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Chemical and Physical Effects of Processing Fats and Oils[1]

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ABSTRACT

Soybean oil is processed for a variety of food uses, salad/cooking oil, margarine and shortening. Crude soybean oil is composed mainly of triglycerides but also contains measurable amounts of minor constituents that may have beneficial or detrimental effects on oil characteristics. The nature of these minor constituents, the role they play in oil stability or deterioration and their fate during processing are subjects of this review. Iodine value, fatty acid composition, solid fat index and congeal point are chemical and physical characteristics of oil that are affected by the hydrogenation process. Techniques and effects of degumming, alkali refining, bleaching, hydrogenation, winterization and deodorization are discussed. Utilization or disposal of by-products or wastes from each processing step is reviewed.

INTRODUCTION

In many countries, the major edible oils traditionally are consumed in a clean but unrefined form. Apart from hydrolysis, which releases free fatty acids, and oxidation, which causes rancidity, these oils are unaltered and any materials naturally present remain in the product. Examples of vegetable oils that are consumed in the unrefined state are peanut, coconut, rapeseed, mustard seed, palm, olive and sesame seed oils. However, processing crude oils to finished edible food products is practiced worldwide and is dictated by several factors: (a) consumer preferences, (b) flavor and stability characteristics of particular oils, and (c) preparation of hardened products from liquid vegetable oils, i.e., margarines and shortenings. These factors have lead to development of technological processes for treatment of crude oils to make them as bland and colorless as possible and for modification of the physical characteristics of the oils. The refining techniques consist of water or acid degumming, alkali refining, bleaching and deodorization. The refined oils and fats may be further processed by hydrogenation and winterization for different food uses. Each of these technological processes affects the nature of the oil; the character of these effects forms the basis of the current discussion.

In the United States soybean oil is the major vegetable oil used for production of edible food products. Significant quantities of cottonseed, corn, peanut, safflower and sunflower seed oils also are utilized in our domestic market. In general, the same technological processes are applied for the refining of all these oils with minor modifications based on the characteristics of the particular oil. Therefore, this paper will be directed to a consideration of processing soybean oil.

Composition of Soybean Oil

The typical compositions of crude and refined soybean oils are given in Table I (1). The refining process does not affect the fatty acid composition of the glyceride but does essentially remove phosphatides and free fatty acids and lower the contents of some lesser constituents such as the tocopherols, the sterols and squalene (2). Also present in very small quantities are a number of other materials including waxes, pigments and minerals. Waxes are the esters of long chain fatty alcohols and acids that originate from seed coats. Although waxes are a minor consideration with soybean oil, other oils such as sunflower seed, corn, safflower and sesame contain sufficient amounts of waxes (0.2-3.0%) to require their removal by a special dewaxing (3). One of the more prevalent pigments is β-carotene, which is the most important of the provitamins A. When present in higher concentration, β-carotene is also responsible for the red color of palm oil. Hydrogenation and high-temperature deodorization destroy the chromophore groups of β-carotene. Chlorophyll is also present and gives a greenish cast to soybean oil after the removal of the yellow color of β-carotene during hydrogenation. If immature or freeze-damaged soybeans are used for oil extraction, the content of chlorophyll can be sufficient to cause color problems in producing a finished oil (4). Minerals present in trace amounts include phosphorus, sodium, iron and copper. Iron and copper have been shown to be active catalysts for the oxidation of soybean oil (5) and their removal or inactivation is essential for oil stability.

PROCESSING

The processing techniques employed to produce a finished edible oil from crude oils are outlined in the flowsheet shown in Figure 1.

