Consortium for
Educational
Communication

Module
on
Fats And Oils

By

DR. OMAR BIN HAMEED
PhD Research Scholars
Department of Post Harvest
Technology (SKUAST-K).
E-mail: omargojwari@gmail.com.
Phone No.: 9796661750

Text

Chemical Composition

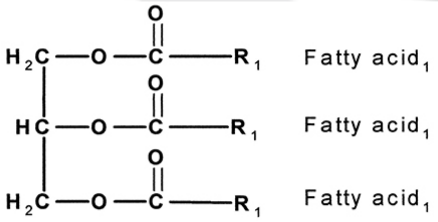
The main components of edible fats and oils are triglycerides. The minor components include mono- and diglycerides, free fatty acids, phosphatides, sterols, fat soluble vitamins, tocopherols, pigments, waxes, and fatty alcohols. The free fatty acid content of crude oil varies widely based on the source. Other than the free fatty acids, crude vegetable oils contain approximately two percent of these minor components. Animal fats contain smaller amounts.

A. The Major Component – Triglycerides

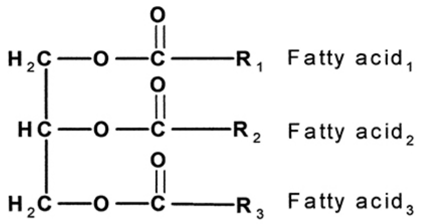
A triglyceride consists of three fatty acids attached to one glycerol molecule. If all three fatty acids are identical, it is a simple triglyceride. The more common forms, however, are the “mixed” triglycerides in which two or three kinds of fatty acids are present in the molecule. Illustrations of typical simple and mixed triglyceride molecular structures are shown below.

Figure 1

Diagrams of simple and mixed triglycerides



Simple Triglyceride



Mixed Triglyceride

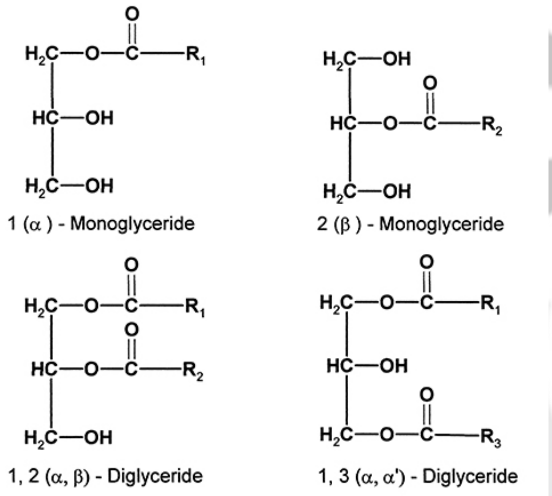
The fatty acids in a triglyceride define the properties and characteristics of the molecule.

B. The Minor Components

1. *Mono- and Diglycerides:* Mono- and diglycerides are mono- and diesters of fatty acids and glycerol. They are used frequently in foods as emulsifiers. They are prepared commercially by the reaction of glycerol and triglycerides or by the esterification of glycerol and fatty acids. Mono- and diglycerides are formed in the intestinal tract as a result of the normal digestion of triglycerides. They occur naturally in very minor amounts in both animal fats and vegetable oils. Oil composed mainly of diglycerides has also been used as a replacement for oil composed of triglycerides. Illustrations of mono- and diglyceride molecular structures are provided below:

Figure 2

Diagrams of mono- and diglycerides.



1 (α) - Monoglyceride

2 (β) - Monoglyceride

1, 2 (α, β) - Diglyceride

1, 3 (α, α') - Diglyceride

2. *Free Fatty Acids.* As the name suggests, free fatty acids are the unattached fatty acids present in a fat. Some unrefined oils may contain as much as several percent free fatty acids. The levels of free fatty acids are reduced in the refining process. Fully refined fats and oils usually have a free fatty acid content of less than 0.1%.

3. *Phosphatides.* Phosphatides, also known as phospholipids, consist of an alcohol (usually glycerol) combined with fatty acids, and a phosphate ester. The majority of the phosphatides are removed from oil during refining. Phosphatides are an important source of natural emulsifiers marketed as lecithin.

4. Sterols. Sterols are found in both animal fats and vegetable oils, but there are substantial biological biological differences. Cholesterol is the primary animal fat sterol and is found in vegetable oils in only trace amounts. Vegetable oil sterols are collectively called "phytosterols." Stigmasterol and sitosterol are the best-known vegetable oil sterols. Sitosterol has been shown to reduce both serum and LDL cholesterol when incorporated into margarines and/or salad dressings. The type and amount of vegetable oil sterols vary with the source of the oil.

