properties of margarines and spreads, especially texture, spreadability, color, appearance, and melting profile are functions of the structure of the fat and the processing conditions used in manufacture. Margarines and spreads are composed of liquid oil, solid fat crystals, and the aqueous phase. The crystals give margarine the required consistency and stabilize the water droplets. The fat crystals are in effect frozen oil (4).

Margarine, a water-in-oil emulsion, is a semistable suspension of dispersed aqueous materials within a continuous matrix of fat. The predominant vegetable oil in the United States is soybean oil, a by-product of soybeans. The soybean is grown to produce proteins for animal and human foodstuffs; soybean oil comprises ~18% of the soybean. Additional vegetable oils used in margarines are corn, cottonseed, safflower, sunflower, and palm. Lauric oils are seldom seen. Oils of marine origin that are considered GRAS by regulatory bodies are permitted also. Lower-priced margarines, especially in private-label segments, may contain lard, beef tallow, or combinations of these with soybean oil.

Margarine fats are generally blends of hydrogenated and nonhydrogenated oils mixed in appropriate proportions for functional effect. The functional effect can be predicted from the measurement of solid fat index (SFI), which is the ratio of solid fat to liquid fat at specified temperatures. Hydrogenation is energy intensive, and also produces *trans* fat isomers. Partially hydrogenated oil use in margarine is generally minimized for economic as well as functional effect. For example, stick margarine fat may be a blend of 50% partially hydrogenated soybean oil of iodine value (IV) 68 and 50% refined, bleached, and deodorized liquid soy oil of IV 135. Tub margarine may be a blend of the same components, with the sole difference being the ratio of liquid oil to hard fat at 2:1 rather than 1:1 as for stick product. The liquid product may be a blend of ~98% liquid soy oil and 2% almost fully hydrogenated soybean oil. Bakery products typically combine partially hydrogenated oil and liquid oil with a low-IV β′ hard fat to maintain structure in warm bakeries.

Aqueous Components

The dispersed phase typically contains droplets 1–20 μm in size. The primary aqueous material is water, to which may be added skim milk, salt, and water-soluble preservatives, and/or flavorants. A typical salt concentration in the finished margarine is ~1.5%. Skim milk, whey, or other edible proteins are added to enhance the release of the flavors and to permit the margarine or spread to perform similarly to butter in shallow pan frying. Milk solids and protein will brown in the pan, leaving a golden color for frying. Water-based margarines contain no milk products. Lactic acid, if added, is both a flavorant and an acidulant. Addition of ~0.05–0.1% lactic acid will reduce the typical serum phase pH to <5.5, which increases the effect of the preservatives. The preservative system in a margarine or spread may be a mixture of potassium sorbate and sodium benzoate, each added at ~0.10% by weight. These preservatives are added to sustain the resistance to microbial spoilage after the package has been opened.

Spreads

Since 1975, there has been increased emphasis on "spreads." There are many new varieties of margarine products in addition to conventional table-grade margarines. Most of the new retail products focus on lower-calorie products; others are blends of margarine and butter. The 80% fat products include stick, soft (tub) and liquid (squeeze bottle). Two substitute types are the vegetable oil spreads, which have less total fat than regular margarine, and the diet, or reduced-calorie margarines, which have about half as much fat. One type that falls into both categories is the "butter" blend. The list of table-grade margarine products can be expanded by including whipped margarine, "reddies," which are ready-to-use portions as well as "country patties."

Industrial Margarines

Certain other margarine products are formulated for commercial applications. Different types of baker's margarine have been in use for a long time. Puff pastry margarines are of a more recent origin. One such type has been made from a base fat composed of 42% unhydrogenated soybean oil, 40% edible tallow, and 18% tallow, hydrogenated to a low IV. The margarine itself contains 0.4% hard monoglycerides, 8.9% water, and 1.7% salt. This product is reported to have excellent plasticity when crystallized over a chill roll and tempered overnight at 27–29°C and then printed or formed into blocks or sheets. Suggested SFI. values for this puff pastry fat are as follows: 30.0–33.5 at 10.0°C, 28.0–30 at 21.1°C, 24.5–26.5 at 33.3°C, and 19 minimum at 40.0°C (5).

Manufacturing Process

The process of manufacture of margarine begins with the premixing of ingredients followed by rapid chilling (solidification), homogenization, mechanical mixing or quiescent crystallization, and then packaging. The margarine consistency depends principally on the fats used in manufacture, but it is also influenced by ordinary variations in methods of solidifying and emulsifying the product, and by variations in the relative properties of milk and fat. It should be noted that baker's margarines and puff pastry margarine are not required to melt at body temperature as is the case for table-use margarine. Puff pastry margarines usually have a very high melting point, ranking among the highest of the edible fat products.

All fat products that are solidified in the course of their manufacture are actually plastic solids, except at extremely low temperatures; that is, they consist of an intimate mixture of liquid and very small solid particles. The liquid is retained in the framework of solids by capillarity, and the tendency of the solid particles to interlock and cohere gives the material the resistance to limited deforming stresses characteristic of plastic systems. Obviously the plastic properties of such a material are very largely dependent upon such factors as the relative proportions of solids and liquids, the size and distribution of the solid particles, the shape of the particles, and their rigidity and degree of mutual attraction.

Because some of these factors are influenced by the manner in which solidification is conducted, care is required in this operation to obtain desirable properties in the solidified product. Solidification of fats is complicated by the fact that these materials are polymorphic, that is, they may exist in different crystal modifications according to the conditions under which they are solidified. Different solid modifications of the same material vary in melting point and other physical characteristics. Hence, polymorphism alone may account for wide variations in the properties of a single plastic product solidified by different methods (6).

Scraped-Surface Heat Exchange

The consistency of an emulsion, as well as its stability, depends to a considerable degree upon the extent to which the discontinuous liquid phase is dispersed. The first chilling device was a refrigerated steel roll. This device had certain inherent defects such as inefficiency, moisture condensation on the surface, and lack of product uniformity. These disadvantages were overcome by the introduction of closed chilling machines, which incorporated the use of scraped-surface heat transfer units. Virtually all margarines are now processed by scraped-surface heat exchange. The Votator system was the first such process, and it is still a very much sought after installation. The sequence of operation in the solidification of a spread is as follows:

1. From holding tanks, the melted fat is fed into a small float-controlled supply tank, from which it is picked up by a gear pump and forced first under pressure through one or more chilling cylinders called "A" units.

2. Air or nitrogen to be dispersed in the product is admitted in controlled flow into the suction of the pump.
3. Within a period of 9–18 s, the fat is chilled to 50–65°F. It leaves the chilling cylinders in a supercooled and highly fluid condition, but with nuclei established for the formation of a very fine crystal structure.
4. Crystallization is substantially completed in closed cylinders somewhat larger than the chilling cylinders, known as "B" units, which are equipped with rotating shafts set with projecting fingers. These fingers are placed on the shaft in a spiral manner, to produce a helical movement of the fat through the cylinder, and they intermesh with similar stationary fingers projecting from the cylinder wall. The B unit is not jacketed or cooled. Its function is merely to maintain the fat in a state of uniform agitation while crystallization proceeds.

The scraped-wall heat exchanger is an efficient heat transfer device. Inside every such unit, a mutator shaft rotates within a tube. The product passes through an annulus formed by the shaft and heat transfer tube. Heating or cooling medium flows in a jacket. The unit is insulated to minimize energy loss and protect personnel. A polished, easily cleaned, stainless steel cover protects the insulation. In operation, the blades of the rotating shaft continuously scrape product film from the heat transfer tube wall, thereby enhancing heat transfer and vigorously agitating the product to produce a homogenous mixture.

Scraped-surface heat exchanger components are manufactured in a variety of configurations and materials so that each unit can be assembled to meet the specific processing requirements of each application. Thermal conductivity and wall thickness are the key design considerations of scraped-surface heat transfer tubes. Tube wall thickness is engineered precisely to minimize heat transfer resistance while maximizing structural stability. Pure nickel tubes, which provide high thermal conductivity, are standard. The inside of the tube is hard chrome–plated, then honed and polished to a smooth finish for resistance to wear from scraper blades and abrasive products. Although stainless steel tubes are available, it has been found that heat transfer is not as good as in the standard chrome-plated nickel tubes for shortening and margarine applications. Scraper blades are relatively short and arranged on the shaft in staggered rows. The blades are held on the scraped-surface heat exchanger shaft by strong, durable, specially designed "universal pins," which are welded to the shaft. There are no threaded areas to cause product buildup and possibly unsanitary conditions. These pins allow quick, easy blade removal and correct replacement; they hold blades ranging from 0.125-in thick metal to 0.254-in thick plastic. A variety of blade materials are available. Durable plastic blades can accept a wide temperature range, corrosive conditions and abrasive products. However, shortening and margarine production experience has indicated that stainless steel blades are more suitable. Most applications are met with the standard floating blade configuration, but for very viscous products, such as peanut butter, eccentrically mounted shaft units or oval tube design is beneficial.

Solidification Processes

Although methods for the solidification of margarine are in most respects similar to those employed for the solidification of shortening, certain complications are introduced because margarine is not a pure fat, but an emulsion consisting of ~80% plastic fat, 20% milk, and other aqueous phase ingredients, such as salt. Three different processes have been used for solidifying this product. In these, the emulsion of oil and aqueous liquid is sprayed into cold water, solidified on the surface of a chilling roll, or solidified in a closed chilling apparatus, respectively. The three processes were developed in the order mentioned. Today, the cold-water method is obsolete, at least in the United States, and the roll method has been at least 90% supplanted by solidification in the closed chilling machine. In addition to the Votator process, there are at least two other systems that employ scraped-surface heat exchangers. The Gerstenberg and Agger systems, such as the Prefector, are manufactured in Denmark. The "Kombinator" apparatus has been in use for over 40 years and is used worldwide in the production of shortening, monoglycerides, and many other products. It is manufactured by Schroeder and Company, of Germany.

Stick and brick product can be packed by either of the following two processes: (i) form the stick, then apply wrap, collect and carton, as typified by the Morpac machine or (ii) insert cut wrapping material into a mold, then inject the fluid product into the mold cavity, wrap, collect, and carton, such as accomplished by machines designed by the Benz and Hilgers Company of Germany. Soft product is dispensed into preformed and printed cups or tubs, capped, then sleeved. Many soft products are packaged with a plastic "shrink wrap" band for package surety. Packed units are collected into cases, stacked on pallets, then moved to cold store for temporary storage until quality testing is completed.

For cup filling, the product must be maintained in a fluid state for ease of filling and leveling in plastic containers (8 or 16 oz). The product is maintained in a fluid state by subjecting it to an agitated holding period in an agitated holding unit. This unit is comprised of intermeshing pins from the tube wall of the unit and spirally wound pins on the shaft of the unit. The degree of agitation is controlled by driving the unit with a variable speed arrangement. The holding time in this unit is designed to satisfy the specific formula being filled. The unit is of stainless steel construction and may include a jacket. These process steps represent the more common practice in the United States. Modifications of this process include the precrystallization technique, which includes recycling some of the crystallized product back to the entrance of the heat exchanger step. This technique is intended to modify the crystal structure and, in turn, the melting characteristics and spreadability of the product. Another variation involves injection of a portion of the cooled milk at the outlet of the heat exchanger. This cooled milk and the precooked emulsion are then mixed in an agitated worker unit to ensure an adequate blend of these two components. The object of this technique is to produce two intermixed dispersions of the aqueous phase, one of which is very finely subdivided and represents ~25%of what is mixed with the remaining portion, which has relatively large aqueous droplets. Gerstenberg and Agger

(G&A) has designed a machine that is capable of producing puff pastry, stick and cup margarine as well as shortening. The flow sheet for this plant is shown in Fig. 23.1.

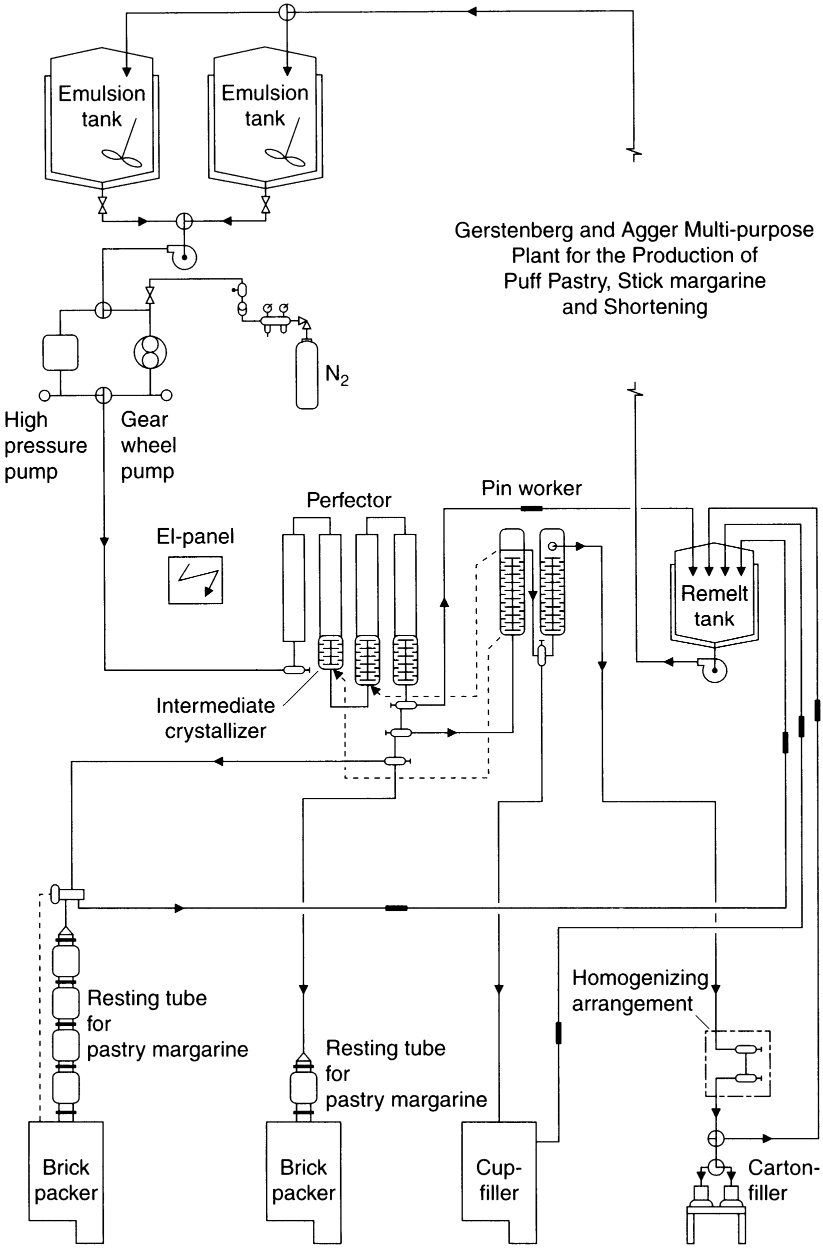

Fig. 23.1. Flow sheet for Gerstenberg & Agger multipurpose plant.

The puff pastry product flow is as follows: (i) The emulsion is pumped through the equipment by a high-pressure piston pump. It passes through two chilling tubes and the intermediate crystallizer. Then it leaves the Perfector and passes through a pin worker mounted between chilling tube Nos. 2 and 3 and associated crystallizers. (ii) From the Perfector, the semisolid emulsion enters the large puff pastry resting tube, which must have a capacity of at least 10-15% of the hourly production. G&A claims that the puff pastry produced in a tubular plant is as good as the product from the European roll systems.

Low-calorie spreads can be produced in the G&A system, but throughput must be lower because of the greater amount of aqueous phase. Undesirable oil-in-water emulsions can form easily if care is not exercised during processing. A moderate cooling temperature of –5°C to –1°C (12–23°F) and reduced pin worker volume are recommended. Table margarine and margarine/butter blends are produced by using a cooling temperature of –18°C to –20°C (0 to –4°F). For brick (solid) style, the flow is directly from the Perfector to the resting tube, which should have a capacity to provide 1 min of dwell time. Soft (tub or cup) margarine differs in that the margarine is worked in pin machines (similar to shortening) before packaging.

Low-Fat Spread Processes

The Schroeder Company, through application of their Kombinator system, has designed plants for the continuous production of shortening, margarine, and other edible fat products such as low-fat dairy spreads. These last-mentioned products were first produced in Great Britain in 1967, some eight years before their introduction in the United States. After introduction in the U.K., they were produced in the Netherlands in 1968, in Sweden in 1971, in Switzerland in 1972, in Denmark in 1973, and in West Germany in 1974. Three different methods have been used to make low-fat spreads:

- Mixing of cream and vegetable oil, followed by homogenization and pasteurization and, finally, churning.
- Mixing of butter with an aqueous phase containing oil, water, and protein.
- Margarine production process consisting of emulsion preparation, pasteurization, cooling and solidification/plasticizing, and filling and packaging.

The first two methods have the inherent defects of poor bacteriology control and poor emulsion stabilization. The processing sequence for the third method is as follows:

1. Liquid butterfat is measured into a mixing tank where the oil-soluble ingredients are added, and the mix is heated to 66°C (140°F).
2. After mixing, the oil phase is cooled to 40°C (104°F) and tempered.
3. The aqueous phase is prepared by adding the milk protein, salt, and stabilizers and water-soluble flavors to 40°C (104°F) water in the aqueous phase mix tank. (Homogenization and pasteurization may be necessary depending on the kind of milk protein used.)

4. Pasteurization is accomplished by heating from 40°C (104°F) to 85%C (185°F) with indirect steam and holding at temperature for 5–15 s, then cooling back to 40°C (104°F).
5. The emulsion is made by slowly adding the aqueous phase to the oil phase under vigorous agitation. The finished emulsion must be a water-in-oil type, which can be determined by conductrimetric measurement.
6. The finished emulsion is pumped to a surge tank and then is handled in a closed system.
7. The emulsion is pumped from the surge tank through a Kombinator pasteurizer, then through a Kombinator plasticizer and crystallization tube to the filling/packaging machine.

Shock cooling is effected by means of a second Kornbinator operating with either indirect ammonia or Freon evaporation, cooling the product from ~40°C (104° F) to 10°C (50°F) in ~30 s. Consistency is improved by passing the chilled product through a pinworker machine. From the pin machine, the product passes to either a cup filler or to a block-forming machine through a resting or crystallization tube. The Kombinator plants can be built for production capacities ranging from ~500 kg/h to ~10 t/h.

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Chapter 24

Liquid Oils Technology

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Introduction

The terms "oils and fats" refer to a class of lipid materials, consisting of the glyceride esters of fatty acids and their associated phosphatides, alcohols, hydrocarbons, pigments, and other products that are obtained from plants or animals by processes such as rendering, pressing, extraction, or a combination of these processes. Whether any particular lipid should be referred to as an oil or a fat depends on the physical state. It has become common practice to refer to a solid lipid as a fat and a liquid one as an oil, regardless of whether the source material was an animal fat or a vegetable oil. Some vegetable oils appear to disagree with this designation until the place of origin and the ambient temperature experienced are considered. For example, vegetable oil products such as palm, coconut, and palm kernel oils are solid materials at ambient temperatures in moderate climates, but are liquids at the ambient temperatures in the tropical areas in which they are grown.

The physical state of a lipid product may also be the result of processing. Changes in the physical state of the lipids to either a solid or a liquid can be effected by processing to change the melting or solidification points. These physical properties can be modified by several different processes available to the fats and oils industry including the following: (i) hydrogenation, which saturates the unsaturated fatty acids, increasing both the oxidative stability and melting point; (ii) interesterification, which interchanges the fatty acids among the triglycerides, changing the melting, oxidative stability, and crystallization tendencies of the oil; and (iii) fractionation, which physically separates hard and soft fractions to provide different functional properties. Most recently, genetic engineering procedures have been developed which modify vegetable oil compositions and consequently the physical characteristics.

Clarity at or below ambient or room temperature is the primary characteristic of a liquid oil. Natural vegetable oils that are liquid at room temperatures (75 ± 5°F or 23.9 ± 2.8°C) in temperate climates contain high levels of unsaturated fatty acids with low melting points. Fatty acids containing double bonds, and 18 carbon atoms are the most important unsaturated fatty acids for liquid oils. Oleic ($C_{18:1}$), a monounsaturated fatty acid, is the most widely distributed of all fatty acids. The di- and triunsaturated fatty acids most widely distributed are linoleic ($C_{18:2}$) and linolenic ($C_{18:3}$). Both of these acids are termed essential because they cannot be synthesized by the human body and must be supplied in the diet. Complete exclusion of the essential fatty acids results in scaly skin, loss of weight, kidney lesions, and death.

Three major oil types have been developed that maintain different degrees of clarity at and below room temperature in temperate climates, i.e., cooking oils, salad oils, and high-stability oils. The major differences among these three liquid oil types are described below.

Cooking Oil. This describes an oil that has *not* been processed beyond refining, bleaching, and deodorization. Some cooking oils may crystallize, cloud, or become semisolid at temperatures <70°F or 21.1°C. Stronger flavors are sometimes acceptable in cooking oils. For example, olive oil is rarely processed beyond extraction to preserve its distinctive flavor. In some parts of the world, all vegetable oils are still used in their natural state after extraction; however, a majority of the cooking oils are refined, bleached, and deodorized (RBD) for a light color and a bland flavor.

Salad Oil. This describes a liquid oil that will maintain clarity at refrigerator temperatures of 40–50°F or 4.4–10°C. The standard evaluation method for a salad oil is a cold test analysis. An oil sample that will remain clear for 5 h while submerged in an ice bath meets the criterion for a salad oil. Many oils require either winterization or dewaxing to remove higher melting point triglycerides or waxes, which cloud and solidify at refrigerator temperatures. However, some vegetable oils are natural winter oils that meet the cold test requirements without the benefit of either of these processes.

High-Stability Oil. This describes an oil that is liquid at room temperature and possesses exceptional oxidative or flavor stability. High-stability oils will not maintain clarity under refrigeration conditions. Normally, these oils cloud and solidify at temperatures slightly below room temperature. Most high-stability oils contain a high concentration of the monounsaturated fatty acid, oleic acid. These oils are used for food preparations in which the functional characteristics of a liquid oil are desirable and a long shelf life is required.

Liquid Oil Development

Humans have been familiar with fats and oils since prehistoric times. Long before any knowledge of the chemical nature of these substances existed, people recognized differences in their properties and employed them in a variety of ways. When and how humans first became familiar with oils and their uses is lost in antiquity but certainly they were used by primitive peoples as food, medicines, cosmetics, illuminants, lubricants, and other purposes. Ample evidence exists to attest to the fact that the people of all early civilizations were acquainted with a variety of oils, various methods of producing them, and a considerable number of uses and applications.

Humans existed on earth for more than 2 million years as hunters and gatherers. Therefore, climate and availability had to have had a major influence on the eating habits of our ancestors. Inhabitants of central and northern Europe first derived their edible fats almost entirely from wild animals and later domestic animals.

Consequently, their foods developed around solid fats such as butter, lard, and tallow. In the more heavily populated areas of Asia, southern Europe, and Africa, where it was impractical to dedicate land to livestock grazing, diets were developed with vegetable oils (1).

Probably the first fats used by humans were of animal origin; these were separated from other tissues simply by heating or boiling with water. Certain oily fruits, such the olive, palm, and oil-rich nuts were most likely made to yield their oils in this same manner. Recovery of oil from small seeds with a hard seed coat required the development of more vigorous methods of processing and likely gave rise to cooking, grinding, and pressing processes. These processes were of an ancient origin because ample evidence exists that the people of all early civilizations were acquainted with a variety of oils. Oil was a familiar commodity to the Egyptians and Phoenicians who utilized it as both a food and an anointing agent as early as 259 B.C. The use of oil spread from these peoples to the Hebrews and ultimately to the Greeks. Cottonseed is known to have been crushed for oil by the Hindus and the Chinese as early as the 5th century. The Chinese have also processed soybeans into oil and meal for thousands of years (2). Olive oil, an original cooking oil that dates back to antiquity, was and continues to be prized for its distinctive flavor.

Vegetable Oil Extraction

The practice of warming or steaming the crushed seeds to extract oils appears to have been developed some time between the days of the Romans and the 17th century. By the latter date, oilseed milling had become an established trade in Europe, although the technology had not advanced much since the days of the Roman Empire. Improvements in oilseed extraction machinery and methods began to appear frequently after the 17th and 18th centuries. Foremost among these machines was the wedge press, followed by the hydraulic press, which seems to have been invented in 1795 by Joseph Bramah. Mechanical pressing was the primary method used until the 1940s when successful extraction systems with petroleum solvents were introduced (3). Both mechanical and solvent extraction methods are currently in use to process vegetable oils.

Vegetable Oil Refining, Bleaching, and Deodorization

Like animal fats, vegetable oils had to be consumed in their crude state or as extracted from the seed or fruit for centuries. The natural flavor of crude vegetable oils is still preferred in some parts of the world, such as China, India, and other Asian countries. However, before the seed oils could attain widespread acceptance for use as edible food oils in the United States and other countries in which animal fats were in general use, further refining was necessary to remove the objectionable features of most of the extracted or crude oils. Acid refining techniques were introduced during the last part of the 18th century but never assumed importance. During the 1840s, alkali refining procedures using calcium and potassium hydroxide were developed in Europe but not used in the United States until the 1880s when the use of caustic soda was introduced in refining. The caustic alkali refining removes free fatty acid and a large proportion of the color pigments. However, further removal of color from cottonseed and other vegetable oils was necessary to make them more acceptable for eating purposes.

Cottonseed oil, used to adulterate lard and olive oil, had to have the color intensity reduced beyond that provided by caustic refining. The first bleaching was accomplished using a palm oil technique, which exposed the oil to sunlight in tanks on factory roofs for long periods (up to 18 mo). This practice had serious drawbacks, i.e., the lengthy exposure seriously deteriorated the flavor and keeping quality. Carbon in various forms was the first absorbent bleaching agent used, but it was replaced during the latter quarter of the 19th century by various clays or bleaching earths imported from Europe. Later, deposits of bleaching earth were discovered in Florida, Georgia, Mississippi, Arkansas, Texas, and California. Adsorptive bleaching provided oil colors consistent with those of other fats and oils products (4).

The process of caustic refining reduced the free fatty acid content and removed other gross impurities such as phosphatides, and proteinaceous and mucilaginous substances. The bleaching process removed color-producing substances and purified the oils. Neither of these processes had substantially affected the disagreeable flavors that hampered the acceptance of most vegetable oils until the deodorization process was perfected. Some flavor removal was accomplished as early as 1840 by boiling edible oils in water. In 1891, Henry Eckstein discovered that steam blown through oil heated to 340–350°F removed the unpleasant flavors. Around 1900, David Wesson perfected the deodorization process by using higher temperatures and maintaining the oil under a vacuum while blowing with superheated steam. The superheated blowing steam carried off the unpleasant flavors and odors, free fatty acids, and some color bodies, whereas the vacuum prevented oxidation and the development of other off flavors. Southern Cotton Oil Company marketed a cottonseed cooking oil under the brand name Wesson Oil to commemorate David Wesson's achievements (5).

Winterization

The advent of mechanical refrigeration made the development of salad oils a necessity. Winterization is the process identified around 1900 to produce a cottonseed oil that would remain clear at reduced temperatures. The winterization process evolved from practical experience at refineries when it was observed that storing cottonseed oil in outside tanks exposed to low temperatures during the winter months allowed the higher melting triglycerides to settle to the bottom of the tank, leaving a top layer of clear oil. Winter oil was then obtained either by decanting the liquid oil from the top or filtering to separate the liquid and solid fractions. The liquid oil obtained would remain clear and pourable at moderately low storage temperatures. The solidified fats or stearine could be used as a shortening base stock. The original intent was to retain fluidity and clarity during the cool winter months. Oils marketed in the summer time did not require this treatment because of the warmer temperatures.

Then, introduction of mechanical refrigeration initiated a need for winterized oil year round. This was especially true as the mayonnaise, salad dressing, and sauces industries expanded. These emulsions could not be made from oils that would crystallize in the refrigerator and cause the emulsion to break. New terminology came about because of this association with salad dressings. Winterized oil became "salad oil" and summer oil became "cooking oil." The increased demand for winterized oil made it impossible to rely on natural conditions for the required annual production of salad oil. Edible oil processors seized on the simplest expedient; they created winter conditions indoors (6).

Salad Oil

Salad oil requirements were later changed from an oil processed by the winterization process to an oil than met the specified limits of a winter oil, that is, it was able to resist clouding for more than 5½ h at 32°F or, more specifically, the conditions of the cold test. This revised salad oil specification also encompassed oils identified as natural winter oils. These oils do not require winterization to remain clear and brilliant at refrigerator temperatures due to fatty acid compositions that are high in unsaturates, with a corresponding low saturated fatty acid level. Soybean, corn, canola, safflower, and sunflower oils all have fatty acid compositions that identify them as natural winter oils; unfortunately, all of these oils except soybean contain waxes that are solids at cool temperatures. The waxes do not affect the oil's performance in mayonnaise or spoonable salad dressings but do produce unsightly clouding or wisps in retail bottled oils and pourable salad dressings. The dewaxing process is a cosmetic operation that removes the high temperature melting components such as waxes and trisaturated glycerides present in the oil through chilling and filtration. Dewaxing is rather simple and can be accomplished by rapidly chilling the oil in the presence of a filter aid, holding at this temperature for 1–2 h, and cold filtration.

Soybean Oil Technology

Despite its well-known flavor and odor deficiencies, soybean oil became popular in the United States during World War II as a result of shortages; later, its popularity was due primarily to a 4–9% discount to cottonseed oil. Edible fats and oils processors were able to incorporate soybean oil into hydrogenated shortening and margarine formulations without a noticeable flavor degradation. However, flavor was still a limiting factor for its acceptance as a cooking or salad oil. Two developments were necessary to provide soybean salad and cooking oils with an acceptable flavor stability, i.e., chelating of trace metals and reduction of the linolenic fatty acid content.

German scientists developed a process to cure soybean oil reversion during World War II. It involved the addition of citric acid to the deodorized oil, which complexed trace prooxidant metals. Sensory flavor and odor evaluations substantiated that trace metals were a significant contributor to the soybean oil flavor problem. Other fats and oils can tolerate copper and iron in the parts per million (ppm) range, whereas soybean oil flavor is ruined by as little as 0.5 ppm iron and 0.01

ppm copper. Upon release of this information, edible oil processors in the United States almost immediately adopted the use of metal deactivators or chelating agents; of these, citric acid remains the most popular. The chelating agents were also been found to improve the oxidative stability of other source oils processed; today, they are added after deodorization to most fats and oils.

Chelating of the prooxidant trace metals improved soybean oil's oxidative stability but an offensive fishy, painty, or watermelon type flavor still developed with liquid oil usage. Circumstantial evidence pointed to the 7–8% linolenic fatty acid content. A classic experiment intersterified 9% linolenic fatty acid into cottonseed oil, which typically contains <1% of the $C_{18:3}$ fatty acid. Flavor panels identified this modified cottonseed oil as soybean oil. This result presented the following three alternatives for improving the flavor stability of soybean oil: (i) breed it out; (ii) extract it out; or (iii) hydrogenate it out. Hydrogenation to reduce the linolenic fatty acid content was chosen as the most practical short-term approach (7). Soybean salad oil with linolenic fatty acid reduced to 3–4% was introduced to the U.S. market in the late 1950s. This product was brush hydrogenated and subsequently winterized to remove the hard fractions developed during hydrogenation. The refined, bleached, hydrogenated, winterized, and deodorized (RBHWD) soybean salad oil was accepted by the retail and industrial consumers for use in mayonnaise, salad dressings, frying, and other uses for liquid cooking and salad oils.

Antioxidants

Antioxidants have been used to protect food supplies for hundreds or even thousands of years in the forms of various spices and herbs used for seasonings. Antioxidants for early fats and oils included smoke, cereal flours, and crude vegetable oils to stabilize animal fats against rancidity. Around 1930, researchers discovered a distinct relationship between the tocopherols in vegetable oils and oxidative stability. Flavor stability was reduced to extremely low levels when the tocopherols were stripped from vegetable oils, and the oxidative stability was restored when the tocopherols were added back. However, increased tocopherol levels provided no further benefit but acted as prooxidants to decrease oxidative stability. Synthetic antioxidants, beginning with esters of gallic acid (propyl gallate), were identified and approved in the 1940s, followed by phenolic compounds such as butylated hydroxyanisole (BHA) in 1948, then butylated hydroxytoluene (BHT) in the 1950s and tert-butylhydroquinone (TBHQ) in 1972. TBHQ has been found to be the most effective synthetic antioxidant for vegetable oils; active oxygen method (AOM) stability testing has shown a three- to fourfold improvement for RBD soybean oil treated with 200 ppm TBHQ.

Dimethylpolysiloxane

Liquid shortenings with frying stability superior to that of the heavy-duty solid frying shortenings were introduced in the 1950s. The secret to their improved performance was dimethylpolysiloxane. The addition of this antifoamer retarded oxidation and polymerization effectively to provide more than double the frying life of the then current best, heavy-duty, hydrogenated, solid frying shortening, yielding a pourable product with a high polyunsaturated fatty acid content. The antioxidant effect of dimethylpolysiloxane elevated the frying stability of cooking and salad oils to a level that made them attractive to many food service operators for their convenience as well as for the bright, slightly oily appearance of the fried foods. The stability improvement contributed by the antifoamer was cumulative, that is, the additional frying life was determined by the stability of the product initially without the additive. Acceptance of liquid opaque shortenings and cooking or salad oils with the addition of dimethylpolysiloxane for frying undoubtedly influenced the development of high-stability liquid oils.

High-Stability Oils

The technology developed to improve oxidative stability for soybean salad oil was expanded to create another liquid oil type, i.e., high-stability liquid oils. A liquid oil is hydrogenated to reduce a high proportion of the polyunsaturates to monounsaturates, followed by winterization or another form of fractionation to separate out the solid fractions created; this is done because the hydrogenation process is not selective enough to affect only the change of polyunsaturates to monounsaturates. Some of the monounsaturates are saturated to produce stearic ($C_{18:0}$) fatty acids; these acids have a high melting point, which increases the solidification point and reduces liquidity. As another option, fractionation techniques may be used to separate the hard fractions created by hydrogenation or removal of the hard fractions from a fat or oil product that is naturally a solid at the desired temperature range. For example, high-stability oils can be liquid fractions of tallow or palm oil that has been fractionated with one of the different techniques available. Chapter 11 of this volume presents more detailed information regarding the fractionation processes and techniques. The high-stability oils obtain their improved resistance to oxidation through a higher olein or monounsaturate proportion; in addition, the tocopherols concentrate in the liquid fractions during fractionation (8). Additional protection can be obtained with antioxidant additions; of these, TBHQ is the most effective for vegetable oils.

Another technology developed to provide high-stability oils is plant breeding to produce oils low in polyunsaturates and high in monounsaturated fatty acids. Several commodity oilseed crops have been altered successfully to produce oils with high-oleic fatty acid profiles. The plant breeding program is an alternative to hydrogenation and/or fractionation processing with certain advantages; one of these is the absence of *trans* fatty acids produced during hydrogenation. High-oleic versions of commodity oils that are now or could be available commercially include canola, which is itself a hybrid of rapeseed, safflower, sunflower, and soybean. These oil types are still considered specialties and are processed only on a limited basis because of limited availability, premium price, and a need to preserve identity (9).

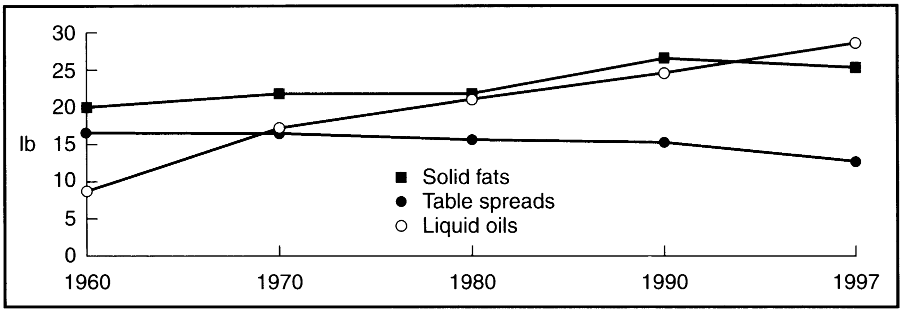

Fig. 24.1. Personal consumption (lb/person) of table spreads, solid fats, and liquid oils.

Emulsifiers

Health concerns regarding cholesterol, saturated fats and *trans* isomers have influenced consumers fats and oils selections. It was an accepted fact that the crystal structure of plasticized shortenings and lard was responsible for their performance in almost all baked products and that liquid oils have no inherent structural characteristics because they do not contain any significant quantities of saturated triglycerides. Nevertheless, the increased popularity of liquid oils prompted the development of product formulations and processes to accommodate liquid oils in the 1970s. Emulsifiers were found to provide the same functions as the solids in plasticized shortenings, with oils providing lubricity and palatability. With the addition of the proper emulsifier systems, liquid oils were found to be effective alternatives to plastic fats in breads, sweet yeast-raised products, and cakes (10).

Liquid Oil Consumption

During the past 37 years, there have been shifts in the types of fat and oil products used, with a significant shift toward softer, less saturated liquid oils. Personal consumption of liquid oils has more than tripled in the United States since 1960 and continues to grow, whereas usage of solid fats and table spreads is decreasing, as shown in Figure 24.1. More than likely, the increased popularity of the liquid oils results from the following: (i) diet modifications to reduce saturated fats, *trans* isomers, and cholesterol; (ii) awareness of the importance of the essential fatty acids in the diet; (iii) reduced dependence on the crystalline properties of solid fats for functionality; (iv) increased oxidative stabilities through the use of processing, plant breeding, antioxidants, and antifoamers; and (v) improved product formulations and processes tailored for the use of liquid oils.

Liquid Oil Characteristics

Chemically, all fats and oils are triglycerides or esters of glycerol and fatty acids. Because all triglycerides have identical glycerol components, the different properties are contributed by the fatty acids. Three aspects can differentiate the fatty acid components, i.e., chain length, the number and position of the double bonds, and the position of the fatty acids with regard to the glycerol. For all practical purposes, fats and oils contain fatty acids with carbon chain lengths between 4 and 24 carbon atoms with 0–3 double bonds. Saturated fatty acids are chemically the least reactive and have a higher melting point than corresponding fatty acids of the same chain length with one or more double bonds. The fatty acids with the most double bonds, or the more polyunsaturated, are the most chemically reactive. The notable polyunsaturated fatty acids or essential fatty acids are linoleic ($C_{18:2}$), which is diunsaturated, and linolenic ($C_{18:3}$), which is triunsaturated. Unsaturated fatty acids have different physical and physiopathologic properties, identified as *cis, trans,* and *positional. Cis* isomers are the natural configuration, whereas the *trans* and *positional* isomers develop with processing or heating, but predominately with hydrogenation. The effect of chain length, unsaturation, and geometric isomerism on the fatty acids melting point is shown in Table 24.1. The triglyceride structure is affected by the following: (i) which carbon atom of the glycerol the fatty acid is linked to, (ii) whether the three fatty acids are all the same or different, and (iii) the position of each fatty acid. When all of the fatty acids in a triglyceride are the same, it is called a simple triglyceride. Different fatty acids within the same triglyceride are referred to as mixed triglycerides. All of these fatty acid and structural variations affect the chemical and physical properties of the resulting triglycerides. Therefore, the characterizations of fat and oil products are the fatty acid and triglyceride compositions. In general, oils that are liquid at room temperature tend to be more unsaturated than those that appear to be solid.

