UNIT - III
FATS AND OILS

Points to be covered in this topic

1. INTRODUCTION
2. NOMENCLATURE OF FATS
3. DIFFERENCE BETWEEN FATS AND OILS

❑ INTRODUCTION

- Fats and oils are the **esters of fatty acids and alcohols** and on hydrolysis gives fatty acids and alcohols.
- Fats and oils are mainly the **glyceryl esters of various fatty acids** like **palmitic, stearic, oleic, linoleic and linolenic.**
- These are also called as **triglycerides** as three molecules of **fatty acids** condense with one mole of glycerol to form fat. **For example**

$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3\ HOOC{-}CH_2{-}CH_2{-}CH_3 \longrightarrow \begin{array}{l} CH_2OCOCH_2CH_2CH_3 \\ | \\ CHOCOCH_2CH_2CH_3 \\ | \\ CH_2OCOCH_2CH_2CH_3 \end{array}$$

Glycerol — Butyric acid — Tributyrin (Fat)

- **Fats on hydrolysis by the enzyme lipases** gives corresponding **fatty acids and glycerol.**
- **Fats and oils are of two types:**

1. **Simple**- When the **three fatty acids of triglyceride are same.**
2. **Mixed**- When the **three fatty acids of triglyceride are not identical.**

NOMENCLATURE OF FATS

- **Glycerol** which is the main part of **fat** is a **trihydric alcohol** and its **triester has three acid residues.**
- If all the **three residues are identical**, it is known as **simple fat** and if they are **not same**, fat is called **mixed glyceride.**
- For **simple fats** the name is given by naming the **alcohol (Glycerol)** or its **radical (glyceryl)** and **naming the acid. For example**

$$\begin{array}{l} CH_2OCOC_3H_7 \\ | \\ CHOCOC_3H_7 \\ | \\ CH_2OCOC_3H_7 \end{array}$$

Glycerol tributyrate

or

Tributyrin

$$\begin{array}{l} CH_2OCOC_{17}H_{35} \\ | \\ CHOCOC_{17}H_{35} \\ | \\ CH_2OCOC_{17}H_{35} \end{array}$$

Glycerol tristearate

or

Tristearin

- In case of **mixed fats/triglycerides**, the positions and the names of the acidic groups are given as **1, 2, 3 or α, β, α'** etc. **For example**

$$\begin{array}{l} CH_2OCOC_{17}H_{35} \\ | \\ CHOCOC_{15}H_{31} \\ | \\ CH_2OCOC_{17}H_{35} \end{array}$$

β-Palmito-α,α'-distearin

❑ DIFFERENCE BETWEEN FATS AND OILS

	Fats	Oils
1.	Fats are solids or semisolids at room temperature.	Oils are liquids at room temperature
2.	Fats contains large amount of saturated fatty acids e.g. stearic and palmitic acids	Oils contain a large amount of unsaturated acids e.g. oleic acid.
3.	Fats meet at higher temperature	Melt at lower temperature.
4.	Fats are animal fats	Oils are vegetable fats.
5.	Fats do not contain double bonds.	Oils have double bonds
6.	Fats are more stable.	Oils are less stable.

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Points to be covered in this topic

1. REACTIONS
2. HYDROLYSIS
3. HYDROGENATION
4. HYDROGENOLYSIS
5. HALOGENATION
6. OXIDATION
7. SAPONIFICATION
8. RANCIDITY OF OILS
9. DRYING OILS

❑ REACTIONS

- **Fats and oils** are **triesters of glycerol** and contain **saturated and unsaturated fatty acids.**
- They undergo reactions of **ester groups in triplicate** and **carbon-carbon double bonds.**
- **Fats and oils give the following reactions:**

