

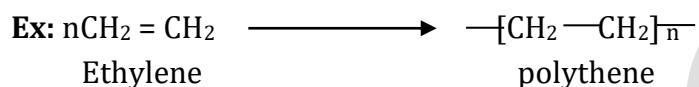
UNIT-II
POLYMERS AND FUEL
CHEMISTRY

POLYMERS

Introduction

Polymers are large class of materials consisting of many small molecules called monomers that can be linked together to form long chains. Thus, they are known as macromolecules.

The overall reaction leading to the formation of polymers from monomers (Ethylene) is called “**Polymerization**”.



Classification of polymers

Polymers are classified into various types depending on:

- i) Origin ii) Chemical nature iii) Thermal property**
iv) Nature of monomers V) Mechanisms

i) Origin of the polymers: Based on the origin polymers are of two types:

- ✚ **Natural polymers:** The polymers which are isolated from natural resources are called natural polymers. **Ex:** Starch, Natural rubber, Cellulose etc.
- ✚ **Synthetic polymers:** The polymers which are isolated from low molecular weight compounds are called synthetic polymers. **Ex:** Teflon, PVC, Polyethylene, etc.

ii) Chemical nature of polymers: Based on chemical nature, polymers are of two types:

- + **Organic polymers:** In organic polymers, the polymer chains are made up of carbon atoms. **Ex:** Styrene
- + **Inorganic polymers:** In inorganic polymers, the polymeric chains are made up of inorganic elements. **Ex:** Silicon rubber

iii) Thermal property: Based on thermal property polymers are classified into two types:

- + **Thermoplastic polymers:** Polymers which become soft on heating and becomes hard on cooling. **Ex:** PVC, Polyethylene etc.
- + **Thermo setting polymers:** During moulding, these polymers get hardened and once they have solidified, they cannot be softened. **Ex:** Bakellite

IV) Nature of monomers: Based on nature of monomers polymers are of two types:

✚ **Homo polymers:** These polymers are derived from identical monomer unit.

Ex: Polyethylene

✚ **Copolymers:** These polymers are derived from two or more different monomer units in the chain are called copolymers. Ex: Nylon 6,6

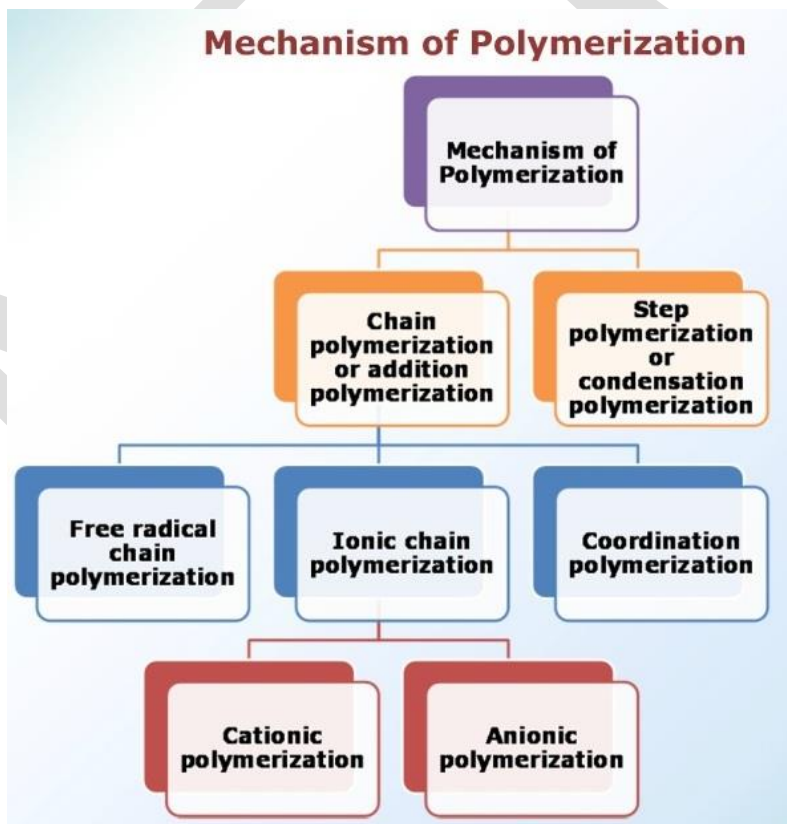
V) Mechanisms: Based on mechanisms polymers are classified into:

✚ **Addition polymers/Chain polymers:** The polymers which are formed by the addition of monomeric units repeatedly. Ex: PVC, Polyethylene

✚ **Condensation polymers/Stepwise:** The polymers which are formed by the process of condensation. Ex: Polyester, Nylon 6,6 etc.

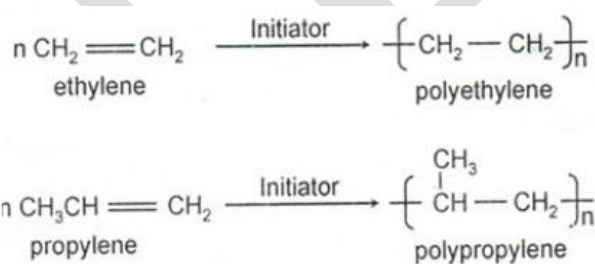
Types of Polymerization

Mechanism of polymerization

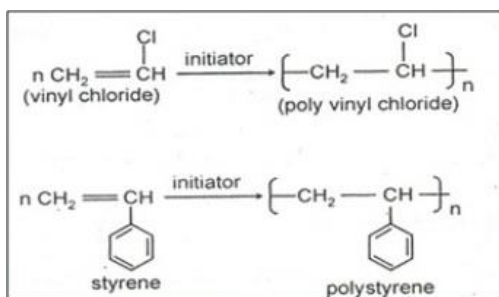


Addition/Chain polymerization

- A chain polymerization is a reaction that yields a polymer product which is the exact multiple of monomers. Thus the mechanism is also called addition polymerization. The following are the characteristics.
- The functionality of the monomer is a double bond and it is bifunctional.
- The polymerization takes place by self-addition of the monomer molecules to each other through a chain reaction.
- No biproducts like H_2O , CH_3OH etc. are produced.
- The polymer has the same chemical composition as that of monomer.
- The molecular weight of the polymer is the exact multiple of the monomers.
- The mechanism is carried out in three steps, i.e. initiation, propagation and termination.
- The mechanism is rapid.
- The conversion of p bond to s bond takes place during the polymerization, liberating 20 Kcal/mole of energy. Hence highly exothermic reactions.
- An initiator is required to start the polymerization reaction.
- The following compounds containing double bonds undergo chain polymerization, For example: **1) Olefins, 2) Vinyl, 3) Allyl 4) Dienes**



2) Vinyl compounds: The general representation of vinyl compounds is $\text{CH}_2=\text{CHX}$, where X = halide, acid, alcohol, amine, phenyl etc.



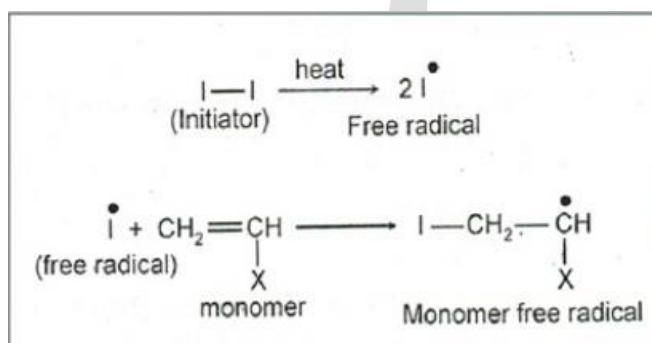
Chain polymerization is initiated by initiators and carried out in three different types of mechanism.

i) Free radical chain polymerization ii) Ionic mechanism iii) Coordination mechanism

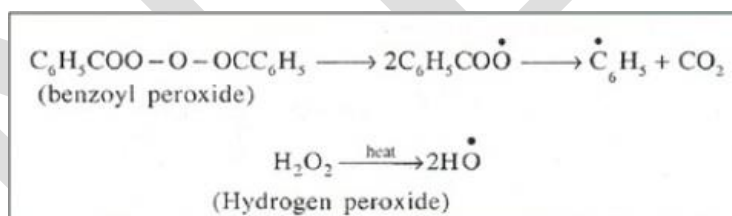
i) Free radical chain polymerization

The initiator undergoes homolytic fission to produce free radicals, which initiates and propagates (rapid chain growth) the polymerization reaction.

