

# Fats and Oils Processing

## 2.1 INTRODUCTION

The crude fats and oils recovered from oilseeds, fruits, nuts, and animal tissues can vary from pleasant-smelling products that contain few impurities to quite offensive-smelling, highly impure materials. Only a few of the crude fats and oils are suitable for edible purposes until they have been processed in some manner. Fortunately, researchers have developed processes for changing fats and oils to make them increasingly more useful to the food industry. Processing techniques allow us to refine them, make them flavorless and odorless, change the color, harden them, soften them, make them melt more slowly or rapidly, change the crystal habit, rearrange their molecular structure, and literally take them apart and put them back together again to suit our requirements of the moment. Advances in lipid processing technology during the past century have resulted in dramatic increases in the consumption of edible fats and oils. Innovations such as deodorization, hydrogenation, fractionation, and interesterification, along with improvements in other processes, have allowed the production of products that can satisfy demanding functional and nutritional requirements.

Throughout the world, processing of fats and oils practically always includes some type of purification to remove impurities, such as gums, free fatty acids (FFAs), pigments, metal complexes, and other undesirable materials. The choice of processing equipment and techniques can depend upon (1) source oils handled, (2) quality of raw materials, (3) available manpower, (4) maintenance capabilities, (5) daily processed oil requirements, (6) available financial resources, (7) proximity of crude fats and oils, (8) product marketing philosophy, (9) governmental regulations, and (10) a number of other considerations. Two general product marketing philosophies practiced in the United States are *crusher/refiner* and *value-added*. The crusher/refiner plant usually concentrates on a limited number of vegetable oils, which are most likely extracted from the oilseed at the same facility. These plants are usually equipped with continuous, automatic, high-volume systems. The value-added processor usually processes fats and oils from several different sources into

a wide range of specialty or tailor-made finished products. The value-added varied and specialized product mix mandates batch or semicontinuous systems with slower throughputs and requiring more manpower.

Fats and oils extraction and processing consists of a series of unit processes in which both physical and chemical changes are made to the raw materials. [Figure 2.1](#) diagrams the typical flow for fats and oils processing in the United States. Changes in the food industry requirements have affected how these raw materials are processed to provide fats and oils products with the functionality required for new and improved prepared foods. Extraction and processing changes have also been motivated by needs of the industry to (1) improve product quality, (2) improve process efficiencies, (3) reduce capital expenses, and (4) solve or eliminate environmental problems. Consideration of the properties of the raw materials, measurement methods, and characteristics of each process or operation is required for process and product control.

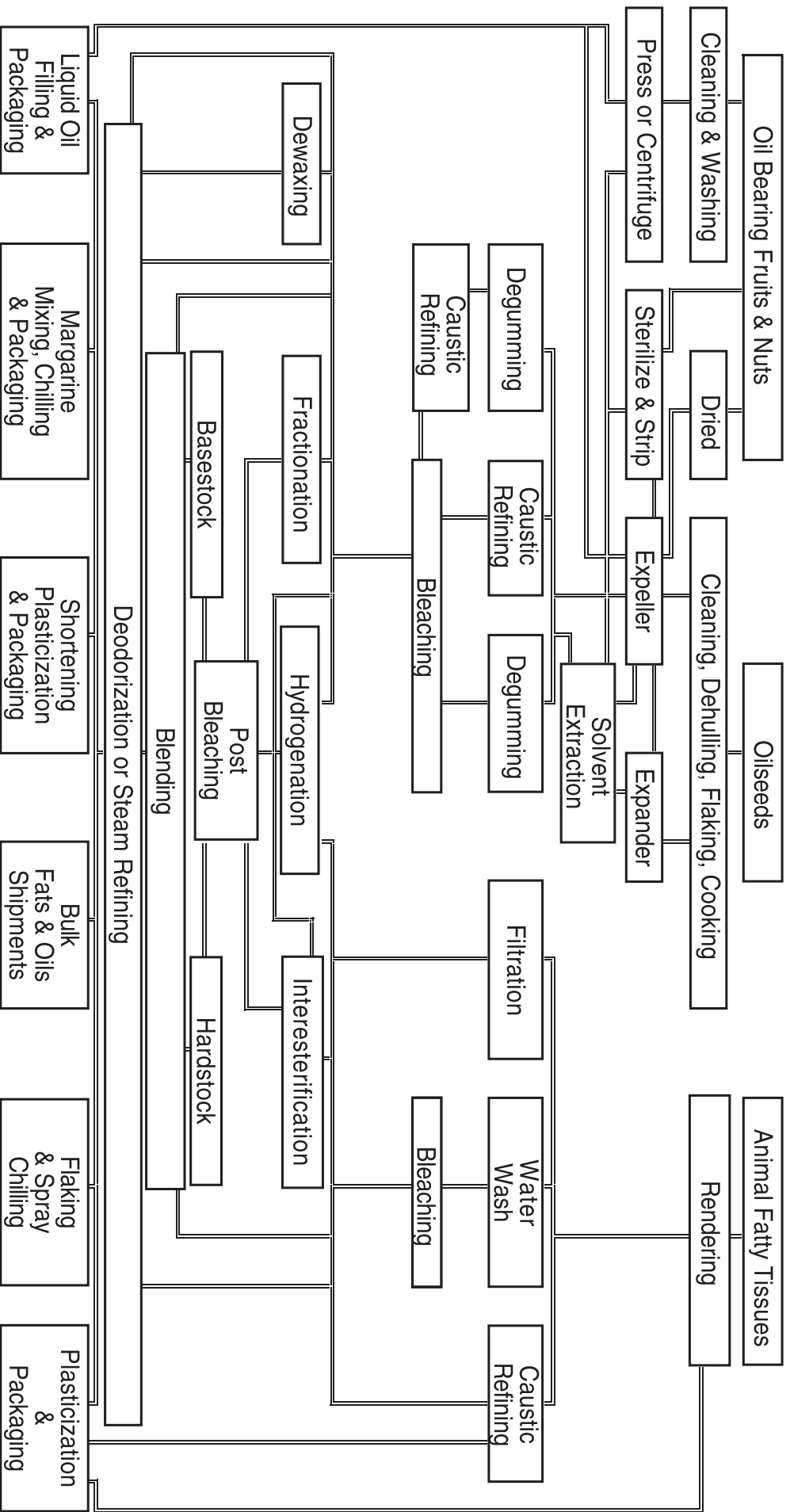
## **2.2 FATS AND OILS RECOVERY**

Edible fats and oils have been separated from animal tissues, oilseeds, and oil-bearing fruits for thousands of years. The purpose of all fats and oils recovery processes is to obtain triglycerides in high yield and purity and to produce coproducts of maximum value. The oilseeds are processed by one of three types of processes: (1) expeller or screw press extraction, (2) prepress solvent extraction, and (3) expander–solvent extraction. The preferred oilseed extraction process depends upon the quantity of oil present in the oilseed, the quantity of oil that can remain in the meal, how much meal protein denaturation is allowed, the investment capital available, and how restrictive the environmental laws are regarding emissions of organic compounds. Oil-bearing fruits are pressed to obtain oil, sometimes after drying (as with coconut copra) or sterilizing (as with palm fruit), or are cold pressed to preserve flavor and odor (as with olives). Animal tissues may be wet- or dry-rendered to separate the fats.

### **2.2.1 Oilseed Extraction**

Most oilseeds require some degree of cleaning and preparation before the oil is separated from the solid portion of the seed. Foreign matter reduces oil and protein yields, adversely affects oil quality, and increases wear and damage to the processing equipment. Stems, pods, leaves, broken grain, dirt, small stones, and extraneous seeds are the typical components of the foreign material found in soybeans, sunflower seeds, safflower seeds, canola seeds, and peanuts. High-capacity dry screeners are used to remove all materials that are over- or undersize by utilizing a combination of screens and aspiration. Permanent or electromagnets are also used for the removal of tramp iron objects. Cottonseed requires an additional delinting process to remove the white or fuzzy linters from the seed.

After cleaning, most of the seeds are dehulled. The hulls have a low oil content (usually less than 1%), will absorb and retain oil in the press cake, and reduce the



**Figure 2.1** Typical fats and oils processing.

capacity of the extraction equipment. Additionally, some oilseed hulls contain high-melting waxes that extract with the oil. The hulls are separated by an aspirator from the kernels or meats, which are further processed to separate the oil and meal. Usually, only about half of the sunflower seed hulls are removed. Canola and safflower seeds are not dehulled because their small size makes it difficult to remove the hulls efficiently.

The oil extraction process is facilitated by the reduction of the seed to small particles. Size reduction to disrupt the oil-bearing cells can be accomplished by grinding or rolling the seeds to produce flakes. Most extraction plants prefer to flake the oilseeds, but it is necessary to rough grind some of the larger oilseeds before sending the pieces through the flaking rollers.

The next step in oilseed preparation is heating or cooking the ground or flaked oilseed. Cooking temperatures can vary with the seed type and may range from 80 to 105°C (176 to 221°F). However, studies have shown that phospholipase D, an enzyme that makes the phosphatides nonhydratable and more difficult to remove, is highly active at 135 to 185°F (57 to 85°C); therefore, this cooking temperature range should be avoided.<sup>1</sup> Proper cooking results in the complete breakdown of the oil cells, coagulation of the proteins to facilitate the oil and meal separation, insolubilization of the phospholipids, increased fluidity of the oil at higher temperatures, destruction of molds and bacteria, inactivation of enzymes, and drying to a suitable moisture content. The effect of the enzymes upon oils are that (1) lipase causes an increase in FFAs, (2) lipoxygenase causes higher peroxide and secondary oxidation products, (3) phospholipase causes elevated nonhydratable phospholipids, and (4) myrosinase causes the formation of sulfur compounds and meal flavor and digestive problems. For cottonseed, cooking also destroys or deactivates gossypol, a complex polyphenolic compound that is toxic to swine and poultry.<sup>2,3</sup>

Before the expander was introduced, cooking was the final oilseed conditioning step. The expander is a low-shear extruder that heats, homogenizes, and shapes oilseeds into porous collets or pellets with a high bulk density. Steam is injected into the oilseed flakes or cake in the expander, under pressure, and then this mixture is extruded through plates to the atmosphere. The collets expand when released to the atmosphere, hence the name *expander*. Some expanders have a drainage cage to reduce the oil content of high-oil seeds to less than 30%, thus enabling the production of intact collets for direct solvent extraction, instead of the prepress extraction process. Other advantages include a 15 to 30% capacity increase for the solvent extraction equipment due to the higher bulk density of the collets and reduced retention time, as well as a lower level of nonhydratable phosphatides in the extracted oil.<sup>4</sup>

### **2.2.1.1 Expeller or Screw Press Extraction**

Expeller pressing mechanically squeezes the oil from the seed. Mechanical pressing is normally applied to seed that is relatively high in extractable oil and is limited to minor oilseeds or locations in which raw materials are not sufficient or local regulations prohibit solvent extraction plants. In the screw press, the cooked

flakes are separated into crude oil and press cake. The press cake, which can contain 3 to 10% oil, is usually ground into meal and sold as a protein source. After settling and filtration to remove fine particles, the crude oil is then transferred to oil refiners for further processing into finished product formulations. Continuous screw presses are used for the mechanical extraction of soybeans, flaxseed, peanuts, copra or coconut, palm kernel, and other oilseed varieties in various parts of the world.

### **2.2.1.2 Prepress Solvent Extraction**

Prepress solvent extraction removes a portion of the oil with expellers, and the remainder of the oil is extracted with an organic solvent. During prepressing, the expeller is choked so that less pressure develops and less oil is recovered. The oil content of the prepress cake is typically 15 to 18%. The remaining oil in this partially de-oiled cake is then solvent-extracted using the same procedure as for direct solvent extraction. The prepressed and solvent-extracted oils are usually mixed before refining. The advantages of this system are that the capacity of the screw press is increased and a smaller solvent extraction plant is required to recover the oil from the de-oiled press cake.

### **2.2.1.3 Direct Solvent Extraction**

Direct solvent extraction removes the oil directly from conditioned oilseeds with an organic solvent. Solvent extraction of soybean flakes was a common practice in the United States as early as 1940, but it was problematic for oilseeds with high oil contents, such as cottonseed, sunflower, rapeseed, safflower, and peanut. The high oil content of the oilseed flakes caused them to disintegrate into fines during the extraction process. A low-shear extrusion method, with equipment identified as expanders, solved this problem. After the oilseeds have been properly prepared, the extraction process can begin. The theory of extraction is very simple: Leach the oil out of the cake, flakes, or collets with a solvent, usually hexane. Even though elevated temperatures reduce oil viscosity and enhance diffusion, the hexane vapor pressure limits the practical operating temperatures of the extractor and its contents to approximately 50 to 55°C (122 to 131°F). Separation of the oil and solvent is accomplished by conventional distillation methods. The full miscella, which is the solvent and oil mixture, is distilled to free the oil from the solvent. The recovered solvent is separated from the accumulated moisture in a gravity separation tank and reused in the solvent-extraction operation. The hexane-free oil is cooled and filtered before storage or further processing.<sup>2-7</sup>

### **2.2.1.4 Oil-Bearing Fruit Extraction**

Two oil-bearing fruits of commercial importance are olive and palm. The oils from these fruits must be recovered by processes different from those used for oilseeds and animal tissues.

### **2.2.1.5 Olive Oil Extraction**

Olives must be harvested as soon as they reach maturity and brought directly to the extraction plant after collection. Being a fruit, it cannot be stored as if it were a seed nor can it be dried to preserve it. Olive oil has to be extracted as soon as possible before the acidity increases and impairs quality. The olives are ground or milled to a coarse paste after separating the foreign material and washing. Milling releases the oil from the oil-bearing cells and helps smaller droplets of oil merge into larger drops. Three general procedures are utilized for oil extraction from the paste: hydraulic presses, continuous centrifuges, or adhesion filtering. The adhesion filtration equipment has a series of steel blades that are dipped into the olive paste and then withdrawn, after which the oil is allowed to drip off the blades. Three fractions are separated from the olive paste: (1) oil, (2) wastewater, and (3) husks or residue. The husks are dried and the remaining oil extracted with solvent; therefore, two oil types are obtained from olives: (1) olive oil, which is pressed without further processing (other than washing, decantation, centrifugation, and filtration) and contains less than 3.5% FFA; and (2) pomace oil, which is obtained by solvent extraction of the husks and does not qualify as olive oil.<sup>5,8</sup>

### **2.2.1.6 Palm Oil Extraction**

In contrast to other oils, palm oil is expressed by cooking and pressing. First, it is sterilized with steam at 266 to 293°F (130 to 145°C) for about 1 hour to inactivate hydrolytic enzymes, loosen the individual fruits, and prepare it for subsequent processing steps. The sterilized fruits are stripped from the bunch stalks by vigorous shaking and beating using drum-type strippers. Then, the fruits are reheated to 95 to 100°C (203 to 212°F) for 20 to 30 minutes in a digester to loosen the pericarp from the nuts and to break the oil cells. The liquid and semisolid phases are then separated with a screw press similar to those used for oilseed extraction. The liquid phase is centrifuged and vacuum dried to remove moisture. The quality of the palm oil is dependent upon the fruit bunches delivered to the oil mill. Overripe fruit bruises easily, accelerating FFA rise through enzymatic hydrolysis and adversely affecting bleachability of the extracted oil.<sup>9</sup>

## **2.2.2 Animal Fat Recovery**

Animal fats are recovered from fatty tissues by cooking processes known as *rendering*. The two predominant rendering processes are wet and dry rendering. Wet rendering produces the better quality oil while dry rendering produces the best quality protein. The wet process is preferred for edible animal fats and the dry process for inedible products. Regardless of the process used, the materials from the meatpacking plant to be rendered are broken up into small pieces (2 to 5 cm) with a crusher or prebreaker. The pieces are then cooked in batch or continuous cookers with agitation to evaporate the moisture, break down the fat cells, and release the fat. The procedure after this point defines the rendering process utilized.

### **2.2.2.1 Wet Rendering**

The two varieties of wet rendering are low temperature, which is conducted at temperatures up to the boiling point of water, and high temperature or steam rendering, which is carried out under pressure in closed vessels. Most of the edible animal fat produced in the United States is rendered by the steam process. Lard produced with this process is identified as *prime steam lard*. The typical equipment used is a vertical cylindrical steel vessel with a cone bottom, designed for a steam pressure of 40 to 60 psi (2.7 to 4 bar) and a corresponding high temperature. The vessel is filled with the fatty material from the cooking operation plus a small amount of water, and steam is injected to boil the water and displace the air. The vessel is then closed, except for a small vent, and steam injection is continued until the operating temperature and pressure are attained. Under these conditions, the fat separates from the solids and rises to the top of the vessel. The pressure is then released and the fat is drawn off and purified by settling or with a centrifuge. Some hydrolysis of the fat occurs during steam rendering to elevate the FFA content above 0.35%.

### **2.2.2.2 Dry Rendering**

Dry rendering involves cooking the material at 115 to 120°C (239 to 248°F) in agitated, steam-jacketed vessels until the moisture has evaporated, usually 1.5 to 4 hours. No steam is injected into the fatty material during processing as with the wet process. The cooked material is then screened to drain off the free fat before pressing the high-protein solids to separate the remaining 6 to 10% residual fat. The fats accumulated are then centrifuged or filtered.<sup>5,6</sup>

## **2.3 REFINING SYSTEMS**

All crude fats and oils obtained after rendering, crushing, or solvent extraction inevitably contain variable amounts of nontriglyceride components such as fatty acids, mono- and diglycerides, phosphatides, sterols, tocopherols, hydrocarbons, pigments (gossypol, chlorophyll), vitamins (carotene), sterol glucosides, glycolipids, protein fragments, traces of pesticides, and trace metals, as well as resinous and mucilaginous materials. The quantities of the nontriglycerides vary with the oil source, extraction process, season, and geographical source. Removal of the objectionable nontriglyceride constituents in the fat or oil with the least possible damage to the triglycerides and minimal loss of desirable constituents is the objective of the refining process. The objectionable components interfere with further processing and cause the oil to darken, foam, smoke, precipitate, and develop off-flavors.<sup>10</sup>

The two major purification processing methods are *chemical refining* and *physical refining*. In chemical refining, FFA, most of the phosphatides, and other impurities are removed during neutralization with an alkaline solution, usually NaOH. In physical refining, the FFA is removed by distillation during deodorization, and the

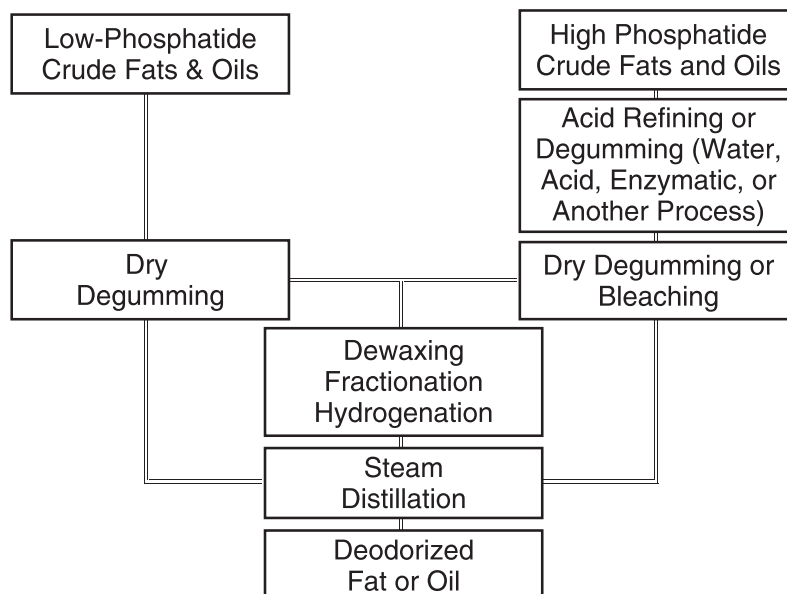
phosphatides and other impurities must be removed prior to steam distillation. Physical refining is still some distance away from being applicable to all fats and oils. Currently, the refining method of choice is determined by the characteristics of the individual crude fats and oils: (1) fats and oils that are normally physically refined, (2) fats and oils that can be physically or chemically refined, and (3) fats and oils that can only be chemically refined. Low-phosphatide crude oils such as palm, palm kernel, and coconut are almost always physically refined. Tallow and lard processing can also be identified as a form of physical refining. Seed oils such as canola, sunflower, and corn fall into the either/or category, the choice being determined by process economics and local environmental requirements for handling soapstock and wastewater generated by chemical refining. Soybean oil can also be physically refined depending upon the treatment of the bean before and during extraction. To obtain good-quality fats and oils with physical refining, it is essential to have a phosphorus content lower than 5 ppm before steam stripping. Some oils, such as cottonseed, cannot be physically refined; an alkali treatment is required to remove the gossypol pigment.

## 2.4 PHYSICAL REFINING

Physical refining was utilized as early as 1930 as a process for the preneutralization of products with a high initial FFA content. In this case, preneutralization was followed by caustic refining. Later, it was found possible to physically refine lauric oils and tallow if the proper pretreatment was applied before steam distillation. Physical refining became a reality in the 1950s for processing palm oil, which typically contains high FFAs and low gum contents. The palm oil process subjected the crude feedstock first to pretreatment and then to deacidification. The pretreatment consisted of a degumming step and an earth bleaching step, which together remove certain nonvolatile impurities by filtration. Volatile and thermally labile components are removed during the conditions of steam distillation under vacuum, which originally gave the process its name of steam refining.<sup>11</sup> However, for vegetable oils, such as soybeans, that contain relatively low levels of FFAs and higher amounts of phosphatides, physical refining became a possibility only recently.

The traditional edible oil processing system consists of caustic neutralization, bleaching, and deodorization. Caustic neutralization of vegetable oils with high phosphatide contents delivers a soapstock that is a mixture of sodium salts of fatty acids, neutral oil, water, unused caustic, and other compounds resulting from the reactions of the caustic with various impurities in the oil. Disposal of this soapstock or the waste streams from soapstock processing systems has become increasingly more expensive. A second problem associated with chemical neutralization is the loss of neutral oil, which reduces the overall yield from the crude oil. Elimination of the caustic refining step is economically attractive, but it means that degumming or some other pretreatment process or system must assume all the functions of the alkali refining process, except for FFA removal.





**Figure 2.2** Physical refining process flow diagram.

Physical refining can remove the FFA, as well as the unsaponifiable and other impurities, by steam stripping, thus eliminating the production of soapstock and keeping neutral oil loss to a minimum. However, degumming and pretreatment of the oil are still required to remove those impurities that darken or otherwise cause a poor-quality product when heated to the temperatures required for steam distillation. Crude oil pretreatment is normally a two-step operation — the addition of a chemical is required to remove any trace quantities of gums remaining after water degumming and bleaching. Following pretreatment, all the FFA and any remaining trace impurities are removed by steam distillation in a single unit. Soapstock acidulation is eliminated with physical refining, and a higher grade distilled fatty acid is recovered directly from the oil without major pollution problems. Figure 2.2 compares physical refining processes for low- and high-phospholipid fats and oils.

Vegetable-oil refining has to cope with many minor components. After water degumming, a number of impurities must still be removed or converted: carotenoids, chlorophyll, brown pigments, phosphatides, metals, free sugars, free fatty acids, and oxidizing lipids. Steam stripping can convert the carotenoids and remove FFAs, most off-flavors, and pesticides, but the other impurities must be handled before the distillation step;<sup>12</sup> therefore, the pretreatment step is critical to the success of the physical refining process. The major process variables in pretreatment are (1) pretreatment chemical, concentration, and level; (2) bleaching clay and level; and (3) operating conditions. Normally, for a single-source oil with a history of consistent quality, the pretreatment process variables can be expected to remain fairly constant, but when more than one source oil is processed, varying conditions and chemical treatments must be considered.<sup>13</sup>

Pretreated and bleached oil can be hydrogenated before steam refining to strip the fatty acids, flavors, and odors. The operating temperatures of the steam-refining

deodorizer are the same as those used for deodorization of chemically refined oils, usually over 440°F (225°C). Deodorizers designed for steam refining of the higher FFA oils should experience no reduction in production rates; however, a rate reduction should be expected with deodorizers designed to remove the lower free fatty acid levels from caustic neutralized oils.

The principal advantage for steam refining a low FFA oil, such as soybean, corn, peanut, sunflower, safflower, or canola, is the reduction of plant pollution commonly caused by the acidulation of soapstock produced with conventional caustic refining. The economics for steam refining are usually favorable for high-FFA products such as palm and the lauric oils. Analyses indicate that no operating cost advantages can be gained by physically refining low-acidity oils,<sup>14</sup> which make up the majority of the oils processed in the United States. Additionally, flavor stability and potential unsatisfactory bleached color concerns still exist. Flavor evaluation work at the U.S. Department of Agriculture (USDA) Northern Regional Research Center indicated that steam-refined soybean oil was equivalent to caustic-refined product; however, some of the test results indicated a potential problem with oxidative stability, which was not duplicated with further test work.<sup>15</sup> Another consideration is that certain oils contain impurities that cannot be adequately removed by the pretreatment process to enable them to be physically refined to the required quality standards. Cottonseed oil falls into this category due to its gossypol content. This pigment is sensitive to heat and oxidation and forms color compounds that are difficult to remove from the oil except by reaction with caustic soda.