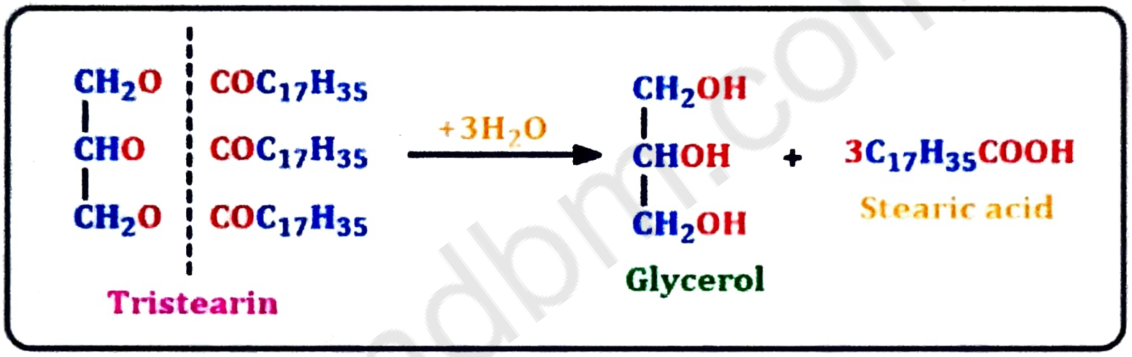
1. **Hydrolysis,**
2. **Hydrogenation,**
3. **Hydrogenolysis,**
4. **Halogenation,**
5. **Oxidation,**
6. **Saponification,**
7. **Rancidity of oils, and**
8. **Drying oils**

HYDROLYSIS

- **Fats and oils undergo the following hydrolysis reactions:**

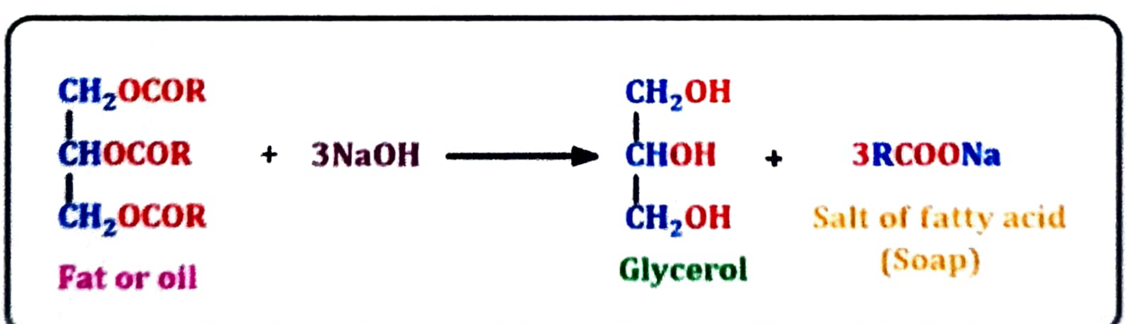
1. By Superheated Steam:

- **Fats and oils undergo hydrolysis** in the **presence of lime, zinc oxide, or magnesia under 8 atm pressure** and at **170°C.**
- **On cooling, free fatty acids separate out** along with some calcium or zinc or magnesium soap. **For example,**



2. Base-Hydrolysis:

- **Glycerol and sodium or potassium salts of higher fatty acids (soaps)** are obtained on **heating fats and oils with NaOH (or KOH) solution.** Base hydrolysis of fats or oils is also known as **saponification.**

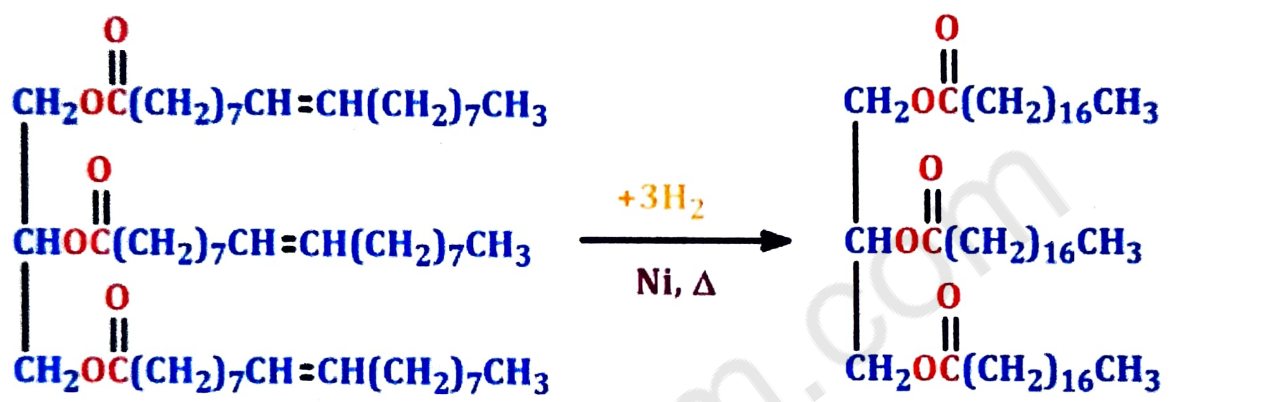


3. Enzyme Hydrolysis:

- **On adding lipase enzyme** to an **emulsion of fat in water, fats** undergo **hydrolysis and form acid** and glycerol in **2-3 days.**