5. *Tocopherols and Tocotrienols.* Tocopherols and tocotrienols are important minor constituents of most vegetable fats. They serve as antioxidants to retard rancidity and as sources of the essential nutrient vitamin E. The common types of tocopherols and tocotrienols

are alpha (α), beta (β), gamma (γ), and delta (δ). They vary in antioxidant and vitamin E activity. Among tocopherols, alpha-tocopherol has the highest vitamin E activity and the lowest antioxidant activity. Delta tocopherol has the highest antioxidant activity.

Tocopherols which occur naturally in most vegetable oils are partially removed during processing. Corn and soybean oils contain the highest levels. Tocopherols are not present in appreciable amounts in animal fats.

Tocotrienols are mainly present in palm oil, but can also be found in rice bran and wheat germ oils.

6. Pigments. Carotenoids are yellow to deep red color materials that occur naturally in fats and oils. They consist mainly of carotenes such as lycopene, and xanthophylls such as lutein. Palm oil contains the highest concentration of carotene. Chlorophyll is the green coloring matter of plants which plays an essential role in photosynthesis. Canola oil contains the highest levels of chlorophyll among common vegetable oils. At times, the naturally occurring level of chlorophyll in oils may cause the oils to have a green tinge. Gossypol is a pigment found only in cottonseed oil. The levels of most of these color bodies are reduced during the normal processing of oils to give them acceptable color, flavor, and stability.

7. Fatty Alcohols. Long chain alcohols are of little importance in most edible fats. A small amount esterified with fatty acids is present in waxes found in some vegetable oils. Larger quantities are found in some marine oils. Tocotrienols are mainly present in palm oil, and can also be found in rice bran and wheat germ oils.

Classification of fats and oils

General

Triglycerides are comprised predominantly of fatty acids present in the form of esters of glycerol. One hundred grams of fat or oil will yield approximately 95 grams of fatty acids. Both the physical and chemical characteristics of fats are influenced greatly by the kinds and proportions of the component fatty acids and the way in which these are positioned on the glycerol molecule. The predominant fatty acids are saturated and unsaturated carbon chains with an even number of carbon atoms and a single carboxyl group as illustrated in the general structural formula for a saturated fatty acid given below:

$$\underbrace{CH3\text{-}\ (CH2)_x -}_{\text{Saturated carbon chain}} \quad \underbrace{COOH}_{\text{carboxyl group}}$$

Edible oils also contain minor amounts of branched chain and cyclic acids. Also odd number straight chain acids are typically found in animal fats.

Classification of Fatty Acids

Fatty acids occurring in edible fats and oils are classified according to their degree of saturation.

*1. **Saturated Fatty Acids**:* Those containing only single carbon-to-carbon bonds are termed “saturated” and are the least reactive chemically.

The saturated fatty acids of practical interest are listed in Table I by carbon chain length and common name. The principal fat sources of the naturally occurring saturated fatty acids are included in the table.

The melting point of saturated fatty acids increases with chain length. Decanoic and longer chain fatty acids are solids at normal room temperatures.

TABLE I

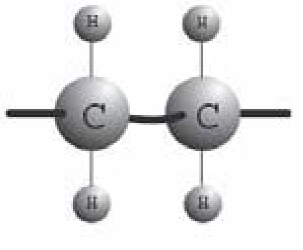
SATURATED FATTY ACIDS

Systematic name	**Common name**	**No. of carbon atoms***	**Melting Point^{0}C**	**Typical fat source**
Butanoic	Butyric	4	-7.9	Butterfat
Hexanoic	Caproic	6	-3.4	Butterfat
Octanoic	Caprylic	8	16.7	Coconut oil
Decanoic	Capric	10	31.6	Coconut oil
Dodecanoic	Lauric	12	44.2	Coconut oil
Tetradecanoic	Myristic	14	54.4	Butterfat, coconut oil
	Palmitic	16	62.9	Most fats and oils
	Margaric	17	60.0	Animal fats
Octadecanoic	Stearic	18	69.6	Most fats and oils
Eicosanoic	Arachidic	20	75.4	Peanut oil
Docosanoic	Behenic	22	80.0	Peanut oil

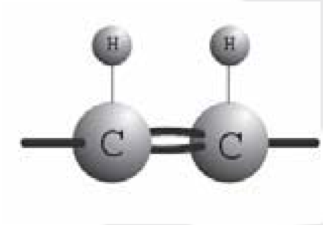
*A number of saturated odd and even chain acids are present in trace quantities in many fats and oils.

*2. **Unsaturated Fatty Acids**:* Fatty acids containing one or more carbon-to-carbon double bonds are termed “unsaturated.” Some unsaturated fatty acids in food fats and oils are shown in Table II. Oleic acid (cis-9- octadecenoic acid) is the fatty acid that occurs most frequently in nature.

Saturated and unsaturated linkages are illustrated below:



Saturated Bond



Unsaturated Bond

When the fatty acid contains one double bond it is called “monounsaturated.” If it contains more than one double bond, it is called “polyunsaturated.”

