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Preface

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Recovery, Refining, Converting, and Stabilizing Edible Fats and Oils

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I. INTRODUCTION

Processing seeds or animal tissues into edible oils can be broken into four sets of operations: recovery, refining, conversion, and stabilization. Oil recovery is often referred to as *extraction* or *crushing* when processing plant sources and *rendering* in the case of processing animal tissues. Oil extraction involves pressing the oil-bearing material to separate crude oil from the solids high in protein or washing flaked or modestly pressed material with solvent, almost always hexane. The defatted solids after pressing are known as *cake* and after solvent extraction as *meal*. The oil, *crude oil* because it contains undesirable components, such as pigments, phosphatides, free fatty acids, and off-flavors and off odors, must be refined to remove these contaminants and produce high quality edible oils. Refined oils consist primarily (>99%) of triglycerides and can be *converted*, usually by hydrogenation; but winterizing, fractional crystallization, and interesterification should also be considered conversion processes because they achieve different properties from the original oil, such as converting liquid oil into semisolid or solid fats. Plasticizing, tempering, and stehling are operations designed to stabilize crystal–oil mixtures used for shortenings and margarines.

II. OIL RECOVERY

For several thousand years, fats and oils have been recovered from oil-bearing seeds, fruits, and fatty animal tissues, and used for food, cosmetics, lubricants, and lighting fluids. Of the more than several hundred plants and animals that produce fats and

Table 1 Major Edible Fats and Oils in the United States and Methods of Processing

Source	U.S. oil consumption[a] (million pounds)	Oil content (%)	Prevalent method of recovery
Soybean	15,655	19	Direct solvent extraction
Corn (germ)	1,397	40	Wet or dry milling and prepress solvent extraction
Tallow (edible tissue)	1,362	70–95	Wet or dry rendering
Canola	1,264	42	Prepress solvent extraction
Coconut (dried copra)	1,021	66	Hard pressing
Cottonseed	772	19	Hard pressing or prepressing or direct solvent extraction
Lard (edible tissue)	988	70–95	Wet or dry rendering
Palm	260	47	Hard pressing
Palm kernel	390	48	Hard pressing
Sunflower	320	40	Prepress solvent extraction
Peanut (shelled)	230	47	Hard pressing or prepress solvent extraction

[a]Data from Ref. 2.
Source: Ref. 1 except as otherwise noted.

oils in sufficient quantities to warrant processing into edible oils, only 11 sources are commercially significant in the United States (Table 1) [1,2]. In other countries the importance of each source may be different, and other sources not on this list may also be important, such as olive oil being consumed in large amounts in Mediterranean countries.

All oil recovery processes are designed to obtain oil triglycerides as free as possible from undesirable impurities; to obtain as high a yield as possible consistent with economics of the process; and to produce cake, meal, or flour (finely ground meal), usually high in protein content, of maximum value [3]. Three general types of processes are used to crush oilseeds: *hard pressing*, *prepress solvent extraction*, and *direct solvent extraction*. The extraction process of choice depends primarily upon the oil content of the source material, the amount of residual oil in the meal allowed, the amount of protein denaturation allowed, the amount of investment capital available, and local environmental laws concerning emissions of volatile organic compounds (VOCs).

A. Extraction of Oil from Oilseeds

The oldest oil recovery method is hard pressing, where the seed is pressed, usually after various pretreatments to enhance oil recovery, to squeeze the oil from the solids known as *cake* (Fig. 1). In the early years, lever presses and screw-operated presses, often driven by oxen or other work animals, were used; then, during the Industrial Revolution, batch hydraulic presses were introduced, which evolved at the turn of the century into continuous screw presses [4] connected to line shafts driven by steam engines. Today, continuous screw pressing and direct solvent extraction have

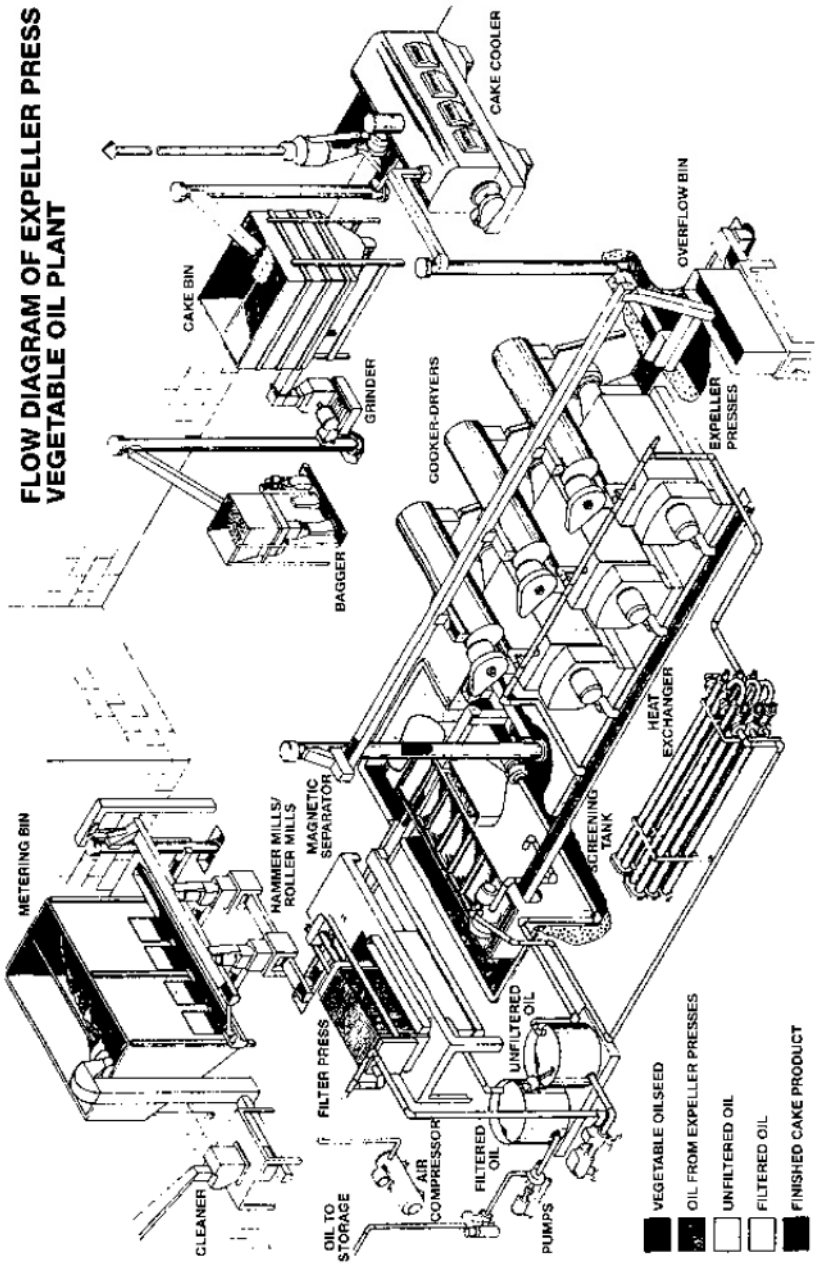


Figure 1 Depiction of hard screw pressing. (Diagram courtesy of Anderson International, Cleveland, OH.)

become the preferred processing methods because the oil is more completely recovered. For a long time, the rule of thumb has been that materials containing more than 30% oil require pressing, either hard pressing or prepressing prior to solvent extraction. Hard pressing involves squeezing as much oil as possible; prepress solvent extraction involves squeezing out only part of the oil before subjecting the partially deoiled material to more complete extraction with solvent. The recent adoption of the expander has largely done away with this rule, and even high-oil content materials can be solvent extracted today with no or little prior oil extraction [5,6]. Direct solvent extraction, without any prior pressing or expanding, has long been the most widely practiced method, the oil is more completely recovered, and the oil and meal are economically recovered undamaged by heat. Both prepress solvent extraction and direct solvent extraction are depicted in Figure 2.

1. Seed Storage

Oilseeds are often harvested at moisture contents higher than levels that allow for long-term storage and must be dried for safe storage. Increasingly, farmers are storing oilseeds, particularly soybeans, on the farm to take advantage of higher prices that are paid later in the crop year.

Storage for extended periods at moisture contents exceeding critical moisture levels will damage oilseeds, reducing the yields of oil and protein, and diminishing the quality of the oil (notably darker color and higher refining loss). Seeds at harvest are alive and respire, converting seed mass to CO_2 and other metabolites, albeit at low rates when the moisture content is below the critical moisture level. The critical moisture level for safe storage varies with the seed specie: usually, the higher the oil content, the lower the critical moisture value (Table 1). At moisture contents exceeding the critical moisture level, respiration rate increases, and the seed can even germinate and become subject to fungi attack. Respiration and germination liberate heat and, when there is insufficient aeration, the heat further accelerates these reactions. Under extreme conditions, the seed may become scorched or even catch on fire (especially cottonseed). Modern seed storage facilities employ temperature-monitoring systems to alert elevator and storage operators when seed temperatures exceed critical set points. Then the seed is moved to another bin to disperse hot spots and/or aerated (blowing air through the seed). The percentage of seed that is heat damaged is often a factor in the U.S. grades and standards (e.g., soybeans).

Overdrying can increase seed fragility, leading to excessive breakage during handling, storing, and processing. In the case of soybeans (a dicot), the cotyledon is prone to splitting into halves when the hull becomes separated from the cotyledon (meat) during conveying and transporting, a problem that becomes worse when the beans are overdried. *Splits* are undesirable because they are difficult to separate from foreign matter, and the oil deteriorates at a faster rate. Oil from soybean splits is higher in free fatty acids, phosphatides, iron, and peroxides due to activation of catabolic enzymes [7]. Oils from field- and storage-damaged seed usually are poor in flavor [8]. For these reasons, damaged kernels and splits are also factors in the U.S. grades and standards for soybeans.

When oilseeds are received at the crushing plant (Fig. 3), samples are often taken for analysis of moisture, foreign matter, damaged seed, oil, protein, and free fatty acid contents. Shipments arriving with similar values for these analyses may be segregated based on actions that are required to minimize further degradation.

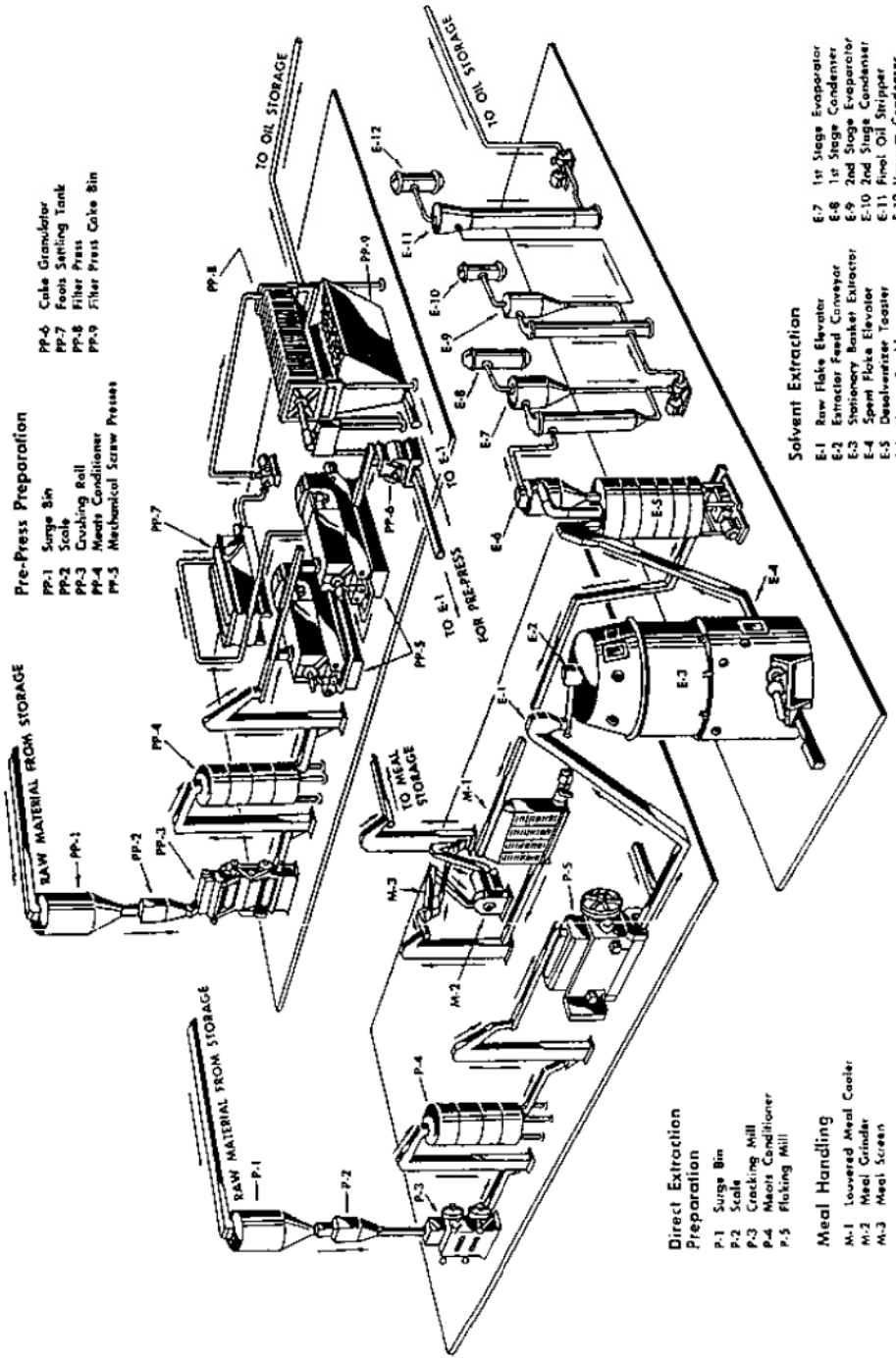


Figure 2 Depiction of prepress solvent extraction and direct solvent extraction. (Courtesy of French Oil Machinery Co., Piqua, OH.)

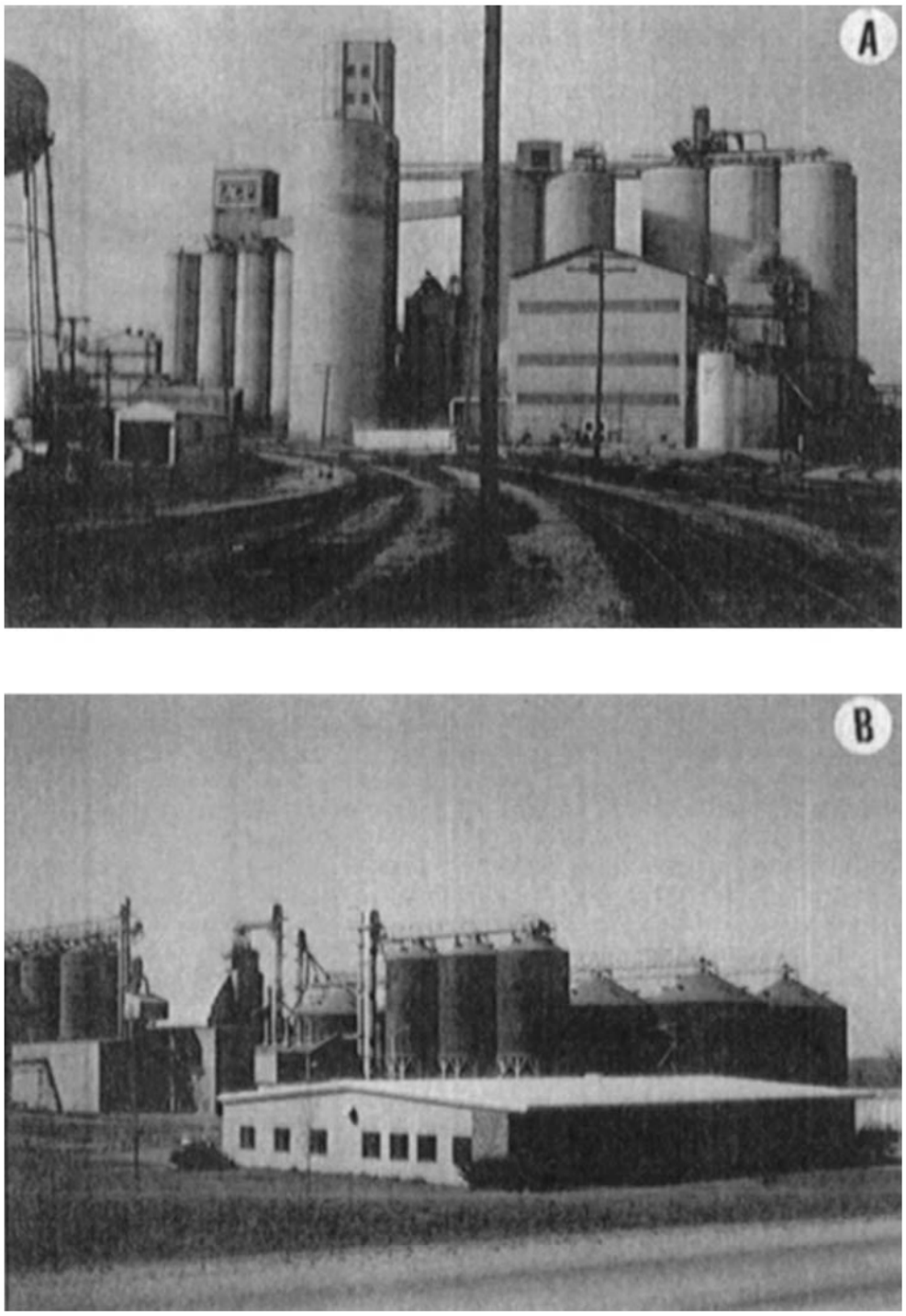


Figure 3 Oilseed mills. (A) Soybean mill in Iowa and (B) sunflower seed mill in North Dakota.

Seed containing more than the critical moisture content is immediately processed or dried. Seed with excessive foreign matter is transferred to scalping operations to reduce the level of contaminants. Foreign matter usually contains more moisture than the seed and the foreign matter tends to become concentrated at certain locations during placement into storage bins. Removing foreign matter reduces bulk moisture content and improves storability. Usually, foreign matter is also a factor in U.S. grading systems.

Both inside and outside storage systems are used (Fig. 4). Metal and concrete bins are used for inside storage. Cottonseed is often stored in special buildings having roof slopes the same as the angle of repose for the seed (Muskogee buildings). Some oilseeds are stored outside on concrete pads, and the piles may be covered with tarpaulins and/or equipped with air distribution systems.

Any handling, including normal harvesting, conveying, and transporting, increases seed damage. Nature has given seeds a high degree of subcellular organization that is affected by seed damage. Seed endosperm is composed of many cells containing oil and storage protein, which supply energy, nitrogen reserves, and other metabolites to support the growth of the embryo during germination. Storage protein (the greatest proportion of seed nitrogen) is concentrated in discrete bodies known as *protein bodies*; and lipids (predominantly triglycerides) are stored in *spherozomes*. Phospholipids are largely associated with pseudomembranes around protein bodies and spherozomes. Enzymes and cellular metabolites are present in the cytoplasm. Some of these enzymes, notably lipase, hydrolyze triglycerides increasing free fatty acid content, which must be removed by refining. Phospholipase activity may render some phospholipids non-hydratable and difficult to remove from the oil by means of normal refining procedures. Lipoxygenases, unique to soybeans and other legumes, oxidize linoleic and linolenic acids causing painty, green, beany flavors in protein; these enzymes may also reduce the oxidative stability of the oil.

