SECOND EDITION

FATS *and* OILS

Formulating and Processing for Applications

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FIRST EDITION PREFACE

This book was written as a practical reference for fats and oils processing and formulation for effective food processor, foodservice, and household applications. It is designed to be an information source for personnel and students of fats and oils processing, as well as for personnel of the user industries.

A number of books are available that cover various aspects of fats and oils chemistry, technology, and processing; however, the author is not aware of a text devoted to fats and oils processing and formulation from an applications and quality control viewpoint. These are important assets for the success of a fats and oils processor. Product application influences the design of the finished product. Quality assurance provides consistent, uniform functionality.

Applications development and quality management begin when the customer's requirements are identified and continue through product design, sales, manufacturing, product costing, delivery, and service. This book was designed to delve into the technical aspects that control the functional characteristics of fats and oils products, how these characteristics can be modified to perform as needed, and the processing control necessary to produce these characteristics on a continuing uniform basis at the most economical cost. A thorough understanding of the functions and properties of the various fats and oil products is the basic key to formulating for the desired attributes. Chapters dealing with the raw material or source oils and fats, performance evaluations, formulation attributes, and application were designed to provide the elements of formulation. Control of these processes requires consideration of the problems associated with the properties of raw materials and each process, as well as customer problems after the sale. Therefore, a quality management chapter was included to help establish when a system is in or out of control, and a trouble-shooting chapter was included to identify solutions to problems or at least stimulate the thought process for solving the problem.

Fats and oils user industries have always shown a great deal of interest in the development, processing, and quality control of shortening, margarine, and liquid oil products. Tailored fats and oils products for specific applications, processes, nutritional contributions, and other functionalities have been successful due to the cooperative development efforts between fats and oils processors and users. Therefore, this text was compiled with the intent of focusing on applications of fats and oils products for both processors and users. The intent was to help better understand the functionalities, limitations, and potential of fats and oils modifications. As stated before, understanding the functions and properties of a shortening, oil, margarine, or other fats-based product is a key element of proper usage and product formulations. Likewise, understanding the requirements of the finished product is necessary to develop fats and oils products that perform more than adequately.

Materials for this book have been gathered over the past 35 years from patents, trade journals, scientific journals, personal experience, and exposure to many of the industry's recognized leaders and many other individuals who have taken a genuine pride in their work and the product produced.

SECOND EDITION PREFACE

The objective of the second edition of this book remains the same as the first: to provide a practical reference for processing and formulation of effective consumer, foodservice, and food processor fats and oils ingredients. Eight major changes or additions were made to improve to the second edition: (1) composition and physical properties for the raw materials have been expanded to provide a more complete information source, (2) information about and characteristics of genetically modified oils have been incorporated, (3) the nutritional aspects of fats and oils are more extensively reviewed, (4) extraction processes have been incorporated, (5) additional alternative processing procedures are reviewed for several areas, (6) formulation alternatives are explored more extensively, (7) source oil and product use statistics have been updated, and (8) the troubleshooting chapter has been expanded. The additions and modifications are designed not only to revise and update the content of the original but also to expand the content to better identify the available source oils, review alternative processes, explore various formulation techniques, and stimulate the development of new and improved products and processes.

The findings of numerous nutritional studies have generated a fair amount of activity since the first edition of this book was prepared. Diet and exercise have been identified as factors that individuals can modify to reduce their risk for chronic diseases such as coronary heart disease. The most important risk factors identified for heart disease are saturated fatty acids, cholesterol, *trans*-isomers, and obesity. A conscious effort to reduce cholesterol considerably reduced the use of animal fats in the past. Now, recent concerns about *trans*-isomers acting like saturated fatty acids have encouraged the pursuit of reduced levels of hydrogenated basestocks in many food products. These formulation changes affect source oil selection, processing, and formulation efforts to produce functional fats and oils products. Fats and oils processors must revise their basestock preparation techniques and other processing parameters to produce acceptable product characteristics. These developments indicate that fats and oils processing and formulation require continual attention to adequately serve the needs of their consumers.

Understanding the functions and properties of the raw materials along with the effects of the purification and modification processes is essential for the formulation of functional fats and oils products; therefore, the continuing purpose of this book is to serve as an information source for personnel and students of fats and oils processors, as well as for those of the user industries.

CONTENTS

Because butter is more expensive than other fats, its use is restricted to those products where the distinctive flavor makes a significant contribution to acceptability or use of the product or has advantageous marketing value. As a raw material, milk fat opportunities are limited for edible fats and oils processors, as most of the processes would destroy or materially change the flavor attributes. The opportunities that have been utilized in the United States are in final blends with margarine and in some cases with other products primarily as a flavorant.

A process utilized in Europe and Japan can effect consistency changes in milk fat without damaging the flavor. Unlike most conventional techniques to modify the consistency of a fat, dry fractionation neither destroys the milk fat flavor nor alters the fatty acid profile. The flavor and the polymorphic crystal form are maintained in the stearine and olein fractions with this process. The milk fat stearine fraction has application as a roll-in for puff pastry, Danish pastry, croissants, and other baked products as well as coating products. The olein fractions have been used in cookies and dairy products and have been blended with other edible oil products to prepare a soft tub-type tablespread.

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CHAPTER 2

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 seed 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 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 olive oil). 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 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

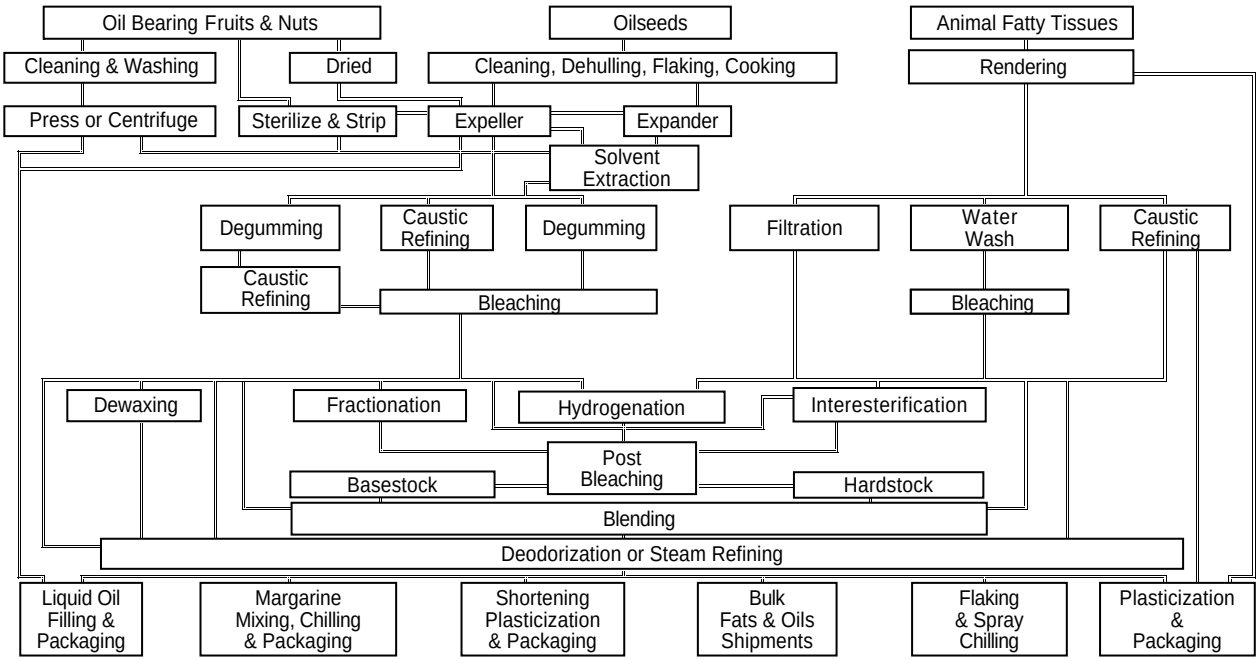


Figure 2.1 Typical fats and oils processing.

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 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.[1] 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 oilseeds is that (1) lipase causes an increase in FFAs, (2) lipoxygenase causes higher peroxide and secondary oxidation products, (3) phosphalipase 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.[2,3]

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 10 to 15% 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.[4]

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 products or formulations. Continuous screw presses are used for the mechanical extractions 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, sunflowerseed, 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 seeds 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 temperature 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.[2-7]

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 course 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 belts 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.[5,8]

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.[9]

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.[5,6]

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.

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 caustic 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 acid 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.[11] 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.

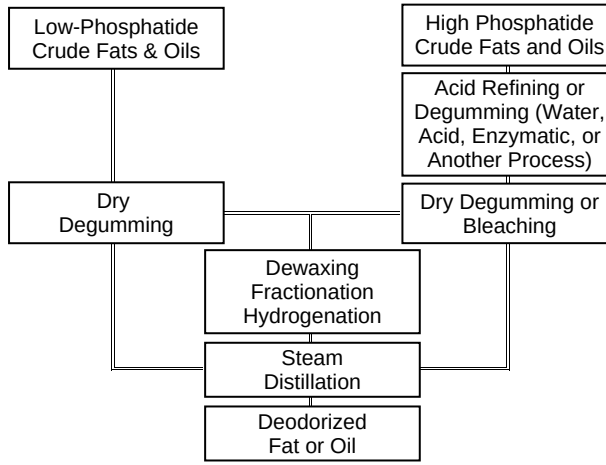


Figure 2.2 Physical refining process flow diagram.

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 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;[12] 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.[13]

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 unfavorable 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,[14] 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.[15] 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.[16] 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 phosphatides 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 loss 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

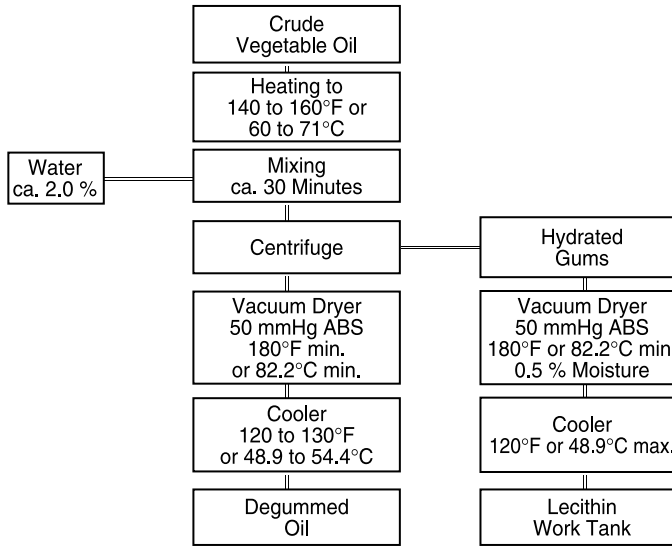


Figure 2.3 Batch water degumming process flow.

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.[17]

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.[18]

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.[19]

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,[20] 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 used to enhance bleaching efficiency before 1 to 3% bleaching earth is added and 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.[21] 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.[14,22,23]

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 soapstock 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 car, 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 treatment 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 weak 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 pigment 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 (2%), because they are refined for FFA reduction only. It should be remembered that the FFAs of 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 °Bé	Concentration NaOH (%) [a]	Excess Treat (%)
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

[a] 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 oil 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 heated to the centrifuges at a temperature suitable for optimum separation. Most soapstocks 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.

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.[17]

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.[25] 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.[10] Some processors add up to 400 ppm citric acid to wash waters to effect the removal of these residuals.[25]

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 these oilseeds of 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

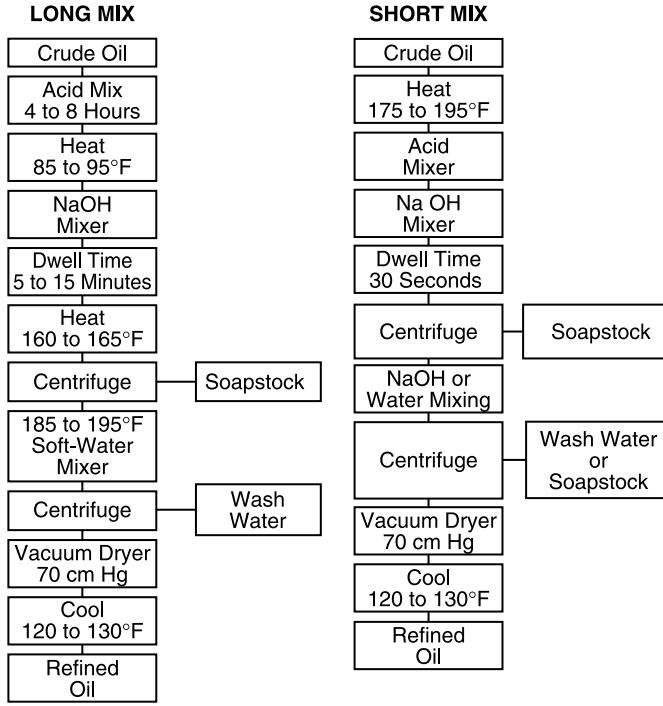


Figure 2.4 Comparison of long-mix and short-mix chemical refining systems.

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 devise 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.[36]

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.[37]

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.[28]

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 mix. 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, precoated, pressure 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 wash, fractionate, or hydrogenate the oil.[29,30]

Obvious disadvantages for the miscella refining process that may have discouraged many processors from adopting this processing system include:[31]

- 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 oilcan 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 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:[31,32]

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 attained, agitation is stopped, heating is discontinued, and the soapstock or foots 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.[21]

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.[23] A second bleaching option adds the silica separately 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 other 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.[33]

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 silicate.[33]

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 by 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),[34] and the refining efficiency is expressed as the ratio of the final oil produced to the laboratory-determined neutral oil in the crude oil. Corn and cottonseed oils trading rules specify

AOCS Method Ca 9a-52,[32] 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.[26] 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:[31]

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

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.[35]

Batch acidulation of the raw soapstock discharged from the caustic refining centrifuges consists of three basic steps:[36]

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.[37]

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.[38] 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.[39]

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,[40] but it does render lecithin toxic, and inorganic salts affect the physical and functional properties.[41] The acid-degummed lecithins have also exhibited poor functionality (i.e., inferior instantizing properties in cocoa powders and milk products).[42]

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 mainly 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.[10,43–48]

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.

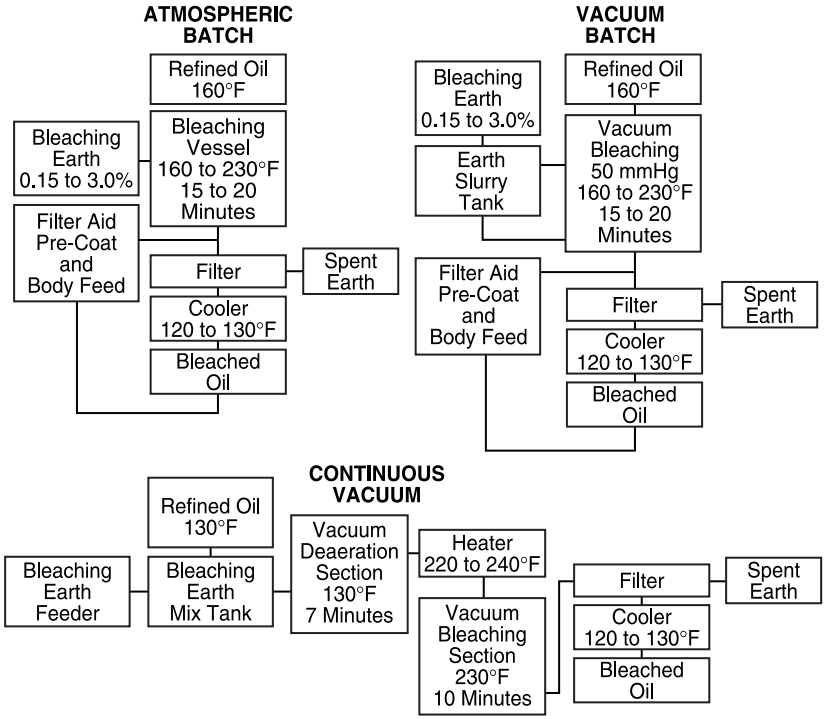


Figure 2.5 Typical bleaching process flow sequence.

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 to be bleached. 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.[48]

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, Fuller's earth. Molecular lattice structure, macropore structure, and particle size 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 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.[44] 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. 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.[45]

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.[46]

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 0.5 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.[46]

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.[18]

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.[47] 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 usually 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 prepared by 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 easily 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 color 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 silicas 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.[23]

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°F to 212°F or 90°C 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.[48]

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 the 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 the 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 may 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.[23]

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 oil 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/m². 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.[49]

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.[50]

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.[51–54] 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 will then 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 needed 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.[55–58] 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.

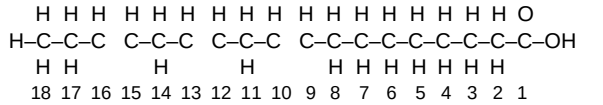
Chemically, fats and oils are a combination of glycerin and fatty acids called triglycerides The portions of triglycerides that can be changed with hydrogenation are classified as unsaturated fatty acids. Saturated fatty acids contain only single carbon-to-carbon bonds and are the least reactive chemically. 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 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 solid fat 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

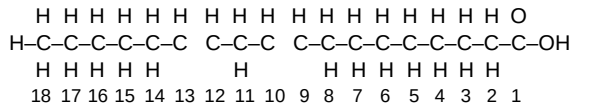
Table 2.2 Fatty Acid Structures

Linolenic fatty acid (C-18:3) melting point 9°F (–13°C)



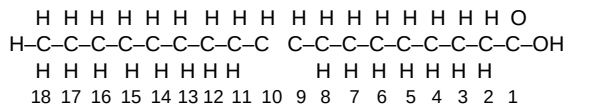
cis, cis, cis isomer
triunsaturate

Linoleic fatty acid (C-18:2) melting point 19°F (–7°C)



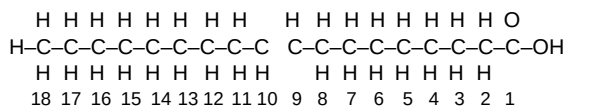
cis, cis isomer
diunsaturate

Oleic fatty acid (C-18:1) melting point 61°F (16°C)



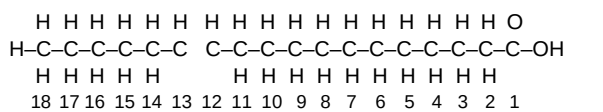
cis isomer
monounsaturate

Elaidic fatty acid (C-18:1) melting point 110.7°F (43.7°C)



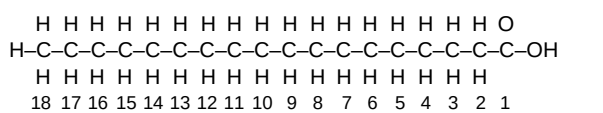
trans isomer
monounsaturate

Petroselinic fatty acid (C-18: 1) melting point 86°F (30°C)



positional cis isomer
monounsaturate

Stearic fatty acid (C-18:0) melting point 158°F (70°C)



saturate

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 treated 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). The 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 increase, 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 proprietary 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.[59] Palladium has been found to be sometimes 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.[60] 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 to 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 base stocks 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[61]:

Fatty Acid	Relative Reactivity
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.

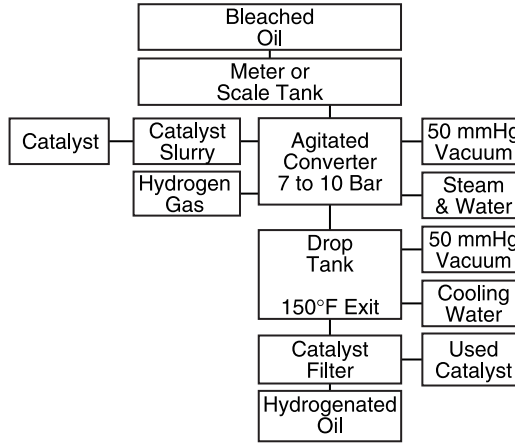


Figure 2.6 Dead-end batch hydrogenation process flow.

A dead-end hydrogenation system is illustrated in Figure 2.6. The converter is loaded with oil from a scale tank or metering devise. 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 triglycerides, 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 ± 0.1°C, and the hardfats would solidify on the prism at this temperature. The hardfat is too hard for dropping point determinations, and IV or final 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 tankage 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.[62] 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 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 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 flavorable 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 demanding 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, 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. Ideal, 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	—	—	—	—	—	—
trans-Acids (%)	14.8	22.7	25.3	44.7	45.5	45.0	Nil
Hydrogenation Conditions	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, organolepic, 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 selective catalyst. The slope of the SFI curve becomes flatter as the hydrogenation reaction conditions are made less selective with lower temperature, higher pressure, and low catalyst levels. These effects are illustrated for the soybean oil basestocks graphically on Figure 2.7.

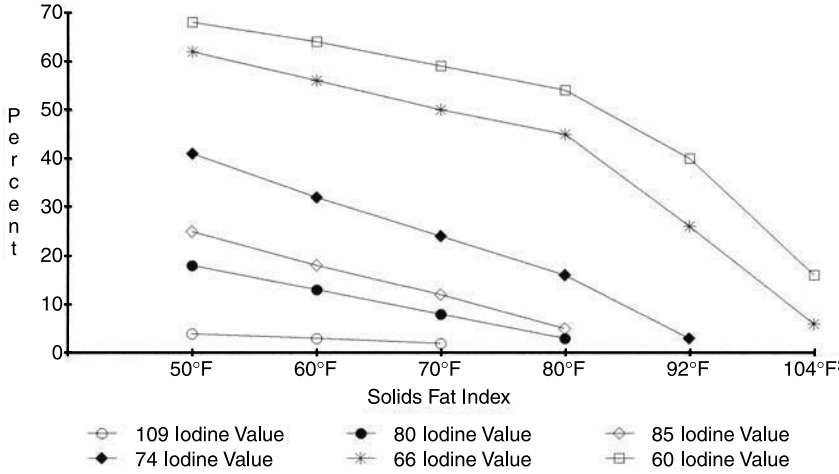


Figure 2.7 Soybean oil basestocks.

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 nm. 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.[63] 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 triglycerides 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 (β) to beta-prime (β′), 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 and 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[69].

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 (71°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[69].

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:[64,65]

- Sodium methylate, an alkali metal (alkylate), is the most widely used low-temperature interesterification catalyst. It is active at 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 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 hydroxides 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 catalysts. 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 so 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

Interesterification 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.[64,66] 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[97,98] 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 butter 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:[64,65,67]

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: (FFA × 0.19) + 0.06 = 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_2) 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_2 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 precipate 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 process 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:[64,67,69]

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.[69,70,71] 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 stable 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 crystal 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

Interesterification 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 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.[72] 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.[73]

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 D-1 crystals, and (2) a high nucleation rate that increases the viscosity, which in turn restricts crystal growth. Slow controlled cooling rates produce stable B or E-2 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 D-1 to the stable B-2 or E-2 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, high agitation rates are recommended because high shear rates fragment the crystals 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:[74]

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[75] and later Neuman[76] 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 to 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 solid 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 stearin crystals in solvent, and less oil is entrapped than with conventional winterization systems. Table 2.5 provides a comparison of cottonseed salad oil stearine typical 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;[34] however, most processors and customers have

Table 2.5 Cottonseed Salad Oil Stearin Analysis

Winterization Process	Conventional	Solvent
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 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 bland 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 Oil Components

Source Oil	Cottonseed Oil			Hydrogenated Soybean Oil		
Oil Component	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 sources are different; the stable crystal form for soybean oil is β, but it is β' for cottonseed oil. β crystals are large, coarse, and self-occluding whereas the β' 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 used. 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 bind the screens almost immediately.[59] A continuous dewaxing process that operates efficiently with low-wax oils (500 ppm or less) has the following process flow:[77]

- 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:[75,78]

- 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).[34] 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 D, E′, and E in that order of stability, melting point, heat of fusion, and density. The rate of crystallization for the D form is higher than for the E′ form, which crystallizes quicker than the E 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 E and E′ crystals that are easily filtered from the liquid phase.

Three distinct unit processes for the fractionation of triglycerides that couple crystallization and separation processes are practiced commercially to produce value-added fractionated fats and oils: (1) dry fractionation, (2) solvent fractionation, and (3) aqueous detergent fractionation.[79] Dry fractionation processes include winterization, dewaxing, hydraulic pressing, and dry 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 quantify 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 liquid 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.[80]

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 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 stearcake. This procedure can produce a very acceptable confectionery coating fat from palm kernel oil.[80] 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.[81]

2.12.2 Detergent Fractionation

The aqueous detergent fractionation process 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.[80,82] 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 solvent, 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.[82,83] 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 3.8. 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.[84] 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.[84] 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 variation 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.[84] 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.[84] 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 45% monoglyceride content, 52 to 56% monoglyceride content, and distilled monoglycerides with 90% mono-glyceride content. There are three basic physical forms of mono- and diglycerides: hard, soft, and intermediate. The difference 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 and heated 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 acid 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 D position of the glyceride, the balance being esterified on the center or E 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

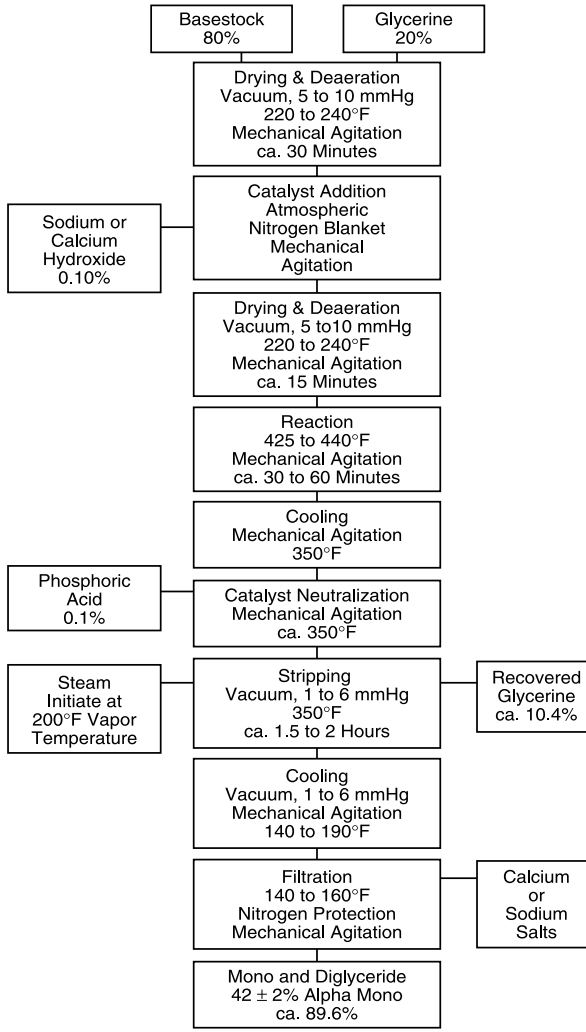


Figure 2.9 Mono- and diglyceride batch process flow.

systems where the reaction time, temperature, and catalyst may be varied. A typical batch process flow to produce a 40 to 46% 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% 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 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.[34] 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 produced 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.[35] 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 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 D-crystal form. These D-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 D-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.[84] 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 alkali catalyst may be needed to accelerate the reaction.[87]

2.13.2 Polyglycerol Esters

Polyglycerol esters have unique physical and chemical properties that provide a broad range of functional properties.[88,89] 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 fatty 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 out through a condenser. Care must be exercised to exclude air from the system. Traces of oxygen can 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 beta-crystalline-tending, surface-active compounds that have proved to be especially effective emulsifiers for cake baking and whipped toppings. The emulsifier forms a beta-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 or 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.[90,91]

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.[91–98] 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 decreases. 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). 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 uniform, 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 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 is stopped or 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.

2.15.2.3 Continuous

Continuous deodorizers provide uniform utility consumption by not being subject to the peak loads attendant with batch type heating and cooling of semicontinuous operations. This permits smaller heating and cooling auxiliaries and optimum heat recovery through interchange between incoming and outgoing oils. Processors requiring infrequent product changes can benefit from continuous deodorization; however, processors requiring multiple stock changes will not realize the benefits. Continuous deodorization benefits are lost with as few as three or four stock changes in a 24-hour period due to loss of production (30 to 60 minutes for each stock change) and the likelihood of commingling product.

Continuous deodorization can involve tray or thin-film deodorizers. Tray deodorizers are based on a series of steam-agitated trays or compartments often stacked vertically in a cylindrical shell. Stripping of FFA and other volatile compounds and heat bleaching are carried out simultaneously. The retention time per tray is usually 10 to 30 minutes. Typically, liquid levels of 0.3 to 0.8 meters are maintained by overflow pipes or weirs. The trays are drained by separate discharge valves.

Physical refining, or the removal of fatty acids from oils by steam distillation rather than by caustic refining, can be carried out in semicontinuous or continuous deodorizers; however, continuous deodorizers containing packed columns are particularly suited to the removal of large amounts of free fatty acids. Thin-film deodorization has structured packing to create maximum surface-to-volume ratio. The oil flows over the packing and meets the rising steam counter-currently for FFA stripping. Heat bleaching is accomplished in a retention section after the packed column. The counter-current principle introduces efficiencies through more effective use of the injected steam to reduce the quantity required and smaller vacuum requirements due to the small volume of oil treated at a time. Also, a large percentage of the heat is recovered by preheating the feedstock oil by passing it counter-currently through a heat exchanger opposite the other oil flow.[9,10]

2.15.3 Deodorizer Heating Systems

Practical, as well as theoretical, considerations indicate that oils should be heated in the range of 410 to 500°F (210 to 260°C) for reasonably rapid and effective deodorization. The Wesson system utilized a direct heat method that circulated the oil through a direct-fired tubular heater. The disadvantages for this system were poor temperature control and localized overheating, which caused hot spots. A more satisfactory system, known as the Merrill system, was used for many years. It heated mineral oil in a direct-fired furnace and circulated it through coils in the deodorization vessel. Pump maintenance, care of the tubes in the direct-fired furnace, and a tendency of the mineral oil to decompose under the heating system conditions were the major shortcomings of the Merrill system. Electrical heating has been used to heat deodorizers either by tube heaters immersed in the oil or by placing the elements around the outside of the tank and heating tubes. Automatic control was achieved

with electrical heating, but the danger of localized overheating as well as high power costs were problems. The use of condensing thermal heating fluids became the most popular method of heating edible oils shortly after introduction in 1932.

All thermal heating fluids (THFs) became suspect carcinogenic materials as a result of several contamination incidents involving THFs containing polychlorinated biphenyls (PCBs). As a result, the use of PCB-containing THFs that could contaminate foods were banned worldwide. THFs with different chemical compositions and low toxicity were adopted in the United States and other countries. Dowtherm A® is a trade name of The Dow Chemical Company for a eutectic mixture of 26.5% diphenyl and 73.5% diphenyl oxide; toxicity and safety data show a negligible health risk for these compounds. This liquid boils with negligible fractionation at 495.8°F (257.7°C) under atmospheric pressure. Dowtherm A is referred to as a liquid because it is used in liquid form, although it is a solid below 53.6°F (12°C). It is relatively stable and has the advantage of low vapor pressure when boiling at high temperature; for example, at 522°F (272°C) the vapor pressure of Dowtherm A is less than 2 bar. Dowtherm A has a pungent odor that is immediately evident in case of a leak. A typical THF heating system consists of a boiler (vaporizer), a burner complete with safety controls required by insurance regulations, and a gravity return system for the condensate from the deodorizer.

The European edible-oil community elected to phase-out THF systems and replace them with hot water/steam heat transfer systems. Conversions to these systems have become the trend in the edible oil industry worldwide for a variety of reasons, including improved heat transfer efficiency, reduced energy costs, reduced maintenance, and reduction in perceived safety risks.[89]

2.15.4 Deodorization Process Control

Deodorization is the last major process step where flavor, odor, and many of the stability qualities of an edible fats and oils product can be affected. From this point forward, all of the efforts are directed toward retaining the quality of the freshly deodorized product. In order to produce a quality deodorized product, attention must be focused on all the factors involved with the process. The various factors that influence the quality of the finished deodorized oil include:

- Undeodorized oil preparation — Preparation of the oil before deodorization has a significant effect upon the finished deodorized product; therefore, the first process control requirement is to assure that the processing steps prior to deodorization have been performed properly as specified. For example, deodorization of high-peroxide oils will thermally decompose the peroxides, but the rate of peroxide formation in the oil during subsequent storage will probably increase and the flavor stability will be compromised. Proper handling of the oil would be to rebleach it prior to deodorization. Steam distillation does not remove secondary oxidation products, soap, or phosphatides, which are adsorbed in bleaching.
- Air elimination — Oil must be scrupulously protected from contact with air throughout the deodorization process. At elevated temperatures, oils react instantly

with oxygen to form polymeric and oxidized triglycerides, which may be detrimental to health. Some potential air sources are:

- Deaeration of the feedstock is essential because the oil may contain dissolved oxygen from previous exposure to the atmosphere. Proper deaeration is achieved by sparging the oil into a tank under reduced pressure. Usually, the oil is heated to >175°F (80°C) and sprayed into a tank kept at a pressure of <50 mbar.[96]
- Air leaks can occur at deodorizer fittings below the oil level and in external pumps, heaters, and coolers; allow the oil to oxidize and polymerize.
- The stripping steam must be generated from deaerated water to be oxygen free.

- Deodorization construction materials — Heavy metals, particularly those possessing two or more valency states, greatly increase the rate of oxidation. Of all metal, copper is the most potent catalyst. A concentration high enough to produce a noticeable oxidative effect lies in the proximity of analytical detection limits, probably 0.005 ppm. The corresponding content for iron is 0.03 ppm. Other metals have exhibited varying catalytic powers; for example, the contents of metal ions required to decrease the lard-keeping time by 50% at 208°F (98°C) are 0.06 ppm manganese, 1.2 ppm chromium, 2.2 ppm nickel, 3.0 ppm vanadium, 19.6 ppm zinc, and 50.0 ppm aluminum.[100] This comparison stresses the importance of avoiding the use of copper, iron, or some other alloy if the highest possible flavor stability is required; therefore, deodorizers are fabricated from type 304 stainless steel at points contacted by the oil.
- Metal chelating — Fats and oils obtain metal contents from the soils where plants are grown and later from contact during crushing, processing, and storage. Many of the metals promote oxidation, which results in off-flavors and odors accompanied by color development in the finished fat and oil products. Studies have identified copper as the most harmful metal, followed by iron, manganese, chromium, and nickel. The effects of pro-oxidants can be diminished by using chelating agents before and after deodorization. The most commonly used chelating agents are citric acid, phosphoric acid, and lecithin. Citric acid is metered into the oil as an aqueous or alcoholic solution at levels of 50 to 100 ppm. Citric acid decomposes at 347°F (175°C), and the usual practice is to add it during the cooling stage in deodorization. Citric acid added prior to deodorization decomposes at deodorization temperatures but still affords a degree of protection from trace quantities of oxygen present during preheating. Phosphoric acid, when used, is added to the deodorizer in an aqueous solution at a concentration of no more than 10 ppm because a slight over-addition can lead to off-flavors in some oils (e.g., watermelon flavor in soybean oil). Lecithin has been used to chelate metals at 5 ppm.
- Oil polishing — The final stage of deodorization should be filtration of the oil. The deodorized oil is normally pumped through an enclosed polishing filter to remove any fine particles of soaps, metal salts, rust, filter aid, polymerized oil, or any other solid impurities. Horizontal leaf filters have long been used as the polishing filter of choice for deodorized oils. These filters are well adapted to this service because oil clarity is excellent and the amount of solids to be removed from the oil is minimal. The disadvantages of this type of filter are the labor requirements to clean and redress the filters and the space requirements; therefore, small cartridge or bag filters have become popular for this purpose. These oil-polishing filters are relatively inexpensive, require a minimum space, and are much less labor intensive; also, the bags are relatively inexpensive.