In the International Union of Pure and Applied Chemistry (IUPAC) system of nomenclature, the carbons in a fatty acid chain are numbered consecutively from the end of the chain, the carbon of the carboxyl group being considered as number 1. By convention, a specific bond in a chain is identified by the lower number of the two carbons that it joins. In oleic acid (*cis*-9-octadecenoic acid), for example, the double bond is between the ninth and tenth carbon atoms.

TABLE II

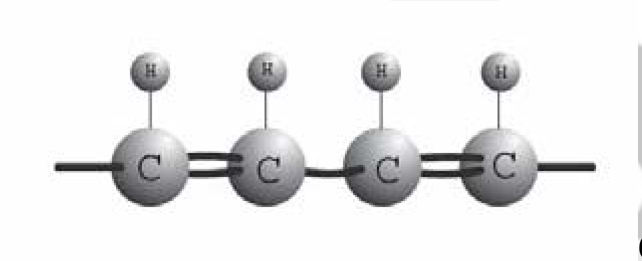
SOME UNSATURATED FATTY ACIDS IN FOOD FATS AND OILS

	Common Name	**No. of Double Bonds**	**No. of Carbon Atoms**	**Melting Point °C**	**Typical Fat Source**
	Caproleic	1	10	-	Butterfat
	Lauroleic	1	12	-	Butterfat
	Myristoleic	1	14	-4.5	Butterfat
	Palmitoleic	1	16	-	Some fish oils

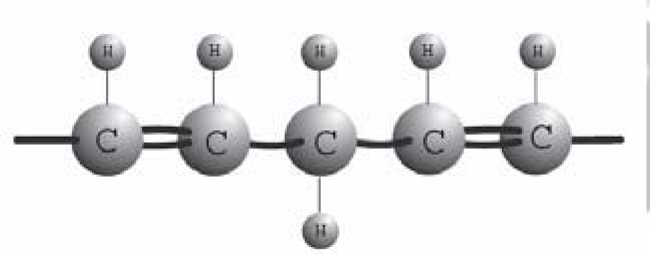
	Oleic	1	18	16.3	Most fats and oils
	Linoleic	2	18	-6.5	vegetable oils

When two fatty acids are identical except for the position of the double bond, they are referred to as positional isomers. Because of the presence of double bonds, unsaturated fatty acids are more reactive chemically than are saturated fatty acids. This reactivity increases as the number of double bonds increases.

Although double bonds normally occur in a non conjugated position, they can occur in a conjugated position (alternating with a single bond) as illustrated below:



Conjugated



Non-conjugated

With the bonds in a conjugated position, there is a further increase in certain types of chemical reactivity. For example, fats are much more subject to oxidation and polymerization when bonds are in the conjugated position.

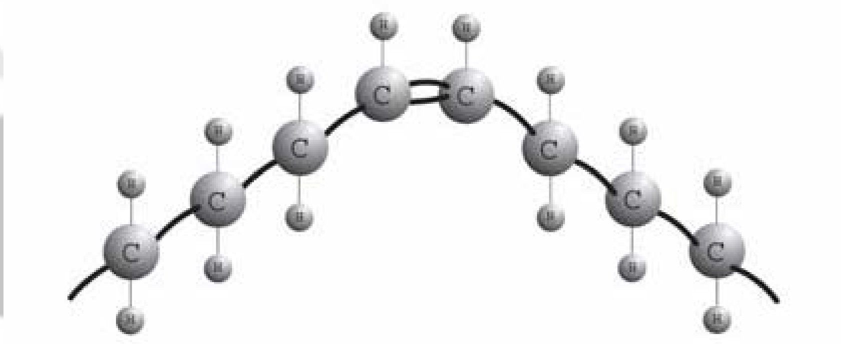
*3. **Polyunsaturated Fatty Acid**:* Of the polyunsaturated fatty acids, linoleic, linolenic, arachidonic, eicosapentaenoic, and docosahexaenoic acids containing respectively two, three, four, five, and six double bonds are of most interest.

Vegetable oils are the principal sources of linoleic and linolenic acids. Arachidonic acid is found in small amounts in lard, which also contains about 10% of linoleic acid. Fish oils contain large quantities of a variety of longer chain fatty acids having three or more double bonds including eicosapentaenoic and docosahexaenoic acids.

