cial processes for upgrading triglyceride structures to more valuable isomers.

APPROXIMATION OF PHYSICOCHEMICAL PROPERTIES

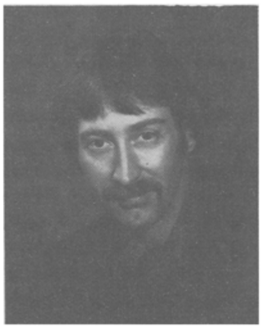
The quickest approach to the formulation of fat systems requires identification of the key functional attributes the fat system is expected to provide to the end use system, and the use of historical knowledge to identify those physicochemical properties which are likely to produce the intended functionality; e.g., the primary functional attribute of coffee cream is to whiten coffee. Secondary attributes may include consideration of flavor, appearance, stability and nutrition. If one wished to produce a coffee whitener derived from vegetable oil, historical data would acknowledge that the physicochemical properties of hydrogenated coconut oil meets fully the primary functional attribute. Secondary requirements are met at least in part. Indeed, coffee whiteners formulated from hydrogeanted coconut oil have been successfully manufactured and marketed for years. Although the triglyceride compositions of butterfat and hydrogenated coconut oil resemble each other little, both fat systems have key physicochemical properties conducive to meeting the primary and, in part, the secondary functional characteristics.

It is important to recognize and to identify key primary and secondary functional attributes and to disregard physicochemical differences which are unimportant to the end use system, when employing this approach to the formulation of fat systems. The utility of this technique is further enhanced when employed to develop new fat systems based on commodity oils such as soybean oil. Using this system, at least one manufacturer has developed a fluidized coffee whitener from soybean oil in which the primary functional attribute (whitening) exceeds that of either butter fat or hydrogenated coconut oil; at the same time, secondary characteristics are equivalent to the desired functional attributes.

A wide range of products has been commercially produced from soybean oil. Key to the efficient utilization of this approach to formulation of new fat systems is the use of experimental design for the systematic evaluation of physicochemical properties as modified fat systems in meeting key primary and secondary attributes. Although triglyceride composition is important to both approaches in product formulation, physicochemical evaluation offers more than one potential solution to the equation. Until a broader range of source-oil triglycerides becomes economically available or until processing technology is developed which will permit modification of triglycerides in existing commodity oils to more valuable triglyceride structures, approximation of physicochemical properties will be the preferred route to formulation of fat systems.

FUTURE

Efforts to broaden the scope and application of formulations based on replication of composition will be increased. Both new processing technology and new source oils will contribute to this increase. However, application will continue to be economical only for scarce, highly functional triglycerides. In the foreseeable future, fat systems based on low-cost commodity oils formulated to meet functional characteristics, rather than compositional criteria, will dominate.



Effects of Processing on Quality of Soybean Oil

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ABSTRACT

The fate of major and minor components of soybean oil is examined at each stage of processing. Relationships are then drawn upon the effect on the quality of finished oil. General topics covered are (a) triglycerides and polyunsaturated fatty acids, (b) free fatty acids, (c) mono- and diglycerides, (d) phospholipids, (e) minor constituents, such as tocopherols, color bodies, and metal ions, (f) rearrangement and decomposition products, (g) foreign or toxic compounds not native to soya and (h) other additives, such as refining aids.

INTRODUCTION

Soybean oil processing technology dates to the 1930s for food use in the United States. Yet, it seems that we learn more precisely how processing affects the oil as each year passes. Basic processing techniques have not changed much. Crude oil is degummed, refined, bleached and deodorized. Each year, minor modifications in techniques are introduced. For example, deodorizers are now built with a heat exchange tray so that the heat from the deodorized oil may be used to heat incoming, nondeodorized oil. This saves energy and is less abusive to the oil.

This paper was written to pull together and summarize various aspects of refining techniques on quality of the resultant oil. For the sake of clarity, each refining term will be defined. Crude soybean oil is generally hexane-extracted, desolventized and filtered. Degumming removes phosphatides. This step is performed by adding water to warm crude oil followed by centrifugation to remove the gummy, hydrated phosphatides. Refining lowers free fatty acid content. Degummed or crude oil is heated and sodium hydroxide solution is added. The mixture is centrifuged to remove the sodium soaps formed, then generally water-washed and recentrifuged to remove final traces of soaps from the oil. Bleaching lowers color intensity; it is done by adding small percentages of bleaching earth to hot, refined oil and filtering. Hydrogenation hardens the oil. Conditions used at this stage are dependent on the resultant oil desired. Nickel catalysts of various activities are used. Hydrogenation pressure, temperature and time will vary, and depend on the solid fat index curve to be obtained. Deodorization, the final step in the processing of oil, removes off-flavor constituents. It is done in a vessel consisting of several stages or levels. Undeodorized oil enters the top, is heated and is then passed down through successive levels where it is sparged with steam and vacuum-stripped of volatiles.