- Operating conditions — Operating variables, such as temperature, pressure, stripping steam rate, and time of steaming affect the quality of the finished product. The temperature of the steam required is proportional to the absolute pressure. The time required for efficient deodorization depends upon the rate at which steam can be passed through the oil and is limited by the point at which appreciable mechanical entrainment occurs. The lower the system pressure at a fixed vapor pressure or temperature and sparge steam rate, the greater the FFA reduction. Because the vapor pressure of the FFA and other volatiles is directly proportional to the temperature, an increase in both temperature and sparge steam rate will increase FFA reduction; however, the maximum temperature that can be used is limited because of the detrimental effects upon oil stability and trans-acids development.

Typical deodorizer conditions practiced in the United States are shown in Table 2.7 for the three types of deodorization systems.[93] Most deodorized oil specifications allow a 0.05% maximum FFA; however, most processors will deodorize to an 0.03% maximum limit internally. The higher published limits allow for the addition of antioxidants or other additives that raise the FFA level.

Table 2.7 Typical Deodorization Conditions

Deodorization Conditions	Range
Vacuum, absolute pressure (mbar)	2–4
Deodorization temperature (°F)	410–500
Deodorization temperature (°C)	210–260
Holding time at deodorization temperature:	
Batch deodorizers (hours)	3–8
Semicontinuous deodorizers (minutes)	15–120
Continuous deodorizers (minutes)	15–120
Stripping steam (wt % of oil):	
Batch deodorizers	5–15
Semicontinuous deodorizers	1.0–2.0
Continuous deodorizers	0.5–2.0
Drop temperature:	
Liquid oils	
°F	100–130
°C	37.8–54.4
Higher melting products	
°F above melting point	10–15
°C above melting point	5.5–8.5
Product free fatty acids (%):	
Feedstock	
Caustic refined	0.05–0.1
Physically refined	1.0–5.0
Deodorized product	0.02–0.03
Product peroxide value (meq/kg)	
Feedstock	2.0 max.
Deodorized product	Zero
Product flavor (minimum)	Bland

2.15.5 Deodorizer Distillate

Typically, deodorizers utilize a three- or four-stage steam ejector system with direct-contact intercondensers to maintain a vacuum within the deodorization vessel at 1 to 6 mbar absolute pressure, and stripping steam is injected into the oil at a temperature of 410 to 500°F (210 to 260°C). The odoriferous compounds, free fatty acids, mono- and diglycerides, oxidation products, tocopherols, sterols, pesticides, other organic materials, and small quantities of triglycerides are carried off by the stripping steam through the primary steam ejector of the vacuum-generating system and are finally condensed along with the stripping and motive steam within the barometric condenser. Scrub coolers are often installed before the barometric condenser to remove as much of the distillate as possible to keep it out of the recirculating cooling water. The distillate stripped from edible oils can be divided into three component groups. The first group will condense between the deodorization and their solidification temperatures, the second group includes those that are condensed and solidify when cooled to a lower temperature by contact with the vacuum system condensing water, and the final group consists of those that remain volatile even at the lower temperature.[101]

Initially, deodorizers used once-through cooling water systems that discharged the wastewater into rivers, lakes, reservoir to a water treatment plant. Closed-circuit water systems were introduced when the discharge of organic materials was restricted by government agencies. These systems recirculated the same water through cooling towers and back to the condensers. A rapid build-up on all the surfaces contacted, such as piping, pumps, valves, cooling tower surfaces, spray nozzles, etc., fouled or plugged the equipment, which led to high maintenance costs and created an offensive odor that drew complaints from the surrounding communities.

A direct contact cooling process was developed in the late 1950s in which the deodorizer discharge vapor and vacuum booster steam flowed into a tower where they were cooled by direct contact with a stream of circulating distillate. The purpose of the distillate recovery tower was to cool the deodorizer discharge to condense as much of the distillate as possible. The location of the scrub cooler within the vacuum system and the operating conditions were selected to maximize distillate recovery, maintain a pumpable liquid in the tower, and prevent condensing of the vacuum system steam. The distillate recovery systems were very successful in reducing maintenance and odor problems; however, some organic material still escaped and ended up in the hot well, which contributed to cooling tower problems. This problem was solved with condenser-water recycle systems. The basic concept of these systems was to keep the cooling tower clean by cooling the dirty, hot well water in a heat exchanger with tower water before recycling to the vacuum system barometric condensers. In this system, there is no direct contact between the two water streams, so the cooling tower water remains clear.[94]

The odoriferous low-boiling compounds that remain volatile at low temperatures continue in the vapor phase through the barometric condenser and exit with the final vacuum stage discharge. The volatile compounds dissolve in the hot well water and are either reintroduced into the air in the cooling tower or build up in the hot well

to cause odor emissions around the deodorizer. Three techniques that have been used for odor control of the noncondensable materials are wet scrubbers, carbon bed systems, and thermal incineration. Carbon beds have not been successful with edible oil systems because of the heat load in the steam being discharged from the deodorizer vacuum system and the regeneration problems encountered with the carbon bed. Thermal incineration has not been adopted for deodorization odor control because of the low cost and availability of energy. Wet scrubbers offer the best solution for eliminating noncondensable odor compounds. A wet scrubber is a device where a liquid is brought into contact with the gas to absorb the soluble components or capture any solid particles. Wet scrubbers normally consist of two components; the first section is a contacting zone where the vapor or particle is captured, and the second section is a disengaging zone where the liquid is eliminated from the cleaned gas.[101]

Deodorizer distillate is the material collected from the steam distillation of edible oils. As a general rule 0.5% of the deodorizer feedstock would approximate the amount of distillate produced by a typical processor of edible fats and oils. The composition of the distillate depends upon the source oil, the refining technique utilized, and the deodorizer operating conditions. The distillate from physically refined oils consists mainly of FFAs with low levels of unsaponifiable components. Distillates from chemically refined oils have higher economic value due to higher sterol and tocopherol contents that are sources for natural vitamin E, natural antioxidants, and other pharmaceuticals.[96] The use of deodorizer distillates in animal feeds is forbidden by U.S. regulations because any insecticides in the source oils are codistilled with the other organic compounds. The distillate can be used as a source of industrial fatty acids or mixed with the fuel oil used to fire the steam boilers; up to 10% of the distillate has been successfully used in fuel oil. The remaining disposal alternatives are deposit in a refuse dump, if permitted, or combustion in a fluidized bed incinerator.[102,103]

2.16 FINISHED FATS AND OILS HANDLING

The last major process that can control the odor and flavor stability of an edible fats and oils product is deodorization. If the conditions of the preceding processing technique and raw material quality have been satisfactory, the result is a tasteless, odorless, and light-colored fat and oil ingredient, free from peroxides and contaminants. Processes for handling and storage of these products must protect the achieved quality prior to packaging or use in a prepared food product. Deodorized fats and oils products must be protected from contamination with foreign flavors, foreign odors, impurities, other fats and oils products, and hydrolysis, as well as thermal decomposition and oxidative deterioration.

2.16.1 Protection against Oxidative Deterioration

Fats and oils containing unsaturated fatty acids are subject to oxidation, a chemical reaction that can occur with exposure to air to make their flavor unacceptable to consumers. The double bonds found in unsaturated fatty acids are the site of this

chemical activity. The oxidation rate is roughly proportional to the degree of unsaturation; linolenic (C-18:3), with three double bonds, is more susceptible than oleic (C-18:1), with only one. Linoleic (C-18:2) is intermediate but twice as susceptible as oleic. Oxidative deterioration results in the formation of hydroperoxides, which decompose into carbonyls, polymerization, and polymerized materials. It is accelerated by temperature increase, oxygen pressure increase, a higher concentration of oxidation products (peroxides and aldehydes), the catalyst, lipoxdases, hematin compounds, antioxidant reduction, absence of metal deactivators, storage time, and ultraviolet or visible light.[100] Extensive oxidation would eventually destroy the carotenoids (vitamin A), the essential fatty acids (linoleic and linolenic), and the tocopherols (vitamin E) contained in most oils. Prevention of oxidation is a major factor that must be designed into all edible fats and oils storage, handling, and processes.

2.16.1.1 Nitrogen Blanketing

Many of the current edible fats and oils storage, handling, and stabilization practices stem from the results of flavor stability research. Determinations that a correlation exists between peroxide value results and off determinations indicate that flavor deterioration can be prevented by excluding air from fats and oils products. The usual procedure involves replacing oxygen with nitrogen. Gas-free finished oil is delivered from the deodorizer to a storage tank under a complete nitrogen blanket supplied by a nitrogen gas generation unit or from liquid nitrogen. A nitrogen blanket is maintained by a pressure system controlled by a regulator. As the tank is filled with oil, the pressure builds and the gas is vented to the atmosphere. Conversely, as the oil is pumped from the tank, the pressure drops and replacement gas enters the tank. It is good practice to install a relief valve or rupture disc for each tank to avoid collapsing a tank with a vacuum. A typical system would be kept under nitrogen pressure of 1 to 15 psi (1 to 2 kg/cm^2). This pressure varies as the tanks are loaded or unloaded, and the pressure relief valves are set to relieve pressures above 15 psi (2 kg/cm^2).

Another nitrogen protective practice utilized is to sparge oils at the exit of the deodorizer or a nitrogen-blanketed vessel. The principle is to saturate the oil with nitrogen while it is completely deaerated. The spargers discharge tiny bubbles of nitrogen directly into the oil stream. As the oil flows into the unprotected vessel, the effusing gas sweeps the headspace, sweeping most of the oxygen from the vessel. This technique is particularly useful for protecting bulk oil shipments in tank cars and trucks.[104]

Oxygen contact can be reduced by keeping the entire edible fats and oils handling process protected with an inert gas. In finished oil processing, preferably the product is protected by nitrogen gas in the storage tanks and bulk transports as well as in the packaging. Effective protection against oxidation for packaged products requires that the air in the oil and the package headspace be evacuated and then replaced by a protective gas such as nitrogen.

2.16.1.2 Temperature Control

Fats and oils temperatures should be maintained as low as possible during handling because heat accelerates the oxidation reaction. Before exiting the deodorizer, while still protected by vacuum, the product should be cooled to 100 to 130°F (37.8 to 54.4°C) for liquid oils and 10 to 15°F (5.5 to 8.5°C) above the melting point of higher melting products. After the polish filter, the liquid oils can be further cooled. The speed of oxidation is doubled for each 27°F (15°C) temperature increase in the 68 to 140°F (20 to 60°C) range. This means that an oil can be held four times as long at 68°F than at 122°F, before the same degree of oxidation occurs.

Hydrogenated and higher melting fats and oils must be kept liquid for transfer with pumps. It is necessary to control the product handling temperature to prevent oxidation and because the pumping rates and volumetric metering systems are dependent upon product viscosity, which is temperature dependent. A good practice, as outlined above, is to keep the product no warmer than necessary to pump conveniently or 10 to 15°F (5.5 to 8.5°C) above the melting point of the product. Bulk handling systems should be designed to accommodate low-temperature product handling and minimize localized overheating with short insulated lines, tank agitators, automatic temperature controllers, hot water or low-pressure steam heating, properly sized tanks, proper placement of temperature probes, and so on.

2.16.1.3 Light Control

Light exposure contributes to the flavor deterioration of all edible fat and oil products. Even limited exposure of an oil product to sunlight or ultraviolet rays from fluorescent lighting will increase peroxide value results and decrease flavor ratings. Normally, light-induced deterioration is not a processing concern because all processing, handling, and storage are accomplished in closed systems; however, two areas of concern are (1) the samples drawn and submitted to the laboratory for analysis, and (2) the liquid oils packaged in clear bottles for the retail market. Transparent or open large-mouth containers should not be used to obtain samples for laboratory testing of organoleptical properties and peroxide value determinations. Oils stored in brown glass bottles have experienced only slightly more deterioration than those stored in metal or otherwise kept away from light, but the U.S. consumer has shown a preference for salad oils packaged in clear containers.

2.16.1.4 Storage Time

All fat or oil products experience deterioration even when handled and stored under ideal conditions. Oils that do not require heating to remain liquid resist deterioration more so than the higher melting products. The higher melting products should not be allowed to solidify and then be reheated for use unless for a downtime of extended duration. Most shortenings and other similar products will maintain an acceptable flavor and oxidative stability for 2 to 3 weeks in melted form with adequate controls. Therefore, edible fats and oils storage systems should be designed for turnovers of less than 2 to 3 weeks within the established storage life of the

product. Additionally, fresh product should not be added to heels of previous lots. The older product will contain concentrations of oxidation products that will accelerate oxidation of the fresh product.

2.16.1.5 Antioxidant Addition

Antioxidants are chemical compounds that provide greater oxidative stability and longer shelf life for edible fats and oils by delaying the onset of oxidative rancidity. Oxidation occurs in a series of steps often referred to as free radical oxidation because the initial step is the formation of a free radical on the fatty acid portion of the fat molecule. The free radical is highly reactive and forms peroxides and hydroperoxides by reaction with oxygen. These free radicals also initiate further oxidation by propagating other free radicals. Finally, the hydroperoxides split into smaller organic compounds such as aldehydes, ketones, alcohols, and acids. These compounds provide the offensive odor and flavor characteristic of oxidized oils.[105] Antioxidants function by inhibiting or interrupting the free-radical mechanism of glyceride autoxidation. Their ability to do this is based on their phenolic structure or the phenolic configuration within their molecular structure. Antioxidants or phenolic substances function as a free-radical acceptor, thereby terminating oxidation at the initial step. Fortunately, the antioxidant free radical that forms is stable and does not split into other compounds that provide off-flavors and odors nor does it propagate further oxidation of the glyceride.[106]

Food products in interstate commerce in the United States are subject to the regulations under the Food, Drug, and Cosmetic Act; the Meat Inspection Act; and the Poultry Inspection Act. These regulations establish limitations on the use of antioxidants and other food additives in food products. Antioxidants cleared under these regulations include the following:[105-112]

2.16.1.6 Tocopherols and Tocotrienols

Nature's fat-soluble antioxidants exist in four homologs: alpha, beta, gamma, and delta. The D-isomer (vitamin E) is widely used as a nutritional supplement. The E-isomers exist in concentrations too low to have any practical significance. Both the J-isomer and the G-isomer are known primarily for their antioxidant properties and are used where consumers require a natural antioxidant. Interestingly, synthetic antioxidants contain the same phenolic structure that makes the tocopherols effective antioxidants.

In most applications, tocopherol addition levels of 0.02 to 0.06% are sufficient to provide good antioxidant properties. The USDA limits the addition level to 0.03% for lard or rendered pork and rendered poultry fat, but the FDA allows the amount required for the intended technical effect for most products. The antioxidant properties of tocopherols can be enhanced by the addition of an acid synergist such as citric or ascorbic acid. Tocopherol additions have the most application for stabilizing edible fats of animal origin because of the absence of natural antioxidants in these products. Vegetable oils are the source of the tocopherols, and enough of the natural antioxidant survives refining, bleaching, and deodorization to provide the optimum stability available from tocopherols. A survival level of 500 ppm for soybean oil is

considered adequate to protect the oil from oxidation. Performance testing has shown that tocopherol levels above the normal survival level do not improve the oxidative stability but in fact act as a prooxidant to enhance oxidation.

2.16.1.7 Propyl Gallate

Propyl gallate, the n-propyl ester of 3,4,5-tri-hydroxybenzoic acid, is an effective antioxidant for shelf-life improvement of vegetable oils at usage levels of 100 to 200 ppm, or the FDA and USDA permitted levels; however, its usage is hampered by solubility problems, discoloration, and poor heat stability. Propyl gallate has significant water solubility and seeks the water phase in water–fat systems which causes a reduction in antioxidant effectiveness and allows complexing with iron to cause iron-gallate discoloration. Darkening of scrambled eggs to a blue-black color when prepared in an iron skillet with an oil stabilized with propyl gallate is an example of the deficiency. Additionally, edible oil products stabilized with propyl gallate can darken while stored in black iron vessels, when packaged in metal containers, or when coming into contact with metal processing equipment. Finally, propyl gallate may be inactivated readily in alkaline systems and particularly at elevated temperatures. These deficiencies have limited the use of propyl gallate in edible fats and oils in the United States, where tertiary butylhydroquinone (TBHG) has been approved as an alternative effective vegetable oil antioxidant.

2.16.1.8 Butylated Hydroxyanisole (BHA)

BHA is outstanding among the antioxidants for its carry-through effect; that is, it can substantially withstand food-processing temperatures such as those experienced in baking and frying. BHA is referred to as a hindered phenol because of the tertiarybutyl group ortho- or meta- to the hydroxyl group. This steric hindrance is probably responsible for the ineffectiveness of BHA in vegetable oils; however, this same steric hindrance is probably responsible for the carry-through effect for baked or fried foods. BHA has a strong phenolic odor that is particularly noticeable with the initial heating of frying shortenings or oils stabilized with BHA and can be described as a chemical odor. Another concern is the development of a pink color, which can occur when BHA comes into contact with fairly high concentrations of alkaline metal ions, such as sodium or potassium.

2.16.1.9 Butylated Hydroxytoluene (BHT)

BHT is another hindered phenol with a molecular structure similar to BHA. BHT is also similar to BHA in performance with regard to its relatively weak stabilization of vegetable oils and ability to survive baking and frying conditions to carry through into the finished food products. Both BHT and BHA are extremely soluble in edible fats and oils and have practically no water solubility. BHT can experience some darkening in the presence of iron, but the degree is not very serious.

2.16.1.10 Tertiary Butylhydroquinone (TBHQ)

TBHQ is a relatively recent addition to the approved antioxidant list in the United States and has not gained approval in many other countries. TBHQ has been found to be the most effective antioxidant for saturated vegetable oils, and it has several other advantages: (1) no discoloration when used in the presence of iron, (2) no discernible odor or flavor imparted to fats and oils, (3) good solubility in fats and oils, (4) effectiveness in poultry and animal fats as well as vegetable oils, (5) carry-through protection in baked and fried products, and (6) stabilizing effect upon tocopherols. The use of TBHQ to protect edible fats and oils from crude to deodorized has been found effective for preventing secondary oxidation products as determined by anisidine value evaluations. This protection is completely removed during steam distillation, and additional TBHQ must be added to the deodorized products for protection of the finished oils. TBHQ, BHA, and BHT are all volatilized at approximately the same rate, but oils stabilized with TBHQ antioxidant consistently have a higher oxidative stability and a better carry-through into fried foods. One concern with TBHQ utilization is the pink color that can develop with an alkaline pH, certain proteins, or sodium salts.

2.16.1.11 Synergistic Antioxidant Mixtures

Much of the success of antioxidants depends upon their being in chemical contact with the product they are protecting; therefore, antioxidant formulations containing various combinations of different antioxidant and chelating agents are generally used in most food applications, rather than individual antioxidant compounds. Not only does the use of such formulations provide convenience, in that it is easier to handle the diluted antioxidants, but it also permits the processor to take advantage of the synergistic properties of the different antioxidant compounds. For example, BHA and BHT used in combination provide a greater antioxidant effect than when either is used alone. Propylene glycol and vegetable oils usually serve as solvents for the antioxidant mixtures. Lecithin, citrate, monoglyceride citrate, and mono- and diglycerides are included in the formulations as emulsifiers.

Synergism is a characteristic common to many antioxidant mixtures. A mixture is designated as synergistic when the effect of the mixture is greater than the effect produced by the sum of the individual components. A synergist, such as citric acid, has two important functions in antioxidant formulations: (1) it increases the antioxidant effectiveness of the combination, and (2) it ties up or sequesters the trace metals, which are fat-oxidizing catalysts, by forming complex, stable compounds (chelates). Other compounds that function as synergists and chelating agents include isopropyl citrate, stearyl citrate, orthophosphoric acid, sodium monohydrogen phosphate, pyrophosphoric acid and its salts, metaphosphoric acid and its salts, calcium disodium ethylenediaminetetraacetate (EDTA), and disodium EDTA.

2.16.2 Protection against Contamination

A contaminant is any undesirable material that may taint, infect, corrupt, modify, or degrade by contact or association. Edible fats and oils must be protected from contamination at all stages of processing and especially after deodorization because that is the last opportunity to remove undesirable flavors, odors, colors, and other compounds. The contaminants most likely to affect the deodorized edible fat and oil products to the degree that would require reprocessing or downgrading to a lesser value product include:

- Moisture — Maintenance of a low moisture content after deodorization will ensure that hydrolysis does not occur. Hydrolysis is the reaction of water with a fat or triglyceride to break it down into a diglyceride and a free fatty acid. This hydrolytic reaction of fats and oils can be prevented by maintaining a moisture-free environment for the product. Some potential sources of moisture contamination during storage and handling are ruptured heating or cooling coils, leaking coolers, inadequate drying of washed tanks, condensation, steaming of lines, etc.
- Impurities — Foreign material in a finished product is usually caused by a malfunctioning polish filter, precipitant of metal salts, polymerized oil from dead spaces in lines, inadequate tank cleaning, etc. It is a good policy to polish filter all finished products during each transfer, preferably near to the destination as possible.
- Commingling — Inadvertent mixing of two different fats and oils products together is serious contamination. Every finished fats and oils product has specific properties designed for the intended application. Commingling with another product can change the composition, consistency, performance, and oxidative stability of the contaminated product. The resultant product in most cases requires reprocessing to another product due to potential changes in labeling, religious constraints, and performance. Commingling is usually the result of human error or malfunction of a valve. Murphy's Law dictates that the highest value product is always mixed with the least-expensive product handled.
- Odors and flavors — Fats and oils easily absorb odors and flavors from other foods, spices, solvents, gases, chemicals, paints, and any other odoriferous or flavorful material; therefore, extreme care must be exercised to protect the fat and oil products at all times after deodorization including storage, handling, and transportation of bulk liquid or packaged products.

2.17 PLASTICIZATION

Considerably more is involved in preparing a shortening and margarine for packaging and eventual use as an ingredient than simply lowering the temperature to cause solidification. For example, a grainy, pasty, nonuniform mass is produced when edible fats and oils are allowed to cool slowly. The more saturated triglycerides crystallize first and grow in size to produce an unsightly, difficult to handle, mushy product that lacks many of the basic qualities necessary for shortening or margarine performance. Development of the desired edibility, appearance, stability, texture, functionality, uniformity, and reproducibility in solidified fat and oil products is a function of controlled crystallization or plasticization.

2.17.1 Plasticity of Edible Fats and Oils

Edible fat and oil products appear to be soft homogenous solids; however, microscopic examination shows a mass of very small interlocked crystals that trap and hold by surface tension a high percentage of liquid oil. The crystals are separate discrete particles capable of moving independently of each other when a sufficient shearing force is applied to the mass. Therefore, shortening, margarine, and other solidified fat and oil products possess the characteristic structure of a plastic solid.

The distinguishing feature of a plastic substance is the property of behaving as a solid by completely resisting small stresses but yielding at once and flowing like a liquid when subjected to deforming stresses above a minimal value. A firm, plastic material will not flow or deform from its own weight; however, it may be easily molded by slight pressure into any desired form. Plastic solids derive their functionality from their unique plastic nature. Three conditions are essential for plasticity:[113]

1. It must consist of two phases, one a solid and the other a liquid.
2. The solid phase must be dispersed finely enough to hold the mass together by internal cohesive forces.
3. The two phases must be in proper proportions. The solid portion must be capable of holding the liquid while enough liquid must be available to allow flow when stress is applied.

Plasticity and consistency of an edible fats and oils product depend upon the amount, size, shape, and distribution of the solid material, as well as the development of crystal nuclei capable of surviving high-temperature abuse to serve as starting points for new desirable crystal growth. The factors that influence these characteristics are as follows:[114,115]

2.17.1.1 Product Composition

The element most directly influencing the consistency of a plastic shortening is the amount of material in the solid phase; the product becomes firmer as the solids contents increase. The solids content is determined by oil source and prior processing, including the degree of hydrogenation, interesterification, fractionation, or naturally solid source oils such as lard, tallow, palm oil, or coconut oil. Solidified fats and oils begin to have enough body to hold their shape well at a solids content as low as 5% and become rigid, losing plasticity as the solids contents reach 40 to 50%. A typical all-purpose bakery shortening, formulated for creaming properties and spreadability or workability, attempts to maintain a solids fat index of 15 to 25% over the widest temperature range possible. However, each product has a satisfactory plastic range, which is the temperature range in which the particular fats and oils product may be used with the intended results.

2.17.1.2 Crystal Size

At elevated temperatures, fats retain enough molecular motion to preclude organization into stable crystal structures; however, edible fats and oils go through a series of increasingly organized crystal phases with cooling until a final stable crystal

form is achieved. All fats crystallize from the liquid phase in the D form and transform more or less rapidly to E and subsequently to the intermediate or the B modifications if they are likely to exhibit these higher polymorphs. This sequence is irreversible; once transformation to the more stable forms has occurred, lower polymorphs can be obtained only by melting the product and repeating the process. This process can occur in fractions of a second or in months. The crystal types formed define the texture and functional properties of most fat-based products. Each crystal form possesses its own specific physical properties; for example, they differ in melting point, solubility, specific heat, and dielectric constants. The crystal lattice formed when the molecules solidify is a relatively loose arrangement. As crystallization proceeds, the molecules tend to pack more closely together. With time, the molecules in the crystal lattice will pack together as closely as their structure permits; therefore, the molecules in the most stable crystal lattice will require the least space.

The body and functionality of plastic fat and oil products are influenced significantly by the size of the crystals formed during solidification. A product becomes progressively firmer as the average size of the crystals decreases and becomes softer as the crystal size increases. A fat that has been melted and allowed to crystallize slowly under static conditions will contain many large crystals plainly visible to the eye. Crystals formed in the same fat by rapid chilling methods will be microscopic in size. Quickly chilled product with very small crystals will be firmer and will have a consistency range much wider than that of a fat slowly crystallized. The slowly crystallized product will also be softer than the rapidly chilled fat.

2.17.1.3 Supercooling

A very critical and complicating factor in plasticizing of edible fats and oils products is the supercooling properties of triglycerides. Fats can remain liquid when chilled below their melting point. Because of this fact and that fats are polymorphic and can crystallize in two or more forms, the solidification and plasticization process requires careful control. The degree of supercooling and the temperature at which the supercooled product is allowed to reach crystal equilibrium is directly related to the temperature range over which the product will be workable. In practice, the temperature to which the product is supercooled, worked, and packaged is controlled to produce the widest plastic range for the individual product formulation. The extent to which a fat is supercooled can affect not only the consistency, but also the melting point of the solidified product.

2.17.1.4 Mechanical Working

Solidification of the supercooled product without working or agitation will produce a firm consistency and a narrow plastic range. The product will also lack smoothness of texture and have a nonuniform appearance. Solidification without working allows the fat crystals to grow together to form a crystal lattice with greater strength than the same product with the crystals broken into smaller discrete particles. Therefore, for optimum plasticity, the supercooled product must be mechanically

worked during this crystal formation period until substantially all of the latent heat of crystallization has been dissipated.

The degree of work applied to shortening and margarine differs due to the finished product consistency desired. Traditional table-grade margarine, packaged in quarter-pound sticks and one-pound solids, must be firm enough to be handled with print-forming and wrapping equipment. Shortening and soft-tub margarines should be in a semifluid condition at the filling station. Traditional stick margarines must be allowed to reach crystallization equilibrium with a minimum amount of work for a homogenous mixture. An important precaution for both stick- and tub-type margarine plasticization is to avoid too fine a dispersion of the aqueous phase while inducing the larger crystal formation. This helps prevent a "waxy" mouth sensation and hastens the liberation of the salty aqueous phase, which contributes some of the flavors and complements others.

2.17.1.5 Gas Incorporation

Creaming gas, preferably an inert gas such as nitrogen instead of air, is incorporated into most standard shortenings at 13 ± 1%, regular soft tub margarines at 4 to 8%, whipped tub margarines at 30 to 35%, and precreamed household shortenings at 18 to 25%. Creaming gas is added to these products to produce: (1) a white, creamy appearance; (2) a bright surface sheen; (3) an easier handling, less dense product; (4) texture improvement; (5) homogeneity; (6) increased volume; (7) reduced calories per serving; and (8) reduced saturated fat grams per serving. Stick, liquid, and most industrial margarines do not have creaming gas added during crystallization. The aqueous phase of a margarine emulsion has the same effect on appearance as does gas incorporation.

2.17.2 Solidification Apparatus Evolution

Most of the first vegetable oil shortenings were grainy and nonuniform with an appearance similar to rendered lard. These products either were filled into containers in a molten state and allowed to cool and solidify or were chilled in tanks until crystallization began and then poured into containers where crystallization and solidification were completed. With this type of processing, the rate and degree of chilling that affected the degree of crystallization before packaging were variable and resulted in products with a nonuniform texture and consistency.[46,116–118]

Probably the earliest device in general use for achieving rapid cooling of fat and oil products was the chill roll, which was a hollow cast-iron, closed-end cylinder, mounted on bearings so it could be leveled. The roll was chilled either by pumping brine through it or by direct expansion of ammonia into its interior. In operation, the roll was rotated, and during rotation it passed through or contacted a trough containing molten fat. A film of fat adhered to the roll surface, where it was chilled to form a solid layer. The solidified sheet of fat was scraped off the roll surface by a doctor blade just prior to the melted fat pickup point after one revolution. The solidified fat dropped from the roll into a horizontal trough or picker box with a longitudinal shaft fitted with a number of paddles or spikes. The purpose of the picker

box was threefold: (1) beat air into the product, which improved the product appearance and texture; (2) serve as a holding vessel while crystallization continued; and (3) dissipate the heat of crystallization. Although the fat sheet from the roll was usually solid, it was in a supercooled condition, and much of the crystallization remained to take place after it left the roll surface. From the picker box, the viscous fat was pumped under pressure through a throttling valve to the container. The pressure and throttling improved the texture and appearance of the shortening by uniformly distributing the air bubbles within the fat and by breaking up any large agglomerates of crystals. Use of the chill roll allowed packaging of a reasonably uniform product. By varying the speed of the roll and the temperature of the refrigerant, it was possible to control the rate of chilling and the degree to which the fat was cooled.

In the early 1930s, work aimed at the development of improved heat-transfer equipment for freezing ice cream led to the perfection of a continuous internal chilling machine that was soon applied to the plasticization of shortenings. Liquid fat to be chilled is pumped into a relatively small annular space between a large mutator shaft and an outer refrigerated jacket. As the shortening contacts the cold jacket wall, it congeals and is instantly scraped off by scraper blades attached to the rapidly rotating mutator. This repeated high-speed congealing/scraping sequence provides extremely high heat-transfer rates and a homogeneous product. The mutator may be hollow and heated slightly with circulating warm water to prevent the formation of adhering masses of crystallized fat.

As the molten shortening is pumped to the scraped-wall heat exchanger, nitrogen, an inert gas, is injected into the stream, where it dissolves in the liquid fat under normal pump pressures. As the product leaves the heat exchanger, it flows into a working or tempering unit that simulates, to some extent, the picker box with the chill-roll procedure. The worker unit is a closed cylinder with stationary pins attached to the walls that intermesh with spirally located pins affixed to a helical rotating shaft inside the unit. The purpose of the worker unit is to dissipate the heat of crystallization while working the shortening to develop fine crystals. The worked shortening passes through an extrusion throttling valve to make a homogeneous product and is pumped to the filling station, where it again passes through another extrusion valve and into the package.

Margarine processing has gone through somewhat the same developments as shortening processing, except that in the beginning it was chilled by continuously pouring or spraying the molten emulsion into a vat of running cold water or brine. The emulsion entered at one end of the vat and solidified before it reached the other end. The solidified material floated to the surface in the form of a flaky mass that was skimmed off. The water was drained from the solidified emulsion before it was worked to give the desired texture and to incorporate flavoring ingredients. This procedure gave way to chill-roll processing, which was replaced with the scraped-wall heat exchanger process in the United States. With this processing, it is customary to make an emulsion containing the fat, moisture, salt, flavoring materials, emulsifiers, color, etc., which is then chilled by using the scraped-wall heat exchanger. The other differences compared to shortening plasticization are lower chilling temperatures, creaming gas or nitrogen is not incorporated for most margarines, and

utilization of a quiescent aging tube instead of the picking or working unit to provide a firm body suitable for printing into quarters or 1-pound solids. Also, margarine handling equipment has to be constructed of corrosion-resistant metals due to the presence of salt, moisture, and acids in the emulsions.

As the continuous closed system for plasticizing margarine was developing in the United States, an intermittent method was becoming popular in Europe. Crystallization in this process is accomplished by delivering the emulsion to internally refrigerated rotating drums or rolls. After crystallization, the product is allowed to temper before it is conveyed through a series of working rolls. It is then transferred to a worker or compactor, cut into slabs, and conveyed to blending machines where the moisture is adjusted. After blending, it is placed in large troughs for chilling to 40°F (4.4°C). The chilled product is then printed and packaged. The advocates of the European process maintain that it provides a preferred product consistency and texture because it more closely approximates butter. Margarine crystallization structure with the continuous process preferred in the United States is finer with a tighter emulsion that does not experience moisture weeping but probably masks flavor more so than does the European process.

2.17.3 Shortening Plasticization Process

The ultimate polymorphic form of plastic shortening is determined by the triglyceride composition, but the rate at which the most stable form is reached can be influenced by mechanical and thermal energy. Thus, it is customary to process plastic shortenings through various heat-exchanger working configurations to remove heat of crystallization and heat of transformation.

A typical U.S. shortening plasticization process, depicted in Figure 2.10, begins when the deodorized shortening blend has been transferred to the packaging department storage vessel, has had all the specified additive materials incorporated, and has met all of the process quality control requirements. The sequence of operations for the plasticization of a shortening are:[46,114–120]

1. The deodorized shortening blend is transferred from the packaging department storage tank to a small float-controlled supply tank adjacent to the chilling unit.
2. The product is picked up by a gear pump that maintains pressures of 300 to 400 psi (20 to 26.7 bar) for some systems and up to 1000 psi (66.7 bar) for others, on the entire chilling system.
3. Nitrogen, an inert gas, is introduced into the suction side of the gear pump, usually at 13.0 ± 1.0% for standard shortening. Creaming gas levels can range from 0 to 30.0%, depending on the product requirements.
4. Pressure throughout the entire solidification system is maintained by the use of a pressure-regulating valve placed in the product line between the pump and the precooler.
5. The oil and nitrogen mixture is precooled to 10 to 15°F (5.5 to 8.3°C) above the melting point of the product. It is important that the shortening blend remain completely melted to prevent precrystallization before rapid cooling is commenced, as this will result in the formation of large crystals that do not provide a good homogeneous crystal structure. The purpose of the precooler is to:

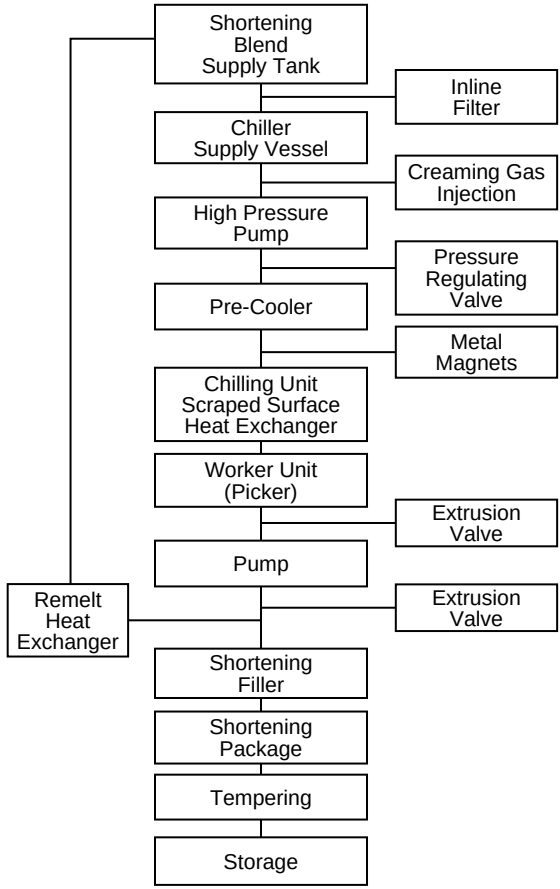


Figure 2.10 Typical process flow for shortening plasticization.

