UNIT- III: Fats and Oils

❖ Fatty acid

- Fatty acid is a carboxylic acid with a long aliphatic chain, which is either saturated or unsaturated. Most naturally occurring fatty acids have an unbranched chain of an even number of carbon atoms, from 4 to 28.

- ***Saturated fatty acids.***

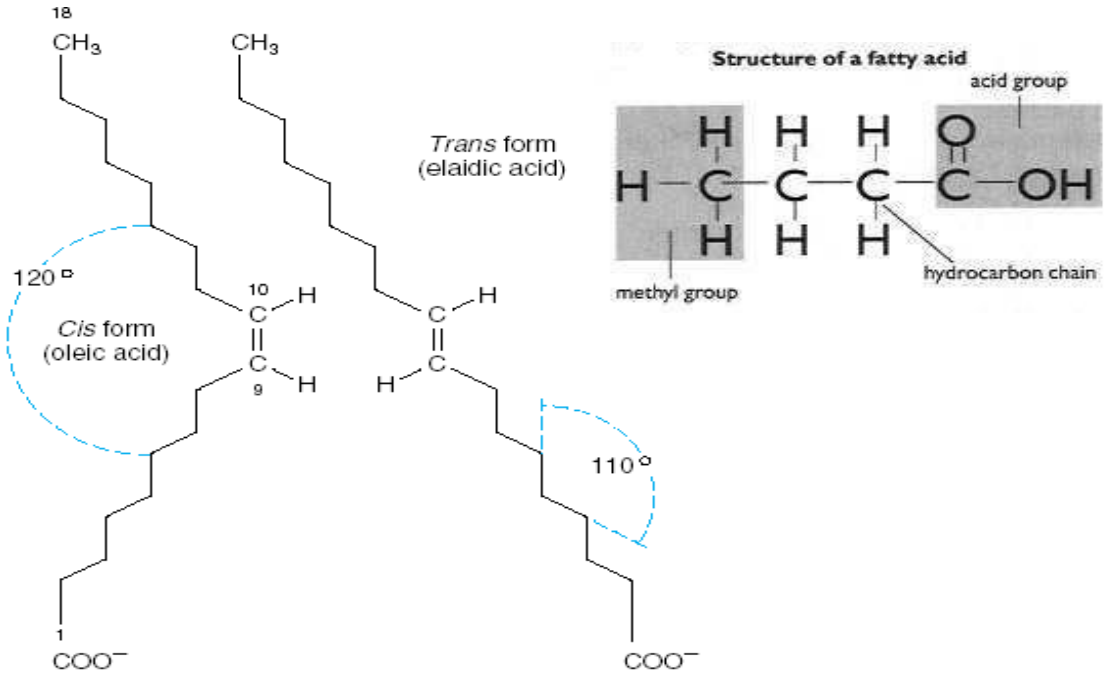
Common Name	Number of C Atoms	
Acetic	2	Major end product of carbohydrate fermentation by rumen organisms[1]
Propionic	3	An end product of carbohydrate fermentation by rumen organisms[1]
Butyric	4	In certain fats in small amounts (especially butter). An end product of carbohydrate fermentation by rumen organisms[1]
Valeric	5	
Caproic	6	
Lauric	12	Spermaceti, cinnamon, palm kernel, coconut oils, laurels, butter
Myristic	14	Nutmeg, palm kernel, coconut oils, myrtles, butter
Palmitic	16	Common in all animal and plant fats
Stearic	18	

- ***Unsaturated Fatty Acids***

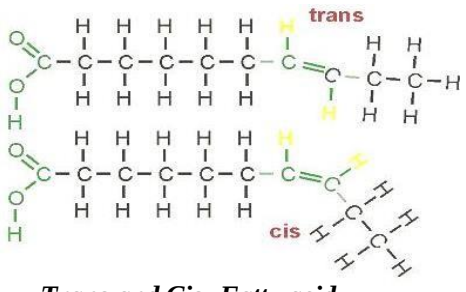
Number of C Atoms and Number and Position of Double Bonds	Common Name	Occurrence
		Monoenoic acids (one double bond)
16:1;9	Palmitoleic	In nearly all fats.
18:1;9	Oleic	Possibly the most common fatty acid in natural fats.
18:1;9	Elaidic	Hydrogenated and ruminant fats.
		Dienoic acids (two double bonds)
18:2;9,12	Linoleic	Corn, peanut, cottonseed, soybean, and many plant oils.
		Trienoic acids (three double bonds)
18:3;6,9,12	γ-Linolenic	Some plants, eg, oil of evening primrose, borage oil; minor fatty acid in animals.
18:3;9,12,15	α-Linolenic	Frequently found with linoleic acid but particularly in linseed oil.
		Tetraenoic acids (four double bonds)
20:4;5,8,11,14	Arachidonic	Found in animal fats and in peanut oil; important component of phospholipids in animals.

- ***Chemistry of Fatty acids***

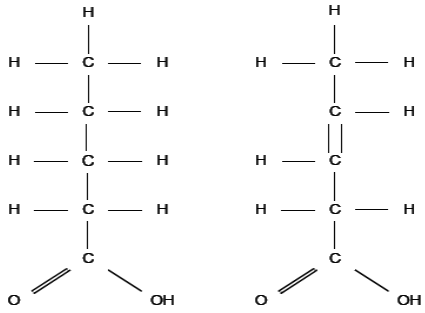
- The carbon chains of saturated fatty acids form a zigzag pattern when extended, as at low temperatures. At higher temperatures, some bonds rotate, causing chain shortening,
- A type of **geometric isomerism** occurs in unsaturated fatty acids, depending on the orientation of atoms or groups around the axes of double bonds, which do not allow rotation. If the acyl chains are on the same side of the bond, it is ***cis-***, as in **oleic acid**; if on opposite sides, it is ***trans-***, as in **elaidic acid**, the ***trans*** isomer of **oleic acid**.
- Naturally occurring unsaturated long-chain fatty acids are nearly all of the ***cis*** configuration, the molecules being **"bent"** 120 degrees at the double bond. Thus, **oleic acid** has an **L shape**, whereas **elaidic acid** remains **"straight."**
- Increase in the number of *cis* double bonds in a fatty acid leads to a variety of possible like **arachidonic acid**, with four ***cis*** double bonds, has **"kinks"** or a **U shape**.
- ***Trans*** double bonds alter these spatial relationships.
- The melting points of even-numbered-carbon fatty acids increase with chain length and decrease according to unsaturation.