Soybean oil may be visualized as a solvent in which numerous components are dissolved. Some of these are beneficial; others are not. Furthermore, the solvent (pure triglyceride oil) itself can decompose. Therefore, processors attempt to remove most of the unwanted components while retaining those that are beneficial without decomposing the oil. This paper examines the fate of these components and oil as a function of processing.

DISCUSSION

Triglycerides and Polyunsaturated Fatty Acids

The polyunsaturated fatty acid content of soybean oil apparently is lowered during processing. This lowering generally results from oxidation or conjugation. An extreme example of this is shown (Table I) in oil extracted from storage-damaged beans (1).

Any stage of processing which oxidizes or polymerizes the oil will result in a reduction of the polyunsaturated fatty acids. Obviously, hydrogenation reduces the polyunsaturated fatty acid (PUFA) content. However, if *trans*-isomers are excluded as PUFA, this factor is reduced further.

Positional distribution of triglycerides apparently is not altered in processing. This was discussed in work by Carpenter et al. (2) when comparing refined vs cold-pressed soybean oil (Table II).

Free Fatty Acid Content

Caustic refining of soybean oil was devised to reduce the free fatty acid content. However, the degumming and deodorization steps are also effective in removing free fatty acids from soybean oil (3). We examined the free fatty acid content as a function of processing step (Table III) (R. Sleeter, unpublished data).

Mono- and Diglycerides

These artifacts are present in crude oil and their fate during processing was studied by Berner (4) using thin layer chromatography to separate the classes and enzymatic quantitative determination following complete saponification (Table IV).

Caustic refining saponifies a small amount of triglycerides forming diglycerides and soap, thereby increasing the diglyceride content at that point. No increase is observed in monoglyceride content due to the small amount of diglyceride available for hydrolysis. Further refining steps tend to lower the content of mono- and diglyceride content in the oil.

Phospholipids

Phosphatides are an unwanted constituent of refined soybean oil. If traces remain, heated oil will form break material consisting of darkened phosphatides. Phosphatides are removed by either degumming by centrifugation following the addition of 2% water to crude oil at 165 F or by straight caustic refining. Table V shows the phosphatide level at each succeeding stage of processing as indicated by phosphorous determination.

Quite a bit of variation is seen in the efficiency of degumming on a plant scale, as shown by the widely variant phosphorous amounts following that step. Caustic refining makes up for poor degumming and reduces the phosphatide content to equivalent levels.

Degumming is hindered by non-hydratable phosphatides (1,5). Hvolby (5) has found that magnesium and calcium salts of phosphatides and lysophosphatidic acids form the greater part of nonhydratable phosphatides. These may be

TABLE I

Relationship between amount of Damage of Soybeans vs Fatty Acid Composition (1)

		Fatty acid composition				
Soybean samples	Degree of damage	16:0	18:0	18:1	18:2	18:3
Undamaged	None	10.5	3.0	21.2	58.3	6.9
Field-damaged	Slight	10.6	4.6	22.6	55.6	6.4
Storage-damaged	Heavy	14.1	4.4	23.6	55.9	2.0

TABLE II

Fatty Acid Distribution As a Function of Triglyceride Position (2)

	Fatty acid distribution	
Fatty acid	2-Position	1,3-Positions
16:0	0	17
18:0	0	6
18:1	25	24
18:2	69	45
18:3	6	8

TABLE III

Relationship of Free Fatty Acid Content As a Function Processing Step[a]

Processing steps	Free fatty acids from two different runs (%)	
Crude	0.61	0.53
Degummed	0.31	0.44
Refined	0.05	0.05
Deodorized	0.02	0.03
Hydrogenated, nondeodorized	0.15	–
Hydrogenated, deodorized	0.025	0.03

[a] R. Sleeter, unpublished data.

TABLE IV

Mono- and Diglyceride Content of Soybean Oil vs Degree of Processing (4)

Degree of processing	Monoglyceride	Diglyceride
	(%)	
Crude soybean oil	0.11	1.10
Refined	0.10	1.44
Bleached	0.06	1.25
Deodorized	0.07	1.05

TABLE V

Phosphorous Content of Soybean Oil As a Function of Processing Step[a]

Processing step	Phosphorous from two different plant runs (ppm)	
Crude	600	603
Degummed	58	423
Refined	13.1	15.1
Deodorized	0.16	.47
Hydrogenated, nondeodorized	0.17	–
Hydrogenated, deodorized	16.1	12.2

[a]R. Sleeter, unpublished data.

reduced using various acids or bases in the hydration water. Several samples are shown in Table VI.