❑ HYDROGENATION

- **Vegetable oils** are **triglycerides of unsaturated fatty acids** (e.g., oleic and linoleic acids).
- **Catalytic hydrogenation** at **low pressures** introduces hydrogen across the **carbon-carbon double bonds** of the acid components of triglycerides, resulting in **saturated glycerides** (solid fats at room temperature).
- This process of hydrogenation is termed as **hardening of oils.**

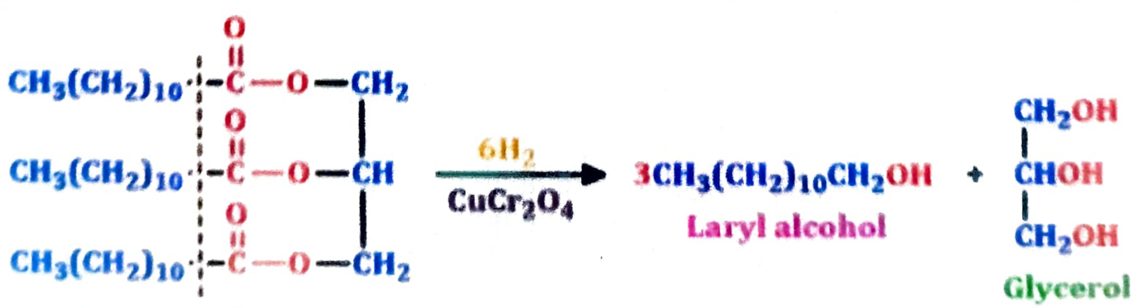


Glyceryl trioleate (mp 17°C)
(A liquid vegetable oil)

Glyceryl trioleate (mp 55°C)
(A solid fat)

❑ HYDROGENOLYSIS

- **Hydrogenolysis** means hydrogenation involving cleavage.
- In this reaction, the **ester groups of triglycerides (fats or oils)** are **reduced with hydrogen** in the presence of **copper chromite ($CuCr_2O_4$, catalyst)** under high pressure and temperature. This reaction gives **glycerol and long-chain primary alcohols** corresponding to the acid portion.

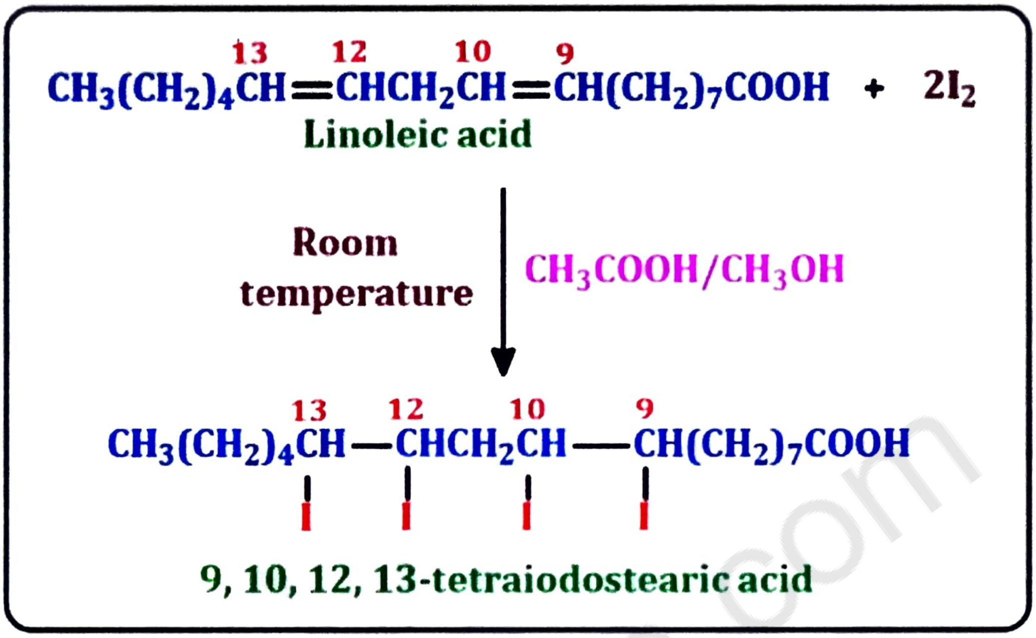


Glyceryl trilaurate

- The obtained **long-chain alcohols** are used for manufacturing detergents.

