# Unit-3

## Pharmaceutical Organic-II

**Unit III** **8 Hours**

### Fats and Oils

- Fatty acids – reactions.
- Hydrolysis, Hydrogenation, Saponification and Rancidity of oils, Drying oils.
- Analytical constants – Acid value, Saponification value, Ester value, Iodine value, Acetyl value, Reichert Meissl (RM) value – significance and principle involved in their determination.

## Fats and Oils:

- Fats & oil belongs to group of natural compound which is soluble in organic solvent such as benzene, chloroform, etc. but insoluble in water these are chemically esters can be further divided into two classes.

1. Fat and oils which give long chain fatty acids and glycerol on hydrolyses.
2. Waxes which on hydrolyses gives long chain fatty acid and long chain alcohol.

- Fatty acid are esterified with glycerol, fatty acid is the main constituent of oil and fat the reactive site of fatty of fatty acid is carboxyl group and double bond present in fatty acid.
- The adjacent methylene carbon increases the reactivity most naturally occurring fatty acid contain 4-22 carbon atom in which 18 carbon containing fatty acid is most common.

$$CH_3\text{-}(CH_2)_4\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}COOH$$

**Fats and oils are called triglycerides or triacylglycerol.**

### Difference between Fat and Oils:-

| Sr. No. | Fat | Oils |
|---|---|---|
| 1. | Fats are solid, semi-solid, at room Temperature. | Oils are liquid at room temperature. |
| 2. | It contains large amount of saturated fatty acid<br>Eg. Stearic acid palmitic acid | It contains large amount of unsaturated fatty acid.<br>Eg. Oleic acid |
| 3. | Fats are melt at high temperature. | Oils are melt at low temperature. |
| 4. | Fats are obtained from animal sources. | Oils are obtained from vegetable sources. |
| 5. | Fats are more stable | Oils are less stable. |

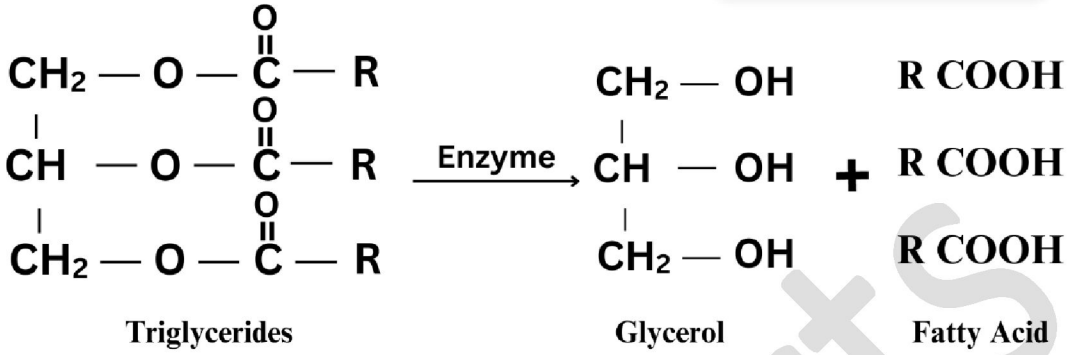
### Physical Properties:

- Oils and fats may be either liquid or non-crystalline solid at room temperatures.
- They are colourless, odourless and tasteless.
- The characteristics colour-odour and flavour associated with natural oil and for example- yellow colour of butter is due to presence of pigment.

### Chemical reaction:

**1. Hydrolysis:**

- Triglyceride are easily hydrolysed by enzyme into fatty acids and glycerol.
- The fatty acid produced get metabolised in human body.

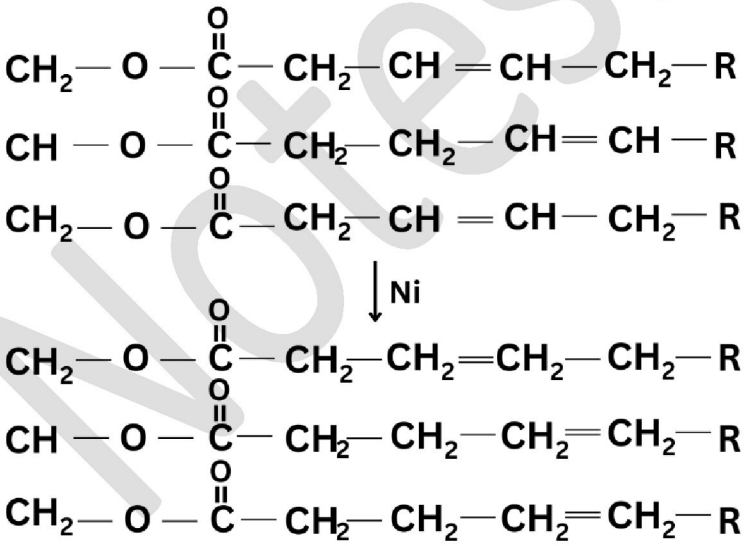



**Triglycerides** **Glycerol** **Fatty Acid**

**2. Hydrogenation:**

- Unsaturated glycerides on hydrogenation in presence of metal catalyst give saturated glyceride this reaction is similar to catalytic hydrogenation of alkenes.