Saturated Fatty Acids

Saturated fatty acids are the least reactive chemically because they contain only single carbon-to-carbon bonds. The melting point of saturated fatty acids increases with

TABLE 24.1 Melting Points of Fatty Acids and Glycerides

			Melting point (°C)			
Fatty acid	Carbon atoms	Double bonds	Acid	1-mono	1,3-di	Triglyceride
Myristic	14	0	54.4	70.5	66.8	57.0
Palmitic	16	0	62.9	77.0	76.3	63.5
Stearic	18	0	69.6	81.5	79.4	73.1
Oleic	18	1 *cis*	16.3	35.2	21.5	5.5
Ricinoleic	18	1 *positional*	5.5			
Elaidic	18	1 *trans*	44.0	58.5	55.0	42.0
Linoleic	18	2 *cis cis*	-7.0	12.3	-2.6	-13.1
Linolenic	18	3 *cis cis*	-13.0	15.7	-12.3	-24.2
Arachidic	20	0	75.3	84.0		
Behenic	22	0	79.9			
Erucic	22	1 *cis*	33.5	50.0	46.5	30.0
Lignoceric	24	0	84.2			

chain length as shown in Table 24.1. The saturated fatty acids all have melting points >70°F or 21.1°C, which indicates that oils with a saturated fatty acid content will not be liquid at ambient temperatures. The principal saturated fatty acids are palmitic ($C_{16:0}$) and stearic ($C_{18:0}$), which occur in most food oils. Other saturated fatty acids in liquid oils are myristic ($C_{14:0}$), arachidic ($C_{20:0}$), and behenic ($C_{22:0}$), which are found in low quantities in most oils. Peanut oil has a relative high level of lignoceric ($C_{24:0}$) fatty acid, typically 1.5%, which has been used as a marker for identification. Canola and traditional rapeseed oils also contain the C_{24} fatty acid.

Monounsaturated Fatty Acids

When a fatty acid contains one double bond it is called monounsaturated. Unsaturated fatty acids are more reactive chemically than the saturated fatty acids due to the presence of double bonds. This reactivity increases as the number of double bonds increases. Accordingly, monounsaturated fatty acids with only one double bond are the least reactive of the unsaturated fatty acids. The principal monounsaturated fatty acid is oleic ($C_{18:1}$), which occurs most frequently in nature. Olive, peanut, and canola oils all have a high-oleic fatty acid content, which contributes to the flavor stability of these oils. The high level of the monounsaturated fatty acid contributes to liquidity due to a relatively low melting point and to oxidative stability by limiting the reaction sites for oxygen. Plant breeding efforts aimed at increasing the oxidative stability of a liquid oil generally concentrate on increasing the oleic fatty acid content of the oil seed.

Erucic ($C_{22:1}$), also a monounsaturated fatty acid, is limited by U.S. Food and Drug Administration (FDA) regulations because of possible physiopathologic harmfulness. Traditional rapeseed oil contains a high-erucic fatty acid content of ~41%. Canola oil, which is a cultivar of rapeseed, was designed to contain <2% of the antinutritional erucic fatty acid.

Diunsaturated Fatty Acids

Unsaturated fatty acids with two double bonds are called diunsaturated. Most of the liquid oils available on a commercial scale are rich in linoleic fatty acid ($C_{18:2}$), which is most likely responsible for both the liquidity and characteristic flavor reversion of these oils. Linoleic fatty acid is one of the fatty acids essential for growth plus skin and hair quality. An essential fatty acid cannot be synthesized by the body and must be supplied in the diet. The dietary fatty acids that can function as essential fatty acids must have a particular chemical structure, namely, double bonds in the *cis* configuration and in specific positions of carbon 9 and 12 from the carboxyl carbon atom (11).

Triunsaturated Fatty Acids

Liquid oils with three double bonds are referred to as triunsaturated. Linolenic ($C_{18:3}$) is the principal triunsaturated fatty acid found in commercially available vegetable oils. Oils with high linolenic fatty acid contents are good drying oils for paints and other industrial uses but relatively poor food oils, unless the unsaturated fatty

TABLE 24.2 U.S. Sources for Salad and Cooking Oils[a]

	1960	1965	1970	1975	1980	1985	1990	1995	1997
	Million Pounds								
Canola oil						W	W	227	301
Corn oil	247	239	246	281	350	515	636	429	364
Cottonseed oil	752	915	527	432	460	384	460	251	248
Olive oil	51	44	62	48	58	105	213	251	360
Peanut oil	28	53	139	100	148	110	139	108[b]	110[b]
Safflower oil		9	12						
Soybean oil	887	1564	2471	3031	4042	4749	4662	5473	6192
Sunflower oil					32[b]	72[b]	50[b]	84[b]	108[b]
Unidentified	1		6	136	77	65	35	243	16
Total	1966	2824	3464	4028	5167	6000	6195	7066	7689
lb/person	9.2	14.1	17.3	17.9	21.2	23.6	24.8	26.9	28.7

[a] W, withheld to avoid disclosing volume for individual companies.
[b] Estimated by author.

acids are in the less reactive 2-position of the triglyceride. Linolenic fatty acid, like linoleic, is also one of the essential fatty acids that must be supplied in the diet.

Liquid Oil Sources

A steady growth in the utilization of liquid oils is evident from the USDA Economic Research Service Oil Crops Situation and Outlook Reports for domestic consumption of salad and cooking oils. Consumption and source oils data for utilization beginning in 1960 are summarized in Table 24.2 (12,13). The overall data showed that the cooking and salad oil quantities used have increased almost fourfold over the 37-y period, and personal consumption has increased 3.1 times over this period.

Soybean Oil

Soybean oil had become the dominant vegetable oil in the United States for use in shortenings and margarines as early as the late 1950s but was not accepted as a cooking or salad oil because of the reverted oil flavor that developed soon after deodorization. Then, citric acid chelating and reduction of the linolenic fatty acid content in soybean oil with hydrogenation and winterization processing were introduced. The source oil data confirm that soybean oil had surpassed cottonseed oil usage as early as 1960; soybean oil had 45.1% of the salad and cooking oil market, whereas cottonseed oil only had 38.3%. Initially, the specially processed or RBHWD soybean oil was offered only to industrial users; then it was cautiously introduced to the retail consumer in blends with cottonseed salad oil. These blends began with a heavy proportion of cottonseed oil, but, over time, soybean oil became dominant and eventually replaced all of the cottonseed oil portion. Thereafter, RBHWD soybean oil had the major share of the liquid oil market in the United States until the late 1970s. A conventional soybean oil with 11.8% palmitic, 4.8% stearic, 24.1% oleic, 52.3% linoleic, and 7% linolenic fatty acids was RBHWD or specially processed. The changes in the fatty acid composition with the special processing to increase oxidative stability and maintain clarity sufficient for a 5 1/2-h cold test were as follows: Linolenic was reduced to 3.5% and linoleic to 40.3%, whereas oleic increased to 39.4% and stearic increased minimally to 5.0%.

In the late 1970s, improvements in the processing of soybean oil enabled processors to produce a RBD soybean oil that was acceptable to industrial customers. This improved RBD soybean oil was then introduced to the retail market as "all natural" and "light." The oil's appearance was almost water white, and processing to change the fatty acid composition of the original oil was no longer required. This product quickly replaced the specially processed soybean salad oil sold in the grocery stores. Technology had provided improved processing and packaging to produce a more stable bland flavor than the RBD soybean oil offered before special processing or RBHWD to reduce the linolenic fatty acid content. Also, it was felt that the U.S. consumer had become more accustomed to the soybean odor and flavor, which also made it less objectionable (14). In any case, soybean oil has experienced an extraordinary growth since the late 1930s to command 80.6% of the salad and cooking oil market in 1997.

Cottonseed Oil

Cottonseed oil contains only minor amounts of linolenic fatty acid and a high level of saturates, composed of ~1% myristic, 25% palmitic, and 2.3% stearic, to make it a relatively stable cooking oil. The remaining unsaturates are 53.3% linoleic and 18.3% oleic fatty acids. An additional benefit is that the natural nutty or buttery flavor of cottonseed oil can often mask less desirable flavors. Cottonseed salad oil production requires winterization to remove the stearine fraction caused by the high level of saturated fatty acids.

Cottonseed oil was the principal cooking and salad oil used in the United States until the late 1950s. As a source oil, it had lost its dominance for usage in shortenings and margarines in the 1940–1950 era, but had remained the preferred liquid oil due to the flavor problems associated with RBD soybean oil. Demand for cottonseed salad and cooking oils in the United States has decreased in both usage percentage and amount. The pounds of cottonseed oil used domestically for salad or cooking oils have decreased 67% since 1960, and the proportion has decreased from 12.6% in 1960 to only 3.2% in 1997. The United States has the distinction of being the major exporter of cottonseed oil to the world. Domestically, the major use for liquid cottonseed oil at home is for snack foods. Cottonseed oil has a unique flavor property that makes it a desirable snack food frying medium. Potato chips fried in cottonseed cooking oil have a pleasant nutty flavor, whereas other frying oils produce chips with clean potato flavors that lack the nutty note. This product usage for cottonseed cooking oil, exports, and any industrial use of cottonseed salad oil account for most of the liquid cottonseed oil production because the retail marketing of cottonseed oil appears to be limited to the gourmet shelves.

Corn Oil

Corn oil is recognized as a premium oil among U.S. consumers and abroad. It is second only to soybean oil in U.S. salad and cooking oil volume, even though or maybe because the availability of corn germ for oil production depends strictly on the amount of corn processed by the dry and wet milling industries. Corn oil possesses an exceptional flavor and resistance to oxidation in spite of a high level of unsaturation. The superior stability is attributable in part to the nonrandom distribution of the fatty acids, i.e., 98% of the fatty acids in the 2-position are unsaturated, which means that all of the saturated and the remaining unsaturated fatty acids are in the 1- and 3-positions. Because the outer positions of the triglyceride are more reactive, the polyunsaturated fatty acids in the 2-position are sheltered from oxidation. Corn oil also enjoys a high level of natural antioxidants, i.e., ferulic acid and tocopherols (15).

Promotion of polyunsaturated oils for nutritional purposes led to an explosion in the commercial use of corn oil in various foods, snack frying, and as a retail bottled oil. Corn oil contains at least 59% linoleic ($C_{18:2}$), ~13% saturated fatty acids, and only a trace of linolenic ($C_{18:3}$) fatty acid. This healthy image and the distinctive musty flavor and odor helped corn oil gain popular acceptance for both home use and prepared food products. Corn oil is a natural winter oil, but it does contain waxes that must be removed to avoid an unsightly wisp or thread of solidified material, which can appear at grocery store temperatures. However, the waxes do not interfere with emulsion stability and need not be removed for production of mayonnaise, salad dressings, and other food products.

Peanut Oil

The peanut crop is subject to mandatory price support in the United States, which maintains a premium price. Only a small amount of the U.S. crop is crushed for oil. Generally, only oversupply, immature seeds, those seeds not considered premium quality for whole nut products, and aflatoxin-contaminated peanuts are crushed for oil. Fortunately, aflatoxins are not oil soluble, so they remain in the meal after crushing. Nevertheless, peanut oil maintains a respectable cooking oil market for snack frying, food service frying, and as a retail bottled cooking oil. Peanut oil cannot be winterized to produce a salad oil due to an unfilterable gel that develops with cooling. Therefore, liquid peanut oil must be classified as a cooking oil. Peanut oil is considered a premium cooking and frying oil due its pleasant flavor, exceptional flavor and frying stability, and price. The oil separated from peanuts is the recipient of the peanut flavor, rather than the meal. The flavor of peanut oil does not revert readily, but when it does, its flavor is mild and similar to that of roasted peanuts. The fatty acids in peanut oil are responsible for its frying and flavor stability, i.e., 80–83% unsaturated and 17–20% saturated. The unsaturated fatty acids consist almost entirely of monounsaturated oleic (50–65%) and diunsaturated linoleic (18–30%).

Olive Oil

Almost all of the olive oil consumed in the United States is imported from the producing countries in Europe, the Middle East, Africa, and Argentina. Consumption of this imported oil has more than tripled in the 12-y period from 1985 to 1997. The substantial increase in olive oil consumption in the United States during the last decade or so is likely due to promotions of the health benefits of the Mediterranean dietary patterns and expansions of gourmet food lines in supermarkets. A Harvard University Press study concluded that the adult populations of Greece and Italy live longer and linked olive oil with lowering the low density lipoprotein (LDL) or bad cholesterol while maintaining the high density lipoprotein (HDL) or good cholesterol levels. Olive oil, produced by crushing and pressing olives, has a high oleic fatty acid content ranging from 55 to 83% and a saturated fatty acid content of only 10–18%. It is more resistant to oxidative changes than most other oils because of its low linoleic fatty acid level. Gourmet consumers often choose olive oil for its unique and distinctive flavor. The good grades of olive oil are produced *without* the usual edible oil processing after extraction other than decantation, centrifugation, and/or filtration.

Canola Oil

The canola oil "healthy oil" promotions apparently were fruitful; this oil has captured almost 5% of the salad and cooking oil market in a little over a decade. It has the lowest levels of saturated fatty acids of any conventional vegetable oil and also contains a relatively high level of monounsaturated fatty acids. Canola oil has been offered for sale in the United States only since 1985 when it was approved as generally regarded as safe (GRAS). During the genetic changes from the original rapeseed varieties to the canola varieties, a major reduction of erucic fatty acid ($C_{22:1}$) occurred; this resulted in a marked increase in oleic fatty acid ($C_{18:1}$) and smaller increases in linoleic ($C_{18:2}$) and linolenic ($C_{18:3}$) fatty acids. As a result, typical canola oil has a fatty acid composition containing 6% saturates, 64% monounsaturates, 20% diunsaturates, and 10% triunsaturates. Canola oil has a fatty acid composition similar to that of olive and peanut oil with the exception of a lower palmitic and higher linolenic fatty acid contents. The high level of triunsaturated linolenic fatty acid is cause for concern for potential oxidative stability problems. However, canola has a relatively high α-tocopherol content (19 mg/100 g), and the 10% linolenic acid content is protected by its attachment to the triglyceride in the 2-position. The 1- and 3-positions or outer positions of the triglyceride are more reactive and shelter the 2-position from oxidation. The oxidative resistance of canola oil has been demonstrated with AOM stability evaluations. Canola oil normally has a 24-h AOM stability, which compares very favorably with the 12–18 h for natural soybean oil and 20–30 h for specially processed RBHWD soybean oil (16).

Sunflower Oil

The sunflower plant is native to North America, but the first oil-producing varieties, imported from Russia, were not grown until the early 1970s. The conventional sunflower oil possesses a clean, bland flavor with a light yellow color and typically contains 68–72% linoleic, 16–19% oleic,<1% linolenic and saturated fatty acids, consisting of 6% palmitic and 5% stearic. Its saturated fatty acid content is lower than that of corn and soybean oils, but 2% higher than safflower oils and 5% higher than canola. The oil has had only limited acceptance in the United States, and ~80% of the oil produced is exported. Retail salad oil bottlers have attempted to create a market for sunflower oil on several occasions. In the early 1990s, branded retail bottled salad oils were introduced nationally but then withdrawn. Later, sunflower was one of the components of blended salad oils introduced and marketed to contain one third less saturates than soybean oil. Salad oil blends are still marketed, but in most cases, canola oil has replaced sunflower oil in the blend. Sunflower oil has become an important seed oil in Russia, the Commonwealth of Independent States, Eastern and Western Europe, South America, South Africa, Australia, France, and the Mediterranean countries. It ranks fourth in world production but only 13th in consumption in the United States.

The most promising future for sunflower in North America may lie in special cultivars. Promoted by nutritional recommendations, sunflower varieties are being developed to produce oils with specific fatty acid profiles. High-oleic sunflower oil has been available commercially since 1988 and probably accounts for 10–15% of the U.S. sunflower oil-producing crop. The oil from the high-oleic varieties is directed toward special food and industrial markets. Like conventional sunflower oil, the high-oleic oil contains a small percentage of saturated fatty acids, 6.7%, but a much lower level of polyunsaturated fatty acids, i.e., 12% linoleic and 0.1% linolenic, and a very large amount of monounsaturated fatty acids, 80% oleic. More recently, the sunflower industry has announced a plan to switch the entire U.S. commodity sunflower crop over to a mid-oleic variety called NuSun, which is expected to lead to a stronger domestic market. This conversion, expected to be completed in the year 2000, will yield an oil typically containing 9.5% saturates, 60% oleic, 30% linoleic, and 0.1% linolenic fatty acids (9). The sunflower industry projections indicate that the chemical composition and commodity pricing of the NuSun variety make it attractive as an oil for frying, home and restaurant cooking, margarines, or liquid shortenings (17).

Safflower Oil

Safflower oil gained and lost appeal as a salad oil during the late 1960s and early 1970s because of its high polyunsaturated fatty acid content. High polyunsaturates have a nutritional appeal, but also equate to poor oxidative stability. Since then, safflower oil has remained a minor oilseed crop, which has maintained about the same planted acreage for the last 10 years. Conventional safflower oil contains 9.7% saturates, 12.2% oleic, 77.7% linoleic, and 0.4% linolenic fatty acids. Because it has the highest level of polyunsaturates available, most of the regular safflower oil is purchased by customers who require its particular fatty acid structure and are willing to pay a premium over other oils. A mutation, high-oleic safflower, produces an oil in which the linoleic and oleic fatty acid level are reversed. This change produces a much more stable oil due to the high monounsaturated fatty acid level. High-oleic safflower oil accounts for more than half of the U.S. safflower oil crop and is used primarily in the formulation of baby formulas, special snack frying, and in blends with other oils (18).

Liquid Oil Markets

Three different markets exist for liquid oils, i.e., retail, food service, and food processor. The retail market consists of the bottled oils sold in grocery stores or other retail outlets. The food service industry is composed of restaurants, hotels, institutions, and other mass feeding operations. The food processor market is made up of the prepared food manufactures of food products sold in retail outlets or utilized by the food service industry. The requirements for each of these markets differ from each other as well as within each market type.

Retail Consumer Oils

Retail bottled oils have benefited from the broad dietary shifts experienced over the past several decades. Since 1950, consumers have moved toward fats and oils from vegetable sources because they contain fewer saturates, no cholesterol, and more polyunsaturates than animal fats. Vegetable oil shortenings were the first beneficiaries of these diet changes because the style of cooking and baking in the United States was based on the use of plastic fats. However, the nutritional benefits of the essential fatty acids and the harmful effects of cholesterol, saturated fats, and *trans* isomers have directed the retail consumers toward liquid oils. The oils favored have reflected somewhat the most recent findings of nutritional studies, usually communicated to the consumers in the form of advertisements; however, soybean oil continually has the highest volume sales.

U.S. Labeling Requirements. Consumers can also consult the nutritional facts panel on each container for information regarding the dietary components. The nutritional facts panel has mandatory and voluntary requirements that were part of the U.S. FDA regulations implementing the Nutritional Labeling and Education Act published on January 6, 1993 for compliance by May 1994. The main purpose of these regulations was to specify the information allowed on food product labels. The mandatory components on the nutritional facts panel are as follows: Serving size, servings per container, total calories, calories from fat, total fat, saturated fat, cholesterol, sodium, total carbohydrate, dietary fiber, sugars, protein, vitamin A, vitamin C, calcium, and iron. The voluntary components, which may refer to fats, include calories from saturated fats, polyunsaturated fats, monounsaturated fats, potassium, and other essential vitamins and minerals. The regulations also spelled out the order in which the components must appear on the nutritional facts panel. The amounts of each nutrient must be listed in grams to the right of each nutrients and another column headed % Daily Value provided. The daily values are comprised of the daily reference values (DRV) and reference daily intakes (RDI). The DRV are designed to help consumers decide how individual foods fit within general recommendations for their daily diet based on 2000 kcal. Reference daily intakes are the U.S. Recommended Daily Allowances (RDA) (20). U.S. FDA regulations, 21 CFR, Part 101 also require an ingredient statement designating each source oil by common or usual name in descending order of predominance by weight. Additionally, if the fat or oil is completely hydrogenated, the name shall include the term "hydrogenated," or if partially hydrogenated, the name shall include the term "partially hydrogenated."

Packaging. The packaging materials and the practices employed for retail liquid oils are a very important contributor to shelf life. The package contains and protects the product from oxidation and other contaminants, starting at the point of manufacture and continuing through usage by the consumer. The ideal retail container has three important attributes, i.e., product protection, product appeal, and cost effectiveness. Currently, most of the regular consumer retail oils are packaged in clear, polyethylene tetraphthalate (PET), rectangular-shaped containers of 16-, 24-, 32-, 38-, 48-, and 64-oz bottle sizes and l-gal polyvinylchloride (PVC) opaque jugs. However, many of the gourmet and specialty oils are still packaged in glass containers with sizes and shapes readily distinguishable from the conventional retail oils. Before the mid-1980s, all consumer oils were packaged in glass containers for product protection. Early testing of polyethylene (PE) containers in 1955, the only food-grade plastic available, showed oxygen permeability, which allowed the oil to oxidize rapidly; the container became sticky as the oil permeated the container and polymers from the bottle migrated into the oil. Later, a food-grade polyvinylchloride (PVC) resin became available that satisfied most of the retail bottled oil criteria (20). USDA research studies in 1973 showed no differences in oil deterioration between glass and PVC packaging. The results of this research had a significant effect on the edible oil industry, which converted almost all consumer oils containers to the translucent plastic bottles by 1985 (21). The next generation of plastic containers for retail oils is currently on the grocery store shelves; polyethylene tetraphthalate (PET). This plastic resin is more glass-like in clarity, shatter resistant, and provides a better oxygen barrier. The rectangle shape is a departure from the traditional round bottle to provide better space utilization in shipping containers, on the grocery store shelves, and in the consumer's pantry.

All liquid oils are sensitive to sunlight and fluorescent lighting, which catalyze oxidative reactions. It has been proven that packaging in metal, foil-lined or waxed paperboard containers, and in tinted or amber glass extends the shelf life stability of liquid oils. However, retail consumers have indicated a preference for clear containers. In their attempts to improve the packaging oxidative stability with the described protective packaging, U.S. retail oil bottlers suffered reduced sales until the container was changed back to clear glass or plastic. Nitrogen gas sparging of the oil and container head space blanketing have been used to prolong the shelf life of the oils effectively by the exclusion of oxygen. Oxidative deterioration has been shown to correlate directly with the amount of oxygen available to react with the oil. Nitrogen protection is ended when the consumer opens the container.

Processing. All of the liquid oils currently available to the U.S. retail consumer can be merchandised as all natural; none of the oils have been chemically modified with hydrogenation. Soybean oil, which is the highest volume retail bottle oil, is refined, bleached, and deodorized (RBD). Many of the other oils contain waxes that are removed with a dewaxing process as well as refining, bleaching, and deodorization; canola, corn, sunflower, and safflower are dewaxed to prevent a wisp or cloud from developing before use. All of these oils can be classified as salad oil because of their ability to resist clouding for 5 1/2 h at cold test conditions. Cottonseed oil must be winterized to remove the hard fractions both to qualify as a salad oil and to prevent clouding on the air-conditioned grocery store shelves. Peanut oil cannot be winterized due to the gel developed at cold temperatures; thus, it must be classified as a cooking oil and may develop a cloud on the grocery store shelf. Virgin or pure olive oil is the most natural of the oils discussed; the best grades of olive oil are produced without any processing after extraction other than decantation, centrifugation, or another filtration process. By U.S. standards, olive oil should be classified as a cooking oil; it cannot pass the cold test requirement for a salad oil.

Plant Genetics. Canola is a success story for plant breeding to control the fatty acid composition of an oilseed to produce a nutritional oil; it is a low-erucic acid/low-glucosinolate rapeseed cultivar. Canola oil's introductory marketing capitalized on a low saturated fatty acid level to claim 94% saturate-free status. Plant breeders have also been successful in altering the fatty acid composition of other oilseeds to improve the nutritional value of the oil. Low-saturated soybeans are aimed at helping food manufactures secure a "low saturated fat" claim on the product label. High-oleic varieties of several different oilseeds are aimed at improving both the health image of the oil and its oxidative stability. Both canola and soybean oilseeds have been modified to reduce the linolenic fatty acid content for oxidative stability; other possibilities include oils high in α-linolenic acid, an n-3 fatty acid (9). Canola oil is the only success of plant genetics for consumer oils, probably due to problems associated with identity preservation and the cost of these specialty oils. Blends composed of soybean, sunflower, and canola oils were introduced and merchandised as containing one third the saturates of soybean oil in the early 1990s. These blends are no longer available, indicating that consumers did not react favorably to this type of marketing. These results may also have discouraged the introduction of other modified oils with a nutritional image.

Food Service Liquid Oils

The food service industry, redefined as "food prepared away from home," continues to grow. It is growing at an inflation-adjusted yearly rate of 2.6% in contrast to a retail food sales growth rate of 0.7%. Fast food continues to represent the largest and fastest rising share of sales among separate eating places (22). Edible fats and oils are major food service ingredients for all of the food service industry. Frying shortenings and oils command the largest portion of this market, whereas salad oils, pan and grill products, margarines, and baking shortenings share equally in the remaining requirements.

Food Service Liquid Oils Frying Applications. Vegetable oils became the leading U.S. food service frying media in 1990 when the major fast-food restaurants switched from tallow to vegetable oils for frying french fries. The vegetable oil products used for frying range from hydrogenated plasticized frying shortenings, to cooking or RBD oils. RBD oils with the lowest initial cost also have the poorest frying stability of all of the available products. RBD and salad oils will perform satisfactorily when the fried food volume is extremely high and an oily product appearance is desired. In some cases, an RBD oil is chosen for a distinctive flavor that the slightly reverted oil contributes; for example, peanut flavor from peanut oil, a musty flavor from corn oil, and a nutty flavor from cottonseed oil. Specially processed or RBHWD soybean oil has also been utilized by food service for frying. This salad oil has better frying stability than RBD soybean oil due to the reduction of polyunsaturates with hydrogenation, and it maintains clarity due to winterization after hydrogenation.

High-stability frying oils comprise another clear liquid frying oil type available to the food service operator. The term high-stability oils describes triglyceride mixtures that are both liquid and stable in the temperature range of 60–85°F or 15.6–29.4°C. In nature, this combination rarely occurs. Natural oils that are liquid under these conditions are generally much less stable with respect to frying stability than solid fats. The oxidative/frying stability of vegetable oils depends on a combination of factors, including the following: (i) degree of unsaturation or number of double bonds; (ii) nature of unsaturation or the position of the double bonds; (iii) prooxidant or trace metals content; (iv) antioxidant content; and (v) exposure to oxygen. In general, the more unsaturated the fatty acid, the faster its rate of oxidation. Natural vegetable oils that are liquid at room temperature generally contain high levels of polyunsaturated fatty acids with low melting points. These polyunsaturated fatty acids, predominately linoleic ($C_{18:2}$) and linolenic ($C_{18:3}$), tend to be very liquid but are also highly susceptible to oxidation; therefore, they exhibit poor frying life in food service applications. Two entirely different techniques have been developed to enhance stability while maintaining liquidity, i.e., processing and plant breeding. Using a combination of hydrogenation and fractionation techniques, it is possible to produce oils that are both stable and liquid from otherwise unstable polyunsaturated raw materials. Plant breeding technology has developed genetically superior varieties of oilseeds that yield oils more suitable for high-temperature frying than the conventional vegetable oils. The high-stability oils, both those produced with processing or plant breeding, have excellent frying stability, approaching the stability of a hydrogenated plasticized shortening. However, high-stability oils produced with either technology have not become as popular as the solid or liquid frying shortenings, probably due to higher product costs.

Most of the clear liquid frying oils are stabilized with dimethylpolysiloxane, an antifoaming agent added to extended the frying stability. Frying life is extended 3–10 times, with the degree of increase dependent on the original frying life without the antifoamer; the more stable products initially show greater increases in frying life than the less stable products.

Other Food Service Liquid Oil Applications. The primary use for a salad or cooking oil in most food service operations is for making salad dressings. Cooking oils are generally not satisfactory for salad dressing use in industrial preparations, but can be used in food service operations in which the salad dressing is prepared fresh and is not expected to withstand prolonged storage periods at refrigerated temperatures. In making salad dressings, ease of blending with other ingredients is quite often an advantage. Most salad dressings depend on the oil to coat the salad ingredients and to hold the flavors of herbs, spices, and vinegars.

Other uses for salad oils include pan frying, griddling, sauces, gravies, dips, and some types of baking. When liquid oils are used in baking, the general use is to make chiffon- or sponge-type cakes and other all-purpose baking applications in which a lubricant is beneficial.

Food Processor Liquid Oils

Food processors often purchase their fats and oils ingredients in bulk quantities to obtain a cost advantage generated by elimination of packaging, lower shipping rates, and reduced labor costs. Liquid oils offer a definite advantage for bulk handling due to the absence of solid fractions at ambient temperatures and below. A major concern with fats and oils bulk handling is that the product may deteriorate before use. This is particularly true of shortenings that must be held in a molten state. Melted products are generally more susceptible to deterioration than packaged products or liquid oils that are normally fluid and pumpable at ordinary ambient temperatures. Autoxidation increases markedly with heating. It has been determined that the rate of oxidation doubles for each 25°F or 15°C increase in temperature within the range of 70–140°F or 20–60°C. Exclusion of oxygen during storage represents an effective method for limiting quality deterioration for all types of fats and oils. The usual procedures replace oxygen with nitrogen during transit and storage before use.

All three of the liquid oil types are utilized by food processors as ingredients for specific product applications. The choice of an oil is the result of a synthesis of many parameters, which explain the variety of solutions chosen. Liquid oils offer a choice of cooking, salad, or high-stability oil types, and functional variations occur within each regarding flavor, degree of unsaturation, fatty acid distribution, essential fatty acids, oxidative stability, frying stability, cost, or availability.

Food Processor Cooking Oils. Food processors utilize cooking oils predominately for frying snack foods, nuts, fish, poultry, meats, potatoes, and other food products for dry, refrigerated, and frozen distribution to retail and food service consumers. Food processors must evaluate the contributions of each cooking fat or oil to their product and identify the most suitable ingredient for use. One role of fat in cooking or frying is essentially to provide an efficient heat transfer medium, transmitting heat rapidly and uniformly to the surface of the food being cooked. Additionally, the oil contributes flavor and palatability to the food fried. Every fat and oil product will experience reversion to characteristic flavor, some of which will complement the food product, whereas others will not. Cooking and frying oils are used at high temperatures, often in the presence of hydrolyzing conditions, namely, water and steam. Hydrolysis causes free fatty acid development, which results in more acidic flavors. Some products that are eaten shortly after preparation do not require as stable a frying oil as other foods that are packaged and require a atmospheric shelf life of several weeks. Products that remain frozen until the consumer thaws them do not require a high degree of oxidative stability. Surface appearance of the fried food is also affected by the frying medium; liquid oils provide a shinny, wet, soft appearance, whereas solid fats impart a dry, somewhat dull appearance. Polymerization, either thermal or oxidative, causes a thicker viscosity, which increases the oil absorption and yields a greasier product.

Successful use of liquid oils in baked products has been a technological advancement for the baking industry. This technology involved the use of emulsifiers to provide the functionality lacking with the liquid oils. Baked products prepared with liquid oils alone had low volume, fair softness, and poor grain; plastic fats provided dough strength, gas retention, aeration, volume, symmetry, fine grain, and even texture. It was found that the use of proper emulsifier systems with liquid oils provided these functions with some added benefits. The liquid oils allowed the bakers to merchandise their products with "all-vegetable" and "polyunsaturated" labeling. Cooking oils are appropriate for these products because refrigeration is not an issue, and the shelf life of baked products is well within the oxidative stability of polyunsaturated oils.

Food Processor Salad Oils. Pourable and spoonable salad dressing preparation for retail and/or food service are the major uses for food processor salad oils. Separating pourable salad dressings are basically a two-phase system of oil and water, some of which contain emulsifying agents. Because most dressings are stored in the refrigerator after being opened, it is important to use a salad oil to resist clouding at these temperature conditions. In addition to the unattractiveness of a product that is cloudy when refrigerated, it is necessary that no solid crystals be present; these would give a waxy, tallowy taste sensation in the mouth. Homogenized pourable salad dressings require the use of noncrystallizing salad oils to prevent separation during refrigeration.

Mayonnaise and spoonable salad dressings are another major food processor use for salad oils. Oil constitutes 80% of mayonnaise formulations and is responsible for the body and viscosity of the product. Spoonable salad dressings have only 35–50% oil, whose function is to modify the mouthfeel of the starch paste that imparts the body. In both cases, a smooth, creamy, nonoily mouthfeel is desired; this will not be present if crystallization occurs. These emulsions are very unstable and the presence of fat crystals will break the emulsion, rapidly causing oil pockets to form (23).

Food Processor High-Stability Oils. The primary characteristics of a high-stability oil are liquidity at ambient temperatures and resistance to oxidation. Most oils that are liquid at room temperature have high polyunsaturated fatty acid contents, which are the most susceptible to oxidation. Two technologies have been developed to enhance the stability of liquid oils while retaining the functional and nutritional properties. The first technology involves processing with hydrogenation to change the polyunsaturates to monounsaturated fatty acids, followed by fractionation to separate the stearine or hard fractions formed during hydrogenation from the olein or soft fraction. The olein fraction, high in oleic fatty acids, becomes the high-stability oil. The alternative high-stability oil technology is the use of plant breeding techniques to produce oilseeds with low levels of polyunsaturates and saturates but high levels of monounsaturates. High-stability oils produced by either technology can be used by food processors wherever liquidity and oxidative stability influence the quality or handling conditions of the finished product. The identified functionalities of the monounsaturated oils are as follows (14):

1. Frying Oils. The high proportion of oleic fatty acid increases frying stability by limiting the opportunities for oxidation and polymerization. High-stability oils have exhibited frying stability results close to those of the selectively hydrogenated heavy-duty frying shortenings.
2. Spray Oils. When applied to the surface of food products, the high-stability oils protect the product from moisture and oxygen invasion, prevent clumping, and impart a glossy appearance. Specific applications include raisins and other fruits, breakfast cereals, nut meats, croutons, bread crumbs, spices, seasonings, crackers, and others.
3. Pan Release Agents. These include aerosol and brushed lubricants for cooking skillets, baking pans, confectionery products, and other food products in which liquidity and oxidative stability are beneficial.
4. Product Carrier. Colors, spices, flavors, vitamins, and other additives may be dispersed in high-stability oils to preserve the flavor, color, or activity during extended shelf life periods with fluidity.
5. Product Compatibility. High-stability oils are compatible with all other fats and oils products because crystal type is not a concern. Liquid oils do not have a crystal structure.

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Chapter 25

Specialty Fats and Oils

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Introduction

Oil and fat processors have developed a variety of tailored fat systems over the years to support product development efforts in the food and beverage, nutritional, pharmaceutical, cosmetic, and personal care industries. Efforts have included the following:

- The introduction of functional and economical alternatives to higher-priced ingredients such as cocoa butter and butterfat
- Development of fat migration inhibitors for peanut butter and nut pastes
- Processing, antioxidant, and biotechnological initiatives to enhance oxidative stability
- Development of medium-chain triglycerides capable of delivering certain nutritional benefits because of their unique metabolic pathway
- Designing encapsulation media to protect core actives and provide controlled release
- Formulation of reduced *trans* and *trans*-free systems
- Tailoring the physical form of products, e.g., flakes and beads, to enhance functionality and performance

The discussion that follows will provide a glimpse into some of the specialty fat systems that are available to support the applications outlined above. Collectively, processing techniques, source oils, and more recently, biotechnology, have contributed to the oil processor's ability to offer an array of specialty fats designed to address functional, nutritional, and economic objectives.

Cocoa Butter Alternative Fats

Cocoa butter alternative fats represent perhaps the most diverse and largest volume specialty fat category. Known generically as hard butters, cocoa butter alternatives exhibit varying degrees of similarity to cocoa butter in terms of melting properties and crystallization tendencies. Major market segments for such fat systems include confectionery, biscuit and cracker, and industrial suppliers who manufacture coatings and drops for user industries. These hard butters generally fall into one of three classifications, i.e., cocoa butter equivalents, cocoa butter replacers, and cocoa butter substitutes.

These categories encompass parameters such as origin, crystallization tendencies, and compatibility with cocoa butter. Because cocoa butter represents the gold standard, producers of cocoa butter alternatives typically compare their products' performance and characteristics to those of cocoa butter.

Products from the Cocoa Bean: Chocolate Liquor, Cocoa Butter, and Cocoa Powder

Chocolate production starts with the *Theobroma cacao* tree, a native of the equatorial Americas. Today, the Ivory Coast produces 41% of the worlds' cocoa, followed by Ghana (15%), Indonesia (13%), Brazil (6%), and Malaysia (3%) (1). Trees require 3–5 y to bear the first fruit and may not reach full yield until y 10. Their productive life can exceed 40 y (2). The fruit, or pod, is unique in that it grows from both the main trunk and large branches. It is similar in appearance to a small furrowed melon, typically with a diameter of 4 in and a length of 8 in. Pulp-covered beans (40–60) are contained within each pod. Subsequent to harvesting, the pods are split open and the beans removed. The harvested beans are fermented in covered heaps or boxes during which time sugar is converted into alcohol and carbon dioxide; the alcohol is subsequently oxidized to acetic acid by bacterial action. This process browns the bean, reduces bitter notes, and hardens the skin to a shell. Fermentation is critical to the development of desirable color and flavor characteristics and generally requires 2–3 d or longer. Thereafter, the beans are dried to a moisture content of ~6% and bagged for shipment. Drying is necessary to preclude mold growth and development of off flavors that cannot be removed in subsequent processing (3). The cocoa bean yields three products fundamental to the manufacture of chocolate and chocolate analogs, i.e., chocolate liquor, cocoa butter, and cocoa powder.

Beans are cleaned, roasted, shelled, and the broken pieces of kernel (nibs) recovered for further processing. The fat content of the nibs, cocoa butter, averages ~55%. The cocoa butter is locked within the cellular structure of the nib; therefore, either a grinding or expeller process is required to liberate the fat. Chocolate liquor is simply finely ground nibs, particles of cocoa solids suspended within cocoa butter; this is also often referred to as cocoa mass, unsweetened chocolate, or baking chocolate. Cocoa butter quality is preserved by naturally occurring flavonoid phenolics, which serve as effective antioxidants.