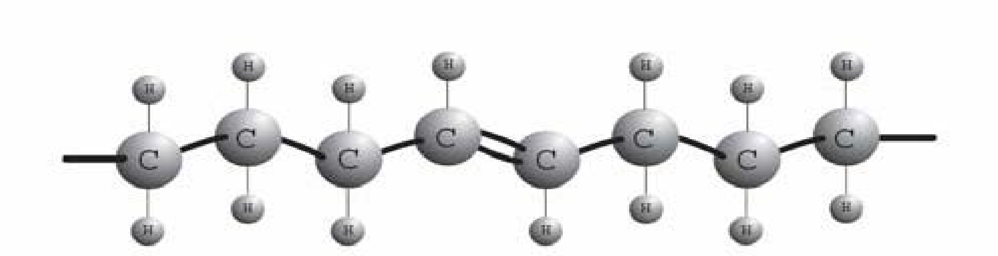
Isomerism of Unsaturated Fatty Acids

Isomers are two or more substances composed of the same elements combined in the same proportions but differing in molecular structure. The two important types of isomerism among fatty acids are (1) geometric and (2) positional.

1. *Geometric Isomerism.* Unsaturated fatty acids can exist in either the *cis* or *trans* form depending on the configuration of the hydrogen atoms attached to the carbon atoms joined by the double bonds. If the hydrogen atoms are on the same side of the carbon chain, the arrangement is called *cis*. If the hydrogen atoms are on opposite sides of the carbon chain, the arrangement is called *trans,* as shown by the following diagram



Cis



Trans

Elaidic and oleic acids are geometric isomers; in the former, the double bond is in the *trans* configuration and in the latter, in the *cis* configuration. Generally speaking, *cis* isomers are those naturally occurring in food fats and oils. *Trans* isomers occur naturally in ruminant animals such as cows, sheep and goats and also result from the partial hydrogenation of fats and oils.

2. Positional Isomerism. In this case, the location of the double bond differs among the isomers. Vaccenic acid, which is a minor acid in tallow and butterfat, is *trans*-11-octadecenoic acid and is both a positional and geometric isomer of oleic acid. The position of the double bonds affects the melting point of the fatty acid to a limited extent. Shifts in the location of double bonds in the fatty acid chains as well as *cis-trans* isomerization may occur during hydrogenation. The number of positional and geometric isomers increases with the number of double bonds. For example, with two double bonds, the following four geometric isomers are possible: *cis-cis, cis-trans, transcis,* and *trans-trans*. *Trans-trans* dienes, however, are present in only trace amounts in partially hydrogenated fats and thus are insignificant in the human food supply.

Omega fatty acids:

A class of essential fatty acids found in fish oils, especially from salmon and other cold-water fish, that acts to lower the levels of cholesterol and LDL (low-density lipoproteins) in the blood. (LDL cholesterol is the “bad” cholesterol).

The three types of omega-3 fatty acids involved in human physiology are α-linolenic acid (ALA) (found in plant oils), eicosapentaenoic acid (EPA), and docosahexaenoic acid (DHA) (both commonly found in marine oils).

PROCESSING

A. General

Food fats and oils are derived from oilseed and animal sources. Animal fats are generally heat rendered from animal tissues to separate them from protein and other naturally occurring materials. Rendering may be accomplished with either dry heat or steam. Rendering and processing of meat fats is conducted in USDA inspected plants. Vegetable oils are obtained by the extraction or the expression of the oil from the oilseed source. Historically, cold or hot expression methods were used. These methods have largely been replaced with solvent extraction or pre-press/solvent extraction methods which give a better oil yield. In this process the oil is extracted from the oilseed by hexane (a light petroleum fraction) and the hexane is then separated from the oil, recovered, and reused. Because of its high volatility, hexane does not remain in the finished oil after processing.

The fats and oils obtained directly from rendering or from the extraction of the oilseeds are termed “crude” fats and oils. Crude fats and oils contain varying but relatively small amounts of naturally occurring non-glyceride materials that are removed through a series of processing steps. For example, crude soybean oil may contain small amounts of protein, free fatty acids, and phosphatides which must be removed through subsequent processing to produce the desired shortening and oil products. Similarly, meat fats may contain some free fatty acids, water, and protein which must be removed. It should be pointed out, however, that not all of the nonglyceride materials are undesirable elements. Tocopherols, for example, perform the important function of protecting the oils from oxidation and provide vitamin E. Processing is carried out in such a way as to control retention of these substances.

B. Degumming

Crude oils having relatively high levels of phosphatides (e.g., soybean oil) may be degummed prior to refining to remove the majority of those phospholipid compounds. The process generally involves treating the crude oil with a limited amount of water to hydrate the phosphatides and make them separable by centrifugation. Soybean oil is the most common oil to be degummed; the phospholipids are often recovered and further processed to yield a variety of lecithin products.

A relatively new process in the United States is enzymatic degumming. An enzyme, phospholipase, converts phospholipids, present in crude oil, into lysophospholipids that can be removed by centrifugation. Crude oil, pre-treated with a combination of sodium hydroxide and citric acid, is mixed with water and enzymes (phospholipase) by a high shear mixer, creating a very stable emulsion. The emulsion allows the enzyme to react with the phospholipids, transforming them into water-soluble lysophospholipids. This emulsion is broken by centrifugation, separating the gums and phospholipids from the oil. This process generates a better oil yield than traditional degumming/refining. Enzymatic degumming is currently not widely commercialized .

