Fuels and Combustion

Introduction: Fuels

❖ Fuels are combustible substance containing carbon as the main constituent

❖ On proper burning gives large amount of heat that can be used economically for domestic and industrial purposes

❖ During the process of combustion of a fuel, the atoms of carbon, hydrogen, etc combine with oxygen with simultaneous liberation of heat

$$C + O_2 \longrightarrow CO_2 + 94 \text{ kcals}$$
$$2H_2 + O_2 \longrightarrow 2H_2O + 68.5 \text{ kcals}$$
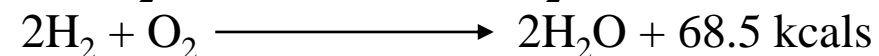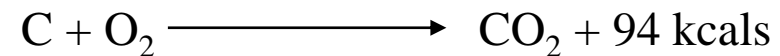
❖ Main source of fuel is coal and petroleum. These are stored fuels available in earth's crust and are generally called fossil fuels because they were formed from the fossilized remains of plants and animals

HEAT PRODUCED ON COMBUSTION OF FUELS
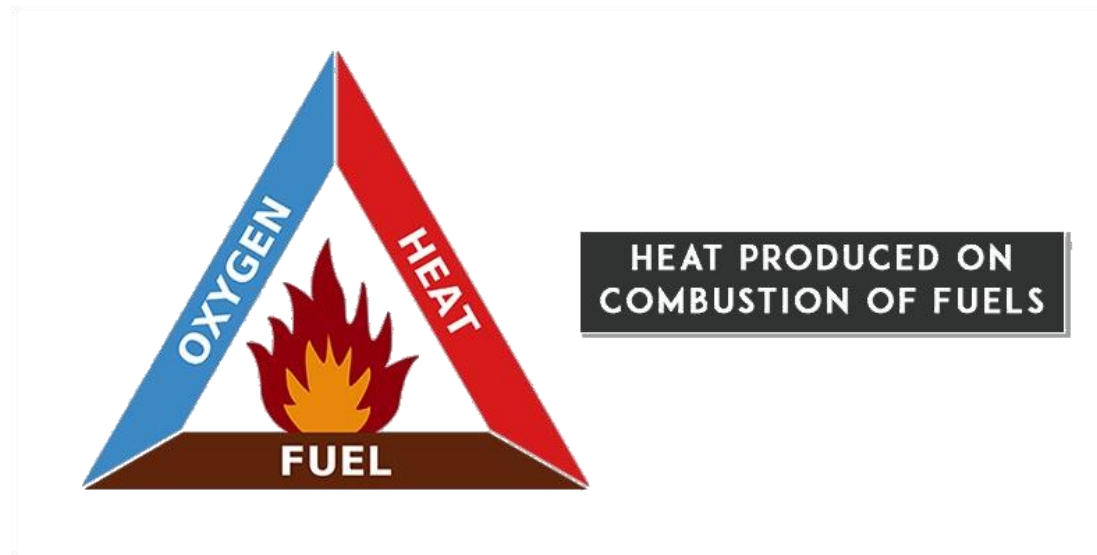
What are the characteristics of a good fuel?

1. High calorific value
2. Moderate ignition temperature
3. Low moisture content
4. Low non-combustible matter content
5. Moderate velocity of combustion
6. Products of combustion should not be harmful
7. Low cost
8. Easy to transport
9. Easy control of combustion
10. Should not undergo spontaneous combustion
11. Storage cost in bulk should be low
12. Burn efficiently without smoke
13. Uniform size in solid fuel for regular combustion.

Transportation of Fuel: (Big issues)