Chocolate liquor is separated into cocoa butter and cocoa solids under hydraulic pressure in a pot press. Residual fat content of the press cake is typically controlled to either 24 or 11%. The cake is crushed and pulverized to the desired fineness for cocoa powder. The demand for cocoa butter generally exceeds that for cocoa powder; hence the butter normally commands a much higher price. The beans, nib, liquor, or powder are often treated with an alkali solution, potassium or sodium carbonate, for example, to improve color and flavor. Product so treated is referred to as "Dutched" or "Alkalized."

Chocolate Production

The manufacture of chocolate entails the following five basic steps: (i) mixing the ingredients; (ii) particle size reduction or refining; (iii) conching; (iv) crystal development (tempering); and (v) crystallization. A typical dark sweet chocolate might contain the following ingredients: 53.0% sugar, 32.0% chocolate liquor, 14.6% cocoa butter, and 0.4% lecithin.

Generally, about one-third fat is required in the recipe to achieve the desired consistency and flow properties. The liquor content of the foregoing example provides only 17.6% fat; thus, without added cocoa butter, a dry powdery product with a fat discontinuous phase results. Additional cocoa butter creates a fat continuum that envelops each sugar or cocoa particle, thereby conveying fluidity to the mass. Lecithin, a surface-active agent, is quite useful in the production of chocolate because it has a profound influence on the fluidity of the non-Newtonian molten mass. The addition of lecithin permits achievement of a given viscosity at much lower cocoa butter content than if it were not included. Therefore, lecithin spares cocoa butter; because it is significantly less costly than cocoa butter, it provides an obvious economic advantage. Lecithin is permitted up to a level of 0.5% and can effectively replace as much as 13% of the total fat requirement (4). Table 25.1 summarizes Minifie's evaluation of the cocoa butter–sparing effect of lecithin (by determining for each 0.1% incremental addition of lecithin to a dark chocolate formulation the cocoa butter reduction required to maintain a constant fluidity). However, the effect of lecithin is strongly dependent on fat content; at higher fat levels, the viscosity-reducing effect of lecithin is rather feeble (5). There is a practical limit, ~0.5%, beyond which additional lecithin no longer reduces viscosity and, in fact, increases it. Furthermore, flavor and crystallization properties of the chocolate will be affected adversely at excessive levels of addition.

TABLE 25.1 Cocoa Butter (CB) Contents Required to Replace Lecithin in Dark Chocolate

Lecithin	CB in formula	CB reduction Formula basis	CB reduction Total fat basis
		(%)	
0	38.0	—	—
0.1	36.2	1.8	4.7
0.2	35.1	2.9	7.6
0.3	34.3	3.7	9.7
0.4	33.6	4.4	11.6
0.5	33.3	4.7	12.4
0.6	32.9	5.1	13.4
0.7	32.8	5.2	13.7

Some means of particle size reduction must be employed to produce a smooth-textured chocolate. Individual sugar crystals are very large; if they are not properly ground, the result will be a very gritty product. Chocolate paste (essentially sugar, chocolate liquor, and cocoa butter) is typically ground with a 5-roll refiner or a ball mill. A final mixing, or conche, follows to develop the texture and flavor. This process is accomplished by kneading, turning, and compressing the mass with heavy arms or rollers for several hours to several days depending on equipment, formula, and organoleptic requirements. This process thoroughly distributes the cocoa butter throughout the mass and ensures that each sugar and cocoa particle is coated. It also disrupts any agglomerates that may have been formed during refining. The result is a homogeneous flowable mass. In addition, the flavor is improved and rounded out because of the evaporation of volatile fatty acids, primarily acetic acid.

Molten chocolate must be properly chilled and crystallized to attain the desirable shiny appearance and textural properties consumers expect. The goal is to establish a stable crystalline matrix within the continuous phase (cocoa butter) that will entrap the dispersed solids (sugar, cocoa, and milk solids) and any uncrystallized fat. Cocoa butter triglycerides are predominantly symmetrical 2-oleo disaturates. Major fatty acid moieties are palmitate (25%), stearate (36%), and oleate (34%); hence, triglycerides are mainly POSt, StOSt and POP (where O = oleate, P = palmitate, St = stearate). These properties promote the triple chain length packing typical of crystallized cocoa butter. Furthermore, they induce a complex array of polymorphic possibilities. Six crystal forms are generally recognized and range from the least stable form I (melting point ~17°C) to the most stable form VI (melting point ~36°C). The lower polymorphs are transitory in nature and reform spontaneously into more stable forms. The final transition from form V to VI is a solid-state conversion; all lower polymorph transitions occur in the liquid state (6,7).

Given the foregoing, it becomes clear that cocoa butter must be steered toward the desired β polymorph to achieve finished product quality. Among the attributes affected are gloss and gloss retention, snap, contraction, and texture. The desired crystals are developed in the molten chocolate mass by a technique known as tempering; the following four basic steps are involved (temperatures are general guidelines and will vary somewhat with formulation): (i) complete melting (45–50°C); (ii) cooling to initiate crystallization (28–29°C); (iii) warming to melt out unstable crystals (30–33°C); and (iv) crystal development. The objective is to develop a small quantity of seed crystal, generally 1–4%, and thereby preclude unmanageable viscosity increases that would result if excessive quantities of cocoa butter were crystallized.

Properly tempered chocolate can then be molded (solid and hollow confections such as bars or eggs), deposited (drops, stars, clusters) or used to coat (enrobing) a substrate such as baked goods or confectionery centers. Thereafter, the product enters a cooling tunnel in which it is chilled under carefully controlled conditions to achieve the proper set, appearance, and shelf life. Products exiting the cooling tunnel will be well set and ready for packaging; however, the crystallization process continues over the subsequent 24–72 h. Hence, storage conditions during this phase are critical to ensure that the final set is achieved; a cool (16–21°C), dry environment is required (8–10). Improper tempering, cooling, or postcooling storage can compromise product appearance in the form of bloom, a white surface haze. Bloom can be either recrystallized fat or recrystallized sugar. The former results from cocoa butter recrystallization on the surface, whereas the latter occurs when excessive humidity dissolves sugar crystals into a syrup, i.e., when the moisture evaporates, the sugar recrystallizes on the surface leaving a gray, rough surface similar in appearance to fat bloom. In either case, the product is safe to consume; it simply does not have eye appeal and presents the impression of mold to many consumers.

Cocoa butter is a natural product whose properties are very much influenced by geography and climatic conditions. Flavor and melting properties are among the most critical considerations *vis-à-vis* the finished chocolate. As plantings have expanded beyond traditional locales, a range of cocoa butter melting properties has emerged. In general, Brazilian butters tend to be softer and Malaysian firmer than are those of West African origin. Cocoa butter fractions are available that permit native butters to be tailored so that, for example, they are more heat resistant, accept more milk fat, or are simply more consistent. Padley *et al.* (11) noted the typical N values (solid fat content) for each origin and also described typical melting curves for stearin and olein fractions compared with the starting cocoa butter (Table 25.2).

Why Cocoa Butter Alternative Fats?

Chocolate and cocoa products must comply with very specific standards of identity promulgated under the Federal Food, Drug and Cosmetic Act. The only fats permitted therein are cocoa butter and dairy fat. However, there are many products that either cannot bear the expense of standard of identity chocolate or are better accommodated by fat other than cocoa butter. The fat phase of chocolate, cocoa butter, is largely responsible for its desirable properties, which include a brittle and nongreasy texture at and below room temperature, excellent keeping qualities, and characteristically rapid

TABLE 25.2 Solid Fat Content for Native Cocoa Butters of Various Origins and for Fractionated West African Cocoa Butter[a]

	Solid fat content			Typical melting curves	
				West African	
	Brazil	Malaysia	West Africa	Stearin	Olein
N20	66	81	76	91	48
N25	60	76	70	95	36
N30	37	55	45	73	0
N35	0	0	0	16	0

[a] *Source:* Ref. 11.

melting near body temperature. However, chocolate exhibits other properties that challenge certain applications:

- Chocolate is sensitive to temperature fluctuations; therefore the environment of distribution systems must be controlled carefully to maintain finished product appearance and integrity.
- A strong contraction and very brittle texture upon crystallizing (setting) characterize chocolate. Such properties are less than optimal if a soft, spongy matrix is to be coated (enrobed); cracking and flaking off of the coating are a certainty.
- The presence of other fats in an enrobed center elicits shelf life concerns because fat migration fosters an exchange of liquid triglycerides between center and coating.
- Chocolate requires careful tempering (controlled crystallization) to ensure good set, gloss, and gloss retention.

Chocolate analogs (often called confectionery coatings) based on cocoa butter alternative fats are available to address the foregoing issues and hence, in certain applications, offer technical advantages over chocolate. Furthermore, the traditionally higher cost of cocoa butter and chocolate liquor with respect to chocolate analogs offers an economic incentive. Hard butters, then, are used to replace or extend cocoa butter in the formulation of confectionery or compound coatings and related products. They are also used in pastels of various colors and flavors, common in seasonal novelties. In addition to being used to enrobe confections and bakery products, confectionery coatings can also be molded or deposited. Selection of the appropriate hard butter is key to product success because the fat is largely responsible for the final appearance, mouthfeel, texture, flavor release/impact, and shelf stability of the finished good. It is important to note that cocoa butter alternative fats do not deliver any "chocolaty" notes; rather, coatings so formulated rely upon cocoa powder and/or chocolate liquor for such. In fact, hard butters are expected to be quite bland and odor free so that they do not interfere with organoleptic objectives.

Cocoa Butter Equivalents (CBE)

CBE are formulated from fats whose melting and crystallization properties rather closely resemble those of cocoa butter. As such, they tend to be quite compatible with cocoa butter and hence perform well at all levels of addition. They serve a variety of roles including the following: (i) improve softer cocoa butters; (ii) firm up chocolates that contain high levels of milk fat; (iii) stabilize liquid oils in nut-containing fillings; (iv) enhance the heat resistance of chocolate; and (v) serve as an economical alternative to the additional cocoa butter required for chocolate formulation.

Raw materials for CBE production are of tropical origin; with the exception of palm, most are wild jungle crops rather than cultivated on plantations. Hence, supply and quality are a constant challenge for processors. Major sources and origins include palm from Malaysia, Indonesia, West Africa, Papua New Guinea and South

TABLE 25.3 Typical Fatty Acid Compositions and Triglyceride Profiles for Selected Cocoa Butter Equivalent Feedstocks[a]

	Cocoa butter	Palm	Illipe	Shea	Sal	Kokum
Palmitic (P)	25	45	16	4	5	2
Stearic (St)	36	5	46	43	44	57
Oleic (O)	34	38	35	45	40	40
Linoleic (L)	2	10	—	7	2	1
Arachidic (Ar)	1	—	2	—	7	—
PPP	—	5	—	—	—	—
POSt	39	3	35	5	11	5
StOSt	26	—	45	40	42	72
POP	16	26	7	—	1	—
StOAr	2	—	4	2	13	—
StLP	4	2	—	—	—	—
PLP	2	7	—	—	—	—
StLSt	1	2	—	—	—	—
PPO	—	5	—	—	—	—
StOL	—	—	—	6	1	—
OOO	—	3	—	5	3	2

[a]*Source:* Ref. 12.

America; illipe (sometimes referred to as green butter) from Borneo; shea from West and Central Africa savannah regions; sal from India; and kokum from India. Table 25.3 summarizes typical fatty acid compositions and major triglyceride families for CBE raw materials and cocoa butter. Illipe and kokum are so similar to cocoa butter that they often require only minimal processing (refining and deodorization) to make them suitable components. Palm and shea, on the other hand, although good sources of symmetrical triglycerides, also are rich in di- and triunsaturates and thus are significantly softer than cocoa butter. Palm also contains a substantial quantity of PPO, whose crystalline behavior exhibits only feeble compatibility with that of cocoa butter. Consequently, these fats require the sophisticated modification offered by fractionation to remove undesirable triglyceride families and render them suitable CBE components.

The process of enzymatic hydrolysis and reesterification has been commercialized in recent years and presents another option for triglyceride structuring, allowing more abundant materials such as palm mid-fraction or high-oleic oils to be used as feedstocks. A regiospecific lipase is employed to tailor the α position fatty acid moieties on the triglycerides. For example, high-oleic sunflower oil and stearic acid combine in the presence of a 1,3-specific lipase to yield StOO, StOSt, and OOO glycerides plus a variety of by-products including undesirable but largely unavoidable diglycerides (they depress melting point and retard crystallization).

CBE describes a range of products, some of which are designed for total replacement of cocoa butter, whereas others are partial replacers. The former are more costly products because they have a triglyceride profile that closely mirrors that of cocoa butter. Considerable effort is required to produce the pure fractions of symmetrical triglycerides required for these products. They can be used to replace all of the free cocoa butter in a recipe—typically, the ratio between the CBE and cocoa butter (from chocolate liquor) will be nearly 50:50. As the POP content increases, temper time increases, and the crystallized product becomes progressively softer. POP is typically a lower-cost component and hence occupies a larger portion of the lower-cost CBE. These CBE are usually softer than cocoa butter and less tolerant toward milk fat.

Cocoa Butter Replacers (CBR)

CBR are derived from nonlauric partially hydrogenated oils and fats (most typically soybean, cottonseed, or palm). Hydrogenation parameters are manipulated (elevated reaction temperatures, reduced hydrogen gas pressure, and partially inactivated or sulfur-promoted catalyst) such that *trans*-octadecenoic isomer formation is maximized in an effort to achieve the required steep melting profile. However, their melting curves are inferior to that of cocoa butter, and hence eating quality suffers. They are best-suited for enrobing bakery products in which the mass and texture of the substrate tend to dominate the eating experience. CBR quality can be enhanced by fractionation whereby the triglyceride families that detract from performance are removed selectively to a large extent. The resultant hard butter exhibits an improved melting profile and thus much improved eating quality. CBR processed in this manner are suitable for high-quality bakery products as well as many confectionery applications. They offer the following advantages:

- Tempering is not required because they crystallize spontaneously in the β' polymorph; practically speaking, this is the stable crystal form for CBR.
- Good gloss and gloss retention.
- Good compatibility with other nonlauric fats.
- Good miscibility with cocoa butter, up to 20–25% (fat basis) depending upon the CBR. This property provides the option of chocolate liquor inclusion, thereby improving flavor impact and flavor release. It also facilitates changeovers between chocolate and chocolate analogs because each product will tolerate some commingling with the other.
- Coatings tend to be more pliable and thus are well-suited for enrobing soft or spongy substrates.

Cocoa Butter Substitutes (CBS)

CBS are produced primarily from lauric fats such as coconut and palm kernel, although lesser quantities of hydrogenated soybean, cottonseed, palm, or other nonlaurics are frequently used in many CBS. Processing techniques include hydrogenation, interesterification, and fractionation. The triglyceride families of lauric fats are characterized

TABLE 25.4 A. Typical Melting Curves for Palm Kernel (PK) Oil, Hydrogenated Palm Kernel (HPK) Oil, and Hydrogenated and Interesterified Palm Kernel (HIPK) Oil

		PK	HPK	HIPK
Solid fat content at	10.0°C	73	95	93
	21.1	38	84	74
	26.7	8	54	45
	33.3	0	17	9

B. The Wide Range of Possible Cocoa Butter Substitutes From Hydrogenation and Interesterification

Mettler dropping point (°C)		36	39	42
Solid fat content at	10.0°C	93	94	95
	21.1	74	76	80
	26.7	45	45	48
	33.3	9	12	15

C. Results of Fractionating Palm Kernel (PK) Oil

		Whole PK	PK stearin	PK olein
Solid fat content at	10.0°C	73	92	62
	21.1	38	82	19
	26.7	8	59	0
	33.3	0	0	

by significant quantities (50% or more) of shorter-chain length fatty acids (C_8–C_{12}); they tend to be small and uniform and hence crystallize well and melt sharply. Palm kernel is an especially useful feedstock; it can be tailored such that it rivals the steep melting profile of cocoa butter. Hence, CBS offer very high quality alternatives in terms of flavor impact and sharp melting properties. Native palm kernel is too soft for most confectionery applications because it is largely liquid slightly above room temperature. Complete hydrogenation yields a very firm fat that is too high melting (~45°C) for many formulations. However, random interesterification of hydrogenated palm kernel dramatically improves its melting properties in that the firm brittle nature is largely maintained up to 25–30°C; at higher temperatures, the fat begins to melt away quickly and exhibits a final melting point of ~36°C. Typical melting curves for palm kernel oil (PK), hydrogenated palm kernel oil (HPK) and hydrogenated and interesterified palm kernel oil (HIPK) are described in Table 25.4A When combined, these two processes provide an array of CBS that cover a wide melting range (Table 25.4B). Alternatively, palm kernel oil can be fractionated to produce an extremely brittle and sharp melting stearin and a very soft olein as shown in Table 25.4C. Selective partitioning significantly reduces the content of the lower-melting triglycerides laden with shorter-chain acids and/or less saturated acids; thus, the stearin is enriched with

TABLE 25.5 Typical Fatty Acid Distribution (%) for Palm Kernel (PK) and PK Fractions

Distribution	Whole PK	PK Stearin	PK Olein
C_8	3.5	2.5	4.5
C_{10}	3.5	3.0	4.0
C_{12}	48.0	55.0	42.0
C_{14}	16.0	20.0	12.5
C_{16}	8.0	8.0	8.5
C_{18}	2.5	3.5	2.5
$C_{18:1}$	15.5	7.0	22.0
$C_{18:2}$	2.5	0.8	3.5
Iodine value	13–18	6–9	25–31

lauric-, myristic-, and palmitic-containing triglycerides (Table 25.5). Palm kernel stearin can be hydrogenated to produce an even harder product; the reduced content of longer-chain acids limits the melting point of fully hydrogenated stearin to ~37–39°C.

A variety of intermediates are possible from hydrogenation, interesterification, fractionation, and combinations thereof, all of which can be blended to tailor a broad range of CBS products. The following two critical properties of CBS fats must be considered for all formulation efforts: (i) Their triglyceride profile deems them incompatible with cocoa butter; hence, chocolate flavored coatings or confections must be formulated with low-fat cocoa powder. The cocoa butter content of the finished recipe must be limited to <5% (fat basis) to prevent excessive softening and bloom. (ii) All sources of lipase and other factors that promote hydrolysis must be avoided. Shorter-chain length free fatty acids present extremely low flavor thresholds and are quite objectionable to the palate in that they are typically perceived as soapy.

CBS offer the following advantages: (i) tempering is not required; (ii) they crystallize quickly and exhibit strong contraction when cooled; (iii) melting properties and flavor release are comparable to those achieved with cocoa butter; (iv) gloss and gloss retention are good; (v) they possess high tolerance to diluent fats such as nut oils.

Center Fats

Centers or fillings are dispersions of solid particles (sugar, starch, protein, fibers, and fat crystals) within a fluid medium (oil). A major consideration is flavor stability; hence, lauric-based fats are often natural choices for such applications given their inherently excellent oxidative stability and rapid melt down. A variety of specialty center fats have been developed over the years to support the diverse range of textural properties confectioners have devised for fillings and centers. Depending on the structure and melting properties required of the center fat, processing techniques include hydrogenation, interesterification, fractionation, and combinations thereof. Lipid systems range from fluid or semifluid to firm and steep melting.

Oil migration presents a significant technical challenge to many confectionery products. A primary consideration during new product concept development must be to evaluate the total confection in terms of the oils and fats present. Generally, the chocolate (standard of identity or compound) shell material of a filled confection will contain about one-third fat. The center material, on the other hand, can be very lean to quite rich in terms of its fat content; furthermore, the fat might be completely liquid (nut oil for example) or rather firm (fractionated palm kernel oil). Herein resides the challenge for maintenance of product quality. Liquid triglycerides will migrate throughout the finished piece such that phase equilibrium is established. In the case of centers that contain generous portions of chopped nutmeats, significant quantities of nut oil will move throughout the mass seeking phase equilibrium. The typical outcome is softening of the chocolate shell, loss of gloss, and bloom. Judicious selection of both the cocoa butter alternative fat for the shell and the center ingredients, with the objective of maximizing compatibility, will greatly improve the finished product stability. In addition to the previously described surface defects that can occur, the center quality might also suffer; for example, it might dry out or even collapse. To inhibit or at least retard migration, particle interaction must be increased to a critical point, at which time the environment becomes so crowded that mobility is virtually eliminated. Specialty fats can provide a structural network that elevates particle interaction. The fine-grained morphology of the β' polymorph has the ability to interlock in a rigid manner and thus entrap substantial quantities of liquid components. β'-tending hard stocks are characterized by a heterogeneous saturated fatty acid moiety mix and include fully hydrogenated cottonseed, palm, and rapeseed. These hard fat components behave much like plasticizers in shortenings. Colby and Japiske (13) described synergistic actions they observed among β'-tending hard fats. They prepared hard stocks from fully hydrogenated rapeseed and fully hydrogenated palm or cottonseed or fractionated cottonseed. To evaluate polymorphic stability, shortening compositions were melted at 60°C and rapidly chilled to a solid at 10°C in ~15 s. The samples were stored at 46°C for 7 d and then analyzed for percentage of β crystals in the crystalline phase. The plastic shortening compositions were comprised of 94% base stock (90% soybean oil/10% cottonseed oil hydrogenated to 98 iodine value) and 6% test hard stock. Rapeseed/palm was found to be the best hard stock on the basis of the improvement conveyed upon β' stability as evidenced by a reduction in β crystals (Fig. 25.1).

Conversely, there are situations in which specialty fats that are normally considered incompatible are blended in an effort to achieve a specific technical effect. For example, a melt-away center can be formulated with a combination of cocoa butter and fractionated palm kernel oil. Admixture of these fats creates a severe eutectic in which the melting point of the blend is lower than that of either component (Fig. 25.2). The result is a very pleasant eating quality that is characterized by rapid and complete melting accompanied by a cooling sensation on the palate.

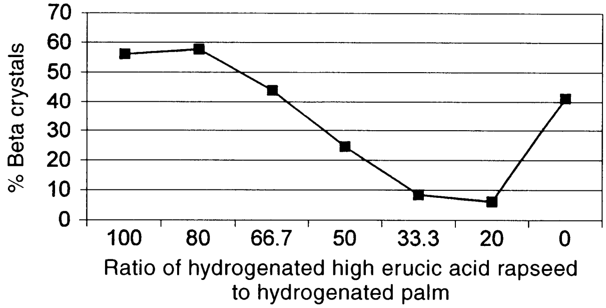

Fig. 25.1. The percentage of β crystals vs. the percentage of hydrogenated rapeseed in shortening formulated with 6% hardstock composed of varying ratios of hydrogenated rapeseed/hydrogenated palm.

Ice Cream Coatings

Often referred to as pail coatings, these are very-high-fat content products, typically 55–70%. Traditional chocolate and confectioners' coatings are too viscous and the fat is too hard for frozen novelties. Coatings must crystallize rapidly and leave a very thin yet nontransparent layer. Because the confection is consumed frozen, the normal mouth temperature is significantly reduced. Therefore, the coating fat must be designed to melt away without a waxy residue; these fat systems normally melt below 30°C. The required snap and rapid melt dictate a steep melting curve. Laurics, especially coconut oil, are a natural for this application. Furthermore, these coatings must set quickly to ensure uniform coverage, good appearance, and production efficiency.

A very basic recipe is 60% coconut oil, 33.5% sugar, 6% cocoa powder, and 0.5% lecithin. Alternatively, 60% chocolate (or confectioners' coating) is blended with 40% coconut oil. It is also quite common to incorporate 10–20% of a stable nonlauric oil (peanut or sunflower, for example) with the coconut oil to create a eutectic that depresses the melting point further, hence improving flavor release. This also has the effect of damping the inherent coating brittleness, thereby reducing its tendency to crack and flake off the ice cream bar during consumption. However,

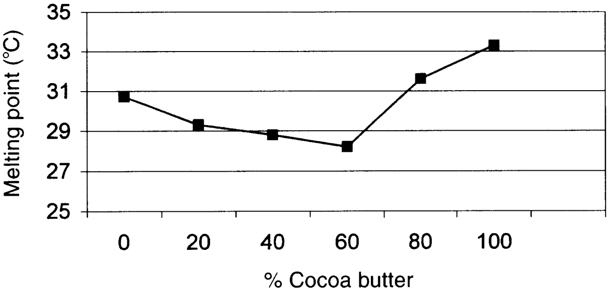

Fig. 25.2. Admixture of cocoa butter with cocoa butter substitute: melting point eutetic.

such formulations will require longer crystallization times and show increased drip and dry times. Partially hydrogenated and fractionated soybean and soybean/cottonseed specialty fats have also been used successfully. These are designed to mirror rather closely the melting profile of coconut oil, but they tend to be more pliable.

Peanut Butter Stabilizers

Peanut butter is a relatively simple product and, in fact, may consist only of shelled, roasted, ground peanuts. Optional ingredients include sweetener, stabilizer, and salt. Raw peanuts typically contain at least 48% oil; clearly, grinding roasted peanuts for the production of peanut butter releases substantial quantities of oil. Herein resides the fundamental challenge, i.e., peanut oil, like all fats and oils, is hydrophobic. Furthermore, peanut oil, with a cloud point and melting point of 4 and –2°C respectively, is completely liquid at typical distribution, storage, and use temperatures. The peanut solids, on the other hand, are largely hydrophilic. Such a mixture is inherently unstable, and the hydrophobic and hydrophilic components will tend to migrate away from one another. This gravitational instability is clearly evident in a jar of natural peanut butter. Shortly after production, the denser substantially proteinaceous solid materials separate from the lighter oil and settle to the bottom.

One time-honored approach to resolving this gravitational instability problem has been entrapment of free oil within a crystalline structure of hard fat. The fine-grained morphology of the β′ polymorph has the ability to interlock rigidly and thus entrap substantial quantities of liquid components. Typically, 1.5–3% fully hydrogenated β′-tending hard fat, (palm, cottonseed, high-erucic acid rapeseed oil, and combinations thereof) are incorporated to maintain phase stability. These hard fat compounds behave much like plasticizers in shortenings. A patent issued to Sanders (14) describes the stabilization of peanut butter with added rapeseed oil that has been hydrogenated to a 10 maximum iodine value. The resultant spongy matrix of fat crystals holds the peanut solids in suspension.

Emulsifiers are often added either alone or as an adjunct to fully hydrogenated triglycerides. Given the low moisture content of peanut butter, emulsifiers do not behave in the classic sense. Woodroof (15) postulated that they complex with the protein and cause it to form a more readily suspendible solid in the oil phase. The combination of β′ hard fat and monoglyceride hardens into a fine-grained structure, giving the peanut butter a glossy surface, stability over a wide temperature range, and improved mouthfeel.

Seiden and White (16) claimed a β′ stable tailored triglyceride hard stock that when incorporated into peanut butter provides a softer butter with improved storage stability "by facilitating more effective entrapment of the liquid oil components." They further claimed that their invention yields a peanut butter exhibiting less stickiness. Traditional β′-tending hard stocks contain 20–30% glycerides that are not β′ stable; for example, StStSt, PPP, and 1,3-diglycerides. Fractionation techniques can be employed to tailor triglycerides to position-specific compositions to minimize the content of those triglycerides that compromise β′ stability. Such a stabilizer was prepared by fractionation of palm to produce a component that was very rich in SOS (71.2%) triglycerides. This fraction was subsequently fully hydrogenated to produce a PStP fat. Fully hydrogenated rapeseed oil was blended 21:79 with the PStP fat to produce the claimed stabilizer.

Vegetable Dairy Fats

Functional and economic incentives fostered the development of specialty fats designed to replace butterfat in a variety of dairy products including dressings, dips, toppings, creamers, and cheese. Imitation dairy products have been on the market for many years. The Filled Milk Act of 1923 defines these products as "any milk, cream, or skimmed milk...to which has been added, or which has been blended or compounded with, any fat or oil other than milk fat, so that the resulting product is an imitation or semblance of milk, cream, or skimmed milk." The Act prohibits "manufacture, shipment or delivery for shipment in interstate or foreign commerce" of any filled milk. Simulated or imitation dairy products contain no milk and are generally formulated from vegetable fat, protein (sodium caseinate, soy protein, or whey protein), carbohydrate (corn syrup solids, lactose), emulsifier, butter salts, stabilizer, vitamins, and flavor.

Nondairy liquid, spray-dried, and frozen coffee whiteners, toppings, cultured products, eggnogs, and "milk" shakes began to appear in the early 1960s. The butterfat alternatives developed for these products provided improvements such as freeze-thaw stability, improved whipping properties and whip stability, and longer shelf life, especially for spray-dried products, because butterfat alternatives could be formulated with significantly improved oxidative stability compared with dairy fat (18).

Vegetable dairy products produced with filled milk are conventionally processed. The fat content and characteristics can be manipulated to produce a variety of fat levels and physical properties. Vegetable fat and emulsifier are co-melted and then pasteurized together with water and nonfat milk solids. The product is then homogenized and cooled for either culturing or storage and subsequent incorporation into other formulations. Examples include filled milk, mellorine, simulated sour cream, and imitation cheese. Alternatively, vegetable dairy products can be formulated directly rather than *via* a filled intermediate. Processing can often be simplified and ingredient flexibility is generally enhanced significantly. Ingredients are simply blended, pasteurized, homogenized, and cooled.

Coffee whiteners and whipped toppings represent widely recognized examples of imitation dairy products. Liquid and frozen coffee creamers typically contain 3–18% fat and powdered products 30–40%. Fat is largely responsible for the whitening effect of these products; if the fat is too low melting, it will interfere with dispersibility of the creamer. High-melting fats, i.e., above 45°C, tend to detract from palatability and produce a more viscous product that does not disperse readily. Whipped toppings are available in a variety of formats including frozen,

frozen concentrate, dry, and aerosol. Finished toppings generally contain ~30% fat. Fat is critical to topping quality; it must be completely bland, exhibit excellent oxidative stability, provide the required structure for good whipping performance and overrun, contribute to structural whipped stability, and melt away rapidly and completely at mouth temperature to avoid waxiness.

A variety of butterfat alternatives have been developed to support this industry. Key criteria include the following: (i) bland and stable flavor and (ii) melting properties similar to those of butterfat, i.e., good body with a sharp melting point near mouth temperature. A clean flavor is critical because these products are emulsions, which present a very large surface area to the tongue; thus, any off notes will be accentuated. The melting point must be managed such that it occurs near mouth temperature; higher melting fats will leave a greasy or waxy palate impact. Lauric fats are commonly employed because of their bland flavor and steep melting profile. Suitable candidates include coconut oil, hydrogenated coconut oil, and hydrogenated and interesterified lauric systems. It is critical that hydrolytic stability be maintained in these formulations; otherwise, liberated shorter-chain fatty acids will impart a disagreeable sharp soapy flavor to the product. Nonlauric systems are sometimes employed, especially in formulations in which other ingredients present the potential to initiate hydrolysis. These products are typically produced with partially hydrogenated soybean and/or cottonseed oils and can be tailored further by recovering selected triglyceride families *via* controlled crystallization and fractionation. However, whether lauric or nonlauric vegetable dairy alternatives are selected, neither is capable of delivering the traditional butter and milky notes expected from dairy products because they lack butyric acid. Hence, such products often contain flavor concentrates designed to convey the lacking dairy notes. For whipped toppings, hydrogenated lauric fats, including palm kernel, palm kernel, and coconut oil blends, hydrogenated interesterified palm kernel, and fractionated palm kernel oil, are among the products that have been used successfully in such formulations. To a lesser extent, high-quality hydrogenated fractionated nonlauric fat systems are used as well.

High-Stability Oils

Traditional liquid oils are quite often not oxidatively robust enough to satisfy product shelf life requirements. Flavor stability (a function of oxidation) of oils and fats is critical to consumer acceptance of finished products because any off notes will suggest that products are of poor quality. Some items, cookies and crackers, for example, require a shelf life of many months. Oxidative stability is largely a function of the component triglyceride families; those that are the most unsaturated tend to be less stable. Nasner (18) assigned the following relative rates of autoxidation to C_{18} fatty acids at 20°C: Stearic (18:0), 1; oleic (18:1), 100; linoleic (18:2), 1200; and linolenic (18:3), 1500.

Oxidative stability is a key consideration for product development and is typically assessed *via* techniques such as the oxidative stability index (OSI) and Schaal oven test. Both test methods accelerate the oxidation process by subjecting samples to elevated temperatures and then measuring oxidation products that develop against time. For OSI, a continuous stream of air is bubbled through the test sample, which is typically maintained at either 110 or 130°C. As the oil degrades, volatile organic acids are produced (these are stable secondary oxidation products) and subsequently swept into a vial of deionized water whose conductivity is monitored. The reaction proceeds slowly at first (the induction period) and little acid is produced; eventually, a rapid rise in conductance occurs as significant quantities of acid are generated—this is taken as the endpoint and reported in hours. Although OSI is now the official AOCS method for determination of oxidative stability, references to the obsolete AOM method persist. The biscuit and cracker industry developed the Oven Test (also often termed Schaal Test) in the 1920s to rank the relative keeping quality of shortenings being offered by suppliers. The test is simple and does not require any specialized equipment. The shortening to be evaluated is placed into a watchglass covered beaker and stored in a temperature-controlled oven at 63°C. The test material is removed daily and the odor evaluated. Because the temperature is considerably lower than that employed for the accelerated testing described above, this test is deemed useful for the characterization of odors and flavors other than rancidity that might develop during the product's shelf life. Finished goods, such as crackers, can be evaluated similarly. Variations include assessment of flavor and peroxide value during the testing period as a means to quantify storage degradation. It is also common to incorporate antioxidants into duplicate samples and thereby assess their efficacy (19).

Selective partial hydrogenation is an effective vehicle whereby the oxidative stability of highly unsaturated oils can be enhanced significantly. Ideally, linolenic and linoleic acids are preferentially converted to oleic acid with concurrent minimal formation of stearic acid. Unfortunately, selectivity is not perfect, and some higher-melting triglycerides are formed as well. Thus, there are practical limitations beyond which the hydrogenation reaction cannot be carried when the required product must remain relatively clear at room temperature. Soybean oil stability, for example, can be approximately doubled with this technique. On the other hand, natural more highly saturated oils, such as coconut, can be ≥15-fold more stable than soybean oil and yet remain relatively liquid at temperatures near or slightly above room. For applications that demand lower saturate levels or greater stability in liquid form, selective partial hydrogenation is carried further. However, as the level of unsaturates is reduced, the amount of higher-melting glycerides formed by both carbon-carbon double bond saturation and *trans* isomerization steadily increases; hence, the product is no longer liquid but rather a semisolid. To achieve the required fluidity or clarity, the partially hydrogenated stock can be melted completely, crystallized under a controlled regime, and subsequently fractionated to recover an olein that remains clear at room temperature and concurrently exhibits exceptional oxidative stability. The oxidative stability of soybean oil so processed can be enhanced ~35-fold. This significant oxidative improvement is a function of both the reduction in unsaturates realized *via* partial hydrogenation and a modest preferential partitioning of tocopherols into the olein fraction.

Biotechnology, both hybridization and genetic modification, has produced a variety of property-enhanced oilseeds in recent years. The object of many of these programs is to reduce polyunsaturates, thereby significantly enhancing oxidative stability. Noteworthy commercial introductions include high-oleic (HO) sunflower, canola, and soybean varieties. The following stabilities (as determined by OSI induction time at 110°C) have been reported for these oils compared with traditional soybean oil (20): Soybean, 6.9 h; HO sunflower, 18.2 h; HO canola 20.9 h; and HO soybean, 80.7 h.

High-stability oils are well suited to a vast array of applications including the following:

1. Many dried fruits are coated with oil to preserve quality, appearance and flavor. The oil barrier minimizes moisture loss, enhances appearance and sheen, prevents clumping, and controls surface sugar crystallization. Usage levels are low, typically <0.4%.
2. Breakfast cereals are often fortified with vitamins and minerals and frequently colored and flavored as well. High-stability oils serve as effective vehicles for these additives and ensure consistent dosing. They also serve as dust control agents, coatings for inclusions (dried fruits or nuts), and spray oils for gloss and bowl life enhancement.
3. Spice and seasoning blends incorporate high-stability oil for dust control and as a moisture barrier. Their bland and stable flavor also makes them well-suited vehicles for both suspensions and solutions of flavorants and seasonings.
4. The food contact surfaces of many pieces of equipment, such as containers, trays, molds, or conveyors, require lubrication to ensure clean product release. High-stability oils are widely used to lubricate pans, trays, belts, cutters, wrappers, bands, molds and so on. They provide both release properties and lubrication, thereby promoting production efficiencies by reducing downtime required for cleanup and the percentage of damaged product. Electrostatic delivery devices are available that permit extremely clean (no fogging) and accurate dosing.
5. They are applied as surface sprays to many baked items to promote richness, improve mouthfeel, enhance surface sheen, provide a moisture barrier, and facilitate the adhesion of seasoning agents added during tumbling and shaking. The large surface-to-volume ratio and extended shelf life requirement presented by such products dictate that the surface spray be extremely robust toward oxidative degradation.
6. Cooking products within a hot oil bath both drives product moisture down and renders out native oil. In both cases, the frying medium diffuses into the substrate and becomes an integral component thereof. Because nut oils are generally highly unsaturated, selection of a high-stability roasting medium provides the opportunity to enhance the shelf life of oil-roasted products. Native oil freed as a result of cell wall rupture is quite labile, and the exchange that occurs between frying medium and na-

tive oil, as well as oil uptake that occurs as moisture is boiled off, infuses the nutmeat with roasting oil. Hence, if a high-stability roasting oil is selected, some partitions into the nutmeat and subsequently enhances storage stability.

Medium-Chain Triglycerides

Medium-chain triglycerides (MCT) were developed at E.F. Drew & Co. in the early 1950s. The genesis, as described by V. K. Babayan (21), was a directive by Ernest Drew, company president, to develop a "fatless" fat. Drew wanted the product to taste like fat and deliver the eating pleasure of fat, but not contribute to obesity. Babayan's research team focused on glycerin esters of C_6, C_8 and C_{10} (medium chain length) fatty acids as candidates for the following reasons: (i) MCT contribute ~8.3 kcal/g compared with 9.2 for conventional fats and oils; (ii) MCT readily solubilize, oxidize, and metabolize upon ingestion; (iii) the E.F. Drew Co. was in the business of processing and fractionating coconut oil fatty acids. They essentially recovered three fractions, two of which were used in the production of synthetic detergents, cocoa butter alternative fats, and mono/diglycerides. The top fraction, composed mainly of C_8 and C_{10} fatty acids, was a by-product and simply accumulated. Hence, a profitable outlet for this fraction certainly motivated Drew's interest in the project.