Soybean oil from field- or storage-damaged beans contains increased amounts of nonhydratable phospholipids (1). However, if crude oil itself is damaged, e.g., as a result of abuse due to overheating to remove hexane during desolventizing, the phosphatide content is lowered (6).

Failure to remove trace levels of phosphatides can result in poor hydrogenation later in the processing. Figure 1 shows the direct relationship between inhibition of hydrogenation and the phosphorous content (7,8).

It has been reported that having residual phosphatides in the oil may be beneficial because of the antioxidant properties claimed for soy phospholipids (9,10). Other workers have found pro-oxidative effects of phospholipids (11,12). Part of this controversy has been answered in a paper by Mieth and Linow (13). Figure 2 shows the antioxidant properties of soy phospholipids.

Their further investigations of isolated fractions (shown in Fig. 3) tell a different story. The authors attribute the antioxidant properties to accompanying substances such as

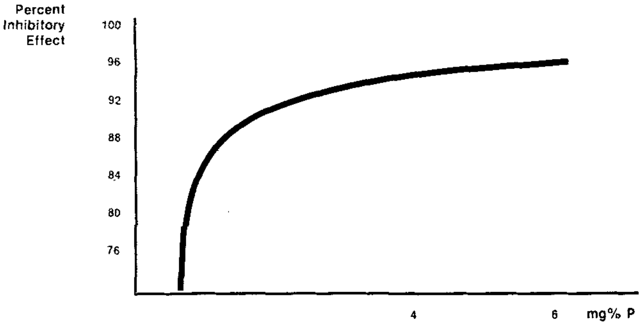
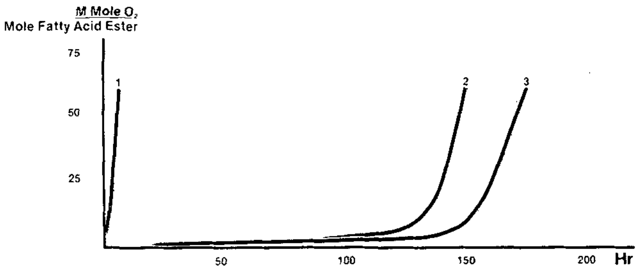
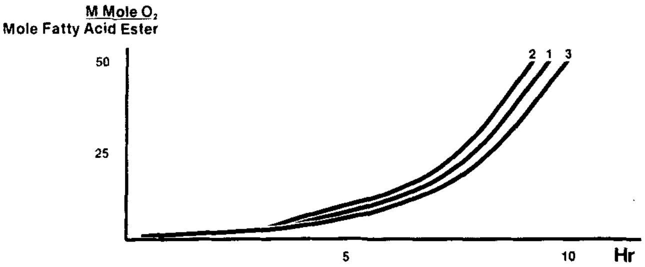


FIG. 1. Inhibitory effect of soy lecithin on hydrogenation of soybean oil (6).



1) Blank oil, 2) Blank oil plus 1% Soy Phospholipids, and 3) Blank oil plus 0.01% propyl gallate

FIG. 2. Influence of phosphatides on the oxygen absorption of methyl linoleate (13).



1) Blank oil, 2) Blank oil plus 1% Phosphatidyl Choline, and 3) Blank oil plus 1% Phosphatidyl Ethanoamine

FIG. 3. Influence of purified soybean phospholipid fractions on the oxygen absorption of methyl linoleate (13).

TABLE VI

Relationship of Phosphorous, Magnesium and Calcium Content of Soybean Oils Degummed at Various pH Values (5)

Sample	mmol/kg		
	Phosphorous	Magnesium	Calcium
Crude oil	16.9	2.84	2.64
H_2O degummed	5.51	1.74	2.31
pH 0 degummed (1 N HCl)	.30	0.01	0.00
pH 2 degummed (HCl, NaCl, citric acid)	1.02	0.27	0.43
pH 4 degummed (NaOH, HCl, citric acid)	2.99	0.85	1.41
pH 6 degummed (NaOH, citric acid)	4.15	1.26	1.96
pH 8 degummed (HCl, $Na_2B_4O_7$)	4.18	1.25	2.08
pH 10 degummed (NaOH, $Na_2B_4O_7$)	2.55	1.02	1.54
pH 12 degummed (NaOH, NaCl, NH_2 CH_2COOH)	1.83	.71	1.07
pH 14 degummed (NaOH)	0.00	0.00	0.00

tocopherols, amino acids or Maillard products, and not to phosphatides themselves.

