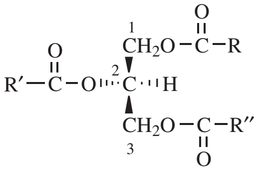
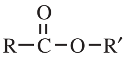
FATS AND FATTY OILS

1. Introduction

Fats and oils are one of the oldest classes of chemical compounds used by humans. Animal fats were prized for edibility, candles, lamp oils, and conversion to soap. Fats and oils are composed primarily of triacylglycerols (**1**), which are esters of glycerol and fatty acids. However, some oils such as sperm whale (1), jojoba (2), and orange roughy (3) are largely composed of wax esters (**2**). Waxes (qv) are esters of fatty acids with long-chain aliphatic alcohols, sterols, tocopherols, or similar materials.



(**1**)



$$R-\overset{O}{\overset{\|}{C}}-O-R'$$

(**2**)

Fatty acids derived from animal and vegetable sources generally contain an even number of carbon atoms since they are biochemically derived by condensation of two carbon units through acetyl or malonyl coenzyme A. However, odd-numbered and branched fatty acid chains are observed in small concentrations in natural triacylglycerols, particularly ruminant animal fats through propionyl and methylmalonyl coenzyme A, respectively. The glycerol backbone is derived by biospecific reduction of dihydroxyacetone. Chain lengths of even-numbered fatty acids range from 4 to 22.

Structure (**1**) shows the stereochemistry of the triglyceride molecule. Positions are numbered by the stereochemical numbering (sn) system. In chemical processes the 1 and 3 positions are not distinguishable. However, for biological systems, the enantiomeric (*R* or *S*) form is important. Simple triglycerides contain only one type of fatty acid, eg, tristearin [555-43-1], and since the fatty acid residues in the 1 and 3 position are identical, do not exhibit enantiomeric forms. If more than one fatty acid is present, mixed triacylglycerols are distinguished. Naming mixed triacylglycerols without regard to stereochemistry involves two conventions: (*1*) the fatty acid with the shortest carbon chain is named first, eg, palmitodistearin, and (*2*) for fatty acids with an equal number of carbon atoms, the acid with the lesser number of double bonds is named first, eg, stearodiolein. When stereochemistry is taken into account, the acids are numbered as they occur, eg, *sn*-1-oleo-2-palmito-3-stearin.

Fatty acids may be saturated, monounsaturated, or polyunsaturated according to the number of double bonds in the alkyl chain. Naturally occurring double bonds are almost exclusively cis (*Z*) in configuration. Table 1 lists the fatty acids found in representative triacylglycerols. Fatty acids are often referred to by their common names (see CARBOXYLIC ACIDS). For example, 9-(*Z*)-octadecenoic acid has long been known as oleic acid. A convenient shorthand notation for fatty acids identifies the chain length followed by a colon and the number of double bonds in the chain, eg, oleic acid is 18:1. The most common fatty acids in animal and vegetable fats and oils are dodecanoic (lauric, 12:0), hexadecanoic (palmitic, 16:0), octadecanoic (stearic, 18:0), 9-*cis*-octadecenoic (oleic, 18:1), 9-*cis,* 12-*cis*-octadecadienoic acid (linoleic, 18:2), and 9-*cis,* 12-*cis,*15-*cis*-octadecatrienoic acid (linolenica, 18:3).

Fats and oils are distinguished by their physical state; fats are solid at ambient temperature, whereas oils are liquid. Some edible triacylglycerols, such as butter, lard, vegetable oils, shortenings, and margarines, have substantial quantities of both liquid and solid components at ambient temperature. Commercial products may be derived from animal carcasses by rendering, or vegetable sources by pressing or solvent extraction (4).

2. Composition

Natural fats and oils are composed principally of triacycerols, but other components may be present in minor quantities. These components may have important effects on the nature and quality of the oil or fat.

2.1. Free Fatty Acids and Partial Glycerides.

After harvest, many crude oil crops contain lipase enzymes that cleave triacylglycerols into fatty acids and partial glycerides. For example, free fatty acid content of rice bran oil and palm oil can reach high concentrations if the enzymes are not denatured promptly by heat treatment. Acids, bases, and heat abuse in the presence of moisture can lead to high free fatty acid concentrations as well as oxidative degradation. Elevated free fatty acid concentrations are undesirable because they cause high losses during further processing of the oil.

Diacylglycerols and monoacylglycerols are formed by hydrolysis. Diacylglycerols formed by lipolysis may initially have a 1,2-configuration. However, a 1,2

Table 1. **Fatty Acids Found in Naturally Occurring Triglycerides**

Fatty acid	CAS Registry number	Common name	Designation[a]	Principal sources
butanoic	[107-92-6]	butyric	4:0	butter
hexanoic	[142-62-1]	caproic	6:0	butter
octanoic	[124-07-2]	caprylic	8:0	coconut
decanoic	[334-48-5]	capric	10:0	coconut
dodecanoic	[143-07-7]	lauric	12:0	coconut, palm kernel, butter
tetradecanoic	[544-63-8]	myristic	14:0	coconut, palm kernel, butter
hexadecanoic	[57-10-3]	palmitic[b]	16:0	palm, cottonseed, butter, animal fat, marine fats
cis-9-hexadecenoic	[373-49-9]	palmitoleic	16:1 (9*c*)	butter, animal fats
octadecanoic	[57-11-4]	stearic[b]	18:0	butter, animal fats
cis-9-octadecenoic	[112-80-1]	oleic[b]	18:1 (9*c*)	olive, tall oil, peanut, canbra[c], animal fats, butter, marine fats
cis,cis-9,12-octadecadienoic	[60-33-3]	linoleic[b]	18:2 (9*c*, 12*c*)	safflower, sunflower, corn, soy, cottonseed
cis,cis,cis-9,12,15-octadecatrienoic	[463-40-1]	linolenic	18:3 (9*c*, 12*c*, 15*c*)	linseed
cis,cis,cis,cis-6,9,12,15-octadecatetraenoic	[20290-75-9]		18:4 (6*c*, 9*c*, 12*c*, 15*c*)	marine fat
cis,trans,trans-9,11,13-octadecatrienoic	[506-23-0]	α-eleostearic	18:3 (9*c*, 11*t*, 13*t*)	tung
12-hydroxy-*cis*-9-octadecenoic	[141-22-0]	ricinoleic	18:1 (9*c*) 12-OH	castor
cis-9-eicosenoic	[29204-02-2]	gadoleic	20:1 (9*c*)	marine fat
cis-11-eicosenoic	[5561-99-9]		20:1 (11*c*)	rapeseed
all *cis*-5,8,11,14-eicosatetraenoic	[506-32-1]	arachidonic	20:4 (5*c*, 8*c*, 11*c*, 14*c*)	animal, marine fats
all *cis*-8,11,14,17-eicosatetraenoic	[24880-40-8]		20:4 (8*c*, 11*c*, 14*c*, 17*c*)	marine fats
all *cis*-5,8,11,14,17-eicosapentaenoic	[10417-94-4]		20:5 (5*c*, 8*c*, 11*c*, 14*c*, 17*c*)	marine fats
docosanoic	[112-85-6]	behenic	22:0	
cis-11-docosenoic	[506-36-5]	cetoleic	22:1 (11*c*)	marine fats
cis-13-docosenoic	[112-86-7]	erucic	22:1 (13*c*)	rapeseed
all *cis*-7,10,13,16,19-docosapentaenoic	[24880-45-3]		22:5 (7*c*, 10*c*, 13*c*, 16*c*, 19*c*)	marine fats
all *cis*-4,7,10,13,16,19-docosahexaenoic	[6217-54-5]		22:6 (4*c*, 7*c*, 10*c*, 13*c*, 16*c*, 19*c*)	marine fats

[a] Number of carbon atoms: number of double bonds [geometric (cis, trans) isomerism].

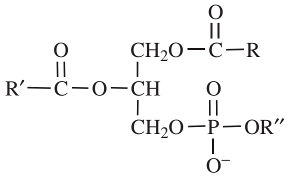
[b] Constituent of most fats.

[c] Low erucic rapeseed.

acyl shift often occurs to form the less sterically crowded 1,3 isomer. This rearrangement has even been shown to occur in the solid state (5). 2-Monoacylglycerols undergo a 1,2 acyl shift to form the more stable 1-monoacylglylglycerols (6). Monoacylglycerols are interfacially active and may form emulsions in the presence of water.

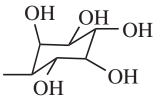
Free fatty acids are removed by alkali refining, physical refining, or deodorization. Mono- and diacylglycerols are not removed by alkali refining or bleaching and may have an adverse effect on the quality of the oil. However, during deodorization (vacuum steam distillation), partial glycerides may disproportionate to triacylglycerols and glycerol [56-81-5]. The glycerol (qv) is removed with the steam deodorization distillate. A method has been reported where monoacylglycerols and other surface-active materials may be removed by treatment with Florisil (7).

2.2. Phospholipids. Glycerides esterified by fatty acids, at the 1,2-positions, and a phosphoric acid, a residue at the 3-position, constitute the class called phospholipids (**3**). In older literature and in commercial practice, these materials are described as phosphatides or lecithins.



(**3**)

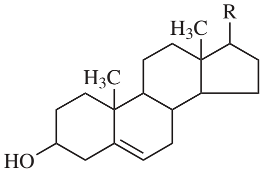
where R″ = $-CH_2CH_2\overset{+}{N}(CH_3)_2$ (**3a**), $-CH_2CH_2NH_2$ (**3b**), or



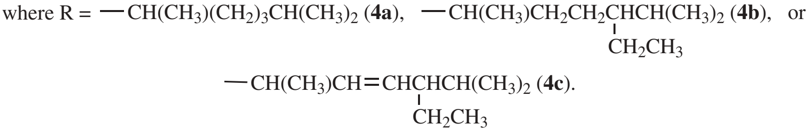
(**3c**)

The identity of the moiety (other than glycerol) esterified to the phosphoric group determines the specific phospholipid compound. The three most common phospholipids in commercial oils are phosphatidylcholine or lecithin [8002-43-5] (**3a**), phosphatidylethanolamine or cephalin [4537-76-2] (**3b**), and phosphatidylinositol [28154-49-7] (**3c**). These materials are important constituents of plant and animal membranes. The phospholipid content of oils varies widely. Lauric oils, such as coconut and palm kernel, contain a few hundredths of a percent. Most oils contain 0.1–0.5%. Corn and cottonseed oils contain almost 1% whereas soybean oil can vary from 1 to 3% phospholipid. Some phospholipids, such as dipalmitoylphosphatidylcholine (R = R′ = palmitic; R″ = choline), form bilayer structures known as vesicles or liposomes. The bilayer structure can microencapsulate solutes and transport them through systems where they would normally be degraded. This property allows their use in drug delivery systems (qv) (8).

2.3. Sterols. Sterols (**4**) are tetracyclic compounds derived biologically from terpenes. They are fat-soluble and therefore are found in small quantities in fats and oils. Cholesterol [57-88-5] (**4a**) is a common constituent in animal fats such as lard, tallow, and butterfat. The hydroxyl group can be free or esterified with a fatty acid.



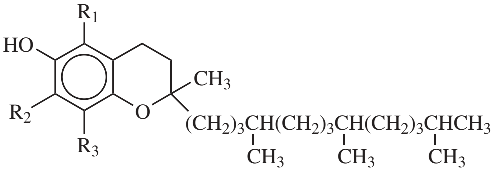
(**4**)



where R = $-CH(CH_3)(CH_2)_3CH(CH_3)_2$ (**4a**), $-CH(CH_3)CH_2CH_2\underset{\displaystyle CH_2CH_3}{\underset{|}{C}}HCH(CH_3)_2$ (**4b**), or $-CH(CH_3)CH{=}CH\underset{\displaystyle CH_2CH_3}{\underset{|}{C}}HCH(CH_3)_2$ (**4c**).