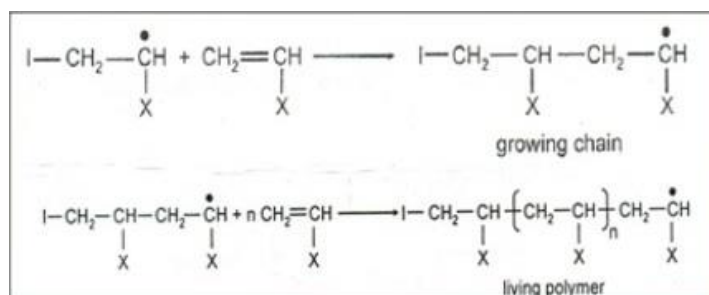
a) Initiation: Initiators are unstable compounds and undergo homolytic fission to produce free radicals which react with electrons of the monomer to produce monomer free radical.



Benzoyl peroxide, hydrogen peroxide are good initiators for free radical chain polymerization.

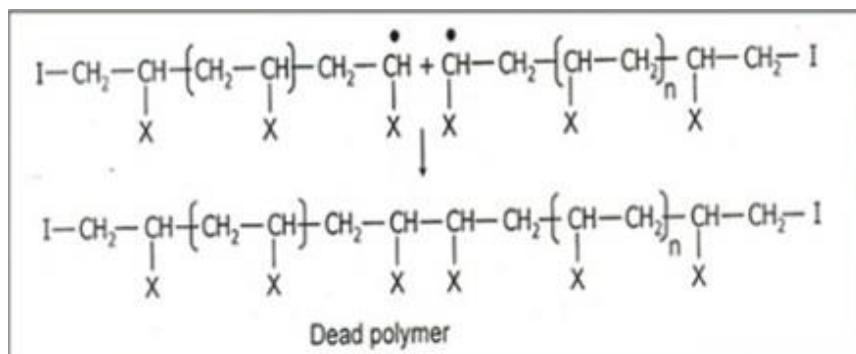


b) Propagation: The monomer free radical reacts with a number of monomers rapidly resulting in the chain growth with free radical site at the end of the chain producing a living polymer. By adding fresh monomer to the living polymer with free radical site, again chain growth starts. Hence it is known as living polymer.

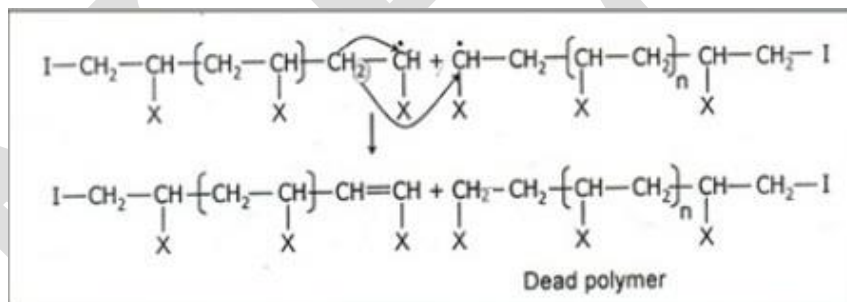


c) Termination: Termination (to stop chain growth) of the growing polymer chain is carried by “coupling” and “disproportionation” resulting in the dead polymer.

Termination by coupling: In coupling the collision of two growing chains causes the union of the two chains at their free radical site producing a dead polymer.



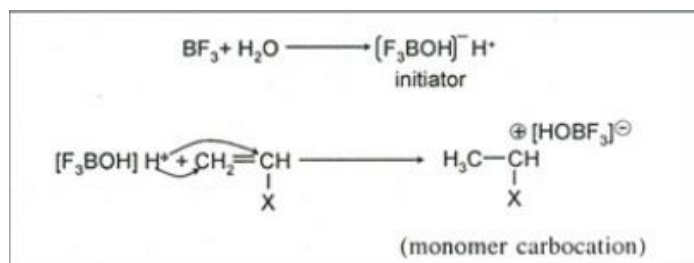
Termination by disproportionation: In termination by disproportionation, H from growing chain is abstracted by the other growing chain, utilizing the lone electron for getting stabilized, while the chain which has donated the H gets stabilized by the formation of a double bond.



ii) Ionic chain polymerization

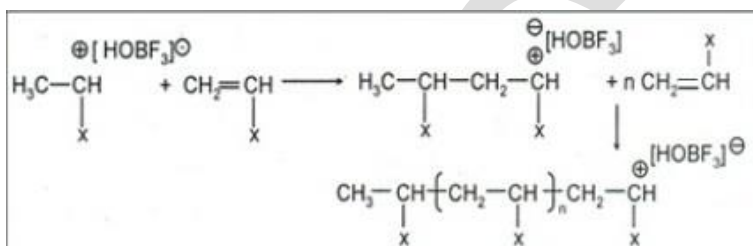
Cationic chain polymerization: The heterolytic fission of the initiator results in cationic and anionic chain polymerization.

a) Initiation: In cationic chain polymerization the cation produced by the initiator attacks the electrons of the monomer forming a monomer carbonium ion. The strong lewis acids like BF_3 , AlCl_3 etc. in presence of small amount of water initiates the reaction as follows.

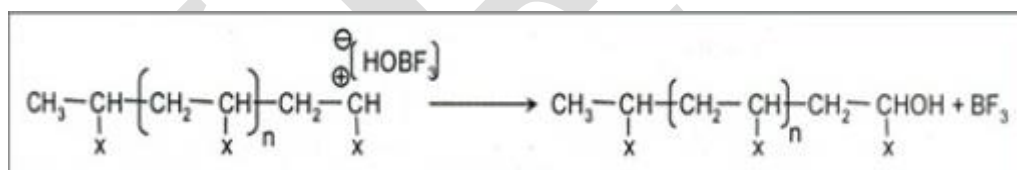


$[\text{HOBF}_3]^-$ is called counter ion, because it is always with carbonium ion of the monomer.

b) Propagation: The monomer carbocation attacks electrons of the other monomers resulting the chain growth with carbocation at the end of the chain.

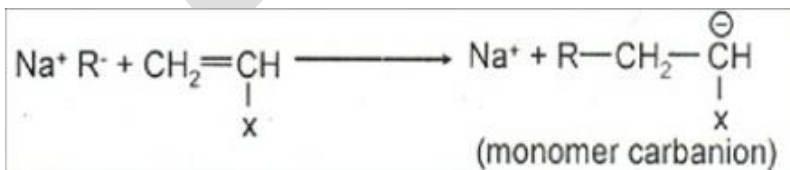


c) Termination: Termination of cationic chain polymerization is done by coupling where the OH^- ion from the counter ion terminates the polymerization.

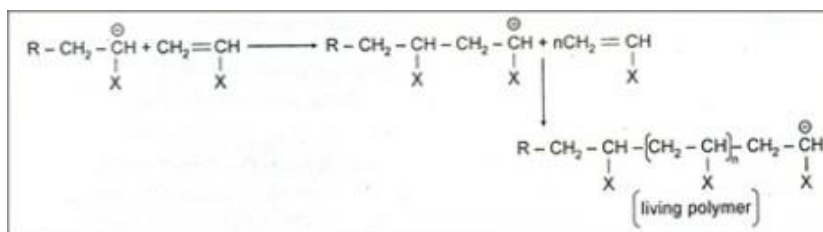


✚ **Anionic chain polymerization:** An anion produced by organo-alkali compounds like ethyl sodium, methyl potassium, butyl lithium etc. initiates the chain polymerization.

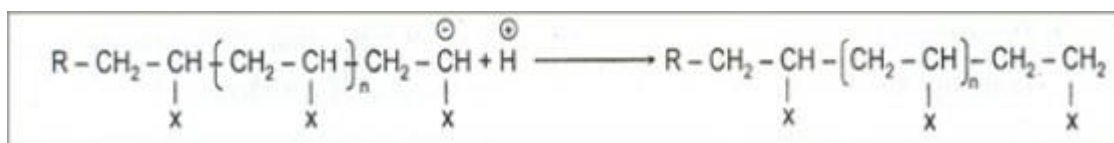
a) Initiation: An anion produced by the initiator will react with the monomer to produce monomer carbanion.



b) Propagation: Attack of the monomers by monomer carbanion results in chain growth.



c) **Termination:** Termination of the chain is carried out by H^+ ion.



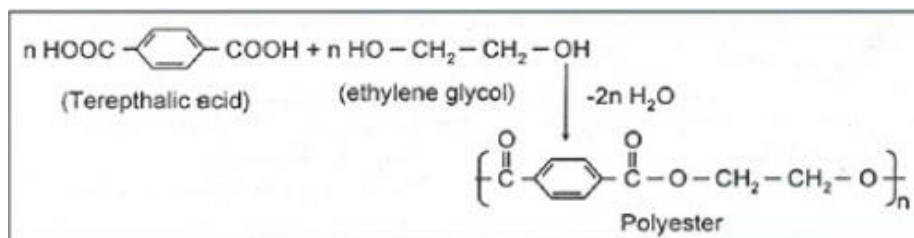
Condensation or step polymerization

Step polymerization takes place by condensation reactions of the functional groups of the monomers, with the elimination of biproducts like H_2O , HCl etc. hence known as condensation polymerization. The following are the characteristics of condensation polymerization.