Cars (growing rapidly in Asia)
Trucks (Critical for economy everywhere)
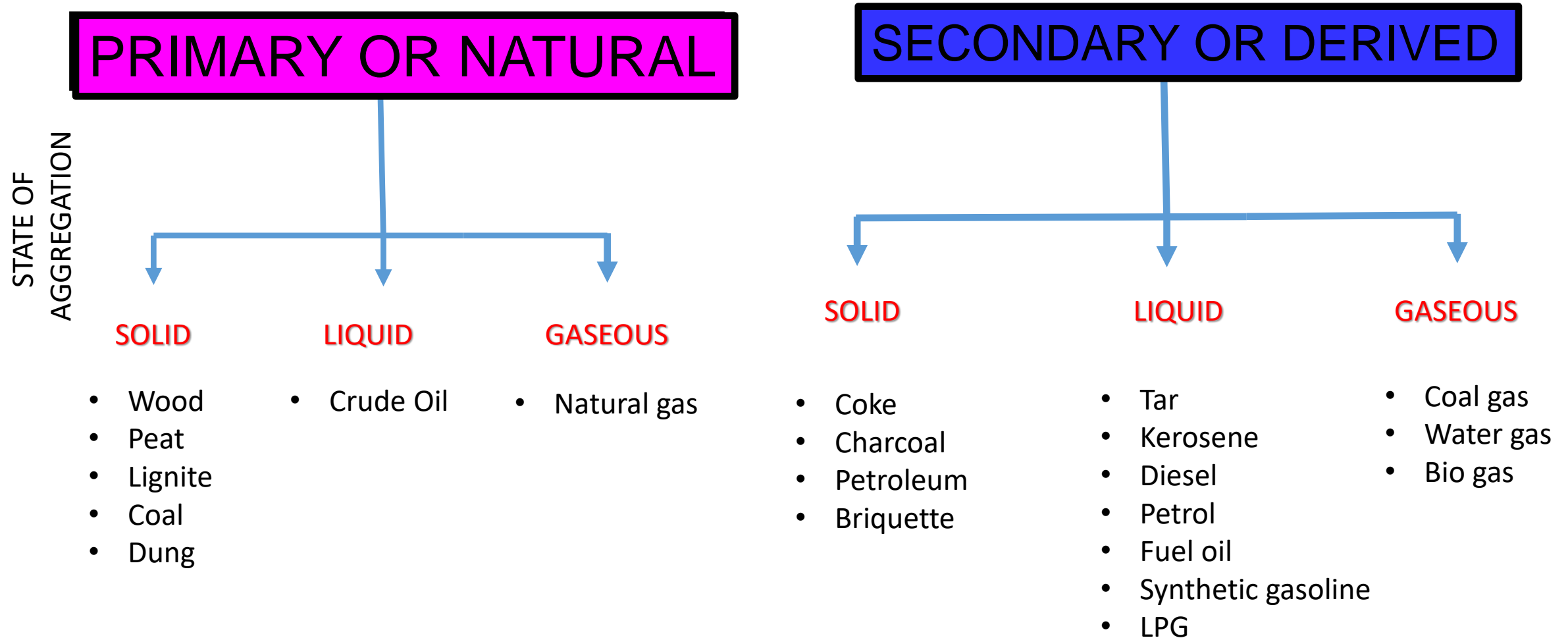Air Planes (Growing rapidly everywhere)

Liquid Fuels:

Liquids Flow (Solids are hard to handle)
High volumetric and mas-energy density.
Easy to store and distribute

Classification

CHEMICAL FUELS

PRIMARY OR NATURAL	SECONDARY OR DERIVED

STATE OF AGGREGATION

PRIMARY OR NATURAL

SOLID
- Wood
- Peat
- Lignite
- Coal
- Dung

LIQUID
- Crude Oil

GASEOUS
- Natural gas

SECONDARY OR DERIVED

SOLID
- Coke
- Charcoal
- Petroleum
- Briquette

LIQUID
- Tar
- Kerosene
- Diesel
- Petrol
- Fuel oil
- Synthetic gasoline
- LPG

GASEOUS
- Coal gas
- Water gas
- Bio gas

Higher or gross calorific value (HCV):

- Usually, all fuels contain some hydrogen and when the calorific value of hydrogen-containing fuel is determined experimentally, the hydrogen is converted into steam. If the products of combustion are condensed to the room temperature (25°C), the latent heat of condensation of steam also gets included in the measured heat, which is then called "higher or gross calorific value". So, gross or higher calorific value (HCV) is "the total amount of heat produced, when unit mass/volume of the fuel has been burnt completely and the products of combustion have been cooled to room temperature"(i.e., 25°C).

Lower or net calorific value (LCV):

- In actual use of any fuel, the water vapour and moisture, etc., are not condensed and escape as such along-with hot combustion gases. Hence, a lesser amount of heat is available. So, net or lower calorific value (LCV) is "the net heat produced, when unit mass /volume of the fuel is burnt completely and the products are permitted to escape".

- Net calorific value = HCV - Latent heat of water vapours formed

     = HCV - Mass of hydrogen x a x Latent heat of steam

Since 1 part by mass of hydrogen produces 'a' part by mass of water.

CALORIFIC VALUE

Calorific value of a fuel is "**the total quantity of heat liberated, when a unit mass (or volume) of the fuel is burnt completely**."

Units of heat :

(1) **'Calorie'** is the amount of heat required to raise the temperature of one gram of water through one degree Centigrade (15-16°C).