In milk fat, cholesterol is associated with lipoproteins in the milk fat globule. It is also a component of animal membranes and controls rigidity and permeability of the membranes. Cholesterol has interesting surface properties and can occur in liquid-crystalline forms. Plants contain sterols such as β-sitosterol [83-46-5] (**4b**) or stigmasterol [83-48-7] (**4c**). Their functions in plant metabolism are not yet well understood. Analysis of sterols has proven useful for detection of adulteration of edible fats (9).

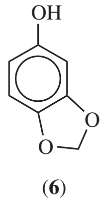
2.4. Tocopherols and Tocotrienols. Algae and plants used as sources of edible oils contain tocopherols, phenolic materials that function as antioxidants (qv). Mammals do not synthesize these compounds and residues present in their bodies are present because of ingestion. Concentrations of tocopherols in commercial vegetable oils vary widely from 0.01% or less in coconut and olive oils; up to 0.05% in palm and peanut oils; ~0.1% in corn, cottonseed, and linseed oils; up to 0.2% in soybean oil; and to as high as 0.5% in wheat germ oil. Tocopherols are designated as being vitamin E active (10). Other structural features of the tocopherols are the chromane heterocyclic ring and the extensively branched side chain that arises biologically from condensation of isoprene units. The α-, β-, γ-, and δ-tocopherols are represented by (**5**), where $R_1 = R_2 = R_3 = CH_3$ is α-tocopherol [59-02-9]; $R_1 = R_3 = CH_3$, $R_2 = H$ is β-tocopherol [148-03-8]; $R_2 = R_3 = CH_3$, $R_1 = H$ is δ-tocopherol [7616-22-0]; and $R_1 = R_2 = H$, $R_3 = CH_3$ is γ-tocopherol [119-13-1].



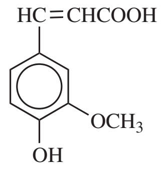
(**5**)

Tocotrienols differ from tocopherols by the presence of three isolated double bonds in the branched alkyl side chain. Oxidation of tocopherol leads to ring opening and the formation of tocoquinones that show an intense red color. This species is a significant contributor to color quality problems in oils that have been abused. Tocopherols function as natural antioxidants (qv). An important factor in their activity is their slow reaction rate with oxygen relative to combination with other free radicals (11).

Several other naturally occurring antioxidants have been identified in oils. Sesamol [533-31-3] (**6**) occurs as sesamoline [526-07-8], a glycoside, in sesame seed oil. Ferulic acid [1135-24-6] (**7**) is found esterified to cycloartenol [469-38-5] in rice bran oil and to β-sitosterol in corn oil. Although it does not occur in oils, rosemary extract has also been found to contain powerful phenolic antioxidants (12).



(**6**)



(**7**)

2.5. Carotenoids and Other Pigments. Carotenoids contain conjugated double bonds, a strong chromophore that produces red and yellow coloration in vegetable oils. Carotenoids are tetraterpene hydrocarbons formed by the condensation of eight isoprene units. Another class of compounds, the xanthophylls, is produced by hydroxylation of the carotenoid skeleton. β-Carotene [7235-40-7] is the best known component of the carotenoids because it is the precursor for vitamin A. Carotenoid pigments are unstable toward heat, light, and oxidation. Oxidative bleaching is occasionally used but great care must be taken to remove excess peroxides. Reaction of peroxide with tocopherols may produce an even deeper red coloration. In the process of deodorization, heat destroys the red carotenoid pigments (heat bleaching).

Green coloration, present in many vegetable oils, poses a particular problem in oil extracted from immature or damaged soybeans. Chlorophyll is the compound responsible for this defect. Structurally, chlorophyll is composed of a porphyrin ring system, in which magnesium is the central metal atom, and a phytol side chain which imparts a hydrophobic character to the structure. Conventional bleaching clays are not as effective for removal of chlorophylls as for red pigments, and specialized acid-activated adsorbents or carbon are required.

3. Processing of Fats and Oils

Fats and oils are derived from animals, plants, or fish by rendering (animal tissues), pressing, or solvent extraction. Animal fat may be obtained from carcasses by trimming the fat from the carcass, treating the trimmings with live steam to melt the fat, and filtering to remove proteinaceous material and debris, such as plastic wrapping, that may be carried along with the trimmed fat.

Vegetable seeds having high oil contents may be extruded through a mechanical press to separate oil from the other components. Peanut oil and cocoa butter are often obtained using this process. With the most modern mechanical screw press, the pressing method leaves ~3–5% residual oil in the meal. Older presses may leave as much as 6% oil in the press cake. Solvent extraction provides higher yields because it leaves less ($\leq$1%) oil residue in the meal. Soybeans, eg, are mechanically pressed into flakes and then extracted using a solvent such as hexane or isooctane. After filtration, the solvent is recovered for reuse from the oil and meal. In a few specialized cases, the solvent is not removed but refining is performed on the solution. This process is known as miscella refining.

Crude oils from these processes are often of insufficient quality to be used directly, particularly for edible products. Impurities such as pigments, phosphatides, volatile odorous compounds, and certain metals must be removed by further processing (13,14).

3.1. Degumming and Dewaxing. Some oils, such as soybean, contain appreciable amounts of phospholipids. These materials are often referred to as gums because of their high viscosity and sticky texture. Hydratable phosphatides are removed by treating the crude oil with hot water or dilute acid. In older manufacturing facilities, hydration is carried out as a batch process. The hydrated oil is allowed to stand in a tank and then the precipitated phospholipids are skimmed from the top. In modern processing plants, the oil is hydrated continuously and the phosphatides are removed in a centrifuge. The vacuum-dried sludge from soybean processing is known as lecithin. This material may be used crude or may be further purified. Lecithin (qv) is a surfactant with several applications in foods or specialty chemical products.

Many seed oils, especially sunflower and linseed, contain waxes that serve as a protective coating for the seed. These waxes solidify at colder temperatures and impart turbidity to the oil and interfere with subsequent processing. They are commonly removed from the crude oil by refrigeration followed by filtration, a process commonly known as winterization.

3.2. Refining. Stored crops undergo gradual hydrolysis because of the presence of lipolytic enzymes and moisture. The resulting presence of free fatty acids is undesirable for an edible oil and is referred to as hydrolytic rancidity. Free fatty acids in cooking oils cause the oils to smoke when they are heated. Free fatty acids in lauric oils, such as palm kernel and coconut impart a soapy off-flavor to edible products. Removal of the free fatty acid may be accomplished by vacuum steam distillation (physical or steam refining) or extraction with aqueous alkaline solution (alkali refining) (15). Physical refining has the advantages of selectively removing free fatty acids with minimal oil loss and deodorizing the oil simultaneously. In addition, the environmental problem of disposing of acidified caustic solution is eliminated. However, physical refining only works well for oils that are low in phosphatides and are stable to heat in an unrefined form. Palm, coconut, and palm kernel oils are well suited to physical refining. Other oils may be subjected to extremely efficient degumming followed by physical refining (16).

In alkali refining, a solution of caustic soda (sodium hydroxide) is mixed with the oil to form soaps. These soaps are dispersed in the aqueous phase together with phospholipids, some pigments, and other compounds. Aqueous and oil phases are separated by centrifugation. The oil is subsequently extracted with water to remove the bulk of the residual soap. Refining losses may occur during the process because of saponification of the oil or emulsification of some neutral oil in the aqueous phase, particularly if the free fatty acid content of the incoming oil is high resulting in a high soap concentration. Phosphatides act as surfactants and tend to increase refining losses if they are not removed by degumming. Conversely, the alkali process effectively removes residual phosphatides.

Strength of the caustic solution, temperature, contact time, and amount used are the critical parameters used to set optimum refining conditions. The type of oil and its free fatty acid and phosphatide content greatly influence refining behavior. An oil with a high phosphatide content requires a greater excess of sodium hydroxide than an oil with low phosphatide concentration. Soapstock is a by-product of alkali refining. It is commonly acidified and the fatty acids are utilized for animal feed. Alternatively, the acidified soapstock may be treated to split fatty acids from residual glyceride and the fatty acids distilled and sold as commercial products. A modification of alkali refining has minimized or eliminated the water stream associated with alkali refining (17). Silica is utilized with a lower concentration of alkali to refine the oil. Soap is absorbed on the silica and subsequent bleaching clay rather than being washed out and neutralized. Soap is therefore disposed of as solid waste along with the bleaching clay and silica rather than acidified and concentrated to crude fatty acid.

3.3. Bleaching. Light color and a clear bright appearance have long been associated with oil quality. Removal of pigments is accomplished by absorption on solid materials (absorption bleaching) or by treatment with oxidizing agents such as hydrogen peroxide or hypochlorite solutions. Bleaching absorbents are derived from bentonite or montmorillonite clays (qv). The activity of these clays may be increased by treatment with acid. In addition to removing pigment, an important function of bleaching clays is the reduction of concentrations of metals such as copper, iron, manganese, and cobalt, which catalyze oxidation of oils and reduce the shelf life of edible products. Activated carbon is an effective bleaching agent but also absorbs a high percentage of its own weight in oil resulting in increased oil loss. Carbon may be used effectively in small amounts in combination with activated bleaching earths.

Absorbents may be selected according to the specific pigments to be removed from an oil (18). Carotenoid pigments, which produce red colors, are effectively removed by activated clays. Carbon is quite effective for removing green chlorophyll pigments from soybean oil obtained from damaged beans. Brown pigments, which may be extremely difficult to remove, result from oxidation of carotenoids and are encountered in abused oils. Type of absorbent and concentration are selected considering activity, absorbent cost, oil loss, and metal removal.

The efficiency of a particular absorbent or blend of absorbents is determined using the Freundlich equation:

$$\log \frac{x}{m} = K + n \log c$$

where x is the amount of pigment absorbed, m is the amount of absorbent, c is the amount of residual pigment, and K and n are constants. Absorption isotherms are generated by a plot of x/m vs c on a log–log scale. Concentrations for the initial $(x + c)$ concentration of pigment and the residual (c) may be measured by spectrophotometry or comparison to standard reference colors.

The principal disadvantage of absorption bleaching is the problem of disposal of spent bleaching clay. Oil absorbed on the clay is exposed to air and is generally too oxidized to recover. Furthermore, spontaneous combustion of the oil-laden clay is a possibility in a landfill. Incineration of the spent clay along with solid municipal waste to recover otherwise wasted energy is an attractive alternative.

Chemical bleaching is never used on oils intended for edible use because it oxidizes unsaturated fatty acids to cause off-flavors. However, it does find wide usage for specialty linseed oil, for the paint industry, and fatty chemicals such as sorbitan esters of fatty acids and sodium stearoyl lactylate. Residual peroxide is destroyed by heating above its decomposition temperature.

4. Hydrogenation of Fats and Oils

4.1. Hydrogenation. Solid and semisolid fats have been used in food products such as margarines and shortenings and in nonedible applications such as candles (19). Historically, such solid fatty products were derived from animal fats or solid fractions of these fats. The discovery of catalytic hydrogenation in the early 1900s (20) allowed liquid oils to be converted into solid and semisolid fats with similar consistency. Solid supported nickel catalysts are most commonly used for addition of hydrogen to unsaturated and polyunsaturated fatty acid side chains (19). Addition of hydrogen to the double bond is the primary reaction, but isomerization of the double bond can also occur. As shown in Figure 1, the semihydrogenated transition state may (*a*) add another hydrogen to yield the saturated fatty acid, (*b*) lose another hydrogen atom to re-form the double bond at a different position, or (*c*) rotate 180° around a sigma bond and lose a hydrogen atom to form a trans (*E*) fatty acid. Double bonds may migrate along the entire length of the chain. Trans isomers increase until the cis (*Z*) monoenes are hydrogenated (21). Because naturally occurring oils contain a mixture of unsaturated triacylglycerols, hydrogenation results in a complex mixture of products.