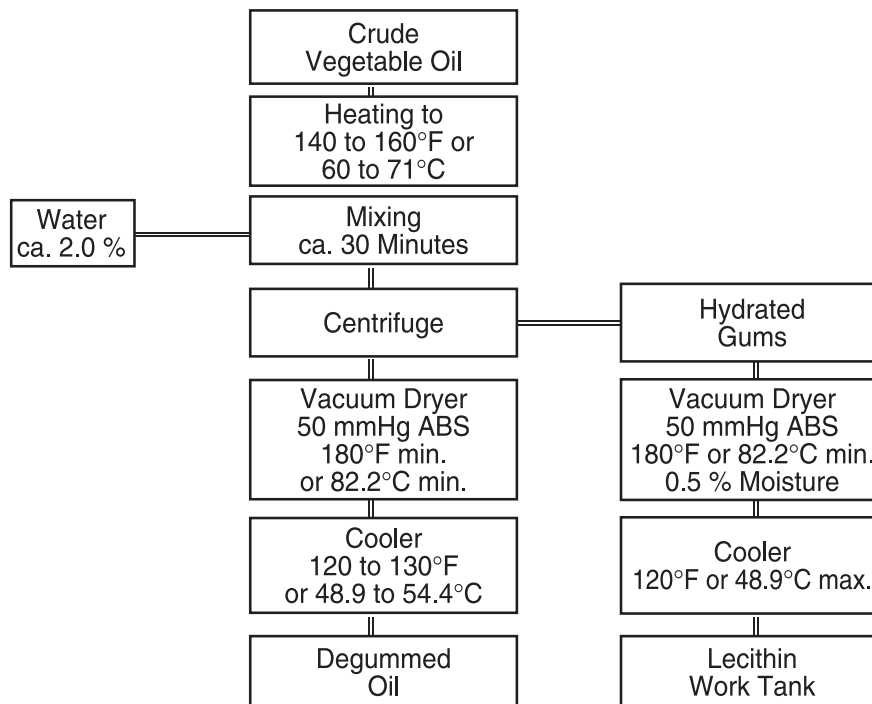
#### **2.4.1 Physical Refining Pretreatment**

A degumming process is crucial for physical refining but optional for chemical refining. It consists of the treatment of crude oils, with water, salt solutions, enzymes, caustic soda, or dilute acids such as phosphoric, citric, or maleic to remove phosphatides, waxes, prooxidants, and other impurities. The degumming processes convert the phosphatides to hydrated gums, which are insoluble in oil and readily separated as a sludge by settling, filtering, or centrifugal action. For physical refining, phosphorus must be reduced to less than 30 ppm with degumming so that bleaching or dry degumming can further reduce this level to less than 5 ppm and remove all traces of iron and copper. Acid or enzymatic degumming processes are normally employed to achieve these results, especially with seed oils. With chemical refining, the phosphatides can either be recovered for their byproduct value through water degumming or be treated as impurities that must be removed from the crude oil. Most of the vegetable oils processed in the United States are chemically refined without degumming. It has been estimated that less than one third of the processed soybean oil will satisfy the demand for lecithin.<sup>16</sup> Crusher/refiners can add the separated gums back to the meal, but most stand-alone processors lack a market or profitable outlet for the gums and forgo degumming. The decision not to degum oil can be based both on energy conservation and capital savings; a separate, combined degumming and refining process can be carried out in one step with the primary centrifuge for caustic refining. However, vegetable oil degumming offers several potential advantages:

- It is necessary for lecithin production. The hydrated gums are the raw materials for lecithin processing.
- It satisfies export oil requirements for a product free of impurities that could settle out during shipment.
- It reduces the chemical refining neutral oil loss. Gum removal prior to alkali refining often improves yield because the phosphates can act as emulsifiers in a caustic solution to increase the neutral oil entrained in the soapstock.
- It substantially reduces refinery waste load due to the lower neutral oil losses and the reduction of gums discharged.
- It improves acidulation performance. The soapstock from alkali refining is easier to acidulate due to a lower emulsifier content, and the acid water has less impact upon the wastewater treatment systems.
- It prepares the oil for physical or steam refining. Degummed oil is more suited to physical refining techniques due to the significant reduction in nonvolatile impurities, such as phosphatides and metallic prooxidants.

## 2.4.2 Water Degumming

The main purpose of the water degumming process is to produce an oil that does not deposit a residue during transportation and storage. The batch water degumming process most commonly practiced in the United States is diagrammed in Figure 2.3. Approximately 2% water, by oil volume, is brought into contact with the crude oil by mechanical agitation in a mix tank. The proper amount of water is normally about 75% of the phosphatide content of the oil. Too little water produces dark viscous gums and a hazy oil, while too much water causes excess oil losses through hydrolysis. Complete hydration requires approximately 30 minutes of agitation at 140 to 160°F (60 to 71°C) for batch processing. Temperature is important because degumming is



**Figure 2.3** Batch water degumming process flow.

less complete at higher temperatures due to the increased solubility of the phosphatides in the oil; also, at lower temperatures the increased oil viscosity makes separation of the phosphatides more difficult. For continuous systems, preheated oil (80°C or 176°F) is treated with water and mixed in a holding tank for approximately 15 minutes (or for less than 1 minute with continuous in-line agitators). The water–oil mixture must be treated very gently to avoid developing an emulsion; high shear stress in the feed pump and at the centrifuge inlet must be avoided. After hydration, centrifuges separate the sludge and degummed oil phases. The degummed oil can be vacuum dried and pumped to degummed oil storage or it can proceed directly to the refining process. The hydrated gums can be vacuum dried for crude lecithin processing or added back into the meal.<sup>17</sup>

Water-degummed oil still contains phosphatides; only the hydratable phosphatides are removed with water degumming. Typically, oils will have an 80- to 200-ppm phosphatide content after water degumming, depending upon the type and quality of the crude oil. The nonhydratable phosphatides, which are the calcium and magnesium salts of phosphatidic acid and phosphatidyl ethanolamine, remain in the oil after water degumming. The amount of the nonhydratable phosphatides in the oil is related to the general quality of the oil and, in particular, to the degree of action of the enzyme phospholipase. This enzyme is responsible for the production of phosphatidic acid from hydratable phosphatides.<sup>18</sup>

### **2.4.3 Acid Degumming**

Acid degumming leads to a lower residual phosphorus content than water degumming and is therefore a good alternative if dry degumming and physical refining are to be the next refining steps. The acid degumming process might be considered as a variant of the water degumming process in that it uses a combination of water and acid. The nonhydratable gums, consisting mainly of the calcium and magnesium salts of phosphatidic acid and phosphatidyl ethanolamine, can be conditioned into hydratable forms with a degumming acid. This acid liberates the phosphatidic acid and phosphatidylethanolamine and forms a binding complex with the calcium and magnesium divalent metal ions that can be removed with the aqueous phase. Phosphoric and citric acids are used because they are food grade, sufficiently strong, and they bind divalent metal ions. Citric acid is usually preferable because it does not increase the phosphorus content in the oil. Because they do not dissolve in oil, the degumming acids must be finely dispersed for maximum contact with the nonhydratable phosphatide complexes. To facilitate their removal, the salts formed with the degumming acid must not be oil soluble. For this reason, acetic acid or its anhydride, although strong enough and food grade, is not an appropriate degumming acid. The gums isolated with an acid degumming process are not suitable for standard lecithin because their phosphatide composition differs from those obtained with water degumming (higher phosphatidic acid) and they contain the degumming acid.<sup>19</sup>

Several acid degumming processes have been developed to attain a phosphorus value lower than 5 ppm that is required for good-quality physically refined oils. In the super-degumming process developed by Unilever,<sup>20</sup> mild temperatures are used in a complicated multiple-holding steps process. First, the oil is heated to 70°C,

modified lecithin is optionally mixed into the oil, and then a strong solution of citric acid is added as a degumming acid to decompose the nonhydratable phosphatides. After a reaction period, the mixture is cooled to below 40°C, and water is added to promote the dissociation of the liberated free phosphatidic acid and phosphatidyl ethanolamine. A further 3-hour holding time is provided to form liquid phosphatide crystals at this reduced temperature. These crystals are then removed by centrifuge, and the oil mixture is heated again before being fed to the centrifugal separator. The residual phosphorus content is generally below 30 ppm, probably due to the increased phosphate hydration; however, these levels are quite dependent upon the starting oil quality.

#### **2.4.4 Dry Degumming**

In dry degumming, the oil is treated with an acid to decompose the metal ion/phosphatide complexes and is then mixed with bleaching earth. The earth containing the degumming acid, phosphatides, pigments, and other impurities is then removed by filtration. Its main advantage is that it does not generate an aqueous effluent, apart from the water involved in the vacuum system. Typically, this process is utilized for oils with low phosphatide contents such as palm oil, palm kernel, coconut, and tallow. Seed oils that have been water- or acid-degummed may also be dry degummed to ensure a low phosphorus oil to steam distillation.

The dry degumming process uses standard bleaching equipment. Acid, usually 85% phosphoric, is dispersed in 80 to 100°C oil at 0.05 to 1.2% of the oil. After a short reaction time, some water can be added to enhance bleaching efficiency before 1 to 3% bleaching earth is added and the vacuum applied. The amount of bleaching earth is dependent upon the phosphatide content of the oil. Normally, this process requires about 115% of the level used to bleach chemically refined oils or fats. The oil is then heated to bleaching temperature (120 to 140°C) for about 15 minutes and then cooled below 100°C. Finally, the bleaching earth is removed by filtration. An increase in FFA of less than 0.2% should be expected, but the final phosphorus content must be reduced to less than 5 ppm.

#### **2.4.5 Enzymatic Degumming**

The EnzyMax enzymatic degumming process has been proven commercially in Mannheim, Germany. Phospholipase A1, the preferred enzyme for degumming, is produced by microbial fermentation. The degumming enzyme changes the phospholipids into lysophospholipids and free fatty acids. The process advantages include:

1. Enzymatic reactions are usually carried out under mild conditions.
2. The enzymes are highly specific.
3. The process has acceptable reaction rates.
4. Only small quantities of the enzyme are required to carry out the chemical reactions.
5. Degummed oils with a low phosphorus and iron contents are produced even with poor-quality starting oils.

The enzymatic process has three important steps: (1) adjustment of the pH with a buffer, (2) enzymatic reaction in the holding tanks, and (3) separation of the sludge from the oil. The buffer, a weak solution of approximately 1.4 parts citric acid to 1 part NaOH, is added to oil at 70 to 75°C to adjust the pH to about 4.5. The oil temperature is reduced to 40°C before adding the liquid enzyme phospholipase A1. The enzyme is added at a level of 200,000 units in 7.5 liters of water per ton of oil. A high-shear mixer is used to mix the enzyme with the oil before the mixture is pumped to a holding tank for a period of less than 6 hours. After the reaction has been completed, the temperature is raised to 75°C for more efficient separation of the gums in a centrifuge. The phosphorus content of crude soybean, canola, and sunflower has measured consistently below 10 mg/kg with an iron content below 0.5 mg/kg even with poor-quality crude oils. The gums recovered from this process were found suitable for lecithin production.<sup>21</sup> The enzymatic degumming process has been found to be applicable to most vegetable oils except for cottonseed and corn oils.

#### **2.4.6 Acid Refining**

Acid refining is a physical refining pretreatment that incorporates the benefits of caustic soda neutralization. This physical refining preparatory process treats the oil with a degumming acid and then partially neutralizes it with NaOH in solution. The amount of NaOH used is limited to prevent soap formation. The metal-phospholipid complexes are dissociated by the acid into insoluble metal salts and phospholipids in their acid form, which are still soluble in oil. The NaOH addition raises the pH and converts the phospholipids into sodium salts that are hydratable. The hydrated salts can be centrifuged for separation or dried to form agglomerates for adsorption on silica, which can be removed with filtration.

The acid degumming treatment will generally reduce phosphorus to between 25 and 35 ppm. Neutralization with NaOH after the acid treatment should reduce the phosphorus content to 15 to 25 ppm. These treatments followed by either a water wash or the use of silica will further reduce the phosphorus to the 5-ppm maximum required for physical refining. Silica adsorbents are added with a separate mixing step before bleaching and can be removed with a separate filtration or with the spent bleaching earth. Some consider acid refining an intermediate between acid degumming and chemical refining. This process should be applicable to all types of oils, either crude or previously degummed.<sup>14,22,23</sup>

### **2.5 CHEMICAL REFINING**

The conventional caustic soda process is the most widely used and best-known refining system. The addition of an alkali solution to a crude oil brings about a number of chemical and physical reactions. The alkali combines with the FFA present to form soaps; the phosphatides and gums absorb alkali and are coagulated through hydration or degradation; much of the coloring is degraded, absorbed by the gums, or made water soluble by the alkali; and the insoluble matter is entrained

with the other coagulable material. With heat and time, the excess caustic can also bring about the saponification of a portion of the neutral oil; therefore, selection of the NaOH strength, mixing time, mixing energy, temperature, and the quantity of excess caustic all have an important part in making the alkali refining process operate effectively and efficiently.

The current alkali refining practices are a result of the gradual application of science to the basic art of batch refining originally performed in open-top, cone-shaped kettles during the first part of the last century. Efficient separation of soap-stock from neutralized oil is the significant factor in alkali refining; the technique of using centrifugal separators was conceived before the last century but did not become a commercial reality until 1932. The conventional caustic-soda continuous system that evolved has the flexibility to efficiently refine all the crude oils presently utilized in the United States. The system may be outlined as follows.

### ***Crude Receipts***

Crude or degummed oils are received by railcar, truck, or barge or from on-site extraction or degumming operations.

### ***Sampling***

Receipts are sampled, analyzed, and then transferred to the appropriate storage tanks. For optimum performance, degummed soybean oil should have a phosphatide content below 0.3%. If this level is exceeded, nondegummed oil should be blended with the degummed oil to attain a 1.0% phosphatide content.

### ***Crude Oil Conditioning***

As needed, the oils are transferred to the appropriate pretreatment or supply tank. Crude oils with high levels of phosphatides such as soybean and canola oils are usually treated with food-grade phosphoric acid for a minimum of 4 hours (8 hours preferred) before refining — 300 to 1000 ppm for soybean and 1000 to 3000 ppm for canola. The purpose of the acid pretreatment is to (1) precipitate phosphatidic materials, (2) precipitate natural calcium and magnesium as insoluble phosphate salts, (3) inactivate trace metals such as iron and copper that may be present in the oil, (4) reduce the neutral oil losses, (5) destabilize and improve the removal of chlorophyll in bleaching, and (6) improve the color and flavor stability of the finished deodorized oil.

### ***Caustic Treatment***

The degummed or acid-conditioned crude oil is continuously mixed with a proportioned stream of dilute caustic soda solution and heated to break the emulsion. Selection of the caustic treatment is determined by the type of crude oil, FFA content, past refining experience with similar oils, and the refining equipment available. In general, the minimum amount of the weakest strength necessary to achieve the

desired endpoint should be used to minimize saponification of neutral oil and prevent “three phasing” or emulsions during separation. Usually, the best results are obtained with relatively weak caustic solutions or lyes on low FFA oils and with stronger lyes on high FFA oils. The strength of the caustic solution is measured in terms of specific gravity, expressed in degrees Baumé (°Bé). The caustic treat selected for the crude oil will vary with the free fatty acid content, the amount of acid pretreatment, and the level of caustic “excess” over “theoretical” determined for each oil type from previous experience. The theoretical quantity of caustic is based on the ratio of molecular weights of sodium hydroxide to oleic fatty acid. This factor is determined as follows:

$$\text{Factor} = \frac{\text{NaOH molecular weight}}{\text{Oleic fatty acid molecular weight}} = \frac{40}{282} = 0.142$$

Thus, the formula for caustic treatment is:

$$\% \text{ Treatment} = \frac{(\% \text{FFA} \times 0.142) + \% \text{Excess} + \text{Acid addition}}{\% \text{NaOH in caustic}} \times 100$$

The phosphorus reduction during refining is determined largely by the amount of water present in the caustic solution. Higher excess caustic treatments remove more phosphorus, but the increase in removal is due more to the increased water than NaOH. Comparative studies have shown that more dilute caustic solutions will remove more phosphorus; therefore, crude oils with high phosphorus levels are best refined with dilute caustic solutions, but if they become too dilute then difficult emulsion separation characteristics develop. For this reason, dilute caustic solutions or low Baumé concentrations are recommended for soybean, peanut, safflower, sunflower, and canola oils.

The refining conditions for cottonseed oil are chosen more for the improvement of color because of the presence of the gossypol. This pigment is sensitive to heat and oxidation and forms colored compounds that are difficult to remove from the oil other than by reaction with caustic. Therefore, the caustic treatment has a greater excess of a more concentrated NaOH solution. Palm, palm kernel, and coconut oils require a weaker caustic of approximately 12°Bé to optimize centrifugal separation, reduce saponification of the neutral oil, and minimize emulsions. The diluted caustic for use with the lauric and palm oils is usually preheated to 150°F (65°C) to minimize emulsion formation in the separators. These oils also require only a minimum of excess treatment as well (0.02%), because they are refined for FFA reduction only. It should be remembered that the FFAs for coconut and palm kernel oils are calculated on the basis of lauric fatty acid instead of oleic as for the other vegetable oils.

Suggested caustic concentrations and excess treatments for various crude vegetable oils as a starting point before experience is gained are shown on [Table 2.1](#). A smooth reproducible flow of the caustic solution into the oil stream is important because pulsating delivery will carry through the mixers and produce varying mixture densities in the centrifuge.



**Table 2.1 Caustic Treat for Vegetable Oils**

Crude Oil	Concentration		Excess Treat (%)
	°Bé	NaOH (%) <sup>a</sup>	
Cottonseed	19–21	13.52–15.23	0.16
Corn	16–20	11.06–14.36	0.13
Canola	16–18	11.06–12.68	0.07
Soybean:			
Crude	12–16	8.0–11.06	0.12
Degummed or mixed	12–16	8.0–11.06	0.10
Safflower	14–18	9.5–12.68	0.12
Sunflower	14–18	9.5–12.68	0.12
Peanut	13–15	8.75–10.28	0.12
Coconut	11–12	7.29–8.00	0.02
Palm kernel	11–12	7.29–8.00	0.02
Palm	11–12	7.29–8.00	0.02

<sup>a</sup> At 15°C (59°F).

### ***Caustic-Oil Mixing***

After the caustic reagent has been proportioned into the crude oil, it must be adequately blended to ensure sufficient contact with the free fatty acids, phosphatides, and color pigments. The gums are hydrolyzed by the water in the caustic solution and become oil insoluble. The caustic and soft oils are mixed at 30 to 35°C (86 to 95°F) in a dwell mixer with a 5- to 15-minute residence time. High oil temperatures during the caustic addition must be avoided because they can increase the neutral oil saponification and reduce the refined-oil yield. Many refineries will use an inline shear mixer to obtain the intimate contact time between caustic and oil followed by a delay period in the dwell mixer prior to centrifugation. After the caustic-mixing phase is complete, the mixture should be delivered to the centrifuges at a temperature suitable for optimum separation. Most soft oils are heated to 165°F (74°C) to provide the thermal shock necessary to break the emulsion.

### ***Soap–Oil Separation***

Refining-yield efficiency is dependent on the primary separation step. From the caustic-oil mixer, the resultant soap-in-oil suspension is fed to high-speed centrifuges for separation into light- and heavy-density phases. These separators are designed to divide suspensions of insoluble liquids and solids in suspension with different specific gravities. The light-phase discharge is the neutral oil containing traces of moisture and soap. The heavy-phase, or soapstock, discharge is primarily insoluble soap, meal, free caustic, phosphatides, and small quantities of neutral oil. Refined-oil yield and quality depend upon a uniform feedstock and separation of the heavy phase with the least amount of entrained oil; however, even under the most optimum conditions, complete separation of the two phases cannot be achieved. Therefore, the primary separation is accomplished by allowing a small amount of the soapstock phase to pass along with the refined oil for removal by the water wash centrifuge.<sup>24</sup>

Various types of centrifuges are used in vegetable-oil refining; however, most centrifuges contain a bowl or hollow cylinder that turns on its axis. The flow of material enters the rotating bowl and is forced outward to a disc stack. The heavier density soapstock is forced to the outside of the bowl and flows over the top disc and out the discharge port. The lighter neutral-oil phase moves to the center of the bowl for discharge from the neck of the top disc. The major factors to consider for improvement of separation completeness include: (1) greater differences in the specific gravity of each phase, (2) lower viscosities, (3) higher temperatures, (4) shorter travel distance for the heavy particles, (5) increased centrifugal forces, and (6) longer centrifugal dwell times.<sup>17</sup>

### ***Water Washing***

Refined oil from the primary centrifuge is washed with hot softened water or recovered steam condensate proportioned into the oil at a rate of 10 to 20% of the oil flow. Softened water must be used to avoid the formation of insoluble soaps. Sodium soaps remaining from the primary centrifugation phase are readily washable and easily removed from the oil with either a single or double wash. A single wash is usually sufficient; however, two washes may provide savings in bleaching earth and hydrogenation catalyst usage, as well as a reduction in washwater volume.<sup>25</sup> The water–oil mixture passes through a high-speed, inline mixer to obtain intimate contact for maximum soap transfer from the oil to the water phase. The soapy water–oil mixture continues through to the washwater centrifuge. Similar in action to the refining centrifuge, water-washed oil is discharged as the light phase and the soapy water solution as the heavy phase. The water-washing operation will remove about 90% of the soap content in the refined oil.

Washwater temperature is important for efficient separation in the centrifuge. The water temperature should be 185 to 195°F (85 to 90°C), preferably 10 to 15°F (5 to 8°C) warmer than the oil temperature. The washwater flow rate controls soap removal and affects the oil losses in the wash water. As with the primary centrifuge, a pulsating flow of water must be avoided.

Two things that water washing will not do are remove phosphatides left in the oil after the primary centrifuge and remove unwashable soaps related to the calcium and magnesium content of the crude oil. These metal complexes should have been removed in either the degumming or refining steps. Iron soaps are prooxidants, while calcium and magnesium result in nonwashable soaps.<sup>10</sup> Some processors add up to 400 ppm citric acid to wash waters to effect the removal of these residuals.<sup>25</sup>

### ***Vacuum Drying***

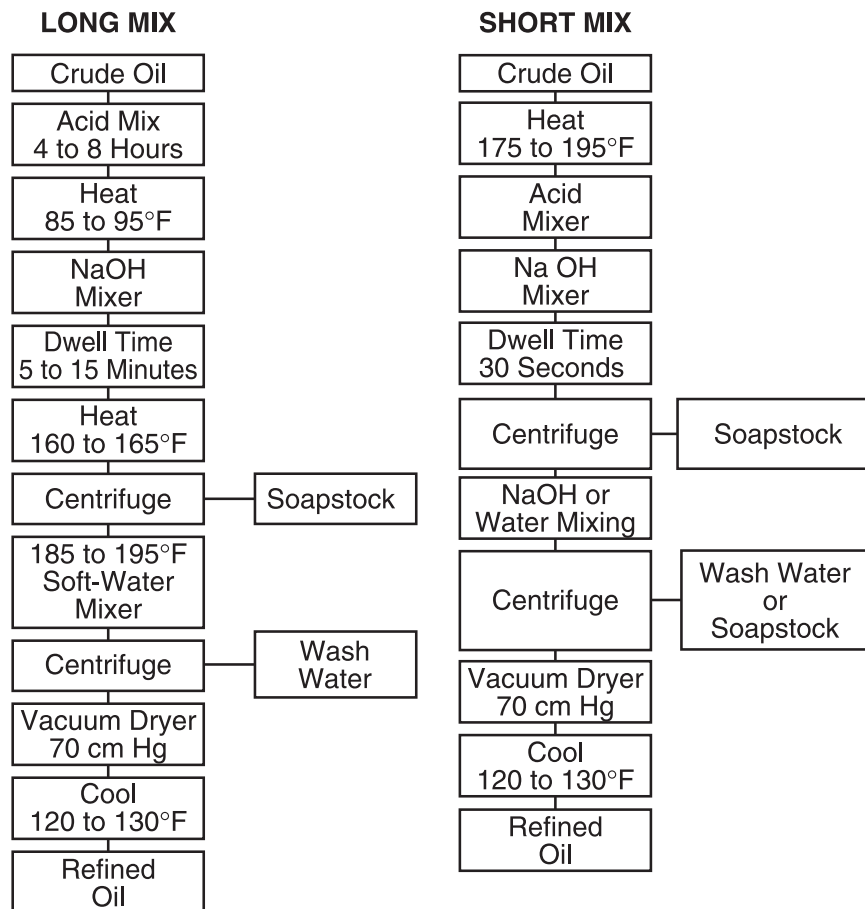
Water-washed oil is usually dried with a vacuum dryer before storage or bleaching. Washed oil at approximately 185°F (85°C) is passed through nozzles into the evacuated section of a continuous vacuum dryer that controls the moisture content of the washed oil to below 0.1%, most often in the range of 0.05%. A typical dryer operates at 70 cm of mercury (Hg) and is equipped with a high-level alarm and

automatic shutdown capability. After drying, the refined oil should be cooled to 120 to 130°F (49 to 55°C) before storage. For extended storage periods, a nitrogen sparge or a nitrogen blanket applied to the surface of the oil will minimize oxidation before use.

### 2.5.1 Short-Mix Caustic-Soda Refining

Refining practices vary between countries and plants due to the number, quality, and kind of source oils processed. The refining practices in Europe differ from those used in the United States mainly because of the need to process all types of oils and typically poorer-quality oils. The European oilseeds or crude oils must be imported, and a typical refinery must be equipped to handle all kinds of oils, depending upon availability and price. The quality of the oilseeds or crude oils imported is variable, but normally a higher FFA oil is processed. The short-mix process was adopted in Europe after World War II because the relatively high FFA oils made it necessary to avoid the long contact time and the larger excess of caustic used with the conventional caustic-soda refining system utilized in the United States. Figure 2.4 compares the differences between the long- and short-mix refining processes.

For the short-mix process, the oil temperature is raised to 80 to 90°C (175 to 195°F) before the addition of the caustic soda. A break between the neutral oil and



**Figure 2.4** Comparison of long-mix and short-mix chemical refining systems.

soapstock takes place immediately, reducing the losses due to emulsification. The contact time between the caustic and oil is reduced to 30 seconds maximum, which helps to reduce the saponification losses. Because it is standard in Europe to degum solvent-extracted oils and to condition the oils with phosphoric acid before refining, the excess caustic treat can be eliminated or reduced substantially. In the case of an oil such as cottonseed refined for color removal, a second caustic treatment is used. This additional phase is called *re-refining*. Because the bulk of the soapstock has already been removed with degumming and the initial caustic treatment, the additional losses with the second caustic treatment are relatively low. The oil is finally washed with demineralized water to help remove the traces of soap remaining in the oil and dried with processes similar to the systems used for the long-mix caustic refining process.

An ultra-short-mix method is used for oils with high acidity to reduce the losses more than the regular short-mix process. For palm and other oils with high acidity levels, the caustic soda is introduced directly into the hollow centrifuge spindle where a special mixing device is located. The very short contact time allows the use of stronger caustic concentrations without excessive saponification of the neutral oil. Comparisons of palm oil refined with the ultra-short-mix process contributed considerable yield improvements over product refined with the short-mix process — 7.0 to 16.5% less loss for one evaluation.<sup>26</sup>

### 2.5.2 Zenith Process

The Zenith process was developed in Sweden in 1960 to enable better refining of the only oilseed crop grown in that country: rapeseed. The stainless steel continuous process consists of three main refining steps, two of which are semicontinuous to maintain the desired reaction times:

- *Step one.* The oil is treated with concentrated phosphoric acid to remove the nonfatty impurities that influence emulsions. The amount of phosphoric acid depends upon the oil quality but normally is about 0.2% by oil volume for rapeseed oil. The reaction, performed under a vacuum, requires 20 minutes. The acid sludge formed with the pigments, phosphatides, calcium, magnesium, and other impurities is removed with a sludge separator. Water is introduced in the form of live steam to form liquid crystals of the remaining phosphatides at the interface between the water and the oil.
- *Step two.* Neutralization is performed by introducing the oil at 90°C (194°F) in the form of droplets to the bottom of a vessel almost filled with 0.35-N (2.0 °Bé) alkaline solution. The 1- to 2-mm diameter droplets rise by the difference in specific gravity and are collected in the upper conical part of the vessel, thus forming an oil layer with a typical analysis of 0.05% FFAs, 0.2 to 0.3% moisture, and 100 ppm soap.
- *Step three.* The neutralized oil is treated with citric acid to help separate the trace quantities of soap for adsorption by the bleaching earth. The oil is dried and bleaching earth added before it is vacuum bleached for 30 minutes before filtering.