(2) "**Kilocalorie**" is equal to 1,000 calories. It may be defined as 'the quantity of heat required to raise the temperature of one kilogram of water through one degree Centigrade. Thus**:   1 kcal = 1,000 cal**

(3) "**British Thermal unit" (B.T.U.)** is defined as "the quantity of heat required to raise the temperature of one pound of water through one degree Fahrenheit (60-61°F). This is the English system unit.

1 B.T.U. = 252 cal = 0.252 kcal   1 kcal = 3.968 B.T.U.

Units of calorific value	Solid fuel	Liquid fuel	Gaseous fuel
CGS method	cal/g	cal/g	cal/cm^3
MKS method	Kcal/Kg	Kcal/Kg	Kcal/m^3
FPS method	B.Th.U/Ib	B.Th.U/Ib	BTU/ft^3
SI method	Joule/Kg	Joule/Kg	Joule/m^3

Determination of Calorific Value

1. BOMB CALORIMETER

The apparatus which is used to determine the calorific value of solid and liquid fuels is known as Bomb Calorimeter.
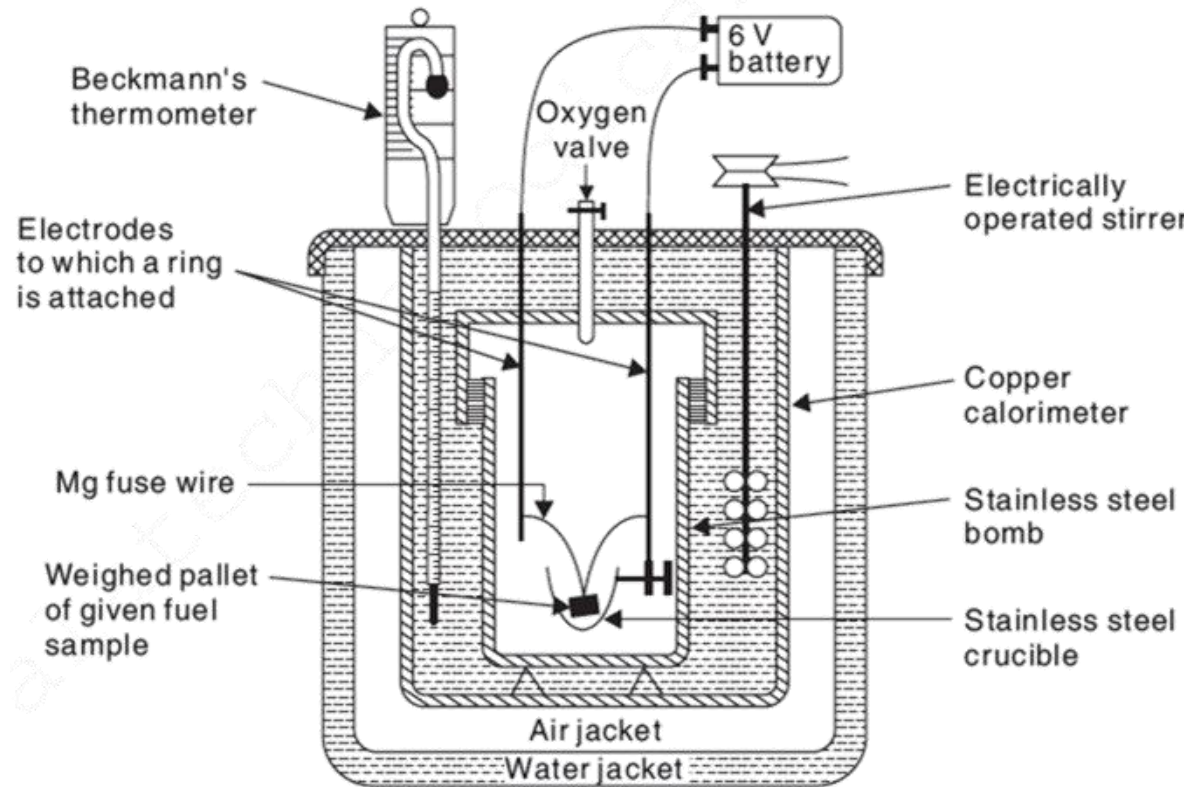

Fig. 1: Bomb Calorimeter

Bomb Calorimeter

Calorific value determination

- A weighed mass of fuels placed in the crucible is allowed to burn in oxygen by electric spark across the electrode
- Heat liberated is measured by principle of calorimetry i.e. taken by water and calorimeter
- Initial and final temperatures of calorimeter are noted

Calculation

m = mass of fuel pellet

W = mass of water in the calorimeter

w = water equivalent of calorimeter

t_1 = initial temperature of calorimeter

t_2 = final temperature of calorimeter

HCV = gross calorific value of calorimeter

$$ \text{L} = HCV = \frac{(W+w)\,(t_2 - t_1)}{m} \, cal/gm $$

Fuel used = benzoic acid (GCV = 6325 kcal/kg)

Correction

Correction factors are used to get accurate results which include:

A. Fuse Wire Correction:

Heat liberated during sparking should be subtracted from heat liberated.