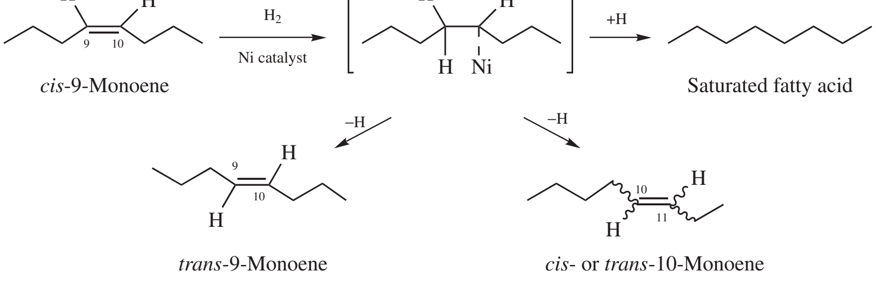


Fig. 1. Alternative pathways for hydrogenation in oils.

Multiply unsaturated linolenic and linoleic acid residues make triacylglycerols more vulnerable to oxidative degradation than oleic acid which is relatively stable. Therefore, where shelf-life is a critical factor, it is desirable to hydrogenate the most unsaturated residues selectively without production of large quantities of stearic (fully saturated) acid. The stepwise reduction of an unsaturated oil may be visualized as:

$$\text{linolenic} \xrightarrow{k_1} \text{linoleic} \xrightarrow{k_2} \text{oleic} \xrightarrow{k_3} \text{stearic}$$

If first-order kinetics are assumed, k_2/k_1 is the linoleic selectivity ratio and k_2/k_3 is the selectivity ratio for reduction of linoleic acid to stearic acid. Figure 2 shows a typical course of hydrogenation for soybean oil; the rate constants are $k_1 = 0.367$, $k_2 = 0.159$, and $k_3 = 0.013$. With a selective nickel catalyst, linolenic acid may be reduced without an appreciable buildup of undesirable saturates. Platinum catalyst, on the other hand, hydrogenates straight through to saturates, ie, shows no selectivity.

Conditions of hydrogenation also determine the composition of the product. The rate of reaction is increased by increases in temperature, pressure, agitation, and catalyst concentration. Selectivity is increased by increasing temperature and negatively affected by increases in pressure, agitation, and catalyst. Double-bond isomerization is enhanced by a temperature increase but decreased with increasing pressure, agitation, and catalyst. Trans isomers may also be favored by use of reused (deactivated) catalyst or sulfur-poisoned catalyst. Trans fats in the diet tend to raise LDL serum cholesterol while lowering the

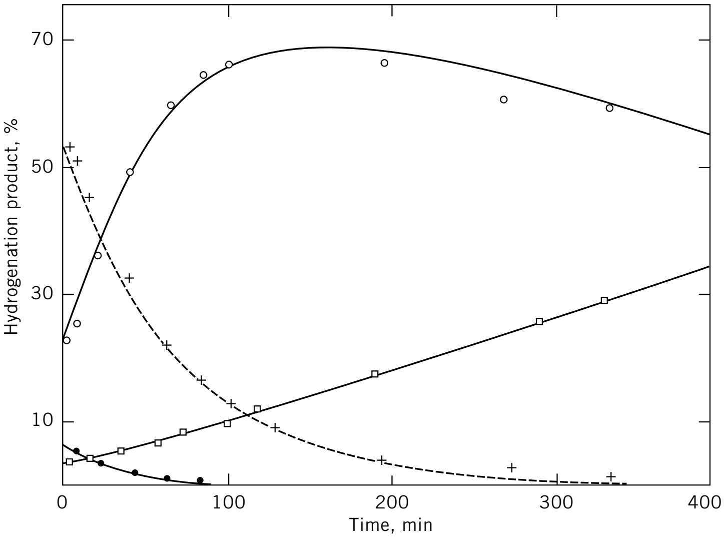


Fig. 2. Typical products from hydrogenation of soybean oil. Reaction conditions are 175°C, 0.02% Ni, 113 kPa (15 psig), and 600 rpm agitation. A′ is oleic; +, linoleic; ○, stearic; and ●, linolenic (19).

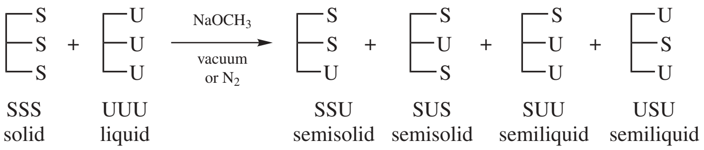
HDL component (22). The U. S. Food and Drug Administration has proposed labeling requirements for trans fats in packaged foods (23).

Commercially, hydrogenation is still carried out using a batch process. A typical "dead end" reactor is shown in Figure 3. The heated oil is stirred with the heterogeneous catalyst while hydrogen is bubbled through the bottom. Efficiency of mixing gas, solid, and liquid phases is critical. Agitation is reported to be increased by ultrasonic energy (24). Batch processes are favored for production of smaller quantities of specialty fats. Continuous hydrogenation processes have been developed and are preferred for production of large amounts of commodity fats.

Hydrogenation is an exothermic reaction. The heat generated is a function of the number of hydrogenated double bonds in a glyceride and the molecular weight. Initially, the oil is heated to an intermediate temperature. When hydrogen is introduced, heat is evolved and the desired reaction temperature is reached. Additional energy savings may be achieved if the finished product is passed through a heat exchanger to heat incoming oil for the next batch.

Disposal of spent hydrogenation catalyst requires a special chemical waste landfill because of its nickel content and the fact that oil-soaked catalysts tend to be pyrophoric. Compared to disposal costs, reprocessing to recover the nickel may become economically viable.

4.2. Randomization/Interesterification. Transesterification occurs when a carboxylic acid (acidolysis) or alcohol (alcoholysis) reacts with an ester to produce a different ester (25). Ester–ester interchange is also a form of transesterification. If completely unsaturated triglyceride oil (UUU) reacts with a totally saturated fat (SSS) in the presence of an active catalyst such as sodium, potassium, or sodium alkoxide, triacylglycerols of intermediate composition may be formed.



Many seed oils have specific triglyceride structures with unsaturated fatty acids in the 2-position. Methoxide rearrangement of these oils randomizes the distribution of fatty acids on the glyceride. The most apparent result is a change in melting behavior (26). For animal fats, randomization has little effect on the melting point. However, the polymorphic crystal pattern and functional properties may be changed. Lard, eg, has been rearranged to improve its functionality in baking applications (27).

Recently, the use of lipase enzymes to interesterify oils has been described (28). In principle, if a 1,3-specific lipase is used, the fatty acid in the 2-position should remain unchanged and the randomization occur at the terminal positions of the glycerol chain. However, higher temperatures, needed to melt solid fats, may cause a 1,2-acyl shift and fatty acids are scrambled over all positions.

The reaction is generally carried out in a batch reactor equipped with agitation and vacuum. Heated oil is first dried under vacuum to remove traces of water. Water has a low molecular weight and deactivates sodium methoxide

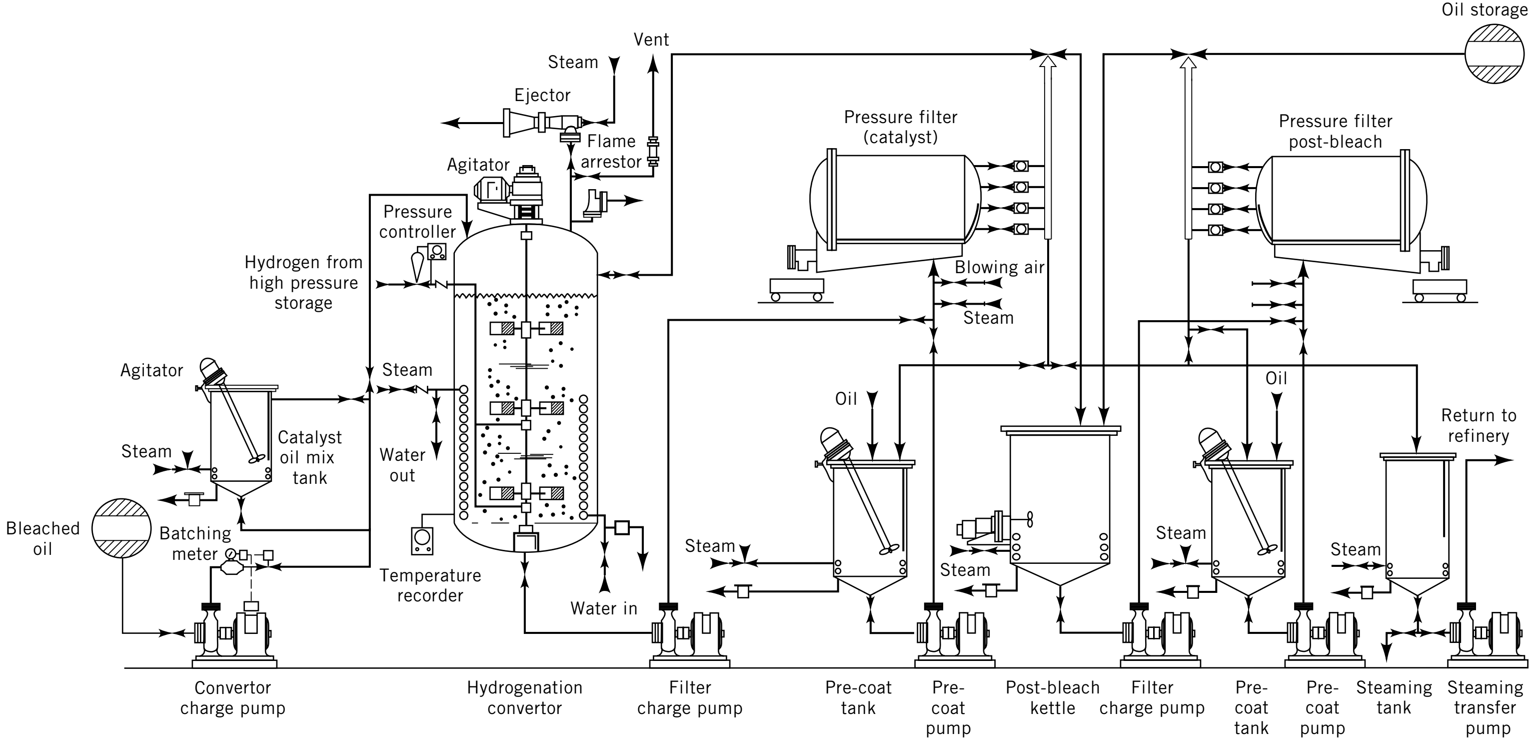


Fig. 3. Diagram of a typical “dead end” hydrogenation reactor (19).

catalysts by reaction to form sodium hydroxide, inactive as a catalyst under these conditions, and methanol. A freshly refined oil must be used to minimize catalyst deactivation by free fatty acid. A small amount (~0.1–0.3%) of sodium methoxide catalyst is added and the mixture is allowed to react for a limited time. Darkening of the oil indicates onset of reaction, probably resulting from formation of enolate ions. Following the reaction, catalyst may be removed by water washing or acidification of the oil.

Filtration through an acidic filter aid or silica removes the last traces of soap from the oil. The finished oil is heated under vacuum to remove small amounts of fatty acid methyl esters.