In intact seeds, these enzymes are kept away from the oil by natural compartmentalization within the cells of the seeds. However, damage by weather, harvesting, and/or handling bruises the seed, breaking cell walls and membranes, allowing the oil and enzymes to come into contact with one another. This accelerates adverse reactions whose rates are dependent on temperature, moisture, and extent of damage.

2. Cleaning

The first step in processing oilseeds usually involves cleaning the seed (Fig. 5). Unless removed by cleaning operations, foreign matter reduces oil and protein contents and increases wear and damage to expensive processing equipment; in addition, foreign matter may adversely affect oil quality (especially color). Magnets are placed in chutes just ahead of processing equipment to prevent damage by tramp iron. Vibrating and/or shaker screens with or without aspiration are used to remove stems, pods, leaves, splits, broken grain, dirt, and extraneous seeds (Fig. 6).

3. Dehulling

Usually, it is desirable to remove the hull or seed coat that surrounds the oilseed meat. Hulls always contain much less oil and protein than do meats. Removing the hull reduces the amount of material that must be handled, extracted, and desolventized, thus increasing downstream plant capacity. The protein content of the meal is raised by removing the hull. Oftentimes, as with corn and sunflower seed, the hull

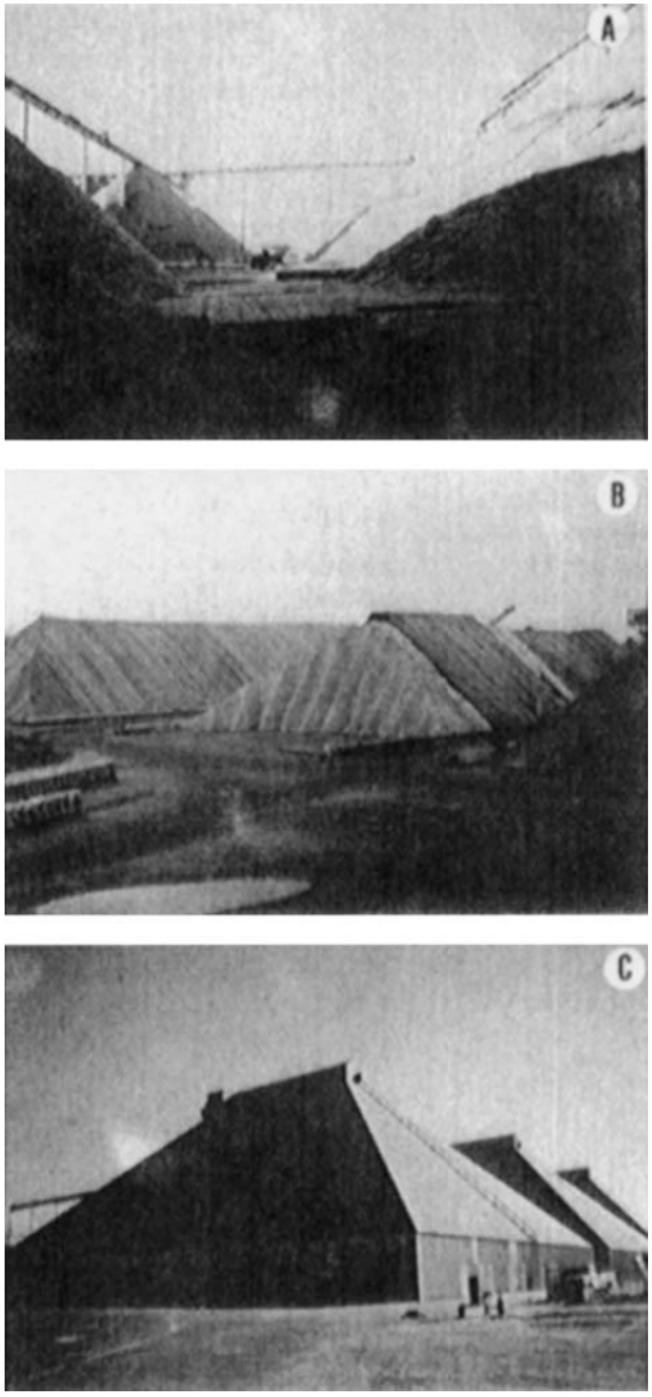


Figure 4 Cottonseed storage systems. (A) Uncovered, outside storage piles; (B) covered, outside storage piles; and (C) Muskogee buildings.

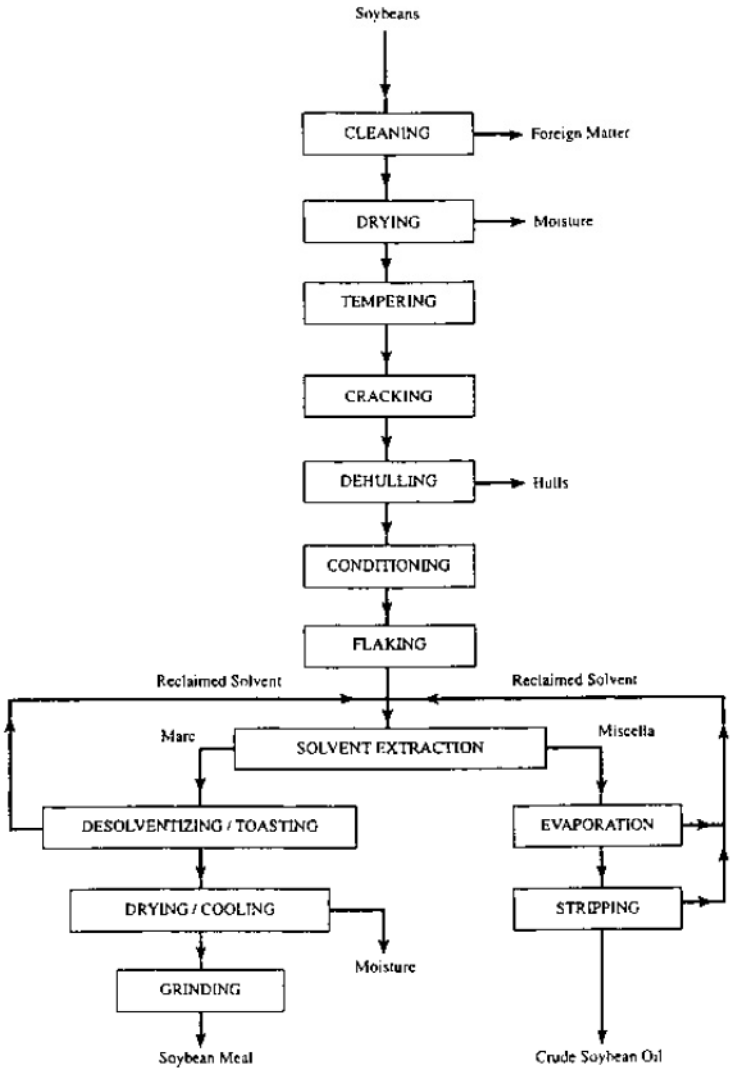


Figure 5 Steps in processing soybeans into meal and edible oil.

contains waxes on the outer surface as a natural protective mechanism of the seed. These waxes must be removed during latter oil-refining steps, often by winterization or cold centrifugation; otherwise, the wax may become insoluble at cold temperatures and make the oil unattractively cloudy and cause emulsions such as mayonnaise to separate. Removing the hulls can alleviate these wax problems. On the other hand, hulls can be helpful at times, such as by providing fiber to allow easier hard pressing or to enhance solvent drainage, and thus they are not always removed.

Dehulling must be done carefully, to ensure that the meat is not broken into too many small pieces, which would be difficult to separate from the hull. Also, crushing of meats during dehulling causes oil cells to be ruptured, freeing the oil. This damage should be minimized to prevent absorption of liberated oil by hulls that are removed. Either one of these problems increases the oil content of the hulls and

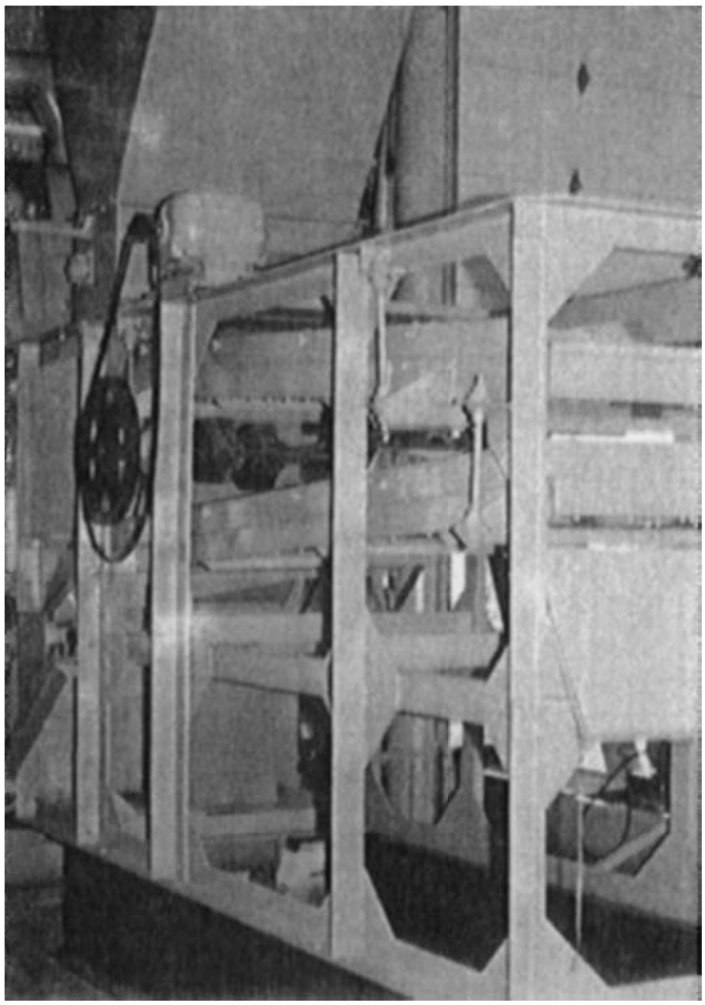


Figure 6 Seed cleaner (shaking screens and aspiration).

reduces the yield of oil. Some seeds, such as soybeans, are often dried, dried and conditioned, or heated prior to dehulling to help free the meat from the hull.

Corrugated roller mills or bar mills, which shear the seed, and impact mills, which shatter the brittle seed coat, are used. The equipment cuts or breaks the hull, respectively, to free the meat, a step often referred to as *decortication*. Sometimes, the combination of sizing the seed with shaker screens prior to decortication and using mills with different settings optimized for each seed size increases the efficiency of decortication. Hull/meat separation systems comprising one or more shaker screens, aspirators, and gravity tables are effective because the hull is often larger and almost always lower in density and more buoyant in an airstream than the oil-rich meat. Hulls may be blended back with meal to control protein level, sold as a separate coproduct for cattle roughage, or burned in boilers to generate steam and electricity in the process known as *cogeneration*.

When making edible flours, more complete removal of hulls is required. More than 90% of the hulls from soybeans must be removed to assure that the minimum

specification of 50% protein is met. Even in the livestock feed industry, the trend is toward meals containing higher protein and lower fiber contents. It is becoming increasingly difficult to produce soybean meal with high protein content because increasing farm yields are depressing protein content.

4. Hard Screw Pressing

Since flakes transfer heat more rapidly than do cracked meats, the seed is usually flaked [0.38–0.50 mm (0.015–0.020 in.) thickness] prior to hard pressing (Fig. 1), before cooking at 115°C over a 60-minute period. Initial stages of cooking should be done with moist heat (seed moisture maintained at 10%) injecting steam or spraying water into the top deck. Cooked flakes are dried in lower trays and should exit the cooker at less than 2.5% moisture [9]. The cooked and dried flakes are then conveyed to screw presses. If proper cooking methods are employed, in conjunction with a well-maintained, modern, screw press, a residual oil content as low as 3–4% can be achieved. Many screw press plants are quite small and do not optimally, if at all, flake, cook, and dry before screw pressing; so as much as 6–10% oil often remains with the cake. Ultimately, hard pressing with more and more pressure is self-defeating because application of pressure causes capillaries to be reduced in volume, sheared, and eventually sealed by coagulation of protein. This places the lowest practical limit at about 3% residual oil.

A screw press (Fig. 7) is basically a continuous screw auger designed to accept feed material and subject it to gradually increasing pressure as it is conveyed through the barrel cage. The barrel is composed of bars surrounding the screw and oriented parallel to the screw axis. The bars are separated by spacers decreasing in size toward the solids discharge end, which allow the oil to drain. A plug of compressed oil-lean solids, the *cake*, forms at the discharge end. Increasing pressure down the length of the barrel is achieved by increasing the root diameter of the screw, decreasing the pitch of the screw flights, and controlling the opening for the discharging cake by means of a choke. This design causes fresh material to be rammed against the plug [10,11].

Screw presses are composed of three sections: feeding, ramming, and plugging. The meats or flakes fall into a rapidly rotating feed screw, which feeds them into the pressing cage to expel entrapped air and squeeze out the easily removed oil. In some screw presses, the feeding section may be a separate vertical screw, or it may be mounted directly to the ramming screw. In either case, the feeding screw turns faster than the ramming screw. Knife bars with projecting nibs are clamped between the half cages to prevent cake slippage and rotation. Maximum pressure is developed in the ramming section as partially deoiled cake is rammed against the deoiled plug. The plug section provides the resistance against which the ramming occurs. The friction in the barrel generates heat that must be removed to achieve low residual oil. Some screw presses recycle cooled pressed oil over the cage to remove excess heat, while others use water-cooled shafts and bar cages.

In hard pressing, screw presses are choked to put maximum pressure on flaked, cooked seed while maintaining cake discharge. The oil drains from the screw press cage and is pumped or flows by gravity to a basin to allow settling of cellular debris (foots) that was removed with the oil. The cake is then ground into meal.

In the United States, hard pressing is largely limited to minor oilseeds (e.g., peanuts and rapeseed), or in areas where supplies are not sufficient for large-scale

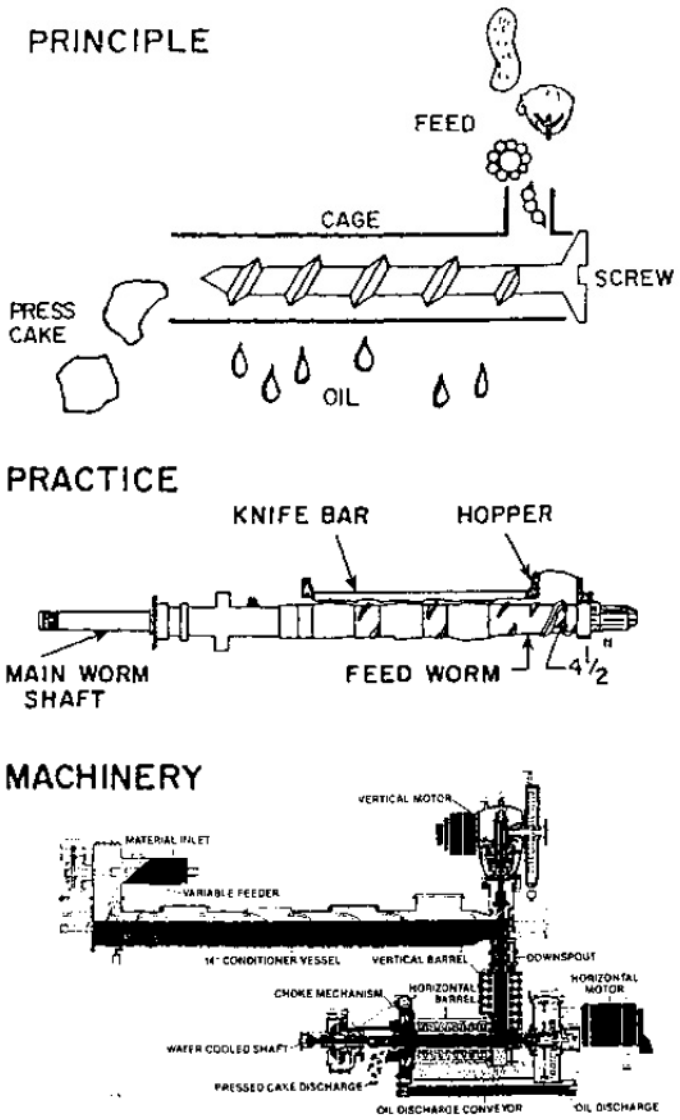


Figure 7 Screw press principles, practice, and machinery.

solvent plants (in cottonseed). There is interest in hard screw pressing oilseeds to produce organically grown or certifiable non-generating modified vegetable oil or to comply with local laws that prevent construction of new solvent plants such as in California. A small amount of soybean is hard-screw-pressed where the meal has particularly high value (e.g., high rumen bypass meal for dairy cattle feed). Screw pressing of copra, peanuts, sesame, and cocoa butter also remains popular in developing countries where investment capital is limited.

5. Prepress Solvent Extraction

In prepress solvent extraction (Fig. 2), part of the oil that is easily removed, is pressed out as described above. The press is choked such that less pressure is developed. Consequently, less oil is extracted and throughput is increased. Usually, the oil con-

tent of prepress cake is 15–18%, and the partially deoiled cake is then extracted with solvent. The cake may be broken into pieces and even flaked to increase bulk density and extractor capacity, and to speed extraction. The remaining steps are the same as for direct solvent extraction, described in the next section.

6. Direct Solvent Extraction

Cell walls are impermeable to oil and nearly so to extraction solvents. Consequently, cell walls and membranes must be *distorted* or ruptured to get the oil out, regardless of whether solvent extracting or screw pressing is done. This requirement often calls for reducing the size of seed particles. Small pieces also transfer heat and moisture more readily during conditioning or cooking. But excessive size reduction reduces mechanical distortion during flaking. Flaking mills distort larger particles more than smaller particles [12]. Of course, particles must be small enough to pass into the nip between rolls of the mill. Heating prior to flaking reduces oil viscosity, inactivates enzymes, coagulates protein, ruptures some cell walls and membranes, and makes the seed particle plastic for subsequent flaking or pressing. Proper plastic texture is necessary to produce thin, nonfragile flakes with minimal fines and maximal cell distortion. The flaked material must have tenacious, thin structure, with porosity that allows transport of the oil or *miscella* (solvent-oil mixture).

It has long been recognized that flake thickness influences the rate of oil extraction. Oilseeds are conditioned prior to flaking by using vertical stack cookers or rotary steam tube driers to heat the seed to 70–80°C over 20–30 minutes, while maintaining 10.5–11.5% moisture [13,14]. This treatment makes the meats soft and pliable enough to be flaked with smooth-surfaced roller mills to low thickness, 0.25 mm (0.010–0.012 in.) without producing excessive fines, which adversely affect other operations.