TABLE I

Average Compositions for Crude and Refined Soybean Oil (1)

Component	Crude oil	Refined oil
Triglycerides, %	95-97	>99
Phosphatides, %	1.5-2.5	0.003-0.015
Unsaponifiable matter, %	1.6	0.3
Plant sterols, %	0.33	0.13
Tocopherols, %	0.15-0.21	0.11-0.18
Hydrocarbons (squalene),%	0.014	0.01
Free fatty acids, %	0.3-0.7	<0.05
Trace metals		
Iron, ppm	1-3	0.1-0.3
Copper, ppm	0.03-0.05	0.02-0.06

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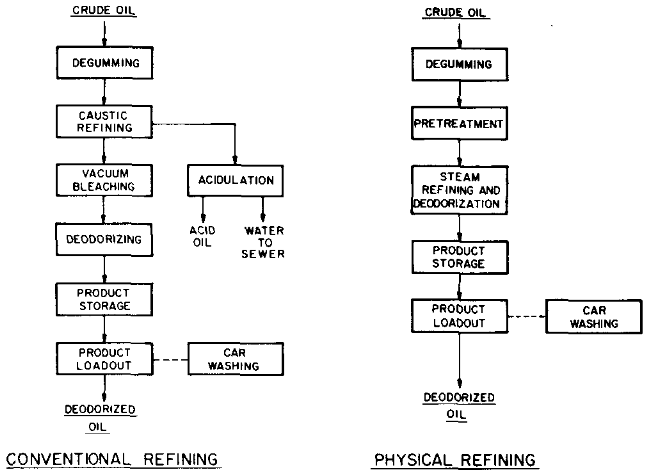

FIG. 1. Processing of edible oils.

Degumming

Crude soybean oil is degummed for one or more of the following reasons: (a) to produce for export an oil substantially free of materials that settle out during shipment or storage, (b) to recover phosphatides that can be processed to make soybean "lecithin" or (c) to remove emulsifying agents (i.e., phosphatides and mucilaginous gums) that increase loss of neutral oil when the oil is alkali refined (6). Degumming with phosphoric acid has been proposed as a necessary pretreatment to lower the content of phosphatides and metallic prooxidants sufficiently prior to physical refining (i.e., steam refining) of edible oil (7).

The principal method of degumming employed in the United States is a batch treatment of the oil with 1 to 3% of water, based on oil volume (8). The mixture is agitated for 30-60 min at 70-80 C. The hydrated phosphatides and gums can be separated from the oil by settling, filtering or centrifuging. The sludge obtained upon degumming soybean oil is a mixture of several phosphatides plus an oil carrier and other ingredients (Table II) (9). After drying, this mixture is marketed as commercial soybean lecithin and finds wide application as a wetting and emulsifying agent. Optionally, the lecithin may be bleached before marketing. About 90% of the phosphatides are removed from the oil by water degumming (10). Although most of the remaining phosphatides are removed during alkali refining, vegetable oils often contain some phosphatides that are not removed by hydration (5). These phosphatides can have a deleterious effect on oil quality. European processors use a phosphoric acid treatment of the degummed oil before alkali refining to facilitate removal of these nonhydratable phosphatides. If phosphoric acid is employed, chlorophyll is partially removed from the oil.

TABLE II

Approximate Chemical Composition of Natural Commercial Soybean Lecithin (9)

Fraction	%
Soybean oil	35
Phosphatidylcholine	16
Phosphatidylethanolamine	14
Phosphatidylinositol	10
Phytoglycolipids and other minor phosphatides and constituents	17
Carbohydrates	7
Moisture	1

Alkali Refining

Refining of soybean oil is practiced as a purifying treatment designed to remove free fatty acids, phosphatides and gums, coloring matter, insoluble matter, settlings and miscellaneous "unsaponifiable" materials. The treatment has little effect on the triglycerides of the oil. If crude oil is to be alkali refined it is conditioned with phosphoric acid to facilitate the purifying treatment (8).

