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ONLINE COURSE WARE

SUBJECT NAME: Food Process Technology IV (Fats& Oils)

SUBJECT CODE: FT 602

CREDIT: 4

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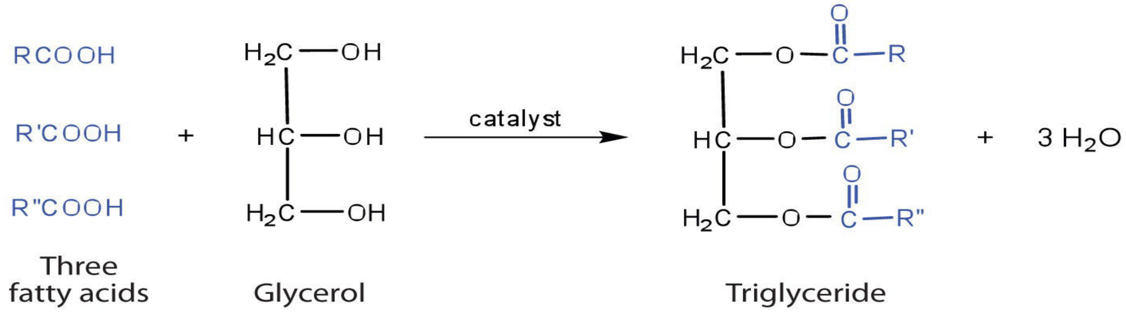
MODULE:I

Lecture 1

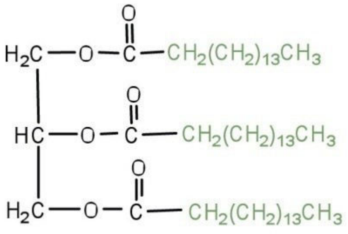
Fats and oils are the most abundant lipids in nature. They provide energy for living organisms, insulate body organs, and transport fat-soluble vitamins through the blood.

Structures of Fats and Oils

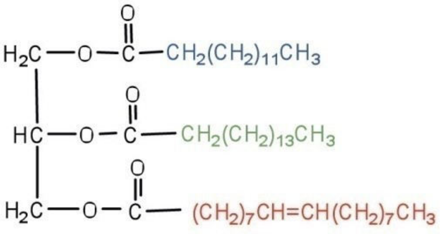
Fats and oils are called triglycerides (or *triacylcylgerols*) because they are esters composed of three fatty acid units joined to *glycerol*, a trihydroxy alcohol:



If all three OH groups on the glycerol molecule are esterified with the same fatty acid, the resulting ester is called a *simple triglyceride*. Although simple triglycerides have been synthesized in the laboratory, they rarely occur in nature. Instead, a typical triglyceride obtained from naturally occurring fats and oils contains two or three different fatty acid components and is thus termed a *mixed triglyceride*.



Tristearin
a simple triglyceride



a mixed triglyceride

A triglyceride is called a fat if it is a solid at 25°C; it is called an oil if it is a liquid at that temperature. These differences in melting points reflect differences in the degree of unsaturation and number of carbon atoms in the constituent fatty acids. Triglycerides obtained from animal sources are usually solids, while those of plant origin are generally oils. Therefore, we commonly speak of animal fats and vegetable oils.

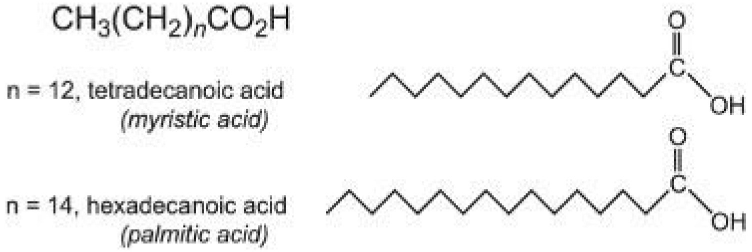
	Lauric	Myristic	Palmitic	Stearic	Oleic	Linoleic	Linolenic
Fats							
butter (cow)	3	11	27	12	29	2	1
tallow		3	24	19	43	3	1
lard		2	26	14	44	10	
Oils							
canola oil			4	2	62	22	10
coconut oil[†]	47	18	9	3	6	2	
corn oil			11	2	28	58	1
olive oil			13	3	71	10	1
peanut oil			11	2	48	32	
soybean oil			11	4	24	54	7

Terms such as *saturated fat* or *unsaturated oil* are often used to describe the fats or oils obtained from foods. Saturated fats contain a high proportion of saturated fatty acids, while unsaturated oils contain a high proportion of unsaturated fatty acids. The high consumption of saturated fats is a factor, along with the high consumption of cholesterol, in increased risks of heart disease.

Oils and fats have similar compositions, but oils are liquid at room temperature and fats are partially solid. They both contain esters derived from propane-1,2,3-triol (glycerol) and carboxylic (often called fatty) acids, known as triglycerides.

In the body, fats provide a concentrated energy source and are broken down and modified to supply the carboxylic (fatty) acids necessary for health. Fats also act as carriers for the vitamins A, D, E and K which are soluble in fats and not in water, and vitamins B and C which are water soluble.

The fatty acids found in natural fats are generally straight chain compounds and can be saturated or unsaturated. For example, saturated acids found naturally include:



However, the most commonly occurring of all fatty acids are unsaturated, for example:

$CH_3(CH_2)_4\text{-}(CH{=}CHCH_2)_2\text{-}(CH_2)_6CO_2H$

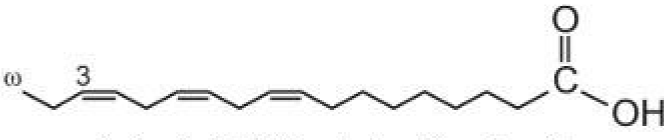
octadeca-9,12-dienoic acid *(linoleic acid)*

$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H$

octadeca-9-enoic acid *(oleic acid)*

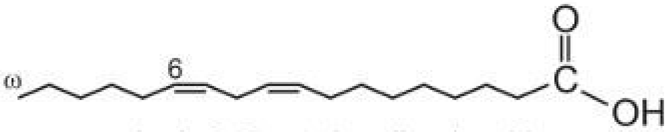
Some of the fatty acids needed by the body cannot be produced by the body's metabolism and must come directly from the diet. These are known as essential fatty acids. The most well known are omega-3 and omega-6 acids, so named by the position of the first carbon-carbon double bond, counting from the terminal methyl group (the omega (co) carbon atom).
Examples are:

An example of a polyunsaturated omega-3 fatty acid. The first double bond is located at the third carbon atom from the ω end.



cis,cis,cis-9,12,15-octadecatrienoic acid
(linolenic acid)

An example of a polyunsaturated omega-6 fatty acid.



cis,cis-9,12-octadecadienoic acid
(linoleic acid)

Chemical processes are used to convert mixtures of naturally occurring oils and fats into margarine and other spreads that are used as substitutes for butter. The major vegetable oils used are palm, sunflower, rapeseed and soya bean oils.

Lecture 2

Chemical composition of fats

Although natural fats consist primarily of glycerides, they contain many other lipids in minor quantities. Corn oil, for example, may contain glycerides plus phospholipids, glycolipids, phosphoinositides (phospholipids containing inositol), many isomers of sitosterol and stigmasterol (plant steroids), several tocopherols (vitamin E), vitamin A, waxes, unsaturated hydrocarbons such as squalene, and dozens of carotenoids and chlorophyll compounds, as well as many products of decomposition, hydrolysis, oxidation, and polymerization of any of the natural constituents.

Fatty acids contribute from 94 to 96 percent of the total weight of various fats and oils. Because of their preponderant weight in the glyceride molecules and also because they comprise the reactive portion of the molecules, the fatty acids influence greatly both the physical and chemical character of glycerides. Fats vary widely in complexity; some contain only a few component acids, and at the other extreme more than 100 different fatty acids have been identified in butterfat, although many are present in only trace quantities. Most of the oils and fats are based on about a dozen fatty acids (*see* table). In considering the composition of a glyceride it is particularly important to distinguish between the saturated acids (acids containing only single bonds between carbon atoms, such as palmitic or stearic), with relatively high melting temperatures, and the unsaturated acids (acids with one or more pairs of carbon atoms joined by double bonds, such as oleic or linoleic), which are low melting and chemically much more reactive.

Common fatty acids

common name	**systematic name**	**formula**	**carbon atoms**	**double bonds**	**melting point (°C)**
caprylic	octanoic	$C_7H_{15}COOH$	8	0	16.5
capric	decanoic	$C_9H_{19}COOH$	10	0	31.5
lauric	dodecanoic	$C_{11}H_{23}COOH$	12	0	44
myristic	tetradecanoic	$C_{13}H_{27}COOH$	14	0	58
palmitic	hexadecanoic	$C_{15}H_{31}COOH$	16	0	63
stearic	octadecanoic	$C_{17}H_{35}COOH$	18	0	72
arachidic	eicosanoic	$C_{19}H_{39}COOH$	20	0	77
oleic	cis-9-octadecenoic	$C_{17}H_{33}COOH$	18	1	13.4
linoleic	cis-9, cis-12-octadecadienoic	$C_{17}H_{31}COOH$	18	2	−5
linolenic	cis-9, cis-12, cis-15-octadecatrienoic	$C_{17}H_{29}COOH$	18	3	−11.3
eleostearic	cis-9, cis-11, cis-13-octadecatrienoic	$C_{17}H_{29}COOH$	18	3	49
ricinoleic	12-hydroxy-cis-9-octadecenoic	$C_{17}H_{33}COOH$	18	1 + OH	16
arachidonic	5, 8, 11, 14-eicosatetraenoic	$C_{19}H_{31}COOH$	20	4	−49.5
erucic	cis-13-docosenoic	$C_{21}H_{41}COOH$	22	1	33.5

In the series of saturated acids, the melting point increases progressively from below room temperature for the acids of lower molecular weight to high melting solids for the longer chain acids. Unsaturated acids may contain up to six double bonds, and as unsaturation increases the melting points become lower. Glycerides based predominantly on unsaturated acids, such as soybean oil, are liquids; and glycerides containing a high proportion of saturated acids, such as beeftallow, are solids. The carbon atoms in fatty acids are arranged in straight chains, and the first site of unsaturation (double bond) in most of the unsaturated acids appears between the ninth and tenth carbon atoms, starting the counting from the terminal carboxyl group (*see* table). The specificity of location of unsaturation in fatty acids obtainable from both plant and animal sources suggests that all are formed by a common enzymatic dehydrogenation mechanism.

Lecture 3

Saturation and unsaturation in fatty acids

lauric acid	$CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}COOH$	a saturated fatty acid with 12 carbon atoms
oleic acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	an unsaturated fatty acid with one double bond and 18 carbon atoms
linoleic acid	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$	an unsaturated fatty acid with two double bonds and 18 carbon atoms
linolenic acid	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$	an unsaturated fatty acid with three double bonds and 18 carbon atoms
arachidonic acid	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_3COOH$	an unsaturated fatty acid with four double bonds and 20 carbon atoms

Since the glycerides, which make up 90 to 99 percent of most individual fats or oils of commerce, are esters formed by three fatty-acid molecules combining with one molecule of glycerol, they may differ not only in the fatty acids that they contain but also in the arrangement of the fatty-acid radicals on the glycerol portion. Simple triglycerides are those in which each molecule of glycerol is combined with three molecules of one acid—e.g., tripalmitin, $C_3H_5(OCOC_{15}H_{31})_3$, the glycerylester of palmitic acid, $C_{15}H_{31}COOH$. Only a few of the glycerides occurring in nature are of the simple type; most are mixed triglycerides (i.e., one molecule of glycerol is combined with two or three different fatty acids). Thus stearodipalmitin, $C_3H_5(OCOC_{15}H_{31})_2(OCOC_{17}H_{35})$, contains two palmitic acid radicals and one stearic acid radical. Similarly, oleopalmitostearin, $C_3H_5(OCOC_{15}H_{31})(OCOC_{17}H_{33})(OCOC_{17}H_{35})$, contains one radical each of oleic, palmitic, and stearic acids. Each mixed triglyceride containing three different acid radicals may exist in three different isomeric forms, because any of the three can be linked with the centre carbon of the glycerol molecule. A mixed triglyceride containing two radicals of the same acid and one radical of another acid has only two isomeric forms.

Monoglycerides and diglycerides are partial esters of glycerol and have one or two fatty-acid radicals, respectively. They are seldom found in natural fats except as the products of partial hydrolysis of triglycerides. They are easily prepared synthetically, however, and have important applications mainly because of their ability to aid in the formation and stabilization of emulsions. As constituents of shortening in baked products they increase product volumes, improve tenderness, and retard staling. They also have technical importance as intermediates in the manufacture of coatings and resins.

Physical and chemical properties

Fats (and oils) may be divided into animal and vegetable fats according to source. Further, they may be classified according to their degree of unsaturation as measured by their ability to absorb iodine at the double bonds. This degree of unsaturation determines to a large extent the ultimate use of the fat.

Liquid fats (i.e., vegetable and marine oils) have the highest degree of unsaturation, while solid fats (vegetable and animal fats) are highly saturated. Solid vegetable fats melting between 20 and 35 °C (68 and 95 °F) are found mainly in the kernels and seeds of tropical fruits. They have relatively low iodine values and consist of glycerides containing high percentages of such saturated acids as lauric, myristic, and palmitic. Fats from fruits of many members of the palm family, notably coconut and babassu oils, contain large amounts of combined lauric acid. Most animal fats are solid at ordinary temperatures; milk fats are usually characterized by the presence of short-chain carboxylic acids (butyric, caproic, and caprylic); and marine oils contain a large number of very long chain highly unsaturated acids containing up to six double bonds and up to 24 or even 26 carbon atoms.

Fats are practically insoluble in water and, with the exception of castor oil, are insoluble in cold alcohol and only sparingly soluble in hot alcohol. They are soluble in ether, carbon disulfide, chloroform, carbon tetrachloride, petroleum benzin, and benzene. Fats have no distinct melting points or solidifying points because they are such complex mixtures of glycerides, each of which has a different melting point. Glycerides, further, have several polymorphic forms with different melting or transition points.

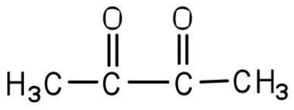
Fats can be heated to between 200 and 250 °C (392 and 482 °F) without undergoing significant changes provided contact with air or oxygen is avoided. Above 300 °C (572 °F), fats may decompose, with the formation of acrolein (the decomposition product of glycerol), which imparts the characteristic pungent odour of burning fat. Hydrocarbons also may be formed at high temperatures.

Fats are hydrolyzed readily. This property is used extensively in the manufacture of soaps and in the preparation of fatty acids for industrial applications. Fats are hydrolyzed by treatment with water alone under high pressure (corresponding to a temperature of about 220 °C [428 °F]) or with water at lower pressures in the presence of caustic alkalies, alkaline-earth metal hydroxides, or basic metallic oxides that act as catalysts. Free fatty acids and glycerol are formed. If sufficient alkali is present to combine with the fatty acids, the corresponding salts (known popularly as soaps) of these acids are formed, such as the sodium salts (hard soap) or the potassium salts (soft soaps).

Lecture 4

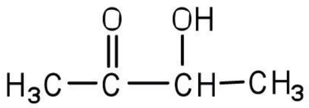
Physical and Chemical Properties of Fats and Oil

Contrary to what you might expect, *pure* fats and oils are colorless, odorless, and tasteless. The characteristic colors, odors, and flavors that we associate with some of them are imparted by foreign substances that are lipid soluble and have been absorbed by these lipids. For example, the yellow color of butter is due to the presence of the pigment carotene; the taste of butter comes from two compounds—diacetyl and 3-hydroxy-2-butanone—produced by bacteria in the ripening cream from which the butter is made.



$H_3C-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-CH_3$

Diacetyl



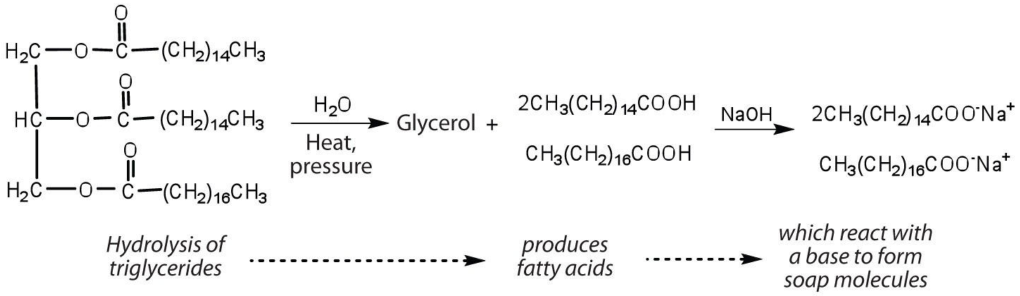
$H_3C-\overset{\overset{O}{\|}}{C}-\overset{\overset{OH}{|}}{CH}-CH_3$

3-hydroxy-2-butanone

Fats and oils are lighter than water, having densities of about 0.8 g/cm^3. They are poor conductors of heat and electricity and therefore serve as excellent insulators for the body, slowing the loss of heat through the skin.

Chemical Reactions of Fats and Oils

Fats and oils can participate in a variety of chemical reactions—for example, because triglycerides are esters, they can be hydrolyzed in the presence of an acid, a base, or specific enzymes known as lipases. The hydrolysis of fats and oils in the presence of a base is used to make soap and is called saponification. Today most soaps are prepared through the hydrolysis of triglycerides (often from tallow, coconut oil, or both) using water under high pressure and temperature [700 lb/in^2 (~50 atm or 5,000 kPa) and 200°C]. Sodium carbonate or sodium hydroxide is then used to convert the fatty acids to their sodium salts (soap molecules):



Lecture 5

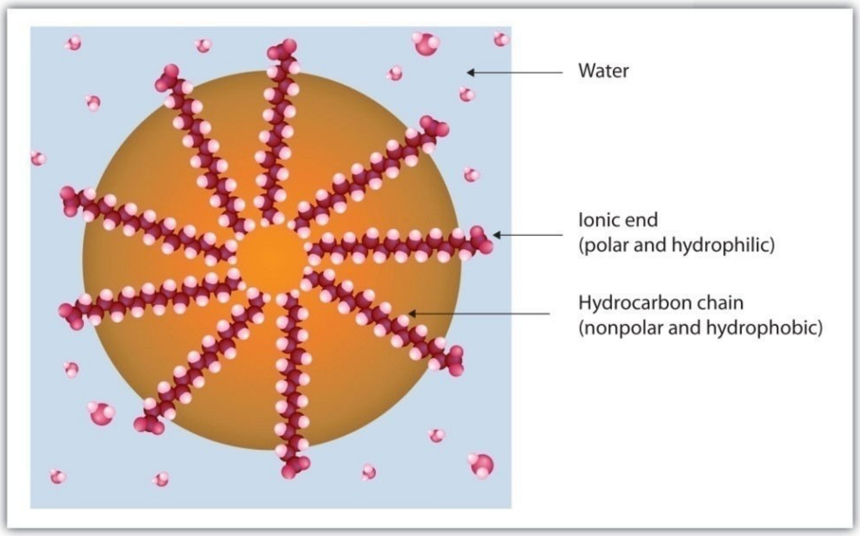
Physical and Chemical Properties of Fats and Oil

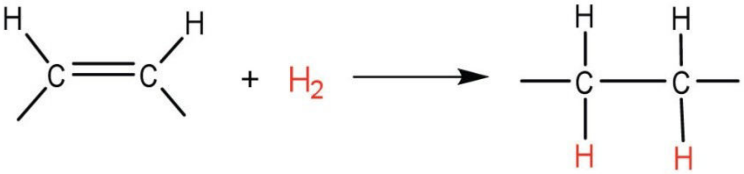
Looking Closer: Soaps

Ordinary soap is a mixture of the sodium salts of various fatty acids, produced in one of the oldest organic syntheses practiced by humans (second only to the fermentation of sugars to produce ethyl alcohol). Both the Phoenicians (600 BCE) and the Romans made soap from animal fat and wood ash. Even so, the widespread production of soap did not begin until the 1700s. Soap was traditionally made by treating molten lard or tallow with a slight excess of alkali in large open vats. The mixture was heated, and steam was bubbled through it. After saponification was completed, the soap was precipitated from the mixture by the addition of sodium chloride (NaCl), removed by filtration, and washed several times with water. It was then dissolved in water and reprecipitated by the addition of more NaCl. The glycerol produced in the reaction was also recovered from the aqueous wash solutions.

Pumice or sand is added to produce scouring soap, while ingredients such as perfumes or dyes are added to produce fragrant, colored soaps. Blowing air through molten soap produces a floating soap. Soft soaps, made with potassium salts, are more expensive but produce a finer lather and are more soluble. They are used in liquid soaps, shampoos, and shaving creams.

Dirt and grime usually adhere to skin, clothing, and other surfaces by combining with body oils, cooking fats, lubricating greases, and similar substances that act like glues. Because these substances are not miscible in water, washing with water alone does little to remove them. Soap removes them, however, because soap molecules have a dual nature. One end, called the *head*, carries an ionic charge (a carboxylate anion) and therefore dissolves in water; the other end, the *tail*, has a hydrocarbon structure and dissolves in oils. The hydrocarbon tails dissolve in the soil; the ionic heads remain in the aqueous phase, and the soap breaks the oil into tiny soap-enclosed droplets called *micelles*, which disperse throughout the solution. (For more information about cell structure, see Section 17.3 "Membranes and Membrane Lipids".) The droplets repel each other because of their charged surfaces and do not coalesce. With the oil no longer “gluing” the dirt to the soiled surface (skin, cloth, dish), the soap-enclosed dirt can easily be rinsed away.





In commercial processes, the number of double bonds that are hydrogenated is carefully controlled to produce fats with the desired consistency (soft and pliable). Inexpensive and abundant vegetable oils (canola, corn, soybean) are thus transformed into margarine and cooking fats. In the preparation of margarine, for example, partially hydrogenated oils are mixed with water, salt, and nonfat dry milk, along with flavoring agents, coloring agents, and vitamins A and D, which are added to approximate the look, taste, and nutrition of butter. (Preservatives and antioxidants are also added.) In most commercial peanut butter, the peanut oil has been partially hydrogenated to prevent it from separating out. Consumers could decrease the amount of saturated fat in their diet by using the original unprocessed oils on their foods, but most people would rather spread margarine on their toast than pour oil on it.

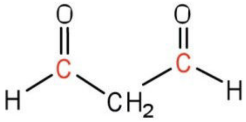
Many people have switched from butter to margarine or vegetable shortening because of concerns that saturated animal fats can raise blood cholesterol levels and result in clogged arteries. However, during the hydrogenation of vegetable oils, an isomerization reaction occurs that produces the *trans* fatty acids mentioned in the opening essay. However, studies have shown that *trans* fatty acids also raise cholesterol levels and increase the incidence of heart disease. *Trans* fatty acids do not have the bend in their structures, which occurs in *cis* fatty acids and thus pack closely together in the same way that the saturated fatty acids do. Consumers are now being advised to use polyunsaturated oils and soft or liquid margarine and reduce their total fat consumption to less than 30% of their total calorie intake each day.

Fats and oils that are in contact with moist air at room temperature eventually undergo oxidation and hydrolysis reactions that cause them to turn rancid, acquiring a characteristic disagreeable odor. One cause of the odor is the release of volatile fatty acids by hydrolysis of the ester bonds. Butter, for example, releases foul-smelling butyric, caprylic, and capric acids. Microorganisms present in the air furnish lipases that catalyze this process. Hydrolytic rancidity can easily be prevented by covering the fat or oil and keeping it in a refrigerator.

Another cause of volatile, odorous compounds is the oxidation of the unsaturated fatty acid components, particularly the readily oxidized structural unit

$$\sim CH{=}CH{-}CH_2{-}CH{=}CH\sim$$

in polyunsaturated fatty acids, such as linoleic and linolenic acids. One particularly offensive product, formed by the oxidative cleavage of both double bonds in this unit, is a compound called *malonaldehyde*.



Malonaldehyde

Rancidity is a major concern of the food industry, which is why food chemists are always seeking new and better antioxidants, substances added in very small amounts (0.001%–0.01%) to prevent oxidation and thus suppress rancidity. Antioxidants are compounds whose affinity for oxygen is greater than that of the lipids in the food; thus they function by preferentially depleting the supply of oxygen absorbed into the product. Because vitamin E has antioxidant properties, it helps reduce damage to lipids in the body, particularly to unsaturated fatty acids found in cell membrane lipids

Lecture 6

General methods of extraction

The raw materials for the fat and oil industry are animal by-products from the slaughter of cattle, hogs, and sheep; fatty fish and marine mammals; a few fleshy fruits (palm and olive); and various oilseeds. Most oilseeds are grown specifically for processing to oils and protein meals, but several important vegetable oils are obtained from by-product raw materials. Cottonseed is a by-product of cotton grown for fibre, and corn oil is obtained from the corn germ that accumulates from the corn-milling industry, whose primary products are corn grits, starch, and syrup.

Fats may be recovered from oil-bearing tissues by three general methods, with varying degrees of mechanical simplicity: (1) rendering, (2) pressing with mechanical presses, and (3) extracting with volatile solvents.

Rendering

Fruits and seeds

The crudest method of rendering oil from oleaginous fruits, still practiced in some countries, consists of heaping them in piles, exposing them to the sun, and collecting the oil that exudes. In a somewhat improved form, this process is used in the preparation of palm oil; the fresh palm fruits are boiled in water, and the oil is skimmed from the surface. Such processes can be used only with seeds or fruits (such as olive and palm) that contain large quantities of easily released fatty matter.

Animal fats

The rendering process is applied on a large scale to the production of animal fats such as tallow, lard, bone fat, and whale oil. It consists of cutting or chopping the fatty tissue into small pieces that are boiled in open vats or cooked in steam digesters. The fat, gradually liberated from the cells, floats to the surface of the water, where it is collected by skimming. The membranous matter (greaves) is separated from the aqueous (gluey) phase by pressing in hydraulic or screw presses; additional fat is thereby obtained. The residue is used for animal feed or fertilizer. Several centrifugal separation processes were developed in the 1960s. Cells of the fatty tissues are ruptured in special disintegrators under close temperature control. The protein tissue is separated from the liquid phase in a desludging type of centrifuge, following which a second centrifuge separates the fat from the aqueous protein layer. Compared with conventional rendering, the centrifugal methods provide a higher yield of better-quality fat, and the separated protein has potential as an edible meat product.

Pressing

Pressing processes

With many oil-bearing seeds and nuts, rendering will not liberate the oil from the cellular structures in which it is held. In these cases the cell walls are broken by grinding, flaking, rolling, or pressing under high pressures to liberate the oil. The general sequence of modern operations in pressing oilseeds and nuts is as follows: (1) the seeds are passed over magnetic separators to remove any stray bits of metal; (2) if necessary, the shells or hulls are removed; (3) the kernels or meats are converted to coarse meal by grinding them between grooved rollers or with special types of hammer mills; and (4) they are pressed in hydraulic or screw presses with or without preliminary heating, depending on the type of oil-bearing material and the quality of oil desired. Oil expressed without heating contains the least amount of impurities and is often of edible quality without refining or further processing. Such oils are known as cold-drawn, cold-pressed, or virgin oils. Pressing the coarse meal while it is heated removes more oil and also greater quantities of nonglyceride impurities such as phospholipids, colour bodies, and unsaponifiable matter. Such oil is more highly coloured than cold-pressed oils. Residual meals are concentrated sources of high-quality protein and are generally used in animal feeds.