Further, it has been shown that phosphatides act as sequestering agents. Lunde et al. (14) have shown that metal ions are transferred from water into vegetable oil when these oils contain phosphatides. This would tend to result in an oil of lower stability if these ions were prooxidants, such as copper and iron, present in water during the degumming and caustic washing steps.

Naturally Occurring Trace Constituents of Soybean Oil

There are numerous classes of compounds found in varying amounts in soybean oil which are not formed as a result of decomposition or rearrangement. These would include tocopherols, sterols (free and bound), triterpene alcohols, hydrocarbons, color bodies (chlorophylls), trace metals and residual proteins. These constituents make up the unsaponifiable fraction of soybean oil.

Tocopherols

Of these various components, most attention is given to the tocopherols. Kanematsu et al. (15) and Carpenter et al. (2) have studied the tocopherol content at various stages of processing for the α-isomer and for all isomers in the finished oil, respectively. Gutfinger and Letan (16) studied the total tocopherol content at all stages of processing (Table VII). As shown, the tocopherol content decreases during each step of processing and may be markedly reduced during deodorization, as the tocopherols are volatile under these conditions.

Bleaching clay was studied for its effect on the tocopherol content (17). The amount of α and δ tocopherols changed very little. γ-Tocopherol was partially adsorbed and oxidized by the clay. It is anticipated that bleaching would lower the tocopherols. Because the tocopherols are powerful natural antioxidants, optimal processing conditions are those which retain these compounds in their active form. Therefore, abuse of the oil by exposure to air or heat will reduce the content by oxidation and polymerization.

Sterols and Hydrocarbons

Sterols present in soybean oil also tend to be reduced in processing and the magnitude of reduction is about the same as the tocopherols (16) (Table VIII).

Squalene is reduced during processing (16), but not drastically until deodorization, when it is reduced because of volatility. It has been shown (17) that the absorption of sterols is increased extensively with increased amounts of bleaching clay. The lipid extract from the bleaching clay had high concentrations of sterols in unchanged form. Popov and coworkers (18) (Table IX) have found that the total sterol and steryl glycoside content of the oil is reduced in the degumming step, as shown by their enrichment in the lecithin.

Triterpene Alcohols

Triterpene alcohols have been found in degummed soybean oils to the extent of 0.06% (19). These included cycloartenol, α-amyrin, β-amyrin and cyclolaudanol. These were not quantified or examined at various stages in processing.

Chlorophylls and Related Compounds

Early frosts while beans are immature cause soybean oil to have a greenish color. This oil has an absorbance maxima at 660 nm. Hydrogenation of this oil produces a gray

TABLE VII

Tocopherol Content at Various Stages of Processing

Processing step	α-Tocopherol (ppm) (15)	Loss (%)	Total tocopherols (ppm) (10)	Loss (%)
Crude oil	302		1132	
Degummed			1116	1.4
Refined	289	4.3	997	11.9
Bleached	257	14.9	863	23.8
Deodorized	242-146[a]	19.8-51.2	726	35.9

[a]Depending on conditions.

TABLE VIII

Effect of Processing Step on Sterol and Squalene Content (16)

Processing step	Sterols (ppm)	Loss (%)	Squalene (ppm)	Loss (%)
Crude oil	3870		143	
Degummed	3730	3.6	142	0.7
Refined	3010	27.2	140	2.1
Bleached	3050	21.2	137	4.2
Deodorized	2620	32.3	89	37.8

TABLE IX

Effect of Degumming on Sterol Content (18)

Oil or fraction	Free sterols	Sterol esters	Sterol glycosides	Total sterols
			(%)	
Crude oil	0.30	0.01	0.23	0.55
Phosphatides following degumming	0.74	0.01	1.93	2.68

appearance and shifts the absorbance maxima to 642.5 nm while the oil retains a greenish cast. Chlorophyll A has an absorbance maxima of 660 nm whereas chlorophyll B is at 642.5 nm. Yellow and red pigments also are present. In salad oils, these pigments tend to mask the green color. However, these pigments are reduced during hydrogenation, thereby amplyifying the green color.

Pritchett and coworkers (20) produced data on the effect of processing on the chlorophyll content. Table X summarizes their work. Obviously, since bleaching has the greatest effect, the amount of bleaching an oil receives is governed by the chlorophyll content. This aspect was studied by Hinners and coworkers (21), who examined various amounts and pH levels of bleaching earths on the chlorophyll content (Table XI).

The more bleach used, the lower the color intensity and, furthermore, the more strongly acidic or basic, the more effective the bleach.