Geometric isomerism of fatty acids (oleic and elaidic acids)



Trans and Cis- Fatty acid



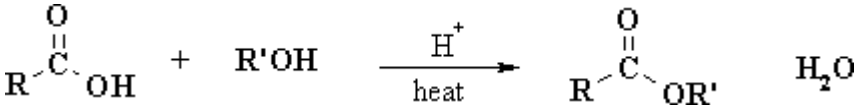
Saturated Fatty acid Unsaturated Fatty acid

Note By: ► Naturally, occurring unsaturated vegetable oils have almost all **Cis** bonds, but using oil for frying causes some of the **Cis** bonds to convert to **Trans** bonds.

► Fatty acids with **Tran's** bonds are **carcinogenic**.

- **Fatty acids -Reactions: Fischer esterification.**

- **Fischer esterification** is the **esterification** of a Carboxylic acid by heating it with an alcohol in the presence of a strong acid as the catalyst.
- ***Reaction type:*** *Nucleophilic Acyl Substiution*



Step 1: An acid/base reaction. Protonation of the carbonyl makes it more electrophilic.

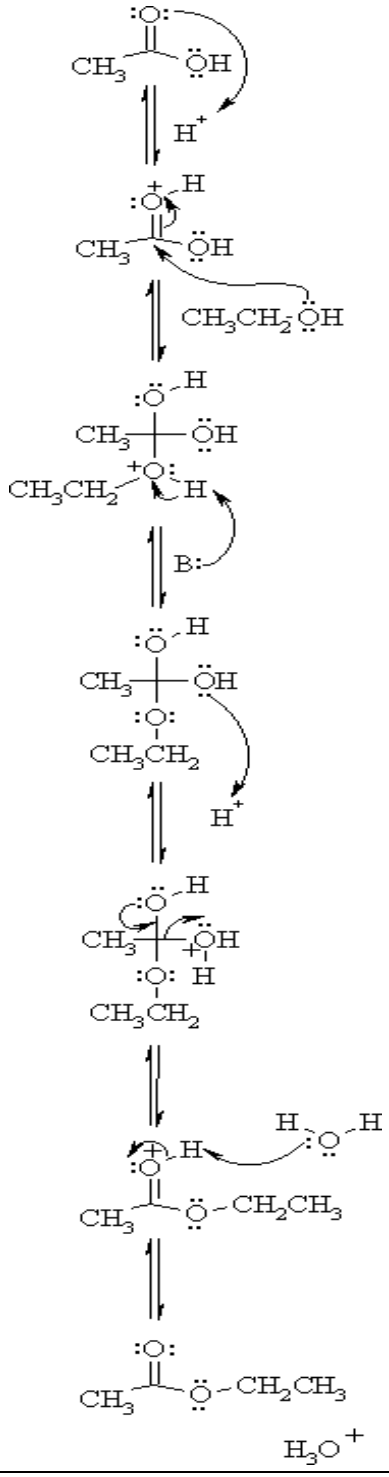
Step 2: The alcohol O functions as the nucleophile attacking the electrophilic C in the C=O, with the electrons moving towards the oxonium ion, creating the tetrahedral intermediate.

Step 3: An acid/base reaction. Deprotonate the alcoholic oxygen

Step 4: An acid/base reaction. Need to make an -OH leave, it doesn't matter which one, so convert it into a good leaving group by protonation.

Step 5: Use the electrons of an adjacent oxygen to help "push out" the leaving group, a neutral water molecule.

Step 6: An acid/base reaction. Deprotonation of the oxonium ion reveals the carbonyl in the ester product.



- **Hydrolysis of fatty acid**

- The reaction can be catalyzed by acid, base, or lipase, but it also occurs as an uncatalyzed reaction between fats and water dissolved in the fat phase at suitable temperatures and pressures.

1. Nonenzymatic ester hydrolysis and the soap-making process

- In aqueous solution, esters are subject to hydrolysis to the corresponding carboxylic acid and alcohol components.

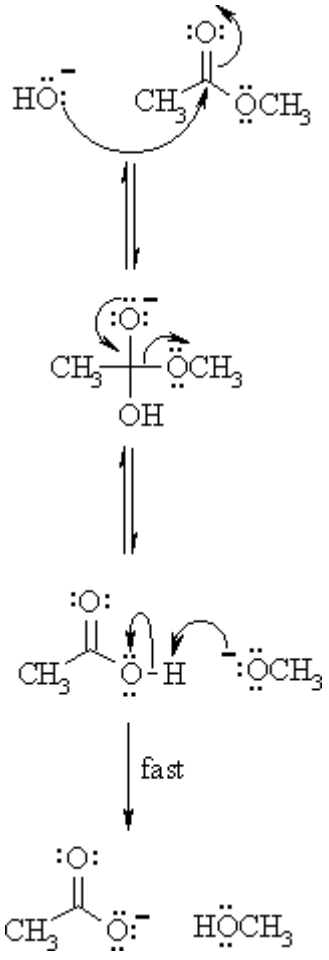
Esters Carboxylic acid Alcohol

- ***Mechanism of the base hydrolysis of esters***

Step 1:
The hydroxide nucleophiles attacks at the electrophilic **C** of the ester **C=O**, breaking the π bond and creating the tetrahedral intermediate.

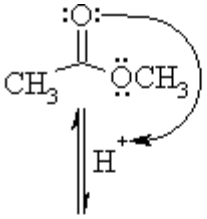
Step 2:
The intermediate collapses, reforming the **C=O** results in the loss of the leaving group the alkoxide, **RO^-**, leading to the carboxylic acid.

Step 3:
An acid / base reaction. A very rapid equilibrium where the alkoxide, **RO^-** functions as a base deprotonating the carboxylic acid, **RCO_2H**, (an acidic work up would allow the carboxylic acid to be obtained from the reaction).

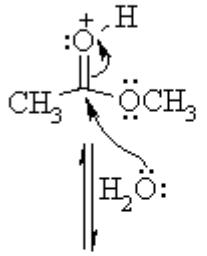


- ***Mechanism of the acid catalysed hydrolysis of esters***

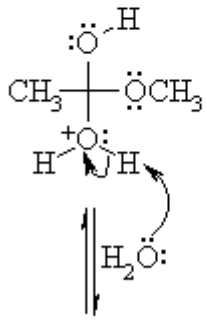
Step 1:
An acid/base reaction. Since we only have a weak nucleophile and a poor electrophile we need to activate the ester. Protonation of the ester carbonyl makes it more electrophilic.