Randomization technology can be applied to create products, such as margarines or shortenings, which are low in trans fatty acids. Although the physical consistency may be similar to trans containing products, melting properties and functionality may be vastly different.

4.3. Physical Fractionation.

Specific fractions of glyceride oils may be separated according to their melting points by fractional crystallization and filtration (winterization) or solvent fractionation. Melting points of triacylglycerols are determined by the number and position of unsaturated fatty acids and fatty acid chain length. Short-chain fatty acids are liquid whereas longer chains are solid. For fatty acids of the same chain length, melting points of triacylglycerols in decreasing order are $SSS > SUS$, $SSU > SUU$, $USU > UUU$, where $S = \text{saturated}$ and $U = \text{unsaturated}$ fatty acid.

Fats high in trisaturates (SSS) are used for encapsulation and as crystal nuclei and stiffening agents for applications such as shortenings and margarine oils. Oils with high levels of disaturates (SSU,SUS) are utilized for confectionery fats because they melt sharply near body temperature. Monosaturates (SUU,USU) are semisolid triglycerides and function as consistency modifying agents in margarine and frying oils. Oils with a high content of triunsaturates are utilized as salad oils, spray oils or base oils for salad dressings and mayonnaise.

Fractional crystallization may be accomplished on a batch, continuous, or semicontinuous basis. Oil is chilled continuously while passing through the unit and is then passed over a continuous belt filter that separates solid fat from the liquid oil. The process gives poorer separation compared to solvent fractionation because oils are viscous at crystallization temperatures and are entrained to a significant extent in the solid fraction. The liquid fraction, however, is relatively free of saturated material.

Winterization is a specialized application of fractional crystallization that is utilized to remove saturates or waxes from liquid oils. Salad oils, which do not cloud at refrigerator temperature, have been produced by winterizing lightly hydrogenated soybean oil. However, many producers now use refined, bleached, deodorized oils for this purpose (29).

Solvent fractionation requires greater capital cost than fractional crystallization but produces more efficient separation of saturated triacylglycerols. Because of dilution and lower viscosity of the filtrate, little liquid oil is entrained in the solid fraction. Acetone (30), hexane (31), and 2-nitropropane (32), have been used as solvents for fractionation of oils. Partially hydrogenated soybean oil, palm oil, and palm kernel oil are common feedstocks that yield products for extension or replacement of cocoa butter in confectionery coatings. The historical high cost of cocoa butter has been the economic driving force for the capital-intensive construction of solvent fractionation plants.

4.4. Deodorization. Removal of volatile odorous material and residual fatty acids is the final step in oil processing prior to packaging or filling for bulk shipment (33). The oil is heated to 230–260°C under vacuum. Steam is passed through the oil to assist in carrying over the volatile material. Aldehydes, enals, dienals, ketones, and hydrocarbons, which are responsible for disagreeable odors, generally boil at lower temperatures than fatty acids. Analysis showing a free fatty acid concentration of $<0.05\%$ is an indication that deodorization is sufficiently complete. Some of the dienals have very low odor thresholds and sensory evaluation of the finished oil is a judicious quality assurance step.

Deodorization can be carried out in batch, continuous, or semicontinuous systems. Figure 4 shows a typical design for a semicontinuous deodorizer. The heated oil is passed through a series of trays under vacuum. Steam is passed through the oil through a steam sparge in the bottom of the tray. Volatiles are carried through the headspace and condensed. In addition to fatty acids and compounds responsible for odor, some tocopherols and sterols are also distilled into the condensate. The amount of tocopherols distilled depends on deodorization temperature and vacuum.

5. Sources of Fats and Oils

Fats and oils may be synthesized in enantiomerically pure forms in the laboratory (35) or derived from vegetable sources (mainly from nuts, beans, and seeds), animal depot fats, fish, or marine mammals. Oils obtained from other sources differ markedly in their fatty acid distribution. Table 2 shows compositions for a wide variety of oils. One variation in composition is the chain length of the fatty acid. Butterfat, eg, has a fairly high concentration of short- and medium-chain saturated fatty acids. Oils derived from cuphea are also a rich source of capric acid, which is considered to be medium in chain length (37). Palm kernel and coconut oils are known as lauric oils because of their high content of C-12 saturated fatty acid (lauric acid). Rapeseed oil, on the other hand, has a fairly high concentration of long-chain (C-20 and C-22) fatty acids.

Another variation of the fatty acid is the degree of unsaturation. Cocoa butter and butterfat have a high concentration of saturated fatty acids which accounts for their solid physical state. Oils such as sunflower, soybean, linseed, and safflower have a high proportion of unsaturated and polyunsaturated fatty acids. Olive oil has a high level of monounsaturated (oleic) fatty acid. Even within a species, there may be some variation in unsaturation depending on the climate in which it is grown. In cold climates, polyunsaturates occur at higher levels. This is apparently important for the plant to maintain fluidity of storage fats and membranes at colder temperatures. The most striking seasonal variation is seen with sunflower oil (38). Fish oils display even higher unsaturation as well as elongated fatty acid chains. They are sources for the biologically important eicosapentaenoic acid [90417-94-4] (EPA, 20:5) and docosahexaenoic acid [6217-54-5] (DHA, 22:6). Double bonds in polyunsaturated oils usually occur as methylene-interrupted dienes. Linoleic acid, eg, is 9,12-octadecadienoic acid. One exception to this generalization is tung oil. Approximately 85% of its

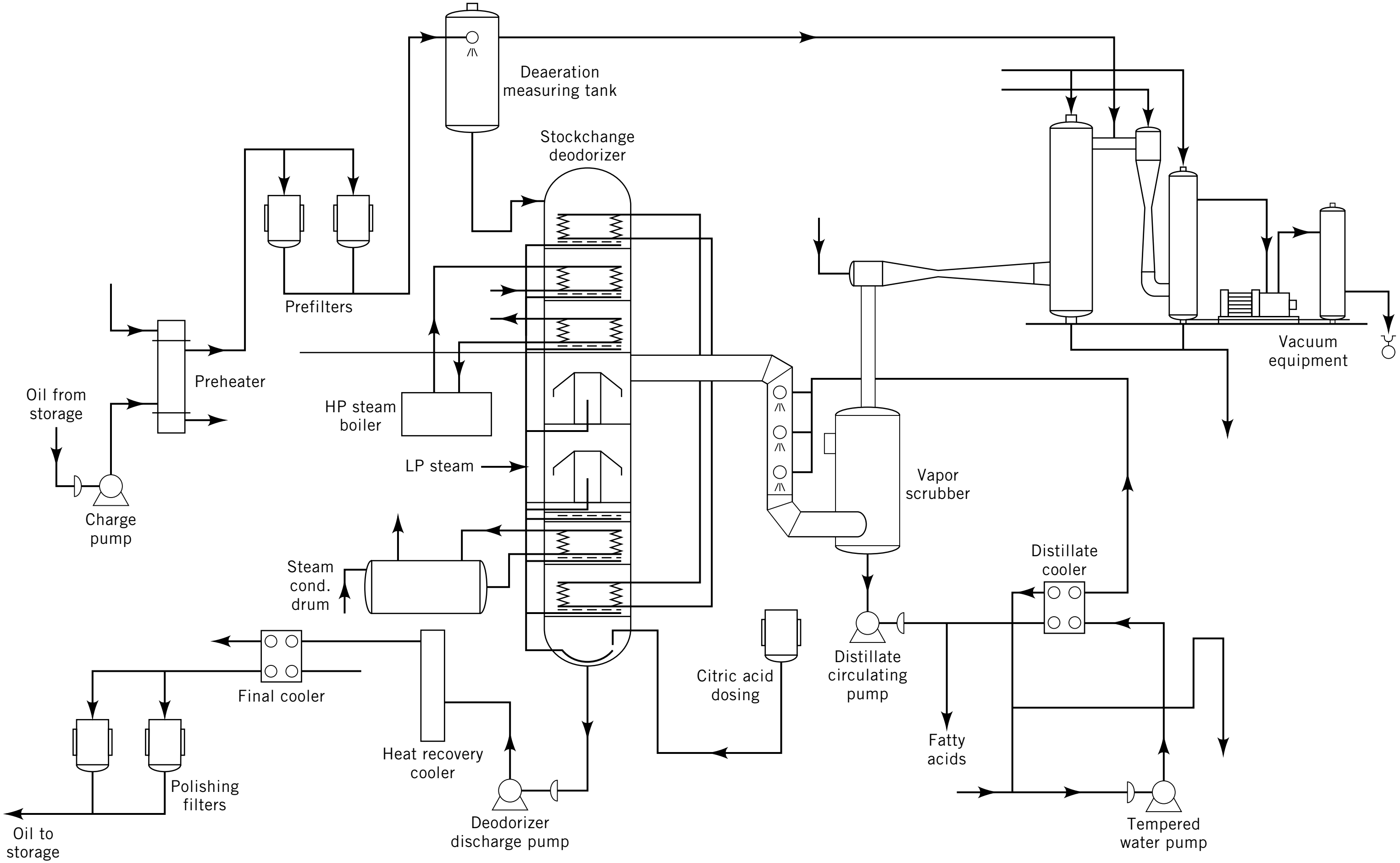


Fig. 4. Schematic diagram of a semicontinuous deodorizer (34).

Table 2. **Fatty Acid Compositions of Naturally Occurring Fats and Oils**[a]

Fat or oil	CAS Registry number	Fatty acid,[b] %													
		6:0	8:0	10:0	12:0	14:0	16:0	16:1	18:0	18:1	18:2	18:3	20:0	22:0	22:1
butterfat[c]		2.3	1.1	2.0	3.1	11.7	28.6	1.9	12.5	28.2	1.7		0.1		
canola oil							3.9	0.2	1.9	64.1	18.7	9.2	0.6	0.2	
castor oil[d]	[8001-79-4]						0.9	0.2	1.2	3.3	3.7	0.2			
chicken fat					0.2	1.3	23.2	6.5	6.4	41.6	18.9	1.3			
citrus seed oil					0.1	0.5	28.4	0.2	3.5	23.0	37.8	5.7	0.8		
cocoa butter						0.1	25.8	0.3	34.5	35.3	2.9		1.1		
coconut oil	[8001-31-8]	0.5	8.0	6.4	48.5	17.6	8.4		2.5	6.5	1.5		0.1		
cod liver oil[e]	[8001-69-2]					2.8	10.7	6.9	3.7	23.9	1.5	0.9			5.3
corn oil	[8001-30-7]						12.2	0.1	2.2	27.5	57.0	0.9	0.1		
cottonseed oil	[8001-29-4]					0.9	24.7	0.7	2.3	17.6	53.3	0.3	0.1		
cuphea oil				84.6	2.3	1.7	2.6			4.0	3.1				
lard					0.1	1.5	24.8	3.1	12.3	45.1	9.9	0.1	0.2		
linseed oil	[8001-25-0]						7.0		4.0	39.0	15.0	35.0			
menhaden oil[f]	[8002-50-4]					6.6	15.7	8.7	2.7	14.3	1.8	1.5	0.2		0.8
oat oil						0.2	17.1	0.5	1.4	33.4	44.8		0.2		
olive oil	[8001-25-0]						13.7	1.2	2.5	71.1	10.0	0.6	0.9		
palm oil	[8002-75-3]				0.3	1.1	45.1	0.1	4.7	38.5	9.4	0.3	0.2		
palm kernel oil	[8023-79-8]	0.3	3.9	4.0	49.6	16.0	8.0		2.4	13.7	2.0		0.1		
peanut oil	[8002-03-7]					0.1	11.6	0.2	3.1	46.5	31.4		1.5	3.0	
rapeseed oil	[8002-15-9]					0.1	2.8	0.2	1.3	21.8	14.6	7.3	0.7	0.4	34.8
rice bran oil			0.1	0.1	0.4	0.5	16.4	0.3	2.1	43.8	34.0	1.1	0.5	0.2	
safflower oil	[8001-23-8]					0.1	6.5		2.4	13.1	77.7		0.2		
safflower oil (high oleic)						0.1	5.5	0.1	2.2	73.7	12.0	0.2	0.2		
sesame oil	[8008-74-0]						9.9	0.3	5.2	41.2	43.2	0.2			
soybean oil	[8001-22-7]						0.1	11.0	4.0	23.4	53.2	7.8	0.3	0.1	
sunflower oil	[8001-21-6]				0.5	0.2	6.8	0.1	4.7	18.6	68.2	0.5	0.4		
sunflower oil (high oleic)							3.3		4.8	81.9	7.6	0.4	0.5	1.5	
beef tallow				0.1	0.1	3.3	25.5	3.4	21.6	38.7	2.2	0.6	0.1		
tung oil	[8001-20-5]						3.1		2.1	11.2	14.6	69.0[g]			

[a] Ref. 36.