B. Acid Correction:

Fuels containing sulphur and nitrogen if oxidized, the heat of formation of H_2SO_4 and HNO_3 should be subtracted (as the acid formations are exothermic reactions).

C. Cooling Correction:

Rate of cooling of temperature from max. temperature to room temperature is noted. From the rate of cooling and the actual time taken for cooling then correction is called cooling correction and is added to the $(t_2\text{-}t_1)$ term.

$$L = \frac{(W + w)\,(t_2 - t_1 + cooling\ correction) - (Acid\ + Fuse\ correction)}{m}\,cal/gm$$
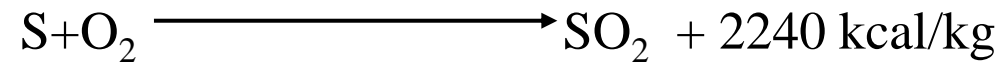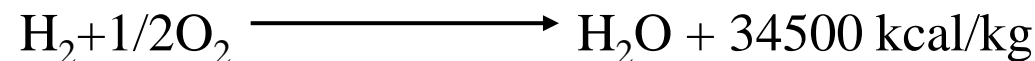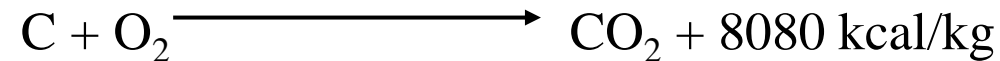
2. Dulong's Formula

➢ is used for the calculation of calorific value from the chemical composition of fuel.

  i.e. HCV = sum of HCV's of individual elemental constituents present in the fuel

• **Derivation:**

  Exothermic reactions during the process of combustion with their respective HCV values are:

$$C + O_2 \longrightarrow CO_2 + 8080 \text{ kcal/kg}$$

$$H_2 + 1/2O_2 \longrightarrow H_2O + 34500 \text{ kcal/kg}$$

$$S + O_2 \longrightarrow SO_2 + 2240 \text{ kcal/kg}$$

Oxygen present in the fuel is assumed to be present as water and which also prevents some part of hydrogen available for combustion

$$H_2 + \quad 1/2O_2 \longrightarrow H_2O + 34500 \text{ kcal/kg}$$

  2g   16g   18g

  1   **8**   9
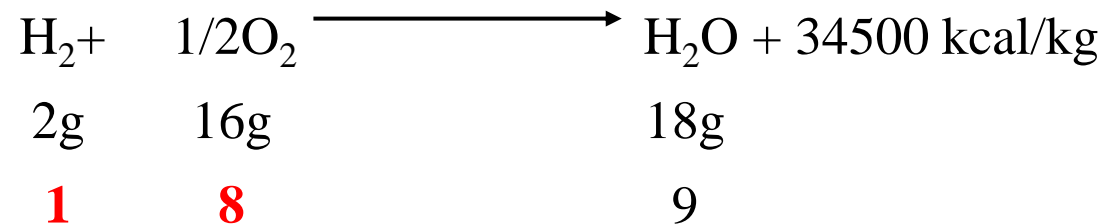
Dulong's formula

So, Available hydrogen for combustion = Total hydrogen – Fixed hydrogen in the form of H_2O

= Total hydrogen – 1/8 (mass of oxygen in fuel)

So if C, H, O and S percentages of carbon, hydrogen, oxygen and sulphur, respectively are known then,

$$\Rightarrow HCV = [8080 \times \frac{C}{100} + \frac{34500}{100}\left(H - \frac{O}{8}\right) + 2240 \times \frac{S}{100}] \, kcal/kg$$

or, $\quad \textbf{HCV} = \frac{1}{100}[\textbf{8080C} + \textbf{34500}\left(\textbf{H} - \frac{\textbf{O}}{\textbf{8}}\right) + \textbf{2240S}] \, \textbf{kcal/kg}$

and, $\quad \textbf{LCV} = \textbf{HCV} - \textbf{0.09H} \times \textbf{587 kcal/kg}$

as 1 part of H by mass gives 9 parts of H_2O, and latent heat of steam is 587 kcal/kg