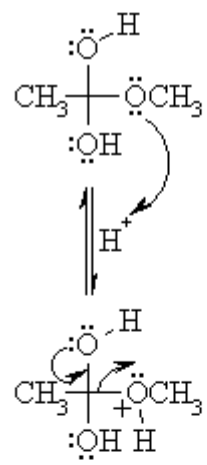
Step 2:
The water **O** functions as the nucleophile attacking the electrophilic **C** in the **C=O**, with the electrons moving towards the oxonium ion, creating the tetrahedral intermediate.



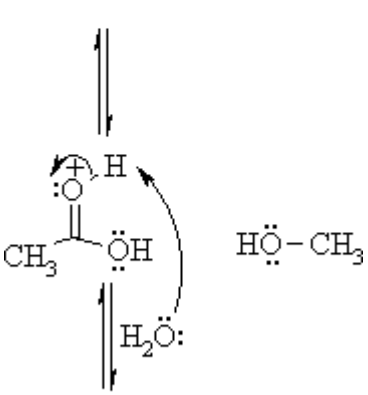
Step 3:
An acid/base reaction. Deprotonate the oxygen that came from the water molecule to neutralise the charge.



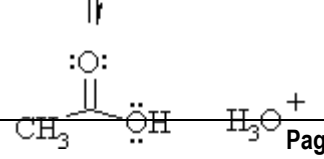
Step 4:
An acid/base reaction. Need to make the **-OCH_3** leave, but need to convert it into a good leaving group first by protonation.



Step 5:
Use the electrons of an adjacent oxygen to help "push out" the leaving group, a neutral methanol molecule.



Step 6:
An acid/base reaction. Deprotonation of the oxonium ion reveals the carbonyl **C=O** in the carboxylic acid product and regenerates the acid catalyst.



❖ Analytical constants: Acid value

- In chemistry, acid value (or neutralization number or acid number or acidity) is the mass of potassium hydroxide (KOH) or sodium hydroxide (NaOH) in milligrams that is required to neutralize the free fatty acids in 1 g of the fat.
- The acid number is a measure of the number of carboxylic acid groups in a chemical compound, such as a fatty acid, or in a mixture of compounds.
- The acid number is used to quantify the acidity of a substance. It is the quantity of base, expressed in milligrams of potassium hydroxide or sodium hydroxide, which is required to neutralize the acidic constituents in 1 g of sample.
- ***Method and procedure:***

(a) Reagents

- *Phenolphthalein indicator:* Weigh 1 g of phenolphthalein and dissolve in 100 mL of ethanol.
- *Sodium hydroxide titrant:* Weigh accurately 4.0 g of sodium hydroxide and place it in a 1000-mL volumetric flask. Make up to the mark with water.
- *Ethanol-ether solution:* Prepare a mixture of ethanol and diethyl ether (1:1, v/v). Neutralize with sodium hydroxide titrant and add 1.0 mL of phenolphthalein indicator until pink coloration is observed. Freshly prepare the solution.

(b) Standardization of sodium hydroxide titrant

- Weigh accurately 0.6 g of potassium hydrogen phthalate, previously dried to constant weight at 105°C, and place it in a 250-mLconical flask, then add 50 mL of water. Shake it well.
- Then add 2 drops of phenolphthalein indicator.
- Titrate the solution with the sodium hydroxide titrant until pink colouration can be observed.
- Towards the end of titration, potassium hydrogen phthalate should be completely dissolved.
- Calculate the concentration of the sodium hydroxide titrant according to the following equation:

$$C_{NaOH} = \frac{W_{C_8H_5KO_4} \times P_{C_8H_5KO_4} \times 1000}{V_{NaOH} \times Mw_{C_8H_5KO_4}}$$

where C_{NaOH} = Molarity of sodium hydroxide titrant (mol/L)
V_{NaOH} = Volume of sodium hydroxide titrant used (mL)
$Mw_{C_8H_5KO_4}$ = Molecular weight of potassium hydrogen phthalate (204.22 g)
$W_{C_8H_5KO_4}$ = Weight of potassium hydrogen phthalate used (g)
$P_{C_8H_5KO_4}$ = Purity of potassium hydrogen phthalate (%)

(c) Titration of test solution

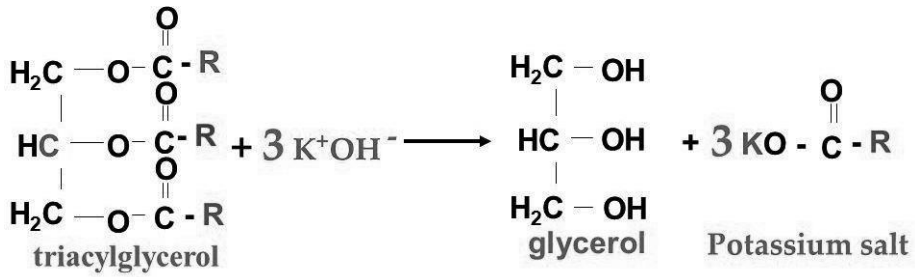
- Weigh accurately a quantity of the fatty oil and place it in a 250-mL conical flask, then add 50 mL of ethanol-ether solution.
- Shake it well. If necessary, reflux the mixture gently until the substance is completely dissolved.
- Titrate the solution with sodium hydroxide titrant until pink colouration can be observed which persists for 30 second.
- Measure the volume of sodium hydroxide titrant used and calculate the acid value according to the following equation:

$$\textit{Free fatty acid}\ (\%) = \frac{\textbf{Titre volume} \times \textbf{normality of NaOH} \times \textbf{28.2}}{\textit{Weight of sample}}$$

Acid Value = % FFA × 1.99

❖ Analytical constants: Saponification value

- Fats and oils are the principle stored forms of energy in many organisms. They are highly reduced compounds and are derivatives of fatty acids.
- Fatty acids are carboxylic acids with hydrocarbon chains of 4 to 36 carbons; they can be saturated or unsaturated. The simplest lipids constructed from fatty acids are triacylglycerol‟s or triglycerides.
- Triacylglycerol‟s are composed of three fatty acids each in ester linkage with a single glycerol. Since the polar hydroxyls of glycerol and the polar carboxylates of the fatty acids are bound in ester linkages, triacylglycerol‟s are non-polar, hydrophobic molecules, which are insoluble in water.
- Saponification is the hydrolysis of fats or oils under basic conditions to afford glycerol and the salt of the corresponding fatty acid.