MCT are produced by reacting together glycerine and medium-chain fatty acids; esterification is random and all possible isomers are formed. Caproic (C_6), caprylic (C_8) and capric (C_{10}) acids were recovered originally in the approximate ratio of 2:52:46 (21). Today, very pure C_8 and C_{10} fractions are available and can be used to produce triesters as well as mono- and diesters having essentially only one fatty acid species. An early MCT specification described by Babayan (21) is shown in Table 25.6. These products are essentially colorless and odorless, exhibit excellent oxidative stability, are very low viscosity (typically <35 cP at 25°C), display excellent solvency and miscibility, and have good lubrication properties.

The transport and metabolism of MCT are unique compared with traditional fats and oils. Bloom, Chaikoff, and Borgström demonstrated in the early 1950s that after intestinal absorption, fatty acids with C_{10} and lower chain lengths were transported

TABLE 25.6 Typical Medium-Chain Triglyceride Specification[a]

Free fatty acid (as oleic)	0.05% maximum
Saponification value	345–355
Iodine value	1.0 maximum
Acetyl value	5.0 maximum
Setting Point	–5°C maximum
Color, Lovibond	10 Yellow/1.0 Red
Unsaponifiables	0.5 maximum

[a] *Source:* Ref. 21.

primarily *via* the portal vein, whereas those C_{16} and higher were transported mainly in the lymph (22). Babayan (21) reported that the portal system transport cut-off was at C_{12} and thus used minimal C_{12} content in his formulation to ensure "clean, rapid metabolism of MCT oils." Upon reaching the liver, medium-chain fatty acids are degraded to two-carbon fragments and ketones or are oxidized completely (22). Both the hydrolysis of MCT and absorption of medium-chain fatty acids are much more rapid than those of their long-chain counterparts. Long-chain triglycerides are hydrolyzed for transit across the lumen wall and thereafter reesterified into triglycerides and packaged into chylomicrons for transport thorough the lymphatic system. Surplus chylomicrons eventually reach the liver where the fatty acids are either oxidized or become available for storage as depot fat.

MCT are well-accepted ingredients in clinical foods. These specialty oils provide readily available energy for those with either compromised or poorly functional gut metabolism; thus they are beneficial for premature infants, AIDS and cancer patients, burn victims, and people with shortened bowel syndrome. Medium-chain esters are useful for such applications because they are hydrolyzed and absorbed much more rapidly than long-chain esters; thus they represent a way in which to deliver adequate amounts of energy more efficiently (22,23). However, when fed as the sole lipid source, medium-chain esters possess some inherent drawbacks for certain clinical situations. For example, they contain no essential fatty acids; furthermore, their metabolic rate may be so great that an intravenous feeding formula cannot be sufficiently laden with calories to supply nutritional requirements adequately without undesirable side effects. Oils rich in longer-chain n-3 and n-6 unsaturated fatty acids have been co-randomized with MCT to address such issues (24). This permits delivery of the quick energy available from MCT metabolism while also providing essential fatty acids. Inclusion of longer-chain acids can also mediate the metabolic rate. The ω fatty acids distributed at the 1- and 3-positions might also be beneficial for visceral trauma patients to help ward off opportunistic infection (25).

The unique metabolism of MCT provides the opportunity for the formulation of specialized products with specific nutritional orientations. For example, infant formulas, geriatric preparations, sports (energy) bars and drinks, and reduced-calorie products are but a few of the categories that might derive a significant portion of their unique nutritional benefits from MCT. In addition, their unique physical properties offer a variety of functions for food processors including the following: Solvent or carrier for flavors and colors; antistick/release agent for candies, baked goods, dried fruits, wrappers, or cutting devices; gloss and gloss-enhancing coating component in combination with beeswax or carnauba wax, for example; and mineral oil alternative.

MCT are also quite functional in a variety of pharmaceutical, cosmetic, and personal care products. Desirable properties include excellent emolliency, skin penetration, solvency, oxidative stability, and compatibility with a wide range of ingredients. In addition, they are nonirritating and do not leave a greasy residue on the skin. Hence, they are often found in skin care products, tanning ointments, color cosmetics, fragrances, and bath products. In addition to fully substituted esters, mono- and diesters of medium-chain fatty acids are also produced. They are very efficient and effective carriers for many compounds that are especially difficult to solubilize, e.g., protein drugs. MCT functionality can be varied further by substitution of propylene glycol for glycerine during synthesis. The resultant medium-chain propylene glycol diesters possess many of the properties previously described for MCT. However, the propylene glycol backbone conveys a lower cloud point and viscosity to the esters than does glycerine.

Encapsulants

Physiologically active substances, acidulants, salt, leavening agents, colorants, or thickeners, are often introduced into environments in which their efficacy is severely constrained. Such lability generally dictates that less efficient modes of addition or incorporation be applied. Alternatively, the active material(s) can be protected by enclosing them within a fat shell matrix. The properties of the fat system are carefully manipulated such that the core material activity is preserved until it is required by the "system." Some examples are given.

Feed Additives. A variety of feed additives exist for ruminants to enhance breeding efficiency, growth, or lactation. Physiologically active substances that might be contained therein include amino acids, vitamins, enzymes, drugs, hormones, microorganisms, and/or minerals. When fed orally, many such substances are decomposed by microorganisms and enzymes in the rumen; hence, their physiologic activities are often severely degraded or even eliminated. A hydrophobic coating protects the core material during transit through the rumen and must have a melting point higher than that of the rumen fluid (~40°C). The shell material is designed such that it becomes permeable only in the abomasum or beyond in the intestinal tract (26,27).

Meat Products. The flavor, color and shelf life of many meat and meat emulsion products are enhanced *via* acidulation. However, pH reduction often compromises processability because emulsions firm up significantly in more acidic environments. This is especially problematic for sausages and related products because the firm emulsion cannot be stuffed properly into casings. This problem can be overcome by coating solid granular acids with a fat that is designed to remain solid over the temperature ranges encountered during emulsion formation and stuffing operations, and melt at the higher temperatures encountered in the smokehouse, thereby releasing the acidulant (28,29).

Reduced *Trans* Systems

Animal fats were traditionally employed for bakery and frying applications because they were available, economical, and generally performed well; their physical properties and stability made them a natural choice. Vegetable oils lacked functionality because of their liquid nature and relatively poor stability toward oxidative degradation. The advent of commercial hydrogenation provided the opportunity to improve upon the natural properties of vegetable oils, thus rendering them suitable for

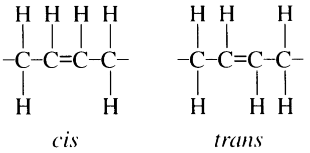

Fig. 25.3. Naturally occurring and alternate geometry demonstrating the hydrogen atoms in the *cis* and *trans* positions.

many of the applications traditionally occupied by lard and tallow. This technology also offered what were deemed nutritionally superior vegetable oil alternatives as scientists began to recognize the baggage represented by the cholesterol content and high saturate level characteristic of animal fats. Simply put, hydrogenation is the addition of hydrogen atoms across the double bonds in unsaturated fatty acids. This reaction is extremely important to the food industry because it permits oils and fats to be tailored, in terms of stability and melting properties (and hence functionality) to the end application. Edible oil processors are capable of exercising a fair degree of control over the hydrogenation reaction. Process variables are manipulated to arrive at the desired functional parameters, i.e., the reaction can be terminated anytime before complete saturation, as required.

In addition to saturation, the melting point and firmness of fat are also influenced by a phenomenon known as isomerization. In that process, rather than a double bond becoming saturated with hydrogen, the position of the hydrogen atoms across the double bond is transferred. For most naturally occurring vegetable oils and fats, hydrogen atoms about any double bonds are in the *cis* conformation, or on the same side of the carbon atoms. An alternate geometry is possible in which the hydrogen atoms are in the *trans* conformation, or on opposite sides of the carbon atoms (Fig. 25.3). Fats from ruminants (cattle and sheep) typically contain from 4-11% *trans* fatty acids and hence represent a naturally occurring dietary source. The majority of dietary *trans* (~75–80%), however, is consumed in the form of partially hydrogenated vegetable fats and oils.

In practice, commercial hydrogenation concurrently both saturates carbon-to-carbon double bonds and promotes geometric isomerization. Although reaction parameters can be manipulated to favor one reaction over the other, it is not possible at present to exclude either preferentially. Eventually, the reaction reaches the point at which all fatty acids are completely saturated—at that time, *trans* are essentially eliminated. The formation of *trans* isomers is a critical functional parameter because they contribute significantly to melting and textural properties. For example, the melting point of the monounsaturated oleic acid is 13°C, whereas that of its *trans* isomer elaidic acid is 44°C. By way of comparison, the melting point of the saturated acid is 70°C. Hence, isomerization represents an alternative to saturates for building functionality into fat.

Recent clinical studies have shown an association between dietary *trans* and elevated levels of total cholesterol and low-density lipoprotein (LDL) cholesterol together with unchanged or reduced high-density lipoprotein (HDL) cholesterol relative to control diets. Levels of *trans* fed during these studies ranged between 4 and 11 en%.

Average *trans* intake has, in fact, been debated. David Allison and co-workers (30) reported that "on average, the US population consumes a mean of 5.3 g *trans* fatty acids per day—about 2.6% of their total energy and 7.4% of their fat energy." This research confirmed earlier findings of others that saturated fatty acid intake remains high, 12.5% of total energy, and is, "relatively speaking, of greater concern." It is also important to note that the majority of *trans* isomers formed during the partial hydrogenation of vegetable oils and fats are in positions along the fatty acid backbone different from those that occur naturally in animal fats. It was stated earlier that fats from ruminants account for 20–25% of *trans* fatty acid intake. However, these two sources might present different associations with risk factors for heart disease. Many nutritionists caution against replacing *trans* fatty acids in the diet with saturates. Rather, the American Heart Association recommends "that naturally occurring unhydrogenated oil be used when possible and attempts made to substitute unhydrogenated oil for hydrogenated or saturated fat in processed foods. Additionally, the recommendation to substitute softer for harder margarines and cooking fats seems justified" (31).

Many of the oils and fats processed for the food industry have been subjected to partial hydrogenation to impart the required functionality and shelf life. The industry has been working diligently to continually improve the nutritional profiles of products in an effort to satisfy market demands. Some examples are the following: (i) many food service deep-frying media are lightly hydrogenated liquid products compared with the heavy-duty plastic products used previously; (ii) several fluidized systems in which lightly hydrogenated or even nonhydrogenated oils replace traditional plastic products are offered for the bakery trade; (iii) the tablespreads category is now largely softer tub type products most of which contain less than the 80% fat required by margarine standards of identity.

Beyond these improvements, a variety of options exist for those situations in which further change is deemed appropriate. However, in general, the penalty is higher saturates and increased ingredient costs. The former is especially apparent in applications in which the fat is required to convey structure and body. Saturates and geometric isomers are largely responsible for contributing structure because they are higher melting. Thus, reduction in either category necessitates an increase in the other to maintain texture; otherwise, the resultant triglyceride families will soften.

Random interesterification represents a particularly functional process for the production of reduced *trans* and *trans*-free fat systems. More than 40 years ago, Melnick and Gooding (32) used interesterification to produce novel margarines having high essential fatty acid and low *trans* fatty acid contents. They co-randomized blends containing 10–30% completely hydrogenated fat with 70–90% oil rich in essential fatty acids. Table 25.7 illustrates proportions they found to be well-suited for margarine production. Compared with traditional margarines evaluated at the time, these fats were deemed improvements because they were softer at cold temperatures and hence more easily spread. List *et al.* (33) investigated the properties of interesterified soybean oil (SBO)/fully hydrogenated soybean oil (FHSBO) blends over the range of 90/10 to 80/20 SBO/FHSBO. Among the co-randomized blends evaluated,

TABLE 25.7 Cottonseed Oil (CSO) Blends Before and After Ester Interchange[a]

	%CSO	% Saturated CSO	Melting point (°C)	Solid fat index			
				10.0	21.1	26.7	33.3
Blend	85	15	50.2	17.0	17.3	16.7	17.0
Randomized	85	15	36.0	12.8	7.3	5.7	3.9
Blend	82.5	17.5	51.2	19.5	19.7	19.2	19.5
Randomized	82.5	17.5	38.2	16.5	10.1	8.2	6.0
Blend	80	20	52.0	21.8	22.3	22.0	22.4
Randomized	80	20	39.4	18.3	11.9	9.6	7.2

[a] *Source:* Ref. 32.

these researchers determined that 80% SBO oil/20% FHSBO yielded the best melting curve for tub margarine. The solid fat index for tub margarine vs. 80/20 interesterified SBO/FHSBO at 10.0, 21.1, and 33.3°C was 7.1 vs. 8.0, 4.5 vs. 3.5, and 2.0 vs. 2.2, respectively.

Using X-ray diffraction, they demonstrated that such blends exhibit the β′ crystal structure that is desired for margarine products, whereas simple mixtures crystallized in the β polymorph. The glyceride families determine physical properties such as melting point and melting curve; thus, tailoring is possible *via* manipulation of triglyceride composition. β′ crystals are important in margarines because they can entrap significant quantities of oil and provide good mouth melt and glossy appearance. Palmitic acid at the 1- or 3-position of a triacyglycerol encourages β′, whereas triacylglycerides of the same fatty acid are very strongly β. A β′ hard stock at room temperature may become β-tending upon dilution with oil. Polymorphic tendencies of major solid triacylglycerides in vegetable margarines and shortenings have been reported by deMan (34) and are shown in Table 25.8.

Ward (35) applied interesterification for the production of high-polyunsaturate, low-*trans* stick, pat, tub, and fluid margarines and spreads. Hard stock was prepared

TABLE 25.8 Polymorphic Tendencies of Major Solid Triglycerides in Vegetable Margarines and Shortenings[a,b]

Carbon number	Triacylglyceride species	Polymorphic form
48	PPP	β
50	PStP	β′
52	PStSt	β′
54	StStSt	β

[a] *Source:* Ref. 34.

[b] Abbreviations: P, palmitate; St, stearate.

TABLE 25.9 High-Polyunsaturated Low-*Trans* Margarines and Spreads

		Stick margarine	Tub margarine
		23% 70/30 babassu/palm Saturated and interesterified 77% sunflower oil	16% 50/50 babassu/palm Saturated and interesterified 84% sunflower oil
Solid fat index at	10.0°C	13.9 (12 minimum desired)	9.4 (9–12 desired)
	21.1	9.1 (7 minimum desired)	6.2 (5–7 desired)
	26.7	2.4 (2 maximum desired)	2.0 (2 maximum desired)
Penetration at 7.2°C (0.1 mm)		95 (65–120 desired)	160 (130–210 desired)

[a] *Source:* Ref. 35.

from a randomized blend of fully hydrogenated babassu and fully hydrogenated palm fats; this was blended subsequently with sunflower or other liquid vegetable oils to complete the composition (Table 25.9).

Van Heteren and co-workers (36) developed an interesterified hard stock blend suitable for margarines and spreads in which the amount of hard stock required was 2–35 parts by weight of the oil phase. The advantage claimed was that the margarine fats had little solid phase at body temperature and hence melted rapidly in the mouth and spread well over their entire application range. The example cited in their patent involves randomization of 56% fully hydrogenated palm kernel olein with 44% of either fully hydrogenated palm stearin (hard fraction from palm) or fully hydrogenated whole palm for the hard stock. Margarine fats were prepared by blending 12.9% hard stock with 87.1% sunflower oil. The resultant melting curves were consistent with the requirements of tub margarine.

Lansbergen and Schijf (37) described a hard stock for use in spreads having a low content of saturated fat, reduced palmitate, and almost zero levels of *trans* fatty acids. The interesterified hard stock for the blend comprised ~27% behenic, 35% palmitic, and 35% stearic acids. This can be derived from 40% fractionated palm (80% C_{16}) and 60% fully hydrogenated rapeseed oil. Spreads were prepared with hard stock produced by both a physical blend as well as randomization. In both cases, the hard fat was used at 6% on a fat basis with sunflower oil comprising the balance. Spreads containing the interesterified hard stock (A) were quite acceptable while those prepared from the physically blended hard stock (B) were much too soft (Table 25.10).

In the early 1990s, a variety of nonhydrogenated tablespreads appeared on the Canadian market in response to consumer pressure for products made without hydrogenated fats. Structuring fats were developed from hard fractions of palm and palm kernel oils, many of which were interesterified. For example, Unilever's Becel margarine was formulated from an interesterified blend of palm and palm kernel hard fractions that was subsequently mixed with 85–88% liquid vegetable oil (38).

Genetically modified high-stearic soybean oil was investigated recently by List *et al.* (39) as a potential candidate for nonhydrogenated margarine fat. High-stearate

TABLE 25.10 Interesterification (A) vs. Physical Blending (B) for Spread Production: Effects on Melting Profile and Textural Properties[a]

	Solids content		Stevens consistency			Hardness value		
	A	B		A	B		A	B
N-10[b]	7.4	6.1	S-05[b]	47	20	C-05[b]	210	95
N-20	5.4	4.7	S-10	44	19	C-10	195	90
N-30	3.9	3.7	S-15	47	19	C-15	210	90
N-35	2.5	2.2	S-20	32	19	C-20	150	90

[a] *Source:* Ref. 37.
[b] Numbers in each of these columns refer to the temperature (°C) at which the measurement was obtained.

varieties with a range of 17–33% C_{18} were evaluated. The glyceride structure is generally similar to that of ordinary soybean oil in which the saturates occur primarily at the outer *sn*-1,3-positions, oleic and linolenic are distributed randomly across all three positions, and linoleic shows a high preference for *sn*-2. This distribution dictates that most mono- and disaturated glycerides are SUU and SUS. Interesterification forms significant quantities of USU and SSU species; these researchers hypothesized that those triglyceride species are quite likely largely responsible for the significant differences in melting properties measured between natural and randomized oils. Selected examples and their properties, representing suitable candidates for tub margarines, are listed in Table 25.11.

Interesterification has also been applied for the production of *trans* free shortenings. Melnick and Gooding (32) co-randomized 70% cottonseed oil and 30% fully hydrogenated cottonseed to produce an all-purpose type shortening rich in essential fatty acids (Table 25.12).

List *et al.* (40) evaluated a variety of co-randomized base stocks (blends of liquid oil and fully hydrogenated fats) mixed with oil to produce shortening-type products.

TABLE 25.11 The Effect of Random Interesterification on the Melting Properties of High-Stearate Soybean Oil[a]

			Solid fat index			
	State	%C_{18}	10.0°C	21.1°C	33.3°C	MDP(°C)[b]
A	Natural	23.9	11.2	0.0	0.0	19.7
	Interesterified	23.9	6.8	3.3	1.5	23.2
B	Natural	27.1	22.8	12.1	0.0	18.7
	Interesterified	27.1	13.7	4.5	2.6	38.2
C	Natural	33.0	18.7	7.9	0.0	19.9
	Interesterified	33.0	13.5	5.5	3.5	36.4

[a] *Source:* Ref. 39.
[b] Mettler dropping point.

TABLE 25.12 Interesterification for the Production of *Trans*-Free Shortenings[a]

	Blend[b]	Interesterified blend[b]
Melting point (°C)	53.5	43.0
Solid fat index at 10.0°C	31.2	24.3
21.1	31.3	16.4
26.7	31.0	14.5
33.3	31.4	12.5

[a] *Source:* Ref. 32.

[b] 70% cottonseed oil/30% fully hydrogenated cottonseed oil.

They found that 75–80% palm interesterified together with 20–25% fully hydrogenated soybean or fully hydrogenated cottonseed oils were suitable base stocks. The addition of 35% liquid soybean oil to any of these base stocks yielded melting curves consistent with commercial all-purpose shortening. Crystal structures, as determined by X-ray diffraction, showed a predominance of the desirable β' polymorph.

The variety of high-oleic/reduced polyunsaturate oils available today offer the opportunity for further product enhancements. For example, oxidative stability can be improved significantly by replacing standard liquid soybean oil with a more stable high-oleic oil.

In summary, options for *trans* reduction include the following:

- Nonhydrogenated hard fractions can be added to nonhydrogenated or minimally hydrogenated stocks in an effort to convey body. Typically, such hard fractions are derived from palm or palm kernel fats, both of which are significantly higher in saturates than the partially hydrogenated components they replace.
- Fully hydrogenated components (e.g., soybean or cottonseed) can be blended with liquid components and interesterified subsequently to improve the melting curve and crystallization properties. Interesterification reorders the triglycerides from their naturally occurring nonrandom distribution to one that is random and consequently improves melting and crystallization properties.
- Inherently higher oxidatively stable oils and fats can be substituted for partially hydrogenated components. For example, nonhydrogenated coconut oil represents a functional alternative to partially hydrogenated vegetable oil sprays.
- Many of the identity preserved oils, e.g., high-oleic and/or reduced polyunsaturate sunflower, canola, and soybean, present the possibility of replacing traditional varieties with nonhydrogenated oils of superior oxidative stability.

Most of the foregoing options involve higher-cost precursors and/or additional processing (e.g., interesterification); consequently, they typically represent higher-cost alternatives. Preservation of performance for some of the more demanding applications also presents a challenge. Therefore, it is prudent to consider the serving size when such reformulation efforts are undertaken to quantify accurately the magnitude of change required and to appreciate the implications for the nutritional panel.

Flakes

Flakes represent a convenient and functional format for a variety of applications. The more brittle and/or higher melting point fat systems are typical candidates for this process. Generally, most fats that are suitable for flaking melt at ≥35°C and possess a crystallized phase sufficient to form a brittle flake during the chilling process and to maintain the flake integrity throughout storage and distribution. Typically, a thin layer of molten fat is applied to either a chilled drum or belt on which the product is crystallized. Thereafter, crystallized material is removed, often with the aid of a doctor blade, resulting in the production of thin, irregularly shaped flakes of fat. It is important that the relative humidity in the flake production area be controlled such that excessive condensation does not accumulate on the chilled roll surface or on the flakes themselves. It is common to incorporate additional ingredients to further enhance functionality. Fat-soluble ingredients might include lecithin or other emulsifiers, flavors and coloring agents; components such as cinnamon, sugar and other nonsoluble components can be suspended within the flake matrix as well. These products represent a very convenient format for those applications that require small levels of addition, i.e., they can be conveniently parceled out with a scoop, for example. Because they are quite thin, thermal penetration is rapid compared with large chunks, slabs, or cubes of the same material; thus, they tend to melt quickly and efficiently. For larger-scale operations, they offer the benefit of evenly distributing fat throughout a matrix. Many bakery products, for example, require the distribution of discrete pockets of fat (and coloring or flavoring contained therein) throughout the dough or mix matrix; flakes offer an efficient medium to accomplish this and thus are quite useful for the production of bakery items such as pizza crusts and biscuits. Furthermore, they can be readily delivered to a process step by conveyor belts or buckets and pneumatic devices such as those used for sugar, flour, and other dry ingredients.

Spray Chilled Fats

A variety of specialty fats are beaded or spray chilled. These are typically hydrogenated higher-melting (50°C) firm fats. In one embodiment, molten oil droplets are delivered into a chilled chamber in which they crystallize during their freefall to the collection area. Process variables are manipulated to control particle size, which can range from a small bead to a very fine particle. To maintain the free-flowing properties of these materials, they are often either postconditioned (tempered) or processed though a fluidized bed to extract the heat of crystallization. Such post-treatment is necessary to prevent exothermic energy from partially melting the beads; the molten particle surface film that results eventually resolidifies upon cooling. The result is that neighboring particles fuse together and, in extreme cases, the entire package contents can completely associate into an extremely hard and unfriable mass. Typically, 95–97% of the finer powder type material will pass through a 100-mesh sieve. Like flakes, they provide for ease of addition, especially in situations in which small quantities are required. Their consistent size and geometry permit very accurate automated dosing and even distribution for a variety of applications including dough laminates, dry mixes, and nut butter stabilization. Powdered fats are also widely used for the production of tablets and other compressed items in the food, pharmaceutical, cosmetic and personal care, powder metallurgy, and catalyst and ceramic industries in which they serve as binders and lubricants. They have been shown to be advantageous compared with magnesium stearate when used for tablet production.

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Chapter 26

Design and Application of Fat-Based Surfactants

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Introduction to Surface and Interfacial Activity

Introduction

The principles of surface and interfacial activity represent a vast array of literature. Only a brief summary of these topics will be attempted in this chapter. For more detailed treatments, the reader is referred to other significant sources (1–3).

A surface may be visualized as a boundary between two distinct phases. For mixtures, one phase (the dispersed phase) may be distributed in another (the continuous phase). Some common examples are given in Table 26.1. Where phases are mutually soluble, for example, a mixture of gases, no boundary exists. Where phases are not mixed, for example, in a container of water, the surface of the water is actually an air-water interface.

The phase volume of the dispersed phase is an important measure. It is easily determined and controlled by the volume of each phase in the formulation. The size of particles in a colloid, droplets in an emulsion, or air cells in a foam may be measured by a number of techniques (4). A system is described as monodisperse if the size distribution of the dispersed phase has a narrow range. It is polydisperse if the size range is relatively broad or bimodal. Phase volume and size distribution determine important properties of a product such as rheology and appearance.

A surfactant is a molecule that is not completely soluble in either phase and therefore tends to concentrate at the interface. This excess concentration of surfactant influences a number of measurable interfacial properties.

TABLE 26.1 Common Examples of Phase Distribution

	Dispersed phase		
Continuous phase	Solid	Liquid	Gas
Solid	Alloys	Gel	Solid foam
Liquid	Colloid	Emulsion	Foam
Gas	Smoke, aerosol	Fog, aerosol	Gas mixture (one phase)

Surface and Interfacial Tension

Molecules located at the boundary of two phases experience unbalanced intermolecular forces. For example, in a glass of water, molecules at the surface experience attractive forces from water molecules from below, whereas air molecules above exert very little force. These unbalanced forces give rise to surface tension. The surface tension of water and the surface tension of oil are unequal. Therefore, when water and oil are mixed, the boundary phase displays an increased free energy due to the increased contact area, which is described in the equation:

$$\Delta G = \gamma_i \Delta A$$

where ΔG is the free energy necessary to increase contact area, ΔA is the increase in contact area, and γ_i is the proportionality constant, the interfacial tension.

Wetting of a solid surface by a liquid film is an important property in a number of applications. When an aqueous spray impacts a hydrophobic surface, distinct drops are formed. The shape of the droplet and its ability to wet the surface are determined by the balance among air-liquid, air-solid, and liquid-solid interfacial tensions. The surface line and the tangent to the droplet originating from the point at which air, liquid, and solid meet define the contact angle. As the contact angle decreases, wetting power increases. A spreading coefficient is defined by the following equation:

$$S = \gamma_{SG} - (\gamma_{SL} + \gamma_{LG})$$

where S is the spreading coefficient, γ_{SG} is the solid-gas interfacial tension, γ_{SL} is the solid-liquid interfacial tension, and γ_{LG} is the liquid-gas interfacial tension.

Static and dynamic surface and interfacial tensions may be measured by a number of methods including (i) the DuNouy Ring, (ii) the Wilhelmy Plate, and (iii) sessile, spinning, or pendant drop methods (5). The DuNouy method places a platinum ring on the surface or interface and gradually increases the force applied to it. A single value is recorded at the moment of detachment from the surface or interface. Surface tension is calculated from the following equation:

$$F = 4\pi r\gamma$$

where F is the force required to detach the ring, r is the radius of the ring, and γ is the surface tension. In the Wilhelmy method, probably the most common example of a dynamic method, a plate is suspended in contact with the surface or interface. Platinum or iridium plates are used because these materials have an essentially zero contact angle. Tension is measured by a torsion microbalance and plotted vs. time. Surface tension is expressed by the equation:

$$F = 2(l + L)\gamma\cos\theta$$

where F is the force required to detach the plate, l and L are the length and thickness of the plate, γ is the surface tension, and θ is the contact angle.

Because interfacial tension is a driving force for separation of emulsions, lower interfacial tensions tend to promote emulsion formation and emulsion stabilization. Spinning drop tensiometry is a method that is useful for measuring formulations that have very low interfacial tensions. A drop of liquid is placed in a tube with an immiscible liquid. The tube is then subjected to an angular force and the shape of the drop is measured by optical imaging. Contact angle may be measured by observation of a drop on a microscope slide. The shape of the droplet may then be analyzed using optical imaging software.

Rheological Properties

Although bulk rheology of a colloid or emulsion is determined largely by the viscosity of the continuous phase, the concentration of the dispersed phase, the particle size, and the interaction between the particles may have major effects. If the dispersed phase is a solid, the particle shape is fixed, whereas liquid droplets may be deformed at higher concentrations. For example, mayonnaise has 80% oil as the dispersed phase, and droplets are distorted to achieve optimum packing. Emulsions tend to be non-Newtonian and often are shear thinning due to disruption of intermolecular forces. Formation of an interparticle network may also produce a yield stress in the system.

Interfaces between immiscible phases in emulsions may also display discrete rheological properties. The interface may have a solid character or the molecules may slide over one another when a deforming force is applied. Most heterogeneous oil-water systems display a mixture of these characteristics and are therefore described as viscoelastic. High interfacial elasticity is a major contributing factor to the prevention of coalescence. Interfacial rheology may be measured by placing a circular plate at the interface (6). The plate may then be rotated through a fixed angle or oscillated and the resultant force measured directly.

Adsorption of Surfactants at Interfaces

Surfactant molecules may migrate to the interface or remain dispersed in the continuous phase depending on the free energy. Migration of surfactant to the interface may be diffusion controlled. This favors small molecules, which migrate at higher velocities. Under turbulent conditions, the opposite tendency is observed in which large particles bind preferentially to the interface. During aging, thermodynamic properties determine the composition of the interface. However, macromolecules may undergo changes that alter their stability at the interface. For example, globular proteins may unfold to expose more hydrophobic residues to the interface. Also, sulfhydryl groups may form disulfide bonds, which cross-link the protein and anchor it to the interface.

Adsorption of surfactants at the interface decreases interfacial tension and may increase interfacial elasticity. Emulsion formation and stabilization are increased as a result. Macromolecules adsorbed at the interface may also stabilize emulsions and dispersions by electrostatic repulsion or steric hindrance toward particle/droplet aggregation.

Adsorption of surfactants may be measured by a number of methods. For example, the decrease of interfacial tension may be measured as a function of concentration. As the concentration is increased, a linear decrease in interfacial tension is observed. At some point, the line breaks and becomes almost parallel to the x-axis. This point is referred to as the critical micelle concentration (cmc). Another method utilizes a film balance to measure surface pressure. A film is cast onto the surface of a liquid (most often water), which is confined by one or two movable barriers. The movable barriers compress the film as the surface pressure is measured by a torsion microbalance. A rapid increase in surface pressure is observed when the molecules are tightly packed into a monolayer. The area/molecule may be calculated from this result. Another method utilizes a radiolabeled surfactant dispersed in the continuous phase. A radioactivity detector above the surface monitors the increase in radiation as the concentration at the interface increases.

The composition of surfactant at the interface may be determined by a number of physical methods, such as X-ray diffraction, infrared and ultraviolet spectroscopy, and fluorescence microscopy. Enzymatic hydrolysis of proteins provides insights into protein conformation. Residues that are tightly bound to the interface are not susceptible to hydrolysis, whereas segments extending into the continuous phase are rapidly cleaved.

Emulsion Formation and Stabilization

Preparations of heterogeneous formulations have been among the most difficult commercial processes to model and understand. Adding to the difficulty is the fact that most commercial products are complex mixtures rather than purified materials. However, principles derived from pure materials may be used to predict properties with appropriate corrections from ideal behavior (7,8).

Emulsion and Dispersion Types

Colloids are fine particles dispersed in a liquid phase. The particles may be spherical or irregularly shaped. They may be rigid or they may be deformable. Individual particles may be discrete or they may form loose or tight aggregates.

Emulsions are formed when an immiscible liquid is divided into droplets and dispersed into another immiscible liquid. Examples are oil-in-water (O/W) or water-in-oil (W/O). Macroemulsions, termed emulsions by default, are thermodynamically unstable due to the unfavorable surface forces that exist between immiscible liquids. By contrast, microemulsions are thermodynamically stable. They also differ from macroemulsions because they are transparent and do not scatter light.

Foams are dispersions of gas in liquids or solids. As the volume fraction of gas is increased, the density of the mixture decreases. The volume fraction of gas can be calculated from the specific gravity and is often converted to overrun, which is the reciprocal of the volume fraction multiplied by 100.

Preparation of Emulsions and Colloids

Colloidal particles must be small to avoid separation by sedimentation (see below). Large rigid particles are therefore generally reduced in size by grinding before dispersion in the liquid continuous phase. Dispersion into the liquid is accomplished with high-shear mixing. An alternative approach is to grind the particles after dispersion in the liquid phase. An example is the processing of chocolate in which sugar crystals and cocoa particles are reduced to fine particles in a roller refiner. The advantage of the latter approach is that the cocoa butter acts as a lubricant and heat-transfer medium. Microprecipitation may also be used to prepare colloidal dispersions. In this process, a solution of a solid is added to another liquid in which the solid is insoluble. Fine dispersions are obtained when the process is accomplished using high-speed agitation.

To disperse one liquid in an immiscible second liquid, energy must be provided to overcome the unfavorable interfacial forces of the interaction. The Weber number is defined as the ratio of energy input to the interfacial destabilization energy.

Factors affecting the Weber number depend on whether laminar flow, turbulence, or cavitation accomplishes droplet formation. In laminar flow, such as pumping a liquid through a long pipe, the viscosities of the phases play an important role. Higher viscosity requires more energy to deform and disrupt drops. Turbulent flow is associated with high-shear mixing devices that produce eddy currents. Equipment is usually designed to minimize small and large eddies because they are less efficient in drop disruption. Cavitation occurs when highly localized energy causes a cavity in the continuous phase. Collapse of the cavity causes a shock wave that disrupts drops in the region into smaller droplets.

Emulsion formation may be conducted as a two-stage process. The first stage mixes the two phases into a coarse emulsion, and the second stage reduces the size of the droplets. The latter stage requires high energy because it must overcome the unfavorable forces caused by the exposure of larger surface contact of the immiscible phases. Droplet size reduction is in equilibrium with recoalescence back to larger droplets. Surfactants adsorbed at the interface reduce the interfacial tension and the associated free energy required for droplet disruption. The adsorbed layer may also increase interfacial elasticity which prevents recoalescence. The surfactant must be able to migrate to the interface rapidly enough to accomplish this latter function.

Droplet size reduction may be carried out in high-shear equipment. Rotor stator devices act by passing the mixed liquids through rotating concentric holes. However, rotating bars may be used to disrupt solid particles in the preparation of colloids. A special type of rotor-stator device, referred to as a colloid mill, uses a conical gap through which liquids flow and droplets are disrupted. This device is particularly useful for medium-to-high viscosity liquids.

Homogenizers act by passing a coarse emulsion through an orifice at high back pressure to form small droplets. High back pressures provide high energy input but reduce the throughput of the device, which raises production cost. Commercial processes are therefore optimized to balance small droplet sizes against rapid throughput. In a similar device, the microfluidizer, two liquid streams are impacted into a barrier, thereby producing small drops through shear and turbulence. Recirculating the resulting emulsions may produce smaller droplets.

Ultrasonic devices disrupt droplets by producing cavitation through localized energy within a small area. One major advantage of an ultrasonic probe is that it may be used to produce fine emulsions on a small scale for research purposes. A commercial ultrasonic device utilizes a vibrating plate impacted by a high velocity stream of liquid. The major disadvantage of these devices is that shock waves eventually damage the blades, leading to their frequent replacement.

A glass membrane device produces an emulsion by extruding a disperse phase liquid through the membrane into the continuous phase. A commercial version of the apparatus is a concentric flow-through device. The advantage of using a membrane is that essentially monodisperse emulsions may be produced. However, membranes may be easily plugged if solid particles are present in the stream.

Mechanisms of Instability

Because macroemulsions are thermodynamically unstable, they will eventually separate into their component phases. Kinetic barriers may slow the process but separation is inevitable, Several distinct mechanisms have been identified as shown in Figure 26.1. Practitioners may find it useful to identify the mechanism(s) that cause the destabilization of colloids because steps may then be taken to minimize the effects of the specific mechanism.

Colloids and emulsions experience gravitational force that tends to fractionate the phases according to their specific gravity. Creaming occurs when a less dense dispersed phase rises to the top of a dense continuous phase. Sedimentation is the process in which a dense dispersed phase settles to the bottom. An increase in the phase

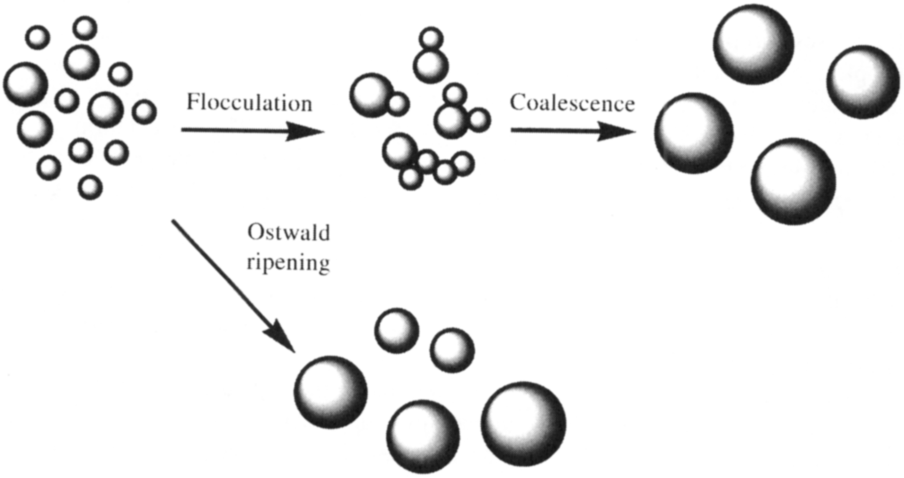


Fig. 26.1. Emulsion destabilization mechanisms.

volume of the dispersed phase may result in a larger number of interparticle forces, resulting in the formation of a network. Mobility of the particles or droplets is therefore reduced, resulting in less creaming and sedimentation. Increasing the viscosity of the continuous phase also retards particle migration, which leads to improved stability.

Droplet and particle flocculation is a function of collision frequency and collision efficiency. Brownian motion, convection currents, agitation, and shearing forces increase the frequency of collisions. The efficiency of collisions depends upon whether particles stick together or bounce off one another in a collision. Particle shape, size, and surface character determine the collision efficiency. Flocculation occurs more frequently in creamed or sedimented phases in which the particles are in close proximity than when particles are distributed uniformly. Aggregates produced by flocculation may be tightly or loosely aggregated. Loose aggregates may be redispersed by mild agitation, whereas more energy may be necessary for more tightly packed formulations. Collision frequency may be minimized by retarding droplet motion, such as by increasing the viscosity of the continuous phase. Surfactants adsorbed at the interface may provide properties that minimize collision efficiency. For example, proteins on particle surfaces produce electrostatic and steric repulsion.

Coalescence occurs when two drops in contact with one another merge together to form a larger droplet. This is caused by drainage of the interfacial membrane, which separates the droplets. As previously mentioned, coalescence is in equilibrium with droplet disruption during emulsion preparation. Keeping droplets separated may minimize coalescence. Adsorbed proteins achieve this effect by steric repulsion. Surfactants, which increase interfacial viscoelasticity, reduce the rate of film, drainage between adjacent droplets.