Protein and Nitrogen Content

The nitrogen content of soybean oil is primarily in the form of nitrogen-containing phospholipids and would, therefore, be expected to decrease as the phosphatides are removed. The reduction of the nitrogen content as a function of processing was shown experimentally by McGuire et al. (22) (Table XII). A portion of this trace nitrogen in fully processed soya oil was residual protein. Tattrie and coworkers (23), in a nice piece of work, fractionated refined and bleached soybean oil. One fraction which showed traces of protein was acid-hydrolyzed and analyzed for individual amino acids. They found, e.g., the following amounts of amino acids in 10 g of oil: aspartic acid, 7.5 nmol; serine, 5.1 nmol; isoleucine, 13.6 nmol and lysine, 3.7 nmol. A total of 74.0 mmol of amino acids/10 g of oil was found. This translates to 0.01313 ppm nitrogen in the oil.

Trace Metals

Trace metals have been studied by numerous workers. King and coworkers (24) found the amounts of the metals listed in Table XIII reduce the keeping time of lard by one-half at 208 F.

In another study (25), copper and iron were added to processed soybean oil and stored at 18 C. the oils were then analyzed for decomposition products. The results are shown in Table XIV.

Because of the degree of instability these trace metals cause, it is imperative to keep the copper and iron content as low as possible. We examined the concentration of copper and iron as a result of processing of soybean (R. Sleeter, unpublished data) by flameless atomic absorption spectroscopy (Table XV).

Other metals, such as lead and mercury, are important because of their toxicity to humans. Thomas (26) followed the fate of arsenic, lead, cadmium and mercury vs processing step (Table XVI). As expected, degumming/refining reduces trace elements, whereas further processing has little effect.

Rearrangement and Decomposition Products

Numerous unwanted rearrangement and decomposition products occur during processing. Oxidation and polymerization may occur throughout all of the processing steps, whereas other transformations are processing-step specific, such as *trans-* and positional isomer formation during hydrogenation.

TABLE X

Summary of the Effect of Processing Steps on the Chlorophyll Content

Processing step	Effect on chlorophyll content
Crude oil (no processing)	150 µg/ℓ
Refining	25% reduction
Deodorization	Little, if any, effect
Hydrogenation	Variable–depending on degree
Bleaching (0.25% earth)	74% reduction
Bleaching (0.75% earth)	91-92% reduction

TABLE XI

Effect of pH and Amount of Bleaching Earths on Color Factors (21)

		Color		
Bleaching earth pH	Bleaching earth used (%)	Yellow	Red	Chlorophyll density
3.04	1.0	35	3.0	0.18
3.04	1.5	35	2.1	0.090
3.04	2.0	20	1.8	0.041
3.10	1.0	35	3.9	0.40
3.10	2.0	35	2.8	0.16
3.10	3.0	25	1.7	0.071
3.10	4.0	20	1.6	0.037
7.4	2.0	35	3.9	0.75
7.74	1.0	76	7.2	0.58
7.74	2.0	35	4.8	0.43
7.74	4.0	35	2.3	0.19
7.74	6.0	35	1.7	0.093
Original oil		70	7.7	0.80

TABLE XII

Effect of Processing Step on Nitrogen Content (22)

Processing step	Nitrogen (%)
Crude soybean oil	0.019
Degummed	0.00044
Refined and bleached	0.00016
Deodorized	0.00001 (0.1 ppm)

TABLE XIII

Amount of Trace Metals Which Lower the Keeping Time of Lard by One-Half at 208 F (24)

Metal	Amount (ppm)
Copper	0.05
Manganese	0.6
Iron	0.6
Chromium	1.2
Nickel	2.2
Vanadium	3.0
Zinc	19.6
Aluminum	50.0

Rearrangement and Decomposition Reactions for Processing Steps Other Than Hydrogenation

Oxidized fatty acids. Very little work has been undertaken to characterize the effect of each processing step on oxidation, conjugation and polymerization of soybean oil. Studies focus mainly on one particular processing step and neglect the others entirely. Frequently, data are presented to contrast the amounts of these products in crude vs refined oils only. For example, epoxiacids which are formed as a preliminary step in fat oxidation have been determined in crude and refined oils (27). These values are 0.08-1.04% and 0.01-0.46%, respectively.