Pressing machines

Many different mechanical devices have been used for pressing. The Romans developed a screw press, described by Pliny, for the production of olive oil. Centuries ago, the Chinese employed the same series of operations followed in modern pressing mills—namely, bruising or grinding the seeds in stone mills, heating the meal in open pans, and then pressing out the oil in a wedge press. The Dutch, or stamper, press invented in the 17th century was used almost exclusively in Europe for pressing oilseeds until the early part of the 19th century, when the hydraulic press was developed. The yield of oil from the hydraulic press was considerably higher than that from earlier processing methods because of the much higher applied pressures. In open presses, the ground seed material was confined in cloths of human hair or, less commonly, camel hair. Pressures on the cake varied from approximately 70 to 140 kilograms per square centimetre (1,000 to 2,000 pounds per square inch), and in the closed-type press, in which the oil-containing material was confined in a strong perforated steel cage during the pressing operation, pressures of approximately 400 kilograms per square centimetre or more were attained. Under ideal conditions the oil content of the hydraulic-press cake can be reduced to about 3 percent, but in practical operation a 5 percent level is average. The modern screw press replaced many of the hydraulic presses because it is a continuous process, has greater capacity, requires less labour, and will generally remove more oil. As ground seed is fed continuously into the mechanical press, a worm screw increases the pressure progressively as the material moves through a slotted barrel. Pressures from 700 to 2,100 kilograms per square centimetre are attained, and the oil is squeezed out through the slots, leaving a cake containing 3 to 3.5 percent oil under optimum processing and 4 to 5 percent oil under average conditions.

Lecture 7

Solvent extraction

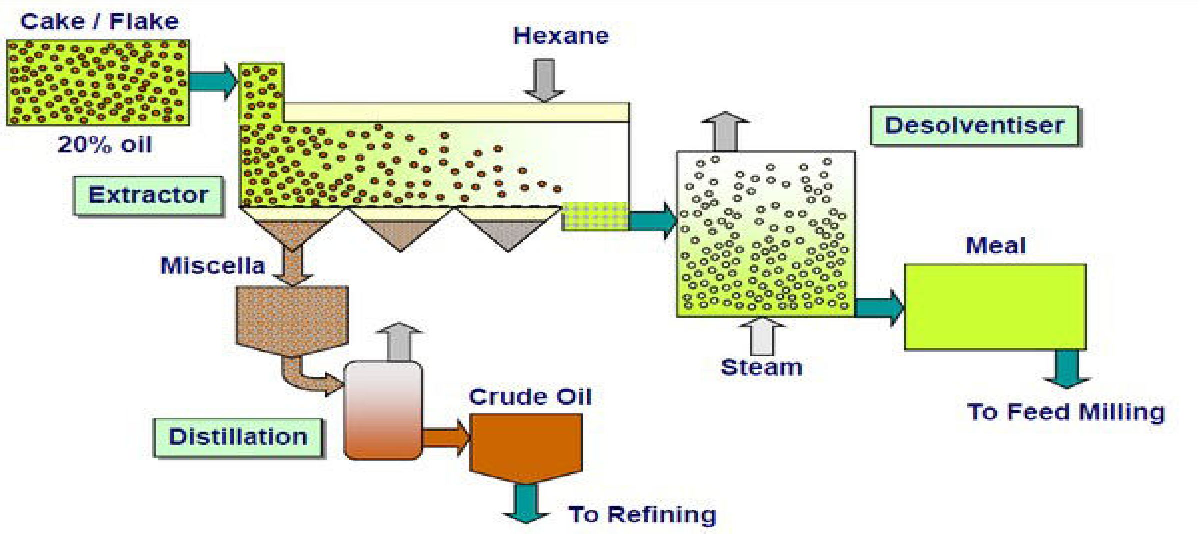
Processes

Cakes obtained by pressing operations still retain 3 to 15 percent of residual oil. When the value of the oil is considerably greater as oil than as a part of the meal, it is desirable to obtain more complete extraction with solvents. Modern commercial methods of solvent extraction use volatile purified hydrocarbons, especially the various grades of petroleum benzin (commonly known as petroleum ether, commercial hexane, or heptane). In large-scale operations, solvent extraction is a more economical means of recovering oil than is mechanical pressing. In the United States and increasingly in Europe, there are many instances of simple petroleum benzin extraction of seeds, mainly soybeans. For seeds or nuts containing a higher oil content than soybeans it became customary to press the material in screw presses to remove a large proportion of the oil before extraction. Since this prepressing also ruptures the cellular structures of oil-bearing materials, most of the residual oil is easily removed with solvents.

A typical extraction system consists of (1) cleaning to remove tramp iron, dirt, foreign weed seeds, and stones, (2) removing hulls or cortex in cracking, aspirating, or screening operations, (3) cracking or rough grinding the kernels, meats, or prepressed cake, (4) steaming (tempering or cooking) of the meats, (5) flaking the small pieces between smooth flaking rolls, (6) extracting the oil with solvent, (7) separating the meal, or marc, from the oil-solvent solution, called miscella, and (8) removing the solvent from both the miscella and the marc. The marc may be toasted or pelletized, or both, for use in animal feeds. Most extracted meals contain less than 1 percent of residual oil. The amount varies depending on the amount of prepressing, the type of material being extracted, and the efficiency of the extracting system.

Extractors

Solvent extraction was first practiced in Europe, using batch extractors for the recovery of additional oil from the residues obtained from mechanical pressing. The greater efficiency of solvent extraction encouraged direct application to oilseeds, and the batch extractor gradually gave way to continuous units in which fresh flakes are added continuously and subjected to a counterflow of solvent. One of the earliest continuous extractors, and a type still considered to be one of the best, was the Bollman or Hansa-Mühle unit from Germany, in which solvent percolates through oilseed flakes contained in perforated baskets moving on an endless chain. After the extraction cycle is complete, the baskets of extracted flakes are dumped automatically and then refilled with fresh flakes to initiate another cycle. Many extractor designs have been proposed, but only a few have found wide acceptance. In the DeSmet extractor, popular in Europe and in a number of developing countries, a bed of flakes on an endless horizontal traveling belt is extracted by solvent percolation. The Blaw-Knox Rotocell has become the most popular extractor in the huge American soybean industry. The flakes are conveyed into wedge-shaped segments of a large cylindrical vessel. Solvent percolating through the cells falls into the bottom of the extractor housing, where it is picked up by a series of pumps and recirculated countercurrent to the flakes.



Processing of extracted oil

The extent of processing applied to fats depends on their source, quality, and ultimate use. Many fats are used for edible purposes after only a single processing step—*i.e.,* clarification by settling or filtering. Most cold-pressed oils (for example, cold-pressed olive, peanut, and some coconut and sunflower oils) can be used in food products without further processing. Tremendous quantities of butter and lard are used without special treatment after churning or rendering. The growing demand for bland-tasting and stable salad oils and shortening, however, has led to extensive processing techniques.

Lecture 8

Supercritical Fluid Extraction:

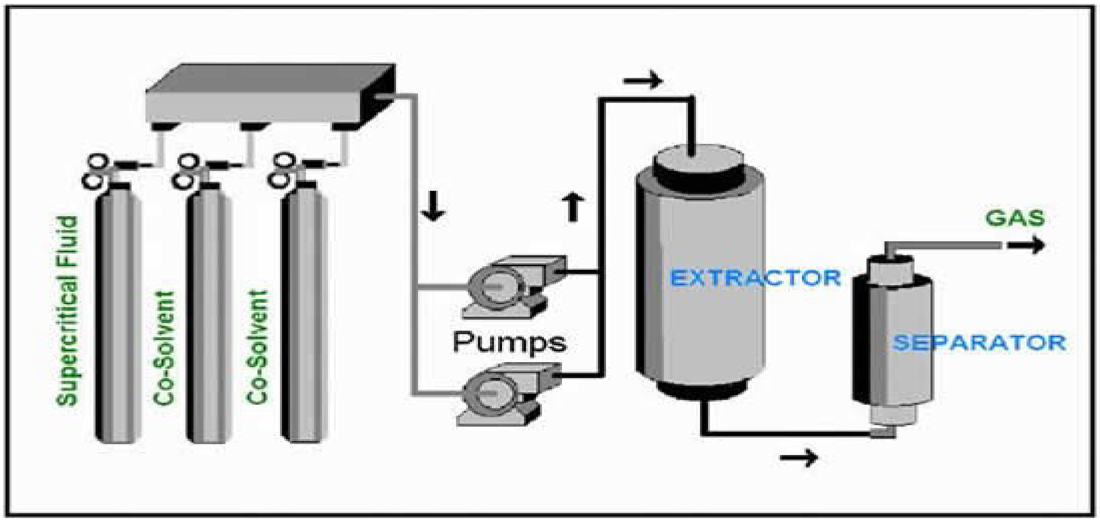
The term “supercritical fluid extraction” (SFE) in the field of oils and fats processing often brings to mind a technology that emerged in the early 1980s as a potential replacement for hexane extraction of commodity seed oils [1]. Despite promising laboratory and pilot plant-scale tests, the technology’s application to seed oils languished owing to high capitalization costs and the inability to develop a consistent solids feed system comparable to those used in conventional organic solvent-based processes. Industrial adoption waned in ensuing years even though several novel approaches to feeding solids into high-pressure extractors, such as high-pressure lock hoppers or auger-based screw conveyors, were developed [2].

Despite this setback, SFE is alive and well and being applied to many substrates that contain lipid matter. If a “production plant” is defined as a process that produces a product for sale, then it has been estimated that there are over 125 plants worldwide using critical fluids. Most of these facilities use supercritical carbon dioxide (SC-CO_2) since CO_2 is environmentally benign and readily available from the atmosphere, geological deposits, and fermentation processes (such as bioethanol production). Indeed, in this author’s 40 years of association with this field, the concept of locating an SFE-based processing facility next to a bioethanol production facility has often been mentioned.

Both sub- and supercritical propane have also been used to produce food products, particularly those with a lowered fat content. SC-CO_2 and propane are GRAS-approved (i.e., are Generally Recognized

As Safe by the US Food and Drug Administration) for contact with foodstuffs; and the use of food-compatible co-solvents with SC-CO_2, such as ethanol, extends the range of SFE for processing substrates that can contain polar lipids (such as phospholipids) and related compounds .

Figure illustrates the spectrum of critical fluid-based solvents that can be applied to lipophilic substrates to produce food and nutraceutical ingredients from lipid-containing feedstocks. In applying SFE to foods and agricultural materials processing, issues such as the degree of comminution and substrate water content have a significant effect on the resultant extract and must be controlled to ensure the desired result. A prime example is the often-cited SFE of water-tempered coffee beans and teas that have been used to produce commercial products for some time now using SC-CO_2 extraction.



Expanding the role of supercritical fluids

It is interesting to examine the developmental eras of critical fluid-based technology (Fig. 2) and their relevance to lipids processing. From the early 1980s, the processing technology expanded into modes other than just SFE. The rise of supercritical fluid fractionation (SFF) methodology, embracing columnar-based schemes using distillation-type towers, as well as production-scale supercritical fluid chromatography (SFC), is documented in the literature [4], but these techniques have faced stiff competition from technologies such as molecular distillation and high-performance liquid chromatography (HPLC). Columnar fractionation-based methods, based on longitudinal temperature gradients along the column, can be operated in either concurrent or countercurrent modes with respect to substrate feeds vs. flow of the critical fluid. Such an approach can enrich lipid-containing mixtures with respect to their concentration in the natural oil matrix, resulting in extracts or raffinates with potential value as nutraceutical ingredients or functional food additives. Toward that end, production plants have evolved to concentrate lipids such as tocopherols, pigments, and sterols.

During the late 1980s and early 1990s, critical fluid-based techniques were gradually adopted by analytical chemists. Regulatory pressures to reduce the use of organic solvents in laboratory environments made SFE attractive to chemists because SC-CO_2 is a virtually solventless extraction medium. Considerable effort was made to develop extraction and cleanup techniques. With respect to lipid matter and food analysis, three main themes emerged: (i) application for total fat/oil content as a replacement for Soxhlet-based methods, (ii) extraction of trace analytes followed by fractionation of lipid-containing material, and later (iii) assays compatible with the demands of the US Nutritional Labeling and Education Act of 1990. Although many sophisticated methods and types of instrumentation were developed during this period, competition from reduced solvent-based techniques lessened the use and impact of SFE in analytical chemistry. Nevertheless, many SFE techniques became standard operating procedures both in the United States and abroad, and these instrumental approaches continue to be used in support of process research and development.

Likewise, supercritical fluid chromatography (SFC) has found a particular niche in the pharmaceutical industry for the rapid characterization of chiral compounds. From the perspective of current applied lipid analysis, SFC is a very complementary and perhaps preferred technique to gas chromatography and HPLC for the rapid characterization of the major groups in biodiesel synthesis, as demonstrated in the early 1990s. Within 30 minutes or less, SFC can break down the major functional lipid groups such as fatty acids, mono-, di-, and triglycerides found in biodiesel so they can be quantified.

Reactions of interest to the oils-fats-lipids community have been developed using sub- and supercritical fluid media. Although there are exceptions, most reaction scenarios fall into one of three categories: (i) enzymatic-initiated reactions, (ii) hydrogenation of oils and oleophilic derivatives, and (iii) hydrolysis-based transformations produced in the presence of subcritical water and SC-CO_2—both neat and in the presence of various catalysts. Initial studies using primarily lipases in the presence of predominantly SC-CO_2 appeared in the early 1990s [7]. Enzymatic catalysis in the presence of supercritical fluids may not be practical for large-scale transformation of the lipids because of the sensitivity of enzymes to the presence of water, their denaturation at high temperatures and pressures, and their cost. However, niche applications in the synthesis of specialty chemicals or aroma compounds, in which avoidance of organic solvents is desired and consumer safety a concern, appear more feasible.

Hydrogenation in the presence of supercritical fluids offers some interesting possibilities since the kinetics for such reactions can be accelerated by 500–1000 times and offer benefits in product selectivity and postreaction isolation of products [8]. The synthesis of oleochemical derivatives such as fatty alcohols, using either SC-CO_2, propane, or *n*-butane, can be more environmentally benign, as demonstrated by van den Hark *et al.* [9] on a pilot plant scale, and by others.

Although traditional fat splitting is often recognized as a hydrolysis process, it actually is using water in its subcritical state, and actually offers a "green," catalyst-free method for the hydrolysis of oils-fats and related materials. By exploiting the temperature dependence of water's hydrolysis constant (K_w), acid-base chemistry becomes possible even at modestly elevated pressures and temperatures, in contrast to the higher pressures required in supercritical fluid-based processes. In terms of biofuels, the treatment of recycled synthetic and bio-derived wastes using subcritical water for hydrolysis has been demonstrated as an appropriate method for the conversion of waste fats into biodiesel, or for the production of methane and methanol fuels from mixed biowaste streams, and it is appropriate for integration in a sequential manner with a liquid or SC-CO_2-based unit process.

One large-scale example of a subcritical water-based processing plant is shown in Figure 4, located in "Eco-Town" in Osaka, Japan, which is capable of processing industrial and biowaste into useful energy-related products, such as methane, methanol, and fatty acids for conversion to biodiesel.

CO_2 and water for lipids?

The mixing of CO_2 both at low and high pressures with water as well as the addition of CO_2 to organic liquids has fostered some unique chemistry that is green and sustainable and that often results in superior products. The addition of CO_2 to water, of course, results in its acidification below a pH~3.0, depending on the CO_2 pressure and temperature of the aqueous solution. As noted previously, these conditions can be exploited for acid hydrolysis of lipid moieties. Even oil and fat mixtures containing low levels of moisture are not immune to an autocatalytic effect in the presence of CO_2. The glycerolysis or methanolysis of oil-/fat-containing materials can be accomplished in the mere presence of CO_2 without resorting to the addition of a catalyst to initiate the reactions. Such an approach is very attractive from a green synthesis perspective. The addition of pressurized CO_2 to some conventional organic liquids results in a gas-expanded fluid that exhibits properties intermediate between those of a gas and liquid.

MODULE:II

Lecture 9

Edible Oil Processing: Introduction to Degumming

1. The Nature of Gums and Phosphatides

Crude oil obtained by screw pressing and solvent extraction of oilseeds will throw a deposit of so-called gums on storage. The chemical nature of these gums has been difficult to determine. They contain nitrogen and sugar and can start fermenting so they were at one stage thought to consist of glycolipids and proteins. Now we know that these gums consist mainly of phosphatides but also contain entrained oil and meal particles. They are formed when the oil absorbs water that causes some of the phosphatides to become hydrated and thereby oil-insoluble. Accordingly, hydrating the gums and removing the hydrated gums from the oil before storing the oil can prevent the formation of a gum deposit. This treatment is called water degumming. It is never applied to fruit oils like olive oil and palm oil since these oils have already been in contact with water during their production.

Water degumming is the oldest degumming treatment and also forms the basis of the production of commercial lecithin. I use the term 'commercial lecithin' here to make a distinction from the use of the word 'lecithin' as the trivial name for the compound phosphatidylcholine (PC). Similarly, phosphatidylethanolamine (PE) has the trivial name 'kephalin'. Since the water degumming process involves more water than when crude oil is allowed to absorb moisture from the atmosphere, the gums resulting from the water degumming process also remove hydrophilic substances such as sugars from the oil.

Lecithin as obtained by drying the gums resulting from the water degumming process contains a mixture of different phosphatides. The structural formulae of the main phosphatides present in lecithin are shown in **Figure 1** (further information on phosphatides is available here...).

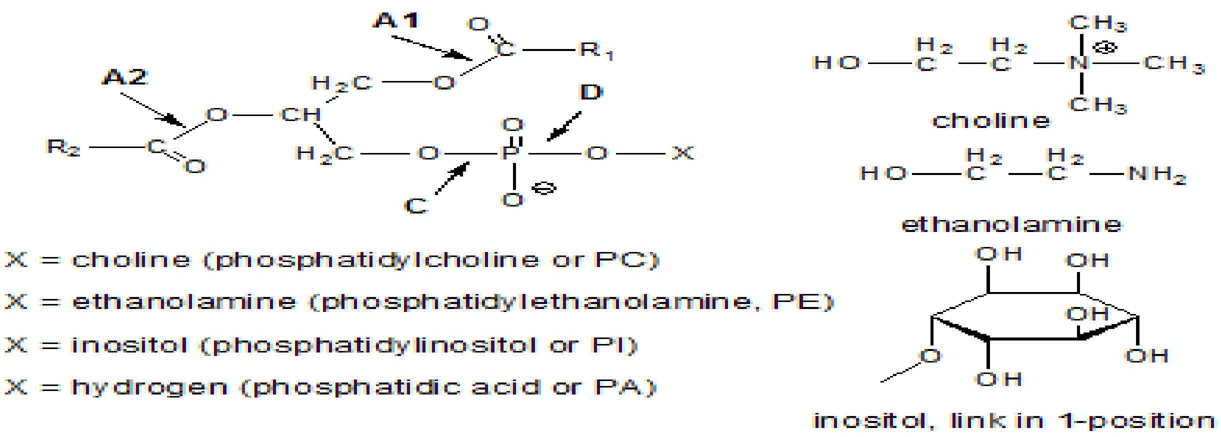


Figure 1.Chemical structure of most common phosphatides and indication of bonds that are hydrolysed by various phospholipase enzymes.

Table 1 gives the phosphatide composition of the phosphatide fraction in lecithins obtained from different oils.

Table 1. Composition (wt %) of phosphatides of various lecithins, adapted from [1]

Phosphatide	**Soyabean**	**Sunflower seed**	**Rapeseed**
PC	32	34	37
PE	23	17	20
PI	21	30	22
PA	8	6	8
Others	15	13	13

Please keep in mind that Table 1 refers to lecithins, the mixture of phosphatides that has been obtained by degumming crude oil with water. Since this water degumming process does not remove all phosphatides from the oil, Table 1 does not reflect the composition of the phosphatides present in the crude oil itself.

Just as a triglyceride oil is a mixture of triacylglycerols with different fatty acids, each phosphatide is also a mixture of different compounds. These compounds differ in their fatty acid composition and isomerically, in their location on the glycerol backbone. In general, the fatty acid composition of the phosphatides reflects the fatty acid composition of the oil in which these phosphatides occur but it tends to have a higherpalmitic acid content and a lower oleic acid content than the oil as illustrated by **Table 2**.

Table 2. Fatty acid compositions of vegetable lecithins and oils. Adapted from [1] and [2]

Fatty acid	Soya bean		Sunflower seed		Rapeseed	
	Lecithin	**Oil**	**Lecithin**	**Oil**	**Lecithin**	**Oil**
	16	11	11	7	7	4
18:0	4	4	4	5	1	2
18:1	17	23	18	29	56	61
18:2	55	54	63	58	25	22
18:3	7	8	0<	0	6	10
Others	1	0	4	1	5	1

The above table contains the data required for arriving at a conversion factor that permits the amount of phosphatides present in the oil to be calculated from its phosphorus content. For the oils represented in Table 2, this factor equals about 25 to 26. In other words, oil containing say 200 ppm of phosphorus contains about 0.5 wt% phosphatides.

On the other hand, the literature often uses a factor of 31.5 or thereabouts to arrive at the acetone-insoluble component of the lecithin. This difference stems from the fact that the acetone-insoluble component of lecithin also comprises glycolipids and sugars. The factor of 31.5 is therefore very much an empirical value. It should only be used for oils that have not yet been water-degummed since on water degumming, sugars are removed. For water-degummed oils, which contain alkaline earth salts of PA and lysophosphatidic acid (LPA) and some PE and lysophosphatidylethanolamine (LPE) and do not contain any more sugars, a factor of 23 to 24 should be used to convert phosphorus to phosphatides.

2. Hydratability of Phosphatides

The extent to which a phosphatide present in the crude oil is removed during water degumming depends on its hydrophilicity. Phosphatidylinositol has five free hydroxyl groups on the inositol moiety that make PI strongly hydrophilic. Consequently, PI present in crude oil will be hydrated during the water degumming treatment and the PI content of properly water-degummed oil is negligible. Similarly, the positive charge of the trimethylamino group in phosphatidylcholine makes this phosphatide hydrophilic. This hydrophilicity does not depend on the pH of the water used to degum the oil since even at pH > 5, when the phosphate group in the PC is dissociated and therefore carries a negative charge, it does not form an internal salt with the quaternary amino group for steric reasons. Consequently, the positive quaternary amino group remains isolated at all pH values and causes PC to be hydrophilic at all pH values.

Table 3 shows what charges the various phosphatides carry at which pH.

Table 3. Charges of phosphatides as a function of pH

pH	PC	PE	PI	PA	Ca-PA
2	+	+	0	0	0
3	(+)	(+)	(0)	(0)	0
4	(±)	(±)	(-)	(-)	0
5-7	±	±	-	-	0
8-9	±	±	-	(2-)	0
>10	±	-	-	2-	0

Some charges in Table 3 have been put between parentheses. They indicate a transition between the value at lower pH and the value at higher pH. So according to Table 3, almost all phosphatidylethanolamine (PE) molecules have a positive charge at pH = 2. This charge causes these molecules to be hydrophilic so at that pH, PE is hydratable. When the pH is increased, more and more phosphate groups dissociate and so a zwitterion (indicated by ±) is formed in which the positive amino group forms an internal salt with the negative phosphate group. The positive and negative charges are so close together that the hydrophilicity of this zwitterion is quite weak and on water degumming, the hydration of PE is incomplete. Accordingly, water-degummed oil still contains some PE.

Now we come to phosphatidic acid (PA). In an acid environment, the hydroxyl groups of its phosphate moiety will not dissociate since the $\mathrm{p}K_\mathrm{a}$ value of the first hydroxyl group equals 2.7-3.8 [4]. Consequently, PA will be poorly hydratable and remain in the oil when this is brought into contact with acid water. When the pH of this water is raised to 5, most of the PA will be dissociated so that the molecule has a negative charge giving it a hydrophilicity that makes it hydratable. Accordingly lecithin contains some PA as illustrated by Table 1. When the pH of the water is raised even further, the second hydroxyl will also dissociate since its $\mathrm{p}K\mathrm{a}$ is 7.9-8.6 [4], whereby the actual value depends on what other salts are present in the water.

But what about the calcium salt of PA? According to the column on the far right in Table 3, this remains without charge at all pH values because the divalent calcium forms a salt with the two dissociated hydroxyl groups of the phosphate moiety. That is the reason that alkaline earth salts of PA remain in the oil when it is degummed with water. They are the main constituents of the nonhydratable phosphatides (NHP). However, when the oil is alkali refined, these salts are removed. Two possible mechanisms have been shown in **Figure 2**:

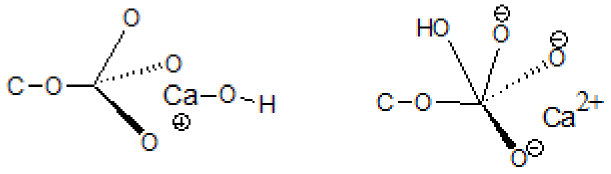


Figure 2.Calcium phosphatidate at high pH.

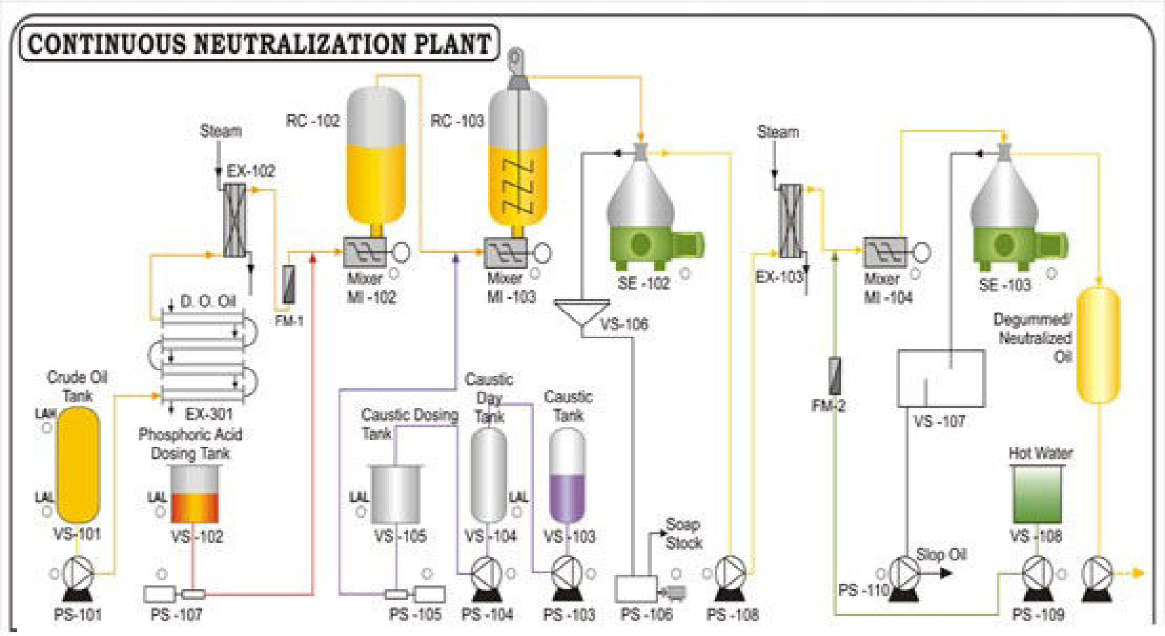
In the lefthand structure in Figure 2, a hydroxyl ion has been linked to the Ca^{2+} ion so that it only has a single positive charge and the salt itself has a negative charge making it hydratable. In the righthand structure, the hydroxyl ion has been linked to the phosphorus of the phosphate moiety so that the calcium retains its 2+ charge. Because of the addition of a negative hydroxyl group the salt itself becomes negatively charged and thus hydratable.