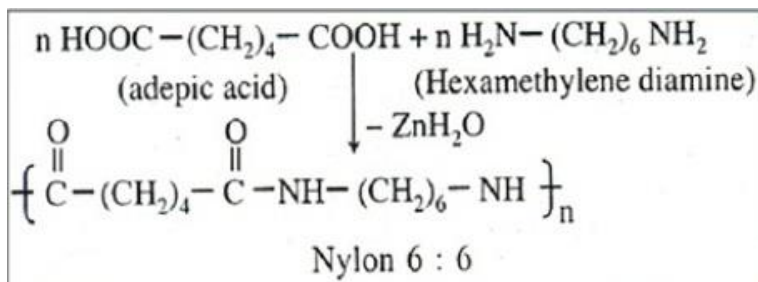
- ✚ The monomers contain functional groups like OH , $-\text{COOH}$, NH_2 , RCOOR' , halides etc.
- ✚ The functionality of the monomer must be two or more than two. The monomers must be dibasic acids, dioles, diamines or triols etc.
- ✚ The polymer is built up by a slow step wise condensation reaction of the functional groups of the monomer.
- ✚ The polymerization reaction is accompanied by the elimination of biproducts like HCl , CH_3OH , H_2O etc.
- ✚ The reactions are not exothermic.
- ✚ The molecular weight of the polymer is not the sum of the molecular weights of the monomers.
- ✚ The polymers produced are living polymers containing functional groups at the end of the chain.
- ✚ It is not a step mechanism of initiation, propagation and termination.
- ✚ The reactions are catalyzed by catalysts.

Examples of step polymerization:

- The polymerization of a diacid with diol produces polyester.



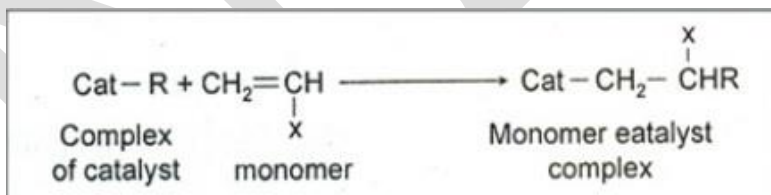
- The polymerization of a diamine with diacid gives Nylon a polyamide.



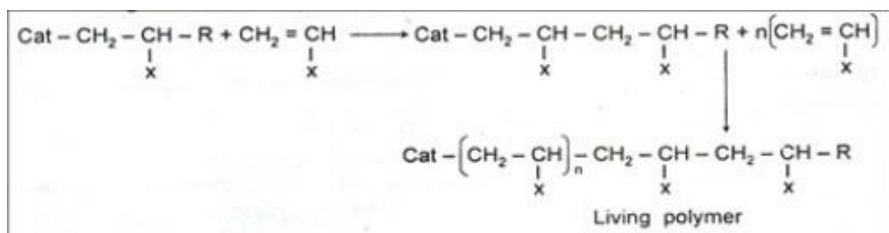
Co-ordination polymerization or Zeigler-Natta polymerization

Zeigler (1953) and Natta (1955) discovered that in the presence of a combination of transition metal halides like TiCl_4 , ZnBr_3 etc. with organometallic compounds like triethyl aluminium or trymethyl aluminium, stereospecific polymerization can be carried out. **Combination of metal halides and organometallic compounds are called “Zeigler Natta catalysts”.** The mechanism is as follows.

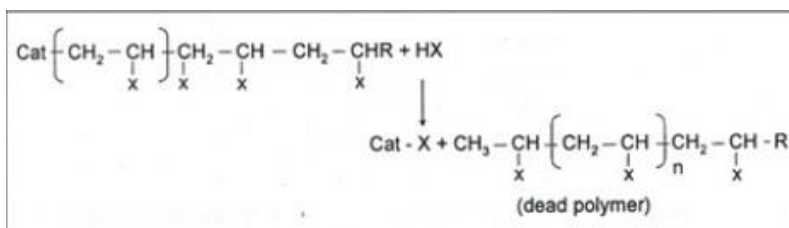
- a) Initiation:** The catalyst form monomer catalyst complexes by reacting with monomer molecules.



- b) Propagation:** The monomer catalyst complex reacts with fresh monomers resulting the chain growth.



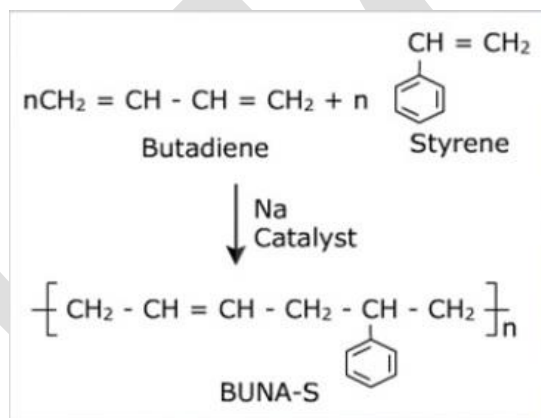
- c) Termination:** Termination is carried out with an active halogen compound.



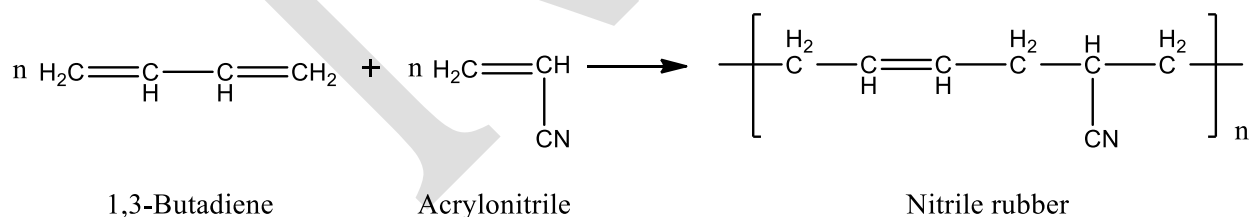
Copolymerization

It is the joint polymerization of two or more monomer species. High molecular weight compounds obtained by copolymerization are called copolymers. Preparation of Styrene rubber (BUNA-S) and Nitrile rubber (BUNA-N) are examples of this polymerization.

- i) **Styrene rubber (BUNA-S) (GRS):** Styrene rubber is prepared by the copolymerization of butadiene with styrene using sodium as a catalyst.



- ii) **Nitrile rubber/Acrylonitrile (BUNA-N) (GRA):** It is a polymer of butadiene and acrylonitrile (vinyl cyanide).



Plastics

- ✚ Plastics are high molecular weight organic compounds, which can be moulded or formed into stable shapes by the application of heat and pressure. The term plastic must be differentiated from resin.

✚ Resins are basic binding materials, which form a major part of the plastics and which actually has undergone polymerization and condensation reactions, during their preparation. Plastics are of two types. **1) Theroplasts** **2) Thermosets.**

1) Thermoplasts: Thermoplasts are those which can be softened on heating and harden on cooling. These are formed as a result of addition polymerization and have long molecular structure.

Ex: PVC, Polyethelene, etc.

2) Thermosets: During fabrication process these resins are moulded. Once they are solidified they can't be softened.

Ex: Bakelite, Nylon etc.

Differences between thermoplastic and thermosetting polymers

Thermoplastic polymers	Thermosetting polymers
1. They soften on heating readily.	1. They do not soften on heating. On prolong heating, however, they burn.
2. They consist of long-chain linear macromolecules.	2. The set of these polymers set molecules have three dimensional network structure, joined by strong covalent bonds.
3. They are formed mostly by addition polymerization.	3. They are formed by condensation polymerization.
4. By reheating to a suitable temperature, they can be softened, reshaped and thus reused.	4. They do not retain their shape and structure, even on heating. Hence, they cannot be reshaped and reused.
5. They are usually soft, weak and less brittle.	5. They are usually hard, strong and more brittle.
6. These can be reclaimed from wastes.	6. They cannot be reclaimed from wastes.
7. They are usually soluble in some organic solvents.	7. Due to strong bonds and cross linking, they are insoluble in almost all organic solvents.