❑ HALOGENATION

- In this reaction, **unsaturated fatty acids and their esters** take up halogens **(Br_2 and I_2)** at their double bond's at room temperature in **acetic acid or methanol solution**. **For example,**



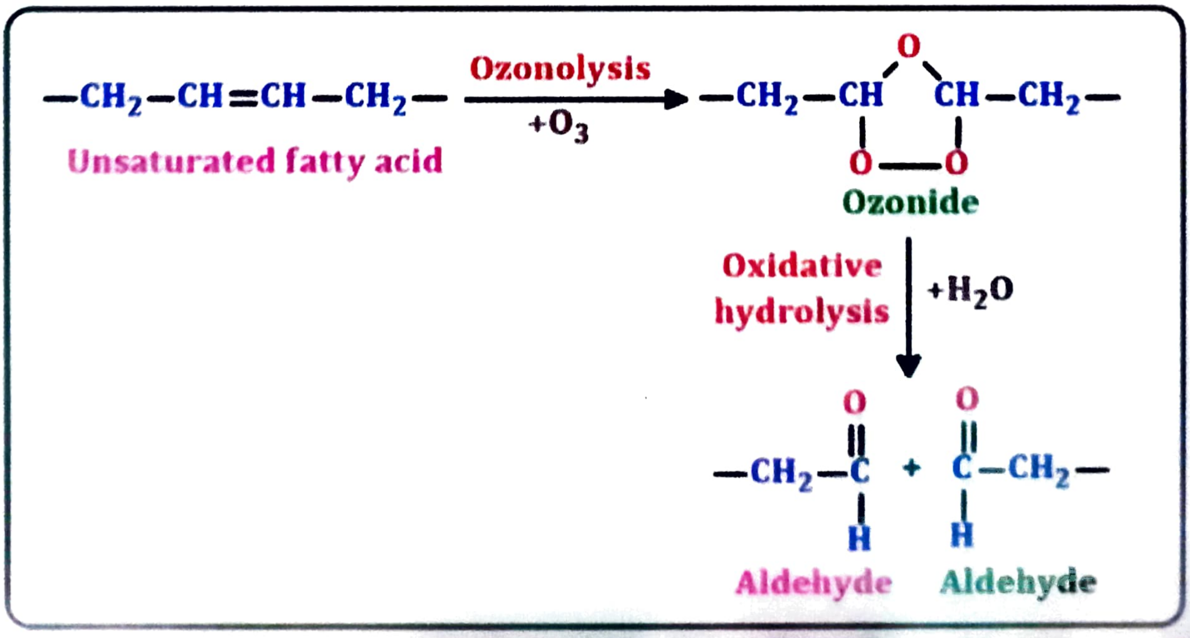
- This reaction forms the **base of iodine number determination**

❑ OXIDATION

- **Oxidation of unsaturated fatty acids** can occur at their **double bonds** as follows:

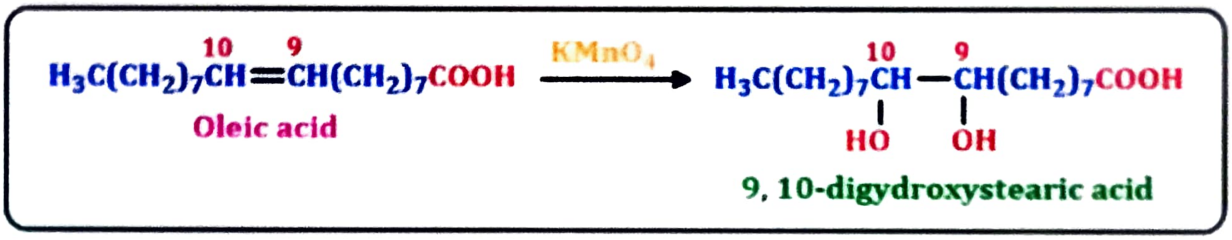
1. With Ozone:

- **Fats** undergo **oxidation with ozone** to form an **unstable ozonide** which is cleaved by water to form two **aldehydic groups.**