- Ensure that the shortening blend entering the scraped-wall heat exchange is at a constant temperature.
- Reduce the load on the scraped-wall heat exchanger.
- Ensure the presence of a large number of crystal nuclei in the product as it is chilled in the scraped-wall heat exchanger .

6. The precooled shortening blend enters a scraped-wall heat exchanger, where it is rapidly chilled (usually less than a 30-second residence time) to temperatures ranging from 60 to 78°F (15.6 to 25.6°C), depending upon the product type and desired firmness.
7. The supercooled product then passes through one or more worker tubes, where the fat crystals are subjected to a shearing action while the heat of crystallization dissipates. The shaft in the worker unit revolves at approximately 125 rpm, and the residence time of the chilled product in this unit is usually about 3 minutes. During this time, the temperature of the product rises approximately 10 to 15°F (5.6 to 8.3°C) due to the heat of crystallization.

8. The worked product is then forced through an extrusion valve that contains a slot or other form of constriction to aid in making the product homogeneous by breaking up any remaining crystal aggregates with an intense shearing action.
9. A rotary pump delivers the substantially solidified product at pressures in the range of 20 to 26.7 bar (300 to 400 psi) to a second extrusion valve located near the filling station.
10. The solidified shortening can now be filled. The temperature rise in the container should not be in excess of 1 or 2°F (0.6 to 1.1°C). Increases above this level are indicative of substantial crystallization under static conditions and will cause the consistency to be firmer than desired.

2.17.4 Liquid Shortening Crystallization

The major attribute of liquid shortenings is fluidity at room temperature. Liquid shortenings are easily poured, pumped, and metered under normal atmospheric conditions, which reduces handling problems for the consumer. Properly processed liquid shortenings do not require agitation to ensure uniformity. Also, oxidative stability is prolonged because no heat is required for fluidity at temperatures as low as 50°F (10°C) for most liquid shortenings. The products are milky white in appearance due to the dispersion of hardfats in the form of microcrystalline particles, which do not settle out because of the crystallization process. Fluid shortenings are composed of components that are stable in the E-crystalline form. Low-iodine-value, E-crystal-forming hardfats seed crystallization for liquid shortenings. The hardfat level that can be added is limited by the desired fluidity of the shortening and the eating quality requirements of the finished products. A stable fluid system in the E-crystalline form will not increase in viscosity or gel once it is properly processed. Hardfats with E-crystal habits are unacceptable for liquid shortenings because the tight-knit crystal lattice structure initiates a viscosity change with crystallization to a nonfluid product. Aeration properties normally associated with E small crystals are achieved by the addition of appropriate emulsifiers. Emulsifiers are also included in some formulations to retard staling of yeast-raised breads and rolls to increase shelf life.

The rate at which a fat transforms into its stable crystal form is important in liquid shortening processing because it must be in the stable form before packaging to avoid solidification in the package; therefore, the transformation of a liquid shortening into the stable form must be accomplished in a few hours. The quickest transformation of a fat to its stable crystal form can be attained by the following:

1. Heat the fat until completely melted.
2. Rapidly cool the fat to just below the D-crystal melting point. Theoretically, the D-crystal melting point is very nearly the lower limit to which fatty materials can be cooled without forming any crystals. AOCS Method Cc 6-25[34] determines the temperature at which a cloud is induced in a fat caused by the first stage of crystallization.
3. Heat to just above the E-crystal melting point but below the E-crystal melting point. The E-crystal melting point or the highest melting form can be estimated with a capillary melting point (AOCS Method Cc 1-25[34]).

Many different processes have been proposed and patented for preparing liquid shortenings. Most of the methods require a chilling of the product with a scraped-surface heat exchanger followed by a crystallization period in an agitated vessel. Two process procedures that have produced acceptable liquid shortenings are diagrammed in Figure 2.11. Process A has been found acceptable for liquid shortenings with hardfat levels below 5%, and process B, which requires more process time, has been found acceptable for products with more than 5% hardfat or emulsifier additions.

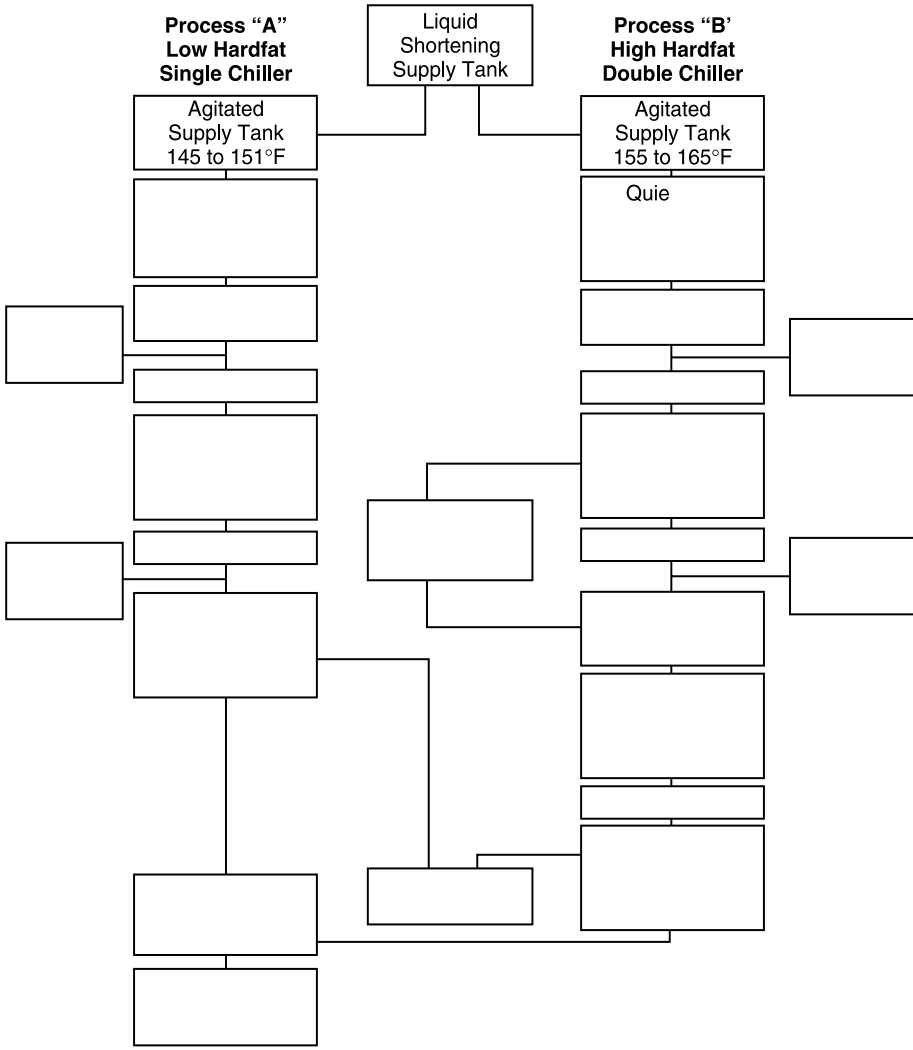


Figure 2.11 Liquid shortening crystallization process flow.

conditions have not been successful.[120] Once transformation to the more stable crystal form has occurred, lower polymorphs can be obtained again only by melting the product, crystallizing the D form, and repeating the sequence of transformations.

2.17.6.1 Quick Tempering

The expense and logistical problems associated with constant-temperature rooms for tempering have led several equipment manufacturers to develop mechanical systems in an attempt to eliminate tempering. Most of these systems do not claim complete elimination but a 50% or more reduction in tempering time. Most of the quick-tempering processes add a post-cooling and -kneading, or working, unit to the conventional type of chilling and working systems utilized with tempering. The theory behind these systems is that liquid fat is forced to crystallize individually and rapidly, thus creating small, more stable crystals rather than crystallizing onto existing crystals, causing an increase in crystal size or agglomeration as happens in normal tempering. Two basic systems utilizing additional chilling to reduce tempering have been developed to more completely crystallize the product into a stable polymorphic form mechanically. The two systems are compared in Figure 2.13. In both systems, the viscous crystalline material that has been supercooled and worked is recooled to remove the heat of crystallization developed in the working unit. One of the systems employs another working unit after the second chilling cycle, whereas the other is filled immediately after the second chilling unit. The best product quality with post-chilling temper is achieved when the product discharge temperature from the second set of chilling units is equivalent to or slightly lower than the exit temperature from the first chilling units. Most shortening and margarine products using a post-chilling temper process are filled within a temperature range of 65 to 85°F (18.3 to 29.4°C).

Performance characteristics equivalent to well-tempered shortening with only 24 hours of conditioning have been claimed for the post-chilled, quick-temper products.[121] These systems have received acceptance from many edible-oil processors, but the standard tempering procedures are still practiced by other processors for plastic shortenings and margarines. In many cases, versions of both conventional and quick-temper systems are being utilized to produce the various specialized shortening and margarine products — for example:

- Frying shortenings that do not require plastic consistency are produced with the conventional process with a rapid throughput and are tempered for solidification purposes only.
- All-purpose shortenings requiring a wide plastic range either are plasticized conventionally and tempered or utilize a quick temper process.
- Pastry or high-solids products are plasticized with one of the two specialized systems, and a short conventional quiescent tempering stage is also employed.

Another procedure developed to instantaneously crystallize fat products to the desired final form utilizes energy instead of cooling. Endres et al.[122] found that tempering of shortening with microwave energy produces a substantially improved

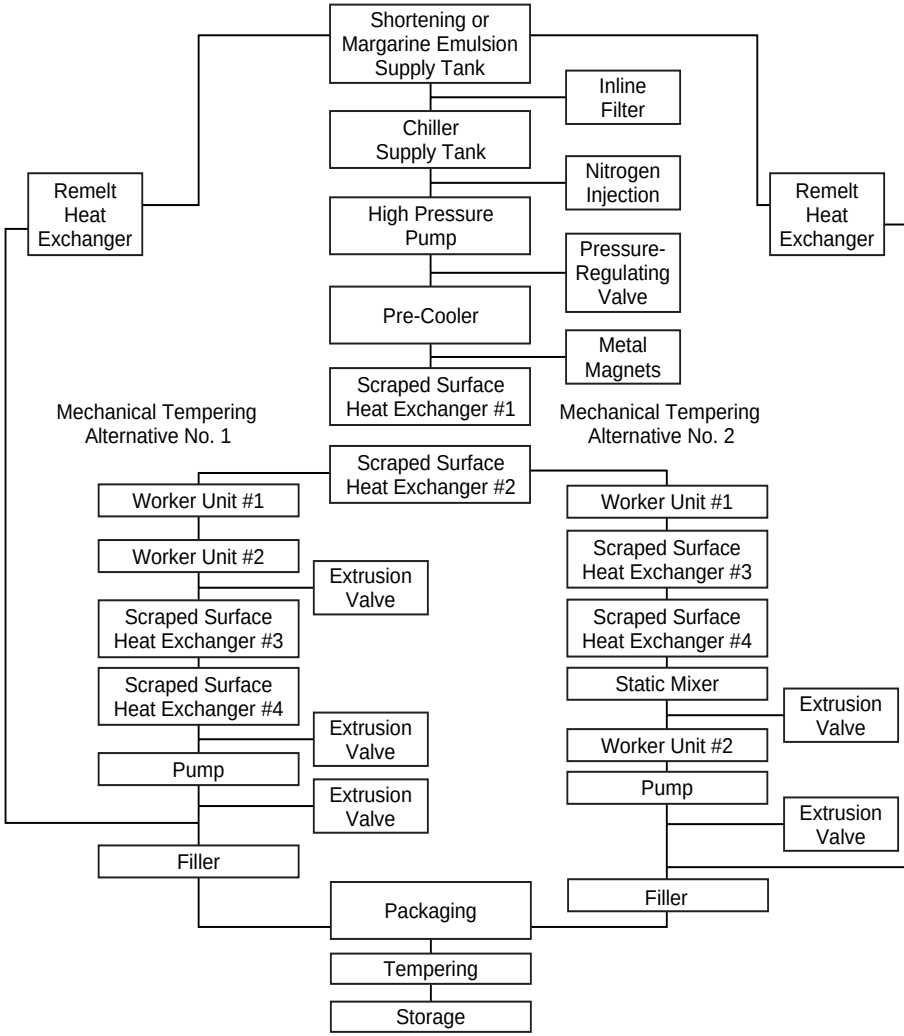


Figure 2.13 Mechanical tempering alternatives.

product with 0.25 to 10 minutes' exposure. U.S. Patent No. 3,469,996 indicates that the microwave tempering could be performed before packaging continuously or after packaging on a batch basis. The typical microwave exposure time was 2 minutes with a product exit temperature of 95 to 103°F (35.0 to 39.4°C).

2.18 FLAKING

Fat flakes describes the higher melting, edible-oil products solidified into a thin flake form for ease of handling, for quicker remelting, or for a specific function in a food product. Flaking rolls, utilized for the chilling of shortening and margarine

prior to the introduction of scraped-wall heat exchangers, are still used for the production of fat flakes. Chill rolls have been adapted to produce several different flaked products used to provide distinct performance characteristics in specialty formulated foods as well as the traditional melting-point adjustment function. Consumer demands have created the need for specialty fat products. Specialty high-melting-fat flakes have been developed for specific applications with varied melting points:

Product	Melting Range °F	°C
Low-iodine-value hardfats	125–150	52–66
Hard emulsifiers	140–150	60–66
Icing stabilizers	110–130	43–54
Shortening chips	110–115	43–46
Confectioners' fats	97–112	36–44

2.18.1 Chill Rolls

Chill rolls are available in different sizes, configurations, surface treatments, feeding mechanisms, etc., but most used flake fats are 4-foot-diameter hollow metal cylinders either 9 or 12 feet long, with the surface machined and ground smooth to true cylindrical form. Flaking rolls, internally refrigerated with either flooded or spray systems, turn slowly on longitudinal and horizontal axes. Several options exist for feeding the melted oil product to the chill roll: (1) a trough arrangement positioned at varying locations on the top quarter section of the roll, (2) a dip pan at the bottom of the roll, (3) overhead feeding between the chill roll and a smaller applicator roll, and (4) a double- or twin-drum arrangement operating together with a very narrow space between them where the melted fat product is sprayed for application to both rolls. A thin film of liquid fat is carried over the roll, and as the revolution of the roll continues the fat is partially solidified. The solidified fat is cleanly scraped from the roll by a doctor blade positioned ahead of the feed mechanism with all of the designs.

2.18.2 Flake Crystallization

During chilling, a portion of the fat is supercooled sufficiently to cause very rapid crystallization. The latent heat released by fat crystallization is absorbed by the cooling medium in the roll. In the crystallization of hydrogenated edible-oil products, the sensible heat of the liquid is removed until the temperature of the product is equal to the melting point. At the melting point, heat must be removed to allow crystallization of the product. The quantity of heat associated with this phenomenon is called the heat of crystallization. The sensible heat or specific heat of the most common hardfat products is equal to 27.8 calories per gram (50 BTU/pound). The amount of heat that must be removed to crystallize low-iodine-value hardened oil is 100 times the amount of heat that must be removed to lower the product temperature. Typical coolant temperature requirements for flaked products are:

Product	Coolant Temperature °F	°C
Low-iodine-value hardfats	70 max.	21.1 max.
Hard emulsifiers	70 max.	21.1 max.
Icing stabilizers	30 max.	–1.1 max.
Shortening chips	5 max.	–15.0 max.
Confectioners fats	30 max.	–1.1 max.

2.18.3 Flaking Conditions

The desired flake product dictates the chill-roll operating conditions and additional treatment necessary before and after packaging; however, some generalizations relative to chill-roll operations and product quality can be made:

- Crystal structure — Each flaked product has crystallization requirements depending upon the source oil, melting point, degree of saturation, and the physical characteristics desired.
- Flake thickness — Four controllable variables help determine flake thickness: (1) oil temperature to the roll, (2) chill-roll temperature, (3) speed of the chill roll, and (4) the feed mechanism. Normal flake thickness for most flaked products is 0.03 inches, but it increases for most shortening chips to 0.05 inches.
- In-package temperature — Crystallization of the fat flakes is not complete before removal from the chill roll, and heat continues to be released. Heat of crystallization will cause the temperature of a product to rise after packaging if it is not dissipated prior to packaging. The product temperature can increase to the point where partial melting coupled with pressure from stacking will cause the product to fuse together into a large lump.
- Flake condition — Glossy or wet flakes are caused by a film of liquid oil on the flake surface due to incomplete solidification. Chill-roll temperatures that are too warm or too cool can cause this condition. High-roll temperatures may not provide sufficient cooling to completely solidify the flake. Low-roll temperatures may shock the oil film, causing the flake to pull away from the surface before it is completely solidified. Under either of these conditions, wet flakes will lump in the package.

2.19 POWDERED AND BEADED FATS

Powdered and beaded fats are specialized products developed for ease of incorporation, handling, melting efficiency, uniform delivery with vibrator addition systems, etc. These products may be produced using a hydrogenated fat only, a hard emulsifier only, a blend of hydrogenated fats and emulsifiers, or fats or emulsifiers incorporated with other ingredients such as skim milk, corn syrup solids, sodium caseinate, powdered eggs, starch, and flavorants. The blended products are formulated for specialized functions in dairy systems, fillings, prepared mixes, candies, sauces, and other prepared food products. Powdered hard emulsifiers serve the same function as flaked product but will melt more quickly and can be incorporated into some finished products as is. The hard emulsifiers, hydrogenated fats, or blends of the two serve as stabilizers for peanut butter and other products and act

as crystallization promoters, lubricants for breading mixes, pan release agents, pharmaceuticals, cosmetics, melting point adjustment, etc.

Three principal methods of forming powdered or beaded fats are practiced in the United States: (1) spray cooling, (2) grinding flaked product, or (3) spray flaking and grinding. Formulated products with fats, emulsifiers, milk solids, etc. for specialized uses are usually spray-chilled powders. Hardfats and hard emulsifiers are also spray-chilled but may have a disadvantage for feeding or blending accuracy. The spherical shape of the spray-chilled powders may act as roller bearings to give erratic feeding rates with vibratory feeding systems or may stratify in blends of dry materials. Beaded products produced by grinding flakes or spray flaking and grinding have granular shapes that can be metered at uniform rates with vibratory or screw feeders and resist stratification or separation in mixes with other granular materials.

2.19.1 Spray Cooling

Generally, this process consists of atomizing a molten fat in a crystallization zone maintained under temperature conditions where a very fine mist of the melted fat is contacted with cooled air or gas to cause crystallization of the fat without marked supercooling. By controlling the temperature conditions and residence time in the cooling chamber, all of the sensible heat and virtually all of the latent heat of crystallization are removed with the formation of many crystallization centers by rapid nucleation, accompanied by an optimum of crystal growth of these nuclei. By controlling the crystal growth with conditions of no appreciable supercooling and almost complete dissipation of the heat of crystallization, the equilibrium condition is achieved almost instantly. This equilibrium condition achieves homogeneity in both inter- and intracrystal composition of the fat to produce free-flowing, tempered particles.

2.19.2 Flake Grinding

Flaked, low-iodine-value hardfats and hard mono- and diglycerides can be ground with attrition-type mills. This type of mill involves impact of the particles both with each other in the air and against a plate. Air flow can be used to move the ground fats through the equipment. The required air flow is less than involved in spray cooling, but the ground flakes must be separated from the air stream. Precooling of the flakes or dry-ice addition must be used to lower the temperature of the product below 40°F (4.4°C) before grinding at a sustained rate is possible. The grinding process causes a rise in temperature, which results in material which is too gummy to grind properly. Flakes can be ground successfully if they are well cooled before the grinding operation begins, with the addition of dry ice or air circulation at low enough temperatures to dissipate the heat generated.

2.19.3 Spray Flaking and Grinding

This patented continuous process allows the manufacture of powdered fats utilizing a chill roll and permits the immediate grinding of the fat into powder without excessive refrigeration in the flaking roll or further cooling of the product. This process consists of the following steps:

1. Spray liquid droplets of molten fat onto the cool chill-roll surface, which then solidify rapidly.
2. Remove the solidified droplets from the chill roll with a doctor blade.
3. Classify the solidified fat droplets by size with a vibrating sizing screen. The larger particles are diverted to the grinder, whereas the smaller acceptable-size particles proceed directly to the packaging operation.
4. Return ground material to the vibrating screen for resizing until an acceptable particle size is obtained for packaging
5. Temper the product at an elevated temperature to transform the crystals to the stable polymorphic form.

2.20 SALAD AND COOKING OILS PACKAGING

Clear salad and cooking oils do not require any further processing after deodorization for packaging except for temperature control for flavor, consistency, and weight control plus nitrogen protection for oxidative stability. Liquid oils are currently packaged in 8-, 16-, 24-, 32-, 48-, and 64-ounce clear plastic containers as well as 1-gallon opaque plastic containers for the retail market. The same oils and some additional products with additives, such as antifoamers and antioxidants, are packaged in 35-pound or 5-gallon plastic jugs and 425-pound closed-head drums for foodservice and food processor customers. Plastic containers have replaced glass and metal containers due to improved economics. Both lower package costs and lighter weight packaging contribute to lower product costs.

Salad and cooking oils are sensitive to light, which catalyzes oxidation to produce off-flavors. Sensitizers such as chlorophyll may promote photooxidation. Artificial lighting, as well as sunlight, causes this deterioration in oils. Industrial packaging protects the oils, but the clear plastic retail container, like glass, offers little protection after removal from the case at the store.

Oxygen contact contributes to the degradation of an oil and is the most critical factor affecting flavor stability. It may gain access to packaged oil in several ways:

- Atmospheric oxygen may be entrained in the oil at packaging.
- Oxygen may be available in the container headspace.
- Oxygen may permeate the walls of plastic containers.
- Impure nitrogen may contain oxygen.

Liquid oils should be protected from both heat and refrigerated temperatures. High temperatures accelerate flavor degradation, and cold temperatures cause crystallization and clouding; therefore, salad and cooking oils should not be stored in shortening-tempering rooms nor in marginarvaults. Storage and shipment should be at 70 to 75°F (21.1 to 23.9°C).

2.21 BULK OIL SHIPMENTS

Food processors that use edible fats and oils in large quantities frequently purchase their requirements in bulk. All the packaged fat and oil products can be shipped as bulk liquids in tank cars or tank trucks, except complete margarines and

spreads. In this case, the margarine oil base can be shipped to the customers. These products must be handled properly during loading, transit, unloading, and storage in the customers' tanks to ensure acceptable quality at the time of use and consumption.

Bulk handling systems for shipping fat and oil products must be designed and operated with three primary considerations for the maintenance of quality: (1) avoid contamination, (2) avoid overheating, and (3) minimize exposure to air.

2.21.1 Contamination

A contaminant is any undesirable material that may taint, infect, corrupt, modify, or degrade by contact or association. The contaminants most likely to affect bulk shipments are:

- Moisture — Precautions must be taken to protect the fats and oils product from hydrolysis and development of free fatty acids. Moisture sources may be wet tank cars or trucks, steamed lines, ruptured tank car coils, leaking coolers, condensation, rain during loading, etc.
- Impurities — The presence of foreign materials in bulk oil shipments is usually caused by a malfunction in the inline clay-out filter, inadequate tank cleaning or rinsing, open hatch covers, etc. Rail tank car cleaning is somewhat difficult because of the black iron construction and heating coils that tend to become coated with oxidized and polymerized oil.
- Commingling — Inadvertent mixing of two different fats and oils products is a serious contamination. Every fats and oils product has its own specific properties, and depending upon its field of application the tolerance for admixture of other fats is usually very low. Product mixing is usually the result of a mispumping, failure to remove a returned heel in a tank car before loading fresh product, or a malfunctioning valve.

2.21.2 Overheating

Most bulk-shipped fats and oils must be heated for pumping to tank cars and trucks and again at the customer's location with rail cars. Product temperatures should never be at a higher level than necessary. The oxidation rate for fats and oils increases by a factor of 3 for each 20°F (11°C); normally a temperature 10 to 15°F (5.6 to 8.3°C) above the melting point is adequate to keep a fats and oils product liquid for pumping. Products received at the customer's location in a solid or semisolid state should be heated slowly so that they are liquid and homogenous before pumping. Rail tank car overheating can occur with high-pressure steam usage or even with low-pressure steam handled improperly. Heating should start at a time calculated to provide the required temperature without exceeding the maximum rate of 10°F (5.6°C) per 24 hours. When steam is used, the steam pressure should not exceed 1.5 kg/sq cm to prevent localized overheating.

2.21.3 Air Exposure

Oxidation results when fats and oils are exposed to air, which decreases stability and produces poor flavors. Air can be almost completely excluded by maintaining

a nitrogen atmosphere at all stages after deodorization; however, most tank cars and trucks cannot be pressurized to maintain a complete nitrogen blanket. Nitrogen sparging into the stream of oil as it is loading will saturate the oil plus an excess. This excess is released when the oil is cooled into the tanker to displace air in the headspace. This practice requires about 5 cubic feet of nitrogen per 1000 pounds of oil. Additionally, the loading lines should discharge near the bottom of the tanker to minimize aeration of the product. Allowing heated fats and oils to cascade or fall through the air into the tanker allows the product to splash and aerate.

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CHAPTER 3

Fats and Oils Analysis

3.1 INTRODUCTION

The use of fats and oils prior to the beginning of the 19th century was based on practical knowledge that had been accumulated slowly over many centuries. Today, fats and oils products are developed and subsequent production controlled with a knowledge of their composition, structural and functional properties, and the expected reactions obtained through the application of scientific research. Progress in the utilization of fats and oils for the production of useful products is dependent upon a thorough knowledge of the characteristics of the raw materials, the changes effected by each process, and the requirements of the individually prepared food product. Physical, chemical, and performance analyses are the tools available to fats and oils processors for the purchase of raw materials, development of new products, and evaluation of the products produced.

Analyses of fats and oils are required for a number of applications, beginning with commodity trading. In every fat and oil processing plant, there are analytical requirements for process quality control. Refining, for example, evaluating the free fatty acid (FFA) content of the oil is necessary to determine the caustic treat, to determine if the oil has been properly deodorized, and to serve as a quality indicator in other areas. Melting points, solids fat index (SFI), and other physical evaluations indicate that the product will function as developed. For final edible-oil products, organoleptic evaluations, peroxide value, FFA, and other analyses are utilized for assurance that the product has the required bland flavor, with predictive analysis such as active oxygen method (AOM) stability being utilized to ensure proper shelf life.

Nutritional listings of saturates, polyunsaturates, cholesterol, vitamins, and other product characteristics on food product labels require accurate analysis to identify the original values and to ensure compliance with any claims. Also of importance are analyses for trace constituents, such as pesticides or trace metals, to ensure compliance with governmental regulations.

Investigative analyses are frequently required in fats and oils processing. Identifying the oils and physical characteristics of a somewhat mysterious product that

arises as a result of a mispumping or some other mishap is required to determine the opportunities to salvage the product. Analyses are also needed to determine the cause of product failures identified by quality evaluations of finished products or as a result of customer complaints.

Specialty and tailored fats have individual analytical requirements in terms of chemical, physical, consistency, nutritional, performance, and other properties that must be measured and maintained to ensure that products function as designed. The diversity of products and applications amplifies the need for analytical information and the ability to interpret the meaning of the results.

The analytical methods employed should be those that are universally accepted in the industry, both by the suppliers of the raw materials and by the purchasers of the finished products. Historically, development of analytical methods for fats and oils has been undertaken by the processors, professional societies, end users, academic community, and government-sponsored research agencies. Development of analytical procedures was one of the main reasons for forming the Society of Cotton Products Analysts, which became the American Oil Chemists' Society (AOCS). Methods standardization remains a major goal for AOCS, and procedures with wide interest and application become a part of the Official Methods and Recommended Practices of the American Oil Chemists' Society. The AOCS methods are continually updated, with unused or less satisfactory methods being dropped and new procedures being added. Other standardized methods of potential application are published by the Association of Official Analytical Chemists' (AOAC), American Society for Testing and Materials (ASTM), and American Association of Cereal Chemists (AACC).

3.2 NONFATTY IMPURITIES

Impurities present in fats and oils are contaminates that must be removed during processing to prevent an adverse reaction and undesirable appearance. Most of the trading rules for edible oil products have specific limits for the various nonfatty materials. Analysis for these materials during processing is part of good process control, and quality processors have stringent as-shipped requirements for finished products to prevent these contaminants from reaching the customer. The nonfatty impurities analytical methods are identified by the predominate contaminant in most cases.

3.2.1 Moisture Analysis

Moisture can contaminate a fat or oil in many different ways: condensation, broken coils, intentional addition during processing, etc. Continued presence of moisture will induce hydrolysis with a resultant FFA increase and off-flavors. Some of the analytical methods to identify and quantify moisture include:

- Hot-plate method — One of the most common methods of determining moisture in a fat or oil is AOCS Method Ca 2c-38 for Moisture and Volatile Matter.[1] Approximately 10 grams of a representative sample is heated in a beaker with gentle agitation on a hot plate until foaming stops and incipient smoking begins.

The loss in weight between the beginning and the ending sample represents the moisture and volatile matter.

- Air oven method — The results of the air oven method (AOCS Ca 2e-25) are more accurate and reliable but also more time consuming than the hotplate method. For the air oven method, approximately 5 grams of a representative sample is weighed into a dried, tared moisture dish and dried in the oven for 30 minutes at 101 ± 1°C. This procedure is repeated until a constant weight is determined. The loss in weight is calculated as the moisture and volatile matter.
- Vacuum oven method — AOCS Ca 2d-25 provides more accurate results than the hotplate and air oven procedures and is especially applicable where moisture is deep seated and must diffuse largely through the capillaries. The same procedure as for the air oven method is observed, except that the vacuum should not exceed 100 mmHg at a temperature 20 to 25°C above the boiling point of water at the operating pressure until a constant weight is obtained in successive 1-hour drying periods. Again, the weight loss is calculated as the moisture and volatile matter.
- Karl Fisher method — This method is adaptable for determining moisture in a wide variety of materials and has been adapted by many laboratories as a standard test procedure for moisture. The Karl Fisher volumetric method for moisture may be determined by ordinary visual titration or by an electrometric method. The titration endpoint is a color change from yellow to brown. The electrometric method of titration for moisture is more accurate when dark solutions are encountered and enables a less experienced technician to correctly identify the endpoint. An automatic titration speeds up the analysis with an even better degree of accuracy. AOCS Method Ca 2e-84 indicates that the precision for the Karl Fisher moisture determination by the same operator is 0.6% relative.
- Skillet moisture — This simple, qualitative method determines very quickly if moisture is present in a sample. It involves pouring a small amount of the sample into a hot skillet previously heated until the sample begins smoking. An absence of moisture is indicated by a lack of reaction, and any popping or spitting indicates the presence of moisture. This qualitative evaluation, with results usually reported as simply wet or dry, can be used to determine if a more quantitative result is required.

3.2.2 Impurities Analysis

Foreign material in incoming crude edible oils or incorporated during processing must be removed by filtration or another process to produce an acceptable finished product. The following methods and procedures have been effective for identifying the existence of a problem and confirming that the impurities have been removed before subsequent processing or shipment:

- Insoluble impurities — Meal, dirt, seed fragments, and other substances insoluble in kerosene or petroleum ether are the impurities identified by AOCS Method 3a-46 normally identified by trading rules for crude vegetable oils. This method utilizes the residue from the moisture and volatile matter determinations or another sample prepared in the same manner is dissolved in 50 milliliters of kerosene and then vacuum filtered through a Gooch crucible. After washing with warm kerosene and petroleum ether, the crucible is dried and weighed. The gain in weight of the crucible is noted and the percentage of insoluble impurities is calculated.

- Filterable impurities (standard disc method) — During processing, small quantities of undissolved impurities may be picked up from polymerized oil deposits, charred materials, salt formed after a reaction, filter aids, bleaching earths, or some other foreign material. These materials should be removed by one or more of the filtering systems in the process, but an evaluation procedure will ensure that the systems are operating properly and are properly sized to remove all of the foreign materials before shipment to the consumer. A suggested procedure for evaluating filterable impurities is to filter a standard quantity (500 grams) of heated (70 to 90°C) oil sample with a vacuum suction funnel through a Whatmann No. 2 filter disc. After filtering, wash the funnel and filter disk with a suitable solvent. Compare the filter disk to standard impurities discs previously prepared to identify the degree of acceptability.
- Turbidimeter impurities — The amount of undissolved impurities in oil can be rapidly determined with the use of a turbidimeter. Product samples are usually heated to 70° ± 1.0°C and allowed to stand 5 to 10 minutes in a controlled-temperature oven after being poured into the prescribed sample bottles to eliminate air bubbles. The turbidimeter readings can be converted to part-per-million (ppm) impurities with a predetermined calibrated curve. Experience has shown that this method cannot be used for animal fats and products containing emulsifiers, because they contain turbid materials other than those effectively measured by this procedure.

3.2.3 Trace Metals Analysis

Throughout the processing of edible fats and oils, metals can be encountered, many of which reduce the efficiency of the process or cause deterioration of the product quality. The most notable of these metals are copper, iron, calcium, magnesium, sodium, lead, zinc, and nickel. Various procedures have been used for determining minute quantities of the trace metals in edible-oil products. Several qualitative methods for iron and nickel are available, but the sensitivity for these methods is limited. These evaluations perform adequately only when it is necessary to confirm that a product contains less of a trace metal than the established limits of the procedure. Initially, these wet chemical analyses were the only quality control analyses available, but improved trace metal determination procedures have been introduced; flame atomic absorption spectroscopy was improved by replacing the flame with a graphite furnace, and more recently plasma emission spectroscopy, inductive coupled plasma (ICP) has been introduced. At one time, these procedures were initially performed only by technical research laboratories or by a centralized quality control laboratory; however, now it is recommended that each refinery have the capability to perform these sensitive trace metal analyses 24 hours a day, 7 days a week. These procedures do require well-trained operators, but reliable trace metal information is necessary to maintain refinery yields and improve quality.[2]

3.2.4 Soap Analysis

In caustic refining, sodium hydroxide is introduced to the oil to react with the FFAs and produce soaps. Traces of soap remaining in the oil after refining and bleaching poison hydrogenation catalysts and have a detrimental effect upon the oxidative stability of deodorized oils at levels below 5 ppm. Two AOCS methods are

available for determining soap: Cc 15-60, a conductivity procedure, and Cc17-79, a titration procedure. Soap analyses are also useful investigative tools for evaluating the cause of early breakdown of frying fats. Trace amounts of caustic cleaning materials left in deep-fat fryers will react with the FFAs present to produce soaps, which shorten the frying life of the shortening as exhibited by foaming, off-flavor, high absorption, etc.