PA moieties present in crude oil are generally considered to originate from the hydrolysis of phosphatides such as PC, PE and PI. This hydrolysis is most likely catalysed by phospholipase D (see Fig. 1). Phospholipase A_1 and A_2 on the other hand lead to the formation of lysophosphatides by hydrolysing one of the ester bonds between a fatty acid and the glycerol moiety in the phosphatide. What about the hydratability of these lysophosphatides? Their free hydroxyl group is more hydrophilic than the original fatty acid ester, but does this make them hydratable when the parent compound is nonhydratable?

The answer to this question is not straightforward. According to, the nonhydratable phosphatides (NHP) comprise lysophosphatidic acid (LPA) and lysophosphatidylethanolamine (LPE), indicating that lysophosphatides are not completely hydratable. According to [6], enzymatic hydrolysis of the NHP present in the oil phase using phospholipase A_1 and phospholipase A_2 led to lyso-compounds that were only detected in the aqueous phase indicating the hydrolysis of NHP causes the resulting lyso-compounds to migrate to the aqueous phase.

In the case of partial glycerides, 1,3-diglycerides are more stable than 1,2-diglycerides. Similarly, 1-/3-(α)-monoglycerides are more stable than 2-(β)-monoglycerides so there is a preference for the fatty acid to be bound to the 1- and 3-positions. It is therefore to be expected that 1-acyl lysophosphatides are more stable than 2-acyl lysophosphatides and that the 2-acyl lysophosphatides formed by the action of the phospholipase A_1 will isomerise to 1-acyl lysophosphatides. These have a fatty acid linked to a terminal carbon atom of the glycerol moiety and will therefore be prone to phospholipase A_1-catalysed hydrolysis. This will lead to formation of a glycerophosphate and indeed glycerophosphates have been observed in the aqueous phase of oils treated with phospholipase A_1 [7]; their concentrations were about equal to those of the lysophospholipids. However, in, the use of Lecitase® 10L (a phospholipase A_2) led to lower concentrations of lysophosphatides in the aqueous phase than when a phospholipase A_1 was used. This might indicate a higher stability of the 2-acyl lysophosphatides in comparison with their 1-isomers.

Lecture 10



Vegetable Oil Refining

Vegetable Oils Refining is necessary for vegetable oils & fats or animal oils & fats so they can be used for cooking and frying foods. Chemically speaking, oils are Tri-Glycerides or "Fatty-Acid Glycerin Esters" (FAGE). One Glycerin molecule combines with three Fatty-Acid molecules to form one FAGE. Oils are a blend of different types of FAGEs. The Oils can be differentiated on the basis of the length of carbon chain in the Fatty Acids and the number and location of double bonds in the carbon chains of the Fatty Acids. Greater the number of double bonds between two carbon atoms, the greater is the extent of "unsaturated" fatty-acids in the fatty-acid profile of the oils. "Unsaturated" oils and fats are considered more desirable than "saturated" oils and fats from health point of view.

Why is Vegetable Oil Refined?

Vegetable and Animal Oils and Fats have impurities such as Moisture, Solids (Insolubles), Gums (Lecithins), Free-Fatty Acids (FFA), Waxes, and Compounds of Sodium, Potassium, Magnesium, Calcium, and other metals. These impurities must be removed to improve the functionality of the oils. Other characteristics of oils (such as Color, odor, and taste) are also considered impurities by modern consumers. These impurities are removed in a series of steps such as degumming (to remove gums), neutralizing (to remove FFA), bleaching (to remove color), deodorizing (to remove odor and taste), and dewaxing or winterization (to remove waxes).

What is RBD Oil?

Refined Vegetable Oil is commonly called Refined, Bleached, and Deodorized (RBD) oil. As described earlier, these are the three main steps in the refining process; although additional steps are required in most cases.

Chemical Refining

In this process, first the crude oil undergoes degumming process where it is treated with food grade processing acids or water to remove seed particles, impurities, phosphatides, carbohydrates, proteins and trace of metals. Later to neutralize free fatty acids, it is treated with sodium hydroxide alkaline solution, followed by the washing out of soaps and hydrated phospholipids. Then follows bleaching and deodorization where unwanted pigments, odours and traces of impurities are removed.

Physical Refining

In physical refining process no chemical is added to remove the acids of crude oil. Once the crude oil undergoes degumming process it is sent for steam distillation under vacuum. The process of neutralization using alkaline solution is avoided and steam distillation method is used in the process of deodorization to remove free fatty acids.

Physical vs Chemical Refining

It depends mainly on the free fatty acid (FFA) content of the oil. If FFA content is very low then physical refining is very useful because by using lesser steam, oil can be refined to the purest form. Physical refining methods do not involve any chemicals or soap stocks to remove the FFA content. However, this method doesn't yield effective results if crude oil quality is low.

In chemical refining soap stocks can hold 50% of the neutral oil. Hence there is a chance of high wastage in this method. Also, care should be taken to maintain balanced temperatures throughout the process. If temperatures are high, the fundamental structure of oil can change by the process called isomerization, which increases trans-fatty acids in the oil. By using chemical refining, maximum reduction of FFA content can be achieved but care should be taken not to exceed the defined temperatures.

Which Oil is Better to Consume?

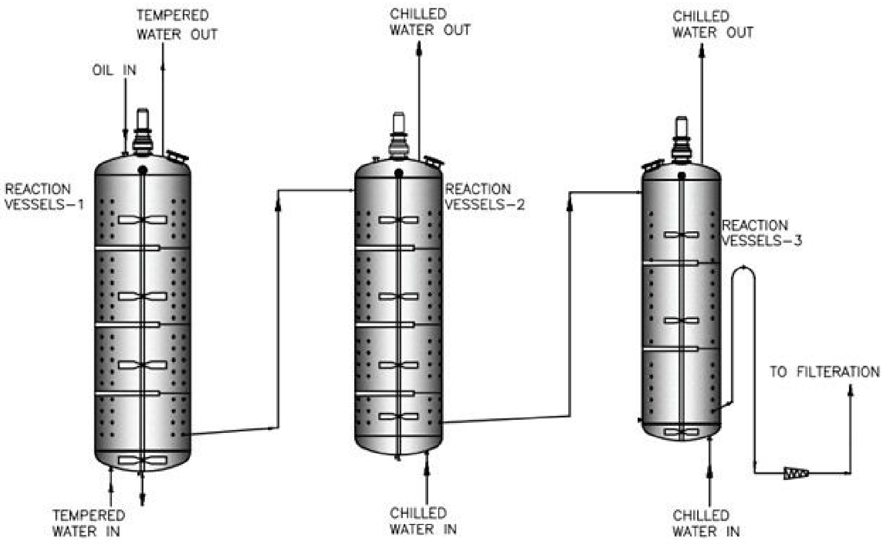
In chemical refining, oils are exposed to several chemicals, bleaching agents and high temperatures which may lead to many chemical changes that are not good for health. On top of it, many chemicals get added as preservatives to keep the oils for long. For instance, when oil is exposed to high temperatures and low pressures, there could be loss in nutritional value and may also lead to the formation of trans fatty acids that are considered as harmful for heart wellbeing. On contrary, physically refined oils are extracted in a much healthier process without exposure to harsh chemicals or high temperatures. Since they do not lose out on the natural nutritional values, they are much healthier to consume.

Lecture 11

Dewaxing or Winterization

A method for winterizing (dewaxing) of vegetable oils is described. The method is of an art, comprising the steps of neutralizing the oil, chilling it, mixing in an alkali solution, slow stirring during a residence time to make waxes and other high melting matters precipitate, and removal of same.

The present method is especially characterized by the fact that the neutralizing is driven to a soap content of 100-7000 ppm, and that the oil is chilled to a temperature below 15° C., preferably 5°-15° C., and that lye or other alkali is added, corresponding to 0.01-0.06 kgsNaOH per 100 kgs oil, the sequence chilling/addition being optional, whereupon 3-10 kgs water per 100 kgs oil are added with intense agitation, and the mixture so obtained is stirred slowly for more than 1 hour, preferably 1-7 hours, whereupon the mixture so obtained is separated into a heavy fraction, containing water- lye- soap- waxes- and other high melting matters and a lighter fraction consisting of the winterized oil.



PFD - Continuous Dewaxing

Winterization is another name to the process of dewaxing. The name winterization appears as during winter when the temperature is low,waxes present in the oil crystallizes,they give hazy appearance to the oil.

Description of dewaxing in sunflower oil refining plant

Dewaxing (also called winterization) of sunflower oil is essential when the oil is to be used as salad oil. The presence of wax makes the oil appear cloudy at room temperature. The oil normally becomes cloudy in 5–6h but with proper dewaxing the oil remains clear after 24h of storage at 0˚C.

The following steps are used to dewax sunflower oil:

Crude oil is refined and bleached to low phosphorus (<1ppm) and low moisture content (<0.1%).
The oil is heated to 55˚C to make sure the oil is fully liquid.
The oil is cooled slowly to 7–8˚C.
Cooled oil is held in a specially insulated tank with a special slow-speed mechanical agitator.
Preferably, the oil is held for 12–24h at this temperature.
The oil is mixed with diatomaceous earth/filter aid through an in-line mixing system and filtered through a pressure leaf filter pre-coated with diatomaceous earth/filter aid.
The filtered oil is collected, checked for cold test and filterable impurities, and then deodorized.
The deodorized oil is checked again for cold test along with the other analyses listed earlier.

Lecture 12

Bleaching

The bleaching of edible oils and fats is a part of the refining process of crude oils and fats, which removes contaminants that adversely impact the appearance and performance of these triglyceride (triacylglycerol)-based materials. Typically, edible oils and fats, ranging from soybean and palm oils to edible lard and beef tallow, are extracted together with impurities in various quantities. Many of these impurities have to be removed from the oil to achieve the high quality oil standards necessary for edible applications. Preceded generally by degumming and refining (neutralization) processes, bleaching is required to remove specific detrimental contaminants that are not effectively removed by these processes before the oil progresses through deodorization.

Originally described as a process of mixing oil and clay adsorbent to remove color, the bleaching operation effectively removes some of the color, reduces the contents of chlorophyll, residual soap and gums, trace metals, oxidation products, and indirectly impacts on deodorized oil color. While the bleaching process appears to be a simple mixing of adsorbent and oil followed by filtration, the chemical and physical reactions occurring are complex and greatly reliant on process variables (i.e. moisture levels, temperature, contact time, and vacuum), oil quality entering the bleacher, the amount and characteristics of the adsorbent and the type of equipment employed. The success or efficiency of the bleaching operation is interdependent on the effectiveness of upstream processes where contaminants that have the potential to interfere with the bleaching mechanisms should be removed (**Fig. 1**). Some consider bleaching the "safety net" of the refining process in that it is the last operation in the oil refining process before going to deodorization. As the focus of this paper would suggest, optimization of the bleaching process is considerably important to both achieving high quality refined oil products and the economic viability of the oil purification process.

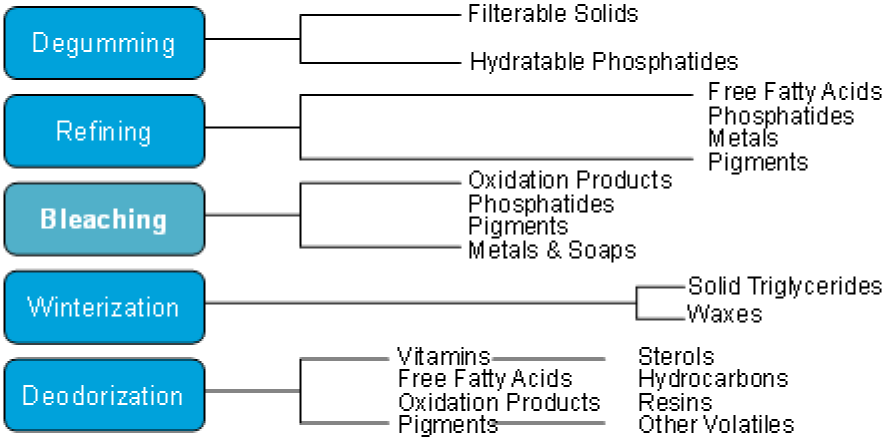


Figure 1.Processing efficiency - process-dependent removal of contaminants.

Bleaching Clay – Characteristics

The adsorptive capacity of sorbent minerals depends on their mineralogical structure and adsorptive properties, such as surface area, particle size distribution, porosity, and surface acidity. Bleaching clays or earths are generally composed of one or more of three types of clay minerals: calcium montmorillonite, attapulgite, and sepiolite. Microscopic views of two of these clay-based minerals are depicted in **Figure 2**. One is calcium montmorillonite (commonly referred to as bentonite) and the other is a naturally occurring blend of attapulgite and montmorillonite from the Georgia region in the USA.

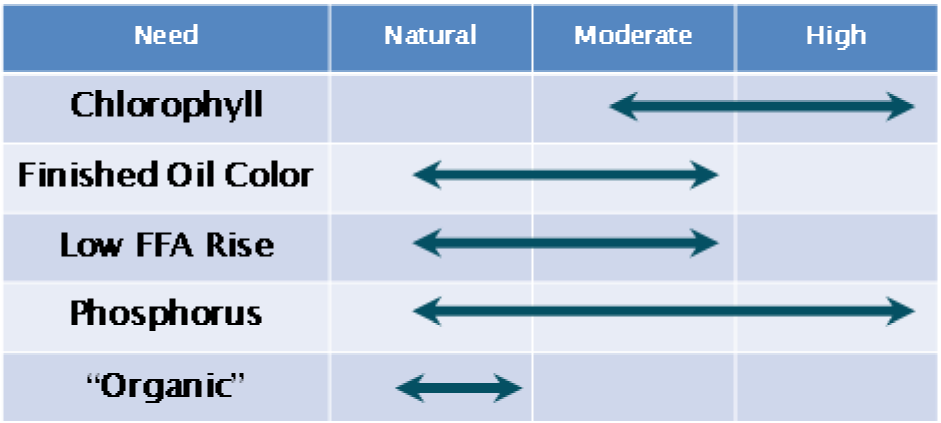
Figure 2.Bleaching clay base minerals.

Bentonite minerals have limited sorptive properties in the natural state and require chemical treatment by acids to create the surface area and porosity needed for bleaching vegetable oils. Bleaching clays of this nature are commonly referred to as “acid” or “acid-activated” clays.

Attapulgite and sepiolite minerals have a naturally high affinity for adsorbing oil contaminants without any acid treatment. These natural clays can be acidified with mineral acids as well as used in conjunction with chelating acids such as citric or phosphoric acids to improve bleaching activity with respect to chlorophyll.

Bleaching Clay – Activation

Bleaching clays are activated to varying degrees via interaction with acids ranging from completely natural clays, as explained above, to highly acid-treated clays (**Fig. 3**). The benefits to having increased adsorbent activity and/or impurity removal (i.e. bleaching efficiency) improve as the clay acidity of a base mineral is increased (pH lowers with limit approaching pH 2). However, employing acid-activated clays can have detrimental side effects in the oil; these include increased levels of free fatty acids, and the formation of undesirable 3-monochloropropane-1,2-diol esters (MCPD). Natural clays are often preferred by refineries that are sensitive to these contaminants.



Need	Natural	Moderate	High
Chlorophyll		⟷	⟷
Finished Oil Color	⟷	⟷	
Low FFA Rise	⟷	⟷	
Phosphorus	⟷	⟷	⟷
“Organic”	⟷		

Figure 3. Influence of bleaching earth activation levels. Typical activation levels for quality variables.

Furthermore, natural clays are the only bleaching clay option that meets the “Organic” oil certification because their manufacture does not involve any restricted chemical agent. In some situations, “organic” approved natural acids such as citric acid can further enhance the bleaching effectiveness of natural clays and still meet “organic” labeling requirements for chlorophyll-rich oils. This acid can be added to the oil being bleached, or acid-treated clay can be prepared in advance.

Bleaching Mechanisms

During the bleaching process adsorption occurs via many different mechanisms involving various physical and chemical interactions; most of them improve the quality of the oil, but some of them may reduce it (**Fig. 3**). These mechanisms include the following:

Adsorption ─ mechanism by which the sorbent binds a contaminant. This can occur in three different ways:

- Physically through surface attraction involving van der Waals' forces
- Chemically by “chemisorption” by electrochemical bonding to the surface of the clay
- By molecular sieves which trap contaminants under pressure inside the pores of the clay during filtration

Absorption ─ mechanism by which the intra-granular pores are filled with some fluid—mainly oil — and in turn whatever contaminants came along with it. Oil retention is reported in two ways: as weight loss by Soxhlet extraction (with hexane being used as solvent), and as total organic matter determined by ashing.

Total oil retention depends on a number of variables including clay dosage levels, clay characteristics (e.g. particle size distribution and mineral type), permeability of the filter bed, incoming feedstock quality, cleanliness of the filter screen and the conditions used to purge the filter before disposal of the “spent” filter cake. Excessive oil retention increases the cost of running the process; oil loss through spent earth can typically range up to 35 weight percent solvent extractable and 50 weight percent for total organic matter of the earth used.

Filtration ─ mechanism of trapping or physically removing suspended contaminants: the physical act of filtering out the suspended clay that simultaneously removes the minor contaminants adsorbed to the clay particles. Filters used in the bleaching process include (1) processing filters (horizontal and vertical leaf filters) and (2) polishing filters (bag, cartridge, paper).

Catalysis ─ mechanism by which contaminants are degraded by interaction with the surface of the clay. For example, peroxides are effectively reduced (polymerized and/or decomposed into volatile oxidation by-products) by clay/oil interaction. With excessive heat and oxidation, pigments can form color compounds that are difficult to remove or said to be “fixed.” In the event of color fixation, red color is more difficult to remove by bleaching clays alone and resistant to thermal degradation leading to higher red color after deodorization.

Process Options

The bleaching process configurations have advanced from the slow, less efficient batch process to the highly efficient countercurrent process options including true countercurrent and lead-lag or double pass bleaching systems currently offered and discussed in the literature (see **Figs. 4**). Batch bleaching systems continue to be the process of preference for those who process many different products per day in small quantities. Countercurrent bleaching systems [7] find more favor in modern facilities because they maximize bleaching efficiency by utilizing the spent clay to exhaustion, which results in substantial savings (up to 40% reported) with 20-30% reported clay reduction.

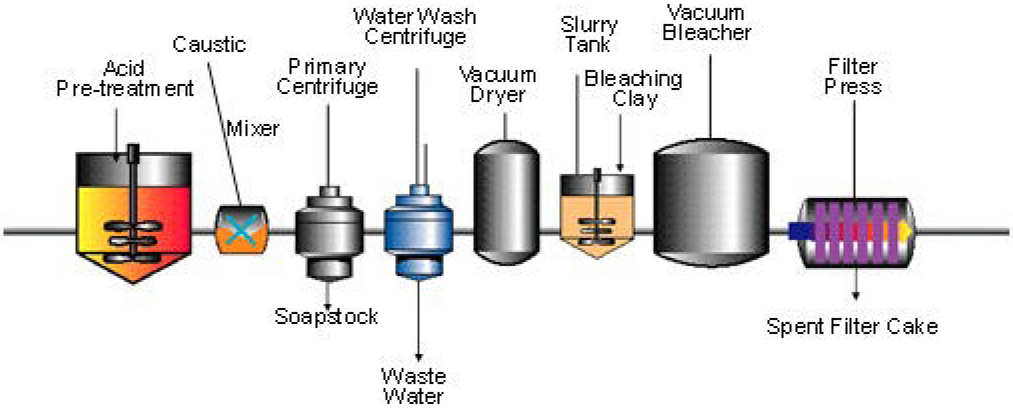


Figure 4. Continuous bleaching .

Improved Oil Quality

Bleaching is the physical and chemical interaction of an oil or fat with bleaching earth to improve its quality. One definition of quality is "to reach a level of excellence." However, with respect to oil specifications, it is quite variable and depends on the product and market we are dealing with. For example, for deep-frying oils, it is very important that phosphorus (P) be as low as possible and a residual content of <0.5 ppm is desired, but for salad oil, a level of <2 ppm may be specified.

Various processing conditions can affect one or more of the oil characteristics that have been listed in quality specifications. By balancing these conditions one against the other, you will be one step closer to a more efficient bleaching process.

To arrive at an optimal bleaching process, you must first establish what the primary target specifications will be and make sure that you are getting the appropriate contaminants removed by the overall refining process (see Fig. 1). Good refined oil must be [1] :

- Low in phosphorus (good if <15 ppm, very good if <10 ppm and excellent if <5 ppm)
- Low in free (unesterified) fatty acids (FFA <0.1 % unless some adaptation of physical refining is being employed)
- Low in soaps (<50 ppm unless silica/silicate refining is used)

Once you have this under control you can begin the bleaching stage where:

- Soaps are completely removed
- Phosphorus content is reduced to below 2 ppm

- Iron content is reduced to below 0.2 ppm
- Chlorophyll content is reduced to below 0.05 ppm
- Peroxide Value is reduced to below 0.5 mEq/kg

All values cited herein serve as industry guidelines to meet product specifications. Each refinery is unique, having any assortment of equipment and production lines set up to meet customer driven specifications.

Lecture 13

Deodorization

In the early days of the edible oil processing industry, in the first half of the 19th century, there was little or no need for refining. Food fats (e.g. lard, olive oil, milk fat, etc.) were mostly consumed unrefined and their typical flavour was even an attractive characteristic. It was the growth of the margarine industry in Europe at the end of the 19th century that resulted in the development of the edible oil deodorization process (**Table 1**). At first, industrial deodorizers were mostly batch-type with the ‘Bataille’ and ‘Lurgi’ deodorizers being the most widely used in Europe (**Fig. 1**). These deodorizers operated under vacuum (to facilitate stripping and protect the oil against oxidation) and also used superheated steam as a stripping agent (to avoid hydrolysis).

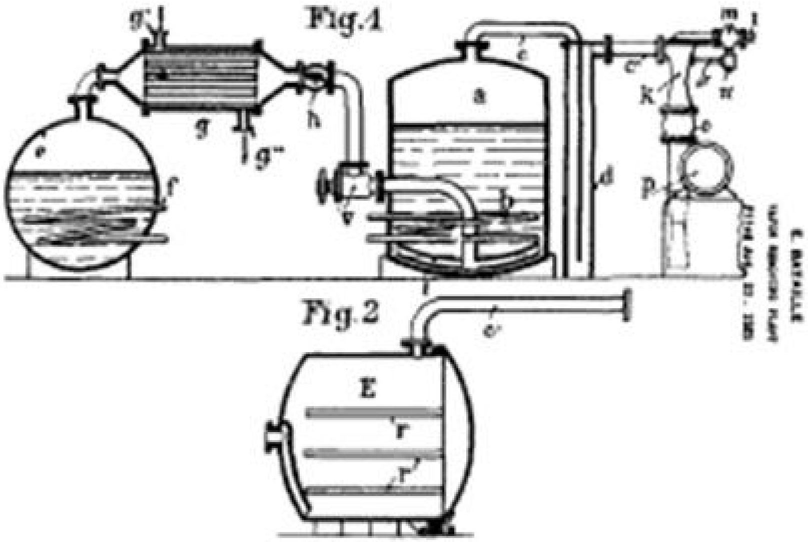


Figure 1.Bataille High Vacuum Batch Deodorizer.

Deodorization principle

Deodorization is actually a stripping process in which a given amount of a stripping agent (usually steam) is passed for a given period of time through hot oil at a low pressure. Hence, it is mainly a physical process in which various volatile components are removed. However, since it is usually carried out at high temperature (>200°C), some chemical and thermal effects may take place as well.

Vacuum stripping of volatile components

Theoretical aspects of vacuum stripping have been described extensively by many authors. Stripping of a given volatile component from the oil is determined by its intrinsic volatility (vapor pressure curve) and the deodorizing conditions applied (temperature, pressure and amount of sparge steam).

For a batch and cross-flow deodorization process, the stripping effect is described by the following mathematical equation:

$$S = \frac{P_t}{\mathrm{E}.P_i^0}.\ln\frac{V_a}{V_0} + \left(\frac{P_t}{\mathrm{E}.P_i^0} - 1\right).(V_a - V_o) \qquad [1]$$

- with S = total moles of steam or any other stripping agent per mole of oil (to express the amount of steam as a percentage of the oil, the factor S has to be multiplied by a factor of 2.); P_t = total pressure of the gas phase = system pressure; P_i^0 = Vapor pressure of a given fatty acid i; E = vaporization efficiency; V_a = initial amount of the volatile component in the oil (moles), V_0 = final amount of the volatile component in the oil (moles).

The vaporization efficiency E in equation (1) is a deodorizer design-specific factor. It should be seen as a measure of how saturated with volatile components the stripping agent (steam) becomes during its contact with the oil. In an ideal (theoretical) case, E = 1, but industrial deodorizers usually have a vaporization efficiency of 0.3-0.7, depending on their design (steam injection geometry, depth of oil layer, elimination of reflux, etc.).

Thermal effects

Another objective of deodorization is the thermal destruction of flavor precursors and heat-sensitive color pigments. The latter effect is called ‘heat bleaching’ and it is most pronounced during deodorization/steam refining of palm oil, where the thermal breakdown of carotenes is targeted. Heat degradation of carotene is very slow at 210°C, but takes only a few minutes at T > 260°C. This is one reason why palm oil is typically deodorized at 260°C.

However, there is a general trend to lower the ‘heat load’ (residence time at high temperature) used during deodorization. This evolution towards milder process conditions is caused by the increasing awareness of the potentially harmful health effects of thermal degradation products (*trans* fatty acids, polymeric triglycerides and glycidyl esters) that can be formed during deodorization. In addition, there is the desire for maximum retention of the natural oil characteristics.

Deodorized oil quality

Deodorized oil quality is evaluated primarily by traditional quality parameters such as a low residual FFA content, a high oxidative stability, a light color and a bland odor and taste. In addition, high-quality food oils need to contain low *trans* fatty acid (TFA) levels, high amounts of natural antioxidants (tocopherols), low levels of polymeric and oxidized triglycerides and no contaminants or degradation products. Refining targets for these minor components are given in **Table 2**.

Table 2. Refining targets for various minor components in edible oils

Minor component	**Refining target (concentration in fully refined oil)**

trans Fatty acids	<1.5% for oils rich in linolenic acid (soybean oil, rapeseed oil, canola, etc.) <1.0% for other vegetable oils (corn oil, sunflower oil, etc.)
Tocopherols	min. 500 ppm (to guarantee good oxidative stability)
Polycyclic aromatic hydrocarbons (PAH)	New EU regulation 835/2011 in force since September 1, 2012 <2 ppb BaP and <10 ppb PAH4 for most food oils; <2 ppb BaP and <20 ppb PAH4 for refined coconut oil; <5 ppb BaP and <30 ppb PAH4 for cocoa butter BaP = benzo(a)pyrene PAH4 = sum of BaP, benz(a)anthracene, benzo(b)fluoranthene and chrysene
Dioxins and PCB	New EU regulation 1259/2011 in force since January 1, 2012 For refined vegetable oils: <0.75 ppt WHO-TEQ (dioxins) and <1.25 WHO-TEQ (dioxins + dioxin-like PCB) For marine oils : < 1.75 ppt WHO-TEQ (dioxins) and < 6 WHO-TEQ (dioxins + dioxin-like PCB) WHO-TEQ = World Health Organization toxic equivalent PCB = polychlorinated biphenyls ppt = parts per trillion
3-MCPD + GE[1]	No legal specifications yet; only trade specifications which are especially challenging for palm oil <2 ppm for refined oils for use in standard food applications; <0.5 ppm for refined (palm) oil for use in infant food.