TABLE XIV

Amount of Some Volatile Oxidation Products in Relation to Metal Content (25)

Oil examined	Metal content (ppm) Copper	Iron	Relative amounts Hexanal	Heptanal	2-Heptenal	Oct-1-en-3-ol Oct-1-en-3-one
Soybean oil	<0.05	0.1	1.0	–	–	–
Soybean oil stored 7 wk	<0.05	0.1	8.0	2.0	0.1	0.5
Hydro-soy oil blend stored 3 wk	0.1	0.7	9.0	2.6	10.2	5.8
	0.2	1.2	16.0	3.0	17.0	14.0

TABLE XV

Correlation of Trace Copper and Iron As a Function of Processing Step[a]

Degree of processing	Copper (ppb)	Iron (ppm)
Crude soybean oil	13.2	2.8
Degummed	3.7	2.1
Refined	2.5	0.2
Deodorized	1.1	0.2
Hydrogenated, nondeodorized	3.7	0.01
Hydrogenated, deodorized	1.2	0.02

[a] R. Sleeter, unpublished data.

TABLE XVI

Toxic Trace Elements As a Function of Processing Step (26)

Processing step	Arsenic	Lead	Cadmium	Mercury
		(ppm)		
Crude soybean oil	0.02	0.06	0.005	<0.01
Refined	0.02	0.04	0.003	<0.01
Bleached 0.1%	0.01	0.04	0.005	0.01
Bleached 1.0%	0.01	<0.04	0.005	0.03
Deodorized	<0.01	0.04	0.004	<0.01

In one study (28), however, most processing steps were examined and changes in oxidized fatty acids (OFA) were measured by relating chromatoplates and weight-related histograms of each constituent. Individual OFA were not identified. The data showed that at each stage of operation, the concentration of individual OFA could decrease, increase, or remain constant. The overall concentration of OFA fell by ca. 20% during caustic refining and 10% during bleaching and rose by ca. 10% during deodorization (Fig. 4).

Conjugated fatty acids. O'Connor and coworkers (31) observed an increase in the absorption in the far UV at 260 nm. This was related to oxidized oleic, linoleic and linolenic acids. Caustic refining had no effect, whereas bleaching and deodorization increased the intensity. In other studies (30-31), absorbance peaks around 260 nm were attributed to conjugated dienes, trienes and tetraenes produced during bleaching of soybean oil. It was estimated that most commercially bleached oil contained 0.1-0.2% conjugated material.

It is worth noting a demonstration of the ineffectiveness of peroxide value for determining the quality of oil (31) (Table XVII). Bosch (30), in a study of the effect of bleaching of vegetable oils, found that with low initial peroxides and in the absence of air, little additional conjugation was found. However, with high initial peroxides or in the presence of air, conjugated dienes and trienes were formed.

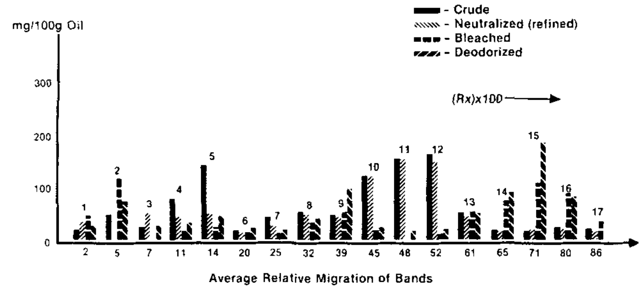


FIG. 4. Comparison of the weight related histograms of chromatoplate bands of different stages of processing for soybean oil (28).

TABLE XVII

Peroxide Value Variation Resulting from Increased Bleaching Time (31)

Bleach time	PV	Absorbance (%) 230 nm	268 nm
0	1.2	.51	.62
1	0.67	.74	.95
2	0	.77	.97
3	0.75	.85	1.05
4	1.0	.97	1.19
6	1.2	1.58	1.96

Oxidative decomposition products. Oxidative decomposition products which normally occur when an oil is exposed to oxygen would be expected to appear during processing. Yasuda and coworkers (33) have identified 47 volatile flavor components developed during storage of deodorized soybean oil. These included ketones, aldehydes, alcohols and lactones. Some of these, notably *n*-hexanal, have been said to impart a green-beany odor.

Polymerization. Polymerization also may occur and may be formed by two major processes: thermal polymerization (in the absence of air as in a deodorizer) or oxidative polymerization, which occurs when oxygen is present (34). Thermal polymerization produces dimers and polymers which result from Diels Alder additive reactions. Air oxidation of polyunsaturated fatty acids at temperatures below 100 C yields conjugated hydroperoxides which produce free radicals. These may proceed to form polymers. Most of these investigations were performed on model systems, such as pure linoleic acid, but would be expected to occur whenever conditions were favorable (i.e., when the oil is heated or when in the presence of air).

Other oxidations. When oils are subjected to these conditions, changes also occur in the composition of minor constituents. As already mentioned, tocopherols are oxidized or dimerized. Kaufmann and coworkers (35) have shown that 7-hydroxysterols are formed when soybean oil is heated in the presence of oxygen. Hydrocarbons and distearyl ethers are formed by bleaching earth treatment of sterols. These artifacts have been detected in commercial oils.