[b] Designations as explained in Table 1.

[c] Also, 3.9% 4:0.

[d] Castor oil is 89% C-18 acid with a 9,10 double bond and an OH substituent on the chain at C-12.

[e] Also 14.3% 22:6 and 6.0% 20:5.

[f] Also 12.1% 22:6 and 15.6% 20:5.

[g] The 18:3 in tung oil is *cis*-9,*trans*-11,*trans*-13-octadecatrienoic acid [506-23-0].

fatty acid composition consists of 9,11,13-octadecatrienoic acid. The conjugated triene system allows rapid thermal polymerization of tung oil making it useful as a protective coating material.

Castor oil (qv) contains a predominance of ricinoleic acid which has an unusual structure inasmuch as a double bond is present in the 9 position while a hydroxyl group occurs in the 12-position. The biochemical origin of ricinoleic acid [141-22-0] in the castor seed arises from enzymatic hydroxylation of oleoyl-CoA in the presence of molecular oxygen. The unusual structure of ricinoleic acid affects the solubility and physical properties of castor oil. Also, since the molecule has both hydroxyl and carboxylic acid functioal groups, it may undergo dehydration to form polymers.

Solid fats may show drastically different melting behaviors. Animal fats such as tallow have fatty acids distributed almost randomly over all positions on the glycerol chain. These fats melt over a fairly broad temperature range. Conversely, cocoa has unsaturated fatty acids predominantly in the 2-position and saturated acids in the 1- and 3-positions. Cocoa butter is a brittle solid at ambient temperature, but melts rapidly just below body temperature.

Historically, many attempts have been made to systematize the arrangement of fatty acids in the glyceride molecule. The even (39), random (40), restricted random (41), and 1,3-random (42) hypotheses were developed to explain the methods nature utilized to arrange fatty acids in fats. Invariably, exceptions to these theories were encountered. Plants and animals were found to biosynthesize fats and oils very differently. This realization has led to closer examination of biosynthetic pathways, such as chain elongation and desaturation, in individual genera and species.

Biotechnology is rapidly revolutionizing the edible oils industry. Crop breeding (43), genetic engineering (44), tissue culture (45), and mutation selection (46) are avenues being pursued to deliver desirable fatty acid compositions into agronomically favored plants. Oils from microbial sources may offer unique fatty acid compositions (47). Canola, high oleic sunflower, and high oleic canola oils are recent successes in harnessing the biosynthetic factories.

Separation of a fat or oil from its source material can be accomplished by several different methods. Selection of an extraction process is based on: (*1*) obtaining oil substantially undamaged and relatively free of undesirable impurities, (*2*) achieving the highest practical yield, and (*3*) obtaining the maximum economic return on the oil and coproducts.

5.1. Rendering. Separation of animal fats from water and connective tissue in crude trimmings from carcasses is accomplished by treatment with heat. The process may also be applied to whole small fish such as sardines or herring. Nonedible fats are generally obtained by dry rendering where moisture is removed and the melted fat is drained and pressed away from connective tissue. Wet rendering can be carried out by treating fat-bearing material with boiling water (low temperature) or with high temperature steam. Edible materials with good color, flavor, and stability can be obtained from wet rendering.

5.2. Mechanical Pressing. Historically, the first large commercial production of oils from seeds and nuts was carried out using labor-intensive hydraulic presses. These were gradually replaced by more efficient mechanical and screw presses. Solvent extraction was developed for extraction of seeds having low oil content. For seeds and nuts having higher oil content, a combination of a screw press followed by solvent extraction is a common commercial practice (prepress–solvent extraction).

Prior to pressing, the material is heat treated to inactivate enzymes that are detrimental to oil or meal quality and to allow oil droplets to coalesce into larger drops. Proteins in the structure are denatured and set into a structure that is more porous to the flow of the oil. Residual oil is commonly left in the meal after pressing. This can range from a few percent as in cocoa butter to a much higher percentage as seen in peanuts. The pressing operation can be a batch process, such as a hydraulic box press, or continuous by use of a mechanical screw press. The latter is more efficient for removal of oil from materials such as cottonseed. Some higher value oils, such as olive, may be extracted by prepress–solvent extraction. The method is also practiced for lower value seeds such as flax, rape, sunflower, and cottonseed.

5.3. Solvent Extraction. Treatment of oil-bearing materials with solvent can effect virtually complete removal of oil from meal. However, the capital cost of equipment is higher and subsequent processing to remove traces of flammable or toxic solvent from both oil and meal is necessary. Straight or branched chain hydrocarbons obtained as light petroleum distillates, are used almost exclusively as solvent. Other solvents such as 2-propanol and methylene chloride have been used alone or as blends with hydrocarbons. The more polar solvents promote the extraction of more polar components such as phospholipids. Gossypol, a toxic substance to domestic animals, may be removed from cottonseed meal with 2-propanol and then removed from the oil by alkali refining. Soybeans are almost exclusively solvent-extracted in the United States and other developed countries. The soybeans are heat treated and then mechanically pressed into flakes in order to render the structure more porous to solvent. The use of expanders to further open the structure has become widely used (34). Another exciting development in extraction technology is the use of supercritical fluids, such as carbon dioxide, to extract oil from its source (48,49). The greatest advantage is that flammable potentially toxic solvents are avoided. The supercritical fluid is a gas at ambient conditions and is easily removed. The principal barrier to commercialization is the high capital cost of continuous equipment designed for use at high pressures.

5.4. Oil Production. World vegetable oil production in 2001/2002 was forecast at 90 million metric tons with all significant oils except sunflower and coconut showing increasing trends (50). Some specialization for specific countries and regions are evident: palm oil is produced mostly in Malaysia, coconut in the Philippines, and rapeseed and sunflower in Europe. Soybean oil is most common in the United States. Commodity prices can range relatively low for soybean oil to relatively high for cocoa butter. These price differentials have stimulated a great deal of research effort to develop functional equivalents to cocoa butter using less expensive fats.

6. Physical Properties of Fats and Oils

The physical properties of fats and oils have been reviewed (51).

6.1. Crystallization and Melting Behavior. Pure compounds usually display sharp melting points and impure compounds show broad melting behavior. However, even pure triglycerides show complex melting behavior because of their tendency to pack in several different crystal lattice forms (polymorphism). Complete crystal structures have been obtained for tricaprin (52), trilaurin [538-24-9] (53), and the triacylglycerol of 11-bromoundecanoic acid (54). Structures of other triacylglycerols relate back to these determinations by analogy.

Triacylglycerols having three identical fatty acids pack into three distinct polymorphs: (*1*) β, the most stable form shows a triclinic subcell, (*2*) β′, a less stable crystal that suggests orthorhombic packing, and (*3*) α, a loosely packed triacylglycerol that packs hexagonally. Rapid cooling of the triacylglycerol leads initially to the α form followed by slow reorganization to β′ and β forms. Mixed glycerides, with more than one type of saturated fatty acid, pack with defects in the structure and chains appear to tilt to correct for these defects. Glycerides with unsaturated fatty acids must pack to accommodate the bend in the alkyl chain caused by the cis double bond. Perhaps the most widely studied fat, cocoa butter, may show as many as seven distinct polymorphic forms (55).

The crystal structure of glycerides may be unambiguously determined by X-ray diffraction of powdered samples. However, the dynamic crystallization may also be readily studied by differential scanning calorimetry (dsc). Crystallization, remelting, and recrystallization to a more stable form may be observed when liquid fat is solidified at a carefully controlled rate in the instrument. Enthalpy values and melting points for the various crystal forms are shown in Table 3 (56).

Specific heats of fats and oils may be calculated with some precision as a function of temperature, t, in °C (57): *Liquid oils*

$$C_p = 1.93 + 0.0025\,t \ (t = 15 - 60^\circ\mathrm{C})$$

Tallow, palm oil, and partially hydrogenated fats

$$C_p = 1.99 + 0.0023\,t \ (t = 40 - 70^\circ\mathrm{C})$$

Fully hydrogenated fats

$$C_p = 1.92 + 0.003\,t \ (t = 60 - 80^\circ\mathrm{C})$$

Some general trends in specific heats have been suggested: (*1*) for solid fats, there is little variation in specific heat for saturated fats and their fatty acids as chain length varies. Specific heat varies directly with the degree of unsaturation. Specific heat of a solid is less than that of the liquid at the same temperature; (*2*) specific heat of liquid fatty acids and glycerides increases with increasing chain length but decreases with increasing unsaturation. For both liquids and solids, specific heat increases with increasing temperature; and (*3*) mixed-acid glycerides have lower specific heats than their corresponding simple glycerides.

Practical consequences of polymorphism may be seen in some food products. In the preparation of chocolate products it is difficult to blend other fats with cocoa butter. Cocoa butter is required to be in the β form for optimal melting and mouthfeel. If another fat with differing crystallization tendencies is

Table 3. **Melting Points and Enthalpy Values for Selected Triglycerides**[a]

		Mp, °C			ΔH, kJ/mol[b]	
n	C:Δ[c]	α	β′	β	α	β
		Simple saturated triacylglycerols				
	6:0			−25		
	8:0		−21	8.2		67.4
	10:0	−15	18.0	31.5		93.3
	11:0	1.0	26.5	30.5		
	12:0	15	35.0	46.5		123
	13:0	25	41.0	44.0		
	14:0	33	46.5	57.0	105	148
	15:0	40	51.5	54.0		
	16:0	44.7	56.5	66.4	126	172
	17:0	50	61.0	64.0		
	18:0	54.9	64.0	73.1	145	197
	20:0	61.8	69.0	78.0		223
	22:0	68.2	74.0	82.5		262
		Simple unsaturated triacylglycerols				
cis-18:1-Δ9		−32	−12	5.5		95.3
trans-18:1-Δ9		15.5	37	42		146
cis-18:1-Δ6				26.2		
18:2-Δ9,12		−43		−13.1		83.3
18:3-Δ9,12,15		−44.6		−24.2		
cis-22:1-Δ13		6	17	30		
trans-22:1-Δ13		43	50	59		

[a] Ref. 56.

[b] To convert kJ to kcal, divide by 4.184.

[c] Δ designates double bond.

incorporated, the foreign fat crystallizes separately and a whitish coating referred to as "bloom" appears on the surface of the product. In margarine manufacture, a β′ crystal is desired because it forms small crystals that feel smooth and melt easily in the mouth. If a fat forms a β crystal, the margarine appears "grainy" or "sandy" and is unacceptable to consumers; Bakery shortenings also require this crystal form to provide proper aeration and texture to the finished product. X-ray diffraction clearly shows the two forms. Examples of mesomorphic forms, or liquid crystals, may be of importance to other industrial technologies, such as manufacture of waxes.