- ***Defination:*** Saponification value of oil, fat or of an ester is defined as the number of milligrams of potassium hydroxide (KOH) required to completely neutralizing the free acids to saponify the esters present in 1gm of the substance. (i.e. to neutralize the fatty acid resulting from the complete hydrolysis of 1gm of the oil or fat.)
- ***Significance of Saponification Value:***
  - The magnitude of saponification value gives an idea about the average molecular weight of the fat or oil.
  - Higher the molecular weight of the fat, the smaller is its saponification value.
  - Saponification Value also indicates the length of carbon chain of the acid present in that particular oil or fat.
  - Higher the saponification value, greater is the percentage of the short chain acids present in the glycerides of the oil or fats.
- ***Reagents Required:***
  i. Ethanolic KOH (95% ethanol, v/v)
  ii. Potassium hydroxide [0.5N]
  iii. Fat solvent
  iv. Hydrochloric acid [0.5N]
  v. Phenolphthalein indicator (1%in ethanol)
- ***Procedure:***
  i. Weigh 1g of fat in a tared beaker and dissolve in about 3ml of the fat solvent [ethanol /ether mixture].
  ii. Quantitatively transfer the contents of the beaker three times with a further 7ml of the solvent.
  iii. Add 25ml of 0.5N alcoholic KOH and mix well, attach this to a reflux condenser.
  iv. Set up another reflux condenser as the blank with all other reagents present except the fat.
  v. Place both the flasks in a boiling water bath for 30 minutes.
  vi. Cool the flasks to room temperature.
  vii. Now add phenolphthalein indicator to both the flasks and titrate with 0.5N HCl.
  viii. Note down the endpoint of blank and test.
  ix. The difference between the blank and test reading gives the number of millilitres of 0.5N KOH required to saponify 1g of fat.
- ***Calculate the saponification value using the formula:***

$$Saponification\ value = \frac{28.05\ (Titrate\ value\ of\ Blank - Titrate\ value\ of\ Test\ Sample)}{\text{Weight of sample (1g)}}$$

❖ Analytical constants: Ester value

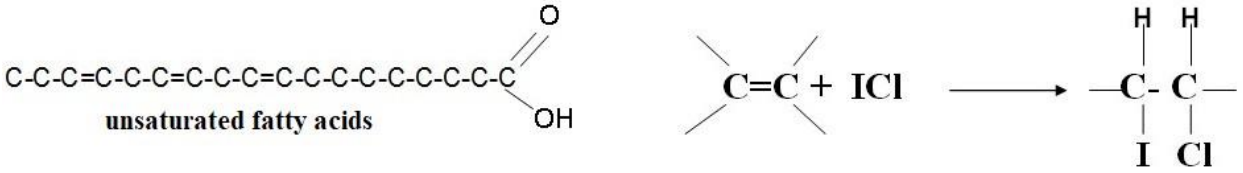
- The ester value is defined as the mg of KOH required to react with glycerin (glycerol / or glycerin) after saponify one gram of fat. It is calculated from the saponification Value (SV) and the acid Value (AV):

Ester Value (EV) = Saponification Value (SV) – Acid Value (AV)

% *glycerin* = *Ester Value* × 0.054664

❖ Analytical constants: Iodine value

- The iodine value (IV) gives a measure of the average degree of unsaturation of a lipid: the higher the iodine value, the greater the number of C=C double bonds. By definition the iodine value is expressed as the grams of iodine absorbed per 100g of lipid.
- Iodine value (I.V.) is directly proportional to the degree of unsaturation (No of double bonds.) and inversely proportional to the melting point (M.P.) of lipid.
- An increase in I.V. indicates high susceptibility of lipid to oxidative rancidity due to high degree of unsaturation.
- Fatty acids react with a halogen [iodine] resulting in the addition of the halogen at the C=C double bond site. In this reaction, iodine monochloride reacts with the unsaturated bonds to produce a di-halogenated single bond, of which one carbon has bound an atom of iodine.



- After the reaction is complete, the amount of iodine that has reacted is determined by adding a solution of potassium iodide to the reaction product.: **$ICl + KI \leftrightarrow KCl + I_2$**
- This causes the remaining unreacted **ICl** to form molecular **iodine**. The liberated **I_2** is then titrated with a standard solution of **0.1N sodium thiosulfate**. **$I_2 + 2\ Na_2S_2O_3 \rightleftharpoons 2\ NaI + Na_2S_2O_4$**
- Saturated fatty acids will not give the halogenation reaction. If the iodine number is between **0-70**, it will be a fat and if the value exceeds **70** it is oil. Starch is used as the indicator for this reaction so that the liberated iodine will react with starch to give purple coloured product and thus the endpoint can be observed.
- ***Materials Required:***
    - Iodine Monochloride Reagent
    - Potassium Iodide
    - Standardized 0.1 N Sodium thiosulphate
    - 1% Starch indicator solution
    - Chloroform
    - Fat sample in chloroform
    - Iodination flask
    - Burette and burette stand with magnetic stirrer
    - Glass pipette
    - Measuring cylinder, distilled water

- ***Method:***
  - Arrange all the reagent solutions prepared and the requirements on the table.
  - Pipette out 10ml of fat sample dissolved in chloroform to an iodination flask labelled as “TEST".
  - Add 20ml of Iodine Monochloride reagent in to the flask. Mix the contents in the flask thoroughly.
  - Then the flask is allowed to stand for a half an hour incubation in dark.
  - Set up a BLANK in another iodination flask by adding 10ml Chloroform to the flask.
  - Add to the BLANK, 20ml of Iodine Monochloride reagent and mix the contents in the flask thoroughly.
  - Incubate the BLANK in dark for 30 minutes.
  - Meanwhile, Take out the TEST from incubation after 30 minutes and add 10 ml of potassium iodide solution into the flask.
  - Rinse the stopper and the sides of the flask using 50 ml distilled water.
  - Titrate the “TEST” against standardized sodium thiosulphate solution until a pale straw colour is observed.
  - Add about 1ml starch indicator into the contents in the flask, a purple colour is observed.
  - Continue the titration until the color of the solution in the flask turns colourless.
  - The disappearance of the blue colour is recorded as the end point of the titration.
  - Similarly, the procedure is repeated for the flask labelled „Blank'.
  - Record the endpoint values of the BLANK.
  - Calculate the iodine number using the equation below:

Volume of Sodium thiosulphate used = [Blank- Test] ml

$$Iodine\ No.of\ fat = \frac{Equivalent\ Wt.of\ Iodine \times Volume\ of\ Na_2S_2O_3\ used \times Normality\ of\ Na_2S_2O_3 \times 100 \times 10^{-3}}{Weight\ of\ fat\ sample\ used\ for\ analysis(g)}$$

Equivalent Weight of Iodine = 127

Normality of sodium thiosulphate ($Na_2S_20_3$) = 0.1

Or

$$Iodine\ Value = \frac{\text{Volume of Sodium thiosulphate used x Normality of Sodium thiosulphate x } 0.127g/meq \text{ weightof Iodine x } 100}{\text{Weight of the fat sample used for analysis}}$$

❖ Analytical constants: Acetyl value

- Acetyl value measure of the free hydroxyl groups in a substance (as a fat or oil) as determined by acetylation, being the number of milligrams of potassium hydroxide required for neutralization of the acetic acid formed by hydrolysis of one gram of the acetylated substance.
- Some fatty acids contain hydroxyl groups. In order to determine the proportion of these, they are acetylated by means of acetic anhydride.
- This results in the introduction of acetyl groups in the place of free hydroxyl groups.
- The acetic acid in combination with fat can be determined by titration of the liberated acetic acid from acetylated fat or oil with standard alkali.
- Acetyl number is thus a measure of the number of hydroxyl groups present in fat or oil
- ***Methods:***
  - Determination of the saponification value of the substance under examination. Acetylate the substance under examination by the following method. 10 g with 20 ml of acetic anhydride in a long-necked, round-bottomed 200-ml flask attached to a reflux air condenser. Support the flask on a sheet of resistant material in which a hole of about 4 cm in diameter has been cut and heat it with a small, naked flame, not more than 25 mm in height and which does not impinge on the bottom of the flask.
  - Boil gently for 2 hours, allow to cool, pour into 600 ml of water contained in a large beaker, add 0.2 g of pumice powder and boil for 30 minutes.
  - Cool and transfer to a separator and discard the lower layer. Wash the acetylated product with three or more quantities, each of 50 ml, of a warmed saturated solution of sodium chloride until the washings are no longer acid to litmus paper.
  - Finally, shake with 20 ml of warm water and remove the aqueous layer completely as possible. Pour the acetylated substance into a small dish, add 1 g of powdered anhydrous sodium sulfate, stir thoroughly and filter through dry pleated filter.
  - Determine the saponification value of the acetylated substance.
- ***Calculate the Acetyl value from the expression***

$$\textbf{Acetyl value} = 1335(b - a) / (l335 - a)$$

Where, ***a*** *= saponification value of the substance*;

b **=** *saponification value of the acetylated substance.*

❖ Analytical constants: Reichert Meissl (RM) value

- The ***Reichert value*** (*The Reichert-Meissl-Wollny Value* or *Reichert-Meissl-Wollny Number*) is a value determined when examining fat.
- The ***Reichert value*** is an indicator of how much volatile fatty acid can be extracted from fat through saponification. It is equal to the number of **millilitres of 0.1 normal hydroxide** solution necessary for the neutralization of the **water-soluble volatile fatty acids** distilled and filtered from 5 grams of a given saponified fat. (The hydroxide solution used in such a titration is typically made from sodium hydroxide, potassium hydroxide, or barium hydroxide.)
- The material is saponified by heating with glycerol sodium hydroxide solution and then split by treatment with dilute sulfuric acid. The volatile acids are immediately steam distilled. The soluble volatile acid in the distillate are filtered out and estimated by titration with standard sodium hydroxide solution.
- These determinations have been used principally for analysis of butter and margarines. Butter fat contains mainly butyric acid glycerides. Butyric acid is volatile and soluble in water.
- Butter fat contains mainly butyric acid glycerides. Butyric acid is volatile and soluble in water. No other fat contains butyric acid glycerides, and therefore, the ***Reichert Meissl value*** of the butter fat is higher than that for any other fat.
- **Reagents:**
  (a) Glycerine
  (b) Concentrated sodium hydroxide solution: 50 % (w /w) Dissolve
  (c) Dilute sulfuric acid solution: Approximately 1.0 N
  (d) Sodium hydroxide solution: 0.1N solution in water, accurately standardised
  (e) Phenolphthalein indicator: Dissolve 0.1 g of phenolphthalein in 100 ml of ethyl alcohol.
  (f) Ethyl alcohol: 90% by volume and neutral to phenolphthalein.
- **Procedure**
  - Weigh accurately 5 ±0.1g of filtered oil or fat sample into a clean, dry, 300 ml distilling flask. Add 20 ml of glycerine and 2 ml of concentrated sodium hydroxide solution, and heat with swirling over a flame until completely saponified, as shown by the mixture becoming perfectly clear. Cool the contents slightly and add 90 ml of boiling distilled water, which has been vigorously boiled for about 15 min. After thorough mixing the solution should remain clear. If the solution is not clear (indicating incomplete saponification) or is darker than light yellow (indicating over-heating), repeat the saponification with a fresh sample of the oil or fat. If the sample is old, the solution may sometimes be dark and not clear.
  - Add about 0.6 - 0.7 gm of pumice stone grains, and 50 ml of dilute sulfuric acid solution. Immediately connect the flask to the distillation apparatus. Place the flask on asbestos board so that it fits snugly into the aperture. This will prevent the flame from impinging on the surface of the flask above the level of the liquid and avoid super heating. Heat very gently until the liberated fatty acids melt and separate. Then set the flame so that 110 ml of distillate shall be collected within 19 to 21 min. The beginning of the distillation is to be taken as the