Exercise

Que: Calculate the gross and net calorific value of coal having the following composition

C	85 %
H	8 %
S	1 %
N	2 %
ash	4 %
Latent heat of steam = 587 cal/g	

3. BOY'S GAS CALORIMETER

➤ Used for measuring the calorific value of gaseous and liquid fuels
➤ A known volume of gas is burnt at a uniform rate
➤ Around the burner there is a chimney containing coils wherein water is passed with a constant rate
➤ Separate thermometer are used to measure the incoming and outgoing water temperatures (t_1 and t_2)
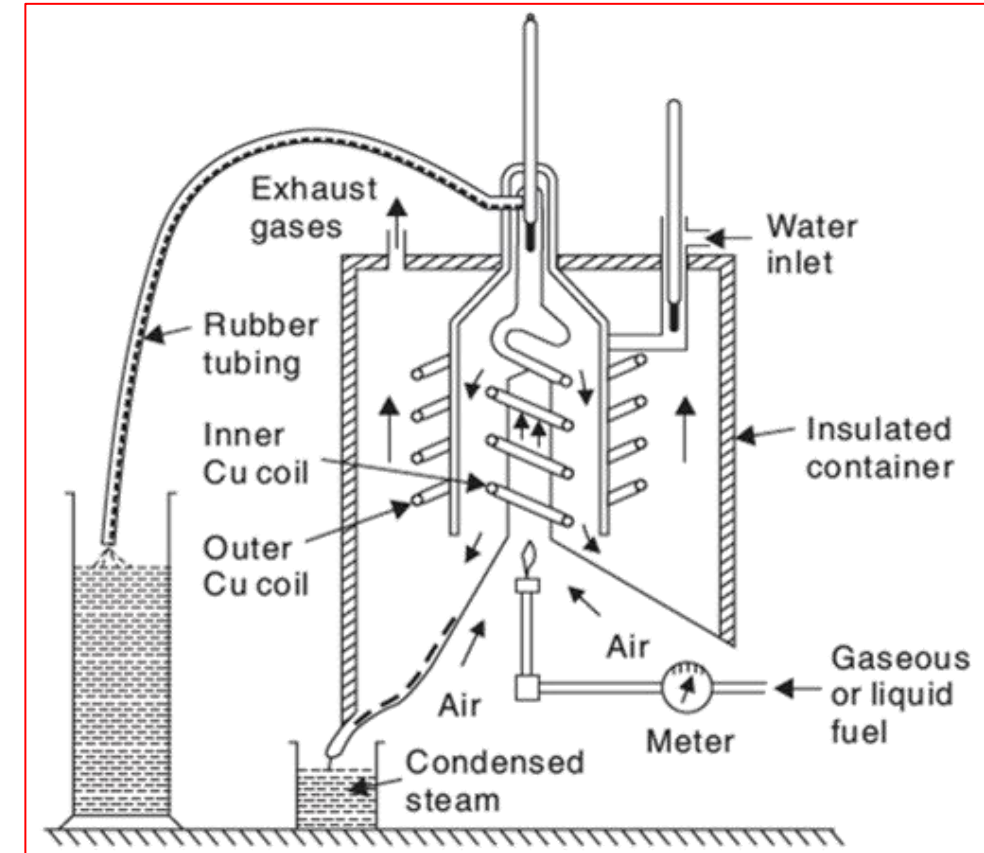
Fig. 2: Boy's Gas Calorimeter

CALCULATION

Let V = volume of gas burning

W = mass of cooling water used in time t

t_1 and t_2 = incoming and outgoing water temperatures respectively

m = mass of steam condensed in time t

Total heat liberated = V x HCV

Total heat absorbed = W x (t_2 - t_1)

So, we get $\boxed{HCV = \dfrac{W \times (t_2 - t1)}{V}}$

Also mass of water condensed per m^3 of gas = m/V kg

So latent heat of steam per m^3 of gas = $\dfrac{m \times 587}{V}$ kcal

So, $\boxed{NCV = \left[HCV - \dfrac{m \times 587}{V}\right] kcal/m3}$

Liquid Fuels

❑ The important liquid fuels are petroleum, petroleum products, tar, alcohols.
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Petroleum (*petra* = **rock**; *oleum* = **oil**)

➤ Petroleum or crude oil is a dark greenish brown or black colored viscous oil found deep in earth's crust.
➤ The oil is usually floating over a brine solution and above the oil, natural gas is present. Crude oil containing mixture of paraffinic, olefinic and aromatic hydrocarbons with minor amounts of organic compounds like N, 0 and S.
➤ The average composition of crude oil is C =80 - 87 %, H =11-15%, S = 0.1 -*3.5%*, (N +O) =0.1-0.5%.

