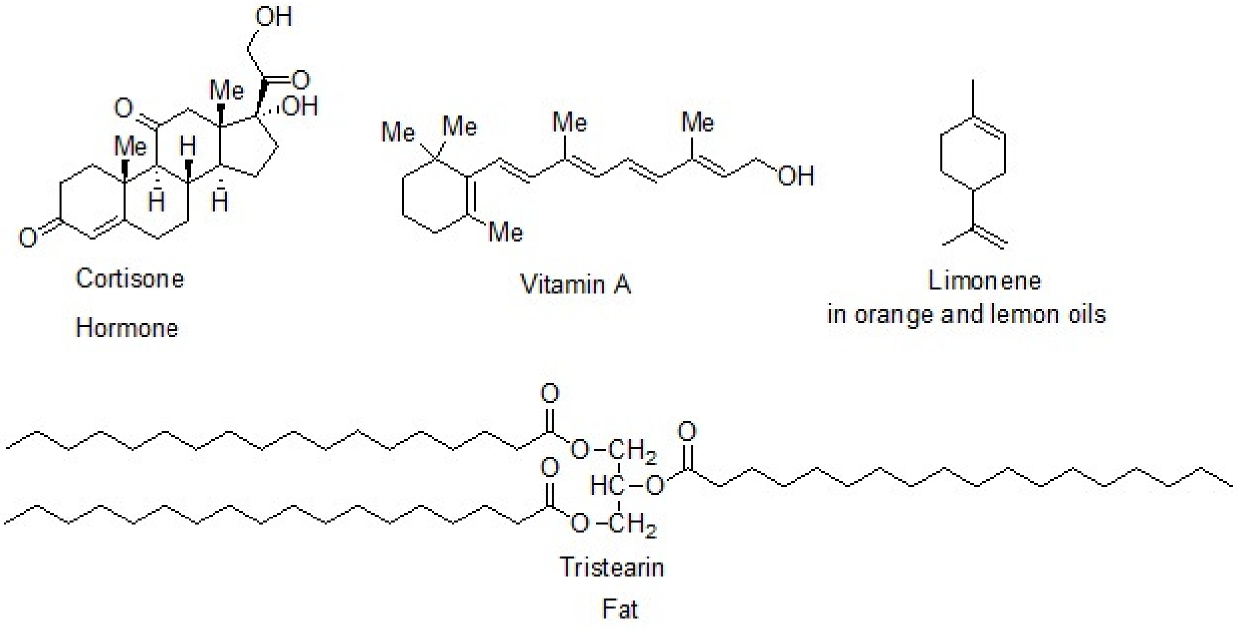
Oils Fats and Waxes

Introduction

Lipids form the third type of natural substance, apart from carbohydrates and proteins. Lipids are organic compounds that are found in living organisms. They have variety of structures and functions, and soluble in organic solvents due to their hydrocarbon componentr. Figure 1 illustrates some of them.



Cortisone
Hormone

Vitamin A

Limonene
in orange and lemon oils

Tristearin
Fat

Figure 1

Lipids are oily substances that have poor solubility in water. There are four types of lipids: (i) Mineral oils, (ii) Essential Oils, (iii) Oils and Fats and (iv) Waxes. We will briefly touch upon the first two, but we are more interested in the third and fourth type, namely oils, fats and waxes.

(i) Mineral Oils: Oils from under the earth’s crust such as petroleum and kerosene
(ii) Essential Oils: Of plant origin and have a pleasant smell such as lemon oil (Scheme 1).
(iii) Oils and Fats: These are esters of glycerol (in green color font) with higher fatty acids (in red color font) and are also called glycerides (Figure 2). The fatty acids involved have even number of carbon atoms.

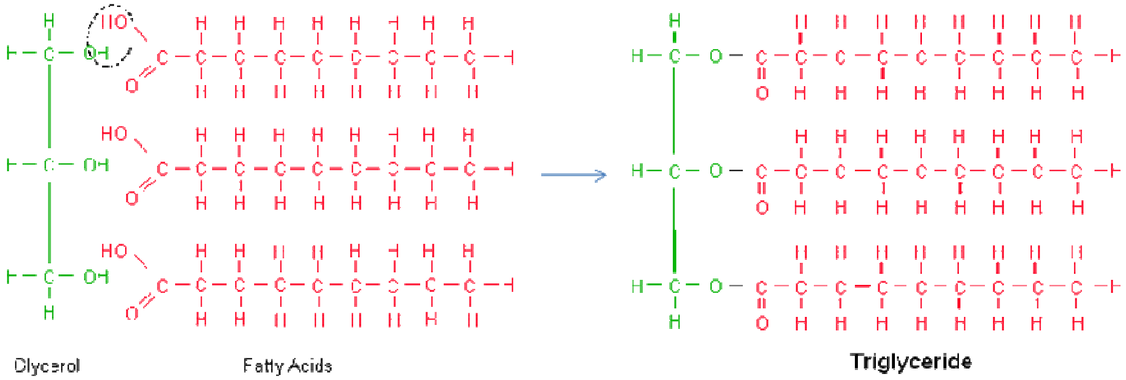
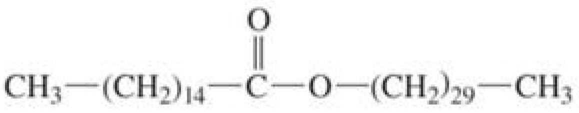