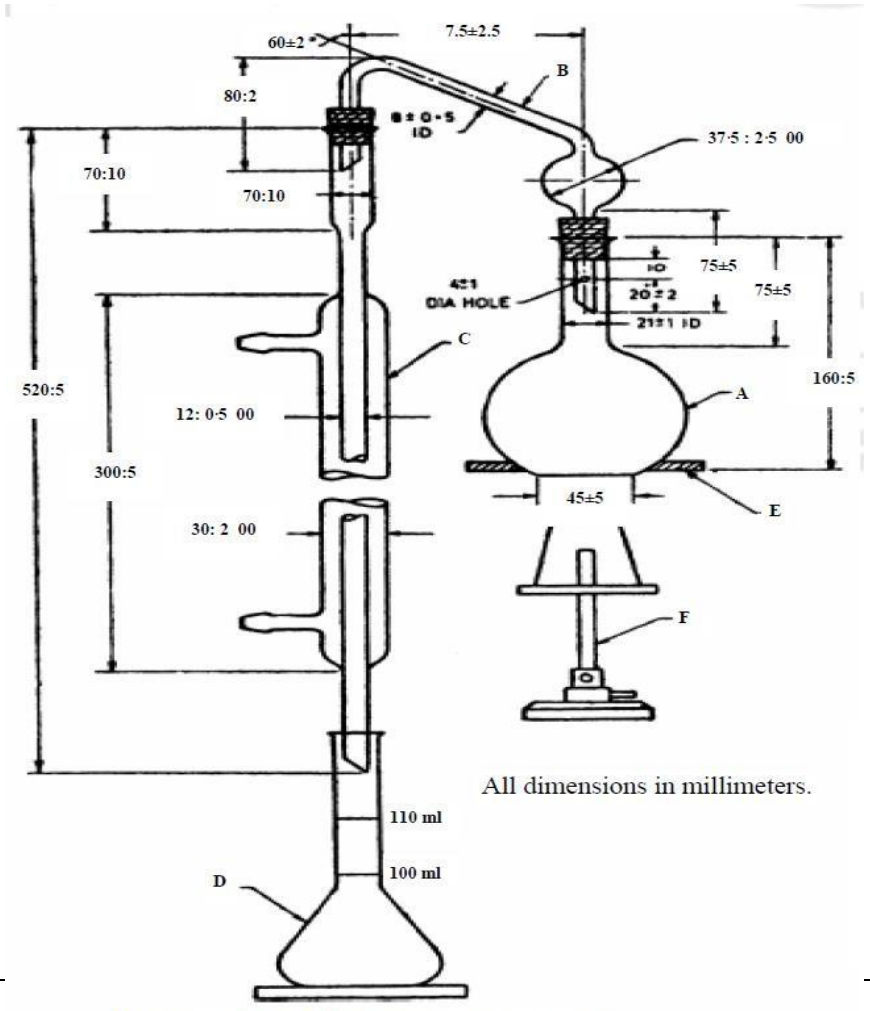
moment when the first drop of the distillate falls from the condenser in the receiving flask. Keeps the water in the condenser flowing at a sufficient speed to maintain the temperature of the outgoing water from the condenser between 15 and 20°C. Collect the distillate in a graduated flask.

- When the distillate exactly reaches the 110 ml mark on the flask, remove the flame and quickly replace the flask by a 25 ml measuring cylinder. Stopper the graduated flask and without mixing place d it in a water bath maintained at 15ºC for 10 min so that the 110 ml graduation mark is 1 cm below the water level in the bath. Swirl round the contents of the flask from time to time. Remove the graduated flask from the cold water bath, dry the outside and mix the content gently by inverting the flask 4 to 5 times without shaking. Avoid wetting the stopper with the insoluble acids. Filter the liquid through a dry, 9 cm Whatmann No. 4 filter paper. Reject the first 2-3 ml of the filterate and collect the rest in a dry flask. The filtrate should be clear. Pipette 100 ml of the filtrate and add 5 drops of the phenolphthalein solution, and titrate against standard 0.1N sodium hydroxide solution.
- Run a Blank Test without the fat, but using the same quantities of the reagents.

- **Calculation**

Reichert-Meissl Value = (A – B) x N x 11

where,
A = *Volume in ml of standard sodium hydroxide solution required for the test*
B = *Volume in ml in standard sodium hydroxide solution required for the blank*
N = *Normality of standard sodium hydroxide solution.*



Reichert-Meissl Distillation Apparatus

❖ Rancidification

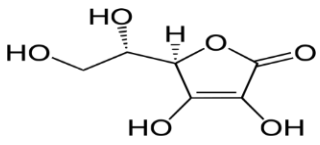
- Rancidity is the complete or incomplete oxidation or hydrolysis of fats and oils when exposed to air, light, moisture or by bacterial action, resulting in unpleasant taste and odor. Specifically, it is the hydrolysis or autoxidation of fats into short-chain aldehydes and ketones, which are objectionable in taste and odor.
- Three pathways for Rancidification:

(i) ***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.

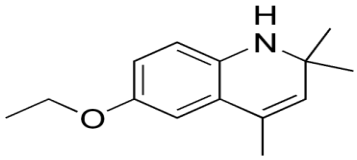
(ii) ***Oxidative:*** Oxidative rancidity is associated with the degradation by oxygen in the air. The double bonds of an unsaturated fatty acid can be cleaved by free-radical reactions involving molecular oxygen.

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 **butylated hydroxyanisole** (BHA), **butylated hydroxytoluene** (BHT), tert-Butylhydroquinone (TBHQ), **propyl gallate** and **ethoxyquin**.

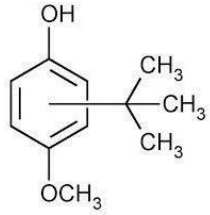
(iii) ***Microbial:*** Microbial rancidity refers to a process in which microorganisms, such as bacteria or molds, use their enzymes such as lipases to break down fat. Sterilization can reduce this process.



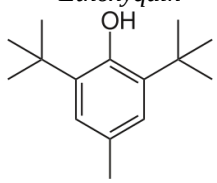
Ascorbic acid



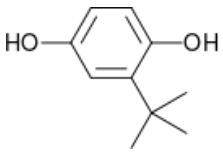
Ethoxyquin



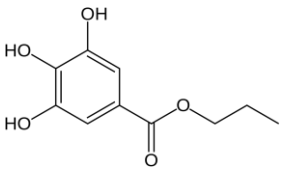
Butylated hydroxyanisole (BHA)



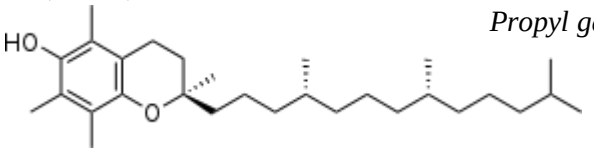
Butylated hydroxytoluene (BHT)



tert-Butylhydroquinone (TBHQ)