Partial glycerides tend to melt higher than their triacylglycerol counterparts, as shown in Figure 5. This observation is consistent with the presence of free hydroxyl groups that can participate in increased intermolecular hydrogen bonding.

6.2. Viscosity. Fats, oils, fatty acids, and other fatty acid derivatives show relatively high viscosities compared to other liquids because of the intermolecular interaction of long alkyl chains (Table 4). They are similar to paraffinic hydrocarbons in this respect. Some general trends are that longer chain lengths and lower unsaturation produce higher viscosities. Fatty acids are more viscous than esters because of the greater tendency to form hydrogen bonds. Castor oil is

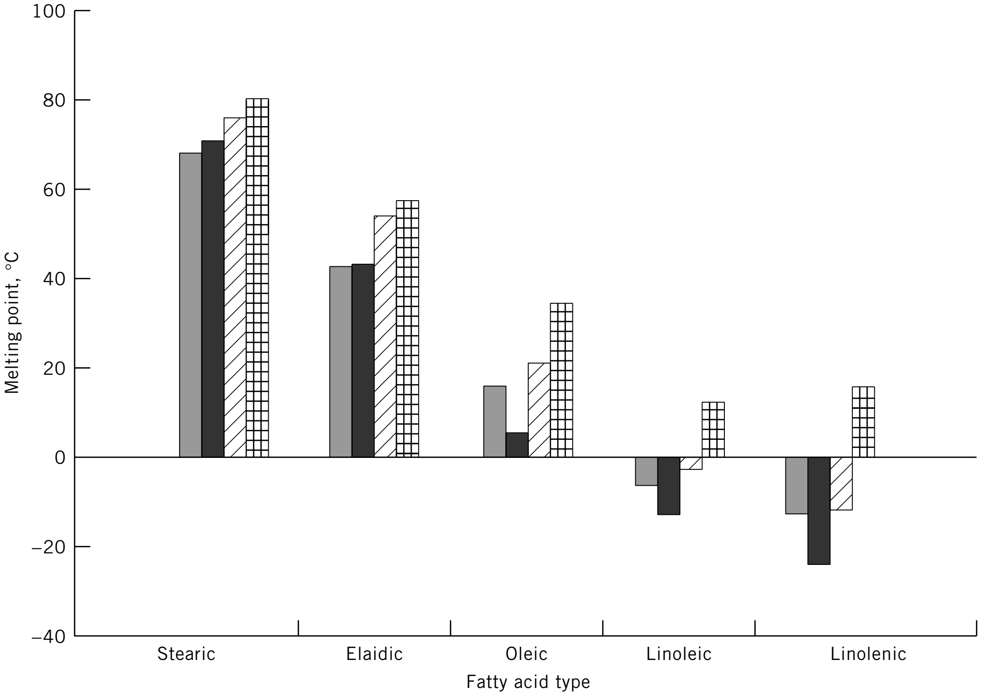


Fig. 5. Melting points of mono-, di-, and triglycerides, where ■ is fatty acid; ▪, triacylglycerol; ▨, 1,3-diacylglycerol; and ⊞, 1-monoacylglycerol.

Table 4. **Viscosity of Deodorized Oils and Fats at Different Temperatures**[a]

	Viscosity,[b] mPa · s (= cP)				Constants[c]	
Oil or Fat	IV[d]	20°C	40°C	60°C	*a*	*b*
soybean oil	134	60	28	15	−0.073	46.6
medium-chain triglycerides	0		21	11	−0.306	50.1
sunflower seed oil	132	63	29	16	−0.038	44.8
corn oil	122	70	30	16	−0.142	49.9
coconut oil	9		27	14	−0.242	51.0
hydrogenated soybean oil, mp 28°C	101		33	18	−0.148	51.1
butterfat	38		34	17	−0.151	51.2
groundnut oil	89	81	36	19	−0.080	50.5
olive oil	83	82	35	17	−0.102	50.1
hydrogenated cottonseed oil, mp 32°C	76		45	23	−0.166	55.9
rapeseed oil	104	93	41	21	−0.023	50.1
lard olein	73		36	18	−0.151	51.9
palm olein	64		37	19	−0.145	52.2
palm oil	51		37	19	−0.192	53.8
lard	63		36	19	−0.068	48.2
hydrogenated rapeseed oil, mp 32°C	81		49	24	−0.140	56.0

[a] Ref. 59.

[b] Standard deviation of replicates 1%.

[c] Constants in the equation $\log \rho = a + 10^6 b t^{-3}$ (t = °C).

[d] IV = iodine value, a measure of unsaturation.

in a class by itself because of its side chain hydroxyl group that can form hydrogen bonds. The free fatty acid of castor oil may condense to form polymers. Derivatives of castor oil are consequently useful as specialty lubricants. Polyglycerol polyricinoleate is used as a crystal modifier in the production of chocolate products (58). Fats and oils behave as Newtonian liquids except at very high shear rates where degradation may begin to occur.

6.3. Surface and Interfacial Tension.

Data for surface tension of fats, fatty acids, and derivatives are relatively sparse. Commercial oils tend to have lower surface and interfacial tensions because of the presence of polar surface-active components such as monoacylglycerols, phospholipids, and soaps. Purification of oils on a Florisil column can be used to obtain higher and more consistent values (60). Monoacylglycerols and phospholipids can reduce the interfacial tension between an oil and water. Emulsions (qv) may be formed that are relatively stable. Food products such as mayonnaise, margarine, and nonseparating salad dressings are commercial examples of stable emulsions.

6.4. Density.

The density of liquid oils at 15°C does not vary markedly with changes in composition. Values generally range from 0.912 to 0.964 g/mL. Density increases with decreasing molecular weight and increasing unsaturation. An approximate equation (61) for determination of specific gravity from saponification number (SN) (function of chain length) and iodine value (IV) (function of unsaturation) at 15°C is $\text{sp pgr} = 0.8475 + 0.00030(\text{SN}) + 0.00014\ (\text{IV})$. Density decreases approximately linearly with increasing temperature. Densities of fats in the solid state are much higher, approximating the values for water (1.0 g/mL).

6.5. Smoke, Flash, and Fire Points.

These thermal properties may be determined under standard test conditions (62). The smoke point is defined as the temperature at which smoke begins to evolve continuously from the sample. Flash point is the temperature at which a flash is observed when a test flame is applied. The fire point is defined as the temperature at which the fire continues to burn. These values are profoundly affected by minor constituents in the oil, such as fatty acids, mono- and diacylglycerols, and residual solvents. These factors are of commercial importance where fats or oils are used at high temperatures such as in lubricants or edible frying fats.

6.6. Refractive Index.

Refractive index of a fat or oil increases with molecular weight and unsaturation. For this reason, the method is used to monitor the progress of processing operations such as hydrogenation. In order to obtain values for both liquids and oils, most control laboratories operate the instrument at increased temperature (48–60°C), rather than the standard 25°C used for other liquids. Refractive indexes of simple glycerides are significantly higher than those of fatty acids. Values for partial glycerides are higher than their triacylglycerol counterparts. The presence of conjugated double bonds, as in tung oil or dehydrated castor oil, leads to a marked elevation of the refractive index.

6.7. Absorption Spectra.

Double bonds in naturally occurring fats and oils are interrupted by methylene groups and, except for a few unusual oils, they are not conjugated. For this reason they are transparent to most of the ultraviolet spectrum. However, conjugated systems can be produced by autoxidation, chemical reactions, or processing and the conjugated isomers can be conveniently detected by ultraviolet (uv) spectroscopy. Bands for dienes (233 nm), trienes (270 nm), and tetraenes (305 nm) are diagnostic for conjugated systems. Caution must be exercised in interpretation because minor constituents in fats or oils may also contain chromophores absorbing in the same regions. Absorption of light in the visible range results in a colored appearance to oils. Color is an important specification in trading of oils.

Infrared (ir) spectra of fats and oils are similar regardless of their composition. The principal absorption seen is the carbonyl stretching peak, which is virtually identical for all triacylglycerol oils. The most common application of ir spectroscopy is the determination of trans fatty acids occurring in a partially hydrogenated fat (63,64). Absorption at 965–975 cm^{-1} is unique to the trans functionality. Near-ir spectroscopy has been utilized for simultaneous quantitation of fat, protein, and moisture in grain samples (65). The technique has also been reported to be useful for instrumental determination of iodine value (66). This method can be used in place of refractive index to determine the degree of unsaturation. As in refratometers, ir cells must be heated to analyze solid fats.

Absorption of X-rays by a powdered sample of solid fat has been a useful method for determination of polymorphic character as discussed earlier. The α, β', and β forms may be distinguished; however, interpretation is made more difficult because subsets of the β' and β forms have often been encountered. Also, a fat may contain mixtures of polymorphic forms and properties may therefore be difficult to relate to the spectra.

Proton chemical shift data from nmr has historically not been very informative because the methylene groups in the hydrocarbon chain are not easily differentiated. However, this can be turned to advantage if a polar group is present on the side chain causing the shift of adjacent hydrogens downfield. High resolution C-13 nuclear magnetic resonance (^{13}C nmr) has been able to determine position and stereochemistry of double bonds in the fatty acid chain (67). Broad band nmr has also been shown useful for determination of solid fat content.

6.8. Solubility Properties. Fats and oils are characterized by virtually complete lack of miscibility with water. However, they are miscible in all proportions with many nonpolar organic solvents. True solubility depends on the thermal properties of the solute and solvent and the relative attractive forces between like and unlike molecules. Ideal solubilities can be calculated from thermal properties. Most real solutions of fats and oils in organic solvents show positive deviation from ideality, particularly at higher concentrations. Determination of solubilities of components of fat and oil mixtures is critical when designing separations of mixtures by fractional crystallization.

7. Chemical Properties

Most triacylglycerol fats and oils have only two reactive functional groups: the ester linkage joining the fatty acid to the glycerol backbone and double bonds in the alkyl side chain. There is a free hydroxyl group in the side chain of ricinoleic acid found in castor oil and a carbonyl group in the licanic acid side chain of oiticica oil. The double bond influences the reactivity of the adjacent allylic carbon atom, particularly when multiple double bonds are present. Figures 6 and 7

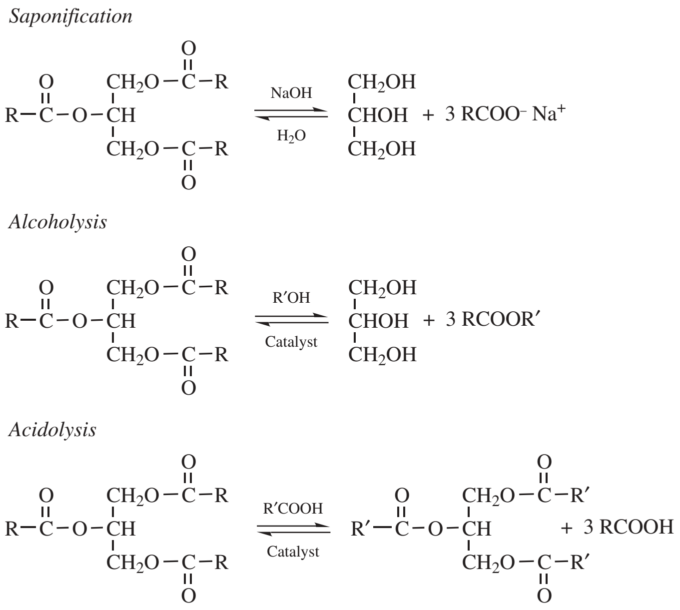


Fig. 6. Reactions of triacylglycerols at the carbonyl ester linkage. R represents the alkyl side chain.