[1] 3-Monochloropropane-1,2-diol and glycidyl esters

Deodorizing process conditions

The deodorization process is fully determined by four process parameters : (1) temperature, (2) time, (3) pressure and (4) amount of stripping steam. The effects of process conditions on the standard quality parameters and the nutritional quality of the refined oil are well understood and are described in the literature (**Table 3**).

Table 3. Effect of process variables on deodorized oil quality

Quality	Temper	Ti	Press	Stea

parameter	**ature**	**me**	**ure**	**m**
Taste	+	++	+	++
Color (heat bleach)	++	+	-	-
FFA stripping	++	-	++	+
trans Fatty acid formation	++	++	-	-
Tocopherol /sterol stripping	++	-	++	+
Contaminant removal[1]	+	-	++	+
Glycidyl ester formation	++	++	-	-

[1] Pesticides, PAH, dioxins; - : little or no effect, + : significant effect, ++ : large effect

Oil deaeration

Degummed, bleached oil is deaerated prior to heating to deodorizing temperature to avoid oxidation and polymerization. It is accomplished in a separate external vessel connected to the vacuum system of the bleacher (50 mbar) or, at even lower pressure, in an integrated compartment of the deodorizer. Some refiners add a bit of sparge steam to improve deaeration.

Industrial deodorizers

Edible oil deodorization is performed industrially in different ways (continuous, semicontinuous or batchwise) with various configurations of deodorizers (horizontal or vertical vessels, tray-type or packed columns). Selection of the most appropriate process technology is mainly determined by the total plant capacity and the number of feedstock changes.

Batch deodorizers

Overall, batch deodorization has become less attractive because of its higher operating cost (higher steam consumption, low heat recovery) and longer processing time. However, for small-capacity plants (<50 tons/day) or plants that process smaller batches of varying quality (e.g. fish oil refiners), a batch deodorizer is still the best option. Apart from the lower capital cost, the main advantages of a batch deodorizer are the higher flexibility (process parameters can easily be adjusted according to the incoming oil quality) and the minimal intermixing between two consecutive batches.

Semicontinuous deodorizers

Semicontinuous deodorizers are basically batch systems designed for larger capacities. Their main application is in plants with frequent feedstock changes of oils sensitive to intermixing (e.g. plants producing margarine fats and shortenings). Heat recovery is effected by means of indirect economizers (e.g. thermosiphon systems, Fig. 4) which recover more heat than can be achieved in a batch deodorizer. The lower intermixing and the shorter time for feedstock changes are the main advantages of semicontinuous deodorizers over continuous deodorizers.

Continuous deodorizers

Continuous deodorizers are the best option for high-capacity plants running on a single feedstock (which is how most refining plants operate nowadays). The main advantages are the moderate investment costs, potentially high heat recovery and easy maintenance. An overview of the various configurations can be found in the literature [5,6].

Vertical tray-type deodorizers are the most commonly used type of continuous deodorizers. Their design is based on a series of trays (compartments) stacked vertically in a cylindrical shell with each tray designed for a specific task. All processes (heat recovery, final heating and cooling, deodorization) are combined in one single vessel. This single vessel concept allows an easier and less costly installation and maintenance and also gives a lower risk of unwanted air leakages.

Most edible oils are deodorized at high temperature (230-260°C), but there is a growing demand from oil processors to lower the heat load (residence time at higher temperature) during deodorization. This is especially required to minimize thermal degradation reactions (e.g. formation of *trans* fatty acids in soybean and canola oil, formation of glycidyl esters in palm oil). These negative thermal effects can be minimized by using packed columns or dual-temperature deodorizers (**Fig. 9**). These deodorizers operate at two different temperatures in order to reach the best compromise between required residence time for actual deodorization (longer time at lower temperature) and heat bleaching and stripping of volatile components (shorter time at higher temperature). The dual temperature concept has been successfully introduced on an industrial scale. Both the low/high temperature and the high/lower temperature concept can be applied.

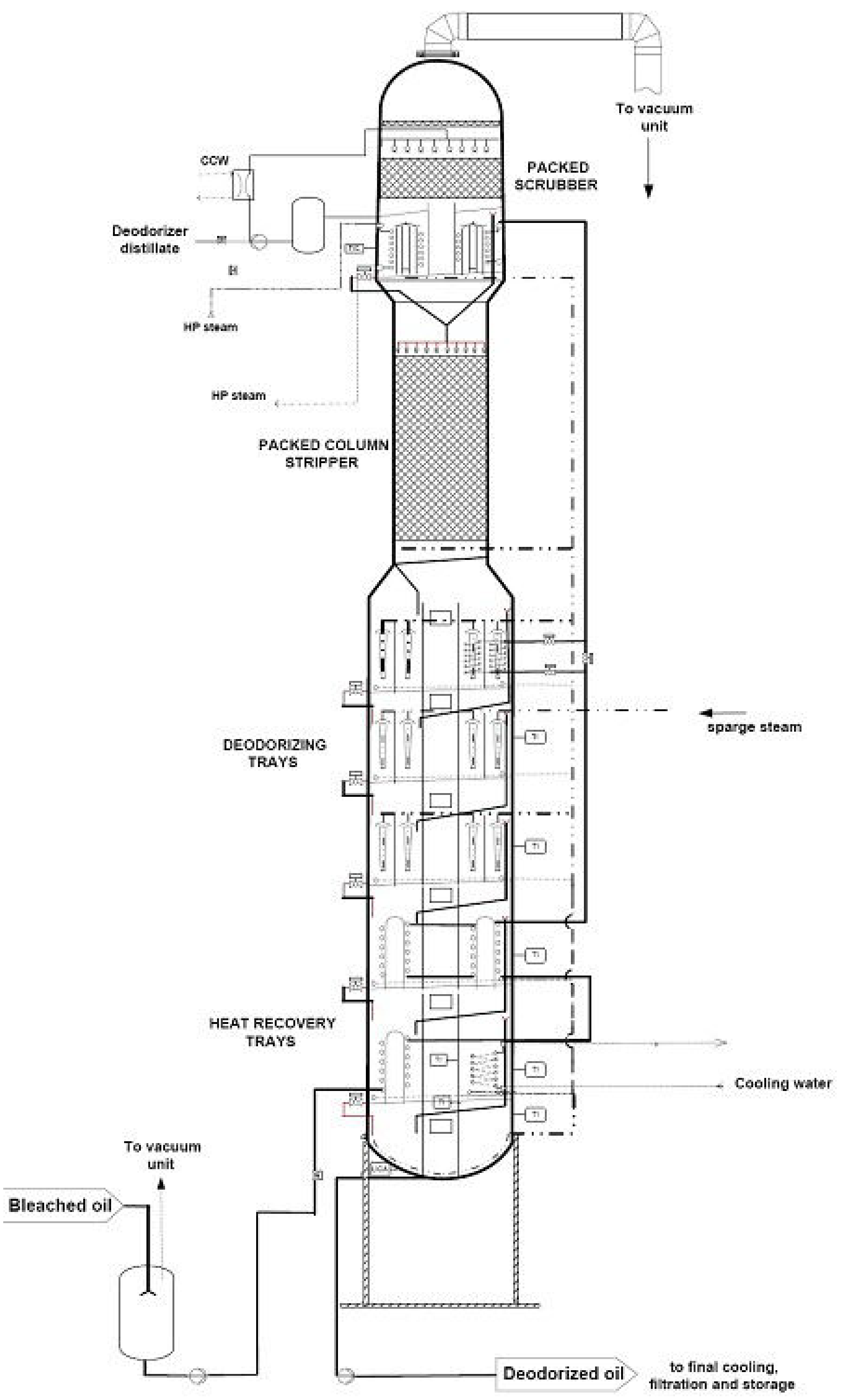


Figure 9.Dual temperature with packed column.

Lecture 14

Fractionation

In edible oil processing, a fractionation process consists of a controlled cooling of the oil, thereby inducing a partial, or ‘fractional’, crystallization. The remaining liquid (olein) is then separated from the solid fraction (stearin) by means of a filtration or centrifugation.

- Dry fractionation, also known as crystallization from the melt, is fractional crystallization in its most simple form, and the economy of the technology allows it to be used for production of commodity fats. Dry fractionation has long been regarded as an unpredictable, tedious and labor-intensive process. However, the relatively cheap dry fractionation technique has evolved to the modification technology of the 21st century [4], as without additives, polluting effluents or post-refining involved, the sustainability and safety of the process aresecond to none.
- Solvent fractionation, already patented in the 1950s, involves the use of hexane or acetone to let the high-melting components crystallize in a very low-viscosity organic solvent. This can be helpful with respect to the selectivity of the reaction, but mainly offers advantages in the field of phase separation: Much purer solid fractions can be obtained, even with a vacuum filtration. Being a more expensive process, it is less common than dry fractionation and only comes into the picture when a very high added value of (at least one of) the resulting fractions makes up for the high cost.

The Fractionation Plant Assembly

Figure 1 presents a general layout of a present-day dry fractionation process. Often multiple crystallizers are used in (overlapping) series. This is not only a matter of capacity, it is also in order to maximize the use of the filter; by a good planning of the crystallization times of filtration, the expensive (batch) filter should be in constant operation.

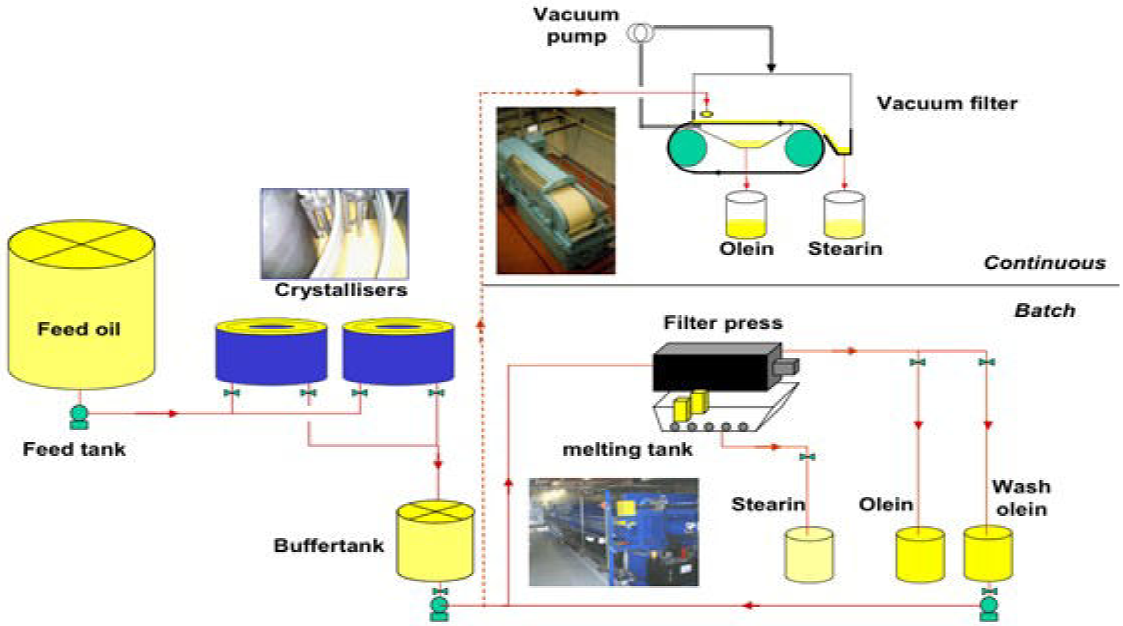


Figure 1. Layout of a typical dry fractionation process.

The reduction of dead time of a filter can also be established by means of a crystallized offer buffer tank; each crystallizer can be quickly drained and made ready to receive the next batch of oil, while the cooled buffer tank will send set volumes of crystal slurry to the filter, whenever it is ready. Continuous filtration systems have been a very elegant strategy in dry fractionation as well, although currently, the demand for purer solid fractions as obtained by filter chamber compaction has pushed continuous belt filters somewhat out of the dry fractionation market.

It should be kept in mind that fractional crystallization of a triglyceride oil is a relatively slow process and is therefore the time-determining stage; some simple fractionations can be established in about 5 hr crystallizer residence time, whereas more complex oils can require up to 3 days of cooling and crystal maturation before being sent to the filter.

Applications and Future Developments

In essence, the goal of fractionation is to create the biggest possible difference between two fractions. Palm oil is by far the most fractionated oil in the world. Given the broad spectrum of triglycerides and also its naturally high amount of palmitic acid that gives a fat 'body' at room temperature, the separation of palm oil into sharply defined fractions usually happens in a multi-stage process (**Fig. 2**).

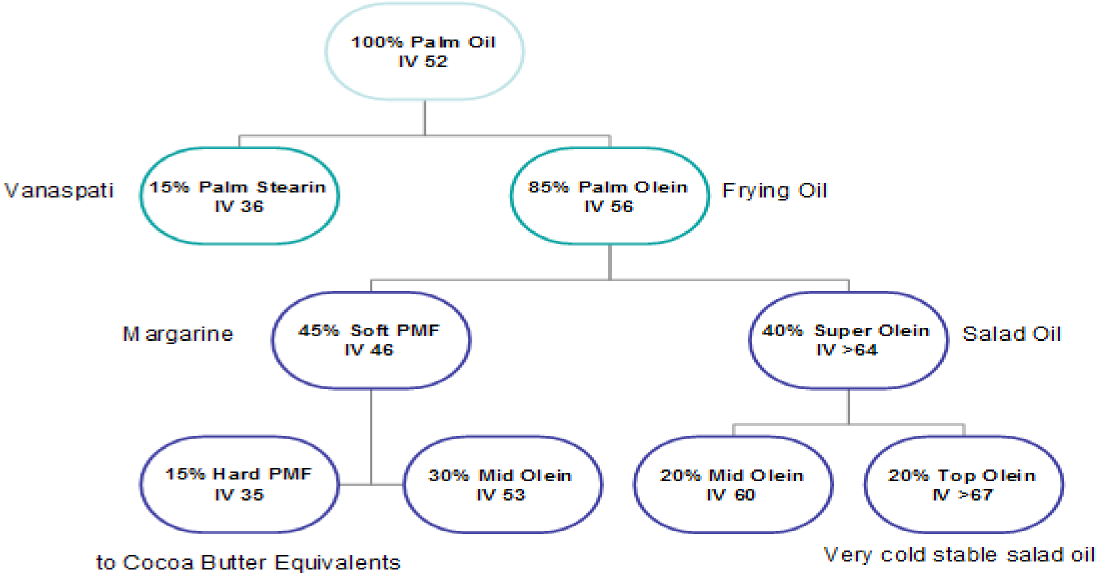


Figure 2.Multistage fractionation of palm oil with possible food applications for the various fractions.

The first step of dry fractionation of palm oil yields olein fractions with a cloud point below 10°C. The olein fractions are used as a substitute for soft oils in frying, cooking and salad oils or are being further fractionated. Together with a further development of single-stage palm oil fractionation by technological improvements, there is an increased tendency to execute a double or triple fractionation of palm oil in order to produce fractions with specific characteristics such as high IV superoleins (IV > 65) and hard palm-mid-fractions (hard PMF) (IV < 36).

The latter fraction can serve as a feedstock for the production of typical cocoa butter equivalents (CBE), which are non-lauric fats similar in their physical and chemical properties to cocoa butter. They are often prepared by solvent fractionation [7], though the more contemporary developments within dry fractionation (better suited crystallizers, improved separation technologies) are closing the gap between the quality of solvent- and dry-fractionated hard PMF.

Another technological field of interest is the use of plug flow reactors that allow the fractional crystallization in a continuous fashion, offering considerable reduction in operation costs (such as steam usage and cooling power). Indeed, just as in any other edible oil processing technology, there is a continuous quest for economization and process optimization. Heat recovery systems, crystal seeding installations, optimized mixing procedures and elegant plant layouts can all contribute to maximize capacity and minimize costs for a dry fractionation plant.

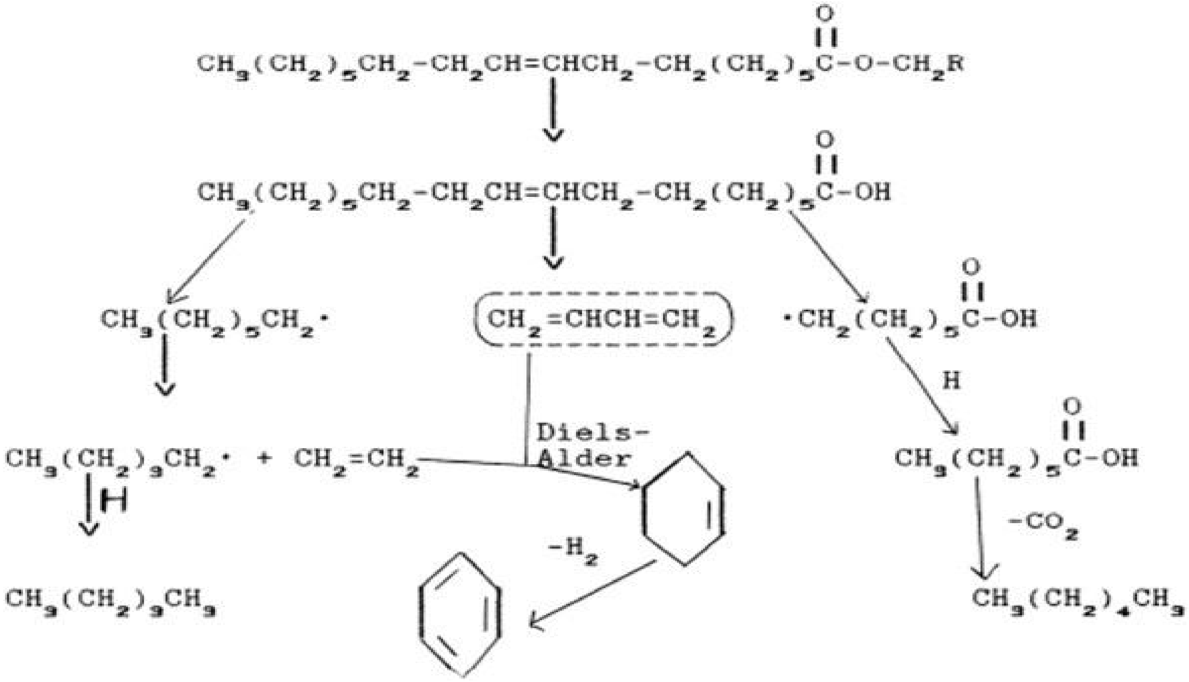
One final comment is that the process technologist should always remember that a fractionation process yields two products, and thus that the sum of the value of the two fractions should always exceed the processing cost and feedstock cost. This is why the feasibility of multistage fractionation is not only a matter of technological know-how, but also a matter of having markets for all 'by-products' generated along the way.

Lecture 15

Pyrolysis

The primary goal of this process is to study the thermal conversion of polyunsaturated fatty acids to hydrocarbon for use as renewable chemicals and fuels. Linoleic acid (*cis,cis*-9,12-octadecedienoic acid) was selected as a model polyunsaturated fatty acid. Batch pyrolysis reactions were conducted at temperatures from 350 to 450 °C for 0.5 to 8 h reaction times. Gas chromatography and mass spectrometry were used to analyze and identify products in the gas and liquid product fractions. Analysis of the gas phase showed concurrent production of CO and CO_2, indicating that deoxygenation reaction proceeded through both decarbonylation and decarboxylation mechanisms. The gas product encompassed alkanes and alkenes with carbon numbers ranging C1–C5 with ethane and propane as the major products. Analysis of the liquid fraction revealed series of *n*-alkanes, alkenes, cyclic alkanes and alkenes, and fatty acids. The presence of the unsaturation resulted in cracking at the allylic C C and predominance of C6 to C10 hydrocarbons and C9 and C10 fatty acids. This work uncovers the dominant reaction pathways in the pyrolysis of free polyunsaturated fatty acids and demonstrates the viability of this pyrolysis to produce renewable hydrocarbons immediately compatible with the existing petrochemical infrastructure.

It is necessary to utilize waste cooking oil as a raw material of biodiesel because the land area available for cultivation in Japan is limited. Waste cooking oil also includes long-chain saturated compounds and free fatty acids derived from animal fats. The former has a high freezing point and the latter forms a soap with the alkali catalyst typically used in biodiesel production, reducing the yield. To make waste cooking oil available for biodiesel production, pyrolysis of the waste oil was attempted. The resulting triacylglycerols were found to decompose at 360 to 390 °C, fatty acids were generated by cleavage of the ester bond, and short-chain hydrocarbons and short-chain fatty acids were generated by cleavage of the unsaturated bonds in the hydrocarbon chain. When the retention time was extended with a reaction temperature of 420 °C, light-oil hydrocarbons were generated by decarboxylation of the fatty acids. By adding palladium supported by activated carbon (Pd/C) as a catalyst, decarboxylation was promoted, and hydrocarbons comparable to light oil were selectively obtained in high yield at 85 wt.%. Compared to the biodiesel obtained by transesterification, the biodiesel obtained by pyrolysis showed improvement of about − 5 °C in the pseudo-cold filter plugging point.



Lecture 16

Rancidity is the complete or incomplete oxidation or hydrolysis of fats and oils when exposed to air, light, moisture or by bacterial action, resulting in unpleasant taste and odor. Specifically, it is the hydrolysis or autoxidation of fats into short-chain aldehydes and ketones, which are objectionable in taste and odor. When these processes occur in food, undesirable odors and flavors can result. In certain cases, however, the flavors can be desirable (as in aged cheeses). In processed meats, these flavors are collectively known as warmed-over flavor. Rancidification can also detract from the nutritional value of food, as some vitamins are sensitive to oxidation. Similar to rancidification, oxidative degradation also occurs in other hydrocarbons, such as lubricating oils, fuels, and mechanical cutting fluids.

Pathways

Three pathways for rancidification are recognized:[5]

Hydrolytic

Hydrolytic rancidity refers to the odor that develops when triglycerides are hydrolyzed and free fatty acids are released. This reaction of lipid with water may require a catalyst, leading to the formation of free fatty acids and glycerol. In particular, short-chain fatty acids, such as butyric acid, are malodorous.[6] When short-chain fatty acids are produced, they serve as catalysts themselves, further accelerating the reaction, a form of autocatalysis.[6]

Oxidative

Oxidative rancidity is associated with the degradation by oxygen in the air. The double bonds of an unsaturated fatty acid can be cleaved by free-radical reactions involving molecular oxygen. This reaction causes the release of malodorous and highly volatilealdehydes and ketones. Because of the nature of free-radical reactions, the reaction is catalyzed by sunlight.[6] Oxidation primarily occurs with unsaturated fats. For example, even though meat is held under refrigeration or in a frozen state, the poly-unsaturated fat will continue to oxidize and slowly become rancid. The fat oxidation process, potentially resulting in rancidity, begins immediately after the animal is slaughtered and the muscle, intra-muscular, inter-muscular and surface fat becomes exposed to oxygen of the air. This chemical process continues during frozen storage, though more slowly at lower temperature. Oxidative rancidity can be prevented by light-proof packaging, oxygen-free atmosphere (air-tight containers) and by the addition of antioxidants.[6]

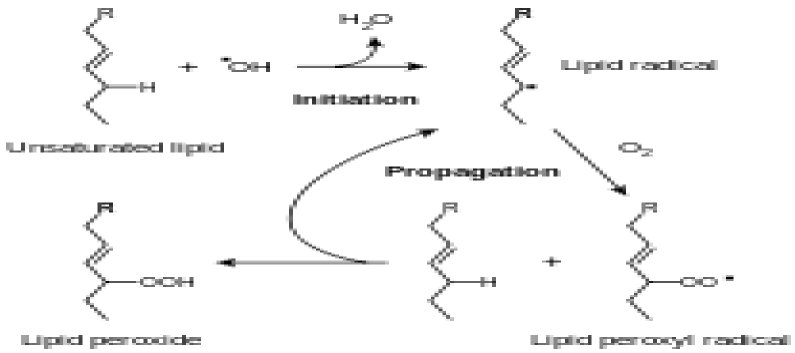
Microbial

Microbial rancidity refers to a process in which microorganisms, such as bacteria or molds, use their enzymes such as lipases to break down fat.[7] Sterilization can reduce this process.

Health effects

Consuming rancid food products is unlikely to cause immediate illness or harm, although rancidification can reduce the nutritional value of food by degradation of nutrients.[3]

Prevention



Antioxidants are often used as preservatives in fat-containing foods to delay the onset or slow the development of rancidity due to oxidation. Natural antioxidants include ascorbic acid (vitamin C) and tocopherols (vitamin E). Synthetic antioxidants include butylatedhydroxyanisole (BHA), butylatedhydroxytoluene (BHT), TBHQ, propyl gallate and ethoxyquin. The natural antioxidants tend to be short-lived,[8] so synthetic antioxidants are used when a longer shelf-life is preferred. The effectiveness of water-soluble antioxidants is limited in preventing direct oxidation within fats, but is valuable in intercepting free radicals that travel through the aqueous parts of foods. A combination of water-soluble and fat-soluble antioxidants is ideal, usually in the ratio of fat to water.

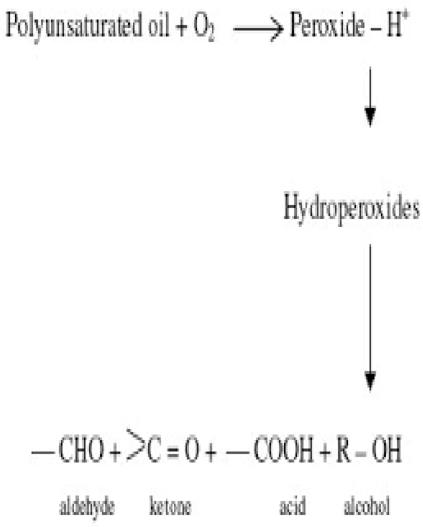
In addition, rancidification can be decreased by storing fats and oils in a cool, dark place with little exposure to oxygen or free radicals, since heat and light accelerate the rate of reaction of fats with oxygen. Antimicrobial agents can also delay or prevent rancidification by inhibiting the growth of bacteria or other micro-organisms that affect the process.[1]

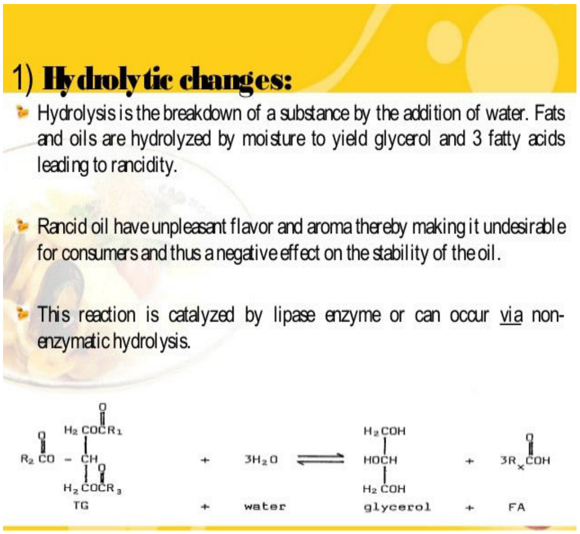
Oxygen scavenging technology can be used to remove oxygen from food packaging and therefore prevent oxidative rancidification.