Improved refined oil yields with excellent quality are claimed for the Zenith process.<sup>27</sup>

### 2.5.3 Miscella Refining

Facilities with an existing oilseed solvent extraction system may find miscella refining to be advantageous because the same solvent recovery unit can be used for both purposes. Miscella is the solution or mixture that contains the extracted oil. Both continuous and batch miscella refining processes are suitable for most fats and oils. Miscella refining is especially beneficial for cottonseed oil to provide an oil with a lighter red color and a high neutral oil yield. This type of refining should be done at a solvent extraction plant as soon as possible, preferably within 6 hours after the oil is extracted from the oil seed or animal. The advantages for miscella refining, as compared to conventional continuous caustic-soda refining, are (1) higher oil yield, (2) lighter color oil without bleaching, (3) elimination of the water-wash step, and (4) extraction of the color pigments before solvent stripping has set the color.<sup>28</sup>

For this purification process, the crude miscella source may be from (1) the pre-evaporator of a direct-solvent extraction plant, (2) a blend of prepressed crude oil and solvent extracted miscella from the press cake, or (3) a reconstituted blend of crude oil with solvent. In the process, a mixture of approximately 40 to 58% oil in solvent is heated or cooled to 104°F (40°C) and filtered to remove meal, scale, and other insoluble impurities. Two solvents that have been used commercially for miscella refining are hexane and acetone.

Hydrolysis of phosphatides and pigments in the crude oil miscella requires an acid pretreatment, which usually varies between 100 and 500 ppm by weight of the oil, depending upon the quality of the crude oil. An acid such as phosphoric or glacial acetic has been found effective in improving oil quality and reducing refining losses. Phosphoric acid is used more commonly due to its less corrosive properties and availability. The acid is mixed with the miscella in a static mixer to provide an intimately dispersed acid phase, which immediately reacts with the crude miscella.

The pretreated crude miscella is then alkali refined using dilute caustic soda with a 16 to 24 °Bé and a 0.2 to 0.5% NaOH excess over the theoretical required to neutralize the free fatty acids. The reaction of the caustic soda with the FFAs proceeds rapidly at 130 to 135°F (54 to 57°C), using homogenizers with a shear mixing intensity capable of homogenizing milk and hydrolyzing the phosphatides and pigments with the caustic soda to produce a two-phase mixture. The miscella temperature is adjusted to 135°F (57°C) to obtain the best separation of the heavy phase or soapstock from the oil or the light phase with the centrifuge. The neutral oil is then filtered through a diatomaceous earth, pre-coated, pressure leaf filter. At this point, the refined and filtered miscella can be stripped of the solvent to produce a neutral yellow oil, or it can be further processed as miscella to dewax, fractionate, or hydrogenate the oil.<sup>29,30</sup>

Obvious disadvantages for the miscella refining process that may have discouraged many processors from adopting this processing system include:<sup>31</sup>

- Equipment — All equipment and facilities must be explosion proof for solvent handling.
- Maintenance — The equipment and facilities must be well maintained to avoid excessive solvent losses and accidents.
- Laboratory — More elaborate laboratory facilities and staffing are necessary to control this process.

## 2.5.4 Batch Caustic-Soda Refining

Batch refining is still practiced for some specialty oils in developing countries for small production lots and in most pilot-plant operations. Batch refining has some basic advantages:

- Investment costs are low.
- Equipment is readily available.
- It is practical for small lots.
- It is suitable for low capacities.
- A quality refined oil can usually be produced.

At the same time, batch refining can have some serious drawbacks:

- Refining losses are high.
- Operational costs are high.
- A high load is imposed on wastewater plants.
- It is very time consuming.

Batch refining is most likely installed only for special conditions where the refined oil requirements are very low.

Generally, two batch-refining procedures are utilized: the dry method and the wet method. The dry method is preferred in the United States for most oils, while the wet method is preferred in Europe. Coincidentally, the batch dry-method parameters resemble the long-mix caustic soda continuous refining procedure preferred in the United States, and the batch wet-method parameters resemble the short-mix continuous procedure preferred in Europe.

### 2.5.4.1 Dry-Method Batch Refining

The equipment required for the batch dry-refining method is simple, consisting of an open-top, conical-bottom tank or kettle equipped with a two-speed agitator and steam coils for heating. The agitator shaft is centered in the vessel and is either suspended from the top or extended to a step bearing on the bottom. The agitator shaft is equipped with sweep arms, each with paddles canted to push the liquid upward during agitation. The usual agitator rates are 30 to 35 rpm maximum and 8 to 10 rpm minimum. The batch dry method consists of the following steps:<sup>31,32</sup>

1. The first stage is carried out with the oil at ambient temperature or at a temperature just high enough to keep the fat molten and liquid. If the oil contains occluded air after pumping to the refining kettle, it must be settled long enough to allow the air to escape. The soapstock can entrain enough air to float, which will prevent it from settling to the bottom of the kettle as desired.
2. The caustic solution or lye is added to the top of the kettle while agitating it at high speed. Agitation is continued to thoroughly emulsify the alkali and oil (usually 10 to 15 minutes), then the agitation is reduced to slow speed and the oil is heated to 135 to 145°F (57 to 63°C) as rapidly as possible.

3. A visible break in the emulsion will occur at about 140°F (60°C) where the soapstock separates from the clear oil in the form of small flocculent particles that tend to coalesce with agitation.
4. After the desired degree of break is obtained, agitation is stopped, heating is discontinued, and the soapstock or foots are allowed to settle to the bottom of the kettle by gravity for 10 to 12 hours minimum.
5. After the soapstock has settled, the neutral oil can be drawn off the top, leaving the soapstock at the bottom of the kettle. For many oils, such as soybean, canola, sunflower, safflower, and peanut, treated with a dilute caustic (usually 12 to 16 °Bé with about 0.25% excess), the settled soapstock should be fluid enough to allow it to be drained from the bottom of the kettle, leaving the refined oil in the kettle.
6. Traces of moisture and soap remain in the refined oil and should be removed if the oil is going to storage before bleaching. The refined oil can be either filtered through spent bleaching earth or water washed. Kettle water washing consists of adding approximately 15% hot, soft water to the refined oil while agitating for uniform dispersion and then allowing the water to settle for decanting. Water washing may be repeated if warranted.

#### **2.5.4.2 Wet-Method Batch Refining**

The preferred European batch-refining method heats the crude oil to a relatively high temperature, 150°F (65°C), before adding the caustic or lye. A high caustic concentration, 20°Bé, is used for the usually high FFA oils processed with about a 0.10% excess treat. In many cases, the addition of salt equivalent to about 0.10% sodium chloride per 1.0% free fatty acid is necessary to break the soapstock and oil emulsion. The precipitated soapstock is washed down with a spray of hot water onto the surface of the oil. Several successive water washes are required to completely remove the soap from the oil, with a settling time required between each wash. The wet method has advantages over the dry method for refining oils with high FFA contents such as some palm and olive oils. It has also been used for refining coconut and other lauric oils. Refining equipment for the wet method is not essentially different from that used for the dry process, except that closed tanks that can also be used for vacuum bleaching are usually used to refine and wash the crude oils with the wet method.<sup>31</sup>

#### **2.5.5 Silica Refining**

Silica processing utilizes a chemically inert synthetic amorphous silica adsorbent with an affinity for polar contaminants. The surface area, porosity, and moisture content of the silica adsorbents provide them with the capability of removing soaps, phospholipids, sulfur compounds, and trace metals from edible oils. The function of the moisture is to hold the pores open and aid in the attraction of polar contaminants. Several different options are offered for the use of silica adsorbents. The simplest option adds silica adsorbent with the bleaching earth prior to bleaching to reduce the clay usage. A 40% reduction in bleaching-earth usage, less neutral-oil loss, and longer filter cycles are claimed by W.R. Grace for their TrySyl® product.<sup>23</sup> A second bleaching option adds the silica separate from the bleaching clay, which

is precoated on the filter press. The silica collapses in the bleaching vessel, trapping the contaminants to preserve the clay for color pigment removal. An 80% reduction in bleaching earth is claimed for this enhanced silica option. The modified caustic-refining procedure eliminates the need for a water-wash centrifuge. The high soap and gum adsorption capacity of the silica replaces the water-wash procedure. The usual washing process produces a high biological oxygen demand effluent as well as a loss of oil. About 0.05% of the oil washed is lost in the wastewater. Also, disposal of wastewater from conventional washing of alkali-refined oils presents a problem to processors because of increasingly stringent laws regarding oil-refinery effluents. The water-washing step may be eliminated by using 0.05 to 0.4% silica hydrogels to absorb residual soap and trace metals from the refined oil. The silica material has a higher ability to absorb soap, secondary oxidation products, and phospholipids than do traditional bleaching clays. The spent silica is removed by filtration before the oil is bleached. Bleaching with clay is still required to remove the color pigments and other impurities; however, the bleaching-earth usage has been reduced 40 to 80% in some operations.<sup>23</sup>

A process using sodium silicate to replace sodium hydroxide in chemical refining has been developed at Texas A&M. Sodium silicate reacts with the nontriglycerides to form a silica hydrogel that is filterable but cannot be centrifuged with current equipment. Conversely, the soaps produced with sodium hydroxide are not filterable but can be centrifuged for separation. Degumming of the oil prior to refining is a prerequisite for this modified process to reduce the quantity of gums absorbed by the sodium silica.<sup>33</sup>

### 2.5.6 Refining Efficiency

Refining efficiency is generally considered to be the yield of dry neutral-refined oil as a percentage of the available neutral-oil content of the crude oil. The dry neutral oil is determined by actual weight in a scale tank or volumetric measurement with adjustments as indicated by the specific gravity or temperature of the product. The crude neutral-oil content is supplied by the laboratory analysis of the incoming crude-oil samples or preferably analysis of the feedstock to the refining system. The refining efficiency is expressed as the ratio of neutral oil produced over the analyzed neutral oil in the crude oil, for example:

$$\text{Refining efficiency} = \frac{\text{Refined-oil yield}}{\text{Crude neutral-oil analysis}} \times 100$$

The specified laboratory loss analysis by trading rules varies with the source oil, which affects the refining efficiency results. Gum-containing crude oils, such as soybean and canola, are usually evaluated by the chromatographic method for neutral oil (American Oil Chemists' Society [AOCS] Method Ca 9f-57),<sup>34</sup> and the refining efficiency is expressed as the ratio of neutral oil produced to the laboratory-determined neutral oil in the crude oil. Corn and cottonseed oils trading rules specify



AOCS Method Ca 9a-52,<sup>34</sup> and the refining efficiency is expressed as savings over cup and determined with the following equation:

$$\text{Savings over cup} = \frac{\% \text{ Cup loss} - \% \text{ Plant loss}}{\% \text{ Cup loss} \times 100}$$

It is customary in Europe to monitor refining efficiency with the *refining factor*, which is the total loss divided by the fatty acid of the crude oil before refining. This factor permits a direct comparison of the refining efficiency of oils with different FFA starting levels. The refining factor can present a false impression when the amount of gums and other impurities is high in proportion to the FFA content. Experience in European facilities with all types of properly filtered and degummed oils shows that the refining factor varies between 1.4 and 1.7.<sup>26</sup> In the United States, lauric and palm oils are refined against free fatty acid, and the efficiency control is measured with the refining factor. The equation for determining the refining factor is:<sup>31</sup>

$$\text{Refining factor} = \frac{\% \text{ Plant loss}}{\% \text{ Free fatty acid}}$$

## 2.5.7 Refining Byproducts

Crude oils contain a number of materials that must be removed to produce neutral, light-colored oils. These impurities have been considered waste products constituting a disposal problem; however, they can be valuable byproducts when effectively recovered and processed. The two major byproducts from the refining processes are soapstock from chemical refining and hydrated gums from the degumming process prior to caustic refining or the physical refining pretreatment stage.

### 2.5.7.1 Soapstock Processing

Soapstock from alkali refining is a source of fatty acids, but it also presents a handling, storage, and disposal problem. Originally, many years ago, the caustic refining byproducts were merely discarded. Then, it became a valuable source of fatty acids for the soapmaker and the fatty acid distiller. Soapstock was shipped from the refiner in the raw form as it was separated from the neutral oil. The growth of synthetic detergents over soaps reduced this market for soapstock considerably, and in the fatty acid field soapstock utilization was replaced with tall oil, a byproduct of the paper industry. These changes turned edible-oil refiners to soapstock acidulation to produce *acid oil*, which is used as a high-energy ingredient in feeds or provides a more refined product for chemical use.<sup>35</sup>

Batch acidulation of the raw soapstock discharged from the caustic refining centrifuges consists of three basic steps:<sup>36</sup>

1. Acidification with 66 °Bé sulfuric acid of the highly basic, diluted soapstock to convert the soap into free fatty acids; the acid level required varies with the amount of caustic used in refining to adjust the pH to 1.5 to 2.0.
2. Breaking the emulsion of fatty acids and foreign materials in water with heat at ~195°F or 90°C with agitation.
3. Separation of the three phases:
  - Top layer — Fatty acid product is recovered and transported to storage.
  - Middle layer — This material, which consists of an emulsion of the top- and bottom-layer material, must be recycled for reprocessing.
  - Bottom layer — The acidified wastewater is removed, neutralized, and disposed of in the wastewater system.

The problems associated with acidulation of soapstock are mainly the corrosive nature of the process and the fact that the separation of the acid-oil phase from the acid-water phase is often relatively poor, which leads to high fat losses and wastewater contamination with fatty material. Federal, state, and municipal legislation enacted for pollution abatement mandated more effective processes for clarification of acid water streams from acidulation. Continuous acidulation of soapstock and washwater as it is discharged from the refinery has provided a byproduct of acid oil with the required quality standards and an acid wastewater with fewer, more manageable contaminants. Soapstock should be processed as soon as possible after it is produced to minimize fermentation and emulsification. Several different continuous acidulation systems of varying designs are available.

The major reason for acidulating soapstock is to remove moisture so that a smaller volume is obtained for handling or storage. Acid oil is essentially the fatty portions of soapstock with the moisture content reduced to 1.0 or 2.0%. It is traded on a total fatty acid (TFA) basis of 95%, and shipments can be rejected if the TFA falls below 85%. The impurities originally in the crude oil, such as phosphatides, carbohydrates, proteins, pigments, sterols, or heavy metals, are transferred in part or in full to the soapstock during refining and then to the acid oil with acidulation.

Probably the greatest volume usage for acidulated soapstock is for animal feeds. Acid oils have become one of the essential components in many animal feeds. They are high-energy ingredients that provide 9 calories per gram when metabolized as compared to 4 calories per gram from starch or protein. Acid oils act as carriers and protectors for several fat-soluble vitamins and antioxidants and are an excellent source of polyunsaturates in most cases. The main competition for the formulated animal feeds is corn, which provides 3.5 calories per gram; therefore, acid oils cannot cost more than 2.6 times the price of corn to be economically competitive. Two potential problems for this application of acid oil are (1) residual sulfuric acid and its reaction products decrease the palatability to most animals, and (2) deodorizer distillates cannot be a component of the acid oil because of the pesticide contents.<sup>37</sup>

An alternative to soapstock acidulation has been used on a limited basis — a neutralized dried soapstock process. This alternative process, which converts the soapstock to a neutral pH followed by drum drying, produces a product that has performed well as a fat source in feeds for chickens and cattle, and the only effluent is evaporated water.<sup>38</sup> This process reduces the load on a plant wastewater treatment facility more than any of the alternatives except for shipping raw soapstock.

### **2.5.7.2 Hydrated Gums Processing**

Lecithin is the preferred outlet for the hydrated gums recovered from water degumming. Commercial lecithin is one of the most important byproducts of the edible-oil processing industry because of its functionality and wide application in food systems and industrial utility; however, the gums hydrated from soybean oil alone far exceed the market requirements for lecithin. Estimates are that less than one third of the soybean oil processed will satisfy the lecithin demands. Another outlet available to the crusher/refiner is to incorporate the recovered gums back into the meal produced. For some operations, this alternative solves a meal-dusting problem, as well as adding value to the gums.

Lecithin is the commercial name for a naturally occurring surface-active agent made up of a mixture of phospholipids. It can be obtained from a number of vegetable oils, but the major source is soybean oil phospholipids or gums, which provide excellent emulsification properties with good flavor and color. Lecithin production starts with degumming the crude oil with approximately 2% steam or water added during slow agitation to hydrate the lecithin. The hydrated gums are separated from the crude oil and dried carefully to below 1.0% moisture to avoid damaging the color. After cooling, ingredients are added to the lecithin to meet the desired specification limits. Soybean oil and fatty acid additions are used to control acetone-insoluble matter, acid value, and viscosity. Lecithin can be chemically bleached with hydrogen peroxide, either before or after drying, to control the color. The National Soybean Processors Association rules define six common grades of lecithin. In addition, a variety of modified lecithins can be produced for specialty uses.<sup>39</sup>

The crude-oil degumming process affects the quality and performance of lecithin products. For example, most additives used to aid degumming are usually deleterious to the lecithin, except for acetic anhydride and enzymes. Other additives, such as phosphoric acid, tend to burn and darken the lecithin on drying and pollute water streams. Oxalic acid does not pollute,<sup>40</sup> but it does render lecithin toxic, and inorganic salts affect the physical and functional properties.<sup>41</sup> The acid-degummed lecithins have also exhibited poor functionality (i.e., inferior instantizing properties in cocoa powders and milk products).<sup>42</sup>

## **2.6 PREBLEACHING**

The purpose of bleaching is not only to provide a lighter colored oil but also to purify it in preparation for further processing. Refined oil contains traces of a number of undesirable impurities either in solution or as colloidal suspensions. These impurities compete with the color pigments for space on the adsorbent surface. In many cases, the bleaching process is performed more for the removal of the nonpigment materials such as soap, gums, and prooxidant metals, which hinder filtration, poison hydrogenation catalyst, darken the oils, and affect finished oil flavor. Another function considered primary by many quality processors is the removal of peroxides and secondary oxidation products. The key parameters for the bleaching process are (1) procedure, (2) adsorbent type and dosage, (3) temperature, (4) time, (5) moisture,

and (6) filtration. Each variable must be considered in light of the system used and the oil to be bleached.<sup>10,43–48</sup>

## 2.6.1 Procedure

The three most common types of contact bleaching methods used for edible fats and oils are batch atmospheric, batch vacuum, and continuous vacuum. This sequence is also the chronological order in which the different methods were developed. Figure 2.5 diagrams the process flow for the three types of bleaching systems.

### 2.6.1.1 Batch Atmospheric

Oil at approximately 160°F (71°C) is pumped into an open-top tank equipped with steam coils, or a steam jacket, and a paddle agitator. Bleaching earth is added from the top of the tank with the agitator running; the temperature is raised to bleaching temperature and maintained for a short time. Next, the oil is recirculated through a filter press and back to the bleaching vessel until the oil is clear, then it is pumped to storage.

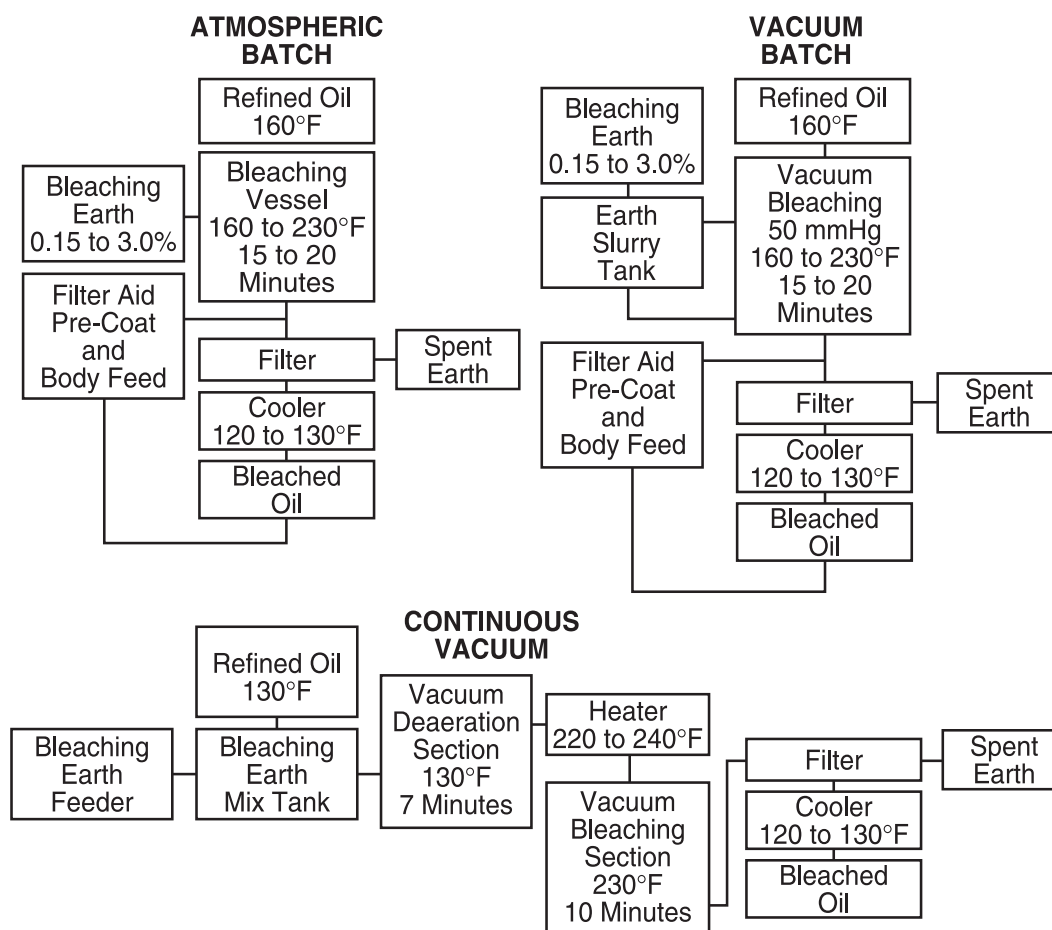


Figure 2.5 Typical bleaching process flow sequence.

### **2.6.1.2 Batch Vacuum**

Bleaching earth is added to an agitated slurry tank containing a small portion of the refined oil at 160°F (71°C). This slurry is transferred to the vacuum bleacher, which contains the balance of the oil batch. The bleaching vessel is equipped with coils or a steam jacket, an agitator, and a vacuum system. After the prescribed time at bleaching temperature under vacuum, the bleached-oil batch is cooled to 160°F (71°C), the vacuum is broken, and the oil is filtered.

### **2.6.1.3 Continuous Vacuum**

Bleaching clay is continuously fed into a stream of oil at 160°F (71°C), and this mixture is sprayed into a vacuum chamber to remove both water and air from the clay and the oil. The product temperature is raised to bleaching temperature with a heat exchanger and then sprayed into a second chamber for bleaching. After the bleaching retention time, it is filtered in a closed-type filter and cooled before the vacuum is broken.

The use of activated clays and higher-temperature bleaching led to the need for protection from atmospheric oxidation, which is provided by the vacuum-bleaching process. Oxidative reactions during atmospheric bleaching cause a fading of some color pigments to lighten the color but also the formation of new nonabsorbent colors and fixation of other colors that darken the oil instead of lightening it. New color formation is believed to be the result of oxidation of red chroman-5,6 quinones from tocopherol, which does not respond to adsorption. Vacuum bleaching is more effective than atmospheric bleaching because it can use less clay, operates at lower bleaching temperatures, effects quicker moisture evacuation for less free fatty acid development from hydrolysis, and does not expose the oil to oxidation at high temperatures. Many versions of the bleaching process are in use; however, most edible-oil processors will prebleach with a continuous vacuum type of system. Continuous bleaching is preferable because large volumes can be processed without interruptions to empty and refill the bleacher, and the process conditions can be adjusted as the operation progresses.<sup>48</sup>

## **2.6.2 Bleaching Agents**

Chemical agents have been used or proposed for use, but practically all edible-oil decoloration and purification is accomplished with adsorptive clays, synthetic silica, and carbons. The basic kinds of adsorbents used in edible-oil bleaching are neutral clays, activated earths, activated carbon, and synthetic amorphous silica.

### **2.6.2.1 Natural Bleaching Earth**

Bentonite clays that exhibit absorptive properties in their natural state are classified as natural bleaching earths, or *Fuller's earth*. Molecular lattice structure, macropore structure, and particle size all affect the capacity of earths to adsorb water,

oil, phosphatides, soap, color bodies, and metals. The better natural earths can absorb 15% of their own weight in pigments and other impurities but also retain about 30% neutral oil. Natural clays perform best with atmospheric bleaching and are employed for easily bleached oils such as coconut, lard, and tallow. The natural earths do not elevate the free fatty acid content nor isomerize unsaturated fatty acid groups; however, for dark or difficult-to-absorb pigments or impurities, prohibitive levels of the natural earths are required, which make the activated materials more attractive.

### **2.6.2.2 Activated Bleaching Earth**

Bentonite clays are also used to produce activated bleaching earths, but the clays are a type that contains a high proportion of montmorillonite. This hydrous aluminum silicate has considerable capacity for exchanging part of the aluminum for magnesium, alkalies, and other bases. Interestingly, most bentonites that exhibit high natural bleaching power are not suitable for activation, and most clays used for activated clay products have a poor natural bleaching activity. Treatment, to varying degrees, with sulfuric or hydrochloric acid, washing, drying, and milling alter the bleaching media's degree of acidity, adsorption capabilities, and particle size distribution.<sup>44</sup> The acid treatment of montmorillonite clay produces a specialty adsorbent from a naturally occurring mineral. During this process, the physical structure and chemical composition are altered in a controlled way to maximize specific properties. An efficient bleaching earth is produced with a surface of the correct chemical composition and pore distribution selectively attractive to the detrimental components of the refined oils.

Particle size is also a major physical parameter affecting bleaching-earth performance, as all adsorption theory considers adsorption as a surface phenomena. In general, the finest particle size clays have the best bleaching power, but particles that are too small create severe filtration problems and oil retention is increased; therefore, the adsorbent used should have as small a particle size as can be effectively handled by the filter system. In practice, a compromise particle size provides acceptable filtration performance and minimizes oil loss without diminishing bleaching performance.<sup>45</sup>

Activated bleaching earths normally contain 10 to 18% moisture, which supports the montmorillonite layers in the clays. If the clay is completely dried prior to bleaching, the layers collapse to decrease the surface area available to adsorb the pigments and other impurities.

Apparent bulk density (weight per unit volume) is dependent upon the amount of void space in the clay — the more void space, the lower the density. Activated clays have a lower bulk density than do natural clays for increased oil retention. The increased void space and total surface area can retain as much as 70% of the bleaching earths, weight in oil; however, lower activated clay usage level requirements normally result in a lower overall bleached oil loss with a lower bleach color and increased impurity removal.<sup>10</sup>

The activated bleaching earths are more likely to split soap residues to elevate FFAs, destroy peroxides and secondary oxidation products, and promote isomerization. The latter effect is more pronounced at temperatures above 300°F (150°C), which is well above the optimum bleaching conditions. The modified bleaching

earths are especially useful for bleaching the most difficult oils, such as palm, soybean, and canola, or as part of the physical refining pretreatment process for the removal of metals and phosphatides.