Figure 2

(iv) Waxes: These are mixtures of esters of higher fatty acids with higher monohydric (in contrast to glycerol which is trihydric) alcohols such as cetyl ($C_{16}H_{33}OH$), myricyl ($C_{30}H_{61}OH$) *etc.* For *eg.* Myricyl palmitate (Figure 3, $C_{15}H_{31}COOC_{30}H_{61}$) is a wax secreted by bees and used in shoe polish, furniture polishes etc.



$$CH_3-(CH_2)_{14}-\overset{\overset{\large O}{\|}}{C}-O-(CH_2)_{29}-CH_3$$

Figure 3

Fatty Acids

Fatty acids are unbranched carboxylic acids having long hydrocarbon chains (Figure 4). Most of the naturally available fatty acids bear an even number of carbon atoms due to their biosynthesis from acetate in living organisms. Some examples are listed in Figure 4. They are subdivided into "saturated" and "unsaturated" fatty acids.

Saturated and Unsaturated Fatty Acids

The terms saturated, mono-unsaturated, and poly-unsaturated refer to the number of hydrogen atoms attached to the hydrocarbon tails of the fatty acids as compared to the number of double bonds between carbon atoms in the tail (Figure 5). Fats, which are mostly from animal sources, have all single bonds between the carbons in their fatty acid tails, thus all the carbons are also bonded to the maximum number of hydrogen atoms possible. Since the fatty acids in these triglycerides contain the maximum possible amount of hydrogen atoms, these would be called saturated fats. The hydrocarbon chains in these fatty acids are, thus, fairly straight and can pack closely together, making these fats solid at room temperature.

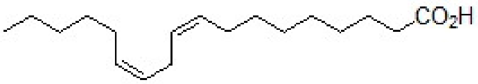
Number of Carbons	Common Name	Structure	Melting Point (°C)
Saturated			
12	Lauric acid		44
14	Myristic acid		58
16	Palmitic acid		63
18	Stearic acid		69
20	Arachidic acid		77
Unsaturated			
16	Palmitoleic acid		0
18	Oleic acid		13
18	Linoleic acid		-5
18	Linolenic acid		-11

Figure 4

Oils, mostly from plant sources, have some double bonds between some of the carbons in the hydrocarbon tail, causing bends or "kinks" in the shape of the molecules. Because some of the carbons share double bonds, they're not bonded to as many hydrogens as they could if they weren't double bonded to each other. Therefore these oils are called unsaturated fats. Because of the kinks in the hydrocarbon tails, unsaturated fats can't pack as closely together, making them liquid at room temperature. Unsaturated fatty acids have less intermolecular interactions compared to saturated fatty acids. As a result, the unsaturated fatty acids have lower melting points in comparison to saturated fatty acids. The melting point decreases as the number of double bonds increases.

Hydrogenated vegetable oil, known as vanaspati in India is artificially saturated oil. The double bonds in unsaturated oils are all artificially broken and hydrogen atoms artificially added to turn it into saturated fat that bears no resemblance to the original oil from which it came from and this is solid at room temperature. In naturally available glycerides, both saturated and unsaturated fatty acid residues may be found.