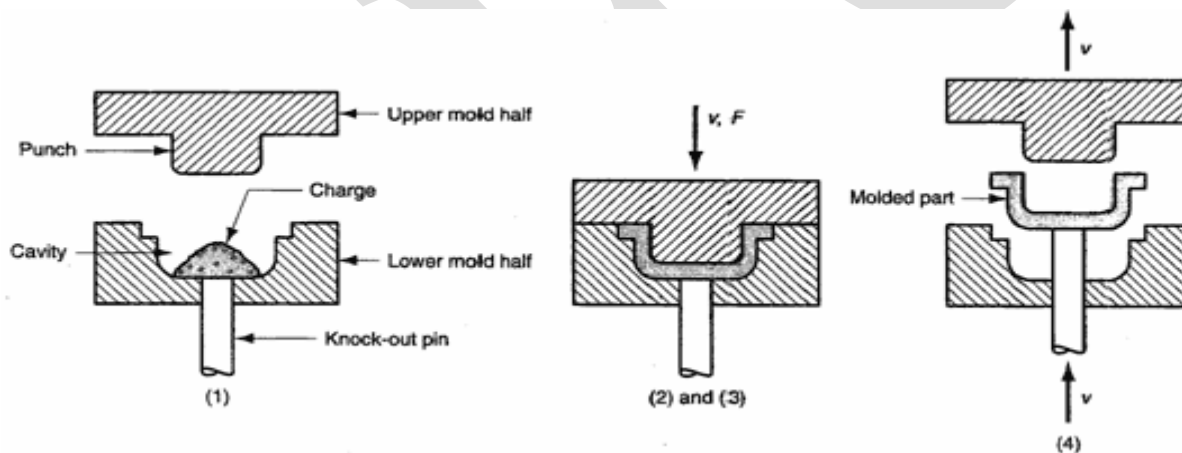
Plastic moulding methods

Depending on the type of resin, whether thermoplastic or thermoset the following fabrication of plastics are used.

1. Compression moulding
2. Injection moulding

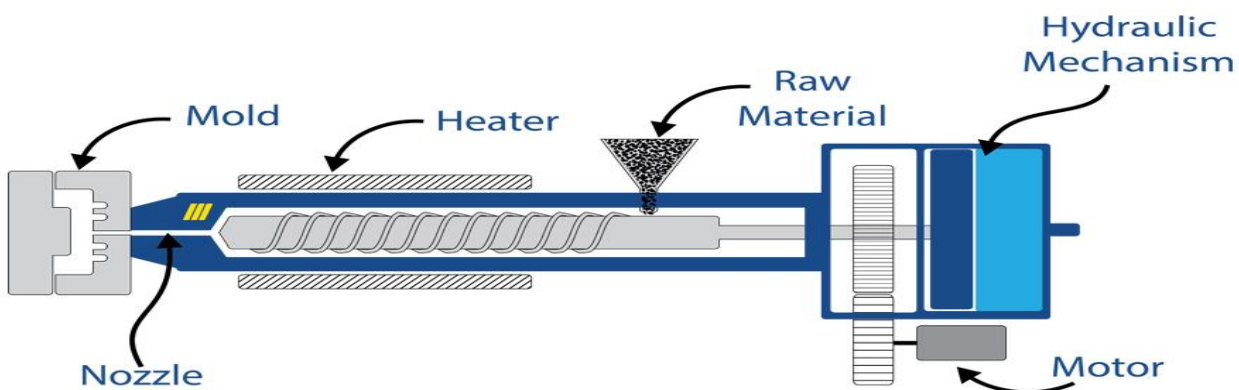
1. Compression moulding

- ✚ This method is applicable to both thermo plastics and thermo setting resins. The predetermined quantity of plastics powder in proper proportions is filled between two halves pieces of mould which are moved relative to each other.
- ✚ Heat and pressure are then applied according to specification, and then cavity gets filled with fluidized plastics. Two halves are closed very slowly.
- ✚ Finally curing is done either by heating or cooling. Heating is applied in the case of thermo settings and cooling is applied in the case of thermo plastics.
- ✚ After curing the mould article is taken out by opening the mould parts.



2. Injection moulding

- ✚ It is applicable to thermo plastics polymers. In this the moulding plastics powder is introduced into hot cylinder heated by hot air jacket which is injected at a controlled rate into mould by using piston.
- ✚ The mould is kept cold to allow the hot plastics to cure and become rigid. After curing the mould article is taken out by opening the mould parts.

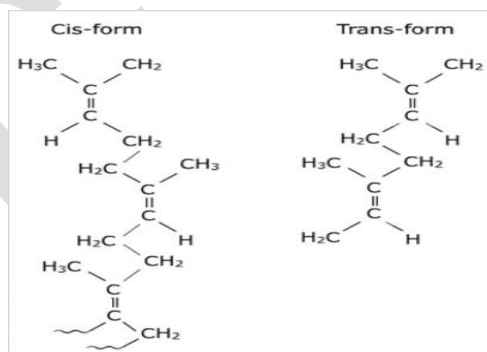
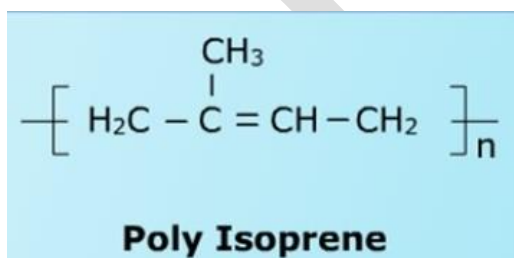


Rubbers and elastomers

Natural rubber:

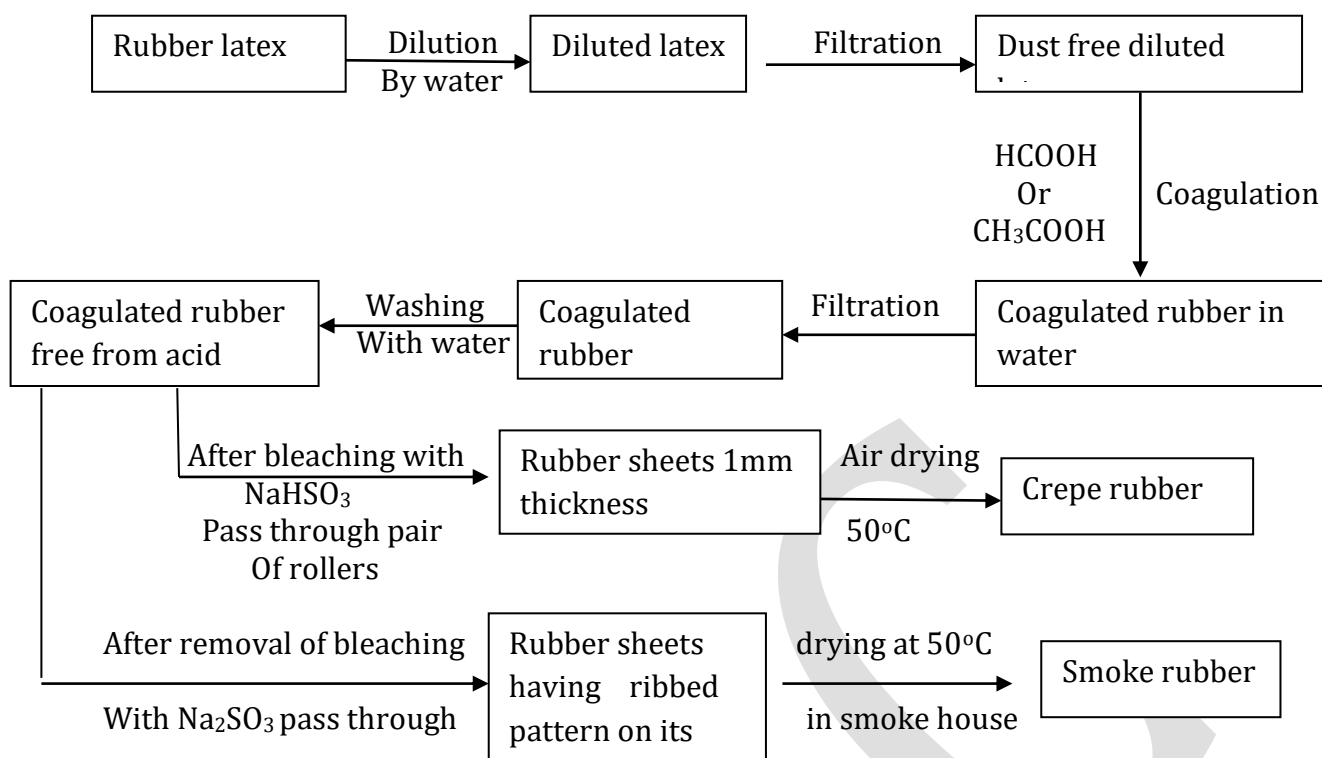
It is believed to be a polymer of isoprene.