### **2.6.2.3 Activated Carbon**

A wide variety of carbonaceous raw materials can be used to form activated carbon by carbonization at high temperatures, combined with the use of activating materials such as phosphoric acid, metal salts, etc. The treated material is washed, dried, and ground to produce activated carbons of various pore sizes, internal specific surface areas, and alkalinity or acidity. Activity is determined by the chemical state and a large specific surface area. Carbon is used sparingly by most processors due to problems with filtration, relatively high cost, and high oil retention; carbon can retain up to 150% of its weight of oil. When utilized, it is normally added in combination with bleaching earths at 5 to 10% of the earth volume. Carbon is effective in adsorbing certain impurities not affected by earths; for example, some aromatic materials that are not volatilized by deodorization can be satisfactorily removed with activated carbon.<sup>46</sup>

### **2.6.2.4 Silica Adsorbent**

Silica is a chemically inert synthetic amorphous silica adsorbent with an affinity for polar contaminants. The surface area, porosity, and moisture content of the silica adsorbents provide them the capability of adsorbing secondary oxidation products (aldehydes, ketones), phosphatidic compounds, sulfur compounds, trace metals, and soap. The function of the moisture is to hold the pores open and aid in the attraction of the polar contaminants. Most of the synthetic silicas do not have significant direct adsorption capabilities for carotenoid or chlorophyll compounds, but the removal of the other impurities enhances the efficiency of the bleaching earths.<sup>18</sup>

### **2.6.3 Bleaching Earth Dosage**

The amount of bleaching earth used depends upon the type of absorbent used and the type of refined oil, as well as the adsorption of color bodies and other impurities required. The percentage of clays used vary in a wide range from 0.15 to 3.0%, and only in extreme cases are higher quantities used.<sup>47</sup> Use of acid-treated or -activated earths far exceeds that of natural clays due to the higher bleaching efficiency, particularly with dark or high chlorophyll oils. On the basis of adsorbent activity, the acid-activated clays are generally 1.5 to 2 times more effective as bleaching agents than are the natural earths. The efficiency of an absorbent is measured by the minimum dose required to reduce the concentration of adsorbate to the required level. Therefore, the kind and amount of earth or carbon used need only be enough to clean up the oil preparatory to hydrogenation or deodorization and to remove any undesirable impurities and pigments that will not be removed in later processing. The minimum required bleach is usually best as overbleaching increases oil losses and can lead to flavor, oxidative, and even color instability. The removal

of color pigments is a common, simple visual guide, often used to gauge the overall performance and adjust levels required of a bleaching earth; however, the ability to remove other undesirable impurities is less readily apparent. The choice of the correct bleaching earth and the level to use in any specific application must take into consideration the removal of all the impurities as measured by peroxide value reduced to zero, chlorophyll reduced to less than 1.0 ppm, phosphorus reduced to less than 1.0 ppm, negative soap, and the Lovibond red determined for the specific source oil.

The bleaching step in fats and oils processing has benefited in recent years from increased interest in physical refining due to the development of different ways to improve the removal of the nontriglyceride materials. One such development has been the introduction of the use of synthetic silica as part of the adsorption process. It is particularly recommended for use with, and preferably before, bleaching-earth treatment. It has been found to have an affinity for the compounds that reduce the efficacy of bleaching earths. Several different options are offered for the use of silica adsorbents. The simplest option adds silica adsorbent (~0.2%) with the bleaching earth prior to bleaching to reduce the clay usage. A 40% reduction in bleaching earth usage, less neutral-oil loss, and longer filter cycles are claimed by W.R. Grace for their TrySyl product. A second bleaching option adds the silica separate from the bleaching clay, which is precoated on the filter press. The silica collapses in the bleaching vessel, thus trapping the contaminants to preserve the clay for color pigment removal. An 80% reduction in bleaching earth is claimed with this enhanced silica option.<sup>23</sup>

#### 2.6.4 Temperature

Both the synthetic silicas and bleaching earths should be slurried with the oil at relatively low temperatures (158°F or 70°C), and then the complete mixture is increased to the final bleach temperature (194 to 212°F or 90 to 100°C). Experience has shown that final bleach colors are darker when the adsorbents are added to hot oil. Evidently, this effect is due to one or both of the following two factors:

1. Adding the adsorbent to hot oil reduces its adsorptive capacity because the moisture is driven off too rapidly, causing a collapse of the lattice structure, which reduces the effective surface area to adsorb impurities and pigments.
2. The oil is unprotected against oxidation when heated before the adsorbent is added, which can cause some color fixation or set.

Bleaching-clay activity increases as the temperature is increased by reducing the viscosity of the oil, but decoloration declines after the optimum temperature has been reached and color fixation occurs. The optimum earth–oil contact temperature is dependent upon the oil type and the type of bleaching system. Temperature requirements for vacuum bleaching systems are normally lower than those for atmospheric bleaching to reach optimum color removal. Temperature also affects other properties of the oil, so it should be kept as low as possible to minimize product damage but high enough for adequate adsorbance of the impurities and color pigments.<sup>48</sup>

Production of an oil with acceptable oxidative stability requires careful control of the process temperatures. Few problems are encountered when the bleaching temperatures remain below 230°F (110°C) and steps are taken to control air oxida-



tion. Anisidine values begin to rise with bleaching temperatures above 230°F (110°C), indicating damage to the oxidative stability. The optimum bleaching temperatures of nearly all edible oils range between 160 and 230°F (70 to 110°C). The activity of an absorbent in bleaching an edible fat or oil is at a maximum at some particular temperature that varies with oil type and process. Low temperatures favor the retention of the adsorbed pigment on the bleaching media surface, while higher temperatures favor movement into the pores where chemisorption is most likely, which promotes structural changes in the unsaturated fatty acid groups. Extremely high-temperature processing must be avoided to prevent isomerization of the unsaturated fatty acid groups and excessive FFA development.

### 2.6.5 Time

In theory, adsorption should be practically instantaneous; however, in practice this is not the case. The rate of color decrease is very rapid during the first few minutes that the adsorbent is in contact with the oil and then decreases to a point where equilibrium is reached and no more color is removed. Time is required for the adsorbent to release all of the bound moisture and take up the color pigments and impurities to maximum capacity. Usually, a contact time of 15 to 20 minutes is adequate at a bleaching temperature above the boiling point of water. The usual error is to extend bleaching time beyond the optimum.

Contact time for bleaching is made up of two time periods: (1) the time in the bleaching vessel or continuous stream, and (2) the contact time in the filter during recirculation or final filtering. Continued or progressive reduction in peroxides and the other impurities as filtering continues is caused by *press effect*, a benefit provided by the earth buildup in the filter with continued use. Some processors take advantage of this effect by decreasing the level of earth used in oils to be filtered with partly filled filters.

When silica is used, it is recommended that it be added to the oil first, with strong agitation and vacuum for 15 minutes, before the bleaching earth is introduced. During this time the silica should adsorb soaps, secondary oxidation products, phosphatides, and trace metals, which normally compete with the color pigments for space on the bleaching earth surface. The absence of these impurities increases the efficiency of the bleaching earths to adsorb the chlorophylloid and carotenoid pigments. Experience has also indicated that the press effect may be more effective than the normal bleaching earth and oil mixing with the use of the synthetic silicas. W.R. Grace has advocated the use of packed bed filtration to take advantage of the press effect.<sup>23</sup>

### 2.6.6 Moisture

The presence of some moisture seems to be essential for good adsorbance and bleaching action. Bleaching earths that have been completely dried before use have been found to be inactive. The adsorbents normally contain from 10 to 18% moisture, which acts as a structural support to keep the montmorillonite layers apart. During bleaching, it is necessary to remove the moisture in the adsorbent to obtain optimum

adsorption capacity; the color bodies and other impurities cannot be adsorbed to maximum capacity until all the water has been removed. The bound moisture is not released until the elevated bleaching temperatures are attained. Refined oil can contain moisture levels from less than 0.1 to as high as 1.0%, which must also be removed for effective adsorption of the traces of soap remaining after refining. Experience has indicated that a slightly wet oil may be beneficial for the removal of color pigments and flavor precursors to provide a lighter, more stable oil. Maximum adsorption is achieved when the silicas and bleaching earth are slurried with the oil below the boiling point of water, then gradually increasing the mix to bleaching temperature. Adding the bleaching earth before heating the oil has also been found to inhibit heat darkening.

### 2.6.7 Filtration

After an adsorbent has selectively captured the impurities, it must be removed from the oil before it becomes a catalyst for color development or other undesirable reactions. Filtration, the separation method most often used for spent bleaching-earth removal, is the process of passing a fluid through a permeable filter material to separate particles from the fluid. Examples of the filtration materials utilized include filter paper, filter cloth, filter screen, and membranes. Filter aids such as diatomite, perlite, or cellulose are usually used in conjunction with the permeable filters for surface protection.

The three steps of filtration are precoating, filtering, and cleaning. The purpose of the precoat is to protect the filter screens, provide immediate clarity, improve the flow rate, and aid in filter cake removal during cleaning. It also helps to prevent blinding, which stops the product flow. Precoating is accomplished by slurring filter aid with previously filtered oil and allowing the oil to carry the filter aid to the filter, deposit it on the filter screen, and return to the precoat slurry tank to pick up more filter aid. The amount of precoat is determined by the filter area, usually 5 to 11 kg/m<sup>2</sup>. The flow rate during precoating should be the same as during filtration to obtain an even coating on the filter. Uneven coatings results in blinded filters and short filtration cycles.

During filtration, *body feed*, or the continuous addition of filter aid, can be used to help prevent blinding of the suspended solids on the precoat. The body feed surrounds the suspended solids to provide flow around them. The body feed slurry of filter aid and oil is injected into the system prior to the filter. The suspended solids are ridged or deformable and can elongate under pressure to extrude through the filter cake and slow or block the product flow. Body feed will coat the deformed solids, allowing them to be retained on the filter cake.

Several indicators are utilized to determine the point at which the filter space has been filled with solids from the bleached oil: when the pressure drop across the leaves reaches a predetermined level, when a predetermined decrease in flow rate occurs, or when a calculated load level is reached. Short cycles or premature filter stoppages are usually the result of (1) inadequate body feed; (2) too high flow rate, which can cause the solids to pack; (3) too low flow rate, which can allow the solids to settle and block the flow rate; (4) blinded screens, which reduce the filter surface

area; or (5) solid load exceeding filter capacity. The perfect circumstance is when the differential pressure is reached and the flow rate is severely reduced at the same time that the calculated filter capacity is exhausted. Once the filter cycle is complete, the filter cake must be removed and the process repeated all over again.<sup>49</sup>

Traditionally, either plate and frame filters or pressure leaf filters have been used for bleach-clay removal. The sequence of change in usage was approximately as follows: plate and frame filters, pressure leaf filters, self-cleaning closed filters, and automated filters. Pressure leaf filters began to replace plate and frame presses for several reasons. One of the major reasons was that the leaf filters were easier to clean than the plate and frame presses, and labor costs were less. Labor costs have been the impetus for more complete automation of the bleaching operations and all the other processes. Currently, completely self-cleaning closed filters that operate on an automated cycle are available.<sup>50</sup>

### 2.6.8 Bleaching Byproduct

The spent bleaching earth removed from the bleached oil with filters represents a substantial amount of waste material. The most common handling procedure is to discard spent bleaching earth directly from the filters to a landfill. The spent bleaching earth oxidizes rapidly when exposed to the air to develop a strong odor, and spontaneous combustion easily occurs, especially with oils high in polyunsaturates. Therefore, the spent bleaching earth must be covered with soil or sand soon after dumping.

The oil content of the spent bleaching earth may range from 25 to 75% of the weight of the earth. Oil retention is affected by the type of filters, the type of refined oil bleached, and the degree of color reduction. It is important to recover as much of this oil as possible, but methods that are too efficient may cause desorption of the impurities adsorbed by the bleaching earth from the refined oil. Because it is possible to remove a substantial portion of the oil from the spent earth, it may become a legal requirement in the future. Oil can be recovered by several methods, some performed on the cake while it is still in the filter and others after it has been removed from the filter.<sup>51-54</sup> Some of the procedures for oil recovery include:

- *Cake steaming* — Blowing steam through the cake in the filter can reduce the oil content to as low as 20%; however, the oil content should not be reduced below 25% because the steam wetting may cause desorption of the impurities below this point to lower the quality of the recovered oil. Also, spent earth with a low oil content oxidizes more rapidly when exposed to the atmosphere.
- *Hot water extraction* — Circulation of hot water at 200°F (95°C) through the filter cake while maintaining a pressure of 5 atm at a rapid flow rate can displace as much as 55 to 70% of the oil for collection and separation. Washing time may be extended to 30 minutes, but 90% of the recoverable oil is obtained in the first 10 minutes. After water washing, the filter cake may be partially dried with steam. Drying with air can cause the filter to catch on fire, especially when oils high in unsaturates are processed.
- *Solvent extraction* — Organic solvents can be used to extract the oil from the filter cake in certain enclosed filters as a separate process. Hexane, a nonpolar solvent, has performed well but strong polar solvents such as acetone or trichlorethylene

may also recover the impurities separated from the refined oil. Solvent extraction provides oil yields of over 95% with a quality comparable to the originally filtered oil. Explosion-proof environments, buildings, and equipment, which are quite expensive, are required for solvent extraction. In most cases, the less efficient hot-water extraction will be more practical than solvent extraction, and it may be feasible only for very large processing facilities that generate large quantities of spent earth.

- *Solvent extraction with oilseeds* — Extraction of the bleaching earths in a mixture with oilseeds has been practiced by some extraction plants with processing capabilities, but the potential problems for this type of recovery may outweigh the savings; for example, the mineral content of the meal may be increased beyond the acceptable limits, and the recovered oil may decrease the quality of the new oil extracted. The oxidation products and polymers from the recovered oil could contaminate the fresh oil.
- *Water/lye extraction* — Oil can be extracted from the spent bleaching earth by suspending it in double the amount of water and boiling with a concentrated lye. The oil accumulates on the surface of the slurry for recovery. The remaining slurry can be centrifuged with separations as high as 85% efficiency. The separated bleaching clay has a light gray color, is almost odorless, and does not ignite spontaneously. It can be used as a landfill material to cover other refuse, instead of requiring soil or sand to cover it. The procedure is simple and relatively inexpensive, but a dark-colored, low-quality oil suitable only for technical purposes or possibly cattle feed is obtained.

## 2.7 HYDROGENATION

In the United States and Northern Europe, animal fats in the form of butter, lard, and tallow were the major source of edible fats until development of the hydrogenation process. This process made it possible for vegetable oils to be converted into plastic fat forms that people were accustomed to, with greater flavor stability at a lower cost. From the time that the British patent on liquid-phase hydrogenation was issued to Norman in 1903 and its introduction in the United States in 1911, few chemical processes made as great an economic impact on any industry. Hydrogenation opened new markets for vegetable-oils processing and provided the means for the development of many specialty fats and oils products.

Oil is hydrogenated for two reasons. One reason is to change naturally occurring fats and oils into physical forms with the consistency and handling characteristics required for functionality. Hydrogenated edible fats and oils products can be prepared with creaming properties, frying stability, sharp melting properties, and the other functional characteristics desired for specific applications. The second reason for hydrogenation is to increase oxidative stability. Flavor stability is necessary to maintain product acceptability for prolonged periods after processing and packaging and for use as an ingredient in a finished product. A wide range of fats and oils products can be produced with the hydrogenation process depending upon the conditions used, the starting oils, and the degree of saturation or isomerization.

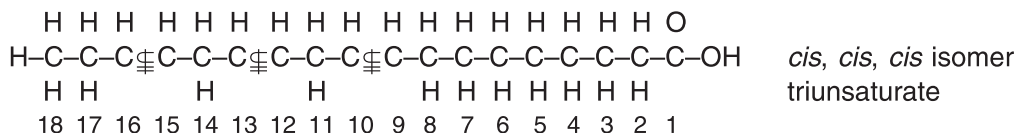
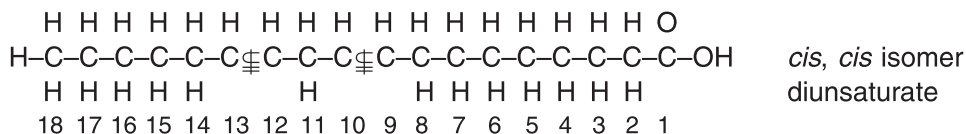
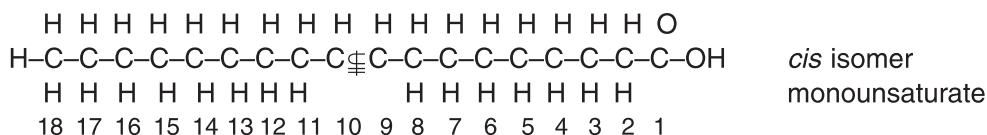
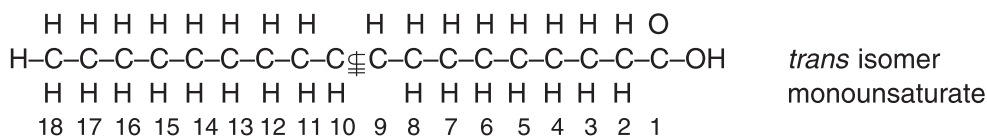
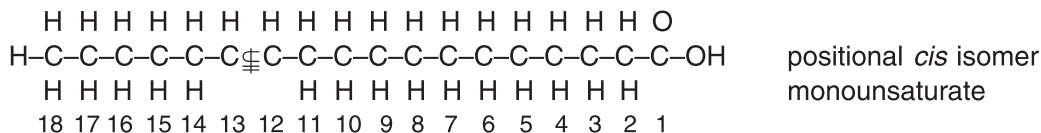
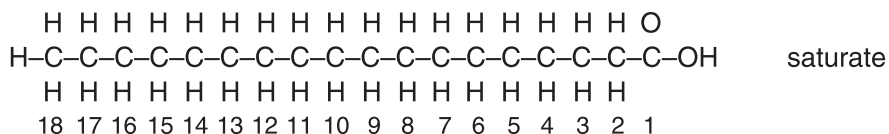
Liquid-phase, catalytic hydrogenation is one of the most important and complex chemical reactions carried out in the processing of edible fats and oils.<sup>55-58</sup> Most

chemistry textbooks describe hydrogenation of oils as a simple saturation of double bonds in an unsaturated fat with hydrogen, using nickel as a catalyst. Actually, that is only one of several very complex reactions during hydrogenation. The products of hydrogenation are a very complex mixture because of the simultaneous reactions that occur: (1) saturation of double bonds; (2) *cis-trans*-isomerization of double bonds; and (3) shifts of double-bond locations, usually to the lower energy conjugated state.

Chemically, fats and oils are a combination of glycerin and fatty acids called *triglycerides*. The portions of triglycerides that can be changed with hydrogenation are classified as unsaturated fatty acids. Saturated fatty acids contain only single carbon-to-carbon bonds and are the least reactive chemically. Physically, they have higher melting points and are solid at room temperature. Unsaturated fatty acids contain one or more carbon-to-carbon double bonds and are liquid at room temperature with substantially lower melting points than their saturated fatty acid counterparts. In the process of hydrogenation, it is possible to chemically react hydrogen gas with the double bonds in the carbon chain of the unsaturated fatty acid, converting it to a more saturated fatty acid, shifting it to a new position, or twisting it to the *trans* configuration, all of which increase its melting point. [Table 2.2](#) illustrates the chemical structure of the natural 18 carbon fatty acids and the changes possible with hydrogenation.

Hydrogenation can take place only when the three reactants have been brought together: unsaturated oil, catalyst, and hydrogen gas. The hydrogen gas must be dissolved in the liquid oil before it can diffuse through the liquid to the solid catalyst surface. Each absorbed unsaturated fatty acid can then react with a hydrogen atom to complete the saturation of the double bond, shift it to a new position, or twist it to a higher melting *trans* form. Both positional and geometric or *trans*-isomers are very important to the production of partially hydrogenated fats. If the unsaturated oil to hydrogenation contains mono-, di-, and triunsaturates, there may be competition for the catalyst surface. The di- and triunsaturates are preferentially absorbed and partially isomerized or hydrogenated to a monounsaturate until their concentration is very low, permitting the monounsaturate to be absorbed and reacted.

Achievement of the desired hydrogenated oil product is usually measured with the solids fat index (SFI), which measures the amount of solids present in a fat at different temperatures from below room temperature to above body temperature. Natural fats are not single compounds, and the hydrogenated products are even more complex mixtures due to the simultaneous reactions. Not only are double bonds saturated with hydrogen, but some of the remaining bonds are isomerized: geometric isomerization changes the low-melting *cis* form to a higher melting *trans* form, and positional isomers shift the double bond away from its natural position in the carbon chain. Extensive geometrical or *trans*-isomerization tends to give products that are hard at low temperatures but soft at high temperatures, which results in steep SFI curves. A lesser but significant effect on melting points is contributed by the positional isomerization, as the shift of a double bond in a carbon chain affects the melting point of the hydrogenated oil. Additionally, the bonds that are shifted can

**Table 2.2 Fatty Acid Structures****Linolenic fatty acid (C-18:3) melting point 9°F (-13°C)****Linoleic fatty acid (C-18:2) melting point 19°F (-7°C)****Oleic fatty acid (C-18:1) melting point 61°F (16°C)****Elaidic fatty acid (C-18:1) melting point 110.7°F (43.7°C)****Petroselinic fatty acid (C-18:1) melting point 86°F (30°C)****Stearic fatty acid (C-18:0) melting point 158°F (70°C)**

be in either the *cis* or *trans* form, which further substantiates the complexity of the hydrogenated oil process.

Selective hydrogenation is the tool by which partial hydrogenation can be accomplished in a controlled manner. Selectivity is the saturation with hydrogen of the double bonds in the most unsaturated fatty acid before that of a less unsaturated fatty acid. In a theoretical sense, an oil hardened with perfect preferential selectivity would first have all of its linolenic fatty acids (C-18:3) reduced to linoleic fatty acids (C-18:2) before any linoleic was reduced to oleic (C-18:1); then, all linoleic fatty acids would be reduced to oleic before any oleic was saturated to stearic (C-18:0). Unfortunately, this does not happen in actual practice, but it is possible to vary the hydrogenation rate of linoleic to that of oleic from the very selective conditions of

50 to 1 to the less selective conditions of 4 linoleic to 1 oleic. The latter is generally described as nonselective.

Formation of the high-melting unsaturated fats or isomerization accompanies hydrogenation and appears to be in proportion to the selectivity of the reaction. Therefore, compromises must be made between selectivity and isomer formation when determining the best hydrogenation conditions for the various basestocks. Control of the operating variables that affect the hydrogenation of fats and oils is necessary to produce the desired product functionality.

## **2.7.1 Operating Variables**

Hydrogenation is a reaction of three components: oil, hydrogen, and catalyst. The reaction takes place on the surface of the catalyst where the oil and gas molecules are adsorbed and brought into close contact. Therefore, any condition which affects the catalyst surface or controls the supply of gas to the catalyst surface will, in turn, affect the course and rate of the reaction. The variables that can affect the results of the hydrogenation are temperature, degree of agitation, hydrogen pressure in the reactor, catalyst amount, type of catalyst, hydrogen gas purity, feedstock source, and feedstock quality. The effects of the variables include the following.

### **2.7.1.1 Temperature**

Hydrogenation, like most chemical reactions, proceeds at a faster rate with increased temperatures. An increase in temperature decreases the solubility of the hydrogen gas in the liquid oil while increasing the reaction rate. This causes quicker hydrogen removal from the catalyst to reduce the quantity of hydrogen on the catalyst surface, resulting in a high selectivity and isomer formation; therefore, increased temperature increases selectivity, *trans*-isomer development, and the reaction rate that results in a steep SFI curve.

Because hydrogenation is an exothermic reaction, it will create heat as long as the reaction is active; a decrease of one iodine value increases the reaction temperature by 1.6 to 1.7°C (2.9 to 3.1°F). Temperature increases will increase the reaction rate until an optimum is reached. At this point, cooling of the reaction mixture is required to continue hydrogenation. The optimum temperature varies for different products, but most oils probably reach their maximum temperature at 450 to 500°F (230 to 260°C).

### **2.7.1.2 Pressure**

Most edible fats and oils hydrogenations are performed at hydrogen pressures ranging from 0.7 to 4.0 bar (10 to 60 psig). At low pressures, the hydrogen gas dissolved in the oil does not cover the catalyst surface, while at high pressure hydrogen is readily available for saturation of the double bonds. The increased saturation rate results in a decrease in *trans*-isomer development and selectivity to produce a flatter SFI curve.

### **2.7.1.3 Agitation**

The main function of agitation is to supply dissolved hydrogen to the catalyst surface, but the reaction mass must also be agitated for the distribution of heat or cooling for temperature control and suspension of the catalyst throughout the oil mixture for uniformity of reaction. Agitation has a significant effect upon selectivity and isomerization: Both are decreased because the catalyst is supplied with sufficient hydrogen to increase the reaction rate.

### **2.7.1.4 Catalyst Level**

The hydrogenation reaction rate increases as the catalyst concentration is increased up to a point and then levels off. The increase in rate is caused by an increase in active catalyst surface; however, a maximum is reached because at very high levels hydrogen will not dissolve fast enough to adequately supply the higher catalyst levels. Both selectivity and *trans*-isomer formation are increased with catalyst concentration increases, but only slightly.

### **2.7.1.5 Catalyst Type**

The choice of catalysts has a strong influence on the reaction rate, preferential selectivity, and geometric isomerization. Nickel catalysts are used almost exclusively for edible fats and oils hydrogenation. Catalysts are prepared by a variety of techniques, some propriety to the catalyst supplier; however, nickel catalyst is usually prepared by the reduction of a nickel salt and supported on an inert solid or flaked in hardfat or a combination of the two. The activity of a catalyst depends on the number of active sites available for hydrogenation. These active sites may be located on the surface of the catalyst or deep inside the pores. High-selectivity catalysts allow the processor to reduce the linolenic fatty acid without producing excessive amounts of stearic fatty acid, thus producing a product with good oxidative stability and a low melting point. The selectivity characteristics of a catalyst are unrelated to the ability of the catalyst to form *trans*-fatty acids because the catalyst may have a very low or very high selectivity, but all common nickel catalysts appear to produce the same level of *trans*-fatty acids at the same conditions. However, catalyst may be treated with other materials such as sulfur, which increases the amount of *trans*-fatty acids unsaturation.