Oxidative stability measurement

Oxidative stability is a measure of oil or fat resistance to oxidation. Because the process takes place through a chain reaction, the oxidation reaction has a period when it is relatively slow, before it suddenly speeds up. The time for this to happen is called the "induction time", and it is repeatable under identical conditions (temperature, air flow, etc.). There are a number of ways to measure the progress of the oxidation reaction. One of the most popular methods currently in use is the Rancimat method.

The Rancimat method is carried out using an air current at temperatures between 50 and 220 °C. The volatile oxidation products (largely formic acid[9]p. 47) are carried by the air current into the measuring vessel, where they are absorbed (dissolve) in the measuring fluid (distilled water). By continuous measurement of the conductivity of this solution, oxidation curves can be generated. The cusp point of the oxidation curve (the point where a rapid rise in the conductivity starts) gives the induction time of the rancidification reaction,[10] and can be taken as an indication of the oxidative stability of the sample.





1) **Hydrolytic changes:**

- Hydrolysis is the breakdown of a substance by the addition of water. Fats and oils are hydrolyzed by moisture to yield glycerol and 3 fatty acids leading to rancidity.
- Rancid oil have unpleasant flavor and aroma thereby making it undesirable for consumers and thus a negative effect on the stability of the oil.
- This reaction is catalyzed by lipase enzyme or can occur via non-enzymatic hydrolysis.

MODULE:III

Lecture:17

Plasticity

Fats can be spread, manipulated and shaped. Plasticity means the ability to be spread and shaped.

Seventy five (75) % of world edible oil is vegetable oil

- Shortening
- Margarine
- Mayonnaise
- Confectionary fat
- Less desirable for salad and frying oil, Why?

- **Slip Melting Point**

Official **AOCS (1989)** Method Cc **3-25. A** columnof fat **was** tempered at **10** C for **16** h in an open capillary tube. The tube wasthen heated slowly in a water bath until the fat column started to rise due tohydrostatic pressure. The temperature at which this occurs was determined asSMP using averaging of four replicates.

- **Solid Fat Content (Nuclear Magnetic Resonance, NMR)**

Hydrogenetion of oil

Definition : To treat oil with H_2 and catalyst to decrease double bonds and increase saturated bonds.

Reaction Result

Saturation of double bonds

Migration of double bonds

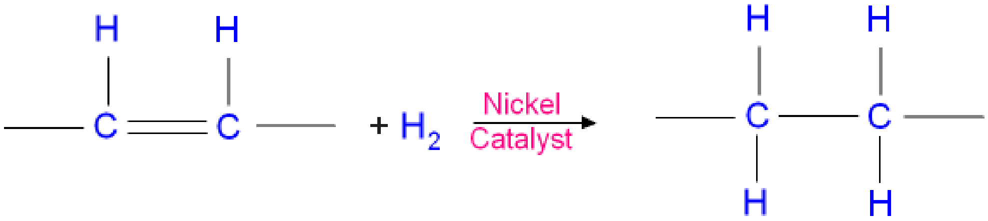
Trans-fatty acid formation

Advantages of Hydrogenation

Making fat suitable for manufacture of margarine, shortening, coating fats, cooking oil and salad dressing oil.

Hydrogenation Reaction Rate

- Nature of the substance to be hydrogenate (Oleic acid vs Linoleic acicd)
- The nature and concentration of the catalyst
- Pressure (reaction) – the concentration of hydrogen
- The reaction temperature
- The degree of agitation



Hydrogenation Steps of Oils

- Transfer and/or diffusion
- Adsorption
- Hydrogenation/isomerization
- Desorption
- Transfer

Transfer and Diffusion

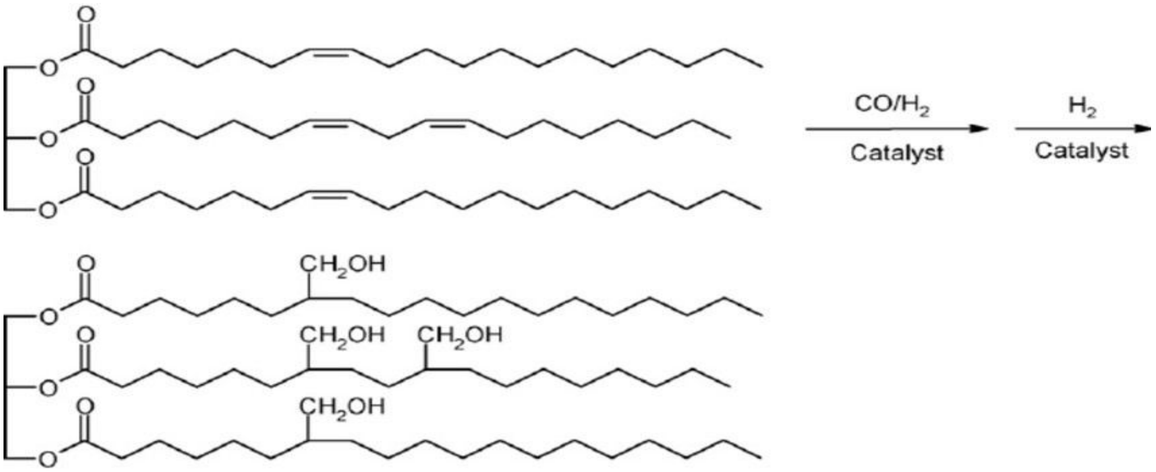
Transfer and adsorption steps are critical steps in controlling the degree of isomerization and selectivity of reactions.

Transfer: Transfer of reactants and products to and from the bulk of the liquid oil phase and outside surface of the catalyst.

Diffusion: Diffusion of reactant into the pores of the catalyst. Diffusion of products out of the pores of catalyst.

Lecture:18

Schematic Diagram of Hydrogenation



Hydrogen sources

For hydrogenation, the obvious source of hydrogen is H_2 gas itself, which is typically available commercially within the storage medium of a pressurized cylinder. The hydrogenation process often uses greater than 1 atmosphere of H_2, usually conveyed from the cylinders and sometimes augmented by "booster pumps". Gaseous hydrogen is produced industrially from hydrocarbons by the process known as steam reforming. For many applications, hydrogen is transferred from donor molecules such as formic acid, isopropanol, and dihydroanthracene. These hydrogen donors undergo dehydrogenation to, respectively, carbon dioxide, acetone, and anthracene. These processes are called transfer hydrogenations.

Substrates

An important characteristic of alkene and alkyne hydrogenations, both the homogeneously and heterogeneously catalyzed versions, is that hydrogen addition occurs with "syn addition", with hydrogen entering from the least hindered side.This reaction can be performed on a variety of different functional groups.

Substrates for and products of hydrogenation

Substrate	**Product**	**Comments**	**Heat of hydrogenation (kJ/mol)[4]**
$R_2C=CR'_2$	$R_2CHCHR'_2$	large application is production of	−90 to −130

(alkene)	(alkane)	margarine	
RC≡CR' (alkyne)	RCH$_2$CH$_2$R' (alkane)	semihydrogenation gives *cis*-RHC=CHR'	−300 (for full hydrogenation)
RCHO (aldehyde)	RCH$_2$OH (primary alcohol)	often employs transfer hydrogenation	−60 to −65
R$_2$CO (ketone)	R$_2$CHOH (secondary alcohol)	often employs transfer hydrogenation	−60 to −65
RCO$_2$R' (ester)	RCH$_2$OH + R'OH (two alcohols)	often applies to production of fatty alcohols	−25 to −105
RCO$_2$H (carboxylic acid)	RCH$_2$OH (primary alcohol)	applicable to fatty alcohols	−25 to −75
RNO$_2$ (nitro)	RNH$_2$ (amine)	major application is aniline[5][6]	−550

Catalysts

With rare exceptions, H$_2$ is unreactive toward organic compounds in the absence of metal catalysts. The unsaturated substrate is chemisorbed onto the catalyst, with most sites covered by the substrate. In heterogeneous catalysts, hydrogen forms surface hydrides (M-H) from which hydrogens can be transferred to the chemisorbed substrate. Platinum, palladium, rhodium, and ruthenium form highly active catalysts, which operate at lower temperatures and lower pressures of H$_2$. Non-precious metal catalysts, especially those based on nickel (such as Raney nickel and Urushibara nickel) have also been developed as economical alternatives, but they are often slower or require higher temperatures. The trade-off is activity (speed of reaction) vs. cost of the catalyst and cost of the apparatus required for use of high pressures. Notice that the Raney-nickel catalysed hydrogenations require high pressures:[7][8]

Catalysts are usually classified into two broad classes: homogeneous catalysts and heterogeneous catalysts. Homogeneous catalysts dissolve in the solvent that contains the unsaturated substrate. Heterogeneous catalysts are solids that are suspended in the same solvent with the substrate or are treated with gaseous substrate.

Homogeneous catalysts

Some well known homogeneous catalysts are indicated below. These are coordination complexes that activate both the unsaturated substrate and the H$_2$. Most typically, these complexes contain platinum group metals, especially Rh and Ir.

- Homogeneous hydrogenation catalysts and their precursors
- Dichlorotris(triphenylphosphine)ruthenium(II) is a precatalyst based on ruthenium.
- Crabtree's catalyst is a highly active catalyst featuring iridium.

- $Rh_2Cl_2(cod)_2$ is a precursor to many homogeneous catalysts.
- (S)-iPr-PHOX is a typical chelating phosphine ligand used in asymmetric hydrogenation.

Hydrogenation of propylene with Wilkinson's catalyst

Homogeneous catalysts are also used in asymmetric synthesis by the hydrogenation of prochiral substrates. An early demonstration of this approach was the Rh-catalyzed hydrogenation of enamides as precursors to the drug L-DOPA.To achieve asymmetric reduction, these catalyst are made chiral by use of chiral diphosphineligands.Rhodium catalyzed hydrogenation has also been used in the herbicide production of S-metolachlor, which uses a Josiphos type ligand (called Xyliphos). In principle asymmetric hydrogenation can be catalyzed by chiral heterogeneous catalysts,but this approach remains more of a curiosity than a useful technology.

Heterogeneous catalysts

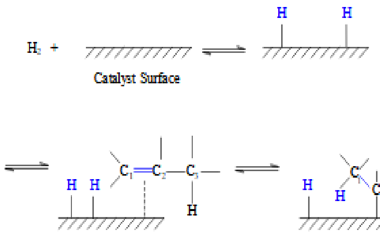
Heterogeneous catalysts for hydrogenation are more common industrially. In industry, precious metal hydrogenation catalysts are deposited from solution as a fine powder on the support, which is a cheap, bulky, porous, usually granular material, such as activated carbon, alumina, calcium carbonate or barium sulfate.[13] For example, platinum on carbon is produced by reduction of chloroplatinic acid*in situ* in carbon. Examples of these catalysts are 5% ruthenium on activated carbon, or 1% platinum on alumina. Base metal catalysts, such as Raney nickel, are typically much cheaper and do not need a support. Also, in the laboratory, unsupported (massive) precious metal catalysts such as platinum black are still used, despite the cost.

As in homogeneous catalysts, the activity is adjusted through changes in the environment around the metal, i.e. the coordination sphere. Different faces of a crystalline heterogeneous catalyst display distinct activities, for example. This can be modified by mixing metals or using different preparation techniques. Similarly, heterogeneous catalysts are affected by their supports.

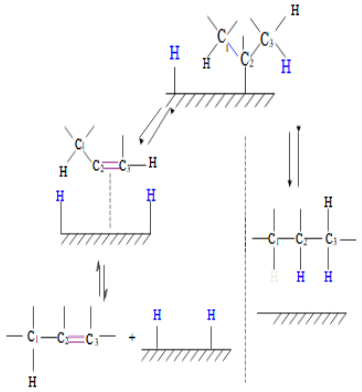
In many cases, highly empirical modifications involve selective "poisons". Thus, a carefully chosen catalyst can be used to hydrogenate some functional groups without affecting others, such as the hydrogenation of alkenes without touching aromatic rings, or the selective hydrogenation of alkynes to alkenes using Lindlar's catalyst. For example, when the catalyst palladium is placed on barium sulfate and then treated with quinoline, the resulting catalyst reduces alkynes only as far as alkenes. The Lindlar catalyst has been applied to the conversion of phenylacetylene to styrene.

Lecture:19

Schematic Diagram of Hydrogenation



Schematic Diagram of Hydrogenation



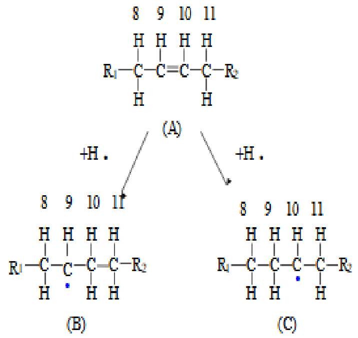
Schematic Diagram of Hydrogenation

Catalysis

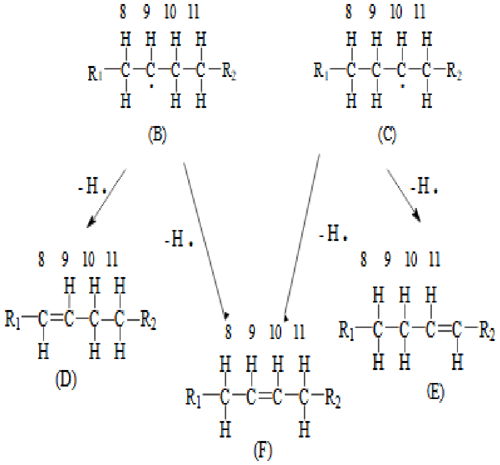
Oil + Catalyst → Oil-Catalyst Complex

Oil-Catalyst Complex + H_2 → Hydrogenated Oil + Catalyst

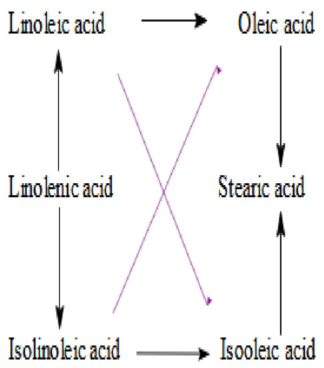
Formation of Double Bond Migration and Transisomers during Hydrogenation



Formation of Double Bond Migration and Transisomers during Hydrogenation



Hydrogenation Scheme



Linoleic acid

Oleic acid

Linolenic acid

Stearic acid

Isolinoleic acid

Isooleic acid

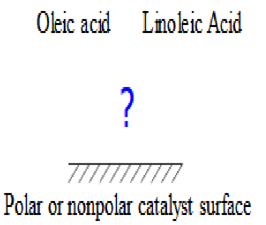
Selectivity

Preferential hydrogenation of more unsaturated acids with minimum formation of completely saturated fatty acids.

	Linoleic acid : Oleic acid
Very selective hydrogenation	50 : 1
Non-selective hydrogenation	4 : 1

Selectivity can be expressed as the ratio K_{LO}/K_O ; the relative rate of hydrogenation of linoleate to that of oleate.

Selectivity for Hydrogenation



The affinity of unsaturated fatty acids to catalyst through hydrogen bond. Geometric configuration and chemical and physical characteristics of catalyst will determine the selectivity of catalyst will determine the selectivity ration of different fatty acids.

Factors Affecting Hydrogenation

The Relationship between Process Conditions and their Effects on Selectivity Ratio, *Trans*-Contents, and the Rates of Reaction

	Selectivity Ratio	*Trans* Content	Reaction Rate
Temperature ↑	↑	↑	↑
Pressure ↑	↓	↓	↑
Agitation ↑	↓	↓	↑
Catalyst ↑	↑	↑	↑

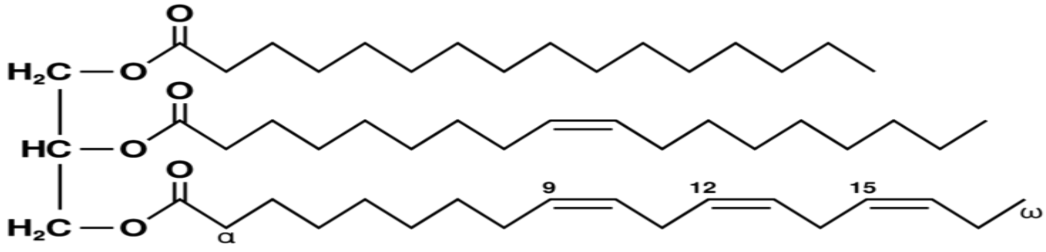
FACTORS AFFECTING HYDROGENATIO

Independent Variables		Dependent Variables
Pressure		Trans fatty acids
Temperature	⟶	Selectivity ratio
Agitation		Hydrogenation rate
Catalyst concentration		

Lecture:20

Esterification

Triglycerides are chemically tri **esters** of fatty acids and **glycerol**. **Triglycerides** are formed by combining **glycerol** with three fatty acid molecules. Alcohols have a hydroxyl (HO–) group. Organic acids have a carboxyl (–COOH) group.



Triglycerides are chemically tri esters of fatty acids and glycerol. Triglycerides are formed by combining glycerol with three fatty acid molecules. Alcohols have a hydroxyl (HO–) group. Organic acids have a carboxyl (–COOH) group. Alcohols and organic acids join to form esters. The glycerol molecule has three hydroxyl (HO–) groups. Each fatty acid has a carboxyl group (–COOH). In triglycerides, the hydroxyl groups of the glycerol join the carboxyl groups of the fatty acid to form ester bonds:

$$HOCH_2CH(OH)CH_2OH + RCO_2H + R'CO_2H + R''CO_2H \rightarrow RCO_2CH_2CH(O_2CR')CH_2CO_2R'' + 3H_2O$$

The three fatty acids (RCO_2H, $R'CO_2H$, $R''CO_2H$ in the above equation) are usually different, but many kinds of triglycerides are known. The chain lengths of the fatty acids in naturally occurring triglycerides vary, but most contain 16, 18, or 20 carbon atoms. Natural fatty acids found in plants and animals are typically composed of only even numbers of carbon atoms, reflecting the pathway for their biosynthesis from the two-carbon building-block acetyl CoA. Bacteria, however, possess the ability to synthesise odd- and branched-chain fatty acids. As a result, ruminant animal fat contains odd-numbered fatty acids, such as 15, due to the action of bacteria in the rumen. Many fatty acids are unsaturated, some are polyunsaturated (e.g., those derived from linoleic acid).

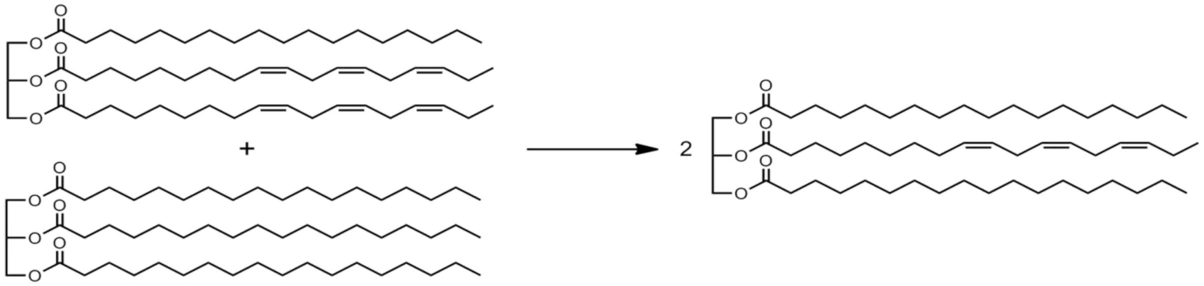
Most natural fats contain a complex mixture of individual triglycerides. Because of this, they melt over a broad range of temperatures. Cocoa butter is unusual in that it is composed of only a few triglycerides, derived from palmitic, oleic, and stearic acids in the 1-, 2-, and 3-positions of glycerol, respectively.

Inter-esterification:

Interesterified fat is a type of oil where the fatty acids have been moved from one triglyceride molecule to another. This is generally done to modify the melting point, slow rancidification and create an oil more suitable for deep frying or making margarine with good taste and low saturated fat content. It is not the same as partial hydrogenation which produces trans fatty acids, but interesterified fats used in the food industry can come from hydrogenated fat, for simplicity and frugality.

Chemistry

Fats such as soybean oil consist mainly of various triglycerides which are made up of a glycerol backbone esterified to three fatty acid molecules. The triglycerides contain a mixture of saturated, monounsaturated, and polyunsaturated fatty acids. Interesterification is carried out by blending the desired oils and then rearranging the fatty acids over the glycerol backbone with, for instance, the help of catalysts or lipase enzymes. Polyunsaturated fatty acids (PUFAs) decrease the melting point of fats significantly. A triglyceride containing three saturated fatty acids is generally solid at room temperature and not very desirable for many applications. Rearranging these triglycerides with oils containing unsaturated fatty acids lowers the melting point and creates fats with properties better suited for target food products. In addition, blending interesterified oils with liquid oils allows the reduction in saturated fatty acids in many trans fatty acid free food products. The interesterified fats can be separated through controlled crystallization, also called fractionation.

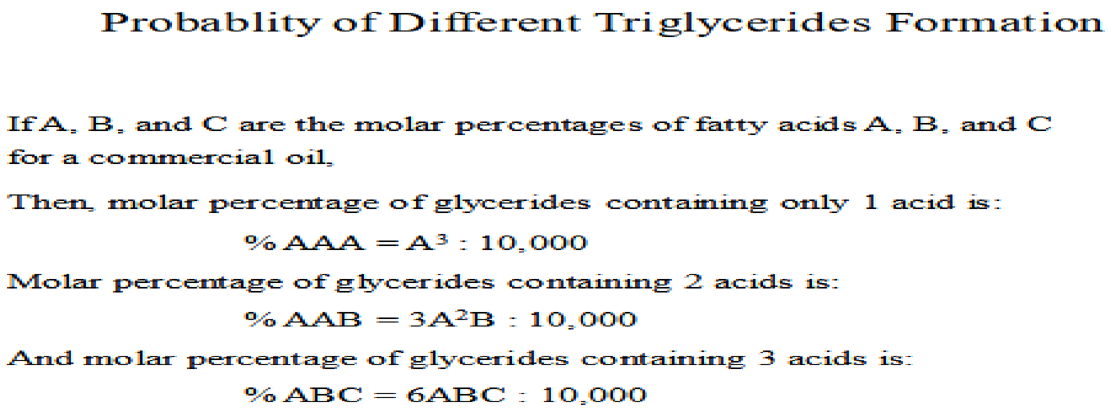


An example of interesterification: A triglyceride with two PUFA (linolenic acid) residues and a saturated one undergo interesterification toward two molecules containing one PUFA residue each.

In vegetable polyunsaturated oils, the PUFA is commonly found at the middle position (sn2) on the glycerol. Stearic acid is not usually found at sn2 in vegetable oils used in the human diet.

Lecture:21

Inter-esterification



Probablity of Different Triglycerides Formation

If A, B, and C are the molar percentages of fatty acids A, B, and C for a commercial oil,

Then, molar percentage of glycerides containing only 1 acid is:

$$\% AAA = A^3 : 10{,}000$$

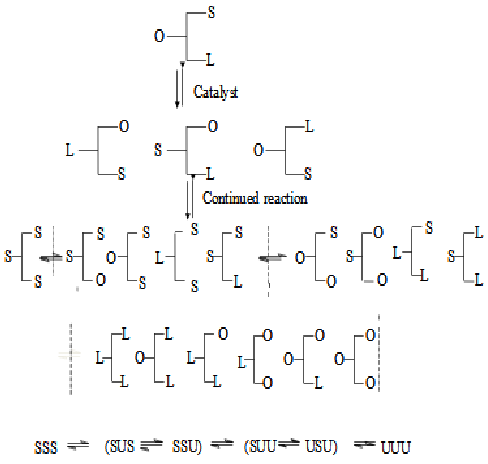
Molar percentage of glycerides containing 2 acids is:

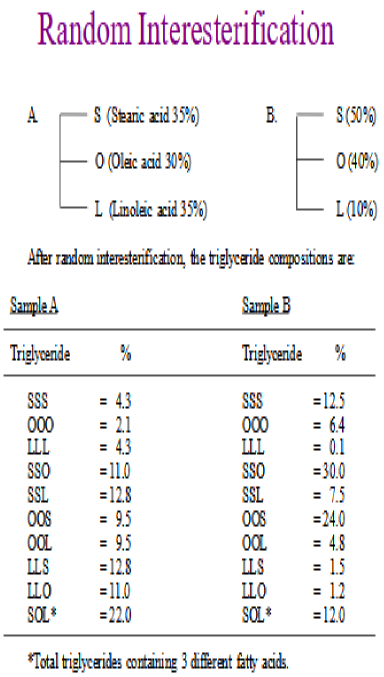
$$\% AAB = 3A^2B : 10{,}000$$

And molar percentage of glycerides containing 3 acids is:

$$\% ABC = 6ABC : 10{,}000$$

Intraesterification, Interesterification and Equilibrium Mixture.




Random Interesterification

A. S (Stearic acid 35%)
O (Oleic acid 30%)
L (Linoleic acid 35%)

B. S (50%)
O (40%)
L (10%)

After random interesterification, the triglyceride compositions are:

Sample A Triglyceride	%	Sample B Triglyceride	%
SSS	= 4.3	SSS	=12.5
OOO	= 2.1	OOO	= 6.4
LLL	= 4.3	LLL	= 0.1
SSO	=11.0	SSO	=30.0
SSL	=12.8	SSL	= 7.5
OOS	= 9.5	OOS	=24.0
OOL	= 9.5	OOL	= 4.8
LLS	=12.8	LLS	= 1.5
LLO	=11.0	LLO	= 1.2
SOL*	=22.0	SOL*	=12.0

*Total triglycerides containing 3 different fatty acids.