Classification of petroleum

Petroleum is classified into three types based on variation of chemical nature of crude oil found in the earth.

- **Paraffinic-base type crude oil**: It contains saturated hydrocarbons from CH_4 to $C_{35}H_{72}$ and little amount of naphthalenes and aromatics.

- **Asphaltic-base type crude oil**: It contains mainly cycloparaffins or naphthalenes with smaller amount of paraffins and aromatic hydrocarbons. Hydrocarbons from $C_{18}H_{38}$ to $C_{35}H_{72}$ are called waxes.
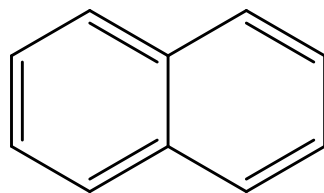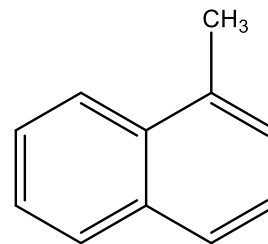
(Naphthalene)   (Methyl naphthalene)

- **Mixed-base type crude oil** : It contains both paraffinic and asphaltic hydrocarbons and are generally in the form of semi-solid waxes.
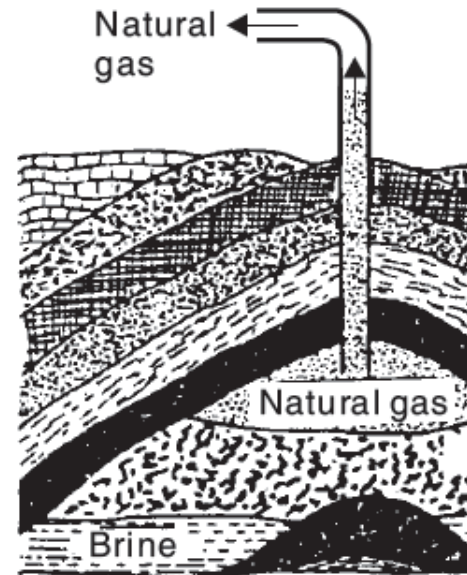
Petroleum

Origin of petroleum

➢ Resulted from the partial decomposition of marine animals and vegetable organisms of pre-historic forests

➢ These materials had buried by changes in earth (like earthquake, volcano etc.) and subjected to high pressure and temperature during the ages of time

➢ Then influenced by either radioactive elements or bacterial decomposition under anaerobic conditions to get converted to various hydrocarbons

Remain plants → Coal   Remain animal → Oil & Gas

Settled and accumulated in the ocean floor

Buried in several kilometers from surface

Sediment

Compressed from the weight

High pressure and temperature, No oxygen

Rock and organic matter

Kerogen

Forming source rock   burial and heating   Petroleum and natural gas
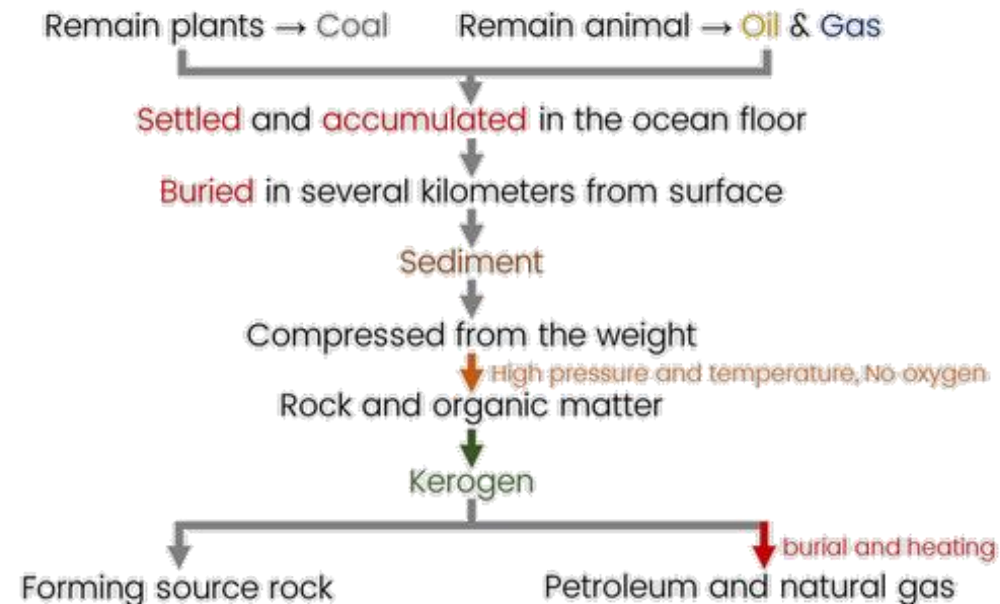
Mining of Petroleum

✓ Done by drilling holes in the earth crust and sinking pipes upto the oil-bearing porous rocks

✓ Oil usually gushes out itself due to hydrostatic pressure of natural gas.