3.3 MELTING, SOLIDIFICATION, AND CONSISTENCY

The data obtained from melting points, solids fat index methods, and other solidification procedures are all used to predict the consistency of the finished product. For edible fats and oils products, the liquid/solids levels at the various temperatures in relation to body temperature can give good indications of the mouth feel, gumminess, workability, and overall general behavior at cool, ambient, and elevated temperatures. The melting and solidification procedures are the most frequently and routinely performed evaluations in fats and oils laboratories, both for quality control and for product development. They are useful to control production and help identify unknown samples and are critical in new product formulation.

3.3.1 Melting Point Analysis

Melting point is usually defined as the point at which a material changes from a solid to a liquid; however, natural fats do not have a true melting point. Pure compounds have sharp and well-defined melting points, but fats and oils are complex mixtures of compounds that pass through a gradual softening before becoming completely liquid. This melting procedure is further complicated by the fact that fat crystals can exist in several polymorphic modifications, depending on the specific triglycerides involved and the temperature/time pretreatment (tempering) of the sample. The different crystal forms are often stable enough to exhibit distinctive melting points; therefore, instead of melting point, melting range or melting interval is more correct. For a melting point, one point within the melting range must be selected with a defined method. Only with ridge and specific definition of the conditions of the fat pretreatment and the test procedure can a melting point be determined. Many methods have been devised to determine the melting point or a point close to it, some by direct observation and some by indirect and objective processes[3]. The advantage of most melting point methods is their relative simplicity, but the dependence of the melting point on the sample pretreatment and on the method used must be considered a disadvantage.

Several fats and oils melting point procedures have been standardized by AOCS and other associations. The melting point methods vary considerably in the endpoint determination, conditioning of the sample, degree of automation, time requirements, attention required, degree of melt, and so on.

- Capillary melting point — AOCS Method Cc 1-25 is essentially the procedure used by the organic chemist for determining the melting point of pure organic

compounds. In this method, capillary tubes (1-millimeter inside diameter) are filled to a height of 10 millimeters with melted fat; the end is sealed and tempered 16 h at 4 to 10°C. After tempering, the tubes are heated in a bath at 0.5°C per minute, starting 8 to 10°C below the expected melting point, until the fat becomes completely clear. It has been difficult to reproduce results with this method because of the subjective interruption of the completely clear endpoint.

- Softening point — This open capillary tube melting point method (AOCS Method Cc 3-25) follows the closed capillary tube procedure, except the tube is not sealed and the endpoint is the physical movement of the fat column under a standardized hydrostatic pressure. This objective determination is a definite advantage for better reproducibility of results.
- Slipping point — AOCS Method Cc 4-25 is based on the same principle as the open capillary melting point or the softening point method, except that only plasticized or solidified samples are placed in metal tubes that are heated at a rate of 0.5°C per minute while immersed in a brine solution in a 600-milliliter beaker. The endpoint for this method is the temperature when the fat rises from the cylinder. This method is useful for solidified products, and the endpoint is determined objectively, but the sample lacks laboratory pretreatment, so the results can be influenced by the nonstandardized thermal history of the product.
- Wiley melting point — At one time, AOCS Method Cc 2-38 was the most popular method in North America for determining a melting point. A solidified fat disc is solidified and chilled in a metal form for 2 hours or more. The disc is then suspended in an alcohol-water bath and slowly heated while being stirred with a rotating thermometer. The Wiley melting point occurs when the fat disc becomes completely spherical. The subjective interpretation of the endpoint is again a major disadvantage, and slight variation in sample tempering or heating rate interferes with reproducibility of the results. Another major disadvantage is the constant attention required to determine the endpoint.
- Mettler dropping point — AOCS Method Cc 18-80 utilizes a Mettler Instrument Corporation, Princeton, NJ control unit and dropping furnace. A sample cup designed for the furnace is filled with approximately 17 drops of the melted fat sample and tempered in a freezer for 15 minutes. The cold solidified sample is warmed in the temperature-programmed furnace until it becomes fluid enough to flow. When the sample flows, it trips a photoelectric circuit, which records the temperature on a digital readout. This procedure has become a standard in most fats and oils laboratories due to the advantages it offers over the other melting point methods: fully automatic endpoint determination, good correlation of results with Wiley melting point results, less than an hour elapsed time required for complete results, and the ability to analyze products with low melting points.

3.3.2 Solids Liquids Contents Analysis

The proportion of solid to liquid fat in a shortening, margarine, or specialty product at a given temperature has an important relationship to the performance of the product at that temperature. This proportion cannot be determined from single-point melting analysis or any other analysis of the physical properties. Estimates of the solids and liquids contents in a fat at different temperatures over the melting range can be made with calorimetric, dilatometric, or nuclear magnetic resonance procedures. Over the past 40 years, the dilatometric procedure (solids fat index) has

gained wide acceptance for the characterization of solid/liquid contents of fats. Methods have also been standardized for the use of nuclear magnetic resonance (NMR) imaging for this purpose, and differential scanning calorimetry (DSC) techniques have been developed for determination of solid/liquid contents.[1]

The usual temperatures at which the solids index/contents determinations are made are 10.0, 21.1, 26.7, 33.3, and 37.8 or 40.0°C. Generally, the SFI may be related to the physical characteristics of the fat or oil product over the temperature range in use.[2] For example, SFI results for margarine-base oils are usually determined at three temperatures to indicate properties for:

- 10.0°C (50°F) — An indicator of printability and product spreadability at refrigerator temperatures
- 21.1°C (70°F) — An indicator of product resistance to oil-off at room temperature
- 33.3°C (92°F) — An indicator of eating or melt-in-the-mouth characteristics

Solids fat index/contents determinations at different temperatures covering the range over which a fat passes from a solid to a liquid can be plotted to produce a curve that illustrates the changes. The solids curves will show:

- Plastic range — Fats and oils products generally have the best consistency for mixing and working within a solids content range of 15 to 25%, which is usually identified as the plastic range.
- Melting point — The dilatometric melting point is the temperature at which the solids curve meets the liquid line, that is, the lowest temperature at which the solids content is zero. This melting point is obtained by extrapolating the solids curve to zero either graphically or mathematically.
- Flat solids curve — Flatter solids slopes generally have a greater plastic range because the solids remain within the plastic range for a wider temperature range.
- Steep solids curve — Sharp melting properties are usually accompanied by a high oxidative stability and characterized by steep solids slope. Frying, cookie filler, and nondairy applications are examples of products benefiting from a steep solids slope. These products require a sharp melt profile with good flavor stability, whereas workability and creaming properties are not required.

Since its beginnings in the early 1930s, dilatometry, now referred to as solids fat index, has become the preeminent analysis performed in fats and oils laboratories. It has become the single most important criterion for establishing specifications regarding melting behavior and crystalline structure. Despite its importance, the SFI method is time consuming and labor intensive and requires more maintenance than the majority of the other analyses performed; therefore, the fats and oils industry has long sought a less time-consuming, more automated, less expensive procedure that would provide comparable results.[3] The SFI remains the preferred method in the United States, whereas the European and Asian fats and oils industries have adopted NMR techniques to determine the solids fat contents.

3.3.2.1 Solids Fat Index

Dilatometry is the basis for the most widely accepted method for solids fat measurement in the United States. AOCS Method Cd 10-57 for the dilatometric solids fat index has been used extensively for product development, process control, and quality specifications for fats and oils products. Solids fat index is an empirical measure of the solids fat content. It is calculated from the specific volume at various temperatures utilizing a dilatometric scale measured in units of milliliters times 1000. It should be recognized that the SFI results are arbitrary because assumptions are made and liberties are taken insofar as precise measurement is concerned, including (1) use of volumetric instead of gravimetric measurements, (2) use of solutions other than mercury as the confining liquid, (3) assumption that the slopes of the liquid and solids lines are parallel, (4) assumption that the slope of the liquid line is the same for all fats, and (5) assumption that the melting dilation is 0.1. Some of the assumptions are made out of necessity and others are made for convenience; however, even with the assumptions and liberties taken, the results have relative significance and are related to other fats and oils properties that are important with respect to performance and use.[6]

3.3.2.2 Solids Fat Content

AOCS Method Cd 16-81 determines the quantity of solid glycerides in a fat by measuring the pulsed NMR signal of the liquid fat.[1] The hydrogen atom in a solid crystal does not give a signal, but a hydrogen atom in a liquid environment does; therefore, NMR measures the actual amount of liquid in a sample. SFI and NMR analysis may be correlated, but the methods do not provide identical results. The most significant difference between the two techniques is experienced with fats containing high solids contents at 10.0 and 21.1°C (50 and 70°F). Solids fat content (SFC) using either pulsed or wideline NMR spectrometers is a direct measurement, whereas SFI is an empirical measure calculated from the specific volumes at various temperatures using a dilatometer.[6] Solids fat content (SFC) using either pulsed or wideline NMR spectrometers is a direct measurement, while SFI is an empirical measure calculated from the specific volumes at various temperatures using a dilatometer.

3.3.2.3 Differential Scanning Calorimetry Fat Solids Content

Measurement of the heat of fusion of fat rather than its thermal expansion appeared to offer promise as a means of determining fat solids content, so methods were developed for measurement of the solids contents of vegetable and animal fats by DSC in the search for a less time-consuming method for determining fat solids content. Briefly, the methods developed measured the heat of fusion of a frozen, completely solid sample of fat. The area under the melting curve (presented on a strip chart) is measured, then selected partial areas are measured as a percentage of the whole. The temperatures selected for partial area measurement are normally those used for the SFI by dilatometry.

Several advantages can be identified for DSC fat solids methods as compared to SFI: (1) the thermal history determined can provide clues to the tempering and

storage conditions for the fat sample; (2) the fat melt curve can help distinguish between two fat products with identical SFI values; (3) a fat solids range from –10°C for soft oils to 70°C for hardfats would be possible; (4) no limit for hardness would be necessary, as is required with SFI by dilatometry; (5) results should be available in approximately 1 hour of elapsed time; and (6) correlation with SFI results appear good. The identified disadvantages were (1) accurately weighing the small sample size (5 to 10 milligrams) poses the problem of representative sampling, (2) variation for fat solids is not constant and is greater at low temperatures, and (3) precision has been found to be poorer than with the standard SFI dilatometric technique.

Fat solids analysis by DSC has never been accepted as a quality control tool to replace SFI. Originally, it had appeared to be an ideal choice because it measured the change in heat absorption vs. the temperature of the sample programmed from one temperature to another to record a melting profile of a sample as it passes through various crystalline states from a solid to a liquid. The primary points of dissatisfaction with the DSC solids measurement techniques were the fact that reanalysis of the same sample is not as reproducible as SFI, the sample minute quantity requires significant weighing accuracy, and DSC provides too much information.[2] It appears that DSC can be a very useful research tool, but not suitable for quality control laboratories.

3.3.3 Solidification Analysis

Solidification of mixed fatty acids is the point at which a balance is attained between the heat generated and the heat lost, which will vary according to the rate of crystallization and the degree of supercooling in the liquid. These evaluations are some of the oldest fat characteristics used for fats and oils control purposes.

- Titer — The titer test (AOCS Method Cc 12-59) measures the solidification point of the fatty acids. First, a fat sample must be saponified and dried before determining titer. Then, a titer tube is filled to the 57-millimeter mark with dried fatty acids and suspended in an air bath, which is surrounded by a water bath at 15 to 20°C below the expected titer result. The sample is stirred until the temperature begins to rise or remains constant for 30 seconds, after which the stirring is stopped and the endpoint is recorded as the maximum temperature the fat reaches with heat of crystallization.[1] Titer is an important characteristic for inedible fats used for soapmaking or as a raw material for fatty acid manufacture. For edible fats and oils, titer is commonly specified for low-iodine-value hardfats, sometimes referred to as titer stocks.
- Quick titer — Hydrogenation control of hardstocks or titer stocks is normally done with a quick titer determination because the official titer (AOCS Method Cc 12-59) is too time consuming for control purposes. A quick titer analysis is performed by dipping the bulb of a glass thermometer into the liquid fat sample and then rotating the thermometer stem between the fingers to cool the fat at room temperature. The endpoint is the temperature reading when the fat on the bulb

clouds. Constants for each oil source have been identified for addition to the quick titer result that approximate the official titer determinations very closely:

Source Fat or Oil	Quick Titer Constant, °C
Cottonseed oil	11.0
Soybean oil	13.0
Peanut oil	14.0
Palm oil	9.0
Lard	11.0
Tallow	12.0

- Congeal point— This solidification method, sometimes referred to as setting point, is a measure of the fat itself rather than the separated fatty acids for titer. The congeal point (AOCS Method Cc 14-59) is determined by cooling a melted sample while stirring until the fat becomes cloudy. The sample is then allowed to remain quietly in the air at 68°F. Under these conditions, a temperature rise occurs. The highest temperature attained is the congeal point, which is an estimate of the solidification temperature of the fat.
- Cloud point— This nonstandard method is a variation of the congeal procedure. An empirical cloud point is obtained by stirring a sample of fat while it is being cooled until the oil has clouded enough to block a light beam of known intensity. The cloud or congeal point values are more closely related to consistency than melting points. A definite relationship exists between the SFI at 92°F (33.3°C) and the congeal or cloud point, especially for meat fats.
- Cold test— The ability of a salad oil to withstand refrigerator storage is determined by the cold test, which measures the ability of an oil to resist crystallization by determining the time (in hours) required for the oil to become cloudy at 0°C (32°F). For the standardized AOCS Method Cc 11-53, dry-filtered oil is placed in a sealed 4-ounce bottle and submerged into an ice bath. The AOCS method stipulates that the oil should be examined after 5.5 hours for clarity to determine if the oil passes or fails. An alternative to the method allows continuation of the cold test until a cloud develops. The alternative procedure is probably the norm, as most salad oil specifications require at least a 10-hour minimum cold test. The cold test was developed to evaluate cottonseed oil for the production of mayonnaise and salad dressing. An oil that will solidify at the refrigerator temperatures used for the preparation of these products will cause an emulsion break and separation. Currently, the cold test is also utilized to ensure that bottled salad oils for retail sale will not develop an unattractive appearance on the grocery shelf.
- Chill test— Natural winter oils with soluble waxes can at times successfully pass an extended cold test but develop a cloudy appearance on the grocery store shelf. A nonstandard chill test has successfully corrected this problem when the cold test failed to do so. For the chill test, dry-filtered oil is placed in a sealed 4-ounce bottle and 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.

3.3.4 Consistency Analysis

Consistency is generally assumed to be a combination of those effects that tend to give the impression of resistance. Plasticity relates to the capacity of the product to be molded. The factor most directly and obviously influencing the consistency of a fat is the proportion of the material in the solid phase. It is well established that a fat becomes firmer as the solids content increases.

Crystal size also has an effect — the smaller the crystals, the firmer the fat. An example is the fact that grainy lards are softer than smooth lards that have been interestified. Persistence of the crystal nuclei is also a factor. As a fat is exposed to temperature fluctuations, a portion of it undergoes melting and resolidification. The ability of certain fats to retain their original crystal form, regardless of temperature variation, is probably due to their capability to leave behind crystal nuclei that serve as starting points for the development of new crystals when the fat is cooled.[10]

Some of the most critical performance factors of fats and oils products are related to the properties commonly referred to as consistency and plasticity. The quality of butter, margarine, and spreads depends upon the consistency of the fat portion and its ability to be spread on bread. A wide plastic range and a smooth consistency are mandatory for roll-in shortenings and margarines used for thin-layer lamination at refrigerator temperatures. Plasticity is also important for the workability and creaming properties required for shortenings used in the preparation of icings and aerated batters. Two measures are used:

- Consistency ratings — Undoubtedly, the first method used for evaluating the consistency of a fats and oils product was to press a finger into the product or squeezing the product in the hand. These testing methods, although very subjective, are still applicable and effective. An experienced evaluator can identify slight differences or imperfections in the finished product more readily than can available instrumentation in regard to body, firmness, softness, and inconsistencies in the feel (e.g., sandiness, lumps, ribby texture), as well as problems with the appearance (e.g., oiling, air pockets, grainy texture). Methods for applying a numerical value to the finished product evaluations have been developed independently by most edible-fats and -oils processors or laboratories for comparison purposes. Suggested methods for shortening and margarine finished product rating are presented in the nonstandardized methods section.
- Penetrations — The most widely used method to measure consistency of a plasticized shortening or margarine involves the ASTM grease penetrometer or an adaptation of it. AOCS Method Cc 16-60 for penetration testing identifies the penetrometer as a mechanical device with a support to grip and release the shaft and cone, a support for the sample, an adjustment capability to level the device, and a gauge graduated in 0.1-millimeter units that conforms to ASTM D5, D217, and D937 designations. Most variations of the method used by different laboratories involve the design of the needle or cone. Penetration evaluations measure the depth to which the cone penetrates into the surface of the shortening or margarine after allowing the cone to settle into the product for 5 seconds, starting from a position where the tip of the cone just touches the surface of the sample. The penetration result for each product is the average of four readings performed at each evaluation temperature.

Penetration results are utilized internally by the most part and are not normally a part of customer specifications for fats and oils products. Nevertheless, uniform procedures must be observed to obtain reproducible results. To avoid overheating or overcooling, evaluation samples must be carefully tempered until the desired product temperatures are achieved, usually 24 hours for 1-pound containers. The sample temperature should be stabilized to within 1.0°C before testing for reproducible results. Temperature abuse at any time can change the penetration results even if the sample temperature is returned to the desired level and especially if the sample has experienced any actual melting.

Figure 3.1 Effect of varied chilling temperatures.

Consistency of a product must be measured at a number of different temperatures to determine its plastic range, that is, the range of temperatures over which the fat has the capability of being molded or worked. Normally, samples are held at three to five different temperatures, ranging from 40 to 100°F (4.4 to 37.8°C), until each sample has equilibrated at the desired temperature. The samples are evaluated to determine the relative softness at low temperature and firmness at high temperature. Products with a wide plastic range are workable at both high and low temperatures. A perfect plastic range, if it could exist, would have the same penetration at all temperatures. Evaluation of penetration data obtained personally, indicated that the penetration plastic range falls between 150 and 300 mm/10 g.

Although the elapsed time required for penetration results is too lengthy for process control, it is a valuable tool for finished products control and product development. A penetration curve can confirm that the desired plasticization and tempering conditions have been achieved for an individual product when the SFI and blend composition are controlled within specified limits. Figure 3.1 illustrates the effect of varied chilling unit temperatures upon consistency of soybean oil hydrogenated basestock as measured by penetrations. The results illustrate the softening effect of cooler chilling unit operating temperatures and that the finished

product consistency can be predicted from the solids fat content when the plasticization and tempering conditions are controlled.

3.4 COMPOSITION ANALYSIS

Knowledge of the composition of fats and oils is very important in nearly every phase of fats chemistry and technology, although often its importance is not fully realized. In fact, progress in the utilization of commercial fats and oils as raw materials in the manufacture of useful products is dependent to a large degree on knowledge of the composition of the starting material and the products derived from it. Methods for determining the fats and oils composition are important not only because of the fatty acid contents and the pattern of glyceride distribution elaborated by plants and animals, but also because the physical character and end-use performance of fats and oils are directly related to composition.

Analytical methods for determining compositions of fats and oils have evolved from chemical separations to instrumental procedures. Instrumental methods are attractive to the analytical chemist because of the time-saving, better accuracy, and less tedious features; however, most instrumental analysis must rely upon a standardization or calibration procedure, usually the original wet chemical analysis.

3.4.1 Saponification Value

Saponification value is a measure of the alkali-reactive groups in fats and oils and is useful in predicting the type of glycerides in a sample. Glycerides containing short-chain fatty acids have higher saponification values than those with longer chain fatty acids. The saponification value, along with the iodine value determination, have been useful screening tests both for quality control and for characterizing types of fats and oils. The results overlap too much to identify individual fats or oils; for example, both domestic vegetable oils and animal fats have saponification values in the 180 to 200 range. Saponification value analysis has been replaced almost exclusively in edible fats and oils processing by fatty acid composition analysis by gas/liquid chromatography (GLC), except that some purchasers may specify it to prevent lauric oil contamination of domestic oils. Lauric oils have saponification values in the range of 240 to 265, which differ substantially from the 180 to 200 range for domestic vegetable oils.

3.4.2 Iodine Value

The iodine value is a simple and rapidly determined chemical constant for a fat or oil. It is a valuable characteristic in fat analysis that measures unsaturation but does not define the specific fatty acids. Iodine value analyses are very accurate and provide nearly theoretical values, except in the case of conjugated double bonds or when the double bond is near a carboxyl group. However, unless the history of the fat or the type of fat in the product is known, an iodine value may be somewhat meaningless by itself. For example, a product prepared with a meat fat with consis-

tency and performance characteristics similar to a vegetable-oil-based product will have a considerably different iodine value. Further, even vegetable oil products with comparable functionality but different source oils will not have like iodine values. Even with these inadequacies, iodine value is a useful tool for process control and product specification. Iodine value is a measure of the unsaturation of fats and oils and is expressed as the number of centigrams absorbed per gram of sample. Determination of the iodine value (AOCS Method Cd 1-25) is carried out by adding an excess of Wijs reagent to the sample, allowing the mixture to react for 30 minutes at 25 ± 5°C, treating the excess reagent with potassium iodide to convert it to equivalent iodine, and titrating with thiosulfate reagent and a starch indicator until the blue color disappears.[1] The iodine-value procedure must be performed very precisely and timed carefully to be reproducible.

3.4.3 Refractive Index

Hydrogenation process control requires a rapid method for the determination of the product endpoint. Refractive index is used by most processors to measure the change in unsaturation as the fat or oil is hydrogenated. By reference to a predetermined curve relating the refractive index to iodine value, a rapid estimation of the iodine value may be made. One source of error in this method is that trans acids formed during hydrogenation affect the refractive index but not iodine value. The index of refraction is the degree of deflection of a beam of light that occurs when it passes from one transparent medium into another. A refractometer with temperature control is used for fats and oils with measurement usually at 25°C. High-melting fats require temperature adjustments to 40 or 60°C depending upon the melting point of the product. Temperature changes affect the results obtained; refractive index decreases as the temperature rises but at the same time increases with the length of the carbon chains and with the number of double bonds present in the fatty acids. AOCS Method Cc 7-25 identifies the procedure used to measure the refractive index for fats and oils.[1]

3.4.4 Fatty Acid Composition

The classical method for identification of fats and oils has been replaced by fatty-acid composition analysis determined by GLC patterns. The classic method was based on the identification of a specific fat or oil by a combination of its iodine value, relative density, refractive index, and saponification value. The advantages of the GLC procedure are that it permits identification of source oils that cannot be identified by the classical methods, plus it offers the ability to identify the source oil proportions in a blended product. Further, because the fatty acid composition requires only one analysis, it can be made more rapidly and applies equally well to refined and unrefined oils, thus requiring only one set of standards.

Gas chromatography includes those chromatograph techniques in which the mobile phase is a moving gas. In general, the procedure involves passing the methyl esters, or transesterified triglycerides, to be analyzed through a heated column by means of a carrier gas such as helium or nitrogen. The components of the mixture

are eluted with the gas and detected and measured at the exit end of the column by a suitable means. The retention time is the time required for a given compound to pass through the column. The fatty acid esters exit in the order of saturation. The retention line is indicated on the horizontal axis of the chart and is a qualitative index of the substance, and the area under the curve is in each case a quantitative measure of the component.

The fatty acid analysis provides a rapid and accurate means of determining the fatty acid distribution of fats and oils products. This information is beneficial for all aspects of product development, processing, and marketing because the physical, chemical, and nutritional characteristics of fats and oils are influenced by the kinds and proportions of the component fatty acids and their position on the glycerol radical. Fatty acids are classified by their degree of saturation:

- Saturated fatty acids — Fatty acids in which all carbon atoms in the chain contain two hydrogen atoms and therefore have no double bonds
- Monounsaturated fatty acids — Fatty acids that have only one double bond in the carbon chain
- Polyunsaturated fatty acids — Fatty acids that have two or more double bonds in the carbon chain

Each fatty acid has an individual melting point. The melting points of saturated fatty acids increase with chain length and decrease as the fatty acids become more unsaturated; for a given fatty acid chain length, the saturated fatty acid will have a higher melting point than the unsaturated fatty acid. Capric (C-10:0) and longer chain saturated fatty acids are solids at room temperature. The unsaturated fatty acids are chemically more active than the saturates because of the double bonds, and this reactivity increases as the number of double bonds increase. The double bonds are subject to oxidation, polymerization, hydrogenation, and isomerization. The physical characteristics of a fat or oil are dependent upon the degree of unsaturation, the carbon chain length, the isomeric form fatty acid forms, and the molecular configuration. Usually, fats are liquid at room temperature when the level of unsaturates is high and solid when the level of unsaturates is low; however, this generalization can be complicated by *trans*-isomers that have different melting characteristics than the *cis*-isomer of the unsaturated fatty acid.

3.4.5 Calculated Iodine Value

Iodine value measures unsaturates or the average number of double bonds in a fat; therefore, it is logical that an iodine value can be easily calculated from a fatty-

acid composition analysis. The constants for the most common unsaturated fatty acids required for calculation of triglyceride iodine value are

Fatty Acid	Constant
Palmitoleic (C-16:1)	0.950
Oleic (C-18:1)	0.860
Linoleic (C-18:2)	1.732
Linolenic (C-18:3)	2.616

The calculated iodine value is determined simply by multiplying the percentage of each unsaturated fatty acid by its constant and addition of the results. This procedure has not replaced the regular iodine value but can be utilized as an audit for the chemical iodine value and does provide the capability of obtaining two results from one analysis.

3.4.6 Glyceride Structure

The chemical, physical, and biological properties of fats and oils depend not only on the kind and quantity of participating fatty acids, but also on the positions of these fatty acids in the glyceride molecule. In general, fats and oils are composed of mixed glycerides rather than mixtures of simple glycerides. When all three fatty acids are identical, the product is a simple triglyceride. A mixed triglyceride has two or three different fatty acids joined to the glycerol. The characteristics of a triglyceride depend on the position that each fatty acid occupies on the glycerin molecule. As a general rule, fats with uniform triglyceride molecules have β crystals in the most stable state. Fats that are stable in the β' crystal form contain mixtures of types of triglycerides that prevent large crystal growth. For example, fully hydrogenated soybean, corn, canola, and peanut oils are essentially all tristearin due to a low level of palmitic fatty acid and form stable β crystals. Cottonseed and palm oils with high palmitic fatty acid levels have mixtures of stearic and palmitic fatty acids when fully hydrogenated, which form β' crystals. Lard and cocoa butter have high palmitic fatty acid levels but crystallize in the β form due to the uniform triglyceride structure. For lard, palmitic fatty acid is always found in the sn-2 position of the glycerin molecule, and cocoa butter always has oleic fatty acid in the sn-2 position.[11]

Analysis of the complex mixtures of triglycerides present in natural fats has been carried out by many methods. Early analytical techniques employing crystallization and counter-current distribution were not reproducible and required large samples and long analysis times. Extensive evaluations of chromatography techniques have led to high-performance liquid chromatography (HPLC), which partially fulfills the ideal requirements of an accurate, quick, and easy analytical procedure. HPLC procedures have provided rapid methods for the determination of relative amounts of glycerides present in a fat. HPLC can be used to monitor the modification of a fat, as well as to detect adulteration, and as a developmental tool for specialty fats and oils. It appears that triglyceride structure analyses can be very useful research and development tools but are not practical for quality control purposes.

3.4.7 Emulsifier Analysis

A rapid, precise, and easily reproducible method for the determination of monoglycerides in fats became an essential requirement from a quality control standpoint when the use of monoglycerides in shortening and margarine blends became widespread. Hydroxyl number determinations, interfacial tension measurement, and alcohol extractions, among other procedures, were investigated and found not specific and sensitive enough or suitable for quality control purposes. The most satisfactory method identified for determining monoglycerides and free glycerin was based upon their quantitative oxidation with periodic acid. AOCS Method Cd 11-57 for D-monoglycerides presents this titration analysis, where the amount of monoglyceride or glycerin is determined by measuring the amount of periodic acid consumed. Free glycerin can also be determined by titration of the formic acid produced.[11]

Several other analytical procedures for monoglycerides based on thin-layer chromatography (TLC), GLC, and HPLC have been developed as substitutes for the periodic acid oxidation method. These procedures provide reproducible results comparable to or better than the periodic acid oxidation method and are fast and easy to perform; however, the total monoglyceride values usually average higher than the titration method. Monoglycerides exist in two isomeric forms: the 2 form and the 1 form. Only the latter responds to periodic oxidation, which is the basic reaction in the normally applied chemical reaction of D-monoglyceride contents.[12,13] The chromatographic procedures are also applicable for determination of other emulsifier types, notably acetylated monoglyceride and propylene glycol esters.

3.4.8 Antioxidant Analysis

Antioxidants are widely used in fats and oils products to delay decomposition processes that result in offensive flavors. Several phenolic compounds have been identified that inhibit oxidation of fats and oils by interrupting the free-radical mechanism of oxidation. The most notable synthetic antioxidants are propyl gallate (PG), butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), and tertiary butylhydroquinone (TBHQ). The U.S. Food and Drug Administration (FDA) permits the use of the antioxidants at a maximum level of 200 ppm singly or in combination by weight in the vegetable oil portion of the food except when prohibited by a Standard of Identity. The U.S. Department of Agriculture (USDA) limits the antioxidant use to 100 ppm singly but allows 200 ppm in combination with no single antioxidant exceeding 100 ppm for meat fat products. Both the USDA and the FDA labeling requirements specify that the antioxidant utilized must be listed in the ingredient statement. These requirements plus the beneficial effect of the antioxidants necessitate good analytical control of their additions. Both qualitative and quantitative analytical methods are available for evaluation of the fats and oils products for the presence of the various phenolic antioxidants:

- Qualitative methods — Rapid color endpoint qualitative process control procedures are available for the detection of PG, BHA, BHT, and TBHQ. These eval-

uations indicate only the absence or presence of the particular antioxidant in the fat or oil product.
- Quantitative methods — HPLC and GLC methods are currently utilized to measure the amounts of PG, BHA, BHT, and TBHQ antioxidants in a fats or oils product. These procedures require less than an hour to provide accurate and reproducible results.

3.4.9 Tocopherols Analysis

Vegetable oils contain tocopherols, which are natural antioxidants that retard oxidative rancidity. The tocopherol content decreases during each step of processing and can be markedly reduced during deodorization, as these compounds are volatile under these conditions. Studies have shown that the deodorizer tocopherol loss can vary from 19.8 to 51.2% depending upon the deodorizer conditions utilized. The amount of tocopherols removed from the oil during deodorization depends on the time, temperature, and stripping steam flow used. It is important that high proportions of the tocopherols survive oil processing to purified optimum oxidation stability. The alternative is the addition of synthetic antioxidants or tocopherols that have been purified from deodorizer distillate of vegetable oils.

Several methods have been developed for tocopherol analysis of the vegetable oils and in deodorizer distillates and soybean sludge and residues. The instrumentation and procedures evaluated have involved colorimeters, paper chromatography (PC), TLC, column chromatography (CC), GLC, GLC/mass spectrometry (GLC/MS), and HPLC separation techniques, all of which are also sometimes used in combination. Four different AOCS methods have been standardized for tocopherol determinations:[1]

- Ce 3-74 — Tocopherols in soya sludge and residue by GLC
- Ce 7-87 — Total tocopherols in deodorizer distillates
- Ce 8-89 — Tocopherols in vegetable oils and fats by HPLC
- Ja 13-91 — Tocopherols in lecithin concentrates by HPLC

Oxidative stability, or lack of it, in the finished fats and oils product may be due to an abnormal reduction of the tocopherols, which act as free-radical chain-breaking antioxidants. Tocopherol analysis of deodorized vegetable oil products or deodorizer distillate can indicate or provide a reason for a stability problem.

3.5 FLAVOR, RANCIDITY, AND STABILITY

Consumers use organoleptic evaluations to judge the quality of fats and oils. Organoleptic evaluation of oil products has long been recognized as the most sensitive method of assessing quality, but it is also recognized that these evaluations generally lack precision and reproducibility. Rancidity is considered to be the objectionable flavor that results from the accumulation of decomposition products of either oxidation or hydrolysis reactions. In the development, evaluation, and quality

control of edible fats and oils, resistance of the products to oxidative and hydrolytic deterioration is of prime importance. Many chemical methods have been developed to measure oxidative deterioration with the objective of correlating the data with flavor characteristics. Various levels of acceptability have resulted from these endeavors, but researchers are still seeking the ideal test; however, experience has shown that when suitable flavor testing methods are employed, the chemical methods become more valuable in assessing the quality as an oil product.

3.5.1 Flavor Analysis

Flavor in foods is a combined result of the senses of taste, smell, touch, and hearing. Taste and smell sensations result from contact stimuli, where the stimulating substances must be placed upon the receptive sensory cells. The taste-sensing organs, called taste buds, are grouped together on the tongue and to a lesser extent on the palate, pharynx, and larynx.[15] Taste has four attributes: sweet, sour, salt, and bitter. It has been determined that most taste receptors respond to most of these attributes. Obviously, such complex taste stimuli cannot be identified with analyses that measure only one aspect; in addition, flavor identity is further complicated by the presence of other substances that block some sensations.[16]

3.5.1.1 Sensory Evaluations

Taste assessment is the ultimate method of grading finished oil quality. To determine oil flavor, 5 to 10 milliliters of oil is taken into the mouth, thoroughly swished throughout the mouth with air drawn over the top, and expectorated into a waste cup.[20] A panel of experienced tasters rates the flavor of the oil according to an established intensity scale. A 10-point scoring system is usually used, and panel members assign numbers representative of the flavor intensity, from which a mean flavor score is determined. The flavor intensity scores of a trained flavor panel should agree within plus or minus one unit. Off-flavors are described with descriptive names such as green, grassy, weedy, fruity, beany, watermelony, nutty, raw, painty, musty, metallic, oxidized, buttery, reverted, fishy, rancid, tallowy, and so on. Agreement among untrained flavorists regarding off-flavor descriptions is often poor due to individual preferences, age, and background.[17]

Organoleptic, or taste, evaluation will always be necessary and probably will remain the most important technique in flavor evaluation. Taste panels for edible-oil evaluations are utilized for several purposes: (1) to serve as a research or developmental tool, (2) to determine consumer acceptance, and (3) to evaluate process quality. The selection of panel members for each application can be different. Consumer panels are usually a random selection of people who constitute the targeted market, whereas research and development evaluations require trained panelists capable of finite discrimination among various oil flavors and intensities. Process quality evaluators must be able to distinguish between a bland or acceptable flavor and an off-flavor. AOCS Method Cg 2-83 provides a standardized technique for the sensory evaluation of edible fats and oils that encompasses standard sample preparation, presentation of samples, and reporting of sensory responses.[1]

3.5.1.2 Volatile Flavor Analysis

Even though sensory evaluation is the most important and common way to determine fats and oils quality, the method is time consuming, tedious, expensive, variable among panel members, and not always available. Advancements in food science analytical instruments have stimulated researchers to work toward development of methods for the evaluation of sensory qualities of fats and oils. The AOCS Flavor Nomenclature and Standard committee studied the objective methods that could complement subjective organoleptic evaluations of oils and found good correlation between actual sensory scores and predicted results by a GLC procedure. The scientific validity of the correlation coefficients and whether GLC analysis performed by one laboratory would correlate with sensory scores obtained at other laboratories was questioned by some scientists. Further evaluations by 94 panel members from eight different laboratories utilizing the same instrumental GLC analysis produced results equivalent to those for panel members from one specific laboratory.[18] The correlation of oil volatiles with flavor scores of edible oils became an AOCS Recommended Practice, Cg 1a-83, and eventually a standardized method.[1]

3.5.2 Rancidity Analysis

Detection of advanced stages of rancidity in a fat or fatty food has never been a problem for people with normal olfactory senses. The sharp pungent odors mixed with stale and musty odors provide the telltale evidence of rancidity. The major causes of these off-flavors are oxidation and hydrolysis. Factors such as temperature, light, moisture, metals, and oxygen contribute to the formation of off-flavors. Preferences for fats and oils products with fresh and bland flavors and odors require keeping qualities and incipient rancidity evaluations both during development and as processed.