Ostwald ripening is a phenomenon in which large droplets grow at the expense of smaller droplets. Unlike the previous mechanisms, droplet collision or contact is not necessary. The process is mediated by partial solubility of the dispersed phase in the continuous phase, allowing molecular diffusion from smaller to larger drops. Pure oil-in-water emulsions do not display this process because of the lack of mutual solubility. Ostwald ripening is often observable in foams. Production of monodisperse droplet distribution and reduction of dispersed phase solubility are strategies to minimize Ostwald ripening.

The Structural Basis of Surface Activity

Polar solutes, such as salt and sugar, are soluble in polar solvents, such as water. Similarly, nonpolar solutes are soluble in nonpolar solvents. Surfactants are amphiphilic molecules, that is, they have both polar and nonpolar functional groups within the same molecule. Surfactants may be obtained from natural sources, such as lecithin and proteins, or they may be designed by organic synthesis. The functionality of surfactants in many applications may be related to their molecular or extended structure. This understanding in turn leads to improved structural design of molecules for specific applications.

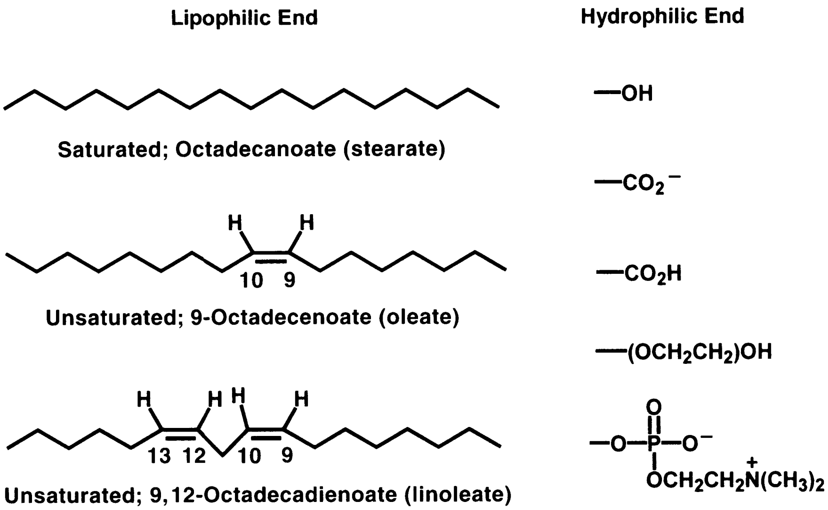


Fig. 26.2. Some common hydrophilic and lipophilic groups found in surfactant molecules.

Elements of Surfactant Structure

Nonpolar functional groups in surfactants are composed of long-chain alkyl, alkenyl, or aromatic structures. Nonpolar groups are referred to as lipophilic (lipid loving) or hydrophobic (water hating). These segments are often large and account for the majority of the molecular weight. Polar groups may contain positively or negatively charged heteroatoms but may also be uncharged groups with high dipole moments. Polar groups are termed hydrophilic (water loving). These components of surfactant structure are shown in Figure 26.2.

Surfactants adsorbed at interfaces reduce interfacial tension and prevent phase separation, as discussed in previous sections. Figure 26.3 shows how the surfactant molecules are oriented at the interface. Polar functions extend as far as possible into the aqueous phase, whereas the nonpolar groups are dispersed into the oil phase. In foams, air assumes the role of the nonpolar component, and hydrocarbon segments extend into the headspace above the liquid phase.

Hydrophile-Lipophile Balance

As previously mentioned, surfactant molecules have an affinity to both the polar and nonpolar phases. However, the relative affinity of the molecule for each phase spans the range from highly oil-soluble to highly water-soluble substances. This range has been defined by placing the surfactant molecules on a scale called the hydrophile-lipophile balance (HLB). A diagram of this scale is shown in Figure 26.4. High numeric values are assigned to surfactants that are water soluble, whereas low values represent molecules that solubilize in oil.

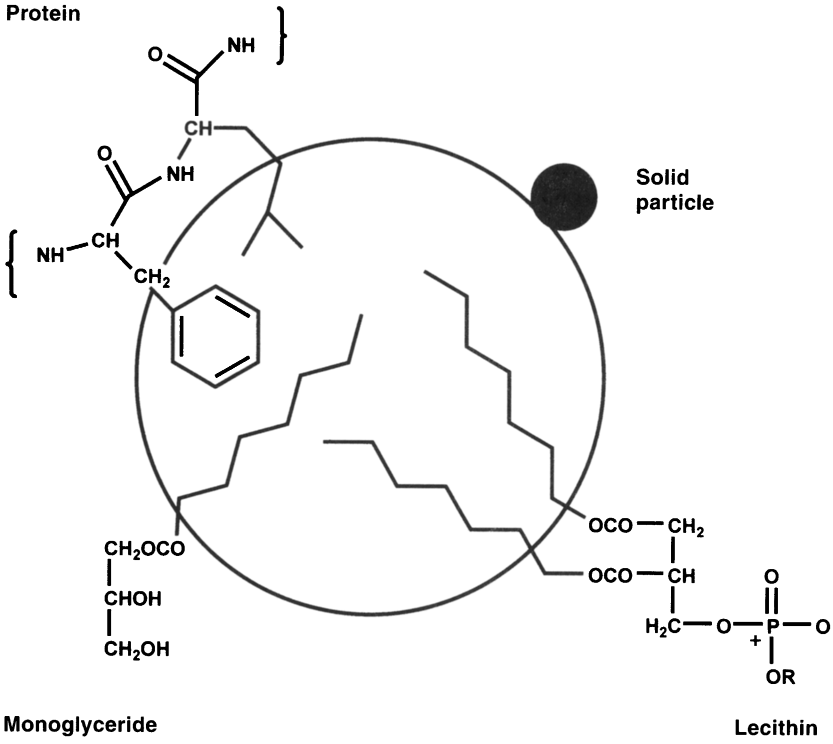


Fig. 26.3. Orientation of surfactant molecules at oil-water interfaces.

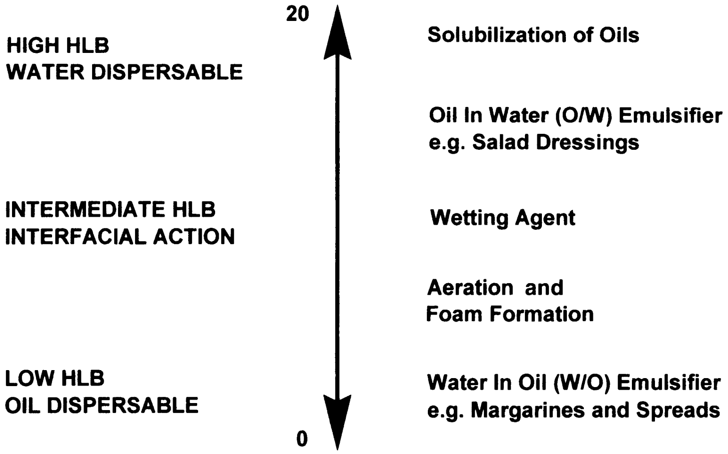


Fig. 26.4. Representation of the hydrophile-lipophile balance (HLB) scale.

The functionality of a surfactant is reflected by its position on the HLB scale. Water-in-oil (W/O) are conventionally prepared by dispersing a low HLB surfactant (lipophilic) in the oil phase followed by slow addition of the aqueous phase. Oil-in-water (O/W) emulsions are prepared analogously with a high HLB surfactant. Functionalities such as aeration, wetting, and texture control are effected by surfactants with intermediate HLB values. These molecules are not dispersed well in either phase and accumulate in high concentrations at the interface.

Several methods have been used to calculate HLB values. The HLB may be calculated by the following equation:

$$\mathrm{HLB} = 20(1 - S/A)$$

where S is the saponification value of the surfactant and A is the acid value of the fatty acid source. This approach works well for nonionic fatty acid esters of polyalcohols. However, an equation that works better for ethoxylated nonionic surfactants is as follows:

$$\mathrm{HLB} = (P + E)/5$$

where P is the wt% polyol fatty ester in the formulation and E is the wt% polyoxyethylene chain.

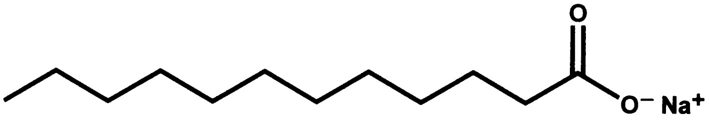
The Davies method utilizes the organic structure of the surfactant molecule to determine HLB. Numerical values are assigned to polar and nonpolar functional groups. The sum of the nonpolar functions is subtracted from the sum of the polar groups to obtain the final HLB value. The major limitation of these calculation methods concerns the compositions of commercial surfactants, which are mixtures rather than a pure chemical entity.

Preparation of Surfactants

Commercial surfactants, in most cases, are prepared by a few simple organic reactions. Processes such as esterification, ethoxylation, and sulfonation are reasonably well understood. However, many manufacturers rely on proprietary reaction conditions to differentiate their products. For pedagogical simplicity, preparations will be discussed according to their structural class. This discussion will be a brief overview of preparation procedures. The reader is referred elsewhere for more detailed treatments (9–11).

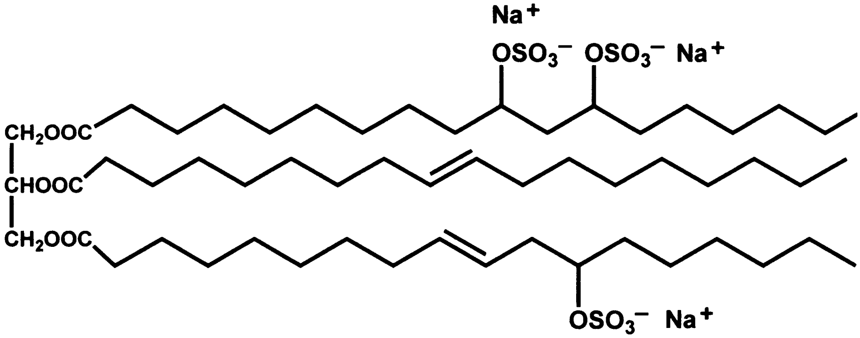
Anionic Surfactants. Anionics have a relatively long history of use. Although many of these compounds have become commodities, many manufacturers are still developing novel formulations.

Soap (Scheme I) is one of the oldest man-made organic chemicals. It was prepared originally by heating animal fats with ashes. The triacylglycerol reaction with sodium hydroxide or sodium carbonate is known as saponification. An alternative preparation is a two-stage process, which first splits and purifies fatty acids from oil or fat. Fatty acids from coconut oil have been found particularly functional. Neutralization with alkali is then used to produce the soap. Although soap is useful for a wide variety of cleaning applications, it has one major disadvantage. Interchange of the sodium or potassium cation with calcium or magnesium forms water-insoluble compounds. Therefore, the use of soap in hard water leaves an undesirable scaly residue.



I

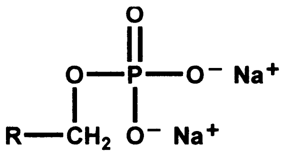
Sulfated oils (Scheme II) are prepared by the reaction of unsaturated oils with sulfuric acid. Addition of the sulfate group across the double bond locates the polar sulfate group in the middle of the alkyl chain. Because of the corrosive properties of sulfuric acid, glass-lined reactors are required for this reaction. Sulfated oils have the advantage over soap of hard-water stability. Sulfuric acid can also react with α-olefins to introduce the functional group at the end of the alkyl chain.



II

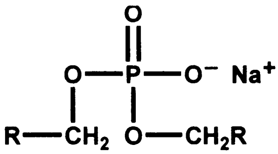
Alkyl phosphates (Scheme IIIa,b) are derived from the addition of phosphoric acid to long-chain alkyl alcohols. As indicated, the surfactant may contain one or two alkyl chains. These compounds are useful for stabilization of foams. Monoacylglycerols may be reacted to produce phosphate derivatives with the functional group positioned on the glycerol chain.

Lactic acid is a bifunctional molecule with a free hydroxyl and a free carboxyl group. Fatty acids can be condensed with the hydroxyl group to give stearoyl lactylic



Disodium alkyl phosphate

IIIa

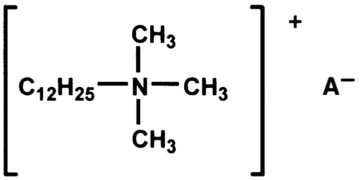


Sodium dialkyl phosphate

IIIb

acid. The presence of sodium or calcium hydroxide converts the surfactant into its anionic form (12). During the course of the reaction, lactic acid can also self-condense to produce a distribution of oligomers. In the older literature, the monomer was designated as 1-lactylate and the dimer as 2-lactylate. This terminology is unfortunate from an organic chemist's perspective because the 1- and 2- do not refer to positional isomerism but degree of oligomerization. In a typical preparation, lactic acid and sodium hydroxide are reacted and water is removed by distillation. Stearic acid is added and the reaction carried out at 160–180°C and reduced pressure. Higher temperatures promote side reactions, which produce dark colors and distinctive odors. Acid value is measured until a minimum value is obtained. The reaction product is characterized by acid value and total lactic acid (13). Lighter colored lactylates can be produced by bleaching with hydrogen peroxide followed by decomposition of the excess peroxide.

Cationic Surfactants. Cationic surfactants are characterized by the presence of the negative charge on the large molecule and a smaller negative counterion. Quaternary ammonium salts (Scheme IV) are the most common type of the cationic category. They are designed in a two-stage process, i.e., tertiary amines are prepared by alkylation or reductive amination as shown in Figure 26.5. The tertiary amine is then reacted with an alkyl halide or sulfate to yield the quaternary ammonium salt. These compounds have a wide variety of applications such as hard-surface cleaners, disinfectants, and fabric softeners.



$$\left[C_{12}H_{25}-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N}}-CH_3\right]^+ A^-$$

IV

Amphoteric Surfactants. Amphoteric surfactants are defined by the presence of both positive and negative charges on the large surfactant molecule. Ion and counterion are

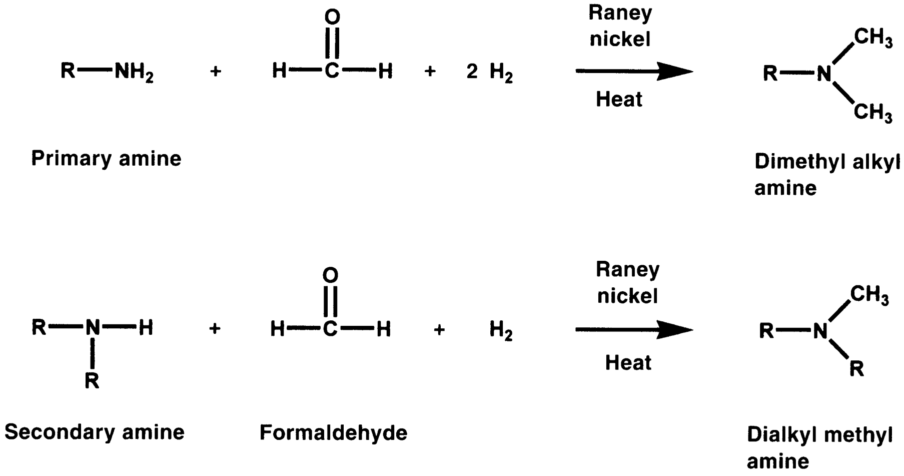
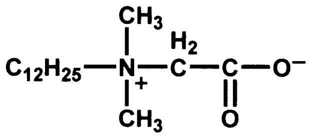


Fig. 26.5. Preparation of tertiary amines by reductive amination.

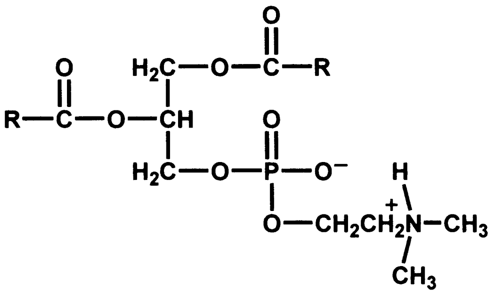
therefore tethered. Betaines, as represented in Scheme V, are the most common category of amphoterics. A betaine is prepared conventionally by alkylation of a tertiary amine with a haloacid, for example, chloroacetic acid. Positively charged amines combined with negatively charged carboxylate ions are present in amino acids, peptides, and proteins.



$$C_{12}H_{25}\text{—}\overset{CH_3}{\underset{CH_3}{N^+}}\text{—}\overset{H_2}{C}\text{—}\underset{O}{\overset{\|}{C}}\text{—}O^-$$

V

Lecithin (Scheme VI) is a naturally occurring amphoteric compound. It is composed of a mixture of phosphatidylcholine, phosphatidylethanolamine, phosphatidylinositol, and other minor components. It is present in membranes and is most commonly obtained from vegetable oils and egg yolks. For example, crude soybean oil is treated with aqueous acid and the insoluble layer is removed by skimming the surface. Crude lecithin contains appreciable quantities of residual oil and may be purified further, e.g., by precipitation from acetone. Purified lecithin may also be fractionated to produce components enriched in phosphatidylcholine or phosphatidylethanolamine. Lecithin may be modified by hydroxylation or enzymatic hydrolysis. These processes increase the HLB value by increasing the ratio of polar to nonpolar functional groups. Lecithins have found widespread use in food applications as coemulsifiers and antisticking agents. In the pharmaceutical industry, they have been used to prepare liposomes for drug delivery applications.



VI

Nonionic Surfactants. The previous discussion concerned surfactant molecules that carry a positive or negative charge. Nonionic surfactants do not bear a formal electrical charge but contain heteroatoms, which cause a dipole moment. The relatively negative region of the molecule is attracted to the aqueous phase, whereas the nonpolar region penetrates into the oil phase. In the case of foam, air assumes the role of the nonpolar phase. The HLB value of a nonionic surfactant depends on the relative number and electronegativity of heteroatoms.

Fatty acid esters of polyols represent a large and diverse group of nonionic surfactants. Some typical polyols used as raw materials in these preparations are shown in Figure 26.6. Esterification can be carried out in either batch or continuous manufacturing processes. A typical batch reactor is illustrated in Figure 26.7. Critical design factors for batch reactors include the following: (i) If corrosive materials such as lactic acid or polyphosphoric acid are used in reactions, the reactor, adjunct vessels, and piping should be constructed of 316 stainless steel. (ii) Meters or scales used to dispense reactants should be accurate in order to produce consistent quality surfactants. (iii) If polyols are to be recycled, fractional distillation capabilities are required. For example, separation of propylene glycol from glycerol must be adequate to prevent cross-contamination in subsequent surfactant batches. In direct esterification reactions, the system should be capable of separating water of reaction from polyol. (iv) Sufficient heat transfer capacity should allow for rapid heating and cooling to minimize reactor cycle time. (v) Enclosed vessels with inert atmospheres should be implemented for starting oils, reactor, piping, and product tanks to minimize degradation. (vi) An adequate cleaning system should be provided to minimize batch-to-batch cross-contamination.

A continuous reactor, as illustrated in Figure 26.8, is the most economical; large quantities are produced by interesterification reactions with minimal product changeover (14). Direct esterification reactions are not amenable to this equipment because of their long reaction times (on the order of several hours) and necessity for removal of water of reaction. Base oil, polyol, and catalyst are metered continuously into the bottom of a heated reactor. Rate of flow through the reactor is adjusted so that reaction temperature is achieved and the reaction is complete as the mixture reaches the top of the reaction vessel. The mixture is passed though a heat exchanger

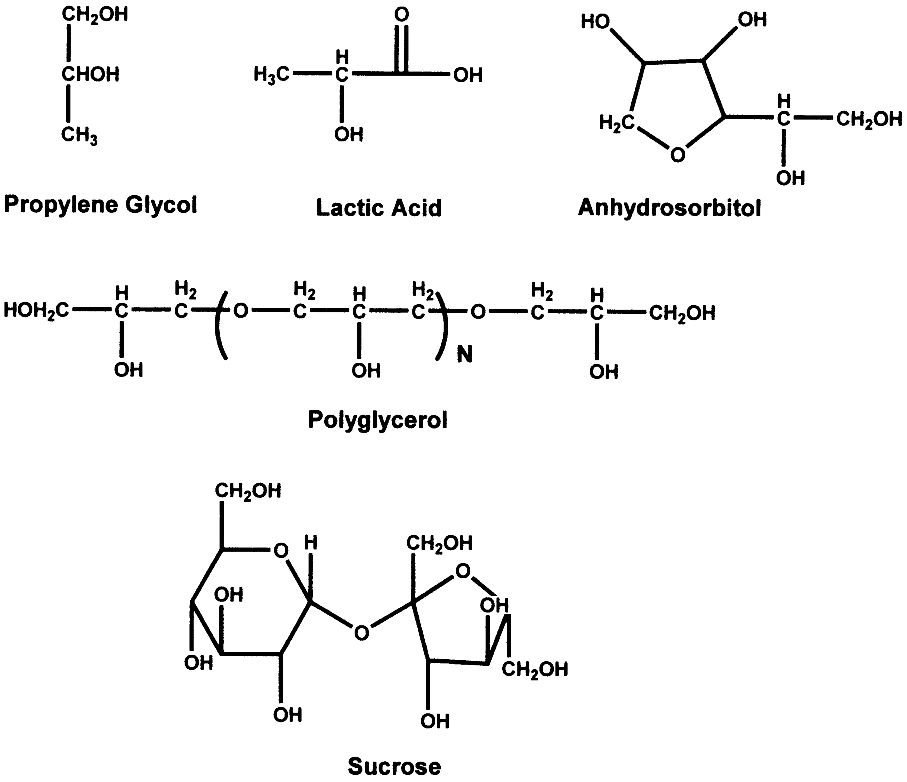


Fig. 26.6. Some polyols used for preparation of polyol fatty acid esters.

and then through a falling film evaporator. Excess polyol is removed by distillation at reduced pressure. Distilled polyols are returned to the polyol raw material tank for recycling. If a mixture of polyols is produced, the distillate stream is diverted to a storage tank and later fractionated to produce individual components, which are recycled. Because the residence time in the falling film evaporator is short, neutralization of the catalyst is not required before polyol removal as is the case in batch systems. Disproportionation reactions are not favored in this short time. The product is then cooled and passed to a holding tank where acid is metered in to neutralize the catalyst. The surfactant is then passed though a filter to remove neutralized catalyst.

Some important design factors for continuous reactors include the following: (i) Because corrosive polar compounds such as lactic or acetic acids are not used, the reactor system may be constructed of lower-grade steels (i.e., carbon or 304 steel). (ii) The multihead metering pump must be sufficiently accurate to produce a consistent quality surfactant. Deficiencies in this component lead to difficulty in setting initial reaction conditions, thus increasing the number of products that do not meet specifications. (iii) Sufficient heat transfer capacity is essential to allow

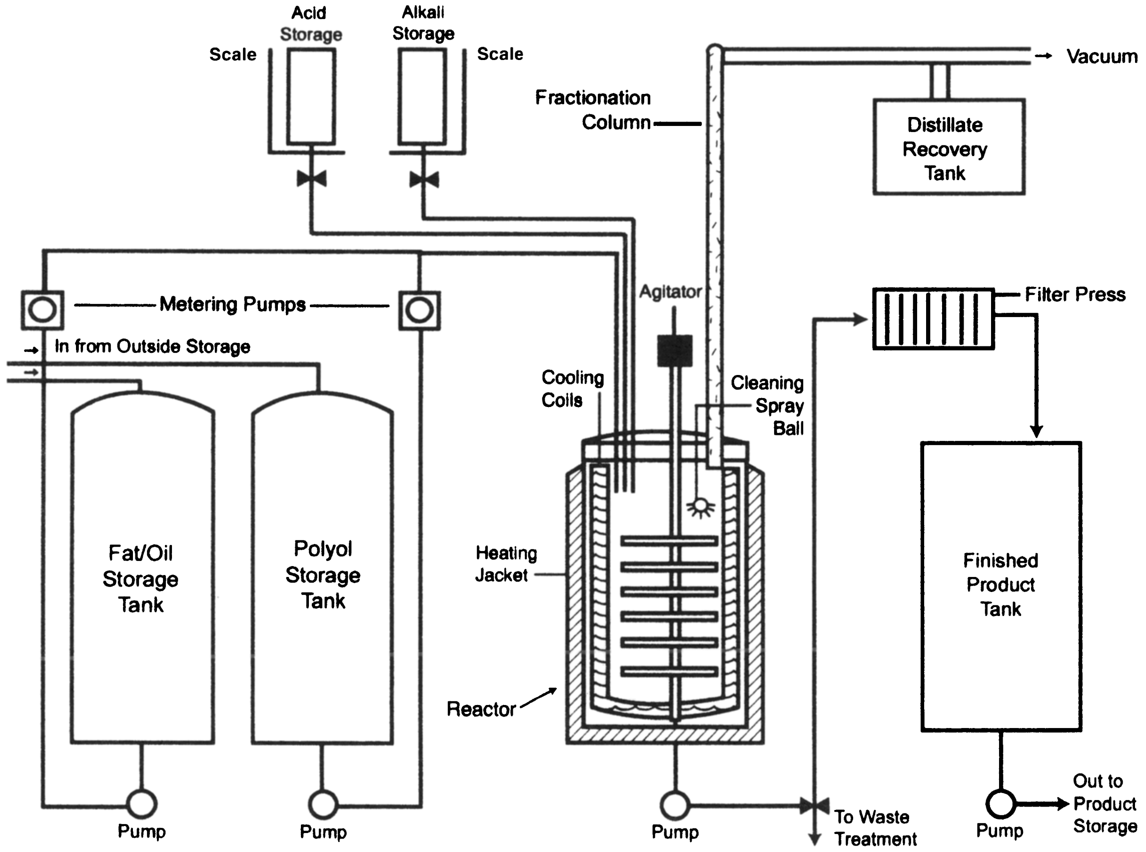


Fig. 26.7. Schematic of a batch ester reactor.

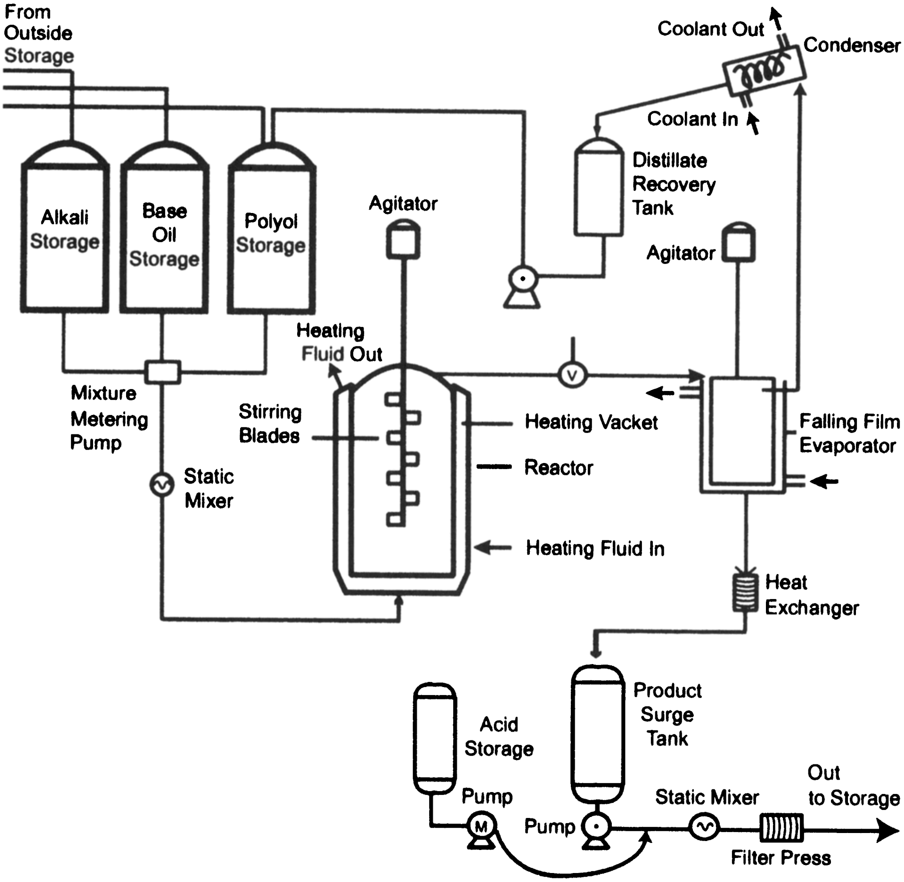
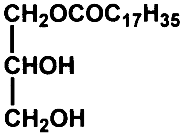


Fig. 26.8. Schematic of a continuous ester facility.

for reasonably rapid flow rate through the reactor and subsequent heat exchanger. (iv) The falling film evaporator must have sufficient surface, heat transfer, and condensing capacity matched to the maximum flow rate from the reactor. Insufficient capacity may result in the inability to produce certain products or result in uneconomical flow rates. (v) A rapid process control analysis is needed to ensure that the process is maintained under good control. A flow-through refractometer is one example of such a control analysis.

Monoacylglycerols (Scheme VII), also known as monoglycerides, are used widely in food and other applications. The two most prevalent commercial routes to monoglycerides are direct esterification of glycerol with fatty acids and glycerolysis of natural or hydrogenated fats and oils. Approximately the same product distribution of mono-, di-, and triglycerides is obtained from both processes. The latter process is more economical because fats are less costly than fatty acids, and therefore most widely utilized. However, if very light color is required for a specific application, e.g., cosmetics, direct esterification is the preferred process.



$$\begin{array}{l} CH_2OCOC_{17}H_{35} \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

VII

Direct esterification has been carried out traditionally using Brønsted or Lewis acid catalysts. However, in the author's experience, alkaline catalysts such as sodium, potassium, or calcium hydroxides may be employed at lower glycerol to fatty acid ratios. High temperatures are required to promote sufficient solubility of glycerol in the fatty acid. Progress of the reaction is monitored by measurement of the acid value decrease by titration with standard base. A pH meter may also be used to estimate the unreacted fatty acid. When the reaction is completed, the catalyst is neutralized and unreacted glycerol is removed by distillation at reduced pressure and recycled. Filtration removes neutralized catalyst from the finished product.

Glycerolysis is carried out with an alkaline catalyst. Sodium hydroxide solution has been widely used at concentrations of 0.01–0.2%. Anecdotal evidence suggests that calcium hydroxide used at 0.035% produces emulsifiers with improved color. However, selection of a low iron–containing sodium hydroxide (e.g., rayon grade) also produces monoglycerides with light color. Additionally, calcium phosphate salts are more difficult to separate from the product by filtration than sodium salts. The reaction is a randomization equilibrium. Temperatures of 220–260°C, depending on glycerol concentration (higher glycerol levels require higher temperatures), are required to promote homogeneity. The reaction proceeds rapidly and is complete usually within 30 min. A rapid indication that equilibrium has been reached is the observation of a single phase when a sample is withdrawn from the reaction. A quantitative determination can be made by titration of α-monoglyceride with periodic acid or measurement of total monoglyceride by gas–liquid chromatography (GLC). Measurement of the hydroxyl absorption by near infrared reflectance (NIR) is an attractive rapid method for monoglyceride determination (15) . As with the direct esterification process, the catalyst must be neutralized and excess glycerol removed. Neutralized catalyst, e.g., sodium or calcium phosphate is removed by filtration.

Propylene glycol esters of fatty acids are similar to monoglycerides but have one less oxygen atom and consequently have lower HLB values. Propylene glycol esters, like monoglycerides, may be prepared using direct esterification or interesterification. However, unlike monoglycerides, the product distribution is significantly different. For interesterification, glycerol from the triglyceride is introduced and produces mono-, di-, and triglycerides in addition to propylene glycol mono- and diesters. As with monoglycerides, the distribution of products is controlled by the ratio of propylene glycol to the fat or fatty acid. Most propylene glycol esters for food are prepared by interesterification because fats and oils are less costly than the fatty acids. Direct esterification is utilized only where light color or specific functionality is required. Progress of the reaction is also monitored by acid value decrease for direct esterification or onset of homogeneity in interesterification. The presence of water in the propylene glycol interferes radically with progress of the interesterification reaction; therefore, dry propylene glycol is required. As with monoglycerides, the reaction catalysts are neutralized and excess polyol is removed by distillation. However, in this case, propylene glycol and glycerol must be separated by fractional distillation before being recycled. Concentration of reaction products is determined by GLC (16).

Polyglycerol esters of fatty acids consist of a polar head group prepared by polymerization of glycerol and one or more fatty acids. The HLB value of the molecule is controlled by the degree of polymerization and the degree of fatty acid substitution. In the first step, glycerol is heated in the presence of a catalyst to produce a distribution of oligomers. In addition to linear condensation, oligomers may self-condense to form a distribution of cyclic isomers. High reaction temperatures also produce byproducts that cause dark colors and objectionable odors and flavors. Low pH at high temperature increases the concentration of colored compounds and cyclic isomers.

One general procedure uses an alkaline catalyst at a concentration of 0.3–1.0%. A reaction temperature of 245–260°C is required to produce an adequate reaction rate (17). Lower temperatures favor the formation of cyclic oligomers. Acid catalysis has been reported by Seiden and Martin (18). Lower reaction temperatures can be used in this system and reaction rate may be more rapid. However, it is not clear whether a higher quality product is produced. Progress of the reaction may be followed by refractive index, near infrared analysis, or hydroxyl value. Because the product is a distribution, the degree of polymerization is characterized as an average. Polyol distributions from diglycerol to dodecaglycerol can be determined by formation of trimethylsilyl ethers followed by analysis with GLC (19). Reaction times vary from ~6 h for diglycerol to 20 h for decaglycerol. Polyglycerol may be used as produced or be stripped of free glycerol and cyclic diglycerol with steam or nitrogen at reduced pressure (20).

Either direct esterification with fatty acid or interesterification with fats or oils may be utilized to produce the polyglycerol esters. Generally, intermediates with a higher degree of polymerization are prepared from fatty acids to avoid introducing glycerol into the polyol distribution. Interesterification may be utilized when lower polyglycerols have been stripped of excess glycerine. The degree of esterification and the resulting HLB are controlled by the ratio of fatty acid to polyglycerol in the reaction mixture. Some selectivity in the production of monoesters by control of reaction temperature has been reported recently (21).

Fatty acid esters of sucrose may be designed with a wide range of HLB values by varying the degree of fatty acid substitution. Only mono-, di-, and triesters have appreciable surface activity. A great deal of work has also been done in the synthesis of these compounds due to the development of sucrose polyesters (e.g., olestra) as a nondigestible fat substitute. The synthetic strategies for these materials are the same. The most common reaction is a base-catalyzed interesterification of fatty acid methyl esters with sucrose. One significant difference from the preceding discussions is the propensity of sucrose to caramelize at temperatures >140°C. High temperatures can therefore not be used to promote homogeneity. One way of overcoming this difficulty is to use a solvent, such as dimethyl formamide (DMF) (22) or dimethyl sulfoxide (DMSO) (23), in which both the fatty component and the carbohydrate are soluble. The disadvantage of this approach is the removal of high boiling and toxic DMSO and DMF from the finished product by vacuum distillation. Another strategy is to use soap or an emulsifier to promote the formation of an emulsion that can react as a two-phase system (24). Excess soap may be neutralized and removed from the product by short path distillation. Acetates of sucrose have been used in place of sucrose to achieve mutual solubility of the two phases (25). High shear can also produce finely divided droplets, which increase the rate of the heterogeneous reaction (26). An emulsifier containing both sucrose esters and glycerides can be prepared by reacting triglycerides with sucrose in the presence of an alkaline catalyst (27). Purification of sucrose esters may be carried out by extraction with solvents such as ethyl acetate/water to remove residual soap.

Sorbitan esters of fatty acids have low HLB values, but are often used in combination with high HLB emulsifiers, such as polysorbates. When sorbitol is reacted with fatty acids, two simultaneous reactions occur. The fatty acid can react with a free hydroxyl group to form an ester bond. At reaction temperatures employed, sorbitol can also self-condense to form the cyclic ethers, sorbitan and isosorbide. An alkaline catalyst such as sodium hydroxide, is used to promote the reaction (28). Zinc stearate has also been used as a catalyst (29). Dark-colored products are produced due to caramelization side reactions at the high temperatures utilized to promote homogeneity. Reducing agents such as sodium hypophosphite (30) can be employed to produce light-colored products. Colors may be improved further by bleaching the product with hydrogen peroxide. Reaction progress is monitored by titration of free fatty acid, and the reaction is observed to be first order in fatty acid concentration. An alternative process (31) is to first cyclize the sorbitol with an acid catalyst to produce sorbitan and isosorbide, which may be purified by treatment with carbon and/or ion exchange resin. The polyol is then reacted with fatty acid to yield the sorbitan ester. The multiple steps involved in this process add significantly to the cost of this process.

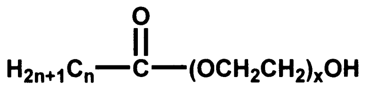
The common nomenclature of sorbitan esters has been determined largely by the ICI trade name Span, combined with a number that designates the fatty acid and degree of substitution. The system is outlined in Table 26.2. Polysorbates follow the same numbering system but are referred to as Tween.

The content of sorbitol, sorbitan, and isosorbide may be measured by cleavage of fatty acids from the polyol, reaction of the polyol with chlorotrimethyl silane, and measurement by GLC (32). Intact sorbitan esters may be separated and analyzed by high-performance liquid chromatography (33).

TABLE 26.2 System of Nomenclature for Sorbitan Esters

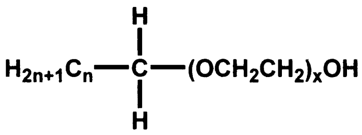
Sorbitan monolaurate	Span 20
Sorbitan monopalmitate	Span 40
Sorbitan monostearate	Span 60
Sorbitan tristearate	Span 65
Sorbitan monooleate	Span 80

Fatty acids and straight-chain fatty alcohols may be reacted with ethylene oxide, resulting in the opening of the oxirane ring and formation of a polyoxyethylene chain. Ethoxylates of the fatty acids (Scheme VIIIa) and fatty alcohols (Scheme VIIIb) have larger and more polar head groups. Reactions employing propylene oxide produce a polyoxypropylene chain.



$$H_{2n+1}C_n{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}(OCH_2CH_2)_xOH$$

VIIIa

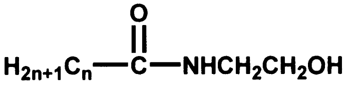


$$H_{2n+1}C_n{-}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}{-}(OCH_2CH_2)_xOH$$

VIIIb

Free hydroxyl groups of sorbitan esters react with ethylene oxide to produce ether linkages to polyoxyethylene chains (34). The molar ratio of ethylene oxide to sorbitan ester is 20. The common nomenclature for polysorbates is analogous to that for the starting sorbitan esters. Thus polyoxyethylene[20] sorbitan monooleate = polysorbate 80; polyoxyethylene[20] sorbitan monostearate = polysorbate 60; polyoxyethylene[20] sorbitan tristearate = polysorbate 65. Products are characterized by saponification number, hydroxyl value, and polyoxyethylene content. Although these specifications mandated by the Food and Drug Administration (FDA) are very tight and manufacturers are highly self-consistent, variations among manufacturers can arise from two factors as follows: (i) Variations in sorbitol/sorbitan/isosorbide ratios in the starting esters. These differences are difficult to determine by analysis because they are "masked" by the addition of the polyoxyethylene chains. (ii) The ethoxylation conditions, such as temperature, rate of addition, or reactor geometry may produce differences in monodispersity/polydispersity of the polyoxyethylene chains. These variations may cause subtle differences in functionality when applied to food products. Negative ion chemical ionization mass spectrometry has been applied to characterization of polysorbates (35). Families of peaks corresponding to oxyethylene units bonded to a fatty acid sorbitan ester were identified. This technique may thus prove a useful "fingerprint" of a unique polysorbate composition.