✓ Then it may be mechanically pumped up by using either lift pump or air-lift pump.

Mining of crude oil and use of air-lift pump

Refining of Petroleum

❏ The crude oil obtained from the earth crust contains water, sulphur and some unwanted impurities.

❏ After removal of water, sulphur and these impurities, the crude oil is separated into various useful fractions by fractional distillation and finally converted into desired specific products having different boiling points. The process is called "Refining of Petroleum" and the refining plants are called "Oil refineries". The process of refining involves the following steps.

Step -I: Separation of water (Cottrell's process)
✓ The crude oil from the oil well is an extremely stable emulsion of oil and salt water. The crude oil is allowed to flow between two highly charged electrodes, where colloidal water droplets coalesce to form large drops, which is then separated out from the oil.

Step - II: Removal of harmful impurities
✓ (a) The presence of NaCI and MgCI in the crude oil can corrode the refining equipment, hence these salts are removed by electrical desalting and dehydration methods.
✓ (b) The sulphur compounds present in the crude oil is removed by treating oil with copper oxide, which results in the formation of copper sulphide (solid), which is then removed by filtration.

Fractional distillation

Step - III: Fractional distillation

✓ The crude oil is then heated to about 400°C in an iron retort, whereby all volatile substances (except asphalt or coke) are evaporated. The hot vapors are then passed up a fractionating column, which is a tall cylindrical tower containing a number of horizontal stainless steel trays at short distances. Each tray is provided with small chimney covered with a loose cap.

✓ When the vapours of the oil go up in the fractionating column, they become gradually cooler and get condensed at different heights of column. The fractions having higher boiling points condense at lower trays whereas the fractions having lower boiling points condense at higher trays. The gasoline obtained by the fractional distillation is called straight --run gasoline. Various fractions obtained at different trays are given in table.
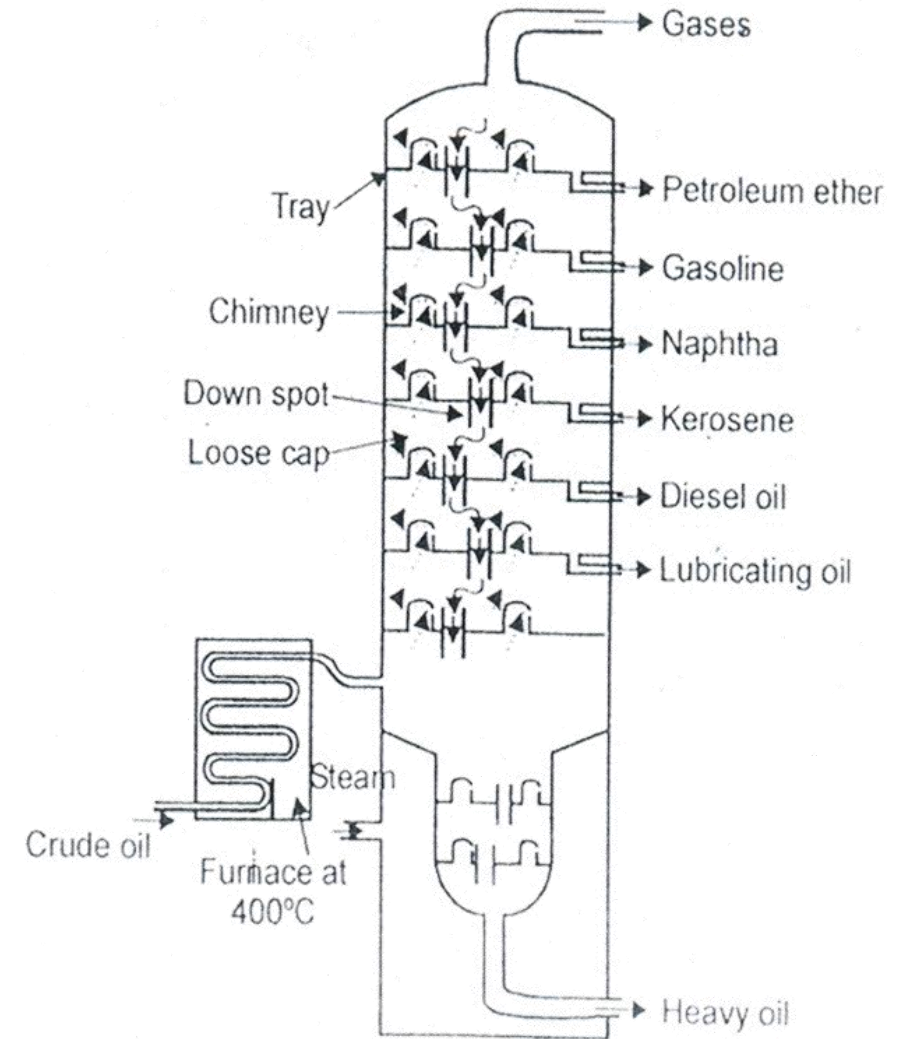
Fractional distillation