3.5.2.1 Peroxide Value

Oxidation of lipids is a major cause of their deterioration, and hydroperoxides formed by the reaction between oxygen and the unsaturated fatty acids are the primary products of this reaction. Hydroperoxides have no flavor or odor but break down rapidly to form aldehydes, which have a strong, disagreeable flavor and odor. The peroxide concentration, usually expressed as peroxide value, is a measure of oxidation or rancidity in its early stages. Peroxide value (PV) measures the concentration of substances (in terms of milliequivalents of peroxide per 1000 grams of sample) that oxidize potassium iodide to iodine. Iodometric AOCS Method Cd 8-53[19] is highly empirical, and any variation in procedure may cause a variation of results. Therefore, it is necessary to control temperature, sample weight, and the amount, type, and grade of reagents, as well as the time of contact. It has also been observed that the standardized method has difficulties in identifying the titration endpoint for low PV levels and is inadequate for products such as phosphatides that develop emulsions.[19]

Peroxide value is one of the most widely used chemical tests for the determination of fats and oils quality. PV has shown good correlation with organoleptic flavor

scores. For soybean oil, a PV of 1.0 or less indicates freshness; 1 to 5 PV, low oxidation; 5 to 10 PV, moderate oxidation; >10 PV, high oxidation; and >20 PV, poor flavor. These quality estimates are specific for soybean oil, and higher or lower PVs may be acceptable for other oils.[20] Still, a peroxide determination does not provide a full and unqualified evaluation of fats and oils flavor because of the transitory nature of peroxides and their breakdown to nonperoxide materials. Although a linear relationship has been observed between peroxide values and flavor scores during the initial stages of lipid oxidation, this method alone is not an infallible flavor indicator because the peroxide value increases to a maximum and then decreases as storage time increases. Therefore, high peroxide values usually mean poor flavor ratings, but a low peroxide value is not always an indication of a good flavor.

3.5.2.2 Anisidine Value

The anisidine value measures the amount of D and E unsaturated aldehydes present in the oil. The method is based on the fact that in the presence of acetic acid, p-anisidine reacts with the aldehydic compounds in an oil, producing yellowish reaction products. The color intensity depends not only on the amount of aldehydic compounds present but also on their structure. Thus, it has been found that the double bond in the carbon chain conjugated to the carbonyl double bond enhances the molar absorbance at 350 nanometers by a factor of 42 or 51.[21] Anisidine value is a measure of secondary oxidation, or the history of an oil, and therefore is useful in determining the quality of crude oils and the efficiency of processing procedures, but it is not suitable for the detection of fat oxidation. AOCS Method Cd 18-90 has been standardized for anisidine value analysis.[1]

3.5.2.3 Free Fatty Acid and Acid Value

Hydrolytic rancidity occurs as a result of a splitting of the triglyceride molecule at the ester linkage with the formation of free fatty acids (FFAs), which can contribute objectionable odor, flavor, and other characteristics. The flavors resulting from FFA development depend upon the composition of the fat. Release of short-chain fatty acids such as butyric, caproic, and caprylic acid cause particularly disagreeable odors and flavors, whereas the long-chain fatty acids (C-12 and above) produce candlelike or, at alkaline pH, soapy flavors.[21] Both acid value and FFA are measures of the free fatty acid content of fats and oils. Acid value is the amount of potassium hydroxide required for neutralization, whereas FFA utilizes sodium hydroxide for neutralization. FFA results may be expressed in terms of acid value by multiplying the FFA percent by 1.99. FFA is calculated as oleic acid on a percentage basis for most fats and oils sources, although for coconut and palm kernel oils it is usually calculated as lauric acid and for palm oil as palmitic acid. The standard AOCS method for free fatty acid is Ca 5a-40, and for acid value it is Cd 3a-63.[1]

Free fatty acid is an important fat quality indicator during each stage of fats and oils processing. It is a measure of deodorizer efficiency and a process control tool for other processes. High FFA results for deodorized oils indicate a poor deodorizer vacuum, inadequate steam sparging, or leaks if the product color is high with an

oxidized oil flavor. The deodorized oil FFA level that has become standard in the United States is 0.05% maximum, but most internal standards require a 0.03% maximum.

Crude vegetable oils may have abnormally high FFA levels if the seed has been field damaged or improperly stored. Seed and fruit enzyme lipases are activated by moisture, and hydrolysis is initiated, which increases the FFA content. Higher crude oil FFA levels equate to higher refining losses.

Free fatty acid content monitoring during and after all processes, including storage, provides process control results that identify potential problems for which corrective actions can be initiated on a timely basis. FFA is the result of hydrolysis of the fat or oil. Moisture must be present for hydrolysis to develop. This reaction is accelerated with heat and pressure, as are most reactions.

Free fatty acid titrations identify all acidic materials in the oil, which includes the acid added to chelate metals, acids leached from the bleaching earths, antioxidant acidity, emulsifiers added, and other acidic materials. Deodorization, the final process, must reduce the FFA content to a level that will still meet the specification requirements even when the required additives have high acidity levels.

During deep-fat frying, FFA analyses are quality indicators that determine the amount of hydrolysis. FFA development results from the reaction of water and fats at frying temperature. The rate of hydrolysis development is due to the amount of moisture in the foods being fried and the frying temperature.

3.5.2.4 Smoke Point

AOCS Method Cc 9a-48 measures the temperature at which smoking is first detected in a laboratory apparatus protected from drafts and equipped with special lighting.[1] The temperature at which smoking will be observed with actual frying or heating situations will be somewhat higher. Smoke point depends primarily on the FFA content because the fatty acids are more volatile than triglycerides. Also, lower molecular weight fatty acids, as well as mono- and diglycerides, have less resistance to smoking. Initially, deodorized shortenings with monoglyceride contents of 0.4% or less and FFA contents of 0.05% or less should have about the same smoke point in the range of 400 to 450°F (204 to 232°C).

3.5.3 Stability Analysis

Stability of a fat or oil is generally accepted as the storage life of the product until rancidity becomes apparent. Oxidative rancidity is usually the principal concern, although other types of deterioration can occur simultaneously and make the problem more complex. For instance, hydrolytic rancidity is sometimes mistaken for oxidative flavor degradation, which can lead to ineffective preventive measures. In general, the methods for measuring fats and oils stability combine the measurement techniques for initial evaluations with the long-term effects of temperature, light, moisture, oxygen, and other abuses.

Most fats and oils products are tested for flavor stability as a part of quality-control programs to ensure that the consumer specification limits are satisfied. The

purpose of these evaluations is to confirm that the product will have a satisfactory shelf life and will not develop an off-flavor prior to incorporation in a finished product. A number of methods have been developed for evaluating the long-range stability of fats and oils products, the majority of which are based on subjecting the sample to conditions that attempt to accelerate the normal oxidation process; however, a direct correlation between the various evaluations is not possible because oxidation of a fats and oils product is a complex mechanism. For each product, the test protocol must be selected that most adequately simulates the end-use performance.

3.5.3.1 Active Oxygen Method Stability

The active oxygen method (AOM) is the most commonly used method for estimating the oxidative stability of fats and oils products. This method has been used for routine quality control and as a research and development tool for new products. AOM employs heat and aeration to accelerate deterioration of the fat and oil sample and shorten the time required to reach the endpoint. AOCS Method Cd 12-57 (AOM for Fat Stability) is performed by placing a 20-milliliter sample in a special aeration tube and then heating it in an oil bath or a heat block controlled at 97.8 ± 0.2°C (208 ± 0.4°F) with an air flow adjusted to 2.33 milliliters per tube per second. The sample is exposed to the elevated temperature and aeration until a predetermined peroxide value is attained, usually 20 PV for meat fats and 70 or 100 PV for vegetable oil products.

The AOM stability analysis has several major disadvantages. First, the procedure involved is highly empirical, requiring close attention to detail if reproducible results are expected. The maximum expected variation in results between laboratories is ±25% for a 100-hour AOM sample. Second, the AOM evaluation is faster than normal aging methods; however, a 100-hour AOM sample will still require 4.2 days to reach the expected endpoint.

3.5.3.2 Accelerated AOM Stability

Active oxygen method stability evaluations began to require greater elapsed time to reach the endpoint after development of product changes that improved the resistance of fats and oils products to oxidation. A comprehensive study of temperature effects indicated that satisfactory correlation with existing AOM data could be obtained by increasing the heating temperature to 110°C with a time savings of 60%. The ratio of time required for the standard AOM to the accelerated procedure is 2.5 to 1.[22]

3.5.3.3 Oxygen Bomb

The petroleum industry has used an oxygen bomb method for many years as a means of determining the resistance of gasoline to oxidation or gum formation. This method has been adapted for use in evaluating oxidative stability of edible fats and oils and fat-containing foods. The material to be tested is placed in a glass container that is inserted into a stainless steel bomb. The bomb is sealed and pressurized with oxygen. The entire bomb is immersed in a bath of boiling water. A pressure recorder

is used to plot a continuous curve of oxygen pressure vs. time. The length of time (in minutes) between the point at which the pressure reaches an initial plateau at the temperature of the bath until a sharp drop occurs in the pressure is taken as a measure of the oxidative stability of the sample. Because it was found that fats and oils do not have a defined pressure drop, an arbitrary endpoint based on comparative pressure drops is generally used.

This method offers several advantages over the standard AOM stability analysis in that it (1) is 1.5 times faster because the increased pressure of the reactive gas speeds up the reaction, (2) is more reproducible, (3) can be used to evaluate fats and oils as well as fatty foods, and (4) requires less technician time and attention to perform. A disadvantage for the bomb stability is that only one sample can be tested at a time, which could more than offset the time savings gained by the reduced elapsed time required.[23]

3.5.3.4 Oil Stability Index

Because of the increased use of two conductivity instruments (Rancimat and the Oxidative Stability Instrument) as AOM stability alternatives, AOCS initiated a collaborative study to investigate these conductimetric methods as official alternatives. As a result of the study, AOCS Method Cd 12b-92 (Oil Stability Index, or OSI) became an official method in 1996.[24] These instruments measure the increase in deionized water conductivity resulting from trapped volatile oxidation products produced when the oil product is heated under a stream of air. The conductivity increase is related to the oxidative stability of the oil product. The evaluation procedure is performed by placing 2 grams of the oil sample into a sample tube that has been preheated to 120°C (248°F), connected on one side to the air source and on the other side to a 50-milliliter cell of deionized water. The conductance of the water is measured automatically over time via a strip chart recorder or data acquisition software. Normally, the oxidation curve indicates the induction period followed by a rapid rising response as the oxidation rate is accelerated.[25] The endpoint for the regular AOM stability is specified as the time in hours required for the sample to reach a peroxide value of 100 milliequivalents per kilogram. The endpoint of this conductivity procedure is the time required for a sudden increase in formic acid production to occur at the end of the induction period.[26] Good correlation has been found to exist between the Rancimat instrument and AOM and the OSI instrument and AOM at various temperatures.

The conductimetric oxidative stability method can be used in applications traditionally utilizing AOM stability (refer to AOCS Method Cd 12-57, Trading Regulations for Finished Fats and Oils Products or Quality Control During Processing). This method automatically delivers rapid oxidation stability data that require less technician time and attention. Additionally, this AOM alternative provides a more precise and reproducible method. The conductivity AOM alternative has not solved the unreliability problem for evaluating natural antioxidants. High-temperature oxidative stability tests, including AOM stability, conductimetric methods, oxygen bomb, and oxygen uptake, are unreliable due to the lipid oxidation mechanism at elevated temperatures. Oxidation stability evaluations based on oils oxidized at 100°C have

peroxide values in excess of 50 milliequivalents per kilogram, while soybean oil flavor is unacceptable at a PV of less than 10 milliequivalents per kilogram[24].

3.5.3.5 Schaal Oven Test

The Schaal oven test was developed by the biscuit and cracker industry to provide an age stability evaluation for shortenings. Because it is performed at temperatures only moderately warmer than those found in ordinary storage conditions, it provides an index of stability that more nearly represents a product under normal use conditions. The Schaal oven test is normally performed in a forced-draft oven at 63°C (145°F). The test sample is stored in beakers covered with a watch glass or in glass jars with loose-fitting caps. The product stability is measured as the number of days before rancidity is detected. The peroxide value can be used as an indicator of rancidity but should supplement only organoleptic evaluations. A distinctive feature of the Schaal oven tests of both fats and oils, plus fatty foods, is that flavors and odors other than oxidative rancidity can be revealed because it does not rely on very high temperatures to accelerate degradation. Also, a minimum of laboratory equipment is required to perform the evaluation.

The relationship between product shelf life, Schaal oven, and AOM stability results varies with each fats and oils product and the processing it has received. It has been suggested that 1 AOM hour or 1 Schaal oven day is equivalent to 15 days of shelf life; however, no overall correlation can be applied in all situations. None of the stability evaluations can be used as an index of shelf stability except when it is applied to a given type of fat and oil formulation for which a specific relationship has been established[27].

3.5.3.6 Pastry Flavor Test

The effects of unsaturation, prooxidants, antioxidants, oxygen, light, moisture, and temperature on lipid products can be measured with the foregoing analytical methods established for fats and oils products. However, the oxidation and hydrolysis resistance factors can change when the fats and oils products are incorporated into a food product and processed. Shortening and margarine products are major ingredients of bakery products. In this application, the fats and oils products must withstand baking temperatures without flavor degradation while in contact with moisture and other ingredients. The pastry flavor test evaluates a shortening or margarine product in a high-fat baked product also containing flour, moisture, and salt for an extended period at baking temperatures. Sensory flavor and odor evaluations of the baked product will identify oxidation, hydrolysis, or other organoleptic problems or changes. This evaluation, outlined in the nonstandardized methods section, can be utilized for product development and to audit the products produced.

3.6 COLOR AND APPEARANCE

Color and appearance of fats and oils are not monitored solely for aesthetic qualities, although this is an important parameter. Color and appearance are important for many reasons, but ultimately the factors of color and appearance relate to the cost of processing, the quality of the finished product, and what the products look like to the end user. Most oils are yellowish-red or amber liquids. The color is due to the presence of carotenoid pigments or chlorophyll pigments, the latter imparting a greenish cast to the oil. Some crude oils can have unexpectedly high pigmentation caused by field damage, improper storage, or faulty handling during crushing, extraction, or rendering. Color measurement will determine the condition of the product as received to identify the necessary blending, processing, and handling procedures; to support claims against vendors; and to prevent contamination of prime-quality oils with problem products. During processing, product appearance may be an indicator of a problem. Improper bleaching, oxidation, ineffective filtration, and other problems can be indicated by color darkening or lack of color change.

Changes in the appearance of fats and oils in finished products are perceived as indicating poor-quality product, regardless of the reason or effect upon performance. Consumers may not consciously notice the color of a bottled oil unless it appears different from other products on the shelf. Marketing has successfully promoted lighter or whiter oil as being better for most salad oils and shortenings. Food processors usually have ingredient specifications that identify the allowable color parameters because the fats and oils product may have the ability to enhance or diminish the appearance of the prepared food product. Product colors of fats and oils must be monitored as they are received to maintain both real and perceived product quality.

Wesson Color Method

AOCS Method Cc13b-45 determines the color of a melted fat or oil product by comparison with red and yellow Lovibond glasses of known characteristics. The oil sample is placed in an optical glass tube with a path length of either 1.0 or 5.25 inches and then viewed by the operator to begin the color match. This is done by superimposing a mixture of red and yellow standards over the reference field, which is adjacent to the oil sample. The 5.25-inch tube is utilized for most samples except for dark oils, which exceed a 40.0 red at this level. It is standard practice to indicate when the 1.0-inch level has been utilized, but the 5.25-inch level is understood.

The Wesson method using Lovibond glasses is an abbreviated version of a method originally developed in England for measuring the color of beer. Color has three attributes, but the Wesson method ignores the brightness factor and is interested only in the degree of redness. Yellow is necessary to make colors look similar to allow assessment of redness, but the amount of yellow is considered unimportant for this method; therefore, the use of a fixed yellow value was adopted with only the red being viewed as critical. The fixed yellow ratio is 10.0 yellow to 1.0 red for most oils with red color readings under 3.5; higher yellow settings are specified for the darker oils.

The Wesson method is the principal color method for the U.S. edible-oil industry and has been utilized for many years primarily because of its simplicity; however,

some difficulties arise as a result of such oversimplification: (1) apparent red values are reduced when chlorophyll is present in the oil, (2) brown pigments interfere with red and yellow comparisons, and (3) visual comparisons must be made. Visual color measurement is less acceptable because the operator must be adept at matching colors and also must have good color vision.[28]

Lovibond (British Standard)

AOCS Method Cc 13e-92 utilizes a Lovibond Tintometer which has become the standard in most countries other than the United States. The geometry and color scales for the Wesson and Lovibond methods are different; consequently, the results are not compatible. The vital parts of the Lovibond Tintometer are the series of red, yellow, and blue permanently colored glass standards. These standards vary from water-white colors to deep reds, yellows, and blues. Each standard color is numbered and subtly different from the one preceding and following it. The addition of the blue color field provides a greater degree of brightness and greenness than for the Wesson method.[29]

Spectrophotometric Color Method for Oils

This method represents an attempt to measure the color of fats and oils with an automatic instrument to eliminate the visual judgment requirement for operators. In 1950, AOCS Method Cc 13c-50 was tentatively adopted for the spectrophotometric determination of oil color to replace the manual Lovibond systems. A collaborative study that included 30,000 color measurements determined the best wavelengths to use to measure the color of oil. These wavelengths were then used to develop an equation to relate the spectrophotometer readings to Lovibond values. The calculations were designed to give values identical to Lovibond color values using the Wesson method.[30] In general, the calculated values agree, but wide discrepancies occur with some oils. The photometric color method has not replaced the Wesson method because of occasional disagreement, economics, and firm entrenchment of the visual procedure. Nevertheless, AOCS Cc 13c-50 (Spectrophotometric Color Method for Oils) is an official method.[1]

Automatic Tintometers

Electronic color instruments with three filters have been introduced by several equipment manufacturers to replace the manual color procedures. The automatic instruments have been designed to conform to AOCS Method Cc 13b-45, as well as the European procedure, or AOCS Method Cc 13e-45. These instruments have performed well with light-colored oils but have had poor agreement with darker oils or products containing certain additives such as emulsifiers.

Fatty Acid Committee (FAC) Color Method

Inedible tallow and grease colors are often too dark or too green to read on the Lovibond tintometer, even with the 1.0-inch column. An arbitrary system of color

standards was developed for identification of the dark colors. AOCS Method Cc 13a-43 employs standard color tubes for comparison of oils in a similar tube. The FAC standards consist of 26 permanent color tubes numbered from 1 to 45 in odd numbers, with three overlapping series: one normal, one green, and one red. The spacing of the tubes is not uniform on purpose. This method, far from precise, has been used mainly for inedible oils because of its ease of application.

Gardner Color

The Gardner scale is a single number scale used mainly to categorize lecithin, paint or drying oils, fatty acids, and some other oil derivatives. These standards are patterned along the same lines as the FAC standard but bear no direct relationship. The Gardner standards consist of glass standards numbered from 1 to 18, lightest to darkest. Gardner color has been standardized with AOCS Method Td 1a-64.

Chlorophyll

The presence of green pigments or chlorophyll is of interest not only because of their impact on the color of the finished product but also because chlorophyll can act as a sensitizer for fats and oils oxidation. These pigments must be removed in the prebleaching process. AOCS Method Cc 13d-55 is used to determine the chlorophyll content (parts per million) of vegetable oils by spectrophotometric absorption measurements at 630, 670, and 710 nm. The method is not applicable to hydrogenated and deodorized oils because the 670-nm absorption is missing in most processed oils.

Coloring Agents Determination

Yellow colors are often added to fats and oils products to simulate the appearance of butter. Carotenes, annattos, and apocarotenals are the primary colorants utilized. Yellow additives are extremely difficult, if not impossible, to control with the two-dimensional Lovibond color measurements. Spectrophotometric measurements of yellow density at wave lengths of 440, 455, or 460 millimicrons, depending upon the product, provide better control for these additives.

3.6.1 Appearance

The first and most obvious product characteristic evaluated by any consumer of a finished fats and oils product has to be its appearance. Appearance is an important attribute because the initial impression usually influences subsequent judgments, even though most of the appearance properties have only an aesthetics value. These characteristics usually have little effect upon performance; however, abnormal appearance characteristics can indicate a handling or storage problem, poor processing techniques, and stability or other quality problems.

3.6.1.1 Product Appearance Ratings

Visual examinations are the best way to get a meaningful evaluation of product appearance as a whole. Appearance ratings use subjective opinions based on experience to assign numerical values for comparison purposes. Product appearance evaluations of solidified products include surface and internal appearance characteristics. The uniformity of color, hue, and textural qualities of a product are rated both for the surface of the product and internally after scratching, cutting, or scraping. The textural ratings evaluate each product for deficiencies such as mottles, streaks, oil separation, and other problems that can be related to specific processing or formulation problems. The apparent color cast and sheen ratings can be related to bleaching deficiencies, color additions, or plasticization problems. Procedures for appearance evaluations and ratings are detailed in the nonstandardized method section. Appearance evaluations are useful measurement tools for product development as well as process quality control.

3.7 REFINING AND BLEACHING

Specific refining and bleaching analyses are necessary for crude oil receipts for three distinct purposes: (1) as a basis for settlement of crude contracts under the trading rules of the various oil trading associations, (2) as a yardstick for the efficiency of the refining and bleaching operations, and (3) as indicators for caustic and bleaching earths types and levels for processing. Most crude vegetable oils are traded on the basis of refining loss out of the oil, refined or bleached color, and flavor. Trading rules for vegetable oils have been established in the United States by three associations: National Cottonseed Producers Association, National Soybean Processors Association, and National Institute of Oilseed Products. All three of these organizations accept the AOCS methods as the basis for trading. For most oils, settlement is based on agreement between the buyer and seller of the results of specified analytical methods within an established variance performed on the same sample. Results beyond the established differences are settled by an Official Referee Chemist's analysis.

3.7.1 Refining Loss

About 75 years ago, cottonseed crushers and oil producers agreed to a series of specifications for crude cottonseed oil. Agreement for price concessions for products less than prime were determined for refining loss, odor, taste, and color. The refining loss penalty assessed was 0.75% for each percent in excess of 9.0% loss. This agreement led to the development of the "cup loss" method for refining a sample of crude oil in the laboratory in a manner that would simulate plant operations to the extent of providing approximate refining losses and refined color assessments. Initially, this method was very subjective, allowing laboratory technicians to rely on their best judgment as to how to perform the evaluation for the best loss result. In 1927, it was agreed that a premium would be paid by the buyer for crude cottonseed

oils with a loss below 9.0%. This agreement offered the crude mills an incentive to produce better grades of oil but at the same time made loss results suspect because the method relied upon the judgment and expertise of laboratory technicians. Standardization of the laboratory cup refining procedure made the results less variable, and the technicians performing the analysis no longer had to be refining experts.[33]

AOCS Method Ca 9a-52 determines the loss of free fatty acids, oil, and impurities when the sample is treated with alkali solutions under the specific conditions of the test.[1] The actual method simulates kettle refining on a laboratory basis with standardized levels and strengths of sodium hydroxide solution, temperatures, and holding periods to promote reproducible results within and between laboratories. The refining loss is calculated by subtracting the refined oil sample weight from the original crude oil sample weight.

3.7.2 Neutral Oil and Loss

The laboratory cup refining test was acceptable when open-kettle refining was common practice but improvements in refining processes provided losses lower than the laboratory estimates. Various methods for estimating the neutral-oil content in a crude oil were explored. These procedures identified the theoretical recoverable oil in the crude oil sample for comparison to actual results to determine refining efficiency. Of the methods and techniques evaluated, an International Chemical Union chromatographic procedure appeared most appropriate because it was found to be reasonably accurate, the most reproducible, easy, and quick to carry out, and it required no special elaborate or expensive equipment.[33] This procedure was the basis for AOCS Method Ca 9f-57 (Neutral Oil and Loss). The neutral oil and loss method extracts the oil or fatty materials on a column of activated alumina by ether-methanol. The mixture extracted consists primarily of triglycerides and unsaponifiable material. Reproducibility has been found to be good; that is, two single determinations performed within a laboratory should not differ by more than 0.15% and not more than 0.30% between laboratories.[1]

3.7.3 Bleaching Analysis

Adsorption bleaching is used both in the plant and in the laboratory. The laboratory technique involves the addition of bleaching earth or carbon, or both, to refined oil, heating it to 120°C, and holding it at that temperature for 5 ± 1 minutes while agitating at 250 ± 10 rpm. Afterward, the earth is removed by filtration and the oil color is determined. Bleaching analyses are performed with oils from the cup-loss evaluation or laboratory-refined samples for the bleach evaluations. Two AOCS methods are available for bleaching fats and oils; both utilize the same procedure, but the specified amount of CAS natural bleaching earth is different and one has a provision for the use of activated bleaching earth for high-green soybean and sunflower oil. AOCS Method Cc 8a-52 is applicable to refined cottonseed oils, and AOCS Method Cc 8b-52 is applicable for soybean and sunflower oils.[1]

3.8 PERFORMANCE TESTING

Some essential attributes contributed by fats and oils cannot be directly measured with chemical or physical analytical methods. In these cases, performance testing is the only means for evaluating the ability of the fats or oils product to perform the desired functions in a food product. Actual determinations of the performance qualities of edible fats and oils products are made with small-scale practical tests that evaluate how the product will perform in a finished product. Successful performance tests are designed with standardized conditions and ingredients, with critical formulations being chosen in regard to the property evaluated to highlight small differences in performance.

Performance testing is essential for the development of new products, especially for fats and oils products designed for a specific food product, formulation, or process. After development, physical or chemical analysis can be related to performance results in most situations; however, continuation of certain performance evaluations is necessary for some products to ensure adequate performance or more timely results in some cases. Initially, most performance testing was designed for bakery products but has now been expanded to every specialty product situation — baking, frying, candy, coatings, formulated foods, nondairy products, and so forth — wherever tailored shortenings, margarines, oils, and other specialty products are utilized. In many cases, the performance tests are developed to evaluate the fat or oil ingredient as it would be used by a specific food processor.

Fats and oils performance testing is performed by most processors, but the procedures utilized have never been standardized for the industry. Performance testing is an analytical technique similar to other laboratory evaluations. The procedures must be designed to incorporate good laboratory techniques, which include standardization of equipment, ingredients, procedures, results reporting, and control of the environment. Performance results must be reproducible to be of value for comparative purposes. Reproducibility is achieved by controlling variables that can be controlled only by the use of standardized methods. The performance test procedures must be written with adequate detail and followed closely. A review of some of the most common performance evaluations follows, and complete performance testing procedures are presented in the nonstandardized methods section of this chapter.

3.8.1 Creaming Volume

Cake batter aeration can be affected by plasticity, consistency, emulsification, basestock formulation, and other fats and oils properties. Creaming-volume evaluations measure the ability of shortening or margarine to incorporate and retain air in a cake batter. In most cases, batter aeration is an indicator of the baked cake volume, grain, and texture and materially affects the handling qualities of the cake batter.

The creaming volume test formula consists of only three ingredients: (1) test shortening or margarine, (2) granulated sugar, and (3) whole eggs. This procedure is the first stage of an old-fashioned pound cake where the cake batter aeration depends upon the creaming properties of the shortening with whole eggs. The

specific gravity of a batter is determined after mixing for 15 minutes and again after 20 minutes. Continued aeration, identified by a decrease in batter-specific gravity, indicates that the fats or oils products has a stable consistency that has not broken down to allow the release of air from the batter. Specific gravity (grams per cubic centimeter) can be converted to specific volume (cubic centimeters per 100 grams) by multiplying the reciprocal of the specific gravity by 100. Specific volume better illustrates the amount or degree of aeration. This performance test is applicable to emulsified, as well as nonemulsified, products to measure aeration potential in a cake batter.

3.8.2 Pound Cake Test

In some cases, shortening or margarine creaming value is most accurately measured by preparing a regular pound cake, omitting the chemical leavener, and measuring the volume, grain, and texture of the baked cake. Creaming value, as determined by this method, is affected by the batter-mixing temperature. Working range, or creaming range, can be measured by adjusting the finished batter temperature over the desired temperature range. Results obtained in this manner provide a good indication of the creaming range or shortening temperature tolerance. The baked pound cake volume is determined by a seed displacement procedure, and the cake appearance is rated numerically on a scale similar to that provided below:

Score Rating	Category	Description
10	Perfect	Fine, regular grain; no holes, cracks, or tunnels; very thin cell walls; and perfect symmetry
9	Very Good	Close, regular grain; free of holes, cracks, or tunnels; thin cell walls
8	Good	Grain very slightly open but regular; free of cracks or tunnels; may have occasional hole; good cell wall thickness
7	Satisfactory	Grain slightly open, mostly regular; a few small holes; no tunnels or cracks; slightly thick cell walls
6	Poor	Open or irregular grain or frequent holes; some cracks or tunnels
5	Unsatisfactory	Very open or irregular grain or numerous holes, cracks, or tunnels; thick, heavy cell walls; may have solid streaks or gum line
4 and below	—	Increasing degrees of unsatisfactory performance

3.8.3 Icing Volume

Shortening and margarine formulation, consistency, and plasticity can affect the ability of a product to produce light creme icings. This property can be measured by making a standardized creme icing under controlled conditions. The evaluation procedure is somewhat similar to the cream-volume evaluation, where the aeration potential and mixing tolerance of fats and oils products are measured with specific gravity determinations. However, the results indicate the ability of a product to aerate and retain the incorporated air in a low-moisture icing. The icing ingredients are (1) test shortening, (2) powdered sugar, (3) nonfat milk solids, (4) salt, and (5) slightly less than 12% water, which are mixed for 12 minutes at high speed, stopping after 7 and 12 minutes to measure the specific gravity of the icing. These measurements determine the aeration potential and the mixing tolerance of the fats and oils product. A fats and oils product with poor mixing tolerance will either aerate very little or will give up a portion of the incorporated air after the first specific gravity determination. This evaluation is applicable to emulsified and nonemulsified fats and oils products to measure the aeration potential in a creme icing.

3.8.4 White Layer Cakes

Fats and oils perform several important functions in all cake products. These functions include entrapment of air during the creaming process, lubrication of the gluten and starch particles to break up the continuity of the gluten/starch structure of the cell walls for a tender crumb, and emulsification or water-holding capabilities that affect moistness and cake-keeping qualities. The emulsification value of a fats and oils product may be defined as its ability to make a white layer cake in which the flour content is low but the sugar and shortening contents are high. The best method for determining emulsion value of a shortening or margarine is to test the product in a high-sugar, white layer cake under standard conditions, evaluating the finished cake for volume, crust characteristics, grain, and texture. Previous results have shown that shortenings with poor emulsification properties produce curdled or separated batters and cakes with low volumes, pasty crusts, and a raw flour taste. Properly

emulsified products will produce smooth cake batters and cakes with golden brown crusts, somewhat dry to the touch without a liquid ring, with a fine grain and texture, and with good eating characteristics[33]. Over-emulsified shortenings produce cakes that dip or have a weak center with a very open grain and a coarse texture.

Three white layer cake performance tests are utilized for the evaluation of general-purpose shortenings and margarines: (1) 140% sugar white cake, (2) 105% sugar white cake, and (3) household white layer cake. The cake performance tests are designed for the fat and oil type product to be evaluated:

- Emulsified product — The high-sugar, egg-white, and liquid cake measures the ability of an emulsified shortening or margarine to produce a high-volume, moist cake with a fine grain and texture.
- Nonemulsified product — A lower sugar, moisture, and egg cake formulation is used for the evaluation of the emulsification properties contributed solely by the product consistency of the all-purpose shortening or margarine product.
- Household shortening — Shortenings produced for household use usually have a low emulsifier content designed to improve baking performance but not enough to drastically affect frying performance; therefore, household baking recipes are designed for this level of emulsifier.

3.8.5 Creme Filling Test

The ability of a shortening or margarine to take up and hold water while aerating to a low-filling specific gravity is an important attribute for creme fillings for snack cakes. Equally important is the resistance of the filling to weep or disappear into the base cake. Shortening plasticity, heat resistance, and emulsification can be measured by creme-filling performance testing. Initially, the ability of the shortening product to aerate the filling is measured during preparation, and subsequently the weep and heat stability of the fillings are evaluated. The evaluation measures the emulsifier system as well as the consistency of the shortening as provided by the basestock formulation.

3.8.6 Cake Mix Evaluation

Originally, cake mix formulations were very similar to bakery cakes and utilized standard high-ratio cake shortenings; however, development of improved cake mixes required rapid aerating shortenings to minimize mixing times for the housewife, while at the same time increasing the products mixing and baking tolerances. The competitive nature of the cake mix industry has continued to generate demands for new and improved products of which shortening has always been a major contributor. A basic white cake mix formulation and makeup procedure can serve to evaluate new or revised emulsifier systems for aeration, eating qualities, and cake shelf life as well as the shortening carrier for lubrication and consistency.

3.8.7 Puff Pastry Testing

The characteristic features of a puff pastry shortening are plasticity and firmness. Plasticity is necessary to produce smooth, unbroken layers of fat between dough layers during repeated folding and rolling operations performed at retarder temperatures

to achieve over 1200 layers. Firmness is equally important, because soft or oily fat products can be absorbed by the dough, thus eliminating its role as a barrier between the dough layers. The laminated puff-pastry dough rises in the oven when the fat layers melt and expand, creating steam if the fat contains moisture, which causes the layers to separate and the product to expand and rise without the benefit of a leavening agent. Satisfactory performance is a five- to sixfold increase in the height of a test patty shell after baking.

3.8.8 Restaurant Deep-Fat Frying Evaluation

A number of factors are studied when evaluating frying shortenings and oils. During deep-fat frying, the fat is exposed continuously to elevated temperatures in the presence of air and moisture. A number of chemical reactions, including oxidation and hydrolysis, occur during this time, as well as changes due to thermal decomposition. As these reactions proceed, the functional, sensory, and nutritional quality of the frying fat changes and eventually reaches a point where it is no longer possible to prepare quality fried products, and the fat will have to be discarded. The rate of frying-fat deterioration varies with the food fried, the frying fat utilized, the fryer design, and the operating conditions.