Monoglyceride functional groups can react with ethylene oxide to add polyoxyethylene chains and effectively increase the size of the head group and the HLB of the surfactant. The first step in their preparation is to produce a mono/diglyceride mixture, generally from a saturated fat or fatty acid. Catalyst is not neutralized but left in the product, which is then subjected to ethoxylation. At the end of the process, the product is steam- or nitrogen-deodorized to remove dioxane and other volatile impurities. Insoluble materials such as residual catalyst are removed by filtration. Ethoxylates have also been produced by reaction of glycidol with fatty acids and ethylene oxide. The reaction of ethanolamine with fatty acids produces ethanolamide (Scheme IX) surfactant molecules. The head group may be modified further by ethoxylation or propoxylation of the molecule.



$$H_{2n+1}C_n-\overset{\displaystyle O}{\overset{\|}{C}}-NHCH_2CH_2OH$$

IX

Some Applications of Surface Active Materials

The driving force behind the development of new products has been an improvement in their functionality in a wide variety of applications. Blends of surfactants are often used to optimize the performance of a particular product. Experienced formulators recognize synergistic and antagonistic interactions with other surfactants or other ingredients. For example, anionic and cationic surfactants interact and neutralize one another's functional properties. Changes in pH also dramatically affect the performance of ionic surfactants.

Soaps and Detergents

Soaps are salts of fatty acid carboxylates and metal ions. They precipitate in the presence of alkaline earth cations, such as calcium and magnesium. Soaps are effective for removing oily dirt through incorporation of oil into the lipophilic core of the micelle formed by the soap in water. Optimum performance is displayed by the 12-carbon sodium dodecanoate (laurate), most often derived from the splitting of coconut or palm kernel oil. Hand soaps may be formulated into bars or liquids. Other ingredients, such as scouring abrasives and fragrances are incorporated. Details of soap formulation and manufacturing have been discussed by Burke (36).

Sulfate-, sulfonate-, and phosphate-based detergents were developed originally to overcome the adverse effects, i.e., precipitation, of hard water on soaps. They have found widespread use in many cleaning formulations such as laundry and dishwashing detergents. Other ingredients, such as foam builders, fiber protectors, and antiredeposition agents are used to improve cleaning properties. Hard-surface cleaners are often formulated to sanitize as well as clean. Quaternary ammonium salts are commonly used as antimicrobial agents for these applications. Principles involved in detergency have been detailed by Lynn (37).

Food Emulsions

Although some food emulsions are obtained by processing foods that contain natural surfactants, many other processed foods employ synthetic food surfactants to improve their appearance, texture, and flavor. Most surfactants used to produce and stabilize emulsions are nonionic because they are less sensitive to pH and the presence of calcium ions. The emulsions may be of the W/O type, such as butter and margarine, or O/W, such as mayonnaise and salad dressing. Some products, for example, whipped toppings and ice cream, are edible foams.

Surfactants provide functionalities in foods beyond emulsion formation and stabilization. Some common examples include the following: (i) lecithin is used to control viscosity in the production of chocolate; (ii) bakery shortenings are used to promote aeration to ensure uniform air cell distribution; and (iii) sodium and calcium stearoyl lactylate retard staling in breads. These secondary functional properties are often more important than emulsifying properties.

Surfactants used in foods are regulated by government agencies responsible for food safety. Strictness of the regulations varies according to surfactant type. Lecithin and monoacylglycerols are approved widely for a multitude of foods. Expansion to other nonstandardized foods is rarely a problem. Other surfactants, such as polysorbates or sodium stearoyl lactylate, are regulated strictly. Using these surfactants for new applications requires lengthy petitions for government approval. Similarly, any new synthetic surfactants would require detailed documentation of their safety for food use. The reader is referred to four recent references fore more complete discussions of principles and practices in food emulsions (38–41).

Agricultural Formulations

Products designed to facilitate agriculture, such as fertilizers, pesticides, and herbicides contain two classifications of ingredients. Active ingredients, often a small percentage of the formulation, perform the desired agricultural function. For example, a herbicide kills weeds. All other ingredients are classified as inert. Although surfactants are highly functional molecules that determine how well the actives are distributed, they are considered inert. Governmental regulations are generally more stringent for active than for inert ingredients.

Contact angle is an important consideration for products that are applied to foliage. The formulation should wet sufficiently to allow the active ingredient to spread over the leaf. The Spreading Coefficient is commonly used to evaluate the performance of agricultural sprays (see the section on surface and interfacial tension for the equation).

Several types of formulations are useful for the application of agricultural chemicals. Emulsifiable concentrates are solutions of active ingredients in oil, which are emulsified into water with simple stirring at the farm location. Emulsion concentrates are preformed emulsions that are simply diluted by addition to water.

Surfactants used in these formulations must be tolerant to hard water, such as that obtained from wells. Invert emulsions are prepared and sprayed as W/O emulsions. The oil continuous phase allows formation of very small droplets, providing more efficient coverage. Microemulsions are thermodynamically stable and therefore tolerate a wide range of storage and use conditions. However, the high level of surfactant makes them relatively expensive. Wettable powders also use surfactants to facilitate wetting of a dry active ingredient. Polymeric additives are included to reduce sedimentation of the dispersion. Microencapsulation of active ingredients allows extended release of the ingredient, requiring less frequent application. However, low loading efficiency has limited the application of this technology. Tadros (42) has discussed formulation of agricultural products in some detail.

Some Pharmaceutical Emulsions

Two important considerations for administration of drugs to treat disease are as follows: (i) Controlled release of the active compound over time. This often involves extending release over a longer time to reduce the number of required doses. (ii) Targeting and delivery of drugs to specific organs or tissues of the body. This technology has the potential to reduce adverse side effects in organs in which the drug is not needed.

Drug delivery can be accomplished using vesicles also known as liposomes. These structures are prepared from natural and synthetic lecithins, which are composed largely of phosphatides. Some sucrose esters are also capable of forming vesicles.

Intravenous emulsions may be used to deliver lipid nutrients to patients whose gastrointestinal system has been compromised. Very small and uniform emulsion droplets are required to prevent adverse effects from blockage of small blood vessels. The nature of the droplet surface is also critical to prevent premature clearance from the bloodstream. Natural and modified egg and soy lecithins have been utilized for this application.

Microencapsulation of drugs can be utilized to extend release times. Also, W/O emulsions tend to be released more slowly than O/W emulsion. Slow release is very useful when administering vaccines because it allows more time for formation of antibodies. For more detailed discussions in these applications of surfactants to pharmaceutical preparations, the reader is referred to a few recent references (43–46).

Cosmetics

As in food and pharmaceutical products, cosmetics interact with the human body. Some surfactants, such as sodium dodecyl sulfate (SDS), are strongly irritating to skin and eyes. Many nonionic surfactants are therefore used because they are milder than anionic surfactants. Cleaning surfactants can also remove protective oils from the skin and hair. Other ingredients are therefore added to the formulation to confer substantivity. Creams and lotions for skin care often contain mesophases, which trap moisture and serve a protective function in the pores of the skin. Shaving formulations contain foam-forming surfactants as well as lubricants, which prevent razor burn irritation. For further information about surfactants and cosmetic formulations, the reader is referred to two works on the subject (47,48).

Some Other Applications of Surfactants

Surfactants can function in any applications that require functions to occur at a surface or interface. Surfactants are added to a number of extruded plastics as lubricants and to allow filling with inert particles. Oil well drilling uses products that assist in removing oil from oil shale and sand. Some of the same principles of surface science may be applied to demulsification. Textile spinning and finishing operations require surfactants for lubrication and surface modification (49). The fat-liquoring operation in leather tanning may use surfactants to facilitate the process (50).

Companies engaged in the manufacturing and sale of surface-active agents face a diversity of challenges. In heavy industries, new products may be applied quickly, and proprietary formulations can be used to preserve intellectual property. Products developed for the pharmaceutical, food, and cosmetics industries require greater effort to prove safety and efficacy. Full label disclosures in these applications also make proprietary formulations easy to reverse engineer. In these markets, new applications are being developed constantly for surfactants that are already approved.

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Chapter 27

By-Product Utilization

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Introduction

During the past 20–30 years, we have seen a significant increase in the usage of fats and oils for both edible and inedible purposes. This has meant an increase in by-products, which are derived from the processing of crude fats and oils into refined products or from the processing of fats and oils into oleochemicals. However, the availability of by-products or the availability of certain types of by-products has changed over the years because of changes that have come about in the methods of processing fats and oils as well as the fact that certain crops grown in the past are not grown in the same quantity today and *vice versa*. For example, in the period of time cited above, there has been a major transition from the alkali refining of oils to the physical refining of oils. Also, today, we have new oils available in larger quantities such as palm oil, palm kernel oil, rapeseed oil, canola oil, and sunflower seed oil; these were not available in significant quantities in the past. Therefore, we are now seeing by-products from these new oils in the marketplace.

A number of by-products exist that are, or could be recovered from the processing of crude fats and oils into refined products or into oleochemical derivatives. However, only a few by-products are produced in sufficiently great quantities to be considered viable raw materials for the manufacture of animal feeds and industrial chemicals. These include the following: (i) soap stocks from the alkali refining of such oils as soybean oil, cottonseed oil, palm oil, corn oil, peanut oil, sunflower oil, rapeseed oil, coconut oil, or palm kernel oil; (ii) steam-refining distillates obtained from such oils as coconut oil, palm oil, soybean oil, palm kernel oil, or animal fats; (iii) deodorizer distillates from all of the above-mentioned oils, which are normally alkali refined; (iv) phosphatides from the degumming of vegetable oils; and (v) residues from the manufacture of fatty acids.

Whenever by-products are considered for the manufacture of animal feeds or chemicals, they must be available in sufficient quantities, and their quality must be such that an excessive amount of processing is not necessary to make them suitable for a specific end-use applications. In addition, the concentration of the active component to be isolated must be at a level to justify its recovery.

The quantity and the quality of by-products recovered from the above-mentioned oils depend upon a number of factors. These include the following:

1. The method used in extracting the oil from the seed, the pulp, or the fruit. For example, the quantity and quality of soap stock derived from cottonseed has been

studied relative to the different methods of extracting the oil from the seed. In these studies, it was shown that refining losses were lowest for direct solvent-extracted oil; at the same time, however, this process gave soap stock with the highest percentage of gossypol and oxidized fatty acids (1). The former can be an undesirable component for use in animal feeds, whereas the latter is not desirable in the manufacture of soap bars.

2. The quantity, quality, or effective concentrations of an active component in soap stocks and steam-refined distillates will depend on how the seeds, pulp, and fruits are handled during harvest and storage; for example, when oil palm fruit is bruised during harvest, the free fatty acid content of the palm oil extracted is increased. In addition, the longer the time between harvesting and sterilization, the higher is the free fatty acid content (2).
3. The quantity and quality of soap stock and steam-refining distillates are related to how the oil is handled and stored before it is processed to remove some of the desirable or undesirable components; oils having high moisture content hydrolyze more readily to give higher free fatty acid content. Also, oils stored at higher temperatures, particularly during summer months, in the presence of air tend to oxidize and form degradation products, which not only increases the amount of by-products recovered from the oil, but also affects the efficiency of removing the by-products from the oil in an adverse manner.
4. The quality and composition of soap stock from alkali refining of oils depend on the type of processing equipment, the efficiency of the process, and the conditions under which the process is operated.
5. Residues from the processing of fatty acids can vary considerably, depending on factors such as the type of distillation, distillation efficiencies, operating conditions, or up-stream processes.

Minor Constituents of Glyceride Oils

Before discussing the chemicals or chemical intermediates that might be derived from the above-mentioned by-products, let us consider the minor constituents of glyceride oils taken as a whole, which may become a portion of one or all of the by-products under consideration.

Fatty Acids

All oils contain varying percentages of free fatty acids, which are removed by alkali and steam refining. Their composition is normally similar to that of the fatty acids derived from the whole oil itself; however, they will vary to a minor degree, depending on how the hydrolysis of the glyceride to produce these acids actually occurred. For example, enzymatic hydrolysis of a glyceride can be very specific in hydrolyzing the fatty acid esters in the α-position of the glycerol molecule. Also, some autocatalytic hydrolysis occurs during the steam refining and steam deodorization of oils. Because both methods of hydrolysis bring about some fractionation of acids, the resulting fatty acid products will vary slightly from the composition of the whole oil. This is illustrated in Table 27.1 relative to the steam refining of palm oil.

In addition, the fatty acids recovered from the oil will contain various percentages of oxidized acids resulting from the exposure of oil to air, whereupon autoxidation of the more unsaturated triglycerides occurs. This is especially true when the oil is subjected to air at higher storage and processing temperatures. The amount of oxidized acids found in these by-products will depend, in certain instances, on how the oil was extracted from the seed, pulp, or fruit. For example, cottonseed oil soap stocks recovered from screw-pressed oils and direct solvent-extracted oils contain higher percentages of oxidized acids compared with soap stocks derived from prepress solvent-extracted oils, high-speed screw-pressed oils, or hydraulic oils. Because these oxidized fatty acids contain other functional groups or may have undergone oxidative polymerization, they can be removed from the fatty acid *via* distillation and be concentrated in the residue fraction.

Unsaponifiables

Vegetable oils can also contain relatively high percentages of unsaponiflable materials, which are normally present in amounts between 1 and 6%. They may occur naturally or result from the degradation of fatty acids and glycerides that have been subjected to high temperatures in the presence of air. In addition, unsaponiflable material can also be artifacts from the growing and processing of oils. An example of the latter occurs in the bleaching and steam distillate refining of palm oil in which thermal and catalytic reactions lead to the formation of normal alkenes, di- and triterpenes, and aromatic chemicals. These products are attributable to the degradation of tocotrienols present in palm oil (3). Other unsaponifiable products that are readily concentrated in soap stocks, steam-refining distillates, and deodorization distillate by-products include tocopherols, color pigments, sterols, gossypol, carbohydrates, oxidized materials, waxes, carotene, pesticides, triterpene alcohols, and 4-methyl sterols (4–7).

TABLE 27.1 Comparative Fatty Acid Compositions

	Fatty acid composition (%)	
Fatty acid	Whole palm oil	Steam-refining distillate
C_{12}	Trace	1.0
C_{14}	1.0	1.3
C_{16}	43.4	46.4
C_{18}	4.5	4.4
$C_{18:1}$	40.0	37.2
$C_{18:2}$	11.0	9.7
$C_{18:3}$	0.1	Trace

As mentioned earlier, high temperatures and/or exposure to air during processing and handling of the various glycerides lead to degradation products that have an adverse effect on the yield of refined oil and on the potential utilization of products recovered from the by-products. For example, some of the volatile substances recovered from soybean oil that result from autoxidation are as follows: acetaldehyde, dimethylsulfide, ethylacetate, 2-butanone, diacetyl, acetic acid, *n*-hexanal, pentanal, acetoin, 5-methyl-2-hexanone, 2-heptanone, butyric acid, 2-nonanone, 2-undecanone, deltanonalactone, 2-tridecanone, ethyl-5-oxo-nonanoate, deltadecalactone, and deltadodecalactone (8).

Commercial Utilization of By-Products

Animal Feeds

One of the major uses for acidulated soap stock and steam-refining distillates and animal fat by-products is in the manufacture of animal feeds (9–11). Dried animal feeds present dust problems in handling and mixing operations and because of their hydroscopic properties, they have a tendency to cake upon storage. The addition of acidulated soap stocks and steam-refining distillates overcomes these problems. In addition, they increase the oil content, increase the weight of the feed, and provide a source of energy.

Incorporating 4–6% of fatty acid by-products into feeds increases the energy density to a level higher than the gross energy value of the by-product itself. This additional metabolizable energy improves feed efficiency or utilization (12). The amount of energy derived from fats or fatty acids is about twice that of other feed constituents such as starch and protein. However, the latter can be less expensive sources of energy. It has also been noted by the National Research Council (NRC) that if the fatty acid by-product contains essential fatty acids, such as linoleic acid, it can be beneficial to the growth of chicks during the early stages (13). The NRC recommends a minimum level of 1%, whereas others recommend higher levels to sustain continued growth response (14).

The literature also notes (15) that conventional cattle foods fail to provide sufficient energy for cattle, especially lactating dairy cattle, during periods of heavy milk production. Although fat can be added to increase the energy level, a fat content >2% in feed for lactating dairy cattle has a toxic effect on the microorganisms in the rumen. To overcome this deleterious effect and at the same time provide additional energy, it is recommended that calcium salts of fatty acids be added to the feed at levels of 3–5%. The specification for the utilization of fatty material in animal feed is given in Table 27.2. Because of the limitation on the percentage of free fatty acids, fatty acid by-products are blended with other low-grade tallows and greases such as yellow grease. Higher levels of free fatty acids yield a feed formulation that is less palatable.

One of the attributes of adding soybean soap stock to poultry feed is that it contains an appreciable amount of xanthophylls, a desirable component of poultry foods.

TABLE 27.2 Specifications for Fatty Material in Animal Feeds

Physical or chemical property	Specification
Free fatty acid	~15%
Titer	44°C maximum
Color	Light
Moisture	0.5–2.0%
Peroxide value	15–20 maximum
Unsaponifiables	3.0% maximum
Impurities	Trace

On the other hand, cottonseed soap stocks contain gossypol, which imparts a dark color to eggs; therefore, it is not used in poultry feed unless the soap stock is derived from glandless cottonseed oil.

Steam-refining distillates at times contain varying amounts of pesticides, which restrict their use in animal foods (16,17). All such distillates should be analyzed for pesticide content before they are incorporated into animal foods. In the United States, federal and state regulations require the testing of fats, oils, and fatty acids before their incorporation into foods.

Tocopherols

Varying amounts of tocopherols are found in most vegetable oils, occurring at levels of 300–2000 ppm in such products as corn oil, wheat oil, cottonseed oil, soybean oil, sunflower oil, safflower oil, olive oil, rapeseed oil, and palm oil. However, coconut oil is practically devoid of these substances. In the refining of oils, tocopherols are concentrated in the deodorizer distillate fractions as well as in steam-refining distillates and are normally recovered using saponification, extraction, and crystallization processes.

Although some oils contain high levels of tocopherols, it may not economically feasible to recover them because of other contaminants. Such is the case for palm oil whose deodorizer distillate contains high levels of tocopherols; because of the presence of tocotrienols, however, it is difficult to fractionate out the tocopherols.

Tocopherols have been proposed, used commercially, and studied as antioxidants for many years. They are classified among the natural antioxidants, which function as electron donors (18). In oleic acid, α-tocopherol is as active as butylated hydroxytoluene (BHT), and γ-tocopherol is more active than BHT or butylated hydoxyanisole (BHA). In linoleic acid, BHT and BHA are more active than the tocopherols (19). Because the production of vitamin E (α-tocopherol) is one of the major uses for vegetable tocopherols, the level of α-tocopherol in each oil is a significant factor. Table 27.3 gives the amounts of the different tocopherols found in the various oils (20).

Although a large portion of the vitamin E manufactured in the United States is utilized in vitamin products sold to the American public, about two thirds of the vitamin E is incorporated into animal feeds, particularly by the poultry industry. A small portion also finds its way into medicinal ointments and cosmetic products. Approximately

TABLE 27.3 Tocopherols in Vegetable Oils

Oils	α-Tocopherol	β-Tocopherol	γ-Tocopherol	δ-Tocopherol	Total
			(mg/100 g)		
Wheat germ	150.75	31.19	3.95	—	240.14
Corn	25.69	0.95	75.23	3.25	108.65
Soybean	9.53	1.31	69.86	23.87	104.57
Rapeseed	18.88	—	48.59	1.20	68.67
Sunflower	62.20	2.26	2.67	—	67.13
Safflower	44.92	1.20	2.56	0.65	49.33
Palm	6.05	—	Trace	—	6.05
Olive	11.91	—	1.34	—	13.25
Peanut	8.86	0.38	3.50	0.85	13.59

5.3×10^3 metric tons of vitamin E from both natural and synthetic sources were produced in the United States in 1984 compared with only 2.4×10^3 metric tons in 1977. Just recently, the Food and Drug Administration (FDA) has permitted the use of vitamin E in pump-cured bacon to inhibit formation of N-nitrosamines (21).

Sterols

All vegetable oils contain varying percentages of sterols. However, of ~10 sterols identified in these oils, only campesterol, stigmasterol, and β-sitosterol occur in quantities that make their recovery worthwhile for commercial purposes (7). The selection of oils for use in preparing these individual sterols depends upon their annual production, their unsaponiflable content, the percentage of sterols present in the unsaponifiable fraction, and the concentration of the desired product. Table 27.4 gives the volume in metric tons of the principal edible vegetable oils consumed domestically worldwide in 1998, the percentage unsaponifiable, and the percentage of sterols in the unsaponifiable fraction (22,23); Table 27.5 shows the percentages of the principal sterols in each oil (6).

TABLE 27.4 Principal Edible Vegetable Oils in 1998

Vegetable Oil	Metric tons ($\times 10^6$)	Unsaponifiables (%)	Sterols in unsaponifiables (%)
Soybean	6630	0.6	60
Coconut	525	0.4	57
Cottonseed	457	0.4	60
Palm	127	0.4	64
Corn	567	0.4	60
Peanut	87	0.4	60
Linseed	70	0.7	60
Sunflower	68	0.7	56

TABLE 27.5 Principal Sterols in Edible Vegetable Oils

	Sterol (%)		
Vegetable oil	Campesterol	Stigmasterol	β-Sitosterol
Soybean	15–21	10–24	57–72
Coconut	6–9	18–19	69–75
Cottonseed	4	1	93
Palm	20–21	12–13	62–69
Corn	23	6	66
Peanut	10–19	6–12	70–76
Linseed	28	10	53
Sunflower	11–12	8–12	62–75

Sterols are found in all three by-products described earlier, but the highest percentages occur in acidulated soap stocks, steam-refining distillates, and deodorizer distillates. They are recovered from these by-products by distilling off the fatty acids and then saponifying the residue fraction, extracting the sterols, and crystallizing them from the extracting solvent. A recent publication describes the isolation of tocopherol and sterols present in soap stock *via* biohydrolysis, bioesterification, and fractional distillation (24).

Sterols, primarily sitosterol as a fatty acyl ester (stanol ester), have been shown to reduce both serum cholesterol and low-density lipoprotein (LDL) when incorporated into margarines (25–27). Another by-product from the processing of corn to yield corn oil is the corn fiber or outer hull of the corn kernel, which contains a corn fiber oil relatively rich in sitostanol ferulate. This ferulate ester has also been shown to have cholesterol-lowering properties (28). In the United States, 3.6×10^6 metric tons of corn fiber are produced each year, which could yield $\sim 7.3 \times 10^4$ metric tons of corn fiber oil.

Both stigmasterol and β-sitosterol are raw materials for the pharmaceutical industry in preparing progesterone and estrone. In addition, campesterol has been promoted for use in cosmetic formulations. Because large quantities of refined soybean oil are being produced daily, soybean soap stocks, which are a major source of sterols, are readily available for the manufacture of sterols.

Fatty Acids

The second largest market for by-products such as soap stocks, steam-refining distillates, and physical-refining distillates is in the manufacture of fatty acids; on the whole, these are poorer quality products compared with the manufacture of similar acids from whole oils. However, top quality fatty acids can be manufactured, but at a much higher cost. As cited earlier, their fatty acid compositions are quite similar to the whole oils, but they do vary slightly. Table 27.6 gives the typical compositions of by-product acids from the various oils that are readily available for the manufacture of fatty acids.

TABLE 27.6 Composition of By-Product Fatty Acids

Length	Soybean	Cottonseed	Canola	Palm oil	Palm olein	Palm stearine	Palm kernel	Coconut
$C_{6:0}$	—	—	—	—	—	—	0.3	0.3
$C_{8:0}$	—	—	—	—	—	—	3.9	7.9
$C_{10:0}$	—	—	—	—	—	—	4.0	7.2
$C_{12:0}$	—	—	—	0.3	0.9	0.1	49.6	54.4
$C_{14:0}$	0.5	0.9	—	1.4	1.6	0.9	16.0	18.8
$C_{16:0}$	16.7	24.7	3.9	47.4	44.9	57.0	8.0	6.2
$C_{16:1}$	—	0.7	0.2	—	—	—	—	—
$C_{18:0}$	7.4	2.3	1.9	4.4	4.0	5.3	2.4	1.2
$C_{18:1}$	24.9	17.6	64.1	36.9	38.1	30.5	13.7	2.6
$C_{18:2}$	44.5	53.3	18.7	8.4	9.2	6.2	2.0	0.9
$C_{18:3}$	5.4	0.3	9.2	0.4	0.6	—	—	0.2
$C_{20:0}$	0.5	0.1	0.6	0.4	0.4	—	0.1	—
$C_{20:1}$	—	—	1.0	0.2	0.3	—	—	—
Others	—	0.1	0.4	—	—	—	—	—

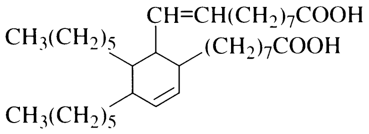
Fatty acids can be recovered from by-products by using the same processes used in the recovery of fatty acids from whole fats and oils. These include pressure splitting, enzymatic hydrolysis, alkaline hydrolysis, distillation, fractional distillation, solvent separation, hydrogenation, and purification. Although by-product acids are generally poorer quality products, they still can be utilized in certain end-use applications for which quality is not a primary factor and cost is of greater significance. Such applications include greases, rubber, compounding agents, or surface-active agents. In considering any of these areas, it must be remembered that competition for these by-products includes low-cost fatty acids derived from low-cost tallows, tallow by-products, and tall oil. Fatty acid by-products can also be considered food grade and kosher when derived from vegetable oils.

Dimer Acids

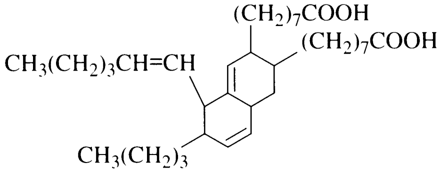
The mono- and polyunsaturated acids isolated from various vegetable oil by-products can be polymerized thermally or catalytically to yield a mixture of dimer, trimer, and higher-molecular-weight polybasic acids (29,30). The predominant product, dimer acid, is normally a mixture of monocyclic, bicyclic, and acyclic isomers as shown in Figure 27.1. These acids are utilized commercially in the manufacture of corrosion inhibitors, polyamide resins, lubricants, fuel additives, antiwear agents, soldering fluxes, or surface coatings. A by-product from the polymerization of unsaturated acids is isostearic acid, which again has a multiplicity of uses (31).

Lubricating Greases

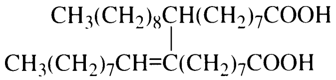
In the manufacture of lubricating greases, soaps of fatty acids are finely dispersed in petroleum oils and processed to form thicker fibers that enmesh and hold the



Monocyclic



Bicyclic



$$\begin{array}{c} CH_3(CH_2)_8CH(CH_2)_7COOH \\ | \\ CH_3(CH_2)_7CH{=}C(CH_2)_7COOH \end{array}$$

Acyclic

Fig. 27.1.

petroleum oil in a three-dimensional network. Greases lubricate by establishing a grease film, by bleeding small quantities of oil, or by a combination of the two.

Sodium, calcium, lithium, and aluminum soaps of fatty acids have been used traditionally to thicken or gel oils. The different soaps give different properties to the grease. Sodium soap greases are heat resistant but susceptible to water washing, whereas calcium and aluminum soap greases are water repellent but are low melting. Lithium soap imparts both heat and water resistance to greases. The average grease consists of 2–15% of one of the above soaps of fatty acids dispersed in mineral oil. Because both saturated and monosaturated acids can be utilized in the manufacture of greases, those acidulated soap stocks or steam-refining distillates that can be fractionated into saturated and unsaturated acids or can be hydrogenated to yield primarily saturated acids could find utilization in the manufacture of greases.

Rubber

The rubber industry consumes large quantities of fatty acids and their derivatives in both the compounding and manufacture of rubber. For example, the so-called rubber-grade stearic acid used in the compounding of synthetic rubber totaled -3.3×10^4 metric tons in 1985.

In the compounding of rubber, fatty acids perform several functions (32). They function as softeners or plasticizers, enabling the stock to be handled more easily during mixing and subsequent operations. They also provide lubrication and release characteristics, which prevent the rubber from sticking excessively to the processing equipment. However, their major function is in the vulcanization of rubber in which they react with zinc oxide to form zinc soaps, which are accelerators.

In this particular end-use application, neither the composition of the fatty acid used, nor its quality are of significant importance. In general, saturated acids are preferred over unsaturated acids because they will not affect aging properties or color adversely. Although as stated, quality is not of major importance, there are some limitations relative to color and undesirable contaminants. The specifications for rubber-grade acids are broad enough so that they can be derived from many raw material sources. However, they must be available in sizeable quantities and at very reasonable prices.

Fatty acid soaps also function as emulsifiers in the emulsion polymerization of monomers to produce synthetic rubbers. One of the largest single-volume synthetic rubbers produced in the world by emulsion polymerization is styrene butadiene rubber, known as SBR. In emulsion polymerization, the monomers constitute the dispersed phase, and water, the continuous phase. The fatty acid soap emulsifier stabilizes the emulsion and creates micelles in which the monomer is solubilized and in which the polymerization occurs.

Fatty acids used in emulsion polymerization are normally partially hydrogenated products of oleic acid; they have low polyunsaturated acid contents because the presence of polyunsaturated acids affects polymer formation adversely. Any fatty acid product derived from acidulated soap stocks or steam-refining distillates and destined for use in rubber will have to be competitive with partially hydrogenated tallow fatty acids.

Surface Coatings

Although we have seen a steady decline in the use of polyunsaturated acids in alkyd coatings in the past 15 years, resulting from the introduction of better resins into the marketplace and a shift from solvent-based coatings to water-based coatings, there still remains a sizeable market for these acids in surface-coating formulations in which alkyds continue to be the primary resin or in which they are used in combination with other resins. Therefore, acidulated soap stocks that contain high percentages of polyunsaturated acids and are recoverable without an excess amount of processing can be marketed in this end-use application. Such soap stocks include soybean, linseed, cottonseed, and sunflower. However, as mentioned earlier, these acids are generally of poorer quality; for this reason, they must be utilized in those coatings in which quality is not a primary factor, e.g., bridge paints and other industrial paints. Pattison (33) offers comments relative to the use of soap stocks in surface coatings. A typical alkyd surface-coating formulation is shown in Table 27.7.

Bar Soaps

Because of an increasingly affluent market, more bathrooms per dwelling, larger markets for treatment-type soaps, and an increasing demand for luxury and deodorant soaps, the soap industry has changed from a staid toilet soap business to a growth industry. This has sparked the development of a number of continuous soap-making

TABLE 27.7 Typical Alkyd Resin Composition

Component	(%)
Fatty acids	63.5
Pentaerythritol	27.0
Ethylene glycol	3.0
Phthalic anhydride	0.5
Xylene	6.0

processes, which are replacing the conventional and cumbersome kettle-process soap making.

Several of the new continuous processes utilize fatty acids rather than whole oils as the raw material feedstock. Normally, a blend of 80% tallow fatty acids and 20% coconut fatty acids is used by most manufacturers. Starting from fatty acids, rather than whole oils, simplifies the process, thus allowing for better process control. Additional refining of distilled coconut oil soap stocks and, in some instances, coconut oil steam strippings, provides products suitable for the manufacture of soap bars. In certain instances, the once-distilled coconut oil acidulated soap stock can be used directly in the manufacture of industrial and pumice-type soap bars without any additional refining.

Liquid hand soaps, which are normally potassium soaps of fatty acids, can be prepared from distilled acidulated soybean and coconut soap stocks. A typical formulation would be 12% coconut fatty acids, 3% soybean fatty acids, 9% 50° Be potassium hydroxide solution, 1% potassium chloride, and 76% distilled water.

Fatty Nitrogen Derivatives

The fatty nitrogen derivative market also represents opportunities for fatty acids derived from acidulated soap stocks and steam-refining distillates, provided they are priced competitively with fatty acids derived from whole fats and oils. It has been estimated that 1.8×10^5 metric tons of fatty nitrogen derivatives are being produced currently in the United States and find use in such products as corrosion inhibitors, fabric softeners, antistatic agents, antislip agents, road construction compositions, ore flotation agents, dye-leveling agents, dispersants, emulsifiers, detergent components, herbicide additives, germicides and bactericides, mold-release agents for rubber and plastics, gasoline additives, hair conditioners, dispersing agents for pigments and fillers, and anticaking agents.

Nitrogen derivatives include such products as fatty amides, fatty diamides, ethoxylated amides, primary, secondary, and tertiary fatty amines, polyoxyethylene alkylamines, amine oxides, fatty diamines, and fatty imidazolines (34–36). The physical characteristics of the fatty acid used to prepare the amine derivative, as well as the physical characteristics of the nitrogen derivatives, determine its use in the various end-use applications. A large amount of physical and chemical data are available for anyone interested in marketing fatty acids into this industry.

Flotation

Fatty acids and fatty nitrogen chemicals are utilized in many ore recovery processes. These processes consumed 4.1×10^3 metric tons of fatty acids in 1985 and 91×10^2 metric tons of fatty amines. Fatty acids and amines function as frothers, promoters or collectors, and modifiers. In the flotation processes, the ores are first ground with water to form slurries, the fatty chemicals are then added, and air is dispersed to form fine bubbles throughout the pulp. The bubbles collect at the surface of the pulp as a froth in which the minerals are collected and concentrated. The concentrates are then refloated to concentrate the ore further. Fatty promoters and collectors alter the surface of the minerals, causing them to adhere to the bubbles. Fatty modifiers also alter the surface of the minerals so as to make them more amenable to flotation.

Paper Coatings

In the manufacture of coated papers, which are used in magazines and for commercial printing papers, pools of coating materials are distributed uniformly across the surface of the paper base stock and then passed over a system of drying rolls onto supercalendering rolls to yield a glossy or semiglossy coated paper. The three major constituents of paper coatings are pigment, adhesive, and vehicle plus various additives. One of the commonly used coating formulations is hydrolyzed starch, clay, and water. To improve upon the rheological properties of such a coating, insoluble metallic soaps such as calcium stearate and palmitate are added. These chemical flow modifiers control, lower, and stabilize the viscosity of adhesives and regulate the flow of the finished coating mixture. In addition, they provide additional latitude to the formulator to meet certain end requirements without impairing the flow properties in actual operations. They also function as a lubricant in both the wet and dry state, reduce dusting on the supercalendering rolls, and improve finished coated paper properties. Because the calcium salts have high meeting points together with fine particle size, they are able to migrate to the surface of the coating where their function is to act as a lubricant.

The optimum dosage level of the calcium salt is ~1.0%, based on dry pigment weight. Little or no additional benefit is realized when the optimum dosage is exceeded. Although this may seem like a small quantity of material, 12.7×10^3 metric tons of metallic stearates were consumed in 1985 and this amount is growing at a rate of 3–3.5%y.

Metalworking Lubricants

Another notable area is the utilization of fatty acids in metalworking lubricants, which include primarily cutting fluids and rolling oils. Cutting fluids are consumed in large quantities by both the machine tool and automotive industries. They are used in metal operations such as drawing, forging, machining, cutting, and grinding and are primarily mixtures of mineral oil and fatty oils plus lubricity additives and emulsifiers. Both the lubricity additives and emulsifiers are generally derived from fatty acids; oleic acid is the one most frequently used. Because quality is not the most significant property of cutting fluids, oleic acid derived from acidulated soap stocks and steam-refining distillates can be of value in this application.

Similarly, the market for rolling oils is large; like cutting fluids, they are composed of mineral oil, fatty oils, additives, and emulsifiers; the two last-mentioned components may be derivatives of fatty acids. Liquidity and mineral oil solubility are of primary concern in formulating a rolling oil; therefore, liquid fatty acids and fatty acid derivatives are desirable. Many rolling oil formulations exist in the literature (37,38); these serve adequately as the basis for developing formulations to satisfy the various idiosyncrasies of a particular rolling mill or the needs of a company that specializes in certain types of metal products. The growth curve for fatty products used in this end-use application parallels the activity and growth of both the automotive and appliance industries.

Methyl Esters

Within the past 10–15 years, a considerable amount of research in both the U.S. and foreign countries has been directed toward the utilization of fatty acid methyl esters as a biodiesel fuel (39,40). Although the methyl esters used for these studies have been derived primarily through the alcoholysis of whole vegetable oils, similar products can be prepared by esterifying by-product fatty acids found in soap stocks, deodorizer distillates, and physical refining distillates. In addition, methyl esters have been shown to be good solvents for the degreasing of metals, as printing ink cleaners, and paint removers.

Phospholipids

A mixture of phospholipids, commonly known as lecithin, is recovered as a by-product during the refining of soybean oil. At an early stage in the refining process, water is added to remove the phosphorous-containing compounds, which become hydrated and insoluble. The oil is centrifuged to recover the phospholipids; these are immediately dried and cooled to yield a purer product, which is a mixture of phospholipids, namely, phosphatidylethanolamine, phosphatidylcholine, and phosphotidylinositol.

The major use of lecithin is as a food emulsifier; the remainder is used in a variety of industrial applications such as pharmaceuticals, agricultural chemicals, and aquaculture. Such end-use applications include adhesives, adsorbents, animal feeds, pet foods, catalysts, soaps, cosmetics, paints, waxes, polishes, and release agents (41).