Extraction has been likened to cleaning paint from a brush [15]. As such, key to getting the brush clean is getting good contact and penetration of the solvent; then there must be enough clean solvent to dissolve the solute (the paint in this example), and enough time and heat to quickly dissolve more solute. However, oilseeds extraction does not follow the single mechanism of leaching as the brush example implies and others have often assumed. Instead, oilseeds extraction involves a combination of leaching, diffusion, and dialysis [12,16–19], which results in an ever-decreasing rate of extraction as the relative importance of each mechanism changes during the course of extraction [20]. For flakes, the larger proportion of readily extractable oil is derived from ruptured cells, especially near the surface. The transfer of oil from distorted interior cells probably is governed by capillary flow, and the rate of oil transfer is partly dependent on viscosity of the miscella. A portion of the slowly extracted oil is contained within intact undistorted cells and must be transferred by osmosis. This transfer is very slow [21]. Presumably, the process of extruding flaked meats, known as *expanding*, shifts the relative importance toward leaching because nearly all the cells are ruptured and the collet structure is quite porous.

Another portion of the slowly extracted oil relates to slowly soluble extractable materials, such as phosphatides, free fatty acids, nonsaponifiables, and pigments, which contribute to refining loss. The best quality oil, high in triglyceride content, is extracted first, while with more exhaustive extraction, poorer quality oil is extracted. Thus, at low residual oil levels, the proportions of free fatty acids and phos-

phatides extracted are greater, as is the refining loss. However, current industry practice is to strive for the most complete extraction possible. Typically, residual oil contents range 0.5–1.0%.

Flake thickness [22–25] and solvent temperature [25,26] have profound effects on extraction rate, and empirical relationships to extraction time have been observed [27]. While these factors are easy to control by adept operators, general lack of understanding and appreciation often exist in practice. The moisture content of the flakes is another factor affecting the rate of solvent extraction [28]. In most cases, 9–11% moisture is ideal. Hexane and water are immiscible, and higher moisture contents interfere with the penetration of hexane. Lower moisture levels reduce the structural strength of the flakes leading to the production of additional fines.

To reduce the amount of solvent used in extractors, countercurrent flow of the solvent to the flakes is used (Fig. 8) [29]. That is, the freshest flakes contact the oldest solvent and progress through the process until nearly oil-free flakes contact fresh solvent. Flakes enter the extractor through a plug vapor seal that allows the material to enter while keeping hexane vapors from escaping. The extractor is an enclosed vessel designed to wash, extract, and drain flakes.

Two principal types of extractor have been employed over the years: *immersion extractors* and *percolation extractors*. An immersion extractor immerses and soaks the material in solvent (an industrial example is the Hildebrandt U-tube extractor, and a laboratory example is the Soxhlet extractor). Generally, more solvent usage is required by immersion extractors. Few immersion extractors processing oilseeds remain; percolation extractors now dominate. In a percolation extractor, the solvent percolates by gravity through a bed of material (a laboratory example of a percolation extractor is the Goldfisch). The solvent flows over the surface of the particles and diffuses through the material during its downward circuitous travel. Miscella flows

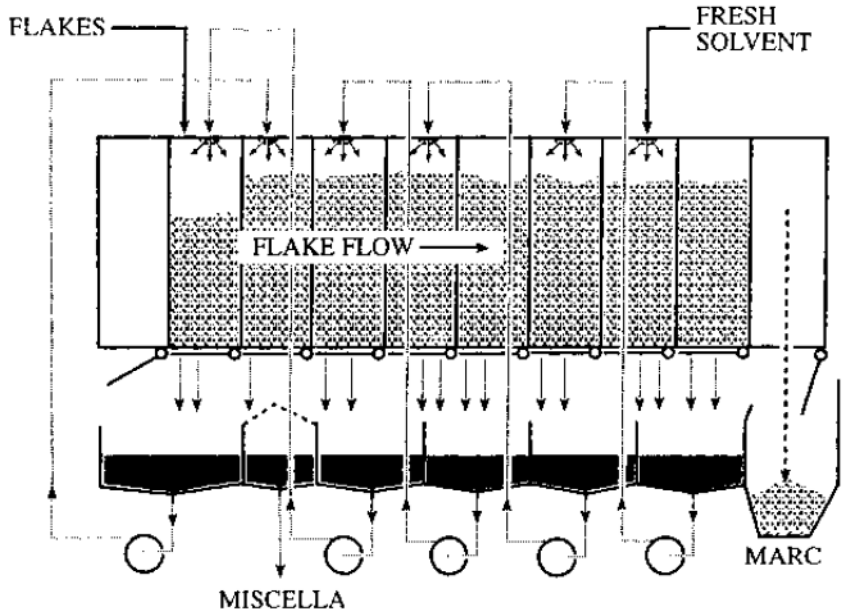


Figure 8 Flake flow relative to solvent flow. (Redrawn from Ref. 29.)

in successive passes through the bed, while the solvent spray and the bed move in opposite directions to each other. Percolation extractors also have larger extraction capacities in less space, and fewer operating problems are associated with these devices than with immersion extractors.

Most modern extractors are of the percolation type (Figs. 9, 10). The extraction principles employed by most extractors are the same, but there are different methods of achieving countercurrent flow of solvent to flakes. The shallow-bed chain extractor (Fig. 9) is one of today's popular extractors and resembles a full-loop conveyor [30]. Flakes fed into an inlet hopper are conveyed down the first leg of the loop, where they are washed with moderately dilute miscella to extract surface oil and penetrate the cells. As the flake bed moves into the bottom horizontal section, full miscella is recycled through the bed for filtering, and then to a liquid cyclone for removing fines and, finally, to the evaporation system. Flakes are conveyed counterclockwise, through a progressively more dilute miscella washes, until a final wash with fresh solvent is used in the top horizontal section of the loop. The latter half of the top loop is used for drainage, after which solvent-laden spent flakes pass to the desolventizer. The following advantages are claimed: the shallow bed (usually about 1 m) promotes drainage and, thus, low solvent carryover to the meal desolventizer and uniform contact of the flakes with solvent, since the bed is turned over while going up the right vertical leg.

Today hexanes (a blend of about 60% *n*-hexane with other hexane isomers) are the solvent of choice, although many other solvents were used during development of solvent extraction technologies. Alternative extraction solvents were extensively reviewed [31,32], but no suitable alternative has been developed. The primary disadvantage of hexane is its flammability and a price structure and supply that are tied to petroleum prices.

Flakes are conveyed to the extractor, where they are extracted for 30–60 minutes. Generally, less than 1% residual oil in the extracted material is achieved, and the amount is lower for soybeans (about 0.5%). The miscella contains 22–30% oil, and the solvent is separated from the crude oil by distillation and stripping columns. The miscella is heated under vacuum to evaporate the solvent, which is usually done in two stages. The first-stage evaporator concentrates the oil to about 90% and uses reclaimed heat from heated solvent vapors from meal desolventization. Steam is used to heat the second-stage evaporator, where the oil is concentrated to >99%. Most of the remaining solvent is removed in a disc-and-doughnut stripping column where evaporation is promoted by means of heat, vacuum (450–500 mm Hg absolute pressure), and steam sparging. Crude oil leaves the stripping column with less than 0.15% moisture and hexane [33]. Trading specifications require the oil to have a flash point greater than 250°C, which is equivalent to no more than 800 ppm of hexane.

The marc generally contains 30–32% solvent holdup, which must be recovered and recycled. Heat must be used to evaporate the solvent holdup from the meal. Live steam is also injected to aid heat transfer and to provide moisture vapor to strip the solvent. Regardless of the type of extractor used, the extracted flakes (*spent flakes*) must be drained of the solvent held by the material. The solvent that will not drain is referred to as ***solvent holdup***, the solvent-laden flakes are called ***marc***. Solvent holdup should be minimized because this solvent must be removed by evaporation

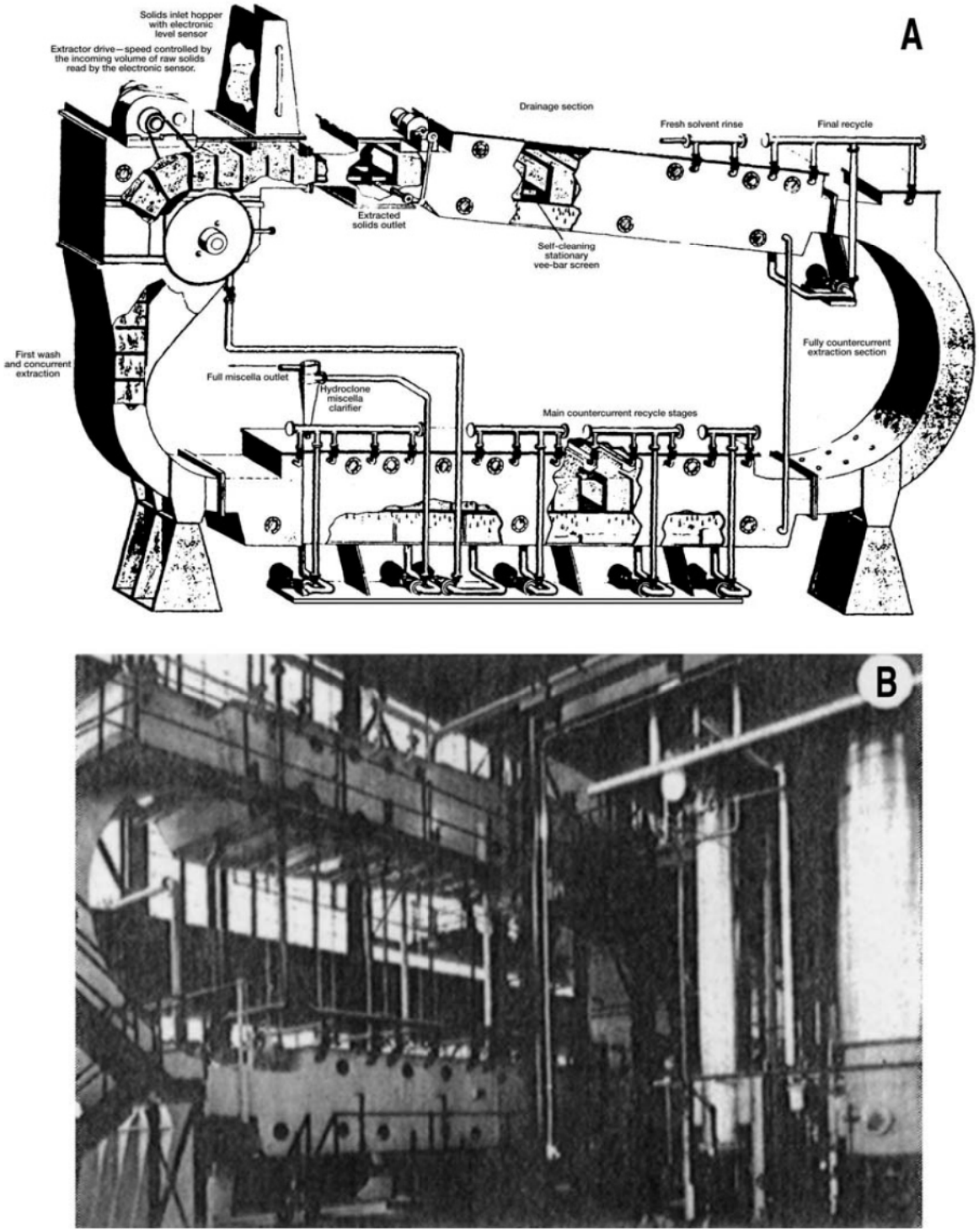
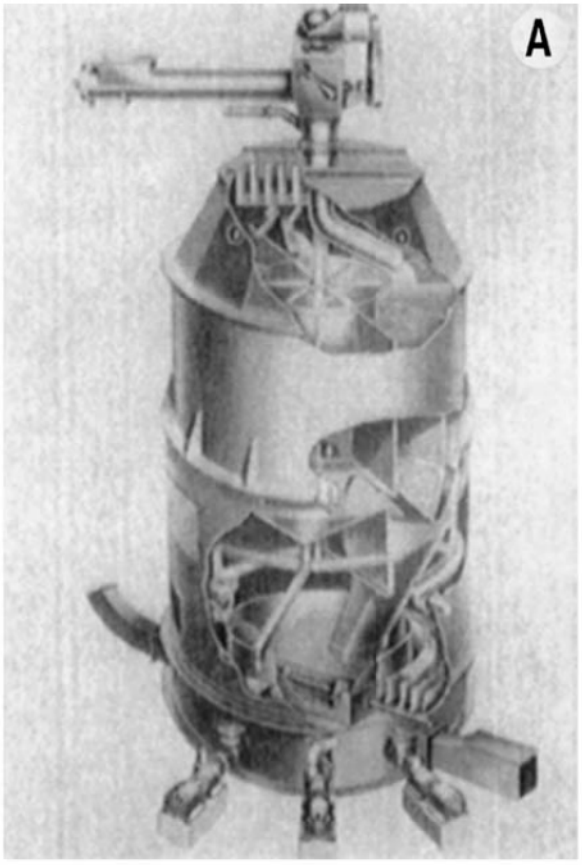


Figure 9 One type of commonly used extractor. (A) Schematic drawing and (B) an actual installation. (Photo courtesy of Crown Iron Works Co., Minneapolis, MN.)



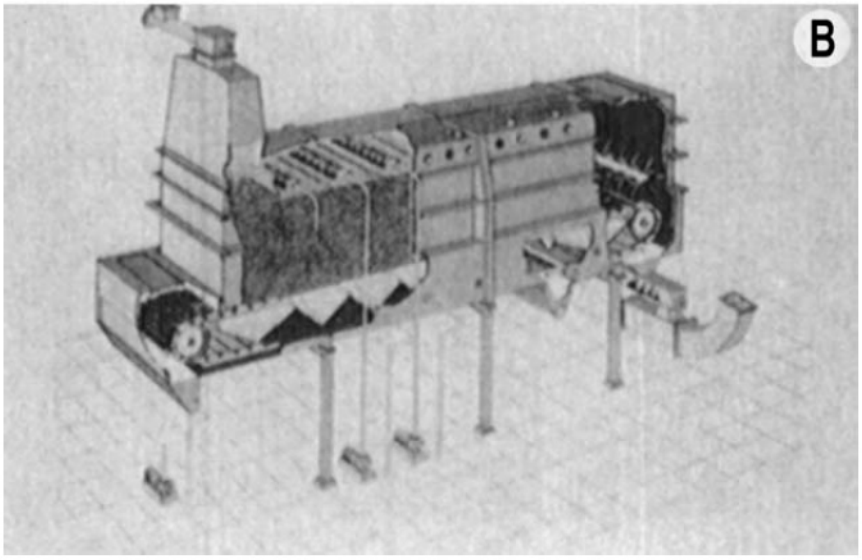


Figure 10 Additional commonly used extractors. (A) Deep-bed rotary basket extractor. (Courtesy of French Oil Mill Machinery Co., Piqua, OH.) (B) Deep-bed chain extractor. (Courtesy of De Smet, Edegem, Belgium.)

using heat. Greater solvent holdup increases the energy required for desolventizing the meal.

Toasting is often needed for feed meals to efficiently denature trypsin inhibitors (protease inhibitors in soybeans affecting protein digestibility) and the enzyme urease (soybeans), bind gossypol to protein (cottonseed), and improve protein digestibility. Of course, none of these objectives can be achieved without considerable protein denaturation and the accompanying loss of water solubility by the protein. However, depending on the method used, meals with great differences in protein solubilities or dispersibilities can be produced.

The preponderance of meal is used for feed, where extensive heat treatment is necessary to maximize feed conversion efficiency by livestock. A conventional desolventizer/toaster (DT) (Fig. 11) is usually composed of about six stacked trays, all with indirect heating. The first two employ live steam injection through nozzles within the sweep arms to evaporate the majority of the solvent. Meal advances down through the trays, and a series of gates and floats control the levels in each tray. The lower four trays are essentially toasting/drying sections, where the meal is held at a minimum temperature of 100°C, and the meal is dried to a value suitable for dryers

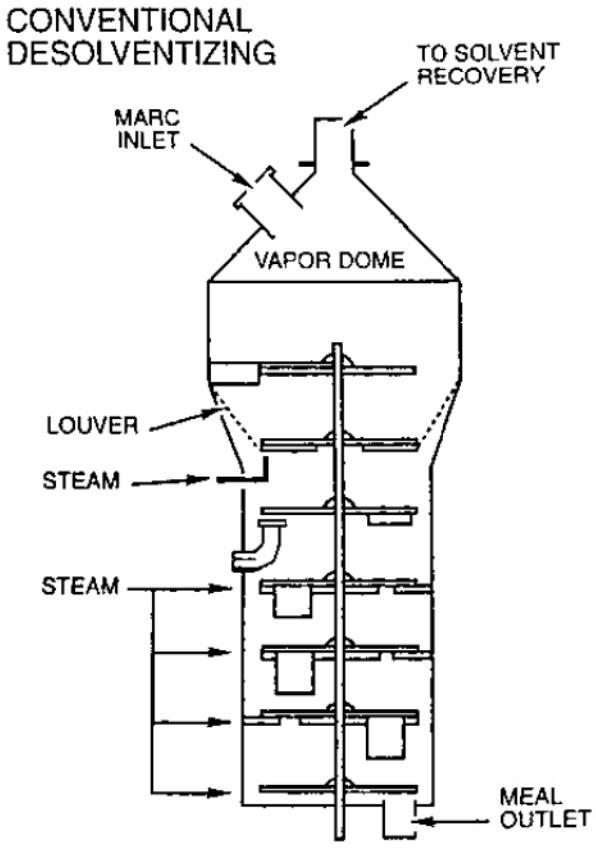


Figure 11 Meal desolventizing/toasting equipment.

that follow the DT. Drying at normal DT conditions to less than 17% moisture is detrimental to available lysine. However, meal should not leave the DT at more than 22% moisture, for this would result in prohibitive drying energy requirements.

In recent years, the Schumacher-type desolventizer/toaster/dryer/cooler has become widely accepted. This device consists of four trays: the top tray is for predesolventizing; the second for desolventizing-toasting with injection of steam through its perforated bottom (achieving countercurrent use of steam relative to solvent evaporation); the third for drying, with hot air blown through its perforated bottom; and the fourth tray is for cooling by blowing cold air through its perforated bottom.

The *flash desolventizer* and the *vapor desolventizer* (Fig. 12) were developed to reduce protein denaturation and produce highly soluble protein food ingredients (e.g., protein isolates) from soybeans [34]. Integrating these systems with cooking systems produces edible protein flours with a broad spectrum of protein dispersibility characteristics. The system includes a desolventizing tube, a flake separator, a circulating blower, and a vapor heater. These units are arranged in a closed loop in which hexane vapor is superheated under pressure and continuously circulated. Solvent-laden flakes from dehulled soybeans are fed into the system and conveyed by the high velocity circulating vapor stream. The turbulent superheated vapor flow (157–166°C) elevates the temperature of the flakes to 77–88°C, well above the boiling point of hexane (65°C), in less than 3 seconds. Because the flakes enter the flash desolventizer at low moisture for a very short period and no steam is injected into the vapor stream, little denaturation of protein occurs. As the flakes travel through the tube to the cyclone separator, the greatest portion of the entrained hexane is evaporated. At this point, if care is taken during conditioning, the protein dispersibility index (PDI) of the meal protein will be 2–5% of the untreated seed (native protein). The substantially desolventized flakes are removed from the system through a cyclone with a vapor-tight, rotary airlock and go to deodorizers.