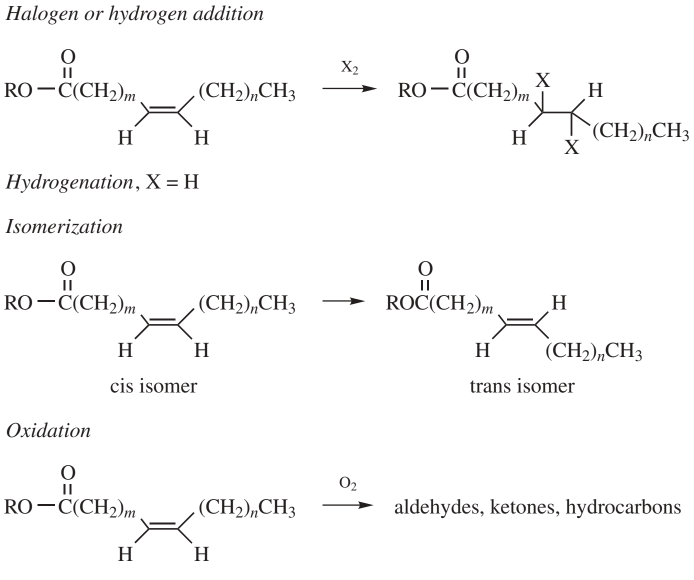


Fig. 7. Reactions of triacylglycerols at double bonds in the alkyl chain. R represents the glycerol backbone.

show some important reactions at the primary reactive sites of triacylglycerols and fatty acids. Minor constituents, such as sterols, may have other functional groups in their structures presenting an opportunity for separation and enrichment of those components. For example, sterols may be comverted to their hemisuccinate esters and removed from the oil by extraction with alkali (68).

Chemical reactions can cause serious quality problems for oils. Hydrolytic and oxidative rancidity can cause oils to become unacceptable to consumers for edible or other uses. Hydrolysis can occur if crops are not dried after harvesting or moisture is in contact with the oil over a large surface area. Hydrolysis may be catalyzed by acids, bases, or lipase enzymes. Lauric oils, such as coconut and palm kernel, acquire a soapy off-flavor after hydrolysis. Oxidation may occur in any oil that contains double bonds. The highly unsaturated oils containing 18:2, 18:3, 20:5, and 22:6 fatty acids are particularly vulnerable. Oxidation is catalyzed by light, as in oxidation of milk lipids, by lipoxygenase enzymes, or by transition metals. After an initiating event, the chain reaction is self-catalyzed (autoxidation). The mechanism of lipoxygenase-catalyzed oxidation (69) and autoxidation (70) have been reviewed. In addition to producing secondary volatile oxidation products having rancid odors and flavors, lipid peroxides may cause oxidation of proteins and thereby cause loss of their nutritional values (71).

8. Analytical Methods

Throughout the history of the development of fats and oils, many wet chemical methods have been developed to assess the quality of the raw materials and products. As sophisticated instrumentation has developed, a number of the wet methods have been replaced. Particular attention has seen given to methods that eliminate the use of solvents that cause an environmental disposal problem. Many in-line sensors are also being developed to allow corrections of critical parameters to be made more quickly in the process.

8.1. Specifications. The quality of individual crude oils is specified by trading rules established by organizations such as the National Soybean Processors Association, National Renderers Association, or National Institute of Oilseed Processors. Standardized tests are defined by the American Oil Chemists Society (AOCS), the Association of Official Analytical Chemists (AOAC), and the American Society for Testing Materials (ASTM). Crude oils must contain minimal amounts of foreign material, protein, volatile or toxic solvents, pesticides, heat-transfer media, moisture, and foreign adulterating fats. They must also not be abused or mishandled which causes them to become oxidized. Crude oils must not show excessive loss on refining which adds to costs and waste disposal problems. Oil processors must also meet specifications for their customers which include measures of oil quality, such as free fatty acid level, color, and oxidation. Other specifications may relate to functionality in the customer's product, such as melting range or fatty acid composition.

8.2. Free Fatty Acid and Saponification Value. High concentrations of free fatty acid are undesirable in crude triglyceride oils because they result in large losses of neutral oil during refining. They are also undesirable in finished oils because they can cause off-flavors and shorten the shelf life of the oil. Free fatty acid is determined by titration with base to a phenolphthalein end point (72). Saponification value is determined by splitting triacylglycerols into free fatty acids in alcoholic base and back-titrating with acid (73). The number obtained is an inverse function of molecular weight and therefore alkyl chain length of the pendant fatty acid.

8.3. Fatty Acid and Triglyceride Composition. Triacylglycerols may be alcoholyzed using alkaline methanol or derivatized as methyl esters using diazomethane. The resulting fatty acid methyl esters may be separated and quantitated by gas–liquid chromatography (glc) (74). The development of capillary columns has greatly improved the resolution and sensitivity of this method (75). Determination of fatty acid composition is the first step in identification of an unknown oil. Triacylglycerols may be broadly grouped into trisaturates, monounsaturates, diunsaturates, and triunsaturates. These broad classes may be determined by thin-layer chromatography (tlc) on a silver-impregnated support (76). A semiautomated tlc unit is commercially available for tlc of lipids. To separate and quantitate mono-, di-, and triacylglycerols, Tlc and glc may also be used.

The arrangement of fatty acids on the glycerol backbone is also an important consideration, particularly where polymorphic properties are critical. Triacylglycerols may be separated by high temperature glc according to their molecular weight and therefore the number of carbon atoms in the fatty acid chain (77). High performance liquid chromatography (hplc) on reversed-phase columns separates glycerides by the number of double bonds and the number of carbon atoms in the side chain (78). Components elute in order of increasing chain length. The presence of a double bond reduces the retention time the same amount as a decrease of two carbon atoms in the chain. Combination of hplc and high temperature glc can yield a complete triacylglycerol profile. An enzymatic technique is used to determine the distribution of fatty acids at the 2-position. Pancreatic lipase hydrolyzes fatty acids at the primary position leaving 2-monoacylglycerols, which are derivatized and injected into a glc (79).

8.4. Measurement of Unsaturation. The presence of double bonds in a fatty acid side chain can be detected chemically or through use of instrumentation. Iodine value (IV) (80) is a measure of extent of the reaction of iodine with double bonds; the higher the IV, the more unsaturated the oil. IV may also be calculated from fatty acid composition. The cis–trans configuration of double bonds may be determined by ir (61) or nmr spectroscopy. Naturally occurring oils have methylene-interrupted double bonds that do not absorb in the uv; however, conjugated dienes may be determined in an appropriate solvent at 233 nm.

8.5. Measurement of Solid Fat. Many commercially used fats and oils are mixtures of liquids and solids and the ratio is largely dependent on composition and temperature. Solid Fat Index (SFI) (81) is a dilatometric method to determine solid fat. Samples are conventionally equilibrated (tempered) and read at several different temperatures and a profile is reported. The profile gives a visualization of how sharp or broad the melting range is for the solid fat. Some applications such as margarines or shortenings benefit from a broad melting range, whereas others such as confectionery products require a sharp melting fat. The method for determination of SFI is laborious and time consuming and has been supplanted by more efficient methods. Differential scanning calorimetry has been used to show the dynamic melting properties of fat (82). More recently another profile, Solid Fat Content (SFC), has been developed. Two low resolution nuclear magnetic resonance techniques, wide-line or continuous nmr (83) and pulsed nmr (84), are utilized to determine the SFC index. Both methods discriminate differences in protons in a liquid state from those in a solid state. Wide-line nmr measures the spin–lattice relaxation time whereas pulsed nmr measures the spin–spin relaxation time. A practical applications-oriented measure of solid fats is the cold test in which oils are chilled to a low temperature and held for a specified period.

8.6. Melting Properties. As previously discussed, because fats are mixtures of triacylglycerols and exhibit polymorphic forms they have broad melting points. Several methodologies have been devised to measure melting points. Capillary melting point (85) and the Wiley melting point were subject to operator variability and have largely been replaced by the Mettler dropping point (86). This technique involves heating a disk of fat at a programmed rate until the disk melts sufficiently to fall through its holder. The motion breaks an electric eye circuit and the temperature is recorded.

8.7. Color. The most common colored materials in oil are naturally occurring pigments such as red from carotenoids and green from chlorophyll. These colors are generally removed substantially in the bleaching and deodorization processes. Measurement of color has been carried out by comparison to reference standards. The three most common scales are the Lovibond (87), the FAC (88), and the Gardner (89). Lovibond colors are generally used to specify vegetable oils for edible purposes whereas the Gardner scale is used for other industries such as paints, cosmetics, and plastics. The FAC scale is useful for animal fats that are mostly yellow with various greenish tones. Spectrophotometric methods in the region of 400–700 nm have been developed because of their objectivity and potential as on-line monitoring possibilities.

8.8. Measurement of Oxidation. The most common cause of rancidity in fat-based products is oxidation. In the initial stages a free radical is produced that captures oxygen and then a hydrogen atom to produce hydroperoxide. The peroxide then decomposes into lower molecular weight secondary oxidation products that have disagreeable odors and flavors. An extraordinary number of tests have been developed to determine the extent of oxidation that has occurred in the oil (90). Peroxide value (91) is an indication of the concentration of hydroperoxides (primary oxidation products). Another method, the thiobarbituric acid test (TBA), presumably measures the concentration of malonaldehyde, a secondary oxidation product (92). During the course of oxidation, conjugated dienes are formed that are measurable by uv absorption. Peroxide value has been generally accepted in the edible oil industry whereas the latter two methods are popular in the measurement of biomedical materials. A comparison of methods for biological samples has been published (93).

Stability of an oil to oxidation has been measured by several techniques. In the Schaal oven test (94), an oil is heated in an oven and the peroxide value is periodically measured. In the Active Oxygen method (AOM) a calibrated stream of air is bubbled through a sample and the peroxide value is measured as a function of time. Alternatively, the oil may be oxidized in a pressurized vessel (bomb). The value is reported in hours to reach a peroxide value of 100 (95). A more automated procedure has been reported where air is bubbled through a heated oil and then through a conductivity cell (96). The induction time is measured by an inflection point where the conductivity begins to increase. Sampling of a headspace above an oil can be used to determine the concentrations of volatile oxidation products. Off-flavor descriptors may be rated on a scale by sensory panels to determine the acceptability of the oil for edible purposes. Many attempts have been made to correlate the sensory experience scores with volatile components by glc (97). Measurement of hexanal may also be used for evaluation of oxidation in biological systems (98). Polar and polymeric oxidation products may be determined by hplc (99).

8.9. Analysis of Trace or Minor Components. Minor or trace components may have a significant impact on quality of fats and oils (100). Metals, for example, can catalyze the oxidative degradation of unsaturated oils that results in off-flavors, odors, and polymerization. A large number of techniques such as wet chemical analysis, atomic absorption, atomic emission, and polarography are available for analysis of metals. Heavy metals, iron, copper, nickel, and chromium are elements that have received the most attention. Phosphorus may also be detectable and is a measure of phospholipids and phosphorus-containing acids or salts.

Antioxidants (qv) have a protective effect on oils when present in the proper concentration. Sterols and tocopherols, which are natural antioxidants, may be analyzed by glc, high performance liquid chromatography (hplc), or tlc. Synthetic antioxidants may be added by processors to improve the performance or shelf life of products. These compounds include butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), *tert*-butylhydroquinone (TBHQ), and propyl gallate. These materials may likewise be analyzed by glc, hplc, or tlc. Citric acid (qv), which functions as a metal chelator, may also be determined by glc.