The importance in considering these degradation products is in their toxicity. Ohfuji and Kaneda (36) have fractionated oxidatively polymerized oil and found several toxic fractions, one of which they postulate as a dimer of triglyceride molecules. This particular fraction was extremely toxic.

Rearrangements and Decomposition during Hydrogenation

Hydrogenation of oils produces isomers peculiar to that process only. These include geometrical and positional isomers and cyclic aromatic fatty acids. Conjugation and polymerization, which occur in other refining steps, also result during hydrogenation.

Geometrical isomerization. Increasing concern is being given to *trans*-isomers formed during hydrogenation. A symposium on "Nutritional Effects of *trans*-Isomers" was held at the American Oil Chemist's Annual Meeting in New York in 1980. Many investigations have been published concerning various aspects of *trans*-isomer formation. Swindells (37) studied the percentage of *trans*-fatty acid isomers formed under selective and nonselective hydrogenation conditions. This paper typifies the general trends found in most other papers and shows the high amounts of *trans*-isomers formed during hydrogenation (Table XVIII).

Ota and coworkers (38) postulated that the precursor of hydrogenation flavor is not only isolinoleic, but also isooleic acid, resulting from *trans*-isomerization. Homogeneous, catalyzed hydrogenation has been shown to reduce *trans*-isomer content to 5-11% for IV drops of 50-55 (39). However, this form of catalysis is not used commercially.

Positional isomerization. Migration of the double bonds is another problem during hydrogenation and arises from contact of the oil with the surface of the catalyst. This will occur with or without the presence of hydrogen. Vigneron and Spict (40) studied this and showed the amounts of migration which resulted for both *cis*- and *trans*-isomers (Table XIX).

Conjugation. As may be expected conjugation is another serious side reaction during hydrogenation and occurs in the presence of hydrogenation catalysts. Desnuelle (41) has produced data on soybean oil showing up to 10% of the 18:2 to be conjugated fatty acids (Table XX).

Other by products. A small portion of cyclic, aromatic fatty acids is formed when soybean oil is hydrogenated at high temperatures (>200 C) and with hydrogen scarcity. Sterols in soybean oil are reduced to stanols during hydrogenation (42). Peroxides are decomposed by hydrogenation to hydrocarbons, aliphatic alcohols, ketones, and ω-hydroxy acids (43).

Generalizations for hydrogenation. Table XXI generalizes aspects of hydrogenation.

TABLE XVIII

trans Fatty Acid Content of Hydrogenated Soybean Oils (37)

Iodine value	Fatty acid composition by GLC					
	C-16	C-18	18:1	18:2	18:3	*trans*-Acid (%)[a]
Nonselective conditions (275 F, 60 psig, 0.2% catalyst)						
132.8	10.4	4.3	22.6	52.6	10.1	0
95.6	10.4	8.6	55.0	24.4	1.6	15.7
87.4	10.4	11.2	57.5	20.2	0.7	20.9
82.2	10.4	12.2	62.2	15.2	0	24.6
75.2	10.4	15.1	62.7	11.8	0	27.3
70.2	10.4	18.4	61.4	9.8	0	32.2
65.6	10.4	20.9	60.4	8.3	0	32.7
61.5	10.4	22.8	59.8	7.0	0	6.6
Selective conditions (400 F, 6 psig, 0.2% catalyst)						
132.8	10.4	4.3	22.6	52.6	10.1	0
96.2	10.4	5.0	57.5	26.3	0.8	24.2
89.5	10.4	5.6	64.3	19.5	0.2	31.0
84.3	10.4	6.6	67.7	15.3	0	36.6
79.1	10.4	7.0	71.0	11.6	0	41.9
75.2	10.4	8.7	72.5	8.4	0	46.3
70.9	10.4	11.8	71.1	6.7	0	51.1
65.9	10.4	16.5	67.7	5.4	0	54.5

[a] Expressed as trielaidin.