Vapor desolventizing is similar to flash desolventizing in that superheated hexane vapor furnishes the required heat energy. Flakes are contacted with hot hexane vapor in a horizontal drum equipped with an agitator/conveyor. Flakes from either system usually enter a deodorizer to be stripped of hexane traces using only indirect heat. A slow moving agitator gently tumbles the spent flakes. The PDI may be further reduced by up to 10 percentage units. The final PDI is controlled at the flake stripper. Sparge steam may be used to minimize solvent loss and produce low PDI products (50–65% PDI). If only indirect steam is used, medium-range PDI products are produced (60–75% PDI). If the stripper is bypassed or operated without any heat or steam, highly dispersible products can be produced (75–90% PDI). However, as PDI increases, more hexane remains with the flakes as they exit the system, 0.5–1.2% hexane for high PDI products.

7. Meal Grinding

Desolventized meal is generally ground so that 95% passes a U.S. 10-mesh screen and a maximum of 3–6% passes through a U.S. 80-mesh screen. Meal for edible purposes is ground, sized, and sold as grits in a wide variety of sizes and as flour (<U.S. 100 mesh).

8. Oil and Meal Storage

Both oil and meal must be cooled before placing in storage because degradation reactions are accelerated at higher temperatures. Neither product should be stored

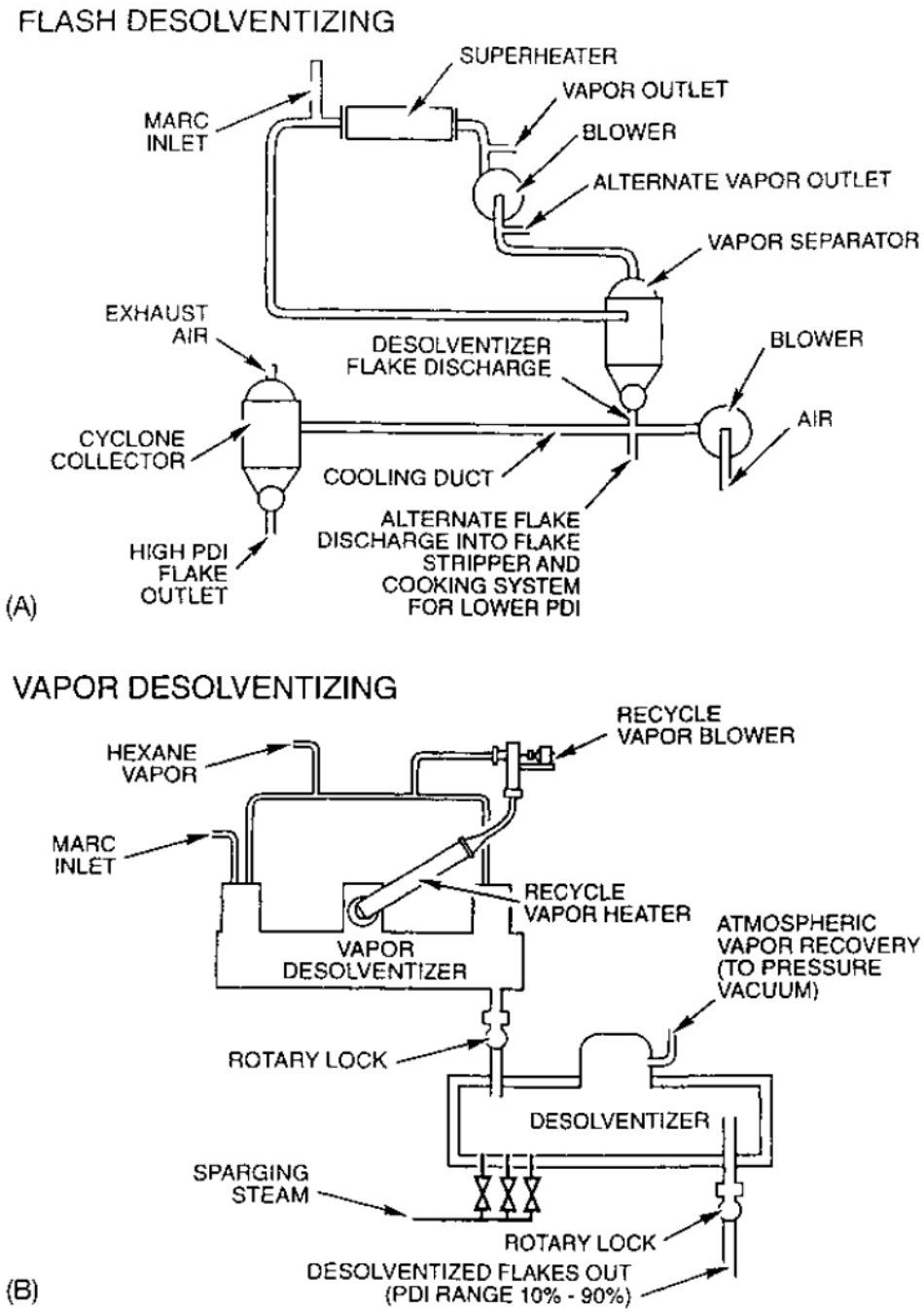


Figure 12 Setups for (A) flash desolventizing and (B) vapor desolventizing.

any longer than necessary. Oil degrades through oxidation, although crude oil is more stable than refined oil because crude oil contains natural antioxidants that are removed in refining steps. Preventing water from contacting the oil is also important to prevent hydrolysis, which increases refining losses. Thus, to extend storability of oil, protection against water, heat, and air is important.

B. Extraction of Oil-Bearing Fruits

Oil palms and olives are two examples of commercially important fruits providing important edible oils. Palm fruit can provide two distinctly different fats, one from the fleshy mesocarp and the other from the seed kernels. While olives and palms are processed slightly differently, space allows discussion of the palm oil production system only (Fig. 13).

Palm trees are perennials grown on plantations, particularly in Malaysia. It takes 3 years for the plantings to mature sufficiently to bear fruit, and they produce for about 25 years. Palm fruits are hand-harvested and immediately transported to the mill, where they are quickly *sterilized*. The fruits are processed within hours after harvesting because the oil immediately begins to degrade after harvesting. The fruits are sterilized by heating under steam pressure (145°C) for 1 hour to inactivate the

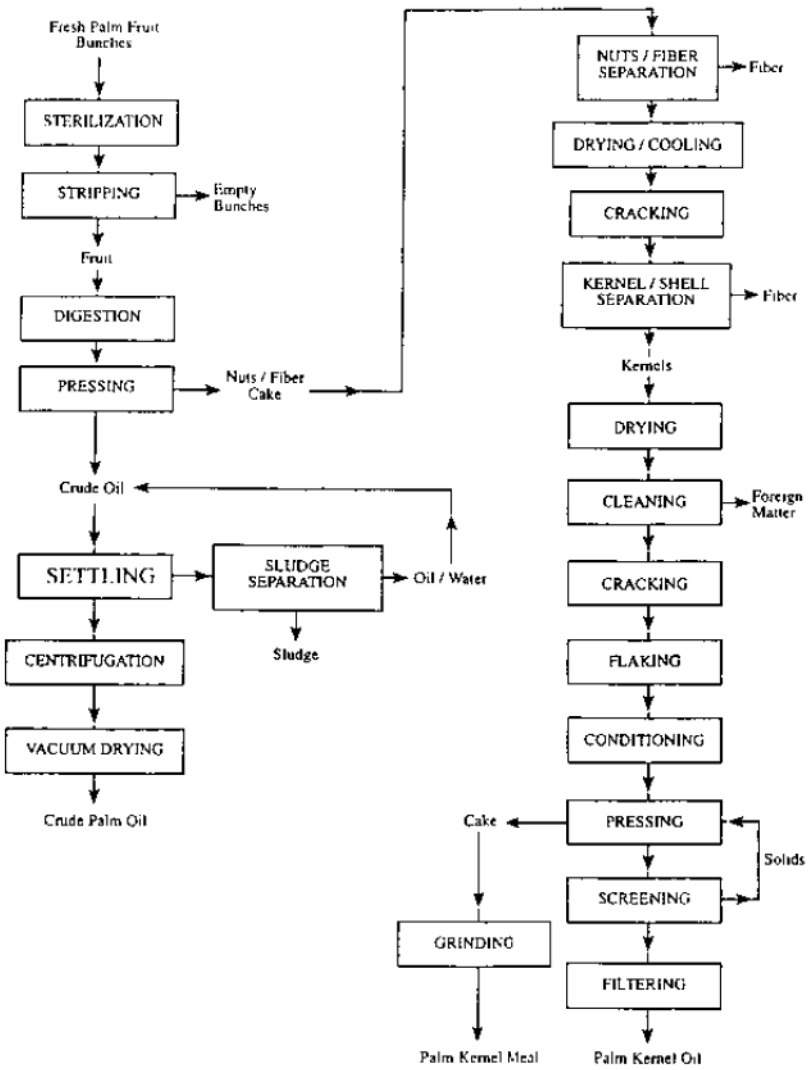


Figure 13 Steps in processing palm fruits.

enzyme lipase, which otherwise would quickly hydrolyze the oil and increase refining loss [35]. Sterilization also aids in stripping the fruit from bunch stalks and preconditions the material for subsequent steps.

The sterilized fruits are stripped from bunch stalks with drum-type strippers. The material is then sent to a digester where it is reheated (95–100°C for 2 minutes) to loosen the pericarp from the nuts and to break the oil cells. The material is conveyed to continuous screw presses similar to, but not quite the same as, those used for oilseeds, to extract oil from the fruit flesh, but not the kernel. The liquid extract, *press liquor*, from the screw press contains about two-thirds oil, one-quarter water, and one-tenth solids. The press cake contains fruit flesh fiber and nuts. Water must be added to the press liquor to facilitate satisfactory settling of solids after screening, an operation referred to as *clarification*. Oil is skimmed off the top and passed to a centrifuge (clarifier) and then to a vacuum dryer. The crude oil is cooled and placed in storage.

The press cake is conveyed by means of a breaking conveyor to an aspirator (a vertical air column), where the nuts fall into a rotating polishing drum at the bottom, and the fruit fiber is blown to a cyclone, where it is separated from discharge air. The fiber is used to fuel the steam boiler. The nuts are conditioned by drying to loosen the kernels from the shell and cool the nuts to harden the shell. The nuts are cracked in an impact mill into two or more pieces. The shells are separated from the kernel with winnowing columns and by hydrocloning or clay bathing. All three of these operations separate shells from kernels based on density differences. The kernels are dried and screw-pressed or solvent-extracted to produce palm kernel oil and meal [36]. For every 10 tons of palm oil produced, 1 ton of palm kernel oil is produced.

C. Recovery of Animal Fats and Marine Oils

Animal fats and marine oils are recovered from fatty tissues by the cooking process known as *rendering*. Both edible and inedible fats are produced; the inedible tallow and grease being the majority in the United States and used as an energy source in livestock feeds. Raw materials include animal offal, bones and trimmings from meat processors, fish species unsuitable for marketing as fillets and other fish products (menhaden, pilchard, herring, etc.), and fish cannery wastes. Until recent years, edible tallow and lard were used for deep-fat frying in fast-food restaurants; but recent consumer concerns over cholesterol and saturated fats have reduced sales in these markets. Increasingly, larger proportions are being used in margarine and bakery shortenings. The defatted solid material is high in excellent quality protein that can be sold for use in livestock feeds as *meat and bone meal* (45–54% protein), *meat meal* (52–60% protein), *poultry by-product meal* (58–62% protein), and *fish meal* (60–65% protein). Fish meal commands high prices because it is especially valued in poultry diets and aquaculture diets.

Both *wet rendering* and *dry rendering* methods are used. Regardless of the process used, the material is conveyed upon receipt to a crusher or prebreaker to break the material into small pieces (2–5 cm). The broken material is conveyed to either batch or continuous cookers, where heating and grinding evaporate the moisture, break down the fat cells, and release the fat, action not too dissimilar from frying bacon.

1. Wet Rendering

Wet rendering is the older method and involves cooking the material (in the presence of water) by steam under pressure [172–516 kPa (25–75 psi)] for 90–150 minutes [37]. When the added water comes only from steam, the process is known as *steam rendering* and this process is used to produce *prime steam lard*. The water, denatured protein, and other solids settle to the bottom, while the fat, being less dense, floats on top of the liquid. Water, known as *stick water*, is drained off, and the remaining *tankage* goes to a press for fat removal.

The presses may be either hydraulic batch type or continuous screw presses similar to those used for processing oilseeds. The high-protein solids portion is known as *cracklings* and typically contains 6–10% residual fat. The cracklings are hammer-milled and screened, with oversized particles being recycled to the mill, thus producing *meal*. The fat discharged from the press must be centrifuged and/or filtered. Most fish, such as anchovy and menhaden, are processed by wet rendering.

2. Dry Rendering

In the newer and more efficient dry rendering process, the material is cooked in its own fat (115–120°C) in agitated, steam-jacketed vessels for 1.5–4 hours, until the moisture has evaporated [37]. No steam or water is added. The cooked material is then passed across a screen to allow the free fat to drain. The remaining tankage is sent to a press, and the remaining steps are the same as for wet rendering.

III. REFINING

A. Background

Consumers usually want bland-flavored or flavor-neutral, light-colored, and physically and oxidatively stable oils. Crude oils are not usually considered to be edible until numerous nonglyceride compounds have been removed through operations collectively known as *refining*. However, some oils, such as olive, tallow, and lard, have been consumed without refining. Undesirable components of crude oils include small amounts of protein or other solids, phosphatides, undesirable natural flavors and odors, free fatty acids, pigments, waxes, sulfur-containing compounds (canola and rapeseed), trace solvent residue, and water. However, not all nonglyceride compounds are deleterious. Tocopherols protect the oil against autoxidation and provide vitamin E activity, and β-carotene provides vitamin A activity. Other phenolic compounds, such as sesamol in sesame oil, act as natural antioxidants. Unfortunately, some of the refining operations are not perfectly selective and also remove some beneficial compounds along with the targeted undesirable ones.

There are two major types of refining: chemical and physical. The major steps involved in chemical refining include degumming, neutralizing, bleaching, and deodorizing (Fig. 14). Physical refining removes free fatty acids and flavors by distillation, to combine the steps of neutralization and deodorization into one operation. *RBD oil* refers to oil that has been alkali-refined, bleached, and deodorized or oil that has been physically refined.

B. Degumming

Degumming (Fig. 15) is a water-washing process to remove phosphatides. Unless removed, phosphatides can spontaneously hydrate from moisture in the air during

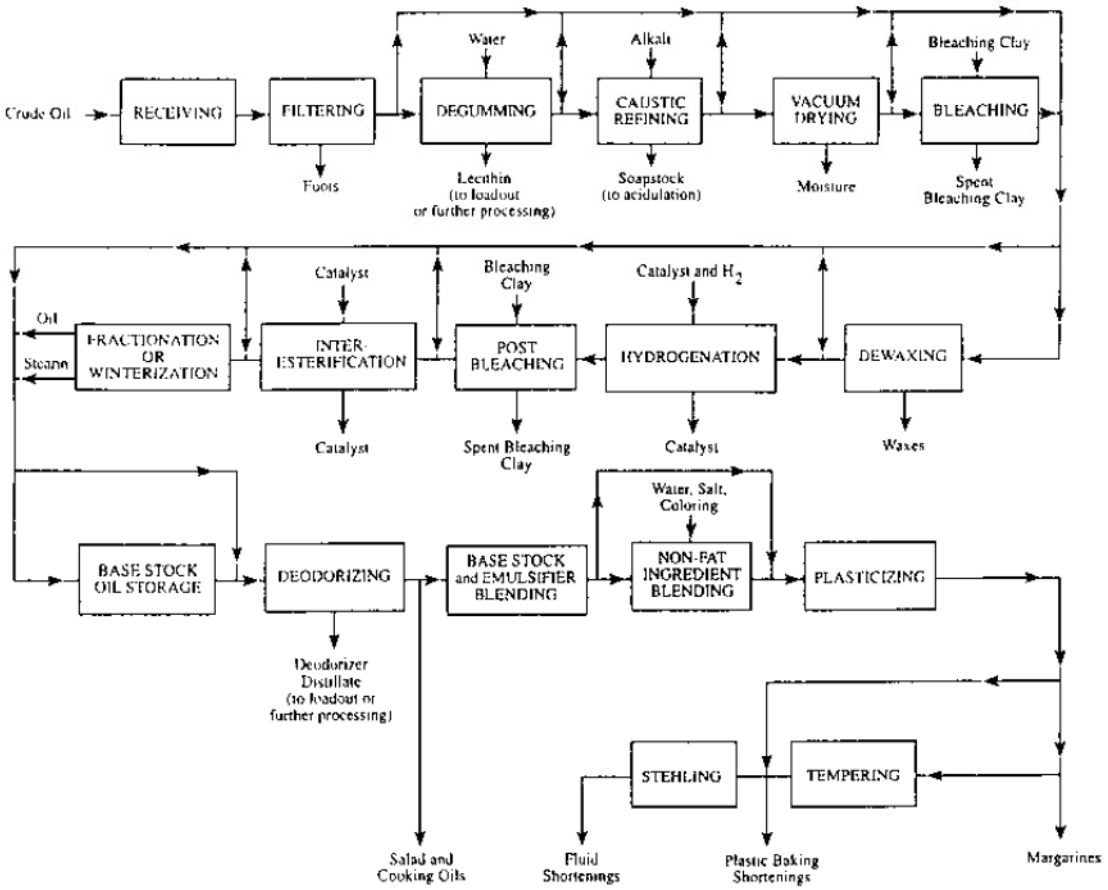


Figure 14 Steps in refining and converting edible oils.

storage or in the headspace. Degumming may be conducted either as a separate operation or simultaneously with neutralization. In the cases of oils rich in phosphatides, such as soybean and canola oils, degumming is usually a separate operation. Hydration makes phosphatides insoluble in the oil, and they precipitate, yielding an oil that is unattractive because of unsightly sludge or *gums*. Phosphatides can degrade and cause dark colors when the oil is heated as in the later deodorization step. All soybean oil in the export trade is degummed [38]. Phosphatides are also surfactants and, if present in frying oils, can cause dangerous foaming. When hot oil foams up and spills over the rim of a cooking vessel, it may burn the user; if it contacts a flame, it will catch fire. Phosphatides, also known as *lecithin*, are important food emulsifiers and, in the case of soybean oil, oftentimes become economical to recover.