Sulfur-poisoned catalysts produce larger quantities of *trans*-isomers in hydrogenated oils. Reaction with sulfur inhibits the capacity of nickel to adsorb and dissociate hydrogen, reducing the total activity of the catalyst. As the ability of the nickel to hydrogenate is reduced, its tendency to promote isomerization is enhanced. Hydrogenated oils with a relatively high melting point at a high iodine value, which results in a very steep SFI slopes, are the result of the high *trans*-isomer content. Commercially, sulfur-treated catalysts have been found to provide more uniform performance than products that are sulfur-poisoned during processing.

Copper-chromite catalyst has been used for selective hydrogenation of linolenic fatty acid to linoleic fatty acid in soybean oil for a more flavorful, stable salad oil with higher winterization yields. The selectivity offered by these catalysts is excellent, but the activity is poor and they are more sensitive to catalyst poisons.



Precious metals have been investigated and found effective as hydrogenation catalysts. Evaluations have shown that basestocks hydrogenated with 0.0005% palladium modified with silver and bismuth were exceedingly more active and slightly more selective with more *trans*-fatty acids development than were equivalent stocks prepared with nickel catalyst. Subsequent evaluations have shown that the precious metals are more active at lower temperatures than nickel. Oils have been hydrogenated at 60°C (140°F) with precious metals, while temperatures above 130 to 140°C (265 to 285°F) are required with nickel catalyst. *Trans*-isomer development is increased as the hydrogenation temperature is increased; therefore, less *trans*-isomer development should be obtained with precious metal utilization at low temperatures.<sup>59</sup> Palladium has been found to be some 30 times as active as nickel, as only 6 ppm is required to replace 200 ppm nickel. The principal deterrent to the use of palladium has been economics, both in the initial costs and recovery problems associated with the minute quantities required.

#### **2.7.1.6 Catalyst Poisons**

Refined oils and the hydrogen gas can contain impurities that modify or poison the catalyst. Catalyst poisons are a factor that can have a significant effect upon the product. The poisons effectively reduce catalyst concentration with a consequent change in the selectivity, isomerization, and rate of reaction. Impurities present in both the feedstock oil and hydrogen gas are known to have a deleterious effect upon nickel catalyst. Hydrogen gas may contain carbon monoxide, hydrogen sulfide, or ammonia. Refined oil can contain soaps, sulfur compounds, phosphatides, moisture, free fatty acids, mineral acids, and a host of other materials that can change the catalyst. Studies have determined that 1 ppm sulfur poisons 0.004% nickel, 1 ppm phosphorus poisons 0.0008% nickel, 1 ppm bromine poisons 0.00125% nickel, and 1 ppm nitrogen poisons 0.0014% nickel. Sulfur primarily affects the activity to promote isomerization by inhibiting the capacity of the nickel catalyst to absorb and dissociate hydrogen. Phosphorus in the form of phosphatides and soaps affects selectivity by residing at the catalyst pore entrance to hinder the triglyceride exit for a higher degree of saturation.<sup>60</sup> Water or moisture and free fatty acids are deactivators that decrease the hydrogenation rate by reacting chemically with the catalyst to form nickel soaps.

#### **2.7.1.7 Catalyst Reuse**

Hydrogenation with used catalyst offers economic advantages when sufficient activity remains after the previous use; however, at some point diminishing returns arise due to filtration problems, as well as changes in reaction rate and selectivity. The filtration problems include: (1) free fatty acids in the oils reacting with the catalyst to form nickel soaps, which can blind filters; (2) decreased particle size from mechanical attrition resulting in colloidal nickel, which will pass through the filter screens; and (3) excessive levels required to maintain the desired nickel content and activity due to catalyst poisons and dilution with filter aid and oil. Selectivity will decrease with each use, while *trans*-isomerization increases with each catalyst

reuse. It has also been observed that *trans*-isomers increase more rapidly when the catalyst is exposed to air after use. Usually, fats and oils processors specify new catalyst for the production of critical basestocks and reuse catalyst for those products for which selectivity is not as important. In a catalyst reuse program, the once-used catalysts are segregated to permit identification and are used by lot, with care taken to maintain the identity of each. The lots are graded down on the basis of the activity during the last use. Each succeeding grade is used for products requiring a lower degree of selectivity until finally it is used to harden low-iodine-value hardfat. In the latter usage, selectivity is of no consequence because the hardstock is substantially completely saturated, and it makes no difference if the catalyst is selective or nonselective.

### 2.7.1.8 Source Oils

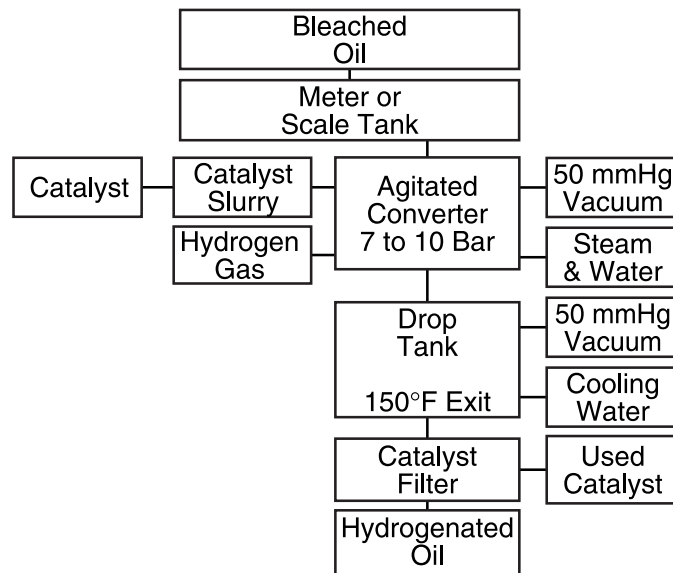
Hydrogenation selectivity depends upon the type of unsaturated fatty acids available and the number of unsaturated fatty acids per triglyceride. Those oils with high linolenic or linoleic fatty acids levels hydrogenate more rapidly and to higher melting points than oils with high oleic fatty acid levels. The relative hydrogenation reactivity for the 18-carbon fatty acids are:<sup>61</sup>

<b>Fatty Acid</b>	<b>Relative Reactivity</b>
Linolenic (C-18:3)	40
Linoleic (C-18:2)	20
Oleic (C-18:1)	1

### 2.7.2 Hydrogenation Systems

Batch hydrogenation is most commonly used in the edible-oil industry, primarily because of its simplicity and flexibility for use with different source oils. Essentially all that is required is a reaction vessel, usually referred to as a *converter*, that can withstand 7 to 10 bar (105 to 150 psig) pressure, with an agitator, heating and cooling coils, a hydrogen gas inlet, piping and pumps to move the oil in and out, and a sample port for process control of the reaction. The converter must also be provided with the means to control the three reaction variables: pressure, temperature, and rate of agitation.

Two different batch converter designs utilized for the partial hydrogenation of edible fats and oils are recirculation and dead-end. In the recirculation system, hydrogen gas is introduced at the bottom of the vessel, and nonreacted hydrogen gas is withdrawn from the headspace, purified, and returned to the converter. The converter is almost always filled with hydrogen under pressure in the operation of the recirculation system. Hydrogenation begins immediately when the catalyst is added with the oil charge during the heating period and thereafter until the endpoint is attained when recirculation is discontinued. Reaction temperature is controlled by circulating water through the cooling coils to carry away the heat of reaction. The hydrogenated oil is pumped out of the converter through an external cooler to a filter for catalyst removal.



**Figure 2.6** Dead-end batch hydrogenation process flow.

A dead-end hydrogenation system is outlined in Figure 2.6. The converter is loaded with oil from a scale tank or metering device. Converter vacuum is utilized to deaerate, dry, and prevent any hydrogenation while heating with steam to reaction temperature. Catalyst, slurried in a portion of the feedstock, is added during the heating period. When the oil reaches reaction temperature, the vacuum is discontinued and hydrogen is added until the specified pressure is attained. This pressure is maintained during the hydrogenation. An agitator designed to provide efficient hydrogen dispersion is necessary to create a vortex to draw hydrogen from the headspace back into the oil. When the exothermic reaction has raised the oil temperature close to the maximum specified temperature, cooling water is introduced into the coils. Samples are drawn from the converter via the sample port as the reaction proceeds to measure the hydrogenation progress. Agitation is suspended whenever awaiting a laboratory analysis to confirm that the endpoint has been reached. When the endpoint has been attained, the hydrogen is vented to the atmosphere through the vacuum system, and the oil is cooled in the converter, in a drop tank, or with a heat exchanger. After cooling to 150°F (65°C), the oil is filtered through a black press to separate the catalyst from the oil. Hydrogenation black presses traditionally have been of the plate and frame or pressure leaf variety.

From an operations standpoint, the two types of converters do not differ very much. In general, the dead-end type is preferred by many processors because it (1) requires less energy, (2) offers more versatility, (3) requires less capital and operating costs, and (4) is safer than the recirculation system. Quality and performance-wise, the advantages for the dead-end system are (1) oxidation and hydrolysis prevention through deaeration and dehydration provided by the vacuum during heat up and cooling, (2) more positive control of the reaction for product uniformity, and (3) the ability to vary the hydrogen pressure as well as temperature.

Most hydrogenations of edible fats and oils are performed both in the United States and in the rest of the world in batch converters. Continuous hydrogenation systems have been available for quite some time, but their commercial usage has

been limited for several reasons. The maximum value for any continuous operation is realized when it is used to produce large quantities of the same product. Considerable out-of-specification product can be produced during a change from one product to another. Because most fats and oils processors produce a variety of products, several different basestocks are routinely required that can be produced more uniformly with batch hydrogenation systems.

### 2.7.3 Hydrogenation Control

In any hydrogenation operation, except those carried out to make low-iodine-value hardfats, the ultimate aim is to produce a partially hydrogenated basestock with a definite preconceived consistency or a basestock suitable for blending with other basestocks or oils to produce the desired finished product functionality. Batch-to-batch variation in consistency is encountered even when the same hydrogenation conditions are maintained due to differences in the feedstock oil, catalyst activity, and selectivity, as well as the other minor variables. It is therefore important to identify controls that will permit the reaction to be stopped at a point that will provide the desired consistency. These controls are usually exercised at the end of the hydrogenation but can be used throughout the reaction to follow the hydrogenation progress. Physical consistency of most finished shortenings, margarines, and other fats and oils products is identified by analytical methods such as solids fat index (SFI), iodine value (IV), and/or melting points. However, time restraints during hydrogenation require more rapid controls. Hydrogenation controls used to determine basestock endpoints include:

- *Refractive index* — Hydrogenation reduces both the iodine value and the refractive index of oils. The relationship between the iodine value and refractive index depends upon the molecular weights of the glycerides, which is very nearly the same for most oils. The exceptions are the oils high in either lauric or erucic fatty acids. Correlation between iodine value and refractive index is not precise but will be within one or two units, which should be adequate to monitor the hydrogenation reaction and indicate when to interrupt the reaction for more precise evaluations.
- *Mettler dropping point* — The relationship of iodine value to melting point can be changed by varying hydrogenation conditions, catalyst types, and levels; therefore, it is necessary to measure both refractive index and melting characteristics for most basestocks with iodine values below 90. Mettler dropping point analysis can provide a reliable result in less than 30 minutes for these basestocks. Usually, the oil is hydrogenated to a refractive index before determining the Mettler dropping point, which is the controlling analysis. If the melting point (dropping point) is lower than desired, hydrogenation is continued and the process is repeated until the specified melting point is obtained.
- *Quick titer* — Refractive indices are rarely used for low-IV hardfat hydrogenation control. The refractometers are generally kept at  $40.0 \pm 0.1^\circ\text{C}$ , and the hardfats would solidify on the prism at this temperature. The hardfat is too hard for dropping point determinations, and IV or official titer determinations are too time consuming. A nonstandardized “quick titer” evaluation is usually used for endpoint control for the hardfats. In this evaluation, a titer thermometer is dipped into a hot sample directly from the converter and rotated in the air until the fat clouds

on the thermometer bulb. The correlation between iodine value and quick-titer results is different for each source oil; therefore, quick-titer limits must be predetermined for each product.

## 2.7.4 Hydrogenated Basestock System

Most prepared foods are formulated with ingredients designed for their application or, in many cases, specifically for the particular product or processing technique employed by the producer. These customer-tailored products have expanded the product base for fats and oils processors from a few basic products to literally hundreds. Each of these products could be formulated to require a different hydrogenated product for each different product. This practice with the ever-increasing number of finished products would result in a scheduling nightmare with a large number of product heels tying-up tank space and inventory. Basestock systems with a limited number of hydrogenated stock products for blending to meet the finished product requirements are utilized by most fats and oils processors. The advantages provided by a well-designed basestock system are basically control and efficiency.<sup>62</sup> The control advantages include:

- Hydrogenated oil batch blending to average minor variations
- Increased uniformity by the production of the same product more often
- Reduced contamination afforded by the ability to schedule compatible products together
- Elimination of product deviations generated from attempts to use product heels
- Elimination of rework generated by heel deterioration before use

The efficiency advantages contributed by a basestock system include:

- Hydrogenation scheduling to maintain basestock inventories rather than reacting to customer orders
- Hydrogenation of full batches instead of producing some partial batches to meet demands
- Better reaction time to meet customer requirements

Basestock requirements will vary with each processor, depending upon the customer requirements, which dictate the finished products produced. The basestock systems can include several source oils or can be limited to almost a single oil type. In either case, the basestock inventories usually consist of a few hydrogenated products that cover a wide range for blending to the desired consistencies:

- *Brush hydrogenated basestocks* — For many edible-fat ingredient specifications, a liquid oil is required. To guarantee an acceptable shelf life, the level of polyunsaturates should be low, with an absence or severely reduced level of linolenic fatty acids (C-18:3). This can be achieved by a light and highly selective hydrogenation of an oil within the oleic/linoleic fatty acid group such as soybean, sunflower, or canola. During hydrogenation, the iodine value drop is kept to a minimum to reduce the formation of saturated fatty acids, and the *trans*-isomers formation is largely suppressed. The hydrogenation should be performed at a low

temperature to reduce the formation of *trans*-isomers. A high pressure of 3 to 4 bar (45 to 60 psig), in combination with new catalyst with high activity, selectivity, and poison resistance should be used. Optimum conditions will vary considerably, depending upon the geometry of the converter, agitator, hydrogen gas purity, and the other hydrogenation variables. After hydrogenation, this basestock can be winterized or fractionated to produce a flavor-stable salad oil or a high-stability liquid oil depending upon the extent of the hydrogenation. This basestock class is also very useful in margarine oil blends, snack-frying oil, and in specialty product formulations.

- *Partially hydrogenated flat basestocks* — Many food products require fats and oils products that have an extended plastic range with good oxidative stability. The products must be soft and plastic at room temperature and still possess some body at temperatures of 100°F (38°C) with melting points only slightly above body temperature. Stability is important because of the probable exposure to baking or frying temperatures and long shelf-life expectancy. These basestock requirements can impose a conflicting set of operating conditions. Highly selective conditions are desirable to convert all linolenic and as much linoleic fatty acids as possible to oleic fatty acids for maximum stability. However, highly selective conditions also favor the formation of *trans*-isomers, which are undesirable for this application. The *trans*-isomers have higher melting points than the normal oleic fatty acid without the stability improvement. Further, the *trans*-isomers restrict the amount of saturated fatty acids that would increase the stability and serve to extend the plastic range while providing the high-temperature body desired. Usually, moderately selective conditions are utilized to produce these flat SFI basestocks — for example, relatively low temperatures of 300 to 350°F (150 to 175°C) with high pressures of 20 to 30 psig (1.3 to 2 bar) with a selective catalyst that has *trans*-isomer suppressant qualities. Reuse catalysts should be avoided, as they enhance *trans*-isomer formation.
- *Partially hydrogenated steep basestocks* — The physical properties of these basestocks are characterized by steep SFI curves or high solids contents at the lower measuring temperatures with an absence of solids at temperatures higher than body temperature. Hydrogenation of these basestocks should be carried out with highly selective conditions or high temperature and low pressure. Used catalyst, sometimes enhanced with new, very selective catalyst, can be utilized to help achieve the desired high selectivity and *trans*-isomer formation. These basestocks are beneficial in blends for margarine oils, high-stability frying shortenings, non-dairy products, fillings, and other products requiring a sharp melting point with good flavor stability while providing the required firmness at room temperature.
- *Low-IV hardfats* — These basestocks are often referred to as *fully hydrogenated hardfats*, or *stearines*; however, regulations require a zero IV for the fully saturated designation. Because catalyst activity is the only criterion with these hydrogenations, used catalyst can be utilized. In general, high-pressure (4 bar or 60 psig, or higher) and high-temperature (450°F or 230°C) conditions are used for these basestocks to make the reaction progress as rapidly as possible.

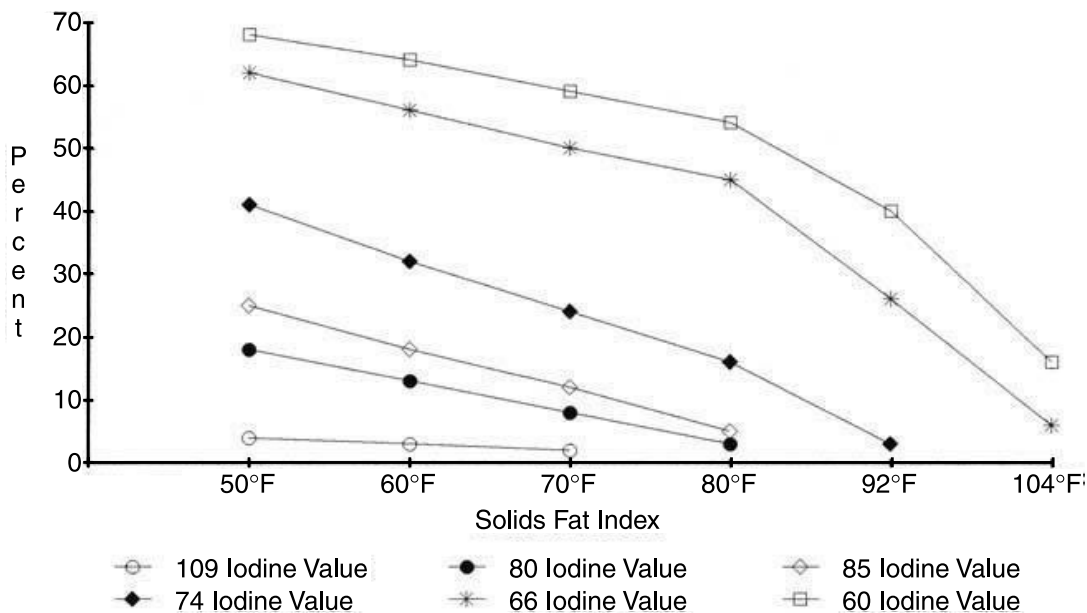
Table 2.3 outlines a soybean oil basestock system with seven hydrogenated stock oils ranging from a lightly hydrogenated 109 IV to a saturated hardfat with a maximum IV of 8. Utilization of a similar basestock system designed for the required product mix should enable fats and oils processors to meet most shortening speci-

**Table 2.3 Soybean Oil Basestock System**

Basestock Type	Brush		Flat		Steep		Saturated
Iodine value	109	85	80	74	66	60	< 8
Mettler dropping point (°C)	—	30 ± 2	33 ± 2	35 ± 1	43 ± 2	46.5 ± 1.5	—
Solids fat index at:							
50°F/10.0°C	4.0 max	18 ± 3	25 ± 3	41 ± 3	62 ± 3	68 ± 3	—
70°F/21.1°C	2.0 max	8 ± 2	12 ± 3	24 ± 3	50 ± 3	59 ± 3	—
80°F/26.7°C	—	3 ± 1	5 ± 1	16 ± 3	45 ± 3	54 ± 3	—
92°F/33.3°C	—	—	—	3.5 max	26 ± 3	40 ± 3	—
104°F/40.0°C	—	—	—	—	6 ± 3	16 ± 2	—
Quick titer (°C)	—	—	—	—	—	—	52 ± 2
Fatty acid composition (%):							
Palmitic (C-16:0)	10.8	10.2	10.1	10.9	10.7	10.7	10.5
Stearic (C-18:0)	4.4	6.4	7.0	8.2	15.2	20.8	86.9
Oleic (C-18:1)	44.3	68.2	72.0	75.0	70.7	66.3	1.7
Linoleic (C-18:2)	37.7	15.2	10.9	5.9	3.1	2.2	—
Linolenic (C-18:3)	2.8	—	—	—	—	—	—
<i>trans</i> -Acids (%)	14.8	22.7	25.3	44.7	45.5	45.0	Nil
<b>Hydrogenation Conditions</b>							
	Nonselective			Selective			Nonselective
Gassing temperature (°F)	300	300	300	300	300	300	300
Hydrogenation temperature (°F)	325	350	350	440	440	440	450
Pressure (bar)	3–4	1.3	1.3	0.7	0.7	0.7	4
Catalyst (% nickel)	0.01	0.02	0.02	0.02–0.04		0.04–0.08	
Agitation	←			Fixed		→	

fications by blending two or more basestocks, except for some specialty products that can be made only with special hydrogenation conditions.

SFI is one of the most important consistency measurements, and it also indicates the selectivity of the conditions used to prepare the individual basestocks. It measures the amount of solids present in a fat at different temperatures from below room temperature to above normal body temperature. A fat can appear to be a solid but really exist as a semisolid and does not have a distinct melting point. Natural and hydrogenated fats and oils melt over a wide range of temperatures. SFI analysis determines the solid or unmelted portion of a fat over a measured temperature range. These results relate to the consistency of the fats and oils product in terms of its softness, plasticity, organoleptic, and other physical properties important for its use as an ingredient in prepared foods. The slope of the SFI curve shows the effects of hydrogenation selectivity as it affects consistency. The SFI curve slope becomes steeper as the hydrogenation conditions are made more selective — that is, the highest temperature, lowest pressure, and highest level of a selective catalyst. The slope of the SFI curve becomes flatter as the hydrogenation reaction conditions are made less selective with lower temperatures, higher pressure, and low catalyst levels. These effects are illustrated for the soybean oil basestocks graphically on [Figure 2.7](#).



**Figure 2.7** Soybean oil basestocks.

## 2.8 POSTBLEACHING

A separate bleaching operation, immediately following the hydrogenation process, has three general purposes: (1) to remove traces of nickel that escape the catalyst recovery filtration; (2) to remove undesirable colors, generally of greenish hue; and (3) to remove peroxides and secondary oxidation products. This bleaching process generally employs a bleaching earth and a metal-chelating acid to reduce the residual nickel content to the lowest possible level. As much as 50 ppm nickel, mostly in colloidal form, can remain in the hydrogenated oil after the black press filtration. Trace amounts of nickel remaining in the oil adversely affect the stability of the oil by accelerating the oxidation process. After postbleaching, the trace metal levels in the oils should be reduced to <0.1 ppm nickel and <0.02 ppm copper for oxidative stability.

Green colors can emerge in the hydrogenated oils because of the heat bleaching of yellow and red masking pigments during hydrogenation. In the course of hydrogenation, the carotenoid pigments can be reduced to a colorless form while the chlorophyllic pigments merely have their absorption maxima shifted from 660 to 640  $\mu\text{m}$ . After the removal of the masking reddish pigments, the greenish pigments predominate, resulting in oils that appear green. The green pigments can be removed by adsorption on acid-activated clays with some difficulty, depending upon the severity. Green colors are more easily removed in the prebleach process before the color has been set by heating during hydrogenation.

Postbleach systems can be exact duplicates of the prebleach process; however, most fats and oils processors prefer batch systems over continuous systems due to the production of a wide variety of hydrogenated basestocks from several different



source oils. Vacuum batch systems are normally selected over atmospheric processes for the oxidative protection afforded the oils. The bleaching conditions are normally 0.1 to 0.2% activated bleaching earth with approximately 10 ppm phosphoric acid or 50 ppm citric acid added as a chelating agent and bleached at 180°F under a 25-inHg minimum vacuum. After bleaching, the spent earth and adsorbed impurities are removed with a pressure filter, and the oil is cooled to 130°F before further processing or is inventoried for basestock blending.

An alternative to postbleaching practiced by some processors is the addition of activated carbon to the oil with the catalyst during hydrogenation. Activated carbon is very effective in removing chlorophyll pigments. After filtering, the oil is treated with citric or phosphoric acid and polish-filtered to capture the colloidal trace metals remaining in the oil and any traces of the carbon that have escaped the catalyst filter.

## 2.9 INTERESTERIFICATION

The term *interesterification* refers to the fats and oils reaction in which fatty acid esters react with other esters or fatty acids to produce new esters by an interchange of fatty acid groups. More simply stated, interesterification can be visualized as a breakup of a specific glyceride, removal of a fatty acid at random, shuffling it among the rest of the fatty acid pool, and replacement at random by another fatty acid. Because of the random rearrangement of the fatty acids of the natural oil, the interesterification process is also commonly referred to as *randomization*, *rearrangement*, or *modification*.

Natural fats and oils are mixtures of mixed triglycerides. Their functional properties as ingredients in prepared foods are directly related to the type of triglycerides in the fats and oils. Triglyceride type is determined by the fatty acid composition 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 type depend on the proportions of the individual fatty acids, the fat or oil source, and the processing history of the product. Nature provides each fat and oil with a selective fatty-acid distribution among the glycerides that affects the consistency of the product as either a solid or a liquid. Trisaturated triglycerides provide structure, disaturated monounsaturated triglycerides provide both structure and lubricity, and the lower-melting unsaturated triglycerides provide lubricity only. [Table 4.4](#), in Chapter 4, shows the melting points of the common triglycerides found in most oleic/linoleic fatty acid group fats and oils.<sup>63</sup> The interesterification processes can alter the original order of distribution of the fatty acids in the triglyceride-producing products with 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 of fatty acids at random from the glyceride molecules, shuffling of these acids, and replacement of them on the glyceride molecules at random. This

change in the distribution of the fatty acids among the glycerides affects the physical nature and behavior of the fats.

Commercially, the interesterification process is utilized for processing edible fats and oils to produce confectionery or coating fats, margarine oils, cooking oils, frying fats, shortenings, and other special application products. Interesterification has not been a preferred process in the United States except for some very specific applications: (1) modification of lard to function as a plastic shortening, and (2) random rearrangement of lauric-oil-based confectionery or coating fats. Interesterification of lard was used to obtain a different triglyceride composition for more desirable physical properties than the original fat. Plasticized shortening made from randomized lard has a smoother appearance and texture because the crystal structure has been changed from beta ( $\beta$ ) to beta-prime ( $\beta'$ ), which also helps it retain its appearance during storage with better creaming properties. Currently, the market for premium lard shortenings no longer exists due to the reduced use of animal fats and the competitive pricing of vegetable oils. The primary, but limited, use of interesterification in the United States is for the processing of value-added specialty fats such as confectionery or coating fats. These fats, called *hard butters*, are used as substitutes for cocoa butter in coatings and other applications characterized by a relatively high solid fat content at room temperature with a sharp melting point. The interesterified hard butters are typically composed of rearranged, hydrogenated palm kernel or coconut oils with lesser quantities of other vegetable oils to adjust the melting point. Outside the United States, interesterification has much wider application to process basestocks or finished products for margarine oils, cooking oils, cocoa-butter equivalents (CBEs), and other specialty products.<sup>60</sup>

Two general types of chemical interesterification or rearrangement processes practiced are random and directed. In random rearrangement, the fatty acid radicals freely move from one position to another in a single glyceride or from one glyceride to another. As the fatty acids rearrange, they reach an equilibrium that is based on the composition of the starting material and is predictable from the laws of probability. Directed rearrangement modifies the fatty acid randomization by upsetting the equilibration mixture. This process is carried out at low temperatures to allow crystallization of a portion of the mixture while the interchange of fatty acids is continuing in the liquid portion. This produces a different composition composed of larger proportions of high-melting glycerides and a corresponding larger proportion of very-low-melting glycerides. The degree of difference depends upon the temperature, time, and other conditions of the reaction.