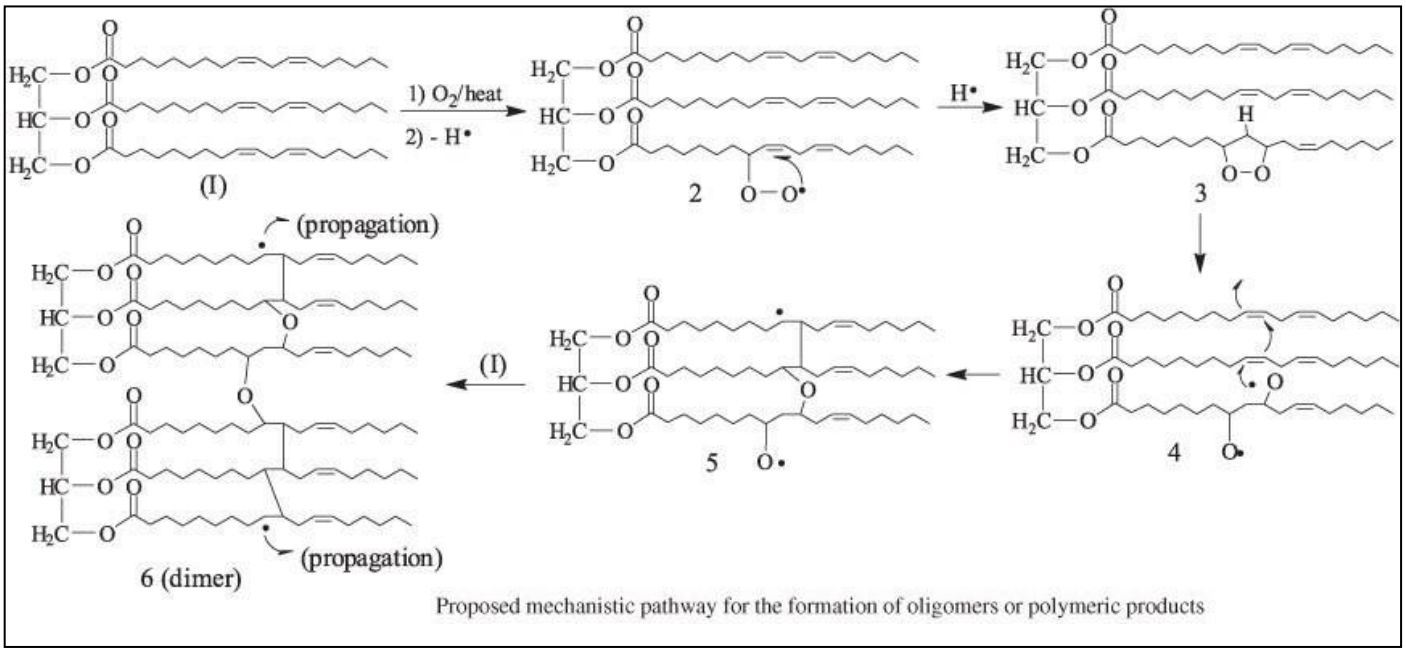
Propyl gallate



Tocopherols (vitamin E)

❖ Drying oil

- A drying oil is oil that hardens to a tough, solid film after a period of exposure to air.
- The oil hardens through a chemical reaction in which the components crosslink (and hence, polymerize) by the action of oxygen (not through the evaporation of water or other solvents).
- Drying and semi-drying oils are the vegetable oils used to make oil colour, namely linseed, poppy and sunflower. The different methods of processing oils produce products with different drying rates, consistencies and colour.
- **Semi-drying** oil is oil which partially hardens when it is exposed to air. This is as opposed to a to drying oil, which hardens completely, or a non-drying oil, which does not harden at all. Oils with an **iodine number of 115-130** are considered semi-drying.
- **Non-drying oil** is oil which does not harden when it is exposed to air. This is as opposed to drying oil, which hardens (through polymerization) completely, or semi-drying oil, which partially hardens. Oils with **an iodine number of less than 115** are considered non-drying.



Proposed mechanistic pathway for the formation of oligomers or polymeric products

❖ Hydrogenation of Oil

- Saturated fats are solid at room temperature due to their molecular shape. The term saturated is in reference to an Sp3 carbon chain that has its remaining Sp3 orbitals bonded with hydrogen atoms. Thus the term “saturated”. It‟s “saturated” with hydrogen.
- Saturated fats have a chain like structure which allows them to stack very well forming a solid at room temperature. Unsaturated fats are not linear due to double bonded carbons which results in a different molecular shape because the **Sp^2 carbons** are trigonal planar, not tetrahedral (**Sp^3 carbons**) as the carbons are in saturated fats. This change in structure will cause the fat molecules to not stack very well resulting in fats that are liquid at room temperature. Butter is mostly saturated fat, that‟s why it‟s solid at room temperature. Olive Oil is liquid at room temperature, thus it‟s an unsaturated fat. An unsaturated fat can be made in to a saturated fat by a Hydrogenation process.
- During the hydrogenation process is the production of **Tran’s fats**. Tran‟s fats are the result of a side reaction with the catalyst of the hydrogenation process. This is the result of an unsaturated fat which is normally found as a cis isomer converts to a Tran‟s isomer of the unsaturated fat. Isomers are molecules that have the same molecular formula but are bonded together differently. Focusing on the **Sp^2 double bonded carbons**, a cis isomer has the hydrogens on the same side. Due to the added energy from the hydrogenation process, the activation energy is reached to convert the cis isomers of the unsaturated fat to a Tran‟s isomer of the unsaturated fat. The effect is putting one of the hydrogens on the opposite side of one of the carbons. This results in a trans configuration of the double bonded carbons. The human body doesn‟t recognized Trans fats.
- Although the Trans fatty acids are chemically "monounsaturated" or "polyunsaturated" they are considered so different from the cis monounsaturated or polyunsaturated fatty acids that they cannot be legally designated as unsaturated for purposes of labelling. Most of the Trans fatty acids (although chemically still unsaturated) produced by the partial hydrogenation process are now classified in the same category as saturated fats.
- The major negative is that trans-fat tends to raise "bad" LDL- cholesterol and lower "good" HDL-cholesterol, although not as much as saturated fat. Trans fat are found in margarine, baked goods such as doughnuts and Danish pastry, deep-fried foods like fried chicken and French-fried potatoes, snack chips, imitation cheese, and confectionery fats.