The gums are rendered insoluble in oil by hydrating them with 1–3% water. As a general rule, the amount of water should be equivalent to the hydratable phosphatide content of the oil. If *single-bleached lecithin* is to be recovered, then hydrogen peroxide may be added to the water; if *double-bleached lecithin* is to be recovered, then benzoyl peroxide may also be added [39]. Alternatively, the degummed lecithin alone may be treated with hydrogen peroxide or both. The mixture is intensively mixed and then agitated for 30–60 minutes at 60–80°C in a slow mixing

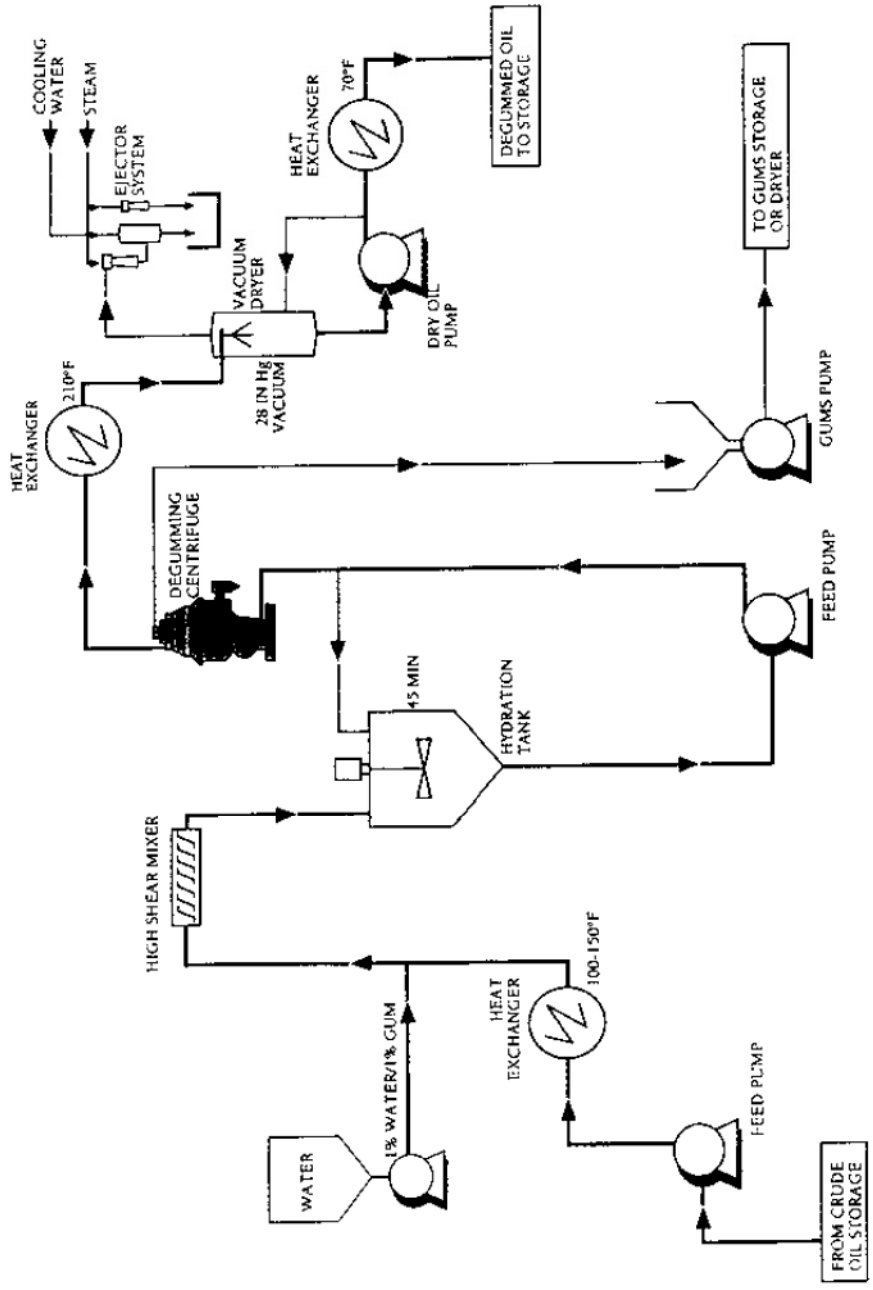


Figure 15 Process flow sheet for degumming. (Redrawn from diagram provided by Delaval Separator Co., Sullivan Systems, Inc., Larkspur, CA.)

vessel (hydration tank) to allow the phosphatides to become fully hydrated and to coalesce. Hydration of the phosphatides is not instantaneous, and adequate time must be allowed. Higher temperatures solubilize more phosphatides, and lower temperatures increase oil viscosity; either one reduces the efficacy of degumming [40]. The gums, being more dense than oil, can be removed by settling or filtering; more often, however, they are centrifuged out. The wet degummed oil is either dried (as described later) or immediately neutralized. Usually, about 90% of the phosphatides are removed by this process. The gums typically contain 25% water and 75% oil-soluble substances (of which one-third is neutral oil).

There are both hydratable and nonhydratable phosphatides. Of the 1–3% phosphatides in soybean oil, 0.2–0.8% are generally regarded nonhydratable. The phosphatides are composed of phosphatidylcholine, phosphatidylinositol, phosphatidylethanolamine, and phosphatidic acid. The first two are always hydratable; but, the latter two can complex with divalent metal ions, rendering them nonhydratable. ***Acid degumming*** and ***superdegumming*** make more of the phosphatides hydratable. Nonhydratable phosphatides remain oil soluble. The nonhydratable phosphatides are believed to be calcium and magnesium salts of phosphatidylethanolamine and, especially, phosphatidic acid, that arise from the enzymatic action of phospholipases when the cellular structure of the seed is damaged [41]. Nonhydratable phosphatides are particularly problematic in soybean oil.

Acid degumming is an improvement over conventional degumming described above and has become the usual practice in the U.S. soybean industry. A small amount (0.05–0.2%) of concentrated phosphoric acid (75%) is added to warm oil (70°C) followed by stirring for 5–30 minutes and degumming as described in connection with conventional degumming. Longer mixing times are often substituted for lower reaction temperatures. Phosphoric acid is added to make the phosphatides more hydratable by binding calcium and magnesium ions before adding water. Phosphoric acid pretreatment also partially removes chlorophyll from the oil.

Phosphatide content varies widely in vegetable oils but is highest in crude soybean oil (Table 2) [42–46]. Soybean oil is the only oil that is regularly degummed. The use of expanders in preparing soybeans for extraction almost doubles the usual phosphatide content of soybean oil. Only about half the phosphatide content of soybeans is extracted with hexane when preparing soybeans by flaking alone. Sometimes, the degumming operation is conducted at the mill so that the gums may be added back to the meal. Gums contribute digestible energy to livestock. The available U.S. supply of soy lecithin is about twice the volume that can be economically sold. The gums for lecithin production are dried and may be further purified and/or bleached. Soybean lecithin is a mixture of about 40% phosphatides (16% phosphatidylcholine, 14% phosphatidylethanolamine, and 10% phosphatidylinositol), 35% oil, 17% phytoglycolipids, 7% carbohydrate, and 1% moisture [49].

Recently ***superdegumming*** processes have been developed in which more of the phosphatides are rendered hydratable. A strong solution of citric acid is added to warm oil (70°C), and the mixture is stirred and cooled to 25°C to precondition the gums. Then water is added with stirring for an additional 3 hours to hydrate the gums. This process causes the phosphatides to form liquid phospholipid crystals, which are easily removed during centrifugation.

Another variation of degumming, ***dry degumming***, is occasionally applied to oils relatively low in phosphatide content, such as palm, coconut, and peanut oils.

Table 2 Properties of Some Crude and Refined, Bleached, Deodorized (RBD) Oils[a]

	Oils									
	Soybean[b]		Cottonseed[c]		Canola[d]		Palm[e]		Sunflowerseed[f]	
Properties	Crude	RBD	Crude	RBD	Crude	RBD	Crude	RBD	Crude	RBD
Triglycerides (%)	95–97	>99	NA	>99	NA	>99	NA	>99	NA	>99
Phosphatides (%)	1.5–2.5	0.003–0.045	0.7–0.9	NA	2.7–3.5	NA	0.006–0.013	0.012	0.5–1.0	NA
Unsaponifiable matter (%)	1.6	0.3	NA	NA	0.5–1.2	NA	NA	NA	<1.3	NA
Plant sterols	0.33	0.13	0.37	NA	NA	NA	0.036–0.062	0.011–0.016	NA	NA
Tocopherols	0.15–0.21	0.11–0.18	0.11	0.06	0.06	NA	0.06–0.10	0.04–0.06	0.05	NA
Hydrocarbons (squalene)	0.014	0.01	NA	NA	NA	NA	0.02–0.05	NA	NA	NA
Free fatty acids (%)	0.3–0.7	<0.05	0.9–37	<0.05	0.4–1.0	<0.05	2.0–5.0	<0.10	0.8–2.4	<0.05
Trace metals										
Iron (ppm)	1–3	0.1–0.3	NA	NA	1.5	<0.1	5–10	0.12	NA	NA
Copper (ppm)	0.03–0.05	0.02–0.06	NA	NA	0.10	<0.01	0.05	0.05	NA	NA

[a]NA, data not available.
[b]From Ref. 42.
[c]From Ref. 43.
[d]From Refs. 44, 45.
[e]From Refs. 35, 46, 47.
[f]From Ref. 48.

The oil is treated with concentrated acid to agglomerate the gums. The gums are then separated from the oil by being adsorbed to bleaching earth during subsequent steps of bleaching and filtering.

C. Neutralization (Alkali Refining)

The term *neutralization* comes from neutralizing the natural acidity of the oil emanating from the presence of free fatty acids. Some use the term *refining* to refer to neutralization. Neutralization is the most important operation in refining edible oils (Fig. 16). An improperly neutralized oil will present problems in subsequent refining steps of bleaching and deodorizing, and in conversion operations of hydrogenation and interesterification.

Neutralization is achieved by reacting the free fatty acid with caustic soda (sodium hydroxide) to form soap referred to as *soapstock*. *Saponification* refers to reactions between glycerides and sodium hydroxide to also form soaps. Neutralization must be done correctly or some of the glycerides will be saponified, resulting in increased refining loss. The oil, low in acid value, is termed *neutral oil*. Removing the soapstock must also be carefully done to prevent high losses of entrained neutral oil, a second means of increasing refining loss.

Soapstock is a coproduct of refineries in that it can be acidulated with sulfuric acid to produce a salable product. Once reacidified, the fatty acids (95% fatty acids) will separate in settling basins as 35–40% free liquid, so-called *acid oil*, from an emulsified layer (high in phosphatides) and a water layer. Most acid oil is used as a high-energy ingredient in livestock feed, but when market prices are attractive, it is sold to fatty acid producers, who distill it to produce feedstocks for various oleochemicals (e.g., surfactants and detergents).

In the case of cottonseed oil, proper and timely neutralization is important to achieve adequate removal of gossypol and oil that is low in red color. For reasons that are not clear, gossypol is adsorbed onto soapstock particles even though gossypol is unsaponifiable.

The amount and strength of sodium hydroxide used depend on the amount of free fatty acids present in the oil. Nearly all oils other than soybean and rapeseed oils are simultaneously degummed and neutralization. Free fatty acids form water-soluble sodium soaps, and any phosphatides become hydrated and water insoluble. The amount of sodium hydroxide used is termed *treat*. The proper treat produces adequately refined oil with the lowest refining loss. Excessive treat can saponify triglycerides and reduce the yield of refined oil. The proper treat is determined by titrating the oil to determine the free fatty acid content and using industry tables, such as those published in the *Official Methods and Recommended Practices of the American Oil Chemists' Society* [50].

Proper neutralization is dependent upon using the proper amount of sodium hydroxide, proper mixing, proper temperature, adequate contact time, and efficient separation. As in acid degumming, some oils are preconditioned with phosphoric acid. That is, prior to neutralizing the oil is treated with 0.02–0.5% phosphoric acid at 60–90°C for 15–30 minutes, making the phosphatides less soluble in the oil and more easily removed. The proper amount of caustic is proportionately metered into the warm oil stream with good mixing and sent to retention, or dwell mixers (5–10 min mixing time). The emulsion is then thermally shocked by heating to about 75°C

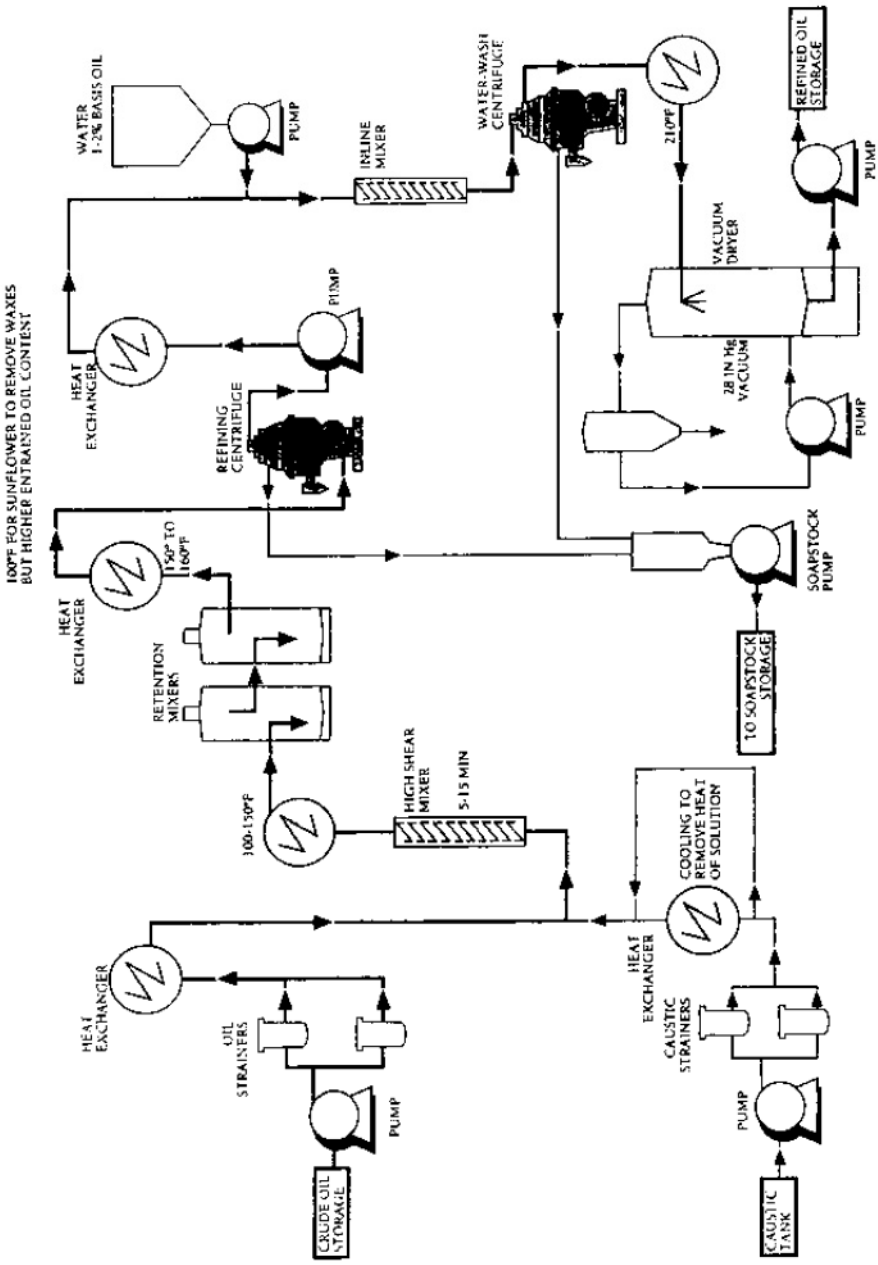


Figure 16 Process flow sheet for alkali refining. (Redrawn from diagram provided by Delaval Separator Co., Sullivan Systems, Inc., Larkspur, CA.)

to break out the soapstock. Soapstock is removed from the oil by using continuous, disk-type centrifuges. Refined oil is then washed with soft water (10–20%) at 90°C and recentrifuged to remove most of the soap. The remaining soap is removed during bleaching. The presence of excessive soap going into the bleaching operation can reduce the effectiveness in removing colors.

D. Miscella Refining (Neutralization)

Alkali refining or neutralizing in the presence of hexane is known as *miscella refining*. In the case of cottonseed, it is desirable to carry out alkali refining as quickly as possible after extraction (about 6 h) at the extraction plant; otherwise, gossypol may become fixed in the oil, hence unremovable [51]. Also, carrying out alkali refining in the presence of hexane reduces viscosity of the oil phase and increases the density difference between the oil phase and the water/soap phase. This improves the separation efficiency and reduces refining loss. Usually the oil content of the miscella is concentrated to 40–60% oil. The oil is mixed with sodium hydroxide with high-shear mixers, sometimes using high-pressure piston pumps with homogenizing valves. The mixture is heated to 65°C to melt the soapstock and then cooled to 45°C, and the aqueous and oil phases are separated by centrifuging. Water washing is not required in miscella refining. The neutralized oil miscella must then be evaporated and the oil stripped, dried, and cooled. Miscella refining produces oil with better color. The soapstock is usually added back to the meal by way of the desolventizer/toaster and contributes digestible energy to the meal.

The oil then is marketed as *once-refined oil*. Once-refined oil is re-refined as any other oil after arriving at the vegetable oil refinery, but much less caustic is required because most of the free fatty acid content has already been neutralized. Although any oil can be subjected to miscella refining, the additional capital investment in the safety features allowing centrifuges to work with hexane is justified only for cottonseed.

E. Drying

The water saturation level in edible fats and oils is about 0.8%; but oils should contain less than 0.3%. Vegetable oils must be dried before heating for prolonged periods to high temperatures as in hydrogenation and deodorization; otherwise, hydrolysis can occur, recreating free fatty acids. Drying is accomplished by spraying the hot oil (115°C) into a vacuum tower (15 mm Hg absolute vacuum). The moisture content of the degummed and neutralized oil is reduced to less than 0.1%. The gums for lecithin production are also vacuum dried in this manner to 0.5% moisture.