C. Refining/Neutralization

The process of refining (sometimes referred to as “alkali refining”) generally is performed on vegetable oils to reduce the free fatty acid content and to remove other impurities such as phosphatides, proteinaceous, and mucilaginous substances. By far the most important and widespread method of refining is the treatment of the fat or oil with an alkali solution. This results in a large reduction of free fatty acids through their conversion into high specific gravity soaps. Most phosphatides and mucilaginous substances are soluble in the oil only in an anhydrous form and upon hydration with the caustic or other refining solution are readily separated. Oils low in phosphatide content (palm and coconut) may be physically refined (i.e., steam stripped) to remove free fatty acids. After alkali refining, the fat or oil is water-washed to remove residual soap.

D. Bleaching

The term “bleaching” refers to the process for removing color producing substances and for further purifying the fat or oil. Normally, bleaching is accomplished after the oil has been refined. The usual method of bleaching is by adsorption of the color producing substances on an adsorbent material. Acid-activated bleaching earth or clay, sometimes called bentonite, is the adsorbent material that has been used most extensively. This substance consists primarily of hydrated aluminum silicate. Anhydrous silica gel and activated carbon also are used as bleaching adsorbents to a limited extent.

E. Deodorization

Deodorization is a vacuum steam distillation process for the purpose of removing trace constituents that give rise to undesirable flavors, colors and odors in fats and oils. Normally this process is accomplished after refining and bleaching. The deodorization of fats and oils is simply a removal of the relatively volatile components from the fat or oil using steam. This is feasible because of the great differences in volatility between the substances that give flavors, colors and odors to fats and oils and the triglycerides. Deodorization is carried out under vacuum to facilitate the removal of the volatile substances, to avoid undue hydrolysis of the fat, and to make the most efficient use of the steam. Deodorization does not have any significant effect upon the fatty acid composition of most fats or oils. Depending upon the degree of unsaturation of the oil being deodorized, small amounts of *trans* fatty acids may be formed. In the case of vegetable oils, sufficient tocopherols remain in the finished oils after deodorization to provide stability.

F. Fractionation (Including Winterization)

Fractionation is the removal of solids by controlled crystallization and separation techniques involving the use of solvents or dry processing. Dry fractionation encompasses both winterization and pressing techniques and is the most widely practiced form of fractionation. It relies upon the differences in melting points to separate the oil fractions.

Winterization is a process whereby material is crystallized and removed from the oil by filtration to avoid clouding of the liquid fraction at cooler temperatures. The term winterization was originally applied decades ago when cottonseed oil was subjected to winter temperatures to accomplish this process. Winterization processes using temperature to control crystallization are continued today on several oils. A similar process called dewaxing is utilized to clarify oils containing trace amounts of clouding constituents.

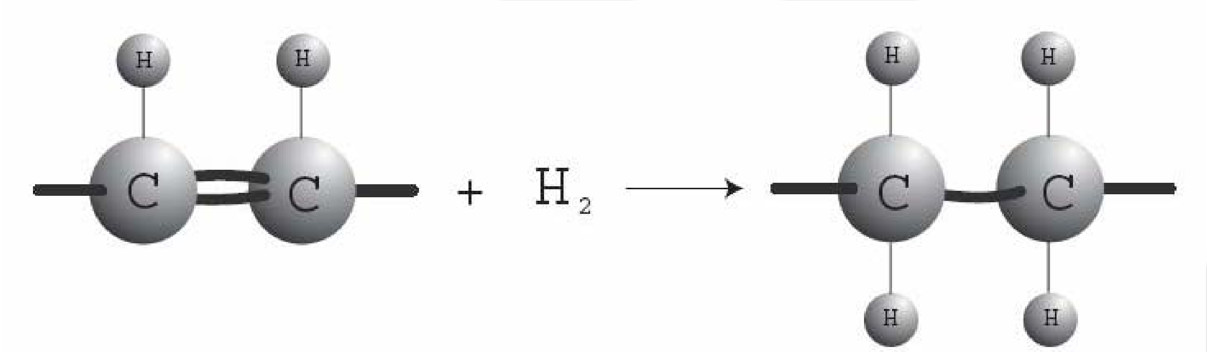
Pressing is a fractionation process sometimes used to separate liquid oils from solid fat. This process presses the liquid oil from the solid fraction by hydraulic pressure or vacuum filtration. This process is used commercially to produce hard butters and specialty fats from oils such as palm and palm kernel.

Solvent fractionation is the term used to describe a process for the crystallization of a desired fraction from a mixture of triglycerides dissolved in a suitable solvent. Fractions may be selectively crystallized at different temperatures after which the fractions are separated and the solvent removed. Solvent fractionation is practiced commercially to produce hard butters, specialty oils, and some salad oils from a wide array of edible oils.