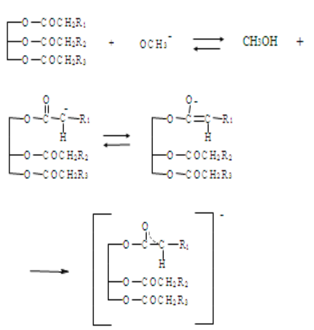
Catalysts

- High temperature catalysts: KOH and NaOH
- Low temperature catalysts: Sodium Methoxide (NaOCH

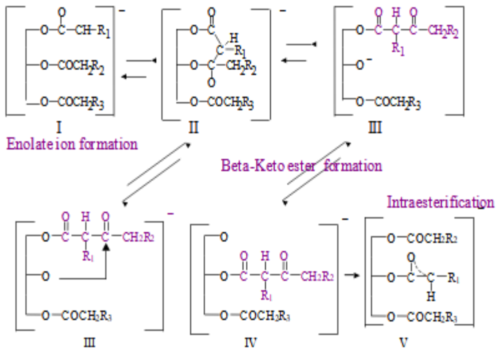
Reaction Mechanisms

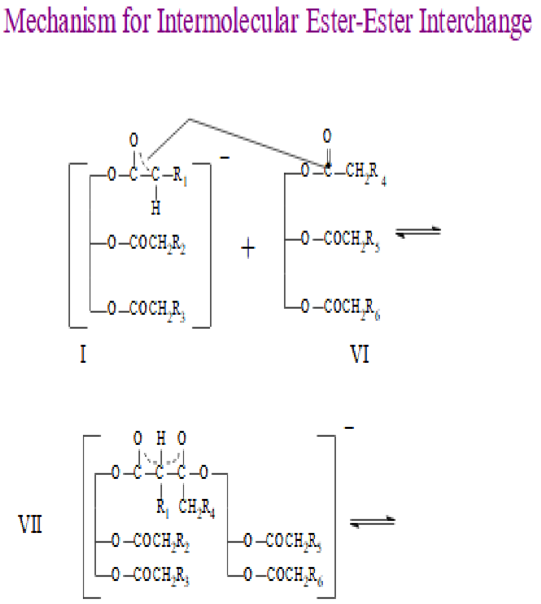
The formation of enolate ion
2. The formation of Beta-Keto ester
3. Interesterification

Enolate Ion Formation



Mechanism for Intramolecular Ester-Ester Interchange





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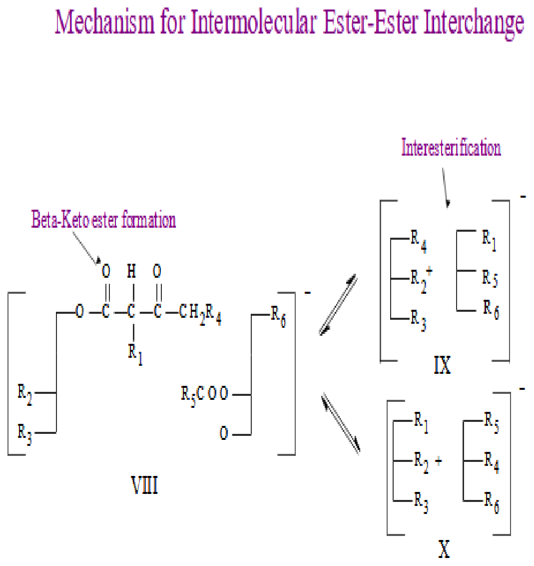

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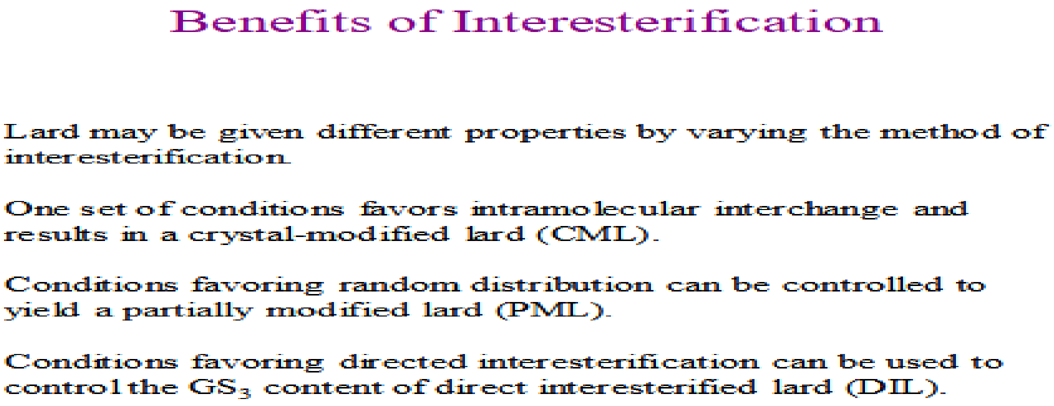


Benefits of Interesterification

Lard may be given different properties by varying the method of interesterification.

One set of conditions favors intramolecular interchange and results in a crystal-modified lard (CML).

Conditions favoring random distribution can be controlled to yield a partially modified lard (PML).

Conditions favoring directed interesterification can be used to control the GS_3 content of direct interesterified lard (DIL).

Lecture:22

Application of plastic fat in bakery, confectionery (including cocoa butter replacers)

Fats and oils are very important raw materials and functional ingredients for several food products such as confectionery, bakery, ice creams, emulsions, and sauces, shortenings, margarines, and other specially tailored products. Formulated products are made with just about every part of chemistry, but they are not simple chemicals. In general, they consist of several, and often many, components. Each of these components has a purpose. Most formulated products have a micro- or nano-structure that is important for their function, but obtaining this structure is often the big challenge. Due to a rise in overweight or obesity, health concerns have increased. This fact has led to the need to the develop products with low fat content, which have become a market trend. In addition, the development of new products using fat substitutes can be a good option for companies that are always trying to reduce costs or substitute *trans* fat or saturated fat. However, the successful development of these products is still a challenge because fat plays multiple roles in determining the desirable physicochemical and sensory attributes, and because the consumers who want or need to replace these ingredients, seek products with similar characteristics to those of the original product. Important attributes such as smooth, creamy and rich texture; milky and creamy appearance; desirable flavor; and satiating effects are influenced by the droplets of fat, and these characteristics are paramount to the consumer and consequently crucial to the success of the product in the market. Therefore, it is important to identify commercially viable strategies that are capable of removing or reducing fat content of food products without altering their sensory and nutritional characteristics. This paper intended to provide an overview about the role of fat in different food systems such as chocolate, ice cream, bakery products like biscuits, breads, and cakes considering the major trends of the food industry to meet the demands of modern society.

Cocoa butter (CB) is the byproduct of cocoa bean processing industry and is obtained from the mature bean from the *Theobroma cacao* plant. It is an important ingredient in the chocolate and other confectionery industries. It's valued for its unique physicochemical properties which is given by its peculiar fatty acid composition. The major triacylglycerols (TAG) present in CB is symmetrical and contains very less amount of highly unsaturated fatty acid. The major fatty acids present in it are palmitic acid, stearic acid, oleic acid and linoleic acid, but low amounts of lauric acid and myristic acid. Increasing demand and shortage of supply for CB, poor quality of individual harvests, economic advantages and some technological benefits have induce for the development of its alternative called cocoa butter replacer (CBR). In the CBRs the TAG compositions are similar but are not identical to genuine CB. Most of them are produced by either modification of natural fat or by their blending in different proportion. However, it couldn't satisfy the consumer and fulfill the demand of confectionery industries. This review gives a brief idea about the processing of cocoa pod, the production of cocoa butter and its composition with fats that are commonly used as its Replacers.

Lecture:23

Shortening is any fat that is a solid at room temperature and used to make crumbly pastry and other food products. Although butter is solid at room temperature and is frequently used in making pastry, the term "shortening" seldom refers to butter, but is more closely related to margarine.

Originally shortening was synonymous with lard, but with the invention of margarine by French chemistHippolyteMège-Mouriès in 1869, margarine also came to be included in the term. Since the invention of hydrogenated vegetable oil in the early 20th century, "shortening" has come almost exclusively to mean hydrogenated vegetable oil. Vegetable shortening shares many properties with lard: Both are semi-solid fats with a higher smoke point than butter and margarine. They contain less water and are thus less prone to splattering, making them safer for frying. Lard and shortening have a higher fat content compared to about 80% for butter and margarine. Cake margarines and shortenings tend to contain a few percent of monoglycerides whereas other margarines typically have less. Such "high ratio shortenings" blend better with hydrophilic ingredients such as starches and sugar.[1]

Hydrogenation of organic substances was first developed by the French chemistPaul Sabatier in 1897, and in 1901 the German chemist Wilhelm Normann developed the hydrogenation of fats, which he patented in 1902. In 1907, a German chemist, Edwin CunoKayser, moved to Cincinnati, Ohio, the home town of soap manufacturer Procter & Gamble. He had worked for British soap manufacturer Joseph Crosfield and Sons and was well acquainted with Normann's process, as Crosfield and Sons owned the British rights to Normann's patent.[2] Soon after arriving, Kayser made a business deal with Procter & Gamble, and presented the company with two processes to hydrogenate cottonseed oil, with the intent of creating a raw material for soap.[2] Since the product looked like lard, Procter &Gamble instead began selling it as a vegetable fat for cooking purposes in June 1911, calling it "Crisco", a modification of the phrase "crystallized cottonseed oil".

A triglyceride molecule, the main constituent of shortening

While similar to lard, vegetable shortening was much cheaper to produce. Shortening also required no refrigeration, which further lowered its costs and increased its appeal in a time when refrigerators were rare. With these advantages, plus an intensive advertisement campaign by Procter & Gamble, Crisco quickly gained popularity in American households. As food production became increasingly industrialized and manufacturers sought low-cost raw materials, the use of vegetable shortening also became common in the food industry. In addition, vast US government-financed surpluses of cottonseed oil, corn oil, and soy beans also helped create a market in low-cost vegetable shortening.

Crisco, owned by The J.M. Smucker Company since 2002, remains the best-known brand of shortening in the US, nowadays consisting of a blend of partially and fully hydrogenated soybean and palm oils.[4] In Ireland and the UK, Trex is a popular brand, while in Australia,Copha is popular, although made primarily from coconut oil.

Shortened dough

A short dough is one that is crumbly or mealy. The opposite of a short dough is a "long" dough or dough that stretches. Vegetable shortening (or butter, or other solid fats) can produce both types of dough; the difference is in technique. To produce a short dough, which is commonly used for tarts, the shortening is cut into the flour with a pastry blender, pair of table knives, fingers, or other utensil until the resulting mixture has a fine, cornmeal-like texture. For a long dough, the shortening is cut in only until the pea-sized crumbs are formed, or even larger lumps may be included. After cutting in the fat, the liquid (if any) is added and the dough is shaped for baking.

Neither short dough nor long flake dough is considered to be creamed or stirred batters.

Lecture:24

Margar*i*ne production process

In margarine manufacturing processes (see Figure 2 as an example of a margarine production process consisting of different unit operations) it has been observed that variations in rework flow, caused by variations in packaging capacity, and switching between pre-mix vessels cause temperature fluctuations in the process line. This is undesired as it leads to a non constant quality of the produced margarine.

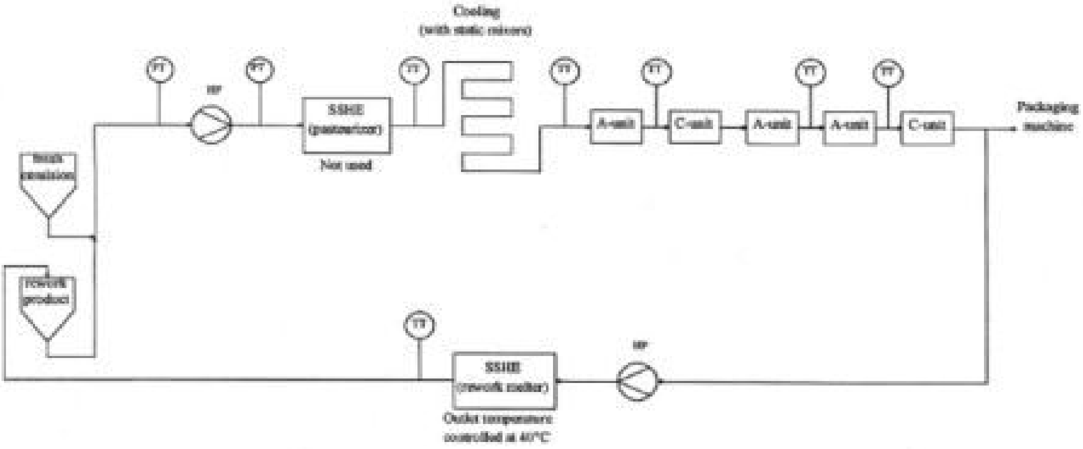
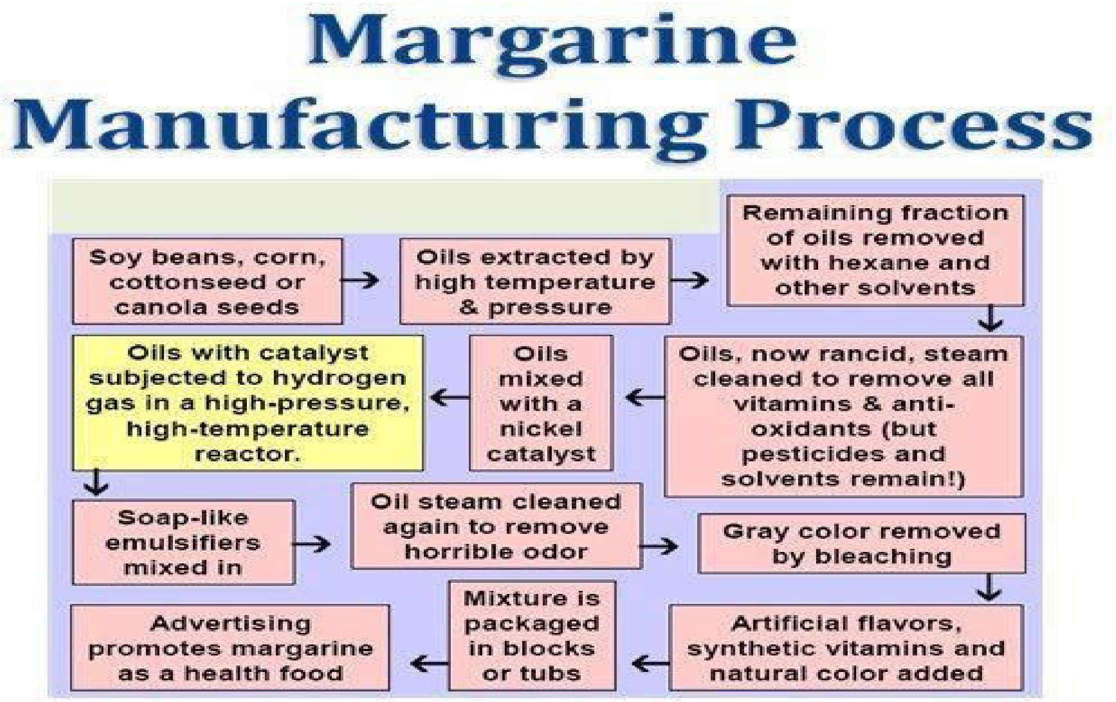


Figure 2. Margarine Processing Unit

To achieve a constant quality, knowledge of the process is necessary. Based on this knowledge acquired control strategies can then be designed and analyzed. The aim of the present work is to gain insight in the temperature variations of the margarine production process. Therefore a model describing the dynamic temperature behaviour in the total process is needed.



MODULE:IV

Lecture:25

By-products of fat/oil processing industries

Fats and oils are very important raw materials and functional ingredients for several food products such as confectionery, bakery, ice creams, emulsions, and sauces, shortenings, margarines, and other specially tailored products. Formulated products are made with just about every part of chemistry, but they are not simple chemicals. In general, they consist of several, and often many, components. Each of these components has a purpose. Most formulated products have a micro- or nano-structure that is important for their function, but obtaining this structure is often the big challenge. Due to a rise in overweight or obesity, health concerns have increased. This fact has led to the need to the develop products with low fat content, which have become a market trend. In addition, the development of new products using fat substitutes can be a good option for companies that are always trying to reduce costs or substitute *trans* fat or saturated fat. However, the successful development of these products is still a challenge because fat plays multiple roles in determining the desirable physicochemical and sensory attributes, and because the consumers who want or need to replace these ingredients, seek products with similar characteristics to those of the original product. Important attributes such as smooth, creamy and rich texture; milky and creamy appearance; desirable flavor; and satiating effects are influenced by the droplets of fat, and these characteristics are paramount to the consumer and consequently crucial to the success of the product in the market. Therefore, it is important to identify commercially viable strategies that are capable of removing or reducing fat content of food products without altering their sensory and nutritional characteristics.

Usually lipids are defined as a heterogeneous group of biological compounds almost insoluble in water but soluble in fats, hydrocarbon type and other fat solvents. Fats and oils are example of lipids and are composed largely of triglycerides with great importance in food systems, and they are formed by esters of a molecule of glycerol and three fatty acid molecules.

Fats and oils are important ingredients in a variety of foods. They confer desirable characteristics on several foods, contribute to tenderness to shortened cake, and by aerating batter, fats aid in establishing texture in cakes; they also add flavor to foods and influence the order in which components of flavor are released when foods are eaten, besides having a lubricating effect and producing a sensation of moistness in the mouth.

For consumers, textural attributes of fats that arise from their molecular states are of primary importance. Food texture is affected by fats by forming structures of crystalline networks and by disruption of structure by interfering with non-fat networks. Fats present polymorphism, an ability to exist in different crystal forms and the three major are α, β, and β' that differ in melting points.

The melting profile of the fat crystals play key roles in determining properties such as texture, stability, spreadability, and mouthfeel. The texture of products such as chocolate, shortenings, and especially butter is determined by the concentration, morphology, and interactions of fat crystals. Shortenings are fats that provide specific functional properties (softness, texture, mouthfeel, structural integrity, air incorporation, heat transfer, and shelf life increase) to pies, breads, pasta and others.

Important attributes such as smooth/creamy/rich texture, milky/creamy appearance, desirable flavor, and satiating effects are influenced by the droplets of fat. Therefore, it is important to identify commercially viable strategies that are capable of removal or reducing fat content of food products without altering their sensory and nutritional characteristics.

Lecture:26

Use of fat in chocolate products

Chocolate is enjoyed by people of all ages, socioeconomic classes, and gender and they can be defined as a suspension of solid particles derived from components such as sugar, milk, and cocoa solids in a continuous fat phase, which in turn contributes to the flavor, aroma, and color, in addition to providing form to the final product.

Primary chocolate categories are dark, milk, and white, and they differ in content of solid cocoa, milk fat, and cocoa butter. Dark chocolate, milk chocolate, and white chocolate contain 28, 30.7, and 30.9 % of fat respectively.

Of the different components in chocolate, the fat phase has the greatest influence on its quality. The fat phase affects the rheological properties of fluid chocolate, release from the mould, snap, gloss, prevention of bloom, melting properties, and flavor release. Milk fat and cocoa butter are the two main forms of fat used in chocolate manufacture to provide these properties.

Chocolate manufacturing process generally follows the common steps. Initially, the ingredients such as cocoa liquor, sugar, cocoa butter, and **skimmed milk powder** (depending on product category) are combined. Then, refining process takes place in a 2, 3, or 5-roll refiner. This is an important step to obtain a smooth texture required in current chocolate products, and the final particle size critically influences the rheological and sensory properties. Next, conching, which is normally carried out by agitating chocolate at more than 50 °C for few hours, takes place. One of the main aims of conching is to produce the optimum viscosity for the subsequent processing, and in this stage fat is very important. Finally, there is the tempering of mass, following the most commonly steps such as: complete melting, cooling to the point of crystallization, crystallization, and melting out of unstable crystals. The objective of tempering is to generate an adequate number of seed crystals to promote the total fat phase to crystallize in a more stable polymorphic form. This in turn will generate a more stable product and a better overall contraction. The most stable form crystals of cocoa butter, which is the form V, is achieved through of systems for heating/cooling (maintained at 35 °C).

Effect of different tempering (under-tempered, optimally-tempered, and over-tempered regimes) on the melting point and particle size in dark chocolate and found that the final structure and melting properties of dark chocolate is defined primarily by the fat crystallization behavior during tempering. With respect to the crystal size distribution (CSD), the under-tempered chocolate showed a broadening in CSD and increases in melting properties, whereas over-tempering caused moderate increases in CSD and melting properties. Under-tempered products showed re-arrangement and re-crystallization of unstable fat crystals to smaller numbers of larger agglomerates with formation of solid bridges between the crystalline network structures with no influence on crystallinity of products, at all temper regimes, the variations in particle size distribution.

Cocoa butter is a main ingredient responsible for the rheological behavior of chocolates. Addition of fat and lecithin in the conching and tempering phase covering the sugar and cocoa particles, reduced interactions and created more void space between them, which is filled with cocoa butter causing an action of lubrication, which involved a decrease in all rheological, textural, and thermal parameters at the end of the process.

Cocoa butter consists mainly of palmitic acid (C16), stearic acid (C18:0), Oleic acid (C18:1), and linoleic acid (C18:2), but it has low amount of lauric acid (C12) and myristic acid (C14). The constitution of fatty acids may be different depending on the location of production, and cocoa butter produced in Brazil has high amounts of linoleic acid (3.5-3.6 %) and minor amounts of stearic acid (33.3-33.8 %) compared with those produced in Ghana, Indonesia, Ecuador, and Malaysia. Brazilian cocoa butter also has around 34.5-36.5 % of oleic acid and 25.1-27.9 % of palmitic acid.

However, for the chocolate industry, cocoa butter is the raw material of high cost and in the leading countries of production, the price of cocoa is affected by weather, pests, and political factors. Coupled with the fact that there is a current trend in the food market to offer consumers low-fat foods and the challenge to reduce fat in chocolate is to find technological solutions to produce a system with increased solid volume fraction and acceptable flow properties, growing interest, in an alternative to cocoa butter.

Some vegetable fats are similar to cocoa butter in triglyceride composition, and cocoa butter equivalents (CBEs) can be added in any proportion to chocolate without causing a significant effect on texture. The use of alternative products depends on the similarity of their physical, chemical, and functional properties to those of cocoa butter; they do not form aneutetic mixture and reduce the product melting point.

Palm kernel and/or coconut oil have characteristics in terms of hardness, mouthfeel and flavor release similar to those of cocoa butter. However, these fats contain a high level of lauric fatty acids and a completely different triglyceride composition from cocoa butter resulting in a considerable degree of incompatibility with cocoa butter.

Milk fat and cocoa butter are the two main forms of fat used in chocolate manufacture. *Milk fat* is a complex mixture of triglycerides (98 %) and other minor lipid components. Milk fat and cocoa butter have different stable crystal forms, and therefore the two fats will not mix completely in the solid state. It changes the temperatures at which the various crystal forms and tends to slow the rate of cocoa butter crystallization in mixtures of cocoa butter and milk fat. Adding increased amounts of milk fat changes the physical and functional properties of chocolate including hardness, ability to temper, and melting point. To cause changes in the crystal forms of cocoa butter it is necessary to add around 50 % of milk fat. Butteroil is also considered.

However, so far, alternatives of cocoa butter fats that could meet the exact demand of cocoa butters have not been found yet. It is necessary to conduct further research on this subject to discover the alternatives of cocoa butter fat that could be able to fulfill the demands of cocoa butter fat.

There is a growing market demand for zero or low-fat food products; therefore, new ingredients and knowledge are needed in order to manipulate these types of product.

Another possibility to replace fat is the use of hydrocolloids.studied chocolate milk added with different levels of gelatin (5, 10 and 15 %) and found that chocolate with 15 % gelatin resulted in a fragile product and with sandy texture. In tests of sensory analysis, it was found the best medium for chocolate with 5 % gelatin, which in turn, had the lowest reduction in fat (3 %). Therefore, a more detailed study on this subject should be carried out in order to achieve a product with reduced fat content. The results showed an increase in hardness jointly with the increasing additional of gums as the development of gel networks. With respect to the melting point, the changes in the amount of cocoa butter had little and insignificant impact on melting profile.

Lecture: 27

The importance of fat in Ice cream

Colloidal dispersions are small particles in a phase (solid, liquid or gaseous) dispersed in another continuous phase, in which the surface properties of the phases exert a great influence on the structure as a whole. There are eight different types of colloidal dispersion that are classified as solid sol, solid emulsion, solid foam, sol, emulsion, foam, and two types of aerosol. Ice cream is a colloidal complex food, which contains fat globules, air bubbles, and ice crystals dispersed in an aqueous phase of high viscosity consisting of proteins, salts, sugars, and polysaccharides.Therefore, ice cream is simultaneously an emulsion (fat globules), a sol (ice crystals), and a foam (air bubbles). Ice cream usually contains about 30 % of ice, 50 % of air, 5 % of fat, and 15 % of sugar solution in volume; therefore, it is composed of all states of matter: solid (ice and fat), liquid (sugar solution), and gas.

An emulsion comprises two immiscible liquids (usually oil and water), with one liquid dispersed as spherical droplets in the other. The emulsions are thermally unstable systems that require energy to increase the surface area between the oil phase and water, maintaining the droplets dispersed in the continuous phase. The stability of the emulsion can be increased by adding surface active agents, called emulsifiers. Some emulsifiers such as yolk substitutes are included in most manufactured products due to the positive effect they have on the structure of the fats.

Sols are dispersions of solids in a liquid continuous phase, for example, ice crystals in ice cream, the pigment particles in the ink, soil particles in the slurry, the particles in the blood. Foam is a dispersion of gas bubbles in a continuous phase liquid. The solid and the gas are small particles dispersed in a continuous phase .

Many advances have been made in the ice cream processing in the last years, in such as the recognition of the importance of adsorption of interfacial material to the fat globule and formation of the fat globule membrane in terms of product behavior and ingredient functionality. In addition, microscopy techniques have been successfully applied to examine the structure of the product. Advances in rheology and their applications have also been made during this period. Thus, all technological advances and research have led to a more complete understanding of the importance of fat and the coalescence of fat globules and how to control it in ice cream.

The setting up of ice cream structure comes from the manufacturing process as well as from the various components used in the formulation. The importance of the structure of fat and colloidal aspects of the ice cream is now widely recognized. Fat appears to contribute largely to the properties of ice cream during freezing and whipping, through the partially coalesced continuous three dimensional network of homogenized globules helping in the air phase stabilization because fat globules surrounds air bubbles, and increased levels of fat aggregation are also correlated to improved melting resistance.

Fat is a multifunctional ingredient in ice cream and promotes flavor, color, texture and mouthfeel. A reduction of fat content in the ice cream can result in the loss of texture and sensory properties because fat is the main carrier of flavor for many compounds, and low flavor intensity may not be overcome by addition of flavoring alone. Fat is essential to explain the "dryness" of ice cream, shape retention, melting in the mouth, and textural creaminess, which is a highly desirable attribute that is contributed by milk fat.

Milk fat is determinant of the body of ice cream because it interacts with other ingredients developing texture, mouthfeel, creaminess, and sensation of lubricity. Typically, ice cream contains 10 to 16 % of fat, but in recent years, some ice cream manufacturers have reduced the amount of fat and replaced those fat solids with carbohydrates or proteins in order to create products that meet the demands of health-conscious consumers. It is essential to understand how to create corresponding structures of fats because a fat replacer should match the texture, mouthfeel, and functionality of the original fat and should convey the desired flavor profile.

Milk fat and vegetable fats can be replaced in order to reduce the fat content or to test new sources. Formulations with low fat or fat free are usually tested adding body agents to minimize the lack of fat in the structure. In addition, fat replacers have been tested due to the availability of new sources, to reduce costs, and to create new products.

The green coconut pulp has been studied as a possible ingredient in chocolate ice cream formulation. The substitution of fat resulted in a very similar product to standard ice cream and was approved by 93 % of participants in the sensory panel. The results of the physicochemical analyzes showed that the coconut pulp has foaming capability and emulsifying action which enables it to be used to produce ice cream, even at low pH values. The frozen product that does not contain milk solids is called Sorbet by law. However, with the composition of coconut pulp it was possible to produce a very similar product with the properties of the real ice cream. Fresh pulp is suitable for producing the "ice cream" because it has little odor and flavor, which makes it the appropriate ingredient to produce products with different flavors. Another positive factor is that the medium chain fatty acids predominate in the coconut pulp (especially lauric acid), which are considered beneficial to health.

A survey tested the quality and structure of ice cream formulations after the partial replacement of skimmed-milk powder for soy extract. The results showed an improvement in the protein content, pH, coefficient of consistency, and it also reduced carbohydrate. The formulations containing soybean extract exhibit improved melting resistance, greater amount of small crystals, and minor crystal growth after heat shock. A substitution of 20 % can be made without affecting the sensory acceptability.

Studies using inulin in ice cream with reduced fat have demonstrated positive results in the texture of the products. Samples containing 4 % and 6 % of inulin have showed the same standard viscosity of the sample. The texture evaluation showed that "low fat" and reduced fat ice cream had a similar response comparing with that of the standard sample. Samples with inulin showed similar consistency and viscosity to that of the standard sample, while samples made with whey protein isolate had higher viscosity than the standard, resulting in a very thick product.