F. Bleaching

The primary purpose of bleaching (Fig. 17) is to improve oil color by removing pigments with neutral clays, activated earths, synthetic silicates, silica gel, and carbon black. Other benefits of bleaching are the breakdown of peroxides and cleanup of residual traces of soaps and phosphatides. The primary pigments of concern are those that give red-brown (carotenoids, xanthophyll, gossypol, etc.) or green colors (chlorophyll). The process is generally done under vacuum because the usual bleaching clays can catalyze oxidation in the presence of air (or oxygen). Adsorbent is mixed

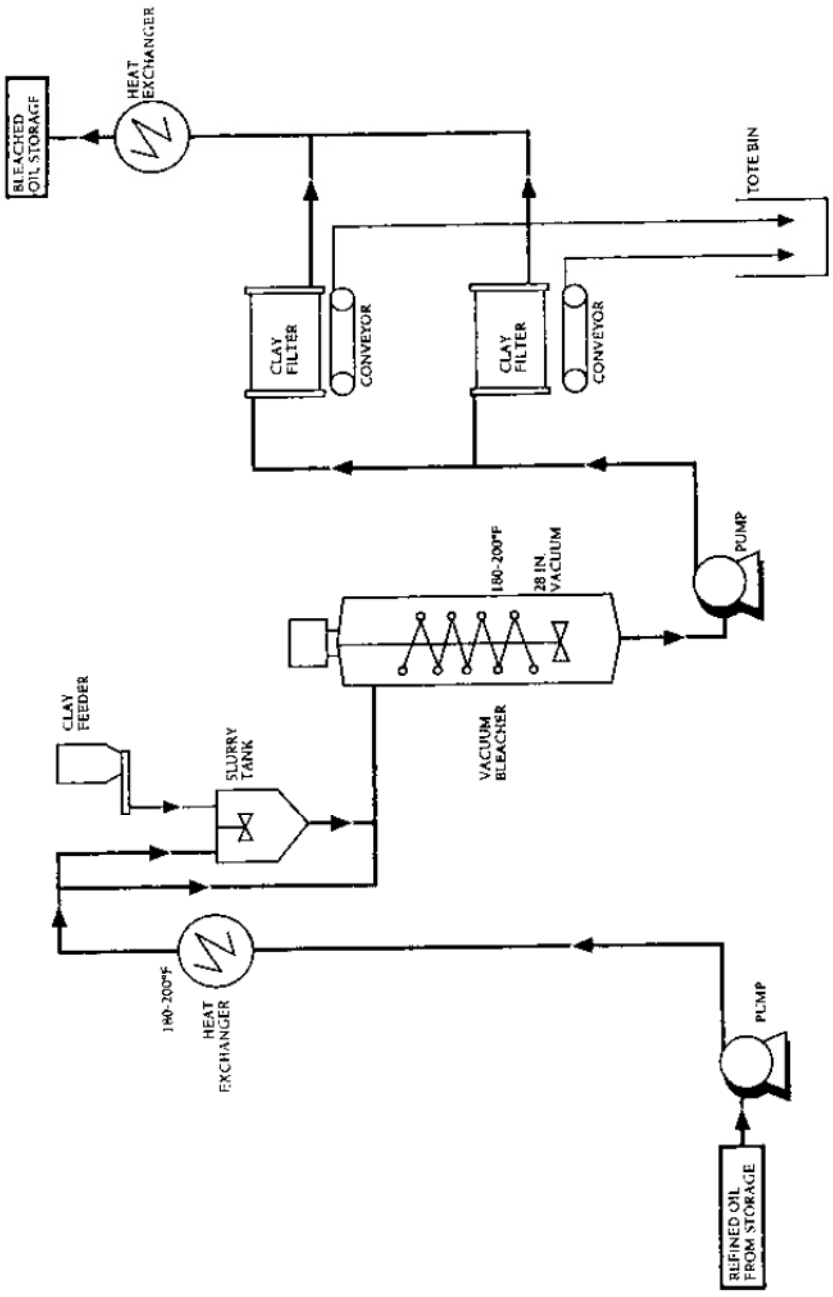


Figure 17 Process flow sheet for vacuum bleaching. (Redrawn from diagram provided by Delaval Separator Co., Sullivan Systems, Inc., Larkspur, CA.)

with hot oil (80–110°C) for 15–30 minutes to form a slurry. Mixing enhances oil contact with the adsorbent. The pigments are adsorbed onto the surfaces of various clays or earths (some may be activated by treatment with acid), even sometimes activated carbon, and the solids are removed by filtration. Activated earths are made from certain bentonites, specifically montmorillonite. Acid activation is believed to be achieved by replacing aluminum ions in the clay structure [52] with hydrogen ions by treating with sulfuric acid; excess acid is removed with water, and the activated earth is dried and milled [38]. The hard-to-bleach oils are normally done so with acid-activated clays.

Bleaching power seems to be a function of the clay's bound acidity, and clays with high total acidity and a reasonable level of acidity are preferred. If a bleaching clay is washed completely free of residual acid, bleaching power is greatly reduced. Clay from which water has been removed gives better results than clays containing adsorbed water; but if the earth is dried to less than 10% moisture, its internal structure will collapse, reducing surface area and thus adsorptive power. This partly explains why heating the oil/clay slurry is important, to remove water that is adsorbed in the clay lattices.

About 0.2–2% bleaching clay is usually used, the precise amount depending upon the amounts of pigments present. At the low end, 0.2–0.4% is used for soybean oil, while rice bran oil requires considerably more (3–5%). In addition to removing pigments and residual soap, bleaching takes out trace metals and some oxidation products. It is important to remove as completely as possible any residual soap (typically <10 ppm) because soaps can *poison* hydrogenation and interesterification catalysts, reducing their activities. Bleaching may be done batchwise or continuously.

Usually the earth is mixed with a small amount of the oil at cool temperatures (80°C), while the bulk of the oil is deaerated and heated to bleaching temperature (100–110°C). Time is not as critical as temperature, usually only 15–20 minutes are all that is required. Once the proper temperature and vacuum have been achieved, the oil/earth slurry is allowed to enter and become mixed with the bulk oil. Good mixing is important to allow for contacting the oil.

Filters are usually precoated with diatomaceous earth to enhance removal of the bleaching earth by leaf filters. Exhaustive removal of the earth is very important to oil stability because the earth acts as a *pro-oxidant*. Used bleaching medium is called *spent earth*. Spent bleaching earth contains some entrained oil, as much as 30–50%. The spent bleaching earth is blown with steam to reduce the oil content of the cake to about 20%. Some processors wash the cake with solvent to reduce the oil content to about 3%. Because of the large surface area that may be exposed to air and the catalytic effect of bleaching earth, spent bleaching earth is prone to spontaneous combustion and is regarded as a hazardous material by landfill operators. Disposal of spent bleaching earth is becoming a problem, and there is considerable interest in regenerating bleaching earth by extracting contaminants.

Edible oils should be pale yellow. Color is measured by the Lovibond tintometer, usually in red and yellow terms. Most finished edible oils are less than 10 yellow and 2.5 red, with high-grade shortenings being less than 1.0 red.

G. Dewaxing

Waxes can harm the appearance of bottled oil by causing unsightly cloudiness or sediments. Corn, rice bran, safflower, sesame, and sunflower seed oils are notorious

for problematic high wax contents (0.2–3.0%) and must undergo dewaxing; occasionally canola oil also has wax problems.

Waxes can be removed by cooling the oil to 6–8°C and filtering or centrifuging at cold temperatures, a process similar to winterization (described in more detail in Sec. IV.B) [52]. To get wax crystals large enough to ease separation, cooling must be done slowly over 4 hours, and the crystals should be allowed to mature for another 6 hours [40]. The oil is then carefully heated to 18°C and filtered.

Sometimes, dewaxing is accomplished simultaneously with removing the gums and/or soapstock by carrying out the centrifugation at cool temperatures. Sunflower seed oil is often predewaxed (from 1500 to 400 ppm) by cooling to 25°C for 24 hours and then degumming with a centrifuge at this temperature. Alternatively, sunflower seed oil may be simultaneously dewaxed and alkali-refined. After neutralization, as already described, the oil–soapstock mixture is cooled to 5–8°C and held there for 4–5 hours under gentle mixing; then the oil is mixed with 4–6% of water heated to 18°C. The soapy water phase wets and causes the small wax crystals to form a heavy suspension in soapy water. The soapy suspension is centrifuged to produce a wax/soapstock fraction and a refined, dewaxed oil [40]. Sometimes sodium lauryl sulfate is added to help wet the crystals [53].

H. Deodorization

The final step in refining fats and oils is deodorization (Figs. 18 and 19). Oils that are converted by a variety of processes are done so before deodorizing. The primary objective of deodorization is to remove compounds responsible for undesirable odors and flavors, such as residual free fatty acids (especially low molecular weight fatty acids), aldehydes, ketones, and alcohols. Deodorization also removes peroxide decomposition products; freshly deodorized oil should have a perioxide value of zero and free fatty acid content of <0.03%. These compounds are more volatile than are triglycerides and are preferentially removed. Lard is one fat that is often not deodorized, since the better grades have mild, unobjectionable flavors. Some losses of monoglycerides, sterols, sterol esters, tocopherols, and other natural antioxidants also result. The tocopherols are potent natural antioxidants and contribute significantly to the greater oxidative stability of crude oil compared to deodorized oil.

Deodorization is essentially steam distillation performed at high temperatures (180–270°C) and under high vacuum (3–8 mm Hg absolute pressure). Steam is sparged to carry away the volatiles and to provide agitation. Vacuum is usually provided by three to five stages of steam ejectors connected in series. Because deodorization is a mass transfer operation, deodorizers are designed to provide large surface areas and shallow oil depths. Only minor amounts of triglycerides are lost. The concentration of materials to be removed is in the range of 0.1–1% for most oils, and the original values should be reduced by over 99% [54]. The usual loss of oil weight is 0.2–0.8%. The amount of stripping steam ranges from 10–50 kg of steam per 100 kg of oil.

Factors that affect the efficacy of deodorization are the vapor pressures of the materials to be removed, the product flow rate, the intimacy of steam mixing with the oil, the absolute pressure achieved during deodorization, the temperature of deodorization (which controls the vapor pressure of the materials being removed), the sparge steam rate, and the time of deodorization [54,55].

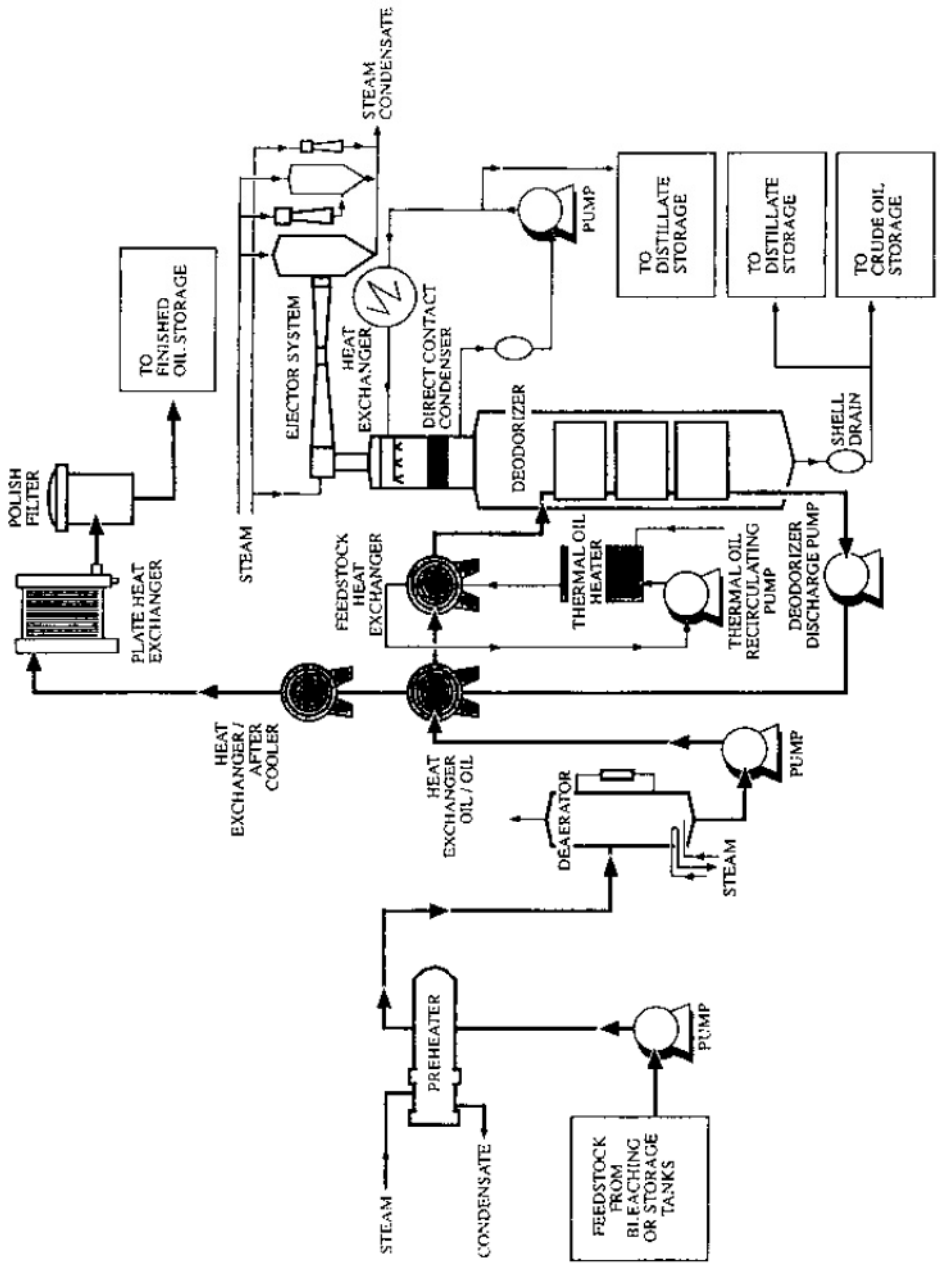


Figure 18 Process flow sheet for deodorization. (Redrawn from diagram provided by Delaval Separator Co., Sullivan Systems, Inc., Larkspur, CA.)

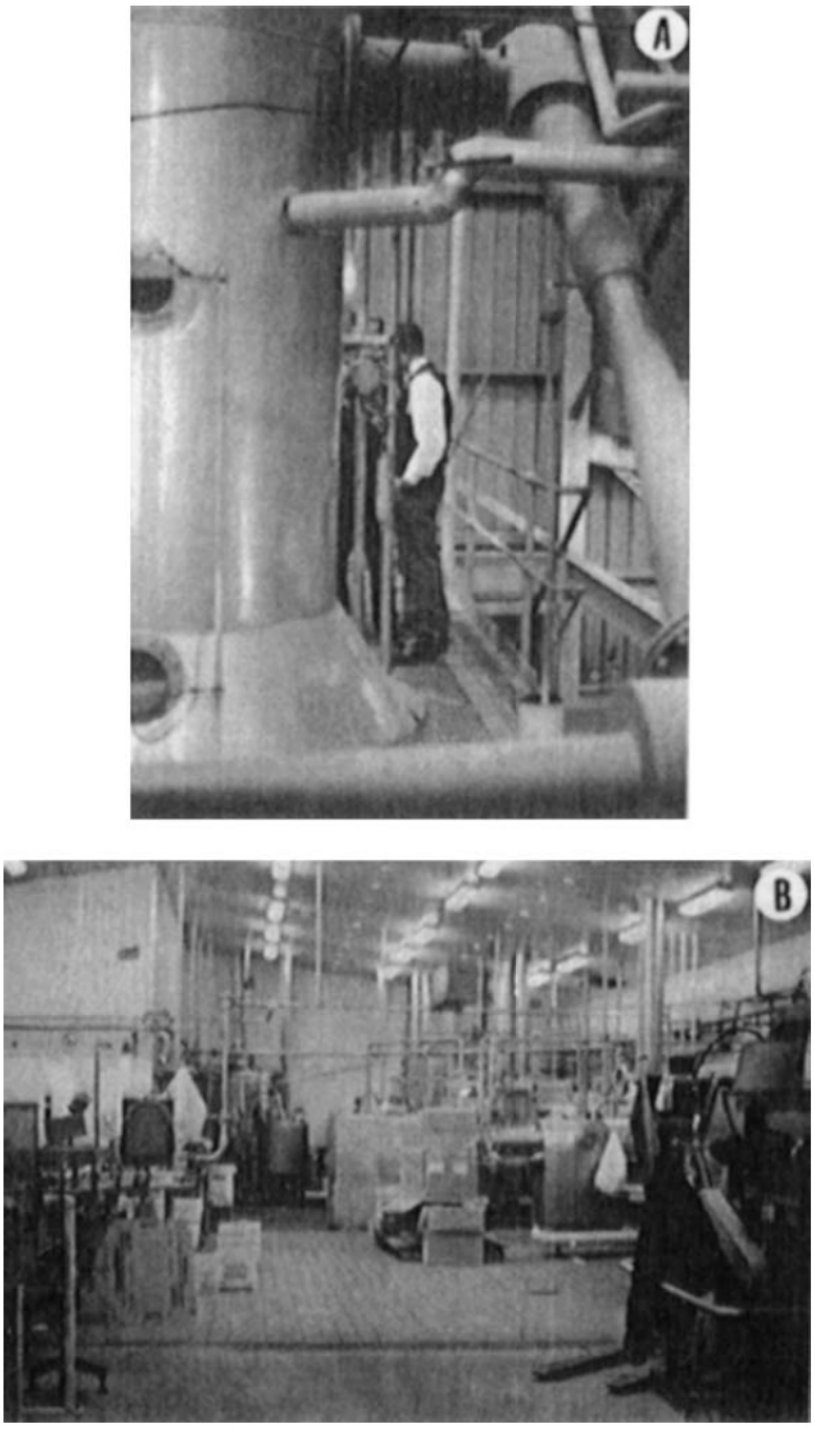


Figure 19 Oil processing facilities. (A) Oil deodorizer and (B) margarine packaging plant in Melbourne, Australia.

Usually steam alone is not used to heat the oil because very high steam pressures would be required to heat the oil sufficiently. Rather, a eutectic mixture of diphenyl and diphenyl oxide, known by the trade name *Dowtherm A*, is used. This product has a boiling point of 258°C and at 304°C generates a pressure of only 110 kPa (16 psi).

Deodorization may be conducted in either batch, semibatch, or continuous vessels. The type of process largely depends on the volume and number of different products being processed. Batch deodorizers have cycle times of 6–8 hours. Continuous deodorizers are most suitable when a limited number of products are manufactured in very large volume. There are five stages in deodorization: deaeration, heating, deodorization/steam stripping, heat recovery/cooling, and final cooling. Stripping steam is provided through sparging rings and airlift pumps. After the deodorized oil has cooled, a small amount (0.005–0.01%) of citric acid is added to chelate metal cations so they would not promote oxidation and reduce shelf life. Crude oils usually have greater oxidative stability than refined oils. Indeed, many processors do not expose deodorized fats and oils to the atmosphere, but discharge oil into tanks blanketed with nitrogen and fill bottled oil under nitrogen.

Deodorization also removes any residual pesticide and hexane. Some pigments, such as β-carotene, are destroyed by the high heat in deodorization and, thus, the yellow and sometimes red colors are reduced. Deodorized oils have improved flavor, odor, and color. The high temperatures used in deodorization cause limited geometric isomerization. Although deodorization removes most peroxides, it cannot reclaim rancid oxidized oils.

Deodorizer distillate is condensed, recovered, and sold at higher prices per pound than the oil itself. Soybean deodorizer distillate typically contains 12.3% tocopherols and 21.9% sterols [49]. Deodorizer distillate may be further processed into valuable fractions rich in tocopherols (vitamin E), which are in high demand by the food and pharmaceutical industries. The sterols may also be purified and sold into the pharmaceutical industry for manufacturing various synthetic hormones.

I. Physical Refining

Physical refining (Fig. 20) is also known as *steam refining*. These terms are applied to the removal of the free fatty acids from the oil rather than reacting them with alkali, as well as to the removal of the compounds normally targeted by deodorization. Physical refining combines both neutralization and deodorization into one operation. Physical refining is always preceded by degumming and bleaching steps. The major advantage of physical refining is that the yield of oil is improved because there is none of the neutral oil loss that accompanies the production of soapstock. This process also affords the possibility of recovering fatty acids for the oleochemical industry without the need for acidulating soapstock and attendant wastewater production. The equipment used for physical refining is similar to deodorization, but with additional steam sparging trays.