A third rearrangement process, enzymatic interesterification, is now used in Europe to produce high-value-added products, such as structured triglycerides for confectionery use. The major advantages of the enzymatic interesterification over chemical processes are the specificity available in lipase catalysts and the greater degree of reaction control. Oil modification by lipases is performed under anhydrous conditions at temperatures up to 160°F (70°C). Two types of enzyme catalysts are currently available commercially: a random lipase that produces products similar to chemical randomization and a 1,3 fatty acid specificity lipase that allows the production of specific triglycerides at high yields.<sup>60</sup>

## 2.9.1 Chemical Rearrangement Catalyst

Fatty acid rearrangement may occur without the use of a catalyst at a temperature of 475°F (250°C) or higher, but most processors use alkali metal alkylates or alkali metals to speed up the reaction. Fats reacted at high temperatures without the assistance of a catalyst proceed slowly to equilibrium and have other undesirable changes as well (i.e., isomerization, polymerization, and decomposition). Some of the chemical rearrangement catalysts commercially utilized include:<sup>64,65</sup>

- *Sodium methylate*, an alkali metal (alkylate), is the most widely used low-temperature interesterification catalyst. It is active at a lower temperature, speeds up the reaction, has a relatively low cost, does not require a vacuum during processing, and is easily dispersed in fat. Sodium methylate is used either as a powder or as a dispersion in solvents such as xylene at very low levels, 0.1% if the starting material has a low free fatty acid level and is dry; however, the average usage range is 0.2 to 0.4%.
- *Sodium potassium alloy*, which has been used as an interesterification catalyst at 0.05 to 0.1%, is liquid at ambient temperature and does not require dispersing in a solvent for introduction to the reaction. It can catalyze low-temperature reactions at faster rates than other catalysts but requires high sheer agitation and is typically more expensive even though it offers a low oil loss. The interesterification reaction starts almost instantaneously with the addition of the catalyst and is complete in as short a time as 5 minutes. The feedstock oil or fat must be very dry before the addition of this catalyst. It will react with moisture to liberate hydrogen gas, which can inactivate the catalyst. Additionally, this creates an explosion potential from the heat and hydrogen gas generated during deactivation.
- *Sodium or potassium hydroxide* are the lowest cost rearrangement catalysts, but they must be used in combination with glycerol and require a two-stage reaction under vacuum at high temperatures to effect a reaction. The first stage is conducted at 140°F (60°C) to neutralize any free fatty acids, dry the oil, and disperse the catalyst. The reaction mixture is heated to 285 to 320°F (140 to 160°F) during the second stage to effect rearrangement. Glycerol is a necessary component of this catalyst for the reaction to occur and usually forms small amounts of mono- and diglycerides.

The compounds described above are probably not the real chemical interesterification catalysts but serve as initiators in the process of forming the true interesterification catalyst. Most likely, intermediates such as sodium glycerate formed in the fat are the active catalyst. When the catalyst is dispersed in a previously dried oil maintained at about 140 to 175°F (60 to 80°C), a white slurry develops. After heating, a characteristic brown color develops indicating that the reaction has begun. The color change is associated with the active catalyst formation, which is probably an intermediate glycerate anion.

Rearrangement catalyst must be inactivated and removed at the end of the process because interesterification is a reversible reaction. Most chemical catalysts can be removed by washing the reaction mixture with water to separate a salt- or soap-rich aqueous phase. An alternative method is to terminate the reaction with phosphoric acid and remove the solid phosphate salts by filtration. Either technique results in product loss:

- *Phosphoric acid termination losses*
  - *Catalyst* — One gram of sodium methylate catalyst yields the interesterified product, 5.519 grams of methyl esters, 5.67 grams of sodium soap, and 2.13 grams of diglycerides. The loss for the catalyst level used can be calculated as 11.2 pounds product loss for each pound of catalyst used.
  - *Bleaching-earth oil retention* — It may be assumed that the bleaching earth will retain its weight in neutral oil or a 0.1% bleaching earth will remove the phosphate salts and retain 0.1% neutral oil.
  - *Deodorizer losses* — Deodorization to a 0.05% FFA would necessitate a loss of the FFA content above this level.
- *Water termination losses* — This neutralization process adds the entrained oil losses experienced with water washing to those for the phosphoric acid termination. The only savings for this procedure are the phosphoric acid costs; however, the oil quality improvement with water termination may justify the added expense.

## 2.9.2 Endpoint Control

A brown color develops when the chemical reaction begins and deepens as the reaction continues. In most operations, the reaction is allowed to proceed for a fixed time period after the appearance of the brown color before sampling to determine if the reaction has been completed. The reaction is most often confirmed by monitoring changes for a characteristic particular to the source oil or mixture of oils processed which usually involve evaluations for specific product changes. The effect of interesterification of glyceride mixtures differs in different cases, depending upon the composition of the original fat, mixture of fats, or prior processing.

### 2.9.2.1 Melting Point

Intesterification may raise, lower, or have no effect upon the melting point, depending upon the starting fat and oil glyceride composition. A high melting mixture of completely hydrogenated fat with a large proportion of a liquid oil will experience a decrease in the proportion of trisaturated glycerides to effect a lower melting point with interesterification. Applied to an oil such as cottonseed, with a substantial proportion of solid fatty acids but hardly any trisaturated glycerides, the randomization process will raise the melting point because it increases the proportion of fully saturated triglycerides. These changes are illustrated by the melting point results before and after the random rearrangements listed in [Table 2.4](#).<sup>64,66</sup> Specific melting point limits must be established to identify the expected change and the suitability of this analytical method for endpoint control. In some cases, no melting point change occurs, or it may be so slight that it will be within the range of normal analytical error. Even though melting point is a rapid, reproducible method, it cannot be used as an interesterification endpoint in all cases.

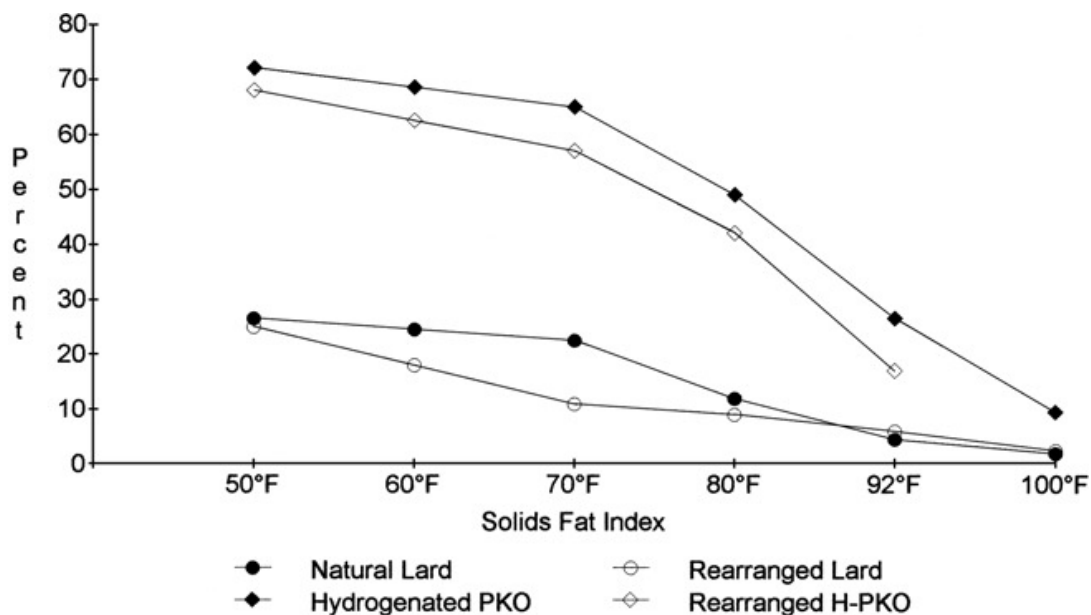
### 2.9.2.2 Solids Fat Index

SFI analysis control requires measurement at several temperatures for definite results to identify a change, and it is very time consuming; however, small changes

**Table 2.4 Melting Point Changes with Random Rearrangement**

Fats and Oils Products	Original		Rearranged	
	°F	°C	°F	°C
Soybean oil	19.4	-7.0	41.9	5.5
Cottonseed oil	50.9	10.5	93.2	34.0
Lard	109.4	43.0	109.4	43.0
Tallow	115.2	46.2	112.3	44.6
Palm oil	102.9	39.4	108.9	42.7
Palm kernel oil	82.9	28.3	80.4	26.9
Coconut oil	77.9	25.5	82.8	28.2
H-palm kernel oil	113.0	45.0	93.9	34.4
H-coconut oil	100.0	37.8	88.9	31.6

in melting point evaluations may be accompanied by more significant changes in the SFI content and slope for the curve throughout the range of functionality-important temperatures. The changes in trisaturate and disaturate glycerides with interesterification are reflected in the SFI contents before and after the reaction. Figure 2.8 shows the effects of interesterification on two different fats and oils sources: natural lard and hydrogenated palm kernel oil. These SFI results<sup>67,68</sup> verify that the rearrangement effects are dependent upon the composition of the original fat or oil product. Rearranged lard has a flatter SFI slope caused by a higher trisaturate level, which is a more desirable shortening base. Rearranged hydrogenated palm kernel oil results in a steeper SFI slope with a lower melting point for improved eating characteristics. SFI analyses are useful for formulation and to confirm that the predetermined results have been attained but are probably too time consuming for interesterification endpoint control.



**Figure 2.8** Rearrangement effect on solids fat index.

### **2.9.2.3 Differential Scanning Calorimetry**

Differential scanning calorimetry (DSC) is most useful for studying the kinetics of crystallization and melting of triglyceride mixtures under dynamic conditions. The heating and cooling thermograms resulting from DSC show distinct differences between some nonrandomized and randomized fats and oils. The basis of the cooling curve is that crystals of fat give off heat upon solidifying from liquid oils and absorb heat upon melting. Large crystals give up heat so rapidly during formation that the temperature of the fat may rise rapidly during the chilling cycle. The endpoint of lard interesterification is best determined by a cooling curve analysis that indicates the absence of the heat of crystallization associated with untreated lard. The endpoint of interesterification for lauric hard butters or coating fats might be determined by a loss of rapid solidification of the fully saturated glyceride component on cooling.

### **2.9.2.4 Glyceride Compositional Analysis**

The basic change that occurs due to interesterification is in the glyceride composition; therefore, analysis that can identify the glyceride composition should be the most definitive endpoint possible. High-performance liquid chromatography (HPLC) methods can separate triglycerides according to their level of saturation or on the basis of molecular weights.

## **2.9.3 Random Chemical Interesterification Process**

Random chemical rearrangement of fats and oils can be accomplished using either a batch or continuous process. Both perform the three important rearrangement steps: (1) pretreatment of the oil, (2) reaction with the catalyst, and (3) deactivation of the catalyst. A typical batch rearrangement reaction vessel is equipped with an agitator, coils for heating and cooling, nitrogen sparging, and vacuum capabilities. The process steps for batch rearrangement are:<sup>64,65,67</sup>

1. Heat the fat to 250 to 300°F (120 to 150°C) in the reaction vessel under a vacuum to dry the oil. Drying is critical because moisture deactivates the catalyst. Moisture levels in excess of 0.01% will require extra catalyst to complete the reaction. Additional catalyst usage results in higher product losses. A rule of thumb is that each 0.1% of sodium methylate catalyst results in 1.1% neutral oil loss.
2. After drying, the fat is cooled to the reaction temperature, which ranges from 160 to 210°F (70 to 100°C), depending upon the product and desired processing conditions. Sodium methylate powder is sucked into the reaction vessel with the vacuum. The amount of catalyst necessary is the amount required to neutralize the free fatty acid, plus a slight excess to catalyze the random rearrangement. Therefore, because one part of sodium methylate will neutralize 5.26 parts of stearic fatty acid and 0.06% excess is enough to catalyze the reaction, the catalyst requirement can be calculated as:  $(\text{FFA} \times 0.19) + 0.06 = \text{the percent sodium methylate catalyst required for the reaction}$ . This mixture is agitated to form a white slurry, which indicates good dispersion, for 30 to 60 minutes or until formation of the distinctive brown color indicates randomization. At this point, the mixture is sampled for laboratory

analysis to determine if the reaction is complete or requires additional catalyst and time to attain the predetermined endpoint.

3. When reaction completion is confirmed by the laboratory results, the catalyst is neutralized in the reaction vessel. Neutralization may include the addition of phosphoric acid or carbon dioxide (CO<sub>2</sub>) prior to water washing to deactivate the catalyst. Water combines with sodium methylate to form sodium hydroxide and methyl alcohol, which react with the neutral oil to form soap and methyl esters. Product losses are kept to a minimum by neutralizing with phosphoric acid or CO<sub>2</sub> prior to water washing.

Continuous interesterification processes follow the same cycle as the batch process but utilize different equipment. The process flow for one continuous system is as follows. The oil is heated with a heat exchanger and flash dried with a vacuum oil dryer to bring the moisture level to 0.01% or less. The catalyst is introduced into the hot oil stream and homogenized for dispersion. The homogenized mixture is then passed through a tubular reactor. The reactor residence time can be adjusted by changing the length of the tube. The catalyst is deactivated with water and centrifuged to separate the soap and oil. After separation the product is vacuum dried to remove the remaining traces of moisture.

#### 2.9.4 Directed Chemical Interesterification Process

In directed rearrangement processes, one or more of the triglyceride products of the interesterification reaction are selectively removed from the ongoing reaction. Trisaturated glycerides crystallize and are separated from the reaction when the mixture is cooled below its melting point. This selective crystallization upsets the equilibrium, and the reaction will produce more trisaturated glycerides to reestablish equilibrium. Theoretically, this process could continue until all the saturated fatty acids are converted into trisaturated glycerides and separated from the reaction. Because this reaction is directed to produce a particular type of glyceride, it is referred to as *directed interesterification*.

In directed interesterification, only catalysts active at low temperatures are effective, and the rate of random rearrangement is important because the trisaturated glycerides can precipitate only as fast as they are formed in the liquid phase. Sodium-potassium alloy (NaK) is more suitable for directed interesterification than either sodium or sodium methylate because of its more rapid activity at low temperatures.

Continuous processes are normally used for directed interesterification because the batch process is difficult to control and would require a number of extra tanks. The process flow for continuous directed rearrangement is as follows:<sup>64,67,69</sup>

1. The oil is vacuum dried to 0.01% moisture or less.
2. After drying, the oil is cooled to a temperature just above its melting point with a heat exchanger.
3. A carefully metered stream of NaK catalyst is added to the product stream and mixed or homogenized to suspend the catalyst throughout the product.
4. The homogeneous mixture is quick-chilled with a scraped-wall heat exchanger to a predetermined point to initiate crystallization of the trisaturated glycerides.

5. The cooled mixture is transferred to an agitated vessel, where interesterification proceeds under carefully controlled agitation. At this stage, trisaturated glycerides are crystallizing while interesterification of the liquid phase is continuing to form more trisaturated glycerides.
6. Crystallization of the trisaturated glycerides liberates a considerable amount of heat due to fusion, which can increase the reaction temperature beyond the desired point, which necessitates a second chilling step with a scraped-wall heat exchanger.
7. After the second cooling, the product is transferred to another vessel with controlled agitation, where the precipitation of trisaturated glycerides and interesterification continues to the desired endpoint. Crystallization slows as the trisaturates diminish, so this stage requires more time for reaction completion. The level of trisaturated glycerides in the final product can be adjusted by varying the time in the crystallizer, the crystallization temperature, or a combination of the two.
8. After the desired endpoint has been reached, the catalyst is “killed” by adding water. The amount of water is calculated to provide the desired fluidity for centrifuging to remove the soap phase. Saponification of the fat can be minimized somewhat by the addition of carbon dioxide with the water to buffer the caustic to a lower pH.
9. After neutralization of the catalyst, the product can be heated to melt the trisaturated glyceride crystals for centrifugation followed by vacuum drying.

### 2.9.5 Enzymatic Interesterification

Enzymes have been used for many years to modify the structure and composition of foods but only recently have been available on a large enough scale for industrial applications. Enzymatic interesterification is now used to produce high-value-added structured fats and oils products.<sup>60,70,71</sup> Useful glyceride mixtures that cannot be obtained by chemical interesterification processes are possible by exploiting the specificity of lipases. In all glyceride reactions, lipases catalyze either the removal or the exchange of fatty acid groups on the glycerol backbone. Different lipases can show preferences for both the position of the fatty acid group on the triglyceride and the nature of the fatty acid. Two types of lipase catalyst identified by application specificity have been identified:

- Random lipases, which catalyze reactions at all three positions on the glyceride randomly
- 1,3-Specific lipases, which catalyze reactions only at the outer 1- and 3-positions of glycerides

Random lipase interesterification has very little advantages over standard chemical techniques. Nonspecific catalyzed reactions with triglycerides produce products similar to those obtained by chemical interesterification. However, with a 1,3-specific lipase as a catalyst, fatty acid migration is confined to the 1- and 3-positions to produce a mixture of triglycerides not possible with chemical interesterification. These specific lipases allow the production of a limited range of glycerides to be produced that can be separated using physical processes.

Lipases are manufactured by fermentation of selected microorganisms followed by a purification process. The enzymatic interesterification catalysts are prepared



by the addition of a solvent such as acetone, ethanol, or methanol to a slurry of an inorganic particulate material in buffered lipase solution. The precipitated enzyme coats the inorganic material, and the lipase-coated particles are recovered by filtration and dried. A variety of support materials have been used to immobilize lipases. Generally, porous particulate materials with high surface areas are preferred. Typical examples of the support materials are ion-exchange resins, silicas, macroporous polymers, clays, etc. Effective support functionality requirements include (1) the lipase must adsorb irreversibly with a suitable structure for functionality, (2) pore sizes must not restrict reaction rates, (3) the lipase must not contaminate the finished product, (4) the lipase must be thermally stable, and (5) the lipase must be economical. The dried particles are almost inactive as interesterification catalyst until hydrated with up to 10% water prior to use.

Lipase-catalyzed interesterification of fats and oils can be accomplished either by using a stirred batch reactor or with continuous processing using a fixed-bed reactor. The latter is the preferred process, offering the advantage of minimized reaction times due to the high catalyst substrate ratio along with the other advantages of (1) catalyst recovery, (2) reduced catalyst damage, and (3) improved operability. The continuous fixed-bed interesterification process begins by dissolving the feedstock in a solvent followed by treatment to remove enzyme catalyst inhibitors, poisons, and particulate materials. This solution is then partially saturated with water prior to pumping through a bed of hydrated catalyst particles. The reaction products are a mixture of triglycerides and free fatty acids. After the reaction, the FFAs are removed by evaporation and processed for recovery. The FFA-free oil is then solvent fractionated to yield the desired triglyceride composition.

## **2.9.6 Interesterified Fats and Oils Applications**

Intesterification processes can be used to produce fats and oils products with different physical and nutritional properties. Rearrangement of the fatty acids on the glycerol backbone affects the structural properties or melting behavior of the fats and oils products. Often, interesterification is combined with other specialized processing techniques such as fractionation or hydrogenation. By combining interesterification with these and other more sophisticated techniques, the fatty acid and glyceride composition can be manipulated to produce the desired physical and functional properties. These products may also be utilized as basestocks for blending with other selected fats and oils products to produce the desired functional properties.

Chemical and enzymatic interesterification processes can affect physical properties by changing the melting properties and in some cases the crystal behavior. The use of these triglycerides in food products can allow the development of specialty fat and oil products more suitable for the desired application performance, nutritional requirements, or both. Interesterification can be utilized to formulate products with less saturated or isomerized fatty acids for the production of products with low or no *trans*-acids. Margarine and shortening finished products have been produced using interesterified fats and oils instead of the traditional hydrogenated basestocks.

## 2.10 WINTERIZATION

The descriptive term of *winterization* evolved from the observation that refined cottonseed oil stored in outside tanks during the winter months physically separated into a hard and clear fraction. Topping or decanting the clear oil from the top of the tanks provided an oil that remained liquid without clouding for long periods at cool temperatures. In fact, some cottonseed salad oils routinely had cold test results of 100 hours or more when topped from outside storage tanks. The clear oil portion became known as winterized salad oil.<sup>72</sup> The hard fraction from the bottom of the tanks was identified as stearine, which is the solid portion of any fat.

A need for a liquid oil with these characteristics was created by the use of refrigerators in the home and the requirements of the mayonnaise and salad dressing industry. Mayonnaise could not be made from oils that would crystallize in the refrigerator and cause the emulsion to break. New terminology emerged because of this association with mayonnaise. Winterized oil became known as *salad oil*. Summer oils, or oils that had not been subjected to winterization, became known as *cooking oils*. As the demand for salad oils increased, it became impossible to rely on long-term storage of refined oils for the winterized oil requirement. Processors recognized the obvious solution and created winter conditions indoors.

### 2.10.1 Classic Winterization Process

The indoor process developed to simulate the natural winter process consisted of a chilled room held at 42°F (5.6°C) with deep, narrow, rectangular tanks to provide the maximum surface exposure to cooling. Warm, dry, refined, and bleached oil pumped into the chill room tanks began to cool and crystallize-out stearine immediately, but slowly. Convection heat transfer simulated the outside storage conditions. Agitation was avoided because it fractured the crystal, causing formation of small, soft crystals that were difficult to filter. Cooling with a 42°F room temperature simulated winter conditions in the southern United States closely and required two to three days to produce the desired large crystals for filtering. After the oil temperature equated with the room temperature, it was held for several hours to allow the stearine or hard fraction to precipitate more fully. The stearine was separated from the liquid oil by filtering with plate and frame presses. Early installations relied on gravity feed to the presses, but later compressed air or positive displacement pumps were utilized to exert a pressure of 5 to 20 psig to increase the filtration rate. Care was exercised to avoid breaking up the crystals excessively. A slow filtration rate was necessary because of the high oil viscosity and excessive pressure pressed the stearine into the filter cloths, causing a blockage that stopped the oil flow. A large filter area on the order of 2 to 3 pounds of oil per hour per square foot was the general guideline. The stearine cake was melted with hot fat for removal after the filter press was full.

Winterization is still performed using the classic techniques outlined above, but many processors have made equipment and process modifications to improve efficiency. Jacketed enclosed tanks equipped with programmable cooling and agitation

have evolved as crystallization cells to replace the open-top, narrow, rectangular tanks cooled by the chill room temperature. However, attempting to force crystallization by means of an excessively cold coolant and rapid agitation results in small crystals that are virtually unfilterable. Recessed plate and frame or pressure leaf filters have been used in winterization because these filters have the cake-holding capacity that the process requires. Obviously, when 15% or more of the feed is removed in the form of stearine, a substantial solids retention capacity is needed. Separation of the stearine from the liquid oil by means of a centrifuge has had some success. The main problem encountered with centrifugal separation is liquid oil yield, as the stearine tends to trap excessive amounts of oil.

## 2.10.2 Winterization Principle

Winterization is a thermomechanical separation process where component triglycerides of fats and oils are crystallized from a melt. The two-component fractional crystallization is accomplished with partial solidification and separation of the higher melting triglyceride components. The complex triglycerides may have one, two, or all three fatty acids, either all the same or different in any of the possible configurations depending upon the source oil and prior processing.

Fat crystallization occurs in two steps: (1) *nucleation*, and (2) *crystal growth*. The rate of nucleation depends upon the triglyceride composition of the oil being winterized, the cooling rate of the oil, the temperature of the nucleation, and the mechanical power input or agitation. Growth rate is dependent on the crystallization temperature, time, and mechanical input or agitation. A careful selection of the process variables for a particular oil is very important. The ideal is to produce a small number of nuclei around which the crystals grow larger in size with cooling. A large mass of small crystals that are difficult to filter results when a large number of nuclei are formed. Poor separation and yield also result when crystals group together in clumps that trap large quantities of the liquid phase. The effect of the major processing variables upon winterization performance include the following.<sup>73</sup>

### 2.10.2.1 Source Oil Composition

Nucleation and crystal growth depend upon the composition of the oil being winterized. The various triglycerides in a particular oil will fractionate in the following order: (1) trisaturate,  $S_3$ ; (2) disaturate monounsaturate,  $S_2U$ ; (3) monosaturate diunsaturate,  $SU_2$ ; and (4) triunsaturate,  $U_3$ . A portion of the higher melting glycerides will be found with the lower melting liquid oils as a result of eutectic formation and equilibrium solubility. Because the mixture of triglycerides in an oil is too complex to predict their phase behavior, a given set of winterization conditions are applicable only for the particular feed oil. For partially hydrogenated oils, the composition of the oil and the hydrogenation conditions affect the winterization yield and quality. Hydrogenation conditions should be selected that produce the lowest level of saturates and *trans*-fatty acids but still effect the desired iodine value endpoint.

### **2.10.2.2 Cooling Rate**

An essential requirement of the winterization process is a slow rate of chilling. Rapid cooling of the oil results in (1) a mass of very small  $\alpha$ -crystals, and (2) a high nucleation rate that increases the viscosity, which in turn restricts crystal growth. Slow controlled cooling rates produce stable  $\beta$ - or  $\beta'$ -crystals, depending upon the dominant crystal habit for the source oil winterized, and the viscosity remains low enough to permit nuclei movement to allow crystal growth. Therefore, the cooling rate is dependent upon the source oil and prior processing.

### **2.10.2.3 Crystallization Temperature**

The crystal growth rate is affected by the temperature of crystallization. A high viscosity resulting from too low a temperature reduces the crystal growth rate. Control of the temperature after crystallization begins is important for transformation from the  $\alpha$  to the stable  $\beta'$ - or  $\beta$ -crystal habit. If the process is not properly controlled at this stage, an unstable crystal will develop. A temperature differential between the coolant and the oil must be maintained to avoid shock chilling. A 25°F (14°C) differential has been found appropriate for oil at the beginning of the process. The differential can be reduced to 10°F (5.6°C) by the time the oil reaches 45°F (7.2°C). If the coolant is allowed to become too cold in relation to the oil, a heavy layer of stearine will build up on the surfaces and insulate the oil from the coolant.