9. Uses of Fats and Oils

9.1. Food Components and Cooking Oils. Fats and oils have a relatively large number of carbon–carbon and carbon–hydrogen bonds. When burned as fuel in the body they provide ~37.7 kJ/g (9 kcal/g) in energy. By comparison, proteins and carbohydrates contribute only ~16.7 kJ/g (4 kcal/g) (one food calorie = 1 kcal). Fat is therefore the most energy dense food available. In addition, fats contribute essential fatty acids. Linoleic acid is the most effective component for prevention of fatty acid deficiency. Fortunately, the daily requirement is very low and extremely severe restrictions are required to induce deficiencies. Fats produce a feeling of satiety and attempts to severely curtail fat may result in a "fat hunger." Vitamins A, D, E, and K are fat-soluble and are generally associated with fats in foods. Highly unsaturated fatty acids, notably linolenic acid (18:3), eicosapentaenoic acid (20:5), and docosahexaenoic acid (22:6), contribute to proper health and development. Fats contribute desirable flavor and texture to food products. In addition to native or modified flavor, fats and oils serve as solvents and modulators for other flavor components present in foods.

Unfortunately, excess consumption of fatty foods has been correlated with serious human disease conditions. Effects on cardiovascular disease (101), cancer (102), and function of the immune system (103) have been shown. Excess consumption of fats can contribute to obesity which, in turn, can aggravate Type II diabetes. Numerous studies have been conducted to determine the effects of saturated, monounsaturated, and polyunsaturated fatty acids on serum cholesterol and more recently high density lipoprotein (HDL) and low density lipoprotein (LDL) present in serum. The effects of saturates, polyunsaturates, and dietary cholesterol on total serum cholesterol have been quantitated (104,105) using the following equations:

$$\Delta SC = 1.35(2\,\Delta S - \Delta P) + 1.4\,\Delta C$$

$$\Delta SC = 2.16\,\Delta S - 1.65\,\Delta P + 0.0677\,\Delta C - 0.53$$

where ΔSC = total serum cholesterol, ΔS = saturated fat, ΔP = polyunsaturated fat, and ΔC = dietary cholesterol. Significant effects were found for saturated fatty acids having 12–16 carbon chain lengths.

Relative amounts of saturated, monounsaturated, and polyunsaturated fatty acids for several oils are shown in Figure 8. Saturated fatty acids have been associated in some studies with increases in total cholesterol and LDL. Trans unsaturates, produced as by-products of hydrogenation, raise LDL and lower HDL. (22,107). Fat and calorie consumption have been correlated with some types of cancer. However, some fat constituents, such as conjugated linoleic acid (CLA) (108), and omega-3 (*n*-3) oils, such as fish oil, have been shown to retard tumor growth. Dietary recommendations (109) have advised the consumption of <30% of calories from fat and equal contributions should be derived from saturates, monounsaturates, and polyunsaturates.

Although most of the fat consumed is indigenous to foods such as meat, poultry, fish, and dairy products, processed fats and oils make a significant contribution in the diet. Cooking oils provide a heat-transfer medium and contribute to flavor development in foods. Partially hydrogenated fats are added to bakery products, icings, and whipped toppings to improve aeration, texture, and mouthfeel. Oil contributes flavor and texture effects to margarine, mayonnaise, salad dressing, and confectionery products. Although many fat replacers (qv) have been developed to allow reduction or elimination of fats in processed food, technology has not yet advanced to a point where these products are perceived as equally preferred to their full fat counterparts.

Derivatives of fats and oils may be used as emulsifiers, stabilizers, and antioxidants in foods (110). Examples are mono- and diacylglycerols, propylene glycol esters, lactylated monoacylglycerols, sodium and calcium stearoyl lactylates, monoacylglycerol citrates, succinylated monoacylglycerols, diacetyltartaric esters of monoacylglycerols (DATEM), sucrose esters, sorbitan esters, polysorbates, and polyglycerol esters.

9.2. Soaps and Detergents. Soap is one of the earliest chemical substances known (111), dating from before 2500 BC. Its original derivation was by boiling ashes rich in alkali with fats to achieve saponification of the fat to soap and glycerol. Modern soaps may be derived from batch or continuous saponification

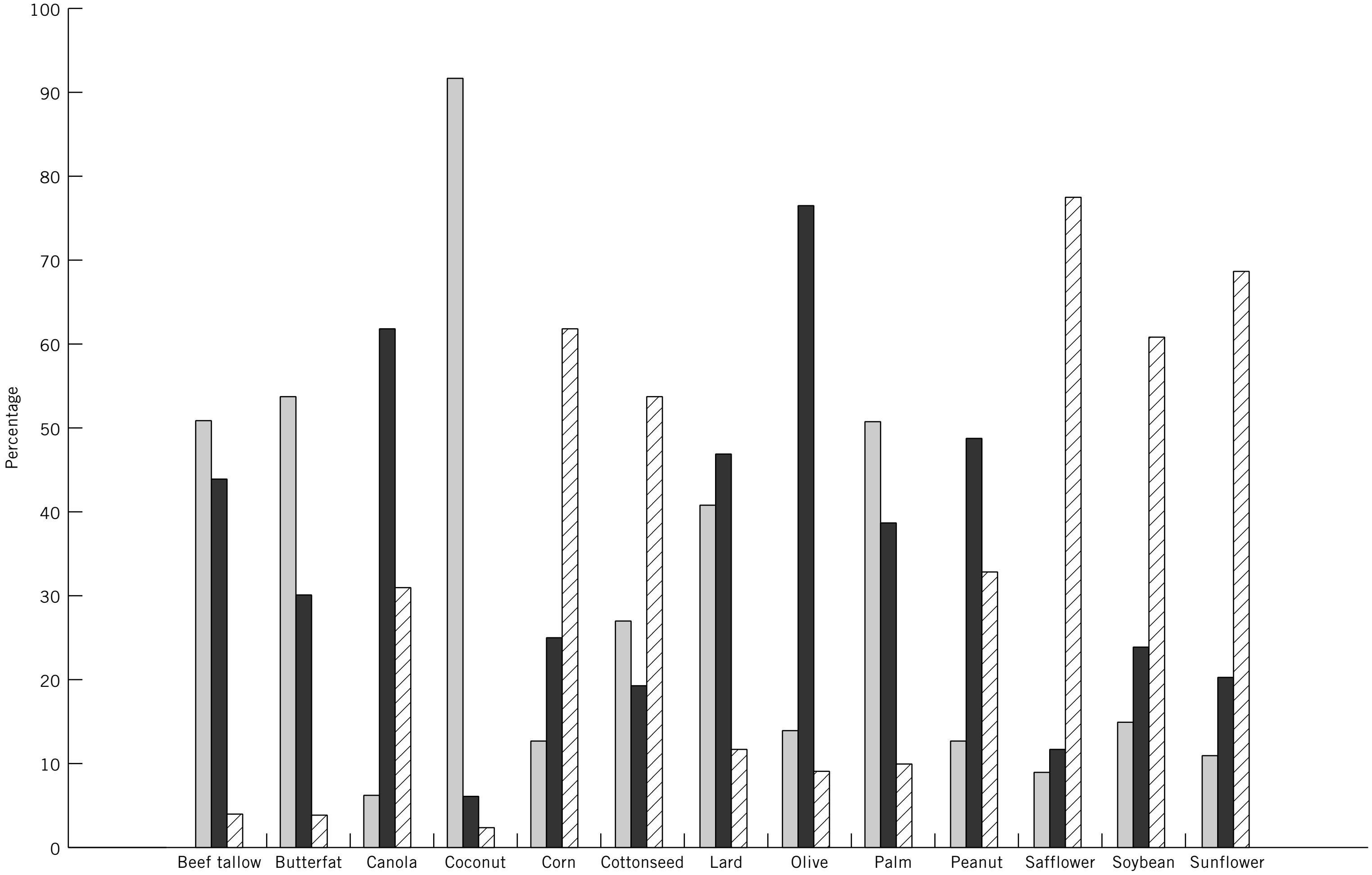


Fig. 8. Saturated, monounsaturated, and polyunsaturated fatty acids in common oils, where ■ is saturate; ▪, monounsaturate; and ▨ is polyunsaturate (106).

or by neutralization of fatty acids that are split from fats. Coconut oil is a very popular starting oil since its soap has high surface activity and residues on the skin are less greasy than soaps with longer alkyl chains.

Detergents may be produced by the chemical reaction of fats and fatty acids with polar materials such as sulfuric or phosphoric acid or ethylene oxide. Detergents emulsify oil and grease because of their ability to reduce the surface tension and contact angle of water as well as the interfacial tension between water and oil. Recent trends in detergents have been to lower phosphate content to prevent eutrification of lakes when detergents are disposed of in municipal waste. Detergent products may be produced in a number of physical forms, such as powders, liquids, or tablets. Formulations may include other functional agents, like fabric protectors and softeners.

9.3. Drying Oils. Liquid oils have a relatively long history of use in paints, lacquers, and varnishes. Flax was grown by the ancient Egyptians as a source of drying oil for their decorative paints. Linseed, fish, tung, soybean, tall oil, and dehydrated castor oil are the most widely used in oil-based coatings. Drying oils (qv) are highly unsaturated and because of their structure are readily polymerized to form cross-linked protective films. Several mechanisms may be operating in the polymerization process. Rearrangement of double bonds into conjugation allows Diels-Alder reactions to occur to produce cross-linking. Oxidation produces free radicals that induce and promote chain-reaction polymerization. Drying may be accelerated by heat, light, or the presence of transition metals (driers) (see DRIERS AND METALLIC SOAPS). Drying oils react with a variety of chemicals to yield resins that produce harder and more durable films. Phenolic resins, alkyd resins (polyesters of polyfunctional alcohols and polybasic acids), and urethanes are the most widely used.

Triacylglycerol oils have declined since the 1980s and have been replaced by petroleum-derived products. However, as fossil fuels deplete the supply of petrochemicals, triglyceride-based oils are available as a renewable resource.

9.4. Manufacture of Fatty Acids and Derivatives. Splitting of fats to produce fatty acids and glycerol (a valuable coproduct) has been practiced since before the 1890s. In early processes, concentrated alkali reacted with fats saponification) to produce soaps followed by acidulation to produce the fatty acids. Acid-catalyzed hydrolysis, mostly with sulfuric and sulfonic acids, was also practiced. Pressurized equipment was introduced to accelerate the rate of the process, and finally continuous processes were developed to maximize completeness of the reaction (111,112). Lipolytic enzymes may be utilized to split fatty acids from oils that would be adversely affected by high temperatures and strongly acidic conditions. The high cost of enzymes and relatively slow rate of reaction have prevented wide-scale commercial use of this process. Regioselective enzymes have been used for analysis of fatty acid residues in the 2-position of triacylglycerols. Transesterification (interesterification) of fats or oils with monohydric alcohols produces alkyl esters of fatty acids and glycerol. Methyl esters from this process are widely used industrial fatty acid derivatives. Figure showed saponification and alcoholysis, which corresponds to interesterification.

9.5. Miscellaneous Uses of Fats, Oils, and Their Derivatives. Fatty-derived materials have been important in a wide variety of industrial applications for many years, although they have been supplanted in some areas with less expensive petroleum-based compounds. Fats, oils, fatty acids, and their derivatives remain in use in industrial areas where their unique structure produces a functional effect. Drying oils for protective coatings depend on oxidation of multiple double bonds. Aldehydes derived from oil oxidation react with collagen in the process of leather tanning. Fatty acids, present in low concentration in oils, allow the formation of thin films on metal parts, providing useful lubricating oils. Wax esters are useful plasticizers because they have a critical balance of alkyl chains and polar functionality. As fossil fuels become more critically managed and more costly, renewable fats and oils are likely to claim an additional share in many industrial applications. Development of biodiesel fuels (113) using fatty acid derivatives, may simultaneously solve two problems; the high cost of fossil fuels and the disposal of used frying oils.

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