Not all oils are suitable for physical refining. The oil must be low in phosphorus content (most comes from phosphatides). The exact upper limit for phosphorus in oil suitable for physical refining is a long-standing controversy, but it may be less than 5 ppm. Higher levels result in dark colored oils. Physical refining is also more appropriate for those higher in free fatty acid contents because the benefit of higher

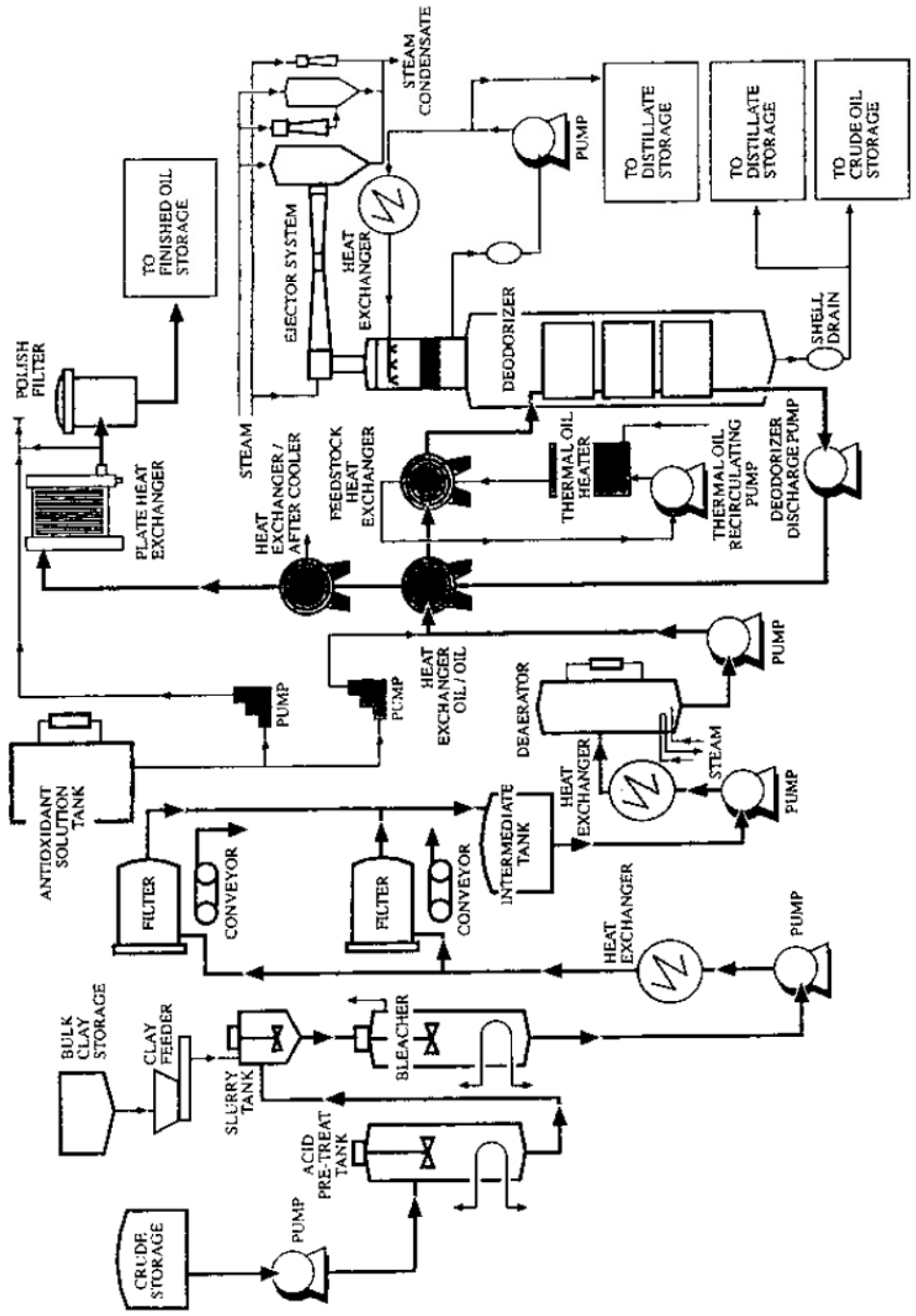


Figure 20 Depiction of physical refining. (Redrawn from diagram provided by Delaval Separator Co., Sullivan Systems, Inc., Larkspur, CA.)

yield justifies the cost of the process. Most regard soybean oil as being unsuitable for physical refining, or at best difficult to physically refine, while palm, rice bran, and coconut oils and animal fats are well suited to physical refining.

IV. CONVERSION

A. Background

Oftentimes, it is desirable or necessary to convert or transform highly unsaturated refined oils into more saturated forms; there may be the requirement for greater oxidative stability or altered physical forms of plastic and solid fats, or for less saturated forms to provide greater physical stability at cold temperatures (Fig. 14). The term *conversion* is often restricted to mean only *hydrogenation*, a process by which hydrogen is added to highly reactive, unsaturated, double carbon–carbon bonds. However, winterization, fractional crystallization, and interesterification, particularly directed interesterification, should also be regarded as modes of conversion, since these processes can also significantly change oxidative stability, physical stability, and functional properties of fats and oils, and their fractions. Stehling, votating, and tempering might also be considered to be conversion processes inasmuch as they are applied to the stabilization of fluid and plastic fats.

B. Winterization and Fractional Crystallization

The saturated fatty acids are not randomly distributed, and the oil can be fractionated into two or more fractions, differing in saturation level (as reflected by iodine value), and thus melting characteristics, oxidative stability, and functional properties. Both winterization and fractionation involve three stages: cooling the liquid oil to supersaturation to form nuclei for crystallization, gradual cooling to remove latent heat of crystallization as the crystals grow in size, and separating the crystalline fraction from the liquid [56]. Supercooling to very low temperatures establishes excessive amounts of nuclei, which results in promotion of very small crystals that are difficult to recover by filtration.

1. Winterization

Winterization was first widely practiced on cottonseed oil. During the early years, the oil was stored in outdoor tanks, exposed to cold temperatures in the winter months. The oil would cloud, and as the crystals grew, they settled to the bottom of the tank. The crystals are composed of triglycerides containing more saturated fatty acids than the triglycerides composing the clear liquid oil. The clear oil was pumped off the lower, crystal-rich fraction, called *stearin*. Typically, 20–25% of the cottonseed oil comprised the crystallized stearin [43]. Cottonseed stearin was blended with other high melting fats to be used as shortening or margarine, where the high palmitic acid content contributes to improved crystal formation with improved functionality. Unwinterized cottonseed oil would cloud when stored under refrigerated temperatures and was unsuitable for salad oils and mayonnaise (the emulsion would break when crystals formed).

Today winterization consists of cooling bleached oil under refrigeration by passing the oil through continuous, chilling heat exchangers to cool the oil to

4–7°C, and then to tanks with slow agitation. The amount of agitation is critical: agitation is required to remove latent heat of crystallization (fusion), but too much agitation breaks up the crystals, making them more difficult to remove. Sometimes, compounds that act as crystal inhibitors are added to increase crystal size and aid filtration [57]. After several days to allow the crystals to grow, they are removed, usually with vacuum filters, but sometimes with plate-and-frame filters or centrifuges. The winterized oil (called *winter salad oil*) is then deodorized and packaged or bulk stored.

Some processors have carried out winterization in solvents, such as hexane. The solvent reduces viscosity, improves the efficiency of filtration, and increases yield of winterized oil. After filtration the solvent must be removed from the two fractions. This process is called *miscella winterization*.

In addition to cottonseed oil, canola oil is often winterized. Sunflower seed oil may also be winterized, not to remove saturated triglycerides, but to remove waxes that cause similar problems. Partially or lightly hydrogenated soybean oil that is winterized to remove saturated triglycerides (GS_3) may be used for salad oils, which will have acceptable cold test values.

In a variation of winterization, some fats are pressed to achieve fractionation. Here a hydraulic press squeezes liquid oil from solid fat crystals. Hard butters for cocoa butter substitution in confectionery products and some specialty fats are produced by pressing of palm kernel and coconut oils [58].

2. Fractional Crystallization

So-called *dry fractionation* is a form of fractional crystallization very similar to winterization, but the term is usually reserved for more saturated fats (palm oil, palm kernel oil, animal fats), as opposed to liquid oils, where one or more cuts of crystallized fats, usually termed *oleins* (high in oleic acid), are removed from higher melting triglycerides, usually termed *stearines* (high in stearic acid). Temperatures higher than those normally reserved for winterization are used. For instance, crystallization of palm oil is carried out at 20°C to produce *palm olein* in about 70% yield and *palm stearin* (for shortening and margarine). A second fractionation at a lower temperature may be carried out to produce *super palm olein* (for frying and cooking oils) and *palm mid-fraction* (for cocoa butter substitutes). Fractional crystallization is used to make a number of cocoa butter substitutes from animal fats and from palm, palm kernel, and coconut oils.

Wet fractionation in various solvents (hexane, acetone, isopropanol, and 2-nitropropane) is also carried out on palm oil and hydrogenated soybean and cottonseed oils. Some confectionary fats and oils high in oxidative stability are produced by means of this form of fractional crystallization.

A third fractionation process is occasionally used, an aqueous detergent phase is mixed into preferentially wet, partially crystallized fat. The aqueous detergent phase contains 0.5% sodium lauryl sulfate, plus magnesium sulfate as an electrolyte. The crystals become suspended in the aqueous phase and are removed from the liquid oil by centrifugation. The water is removed from the crystals by heating the mixture and centrifuging. Both phases are washed with water to remove detergent and vacuum-dried to remove traces of water.

C. Hydrogenation

1. The Process

Hydrogenation was first used industrially to hydrogenate chemical feedstocks; it was first applied to whale oils in 1903 [59]. In 1909, hydrogenation was patented for use in producing shortening from cottonseed oil to replace lard. Hydrogenation is used for two purposes: to improve oxidative stability (by hydrogenating some of the double bonds to saturated ones) and to convert liquid oils or soft fats into plastic or hard fats (facilitating uses for which less saturated forms are unsatisfactory). Liquid oils are converted into shortenings and margarine fats; oils prone to rapid oxidation, such as soybean oil, are partially hydrogenated for use as salad and frying oils.

Unsaturated double bonds are converted to saturated bonds by addition of hydrogen (H_2). The reaction between the liquid oil and H_2 gas is accelerated by using a suitable solid catalyst; thus the reaction is ***heterogeneous*** involving three phases. Hydrogenation is exothermic, and heats about 1.7°C per unit drop in iodine value (IV) [60].

For successful hydrogenation, many of the crude oil impurities must be removed, and refining operations must be correctly carried out beforehand. Many of the contaminants (soaps, gums, sulfur, magnesium, potassium, chromium, zinc, and mercury) can poison the catalyst, reducing its activity. Canola and rapeseed oils are particularly notorious for high levels of natural sulfur content, which can cause problems in hydrogenation.

Both batch and continuous processes are used. For hydrogenation to occur, gaseous H_2, liquid oil, and solid catalyst must be brought together at a suitable temperature. Thus, hydrogenation is a mass transfer issue, and mass transfer of reactants is the rate-limiting factor (Fig. 21). H_2 is first dispersed as bubbles; then it must dissolve in the bulk oil, diffuse to the catalyst particle, and from there diffuse to the catalyst surface. Triglycerides also must diffuse to the catalyst surface, receive the H_2, and then diffuse out into the bulk oil. Therefore, a higher rate of reaction is achieved by raising the temperature and increasing agitation to disperse the gas in bubbles as small as possible. Small bubbles have more surface area for transfer per unit of mass for diffusion into the bulk oil. Agitation also keeps the film thicknesses small. Increasing gas flow rate helps to keep dissolved H_2 at high levels. The reaction is carried out in pressurized reactors because increased pressure increases the saturation concentration of H_2, hence the driving force for dissolution. Other factors that influence the reaction are the quantity and activity of the catalyst.

Pressurized reaction vessels are also used to contain the H_2, which is highly explosive should H_2, air (oxygen), and ignition come together. The reaction is normally conducted at 250–300°C over 40–60 minutes. The catalyst is mixed with a small part of the oil at room temperature. The bulk of the oil is pumped into the reactor, a vacuum is established, de-aerating the oil, and the oil is heated. Finally, the oil/catalyst slurry is added. The extent of reaction is followed by monitoring the refractive index (RI) of the oil, which is directly related to IV.

A catalyst increases the rate of reaction without being consumed in the reaction. Small amounts of catalyst are effective; in the case of hydrogenation, the usual amount is in the range of 0.01–0.02% of the weight of oil. Reduced nickel is the most widely used catalyst by the vegetable oils industry; but copper, platinum, palladium, and ruthenium are also effective. Nickel is the catalyst of choice because of

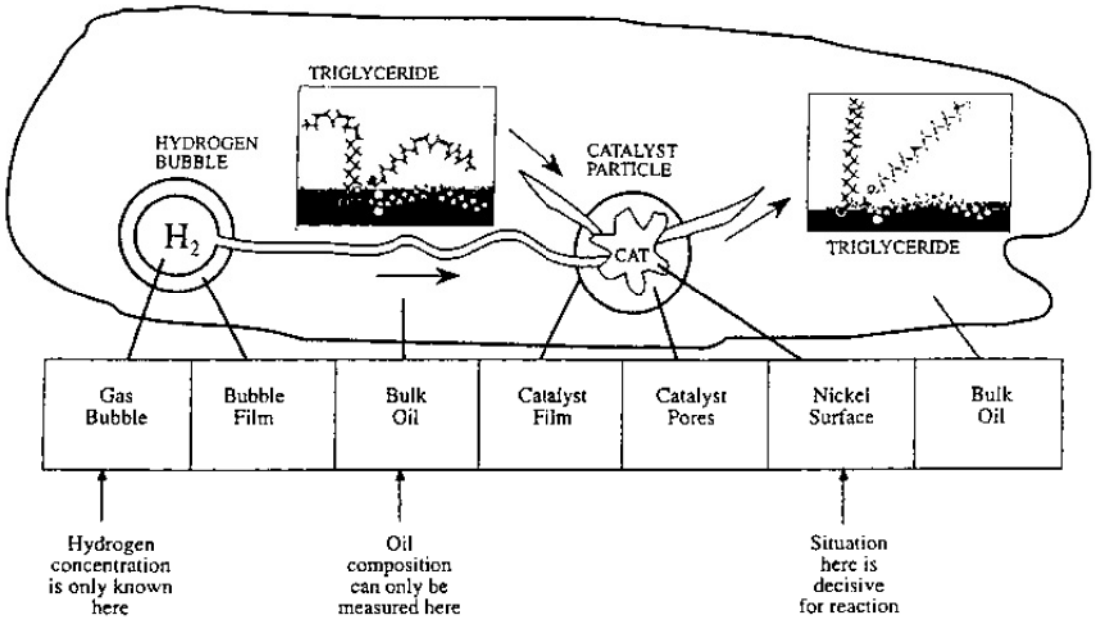


Figure 21 Hydrogenation reaction mechanism. (Modified from Ref. 61; photographs from Ref. 62.)

good activity, selectivity, filterability, reusability, and economical use. Copper has been occasionally used, but it must be completely removed to prevent accelerating oxidation. Since catalytic activity is a surface phenomenon, inducing pore formation increases surface area and thus activity [61]. However, the size and shape of pores in the catalyst are important: pores must be at least 10 nm in diameter in order to accommodate the transfer of triglycerides into them [60].

Catalyst promoters are substances that enhance the activities of catalysts without having catalytic activity themselves. It is believed that the promoter function is structural; that is, these substances somehow permit a larger number of active sites on the catalyst particle. For this reason, hydrogenation catalysts are commonly supported on siliceous materials, aluminum oxide, chromium oxide, cobalt oxide, or copper oxide.

Catalysts are expensive, but they can be reused numerous times. Hydrogenation catalysts can also catalyze oxidation. For these reasons, it is important to efficiently remove the catalyst from the hydrogenated oil and then recover it, which is accomplished by filtration. While surface area per unit weight increases as the size of the catalyst particle decreases, so does the relative difficulty of removing the catalyst by filtration. For that reason, the catalyst is often incorporated onto a support, such as 17–25% nickel fixed onto kieselguhr [60]. The catalyst is removed with leaf filters, and the filtered, hydrogenated oil is bleached to assure removal of all catalyst before deodorizing. This process, though termed *postbleaching*, is carried out in the same manner as normal bleaching.

2. Selectivity

Selectivity refers to the relative rates of hydrogenation of specific fatty acids; selective hydrogenation is the opposite of random hydrogenation. Ideally, the most un-

saturated fatty acids are hydrogenated before the less unsaturated fatty acids have become hydrogenated (Fig. 22). High selectivity gives high oxidative stability for a given IV. For many applications one wants as much oxidative stability as is consistent with producing oil having no solid fat crystals at normal usage temperatures. Selectivity is always relative because perfect selectivity [i.e., all linolenic acid (18:3) converted to linoleic acid (18:2) before any linoleic acid is converted to oleic acid (18:1)] has not been achieved. However, producing catalysts with ever-increasing selectivity is a goal of catalyst suppliers.

3. Isomerization

Two types of isomerization spontaneously occur during hydrogenation: *geometrical and positional*. Only the extent to which isomerization occurs can be affected by processing conditions and catalyst selection. Geometrical isomerization refers to conversion of only *cis* double bonds to *trans* double bonds. Most unhydrogenated plant oils have only *cis* double bonds in their constituent fatty acids; however, milk fat and animal depot fats may have modest amounts of natural *trans* fatty acids, usually attributed biological hydrogenation by rumen bacteria.

Positional isomerization refers to the shift of double-bond position within the chain. If hydrogen atoms exist on the catalyst surface, the double bond opens, and hydrogen atoms add to the carbons atoms at either end [63]. When the catalyst has sufficient hydrogen atoms, another hydrogen atom is added such that the original double bond is converted to a saturated, single bond between carbons. When there are not sufficient hydrogen atoms to cover the catalyst, a hydrogen atom may be removed from either side of the partially saturated bond. This produces a new double

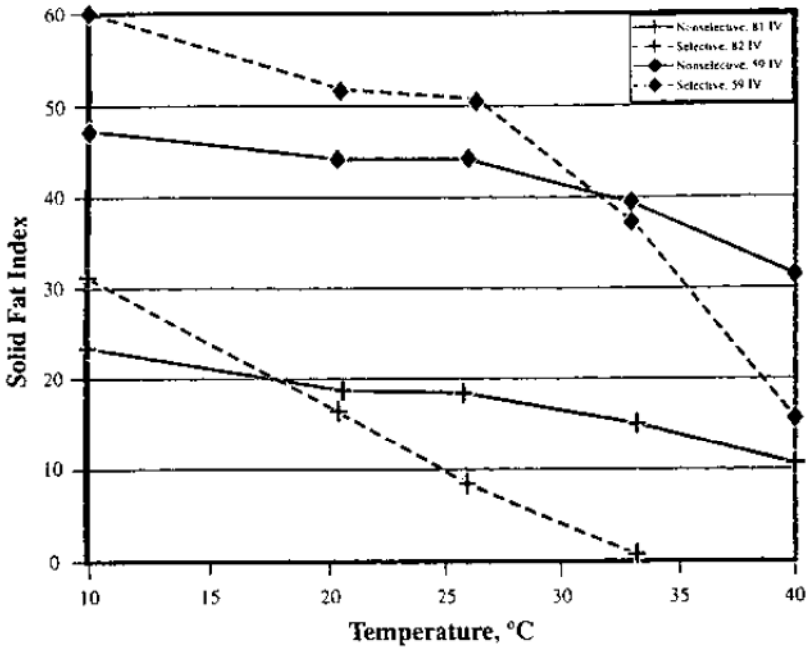


Figure 22 SFI properties of soybean oil hydrogenated under selective and nonselective conditions. (Redrawn from Ref. 53.)

bond, which may form in its original position or moved one carbon away, either up or down the chain. When the double bond re-forms, it may take either the *cis* or the *trans* configuration. These new double bonds may be half-hydrogenated and then dehydrogenated to re-form double bonds even further from the original position.