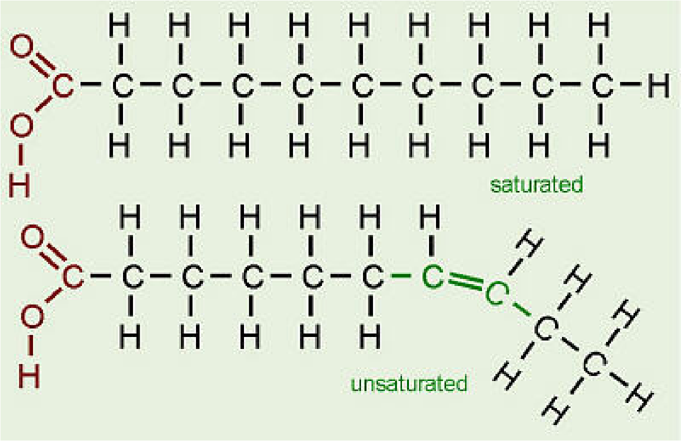


Figure 5

Cis and Trans Isomers of Unsaturated Fatty Acids

In **unsaturated** fatty acids, there are two ways the atoms around a C=C double bond can be arranged (Figure 6). In "***cis"*** bonds, the two hydrogen and two methylene groups attached to the carbon atoms on either side of the double bond are either both "up" or both "down," such that both are on the same side of the molecule. In "***trans***" bonds, these groups are on opposite sides of the double bond, that is, one "up" and one "down" across from each other.

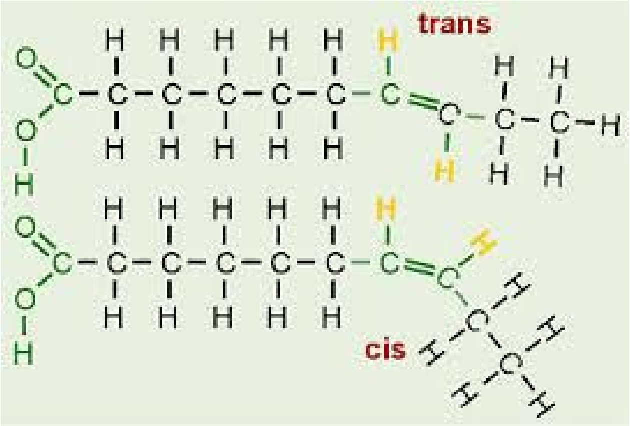
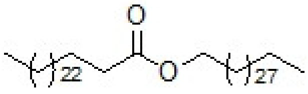


Figure 6

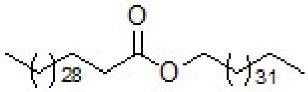
Naturally-occurring unsaturated vegetable oils have almost all cis bonds, but using the oil for frying food causes some of the cis bonds to convert to trans bonds. If oil is used only once, only a few of the bonds get converted. However, if oil is reused, many of the cis bonds may get converted to trans. These trans fatty acids are reported to be carcinogenic, *ie.* cancer-causing.

Waxes

Waxes are esters of long chain carboxylic acids with long chain alcohols. For example, beeswax contains a 26 carbon carboxylic acid and a 30 carbon alcohol component, while carnauba wax has a 32 carbon carboxylic acid component and a 34 carbon alcohol component. The latter is an example for a hard wax, and is widely used as a car wax and in floor polishes (Figure 7).



a major component of beeswax



a major component of carnauba wax

Figure 7

Waxes are also common in living organisms (Figure 8). For example, wax is found on the surfaces of some leaves, where it serves as protectant against parasites and minimizes the evaporation of water. Similarly, the feathers of birds are coated with wax to make them water repellent.

Figure 8

Fats and Oils

The solid or semisolid triglycerides at room temperature are called fats, while the liquid is called oil (Figure 9). Fats are generally obtained from animals, while oils come from plant products. In fats, saturated fatty acids such as oleic acid, linolenic acid are usually involved in the formation of ester with glycerol, whereas in oils, unsaturated fatty acids such as lauric acid, myristic acid, palmitic acid and stearic acid are involved. In case of fats, the saturated fatty acid chain can pack closely together causing them to be solids at room temperature. In case of oil, the unsaturated fatty acid chain cannot pack tightly together, and therefore, that leads to usually have low melting points.