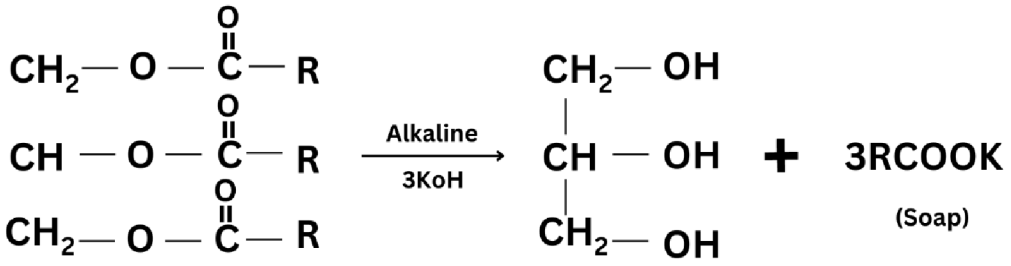



**Unsaturated triglycerides oil**

**Saturated Glycerides Fat**

**3. Saponification:**

- When triglyceride are hydrolysed in alkaline medium they produces glycerol and salt of fatty acid.
- Commonly sodium or potassium salt are used for soap preparation.




**Triglycerides oil** **Glycerol** **Salt of Fatty acid**

**Rancidity (Hydrolysis-Oxidation):**

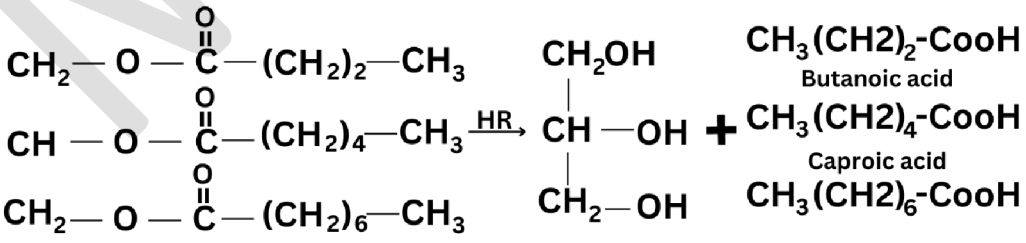
- The term rancidity is applied to any fat or oil when they develop disagreeable odour when exposer to warm and moist air for long time.
- Rancidity is mainly cause by hydrolysis of ester and oxidation of unsaturation present in triglyceride.
- The lower molecular weight acid are produce which are volatile and produces bad (Disagreeable).
- Rancidity may be cause due to Hydrolytic and oxidative rancidity.

1. Hydrolytic rancidity
2. Oxidative Rancidity

**1. Hydrolytic rancidity:**

- This type of rancidity is due to hydrolysis of triglyceride containing lower fatty acid.
- Eg: In case of butter on hydrolytic rancidity they produces butyric acid, Caprylic acid.





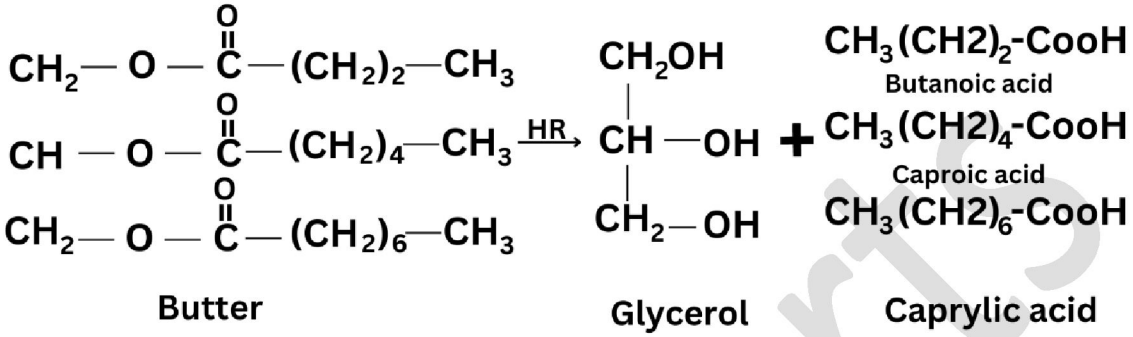

**Butter** **Glycerol** **Caprylic acid**

- The microorganism present in the air participated in hydrolytic process to protect hydrolytic rancidity we preserve the butter top keep in refrigerator.