- Rubber is obtained from the latex of Hevea tree.
- The main composition of natural rubber is polyisoprene
- Isoprene in natural rubber exists in two geometric forms, Cis and Trans.
- Cis-polyisoprene is present in Hevea rubber and trans polyisoprene in Guttapercha.



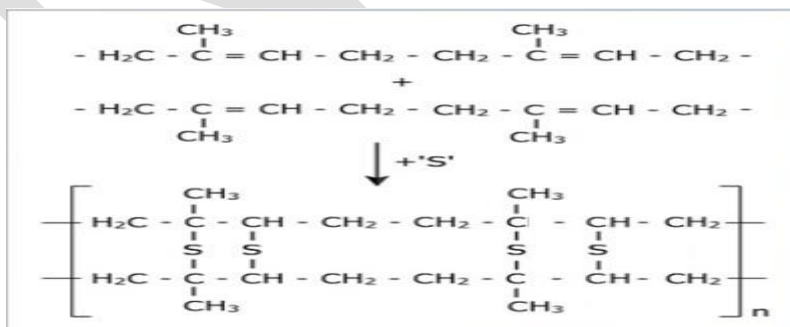
Processing of Natural Rubber:

- By cutting the bark of rubber tree the milky colloidal rubber milk is obtained. The main constituent of rubber latex is 25-45% of rubber and the remaining are water, protein & resinous materials.
- The rubber latex is coagulated by using 5% acetic acid and made in to sheets. The rubber sheets are cured under mild heat and then subjected to further processing.



Vulcanization of Rubber:

- The raw rubber possesses very undesirable properties such as low tensile strength and possesses elasticity over a limited range of temperatures.
- In this process natural rubber is heated with sulphur (or) sulphur compounds at 150°C for few hours.
- Cross linked product is formed when sulphur combines chemically at double bonds of different rubber strips. This process is known as vulcanization.



Advantages:

- Vulcanized rubber has good tensile strength.
- It has good resistant to organic solvents.
- Posses high chemical resistance.
- Posses low water absorption tendency.

FUELS

Introduction

- ✚ Fuel is a combustible substance, containing carbon as main constituent, which on proper burning gives large amount of heat, which can be economically for domestic and industrial purposes.
- ✚ The main sources of fuels are coal and petroleum oils, natural gas etc.
- ✚ During the combustion process of fuels, a redox reaction takes place between fuel and oxygen which is accompanied by a large amount of heat. Hence these fuels are termed as chemical fuels.
- ✚ The energy liberated is due to the rearrangement of valance electrons in the atom of reactants, which results in the formation of compounds like CO_2 , H_2O etc.
- ✚ The products of combustion have less energy than the reactants and therefore, the energy released during the combustion process is the difference in the energy of reactants and products that are formed.
- ✚ The primary or main sources of fuels are coal, natural gas and petroleum. These are stored fuels available in the earth's crust and are called fossil fuels.

Classification of fuels

Fuels are classified into two types

- ❖ Occurrence
- ❖ State of Aggregation
- ❖ **Occurrence:**
 - On the basis of occurrence, fuels are classified in to two types.

Natural (or) primary fuels:

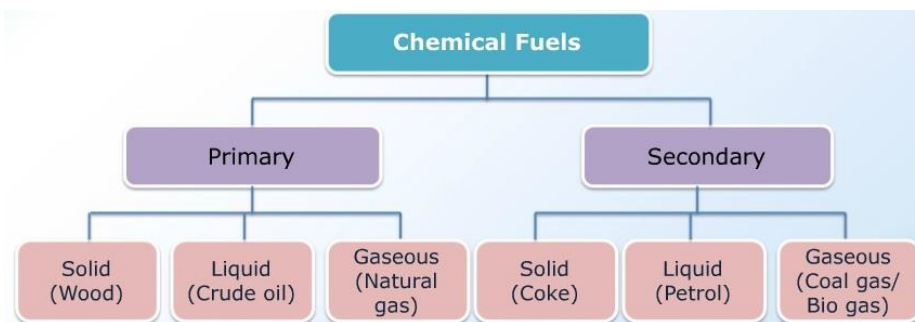
- Fuels which are found in nature are called natural or primary fuels.
- **Ex:** Wood, Coal, Crude oil.

Artificial (or) secondary fuels:

- Fuels which are prepared from the primary fuels are called Artificial or secondary fuels.
- **Ex:** Kerosene, LPG, CNG, Coke.

❖ State of aggregation:

- On the basis of the physical state of aggregation, fuels are classified in to solids, liquids and gases.



Calorific Value

Calorific value of a fuel is the total quantity of heat liberated when a unit mass of the fuel burnt completely.

Units

Calorie: The amount of heat required to raise the temperature of 1g water through 1°C.

Kilocalorie: The quantity of heat required to raise the temperature of 1kg of water through 1°C. 1K. Cal = 1,000 Calories.

B.T.U (British Thermal Unit): Defined as the quantity of heat required to raise the temperature of one pound of water through 1°F. 1B.T.U = 252 cal.

Centigrade Heat Unit (C.H.U): The quantity of heat required to raise the temperature of 1 pound of water through 1°C. 1K.cal = 3.968 B.T.U = 2.2 C.H.U.

✚ Higher (or) gross calorific value (HCV or GCV):

HCV is the total amount of heat produced, when unit mass/volume of the fuel is burnt completely and the products of combustion have been cooled to room temperature.

✚ Lower (or) Net calorific value (LCV or NCV):

LCV is the net heat produced, when unit mass/volume of the fuel is burnt completely and the products of combustion are allowed to escape.

Characteristics of Good Fuel

A good fuel should possess the following characteristics:

High calorific value:

- A fuel should possess high calorific value which results in the liberation of a large amount of heat per unit mass/volume of the fuel.

Moderate Ignition temperature:

- It is the lowest temperature to which the fuel is to preheat so that it burns smoothly. Low ignition temperature is dangerous for storage, since it causes fire hazards.
- Whereas, high ignition temperature causes difficulty in ignition of the fuel. Hence, a good fuel should possess moderate ignition temperature.

Low ash content:

- An ideal fuel should possess low ash content.
- Ash is non-combustible when a sample of coal, with high ash content is used in a furnace, the ash produced in the furnace, fuses due to high temperature and forms hard masses called clinkers.
- Clinkers are bad conductors of heat and causes loss of heat. Further, ash does not contribute to calorific value.

Low moisture content:

- The moisture content of a coal sample reduces the heating value of the fuel. Hence, samples of coal possess low moisture content.

Moderate velocity of combustion:

- If the rate of combustion is low, then the required high temperature may not be possible, because a part of the heat liberated may get radiated, instead of raising the temperature. On the other hand, too high combustion rates are not required.

Low cost:

- A fuel should be available at a cheaper rate.

Combustion nature:

- A good fuel should undergo combustion easily and should controllable when required.

SOLID FUELS

Coal

- Coal is highly carbonaceous matter that has been formed as a result of alteration vegetable matter under certain favorable conditions.
- It is composed of C, H, N and O, besides non-combustible inorganic matter.

Analysis of Coal

To determine quantity of coal, the following two types of analysis are

- ❖ Proximate analysis
- ❖ Ultimate analysis
- ❖ **Proximate analysis**
 - The data varies with the procedure adopted and hence it is called proximate analysis.

Proximate analysis of coal determines:

- ✚ Moisture content
- ✚ Volatile matter
- ✚ Fixed carbon
- ✚ Ash

✚ **Moisture Content**

- About 1 gm of finely powdered air-dried coal sample is weighed in a crucible.
- The crucible is placed inside an electric hot air-oven, maintained at 105°C-110°C for 1hr.
- The crucible is then taken out and cooled in desiccators and weighed. Loss in weight reported as moisture.

$$\% \text{ of moisture} = \frac{\text{loss in weight}}{\text{weight. of coal taken}} \times 100$$

Importance: Moisture in coal evaporates when the coal is burnt and it takes some of the heat liberated in the form of latent heat of evaporation. Therefore moisture lowers the calorific value.

✚ **Volatile matter:**

- The dries of coal left in the crucible is covered with a vented lid and placed in a muffle furnace maintained at 925-970°C for 7 min.
- Crucible is first cooled in air, then inside desiccators and weighed again.
- Loss in weight is reported as volatile matter. The percentage of volatile matter is,

$$\% \text{ of volatile matter} = \frac{\text{Loss in wt}}{\text{wt. of coal sample taken}} \times 100$$

Importance: High volatile matter escapes unburnt and hence a high volatile matter containing coal burns with a long flame, high smoke and has low calorific value. Therefore, lesser the volatile matter, better the rank of coal.