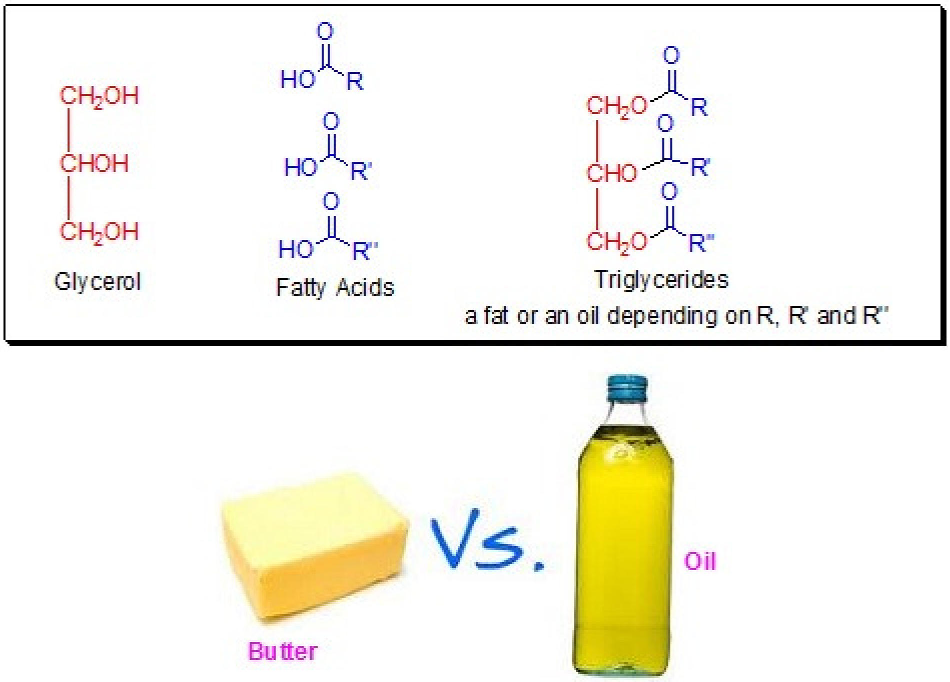
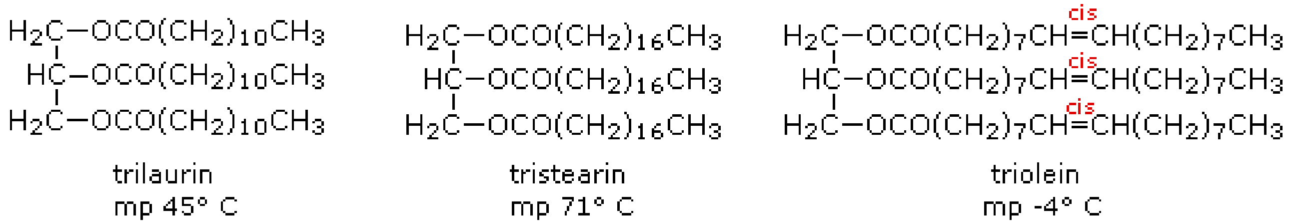


Figure 9

The glycerides are named according to the fatty acid residues present in them by replacing the terminal "ic acid" by "in". So tristearin with 3 saturated stearic acid residues and trilaurin with 3 saturated lauric acid residues attached to glycerol (Figure 10) are solids at room temperture, whereas triolien with 3 unsaturated oleic acid residues attached to glycerol (Figure 10) is a liquid. These glycerides with the same fatty acid residues attached to glycerol are called "simple" glycerides



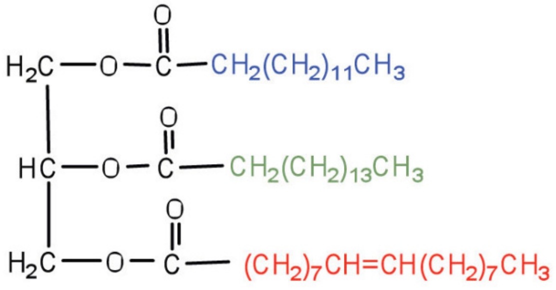
trilaurin
mp 45° C

tristearin
mp 71° C

triolein
mp -4° C

Figure 10

In contrast, when different fatty acid residues are attached to glycerol, they are called "mixed" glycerides (Figure 11).



mixed triglyceride

Figure 11

Polyunsaturated fats and oils are prone to undergo oxidation by O_2 via radical reaction. The allylic H is the one that is easily removed because the resulting radical is resonance stabilized by the pi bonds. The oxidation reaction is responsible for the unpleasant taste and smell associated with sour milk and rancid butter.

Soaps, Detergents and Micelles

Sodium or potassium salts of fatty acids are called soaps. They are obtained by basic hydrolysis of triglycerides which is called saponification as shown in Figure 11. Figure 12 shows the three most common soaps used.