Essentially all soybean oil in the United States is refined by the continuous process. An amount of 17-18° Be′ caustic, based on the free fatty acid content of the oil plus a 0.10-0.13% excess, is proportioned into the crude oil and mixed in a high shear in-line mixer. The soap-oil mixture is heated to 75-80 C and fed to a pressure or hermetic type centrifuge for separation into light and heavy density phases. Light-phase discharge consists of the refined oil containing traces of moisture and soap; the heavy phase is primarily soap, insoluble material, free caustic, phosphatides and a small quantity of neutral oil. Refined oil is washed with 10-20% by weight of soft water at 90 C. The water-washing process removes about 90% of the soap content in the refined oil; the remainder of the soap is removed in the bleaching process (11). Soapstock and wash water are combined and treated with sulfuric acid to convert the soap into crude fatty acids. Most of the acidulated soapstock is used as a high energy ingredient in animal feed. Depending on market demand, acidulated soapstock may be sold to fatty acid producers who recover the crude fatty acid by distillation as a valuable by-product of oil refining (12). Residue from this distillation is a good source of sterols. Nelson and Milun (13) reported that the sterol content of the distillation residue was almost 30%.

Bleaching

Bleaching of alkali-refined oils removes entrained soaps and reduces color bodies in the oil; it is more appropriately referred to as adsorption treatment. Although batch atmospheric bleaching is still used to some extent in the United States, batch or continuous vacuum bleaching is generally practiced. The process consists of agitation of the oil with 0.5-1.5% acid activated earth at 90-95 C for 15-30 min at a vacuum of 26-28 in. Hg followed by filtration to give a clean, clear oil.

Although bleaching generally improves oil quality with respect to color, initial and aged flavor, and oxidative stability, the technique also has other less obvious effects, some of which are desirable and others which are undesirable. Four factors have been determined to affect the degree of bleaching of an oil (14). Adsorption of color pigments by the adsorbent and a reduction in color through oxidation of certain pigments are two favorable factors. Color increases brought about by oxidation of other pigments and the stabilization of these oxidized pigments against adsorption are unfavorable factors. Bleaching earths were shown to catalyze these oxidation reactions. Vacuum bleaching has minimized these unfavorable factors. Such reactions and color changes are complex, i.e., oxidation and heat can bleach carotenoid compounds; these conditions may also encourage the formation of new pigments (15).

Neutral earths and those activated earths that have little or no acidity will produce little or no change in the free fatty acid (FFA) content of the neutralized oil. Some of the more acidic activated earths may add 0.05-0.10% to the FFA content, especially if the contact time is long or if moisture or soap is present.

Good soap removal by washing the refined oil before bleaching is desirable because the adsorption of relatively large amounts of soap lowers the adsorbent's capacity for other constituents in the oil. Generally, the soap content in oil is reduced to 5-10 ppm during bleaching.

Conjugation of oxidized polyunsatured fatty acids during bleaching has been reported (16). Oxidation of the oil before or during bleaching will promote conjugation; therefore, procedures such as deaerating both initial oil and adsorbent and vacuum bleaching help to suppress the conjugation reaction. *trans*-Isomerization has been shown to occur with acid-activated earths, but only at temperatures of 150 C and above, which far exceed those normally employed in bleaching (17).

Deodorization

In the edible oil refinery, deodorization is the last process step used to improve the taste, odor, color and stability of the oil by the removal of undesirable substances. All commercial deodorization, whether in continuous, semicontinuous or batch units, is essentially a steam stripping of the oil for removal of FFA and other volatile compounds. During the process, peroxide decomposition products, color bodies and their decomposition products are eliminated and the contents of sterols, sterol esters and tocopherols are reduced. Conditions of commercial deodorization are presented in Table III (18). The goal of deodorization is to produce a finished oil that has a bland flavor, a maximum FFA content of 0.05% and a zero peroxide value. The modern commercial deodorizer is equipped with a pollution control system that consists of three steps: the deodorizer distillate recovery system, closed circuit condensing water system and the vapor scrubbing system. The distillate recovery system removes 80-90% of the distillate from the steam train before it reaches the condenser. The short-chain fatty acid fractions pass through the recovery unit and are recovered from the vapor scrubbing system. The deodorizer distillate is a concentrate of tocopherols and sterols and is a valuable source of these materials.