G. Partial Hydrogenation/Hydrogenation

Hydrogenation is the process by which hydrogen is added to points of unsaturation in the fatty acids. Hydrogenation was developed as a result of the need to (1) convert liquid oils to the semi-solid form for greater utility in certain food uses and (2) increase the oxidative and thermal stability of the fat or oil. It is an important process to our food supply, because it provides the desired stability and functionality to many edible oil products.

In the process of hydrogenation, hydrogen gas reacts with oil at elevated temperature and pressure in the presence of a catalyst. The catalyst most widely used is nickel which is removed from the fat after the hydrogenation processing is completed. Under these conditions, the gaseous hydrogen reacts with the double bonds of the unsaturated fatty acids as illustrated below:



The hydrogenation process is easily controlled and can be stopped at any desired point. As hydrogenation progresses, there is generally a gradual increase in the melting point of the fat or oil. If the hydrogenation of cottonseed or soybean oil, for example, is stopped after only a small amount of hydrogenation has taken place, the oils remain liquid. These partially hydrogenated oils are typically used to produce institutional cooking oils, liquid shortenings and liquid margarines. Further hydrogenation can produce soft but solid appearing fats which still contain appreciable amounts of unsaturated fatty acids and are used in solid shortenings and margarines. When oils are more fully hydrogenated, many of the carbon to carbon double bonds are converted to single bonds increasing the level of saturation. If an oil is hydrogenated completely, the carbon to carbon double bonds are eliminated. Therefore, fully hydrogenated fats contain no *trans* fatty acids. The resulting product is a hard brittle solid at room temperature.

The hydrogenation conditions can be varied by the manufacturer to meet certain physical and chemical characteristics desired in the finished product. This is achieved through selection of the proper temperature, pressure, time, catalyst, and starting oils. Both positional and geometric (*trans*) isomers are formed to some extent during hydrogenation, the amounts depending on the conditions employed.

H. Interesterification

Another process used by oil processors is interesterification which causes a redistribution of the fatty acids on the glycerol fragment of the molecule. This rearrangement process does not change the composition of the fatty acids from the starting materials. Interesterification may be accomplished by chemical or enzymatic processes. Chemical interesterification is a process by which fatty acids are randomly distributed across the glycerol backbone of the triglyceride. This process is carried out by blending the desired oils, drying them, and adding a catalyst such as sodium methoxide. When the reaction is complete, the catalyst is neutralized and the rearranged product is washed, bleached, and deodorized to give a final oil product with different characteristics than the original oil blends.

The second process is enzymatic interesterification. This process rearranges the fatty acids (can be position specific) on the glycerol backbone of the triglyceride through the use of an enzyme. Higher temperatures will result in inactivation of the enzyme. After interesterification, the oil is deodorized to make finished oil products.

The predominant commercial application for interesterification in the US is the production of specialty fats. These processes permit further tailoring of triglyceride properties to achieve the required melting curves.

I. Esterification

Fatty acids are usually present in nature in the form of esters and are consumed as such. Triglycerides, the predominant constituents of fats and oils, are examples of esters. When consumed and digested, fats are hydrolyzed initially to diglycerides and monoglycerides which are also esters. Carried to completion, these esters are hydrolyzed to glycerol and fatty acids. In the reverse process, esterification, an alcohol such as glycerol is reacted with an acid such as a fatty acid to form an ester such as mono-, di-, and triglycerides. In an alternative esterification process, called alcoholysis, an alcohol such as glycerol is reacted with fat or oil to produce esters such as monoand diglycerides. Using the foregoing esterification processes, edible acids, fats, and oils can be reacted with edible alcohols to produce useful food ingredients that include many of the emulsifiers.

J. Additives and Processing Aids

Manufacturers may add low levels of approved food additives to fats and oils to protect their quality in processing, storage, handling, and shipping of finished products. This insures quality maintenance from time of production to time of consumption. When their addition provides a technical effect in the end-use product, the material added is considered a direct food additive. Such usage must comply with FDA regulations governing levels, mode of addition, and product labeling. Typical examples of industry practice are listed in Table III.

When additives are included to achieve a technical effect during processing, shipping, or storage and followed by removal or reduction to an insignificant level, the material added is considered to be a processing aid. Typical examples of processing aids and provided effects are listed in Table IV. Use of processing aids also must comply with federal regulations which specify good manufacturing practices and acceptable residual levels.