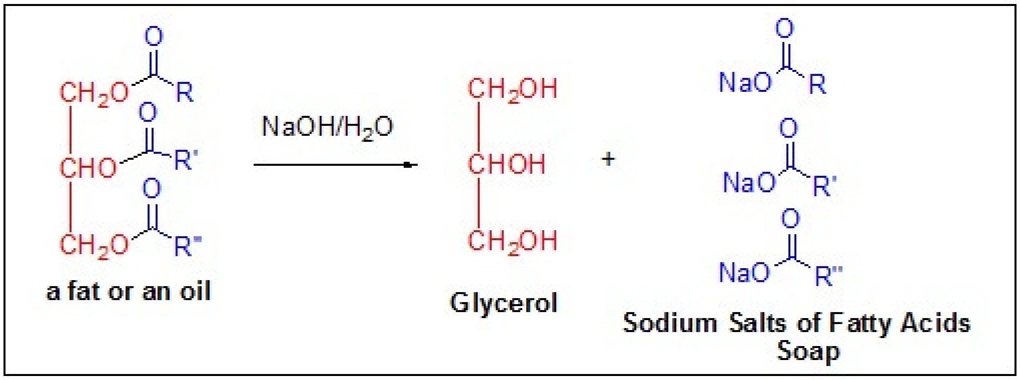


Figure 12

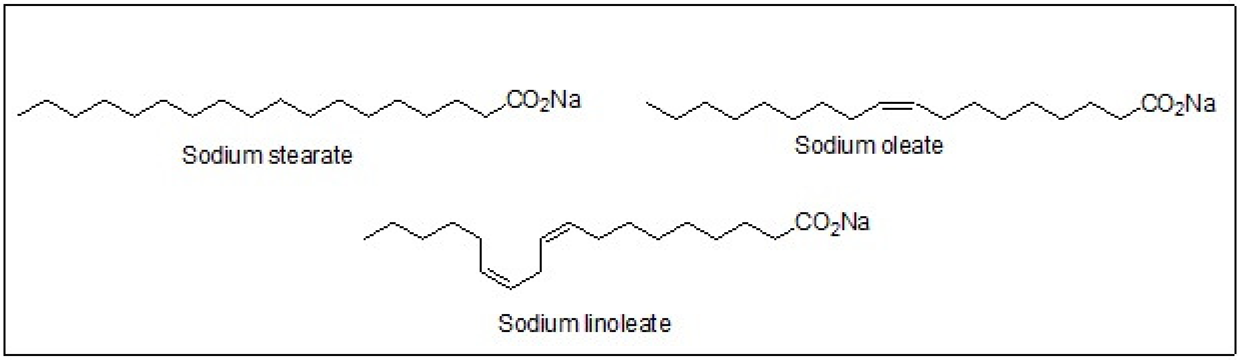


Figure 12

In aqueous solution, the long chain carboxylic acids arrange themselves in spherical clusters called micelles as shown in Figure 13. Each micelle contains 50-100 long-chain carboxylates.

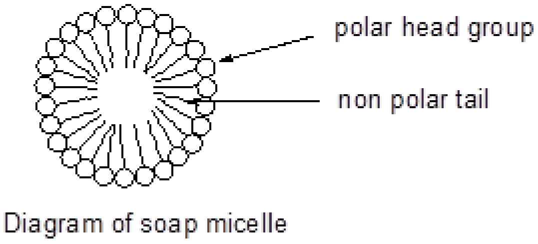


Figure13

Soap contains the cleaning property because nonpolar oil that carry dirt dissolve in the nonpolar interior of the micelle and are carried out away with the soap during rinsing (Figure 14).

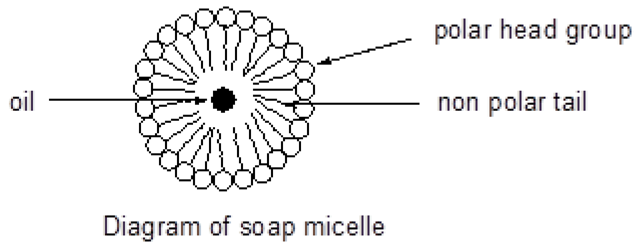


Figure 14

Since soap can undergo precipitation (soap scum) in hard water due to reaction with calcium and magnesium ions, synthetic soaps (salt of benzenesulphonic acid) called detergents have been developed that don't form soap scum in hard water (Figure 15).

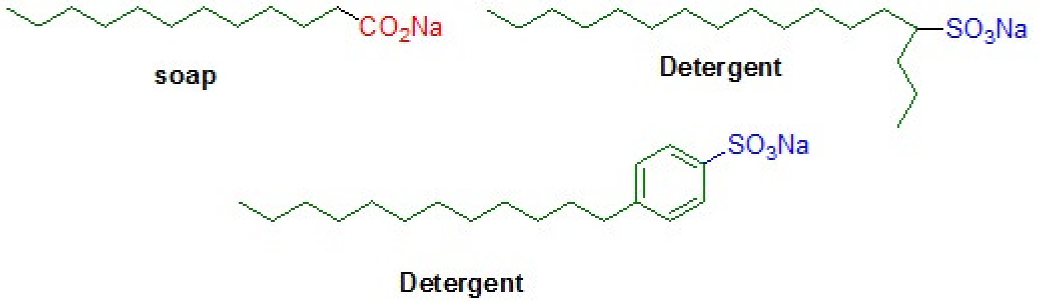


Figure 15

Occurrence of Fats and Oils

Fats and oils can be either of plant or animal origin.
Vegetable oils: Extracted from seeds, *eg.* cotton seed oil, soybean oil etc.
Vegetable fats: Extracted from coconut
Animal oils: *eg.* Cod liver oil, whale oil *etc.*
Animal fats: Lard and butter