Ash:

- The residual coal left in the crucible is then heated without a lid in a muffle furnace at 700-750°C for half an hour.
- The crucible is then taken out, cooled first in air, then in desiccators and weighed.
- Heating, cooling and weighing is repeated, till a constant weight is obtained.
- The residue is reported as ash. Thus the percentage of ash is,

$$\% \text{ Ash} = \frac{\text{wt. of ash left}}{\text{wt. of coal taken}} \times 100$$

Importance: Ash is a non-combustible matter, which reduces the calorific value of coal. Ash causes the hindrances to the flow of air and heat, which lowers the temperature. Also, it often causes trouble during firing by forming clinkers. Hence, lower the ash content, better the quality of coal.

Fixed Carbon:

- The percentage of fixed carbon is given by:

$$\% \text{ of Fixed Carbon} = 100 - (\% \text{ of moisture} + \% \text{ volatile matter} + \% \text{ ash})$$

Importance: Higher the percentage of fixed carbon, greater will be its calorific value and better the quality of coal. Hence, a high percentage of fixed carbon is desirable.

❖ Ultimate analysis

- It is carried out to ascertain the composition of coal.
- Ultimate analysis includes estimation of the following:

Carbon and hydrogen

Sulphur

Nitrogen

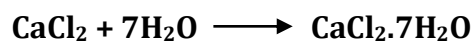
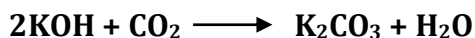
Oxygen

Carbon and hydrogen

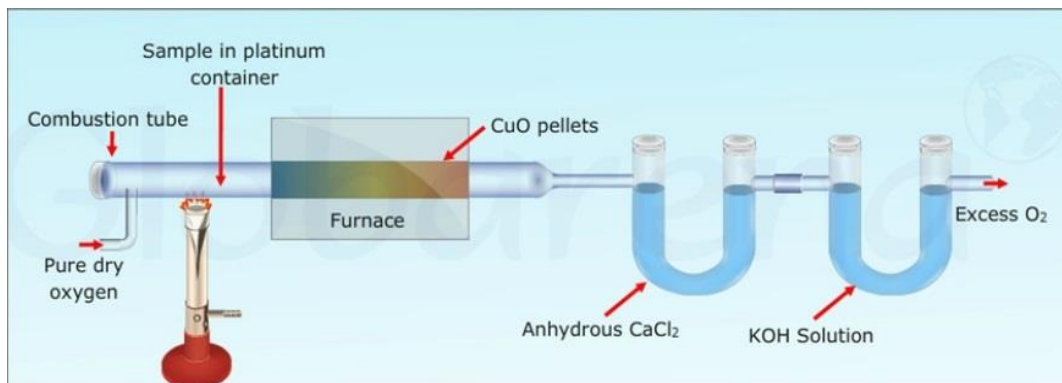
- About 1g of accurately weighed coal sample is burnt in a current of oxygen in a combustion chamber.
- C & H of the coal are converted in to CO₂ and H₂O.



- The products of combustion CO_2 and H_2O are absorbed respectively by KOH and CaCl_2 tubes of known weights.
- The increase in weight of these tubes are then determines.



Estimation of carbon and hydrogen



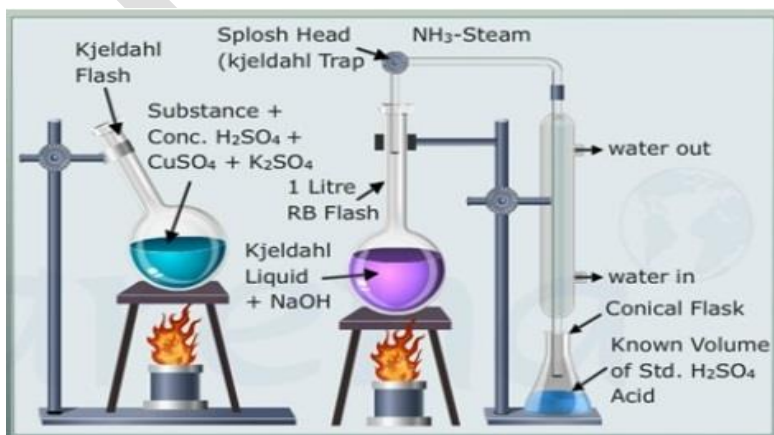
$$\% \text{ C} = \frac{\text{Increases in wt of KOH tube} \times 12 \times 100}{\text{wt . of coal taken} \times 44}$$

$$\% \text{ H} = \frac{\text{Increase in wt . of CaCl}_2 \text{ tube} \times 2 \times 100}{\text{wt . of coal taken} \times 18}$$

Importance:

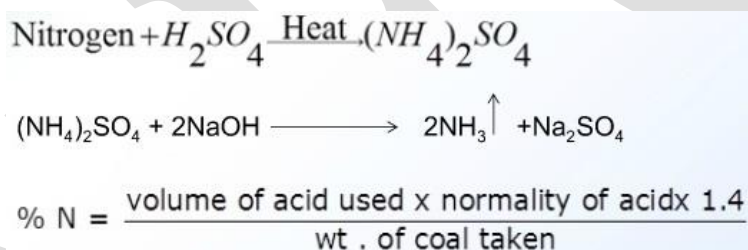
Greater the percentage of carbon and hydrogen, better is the coal in quality and calorific value.

+ Nitrogen



Nitrogen present in coal sample can be estimated by Kjeldahl's method;

- About 1 g of accurately weighed powdered coal is heated with concentrated H_2SO_4 in the presence of a small quantity of K_2SO_4 (catalyst), in a long-necked flask called Kjeldahl's flask.
- After the solution becomes clear it is treated with an excess of KOH (solution) and liberated ammonia is distilled and absorbed in a known volume of the standard acid solution.
- After the solution is clear i.e., when the entire is converted into ammonium sulphate, it is treated with an excess of NaOH to liberate ammonia. The liberated ammonia is distilled into a measured amount of standard acid.
- The volume of unused acid (H_2SO_4) is then determined by back titration with standard NaOH solution.
- The amount of acid neutralized by the liberated ammonia is determined from which the nitrogen present in the sample is calculated.



Importance: Nitrogen has no calorific value and hence, its presence in coal is undesirable. Thus a good quality coal should have very little nitrogen content.

Sulphur

- Sulphur present in coal is determined from the washings obtained from the known mass of coal used in a bomb calorimeter for determination of calorific value.
- During combustion, sulphur is converted into sulphate.
- The washings are treated with barium chloride, whereby $BaSO_4$ is precipitated.
- The precipitate is filtered, washed and heated to constant weight.
- Sulphate washings from bomb calorimeter + $BaCl_2 \longrightarrow BaSO_4$

$$\% \text{ of S} = \frac{\text{wt. of } BaSO_4 \times 32 \times 100}{\text{wt. of coal taken} \times 233}$$

Importance: Presence of sulphur is highly undesirable in coal and is used for making coke in the iron industry, as it transfer to the iron metal and badly affect the quality and properties of steel. Moreover, oxides of sulphur pollute the atmosphere that leads to corrosion of combustion apparatus.

✚ Ash

- Ash determination is carried out as in proximate analysis.

✚ Oxygen

- It is obtained by difference

$$\% \text{ of O} = 100 - \% (\text{C} + \text{H} + \text{S} + \text{N} + \text{ash})$$

Importance: Oxygen content decreases the calorific value of coal. High oxygen-content coals are characterized by high inherent moisture, low calorific value and low coking power. Hence, oxygen is undesirable. Thus, a good quality coal should have a low percentage of oxygen.

Theoretical calculation of Calorific value of a fuel (Dulong's formula)

- The calorific value of fuel can be approximately computed by noting the amounts of the constituents of the fuel. The higher the calorific values of some of the chief combustible constituents of fuel are tabulated below:

Table:1 Calorific values of fuel constituents

Constituent	Hydrogen	Carbon	Sulphur
HCV (Kcal/Kg)	34,500	8,080	2,240

- The oxygen, if present in the fuel, is assumed to be in combined with hydrogen, i.e., in the form of fixed carbon $[\text{H}_2\text{O}]$. So, the amount of hydrogen available for combustion = Total mass of hydrogen in fuel – fixed hydrogen
 = Total mass of hydrogen in fuel – $(1/8)$ mass of oxygen in the fuel.
 (8 parts of oxygen combine with one part of hydrogen to form H_2O .)