**2. Oxidative Rancidity:**

- This type of rancidity occurs in triglyceride continuing unsaturated fatty acid.
- The Unsaturated double bond are get oxidise and form short chain of acid or aldehyde.
- Oxidative rancidity occurs after cleavage of ester link hydrolysis.





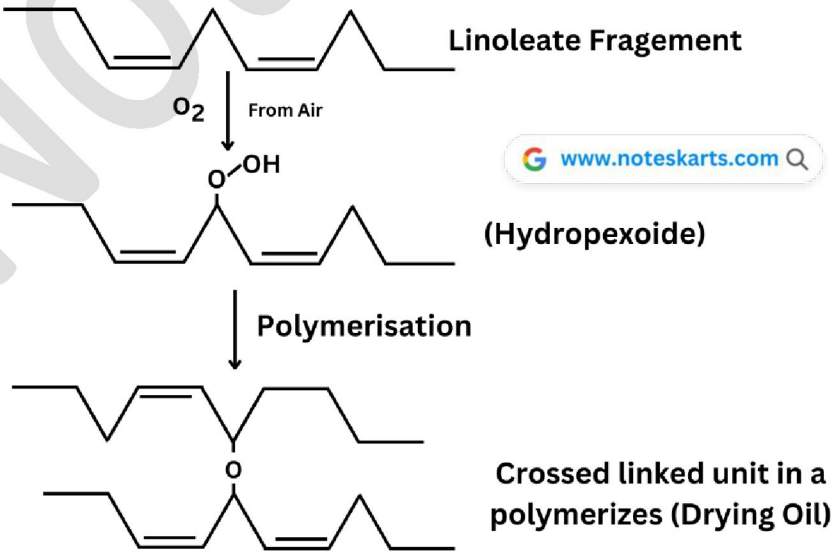

- The addition of antioxidant to be fat or oil will preserve for long period of storage.

**Drying oils:**

- When highly unsaturated oil are exposed to air they undergo oxidation and polymerization to form a thin waterproof film.
- These oils are called drying oil. And reaction and process is known as drying.

Eg:

- Linseed oil, which is rich in linolenic acid is a common drying oil used in oil based paints.



**Analytical constants – Acid value, Saponification value, Ester value, Iodine value, Acetyl value, Reichert Meissl (RM) value – significance and principle involved in their determination.**

## 1) Acid Value:

It ids used to measure the free fatty acid present in fats and oils. And free fatty acids in fats and oils are harmful for human.

**Principle:**

- It is determined by directly titrating the oil/fat in an alcoholic medium against standard potassium hydroxide/ sodium hydroxide solution.
- Dissolved 10gm of Sample in 50 ml of mixtures of equal volume of ethanol (95%) and ether then previously neutralised with 0.1 KOH and add phenolphthalein solution as a indicator.

$$\text{Acid Value} = 5.61\ \frac{n}{w}$$

Where

n= burette reading

w= Sample weight

**Significance:**

- The value is a measure of the amount of free fatty acid which have been liberated by hydrolysis from the glycerides due to the action of moisture, temperature or lypolytic enzyme lipase.
- Therefore oils with increased acid number are unsafe (harmful) for human consumption.

## 2) Saponification value:

- It is the number of mg of KOH required to saponify one gram of a fats and oils.
- It is the measure of average molecular weight of the fatty acids presents.

**Principle:**

- Saponification is the process by which the fatty aids in the triglycerides or fats are hydrolysed by an alkali to give glycerol and potassium/sodium salts of fatty acids.
- A known quantity of fats or oil is refluxed with an excess amount of alc. KOH.
- After saponification it titrate against a standard acid.
- Sample is titrated with 0.5 M HCL (a)
- Perform blank titration (b)
- The value obtained is used for the determination of saponification value of fats and oils.
- Phenolphthalein solution used as a indicator.

$$\boldsymbol{Saponification\ Value} = \frac{\mathbf{28.05\ (b-a)}}{\boldsymbol{W}}$$

**Where,**

W= Weight of sample

**Significance:**

The magnitude of saponification value gives an idea about the average molecular weight of the oils and fat.

$$Molecular\ Weight\ of\ Fat = \frac{mg\ of\ KoH}{Saponification\ valur\ of\ fat}$$

Acc to this,

**Saponification value↑=Molecular weight↓**

**3) Ester Value:**

- The number of mg of potassium hydroxide required to saponify ester present in 1 gm of given sample.
- If saponification value and acid value have be determined than difserence between these two represents the ester value.