Extraction of Fats and Oils

Rendering: After the size reduction in mincer and crusher, the **animal tissues** are melted in a cooker either with direct steam or indirect heat. To avoid damaging the nutritional values, this is carried out at the lowest temperature possible (70-90°C). The separation of the three phases (solids, aqueous phase and melted fat) can be achieved by different techniques. The most common is drainage of the solid phase, which is subsequently pressed and dried. The liquid phase is sent to a decanter (horizontal centrifuge), where the two phases, aqueous and fat phases are separated. The denser aqueous liquid phase is separated and sent to a dryer. The relatively less dense fat is removed from the decanter and filtered before storage.

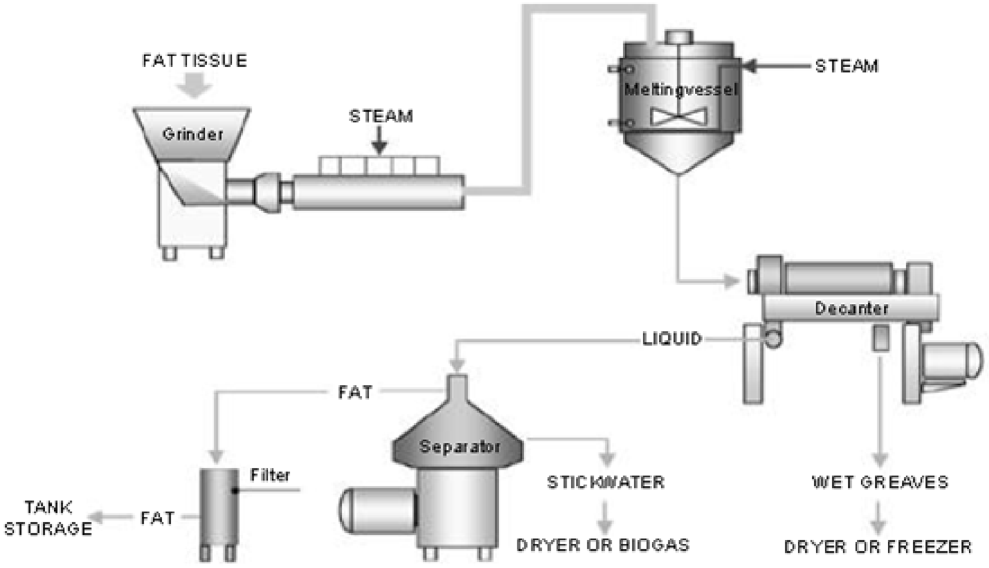


Figure 16

Pressing: Plant raw materials such as seeds, flowers etc are crushed by rollers and the oil extracted in a hydraulic press or expellers. The extracted oil is then refined before filtering. The filtered oil maybe refined and processed further to produce saturated fats.

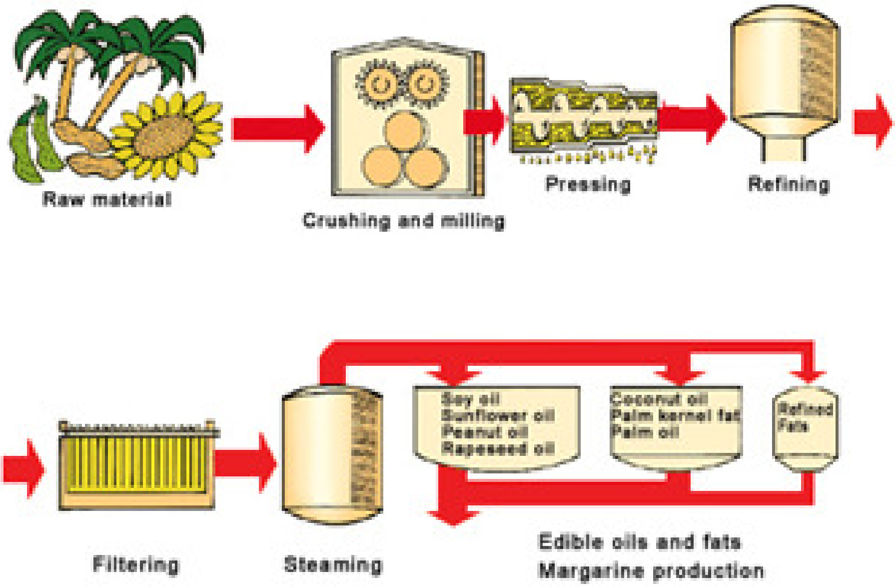


Figure 17

Solvent Extraction: The solid material remaining after the pressing processed is called oil cake. The cake is crushed and subjected to solvent extraction with solvents such as carbon tetra chloride, benzene and/or petroleum ether to extract the residual oil in the cake. The residual cake after solvent extraction maybe used as cattle feed.