2. With $KMnO_4$:

- **Fats** undergo **oxidation with potassium permanganate** under mild conditions to form **glycols at the sites of double bonds**



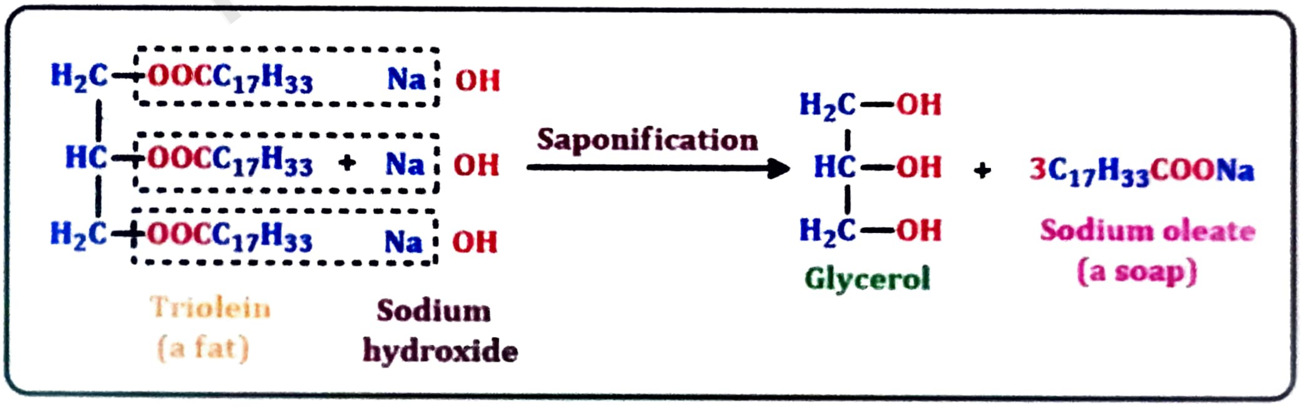
❑ SAPONIFICATION

- **Saponification** is the process of **hydrolysis of fats** in the presence of **alkali.**
- As a result of **saponification, glycerol and salts of fatty acids** which are called **soaps** are formed.

➢ **Soaps are categorized into hard and soft soaps.**

1. **Hard soaps** are the **sodium salts of higher fatty acids** (e.g., **common soap bars**).
2. **Soft soaps** are the **potassium salts of higher fatty acids** (e.g., **semisolids or pastes**).

- The **fatty acid salts** of **calcium, magnesium, zinc, and lead** are water **insoluble.**
- **Zinc soaps** are used for manufacturing **talcum powder** and other **cosmetics.**
- **Lead and magnesium soaps** are used in paint industries to facilitate the drying process.



- **Soaps** are used as **cleansing agents** due to their **emulsifying action** (i.e., capacity to render more prolonged **mixing of oil and water**)
- It acts via **negative charge** which the **soap anion puts on the oil droplets**. The resultant **electrostatic repulsion prevents the coalescence** of soap and oil droplets into an **oil phase**.

❑ RANCIDITY OF OILS

- Oils on exposure to heat, light, air, moisture, and bacterial action, develop an offensive odour and taste; this is termed rancidity.
- Rancid oils have short chain dicarboxylic acids, aldehydes, and ketones of unsaturated fatty acids.
- Rancid oils cannot be consumed by humans due to their harmful physiological effects.

➢ **Rancidity is categorized into the following two types:**

1. Hydrolytic Rancidity

- It is a common reaction which spoils fat.
- In this type of rancidity, fats hydrolyze into free fatty acids by lipase enzyme.
- These low molecular weight fatty acids impart an unpleasant odour to the fats, thus spoiling them.

2. Oxidative Rancidity

- In this type of rancidity, oxygen is attained at the double bonds of the unsaturated glycerides, thus a number of oxidative decomposition products (aldehydes, ketones, low molecular weight fatty acids, hydroxy acids, oxy acids, and gases) are formed.
- Various oxidative decomposition products may be formed, however according to Kerr, the exact nature of these changes is generally unclear.

✓ Oxidative rancidity also results in physical and chemical changes in oils, such as decrease in iodine value, and increase in specific gravity, acid value, and peroxide value.

❑ DRYING OILS

- Highly unsaturated oils undergo oxidation and polymerization to form a thin waterproof film when exposed to air.
- This reaction is termed drying and the resultant oils are termed drying oils.
- For example, linseed oil (rich in linolenic acid) is a common drying oil used in oil-based paints.
- Non-drying oils are either saturated or moderately unsaturated.