**Ester Value = Saponification Value –Acid Value**

**Procedure:**

- Take a given amount of sample in a flask and required alcohol mix it by shaking the content and add phenolphthaline indicator than titrate with 0.5N alcoholic KOH until free fatty acid is completely neutrilised.
- Add excess amount of alcoholic KOH (0.5N) and proceed for saponification value.

$$EV = (56.1\ (V_B\text{-}V_T).N)/W$$

Where,

- $V_B$ = Volume of 0.5 N HCL required in blank sample
- $V_T$= Volume of 0.5 N HCL consumed in test sample titration.
- N= Narmality of HCL
- W= Weight of taken sample

**4) Iodine value:**

- It is the number of grams of iodine that would add to C=C present in 100g of the fats and oil.

**Principle:**

- The oil/fat sample taken in carbon tetrachloride is treated with a known excess of iodine monochloride solution in glacial acetic acid.
- The excess of iodine monochloride is treated with potassium iodine.
- Now this sample is titrate against 0.1 M sodium thio-sulphate solution, starch solution used as a indicator for estimation of liberated iodine (a) then perform a blank titration (b).

$$\text{Iodine Value} = \frac{1.269\ (b-a)}{W}$$

**Significance:**

- The iodine value is a measure of the amount of double bonds (unsaturation) in a fats.
- Iodine Value↑ = Number of double bond↑
- Unsaturated lipids are more susceptible to rancidity.

**5) Acetyl Value:**

- It is the mg of KOH required to acetic acid liberated by the hydrolysis of 1g of the acetylated substances.

**Principle:**

- It is determined through saponification value
- Boil the 10g of sample with 20 ml of acetic anhydside for 2hours.
- Add 600 ml water and boil for 30 min.
- Separate and wash the acetylated product.
- Determine the saponification value of the acetylated substances (b ml)
- Determine the saponification value of the substance (a ml)

$$Acetyl\ Value = \frac{1335(b-a)}{(1335-a)}$$

Where,

- a= saponification of the substance
- b= Saponification value of the acetylate substance.

**Significance:**

- It is the measure of hydroxyl (OH) acids in lipids.

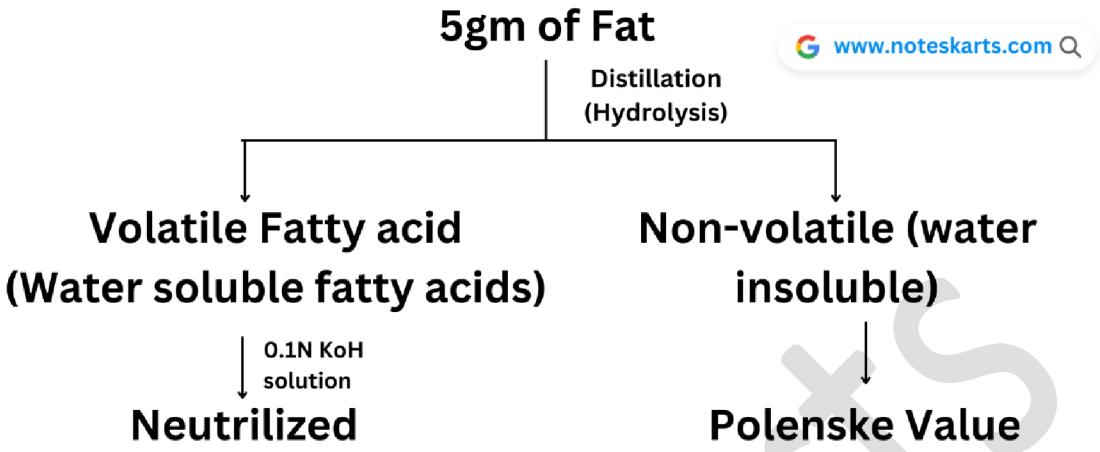
**Acetyl value↑ = more amount of free fatty acids↑**

## Reichert Meissl (RM) value:

- It is useful in testing the purity of butter, since it contains a good concentration of volatile fatty acids butyric acid, caproic acid, and caprylic acid.
- So it is defined as the ml of 0.1 N KOH required to completely neutrilize the soluble volatile fatty acids distilled from 5g fat.

**Principle:**

- Fat is saponified using glycerol-alkali solution and acidified by sulphuric acid to liberate free fatty acids.
- The liberated fatty acids are steam distilled and the steam volatile fatty acids are collected as condensate.
- The cooled condensate of the volatile fatty acids is filtered for separation of water soluble and water insoluble fatty acids.
- The water soluble fatty acids is titrated with alkali to give RM value.




**Eg: Butter (short chain fatty acids) RM value 25-30**

- While RM value is less than 1 for more other edible oils.
- Thus, adulteration of butter can be easily tested by this sensitive RM number.
- Significance:
- It is a measure of water soluble steam volatile fatty acids, specially butyric acid and caproic acid present in oil or fat.
- Butter fat contain butyric acid glycerides, and no other fat contain it so RM value is high for butter fat.
- These determination have been used principally for analysis of butter.