Tocopherols are natural antioxidants found in vegetable oils and contribute significantly to oxidative stability. Due to the high tocopherol content of crude oils, they can be stored for long times if they are protected from air, moisture and high temperature (19). Frankel et al. (20) observed that at high concentrations of tocopherol the synergistic effect between citric acid and tocopherol was decreased. The concentration of natural tocopherols in soybean oil was too high for optimum oxidative and flavor stability. Sterols are complex polycyclic alcohols that are found as a class of compounds in all oils (21). The major sterols in soybean oil are β-sitosterol, campesterol and stigmasterol. Sterols are used for the production of synthetic hormones, whereas tocopherols are marketed as vitamin E. Nelson and Milun (13) determined the sterol and tocopherol contents of soybean deodorizer distillate by gas chromatographic analysis (Table IV).

The high temperatures used in the deodorization process have been shown to cause limited geometric isomerization of polyunsaturated fatty acids. Using capillary gas chromatography, Ackman et al. (22) analyzed the methyl esters prepared from commercial soybean oils undeodorized and deodorized (Fig. 2). They identified two major triene isomers produced by the deodorization: A is *cis*-9, *cis*-12, *trans*-15 and C is *trans*-9, *cis*-12, *cis*-15. Minor amounts of *cis*-9, *trans*-12, *cis*-15, and *trans*-9, *cis*-12, *trans*-15 were also identified.

The authors suggested that this analysis might be a convenient means of determining if a linolenic-acid-containing liquid vegetable oil was subjected to deodorization.

TABLE III

Commercial Deodorization Conditions (18)

Absolute pressure	1-6 mm Hg
Deodorization temperature	210-274 C
Holding time at elevated temperature:	
Batch type	3-8 hr
Continuous and semicontinuous types	15-120 min
Stripping steam: wt % of oil	
Batch type	5-15%
Continuous and semicontinuous types	1-5%
Product free fatty acid:	
Feed, including steam refining	0.05-6%
Deodorized oil	0.02-0.05%

TABLE IV

Unsaponifiables in Soybean Deodorizer Distillates (12)

Compound	%
Tocopherols	12.3
Δ	3.0
β and γ	7.7
α	1.5
Sterols	
Campesterol	5.7
Stigmasterol	5.2
β-Sitosterol	11.0

Hydrogenation

Partial hydrogenation of edible oils is practiced to increase stability by the selective reduction of linolenic acid. Hydrogenation results in extensive changes in the fatty acids of the triglycerides, reduces the carotenoid pigments and lightens the color.

Commercially, soybean oil hydrogenations are carried out with nickel catalysts; selective hydrogenations under conditions such as 5-14 psig, 0.05% catalyst at 177 C; and nonselective hydrogenation under conditions such as 15-50 psig, 0.05% catalyst at 121 C. Saturation of all the unsaturated bonds in one triglyceride molecule or in one molecule of fatty acids is rarely the major effect of partial hydrogenation. Shifts of the unsaturated bonds occur both in poly- and monounsaturated acids to yield a wide range of both positional and geometric isomers with the same number, or fewer unsaturated bonds as the original fatty acids.

For use as a liquid or salad oil, soybean oil is selectively hydrogenated to an iodine value of 115 or less (3). Such oils must be winterized to ensure that a clear, liquid oil is retained even at lower temperatures. The process involves the chilling of the oil to 6 C over a period of 24 hr and

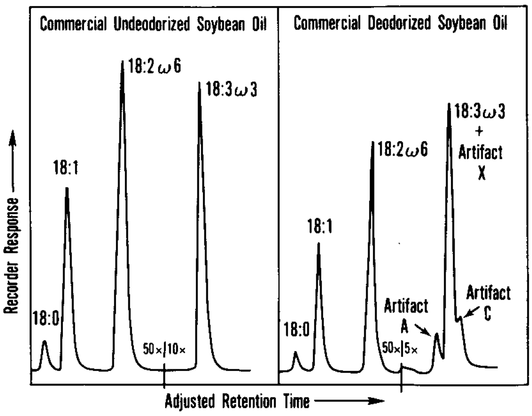

FIG. 2. Comparison of C_{18} group of acids from soybean oils from the same lot of oil before (*left*) and after (*right*) ordinary commercial deodorization. Aged butanediolsuccinate polyester open tubular column operated at 170 C and 40 psig. Elution time ca. 15 min for 18:0 (22).