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Chapter 28

Strategies for Replacement of Fat in Food Products

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Introduction

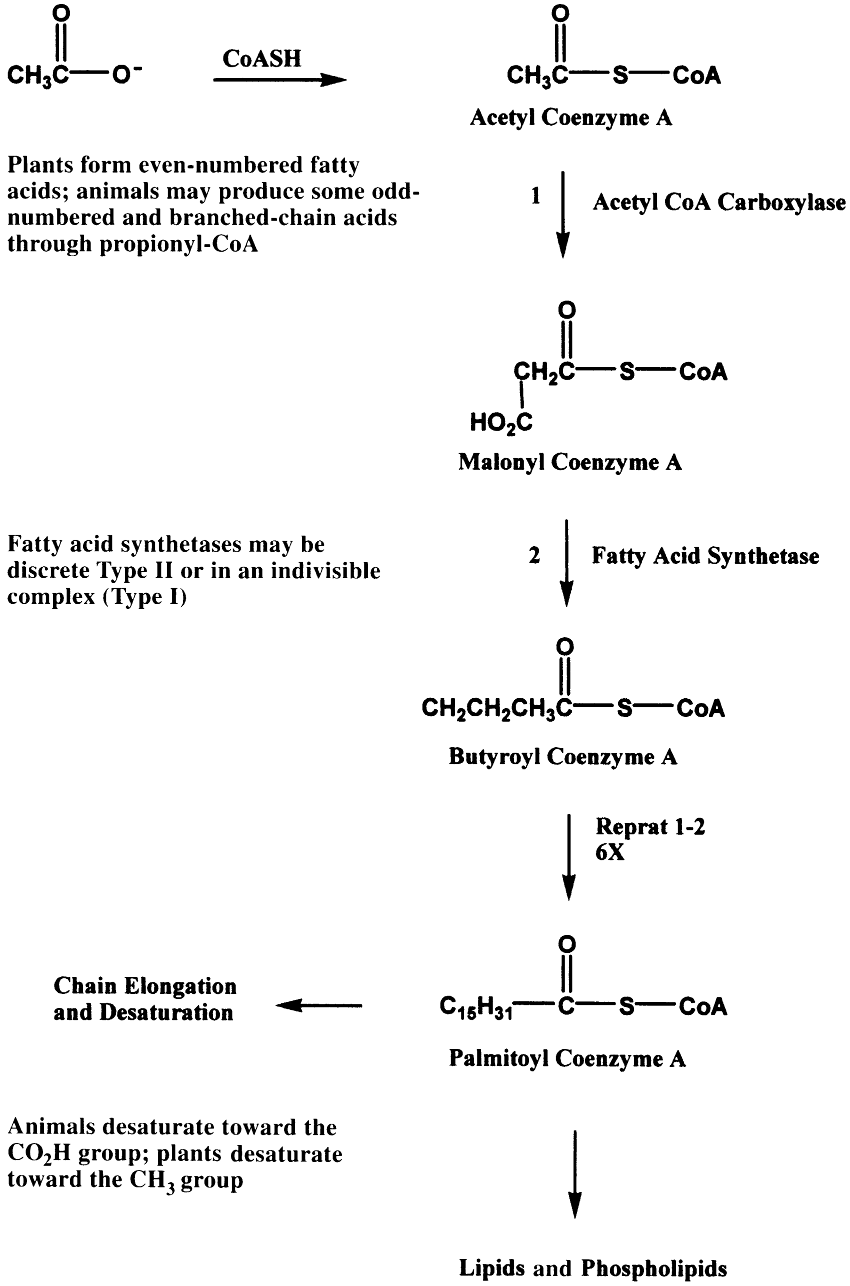
Fats and oils have been valuable articles of human commerce for several millennia. In addition to their use in the preparation and cooking of foods, they have also found use in other industries such as soap and candle manufacturing. In foods, lipids provide ~9 kcal/g compared with ~4 kcal/g for carbohydrates and proteins. This disparity arises from the relative abundance of hydrocarbon chains present in lipids. For cultures in which daily life required hard manual labor, high-fat diets provided a valuable source of energy. However, as technology developed to minimize hard labor, significant populations began to consume more calories than they were expending. The result was a steady increase in obesity.

Consumption of high levels of saturated fats has been blamed for rising levels of serum cholesterol and concomitant increases in arteriosclerotic diseases and heart attacks. Some forms of cancer have also been correlated with high-fat diets. Recently, *trans* fatty acids have been shown to have detrimental effects on levels of serum cholesterol.

Dietary weight control programs have focused on food lipids because a reduction in fat results in twice the reduction of calories compared with reductions in carbohydrate. The American Heart Association and the U.S. Department of Agriculture have established dietary guidelines, which recommend that less than one third of energy intake should be derived from fat and <10% should come from saturated fat. Efforts to reduce the amount of fat in foods have been intensifying through the last 50 years. However, the challenge of accomplishing this will become apparent in the following sections of this chapter.

Nutritional Aspects of Fats and Oils

Fats are produced by living organisms for storage of energy and formation of structure, such as membranes (1). Sources of fat include dietary ingestion and fatty acid biosynthesis. Ingested fats are broken down into fatty acids by lipase enzymes. Fatty acids are produced from carbohydrates by conversion to acetates. The acetate units are then condensed into fatty acids in the fatty acid synthesis pathway shown in Figure 28.1. The fatty acids are then biosynthesized into triacylglycerols for storage or into phospholipids for incorporation into membranes. The nature of the fatty acid (chain length and degree of unsaturation) is determined by elongation and desaturase enzymes in the biosynthetic pathway. Linoleic and linolenic acid are not synthesized by humans and must be ingested in the diet. They are therefore termed essential fatty acids.



Plants form even-numbered fatty acids; animals may produce some odd-numbered and branched-chain acids through propionyl-CoA

Fatty acid synthetases may be discrete Type II or in an indivisible complex (Type I)

Animals desaturate toward the CO_2H group; plants desaturate toward the CH_3 group

Fig. 28.1. *De novo* biosynthesis of fatty acids.

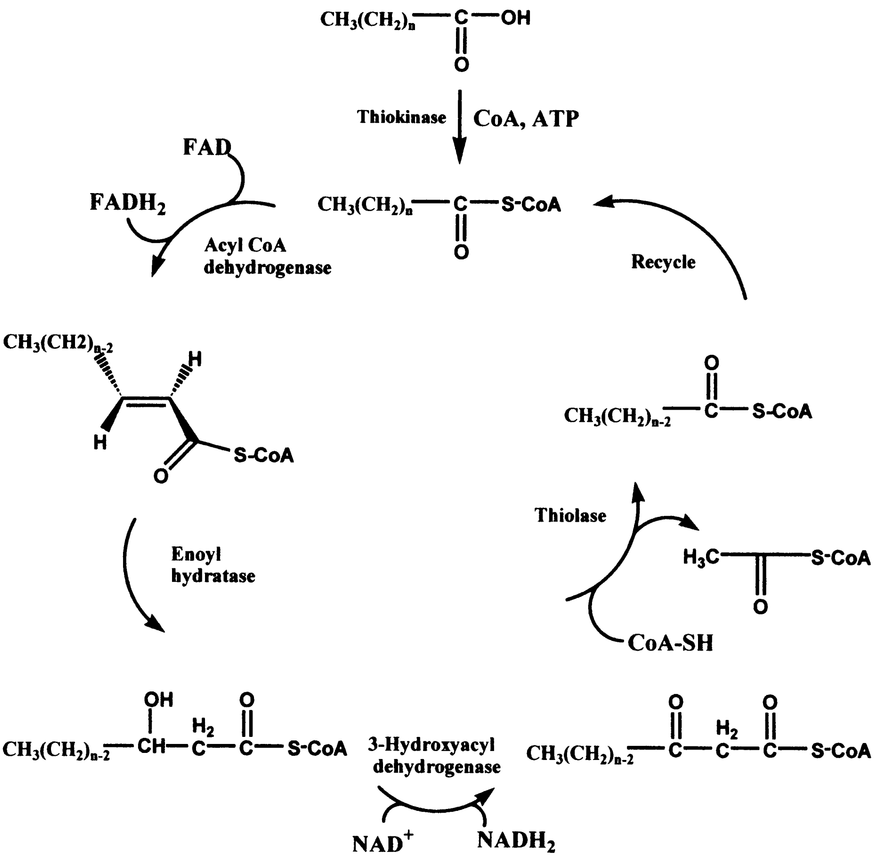


Fig. 28.2. Energy release of fatty acids through β-oxidation.

Stored lipids may be mobilized by the body to provide energy. The biosynthetic pathway through which this occurs is β-oxidation (Fig. 28.2). Fats are also essential for the body to produce prostaglandins and other essential bioregulating compounds. Fat-soluble vitamins, such as tocopherol and β-carotene, are also delivered to the body *via* fat metabolism.

On the basis of this knowledge, there are four logical approaches to reduction of fats in the diet: (i) reduction or replacement of fats in food products; (ii) inhibition of fatty acid synthesis in the human body; (iii) acceleration of the β-oxidation process to burn fat; and (iv) inhibition of lipase enzymes to block the metabolism of ingested fats. The last-mentioned three approaches fall into the realm of pharmaceutical chemistry and will not be dealt with in detail here.

Functional Properties of Solid Fats

One of the major difficulties in reduction of fat, especially with high *trans* and saturated fats, involves the essential functional properties that solid fats perform in food products. Saturated fats provide structure, texture, and mouthfeel to products that contain them. Products high in *trans* fatty acids were developed specifically for their relatively sharp melting points, which decreased the sensation of greasy mouthfeel.

Chocolate is a dispersion of finely ground sugar and cocoa solids in a cocoa butter matrix. Cocoa butter crystallizes into a stable β-polymorphic form. Compatibility with other fats is limited by their crystallization tendencies (2). Small quantities of foreign fats are tolerated but larger quantities of incompatible fats separate, resulting in a whitish coating known as bloom. Cocoa butter itself must be properly tempered to avoid bloom. Cocoa butter provides a shiny surface (gloss), which is considered to be an attractive appearance attribute. The melting properties of cocoa butter are also critical to its sensory properties. It has a very narrow melting range just below body temperature. The result is that chocolate is a somewhat brittle solid (measured by snap) at room temperature but melts completely in the mouth. Higher-melting fats or replacers result in waxiness and poor flavor release. Success in replacing solid fat functionality depends on the ability to match chemical structure to the essential physical properties of the application (3).

Shortenings contribute significantly to the structure appearance and moisture retention of baked products such as bread, cakes, cookies, and doughnuts. These semisolid fats are designed to crystallize into the β′-polymorphic form. This morphology allows air to be incorporated into a fine monodisperse foam, which is set during baking. The result is a light fluffy texture in the product. In sugar-containing products, sugar is creamed into the shortening. This coats the sugar particles, prevents stickiness, and allows proper hydration of the flour. Fat may function as a moisture barrier to prevent the baked piece from drying out. Commercial emulsifiers may be incorporated to improve the functional properties of the fat.

Butter and margarines are dispersions of an aqueous phase in a continuous solid fat matrix. The fat content in these products is 70–80% and represents a significant opportunity for fat reduction. Margarine fats are designed to crystallize into the β′-form. Fats that crystallize into the β-form result in margarines with large crystals which produce a "sandy" or "gritty" mouthfeel. Some consumer complaints have confused this phenomenon with product contamination by ground glass.

Ice creams and whipped toppings rely on solid fats to undergo controlled destabilization and coat air cells during the whipping process. This coating helps prevent collapse of the foam and maintenance of a light smooth texture.

These examples illustrate the difficulty in reducing fat in products in which the functional role of the solid fat is critical.

Contribution of Fat to Flavor Release

Perhaps the overwhelming reason for selecting a particular food product is that we like the flavor. Food products to which we have become accustomed over a lifetime have a specific ratio of fat phase to nonfat phase. Changing this fat/nonfat ratio often significantly alters the perception of flavor in the finished product. Flavor molecules are generally amphiphilic, having both polar and nonpolar functional groups. Flavor

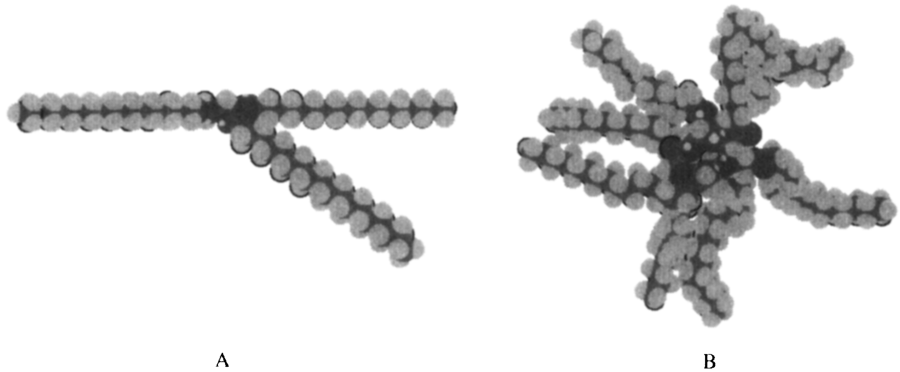


Fig. 28.3. Three-dimensional structures of (A) triacylglycerol and (B) sucrose polyester (SPE).

molecules partition between fat and aqueous phases or may concentrate at the interface between the phases. Reduction of fat in the system should result in increased concentration of nonpolar entities in the remaining fat phase and at the interface.

Qualitative descriptive observations have noted that flavors in low-fat products are harsh initially but disappear quickly. In full-fat products, flavors are described as rounded and relatively persistent. An idealized diagram of this phenomenon is shown in Figure 28.3. To reduce the fat in a product while maintaining flavor perception, the practitioner may adjust individual flavor molecules. However, this task is extremely difficult because little is known about interactions of flavor molecules with flavor and aroma receptors. In addition, natural and synthetic flavors contain a multitude of flavor molecules, which have different thresholds. Intensity of flavor varies over time and is dependent on relative concentrations in each phase.

The nature of an emulsion [water-in-oil (W/O) or oil-in-water (O/W)] determines the flavor release profile. As fat is reduced in a W/O emulsion, the emulsion may invert, resulting in a dramatically different flavor. Melting points of fats in both the bulk phase and emulsions determines the rate of flavor release. For example, as fat is reduced in margarines, the product does not melt as readily and much of the flavor is trapped in the solid and not released.

Lipid-Based Fat Replacement

Perhaps the easiest approach to visualize for fat reduction is the use of a replacement that resembles fat in all or most of its physical properties. If the replacement is heat stable, the replacement can be used for frying and baking applications. One would expect that flavors could be released similarly to full-fat formulations. To maintain the relatively hydrophobic properties of fat, the substitute should contain saturated and unsaturated alkyl chains. However, to prevent utilization of their potential energy, the substitute must be designed to be nonabsorbable. Strategies include a design that

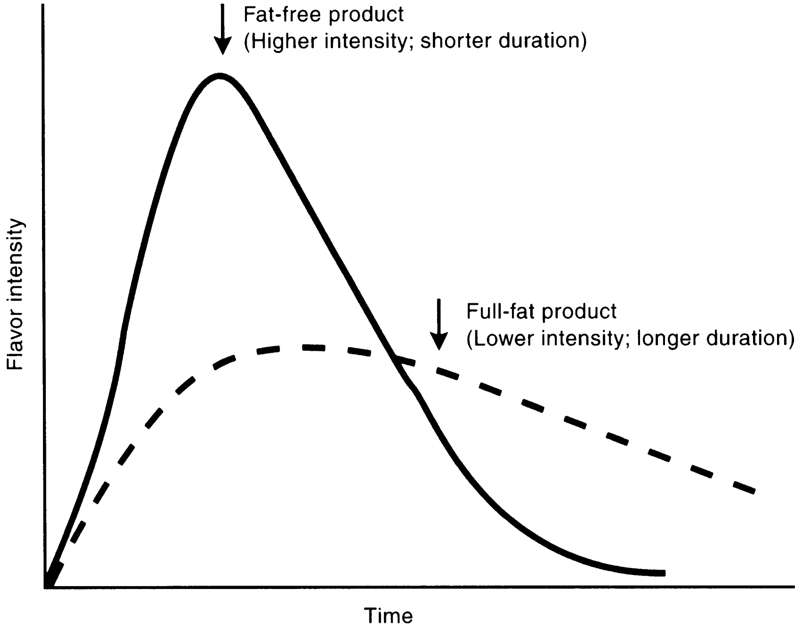


Fig. 28.4. Descriptive time/intensity of flavor release in fat-free and full-fat food products.

limits the reaction to lipase enzymes and melting points that reduce absorption from the gut.

The disadvantages of lipid-based fat substitutes include the following: (i) Synthesis and purification of these compounds involves high cost, which must be passed on to the consumer. Also, the substitutes are commonly used as a one-for-one replacement, which translates into large percentages in the formulations. (ii) Matching the melting points and crystallinity of solid fat is a problem. (iii) Fat substitutes that pass through the body undigested may also carry fat-soluble vitamins through without ingestion (4).

Sucrose Polyesters

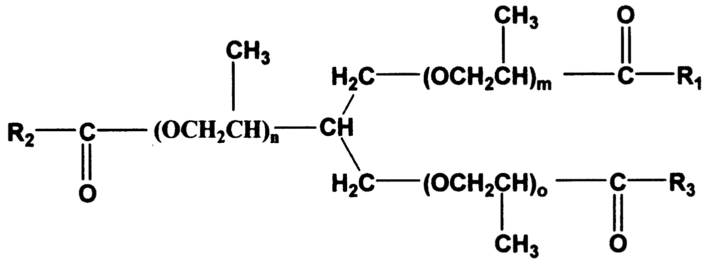
Despite its synthetic-sounding name, sucrose polyester (SPE) is a molecule composed of fatty acids and sucrose in which the eight hydroxyl groups on sucrose are essentially completely esterified. As shown in Figure 28.4, the resulting molecule is much larger than the corresponding triacylglyceerol and may not fit into the active site of digestive lipase enzymes. Sucrose polyester therefore passes through the body without being absorbed.

The synthesis and manufacture of SPE are complicated by the relatively low caramelization temperature of sucrose. The maximum temperature that can be utilized is 140°C. SPE is commonly prepared by interesterification of sucrose with fatty acid methyl esters (FAME). The reaction is generally catalyzed by alkaline compounds. A solvent, such as dimethyl formamide or dimethyl sulfoxide, may be used to produce homogeneity. Because these solvents have significant toxicity, they must be removed completely from the final product. Alternatively, high levels of soap may be used without solvent to interdisperse the phases (5). In the latter case, the presence of high soap concentration poses a significant purification problem. This may be overcome by acidification of the reaction mixture and removal of the free fatty acid by short-path distillation (6). The reaction mixture also darkens dramatically. The problem has been mitigated by incorporation of hydroxy acids into the reaction mixture (7), or by reducing the carbonyl content in the starting methyl esters (8). Color may also be reduced by driving the reaction to more rapid completion through the use of continuous short-path vapor removal (9).

Initially, SPE was envisioned as a therapeutic agent for the reduction of serum cholesterol and the concurrent risk of coronary artery disease (10). Its use as a food additive was vigorously pursued and it is currently used under the trade name Olean as a frying medium for fat-free salty snacks, e.g., potato chips. Sensory panels have reported that flavor and texture of the products are comparable to their full-fat counterparts. One application problem that had to be overcome was that of anal leakage, i.e., liquid SPE behaves very much like mineral oil. This difficulty was overcome by incorporating sufficient saturated fatty acid to maintain integrity at body temperature. This design must be balanced with the design of the molecule to optimize physical and functional properties (11).

Propoxylated Derivatives of Glycerides

Another lipid-based fat substitute (Scheme I) may be prepared by reaction of partial glycerides with propylene oxide or by direct esterification of propoxylated glycerol with fatty acids (12). Opening of the oxirane ring provides an energy release, making the reaction exothermic. The appended methyl groups provide a degree of lipophilic character, which gives some measure of resemblance to hydrocarbon chains. However, the steric factors modify the crystallization tendencies of the molecule. Matching the physical properties to the fat for which the propoxylated



I

glyceride is substituting is therefore a critical strategy. Toxicity data for this fat substitute have demonstrated it to be fairly benign. However, the material has not yet been approved by the Food and Drug Administration (FDA) or marketed commercially in a food product.

Wax Esters

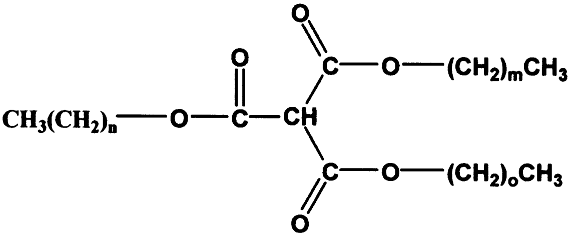
Naturally occurring waxes are monoesters formed between fatty acids and long-chain linear alcohols. This ester linkage is not digested completely by lipase enzymes and the wax is not absorbed. One of the oldest wax esters was derived from the sperm whale (spermaceti). However, as whales became scarce, other naturally occurring wax esters were sought. The seeds of the jojoba plant (*Simmondsia chinensis*) have been an attractive source of waxes because the plant may be grown in arid climates. The oil is composed primarily of C_{20}–C_{26} unsaturated fatty acids esterified to C_{20}–C_{22} linear monounsaturated alcohols. Its use as a fat substitute has been investigated, but to date, it has not seen widespread commercial use.

Orange roughy oil is derived from the heads and entrails of the fish *Hoplostethis atlanticus* and has been known among aboriginal populations as a natural laxative. An oil of similar composition is derived from the fish *Oreosomatidae zeiformus* (Oreo Dory). Both fish are harvested from deep waters off New Zealand. True to its origin, the oil has a fishy odor and flavor. The oil may be purified and deodorized but unless carefully handled, can undergo reversion to the fishy state.

Esters of Polycarboxylic Acids

Di- and polycarboxylic acids may be reacted through esterification with linear long-chain alcohols to produce a class of fat substitutes referred to as "reverse esters" (Scheme II). This backward linkage is not recognized by digestive lipases as a viable substrate and passes through the body undigested. With proper selection of the reactants, these compounds have the physical properties of fats.

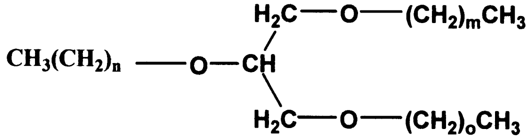
Alkyl esters of di- and polycarboxylic acids were tested as fat-free cooking oils (13), mayonnaise and margarines (14). However, these esters have not yet been approved by the FDA nor have they found commercial use in food products.



II

Glyceryl Fatty Ethers

Lipase enzymes act to hydrolyze glyceride esters. Substitution of an ether linkage for the ester results in an inert molecule. Glyceryl ethers (Scheme III) have been developed as a cooking oil (15). Because ether linkages are much more stable toward hydrolysis than ester bonds, these fat substitutes are not metabolized in the digestive tract. Variation of the chain length and degree of unsaturation of the alkyl chain, properties similar to those of liquid oils or solid fats, may be engineered into the molecule. These fat substitutes have not been approved for use in foods.



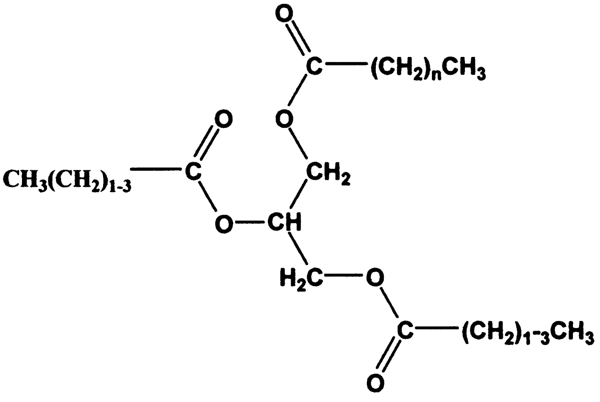
III

Partially Digestible Fat Substitutes

Some naturally occurring solid fats have reduced absorption in the digestive tract, even though they are triacylglycerols (16). For example, cocoa butter contributes only ~7 kcal/g rather than the 9 kcal supplied by other triacylglycerols. This phenomenon arises because the predominant triacylglycerol has the palmitic-oleic-stearic (POS) configuration. Apparently, long-chain saturated fatty acids in 1,3-positions are not fully absorbed in the digestive tract. When pancreatic lipase cleaves the 1- and 3-positions, some of the stearic acid passes through the digestive tract without being absorbed. Partially digestible fat substitutes may be designed using the same rationale.

Caprenin is a triacylglycerol that contains two medium-chain length (C_8,C_{10}) fatty acids and a C_{20},C_{22} acid. Although the structure of the molecule would suggest that it is a fully saturated fat, the long-chain acid is poorly absorbed and the medium-chain fatty acids pass through a different metabolic pathway than other fats and are burned more rapidly, analogous to carbohydrates. However, the U.S. FDA requires labeling of the ingredient as a saturated fat on the basis of its structure; for this reason, the fat substitute has not been widely adopted.

SALATRIM (Scheme IV) is a triacylglycerol composed of a long-chain fatty acid and two short-chain acids selected from acetic, propionic, or butyric. Although it is structurally similar to acetylated monoglycerides, its physical properties may be optimized for specific applications by adjusting the composition of the short-chain acids. The triacylglycerol may be produced by alkali-catalyzed transesterification of a long-chain fat with triacetin, tripropionin, and tributyrin (17). Recently, enzyme-catalyzed processes have also been reported (18,19). Analogous to the cases above, the ingredient is not fully absorbed in the digestive tract (20,21). One of the dilemmas associated with the use of nondigestible and partially digestible fat substitutes is how to distinguish the substitute from normal fats and oils for labeling purposes. Analytical techniques for characterization of SALATRIM have been reported (22).

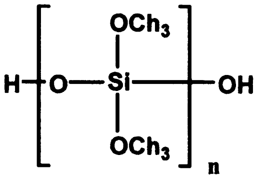


IV

Miscellaneous Lipid-Based Fat Substitute Strategies

Following the basic strategy that a desirable fat substitute is a lipophilic molecule that is not absorbed by the body, a number of strategies are feasible. Mineral oils, which are long-chain hydrocarbons, have a long history as laxatives. Lengthening the chain further can provide solid species. However, the dipole moment is much lower than for triacylglycerols, and the flavor release and emulsification properties are significantly different.

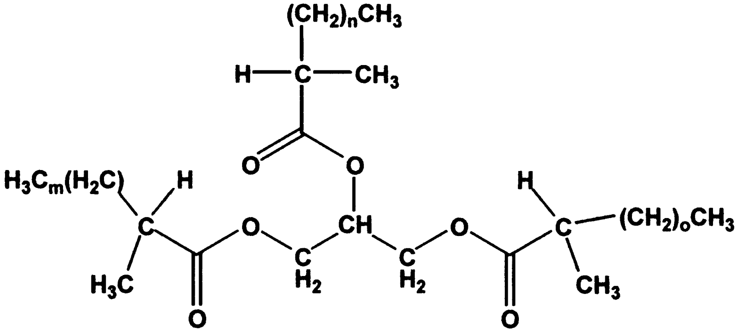
Silicone oil (Scheme V) is an inert polymer, which would pass through the digestive tract unabsorbed. Because of its stability to heat, it has been tested as a frying oil. Sensory properties of the foods are good, although they lack the native flavor of the natural oils. However, given the recent adverse publicity surrounding breast implants, silicone oils are unlikely to gain acceptance as food additives.



V

Analogous to the case for sucrose polyester, esterified oligosaccharides, such as trehalose (23) and raffinose (24), have been reported. One advantage of the oligosaccharides is that their esterification need not be as complete as for sucrose in order to be nondigestible. However, further development of these materials would require extensive testing for safety and utility. Fatty acid esters of sorbitol were synthesized and reaction conditions were optimized using response surface methodology (25). Fatty acid polyesters of polyglycerols were synthesized and applied to the replacement of fat in chewing gum (26).

Triacylglycerols containing α-branched fatty acids (Scheme VI) have been investigated (27). An α-hydroxyl group is esterified by a second fatty acid providing mutual steric hindrance between the glyceryl and α-hydroxy ester linkages. Branching further down the chain is less efficient, and some lipase-catalyzed hydrolysis may occur.



VI

Lipid-based emulsifiers promote the formation and stabilization of emulsions composed of mutually insoluble oil and aqueous phases. In addition, they provide other functional properties such as aeration, crystal modification, antistaling, antistick, and viscosity control. In many cases, a small modification in emulsifier composition and concentration may provide fat-sparing functionality (28). For example, with amphiphilic structures formed by emulsifiers, the lamellar phase may be used to structure the continuous phase of a food emulsion to provide a low-fat system (29).

Replacement of Fats with Mimetic Materials

Protein-Based Fat Replacement

In the absence of lipid-based fat replacers approved for multitudinous food applications, the problem of removing fat in food products becomes more difficult. Two basic approaches may be visualized as follows: (i) Reduction of fat as other ingredients are allowed to increase proportionately. Examples of this approach are trimming visible fat from meat or reducing the percentage of fat in a formulation, such as margarine. Eventually this approach encounters limitations, as in the meat example. The limitations may also manifest themselves in unacceptable physical properties. The fat-reduced food may become resistant to normal processing or the sensory properties may be unacceptable to the consumer. (ii) Fat reduction is compensated by an increase of water in the formulation. In this case, a fat mimetic is introduced to bind the excess water and replace one or more functional properties of the fat. In this section, we will focus on the latter, possibly more useful approach (30,31).

A strong argument for the use of fat mimetics is that they are usually derived from natural materials or are already approved for use in foods. Lengthy toxicity testing and regulatory petitions are rarely necessary. Major disadvantages are that mimetics are not heat stable, are not suitable for frying, and may contain off-flavors or flavors incompatible with the food product. Ingredient interactions also become a more critical area for concern (32).

Important properties of fat that must be mimicked include the following: (i) size distribution and surface properties of oil droplets or fat crystals; (ii) rheological and textural properties; and (iii) fat flavor and control of flavor release. Undoubtedly, these properties are interactive, but for instructional value, they will be discussed individually.

One factor affected by droplet size and distribution is appearance. Small oil droplets scatter light more efficiently; as droplets become larger or reduced in number, the product may take on a blue or gray appearance. To overcome this problem,

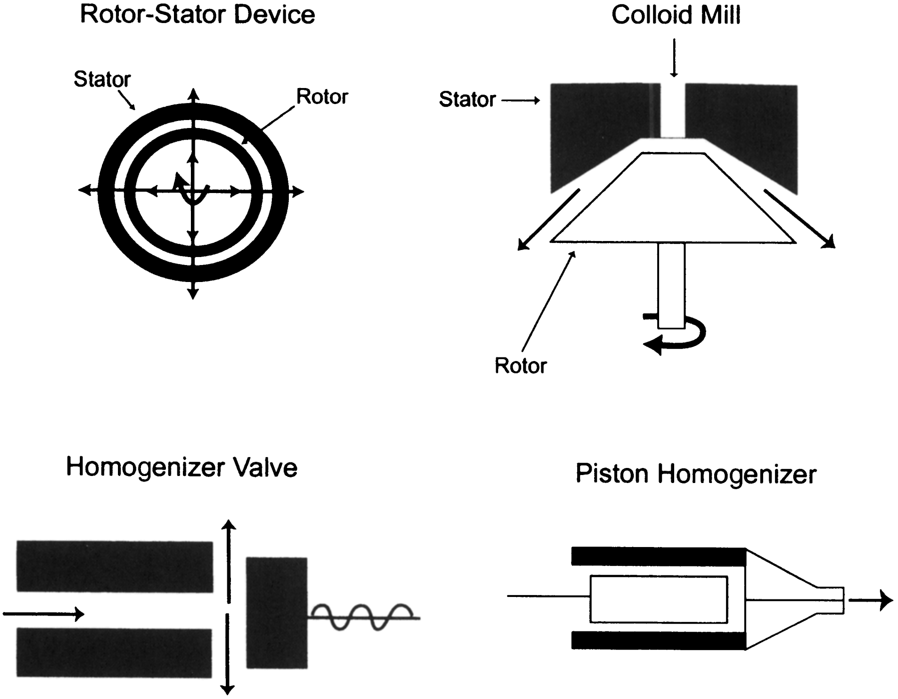


Fig. 28.5. Examples of apparatus utilized for microparticulation of fat mimetics.

particles such as protein or titanium dioxide may be incorporated. Close packing of particles may affect the stability of oil-in-water (O/W) emulsions. Particle-particle interactions may produce a network that retards particles from creaming. In water-in-oil (W/O) emulsions, fat crystals form a continuous phase, which immobilizes water droplets, preventing sedimentation. A lubricating effect is provided by oil droplets, whereas melting of fat crystals enhances mouth cooling.

When fat is replaced by water in a formulation, viscosity is reduced by eliminating the interparticle network described above. This network also contributes to other rheological properties, such as yield stress and shear thinning. Fat mimetics that form networks in the aqueous phase help to replace these rheological properties.

Flavor molecules in emulsions are distributed according to their polarities. Polar molecules concentrate in the aqueous phase, nonpolar molecules accumulate in the fat/oil phase, and amphiphilic flavors may seek the interface. As fat is reduced and water increased, polar compound concentration is diluted and nonpolar flavor molecules are forced into the aqueous phase. Flavor perception is altered dramatically, particularly when the remaining percentage of fat is removed. Compounded flavors may be adjusted to correct for these concentration imbalances. However, because aqueous flavors produce initial effect and nonpolar molecules are responsible for sustained release, the time-intensity profile will remain a problem. In addition, natural complex flavors, such as spices, may not be easy to replace due to distortion of the flavor character. Flavor attributes have been the most difficult of fat functions to replace.

Protein Fat Mimetics. Although proteins are chemically dissimilar to fats, they have found application as fat mimetics (33). In aqueous environments, proteins orient themselves with a hydrophobic core and hydrophilic surfaces. They function as emulsifiers in protein-stabilized emulsions. Therefore, "empty" protein-stabilized emulsion particles can effectively mimic fat. Protein also has a positive image on a label ingredient statement. The major disadvantage of protein-based mimetics is their relative high cost compared with carbohydrates, particularly starch.

Casein micelles are protein particles found in milk. In solution, they are of comparable size to fat particles and are capable of forming network structures. Thus, the emulsion-stabilizing and rheological functions of fat are mimicked. Two examples of their use are addition of nonfat dry milk to cottage cheese (34) and cream cheese (35) for replacement of fat.

Zein protein is a hydrophobic protein derived from corn (36). An alcoholic solution of the protein may be microprecipitated by addition to an aqueous medium. The result is a dispersion of hard spherical particles with hydrophobic surfaces, the same size and surface character as fat droplets. The perception of creaminess is produced by the spheres rolling over one another like ball bearings.

Simplesse is a pioneering protein-based fat mimetic produced by shearing and denaturing either milk or egg protein (37). The combination shearing-heat exchanging apparatus for producing the product has been described (38). The resulting dispersion of deformable spheres imparts a creamy mouth feel by the ball bearing effect and enables the development of fat-free products. Modern microstructural techniques were used to characterize the dispersion and rationalize its functionality (39). The mimetic has been applied to a variety of commercial products. However, as mentioned above, the ingredient is at a cost disadvantage to a number of carbohydrate-based mimetics. An interesting approach forms a fat-free cream base using two aqueous protein phases (40). One example uses gelatin as a continuous "phase" and dispersed whey particulates as the dispersed "phase."

Microfluidized Protein/Hydrocolloid Complexes. Proteins in an aqueous environment below the isoelectric point bear a net positive charge. An insoluble complex may be formed with a hydrocolloid such as xanthan, alginate or low-methoxy pectin. Mictroparticulation of these complexes in a high-shear device yields a dispersion of particles that are nonspherical. Nonetheless, these products (such as Trailblazer) are quite effective fat mimetics (41). Because the protein is denatured during processing, the complex remains largely intact when the pH is again raised above the isoelectric point. The relatively high cost of this system has kept it from being commercialized extensively.

Meat products have proven to be a significant source of "invisible" fat in the diet. Trimming of discrete fat areas is both labor intensive and limited in its efficacy (42). Soy proteins along with hydrocolloids have found use in binding water, which is added to ground meat products (43).

Role of Carbohydrates in the Replacement of Fat

Carbohydrates have a long history of use in building the texture of foods. An example of fat reduction using this approach was the development of Miracle Whip. Starch was used to preserve the viscosity of the product when soybean oil was reduced. Low-fat spreads were formulated using carbohydrates to thicken the aqueous phase (44). Although some gums are quite expensive, they are effective at building viscosity at relatively low concentrations (usually <1%). Starch is also an economical ingredient. Some carbohydrates are not fully digested (45) The major drawback to carbohydrates is their lack of particulate nature, which may contribute to a starchy or slimy mouthfeel.

Starches and Modified Starches. Starch is a biopolymer, which consists of glucose molecules joined by 1,4-linkages. Starch is used by plants as an energy storage mechanism. The polymers have two major morphologies, i.e., amylose is a straight-chain entity, whereas amylopectin is highly branched. Amylose occurs in a helical conformation and interacts with other ingredients, such as emulsifiers. Starches are available that contain relatively high or low concentrations of amylase.

Starch granules are small spherical particles. When the starch is cooked, these granules swell by incorporation of water molecules, thereby increasing the viscosity. However, as cooking time is extended, starch granules burst and the viscosity drops precipitously. Starches may be modified to overcome this problem. Starches may also be prehydrated by ingredient suppliers to be dispersible in cold processes. One application utilizes microparticulated rice starch as a fat replacer (46,47).

Maltodextrin is an acid or enzyme-catalyzed hydrolysis product of starch, which has a dextrose equivalent of <20. It is a useful material for partial replacement of both fat and sugar (48,49). The major advantages of maltodextrin are its ability to form gels with favorable low-shear rheological properties and its heat stability, which allow it to function in baking applications. Some examples of commercial products are Paselli SA2, from potato starch; N-Oil, from tapioca; Maltrin, from corn; Trim Choice, from oats; and Stellar, which is formally regulated as a modified starch rather than as a maltodextrin. A reverse process to starch hydrolysis is the polymerization of dextrose with small quantities of sorbitol and citric acid to form polydextrose (50). The polymer has a highly branched structure; as a result, the energy value is only 1 kcal/g rather than 4 kcal/g from starch. Litesse is a commercial polydextrose product.

Cellulose and Its Derivatives. Cellulose, like starch, is a polymer composed of glucose molecules. However, unlike starch, the glucose units are joined by a 1,4-linkage. Cellulose is insoluble in water, resulting in a zero energy value. However, in its crude form, cellulose may produce grainy texture in some food products. Microcrystalline cellulose is produced by a process that separates the crystalline regions from the amorphous regions of cellulose (51). Avicel products are a commercial class of products that were developed as fat mimetics (43).

Cellulose may be modified chemically to incorporate some hydrophobic character into the molecule. Examples are methyl-, ethyl-, and hydroxypropyl cellulose. These materials have the interesting property of increasing viscosity with increasing temperature in aqueous media. This principle has been applied to reduction of fat absorption in battered fried foods. Carboxymethyl cellulose (CMC) is produced by alkaline treatment of cellulose followed by reaction with chloroacetic acid. The presence of the $-O-CH_2-CO_2^- Na^+$ functional group appended to a polysaccharide chain makes CMC structurally similar to hydrocolloids, such as xanthan and alginate. CMC is used in dairy and egg products to protect against protein precipitation.