TABLE III

SOME DIRECT FOOD ADDITIVES USED IN FATS AND OILS

Additive	*Effect Provided*
Tocopherols Butylated hydroxyanisole (BHA) Butylated hydroxytoluene (BHT) Tertiary butylhydroquinone (TBHQ) Propyl Gallate (PG)	Antioxidant, retards oxidative rancidity
Carotene (pro-vitamin A)	Color additive, enhances color of finished foods
Dimethylpolysiloxane (Methyl Silicone)	Inhibits oxidation tendency and foaming of fats and oils during frying

Diacetyl	Provides buttery odor and flavor to fats and oils
Lecithin	Water scavenger to prevent lipolytic rancidity,emulsifier
Citric acid Phosphoric acid	Metal chelating agents, inhibit metal-catalyzed oxidative breakdown
Polyglycerol esters	Crystallization modifier and inhibitor

TABLE IV

SOME PROCESSING AIDS USED IN MANUFACTURING EDIBLE FATS AND OILS

Aid	Effect	Mode of Removal
Sodium hydroxide	Refining aid	Water wash, neutralization
Carbon/clay (diatomaceous earth)	Bleaching aid	Filtration
Nickel	Hydrogenation catalyst	Filtration
Sodium methoxide	Chemical interesterification catalyst	Water wash, acid neutralization
Phosphoric acid Citric acid	Refining aid, metal chelators	Neutralization with base, bleaching, water washing
Nitrogen	Inert gas to prevent oxidation.	Diffusion, vaporization
Silica hydrogel	Adsorbent	Filtration

K. Emulsifiers

Many foods are processed and/or consumed as emulsions, which are dispersions of immiscible liquids such as water and oil, e.g., milk, mayonnaise, ice cream, icings, and sauces. Emulsifiers, either present naturally in one or more of the ingredients or added separately, provide emulsion stability. Lack of stability results in separation of the oil and water phases. Some emulsifiers also provide valuable functional attributes in addition to emulsification. These include aeration, starch and protein complexing, hydration, crystal modification, solubilization, and dispersion. Typical examples of emulsifiers and the characteristics they impart to food are listed in Table V.

TABLE V

EMULSIFIERS AND THEIR FUNCTIONAL CHARACTERISTICS IN PROCESSED FOODS

Emulsifier	***Characteristic***	***Processed Food***
Mono-diglycerides	Emulsification of water in oil Anti-staling or softening Prevention of oil separation	Margarine Bread and rolls Peanut butter
Lecithin	Viscosity control and wetting Anti-spattering and anti-sticking	Chocolate Margarine
Lactylated mono-diglycerides	Aeration Gloss enhancement	Batters (cake) Confectionery coating
Polyglycerol esters	Crystallization promoter Aeration Emulsification	Sugar syrup Icings and cake batters
Sucrose fatty acid esters	Emulsification	Bakery products

REACTIONS OF FATS AND OILS

A. Hydrolysis of Fats

Like other esters, glycerides can be hydrolyzed readily. Partial hydrolysis of triglycerides will yield mono- and diglycerides and free fatty acids. When hydrolysis is carried to completion with water in the presence of an acid catalyst, the mono-, di-, and triglycerides will hydrolyze to yield glycerol and free fatty acids. With aqueous sodium hydroxide, glycerol and the sodium salts of the component fatty acids (soaps) are obtained. In the digestive tracts of humans and animals and in bacteria, fats are hydrolyzed by enzymes (lipases). Lipolytic enzymes are present in some edible oil sources (i.e., palm fruit, coconut). Any residues of these lipolytic enzymes (present in some crude fats and oils) are deactivated by the elevated temperatures normally used in oil processing.

B. Oxidation of Fats

Autoxidation: Of particular interest in the food arena is the process of oxidation induced by air at room temperature referred to as “autoxidation”. Ordinarily, this is a slow process which occurs only to a limited degree. In autoxidation, oxygen reacts with unsaturated fatty acids. Initially, peroxides are formed which may break down into secondary oxidation products (hydrocarbons, ketones, aldehydes, and smaller amounts of epoxides and alcohols). Metals, such as copper or iron, present at low levels in fats and oils can also promote autoxidation. Fats and oils are normally treated with chelating agents such as citric acid to complex these trace metals (thus inactivating their prooxidant effect).

The result of the autoxidation of fats and oils is the development of objectionable flavors and odors characteristic of the condition known as “oxidative rancidity”. Some fats resist this change to a remarkable extent while others are more susceptible depending on the degree of unsaturation, the presence of antioxidants, and other factors. The presence of light, for example, increases the rate of oxidation. It is common practice in the industry to protect fats and oils from oxidation to preserve their acceptable flavor and to maximize shelf life.

When rancidity has progressed significantly, it becomes readily apparent from the flavor and odor of the oil. Expert tasters are able to detect the development of rancidity in its early stages. The peroxide value determination, if used judiciously, is oftentimes helpful in measuring the degree to which oxidative rancidity in the fat has progressed.

It has been found that oxidatively abused fats can complicate nutritional and biochemical studies because they can affect food consumption under *adlibitum* feeding conditions and also reduce the vitamin content of the food. If the diet has become unpalatable due to excessive oxidation of the fat component and is not accepted by the animal, a lack of growth by the animal could be due to its unwillingness to consume the diet. Thus, the experimental results might be attributed unwittingly to the type of fat or other nutrient being studied rather than to the condition of the ration. Knowing the oxidative condition of unsaturated fats is extremely important in biochemical and nutritional studies with animals.