If hydrogenation is carried out at high pressure, low temperature, high agitation, high gassing rate, and low catalyst levels, then the catalyst is more saturated or covered with free hydrogen atoms, and there is little geometrical and positional isomerization. Also, under these conditions selectivity is low. However, under *starved conditions* of limited hydrogen on the catalyst surface, when the reaction could proceed much faster if more hydrogen were present, both isomerization and selectivity are high.

Hydrogenation cannot be conducted without producing some geometrical and positional isomerization; but a wide range in the extent of isomerization is possible. The more times the catalyst is reused, the less selective it becomes, and the greater its tendency to produce isomerization. This has been attributed to natural poisoning of the catalyst by contaminants even in well-refined oil.

4. Effects on Physical and Functional Properties

Hydrogenation raises the melting point and reduces the IV of the triglycerides, usually to convert oils liquid at room temperature to semisolid plastic fats. Completely hydrogenated fats (IV < 1) are solid and brittle at room temperature and are used to add solids in baking shortenings. An advantage of hydrogenation is that a wide range of physical properties can be achieved, depending on how much H_2 is reacted with the oil. Thus, the processor and the food scientist have great flexibility in developing new products. Solid fat index (SFI) as determined by dilatometry and solid fat content (SFC) as determined by pulsed nuclear magnetic resonance (NMR) allow the analyst to describe the relative amounts of solid fat versus liquid oil over a temperature range usually reported at 10, 21.2, 26.7, 33.3, and 37.8°C, thus affording a measure of plasticity (especially important to margarines, baking shortenings, and confectionery fats).

Since *trans* fatty acids melt at considerably higher temperatures than do *cis* fatty acids, the former contribute considerably to melting and plastic properties of the fats. In some products, a high level of *trans* fatty acids (as high as 55%) is desired for functional reasons, often to achieve proper melting characteristics (e.g., in cocoa butter substitutes). Margarines and shortenings usually contain substantial *trans* fatty acids (12–33%) [44]. However, there has been and continues to be considerable debate about the effect of *trans* fatty acids on health. Many now believe that *trans* fatty acids are not as atherogenic as saturated fatty acids but not as healthy as unsaturated fatty acids [64].

Some catalysts are treated (e.g., H_2S, SO_2, CS_2, and CO) to reduce sites available to hydrogen to increase *trans* fatty acid production. There is also interest in developing catlysts that produce lower amounts of *trans* isomers. Some of the semiprecious metals have this tendency (Fig. 23); but their costs are greater and recovery becomes even more important. Because some have higher catalytic activity than nickel, equivalent hydrogenation rates can be achieved at lower temperatures, reducing formation of *trans* fatty acids, as well as energy usage [65]. Precious metals are normally supported on carbon. Once the catalytic activity is spent, the catalysts

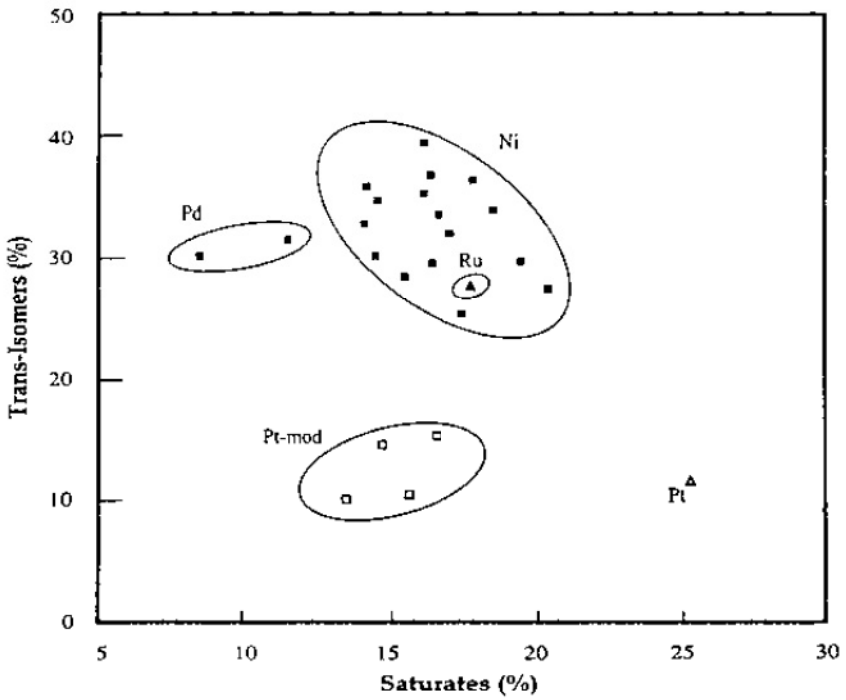


Figure 23 Effect of catalyst type on *trans* fatty acid content of hydrogenated soybean oil. (Redrawn from Ref. 65.)

are returned to the manufacturer for reclamation of the precious metal and remanufacturing of catalysts.

D. Interesterification

Interesterification, especially directed interesterification, can also be used to convert oils into more and/or less saturated fractions and ones with different functional properties from the original fat or oil or blend of two oils. Interesterification is described in much greater detail in Chapters 10 and 27.

V. STABILIZING PHYSICAL FORMS

Shortenings and margarines are *plastic*; that is, they have the appearance of solids in that they resist small stresses but yield to a deforming stress above a certain minimal value (the yield stress) to flow like liquid [66]. Shortenings and margarines are plastic at room temperature because they consist of two phases—solid fat crystals and liquid oil—and the solid crystals are sufficiently finely dispersed to be held together by internal cohesive forces (Fig. 24). Votating is conducted to produce the fine dispersion of solid crystals and entrained liquid oil. The dominant controlling factor for hardness is the relative proportion of solid crystals to liquid oil, followed by crystal size and *polymorphic* form (different crystal forms). The greater the proportion of crystals and the smaller the crystal size, the firmer the product, because there is greater opportunity for crystals to interassociate. The purpose of tempering is to facilitate transformation of the fat into the correct crystalline form.

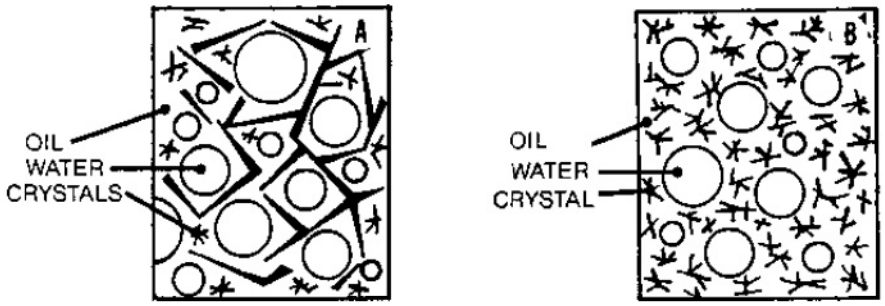


Figure 24 Plasticization of margarine. (A) Firm, with yield value of 1000 g/mL and (B) soft, with yield value of 200 g/mL. (Redrawn from Ref. 67.)

A. Crystallizing

1. Plasticizing

Plasticizing is the most commonly used process for chilling and plasticizing margarines and shortenings. *Votator* is one manufacturer's name for a swept-surface heat exchanger used to plasticize fat and thus the term *votation*. Molten fat is pumped into the first swept-surface heat exchanger known as an A unit, where the fat is supercooled to 15–25°C in 10–20 seconds, depending on the product. Ammonia or *Freon* products are used as the heat exchange media in the exchanger jackets by means of a direct expansion refrigerant system. Oftentimes 5–25 vol % of nitrogen, or in some cases air, is injected along with the melted fat and whipped or dispersed in the crystallized fat. The entrained gas makes shortenings white and may provide some physical leavening in bakery products.

The supercooled fat is then passed through one or more worker tubes, known as B units. Here the fat crystals are sheared while the heat of crystallization is dissipated. The temperature of the fat can rise 5–10°C as a result of the heat of crystallization. The fat at this point may be sent to a filling unit, or it may be subjected to a second but special heat exchanger known as a C unit. The final product will have a temperature of 13–24°C.

Firm table margarine is made with quiescent A units (lacking an internal agitator) replacing worker B units, whereas working B units are used to produce softer margarines.

2. Stehling

Stehling is a process that is often used to produce fluid shortenings, which are suspensions of fine crystals of solid fat in liquid oil. These products are pourable and pumpable, characteristics that are important to liquid frying shortenings, bread and cake shortenings, and nondairy products. Stehling is nothing more than stirring the oil/fat blend (and emulsifiers) after votating for a prolonged period at a precise temperature, to induce the formation of very small crystals that will remain dispersed in the liquid oil and not separate during reasonable transporting and storage periods.

B. Postprocessing Tempering

After plasticizing and packaging, shortenings are often moved to tempering rooms for 2–4 days, where the temperature is controlled at 25–35°C, depending on the

product type and tempering time [67]. During tempering the fat transforms from one crystal form to another more stable form, a phenomenon known as *polymorphism*. Polymorphism refers to the property of fats to exist in several different crystalline forms, depending on the orientation of the molecules in crystallized fat. The crystals spontaneously transform from one crystal type to another, successively to the most stable form, higher in melting temperature. Both the rate and the extent of transformation depend on the fatty acid composition, the votating conditions, and the temperature and duration of storage. Tempering expedites transformation to the most stable form. The least stable form is α, and no fats are stable in this form. The next form is β', and oils high in palmitic acid are stable in this form. This crystal form, characterized by smooth, small, fine crystals, is high functional in cake shortenings and margarines. The highest melting form is β, characterized by large, coarse, grainy crystals and is preferred in bread shortenings and confectionery fats.

Relative to untempered fats, tempering causes the fat to become slightly firmer above the tempering temperature and slightly softer at temperatures below the tempering temperature. The mechanism by which tempering occurs is not well understood, but it is believed to involve melting and recrystallization. Tempering serves to extend the plastic range of a shortening, rendering the product more functional. Untempered shortening may be grainy, brittle, and lacking in proper spreading qualities. Thus, tempering improves plasticity, creaming properties, and performance of baking margarines and shortenings.

VI. PROSPECTS FOR IMPROVED PROCESSES

Even though most regard the fats and oils industry to be mature, exciting new developments are in the process of adoption or testing. These developments involve advances in both processing techniques and equipment. In addition, new feedstocks modified through genetic engineering and traditional breeding could reduce or eliminate the need for some processing.

A. Expander Preparation

In recent years, expanders, an innovation pioneered in Brazil, have found acceptance for preparing flaked soybeans for extraction. Whereas with cottonseed, all the flakes are expanded, most soybean processors expand only part of the extractor feed, generally about 30%. As a result, part of the meal experiences more heat treatment than the unexpanded portion; but these differences are believed to have no practical significance. Expanding produces a porous collet for more rapid extraction, more complete drainage of solvent from the marc, higher miscella concentrations for lower evaporation costs, and higher bulk density for greater extractor capacity. Approximately 70% of the soybean mills in the United States now employ expanders.

In extrusion/pressing or expanding/pressing, whole soybeans are extruded or expanded, usually with an autogenous dry extruder (Fig. 25), followed by screw pressing. This nontraditional process is being used commercially in some unusual situations. In developing countries, for example, local processing of soybeans into crude cooking oils is attractive. Other applications of these extrusion/expansion techniques arise when specialty oilseeds are crushed for high-value oils, such as some genetically modified soybeans, and when high-value feed ingredients are produced

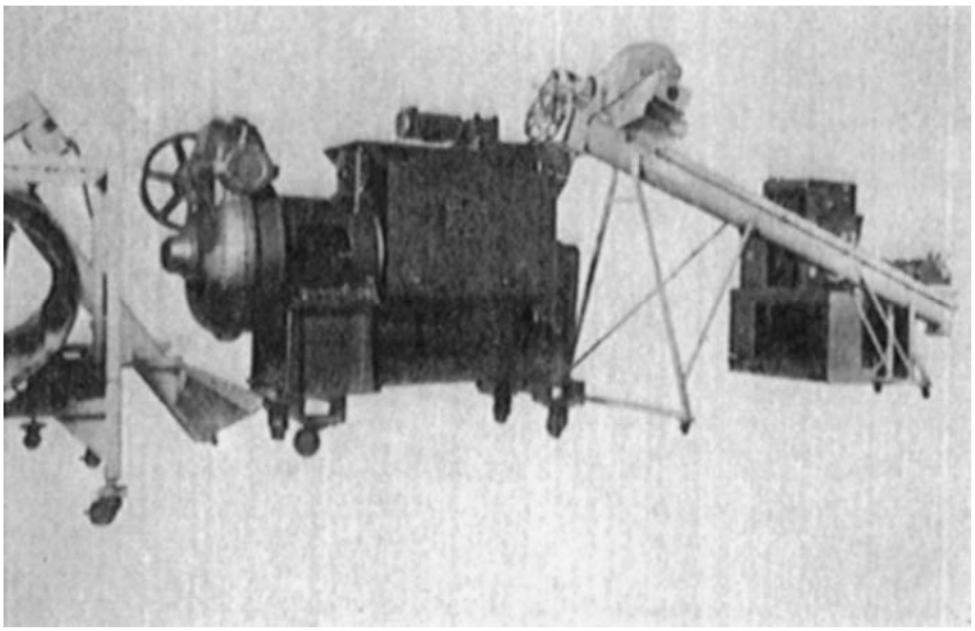


Figure 25 Equipment used in expander/pressing of oilseeds. (Courtesy of InstaPro Division, Triple F, West Des Moines, IA.)

(e.g., high-rumen bypass protein for dairy animals). The advantage is low capital investment, but a significant disadvantage is relatively low yield: about 6–7% residual oil is achieved compared with 0.5% residual oil for solvent extraction. Today, about 1–2% of the U.S. soybean crop is screw-pressed, but the percentage could increase if regulations on hexane emissions become more restrictive and mandated levels become more difficult to achieve.

B. Alternative Solvents for Extraction

The 1990 Clean Air Act is causing much concern over hexane emissions. *n*-Hexane, the main component of commercial hexane, is one of 189 Hazardous Air Pollutants listed in the Clean Air Act, and hexane will be regulated as both a *criteria pollutant* and a *hazardous air pollutant*. The emission limit as a criteria pollutant is 100 tons/year and as a hazardous air pollutant is 10 tons/year. To exceed either limit, a processor must obtain a federal operating permit, and there is an annual fee based on hexane consumption. Great strides have been made recently in reducing hexane loss, and today the average loss in a soybean plant would be about 0.2 gal/ton, down from 1.0 gal/ton 30 years ago. For a 2000 ton/day plant, however, this loss still translates into 460 tons of hexane per year.

While the industry continues to reduce hexane loss through engineering advances, a number of laboratories are researching alternative solvents (e.g., acetone, ethanol, isopropanol, isohexane, heptane) with less serious health and environmental risks. Enthusiasm for supercritical carbon dioxide has waned because of high capital costs and engineering problems in moving large quantities of solids through a reactor operating at very high pressure.

In a recent cottonseed plant trial, isohexane, a major component of commercial hexane, reportedly performed well and resulted in 38% steam savings [68]. But isohexane is even more expensive than hexane.

Work on ethanol and isopropanol has been going on for several years. The solubility of oil in these two solvents is temperature dependent, and this property can be used to advantage. High solvent-to-meal ratios are required because of low solubility compared with hexane. Acceptable energy usage is achieved by reducing evaporation costs by first chill separating. The full miscella is chilled to separate a heavier oil-rich phase containing more than 90% oil, which is stripped, and a lighter oil-lean phase that is recycled to the extractor. The extracted flakes are partially desolventized with mechanical presses followed by heat. Both solvent streams are used to wash the flakes. Although polar solvents usually extract poorer quality oil, the use of alcohols with chill separation produces good quality oil.

C. Membrane Filtration

Membrane technology to separate materials on the basis of molecular size has greatly improved in recent years [69]. *Microfiltration*, *ultrafiltration*, *nanofiltration*, and *reversed osmosis* are terms to designate different molecular weight separations. Membranes have been developed that are now stable to solvents and have greater selectivity. Membranes are being explored to concentrate oil in the miscella before evaporating.

Membrane filtration has considerable potential in degumming. When hydrated, the phosphatide molecule becomes oriented with the hydrophilic portion sequestered in the water droplet. In the nonaqueous environment of degumming, reverse micelles are formed. Micelles are large compared to the triglyceride molecules in which they are dispersed, and they are relatively easy to separate. The gums and pigments are concentrated in the 5% retentate, and high quality oil is recovered in the 95% permeate.

Membranes are also being explored to remove free fatty acids, and this approach appears to work. Perhaps more importantly, membrane-degummed oil is suitable for physical refining. Other applications for using membrane technologies in a vegetable oil refinery showing promise include miscella bleaching and hydrogenation catalyst removal.

D. Enzymatic Degumming

Both soybean and canola oils have high levels of nonhydratable phosphatides. Recently, enzymatic degumming for the conversion of nonhydratable phosphatides to hydratable forms has been perfected [70]. Water-degummed oil is treated with the enzyme phospholipase A_2 after adjusting the pH to 5 with citric acid. Phospholipase A_2 hydrolyzes the *sn*-2 fatty acid to form lysolecithin, which is easily hydrated and removed. The oil is sufficiently low in phosphatides to be suitable for physical refining.

E. Supercritical Fluid Refining

Supercritical fluids have been used to extract oil from oilseeds. The extracted oil is usually lower in phosphatides and free fatty acids. Although some report insufficient

selectivity, others claim success in using supercritical fluids to refine vegetable oils. Liquids are more suitable for supercritical fluid technologies than are solids in terms of material handling properties. Pumping against the high pressure is relatively easy.

F. Bleaching with Silica Gel

Bleaching clays are easily poisoned by residual soaps and phosphatides. Silica gel can be used to preserve adsorption capacity for pigments, especially problematic chlorophyll [71]. In the preferred method, the oil is contacted with silica gel before contact with clay occurs. When silica gel is incorporated, clay levels can be lowered by as much as 50%, reducing solid waste and neutral oil loss.

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