Microcrystalline cellulose may be improved in fatty mouthfeel by microparticulation in a high-shear device. Creamy mouthfeel is greatly enhanced when the majority of particles are <1 μm in diameter. The structure under the microscope resembles aggregated cotton balls. Large quantities of water are trapped in the interparticle spaces to form a cellulose gel. This mimetic has been commercialized widely in fat-free foods such as ice cream, mayonnaise, and salad dressings (52). In an analogous system, oil-coated gellan gum microparticles were claimed as fat replacers, encapsulants, and delivery vehicles for food ingredients (53).

Hydrocolloids. Hydrocolloids or gums have a history of use in foods as thickening agents. When fat is reduced in an O/W emulsion, interparticle forces are diminished and oil particles tend to separate by creaming. Thickening the aqueous phase retards the motion of the oil droplets, resulting in increased emulsion stability. Most hydrocolloids are derived from natural sources, resulting in an attractive label declaration. Although generally expensive, hydrocolloids exert their thickening effect at low concentrations (as much as 10 times lower than starch). Because they do not contribute significantly to fatty mouthfeel, hydrocolloids are generally used in combination with other mimetics, e.g., in a systems approach (30). Caution must be exercised when using gums to guard against interaction with other ingredients such as starch, proteins, and other gums. Many of the gums are negatively charged due to the presence of sulfate groups or carboxyl groups at pH values above their pK_a. This property renders them sensitive to calcium and magnesium concentrations, such as in hard water. When gums are dispersed in aqueous media, they should be premixed with other dry ingredients or slurried in oil to prevent clumping. Sufficient time should also be allowed for the gums to hydrate.

Xanthan gum is a fermentation product derived from *Xanthomonas campestris*. It has a very complex carbohydrate structure, consisting of glucose, mannose, and glucuronic acid. It forms stable hydrates when dispersed in a cold aqueous medium. Xanthan is used in salad dressings and other food products.

Alginic acid is derived from the brown seaweeds *Macrocystis pyrifera* and *Ascophyllum nodosum*. Algin is extracted and may be converted to the sodium salt. The hydrocolloid polymer is composed of units of mannuronic and guluronic acid. Sodium and calcium alginate form gels in aqueous media but do not contribute to fatty mouthfeel. Sodium alginate may be reacted with propylene oxide to form propylene glycol alginate. This synthetic multifunctional ingredient is widely used in salad dressings where it contributes viscosity and suspends spice particles.

Pectins, with a long history of use for thickening jams and jellies, are derived mainly from rinds of citrus fruits and by-products of apple processing. The molecule may be partially or fully demethylated to produce a derivative referred to as low-methoxy pectin. This derivative has a lower gelling temperature and is more sensitive to calcium ion concentrations. It has been used in low-fat and fat-free formulations to increase viscosity.

Tragacanth is a hydrocolloid derived from the exudate of the Middle Eastern shrub *Astragalos gummifer*. It is a complex mixture of galacturonic acid, sugars, and minor amounts of starch and cellulose. It has been recognized for its ability to provide creamy mouthfeel to low-fat and fat-free dairy products.

Carrageenan is extracted from a variety of red seaweeds. Its unique composition includes sulfate groups bonded to the carbohydrate backbone, which imparts a negative charge to the polymer. Three forms of carrageenans are distinguished by the ratio of sulfate groups to carbohydrate. κ-Caraggeenan forms strong brittle gels; the τ-form produces soft gels; λ-carageenan thickens but does not form a gel. These diverse gel-forming properties lend themselves to fat replacement in a number of products, such as ground meats and dairy products. Carageenan/milk gels have been microparticulated and evaluated as fat mimetics (54).

Guar gum is extracted from the endosperm of the guar plant (*Cyamposis tetragonolubus*). The extract is a neutral gum composed of galactose and mannose (galactomannin) and occurs as a branched structure. A closely related galactomannin is locust bean gum, also known as carob gum, which has an essentially linear structure. Both gums produce high viscosities and interact strongly with other gums, such as xanthan, carageenan, and carboxymethylcellulose. Both gums are used as stabilizers in frozen desserts and dairy products. Konjac is extracted from the tuber *Amorphophallus konjac*. It has a long history of use in East Asia. Konjac flour has a very high molecular weight and exhibits pseudoplastic rheology in aqueous media. Konjac is synergistic with xanthan and carageenan.

Dietary Fibers. Because fiber contributes no calories and has a generally favorable nutritional image, it is an attractive candidate to use in fat replacement strategies. The physiologic roles of nondigestible carbohydrates are complex and involve such diverse functions as binding of bile salts, promotion of beneficial intestinal microorganisms, and intestinal mobility (55,56). β-Glucans, which are fiber components, can lower low-density lipoprotein (LDL) serum cholesterol levels. For many low-fat and fat-free applications, the texture of fiber must be modified to avoid a gritty texture.

Inulin is a carbohydrate most commonly derived from chicory root, although it is present in several other plants. It is composed of fructose units and because it is not digestible by humans, it is therefore considered a fiber. Inulin has been promoted extensively as a fat replacer but is limited by its instability toward acid hydrolysis and off-flavors that occur with unfavorable agronomic conditions.

A family of fiber-based fat replacers has been developed by the U.S. Department of Agriculture. Oatrim is derived from oat flour by an enzyme hydrolysis process. It is utilized commercially in low-fat bakery products. Z-Trim is produced from the hulls of soybean and fiber from corn and oats. The fiber is microparticulated to produce a fine powder. The sensory properties have been reported to compare well with full-fat products (57). The most recent product, called Nu-Trim, uses a thermomechanical process to disrupt oat and barley endosperm. Cellulose is separated to leave a product high in β-glucan structure. The product should therefore qualify for a heart-healthy nutritional claim.

From Fat Replacement to Functional Foods

After a great deal of initial interest by food manufacturers and consumers, low-fat and fat-free products appear to have peaked and may become less popular (58). Reasons and trends behind the waning interest are multifaceted.

Traditionally, consumers had accepted that eating a healthy diet involved sacrificing indulgent food products such as ice cream, potato chips, and doughnuts. The publicity around technologies for producing low-fat and fat-free foods implied that consumers could consume these products in a healthy diet and still enjoy all the pleasures of a full-fat product. Because of the myriad technical difficulties described in the preceding sections, food producers have been unable to deliver fully on this promise, particularly in the area of flavor. In the one case for which olestra (SPE) has been approved (fried salty snacks), some consumers may be deterred by the prominent warning label required by the U.S. FDA.

The primary argument for reduction of total fat and saturated fat in the diet has been to lower serum cholesterol and its attendant risk of coronary artery disease.

Recent advancements in the treatment of hypercholesterolemia with drugs such as Lipitor and Zocor have been remarkably successful. As patients gain control of their cholesterol levels, they may become much less compliant with their low-fat diets. In addition, a number of dietary components have been investigated for their cholesterol-lowering functions. Several investigations of palm oil have shown no cholesterol-raising tendencies despite the high levels of saturated fatty acids present (59–61). The mechanism of action is thought to involve the tocopherols and tocotrienols present in palm oil. Recent animal and human studies have suggested that incorporation of soy products into the diet results in lower levels of serum cholesterol (62). Attention has been focused on the phytoestrogens, isoflavones, and lignans found in soy products (63). β-Sitostanol is derived by hydrogenation of the phytosterol β-sitosterol, obtained from the unsaponifiable fraction of vegetable oils. Incorporation of the stanol ester into the diet produces a cholesterol-lowering effect (64). A margarine-type spread is currently being marketed for its positive effects on serum cholesterol.

A great deal of attention has recently been shown by the pharmaceutical industry to the problem of obesity (65). In addition, a great deal more has been learned about fat consumption, energy balance, and the regulation of body weight (66). Lipase inhibitors, which would block the hydrolysis of ingested fat, have the effect of transforming a normal fat into its own nondigestible fat substitute. At the other end of the spectrum, some pharmaceutical agents, such as selective β-adrenergic agonists, can accelerate burning of fat once it is metabolized. Many herbal preparations and other food supplements, such as pyruvic acid, are also being marketed for their alleged promotion of fat burning.

Sales of fat-free and low-fat products have been targeted to the demographic population concerned about obesity and heart disease. As alternative solutions to these problems continue to be discovered, it will be increasingly difficult to persuade consumers to sacrifice their favorite foods for an inferior imitation.

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Chapter 29

Genetically Engineered and Identity Preserved Oils

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Introduction

The commercialization of specialty, or identity preserved (IP) oils has been tedious, if not almost impossible to date. Of the few new oils that have been produced on a small commercial scale, a struggle continues over their functional use and/or health benefits, and more importantly, whether these benefits merit a higher value.

The first hurdle to overcome lies in the fact that specialty seed development companies have had unrealistic goals in terms of the market value of IP proteins and IP oils. The consumer will pay only a slight premium for any protein or oil product, regardless of its functional or health benefits. This chapter describes a logical, straightforward, progression from the developed seed to the commercialization of specialty protein and oil (see Figs. 29.1 and 29.2), and will also describe all specialty varieties of seed that have been developed to date with their current status of commercialization.

Specialty Oils: A Definition

First, we should describe what is meant by "specialty oils." A specialty oil is one that has a unique functionality in food products and/or improved health benefits. A

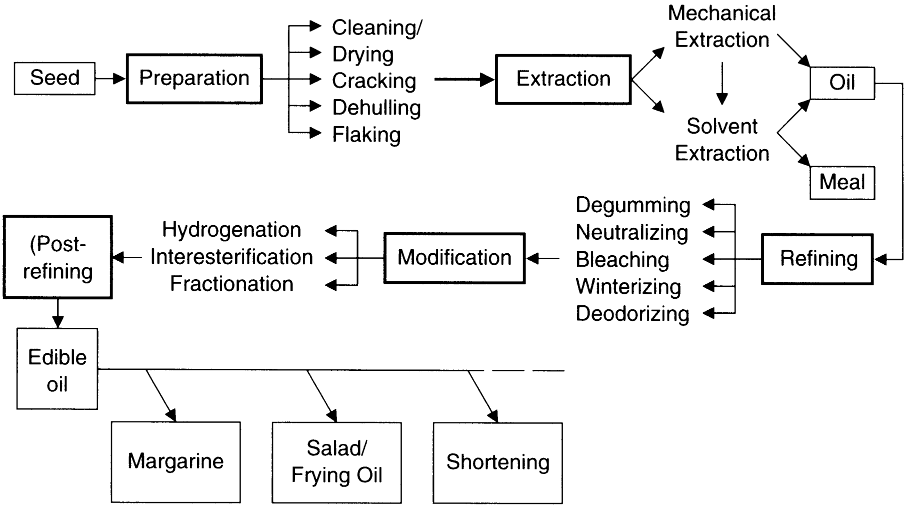

Fig. 29.1. Oils and fats processing. The steps from seed to finished product.

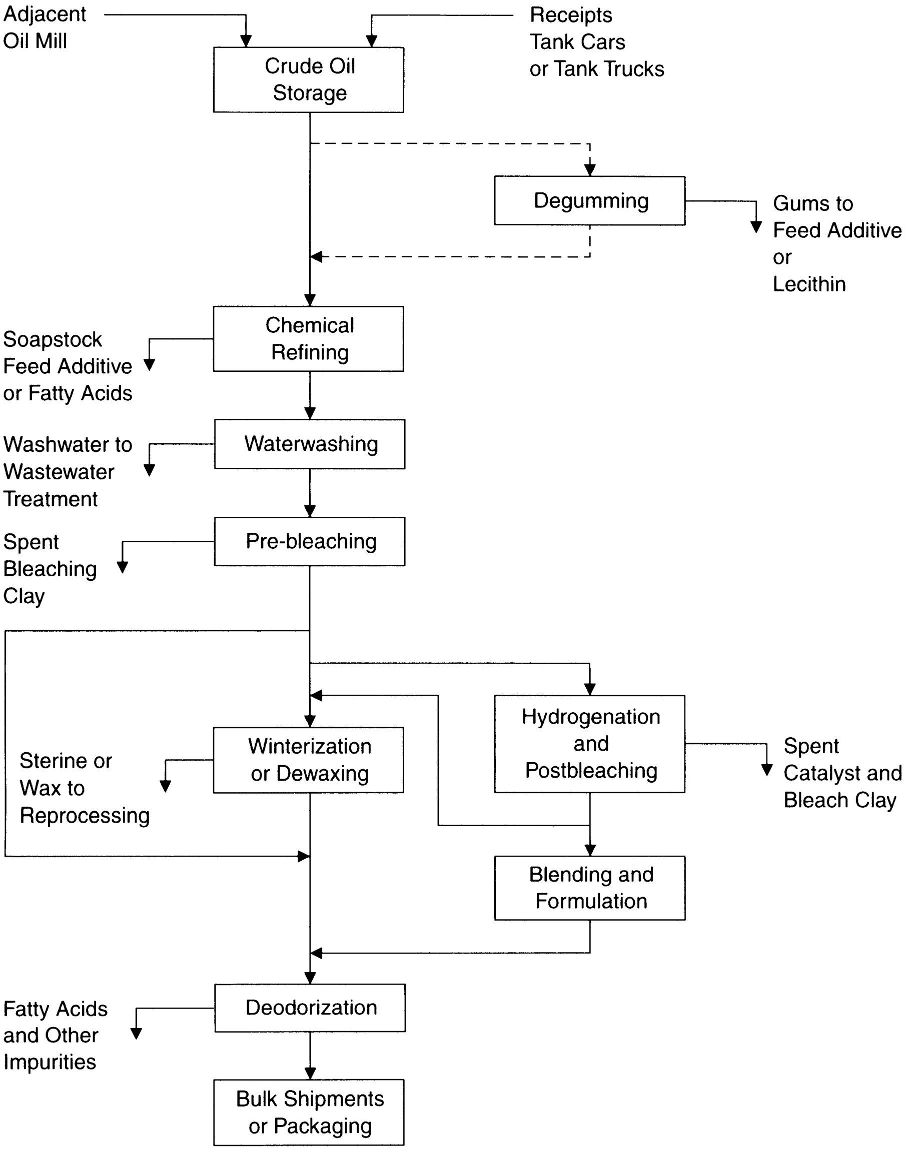

Fig. 29.2. Processing sequence in current systems, from crude to finished oil.

specialty oil is generally one that occurs in low volume compared with commodity oils. In this case, the specialty comes from the special handling required to achieve identity preservation. In addition, specialty oils are not simply those that are developed by genetic modification or breed selection; they may be from naturally occurring oilseeds such as desert plants. In this case, these specialty oils demand special handling and processing to avoid contamination from other oils. The types of specialty oils include the following: (i) genetically modified oils; (ii) oils with special properties created by breed selection; and (iii) low-volume (noncommodity) type oils. Specialty oils are processed in the same manner as high-volume commodity oils, only on a much smaller scale.

Degummability Test for Soybean Oil

A method for determining degumming efficiency is presented below. Depending on the efficiency, one can choose the proper refining process (see Figs. 29.A1–29.A4 in the Appendix). This test is used to determine how well crude soybean oil will degum or refine and to estimate the amount of silica that will be required to purify the oil without water washing. The test procedures are as follows:

1. Analyze the crude oil for P, Ca, Mg.
2. Add 400 g crude oil to a 800-mL beaker.
3. Place on stirrer/hot plate with stirrer bar set at medium speed.
4. Heat to 130°F (do not overheat).
5. Slowly add water (deionized water preferred).
6. Water treat = (P ppm $\times$ 31.7 $\times$ 10^{-4})0.7.
    Example: if P = 800 ppm$\rightarrow$ (800 $\times$ 31.7 $\times$ 10^{-4}) 0.7 = 1.78%
    400 g oil $\times$ 1.78% = 7.1 g water.
7. Agitate at slow speed for 20 min with no additional heat.
8. Turn off agitator and let sit idle for 5 min.
9. Filter through filter paper, by gravity.
10. Analyze filtrate for P, Ca, and Mg.

To compute degumming efficiency (DE), the following formula is used:

$$\text{DE} = (\text{P ppm crude oil} - \text{P ppm degummed oil})/\text{P ppm crude oil} \times 100$$

Example: If P crude oil = 800 ppm and P of degummed oil = 35 pprn,
then DE = (800 – 35)/800 × 100 = 95.6%

Processing Sequence of a New Seed Variety to Commercial-Sized Quantities

Year 0. First, the new seed is developed by genetic engineering or by breed selection. Initially, only a few plants are grown in the greenhouse. Upon maturity, the seed is hand picked and processed in the laboratory to determine protein and oil content. Enough oil is extracted to determine FAC (fatty acid composition).

Year 1. Generally, year 1 will yield a much larger greenhouse crop. The problem with only a few plants lies in the fact that there can be variation from plant to plant. The larger crop will average out these variations. In fact, these variations will be minimized with each subsequent planting, ideally in the direction of establishing the traits desired.

With the larger greenhouse crop, the seed will be analyzed for protein and oil content, and the extracted oil will be completely analyzed for free fatty acids (FFA), neutral oil loss (N. O. L.), and trace metals. The crude oil will be refined, bleached, and deodorized to determine finished oil quality and shelf life. Many seed development companies make a mistake here, particularly if their goal is to make an improved protein product, by not determining finished oil quality. If the quality of the oil is affected negatively, this seed will never see the light of day.

Year 2. Year 2 should bring the first field crop, which could be as small as one acre, to determine how well this seed develops in real-world growing conditions and to produce seed for the next growing season. A few seeds from this crop will be processed in the laboratory to determine protein and oil content, and the extracted oil will be refined in the laboratory to determine finished oil quality and shelf life.

Year 3. If the results of years 1 and 2 were successful, year 3 should bring a large crop to produce seed for a major planting in year 4. Year 3 is the first year to produce pilot plant quantities of defatted meal and oil. Typically this will be 2-4 ton of seed. To produce this quantity will require about 3 days at the Texas A&M oil mill pilot plant (alternate: Iowa State University and POS pilot plants). The solvent-extracted meal is analyzed for quality, protein, and oil. The oil is refined, bleached, and deodorized. This quantity of oil will be sufficient for fry tests and small plant trials.

Year 4. All of the seed saved from year 3 will be planted in year 4. This will be the first year for large-scale oil extraction and refining of the oil, to provide large quantities for food plant trails. The quantity of seed processed could be 10 ton. This quantity is too large for existing pilot plants, but much too small for even the smallest commercial plants. If the extraction is performed at a small extraction plant (small would be 1000 ton/d), the cost of processing would be quite high because all of the lost time in maintaining identity preservation must be paid for.

A number of the problems of identity preservation are minimized if this volume of seed is expeller pressed, with no solvent extraction. We now have several small expeller plants in operation that may not be operating continuously; generally, they can be shut down at any time and run an identity-preserved seed. Very few of these expeller plants have refineries, but this is changing rapidly. This writer will be installing two refineries at expeller plants during the year 2000. Thus, in the fall of year 2001, we will be ideally equipped to handle this mid-sized quantity of seed.

Year 5. Year 5 delivers a large commercial-sized crop. This is the first year to enter the market with meal for animal feed and make a major entry into the food oils market. This quantity of seed will be too large for the small expeller plant and the small refinery, even if they operated on this seed all year. Therefore, this crop must be processed in a large solvent extraction plant. The question is: where? It is highly likely that by the year 2005, there will be no remaining soybean extraction plants producing <3000 ton/d. A plant this size will have no interest in processing an identity-preserved oil unless there is a sufficient supply of seed to run the plant all year.

This writer believes that it will be necessary to build an extraction plant of 1000–2000 ton/d capacity, in the area in which the identity-preserved crop is grown. In later years, as the crop becomes much larger, some of the larger existing plants can be converted to this variety, totally replacing the existing variety.

Modified Oils That Have Been Developed and Commercialized

Canola Oil. The most successful genetically modified oil to date is canola. Canola was developed to have low erucic acid (<2%) because high levels of erucic acid were considered toxic in the human diet. A pleasant and highly significant side effect was that the new canola oil was the lowest of all vegetable oils in saturated fat (7%). This one trait catapulted canola oil into a mainstream oil, grown in large quantities. Very soon, medical doctors began recommending canola oil to their patients who needed to reduce saturated fat intake. Another significant fact led to canola's phenomenal success in respect to hectares planted, i.e., all rapeseed was converted to this variety and all of the problems with identity preservation were eliminated. As we develop new varieties of other oilseeds, it would be wise to follow the canola example; success of the new variety may depend upon it. Other modified oils that have been developed are depicted in Table 29.1.

Cottonseed Oil. The current variety of cottonseed oil is listed for reference only. No new variety of cottonseed oil has been developed, although such development may be in progress.. Cottonseed oil would be a good replacement for hydrogenated fats and would have zero-*trans* fat; however, the saturated fat content is too high (29%). The new variety should contain <10% saturated fat, the palmitic acid content would be reduced dramatically, and a large percentage of the linoleic acid would be converted to oleic acid. Cottonseed oil is already very low in linolenic acid (0.5%).

Even if this variety can be developed, we will still have to maintain the existing variety for those products that require high palmitic acid content, such as household shortening. This should not be disturbing because all that is required is to convert one area of the country into exclusive production of the new variety. For example, if the entire state of Georgia were converted to this new variety, no identity preservation would be required because all of the Georgia cottonseed would be processed in cotton gins, oil mills, and refineries in Georgia. No regular variety cottonseed would be allowed to cross the state line.

Soybean Oil. The current variety of soybean oil is relatively high in saturated fat (15%), certainly higher than canola oil. The linolenic acid content is 8%, preventing its use as a zero-*trans* frying fat. Several new varieties of soybean oil have been

TABLE 29.1 Fatty Acid Composition of Oils with Improved Health Benefits and/or Functionality

	Cottonseed oil	Soybean oil	Low-sat[a] soybean oil	High-sat soybean oil	Low-linolenic soybean oil	High-oleic soybean oil	NuSun mid-oleic sunflower oil
				(%)			
$C_{14:0}$ Myristic	0.8				0.1		
$C_{16:0}$ Palmitic	25.1	10.2	3.1	9.8	10.4	6.5	4.4
$C_{16:1}$ Palmitoleic	0.6	0.1				0.1	0.1
$C_{17:0}$ Margaric	0.1	0.1	0.1		0.1	0.1	
$C_{18:0}$ Stearic	2.4	4.3	2.4	21.7	4.8	3.3	4.3
$C_{18:1}$ Oleic	17.4	24.1	17.4	17.6	23.8	82.0	61.6
$C_{18:2}$ Linoleic	52.2	52.5	65.0	42.8	56.6	3.3	27.2
$C_{18:3}$ Linolenic	0.5	7.6	10.8	5.6	3.0	3.3	0.3
$C_{20:0}$ Arachidic	0.3	0.3	0.2	0.2	0.3	0.3	0.3
$C_{20:1}$ Gadoleic		0.1	0.2		0.1	0.3	0.2
$C_{22:0}$ Behenic	0.2	0.3	0.2	0.2	0.4	0.3	1.0
$C_{24:0}$ Lignoceric	0.1	0.1	0.1	0.1	0.1	0.1	0.3
Total saturated fat	29.0	15.3	6.1	32.0	16.2	10.6	10.3

[a] Abbreviation: sat, saturated fat.

developed, some of which were never commercialized; the few that have been commercialized are far from being considered a success.

Low-Saturated Fat Soybean Oil. A new variety was developed that was low in saturated fat (6%), an improvement over even canola oil. However, the oleic acid (monounsaturates) content was even lower than that of the standard variety, the linoleic acid content was higher than that of the standard variety, and the linolenic acid content (11%) was even higher than the standard variety. Obviously, this variety never saw the light of day. This should be a learning experience for developing the better bean, i.e., examine all of the traits of the current variety and realize that several of the traits must be altered simultaneously.

High-Stearate Soybean Oil. High-stearic acid soybean oil (22%) was developed, but then dropped after a few years of trying to improve the yield with no success. One would question why one would want to develop a soybean oil that was high in saturated fat (32%), particularly during the period of developing concerns over saturated fat levels. High-stearate soybean oil is high in stearic acid content (22%); if the stearic acid content is deducted from the total saturated fat content (32%), the remaining saturated fat content would be 10%. Some medical studies have indicated that stearic acid is neutral in terms of its effect on coronary heart disease, leading to the view that stearic acid would not have to be included in the total saturated fat content; however, this condition did not persist. Our interest in high-stearate soybean oil is that it could allow the production of tub margarine, and even stick margarine, with zero-*trans* fatty acid and no hydrogenation.

Low-Linolenic Soybean Oil. A low linolenic soybean oil variety was developed (3% linolenic), but it proved to be of little value. The saturated fat content was 16% (1% higher than the standard variety); the linoleic acid content was higher (56%) and the oleic acid content was the same as that of the standard variety. The stability and shelf life of the oil were only slightly improved, an insufficient reason for this oil to carry a premium price. This is another example of failure as the result of changing only one trait, while letting other traits become worse that the standard variety.

High-Oleic Acid Soybean Oil. This variety has high oleic acid content (>80%), low linolenic acid content (3%), and lower total saturated fat content at 10%. This is the first new soybean variety that has a chance for success. A small quantity of this oil is in a limited market area, but the oil will go unnoticed without a major marketing campaign and huge advertising. The consumer will pay no more for it unless a benefit can be realized.

Mid-Oleic Acid Soybean Oil. A mid-oleic acid soybean oil is being developed at North Carolina State University. Because this new variety is being developed in the public sector, it will not be indebted for years of research by a private seed company. This mid-oleic variety will have an oleic acid content of ~55%. The linolenic acid content will be 3%, and the palmitic acid content will be lowered to ~3%; linoleic acid content will be low, ~25%, and the total saturated content will be ~7%. This variety may well be the soybean variety for the future. Once past the development stage, identity preservation will not be necessary because all of the soybeans in the United States could be changed to this variety.

This oil will be in great demand because of the mid-oleic acid content, coupled with the low linoleic content and low linolenic acid content. This oil will deliver a retail salad oil with much improved shelf life and flavor stability; it can also displace hydrogenated oils in light-duty frying applications. A frying fat with zero-*trans* fatty acids and low saturated fat will gain wide acceptance.

NuSun Mid-Oleic Acid Sunflower Oil. High-oleic acid sunflower oil (80%) was developed ~10 years ago. The first five years were wasted due to the time required in developing techniques to preserve the identity of this specialty oil. In addition, the seed developer was overly optimistic concerning the premium this oil could bring in the market place.

Even today, this oil is produced in small quantities; its only use has been in an infant formula, which is formulated to closely match mother's milk. The major snack food company in the U.S. invested heavily in development of this oil with the belief that it could be a good substitute for cottonseed oil, particularly in potato chips. This belief was unfounded because the high-oleic variety did not deliver a good fried food flavor, nor was this company prepared to pay a premium for a specialty oil.

The National Sunflower Association has directed the development of a mid-oleic acid sunflower oil, marketed under the brand name of NuSun. This new oil contains 60% oleic (considered mid-oleic because the high-oleic acid variety contains 80% oleic). The linolenic acid concentration is very low at 0.3%. Linoleic acid is low at 27%, and the total saturated fat content is 10%. Extensive fry tests indicate that this oil does develop a good fried food taste.

Conclusion

New genetically altered oils, as well as new oils developed by breed selection, are certainly here to stay, and there will be major developments over the next few years. The greatest contribution the fats and oils industry can make is to deliver new oils that contribute to wellness and health, and to offer significant improvement in health as we age. These oils are needed to feed the world's growing population, and more importantly, to feed them with healthier oils.

Appendix

These figures depict the various refining and degumming processes used to yield refined oil.

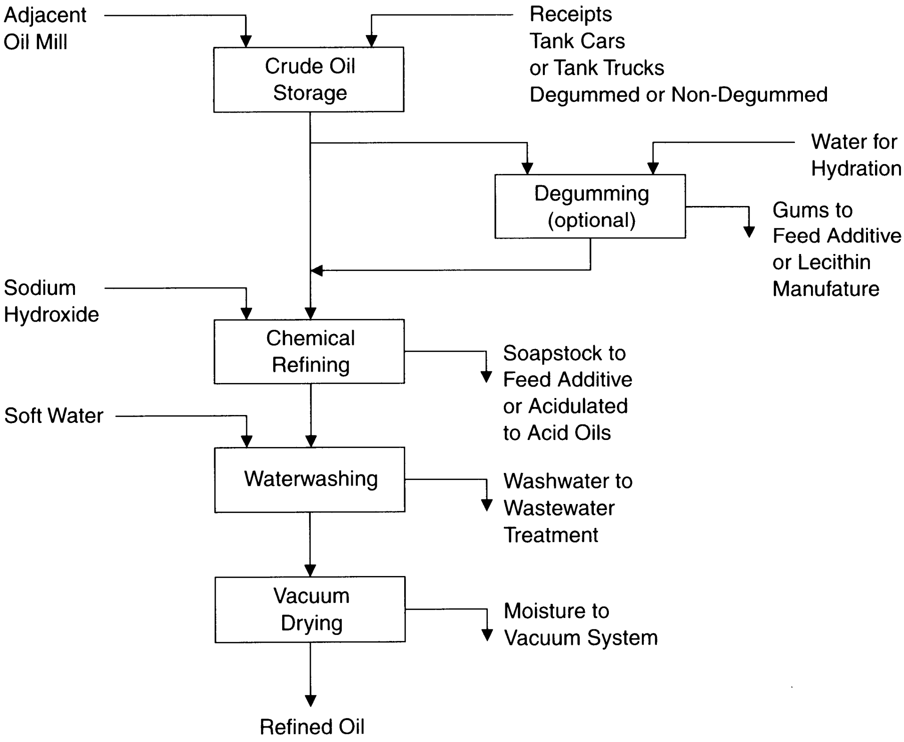

Fig. 29.A1. Chemical refining of vegetable oils, including water washing.

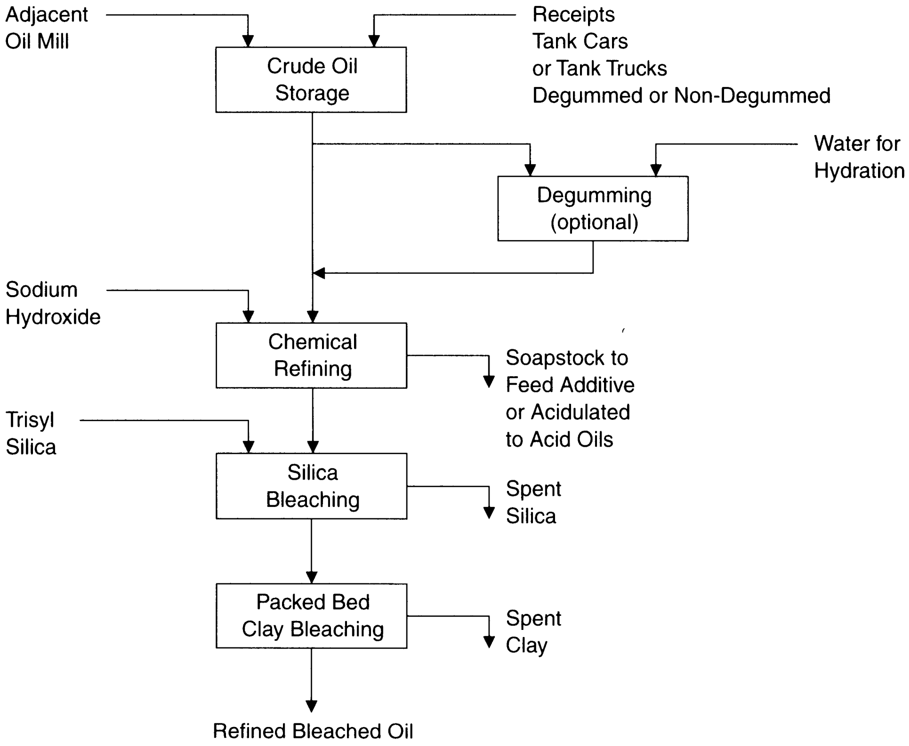

Fig. 29.A2. The modified or silica refining process (caustic refining) in which water washing is replaced by silica purification to remove residual soaps and trace metals. The figure also depicts bleaching close-coupled to the refining or neutralization process.

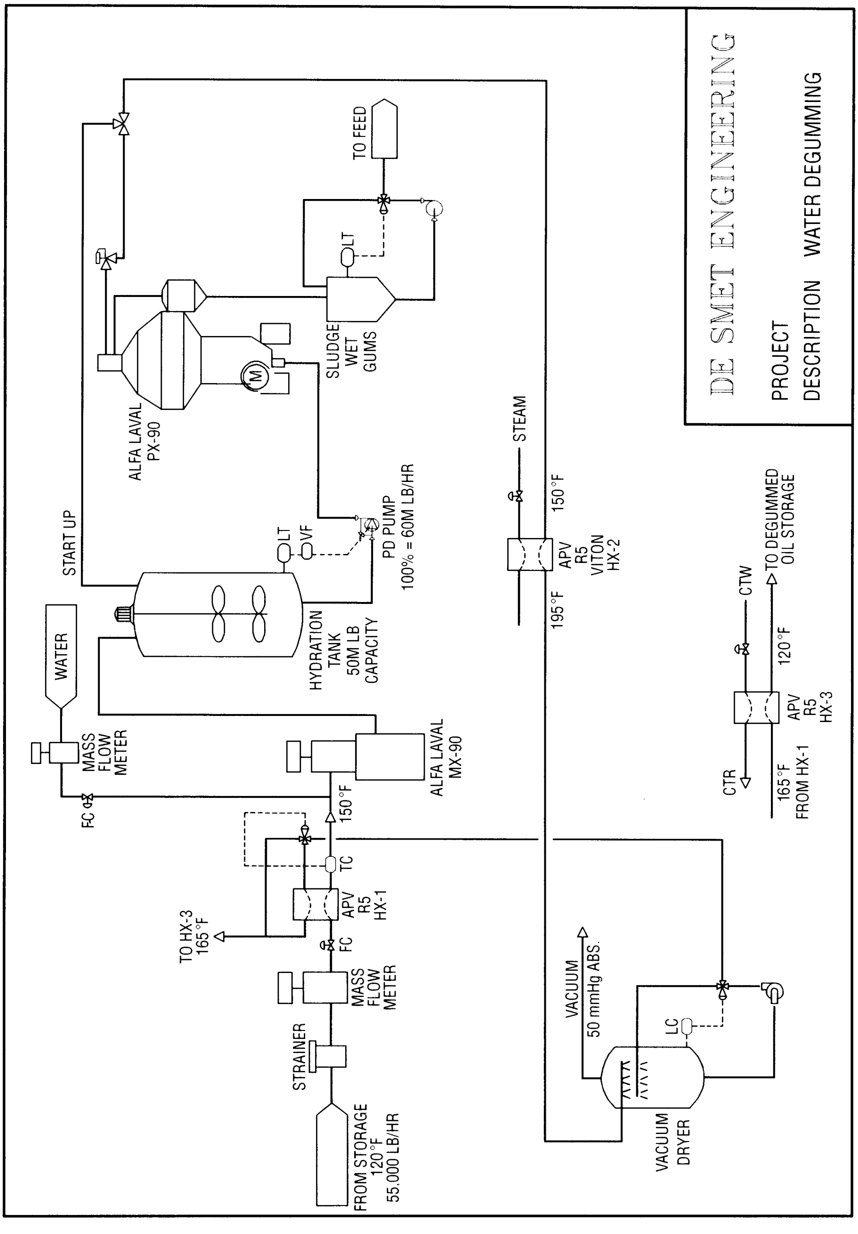

Fig. 29.A3. The water degumming process. Oils that contain relatively high levels of gums or phospholipids (such as the current varieties of soybean and canola) should be degummed before caustic refining. The degumming process reduces the overall refining loss and improves oil quality. Acid degumming is a prerequisite for physical refining pretreatment.

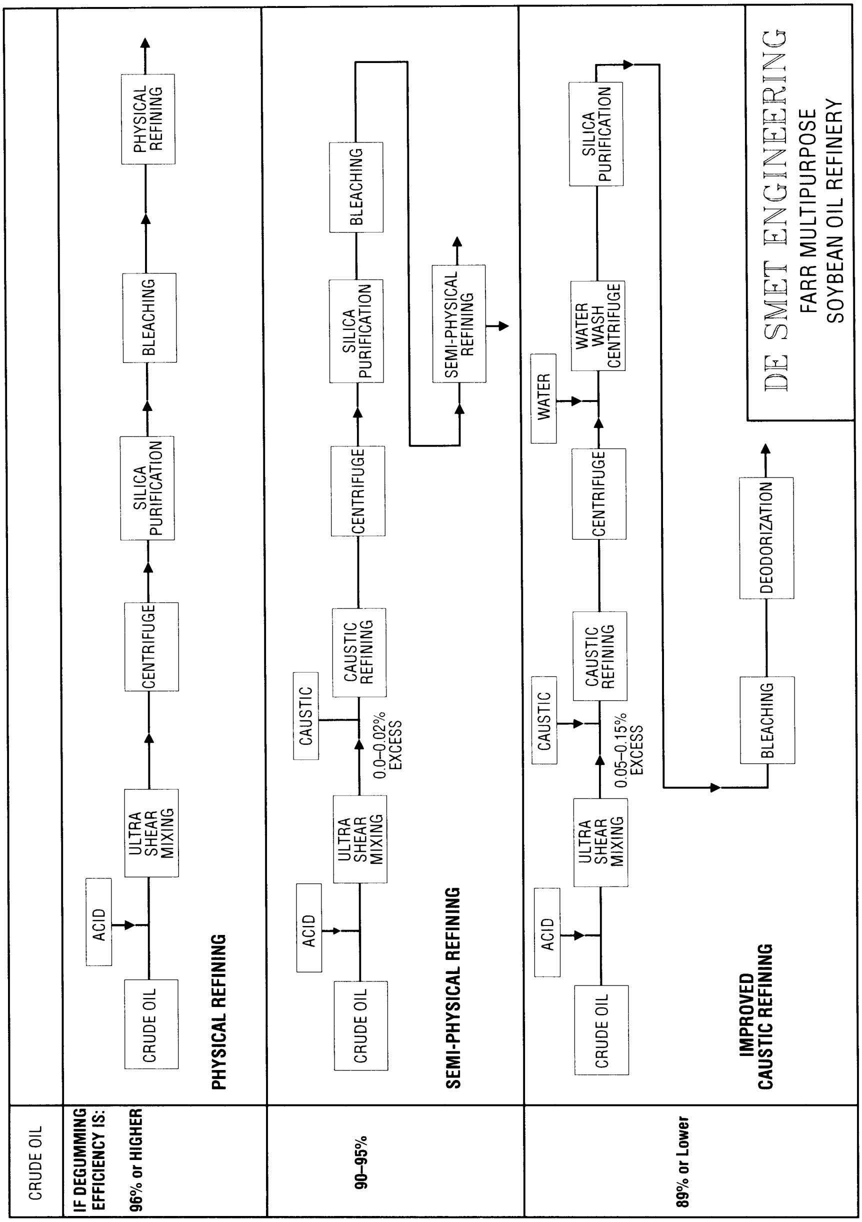

Fig. 29.A4. This flow diagram of a Farr multipurpose refinery depicts the processes of physical refining, semiphysical refining, and improved chemical refining. For soybean oil, the correct process is chosen on the basis of the degumming efficiency of the crude oil.

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