Refining: The free fatty acids in crude oil from plant and animal sources is first neutralized with alkali. The oil is then decolorized by bleaching with animal charcoal, fuller's earth or pla.

0ster of paris. The decolorized oil is then filtered and deodorized. The deodorizing is conducted by passing superheated steam through the oil. The oil is then quickly cooled and stored.

Physical Characteristics of Fats and Oils

They are

- Colorless liquid or solid, but maybe yellow or brown due to impurities.
- Lighter than water and immiscible with it
- Soluble in organic solvents such as petroleum ether, benzene etc.
- Non-volatile
- Upon heating they decompose to give an irritating odor
- Form emulsions in the presence of detergents/surfactants

Chemical Characteristics of Fats and Oils

- **Polymerization**: Unsaturated fats and oils polymerize upon drying and used in paints

- **Rancidity**: it is the natural process of decomposition (degradation) of fats or oils by either hydrolysis or oxidation, or both. The development of rancidity is accompanied by a marked increase in the acid value of the fat. This converts fatty acid esters of oils into free fatty acids, by reaction with air, moisture and/or other materials.

There are three causes for rancidity:

a. Oxidative rancidity, known as autoxidation, occurs when oxygen is absorbed from the environment. In the presence of oxygen and/or ultraviolet (UV) radiation, most lipids will break down and degrade, forming several other compounds.
b. Hydrolytic rancidity, also called hydrolysis or enzymatic oxidation, occurs in the absence of air, but with moisture present. This normally is accomplished through enzymatic peroxidation, where enzymes found naturally in plant oils (i.e., lipoxygenase, cyclooxygenase) and animal fats (i.e., lipase) can catalyze reactions between water and oil.

c. Microbial rancidity is caused by micro-organisms such as bacteria, molds and yeast which use enzymes to break down chemical structures in the oil, producing unwanted odors and flavors.

- **Hydrogenation**: Hydrogenation is a chemical reaction between molecular Hydrogen (H_2) and another compound or element, usually in the presence of a catalyst such as nickel, palladium or platinum. The process is commonly employed to reduce or saturate organic compounds such as unsaturated fatty acids. It adds a pair of hydrogen atoms to a double bond such as cis or trans double bound carbons in a fatty acids as shown in Figure 18.

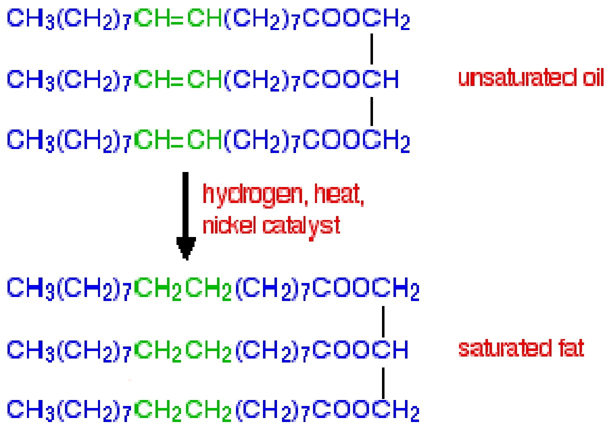


Figure 18

The conversion of double bonds to single bond raises the melting point of the fatty acid/glycerides and changes the texture of the product.

- **Hydrolysis**: Triglycerides can be hydrolyzed to constituent glycerol and fatty acids by dilute acids or alkali. Esterases such as lipases can also catalyze the hydrolysis reaction (Figure 19).

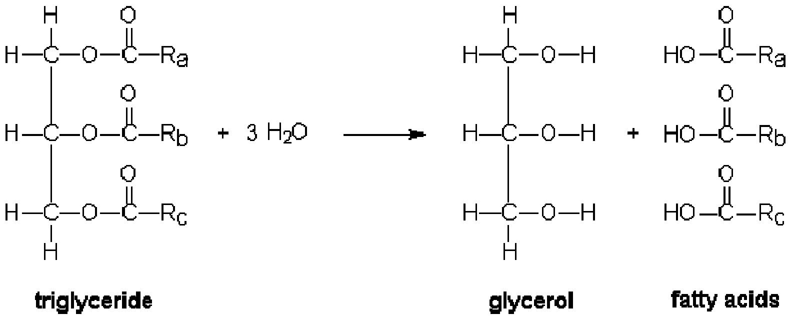


Figure 19

- **Saponification**: When the hydrolysis is catalyzed by base such as sodium hydroxide, the end product is glycerol and sodium salt of fatty acids. The sodium salts of fatty acids are actually soaps and this reaction is called saponification.