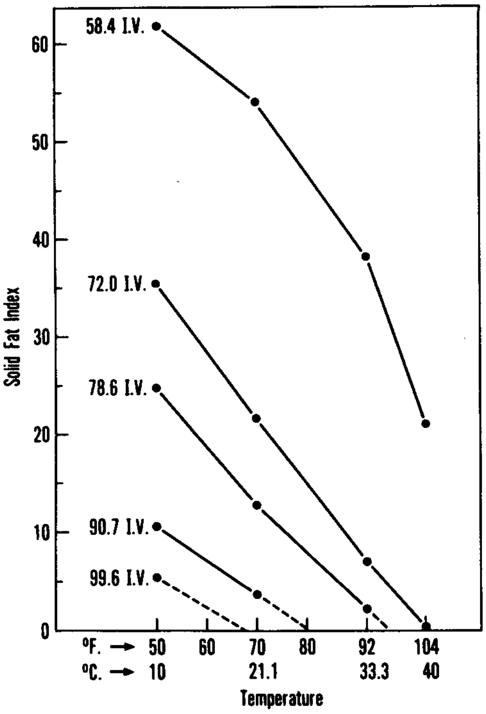

FIG. 3. Hydrogenation of soybean oil to successively lower iodine values increases its firmness as indicated by the solid fat index. Hydrogenation conditions: 0.02% nickel catalyst, 15 psig pressure, 300 F (149 C) temperature (23).

holding at this temperature for 6 to 8 hr. The high melting glycerides, palmitic and stearic acid fractions (mainly dipalmitoolein and dipalmitolinolein) called soy stearine, crystallizes and is removed by filtration. The yield of liquid oil is generally 75-85%. The dewaxing of sunflower oil is accomplished by a process very similar to winterization.

Nonselective hydrogenation yields a physically hardened product. The degree of hardening is determined by the solid fat index (SFI), which is an empirical measure of the solid fat content of an oil. While process variables can significantly affect the slope of the SFI curves, typical SFI curves for the hydrogenation of soybean oil are shown in Figure 3 (23). Examination of the SFI curves shows that as the iodine value end point is decreased, the SFI values at 92 F and 104 F begin to rise rapidly.

Adventitious Materials

Residues of chlorinated pesticides are adventitious materials reported in edible oils (24-26). Results of the analysis for several of these compounds in raw oils and in oils at various stages of processing is shown in Table V (26). Essentially, all of the compounds are removed by deodorization. The pesticide residues are concentrated in the deodorizer distillate and limit the use of this by-product as a feed additive.

TABLE V

Pesticide Residues in Soybean Oil at Various Stages of Processing[a] (26)

Pesticide	Crude oil	Refined oil	Bleached oil	Deodorized oil	Deodorizer condensate
α BHC	18.0	18.6	10.7	1.2	1459.0
Lindane	8.0	9.1	7.4	–	178.8
β BHC	8.5	7.9	2.3	1.7	173.8
Heptachlor	8.8	14.5	3.2	–	426.2
Aldrin	10.4	7.6	4.8	0.9	883.8
Heptachlor-epoxide	40.4	59.7	66.5	1.6	3648.4
Dieldrin	222.6	179.2	142.7	–	8012.9
Endrin	28.3	3.2	–	–	–
OP' DDT	15.4	29.6	1.8	–	822.7
PP' DDD	8.5	3.2	–	–	12.4
PP' DDT	18.8	20.8	12.5	–	768.2

[a] Parts per billion

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