Dulong's formula for calorific value from the chemical composition of fuel is:

$$\text{HCV} = 1/100[8,080\text{C} + 34,500 (\text{H}-\text{O}/8) + 2,240 \text{S}] \text{ Kcal/Kg}$$

- Where C, H, O and S are the percentages of carbon, hydrogen, oxygen and sulphur in the fuel respectively.

$$\text{LCV} = [\text{HCV} - 9/100\text{H} \times 587] \text{ Kcal/Kg} = [\text{HCV} - 0.09\text{H} \times 587] \text{ Kcal/Kg}$$

- This is based on the fact that 1 part of H by mass gives 9 parts of H₂O and latent heat of steam is 587 Kcal/Kg.

LIQUID FUELS

Petroleum

- Petroleum is dark greenish-brown viscous oil found deep in earth's crust.
- It is composed mainly of hydrocarbons together with small amounts of organic compounds containing oxygen, N₂ and sulphur.
- The average composition of crude petroleum is

C	-	79.5 to 87.1%
H	-	11.5 to 14.8%
S	-	01. To 3.5%
N + O	-	0.1 to 0.5%

Refining of crude oil

- The crude is separated into various useful fractions by fractional distillation and finally converted into desired specific products.
- The process is called refining of crude oil and the plants set up for the purpose called refineries.
- Refining of petroleum is done in different stages such as
 - ✚ **Step-1:** Separation of water
 - ✚ **Step-2:** Removal of harmful sulphur compounds
 - ✚ **Step-3:** Fractional distillation

✚ **Step-1: Separation of water**

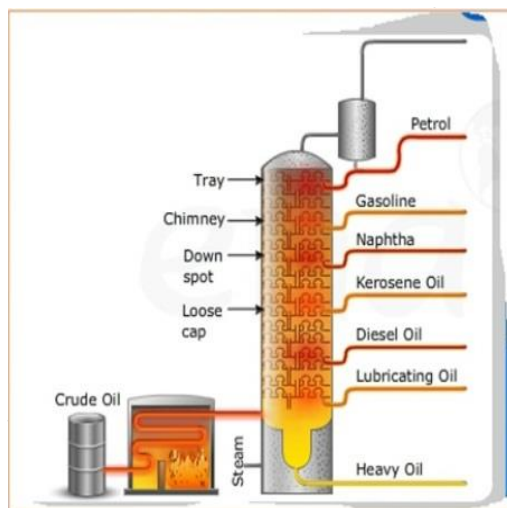
- The crude oil acquired from the earth's crust is in the form of stable emulsion of oil and salt water.
- When this mixture is passed between the two highly charged electrodes they destroy the emulsion films and the colloidal water droplets coalesce into bigger drops and they get separated from the oil.

✚ **Step-2: Removal of harmful sulphur compounds**

- To remove the sulphur compounds in the crude oil, the crude oil is treated with copper oxide.

- The sulphur compounds convert into the insoluble copper sulphide and can be removed by the process of filtration.
- Substances like sodium chloride and magnesium chloride present will corrode the refining equipment and result in the formation of scale.
- These can be removed by techniques like dehydration and electric desalting.

Step-3: Fractional distillation

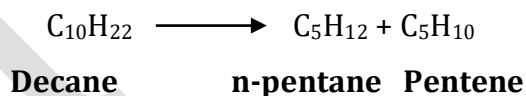


- The crude oil enters through the bottom of the still by an inlet. The crude oil is heated with steam, inside the still to a temperature of about 400°C
- All volatile constituents except the residue are evaporated. The vapours are then passed up a fractionating column.
- Fractional column is a tall cylindrical tower containing a number of the stainless steel trays at short distances.
- Each tray is provided with a small chimney, covered with a loose cap.
- As the vapour goes up, they become gradually cooler and fractional condensation takes place at different heights of column.
- The constituents of fraction and the temperature at which they are obtained are given in the table below.

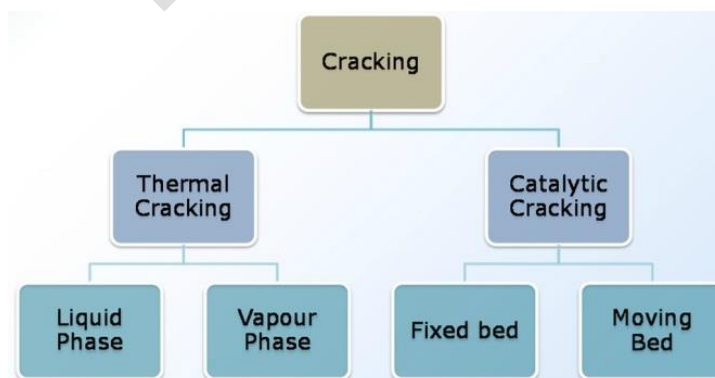
Sl.no	Name of fraction	Boiling range	Approx, composition in terms of hydrocarbon containing C atoms	Uses
1	Uncondensed gas	Below 30°C	C ₁ to C ₄ (such as ethane, propane, isobutene),	As domestic or industrial fuel under the name LPG (liquefied petroleum gas)
2	Petroleum ether	30-70°C	C ₅ -C ₇	As a solvent
3	Gasoline or petrol or motor spirit	40-120°C	C ₅ -C ₉ (calorific value -11, 250 kcal/kg)	As motor fuel, solvent and in dry cleaning
4	Naphtha or solvent spirit	120-180°C	C ₉ -C ₁₀	As solvent and in dry cleaning
5	Kerosene Oil	180-250°C	C ₁₀ -C ₁₆ (calorific value = 11,000 kcal/kg)	As an illuminant, jet engine fuel and for preparing laboratory gas.
6	Diesel oil or fuel oil or gas oil	250-320°C	C ₁₀ -C ₁₈ (calorific value = 11,000 kcal/kg)	Diesel engine fuel
7	Heavy Oil	320-400°C	C ₁₇ -C ₃₀	For getting gaso-line by cracking process
(a)	Lubrication Oil	-	-	As lubricant
(b)	Petroleum jelly (Vaseline)	-	-	As lubricant and in cosmetics and medicines
(c)	Grease	-	-	As lubricant
(d)	Paraffin wax	-	-	In candles, boot polishes wax paper, etc.
(8)	Residue may be	Above 400°C	C ₃₀ and above	
(a)	Asphalt	-	-	Water-proofing of roofs and road making
(b)	Petroleum coke	-	-	As a fuel and in molding are light rods.

Cracking

- The process of breaking bigger hydrocarbon molecular to simpler, low boiling hydrocarbons of low molecular weight is called cracking.



Cracking is carried out in different ways is given below



Thermal cracking

Thermal cracking is the breaking of bigger hydrocarbons into simpler, low boiling, lower molecular weight hydrocarbons making use of high temperature and pressure.

Catalytic cracking

In catalytic cracking, a catalyst is used at low pressure and moderate temperature. The catalyst like aluminum oxide, aluminium metasilicate, etc. is used as catalyst.

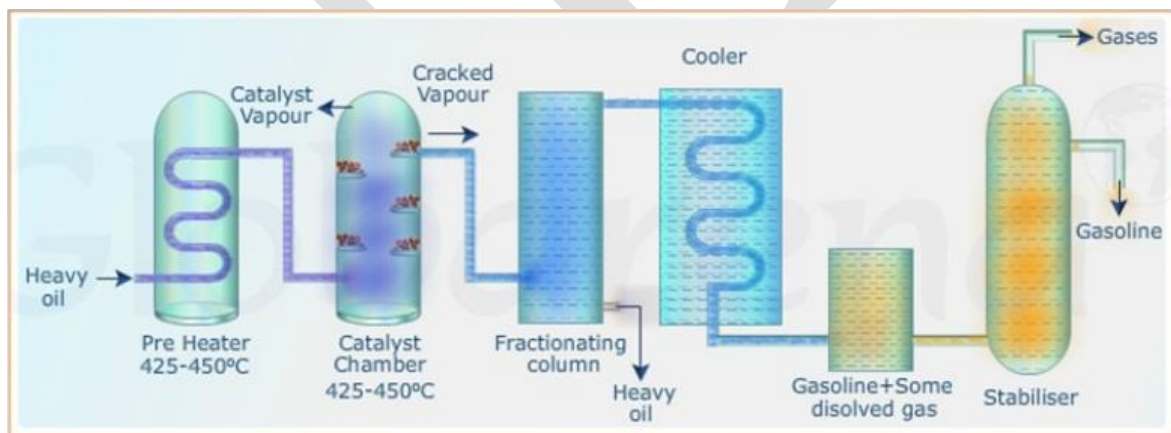
Advantages of catalytic cracking over thermal cracking

- The yield of petrol is higher.
- Quality of petrol is produced is better.
- A much lower pressure is needed in catalytic cracking.
- The product contains very little amount of undesirable 'S'