TABLE XIX

Comparison of Positional Isomerism of Two Hydrogenated Soybean Oils (Nickel-Catalyzed) (40)

Monoenes	Fatty acid (%)	
	Oil 1	Oil 2
trans Isomer		
$\Delta 7$	0.8	–
$\Delta 8$	5.2	5.1
$\Delta 9$	15.0	12.0
$\Delta 10$	25.9	30.4
$\Delta 11$	25.1	27.7
$\Delta 12$	11.8	10.8
$\Delta 13$	9.0	7.7
$\Delta 14$	4.4	3.5
$\Delta 15$	1.9	1.6
$\Delta 16$	1.4	1.0
cis Isomer		
$\Delta 8$	0.8	1.4
$\Delta 9$	84.6	84.3
$\Delta 10$	2.4	3.1
$\Delta 11$	5.1	3.8
$\Delta 12$	6.8	6.3
$\Delta 13$	1.0	0.4
$\Delta 14$	–	–
$\Delta 15$	–	–

TABLE XX

Fatty Acid Composition of a Nickel-Catalyzed, Hydrogenated Soybean Oil (41)

Fatty acid	(%)
16:0	10.7
18:0	7.2
18:1	73.5
18:2 (nonconjugated)	7.8
18:2 (conjugated)	0.8
18:3	–

Foreign Compounds Not Naturally Occurring in Soybean Oil

Numerous chemicals which are foreign or not naturally found may be present in crude soybean oil or may be added during refining. These include pesticides, PCB, residual hexane and heat transfer medium.

Pesticides. Numerous papers have been published studying the fate of pesticides in soybean oil as a function of processing step. The following data illustrate the general trend that pesticides are reduced slightly at each stage of processing and are drastically reduced during deodorization. (Table XXII). Pesticides are concentrated in the deodorizer distillate. For example, we have found <0.05 ppm for dieldrin in crude soybean oil and 2.56-5.44 ppm in deodorizer distillate (R. Sleeter, unpublished). This represents variation in a typical production deodorizer.

Extraction solvent. Residual hexane resulting from soybean oil extraction of the meal was determined (46). Crude soybean oils varied from 3,500 to 1,000 ppm and refined oils varied from 170 to 150 ppm.

Heat transfer media. Heat transfer media, e.g., Dowtherm A, may be present in soybean oil resulting from pinhole leaks in the heat exchange tray of a deodorizer. Takagi (47) was able to detect concentrations as low as 0.2 ppm.

Additives to Soybean Oil to Aid Processing

Very few compounds are added to soybean oil as part of a processing step. Citric acid is one. It is usually added prior to deodorization as a metal scavenger. It also performs as an acidic synergist, like ascorbic acid, by inhibiting the antioxidant catalysis of peroxide decomposition (48).

Sorbitol also has been demonstrated to be an effective substitute for citric acid (59). One study investigated the fate of antioxidants added to soybean oil during processing (45) (Table XXIII). These generally are volatile and are eliminated during deodorization.

There are many factors to consider when oil is processed. One comment is worth noting. Years ago, when routine analyses were rudimentary, it was relatively easy to process an abused oil and make it appear to be in excellent condition. Now, with increased sophistication in quality

TABLE XXI

Effect of Operation during Hydrogenation on the Resultant Oil

Operating parameter	Effect of parameter	Result in oil
Decreased agitation Low catalyst activity Higher temperature	Low dispersion and low concentration of hydrogen Longer hydrogenation time	Increased *trans*, positional and conjugated isomer content Sharpened SFI curve
Good agitation High hydrogen pressure Lower temperature	Good dispersion and high concentration of hydrogen Shorter hydrogenation time	Lower *trans*, positional and conjugated isomer content Flattened SFI curve

TABLE XXII

Effect of Processing Step on Residual Pesticide Level

Processing step	Pesticide (ppm)					
	Aldrin (44)	Dieldrin (44)	β-BHC (45)	ppıDDE (45)	pp′DDT (45)	PCB (45)
Crude	0.03	0.11	1.49	1.42	1.36	3.59
Refined	–	0.09				
Bleached	–	0.07	0.42	0.896	–	3.03
Deodorized	–	–	0.039	0.050	–	.28
Deodorized distillate	0.49	5.99				

TABLE XXIII

Effect of Processing Step on Added Antioxidants (45)

	Recovery (%)	
Processing step	BHA	BHT
Crude	100 (added here)	100 (added here)
Refined	96.9	98.0
Bleached	89.1	92.2
Deodorized	None detected	None detected

control laboratories, abused oils cannot be "fixed" to look good.

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Soybean Oil in Brazil and Latin America: Uses, Characteristics and Legislation

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ABSTRACT

The soybean was introduced into Brazil in 1882. The oil content of different varieties of soya is ca. 22.5% w/w. Now, soya oil is the most popular oil in Brazil. Food standards legislation has been enacted for soya oil and its hydrogenated products in Brazil and the rest of Latin America.

INTRODUCTION

Soya probably was introduced into Brazil in 1882 in Bahia by the agronomic engineer Gustavo Dutra (1). Ten years later, it was grown by the agronomist Daffert (1) in the Agronomical Institute of Campinas. Soya was unsuccessful