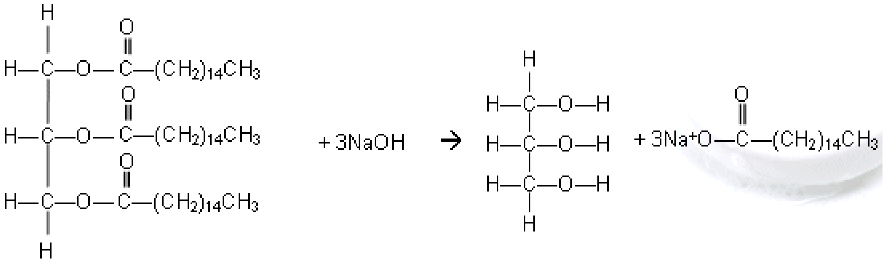


Figure 20

- **Hydrogenolysis**: The process of splitting a compound by means of hydrogen is known as hydrogenolysis. With excess hydrogen and high pressures in the presence of copper or chromium as catalyst, triglycerides are split into glycerol and higher aliphatic alcohols. (Not to be confused with hydrolysis which produces glycerol and fatty acid).

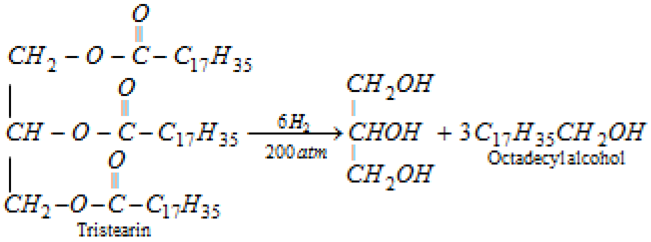


Figure 21

Analysis of Oils and Fats

(i) ***Acid value*** : It indicates the amount of free acid present in the oil or fat**.** *It is defined as the number of milligrams of KOH required to neutralize the free acid present in one gram of the oil or fat*. It is determined by dissolving a weighed amount of oil or fat in alcohol and titrating it against a standard solution of *KOH* using phenolphthalein as an indicator.

(ii) ***Saponification value*** **:** It is a measure of fatty acids present as esters in oils and fats. It is defined as the number of milligrams of *KOH* required to saponify one gram of the oil or fat *ie*. number of milligrams of *KOH* required to neutralize the free acids resulting from the hydrolysis of one gram of an oil or fat.

It is determined by refluxing a standard amount of fat or oil with known excess of standard alcoholic caustic potash solution and back titrating with excess alkali with a standard acid.

The saponification value gives an idea about the molecular weight of the fatty acid. The molecular weight triglyceride is directly proportional to the size of the fatty acids (as the size of the glycerol is fixed). So, a high molecular weight triglyceride upon hydrolysis would yield big fatty acids, which would in turn mean smaller number of free carboxylic acids available for neutralization by the base and consequently a smaller saponification value.

(iii) ***Iodine value*** **:** Iodine value of a fat or oil is a measure of its degree of unsaturation. *It is declared as the number of grams of iodine taken up by 100 grams of fat or oil for saturation.* For a saturated acid glyceride, the iodine value is zero. Thus, the iodine value for a fat is low whereas for oil, it is high. As iodine does not react readily, in actual practice, iodine monochloride is used. Iodine monochloride is known as Wijs' reagent.

(iv) ***Reichert-Meissl value, (R/M value)*** **:** It indicates the amount of steam volatile fatty acids present in the oil or fat. *It is defined as the number of millilitres of 0.1 N KOH solution required to neutralize the distillate of 5 grams of hydrolysed fat or oil.* It is determined by hydrolysing a known weighed amount (5 grams) of the fat with alkali solution and the mixture is acidified with dilute sulphuric acid and steam distilled. The distillate is cooled, filtered and reacted against 0.1 *N KOH*.

Uses of Oils and Fats

- Many oils and fats are used as food material.
- Oils and fats are used for the manufacture of glycerol, fatty acids, soaps, candles, vegetable ghee, margarine, hair oils, etc.
- Oils like linseed oil, tung oil, etc., are used for the creation of paints, varnish, etc.
- Castor oil is used as purgative and codliver oil as a source of vitamins *A* and *D*. Almond oil is used in pharmacy. Olive oil is also used as medicine.
- Oils are also used as illuminants and lubricants.