In a study on the structure of blends/fats as substitutes for hydrogenated fats used in ice cream, same formulations were made by varying only the addition of hydrogenated fat, low *trans* fat, palm fat, or cupuassu fat. A product with Longan, a sweet fruit pulp that has components that are beneficial to health and is commonly used in Asian countries, has also been formulated in order to verify its structure and acceptance. Based on the results of the physicochemical and sensory analyzes, the study concluded that cupuassu fat was effective as a substitute for hydrogenated fat, with a similar profile to that of the standard formulation and a good melting profile. The ice cream made with fruit Longan produced a product with a 25 % reduction of sugar and had good acceptance and purchase intent in sensory analysis. However, the sample made with palm fat showed a significant difference between the formulations in the study of the rheology and had a worse melting profile. Another study showed that the use of palm fat instead of hydrogenated fat caused changes in the melting point of the ice cream formulations; it also investigated the use of oat extract as fat substitute in ice creams.

Improvements in product formulation to obtain lower fat ice cream are required to compensate the lack or the replacement of fat since changes to a food system can impart an imbalance in the flavor profile through various mechanisms. Hence, strategies have been studied by many researchers that have focused on producing highly palatable reduced fat ice cream that meets the demands of health conscious consumers, and there have been favorable results. The development of products with good acceptance and the perceived advances in this area are very positive for the consumer market, which is increasingly looking for healthier alternatives with higher added value.

However, ice cream has not followed the trend in consumption of low-fat products in U.S and Canada as it has been observed in other food categories. Contrary to this trend, in the last 20 years, the development of premium ice cream with around 12 % of fat and super premium ice cream with around 16 % of fat has increased. Healthier options have become popular in recent years in Canada since producers have introduced more all-natural, functional, low-fat, and low-calorie varieties. Smaller, multi-pack products for portion control have seen significant growth. According to the IDFA-International Dairy Foods Association (2012), premium ice cream, which tends to have lower amount of aeration and higher fat content than regular ice cream, is the most popular product among consumers according to a recent survey of U.S. ice cream manufacturers. In this survey, 79.3 percent cited premium ice cream as the most popular product, while 10 percent said that novelties are most popular. Novelties are defined as separately packaged single servings of a frozen dessert, such as ice cream sandwiches and fudge sticks.

Lecture 28

The role of fat in biscuits

Biscuits are one of the most popular bakery items consumed all over the world, and they can be defined as small products from a dough or batter whose mainly ingredients are flour, fat, sugar, milk, water, eggs, and salt and that is viscous enough to allow the pieces of dough to be baked on a flat surface. They come in an infinite variety of sizes, shapes, texture, composition, tenderness, tastes, and colors.

In the formulations of biscuits, sugars and fats appear in large amounts, while moisture content appears in low proportions (1-5 %). Fat functionality is very important in baked products, and it is responsible for tenderness and overall texture of the final product improving mouthfeel, structural integrity, lubrication, incorporation of air, heat transfer, and extended shelf life.

All cookie fillers have the same basic ingredients in order of prominence, sugar, shortening, salt, flavor, and lecithin. The filler consistency and eating character are determined to a large extent by the shortening used. The requisites for a good sandwich cookie or wafer filler shortening have been identified as: Quick getaway in the mouth, oxidative stability, and others.

In cookie production, plastic shortening is creamed with sugar to incorporate air bubbles that are trapped in the liquid phase of the shortening. While the liquid phase is necessary for air incorporation, fat crystals have a structural role and retain air at the end of mixing and during early baking stages.

The fats used for the production of cookies need to be at room temperature on solid or semisolid state to facilitate handling of the batter during the manufacturing, which implies an increase in the content of saturated fatty acids (SFA).

Epidemiological studies have identified the consumption of trans fatty acids (TFAs) as a risk factor in the development of cardiovascular disease .

In order to be effective, shortenings must have plastic properties which are, in turn, exemplified by the correct solid-to-liquid index at dough mixing temperature. High Solid Fat Index (SFI) shortenings do not have enough oil volume for adequate aeration, and low SFI shortenings do not have the ability to hold the air until mixing is complete (O'Brien, 2009).

Another characteristic of fat is its crystalline nature. The three basic polymorphs are designated α, β, and β' (Marangoni et al., 2012). It is essential for the fat to be in the β' crystal form to promote optimum creaming (Wilderjans et al., 2013). Utilization of emulsified bakery shortening helps in the fine dispersion of the fat in the batter or dough system as compared to non-emulsified shortenings (Jacob &Leelavathi, 2007).

Decreasing the amount of fat added to biscuits is a good way to obtain a healthier and lower-calorie product. The effect of partial replacement of fat by different fat replacers on the quality of biscuits has been studied by different authors (Bertolin et al., 2013).

Fat mimetics are substances of carbohydrate or protein origin which can be used in some foods to imitate the functional and sensorial properties of fat (Zoulias et al., 2002).

Rodríguez-García et al. (2013) evaluated the effects of inulin as fat replacer on short dough biscuits and their corresponding dough. A control formulation, with no replacement, and four formulations in which 10, 20, 30, and 40 % of shortening was replaced by inulin were studied. It can be concluded that shortening may be partially replaced, up to 20 %, with inulin. These low fat biscuits are similar to the control biscuits, and they can have additional health benefits derived from inulin presence.

Jacob &Leelavathi (2007) studied the effect of four different fat types on the rheology of the cookie dough, and the consequent effects on the cookie quality using emulsified bakery shortening, margarine, non-emulsified vegetable hydrogenated fat, and sunflower oil. Measurement of the breaking strength showed that cookies containing the oil were the hardest. On the other hand, breaking strength of cookies containing the other three types of fats was not significantly different from each other.

Lecture 29

The influence of fat in cake

Bakery products are among the most consumed products in the world. Among them, cakes are popular and associated by the consumers as tasty products with particular sensory characteristics (Matsakidou et al., 2010).

Cake batter can be considered as an oil-in-water emulsion (O/W) containing dry ingredients such as sugar, flour, milk powder, salt, and yeast, suspended or dissolved in the continuous aqueous phase (Ronda et al., 2011; Sakiyan et al., 2004).

The cake quality is related to its aerated structure, which is formed by the incorporation of air during whipping as well as the development of bubbles during cooking. Batters with a low viscosity trap air during whipping, which leads to a cake with a low volume expansion (Psimouli&Oreopoulou, 2011).

The role of fat in manufactured cakes and bakery products in general is very important both from the technological point of view and the sensory point of view. Many bakery products require a relatively high fat content, as reported by Sowmya et al. (2009). According to Zhou et al. (2011), shortenings have numerous functions in bakery products; among them are: texture, softness, structure integrity, mouthfeel, lubrication, air entrapment, heat transfer, and extended shelf life.

In many systems like cake batters, the air bubbles are incorporated by the action of fat in whipping cream method, where such bubbles are trapped in the continuous phase of the emulsion, at room temperature (Jacob &Leelavathi, 2007; Goldstein &Seetharaman, 2011; Wilderjans et al., 2013), rather than remain in the aqueous phase. However, as the batter is heated during cooking, these air bubbles are transferred from the fatty phase to the aqueous phase structure providing a voluminous and foamed structure after cooking. The baking powder releases carbon dioxide when heated. The gas formed exerts great pressure on the mixture, resulting in increased volume in the final product (Indrani&Rao, 2008; Cauvain, 2003a).

Several studies have been carried out to reduce fat in baked goods, especially in cakes due to the great amount of this raw material in its formulation, especially the *trans* fatty acids present in some formulations.

Trans fatty acids (TFAs) are strongly correlated with an increased risk of many diseases, among them cardiovascular disease (Ansorena et al*.,* 2013).

There are many researches in favor of replacements of hydrogenated vegetable fats in cakes. These substitutions may vary in their ingredients, and this replacers come from lipids (Sowmya et al., 2009), fibers (Lee et al., 2011) and hydrocolloids (Zambrano et al., 2005; Gómez et al., 2007).

Martínez-Cervera et al. (2012) evaluated the effects of partial replacement of fat by cocoa fiber in chocolate muffins. This study evaluated the sensory characteristics of the final product and showed great difficulty in chewing and swallowing the cake when high cocoa fiber content was added. The bitter taste and the decrease of viscosity were also reported.

In a study conducted by Kumari et al. (2011), the authors used two vegetable oils, namely sunflower oil (SFO) and coconut oil (CNO), emulsifiers, and hydrocolloids in pound cakes to evaluate their rheological properties, fatty acid profile, and quality characteristics (texture, color, specific gravity, volume, and sensory analysis) using hydrogenated vegetable fat in the formulation as the control cake. The results of the fatty acid profiles of cakes showed the presence of 48.9 % of lauric acid in the formulation made with coconut oil in comparison to that of hydrogenated vegetable fat (1.2 %). Pound cake formulated with oil resulted in a decrease in batter viscosity, cake volume, and overall quality score. Cakes made with emulsifiers and oils showed improvements in their characteristics. The authors concluded based on these results that cakes with reduced fat showed better fatty acid profile and quality characteristics similar to those of the control cake can be prepared by replacing hydrogenated fat with SFO or CNO.

Lee et al. (2011) studied the effects of β-glucans in cake batters and analyzed texture, color, and volume obtaining satisfactory results as high volume, viscosity, and texture. Texture values were higher than the those of the control cake, whose formulation did not contain β-glucan. Therefore, it was is concluded that the application of these fibers does not degrade the quality parameters of the final product.

Gularte et al. (2012) conducted a study to investigate the effect of different fibers added individually or combined to improve the functional properties of gluten-free layer cakes. The authors applied mixtures of soluble and insoluble fiber in the formulations and obtained better results with the formulations containing oat cakes and inulin than those with oat and guar gum. In all formulations, cake acceptability was related to its specific volume.

Lee et al. (2005) evaluated the physical and rheological properties of cakes using the fat substitute Oatrim®, which is a product obtained by enzymatic hydrolysis of oat flour rich in soluble fiber (β-glucan). The formulations containing fat replacements at 20 % showed no significant differences ($p > 0.01$); softness exhibited properties similar to those of the control without loss in the quality of the final product. There were no significant changes in relation to specific gravity, volume, and rheological properties in formulations with 40 and 60 % substitution.

Salas &Lannes (2010) evaluated the application of fats and margarine on texture and volume of chocolate cakes and showed that these parameters depend on the type of fat base used in the formulation. Rios &Lannes (2012) studied the influence of different fats in cake batter such as vegetable fat, margarine, and soy oil in textural parameters, such as yield value and compression force, showing that they can be considered for the industry very important parameters pointing the need of less energy in processes of pumping to lower the values of these parameters, for example.

Lecture 30

Biodiesel is a well-known renewable commodity. It is composed of fatty acid methyl esters (FAMEs) and its quality and use are covered by several regulations (Lois, 2007; Demirbas, 2009; Lapuerta*et al*., 2008). The production cost for biodiesel is still high compared to diesel fuel (El Bassam, 2010; Berrios*et al*., 2010; Usta*et al*., 2005; Lam *et al*., 2010; Chongkhong*et al*., 2007; Naima and Liazid, 2013), but this can be expected to decrease in the future. More than 75% of the production costs of biodiesel are due to the costs of the raw materials (Ramadhas*et al*., 2004; Lam *et al*., 2010; Rivera *et al*., 2009; Bao-Xiang *et al*., 2008).

Crude vegetable oil is mainly composed of triacylglycerols, but also contains numerous non-edible compounds that need to be removed by a refining process prior to human consumption. For the refining of crude vegetable oils there are two main routes, the chemical and the physical refining.

Some by-products of low commercial value are obtained from these refining processes (Ching*et al*., 2008; Haslenda and Jamaludin, 2011). Important amounts of by-products such as soapstocks (SS), deodorizer fatty acid distillates (FAD) and acid oil (AO) are produced from the oil refining processes. These by-products are harmful to the environment if they cannot be used for any beneficial or industrial activity.

On the other hand, due to the rising world population, the consumption of refined vegetable oils will also increase, resulting in an increase in the production of these by-products. The use of byproducts for biodiesel production is a very good alternative for cost reduction of biofuel production and to solve related environmental problems (Fan and Burton, 2009; Yujaroen*et al*., 2009; Yu *et al*., 2010; Dias *et al*., 2013). This way, the ethical discussion about the competition of land use for food production against energy production (El Bassam, 2010; Balat, 2011) through biofuels can also be avoided (Budiman*et al*., 2012; El Bassam, 2010; Nigam and Singh, 2010).

The scope of this paper is to analyze the state-ofthe-art for obtaining biodiesel from three less used by-products of the refining oil industry (soapstock, acid oil and fatty acid distillate) and their use in internal combustion engines. Although some previous reviews were published (Gunawan and Yi-Hsu, 2009; Dumont and Narine, 2007) these were focused only on one or two of these by-products and the analysis of reports of their use in internal combustion engines was not included, although the main task is to produce energy in a diesel engine. Another motive for including the engines test results in the study is that the biofuel physical properties strongly influence the engine's behavior (Mesquita*et al*., 2012). The updating of these topics is also necessary to cover the recent published results and trends.

VEGETABLE OIL REFINING

Chemical refining is the most widely used technique to purify vegetable oils since it successfully decreases the level of free fatty acids (FFAs), phospholipids, waxes, aldehydes, and ketones among other components; physical refining is also widely used.

Physical refining is preferred as it reduces the loss of triglycerides, minimizes chemical usage and water consumption, and enables the recovery of high quality FFAs, which leads to considerable reduction of the environmental impact. Investigation of the suitability of lower value lipids, primarily animal fats and waste greases, as feedstocks for biodiesel production has also been reported (Haas *et al*., 2001; Haas *et al*., 2003; Chongkhong*et al*., 2007; Chongkhong*et al*., 2009). In order to convert the waste by-products from the oil refining process to biofuels under good yield conditions and reasonable industrial costs, different physico-chemical techniques are modified or developed.

ESTERIFICATION AND TRANSESTERIFICA-TION REACTION

Most oil refining and biodiesel plants use the conventional sodium hydroxide/sodium methoxide and/or sulfuric acid based transesterification processes. This chemical esterification process would be the most convenient to use for conversion of by-products to biodiesel. The primary purpose of the transesterification is to reduce the oil viscosity (Demirbas, 2008; Ranganathan*et al*., 2008).

The technological challenge in the use of these by-products as a feedstock for biodiesel production is the same as using waste greases or other materials containing FFAs: the alkaline transesterification typically employed to synthesize esters is ineffective at esterifying FFAs. A dual reaction approach is therefore required (Haas, 2005).

Acid catalysts are too slow to be practical for converting triglycerides to biodiesel (Canakci and Van Gerpen, 1999; Canakci and Van Gerpen, 2001); however, acid catalysts are quite effective at converting FFAs to biodiesel. Therefore, an acid-catalyzed pretreatment step to convert the FFAs to esters, followed by an alkali-catalyzed step to convert the triglycerides should provide an efficient method to convert high FFAs to biodiesel (Canakci and Van Gerpen, 2001; Bao-Xiang *et al*., 2008; Boonnoun*et al*., 2008; Usta*et al*., 2005; Kartina, 2011; Chongkhong*et al*., 2007). The more suitable alcohol for the esterification reaction is methanol (MeOH) due to economic reasons, but ethanol is also used (Marchetti, 2011).

The FFAs and water content affect the production of biodiesel (Van Gerpen, 2005). The oil acid value should be less than 1 mg KOH/g and the raw materials should be anhydrous (water content < 0.3%). If these requirements are not met, it is still possible to produce biodiesel, but the yield of the reaction is reduced due to the deactivation of the catalyst and the formation of soaps.

USE OF BY-PRODUCTS OF THE OIL REFINING INDUSTRY TO PRODUCE BIODIESEL

Three main by-products from the oil refining industry are obtained, as observed in Figure1. Soapstocks, acid oil and fatty acid distillate represent low value by-products but, according to the composition, they are suitable for the production of biodiesel, adding value to them and a higher efficiency to the vegetable oil refineries.

The concept of reaching zero-waste with regards to utilization of by-products generated in palm oil refineries was applied to the palm oil industry (Haslenda and Jamaludin, 2011). The authors explored the capability of the oil industry to use the residual soapstock and the fatty acid distillates to produce biodiesel, but also for other industrial applications such as the production of animal feed, lubricants and soaps.

Soapstock

Soapstock emerges from the refining process when oil is treated with a dilute alkali solution separating the FFAs as soaps. This wet lipid mixture (Dumont and Narine, 2008; Haas *et al*., 2000; Dumont and Narine, 2007) is separated from the crude oil by centrifugation. It is generated at a rate of about 6% of the input of oil entering the refining operation (Haas *et al*., 2003) and its cost represents 1/10 of the refined oil cost (Kanthavelkumaran and Seenikannan, 2012).

Soapstock is quite alkaline, with pH values between 10-11 (HaasBloomer, 2000; Haas, 2005; Young-Moo *et al*., 2010). This residual is also referred to as residual oleins (Pereda*et al*., 2003) and has poor commercial value, but can be used as an ingredient in animal feed (Haslenda and Jamaludin, 2011; Ching*et al*., 2008). It is a mixture of triglycerides of fatty acids and of the same free fatty acids.

Its physico-chemical properties tend to change with the type of vegetable oil source, seed processing, handling and storage conditions (Dumont and Narine, 2007). Soapstock can be solid (Reaney, 2002; Keskin*et al*., 2008; Haas *et al*., 2001) or liquid; it is also referred to as an emulsified aqueous mixture of glycerides and FFAs (Phillips and Leavens, 1978; Haas *et al*., 2003). The emulsion can contain about 50% of water (Haas, 2005; Young-Moo *et al*., 2010).

The first attempt at soapstocks characterization dates from 1987 (Waliszewski, 1987). The analysis of fatty acids in this matrix is not an easy procedure, because a wide polarity range can be present in it (Dumont and Narine, 2007). The first complete characterization of soapstock from cottonseed was reported in 1996 (Dowd, 1996).

A two-step method for the production of biodiesel from soapstock was initially presented by Haas and Scott (1996), but achieved only an 81% yield. Afterwards, Haas presented a new approach for obtaining biodiesel from soapstock (Haas *et al*., 2000) proposing a lyophilization step to remove the water content and a saponification of the soapstock before the esterification reaction. To assure the total saponification, a minimum addition of 14.6% of NaOH was needed and the reaction took 5 h. Haas reported a yield of 60% of the theoretical amount of product, which is not a good yield compared to other methods.

A three-step method was developed by Jin *et al*. (2008) for producing biodiesel from a mixture of oil sediments and soapstocks. In the first step, the mixture was extracted with ethyl ether and divided into three phases. In the second step, the soap phase was acidified with sulfuric acid to yield fatty acid. Then the acid oil was efficiently converted into methyl esters by acid-catalyzed esterification. In the third step, alkaline-catalyzed transesterification was performed to convert the triglycerides into biodiesel. Biodiesel properties such as density, kinematic viscosity, flash point, calorific value, and acid value were found to be comparable to the reference diesel fuel.

For transformation of the soapstock into biodiesel, the esterification reaction is easily performed by acid catalysis (Benjumea*et al*., 2006) while the transesterification in this medium takes place slowly (Pereda*et al*., 2003). Alkaline catalysis cannot be applied to a material with high FFA content due to soap formation (Keskin*et al*., 2008). Usta*et al*. (2005) obtained biodiesel from a mixture of hazelnut soapstock and waste sunflower oil in approximately equal volume proportions. The soapstock FFA composition was approximately 45-50%, but the final blend had only 20%. Even at this level of FFAs, an acid-catalyzed esterification pre-treatment at 35 ºC was necessary before trans-esterifying the triglycerides with an alkaline catalyst to complete the reaction at 55 ºC.

The ester phase was washed with pure water three times. At the end of the process, the oil was heated to 100 ºC to remove any water from the oil left in the ester. Usta*et al*. (2005) found a very high viscosity compared to the standard diesel fuel for the biodiesel obtained due to the characteristics of the FAMEs and consequently it was not practicable for direct use in a diesel engine.

Pereda*et al*. (2003) reported biodiesel obtained from soapstock with 56% of FFAs (expressed as oleic acid). They reported the use of three steps: esterification in acid medium, transesterification in alkaline medium and neutralization. The transesterification of the esterified olein without neutralization of the residual FFAs yields a product in which no phase separation is observed due to the emulsifier properties of the soaps formed (Pereda*et al*., 2003; Haas *et al*., 2006). This can be avoided by neutralizing the FFAs before the transesterification. Using this treatment, the reaction conversion can be increased from 56% to 72-73% (Pereda*et al*., 2003).

The water content is critical for the transesterification reaction since it competes with the alcohol reactant, transforming the desired esterification reaction into ester hydrolysis and generating FFAs (Haas, 2005).

In the field of patents several are registered. Some of them cover methods for biodiesel production from soapstock (Stern *et al*., 1996; Basu and Norris, 1996), recovering of fatty acid products from soapstock (Phillips and Leavens, 1978), obtaining biodiesel from soapstock using enzymatic esterification (Araujo and Almeida, 2009) or soapstock acidulation (Reaney, 2002).

Fatty Acid Distillate

One of the potential raw materials for biodiesel production is Fatty Acid Distillate (FAD) (Budiman*et al*., 2012; Kartina, 2011; Nang *et al*., 2009), which contains high amounts of FFAs. It is also a byproduct obtained in the final deodorization stage of the refining process (Yang *et al*., 2010).

It is also called deodorizer distillate and contains compounds similar to soapstocks (Dumont and Narine, 2008; Dumont and Narine, 2007). Additionally, it contains material with some commercial value (Dumont and Narine, 2008; Garcia-Zapateiro*et al*., 2010; Verleyen*et al*., 2001; El-Mallah*et al*., 2006) as animal feed ingredient (Nang *et al*., 2009; Haslenda and Jamaludin, 2011). Several methods have been proposed to recover phytosterols from the deodorizer distillate (Yan *et al*., 2010; VerleyenVerhe, 2001; Kasim*et al*., 2010; Fabian *et al*., 2009). The byproduct obtained through physical refining has a higher FFA content than that obtained by chemical refining (El-Mallah*et al*., 2006).

The unsaponifiable materials of FAD have been considered to be a potential source of highly valuable phytochemicals (Gapor, 2000; Naz*et al*., 2012) such as vitamin E, phytosterols, and squalene among others (Verleyen*et al*., 2001; Gunawan*et al*., 2008; Fabian *et al*., 2009; El-Mallah*et al*., 2006). The vitamin E profile of Malaysian FAD is 10.3 wt% of fonte symbol-tocopherol, 18.7 wt% of fonte symbol-tocotrienol, 49.8 wt% of γ-tocotrienol, and 14.6 wt% of fonte symbol-tocotrienol (Bonnie and Mohtar, 2009).

A process to obtain biodiesel from FAD through two simultaneous chemical reactions has been reported (Budiman*et al*., 2012; Kartina, 2011) and referred to as reactive distillation. This procedure can improve the conversion and reduces the catalyst requirement. Biodiesel is produced from FAD in two steps (esterification and transesterification). Both reactions are well described in (Budiman*et al*., 2012).

A method using a column reactor packed with a cation exchange resin was reported for biodiesel synthesis from rapeseed oil deodorizer distillate (Liu and Wang, 2009). Under the optimal conditions, biodiesel production from FAD afforded a methyl ester yield of over 96%. The resin showed good operational stability and the same efficient activity as conventional sulfuric acid catalyst.

Acid Oil

Biodiesel can be obtained from the acid oil (Haas *et al*., 2003; Feng*et al*., 2012b) that results from the treatment of soapstock with sulfuric acid (Zhong-Ming *et al*., 2007; Dumont and Narine, 2007; Yan *et al*., 2010a; Young-Moo *et al*., 2010; Moulay*et al*., 2005; YuLi, 2010). Its use for biodiesel production can also improve the economic feasibility of the biodiesel process.

The acid oil (AO), also known as high-acid oil (Cherng-Yuan and Yi-Wei, 2012), consists of a long chain FFA mixture along with small amounts of mineral acids, glyceride, phospholipids and sterols (Kulkarni*et al*., 2008; Zhong-Ming *et al*., 2007) and is contaminated with fatty matter (Dumont and Narine, 2007). Acid oil characterization is reported in Johansen *et al*. (1996), Mag (1983) and Zhong-Ming *et al*. (2007).

Compared to the two previously analyzed byproducts, acid oil has almost no economic value (Dumont and Narine, 2007). Acidulation of soapstock is one of the least desirable processes in an integrated facility because it is difficult to perform effectively and its cost has no significant return (Zhong-Ming *et al*., 2007).

Additional drawbacks for conversion of acid oil to biodiesel are: addition of an excess of methanol and acid catalyst is required; a complete hydrolysis of the acylglycerols to fatty acids prior to FAME production is required in order to avoid the methanol and acid excess (Watanabe *et al*., 2007).

Nevertheless, several studies covering the conversion of acid oil to biodiesel have been reported. A kinetic study of the acid catalyst used in the reaction was reported (Marchetti*et al*., 2010). Zhong-Ming (Zhong-Ming *et al*., 2007) presented a technology for the production of biodiesel from acid oil after transformation of the soapstock.

Haas *et al*. (2003) proposed a method for obtaining biodiesel from acid oil. The process did not achieve efficient esterification of the fatty acids in the acid oil, but avoids the substantial amount of solid sodium sulfate generated as a by-product verified by Haas *et al*. in a previous approach (Haas *et al*., 2000). The optimal reaction occurred at 1:1.8:0.17 acid/methanol/sulfuric acid, with a reaction time of 14 h at 65 ºC. The authors also found that the accumulation of water released by the esterification prevented the complete esterification.

The process developed by Haas has been criticized (Zhong-Ming *et al*., 2007; Yan *et al*., 2010b; Yan *et al*., 2010a) due to the high temperature required to recover acid oil from soapstock, low efficiency, the additional process required in the technology and mainly for the long esterification reaction time.

Cherng-Yuan and Yi-Wei (2012) used the highacid oil from soybean soapstock as the feedstock for biodiesel production using supercritical-methanol transesterification. The authors analyzed and compared the fuel properties of biodiesel produced using various molar ratios of methanol to high-acid oil.

HETEROGENEOUS AND ENZYMATIC CATALYSTS

The development of heterogeneous catalysts has been a relatively recent area of research in the synthesis of biodiesel (Sharma *et al*., 2011; Trakarnpruk, 2012). Their use has a great potential not only technologically but also economically (Marchetti, 2012; Joon*et al*., 2011). The aim of the development of heterogeneous catalysts is related to the drawbacks of homogeneous catalysts: washing of biodiesel with water to remove the catalyst present, which results in wastewater and loss of biodiesel as a result of water washing.

Heterogeneous catalysts have the benefit of easy separation from the product without washing requirement (Jiang *et al*., 2010). Reuse of the catalyst is another advantage (Sharma *et al*., 2011; Oliveira *et al*., 2010; Bournay*et al*., 2005; Jiang *et al*., 2010). They are categorized as solid acid and solid base catalysts. Solid base catalysts show higher yields of biodiesel; however, they are sensitive to the presence of FFAs and thus solid acids are more recommended.

There are reports of the use of heterogeneous acid catalysis for biodiesel production (Meher*et al*., 2004; Melero*et al*., 2009a; Melero*et al*., 2009b; Semwal*et al*., 2011; Lotero*et al*., 2005; Puna*et al*., 2010; Baig and Flora, 2010). Solid acid catalysts (Chavan*et al*., 2001; Feng*et al*., 2010; Feng*et al*., 2012a; Helwani*et al*., 2009b) and zeolites (Sasidharan and Kumar, 2004) used for triglyceride transesterification showed high catalytic activities. Sulfated zirconia, sulfated tin oxide and sulfated titanium oxide are some of the catalysts that hare shown good catalytic activities (Kiss *et al*., 2006; Furuta*et al*., 2004; Muthu*et al*., 2010). The use of anionic ion-exchange resins as heterogeneous catalyst is also reported (Shibasaki-Kitakawa*et al*., 2007). Much interest has been shown in CaO among other heterogeneous base catalysts due to its economic advantage, lower solubility and easy handling (Peng-Lim *et al*., 2012).