UNIT - III
FATS AND OILS

Points to be covered in this topic

1. ANALYTICAL CONSTANTS OF FATS AND OILS
2. ACID VALUE
3. SAPONIFICATION VALUE
4. ESTER VALUE
5. IODINE VALUE
6. ACETYL VALUE
7. REICHERT-MEISSL (RM) VALUE
8. USES OF FATS AND OILS

❑ ANALYTICAL CONSTANTS OF FATS AND OILS

- The chemical nature of fatty acids and the number of hydroxyl groups present in a fat molecule can be determined from the reactions.
- These chemical determinations are called chemical constants and involve the following analytical tests:

1. Acid value,
2. Saponification value,
3. Ester value,
4. Iodine value,
5. Acetyl value, and
6. Reichert- Meissl (RM) value.

❑ ACID VALUE

- It is the **number of milligrams of KOH** required to **neutralize the free fatty acids** present in **1 gm of fat or oil.**
- Normally, the **free fatty acids** along with the **triglycerides** are present **in oils in small amounts.**
- The **free fatty acid content is the acid number/acid value**, which **increases during the storage period.**
- Thus, the free fatty acid content **influences** the keeping **quality of oil.**

❖ Principle

- The **content of free fatty acid in oil** can be **determined by titrating it against KOH** using **phenolphthalein** as an indicator.

❖ Determination

➢ **Acid value can be finally calculated using the formula:**

$$\text{Acid value (mg KOH/g)} = \frac{\text{Titre value} \times \text{Normality of KOH} \times 56.1}{\text{Weight of the sample (g)}}$$

- The free fatty acid content is **calculated as oleic acid** using the equation:

$$1\text{ml N/10 KOH} = 0.028\text{gm oleic acid}$$

- The **exact strength of KOH** can be determined by **titrating 0.1N oxalic acid solution** (630mg in 100ml water) against KOH using **phenolphthalein** indicator. The strength of KOH can then be determined using the formula:

$$V_1N_1 = V_2N_2$$

❖ Significance

- **Acid value** gives the **free fatty acid content in an oil or fat.**
- A stale or **rancid fat or oil stored** under **improper conditions** possess a **high acid value.**

SAPONIFICATION VALUE

- It is the number of milligrams of KOH required to saponify 1 gm of fat or oil.
- This value is used for comparative study of fatty acid chain length in oils.
- The process of saponification involves hydrolysis of fatty acids in the glycerides by an alkali.

Principle

- With an excess amount of alcoholic KOH, a known quantity of oil is refluxed.
- After saponification, the remaining KOH is determined by titrating it against a standard acid.

Determination

- Saponification value can be finally calculated using the formula:

$$\text{Saponfication value} = \frac{28.05 \times (\text{Titre value of blank} - \text{Titre value of sample})}{\text{Weight of the sample (g)}}$$

Significance

- The saponification value provides information regarding the average chain length of fatty acids present in the fat.
- The saponification value and the chain length of fatty acids are inversely proportional

ESTER VALUE

- It is the number of milligrams of KOH required to react with the esters in 1 gm of a fat or oil.
- Difference between the acid and saponification values gives the ester value.

Principle

- The number of milligrams of KOH required for saponification of esters in sample is determined.

Determination

- Subtracting the acid value of oil from the saponification value of the corresponding oils gives the ester value:

$$\text{Ester Value} = \text{Saponification Value} - \text{Acid Value}$$

Significance

- Ester value gives the number of hydroxyl group present in the fat or oil.

❑ IODINE VALUE (KOETTSTORFER NUMBER)

- It is the **number of grams of iodine absorbed by 100 gm of fat or oil**
- **This value is constant for a particular oil or fat.**

❖ Principle

- **Both saturated and unsaturated fatty acids** are present in oils.
- **Iodine** gets incorporated at the **double bonds** present in the fatty acid chain. Thus, **the iodine amount absorbed** by the oil indicates the **unsaturation degree.**

❖ Determination

- Difference between the **quantity of thiosulphate required for blank** and the quantity required for sample gives **thiosulphate equivalent of iodine absorbed by the sample:**

$$\text{Iodine number} = \frac{(B\text{-}S) \times N \times 12.69}{\text{g sample}}$$