### **2.10.2.4 Agitation Rate**

Crystal formation is hastened by stirring to bring the first crystals into contact with more of the liquid; however, mild agitation rates are recommended because high shear rates fragment the crystal during the growth stage, thus producing more smaller crystals instead of the desirable large crystal.

### **2.10.2.5 Crystallization Time**

Crystallization is inseparably linked to two elements of time: (1) the time it takes to lower the temperature of the material to the point where crystallization will occur, and (2) the time for the crystal to become fully grown. The rate of cooling is a primary factor for determining the size, amount, and stability of the crystals formed. In general, crystals assume their most highly developed and characteristic forms when grown slowly from a melt or solution only slightly supercooled, in which the liquid freely circulates around the crystal. A typical time–temperature sequence for winterization of cottonseed oil is:<sup>74</sup>

1. Refined and bleached cottonseed oil is transferred to the chilling units at 70 to 89°F (21.1 to 26.7°C).
2. The oil is cooled to 55°F (12.8°C) in 6 to 12 hours, when the first crystals usually appear.

3. The oil is cooled to 45°F (7.2°C) in 12 to 18 hours with a reduced cooling rate. At this point, a 2 to 4°F (1.1 to 2.2°C) heat of crystallization temperature increase should be observed.
4. After the oil temperature drops slightly below the previous low, approximately 42°F (5.6°C), it is maintained at this temperature for approximately 12 hours. This period is critical for the effectiveness of the process. Because the oil is viscous and molecular movement is slow, crystals continue to grow after the minimum temperature is reached.

### 2.10.3 Solvent Winterization

Salad oil production with the traditional winterization procedure is a slow process. Two to three days' chilling time is required for good filtration and yield. Most vegetable oils that cloud at refrigerator temperatures can be solvent winterized for better yields and to produce a salad oil of better quality in less time than by the conventional process. Comparison of the two procedures indicates many similarities. The major advantage of a solvent winterization system include: (1) viscosity is considerably lower, which allows a faster crystal growth for more rapid stearine separation; (2) the salad oil produced has a better resistance to clouding at cool temperatures for longer cold tests; and (3) less liquid oil trapped in the stearine component for higher salad oil yields.

An operational continuous solvent process was described by Cavanagh<sup>75</sup> and later Neumanz<sup>76</sup> for winterization of cottonseed oil. Miscella containing 30 to 60% by weight of oil in hexane with a 50% solution preferred is cooled rapidly with a heat exchanger to either 20 to 26°F (−6.6 to −3.3°C) or 8 to 12°F (−13.3 to −11.1°C). After cooling, the miscella passes through a continuous winterizing column, which cools with a series of agitated trays over a 40- to 60-minute period to temperatures as low as −4°F (−20°C). A continuous solids discharge centrifuge separates the solid stearine from the liquid miscella. The solvent is removed from the liquid oil portion with an evaporator system before deodorization. The solid discharge from the centrifuge is filtered to remove any foreign material before the residual 10 to 15% hexane solvent is removed with an evaporator system.

Controlled agitation of 1 to 10 rpm and a controlled temperature drop to 0°F produces harder, firmer, more compact stearine crystals in solvent, and less oil is entrapped than with conventional winterization systems. [Table 2.5](#) provides a comparison of cottonseed salad oil stearine analytical characteristics from a conventional process and a solvent process.

### 2.10.4 Winterization Process Control Procedures

The acceptability of a winterized oil is almost always determined by cold-test analysis. This method measures the ability of the oil to resist crystallization. The cold-test result is the number of hours at 32°F (0°C) required for an oil to become cloudy. AOCS Method Cc 11-53 indicates that an oil has passed the test if it is clear and free of any cloud at 5.5 hours;<sup>34</sup> however, most processors and customers have

**Table 2.5 Cottonseed Salad Oil Stearin Analysis**

<b>Winterization Process</b>	<b>Conventional</b>	<b>Solvent</b>
Iodine value	95.5	71.6
Solids fat index at:		
10.0°C/50°F	21.6	52.3
21.1°C /70°F	1.3	33.7
26.7°C/80°F	—	1.2
33.3°C/92°F	—	0.1
Fatty acid composition (%):		
Myristic (C-14:0)	0.7	0.6
Palmitic (C-16:0)	34.6	52.1
Palmitoleic (C-16:1)	0.6	0.8
Stearic (C-18:0)	2.1	1.9
Oleic (C-18:1)	15.8	9.1
Linoleic (C-18:2)	46.2	35.5

more stringent requirements for cold-test hours. Cottonseed and soybean winterized oil products normally have a minimum cold-test limit of 10 hours, and some are as high as 20 hours for special products.

Processors have investigated many different potential process control evaluations, procedures, and methods to determine that the winterization process is in control on a timely basis; however, cold test is still the most definitive evaluation, even though the results are not available until a lengthy period after the oil has been winterized. Usually, the winterized oil production is segregated in separate tanks until the cold-test results are available. If the oil fails to meet the specific number of hours, it must be rewinterized. Oils that meet the requirements are transferred to salad oil storage for subsequent deodorization, packaging, or shipment as required. This after-the-fact analysis to determine the acceptability of the winterized oil places more emphasis on process control techniques to ensure that all of the best practices are continually observed.

### **2.10.5 Winterization Applications**

Historically, winterization has always been associated with cottonseed oil. It and other liquid oils that contain fractions that solidify when chilled must be winterized or fractionated to remain clear at cool temperatures. Oil that is to be refrigerated or stored in cool warehouses must resist clouding for a period of time to be acceptable aesthetically or for performance. Winterized cottonseed oil was the standard salad oil used by retail-trade food processors to produce mayonnaise and other salad dressing products because of its pleasing flavor and flavor stability.

Soybean oil was rejected as a salad oil both at the retail level and by food processors until the flavor stability problem was remedied with partial hydrogenation to reduce the linolenic (C-18:3) fatty acid content. Hydrogenation to improve flavor stability also produced a hard fraction in the soybean oil, which crystallized at cool temperatures similar to cottonseed oil. Winterization was employed to separate the hard and liquid fractions. Supply-and-demand economics and performance elevated

**Table 2.6 Typical Cottonseed Oil and Partially Hydrogenated Soybean Oil Winterized Salad 0.1 Components**

Source Oil	Cottonseed Oil			Hydrogenated Soybean Oil		
	Whole Oil	Salad Oil	Stearin	Basestock	Salad Oil	Stearin
Fraction (%)	100	84.6	15.4	100	82.9	17.1
Iodine value	109	113.5	90.6	108.7	111.4	95.7
Fatty acid composition (%):						
Myristic (C-14:0)	0.9	0.9	0.7	—	—	—
Palmitic (C-16:0)	24.8	21.3	38.2	11.2	10.2	15.0
Palmitoleic (C-16:1)	0.5	0.5	0.3	—	—	—
Stearic (C-18:0)	2.6	2.9	2.3	4.8	4.1	7.9
Oleic (C-18:1)	16.9	18.0	13.8	45.4	45.2	46.0
Linoleic (C-18:2)	53.7	55.8	44.2	35.4	37.5	29.1
Linolenic (C-18:3)	0.2	0.2	0.1	3.0	2.8	1.9
Arachidic (C-20:0)	0.2	0.2	0.2	—	—	—
Cold test (hours)	—	24	—	—	10.5	—

partially hydrogenated winterized soybean oil to the leading winterized salad oil product in the United States. A comparison of the two winterized oil products is presented in Table 2.6.

Winterization of hydrogenated soybean oil is very similar to that of cottonseed oil, except that less time is required for crystallization and filtration. The inherent crystallization tendencies for the two source oils are different; the stable crystal form for soybean oil is  $\beta$ , but it is  $\beta'$  for cottonseed oil.  $\beta$ -crystals are large, coarse, and self-occluding whereas the  $\beta'$ -crystals are small, needle-shaped crystals that pack together to form dense, fine structures.

## 2.11 DEWAXING

An increased demand for salad oils high in unsaturates has resulted in the marketing of source oils that must be dewaxed to maintain clarity during storage, on the retail store shelf, and at refrigerator temperatures. Many vegetable oils have small quantities of waxes that solidify and cause cloudy oil. Several 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 over 2000 ppm. The wax content must be reduced to less than 10 ppm to ensure that the oil will not cloud or develop a wisp.

The mechanisms for wax removal from oils is different from those applicable to winterization even though the same equipment can be utilized. The classical dewaxing process usually performed after prebleaching and prior to deodorization consists of carefully cooling the oil to crystallize the waxes for removal by filtration. The cooling must be done slowly under controlled conditions. A body feed approximately equal to the wax content of the oils is used to prevent blinding of the filter leaves. Without

a body feed, the waxes slime over and blind the screens almost immediately.<sup>50</sup> A continuous dewaxing process that operates efficiently with low-wax oils (500 ppm or less) has the following process flow:<sup>77</sup>

- The oil is continuously cooled with heat exchangers and a crystallizer to 43 to 46°F (6 to 8°C).
- A quantity of filter aid equal to the wax content is added to the crystallizer to facilitate crystallization and filtration.
- Crystallization time is 4 hours minimum, followed by a holding period of 6 hours to develop the wax crystals.
- The oil is carefully heated to 64°F (18°C) before filtering to separate the wax crystals from the liquid oil.

The typical dewaxing process performs well with low-wax oils, but some vegetable oils have higher wax contents. The filtration time is increased and higher product losses are experienced with the higher wax-content oils. Some of the procedures in use to improve the dewaxing economics include:<sup>75,78</sup>

- *Simultaneous dewaxing and degumming* — The crude oil is cooled to approximately 77°F (25°C) and held at this temperature for 24 hours before water degumming. This process usually reduces the wax content to 200 to 400 ppm.
- *Wet dewaxing* — The phosphatides are first removed from the oil by degumming. The oil is then cooled to 46°F (8°C), and 5% water with sodium lauryl sulfate is added and agitated for 4 hours minimum to crystallize the waxes. The wax crystals should disperse in the water phase for separation with a centrifuge.
- *Simultaneous dewaxing and chemical refining* — The oil is treated with phosphoric acid and neutralized with sodium hydroxide and centrifuged using normal refining techniques. Before water washing, the oil is cooled to 46°F (8°C) and held for 4 to 5 hours with gentle agitation. Then, 4 to 6% water is added and the mixture is heated to 64°F (18°C) with agitation. During this mixing, the wax crystals are wetted and suspended in the soapy water phase. This mixture is centrifuged to separate the water and oil phases. Usually, a second water wash is required to complete removal of the wax and soap traces from the oil.
- *Solvent dewaxing* — This procedure is performed after prebleaching and prior to deodorization if it is not an integral part of a miscella refining process. Dewaxing in solvent consists of mixing the oil with a fixed volume of solvent and, after chilling, to promote crystallization of the waxes for separation by either filtration or with a centrifuge.

### 2.11.1 Dewaxing Process Control

Currently, the analytical method to determine if an oil is adequately dewaxed is the same as for products winterized to remove large quantities of stearine: cold test (AOCS Method Cc 11-53).<sup>34</sup> However, this evaluation may be very misleading. Dewaxed oil, which remains clear and brilliant for 5.5 hours, generally remains so for 24 hours in the ice bath, but the same oil can become opaque after only a few hours at room temperature due to the reappearance of waxes as well as glycerides; therefore, to determine that an oil has been adequately dewaxed, a chill test and a



cold test of 24 hours minimum should be required. The chill test consists of drying and filtering the test sample before hermetically sealing it in a 4-ounce bottle. The sample is held at 70°F (21.1°C) and examined after 24 hours for clarity. Any indication of a cloud or wisp indicates the presence of a wax or hard-oil contamination.

### 2.11.2 Dewaxing Applications

The highly unsaturated vegetable oils marketed in the United States as salad oils, which can cloud due to a wax content, are listed below with their typical wax contents:

Source Oil	Typical Wax Content (%)
Sunflower	0.2–3.0
Safflower	~0.5
Corn	0.5–1.0
Canola	~0.2

## 2.12 FRACTIONATION

Edible fats and oils are fractionated to provide new materials more useful than the natural product. Edible fats and oils are complex multicomponent mixtures of various triglycerides with different melting points. The melting behavior and the clear point of fats are important properties for functionality in the various prepared food products. Fractionation processes separate fats and oils into fractions with different melting points. Fractionation may be practiced merely to remove an undesirable component, which is the case with dewaxing and winterization processes to produce liquid oils that resist clouding at cool temperatures. Separation of a fat or oil into fractions can also provide two or more functional products from the same original product. The production of cocoa-butter equivalents or substitutes is a well-known application for this type of fractionation.

Separation of fats and oils fractions is based on the solubility of the component triglycerides. The solubility differences are directly related to the type of triglycerides in the fat system. The triglycerides types are determined by their fatty acid composition and the distribution of the fatty acids on the individual triglyceride molecule. Components of a fat or oil that differ considerably in melting point can be separated by crystallization and subsequent filtration for removal of the higher melting portions. In any practical process of fractional crystallization the potential for efficient separation of crystals from the liquid is dependent upon the mechanics of separation as well as the phase behavior of the system. The successive stages of fractionation can be distinguished as:

1. Cooling of the oil to supersaturation to form the nuclei for crystallization
2. Progressive growth of the crystalline and liquid phases
3. Separation of the crystalline and liquid phases

Separation efficiency of the liquid and solid fractions depend primarily upon the cooling method, which determines the crystal form and size. Fats and oils can crystallize in several polymorphic forms, specifically  $\alpha$ ,  $\beta'$ , and  $\beta$  in that order of stability, melting point, heat of fusion, and density. The rate of crystallization for the  $\alpha$  form is higher than for the  $\beta'$  form, which crystallizes quicker than the  $\beta$  form. Rapid cooling causes heavy supersaturation, which forms many small, shapeless, soft crystals of mixed crystal types with poor filtration properties. Gradual cooling of the oil results in stable  $\beta$ - and  $\beta'$ -crystals that are easily filtered from the liquid phase.

Three distinct unit processes for the fractionation of triglycerides that couple crystallization and separation process are practiced commercially to produce value-added fractionated fats and oils: (1) dry fractionation, (2) solvent fractionation, and (3) aqueous detergent fractionation.<sup>79</sup> Dry fractionation processes include winterization, dewaxing, hydraulic pressing, and crystal fractionation. It is the most widely practiced form of fractionation in which crystallization takes place without the aid of a solvent. The winterization process is effective for the removal of small quantities of solid fat from a large quantity of liquid oil. Dewaxing can be a variation of the winterization process to remove small quantities of waxes from certain vegetable oils rich in unsaturates. Hydraulic pressing effectively removes small quantities of liquid oil from a large quantity of solid fat. Some oils, such as palm oil, that contain high levels of both liquid and solid fractions can be separated by dry fractionation but not as efficiently as with other processes. Solvent or aqueous detergent fractionation processes provide better separation of specific fractions of the feedstock materials.

### 2.12.1 Dry Crystal Fractionation

The advantages of fractionation were accidentally revealed to European companies with coconut oil imported from Sri Lanka in long wooden barrels called *Ceylon pipes*. The barrels were filled with warm coconut oil, which cooled slowly during the sea voyage to the cooler temperatures in Europe. The slow cooling, coupled with agitation from movement of the ship, caused the coconut oil to crystallize and separate into a hard and soft fraction. Customers receiving the fractionated product evaluated the properties of the components and realized that the fractions were more useful for some applications than the whole or natural products.<sup>80</sup>

Dry crystal fractionation procedures are commonly used for separation of hard stearine and soft olein fractions from natural products that contain high levels of each like palm oil and the lauric fats. The principal of this fractionation procedure is based on slowly cooling the oil under controlled conditions without the aid of a solvent. The stearine and olein fractions can be separated by various processes, such as filtration, centrifugation, hydraulic pressing, rotary drum, or one of the patented processes. In the dry process, large crystals are generally required for efficient separation. The large crystals tend to group together in clumps, which can trap part of the liquid olein phase. This results in a soft stearine or a low olein yield caused by the poorer separation. A low olein yield can also be experienced from the formation of mixed crystals. Controlled slow cooling of the natural oil will diminish these problems to provide cleaner separation of the olein and stearine fractions.

One unique labor-intensive dry crystal fractionation process still utilized to fractionate lauric oils is to slowly cool the oil until it has a plastic consistency. This product is poured into canvas bags and cooled further to the fractionation temperature, and the crystal is allowed to stabilize or mature. Then a hydraulic press is used to squeeze the oil portion out of the stearine cake. This procedure can produce a very acceptable confectionery coating fat from palm kernel oil.<sup>80</sup> Previously, this process was utilized to fractionate lard and tallow to produce hard fractions for use in stabilizing compound shortenings and a liquid oleo oil. High-viscosity-resistant crystallizers and high-pressure membrane filter presses have been developed to replace this labor-intensive process for high-quality specialty fats.<sup>81</sup>

### 2.12.2 Detergent Fractionation

The aqueous detergent fractionation procedure utilizes the same basic principals of dry fractionation; that is, crystallization is induced by cooling the oil under controlled conditions without the addition of a solvent.<sup>80,82</sup> The difference is that an aqueous detergent solution is added to the crystallized material to assist in the separation of the liquid olein and the solid stearine. The aqueous solution contains about 5% of a detergent such as sodium lauryl sulfate, which preferentially wets the surface of the crystals displacing the liquid oil. About 2% of an electrolyte such as magnesium or aluminum sulfate is added to the solution to assist in uniting the liquid olein droplets. Separation is then effected with a centrifuge. The heavier phase containing the stearine is heated to melt the stearine and separate the oil and water phases. Complete separation of these phases is accomplished with a second centrifuge. Aqueous detergent fractionation is more expensive than dry fractionation, but more complete separation of the soft and hard fractions can be achieved, thus producing a higher olein yield and a harder stearine fraction.

### 2.12.3 Solvent Fractionation

Solvent fractionation is an expensive process that can be justified only for preparation of value-added, high-quality products. The ultimate objective for the use of solvent fractionation technology is commercial production of fat and oil products with unique properties. Fractional crystallization from dilute solution results in more efficient separation with improved yields, reduced processing times, and increased purity than can be achieved by fractionation carried out without a solvent. The attractive benefits are partially, and for some products completely, offset by high capital costs for the handling and recovery of the solvents, as well as increased cooling capacity requirements. Some of the product categories that have utilized solvent fractionation technology to produce products with unique functional characteristics include:

- *Cocoa-butter equivalents (CBEs)* — CBEs are fats with chemical compositions similar to cocoa butter and capable of replacing it in any proportion in chocolates.
- *Lauric cocoa-butter replacers (CBRs)* — These are products made from fractionated coconut or palm kernel oils with physical properties closely resembling cocoa butter.

- *Nonlauric CBRs* — The most widely used products in this classification are based on solvent-fractionated, hydrogenated liquid oils, such as soybean, cottonseed, and palm oils.
- *Confectionery products* — Fat systems with a low melting point but a high SFI content at room temperature can provide products with a quick melt at body temperature, which results in a cooling sensation when eaten. High-quality candy centers and whipped toppings are two specific applications for fractionated products.
- *Medium-chain triglycerides* — Lauric oil fractions containing C-6:0, C-8:0, and C-10:0 saturated fatty acids, which are soluble in both oil and water systems for quick absorption by the body and transported via the portal system.
- *High-stability liquid oils* — Modification of oils by utilization of hydrogenation with fractionation has permitted the development of liquid oils with high resistance to oxidative degradation. Liquid oils with an AOM stability of 350 hours are available commercially.

Commercially, solvent fractionation is carried out by a number of different processes that may be batch, semicontinuous, or continuous.<sup>82,83</sup> Crystallizers, filters, and solvent recovery systems can differ in design, and one of several organic solvents may be employed. Solvents that have been used include acetone, hexane, and 2-nitropropane. Some of the processes are protected by patent and are proprietary, but all require control of certain process parameters:

- Feedstock selection, which can include natural oils and blends, hydrogenated oils and blends, randomly rearranged oils and blends, and blends of any or all of these
- Concentration of the fat in the solvent
- Fractionation temperature
- Cooling rate and residence time in the crystallizer
- Separation conditions

A typical solvent fractionation process flow usually begins with heating the feedstock oil to a temperature above the completed melting point and blending with warm solvent in the ratio of 1 part oil to between 3 and 5 parts solvent by weight. The solution is then cooled to crystallize the hard fractions. Crystallization temperatures vary, depending on the nature of the solvent, the concentration of oil in the solution, and the characteristics needed in the final fractions. For example, for lauric oils in acetone solvent, temperatures of 28 to 68°F (−2 to 20°C) have been used to obtain stearine iodine values of 1.8 to 8.3. The crystallized slurry is separated by filtration or by a settling technique. The solid material is then stripped of solvent for one fraction. Removal of the solvent from the filtrate yields another fraction. Further fractionation may then be achieved by redissolving either fraction and repeating the process.

## 2.13 ESTERIFICATION OR ALCOHOLYSIS

Emulsifiers are usually made either by alcoholysis or by direct esterification. In direct esterification, fatty acids and polyalcohols are reacted together under controlled conditions to form esters. In alcoholysis, fats are reacted with polyalcohols

to make the surfactants. For example, the production of mono- and diglycerides from fat is an alcoholysis reaction with glycerine as the alcohol.

Mono- and diglycerides were the first fatty emulsifiers to be added to foods. These emulsifiers were first used in margarine for Danish pastry and puff pastry shortening. The first U.S. patents for mono- and diglycerides granted in 1938 disclosed the usefulness of surfactants in emulsions and margarine.<sup>84</sup> Monoglycerides with only one fatty acid attached to a glycerol molecule and two free hydroxyl groups on the glycerol take on the properties of both fats and water. The fatty acid portion of the molecule acts like any other fat and readily mixes with the fatty materials, whereas the two hydroxyl groups mix or dissolve in water; thus, monoglycerides tend to hold fats and water together. Cake shortenings that offered increased aerating, creaming, and moisture retention properties contributed by the addition of mono- and diglycerides were introduced in 1933, with patents granted in 1938, as well. Shelf-life extension properties for yeast-raised products with the addition of mono- and diglyceride were introduced soon after to bread bakers.<sup>84</sup> Since that time, the uses and demand for food emulsifiers have grown dramatically, and several other emulsifiers have been developed. Most of the fatty emulsifiers produced are either monoglyceride derivatives or utilize an alcohol other than glycerine, such as propylene glycol monoester (PGME) or polyglycerol ester (PGE). Examples of the monoglyceride derivatives include ethoxylated monoglycerides, acetylated monoglycerides, and succinylated monoglycerides.

Emulsifier production is generally performed in versatile batch equipment that is used for a variety of different surfactants. Acid-resistant construction for the tankage and reactors is one or another variant of the 300 series stainless steels. The use of these alloys essentially eliminates the possibility of iron and other metal contamination that may either degrade the product or catalyze undesirable oxidation or other side reactions. Typically, type 304 stainless steel is used for fatty chemical processes where the temperature does not exceed 300°F (150°C), and type 316 is used for temperatures above this level.<sup>85</sup> Internal reactor coils capable of handling high-pressure steam and cooling water, as well as a vacuum system with 0.1-mmHg capabilities, are necessary for emulsifier reactors. A condenser for the recovery of the excess glycerine, glycol, or other alcohols should be sized for the largest volume of the polyalcohol to be recovered.

### **2.13.1 Mono- and Diglycerides**

Mono- and diglycerides are the most dominate food emulsifier both from the standpoint of total use and breadth of use. The mono- and diglycerides consist of glycerol esters of various edible fatty acids and fat blends. Three types of standard mono- and diglycerides are manufactured: 40 to 46%  $\alpha$ -monoglyceride content, 52 to 56%  $\alpha$ -monoglyceride content, and distilled monoglycerides with 90%  $\alpha$ -monoglyceride content. There are three basic physical forms of mono- and diglycerides: hard, soft, and intermediate. The differences in the emulsifier consistency is determined by the physical characteristics of the edible fat or oil used in the reaction. The consistency of the mono- and diglyceride, as indicated by the iodine value or melting point, determines the functionality of the emulsifier. Generally, a higher

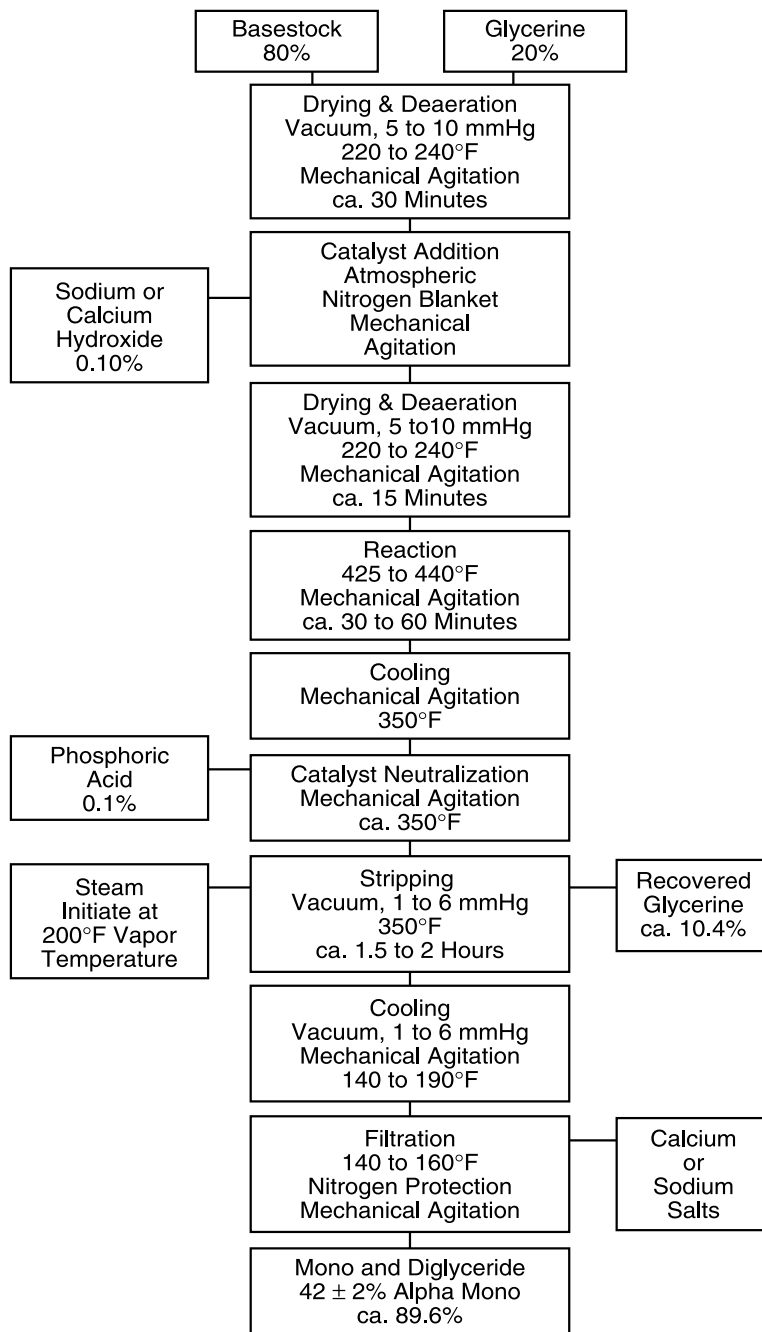
melting point emulsifier is preferred when a tight emulsion is desired, whereas the lower melting or softer products provide better aeration qualities. Intermediate-hardness mono- and diglycerides are compromise products suitable, to a degree, for both application ranges but not specific for either.