Types of catalytic cracking

- ✚ Fixed bed catalytic cracking
- ✚ Moving bed catalytic cracking

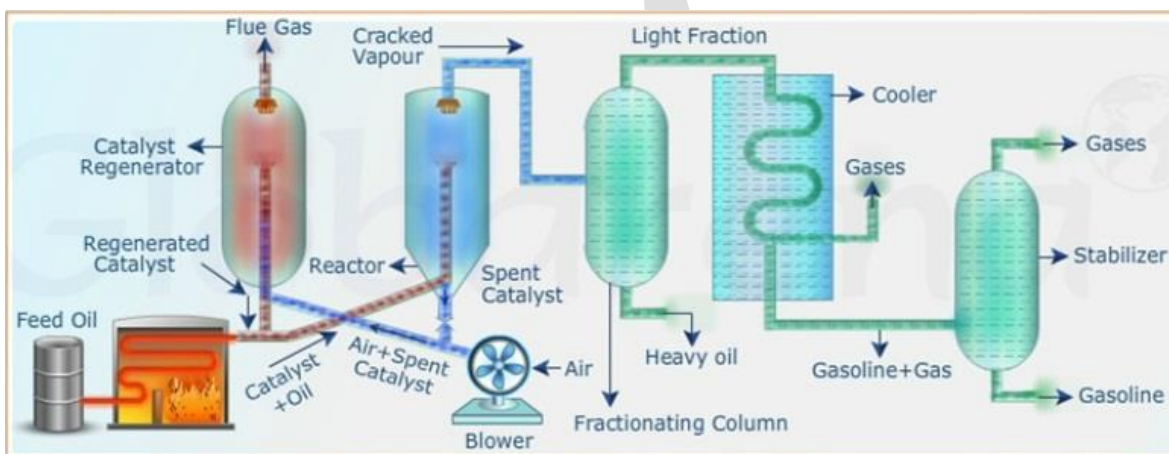
✚ Fixed bed catalytic cracking



- Zirconium oxide mixed with artificial clay is used as catalyst which is placed in the catalytic chamber at fixed places in shelf's. Therefore, it is called fixed-bed catalytic process.
- The oil vapours are heated in a preheater to cracking temperature 425-450°C and forced through a catalytic chamber maintained at 425-450°C temperature and 1.5 Kg/cm² pressure.

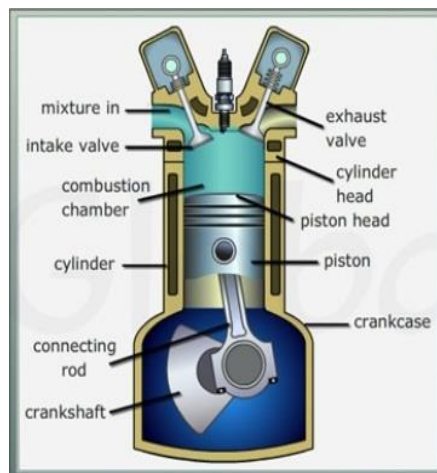
- About 40% of the charge converted into gasoline and about 2.4% carbon is formed. The carbon gets absorbed on the catalyst bed.
- Vapours produced, are then passed through a fractionating column, where heavy oil fractions condense.
- The vapours are then passed through a cooler, where some of the gases are condensed with gasoline and uncondensed gases move on.
- Gasoline containing some dissolved gases then sent to a stabilizer, where the dissolved gases are removed and pure gasoline is obtained.

Moving bed catalytic cracking



- The solid catalyst is very finely powdered, so that it behaves almost as a fluid, which can move freely in the chamber.
- Vapours of cracking stock (heavy oil, gas oil etc.) mixed with fluidized catalyst are forced into a large reactor bed.
- Near the top of the reactor, there is a centrifugal separator (called cyclone), which allows only the cracked oil vapours to pass on to the fractionating column by retaining the catalyst.
- During cracking, carbon is deposited on catalyst and settles to the bottom from where it is forced by an air blast to the regenerator (maintained at 600°C)
- In the regenerator, carbon is burnt and regenerated catalyst flows through a stand-pipe for mixing with the fresh batch of incoming oil.
- As the top of the regenerator there is a separator, which permits only gases (CO_2) to pass out, and hold catalyst particles.

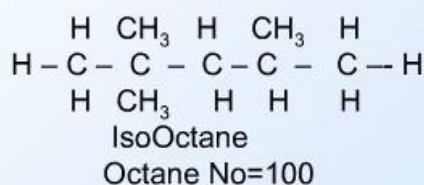
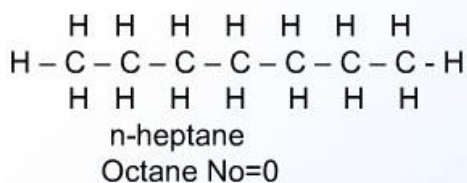
Knocking



- In the combustion of liquid fuel in internal combustion, a spark is struck in the cylinder containing petrol vapour mixed and air for the initiation of the combustion reaction.
- After striking the spark in the cylinder, the flame should spread rapidly and smoothly through the gaseous mixture. This leads to the combustion and expansion of the mixture of products combustion which pushes the piston down the cylinder.
- The ratio of the volume in the cylinder at the end of suction-stroke to the volume at the end of the compression-stroke of the piston is known the compression ratio.
- The efficiency of engine increases with the increase in the compression ratio and the compression ratio is influenced by the composition of petrol used.
- Under certain circumstances, the rate of oxidation becomes so large that the last portion of the fuel-air mixture gets ignited which is called pre-ignition, producing a large thumping sound called knocking. The knocking results in loss of efficiency.

Octane rating

- It has been found that n-heptane knock very badly and hence its anti-knocking value has been given zero.
- On the other hand isooctane given very little knocking. So its anti-knock value has been given as 100.
- Octane number of a gasoline is the % of isooctane in mixture of isooctane and n-heptane which matches the fuel under test in knocking characteristics



Improvement of anti-knock characteristics of a fuel:

- The octane number of internal combustion fuels is increased by the addition of materials as tetra ethyl lead, $(\text{C}_2\text{H}_5)_4\text{Pb}$, MTB ether, benzene etc., however, the usage of tetra ethyl lead is stopped due to its environmental pollution hazards.

Unleaded petrol:

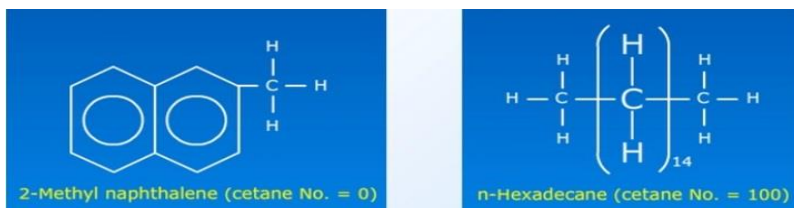
- The method of increasing the octane number of petrol is to add high octane compounds like isopentene, isooctane, ethyl benzene, isopropyl benzene and methyl tertiary butyl ether (MTBE).
- Out of all these compounds, MTBE is preferred as it contains oxygen in the form of ether group and supplies oxygen for the combustion of petrol in an internal combustion engine. This reduces the extent of peroxy compound formation.
- Unleaded petrol is the enhancement of octane rating and is accomplished without the addition of lead compounds.

Uses of unleaded petrol:

- It prevents the use of catalytic converter attached to the exhaust in automobiles.
- A catalytic converter contains a catalyst (Rhodium), which converts the toxic gases (CO and NO) to form gases (CO_2 and N_2 respectively). Moreover, it oxidizes unburnt hydrocarbons into CO_2 and H_2O .

Cetane Rating:

- The suitability of a diesel fuel is determined by its cetane value, which is the percentage of n-hexadecane in a mixture of n-hexadecane and 2-methyl naphthalene, which has the same ignition characteristics as the diesel fuel.
- The cetane number of a diesel fuel can be increased by the addition of a small quantity of "pre-ignition dopes" like ethyl nitrite, acetone peroxide etc.



UNIT-II
POLYMERS AND FUEL CHEMISTRY
IMPORTANT QUESTIONS

1. What is polymerisation? Explain the chain growth & step growth polymerization with examples.
2. Explain about mechanism of Addition polymerization (Free radical, cationic, anionic).
3. Explain the difference between thermoplastics and thermosetting plastics
4. Explain the mechanism of co-ordination polymerization.(Z-N catalysis)
5. What is meant by moulding of plastics? Mention the moulding techniques of Compression and injection moulding with neat diagram.
6. Explain the procedures used in the processing of natural rubber. And how to overcome the drawbacks of natural rubber by vulcanization process?
7. Explain analysis of coal.
8. Describe refining of petroleum with diagram.
9. What is cracking? How gasoline is obtained from moving and fixed catalytic cracking?
10. What is meant by knocking? Explain how molecular structure will affect the Octane and cetane numbers.