C. Polymerization of Fats

All commonly used fats and particularly those high in polyunsaturated fatty acids tend to form larger molecules (known broadly as polymers) when heated under extreme conditions of temperature and time. Under normal processing and cooking conditions, polymers are formed in insignificant quantities. Although the polymerization process is not completely understood, it is believed that polymers in fats and oils arise by formation of either carbon-to-carbon bonds or oxygen bridges between molecules. When an appreciable amount of polymer is present, there is a marked increase in viscosity. Animal studies have shown that polymers present in a fat or oil will be poorly absorbed from the intestinal tract and as such will be excreted in the feces.

D. Reactions during Heating and Cooking

Glycerides are subject to chemical reactions (oxidation, hydrolysis, and polymerization) which can occur particularly during deep fat frying. The extent of these reactions, which may be reflected by a decrease in iodine value of the fat and an increase in free fatty acids, depends on the frying conditions (principally the temperature, aeration, and duration). The composition of a frying fat also may be affected by the kind of food being fried. For example, when frying foods such as chicken, some fat from the food will be rendered and blend with the frying fat while some of the frying fat will be absorbed by the food. In this manner the fatty acid composition of the frying fat will change as frying progresses. Since absorption of fat by the fried food may be extensive, it is often necessary to replenish the fryer with fresh fat. Obviously, this replacement with fresh fat tends to dilute overall compositional changes of the fat that would have taken place during prolonged frying. Frying conditions do not, however, saturate the unsaturated fatty acids, although the ratio of saturated to unsaturated fatty acids will change due to degradation and polymerization of the unsaturated fatty acids. The frying operation also results in an increase in the level of “polar compounds” (mono- and diglycerides, free fatty acids, and other polar transformation products) formed frying/heating of foodstuffs in the oil.

It is the usual practice to discard frying fat when (1) prolonged frying causes excessive foaming of the hot oil, (2) the fat tends to smoke excessively, usually from prolonged frying with low fat turnover, or (3) an undesirable flavor or dark color develops. Any or all of these qualities associated with the fat can decrease the quality of the fried food.

The “smoke”, “flash”, and “fire points” of a fatty material are standard measures of its thermal stability when heated in contact with air. The “smoke point” is the temperature at which smoke is first detected in a laboratory apparatus protected from drafts and provided with special illumination. The temperature at which the fat smokes freely is usually somewhat higher. The “flash point” is the temperature at which the volatile products are evolved at such a rate that they are capable of being ignited but not capable of supporting combustion. The “fire point” is the temperature at which the volatile products will support continued combustion. For typical non-lauric oils with a free fatty acid content of about 0.05%, the “smoke”, “flash”, and “fire” points are around 420°, 620°, and 670°, respectively.

The degree of unsaturation of oil has little, if any, effect on its smoke, flash, or fire points. Oils containing fatty acids of low molecular weight such as coconut oil, however, have lower smoke, flash, and fire points than other animal or vegetable fats of comparable free fatty acid content. Oils subjected to extended use will have increased free fatty acid contents resulting in a lowering of the smoke, flash, and fire points. Accordingly, used oil freshened with new oil will show increased smoke, flash, and fire points.

It is important to note that all oils will burn if overheated. This is why most household fat and oil products for cooking carry a warning statement on their labels about potential fire hazards. Accordingly, careful attention must be given to all frying operations. *When heating fat, do not leave the pan unattended*. The continuous generation of smoke from a frying pan or deep fryer is a good indication that the fat is being overheated and could ignite if high heating continues. *If smoke is observed during a frying operation, the heat should be reduced.* If, however, the contents of the frying pan ignite, extinguish the fire by covering the pan immediately with a lid or by spraying it only with an appropriate fire extinguisher. Do not attempt to remove a burning pan of oil from the stove. Allow the covered frying container to cool. Under no circumstances should burning fat be dumped into a kitchen sink or sprayed with water.

Importance of Fats and Oils

Fats and oils are recognized as essential nutrients in both human and animal diets. Nutritionally, they are concentrated sources of energy (9 cal/gram); provide essential fatty acids which are the building blocks for the hormones needed to regulate bodily systems; and are a carrier for the oil soluble vitamins A, D, E, and K. They also enhance the foods we eat by providing texture and mouth feel, imparting flavor, and contributing to the feeling of satiety after eating. Fats and oils are also important functionally in the preparation of many food products. They act as tenderizing agents, facilitate aeration, carry flavours and colours, and provide a heating medium for food preparation. Fats and oils are present naturally in many foods, such as meats, dairy products, poultry, fish, and nuts, and in prepared foods, such as baked goods, margarines, and dressings and sauces.