Most of the mono- and diglyceride requirements are produced by glycerolysis of triglycerides or fats and oils. In this process, fats and oils of the desired hardness are mixed with an excess of glycerine at elevated temperatures in the presence of an alkaline catalyst, usually either sodium or calcium hydroxide. The reaction mixture is kept at an elevated temperature until the fatty acid radicals of the triglycerides are redistributed at random among the available hydroxyl groups of the glycerine. The reaction mixture is cooled after equilibrium has been attained, and the catalyst is “killed” or deactivated by the addition of a food acid, normally phosphoric acid. The phosphate salts that result from the catalyst neutralization must be removed by filtration. The excess glycerine will separate as a lower layer upon cooling and can be partially removed by decanting. The glycerine that remains dissolved in the reaction mixture must be removed by vacuum distillation during steam stripping to reduce the FFA content and remove the oxidation materials that contribute to undesirable flavors and odors.

This process yields substantial amounts of monoglycerides in addition to diglycerides and triglycerides with altered or rearranged structures and free glycerine. The proportion of monoglyceride to diglyceride may be controlled, depending on the relative proportion of reactants, temperature, time, catalyst, and use of stripping steam or inert gas. The normal distribution is 50% monoglycerides, 40% diglycerides, and 10% triglycerides; approximately 85% of the monoglycerides are esterified on the  $\alpha$  position of the glyceride, the balance being esterified on the center or  $\beta$ -hydroxyl group. The composition of this mixture can be changed by reducing the amount of glycerine added or by changing reaction temperature and catalyst level. Most of the mono- and diglyceride emulsifiers made contain about 50% monoglycerides, but 60% monoglyceride levels can be attained. Higher monoglyceride contents can be obtained by distillation of the mono- and diglyceride products.

The amount of fat that will react with the specified amount of glycerine varies with the molecular weight of the fat involved. A product with a high molecular weight, such as soybean oil, requires more fat per pound of mono- and diglycerides produced than does a lower molecular weight product, such as tallow or cottonseed oil. On the basis of typical fatty acid compositions, the average molecular weight for hydrogenated soybean oil containing 3% oleic acid is 882.6, whereas the corresponding molecular weight for hydrogenated tallow triglyceride is 858.7. Theoretically, it would require 89.37 pounds of hydrogenated soybean oil to produce 100 pounds of glycerine-free mono- and diglycerides, whereas it would require only 88.15 pounds of hydrogenated tallow to produce 100 pounds of mono- and diglycerides. Because it is difficult to strip all the glycerine from the finished emulsifier, the above fat requirements become 88.9 pounds of hydrogenated soybean oil for a mono- and diglyceride containing 0.5% free glycerine and 87.7 pounds of hydrogenated tallow to yield 100 pounds of mono- and diglycerides again containing 0.5% free glycerine.

Mono- and diglycerides can be manufactured with either a batch or a continuous process; however, a large proportion of the U.S. demand is still produced with batch



**Figure 2.9** Mono- and diglyceride batch process flow.

systems where the reaction time, temperature, and catalyst may be varied. A typical batch process flow to produce a 40 to 46%  $\alpha$ -monoglyceride emulsifier is detailed in Figure 2.9. For continuous processing, the process time is considerably less than that required for batch systems, probably less than 30 minutes total, which is promoted in part by the higher reaction temperatures employed; however, the total pounds per man-hour may be equivalent to those produced by a batch system.

Concentrations of monoglycerides to produce the 90%  $\alpha$ -monoglyceride products is achieved by distillation of the mono- and diglyceride emulsifiers. Prior to the actual concentration, the free glycerine content has to be removed to preserve the monoglyceride content. The reaction between triglycerides and glycerine is reversible, especially in the presence of catalyst and at elevated temperatures. Additionally,

monoglycerides are not heat stable and have only limited heat tolerance, so thermal damage must be avoided. Molecular distillation is evaporative distillation where a compound in the liquid state evaporates without boiling, because the high vacuum removes the effect of atmospheric pressure. Monoglycerides vaporize, leaving the heavier di- and triglycerides behind in the distillation residue.<sup>84</sup> The residue is recycled to produce additional mono- and diglycerides for subsequent distillation until the product color becomes too dark.

### **2.13.1.1 Monoglyceride Derivatives**

Monoglycerides not only are used as surfactants as produced but also can be further modified to produce other surface-active products suitable for use in prepared foods. The multiple reactive groups of the monoglycerides allow the formation of other functional emulsifiers. One or both of the hydroxyl groups can be replaced by different groups to form esters with specialized functionality characteristics. Modified monoglyceride surfactants can be obtained by treating monoglycerides with an acid, acid anhydrides, acid chloride, or another ester. Some of the monoglyceride derivatives produced include the following.

### **2.13.1.2 Lactylated Monoglycerides**

The lactoglycerides comprise an important series of edible emulsifiers that are derived from monoglycerides or mixtures of mono- and diglycerides. Lactostearin can be made by subjecting low-iodine-value hydrogenated soybean oil to glycerolysis, using sodium or calcium hydroxide as a catalyst and then esterifying this mixture directly with lactic acid, followed by water washing to remove the bitter-tasting triglycerides of lactic acid. The resultant product can be identified as glyceryl lactostearate and mono- and diglycerides.<sup>86</sup> The lactylated monoglyceride surfactants are utilized primarily for aeration in cakes and whipped toppings.

### **2.13.1.3 Acetylated Monoglycerides**

Acetylated monoglycerides are characterized by sharp melting points with a waxy, rather than a greasy, feel. The physical and functional properties of a particular acetylated monoglyceride depend on the triglyceride from which it is made and the degree of acetylation. Monoacetylated or partially acetylated monoglyceride molecules each contain one long-chain fatty acid plus one acetyl group and one hydroxyl group. Diacetylated or fully acetylated monoglyceride molecules each contain one long-chain fatty acid and two acetyl groups. Acetylated monoglycerides may be produced by either of two procedures:

1. Direct acetylation of monoglycerides with acetic anhydride without a catalyst or molecular distillation with the acetic acid, acetic anhydride, and triacetin removed by vacuum distillation
2. Interesterification of edible fats and oils with triacetin in the presence of a catalyst, followed by molecular distillation or steam stripping



Acetylated monoglycerides are stable in the  $\alpha$ -crystal form. These  $\alpha$ -crystalline-tending emulsifiers promote the agglomeration of the dispersed fat globules that induce clumping of fat globules into clusters to form structural networks in whipped toppings and other foams. Saturated monoglycerides can be stabilized in the active  $\alpha$ -crystalline form with the addition of acetylated monoglycerides.

#### **2.13.1.4 Ethoxylated Mono- and Diglycerides**

Ethoxylated mono- and diglycerides labeled as “polyglycerate 60” are formed when 20 moles of ethylene oxide are reacted with a mono- and diglyceride. The reaction is carried out at 265 to 325°F (130 to 165°C) under pressure because ethylene oxide is a gas catalyzed by a base such as sodium hydroxide. The polymerized ethylene oxide chains combine with the mono- and diglycerides to produce an effective emulsifier with strong hydrophilic characteristics. The presence of many ether oxygen atoms in the polyoxyethylene chains offers sites for hydrogen bonding to water molecules and proteins.<sup>84</sup> The physical form contributed by the triglyceride basestock has a direct affect upon functionality; that is, firm consistencies are preferred for yeast-raised products, and soft consistencies provide better aeration properties for cakes and icings.

#### **2.13.1.5 Succinylated Monoglycerides**

Succinylation of monoglycerides changes the properties of the surfactant from one with essentially only bread-softening properties to one with both softening and dough-strengthening properties. This product is manufactured by reacting monoglyceride with succinic anhydride at temperatures ranging from 175 to 350°F (80 to 180°C). At high temperatures, no catalyst is required but at reaction temperatures below 200°F (95°C) a low level of an alkaline catalyst may be needed to accelerate the reaction.<sup>87</sup>

### **2.13.2 Polyglycerol Esters**

Polyglycerol esters have unique physical and chemical properties that provide a broad range of functional properties.<sup>88,89</sup> Polyglycerols are polymers formed by the dehydration of glycerine. For each molecule of glycerine added to the polymer, there is an increase of one hydroxyl group. The potential number of different possible polyglycerol esters is almost limitless, depending upon the degree of glycerine polymerization. U.S. Food and Drug Administration (FDA) regulations have approved these surfactants, ranging up to and including decaglycerol esters of edible fats and oils from corn, cottonseed, peanut, safflower, sesame, soybean, lard, palm, and tallow. The polyglycerol esters are functional in a very broad range of applications, either singly or blended with other emulsifiers, to include crystal inhibitors; aeration of batters, icings, fillings, and toppings; antispattering agents for cooking oils and margarine; low-fat products; ice cream and mellorine; confectionery anti-bloom agent; viscosity control; nondairy creamers; cake mixes; lubricants; etc.

The esters are made by reacting fat with glycerine that has been polymerized into polyglycerols at high temperatures. To a degree, the polymerization can be controlled to produce varying amounts of diglycerol, triglycerol, tetraglycerol, etc. Two molecules of glycerol will combine to form diglycerol and a molecule of water. The diglycerol is then transformed into triglycerol as another glycerol molecule is added. The water released by the polymerization distills from the reaction mixture at the high temperature used and is lost.

Similarly, tetraglycerol and the higher polymers can be formed from triglycerol. During polymerization of glycerol, these reactions are all occurring at the same time but at different rates. Thus, the polymerized product is a mixture of glycerol and various polymers, with the actual composition depending on polymerizing conditions and its extent. The average molecular weight of the polyglycerol mixture can be either low or high, depending on the extent of the polymerization, with the number of hydroxyl groups per molecule or sites for esterification with fatty acids increasing as the molecular weight increases. Variations in molecular weight of the polyglycerol or the fatty acids and in the fatty acid/polyglycerol ratio will change the solubility characteristics and emulsification properties of the reaction product.

The following procedure has been utilized to polymerize glycerine and esterify the polyglycerol and triglyceride basestock in the same reaction vessel:

1. Charge the reactor with glycerine.
2. Add 1.0% sodium hydroxide (dry basis) to the glycerine while agitating.
3. Start heating and sparge nitrogen through the mixture to provide a positive nitrogen flow through the reactor outlet through a condenser. Care must be exercised to exclude air from the system. Traces of oxygen lead to the formation of acrolein as well as a dark color that is difficult to bleach.
4. Heat to 480 to 500°F (250 to 260°C) and hold while continuing the nitrogen sparge to carry off the water liberated.
5. Determine the polymerization process endpoint using the refractive index or measurement of the liberated water removed.
6. Cool the polyglycerol mixture.
7. Add the triglyceride basestock at equal proportions to the polyglycerol weight while sparging with nitrogen.
8. Stop the nitrogen sparge and initiate a vacuum on the reactor.
9. Heat and maintain the mixture at 410 to 425°F (210 to 220°C) for 2 hours. Approximately 20% of the glycerol should be removed and recovered during the reaction.
10. Cool the polyglycerol ester before exposing it to the atmosphere. From this point, the polyglycerol esters can be treated much the same as triglycerides. They can be bleached and deodorized by the usual procedures used with fats and oils.

### **2.13.3 Propylene Glycol Monoester**

Propylene glycol has the same carbon chain length as glycerine, but it has only two hydroxyl groups. Commonly used propylene glycol monoesters are generally more lipophilic than many glycerol monoesters because they have fewer free hydroxyl groups. Alcoholysis of triglycerides with propylene glycol leads to mixed

partial glycol-glycerol esters or propylene glycol mono- and diesters and mono- and diglycerides. Propylene glycol monoesters are  $\alpha$ -crystalline-tending, surface-active compounds that have proved to be especially effective emulsifiers for cake baking and whipped toppings. The emulsifier forms an  $\alpha$ -crystalline film around entrapped air bubbles to stabilize the food systems.

The process for the preparation of PGME emulsifiers is similar to that used for the manufacture of mono- and diglyceride emulsifiers, except that propylene glycol is reacted with the fat base. Mono- and diesters of propylene glycol are formed and glycerine is liberated from the triglyceride. Some of the liberated glycerine reacts with some of the fat present, forming mono- and diglycerides following the same reaction used for mono- and diglyceride preparation. The propylene glycol monoester composition will vary depending upon the mixture to reaction. A reaction mixture of basefat and pure propylene glycol should yield approximately 70% propylene glycol monoesters and 10% monoglyceride, with the balance consisting of propylene glycol diesters, diglycerides, and a small amount of triglyceride.

## 2.14 BLENDING

Basestocks are blended to produce the specified composition, consistency, and stability requirements for the various edible fat and oil products, such as shortenings, frying fats, margarine oils, specialty products, and even some salad oils. The basestocks may be composed of hydrogenated fats and oils; interesterified products, refined and bleached oils; or fractions from winterization, dewaxing, or 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 evaluations for solids fat index, iodine value, melting points, fatty acid composition, etc. Basestocks should not be blended with a disregard for either specified composition or analytical requirements. It is often possible to meet the specified analytical requirements with several different basestock compositions; however, only the specified composition will perform properly, have the required oxidative stability, or conform to the nutritional and ingredient statements.

The blending process requires scale tanks and meters to proportion the basestocks accurately for each different product. The blend tanks should be equipped with mechanical agitators and heating coils to ensure a uniform blend for consistency control. Capacities of the blend tanks should be sized to accommodate the next process, probably deodorization. Nitrogen protection should be provided for the long holding times required to perform some of the analytical evaluations. A typical blending process sequence is:

1. Determine the proportions for each basestock for the product to be blended.
2. Add the basestocks to the blend tank at the identified proportions.
3. Heat the blend if necessary to the specified temperature and agitate for 20 minutes.
4. Sample and submit to the laboratory for the specified analysis.
5. Transfer to the next process if the analytical characteristics meet the specified limits.

6. Adjust blends outside the specified limits to bring them into the allowed consistency control ranges; however, use only specified basestocks within the allowed ranges for any adjustments.
7. Resample the adjusted blend after agitating for 20 minutes to achieve a uniform product and resubmit to the laboratory for consistency analysis.
8. Transfer to the next process after the specified analytical objectives have been met.

## 2.15 DEODORIZATION

In the early stages of the development of the edible fats and oils industry, offensive odors and flavors were not a problem. Lard and butter were consumed in the same form as produced, and the natural flavors were considered an asset. Olive oil, one of the earliest known vegetable oils, was and still is used for its distinctive flavor; however, the rapid expansion of cotton acreage at the end of the 19th century resulted in large quantities of cottonseed oil, which presented an economic incentive to use this vegetable oil. Caustic refined and bleached cottonseed oil was offered as a cooking or salad oil and blended with tallow or olein stearine as a lard substitute. These products enjoyed a price advantage over lard and olive oil, but the unpleasant flavor was so strong that acceptance was poor. In addition, the hydrogenation process developed to harden vegetable oils imparted a more disagreeable flavor and odor to the oils. Attempts to remove the flavor and odors chemically or to mask them with spices or flavors were unsuccessful. The first successful attempt at removing the disagreeable odors and flavors from a fat and oil consisted of injecting live steam into an oil at high temperatures. It was discovered in England, but this flavor-improvement process was soon adapted by most American fat and oil processors. The advantages of treating oils with steam to remove offensive flavors and odors was recognized in the early 1890s by Henry Eckstein. David Wesson improved the process by using higher temperatures and maintaining the oil under vacuum while blowing with superheated steam.<sup>90,91</sup>

Deodorization is a vacuum-steam distillation process of an oil at an elevated temperature during which FFAs and minute levels of odoriferous materials are removed to obtain a bland and odorless oil.<sup>91-98</sup> Most vegetable oils retain characteristic undesirable flavors and odors and obtain others during processing. Bleaching imparts an “earthy” flavor and odor, and hydrogenation adds an odor and flavor that can be described only as typical and certainly undesirable. The odoriferous substances are FFAs, aldehydes, ketones, peroxides, alcohols, and other organic compounds. Additionally, certain carotenoid pigments are destroyed, resulting in a heat-bleaching effect. Efficient removal of these substances depends upon their vapor pressure, for a given constituent is a function of the temperature and increases with the temperature. Deodorization is the last major processing step during which the flavor and odor and many of the stability qualities of an oil can be affected. From this point forward, effort is directed toward retaining the quality that the deodorized oil possesses; therefore, considerable care must be given to the selection, operation, and maintenance of the deodorizer equipment and the operating conditions.

## 2.15.1 Operating Variables

Deodorization conditions depend upon the particular oil type, the oil quality, and the refining system used. A shift in refining technology toward physical refining where the FFA is removed exclusively by steam distillation requires more severe conditions than do chemically refined oils. With chemical refining, most of the FFA content has been neutralized before deodorization. Physically refined oils have FFA contents between 1.0 and 5.0% compared to 0.05 to 0.1% for chemically refined oils. The steam distillation requirements for both physical and chemically refined oils can be achieved by altering one or more of the operating variables. The four interrelated operating variables that influence deodorized oil quality are vacuum, temperature, stripping-steam rate, and holding time at deodorization temperatures.

### 2.15.1.1 Vacuum

If fatty acids and odoriferous substances are to be distilled at as low a temperature as possible, distillation must be carried out at low absolute pressures effected by the vacuum system. The boiling point of the fatty acids and the vapor pressure of the odoriferous materials decrease as the absolute pressures decrease. 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, vapor condensers, and mechanical vacuum pumps. Special vacuum systems have been developed to reach lower pressures and operating costs and, at the same time, reduce emissions by a more efficient condensing of the volatiles. In the dry condensing systems, the sparge steam is condensed on surface condensers working alternatively. The remaining noncondensables are removed by mechanical pumps or by a vacuum ejector system.

### 2.15.1.2 Temperature

Deodorization temperatures must be high enough to make the vapor pressure of the volatile impurities in the oil conveniently high. The vapor pressure of the odoriferous materials increases rapidly as the temperature of the fat is increased. For example, the vapor pressure of palmitic fatty acid is 1.8 mm at 350°F (176.7°C), 7.4 mm at 400°F (204.4°C), 25.0 mm at 450°F (232.2°C), and 72 mm at 500°F (260°C). Assuming that the vapor pressure–temperature relationship for all the odoriferous materials is similar to that of palmitic fatty acid, each 50°F (27.8°C) deodorizer temperature increase would triple the odoriferous material removal rate. Or, stated another way, it would take nine times as long to deodorize an oil at 350°F than at 450°F. Higher deodorizer temperatures definitely provide shorter deodorization times; however, excessive temperature results in the development of the polymerization, isomerization to produce *trans*-acids, thermal cracking with formation of odoriferous and low boiling products, color reversion, and distillation of tocopherols. Generally, *trans* formation during deodorization is negligible below 428°F (220°C), becomes significant between 428 and 464°F (220 and 240°C), and is nearly exponential above 464°F (240°C). Thermal degradation of the tocopherols becomes

significant at deodorization temperatures above 500°F (260°C).<sup>96</sup> It has been determined that twice as many tocopherols and sterols are stripped out at 525°F (275°C) as at 465°F (240°C), and that pressure variations of 2 to 6 mbar had only a slight effect upon tocopherol/sterol stripping. Deodorizer operation at elevated temperatures can also promote thermal decomposition of some constituents naturally present in oils, such as pigments and some trace metal–prooxidant complexes. The carotenoid pigments can be decomposed and removed by deodorization beginning at 446°F (230°C); therefore, a compromise must be determined between time and temperature for deodorizing particular fats and oils.

Optimum deodorizer operating temperatures vary from product to product. In general, animal fats require less stringent conditions than the vegetable oil products. Chemically refined oils are easier to deodorize than physically refined oils due to lower FFA levels and more effective removal of polar components, oxidation products, and pigments. Among the vegetable oils, those containing relatively short-chain fatty acids such as coconut and palm kernel oils require lower deodorization temperatures than the domestic oils composed of longer chain fatty acids. Hydrogenated oils are usually more difficult to deodorize because of higher FFA contents and the distinctive odor imparted by the hydrogenation reaction. Corn oils usually require a higher temperature or longer residence time to achieve the desired heat bleach. In general, deodorization temperatures will vary from 400 to 475°F (204 to 246°C) and in some cases as high as 525°F (274°C).

### **2.15.1.3 Stripping Steam**

Adequate stripping steam, consistent with the temperature and pressure in the deodorizer, is required. The amount of stripping steam required is a function of both the absolute operating pressure and the mixing efficiency of the equipment design. Agitation of the oil, necessary to constantly expose new oil surfaces to the low absolute pressure, is accomplished by the use of carefully distributed stripping steam. Therefore, oil depth is a primary factor for establishing both the stripping steam requirement and the deodorizing or holding time. The quantity of fatty acids distilled with each pound of steam is directly proportional to the vapor pressure of the fatty acids. Effective steam stripping is dependent upon volume; for example, 1-mbar operation will require a lower weight percentage of stripping steam than will 6-mbar operation. Differences among the source oils also affect steam requirements; for example, canola oil requires more steam than soybean oil to remove the odor. Excessive live steam may cause hydrolysis and increased energy consumption for the vacuum system. Typical stripping steam deodorization conditions for chemically refined oils are 5 to 15 wt% of oil for batch systems and 0.5 to 2% for continuous and semicontinuous deodorizer systems.

### **2.15.1.4 Holding Time**

Deodorizer holding time is the period during which the fat or oil is at deodorizing temperature and subjected to stripping steam. Stripping time for efficient deodorization has to be long enough to reduce the odoriferous components of the fats and

oils products to the required level. This time will vary with the equipment design. For example, a batch deodorizer with an 8- to 10-foot depth of oil above the sparging steam distributor will require a longer deodorization time than will a continuous or semicontinuous system that treats shallow layers of oil. Typically, the holding time at elevated temperatures for batch deodorizer systems is 3 to 8 hours, whereas the holding time for continuous and semicontinuous systems vary from 15 to 120 minutes. Additionally, certain reactions with the oils deodorized are not related to removal of FFAs but instead help provide a stable oil after deodorization. These reactions and the heat bleaching are time and temperature dependent; therefore, deodorizing systems provide a retention period at deodorizing temperatures to allow these reactions and the heat bleaching to occur.

## **2.15.2 Deodorization Systems**

Deodorization equipment in current use can be classified into three principal groups: batch, continuous, and semicontinuous. The system choice depends upon several factors, such as the number of feedstock changes, heat recovery, investment, operating costs, ecology requirements, physical or chemical refining, and so forth.

### **2.15.2.1 Batch**

This is basically the simplest type of deodorization system that can be installed. The principal component parts consist of a vessel in the form of a vertical cylinder with dished or cone heads. The vessel is fabricated from type 304 stainless steel to avoid the deleterious catalytic activity of copper and iron on oils, welded to prevent air leaks, and well insulated to minimize heat loss. The usual range of capacity is 10,000 to 40,000 pounds, although the preference appears to be batch sizes of 15,000 to 30,000 pounds. Vessel diameters are usually chosen to give a depth of 8 to 10 feet of oil and have a similar amount of headspace above the surface of the oil. It is necessary to allow sufficient head space to avoid excessive entrainment losses from the rolling and splashing of the oil caused by the injected steam. Stripping steam is injected into the bottom of the vessel through a distributor. In addition to the steam ejector system, means for heating, cooling, pumping, and filtering the oil are required. The batch system controls include a device for indicating oil temperature and a pressure gauge designed to indicate accurately low pressures within the deodorizer.

Equipment operating at a high temperature and 6- to 12-mbar pressure requires about 8 hours for a complete deodorization cycle of charging, heating, deodorizing, cooling, and discharging the oil. Some systems operating at higher pressures or lower deodorization temperatures may require as long as 10 to 12 hours for a deodorization cycle. The total amount of stripping steam required may vary from approximately 10 to 50 lb per 100 lb of oil, with the average usage probably about 25 lb per 100 lb oil. The stripping steam is ordinarily injected at 3 lb per 100 lb of oil per hour at 6-mbar pressure. The oil must be cooled to as low a temperature as practicable after deodorization before it is discharged to atmospheric conditions to minimize oxidation. A temperature of 100 to 120°F (38 to 49°C) is preferred for liquid oils,

with higher temperatures being necessary for higher melting products but still maintained as low as possible.

Batch deodorization has the advantage of simplicity of design, flexibility, and ease of operation. It can be operated for as long or as short a period as required, with frequent product and even deodorization condition changes. Mechanically, batch deodorizer systems require very little maintenance; however, the cost of utilities for batch deodorization is considerably higher than for the continuous or semicontinuous systems. Batch systems do not provide a convenient means of recovering any substantial portion of the heat required, they have a high stripping steam consumption, and they require large vacuum systems with high steam and water requirements. But, the lower labor and capitalization costs for the original installation may offset a portion of the higher utility costs.

### **2.15.2.2 Semicontinuous**

These systems operate on the basis of handling finite batches of oil in a timed sequence of deaeration-heating, holding-steam stripping, and cooling such that each quantum of oil is completely subjected to each condition before proceeding to the next step. The semicontinuous deodorizer consists principally of a tall cylindrical shell of carbon steel construction with five or more type 304 stainless steel trays stacked inside of, but not quite contacting, the outer shell. Each tray is fitted with a steam sparge and is capable of holding a measured batch of oil. By means of a measuring tank, oil is charged to the top tray where it is deaerated while being heated with steam to about 320 to 330°F (160 to 166°C). At the end of the heating period, the charge is automatically dropped to the second tray, and the top tray is refilled. In the second tray the oil is heated to the operating temperature and again after a timed period is automatically dropped to the tray below. When the oil reaches the bottom tray, it is cooled to 100 to 130°F (38 to 54°C) and discharged to a drop tank from which it is pumped through a polishing filter to storage. Semicontinuous deodorizers are usually automated and controlled from a central panel with a time-cycle controller and interlocks such that the sequence steps are interrupted in the event of insufficient batch size, improper drop-valve opening or closing, or the oil not reaching the preset heating or cooling temperatures in the allotted time.

One of the principal advantages of the semicontinuous deodorization system derives from the fact that all of the trays are under the same relatively high vacuum. All oil receives substantially identical treatment, and the annular space between the trays and the shell provides some insurance against oxidation due to inward leakage of air. The deodorizer arrangement avoids refluxing of once-distilled undesirable materials back into the oil. This reflux, plus any mechanical carryover, is permitted to drain from the bottom of the deodorizer shell. The ability to accommodate frequent stock changes with a minimum of lost production and practically no intermixing is an important advantage for the semicontinuous systems over the continuous deodorization systems; however, heat recovery is less efficient than a continuous operation, and 10 to 20% more sparge steam is required.