Good testing procedure limits the variables to the product being evaluated. The method should be designed to incorporate techniques that are practiced in any good laboratory, including the standardization of equipment, control of the environment, and an explicit evaluation procedure. Frying tests have been attempted in commercial restaurant frying operations; however, cause and effect determinations for the results obtained are difficult to assess due to the changing product mix, handling conditions, and other unknown conditions and contaminants. A laboratory test procedure employing the smallest available commercial fryers to continuously heat the frying shortening and frying of French-cut potatoes at prescribed intervals has been found to adequately evaluate frying fats. This procedure allows the frying-fat deterioration to be monitored visually, organoleptically, and with chemical and physical analytical testing for assessment of the cause and effect.

The deep-fat frying evaluation consists of controlled heating of the test shortening or oils at 360 ± 10°F (182.2 ± 5.6°C) continuously until the test is terminated. Fresh French-cut potatoes (227 grams) fried eight times daily for 7 minutes at 3-hour intervals are flavored once daily. Frying observations recorded after each frying include smoking, odor, clarity, gum formation, and a determination of foam development. Foam development (described as none, trace, slight, definite, and persistent) should also be measured with a foam test daily and each time a change in the observed foam is recorded. Samples are taken after each 24-hour period for analysis of color, free fatty acid, and iodine value for quantitative measurement of darkening, hydrolysis, and polymerization. The frying test is terminated when persistent foam has been observed and substantiated by foam height testing.

3.8.9 Ice Cream Bar Coating Evaluation

Ice cream novelties are usually enrobed with a confectionery coating that utilizes a relatively high fat content. The function of the fats utilized are viscosity control,

crystallization, gloss retention, and eating characteristics. These characteristics must be measured to identify the acceptability of the coating fat by actually dipping ice cream bars into prepared coatings. The qualities measured to determine acceptability are drying time, hardening time, brittleness or snap, bar coverage, flavor, eating characteristics, and gloss retention.

3.9 NONSTANDARDIZED METHODS

A number of nonstandardized methods have been reviewed for the evaluation of fats and oils in this chapter. Complete test methods for these evaluations are presented on the following pages. All these evaluations have been successfully employed for product development, quality control, or auditing of current production products and those of the competition. The methods presented are:

Method	Description
3.1	Shortening consistency and plasticity rating
5.3	Pastry flavor test
6.2	Shortening appearance rating
6.3	Margarine appearance rating
8.1	Creaming volume test
8.2	Pound cake test
8.3	Icing volume
8.4	140% sugar white cake
8.5	105% sugar white cake
8.6	Household white layer cake test
8.7	Creme filling test
8.8	White, dry cake mix test
8.9	Puff pastry testing
8.10	Deep-fat frying test
8.11	Ice cream bar coating test
8.12	Sandwich cookie filler shortening evaluation

Nonstandardized Method 3.1

Shortening Consistency and Plasticity Rating

- Description: A systematic, uniform means of rating the consistency and plasticity of crystallized fats and oils products
- Scope: Applicable to all shortenings, margarines, and other plasticized fats and oils products
- Equipment:
  Constant 80°F-temperature storage room
  Illumination of 50 to 100 foot-candles at the examination surface from cool white fluorescent lamps
  Thermometer with 0 to 120°F range and 1°F gradations
- Procedure:
  1. Temper the samples to achieve the required 75 to 80°F examination temperature.
  2. Determine and record the sample temperature.
  3. Examine the consistency and plasticity of the sample by pressing a finger into the product or squeezing it in the hand, or both. This procedure identifies imperfections in the sample.
  4. Some of the most common consistency problems found with plasticized products include:
     Puffy, a soft product with large air cells or pockets that offer very little resistance when pressed or squeezed
     Sandy, small lumps about the size of grains of sand felt throughout the sample
     Ribby, alternating thin layers of hard and soft product which has been described as feeling like a coarse corduroy cloth surface
     Brittle, a firm resistance that cracks as a finger is pressed through the product
     Mushy, soft and greasy feeling with very little, if any, resistance
     Lumpy, sizable firm clumps within a softer or plastic consistency
     Chalky, a dry putty-like feeling
  5. Plasticity ratings evaluate the workability of a crystallized product. A product with perfect plasticity would retain a good body feel without releasing liquid or remaining rigid when worked in the hand. A plastic material will not flow or deform from its own weight but should be easily molded with only slight pressure.
  6. Consistency and plasticity should each be rated overall using the following 10-point scale:

     10 – Perfect
     9 – Nearly perfect
     8 – Good or satisfactory
     7 – Slightly unsatisfactory
     6 – Moderately unsatisfactory
     5 – Definitely unsatisfactory
     4 – Bad
     3 – Definitely bad
     2 – Very bad
     1 – Terrible

     Note: All products should be rated objectively without reference to the type of product, its age, or other qualifying factors.

Nonstandardized Method 5.3

Pastry Flavor Test

- Description: Subjects the test fat or oil product to prolonged high-temperature heat in the presence of moisture, salt, and flour for oxidative stability measurement by sensory flavor and odor evaluations
- Scope: Applicable to all fats and oils products (i.e., shortening, margarine, flakes, chips, liquid shortenings, and oils)
- Equipment:
  Mixing bowl
  Pastry cutter
  Pastry cloth
  Dusting flour
  Rolling pin

Table 4.8 Mono- and Diglyceride Functionality

Emulsifier Form	Functionality	Food Products
Hard (5 IV maximum)	Moisture retention	All baked products
	Crumb softener	All baked products
	Anti-staling	All baked products
	Volume improver	All baked products
	Tenderness Improver	All baked products
	Grain and texture improver	Cakes
	Batter aeration	Cakes
	Palatability improver	Bread and rolls
	Stickiness retardant	Chewing gum and candy
	Anti-sticking	Pasta
	Oil stabilization	Peanut butter
	Rehydration	Dehydrated potatoes
	Tight emulsion	Margarine
	Freeze/thaw stability	Frozen desserts
	Dispersant	Coffee whiteners
Plastic-like (70 ± 10 IV)	Compromise of hard and soft forms	All products
Soft (90 IV)	Aeration	Icings and fillings
	Water absorption	Icings and fillings
	Texture improvement	Gravies and sauces
	Loose emulsion	Margarine
	Fat dispersant	Pet foods
	Fat dispersant	Cake donuts

Several mono- and diglyceride deviations are produced by using them as raw materials in the production of esters of fatty, water-soluble compounds such as lactic acid, citric acid, acetic acid, diacetyl tartic acid anhydride, and succinic anhydride:[38-42]

- Diacetyl tartaric acid esters of monoglyceride (DATEM) are hydrophilic emulsifying agents with excellent dough-conditioning properties. By strengthening the gluten in the dough, DATEM enhances gas retention, resulting in increased volume in baked products, better dough tolerance to mechanical handling, and improved proofing stability. Gluten strengthening also improves crumb structure and crust characteristics. Even though DATEM is primarily utilized as a dough strengthener, it also has application in extruded products, icings, and margarines.
- Lactic acid esters of monoglycerides, or lactated esters, are a group of food emulsifiers used primarily in applications where aeration is required, such as in toppings, cakes, and icings. The lactated esters have more surface activity and are slightly more hydrophilic than regular mono- and diglycerides. Most lactated esters are processed from saturated or low-iodine-value mono- and diglycerides to give optimum aerating properties.
- Citric acid esters of monoglycerides or monoglyceride citrate are hydrophilic emulsifiers prepared for use as a margarine antispattering agent, for metal chelating, and for use with other surfactants as an emulsion stabilizing agent.
- Acetylated monoglycerides are blending emulsifiers that can be used to promote aeration, volume, foam texture, and stability against syneresis for imitation creams and toppings. Also, acetylated monoglycerides form protective films that are effective against oxidation and moisture loss to keep pie crusts and pizza shells crisp and

fresh. Additionally, the liquid acetylated monoglycerides are effective lubricants and release agents for use in dough grease or bakery product depanning agents.
- Succinylated monoglycerides perform as dough conditioners and strengtheners that are tolerant to mechanical handling and flour variability for uniform good volume, texture, flavor, and crumb softness.

4.8.2 Propylene Glycol Esters

Propylene glycol mono fatty-acid esters are a group of moderately surface active compounds which are effective emulsifiers for cakes and nondairy whipped products such as imitation creams, whipped toppings, and spray dried topping products. The D-tending, propylene glycol monoester (PGME) surfactants are added not for emulsion stability but rather to influence the whipping rate, stiffness, volume, and foam stability. These emulsifiers are able to promote an agglomeration of fat globules for the formation of a good and stable foam while forming a protective crystalline membrane on the liquid droplets that results in a high degree of aeration.

Cake batters aerate rapidly with PGME and produce baked cakes with high volume but fleecy, elongated, even cell structures. Initially, cakes utilizing propylene glycol monostearate (PGMS) had to be low-fat formulations with high PGMS levels, but then it was determined that a combination of PGMS and mono- and diglycerides was more functional for cake baking. The most effective PGME emulsifiers for cakes are produced with a low-iodine-value fat base. For consumer cake mixes, PGME shortenings provide the needed tolerance to mixing conditions at PGME levels of 8.0 to 16.0%, with total monoglyceride levels of 2.0 to 6.0%. Bakery cakes require less functionality from the emulsifier system because the aeration is achieved by more efficient mixing procedures and equipment. These shortenings typically range from 2.8 to 8.5% PGME with 4.0 to 5.5% total monoglyceride.

Whippable emulsions normally contain proteins that provide a great deal of the stability needed by these products in a liquid form. In these emulsions, propylene glycol monoesters function to provide volume, foam texture, and stability against syneresis. Structure building consists of aggregated fat globules forming a network within the foam. The hard form of the 90% monoesters is typically used at 0.2 to 1.5% levels for these products.

Saturated-fat-based emulsifiers function more as defoamers than aerators in low-moisture prepared foods such as icings and fillings; however, the softer based PGME emulsifiers can function in these products. An intermediate-hardness PGME surfactant made with a 50-IV hydrogenated lard and a 70-IV hydrogenated soybean oil base added to an all-purpose shortening base to obtain 2.5 to 3.5% PGME and 4.0 to 5.0% total monoglyceride emulsifier will perform in icings, fillings, and low- as well as high-sugar bakery cakes. The intermediate-hardness PGME emulsifier has also been utilized for lean cakes, cookies, and other fat-reduced foods.

4.8.3 Sorbitan Esters

Sorbitan fatty-acid esters are sorbitol-derived analogs of mono- and diglycerides that are slightly more water soluble. Sorbitan monostearate, the most common of

these surfactants, is a hard solid or bead material that requires dispersion in water or fat before use. Sorbitan fatty-acid esters are lipophilic emulsifiers that can be used in emulsions where less water-binding properties and enhanced aeration properties are desired. Sorbitan monostearate can be used for icing, whipped topping, and coffee whitener applications for aeration, gloss, and stability characteristics; however, the best known application is probably as a crystal modifier or promoter for confectionery coatings. Sorbitan esters are especially effective additives for the improvement and retention of gloss, plus they have a desirable effect upon the fat solids content to improve mouth feel.

4.8.4 Polysorbate Fatty-Acid Esters

Polyoxyethylene sorbitan esters, commonly called polysorbates, are formed from the reaction of sorbitan esters with ethylene oxide. Three of the polysorbate types permitted for food use in limited amounts are polysorbate 60, polysorbate 65, and polysorbate 80. The level of usage of these emulsifiers is restricted by food-additive regulations; however, relatively small quantities of the polysorbates provide the desired effect in most applications, and higher levels impart a bittersweet taste. The polysorbates are hydrophilic emulsifiers that act as powerful surface-active agents to drastically reduce the interfacial tension among water, oil, and other ingredients; to enhance interaction between ingredients; and to promote emulsion stability. Polysorbate 60 is particularly effective in formulating oil-in-water emulsions. These derivatives have found more acceptance than sorbitan esters. Polysorbate 60 can be used in applications similar to those cited for sorbitan esters or cakes, whipped toppings, coffee whiteners, icings, and confectioner's coatings, plus nonstandardized salad dressings. Polysorbate 65 is permitted in ice cream and frozen desserts, mellorine or ice milk, and fruit sherbet, as well as in bakery applications. Polysorbate 80 can be used in a wide range of applications, including use in special dietary foods and gelatin desserts, as a solubilizing and dispersing agent in pickles and pickled products, and in baking applications.

4.8.5 Polyglycerol Esters

These compounds are formed by a reaction of fatty acids with polymerized glycerol consisting of 2 to 10 molecules. Careful control of the polymerization and esterification processes produces emulsifiers that can be used to emulsify, thicken, stabilize, defoam, release, plasticize, modify crystallization, enhance gloss, and also prevent sticking, weeping, lumping, and clouding. Some of the typical applications include:

- Peanut butter — Stabilizer and plasticization aid to prevent oil separation and weeping while improving spreadability and lubrication to prevent the peanut butter from sticking to the roof of the mouth.
- Confectionery coatings — Incorporation of 0.5 to 5% of a specific polyglycerol ester to enhance and maintain gloss properties while minimizing tempering and handling problems.
- Margarine — Excellent as antispattering and emulsifying agents when used at 0.1 to 0.5% for margarines and at 0.1 to 2.0% for low-fat spreads.
- Crystal inhibitor — Retards crystal formation in salad oils to increase the length of time before cloud development at use levels of 0.02 to 0.04%.
- Icings and fillings — Rapid effective aeration and weep stabilization for low-moisture icing and filling products at levels of 1.0 to 2.0% of the shortening.
- Cakes — Layer and loaf cakes with volume, grain, and texture equivalent to mono- and diglyceride-emulsified, high-ratio shortenings can be produced with lower polyglycerol ester use levels of 1.0 to 3.0% of the shortening.

4.8.6 Lactated Esters

Several forms of lactated esters are used in foods. Lactic acid esters of monoglycerides, reviewed previously with mono- and diglyceride, are reaction products of glycerine, lactic acid, and fatty acids. The two most prominent products are glycerol-lacto palmitate (GLP) and glycerol-lacto stearate. These blending emulsifiers are used primarily in applications where aeration is required, such as cakes, cake mixes, and whipped toppings to improve volume and texture. Most of these products have almost fully saturated fat bases and exhibit some oil solubility but no water solubility.

Stearoyl-2-lactylates are reaction products of stearic fatty acid and lactic acid converted to the calcium or sodium salts. Sodium stearoyl-2-lactylates, one of the most hydrophilic emulsifiers in the food industry, is used principally as a dough conditioner in baked products, pancakes, and waffles but is also effective in frozen whipped dairy cream and toppings to improve aeration and stabilization of the foam and to improve fat distribution to enhance the whitening effect in coffee whiteners. Calcium stearoyl-2-lactylate, also a dough conditioner, is used in both fresh and prepared mixes for yeast-raised baked products, as a whipping agent for egg whites, and as a conditioning agent for dehydrated potatoes. Low levels, typically 0.25 to 0.5% of the flour, of the stearoyl lactylate complex with starch delays the staling process in bread. The interaction with the flour gluten results in a finer crumb structure, increased volume, and better crust in the baked bread loaf.

4.8.7 Lecithin

The processed-food industry in the United States utilizes over 350 million pounds of surfactants a year, with 90% being chemically derived and 10% natural. The most prominent, functional, and commonly used natural surfactant is lecithin. This natural emulsifier is found in eggs, dairy products, vegetable oils, and many of the other food products from nature. Lecithin is a phosphorus-containing, lipid phosphatide found in all plant and animal organisms. Commercially, the chief source for lecithin is the gums extracted from soybean oil. Lecithin may also be obtained from other

oilseeds such as corn, cotton, peanut, and sunflower, but little is available for commercial use.

Lecithin has wide use in food and nonfood products, which makes it a very important byproduct of the soybean oil processing industry. The National Soybean Processor Association established criteria in the early 1970s for defining plastic and fluid lecithins, but these lecithin products are only about 15 to 20% of the current products used. Many new types of lecithin have been introduced commercially over the past few years. Some of these new products include oil-free or de-oiled, fractionated, and enzyme-modified lecithins, among others. Phospholipids isolated from soybean lecithin have the following applications in food products[13,14]:

- Protein complexing — The ability to complex with the protein in flour (gluten) provides the basis for a good dough conditioner. Lecithin can function as a natural bread-dough conditioner at addition levels generally between 0.25 and 0.6% based on the weight of the flour.
- Starch complexing — An ability to complex with starch is the basis of some antistaling agents. Certain lecithin phospholipids such as phosphatidylcholine and phosphatidylethanolamine form vesicles or liposomes with excellent antistaling properties.
- Fat reducer — Hydrated lecithin can assume a spherical form that rolls on the tongue to give a mouth feel similar to that of fats. Reductions of 20 to 60% of the fat content have been accomplished with cocoa and chocolate products. In chocolate, about 0.25 to 0.35% lecithin is used to reduce viscosity by coating the sugar, to increase the "snap" by allowing a reduction in cocoa butter content, and to inhibit bloom by allowing a wider range of processing temperatures.
- Egg yolk replacer — Commercial lecithin can duplicate the emulsification characteristics of egg yolk in cakes, sweet goods, and other food products. Lecithin or egg yolks provide cake batter fluidity during baking which prevents a collapse of the cake, or a "dip."
- Antisticking properties — Lecithin is the antisticking agent used in most pan and grill shortening, pan sprays, and baking-pan release products and is used in the candy industry for hard candies and confectionery. Lecithin mixtures in oil or other solvents form a barrier by coating the equipment surfaces.
- Antispattering agent — Lecithin is used in margarines and spreads at 0.1 to 0.5% to act as an antispattering agent. It also serves as an emulsifier to improve texture, absorb moisture, prevent bleeding, and improve spreadability and acts as a browning agent. Spattering is caused by the rapid explosive evaporation of the moisture present in margarine and develops when finely divided water coalesces to form large drops. Lecithin envelops each water particle with a protective membrane to stop the coalescence of the water droplets.
- Wetting — Cocoa powders possess poor wetting properties, regardless of the fat content, without the addition of lecithin. Cocoa and other instant drink powders are instantly wetted and drawn into cold water additions with lecithin levels of 1.0 to 1.5%.
- Antioxidant — Lecithin functions as an antioxidants in some oils at levels of 0.01 to 0.25%. Low-level additions of lecithin can also effectively retard off-flavors caused by hydrolysis by the same action that prevents spattering.

The appearance and flavor requirements of fats and oils can limit the use of lecithin, especially for products that must be heated. Lecithin is quite heat sensitive and can darken, smoke, and develop an objectionable fishy odor and flavor at temperatures above 120°F (49°C). Additionally, the level of lecithin added to a fat or oil product may affect both the color of the ingredient and the finished product. Regular fluid food-grade lecithin has a brown or amber color and a typical flavor. At the normal low usage levels, the color, flavor, and odor imparted by lecithin do not materially affect the appearance and flavor of the product; however, care must be exercised with the formulation and use of lecithin products to avoid problems.

4.8.8 Emulsifier Selection Methods

The process of selecting an emulsifier system has been viewed as more of an art than a science in that it requires experience and performance testing. The synergistic effects observed with various combinations of surfactants provide desirable functional properties not possible with single emulsifiers and complicate the selection process; therefore, development of emulsified shortenings can require a complex evaluation program with numerous surfactant blends of different ratios and use levels. Researchers have concluded that emulsifier selection is not a simple task, and a number of schemes have been developed to assist in identification of optimum systems for individual applications. The most well-known selection scheme is probably the hydrophilic/lipophilic balance (HLB).

4.8.8.1 Hydrophilic/Lipophilic Balance System

Emulsifiers can be classified by their affinity to water and oil. Surfactants with an affinity to oil (the lipid phase) are classified as fat-loving or lipophilic emulsifiers. Surfactants that have an affinity to water (the aqueous phase) are classified as water-loving or hydrophilic emulsifiers. Oil-soluble or lipophilic emulsifiers will absorb water or water-soluble materials into the oil or lipid phase. Hydrophilic emulsifiers will absorb the oil phase into the water or aqueous phase. The measure of an emulsifier's affinity for oil or water may be identified by its HLB.[45,46] HLB is an expression of the relative attraction of an emulsifier for water and for oil or for the two phases of the emulsifier system being considered. In the HLB system, each emulsifier is assigned a numerical value. An emulsifier that is lipophilic is assigned a low HLB value below 9.0, and one that is hydrophilic is assigned a high HLB value above 11.0. Those in the 9.0 to 11.0 range are intermediate. In general, lipophilic emulsifiers such as mono- and diglycerides have HLBs in the 2 to 4 range and tend to form water-in-oil emulsions. Hydrophilic emulsifiers, such as polysorbate esters, have HLBs in the 13 to 17 range and tend to form oil-in-water emulsions.

The following table indicates the relationship of HLB to water solubility at 70°F (21.1°C):

Emulsifier Behavior When Added to Water	HLB Range
Insoluble	1–4
Poor solubility	3–6
Opaque with vigorous agitation	6–8
Stable opaque dispersion	8–10
Translucent	10–13
Clear solution	13 and Above

The best results are usually obtained with emulsifier systems or by blending two or more emulsifiers to obtain a desired HLB value rather than using only one. A blended emulsifier system, usually described as a synergistic emulsifier blend, provides not only the functional properties of each emulsifier but also additional functional properties due to interaction effects. The HLB of the blend is essentially a straight-line relationship that can be determined by multiplying the HLB value of each component in the blend, then adding together these numerical values. The HLB values of various surfactants are listed below:

Emulsifier	HLB Value
Mono- and diglycerides	
40% minimum D-monoglyceride	2.8
52% minimum D-monoglyceride	3.5
90% minimum D-monoglyceride	4.3
Propylene glycol esters	
Propylene glycol mono- and diesters	3.4
Propylene glycol mono- and diesters and mono- and diglycerides	3.5
Sorbitan esters	
Sorbitan monostearate	4.7
Sorbitan tristearate	2.1
Polyoxyethylene sorbitan esters	
Polysorbate 60	14.9
Polysorbate 65	10.5
Polysorbate 80	15.0
Polyglycerol esters	
Triglycerol mono shortening	6.0
Triglycerol monostearate	6.2
Hexaglycerol distearate	8.5
Lactated esters	
Lactylated mono- and diglycerides	2.6
Lecithin	
Standard fluid	3.5
De-oiled, 22% phosphatidylcholine	4.5
De-oiled, 45% phosphatidylcholine	6.5

The HLB selection system consists of the steps: (1) determining the optimum HLB value for the intended product, (2) identifying the best emulsifier types, and

(3) applying final HLB adjustments. In this procedure, emulsifiers and blends with HLB values outside the identified HLB range may be eliminated to reduce the trial-and-error evaluations. The detailed steps to determine the best HLB value are as follows:

1. Select a matched pair of emulsifiers, one lipophilic and one hydrophilic, with known HLB values; for example, mono- and diglycerides with a 2.8 HLB are lipophilic surfactants, and polysorbate 60 with a 14.9 HLB is a hydrophilic surfactant.
2. Prepare a series of test emulsions with the selected emulsifiers blended to give different HLB values ranging from all lipophilic to all hydrophilic surfactants. This range would be from 2.8 to 14.9 for the two surfactants suggested in the first step. An excess of the emulsifier blend should be used, or approximately 10 to 12% of the fat and oil level in the final product.
3. Evaluate the emulsifier's series using appropriate performance methods based on the product requirements. One or more of the emulsifier blends should provide a better emulsion than the others, but if all levels appear good, repeat the series with a lower use level. Conversely, if all are poor, the use level should be increased and the series repeated.
4. The final test results should indicate within approximately 2 units the HLB range that will perform the best for the application. A more accurate HLB value may be determined by another series located around this range if necessary.

The appropriate surfactant chemical type is as important as the HLB value. After the HLB value has been established, it must be determined if some other emulsifier blend would perform better, would be more efficient, or would be more cost effective to produce that HLB value. The evaluation object is to select several pairs of emulsifiers covering a suitably wide area of chemical types. Performance evaluations of these blends should indicate the ideal emulsifier blend for the specific application.

The HLB method is an incomplete system for selecting surface-active agents. Surfactant selection for emulsions using the HLB system functions well in a pure system when a formula is composed of oil, water, and emulsifiers; however, its use is limited in many food systems due to their complexity. The effect of surfactants on starch complexing is an important function for some products, but HLB does not measure this attribute. Emulsifiers with the same HLB value may vary from excellent to poor in their ability to produce an acceptable cake; emulsifier selection becomes more complex with the addition of flour, starch, sugar, milk, salt, eggs, or other similar ingredients, some of which contain natural emulsifiers that react and interact with each other. Thus, the HLB approach can assist in the surfactant selection process, but identification of the optimum emulsifier system for the application still requires experience and detailed experimental work.

4.8.8.2 Emulsifier Functionality Traits

Mono- and diglycerides are probably the most multifunctional emulsifiers. Other emulsifiers generally fit a more specific or limited function. The specificity of surfactant functions provides a selection guide for emulsifier systems development.

Table 4.9 evaluates the functionality of emulsifier types most often used for food

Table 4.9 Emulsifier Functionality Degree

Emulsifier	Emulsion Stability	Starch Complexing	Dough Conditioner	Crystal Modifier	Aeration
Mono- and diglycerides					
Hard or saturated	2	1	4	3	1
Soft or unsaturated	2	3	4	3	2
Propylene glycol esters					
Propylene glycol mono- and diesters	5	2	5	1	1
Propylene glycol mono- and diesters and mono- and diglycerides	3	1	4	1	1
Sorbitan esters					
Sorbitan monostearate	3	5	5	1	3
Sorbitan tristearate	3	5	5	1	5
Polyoxyethylene sorbitan esters					
Polysorbate 60	3	2	1	3	1
Polysorbate 65	3	3	3	3	2
Polysorbate 80	2	3	3	2	2
Polyglycerol esters					
Triglycerol mono shortening	2	3	3	3	1
Triglycerol monostearate	3	3	3	3	1
Hexaglycerol distearate	1	3	3	1	2
Lactated esters					
Lactylated mono- and diglycerides	2	4	5	1	1
Stearoyl-2-lactylates	1	2	1	5	2
Lecithin					
Standard fluid grade	3	3	3	1	4

Note: Emulsifier functionality evaluation: 1 = excellent; 2 = good; 3 = slight; 4 = poor; 5 = none.

applications in five different areas.[47–49]

- Emulsion stability — Emulsifiers create mixtures of two liquids that are normally immiscible. An emulsion can be defined as a dispersion of droplets of one immiscible liquid with another. Emulsifiers promote formation of dispersed systems by lowering the surface tension at the interface of two immiscible substances. The ability of an emulsifier to act at the interface is due to molecular structure. The polar group of an emulsifier has an affinity for water in which it dissolves. The fatty acid part of the emulsifier has affinity for oil and dissolves in this phase.
- Starch complexing — Starch consists of two types of carbohydrates: amylose and amylopectin. A gel is formed when these carbohydrates are mixed with water and heated. The starch components recrystallize from the gel, or retrograde, the process that is responsible for the staling process of baked products, toughness in pasta and potato products, and hardening in starch jelly confections. Emulsifiers that can form complexes with starch retard the retrogradation process.

- Dough conditioning — Gluten, the protein in wheat flour, forms a network that strengthens doughs. Certain emulsifiers can strengthen the gluten, thereby preventing rupture of the cell walls that have entrapped the fermentation gases. This allows the cells to form uniformly, providing even grain in the finished loaf and doughs that are not sticky or bucky for better machinability.
- Crystal modification — Triglycerides are polymorphic, which means that they can exist in more than one crystalline form. Crystal reversion can be retarded by the incorporation of emulsifiers with crystal modification capabilities. The propylene glycol monoesters, acetylated monoglycerides, and lactylated monoglycerides of D-tending surfactants can stabilize mono- and diglycerides in the more active D-form for improved functionality. Sorbitan esters prevent the formation of bloom on chocolate products by retarding B-crystal development. Polyglycerol esters also prevent chocolate bloom and are effective crystal inhibitors for salad oils. Lecithin was the first crystal inhibitor used in salad oil processing.
- Aeration — Many food products are prepared in emulsion form and are aerated to a foam. Aerating emulsifiers facilitate aeration, provides faster whipping rates, evens cell structures, and provides higher volumes in baked products and other aerated products such as icings, fillings, and whipped toppings.

4.8.8.3 Emulsifier Selection Procedure

The emulsifier system of a product must be tailored to the specific application, as its behavior will be influenced by the processing conditions and the presence of other ingredients. Furthermore, a blend of two or more emulsifiers imparts synergistic effects greater than that possible with a single emulsifier. Development of the optimum system requires analyzing the available surfactants in blends of different ratios. The following guidelines summarize a successful technique for the selection of an emulsifier system for specific applications[39]:

1. Consult the applicable regulations for restriction on the use of emulsifiers or for specific requirements for standardized products. Only approved emulsifiers should be considered.
2. Identify the functional requirements of the food system, the method of processing, and the form of the finished product.
3. Identify the surfactants that contribute the functional properties required by the food system. Table 4.9 summarizes the functionality of the emulsifier types most often used for food applications. Also, consult surfactant suppliers for suggested usage levels, incorporation methods, product functionality, and other available information.
4. Screen the approved emulsifiers with functional characteristics applicable to the food product using the HLB system guideline to identify the most promising blends and evaluate further to identify the optimum emulsifier system.
5. Optimize the emulsifier system usage level. Emulsifiers have an optimum usage range or plateau that provides the maximum functionality; levels over and under this plateau level provide lesser degrees of the preferred functionality.

4.9 PRODUCT DEVELOPMENT

Fats and oils are key functional ingredients in a large variety of food products. They have particular physical properties of importance in the processing and final use of both natural and prepared foods. The glyceride structure and composition of the fats present in such foods also differ widely. These fatty acid and triglyceride compositions influence the functional properties of foods and food ingredients that contain even modest fat levels. The relationships between triglyceride composition and end-use characteristics are evident when the physical and chemical properties are evaluated; therefore, fats and oils with similar physical and chemical properties, even with different triglyceride compositions, can provide the desired functional characteristics for the food product. Fat systems for foods and food ingredients may be developed in several ways. Three product development methods used to formulate fats and oils products to perform desired applications are:

1. Application development — Utilize qualitative knowledge regarding the effects of source oils, basestocks, fat fractions, interesterified products, emulsifiers, and other additives on product consistency and behavior in the finished product.
2. Analytical development — Determine the components based on their contributions to satisfying predetermined analytical limits.
3. Triglyceride replication — Carefully blend selected fractions from various source oils to duplicate the triglyceride structure of another product.

4.9.1 Application Product Development

Application development of fats and oils products begins with identification of the key functional attributes the product is expected to provide to the end-use product and the use of historical knowledge to identify and evaluate the physical and chemical properties most likely to produce the intended functionality. Recognition of the primary and secondary functional attributes and disregarding insignificant properties is important for this product development. The results of these studies provide the information necessary to develop a product specification that identifies the physical and chemical requirements that must be met to ensure compliance with the requirements of the application. In most cases, the product is required to meet the performance standards of an existing product; however, the product developed may perform better than the original, or the product currently used may be overqualified for the application.

Performance requirements can usually be translated into analytical measurements for the specification limits of the product in development. For example, the primary performance requirements of a salad oil can be evaluated with the AOCS Cold Test Method Cc 11-53,[30] which determines the resistance of an oil to crystallization while submerged in an ice bath. This analytical method was developed to evaluate the acceptability of salad oil products for the production of mayonnaise and salad dressing. An oil that clouds or solidifies at the cold temperatures used for salad dressing preparation will cause the emulsion to break, which results in product separation. Likewise, the solids fat index (SFI) and solids fat content (SFC) curves are of great importance to achieving the desired consistency and performance of

shortening, margarine, and other fats and oils products. The usual SFI measurements

Table 10.3 Tablegrade Margarine Oils Composition, SFI, and Nutritional Information

Margarine Type	Stick Margarine Oils			Tub Margarine Oils	
	All Hydrogenated	Soft Printable	High Liquid Oil	All Hydrogenated	High Liquid Oil
Basestock (%):					
60-IV H-SBO	—	—	—	18	18
66-IV H-SBO	38	50	15	—	—
74-IV H-SBO	20	—	25	—	—
85-IV H-SBO	—	—	—	—	—
109-IV H-SBO	42	—	—	82	32
RB SBO	—	50	60	—	50
Solids fat index (%) at:					
50°F/10.0°C	28.5±	22.0±	30.0±	12.0±	11.0±
70°F/21.1°C	17.5±	13.5±	17.0±	7.5±	5.5±
92°F/33.3°C	3.0±	2.0±	1.5±	3.0±	0.7±
Saturates (%)[a]	20.0	20.7	17.9	18.3	18.3
trans-Isomers (%)[a]	32.4	22.8	18.0	20.2	12.8

[a] Calculated.
Note: IV = iodine value; H-SBO = hydrogenated soybean oil; RB = refined, bleached.

a steep SFI slope for good eating characteristics. Two different soft tub compositions are shown in Table 10.3. The all-hydrogenated product provides the oxidative stability and firmest margarine consistency. Slight consistency differences can mean the difference between a soft tub margarine with a picture-perfect surface appearance or excessive "lid slosh." The all-hydrogenated margarine base has a better chance of retaining a smooth surface because it will set quicker than the product formulated with liquid oil.

Liquid margarine has been marketed for quite some time, but it has never achieved significant consumer acceptance. Food processors have accepted and utilized this product for specialty applications more so than consumers. Liquid margarine has been prepared using beta and beta prime types of hardfats: 4 to 5% soybean or cottonseed oil hardfat with refined, bleached (RB) soybean oil. The beta hardfats have been found to be more suitable for product packaged without tempering or crystallization process stages. Product prepared with beta crystal-forming hardfats requires tempering of the supercooled mixture at elevated temperature for a period of time under agitation to develop and stabilize the beta crystal. This liquid margarine process resembles the liquid shortening process closely. The beta crystal formulation and procedure produces a more fluid, less viscous product with better suspension stability than the beta prime product but costs more to produce.[20] The beta hardfat direct process provides a better mouth feel and flavor but requires constant refrigeration to avoid separation.

10.4.1 Trans-Free Consumer Margarine Oil Formulation

Clinical nutritional studies showing an association between both dietary trans- and saturated fatty acids have created formulation opportunities for processors relying on hydrogenated basestocks. During hydrogenation, some double bonds change

Table 10.4 Industrial Margarine Types and Butter

Product	Dairy Butter	Margarine			
		Tablegrade	Baker's	Danish Roll-In	Liquid
Mettler dropping point, °C	35.0±	33.0±	49.0±	40.2±	*
Solids Fat Index, % at:					
50°F/10.0°C	33.0±	30.0±	25.0±	43.5±	3.0±
70°F/21.1°C	14.0±	17.0±	19.0±	25.8±	2.5±
80°F/26.7°C	10.0±		18.0±	20.6±	2.0±
92°F/33.3°C	3.0±	1.5±	14.0±	11.1±	2.0±
104°F/40.0°C			9.0±	2.0±	

* Too soft

configuration from cis to trans to form high-melting unsaturated fatty acids, before saturation occurs. The high trans basestocks also contributed greater oxidative stability and stabilization in the E-crystal form. These behavior changes have been utilized by formulators to produce margarines that are less saturated. Interesterification is an alternative process for producing basestocks that can be used to achieve a steep SFI curve without trans-fatty acid production. The effect of interesterification on melting behavior depends upon the starting materials. A steeper SFI and a reduced melting point are produced when a high-melting fat is interesterified with a liquid oil, as shown in Table 4.7 in Chapter 4. Additionally, transition of the crystal to the most stable E form progresses more slowly to stabilize the interesterified blend in the E-crystal form. The common feedstocks for the randomization process are liquid vegetable oils and fully hydrogenated vegetable oils in the United States and liquid vegetable oils, palm oil and fractions, palm kernel oils and fractions, and coconut oil, with or without complete hydrogenation, in Europe and Canada.