Where,
B = Volume of thiosulphate for blank (ml)
S = Volume of thiosulphate for sample (ml)
N= Normality of thiosulphate solution

- The **amount of fat or oil** should be adjusted so that the **excess iodine in the added 25ml of Hanus iodine solution** has around **60% of excess iodine** of the amount added **[i.e., if (B-S) is greater than B/2]**. The process is **repeated with smaller amount of sample.**

❖ Significance

- **Iodine value** is used to study **oxidative rancidity of oils,** since **higher the unsaturation greater the rancidity of oils.**
- **Greater the number of double bonds** in the acid residues of a triglyceride, **greater will be the amount of iodine** that adds to 100 grams. Since a **saturated fatty acid does not have any double bonds**, it does not take up iodine, and has **zero, iodine number.**
- The **iodine number of oleic acid** having a **C=C bond is 90**, of **linoleic acid having two C=C bonds is 181,** and of linolenic acid having **three C=C bonds** is 274. Thus, the **iodine number of animal fats** having a large amount of **saturated** acid residues is low, and of **vegetable oils** having a large amount of **unsaturated acid** residues is high.

❑ ACETYL VALUE

- It is the number of milligrams of KOH required to neutralize the acetic acid obtained by saponification of 1gm of fat or oil after it has been acetylated (treatment fat or fatty acid mixture with acetic anhydride acetylates all the alcoholic –OH groups)

❖ Principle

- On adding acetylating agent, e.g., acetyl chloride (CH_3COCl), the CH_3CO group replaces the hydrogen in alcoholic group (-OH); this process is termed acetylation.
- Alcohol is obtained during saponification of fat or oil.
- This alcohol reacts with CH_3COCl to form an acetyl derivative, which hydrolyses into a volatile acetic acid in the presence of a non-volatile acid (such as benzene sulphonic acid).
- The resultant mixture is distilled when acetic acid distils over.
- The obtained distillate is titrated with standard KOH solution.

❖ Determination

- The acetyl value is calculated using the following formula:

$$\text{Acetyl Value} = 1335\,(b-a)/(1335-a)$$

Where,

a = Saponification value of the sample

b = Saponification value of the acetylated product

❖ Significance

- Acetyl number is the number of OH groups present in a fat or oil. For example, castor oil contains a large amount of ricinoleic acid (a hydroxy acid), thus has a high acetyl number (146).

❑ REICHERT-MEISSL (RM) VALUE

- It is the number of millilitres of 0.1N KOH required to neutralize the soluble, volatile fatty acids derived from 5 gm of fat or oil.

❖ Principle

- The sample is saponified on heating with glycerol sodium hydroxide solution and then split on treating with dilute sulphuric acid.
- The volatile acids are steam distilled.
- The soluble volatile acid in the distillate is filtered and titrated against standard sodium hydroxide solution.

❖ Determination

- The sample is completely saponified using alkali.
- The resultant solution is acidified with dilute sulphuric acid and then steam distilled.
- The obtained distillate is titrated with 0.1N KOH solution and RM value is determined using the formula:

$$\text{R.M.Value} = \frac{\text{No. of ml of 0.1N KOH}}{\text{W(wt. of oil or fat)}} \times 5$$

❖ Significance

- The RM number is the quantity of short chain fatty acids (up to C10) in a fat molecule.
- The RM number of coconut and palm oils ranges between 5 and 8. However, butterfat is an exception whose RM number ranges between 17 and 35.
- This high RM value aids in detecting any foreign fats which adulterate the manufactured butter.

❑ USES OF FATS AND OILS

1. They are energy reservoirs, and are more efficient than proteins and carbohydrates.
2. They are used in soap industries.
3. Linseed oils are used for manufacturing paints, oil cloth, varnishes, linoleum, and liquors.
4. They are used as raw materials for preparing higher alcohols used for manufacturing synthetic detergents.
5. Groundnut oils are used for manufacturing Vanaspati ghee (marketed as Dalda, Rath, Gagan, etc.).
6. By grinding carbon black with oil containing a drier, printing inks can be made.
7. Castor and cotton seed oils are used as purgatives.
8. Cod liver oils are used in vitamin A and D deficiency conditions.
9. Castor oils are used as lubricants.
10. Oils are also used in making hair oils, candles, polishes, etc.
11. They are used for preparing high molecular weight, straight chain carboxylic acids.