A growing number of papers have appeared in this field, including several reviews (Sharma *et al*, 2011; Helwani*et al*., 2009a; Lam *et al*., 2010; Zabeti*et al*., 2009; Kiss *et al*, 2006; Leung *et al*., 2010; Melero*et al*., 2009b; Joon*et al*., 2011). In our paper we focus on the use of these catalysts for biodiesel production from the studied by-products.

Yan *et al*. (2010a) proposed a hybrid of both the traditional chemical method and solid acid catalyst for obtaining biodiesel from acid oil. A first distillation process for the acid oil in order to separate the FFAs from the triglycerides is necessary. Afterwards, they applied conventional alkali catalysis for the triglycerides and super acid catalysis for the FFAs, reaching high conversion into FAMEs.

However, the heterogeneous catalysts have not been widely used in industry because of the high catalyst cost and difficulty in filtering the small catalyst particles. Bao-Xiang *et al*. (2008) evaluated large particles of the $SO_4^{2-}/TiO^2\text{-}SiO^2$ solid acid catalyst for its catalytic activity in biodiesel production.

Next to the heterogeneous catalyst-based synthesis, the use of enzymes (Watanabe *et al*., 2000; Watanabe *et al*., 2007; Demirbas, 2008; Ranganathan*et al*., 2008) has also been reported. Biodiesel production using enzyme catalysts is a more environmentally friendly process and reaches adequate or even higher yields than the previously analyzed processes (Rivera *et al*., 2009; Yujaroen*et al*., 2009; Joon*et al*., 2011). Although these processes involving enzymes are costly (Chongkhong*et al*., 2009; Haas, 2005; Yujaroen*et al*., 2009; Yan *et al*., 2010b; Liu and Wang, 2009; Helwani*et al*., 2009b; Wang *et al*., 2007), the enzyme-based processes reduce energy cost as well as tend to have lower waste treatment costs (Dos Santos Correa *et al*., 2011).

Using enzymes, conversion efficiencies between 70-90% for the transesterification reaction can be obtained (Rivera *et al*., 2009; Haas, 2005; Dos Santos Correa *et al*., 2011; Juan *et al*., 2011; Modi*et al*., 2006). Using lipase, 63% esterification conversion was reported (Haas, 2005) with an overall efficiency of 81%. A combination of enzymes and supercritical fluid extraction/reaction for obtaining biodiesel from soapstocks was also reported (King *et al*., 1998; Cherng-Yuan and Yi-Wei, 2012; Yujaroen*et al*., 2009). Supercritical extraction also has drawbacks, mainly related to the high pressures required and excessive energy costs (Chen *et al*., 2009; Helwani*et al*., 2009b).

Shao *et al*. (2008) proposed the use of *C. rugosa*lipase as catalyst starting from rapeseed soapstock. A conversion of 63.6% was obtained with a methanol molar ratio of 4:1, an enzyme amount of 8%, a water content of 6% and 45 ºC. The methyl ester content was above 95% after molecular distillation.

Watanabe *et al*. (2007) achieved 98% of FAME for acid oil conversion into biodiesel using a twostep enzymatic method. The enzyme used was lipase at 0.5 wt. % for the first step and 6 wt. % for the second step, with the possibility of reusing lipase several times. As an alternative procedure, a non-catalytic supercritical methanol process was proposed (Yujaroen*et al*., 2009). The effect of water content in the feed on the yield of FAMEs was investigated, and also the yield of FAMEs from the non-catalytic esterification was compared to the conventional acidcatalyzed esterification and transesterification in supercritical methanol. The most suitable conditions were FAD to methanol molar ratio of 1:6 and a reaction temperature of 300 ºC during 30 min, in which 95% of FAMEs was produced. Compared to the conventional acid-catalyzed esterification of FAD using a similar molar ratio, they found that only a 75% yield was obtained in 5 h.

Silva *et al*. (2012) obtained biodiesel from beef tallow with ethanol, reaching reaction times between 24-48 hours at 45 ºC. The authors used an enzymatic route with two different lipases.

USE IN INTERNAL COMBUSTION ENGINES

A direct injection single cylinder Petter engine TD111 with a compression ratio of 17:1 and fuel injection timing of 24-33º (before top dead center) was used to test blends of biodiesel obtained from cotton oil soapstock and diesel fuel, increasing the percent of biodiesel in the blend up to 60% (Keskin*et al*., 2008). No differences were found in the measured engine power output between diesel fuel and the blends at lower speeds. However, at higher engine speeds, a nearly 6% decrease in power output of the engine was observed, depending on the amount of biodiesel in the blend and the engine speeds. The authors related this behavior to the lower heating value of the blend compared to diesel fuel. An increase of the specific fuel consumption up to 10.5% was observed using blends compared to diesel fuel, depending on the amount of biodiesel in the blend. For the blends, decreases of 46% in particulate matter in the exhaust emissions were also observed.

A Ford XLD four-cylinder, four-stroke, watercooled, 21.5:1 compression ratio, turbocharged, indirect injection diesel engine was used to test blends of biodiesel-diesel fuel (Usta*et al*., 2005). The volume percent was up to 25% of biodiesel in the blends. Although the heating value of the biodiesel is lower than diesel fuel, they found a slightly higher torque and power output at full load and partial loads for biodiesel blends. At full load, the CO emissions for the blend were higher at low speed and lower at high speeds than those of diesel fuel, while higher CO2 emissions in the speed range were found for the blend. At partial loads, it was found that the blend did not cause significant changes in the CO and CO2 emissions. They also reported a significant SO2 reduction with the blends due to the lower sulfur content of the biodiesel. NOx emissions slightly increased, attributed to the higher combustion temperature and the presence of oxygen with the blend at full load.

Haas (2005) conducted tests in a heavy-duty truck engine, a six-cylinder four-stroke, direct injection, turbocharged, intercooled engine nominally rated at 257 kW at 1800 rpm. As fuel 100% soapstock-based biodiesel, commercial biodiesel prepared from soybean and a reference diesel fuel were tested. For HC emissions they reported between 25-50% reductions compared to diesel fuel. They found an increase in the brake specific fuel consumption around 18%, related to the lower energy density of the biodiesel. When methyl esters obtained from a soapstock were tested in a diesel engine, reductions of particulate matter near 70% and increases in NOx emissions up to 10% compared to diesel fuel were observed (Haas *et al*., 2001; Haas, 2005), but also 40% reductions in CO emissions (Haas, 2005).

Graboski*et al*. (2003) performed tests in a sixcylinder, four-stroke diesel engine, nominally rated at 257 kW and 1800 rpm, direct injected, turbocharged, intercooled and electronically controlled. They tested soapstock methyl esters for exhaust emissions and compared the results with a reference diesel fuel. Important reductions in some pollutants such as total hydrocarbons (80%), CO (66%) and particulate matter (58%) compared to diesel fuel were observed, but also increases in the NOx (10.5%) and CO2 (2.7%) were reported.

Avoiding the chemical transesterification reaction in order to obtain the FAMEs, one solution could be to use these by-products with a preheating system.

The problem is that a higher viscosity and cloud point compared to standard diesel fuel should be expected. Could present long term engine operation durability problems, but also changes in injection, fuel spray characteristics, droplet size and spray penetration. The main problem is that the direct use of these by-products after preheating in a diesel engine will cause serious corrosion problems due to the high acidity of the by-products; therefore this approach should be avoided.

Galle *et al*. (2012) tested fatty acid distillates in a medium speed diesel engine. The by-product was heated to 110 ºC in order to decrease the viscosity to 8 mPas. During the investigation, dark deposits were detected on the piston crown, the rings, the combustion chamber and the injector. In the deposits, amounts of carbon, sodium, magnesium and iron were found. As the authors concluded, most of the damage in the injectors was induced by the fuel characteristics. Heavy erosion produced by particles in the fuel facilitates the start of microcracks, producing fatigue loads and the failure of fuel injectors. The problems encountered during the testing of the engine were related to the fuel composition, mainly related to its contamination content, the water present and the alkali.

Another possibility is the use of an emulsion or microemulsion (Ranganathan*et al*., 2008). As was analyzed in this paper, during biodiesel production, the lack of elimination of the water from these byproducts can cause, in the second step of the synthesis, an emulsion between the oil phase and the water promoted by the soap content. According to the analyzed papers, this should be avoided, but it will be interesting to take into account the possibility of the oil-water emulsion in order to test in engines.

Another topic that enhances de microemulsification is that the water can be generated (even when water-free reactants are used) during the reaction of the hydroxide ion with the alcohol used (Andreani and Rocha, 2012). Therefore, the removal of the residual waste water produced is crucial, leading to more costly processes, which is not necessary if the microemulsification route is followed.

There are a large number of studies and evidence that, in relation to the efficiency of the combustion process, the use of emulsions is favorable for the engine performance and exhaust emissions (Abu-Zaid, 2004; Cherng-Yuan and Li-Wei, 2009; Husnawan*et al*., 2009; Kannan and Anand, 2011; Lif*et al*., 2010; Subramanian, 2011; Demirbas, 2003), although there are also drawbacks (Abbaszaadeh*et al*., 2012).

Alcohol-oil microemulsions for use in diesel engines have been suggested (Yusuf *et al*., 2011). If the use of an emulsion of this nature is feasible, it can also reduce the number of steps in the biodiesel synthesis.

The lack of papers about the use of biodiesel obtained from these by-products means that this is a wide open field for research. Most research is focused on obtaining better yields of biodiesel, more efficient chemical processes and cost reductions.

Lecture 31

Food proteins contain long chains of amino acids held together by peptide bonds. Peptides are the shorter forms of proteins that can be obtained through enzymatic digestion which splits peptide bonds. The products of protein digestion have functional or health-promoting uses that are usually not associated with the native protein. Therefore, customized proteolysis of food proteins can be used to produce peptides for specific functions. All food protein resources can serve as raw materials for peptide production but most common are from milk, fish, eggs, oilseeds, and pulses. After hydrolysis, the mixture of peptides is called a protein hydrolysate, which can be further separated into distinct fractions based on hydrophobicity, charge, or peptide size. Additional separations using several rounds of column chromatography could result in pure peptide fractions that can be used to determine amino acid sequence. Protein hydrolysates and pure peptides are currently used in foods as antioxidants to prolong product shelf life as well as hypoallergenic products. Health applications include relief from oxidative stress, immune modulation, blood pressure reduction, and inhibition of excessive cellular proliferation.

Although seeds are mainly used for food or feed, they are also used as raw materials for various other industrial applications. Improvement of the nutritional quality of protein in legumes and cereals has been the prime aim of plant breeders. Crop breeding has undergone major changes during the last decades and new selection strategies are based on sophisticated genetics, the use of computational power, and biometric methods in field trials. On the other hand, the processing quality of seeds can be modified by altering the structural grain constituents or the enzyme activities that mobilize storage reserves of the seeds. Recent developments in the molecular biology of seed proteins offer breeders new tools for this work.

Seafood is one of the most commercialized, but also perishable, foodproduct. Its proteins offer multiple technological applications due to their inherent functional properties. Postcapture biochemical changes affect its quality. Seafood proteins are sensitive to thermal denaturation which causes structural changes affecting their functional properties. Minimal and nonthermal processing techniques have been proposed as emerging technologies to reduce heat damage and conserve wholesomeness of seafood. Seafood proteins are diverse in structure and properties, which make them attractive for their recovery as concentrates, isolates, hydrolysates, protein fractions (e.g., collagen, gelatin), or peptides due to their nutritional, functional, and biological properties. Useful protein-based techniques for identification and authenticity of seafood species to ensure compliance with labeling regulations to prevent fraudulent substitutions and to promote just trade for exporters, importers, and consumers are addressed.

Lecture 32

Antioxidants are compounds that inhibit oxidation. Oxidation is a chemical reaction that can produce free radicals, thereby leading to chain reactions that may damage the cells of organisms. Antioxidants such as thiols or ascorbic acid (vitamin C) terminate these chain reactions. To balance the oxidative state, plants and animals maintain complex systems of overlapping antioxidants, such as glutathione and enzymes (e.g., catalase and superoxide dismutase), produced internally, or the dietary antioxidants vitamin C, and vitamin E.

The term "antioxidant" is mostly used for two entirely different groups of substances: industrial chemicals that are added to products to prevent oxidation, and naturally occurring compounds that are present in foods and tissue. The former, industrial antioxidants, have diverse uses: acting as preservatives in food and cosmetics, and being oxidation-inhibitors in fuels.

Importantly, antioxidant dietary supplements have not yet been shown to improve health in humans, or to be effective at preventing disease. Supplements of beta-carotene, vitamin A, and vitamin E have no positive effect on mortality rate or cancer risk. Additionally, supplementation with selenium or vitamin E do not reduce the risk of cardiovascular disease.

A paradox in metabolism is that, while the vast majority of complex life on Earth requires oxygen for its existence, oxygen is a highly reactive molecule that damages living organisms by producing reactive oxygen species. Consequently, organisms contain a complex network of antioxidant metabolites and enzymes that work together to prevent oxidative damage to cellular components such as DNA, proteins and lipids. In general, antioxidant systems either prevent these reactive species from being formed, or remove them before they can damage vital components of the cell.[48][49] However, reactive oxygen species also have useful cellular functions, such as redox signaling. Thus, the function of antioxidant systems is not to remove oxidants entirely, but instead to keep them at an optimum level.

The reactive oxygen species produced in cells include hydrogen peroxide (H_2O_2), hypochlorous acid (HClO), and free radicals such as the hydroxyl radical ($\cdot OH$) and the superoxide anion (O_2^-).The hydroxyl radical is particularly unstable and will react rapidly and non-specifically with most biological molecules. This species is produced from hydrogen peroxide in metal-catalyzed redox reactions such as the Fenton reaction. These oxidants can damage cells by starting chemical chain reactions such as lipid peroxidation, or by oxidizing DNA or proteins. Damage to DNA can cause mutations and possibly cancer, if not reversed by DNA repair mechanisms, while damage to proteins causes enzyme inhibition, denaturation and protein degradation.

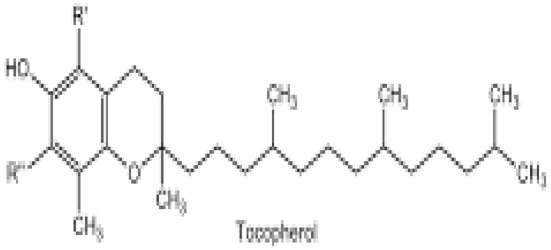
The use of oxygen as part of the process for generating metabolic energy produces reactive oxygen species. In this process, the superoxide anion is produced as a by-product of several steps in the electron transport chain.[58] Particularly important is the reduction of coenzyme Q in complex III, since a highly reactive free radical is formed as an intermediate ($Q\cdot^-$). This unstable intermediate can lead to electron "leakage", when electrons jump directly to oxygen and form the superoxide anion, instead of moving through the normal series of well-controlled reactions of the electron transport chain. Peroxide is also produced from the oxidation of reduced flavoproteins, such as complex I. However, although these enzymes can produce oxidants, the relative importance of the electron transfer chain to other processes that generate peroxide is unclear. In plants, algae, and cyanobacteria, reactive oxygen species are also produced during photosynthesis, particularly under conditions of high light intensity. This effect is partly offset by the involvement of carotenoids in photoinhibition, and in algae and cyanobacteria, by large amount of iodide and selenium, which involves these antioxidants reacting with over-reduced forms of the photosynthetic reaction centres to prevent the production of reactive oxygen species.

Examples of bioactive antioxidant compounds

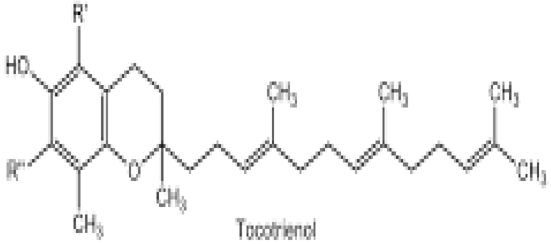
Antioxidants are classified into two broad divisions, depending on whether they are soluble in water (hydrophilic) or in lipids (lipophilic). In general, water-soluble antioxidants react with oxidants in the cell cytosol and the blood plasma, while lipid-soluble antioxidants protect cell membranes from lipid peroxidation.[49] These compounds may be synthesized in the body or obtained from the diet.The different antioxidants are present at a wide range of concentrations in body fluids and tissues, with some such as glutathione or ubiquinone mostly present within cells, while others such as uric acid are more evenly distributed (see table below). Some antioxidants are only found in a few organisms and these compounds can be important in pathogens and can be virulence factors.

The relative importance and interactions between these different antioxidants is a very complex question, with the various antioxidant compounds and antioxidant enzyme systems having synergistic and interdependent effects on one another. The action of one antioxidant may therefore depend on the proper function of other members of the antioxidant system.[50] The amount of protection provided by any one antioxidant will also depend on its concentration, its reactivity towards the particular reactive oxygen species being considered, and the status of the antioxidants with which it interacts.[50]

Some compounds contribute to antioxidant defense by chelatingtransition metals and preventing them from catalyzing the production of free radicals in the cell. Particularly important is the ability to sequester iron, which is the function of iron-binding proteins such as transferrin and ferritin. [62]Selenium and zinc are commonly referred to as *antioxidant nutrients*, but these chemical elements have no antioxidant action themselves and are instead required for the activity of some antioxidant enzymes, as is discussed below.

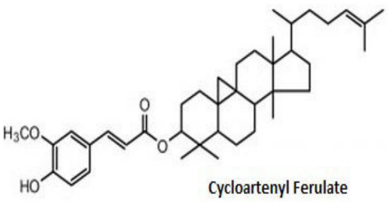


Tocopherol

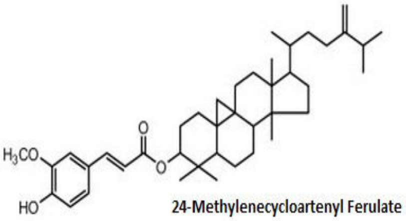


Tocotrienol

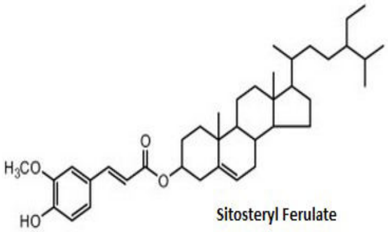
	R'	R''
α	CH_3	CH_3
β	CH_3	H
γ	H	CH_3
δ	H	H



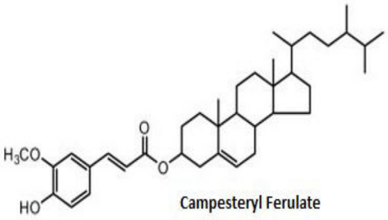
Cycloartenyl Ferulate



24-Methylenecycloartenyl Ferulate



Sitosteryl Ferulate



Campesteryl Ferulate

The antioxidant activities of vitamin E (alpha-tocopherol, alpha-tocotrienol, gamma-tocopherol, and gamma-tocotrienol) and gamma-oryzanol components (cycloartenylferulate, 24-methylenecycloartanyl ferulate, and campesterylferulate) purified from rice bran were investigated in a cholesterol oxidation system accelerated by 2,2'-azobis(2-methylpropionamidine) dihydrochloride. All components exhibited significant antioxidant activity in the inhibition of cholesterol oxidation. The highest antioxidant activity was found for 24-methylenecycloartanyl ferulate, and all three gamma-oryzanol components had activities higher than that of any of the four vitamin E components. Because the quantity of gamma-oryzanol is up to 10 times higher than that of vitamin E in rice bran, gamma-oryzanol may be a more important antioxidant of rice bran in the reduction of cholesterol oxidation than vitamin E, which has been considered to be the major antioxidant in rice bran. The antioxidant function of these components against cholesterol oxidation may contribute to the potential hypocholesterolemic property of rice bran.

MODEL QUESTIONS

Multiple Choice Questions (MCQ)

1. Choose the correct alternatives of the following

(i) The conjugated double bond containing PUFA is

(a) Linoleic acid (b) Linoleic acid (c) Elaidic acid, (d) Both (a)&(b)

(ii) Volatile short chain fatty acid responsible for characteristic aroma in butter in the list

(a) Lauric acid ;(b) Stearic acid ;(c) Myristic acid (d) Caproic acid

(iii) The nonhydratable phosphatide in the following category is

(a)Phosphatidyl ethanolamine (b) Phosphatidyl serine; (c) Phosphatidyl choline; (d) Phosphatidic acid

(iv) Deodorization process is also known as

(a) Steam refining ;(b) Wet degumming;(c) Miscella refining;(d) Desolventisation

(v) Oxidative deterioration of edible oil and fat can be measured by

(a) TBA test ;(b) HPLC; (c) Active oxygen method ;(d) DPPH method

(vi) Fish oil contains

(a) ETA;(b) EPA;(c) DHA;(d) Both(b)&(c)

(vii) The term treat in refining of vegetable oil usually mean

(a) Bleaching earth ;(b) Tocopherol ;(c) Concentrated sodium hydroxide ;(d) fatty acid

(viii) Saponification value signifies

(a) Degree of unsaturation, (b) degree of unsaturation, (c) chain length, (d) none of these

(ix) Mention the name of invisible fat from the following list

(a) Margarine (b) Butter (c) Meat (d) Cheese

(x) F.F.A reduced in the process of deodorization is up to

(a) 1% (b) .1% (c) ≤.03) % (d) None of these

(xi) Pro-oxidant in the following list is

(a) Concentrated phosphoric acid ;(b) Tocopherol ;(c) Bleaching earth;(d) Sterol

(xii)Removal of gossypol from neutral oil deals with the following color

(a) Yellow (b) Red brown (c) Green (d) None of these

(xiii) Example of saponifiable component of crude fat is

(a) Squalene;(b) carotenoid; (c) Phospholipid; (d) Sterol

(xiv)Soybean deodorizer distillate contains

(a)15% tocopherol& 25%sterol; (b)10% tocopherol& 30%sterol; (c)12.3% tocopherol& 21.9% sterol; (d) None of these

(xv) Which one of the following is a nonglyceride component?

(a) vitamin E, (b) sterols, (c) waxes, (d) all of these

(xvi)The potent toxic compound generated during deep fried triglyceride is

(a) HHE (b) HOE (c) HNE (d) HPNE

(xvii) The fat system used for baking in order to tenderize the structure of baked products is

called (a) Confectionery fats, (b) spread fat, (c) margarine, (d) shortenings.

(xviii) The characteristic flavor of butter is due to

(a)linoleic acid, (b) caproic acid, (c) butyric acid, (d) caprylic acid.

(xix). A triglyceride contains lauric acid (12:0), linoleic acid (18:2), and palmitoleic acid

(16:1). How many moles of H_2 are required to completely hydrogenate this triglyceride?

(a) two (b)six (c) three (d) four.

(xx) Zero-Trans of a product can be obtained by the process of

(a) Interesterification; (b) Hydrogenation; (c) Emulsification; (d) esterification.

(xxi) Selectivity I (S_I) refers to the preferentially exclusive hydrogenation of

(a) Oleic to stearic ; (b) Linoleic to oleic ; (c) Linolenic to linoleic ; (d) Linolenic to oleic acid (xxii) Salad oil can be prepared by

(a) Winterization; (b) Deodorization; (c) Hydrogenation; (d) Interesterification.

(xxiii) Which of the following oil gives low cost during hydrogenation?

(a) Palm oil, (b) rice bran oil, (c) sunflower oil, (d) soybean oil.

(xxiv) Butter can be substituted by a product called

(a) Shortenings; (b) Confectionery; (c) Margarine; (d) Hydrogenated fat.

(xxv) According to the legislation of many countries including India the fat content in margarine should not be less than (a) 70% ; (b) 80% ; (c) 50% ; (d) 40% .

(xxvi) The term shortenings is used in bakery industry to impart

(a) The stability of the product ; (b) Taste of the product ; (c) Tender quality ; (d) All of the above .

(xxvii) One important class of cocoa butter replacer is

(a) Cocoa butter substitute; (b) Cocoa butter equivalent; (c) Cocoa butter extender; (d) All of the above.

(xxviii) The most stable crystal structure present in fats is

(a) α-form; (b) β-form; (c) γ-form; (d)$\beta^{\prime}$-form.
(xxix) Major solvent used for SFE of oil is

(a) CO_2, (b) toluene, (c) hexane, (d) heptane
(xxx) Which one of the following is a nonglyceride component?

(a) vitamin E, (b) sterols, (c) waxes, (d) all of these

2. Discuss the conventional degumming process. What is wax?

3 What do you understand by polymorphism? What is cold test and spreadibility of fat?

4. Mention the name of the instrument for measuring color of oil and also indicates its working principle. What is the standard limit of color of finished oil?

5. Differentiate between reversion and rancidity. Describe the process of lipolysis.

6. Briefly describe the continuous deodorization conditions? What is its difference with batch process?

7. What do you understand by the term Cocoa butter replacers? How cocoa butter substitute is produced from natural vegetable oil?

8. Fatty acid composition governs the major characteristics of oils & fats – explain. Distinguish between animal and vegetable fat9. What do you understand by the term shortenings? Explain the processing technology of a shortening fat.

10. Explain the terms acidolysis and alcoholysis.

11. Distinguish between hydrogenated and interesterified product in terms of their stability

frying and nutritional quality.

12. Define the terms DG & MG. The high DG and MG present in oil indicates the spoilage of oil-explain.

13. Distinguish between rice bran & mustard oil in respect of their fatty acid composition and nutritional value.

14 Write short note on

(a) Phosphatides

(b) Tocopherol&Oryzonal

(c) Butter fat/ Milk fat

15. Differentiate between single and double bleached lecithin. Discuss continuous vacuum bleaching techniques with essential conditions. What is spent earth? How oil is extracted from spent earth? Point out the utility of spent earth

16. What do you understand by pyrolysis of triglyceride? Describe the essential stages of chemical conversions during this process

17. Describe the flow process for the production coconut protein isolate. How protein isolate can be recovered from mustard seed? Describe the flow sheet.

18. Write short notes on (any Three):

(a) Fractionation of soylecithin

(b) Chemical constants

(c) Deodorizers distillate

(d) Neutralization loss

(e) Detection of argemone and castor oil in edible oil

19. Discuss the three stage mechanism of generation of toxicity in deep fat frying by mentioning the nature of volatile and nonvolatile substances produced in this process. Which one among these considered as potent carcinogen and why?

20. Give the mechanism of auto oxidation of lipid. What do you understand by ROS? Give the mechanism of action of antioxidant for prevention of oxidative rancidity. Give an example each of ketonic and hydroxyl group containing synthetic antioxidant with structure.

21. What is winterization? Explain with a flow sheet the preparation of salad oil by winterization. Discuss the product characteristics of salad oil.

22. What do you understand by selectivity and isomerization in case of a hydrogenation process? Describe the influence of catalysts for hydrogenation process? What are the product characteristics of hydrogenated fat?

23. What do you understand by ester –ester interchange? Give a brief description of interesterification process. Discuss some important commercial applications of interesterified products.

24. Explain the term plastic fat. Discuss the role of plastic fats in bakery industries. Cocoa butter is considered as confectionery plastic fat –explain. What do you understand by spread fat?

25. Discuss the product characteristics of margarine. Explain the steps used for the manufacture of margarine. Mention the factors which influence the consistency or spreadability of margarine.

26. What do you understand by super critical extraction (SCE)? Explain the super SCE procedure. What are the advantages of SCE over convention extraction method?