10.5 INDUSTRIAL MARGARINE FORMULATIONS

Foodservice and food processor margarines may either be duplicates of the consumer products or designed for a specific use. A popular industrial product is the consumer stick margarine packaged in 1-pound solids for foodservice kitchen use and in 50-pound cases for food processor applications. Individual servings of consumer table-grade margarines and spreads are also large-volume foodservice products. Most of the other foodservice and food processor margarines are formulated for specific uses, with the main analytical criteria being the Mettler dropping point (MDP) to measure melting point and solids fat index (SFI). The differences in functionality are achieved by manipulation of the margarine oil components.

Many of the industrial margarines are formulated for bakery applications. Table 10.4 lists typical SFI and MDP values for the general types of bakery margarines compared to butter. The function and formulation peculiarities for the bakery margarine categories include the following:

- Table-grade margarine — The analytical values closely match butter with a relatively steep SFI and a MDP close to body temperature. Table-grade margarines are formulated like the stick margarines shown in Table 10.3. Typical bakery uses are fillings, crumb crusts, and buttercream icings.
- Baker's margarine — Baker's margarine is designed to have a wide plastic range with good creaming properties like the standard all-purpose shortening. In fact, the margarine oil formulation can be the same composition as the all-purpose one shown in Table 6.1 in Chapter 6: an 80-85-IV basestock with a saturated EMC hardfat. Applications for this margarine include cookies, Danish pastries, croissants, buttercream icings, cakes, and pie crusts.
- Roll-in margarine — Mechanical operations are more demanding than hand make-up, roll-in operations. It is critical that the margarine emulsion does not break when pumped and extruded under high pressure, that it maintains a smooth plasticity and consistency to spread evenly through lamination without bleeding into or tearing the dough, and that the margarine and the dough are compatible to prevent equipment problems. Roll-in margarines are formulated to achieve a relatively shallow SFI profile and are stabilized in the beta crystal phase. The melting point must be, as a general rule, 5°F (2°C) higher than the proofing temperature of the roll-in product to prevent oil-out before baking. The moisture in margarines generates steam in the oven for leavening and flakiness.

10.6 SPREAD FORMULATIONS

All products resembling margarine that contain less than 80%, but more than 40%, fat are required to be labeled spread. However, these products must conform with the margarine standard in all respects except for the fat content and the fact that only safe and suitable ingredients not provided for in the standard may be added to improve functional characteristics so that spreads are not inferior to margarine. Soft tub and stick spreads containing 41 to 75% fat are usually formulated from the same fat and oil blends as those used for regular consumer margarines. The other ingredients utilized are also basically the same with the following exceptions[6,21]:

- Milk protein acts as an oil-in-water emulsifier; consequently, the use of milk, casein, or caseinates can result in a phase inversion, so most spread formulations are milk and milk-protein free.
- Emulsifier levels are increased and a synergetic system has been found most effective for emulsion stability, typically 0.6% intermediate-hardness mono- and diglycerides, 0.1 to 0.2% polyglycerol ester, and 0.3 to 1.0% saturated EMC hardfat.
- Lecithin use in low-fat spreads may decrease the emulsion stability and increase the tendency to oil-off; however, it can also functions to slow emulsion breakdown in the mouth, so the use of lecithin and the level of use must be evaluated for each formulation.
- Gelatin, pectin, carrageenans, agar, xanthan gum, starch, alginates, or methylcellulose derivatives are gelling or thickening agents used in some spreads to improve the body.
- The higher emulsifier levels used for spread can produce tighter emulsions, and the gelling or thickening agents can affect the rate and order in which flavors are

perceived. The flavor content and types must be defined to produce oral responses similar to the high-fat products.
- Preservatives are more important in spreads than in regular margarines because of the higher moisture content.
- The light reflection of a spread is different than that of regular margarine because of the increased number of water droplets present; therefore, it is necessary to add about twice the amount of color used in normal margarine to obtain the same color intensity.

10.7 MARGARINE AND SPREAD PREPARATION

Margarine and spread processing resembles shortening preparation, except that an emulsion is prepared by mixing the water-soluble and fat-soluble ingredients before chilling and crystallization. The basic steps for margarine and spread preparation include (1) margarine-base blending, (2) oil-phase preparation, (3) aqueous-phase preparation, (4) emulsion preparation, (5) chilling and crystallization, (6) packaging, (7) tempering, (8) storage, and (9) distribution. The same procedures work well with both margarine and spread products containing from 52 to 80% fat; however, as the fat level decreases below 52%, strict process control for temperature and addition rates must be used to guard against the formation of a mixture of water-in-oil and oil-in-water emulsions or an all oil-in-water emulsion.[19]

The lipid phase is prepared by heating the margarine base to a temperature of at least 10°F (5.6°C) above the melting point before adding the oil-soluble ingredients. These ingredients include the emulsifiers, vitamins, color, and flavor if it is oil soluble. The aqueous phase is prepared separately. When milk proteins are utilized, the milk or whey product is reconstituted if liquid skim milk is not used, pasteurized, and cooled until required. The water-soluble ingredients are added to the required amount of pasteurized skim milk, whey, or water for the case of protein-free products. The ingredients include salt, preservatives, water-soluble flavors, and any other water-soluble materials. The oil and aqueous phases are blended together with high-shear agitation to form a water-in-oil emulsion. It is important to add the water phase to the oil phase in order to promote the formation of a water-in-oil emulsion. The water addition rate has little effect upon margarine emulsions but is critical for spreads. It is essential that the water addition rate for spreads be reduced, especially in the early stages of emulsion preparation, to prevent inversion of the emulsion. Continuous agitation is necessary to maintain this emulsion; without agitation, the water- or milk-phase droplets immediately begin to coalesce and settle out. After preparation, the emulsion is transferred to an agitated holding tank that supplies the chilling units.

An alternative continuous emulsion preparation process consists of proportioning pump systems capable of metering individual ingredients of the aqueous phase together and also the oil-phase components. In-line static mixers are utilized to blend the separate phases, which are then mixed and emulsified with another static mixer. After inline blending, the loose emulsion is continuously fed to the crystallization system.

The solidification process for the various margarine and spread types all employ a scraped-surface heat exchanger for rapid chilling, but the other steps are somewhat different from shortening and the other margarine types. The solidification or plasticization process for the four basic spreadable types are as follows.

10.7.1 Stick Margarine or Spread

The temperature of the stick margarine emulsion is adjusted and maintained for most table-grade products that melt below body temperature at 100 to 105°F (37.8 to 40.6°C) before pumping to the scraped-surface heat exchanger. If the temperature is allowed to cool below the melting point of the margarine base, precrystallization structures may be formed that affect the consistency of the finished product. It is rapidly chilled to 40 to 45°F (4.4 to 7.2°C) in less than 30 seconds. Stick margarine requires a stiffer consistency than shortening, which is accomplished with the use of a quiescent tube immediately after the chilling unit. This is a warm-water-jacketed cylinder that can contain baffles or perforated plates to prevent the product from channeling through the center of the cylinder. The length of this tube may have to be varied to increase or decrease crystallization time, depending upon the product formulation. The supercooled mixture passes directly to a quiescent resting or aging tube for molded print-forming equipment. For filled print equipment, a small blender may be utilized before the resting tube to achieve the proper consistency for packaging and a slightly softer finished product. A remelt line is necessary because in all closed filler systems some overfeeding must be maintained for a uniform supply of product to the filler for weight control. The excess is pumped to a remelt tank and then reintroduced into the product line.

Two types of stick margarine forming and wrapping equipment are used in the United States: molded print and filled print. The molded print system initially used an open hopper into which the product was forced from an aging tube through a perforated plate in the form of noodles. The margarine noodles were screw fed into a forming head and then discharged into the parchment-paper wrapping chamber and finally cartoned. Closed molded systems use a crystallization chamber instead of the aging tube and an open hopper arrangement that fills the mold cavity by line pressure. The filled print system accepts margarine from the quiescent tube with a semifluid consistency. The product is filled into a cavity prelined with the parchment or foil interwrap. The interwrap is then folded before ejection from the mold into the cartoning equipment.

10.7.2 Soft Tub Margarine or Spread

The oil blends for soft tub margarines or spreads are formulated with lower solids-to-liquid ratios than the stick-type products to produce a spreadable product directly out of the refrigerator or freezer. Crystallization technique contributes to the desirable consistency as well, but the products are too soft to print into sticks; therefore, packaging in plastic tubs or cups with snap-on lids is utilized.

To fill the container properly, the soft margarine or spread consistency must be semifluid like shortening, so the crystallization process more closely resembles shortening plasticization than stick margarine processing. The temperature of a typical soft margarine emulsion would be adjusted and maintained at 95 to 105°F (35.0 to 40.6°C) before pumping with a high-pressure pump to the scraped-surface heat exchanger. Creaming gas or nitrogen, added to further improve spreadability, is injected at the suction side of the pump at 8.0% for the most spreadable product; lower levels are used for a firmer product. Margarine blends are rapidly chilled to an exit temperature of 48 to 52°F (8.9 to 11.1°C). Spread fill temperatures are higher than for margarine products because the emulsion is more viscous. If the fill temperature is too low, the product will mound in the bowl for excessive lid coverage, and the product may become dry and crumbly. The supercooled margarine or spread mixture then passes through a worker unit to dissipate the heat of crystallization. The shaft in the worker unit revolves at about 35 to 50 revolutions per minute with an approximately 3-minute residence time. Worked product is then delivered to the filler where it is forced through an extrusion valve at pressures in the range of 20 to 26.7 bar (300 to 400 psi). Either a rotary or straightline filler may be used to fill the tubs with margarine. The excess product necessary for a uniform supply to the filler is transferred to a remelt tank and eventually reenters the solidification system.

10.7.3 Whipped Tub Margarine or Spread

The same equipment used to prepare, crystallize, and package regular soft tub margarine or spread can be utilized for whipped tub products. The difference during crystallization is the addition of 33% nitrogen gas by volume for a 50% overrun. The nitrogen is injected inline through a flow meter into the suction side of the pump. The larger tubs required for the increased volume necessitate changing parts for the filling, lidding, and packaging equipment.

10.7.4 Liquid Margarine

Both retail and commercial liquid margarine can be crystallized with the same equipment and process flow used for soft tub products, depending upon the formulation and suspension stability requirements. Liquid margarine formulations normally consist of a liquid vegetable oil stabilized with either E or E-forming hardfat. E-stabilized liquid margarine can be prepared utilizing the same rapid crystallization process used to prepare soft tub margarine and omitting the addition of creaming gas. These finished products require refrigerated storage for suspension stability. Liquid margarines formulated with E-forming hardfats and some processed with E formulations incorporate a crystallization or tempering step to increase fluidity and suspension stability. This crystallization step consists of a holding period in an agitated jacketed vessel to distribute the heat of crystallization. The product may be filled into containers after the product temperature has stabilized. Some products with higher solids-to-liquid ratios are further processed to stabilize the fluid suspension with either homogenization or a second pass through the scraped-surface

heat exchanger before filling. The additional processing for more stable crystallization will increase fluidity and suspension stability, but the increased production costs may not be justifiable.

10.7.5 Industrial Margarines or Spreads

Foodservice and food processor margarines and spreads may either be duplicates of the retail products in larger packages or designed for a specific use, either product- or process-related. Among the specific-use margarines, puff paste or Danish pastry applications are the most difficult regarding crystallization. The characteristic features of a roll-in margarine are plasticity and firmness. Plasticity is necessary, as the margarines should remain as unbroken layers during repeated folding and rolling operations. Firmness is equally important as soft and oily margarine is partly absorbed by the dough, thus destroying its role as a barrier between the dough layers. As with shortenings, the ultimate polymorphic form for roll-in margarines is determined by the triglyceride composition, but the rate at which the most stable form is reached can be influenced by mechanical and thermal energy. Therefore, the customary crystallization process for roll-in and/or baker's margarines is a duplicate of the shortening plasticization process depicted in Figure 2.10 in Chapter 2, except that margarines containing water or milk emulsion form are normally not aerated. The aqueous phase of a margarine emulsion has the same effect as gas incorporation on appearance and performance. Food service or margarine products are usually packaged in 50-pound corrugated fiberboard cartons, 5-gallon plastic pails, 55-gallon drums, or special packaging designed for each specific use.

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CHAPTER 11

Liquid Oils

11.1 INTRODUCTION

Clarity at or below ambient or room temperature is the primary characteristic of a liquid oil. Natural vegetable oils that are liquid at room temperature (75 ± 5°F or 23.9 ± 2.8°C) in temperate climates contain high levels of unsaturated fatty acids with low melting points. The 18-carbon-atom fatty acids are the most important unsaturated fatty acids for liquid oils. Oleic (C-18:1), a monounsaturated fatty acid, is the most oxidative stable. Linoleic (C-18:2) and linolenic (C-18:3), referred to as polyunsaturates, are deemed essential fatty acids because they cannot be synthesized by the human body and must be supplied in the diet.

Three major oil types have developed that maintain different degrees of clarity at and slightly below room temperature in temperate climates. Cooking, salad, and high-stability oils are prepared from vegetable oils that are refined, bleached, and deodorized (RBD) at a minimum but can also require modification by dewaxing, winterization, hydrogenation, and fractionation processes. All of these oil types have one common physical property — they are clear liquid oils at room temperature. The three types of liquid oils are defined as:

- Cooking oil — An edible oil that is liquid and clear at room temperature and may be used for cooking. Cooking oils are used for pan and deep-fat frying and in packaged mixes or wherever a clear liquid oil has application without refrigeration. Cooking oils may solidify at refrigerator temperatures.
- Salad oil — An edible oil that will remain substantially liquid at refrigerator temperatures, about 40°F (4.4°C). The standard evaluation method for a salad oil is the cold-test analysis. A salad oil sample that remains clear after 5-1/2 hours while submerged in an ice bath meets the criterion for a salad oil. Salad oils may be used for cooking but are low in saturated fatty acids to prevent or delay clouding and graining during refrigeration.
- High-stability oil — An edible oil that is liquid at room temperature and has exceptional oxidative or flavor stability. High-stability oils are used for food preparation applications where the functional characteristics of a liquid oil are desired and a long shelf life is required.

11.2 DEVELOPMENT OF LIQUID OILS

Climate and availability influenced the eating habits of our ancestors. Inhabitants of central and northern Europe first derived their edible fats almost entirely from wild animals and later from domestic animals. Consequently, their foods developed around the use of solid fats such as butter, lard, and tallow. In the more heavily populated areas of Asia, southern Europe, and Africa, where it was impractical to dedicate land to livestock grazing, diets were developed with vegetable oils as the major fat source. All oil-bearing plants produce oils that are liquid at the prevailing temperatures where the plant grows. Even the tropical oils that are solid at room temperature in cooler climates are liquids in the tropical climates where these plants flourish. North America's preference for animal fats was influenced by the early immigrants who came from northern Europe and adapted large areas of the country to raising domestic animals.[1]

Fats and oils processors in the United States developed the differentiation between cooking and salad oils. The original intent was to retain fluidity and clarity for cottonseed oil during the colder months; oil fluidity and clarity were not a problem during the warmer summer temperatures. Domestic ice boxes and later refrigerators, along with the large-scale commercialization of the mayonnaise and salad dressing industry, increased the need for a liquid oil that remained clear at reduced temperatures. Initially, salad oil was referred to as winter oil as an indication of the fractionation process used to produce the cloud-free oil at cool temperatures. The winterization process evolved from practical experience at refineries when it was observed that storing cottonseed oil in outside tanks exposed to low temperatures during the winter months allowed the higher melting triglycerides to settle to the bottom of the tank, leaving a top layer of clear oil. The top layer was decanted, deodorized, packaged, and marketed as a salad oil. The topping process did not provide consistent results because it depended upon nature to provide the coolant, and as the popularity of the oil increased it became impractical to maintain the quantity of oil in storage tanks at the volume and time required. Therefore, mechanically refrigerated chilling and filtering systems were developed to simulate the outside storage and topping process. Salad oil terminology came about because of the application of winter oil to mayonnaise preparation. At the same time, unwinterized oil, which was known as summer oil, became cooking oil.[2,3]

Salad oil identification later changed from an oil processed by the winterization process to an oil that can meet the requirements of a winter oil: resist clouding for more than 5-1/2 hours at 32°F (0°C). This revised salad oil definition encompassed oils identified as natural winter oils. These oils, which have fatty acid compositions that are high in unsaturates with corresponding low saturated fatty-acid levels, do not require winterization to remain clear and brilliant at refrigerator temperatures. Soybean oil is a natural winter oil and does not require fractionation to meet the cold-test requirements. Corn, canola, safflower, and sunflower oils would be natural winter oils, except for waxes that cloud at cool temperatures. These oils are normally dewaxed with a winterization-type process to remove the waxes. Salad oils cannot be prepared from peanut oil because it gels when chilled to the extent that it cannot

be separated. The saturated fatty-acid levels of tropical oils are too high for consideration as salad oils.

Liquid oils are consumed as naturally (undeodorized) and artificially flavored oils and as neutral, deodorized products. Olive oil is almost always marketed in the undeodorized form. The natural flavor is an important asset that deodorization would destroy. Soybean, peanut, sunflower, and sesame oils are generally consumed in their crude form in India and China; however, the oil seeds are expressed at low temperatures without previous heat treatment. These cold-pressed methods produce low yields, but the oils have a relatively mild flavor and odor. Even though olive oil is growing in popularity as a gourmet oil, consumers in the United States are accustomed to deodorized oils. Cottonseed oil, the only oil consumed in the United States for many years, is so strongly and unpleasantly flavored that deodorization is considered necessary to made it edible. The efficient methods used to separate oils from vegetable seeds involve a cooking, or heating, process before extraction. These methods do not change the stability or nutritive qualities of the oil, but the oils do develop a stronger flavor and odor that are considered objectionable. The higher oil yields compensate for the refining and deodorization expenses required to make the oils palatable. A market has developed for cold-pressed peanut, sesame, safflower, and sunflower oils because of implied nutritional considerations, but no reliable consumption data are available.

In general, a greater utilization of liquid oils has developed in areas that had been partial to solid fats than of plastic fats in oil-consuming countries. Figure 11.1 compares the preference changes for edible fats and oils in the United States beginning in 1950 when liquid oil usage was at a much lower level than that for either shortening or solid fats, as well as the tablespreads (butter and margarine). Liquid oil usage more than tripled during this period. Cooking and salad oil usage surpassed tablespreads in 1970 and exceeded solids fat usage in 1999. This trend has developed because of the following reasons:

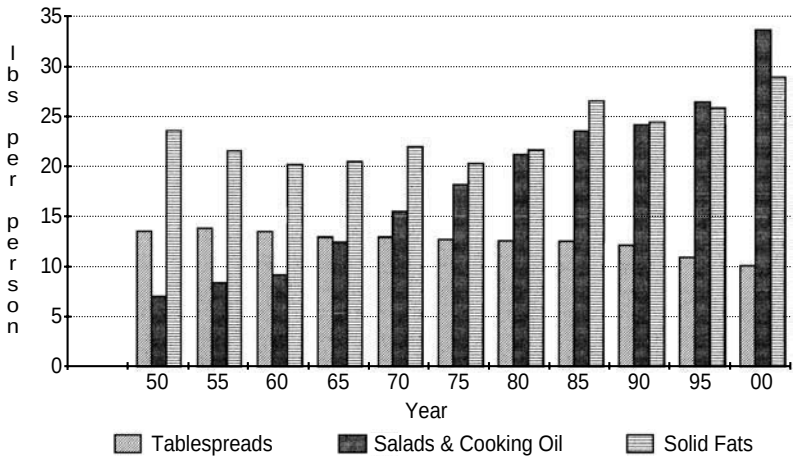

Figure 11.1 Visible fats and oils consumption changes.

- Global movement of people
- High polyunsaturate content of most oils
- Saturated fatty acids being implicated in cardiovascular disease
- Process improvements for more bland and flavors with improved oxidative stability
- Finished product formulations and processdevelopments to accommodate liquid oils
- Emulsifier development that reduced dependence on the crystalline properties of solid fats for functionality
- More convenient handling

Liquid oils are suitable and preferred for many types of food preparation, such as when the food is consumed shortly after preparation, for frying with high absorption rates for rapid turnover, for frozen and refrigerated food preparation, and in other areas requiring protective packaging. These application restrictions still apply for cooking and salad oils, but high-stability oils have been developed for applications requiring a long-term oxidative stability. The primary characteristics of a high-stability oil are liquidity at room temperature with enhanced oxidative stability while retaining functional and nutritional properties. Two techniques for producing a high-stability oil are (1) hydrogenation followed by fractionation to separate the stearine or hard fraction from the olein fraction which becomes the high-stability oil, or (2) use of plant-breeding techniques to produce oils low in polyunsaturates and high in monounsaturated fatty acids. Both of these techniques are used to produce high-stability liquid oils for use wherever stability and liquidity are the important functional requirements.

11.3 COOKING AND SALAD OIL SOURCES

The steady growth in the consumption of cooking and salad oils is evident from the U.S. Department of Agriculture (USDA) Economic Research Service Oil Crops Situation and Outlook Reports for domestic consumption of salad or cooking oils; the consumption and source oils data for salad and cooking oils utilized since 1960 are summarized in Table 11.1.[6-8] Deodorized cooking and salad oils are principally prepared from soybean, corn, canola, cottonseed, and peanut oils. Cottonseed, corn, and peanut oils can be deodorized to bland neutral products that do not develop exceeding disagreeable flavors upon reversion or oxidation. Conversely, the characteristic oxidized flavor of soybean oil kept it from being an acceptable salad or cooking oil for quite some time.

Winterized cottonseed oil was the principal salad oil used in the United States until the late 1950s. Soybean oil surpassed cottonseed oil as the principal vegetable oil in the United States soon after World War II; however, cottonseed oil remained the preferred salad oil source until the flavor and odor deficiencies of soybean oil were addressed. Soybean salad oil with a reduced linolenic fatty acid (C-18:3) was introduced to the U.S. market in the late 1950s and early 1960s. The linolenic fatty-acid content was reduced with hydrogenation and subsequently winterized to remove the hard fraction created during hydrogenation. This specially processed soybean

Table 11.1 U.S. Usage of Source Oils for Salad and Cooking Oils

	Year (million pounds)				
Oil Source	1960	1970	1980	1990	2000
Canola	—	—	—	W	515
Corn	247	247	350	636	502
Cottonseed	752	527	460	460	304
Olive	51	62	58	213	459
Peanut	28	140	148	139	W
Safflower	—	12	—	—	—
Soybean	887	2471	4042	4662	7361
Sunflower	—	—	NR	NR	NR
Unidentified	1	5	109	33	51
Total	1966	3464	5167	6143	9192
Pounds per person	9.2	17.3	21.3	24.2	33.7

Note: W = withheld; NR = not recorded.

oil quickly replaced the more expensive cottonseed salad oil as the preferred food processor salad oil and was cautiously introduced to the retail consumer. It became the preferred retail bottled oil during the 1960s. In the late 1970s, with improvements in the processing of soybean oil, processors were able to produce a refined, bleached, and deodorized (RBD) soybean oil acceptable to industrial customers. This improved RBD soybean oil was introduced to the retail market as "all natural" and "light." The oil appearance was almost water white. This product quickly replaced the hydrogenated, winterized, and deodorized soybean salad oil sold in retail grocery stores. Improved processing and packaging had provided a more bland flavor stable oil than the soybean oil of the 1930s and 1940s, but the U.S. consumer had also become more accustomed to the soybean oil flavor and odor which made it less objectionable.

Cottonseed oil has a unique flavor property that makes it a desirable frying medium for snack foods. Potato chips fried in cottonseed cooking oil have a pleasant nutty character, whereas other frying oils produce chips with clean potato flavors that lack the nutty note.[19] This use for cottonseed cooking oil and other industrial uses of cottonseed salad oil probably account for most of the liquid cottonseed oil usage, as the retail market of cottonseed salad oil appears to be limited to the gourmet shelves.

Corn oil is second only to soybean oil in salad and cooking oil volume, as well as for other products, and has wide consumer recognition even though it is a byproduct of corn sweetener, starch, meal, and ethanol production. Corn oil has been regarded as having exceptional flavor and quality while obtaining a healthy-oil image. Promotion of polyunsaturated oils for nutritional purposes during the 1950s and 1960s exploded the commercial use of corn oil in various foods, for snack frying, and as a retail bottled oil. Corn oil contains 69% linoleic (C-18:2), about 13% saturated fatty acids, and only trace amounts of linolenic (C-18:3) fatty acid. The distinctive musty flavor and odor developed by corn oil has popular acceptance both for home use and for prepared food products such as fried snacks and mayonnaise or salad dressings.

Peanut oil cannot be winterized to produce a salad oil because of the unfilterable gel produced with cooling; therefore, it is marketed as a cooking oil for both industrial and retail uses. Peanut oil is considered a premium cooking and frying oil because of the pleasant flavor and cost. The oil separated from peanuts maintains the pleasant peanut flavor better than the meal. Peanuts, and therefore the oil, are subject to mandatory price supports in the United States, which maintains the premium pricing; nevertheless, peanut oil maintains a respectable cooking oil market for snack and foodservice frying, as well as a retail cooking oil.

The increase in U.S. olive oil consumption over the past decade is due, in part, to promotions of the health benefits of Mediterranean dietary patterns and to market expansion from gourmet shops into supermarkets. The high monounsaturates of olive oil are being promoted by some nutritionists as being healthful. Olive oil, produced by crushing and pressing olives, has a high oleic fatty acid (C-18:1) content ranging from 55 to 83%. The Mediterranean diet is based on the findings of a Harvard University Press study[11] that concluded that the adult populations of countries such as Greece and Italy live longer. This diet allows 25 to 35% of its calories to come from fat as long as that fat is olive oil. This study linked olive oil with lowering low-density lipoprotein (LDL) (problem) cholesterol levels while maintaining high-density lipoprotein (HDL) (good) cholesterol levels. However, these results have not been observed on a consistent basis and are therefore questioned by some researchers.[11,12]

Canola oil has been offered for sale in the U.S. since 1985, when it was approved as generally recognized as safe (GRAS). Initial campaigns promoting it as "healthy oil" and showcasing its low saturates content of 6% or less were fruitful; this oil captured almost 5% of the salad and cooking oil market in a little over a decade, and the volume continues to grow.

Retail salad oil bottlers have attempted to create a market for sunflower oil on several occasions. In the early 1990s, the major branded retail salad oil producers introduced sunflower oil nationally; however, the volume generated has not been identified by the USDA in the Fats and Oils Situation and Outlook Reports to avoid disclosure of individual producer's volume. Canola oil introduced as a retail bottled oil appeared to replace most of the national market for sunflower oil. Then, sunflower oil became one of the components of the blended salad oils introduced in 1991 with a third less saturates than soybean oil. These oils were blend of soybean, sunflower, and canola oils with a 10% saturated fatty-acid content.[13] Blended vegetable oils are still marketed, but the saturates are reduced to 5 to 8% using blends of canola and corn, canola and soybean, soybean and corn, or canola, sunflower, and soybean oils.

The Nutritional Labeling and Education Act, effective May 1994, specified the information allowed on food labels. The mandatory listings on the nutritional facts panel that pertain to the content of fats and oils are serving size, servings per container, total calories, calories from fat, total fat, saturated fat, cholesterol, and vitamin A. The voluntary components, which may refer to fats and oils products, include calories from fats, potassium, and other essential vitamins and minerals. It is speculated that *trans*-isomers will be added to the mandatory listing on the nutritional facts panel.

Problem: High Impurities in the Filtered Oil

Possible Causes and Corrective Actions

1. Inadequate precoating of the filter — Recirculate until the impurities improve; if the impurities persist, stop and precoat the filter properly.
2. Holes in the filter screens, cloths, or papers — Repair or replace.
3. Improper filter assembly — Reassemble properly.
4. Worn seals or gaskets — Replace defective seals or gaskets.

Problem: Poor Bleach Color

Possible Causes and Corrective Actions

1. Low bleaching-earth level — The amount of bleaching earth to be used should be the minimum amount required to effect removal of the impurities as measured by peroxide reduction, with zero as the target. The bleaching-earth level should be guided by performance, not a mandatory addition level.
2. Short contact time — Usually 15 to 20 minutes of contact time between the oil and the bleaching earth is adequate to drive off the moisture in the bleaching earth and complete the bleaching reaction with atmospheric bleaching. In vacuum bleaching, the greatest color reduction is realized within the first 3 minutes of contact because the air and moisture are removed by the vacuum. Extending the contact time does not harm the vacuum-bleached oil because oxidation is prevented by the vacuum.
3. Low bleaching temperature — Bleaching temperatures can be increased but should not exceed 110°C (230°F). Heating of the oil should take place after the addition of the bleaching earth. A higher oil temperature reduces oil viscosity, which improves the adsorptivity of the bleaching earth; however, no significant improvements are experienced above 110°C. Problems with increased free fatty acid development, oxidation, and color fixing can result with temperatures exceeding 110°C.
4. Inadequate refining — Check upstream problems such as caustic treat or mixing in refining.
5. Bleaching-earth addition temperature — Addition of the bleaching medium to hot oil vaporizes the moisture in the earth too soon. The moisture release allows the lattice structure in the clay to collapse, which reduces the effective surface area before it has an opportunity to adsorb the color pigments and the secondary oxidation products.
6. Agitation — Bleaching-vessel agitation should be sufficient to achieve good contact of the earth with the oil without incorporating air.

Problem: High Peroxide Value

Possible Causes and Corrective Actions

1. Product skipped bleaching — Properly bleached oils have a zero peroxide value. High peroxide values for products coming out of bleaching indicate that the product has not been bleached with bleaching earth; it may have been pumped

through the system without the addition of bleaching earth because the color met the required limits before bleaching. Postbleaching is mandatory after hydrogenation to ensure that any trace metals and secondary oxidation precursors are removed. A zero peroxide value output of postbleach indicates that the product has been bleached properly.

13.2.11 Winterization

Problem: Poor Cold Test

Possible Causes and Corrective Actions

1. Filtered-oil temperature too high — Cool the oil to the proper temperature before filtering (45°F or 7.2°C).
2. Rapid cooling rate — Ensure that the oil is not cooled at too rapid a rate to produce the desired crystal; a temperature change from 104 to 45°F (40 to 7.2°C) over a 12-hour period is generally acceptable.
3. Broken screen or torn cloth — Inspect and correct the problem.
4. Leaking seals or gaskets — Inspect and correct the problem.
5. Improper filter cooling after hot-oil wash — Cool the filter to the desired temperature after each hot-oil wash.
6. Warm filter room — Keep the filter cool to prevent stearine from melting and remixing with the salad oil.
7. Mixing low and high cold-test oils — Low cold-test products should be kept separate from salad oils with satisfactory analysis. Blends of winterized oils with good and poor cold-test results normally result in a substandard cold test for the blend. A laboratory-prepared blend of the two products should be evaluated and found satisfactory prior to any blending of batches.

Problem: Slow Filtration Rate

Possible Causes and Corrective Actions

1. Cold oil — Check the oil temperature for adjustment of subsequent batches.
2. Wet oil — Moisture levels above 0.1% will cause filtration problems. Trace and correct the moisture problem to speed up filtration on subsequent batches.
3. High soap content (over 50 ppm) — Take corrective action in refining, waterwashing, or prebleaching to correct the problem for future production.
4. High phosphatide level (over 4 ppm phosphorus) — Remedy the problem upstream in the refining process for future production.
5. Overpressurization of the filter by the feed pump — Make sure that the backpressure control system is operational.
6. Blinded screens — Externally wash blinded screens.
7. Winterized-oil crystal abuse — Do not pump or recirculate winterized oil any more than absolutely necessary before filtration; fractured crystals filter slowly.
8. Low chill-tank loading temperature — Improper graining, which affects the filtration rate, results from cool chill-tank loading temperatures. The chill-tank supply oil temperature should be adjusted to meet the established limits before loading.

Problem: Poor Salad Oil Yield

Possible Causes and Corrective Actions

1. Long graining or chilling time— The solidified oil can entrap the liquid oil decreasing the salad oil yield.
2. Hydrogenation conditions— The hydrogenation conditions for oil to be winterized for salad oil should produce the least possible saturates and trans isomers while reducing the linolenic fatty acid (C-18:3) content. Nonselective hydrogenation conditions of low temperature, high pressure, and a low catalyst concentration normally produce the desired low saturates and trans isomers.
3. Low chilling temperatures— High viscosities caused by low crystallization temperatures inhibit the desired crystal growth. Filtration efficiency is dependent upon the crystal size and entrapped liquid oil within the crystal matrix.