○ *Hydrogenation definition*

- Hydrogenation is a chemical process where hydrogen reacts to an organic compound.
- It refers to the saturation of unsaturated liquid oils with hydrogen atoms.
- Molecules in unsaturated fatty acids are bent (have kinks in them), not allowing them to pack together closely.
- This limits the intramolecular attractive forces and makes their melting point lower, which means that they are liquid at room temperature.
- The hydrogenation process removes those kinks and makes the fatty acids straight, either by making them fully saturated or altering them to **Tran’s** fatty acids.
- Both saturated and **Tran’s** fatty acid chains are straight. Therefore, they can stack up closely together. This

increases their melting point.

✓ **The main purposes of hydrogenation oils to solid or semi-solid fats are:**

- They are a cheap substitute of saturated fats from animal origins, such as lard or butter;
- Hydrogenated oils are more stable than unsaturated oils. The process of hydrogenation transforms fatty acids that are prone to oxidative rancidity, especially in high temperatures during cooking;
- Hydrogenated oils are also more stable than saturated products, such as butter.
- Although butter is considered as a saturated fat food, it contains some short chain fatty acids and unsaturated fats, both of which are more prone to rancidity than long chain saturated fatty acids present in hydrogenated products.

✓ ***Full hydrogenation (full saturation)***

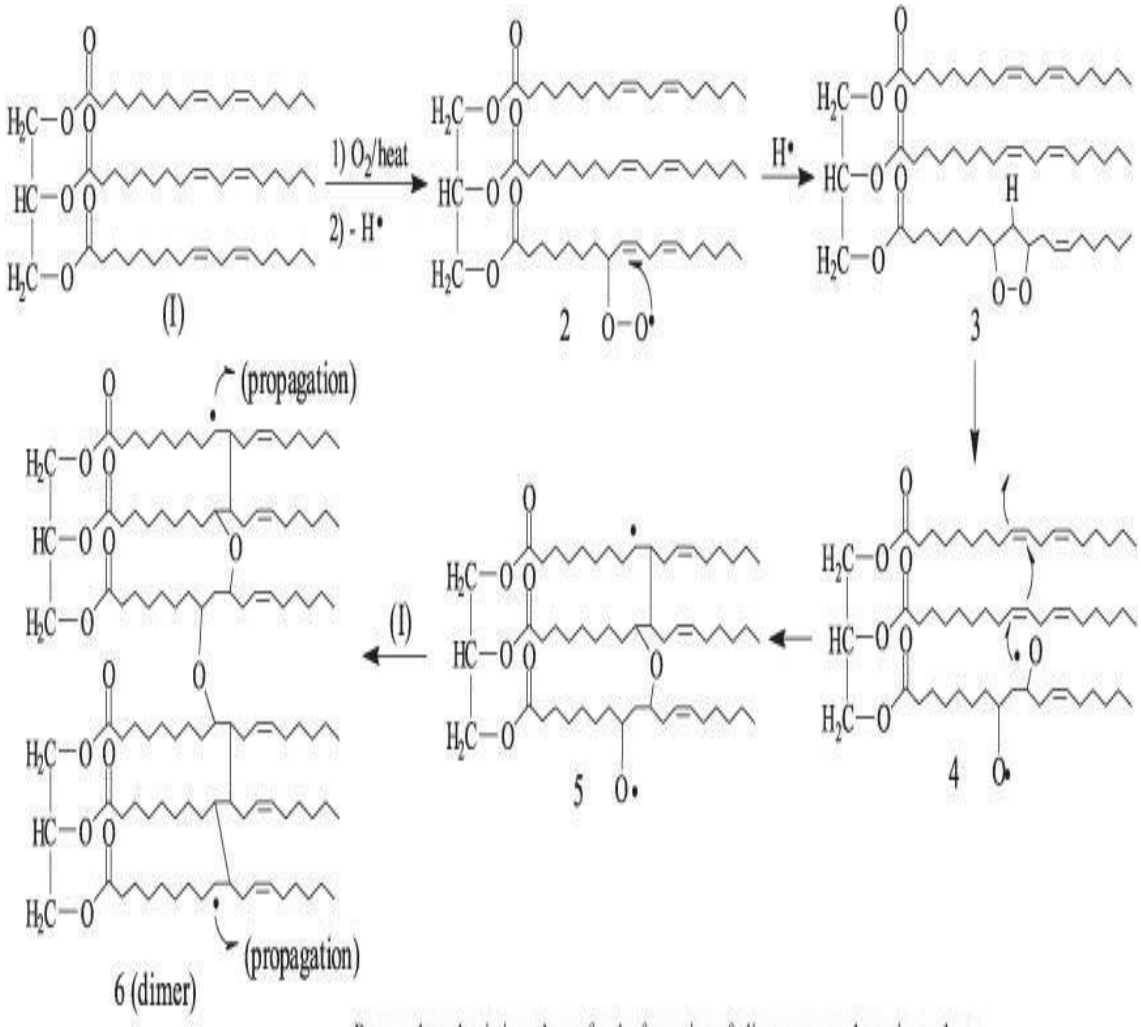
- The full hydrogenation process saturates all carbon atoms with the maximum possible number of hydrogen atoms, making the oil fully saturated (no more hydrogen atoms can be attached and also no Trans fatty acids exist).
- The process of full saturation transforms unsaturated into fully saturated fatty acids. All of the kinks/bends are removed from the structure.
- The shape of the chains becomes straight. Therefore, when they stack up together, they form a solid fat in room temperature.

✓ ***What is partial hydrogenation (partial saturation)***

- Partial hydrogenation is an incomplete process. This means that the hydrogenation process stopped before completing a full saturation of carbons with hydrogen atoms.
- As a result, there are still some double bonds present. Some of these double bonds are of “cis” configuration (normal configuration characteristic for unsaturated fatty acids) and some have been damaged in the process forming a “trans” configuration, where one of the hydrogens at the carbon double bond has been removed and another placed on the opposite side of the chain.
- The purpose of partial hydrogenation of oils is to make their properties optimal for food preparation. Partial hydrogenation results in a product that is more suitable for culinary purposes than fully hydrogenated products.

✓ ***Why are oils only partially hydrogenated?***

- Partially hydrogenated oils can give a wide range of consistencies of the finished fat product.
- Fully hydrogenating oils would make the oils hard at room temperature and not as versatile in food preparation.
- They increase the stability and the shelf life of fats in processed foods.
- They are extremely cost efficient and preferred for their usability in most commercial baked good



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