13.2.12 Dewaxing

Problem: Poor Filtration Rate

Possible Causes and Corrective Actions

1. Sunflower oil temperature— Crystallization and maturation require gradually cooling the oil to 40 to 50°F (4.4 to 10°C) for stable crystals; however, the viscosity does not allow an acceptable filtration rate at this temperature. Heating the oil up to 54 to 57°F (12.2 to 13.9°C) increases the filtration rate approximately 60%.
2. Gums— It is necessary to remove gums before dewaxing. The presence of gums in the oil influences the formation and stability of the formed crystals to diminish the filtration rate of the oil. Dewaxing should be performed after prebleaching and prior to deodorization.
3. Diatomaceous earth addition— The addition of small amounts of diatomaceous earth to cold sunflower oil has been reported to increase the filtration rate by a factor of four.[17]

Problem: Wax Content

Possible Causes and Corrective Actions

1. Hybrid sunflower oil— Hybrid sunflowers that have replaced the open-pollinated varieties have improved plant uniformity, yields, and disease resistance; however, the higher oil-content seeds with reduced hull content have increased wax levels in the hull, and the hulls are more difficult to separate from the kernels when processing to extract the oil. The soluble waxes in the oil at ambient temperature will cause an unsightly cloudy appearance at cooler temperatures. Dewaxing is required to maintain a clear sunflower oil.
2. Hulled vs. dehulled sunflower seeds— The wax content in sunflower oil is dependent upon the seed handling practices. Sunflower oil from dehulled seeds will generally contain 0.011 to 0.015% waxes, whereas seeds with hulls provide waxes in the 0.06 to 0.09% range.[17]

13.2.13 Esterification

Problem: High Color

Possible Causes and Corrective Actions

1. Air contact — Fatty emulsifiers must be protected from air incorporation throughout the alcoholysis process to prevent oxidation of the unsaturated fatty acids or the D-tocopherols with attendant color development. Some potential air sources during fatty emulsifier production are (1) air leaks in fittings below the product level and in pumps, as well as holes in the reaction vessel, heaters, and coolers; (2) improper deaeration of the reaction mixture; and (3) the stripping steam must be generated from deaerated water to be oxygen free.
2. Basestock hydrogenation catalyst — Emulsifier basestocks must be free of the residual nickel that catalyzes oxidation. Reused catalyst can cause filtration problems for two reasons. The first is that the free fatty acids in the hydrogenation feedstock react with the nickel catalyst and form nickel soaps, which pass through filters. Second, the reuse catalyst particle size may have been reduced to sizes that will not be retained on the filter; only new, easily filtered catalyst should be utilized for emulsifier basestocks.
3. Basestock postbleaching — Hydrogenated oils require postbleaching to remove traces of nickel from the finished product. Nickel soaps formed during hydrogenation are oil soluble and remain in the oil after filtration. Addition of 100-ppm citric acid prior to postbleaching will chelate the remaining nickel for more efficient filtration after bleaching. Additionally, the hydrogenated basestock must be bleached with bleaching earth, even when the analytical color limits indicate that bleaching is not required to obtain the specified color. A zero peroxide value indicating removal of secondary oxidation materials is also a prerequisite for emulsifier basestock postbleaching.
4. Nitrogen protection — Relatively low levels of oxidation prior to alcoholysis can significantly impair the oxidative stability of the finished emulsifier. Quality products require a minimum of oxygen exposure before processing, which necessitates effective nitrogen blanketing of all emulsifier basestocks during storage or transportation, including the low-iodine-value bases.
5. Oxidized tocopherols — D-Tocopherol oxides to a very colorful chroman-quinone, which is probably catalyzed by excessive alkalinity of the processed oil or emulsifier at some point during processing of oils, basestocks, or emulsifiers.
6. High discharge temperature — Proper cooling while protected by the vacuum before exposure to the atmosphere is mandatory for oxidative stability and color control. The product discharge temperature must be as low as possible while still maintaining the product as a fluid, pumpable product.
7. Catalyst selection — Less color development in mono- and diglycerides has been experienced with the use of calcium hydroxide as opposed to sodium hydroxide.[18]
8. Filter aid — Only neutral filter aids should be utilized for emulsifier filtration. Modified filter aids can have deleterious effects upon the emulsifier color.
9. Rust — Iron oxides are soluble in monoglycerides and many other emulsifiers. Rust, from washed black-iron surfaces that are not protected or sweetened with oil immediately, will cause darker emulsifier colors.[19]

10. High feedstock color — The color of the feedstock to the reaction should be analyzed to ensure that a color reversion has not occurred between the postbleach process and the glycerolysis feedstock tanks.
11. Incomplete neutralization — The presence of catalyst will catalyze red color development. Neutralization should be confirmed with soap or pH analysis to ensure that the catalyst has been properly neutralized. It is important to maintain a pH of <5 for color stability.
12. Carbon steel reaction vessel — Ordinary carbon steel is not a suitable material for reaction vessels, as it contaminates the product with iron soaps, which cause dark-colored product. Stainless-steel equipment and vessels are preferred.[18]
13. pH control — An emulsifier pH of <5 is necessary to maintain color stability in storage.[20]

Problem: Low α-Monoglyceride Content

Possible Causes and Corrective Actions

1. Reversible reaction — Esterification is a reversible reaction, especially in the presence of a catalyst at elevated temperatures. Reversion of monoglyceride occurs at the point of reaction completion before catalyst neutralization or after if neutralization is incomplete. During cooling prior to glycerol removal, the excess glycerine is less soluble in the fat phase and separates into the lower layer. This shifts the equilibrium somewhat to regenerate diglycerides and triglycerides; therefore, catalyst neutralization and excess glycerine removal are critical stages of glycerolysis, which must be performed with close and precise control.[19]
2. Excessive steam stripping — Most emulsifier specifications allow a 1.0 to 1.5% free fatty acid limit to allow steam stripping to be suspended before the monoglyceride content is reduced below the specified limits.
3. High reaction temperature — The reaction should be performed within a temperature range of 175 to 250°C (347 to 482°F). Higher temperature reactions cause the formation of polyglycerols and polymerized glycerides, which affect both the monoglyceride yield and functionality of the emulsifier product.
4. Low reaction temperature — Glycerolysis is temperature dependent. The monoglyceride level is determined by the glycerol miscibility in oil. For example, no more than 45% monoglyceride can be obtained with a 180°C (356°F) reaction temperature.
5. Low level of glycerin to reaction — It is necessary to maintain the prescribed glycerine level in the reaction mixture to obtain the specified monoglyceride content. Two usual causes for a low glycerin level in the reaction have been (1) incorrect amount added, and (2) glycerin flashed off before the reaction. An incorrect addition level can be a result of calculation error, incorrect pumping, pump failure, etc. Glycerin can be flashed off or lost to entrainment due to high temperature, high vacuum, or stripping steam use during the drying process.
6. Low catalyst level — The amount of reactive glycerin depends upon the level of catalyst used; therefore, additions of catalyst at low levels will result in low monoglyceride contents. A low catalyst level may be a result of a calculation error, a higher dilution than specified, faulty addition procedures or equipment, an excess of other reactants, etc.

7. Incomplete catalyst neutralization— Catalyst presence at the end of the reaction enhances the potential reversion of the monoglyceride reaction. Catalyst neutralization should be monitored by soap content or pH analysis or both. A high soap content or an alkaline pH indicates incomplete catalyst neutralization.
8. Acid addition procedure— Phosphoric acid must be added slowly to allow for proper dispersion. Rapid addition of the neutralization acid, especially with poor agitation, will allow it to drop to the bottom of the reactor, where it can be ineffective. Insufficient catalyst neutralization will allow the reaction to reverse during stripping of the excess glycerine for a low active emulsifier content.
9. Low reaction time or temperature— A low reaction temperature or time can provide an incomplete reaction for a low monoglyceride or propylene glycol monoester (PGME) content, depending upon the product being produced.
10. Reused glycerine— Monoglyceride yield can decrease with the use of recycled glycerine from previous production. Phosphate salts are formed when the catalyst is neutralized with phosphoric acid. Trisodium phosphate is formed by the reaction of the acid with the catalyst, but the excess acid used forms NaH_2PO_4 and some Na_2HPO_4. Trisodium phosphate is crystalline and can be easily removed by filtration; however, the acid salts are not crystalline and remain dispersed in the product. It is necessary to mix the molten still residue with diatomaceous earth to remove these acid phosphates salts by filtration or with a centrifuge.[20]

Problem: Impurities

Possible Causes and Corrective Actions

1. Phosphate salts— Impurities identified as phosphate salts have been found in products shipped to customers shortly after production. Studies have determined that glycerolysis catalyst neutralization is related to time and temperature; at 350°F (176.7°C), neutralization is completed within 10 minutes, whereas it requires 8 to 12 hours at 190°F (87.7°C). Emulsifiers neutralized at low temperatures may require a holding time before filtration or a second filtration to remove all of the phosphate salts.
2. Early delivery— During the startup cycle of the phosphate salt filters, care must be exercised to recycle the initial cloudy emulsifier instead of contaminating the emulsifier storage vessel.
3. Filter-screen holes— Stream and representative batch samples must be evaluated for clarity to determine that the filters are operating satisfactorily. Positive impurities in any of these samples identifies a problem that must be investigated and a solution determined before proceeding.
4. Neutralization— Filtration is affected by the type of phosphate salt produced. Trisodium phosphate is the most desirable because it is crystalline and can be easily removed by filtration; however, the excess phosphoric acid used to produce an acidic pH also produces acid salts. These salts, NaH_2PO_4 and some Na_2HPO_4, which are not crystalline, are difficult to filter and usually remain dispersed in the product. A suggested remedy to remove acid salts is to use diatomaceous earth as an absorbent prior to filtration.[20]

Problem: High Free Fatty Acid

Possible Causes and Corrective Actions

1. Excessive acid neutralization — Phosphoric acid is normally used to neutralize the alkaline catalyst. Excess phosphoric acid usage will be revealed during analysis as free fatty acids and catalyzed additional free fatty acid development.
2. Insufficient stripping — Free fatty acids are removed by steam distillation after the reaction has been terminated. Insufficient steam distillation will not effectively reduce the free fatty acid level; however, overstripping can reduce the monoglyceride content.
3. Wet reactants — Addition of moisture to the reaction will cause hydrolysis, which results in free fatty acid development. A higher free fatty acid level may require additional stripping to meet the required limits, which may in turn lower the monoglyceride content. Wet feedstocks or glycerin can be caused by moisture contamination from wet steam, steaming lines into the storage tanks, leaks in the heating or cooling coils, or the like. The source of the moisture must be identified and the reactants dried before use.

13.2.14 Blending

Problem: AOM Stability

Possible Causes and Corrective Actions

1. Soft basestock addition — Blending a mix with a soft, unspecified basestock will decrease the oxidative stability of the product. Blends should be made only with the basestocks specified to maintain the designed AOM stability of the finished product.
2. Exceeding composition tolerances — Blending with a specified basestock outside the specification tolerances will affect the oxidative stability of the product.
3. Salad oil stearin usage — Natural antioxidants accumulate in the liquid fraction of a winterized or fractionated product; therefore, the stearin fraction has less oxidative protection than oils with the same hardness produced from regular source oils.

Problem: Government Regulations Compliance

Possible Causes and Corrective Actions

1. Ingredient statements — U.S. Food and Drug Administration labeling regulations require identification of each source oil in descending order of predominance. Blending changes outside the specified composition and tolerances can violate the ingredient statement requirements.
2. Nutritional claims — Nutritional claims are made for edible fats and oils products based on the fatty acid compositions of individual products. In most cases, the product tolerances must be established based on the allowed rounding of the values. Blending outside the specified composition tolerance range or with unauthorized basestocks will result in product characteristics outside the nutritional claims. In this case, there is no good or bad — just right or wrong.

Problem: Solids Fat Index Compliance

Possible Causes and Corrective Actions

1. Basestock blending — Fats and oils mixes made with basestocks previously blended for solids fat index (SFI) limits compliance will not have the same effect upon subsequent blends as hydrogenated basestocks produced in limits. Both the fatty acid composition and the triglyceride composition are changed with each blend.
2. Sampling technique — Fats and oils blends should be agitated a minimum of 20 minutes at 10°F (5.6°C) above the expected melting point of the blend. Prior to sampling, the sample line and valve must be flushed with the current product to remove all previous product residue, and the sample container must be clean.
3. Incorrect pumping — Errors in pumping should be indicated first by a high or low melting point analysis. Material balance and a review of the product transfers should help identify the resultant blend composition for determination of corrective actions.

Problem: Poor Performance

Possible Causes and Corrective Actions

1. Substitution basestocks — Substitution or addition of a nonspecified basestock may meet the analytical limits specified but affect the performance of the product. Only specified basestocks should be used for blending. The product composition specified represents the product developed and approved by the customers. Product consistencies and performance are dependent upon compositions as much as, and sometimes more than, the analytical values. It may be possible to meet the specified analytical limits with several different basestock blends, but only one will perform properly.

13.2.15 Deodorization

Problem: High Free Fatty Acid

Possible Causes and Corrective Actions

1. Low vacuum — Identify and correct the vacuum problem. Refer to the poor deodorizer vacuum section for possible problems and solutions.
2. Low oil temperature — Increase oil temperature.
3. High oil-flow rate — Increase residence time by reducing the flow rate.
4. Poor steam distribution — Clean steam sparge ring.
5. Too high or too low sparge steam pressure — Reduce if too high or increase with extreme caution if too low.
6. Supply oil has high free fatty acid — Recirculate to attain the specified free fatty acid level but identify upstream problem and correct for subsequent production.
7. Excessive shell drain (semicontinuous deodorizer) — Drain more frequently until the reason for the increased shell drain can be identified and corrected.
8. High CO_2 content in nitrogen gas — CO_2 will analyze as free fatty acid. It can be determined that CO_2 is causing the high result by evacuating all the gases from

the oil sample with a vacuum and retesting for free fatty acid content. A lower free fatty acid result would indicate CO_2 contamination of the nitrogen gas supply, probably at the in-house gas generating plant. Correction of the gas plant problem or purchase of liquid nitrogen would be two potential corrective actions.

9. Chelating acid addition — Typical chelating acid addition levels are 50 to 100 ppm citric acid or 10 ppm phosphoric acid; 0.0022% citric acid analyzes as 0.01% free fatty acid.[21] The expected free fatty acid rise, due to chelating acid addition, must be accounted for in the equipment design and development of specification limits.
10. Antioxidant addition — Antioxidants will contribute to the apparent fatty acid content because the analytical method does not distinguish between acidity contributed by fatty acids or mineral acids. The free fatty acid level of the deodorized oil must be low enough to allow for the increase contributed by antioxidants and acid chelates.
11. Instrumentation accuracy — Preventive maintenance should be performed on a regular basis and instruments recalibrated whenever poor performance is suspected.
12. Phosphoric acid overdose — Oils are acid treated prior to refining and bleaching to reduce the phosphorus content and chelate the trace metals and again after deodorization to chelate metals. Phosphoric acid is usually less expensive and more effective than the alternative citric acid; however, it has been found to form compounds with the partial glycerides and carbohydrates in the oil, making it difficult to achieve the desired free fatty acid content, or the level of free fatty acids may rise rapidly during storage. These reactions are not experienced with citric acid until the treatment level is increased substantially.

Problem: Dark Oil

Possible Causes and Corrective Actions

1. High soap content — The problem batch must be rebleached and redeodorized to remove the soap and reduce the color. The cause of the problem upstream in refining or prebleaching should be identified to prevent future problems.
2. High phosphatides content — Deodorizer feedstocks with a phosphatide content above 20 ppm will cause high deodorized oil colors. The phosphatides must be removed in refining and bleaching before the deodorization process. Some of the phosphatides and their associated metal complexes are not easily hydratable. These complexes require a phosphoric acid pretreatment for their removal in degumming or refining. The prebleach process removes the traces of soap and phosphatides remaining after the refining process. Oils that do reach the deodorizer with high phosphatide contents will have a darker color and a characteristic fishy odor after deodorization. These products must be bleached and then redeodorized to salvage the oils.
3. Rework quality — A color problem, in most cases, can be corrected with rebleaching and redeodorization, but it may require blending at low levels with subsequent batches. In extreme cases, it may be necessary to sell it as off-quality product. The reclaiming method should be thoroughly evaluated before execution.
4. Secondary oxidation — Oils with severe oxidation abuse will develop a reddish-orange color that will heat bleach readily; however, the secondary oxidation products must be removed with bleaching for oxidative and color stability. Identification of the cause of the oil abuse (probably aeration or overheating) and correction must be given top priority to prevent continuation of the problem, which requires additional processing and affects product quality.

5. Proteinaceous material — Meat fats containing proteinaceous material will turn black in the deodorizer. More effective filtering or water washing of meat fats is required to eliminate this problem. The charred protein material, developed in the deodorizer, can be removed with bleaching.
6. High-temperature air contact — Fats and oils must be protected from air incorporation throughout deodorization to prevent oxidation with attendant color development. Some of the potential air sources during deodorization are (1) air leaks in fittings below the product level, in pumps, holes in the deodorizer shell, heaters, and coolers; (2) improper deaeration of the feedstock; and (3) stripping steam not generated from deaerated water and thus not oxygen free.
7. High discharge temperature — The oxidation rate for edible oils almost doubles with each 20°F rise in temperature; therefore, proper cooling of the oil before it exits the deodorizer is mandatory for oxidative stability, as evidenced by color, peroxide value, and flavor evaluations.
8. Low deodorizer temperature — The thermal treatment that is a necessary part of the deodorization process also heat bleaches the oil by destruction of carotenoids that are unstable at deodorization temperatures. Because the carotenoid pigments can be decomposed and removed at approximately 500°F (260°C), the high side of the normal deodorization temperatures — 400 to 525°F (200 to 274°C) — should deliver the heat bleach desired. However, the maximum deodorizer temperature that can be used must be limited because of the detrimental effect upon oil stability.
9. Oxidized tocopherols — D-Tocopherol oxidizes to a very colorful chromanquinone. The opportunities for oxidation must be evaluated and the cause eliminated for further production. The immediate product must be rebleached to remove the oxidized tocopherol and other secondary oxidation products.
10. Crude-oil storage — Storage of crude oils in contact with atmospheric oxygen can cause oxidative damage, which is ultimately reflected in the quality of the processed oil. Vegetable oils with the lightest colors and the best oxidative stability are either processed immediately or protected with nitrogen immediately after extraction.
11. Phosphoric acid overdose — Oils are acid treated prior to bleaching to reduce the phosphorus content and chelate the trace metals. Phosphoric acid is usually less expensive and more effective than the alternative citric acid; however, it has been found to form compounds with the partial glycerides and carbohydrates in the oil that darken in the deodorizer. Additionally, it may be difficult to achieve the desired free fatty acid content, or the level of free fatty acid may rise rapidly during storage. These reactions are not experienced with citric acid until the treatment level is increased substantially.

Problem: Rapid Peroxide Value Increase after Deodorization

Possible Causes and Corrective Actions

1. Inaccurate analysis — All laboratory utensils must be rinsed with distilled water to remove all traces of soap or detergent which cause high peroxide value results.
2. Light exposure — The deleterious effects of light exposure upon the flavor stability of edible oils is well known. Even limited exposure of the oil to sunlight or ultraviolet rays from fluorescent lightening will increase the peroxide value of the oil and impart off-flavors. Samples from any process should be protected from the light to ensure a representative analysis of the product. Clear glass or plastic containers should not be used to sample in-process oils.

3. Washed tanks — Process tanks must be rinsed with clear water, neutralized, and sweetened with an oil rinse after washing to remove all traces of soap or detergent.
4. Chelating acid addition — 30 to 50 ppm citric acid or 10 ppm phosphoric should be added in the deodorizer cooling tray to chelate metals. Problems with acid addition may be caused by a broken or clogged addition line, an empty acid-supply tank, incorrect preparation of the acid solution, the system being shut off, or something similar.
5. Deodorizer discharge temperature — Rapid oxidation of deodorized oils must be avoided by controlling the oil temperature in the cooling stage before exposure to the atmosphere. Liquid oils high in polyunsaturates should be cooled from 100 to 120°F (38 to 49°C). Higher deodorizer discharge temperatures are necessary for higher melting products but should be maintained as low as possible. The speed of oxidation is doubled with each 27°F (15°C) increase in temperature within the 70 to 140°F (20 to 60°C) interval.
6. Secondary oxidation — The immediate batch may be salvaged by rebleaching with bleaching earth followed by redeodorization; however, the source of the abuse should be identified to prevent a recurrence with subsequent production.
7. Air incorporation — Repair pumps or other sources of air incorporation after deodorization.
8. Polymerized oil buildup — Peroxide values increases can be caused by a buildup of polymerized or oxidized oil, which mixes with the oil in process. The corrective action is to wash the deodorizer. To prevent these problems from occurring, a regular washout schedule should be established. It should be standard procedure to wash the deodorizer every 6 months if it is not operated continuously 7 days a week, or the operation is subject to power failures. Otherwise, deodorizers should not be operated more than 12 months without a thorough washout.[21]
9. Prior oxidation — It is very important that oxidation be prevented during all stages of edible fats and oils processing because of the detrimental effects upon the finished deodorized oils. For example, it has been estimated that a peroxide value increase of only 1.2 meq/kg in neutralized soybean oil after refining may reduce the oxidative stability of the deodorized oil by 50%.[22] Oxidation during processing can be minimized by avoiding contact with air, elimination of prooxidant metallic contaminants, nitrogen protection at all stages of processing, or addition of antioxidants at the initial stages of processing.

Problem: High Loss

Possible Causes and Corrective Actions

1. Excessive blowing steam — A 15% increase in sparging steam will double the entrainment loss, and a 35% increase will result in a fourfold loss; therefore, maintaining the proper blowing-steam level is essential to controlling deodorizer entrainment losses.
2. Wet blowing steam — Make sure that the steam pressure to the deodorizer is within specified limits.
3. Wet oil — Dry wet oil before deodorization to control entrainment loss and evaluate the feedstock origin, and eliminate the moisture source for future production.
4. Charge or batch size — Ensure that the deodorizer charge or batch size does not exceed the capacity.

5. High free fatty acid feedstock — Determine and correct the upstream cause to avoid continued high losses.
6. Leaking drop valves — Timely maintenance is necessary to prevent or repair leaking valves that cause erratic temperature recording and overflowing deodorizer trays.
7. Leaking trays — An increase in the deodorizer shell drain indicates leaking trays that need repair.

Problem: Contamination with Another Product

Possible Causes and Corrective Actions

1. Mixing in the measuring tank — Blow the supply lines into the measuring tank, followed by evacuation of this vessel with the deodorizer vacuum to prevent product heels.
2. No empty trays between products (tray-type deodorizers) — One or two empty trays should separate products that are somewhat similar.
3. No flush oil — Dissimilar products should be separated by flushing the system with a minimum of the first two trays of the new product.
4. Nonrepresentative sample — The sample line and valve must be thoroughly rinsed with the product to be sampled to remove all congealed, oxidized, or gummy deposits; the sample container must be absolutely clean; all products must be liquid when sampled; and the samples must be adequately identified by product and source to avoid sample confusion.

Problem: Reverted Oil Flavor

After deodorization, certain oils develop objectionable flavors that may not be recognized as oxidative in nature. This flavor, representative of the original crude oil, has been described as reversion.

Possible Causes and Corrective Actions

1. Air exposure — Oils containing linoleic and linolenic fatty acids are subject to flavor changes with minimal exposure to air or oxygen of less than 1.0%.
2. Crude vs. refined storage — Most edible oils, with the exception of cottonseed oil, store best in the crude state. Degummed crude soybean oil oxidizes more rapidly than nondegummed crude oil. Apparently, the phospholipids in crude oil provide an antioxidant function above that of the natural antioxidants or tocopherols.
3. Temperature control — The rate of oxidation or reversion is dependent upon temperature. Evidently, oxygen will diffuse into and react with the oil faster at higher temperatures. The oxidation rate approximately doubles with each 20° F (11.1°C) temperature increase; therefore, the rule of utilizing a temperature that is only 10°F above the melting point of the product should be enforced to control reversion.
4. Nitrogen blanketing — Nitrogen blanketing of all tanks is an effective means of protecting edible fats and oils. Peroxide development and flavor instability can be

virtually eliminated by keeping oxygen away from the oil at all stages of processing. Evaluations of soybean oil stored several months with and without nitrogen protection showed a decidedly more rapid flavor deterioration for the oil stored without nitrogen protection.

5. Phosphatide removal — Residual phosphatides will contribute to off-flavors and colors. Some of the phospholipids and their associated metal complexes are not easily hydratable. Removal of these complexes requires phosphoric acid pretreatment in degumming or refining. The preferred process cleans up traces of soap and phosphatides remaining from the refining process. Problems will develop with the deodorized oil if the feedstock has a phosphatide content above 20 ppm.
6. Bleaching-earth filtration — Complete removal of the bleaching medium from the bleached oil is very important because residual earths can act as a prooxidant. The bleaching operation should be combined with filterable impurity evaluations to ensure that the bleached oil transferred to storage or the next process is free of any contaminants that could decrease the oxidative stability.
7. Vacuum bleaching — The primary function of the bleaching process is to remove peroxides and secondary oxidation products. Secondarily, the process cleans up traces of soap and phosphatides remaining after the refining step and adsorption of color pigments. Vacuum bleaching is more effective than atmospheric bleaching. It usually requires less bleaching earth, operates at lower temperatures, and minimizes oxidation by reducing exposure to air and providing an opportunity to cool the oil before returning to atmospheric conditions.[33]
8. High peroxide value before deodorization — Contrary to most beliefs, no significant oxidation breakdown products are removed by deodorization; the only opportunity to remove them is during the bleaching process. The thermal decomposition of peroxides is complete with deodorization, but the rate of peroxide formation in the oil during subsequent storage is increased and the flavor stability of the finished oil is compromised. Rebleaching before deodorization, when the peroxide value has been allowed to increase, is necessary for adequate flavor stability.[33]
9. Deodorizer temperatures — Normally, deodorization temperatures range from 400 to 525°F (200 to 274°C). The deodorization process is time and temperature dependent; lower temperatures require longer times, and higher temperatures require shorter times. Even though elevated temperatures have a favorable effect upon deodorization efficiency, excessive temperatures are detrimental to flavor stability. Twice as many tocopherols are stripped out of the oil at 525°F (275°C) as at 465°F (240°C); therefore, for flavor stability, the lowest practical deodorization temperature should be utilized.
10. Reduced stripping-steam flow — Inability to maintain acceptable oil quality when the deodorizer temperature, vacuum, and feed rate appear normal may be caused by a reduced or restricted stripping-steam flow. It may be necessary to redrill the sparger holes if a boil-out does not correct the problem.
11. Avoid air contact — Fats and oils must be protected from exposure to air throughout deodorization. An oil reacts rapidly with oxygen at deodorizer temperatures with deleterious effects upon flavors and oxidative stability. Potential air sources are (1) air leaks in fittings below the product level, in pumps, holes in the deodorizer shell, heaters, and coolers; (2) improper deaeration of the feedstock; and (3) stripping steam not generated from deaerated water and thus not oxygen free.
12. Chelating agent — Addition of citric acid (0.005 to 0.01% based on the weight of the oil) or phosphoric acid (0.001% based on the weight of the oil) before and

after deodorization helps protect against oxidation and reversion. The acid inactivates the trace metals, particularly iron and copper, which may be present in the crude oil or picked up during processing. These acids decompose rapidly at temperatures above 300°F (150°C). The usual practice is to add the acid during the cooling stage in the deodorizer, during bleaching, and prior to caustic refining. Excessive amounts of phosphoric acid can lead to the development of watermelon- or cucumber-type off-flavors, even with good oxidative stability results.

13. Antioxidant replacement — Fats and oils resist oxidation until the antioxidants are destroyed during the induction period, the interval when oxidation proceeds at a slow rate. After the antioxidant ceases to function as a free-radical terminator, a rapid increase in the rate of peroxide development occurs. Replacement of the destroyed antioxidants with tocopherols or synthetic compounds will significantly improve the oxidative stability of the oil.
14. Light exposure — The deleterious effects of light exposure on the flavor stability of edible oils is well known. Even limited exposure of the oil to sunlight or ultraviolet rays from fluorescent lightening will increase the peroxide value of the oil and impart off-flavors. Samples from any process should be protected from light to ensure a representative analysis of the product. Clear glass or plastic containers should not be used to sample oils in process.
15. Blend stocks before deodorization — Shortenings, margarines, and some salad oils are blends of two or more base stocks or oils to achieve the desired product characteristics. Blending of these stocks before deodorization, rather than after, minimizes the handling and storage of the deodorized oil. It also allows process control to determine if the product has been abused inadvertently. This practice also allows the product to be bleached prior to deodorization when needed for the removal of the secondary oxidation products.
16. Boiler-water treatment — Additives to treat boiler water can provide puzzling flavor results.

Problem: Poor Deodorizer Vacuum

Possible Causes and Corrective Actions

1. Air leaks — Verification of air leaks can be accomplished with a drop test. This test is performed by closing the oil inlet and discharge line valves and then quickly shutting off the steam and water to the vacuum system. The vacuum may drop rapidly at this point, but it should stabilize at a value that must be above 20 inches for a valid test. Then the vacuum should be noted each hour to determine if the drop is within the limits identified by the deodorizer manufacturer. If the vacuum loss exceeds the design limits, tighten all piping connections, valve packing glands, and equipment flanges. If vacuum loss continues after these measures have been taken, the source of the leak may be identified with one of the following test methods:
   - Soap detection test — Large leaks may be detected by painting all possible leak sources with a soapy water solution while the system is under 1.3-bar (20-psig) air pressure. Bubbles should form at the leak points. Mark the leaks, release the pressure, purge the system with air, repair the leaks, restore the equipment and instruments, and then repeat the drop test to determine if the vacuum loss still exceeds the satisfactory rate. If so, smaller leaks can be identified with the next evaluation.

- Ammonia/sulfur dioxide test — Prepare the system by closing all valves, blind the vacuum system tailpipes, disconnect the vacuum gauges, and admit ammonia gas until the system pressure reaches 0.3 bar (5 psig) and then further to 1.3 bar (20 psig) with compressed air. Examine the system by directing a small stream of sulfur dioxide gas around the possible leak points. White fumes indicate the presence of a leak. Mark the leaks, release the pressure, purge the system, and then repair the leaks.[21]

2. High-temperature condenser water — When the vacuum-system water is recirculated through a cooling tower, the average wet-bulb temperature is a parameter used for the system design. Cooling towers will cool water to within a few degrees of the wet-bulb temperature. Normally, the wet-bulb and the corresponding water temperature chosen will not be exceeded 5% to 10% of the time in the summer months; however, the oil quality must be closely monitored during the warm summer days when the warm condenser water prevents operation at the desired vacuum.
3. Other operational problems — Two other problems, in addition to those already reviewed, are (1) low steam pressure or wet steam to the vacuum jets, and (2) insufficient condenser water for one reason or another. Both of these conditions require maintenance or at least investigation to identify the source of the problem for corrective action and installation of preventive measures for the future.
4. Vacuum maintenance — If operational problems are not the cause of a poor vacuum, the steam nozzles, steam chests, and throat of the booster should be examined for wear. Replacement of the worn parts and adoption of a preventive maintenance program to regularly review the vacuum systems should help relieve the poor vacuum problems.

Problem: Poor Steam-Ejector Operation

Possible Causes and Corrective Actions[24]

1. Low steam pressure — This may be caused by clogging of the steam strainers or orifice plates with pipe scale or sediment, improper operation of the steam pressure regulating valve, or low boiler pressure. A steam pressure gauge for measuring the operating pressure should be installed at a point close to the ejector steam inlet in order to determine the true operating pressure.
2. Steam nozzles — In addition to the possibility of a nozzle clogging from pipe scale or dirt, a scale deposit might occur in the throats of the steam nozzles from impurities in the steam. When this occurs, it is necessary to clean out the nozzle with a proper size reamer or drill, taking care not to mar the internal surfaces.
3. Insufficient cooling water — The temperature of water entering and exiting the ejector condensers should be measured. If the temperature rise is not excessive, the cooling water supply is adequate and the source of the problem should be sought elsewhere.
4. High back pressure at ejector discharge — The pressure at the final stage exit should be measured. Excessive pressure indicates that the piping should be changed to reduce the discharge pressure.
5. Nozzle and diffuser wear — Operation of the ejectors with wet steam or corrosive gases or vapors will cause excessive wear and produce a rough wall surface. Periodic checks should be made to compare the throat diameter of the diffuser and nozzle with the original sizes to determine if replacement is required.

13.2.16 Antioxidant Addition

Problem: Antioxidant Activity

Possible Causes and Corrective Actions[25–27]

1. Incomplete dispersion — Dispersion problems may result from inadequate mixing equipment, poor mixing techniques, or shortcuts in procedures established for the antioxidant addition. Several acceptable addition methods are practiced; one of which is outlined below:
   - The quantity of the batch must be large enough to allow adequate mechanical agitation; simply stated, the product must cover the agitator in the tank used for effective mixing.
   - The temperature of the product must be maintained at least 10°F (5.6°C) above the melting point, but not so high that it allows oxidation before addition of the antioxidant.
   - Determine the proper antioxidant quantity for the individual product and weigh antioxidants with a laboratory balance for each batch.
   - Slurry the antioxidant in a portion of the product with vigorous mechanical agitation.
   - Add the slurry to the agitating product tank at a temperature of 10°F (5.6°C) above the melting point of the product.
   - Continue agitation of the batch for a minimum of 20 minutes before sampling.
   - Sample and obtain a positive qualitative antioxidant analysis before packaging or shipping in bulk quantities.
2. Vessel agitation — Addition of a concentrated antioxidant mixture before agitation begins will result in a high level of the additive in a portion of the product while the major portion has little or no antioxidant present. This practice will produce serious stability deficiencies for most of the product, and the very high concentration of antioxidant in the oil at the bottom of the vessel will result in performance problems. First and last piece product evaluations from packaged product should identify this problem. Tank truck or railcar products may indicate a negative antioxidant analysis for the as-shipped sample when the antioxidant is added to the shipper after loading of the oil product has been completed.
3. Improper antioxidant levels — Maximum antioxidant levels are defined by U.S. regulatory agencies. The allowed levels are generally recognized as the optimum for achieving good stability results. In general, successive additions of an antioxidant yield steadily diminishing returns. At higher concentrations, an appreciable portion of the antioxidant is consumed by side reactions and thus does not function as a free-radical terminator. In some cases, decomposition of the antioxidant may produce substances with prooxidant action.
4. Antioxidant storage conditions — Proprietary antioxidant mixtures formulations are available from several suppliers. These mixtures vary in active ingredient contents and the solvent systems utilized to dissolve the antioxidant and keep them in solution until use. Separation or crystallization or other changes can occur if the products are handled improperly. Most antioxidant mixtures solidify at temperatures below 32°F (0°C), but the heating required to liquefy has no detrimental effect on antioxidant properties. Deterioration occurs when the antioxidants are heated above 200°F (93.3°C) for extended periods.

5. Incorrect antioxidants— Significant performance differences exist among the antioxidants in different source oils, processing, and handling conditions. Consideration of the antioxidant type or mixture formulation to be used must be made during product development. Substitution of one antioxidant for another cannot be allowed because of performance and specialized labeling requirements. Each individual synthetic antioxidant must be identified by the prescribed nomenclature in the ingredient statement on the label.
6. Addition stage— Natural and synthetic antioxidants are removed from edible oils during processing, notably by refining, bleaching, and deodorization. Antioxidants can be added to oils at an early stage for protection, but it should be recognized that deodorization will destroy the antioxidants. In this case, the antioxidants will have to be added again after deodorization for oxidative protection.
7. Addition point— Antioxidants will not rejuvenate mistreated fats and oils products. Phenolic antioxidants function by inhibiting free-radical formation, the initial step in oil oxidation; therefore, it is essential that the addition point occurs as soon as reasonably possible after deodorization before the autoxidation reaction has a chance to start.
8. Low antioxidant level— Analysis of the antioxidant level in the finished product will reveal a lower level than was actually added. The antioxidant level decreases as it functions to intercept oxygen before it can attack the fats and oils products.
9. Induction period— The initial period of relatively slow oxidation is called the induction period. Antioxidants prolong the induction period but have no effect after the end of the induction period. Once oxidation has started, the rate is as rapid as experienced with unprotected fats or oils.
10. Prior abuse— Edible fats and oils that have been allowed to oxidize significantly before deodorization will have a poor stability after deodorization. This is because of the formation of oxidation products, which are odorless and tasteless and carry through into the deodorized product, where they initiate and propagate further oxidation. Antioxidant addition to these used oil products will have little or no stabilizing effect. Antioxidants cannot reverse or terminate the autoxidative process after it has passed the early stages.
11. Tocopherols— Tocopherols, natural antioxidants, attain maximum effectiveness at comparatively low levels, roughly equivalent to their natural level of occurrence in vegetable oils. Tocopherol levels above the optimum concentration usually function as prooxidants.

13.2.17 Bulk Railroad Car or Truck Loading

Problem: Impurities

Possible Causes and Corrective Actions

1. No analysis— Evaluate each product load before the shipment is released, and refilter each load that does not meet established limits, followed by upstream evaluations to determine the cause for the impurities.
2. Poor sample— All trucks and cars should be done sampled after loading is completed, while the product is still liquid, to identify problems before shipment. Dip samples, which are easier to obtain, evaluate only the surface oil on the top of the tank. Impurities are normally heavier than oil and sink rapidly to the bottom of the tank.

3. Dirty sampler or container — All sampling apparatus must be cleaned before use to prevent contamination of the sample.
4. No inline filter — All loading lines should be equipped with inline filters to trap impurities caused by polymerization or scale that develops inside the transfer lines.
5. No filter element — Install proper element. The supervisor should ensure that all filters are being utilized properly.
6. Filter not used — Eliminate bypasses around filters.
7. Coarse filter element — Most loading filters should be 25 microns or less to effectively trap the impurities encountered.
8. Faulty filter element — Inspect the filter elements for holes and tears and replace when faulty.
9. Line blowing causing filter failure — Blow the line into a separate container or through another filter to avoid contamination of the oil shipment if the filter is damaged by the nitrogen pressure.
10. Dirty filter shell — impurities from the lid of the dirty filter element can fall off 7.533.s[(dirt