Sn.	Name of the fractions	Boiling range (^{O}C)	Composition of Hydrocarbons .	Uses
1.	Uncondensed gases	Below 30°C	C_1 to C_4	
2.	Petroleum ether	30 70 °C	C_5 to C_7	
3.	Gasoline (or) petrol.	40 - 120 °C	C_5 to C_9	
4.	Naphtha (or}solvent spirit .	120. - 180 °C	C_9 to C_{10}	
5.	Kerosene oil.	180 - 250 °C	C_{10} to C_{I6}	
6.	Diesel oil (or) gas oil	250 320 °C	C_{10} to C_{I8}	
7.	Heavy oil.	320 - 400 °C	C_{17} to C_{30}	

Fractional distillation of Heavy Oil

Sn.	Name of the fractions	Boiling range (^{O}C)	Composition of Hydrocarbons .	Uses
1.	Lubricating oil	-	C_{17} to C_{20}	
2.	Petroleum jelly (Vaseline)	-	-	
3.	Paraffin wax	-	C_{20} to C_{28}	
4.	Grease	-	-	
5.	Asphalt or bitumen	Above 400°C	C_{30} and above	

Cracking

Cracking

➤ The decomposition of bigger hydrocarbon molecules into simpler, low boiling hydrocarbons of lower molecular weight is called **Cracking**.

➤ The gasoline obtained from the fractional distillation of petroleum, has the highest demand as a motor fuel, but the **yield** of this fractions is only 20-30% (Crude oil) and also **quality** as straight-run gasoline which is not good and hence is used only after proper blending. To overcome these difficulties, the higher boiling fractions (e.g. fuel oil and gas oil) are converted into lower boiling fractions gasoline (petrol) by cracking process.

➤ The cracked gasoline gives better engine performance i.e., they are suitable for spark-ignition engines of automobiles. In cracking process, higher saturated hydrocarbon molecules are converted into simpler molecules such as paraffinic and olefinic hydrocarbons.

$$C_{10}H_{22} \xrightarrow{\text{Cracking}} C_5H_{12} \;+\; C_5H_{10}$$

Decane   n-pentane   pentene

B.P. = 174 °C   B.P. = 36 °C
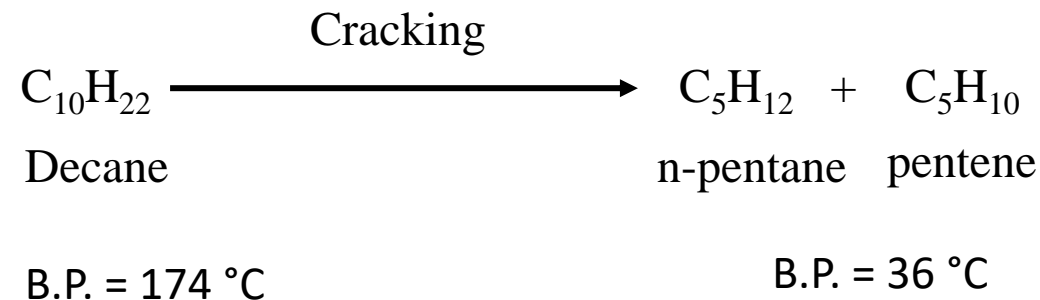
Types of Cracking: Thermal Cracking

There are two methods of cracking in use
1. Thermal cracking   2. Catalytic cracking

Thermal cracking

- ✓ In this process, the heavy oil is subjected to high temperature and pressure, when the bigger hydrocarbon molecules break down to give smaller molecules of the paraffins, olefins and hydrogen.
- ✓ The cracked products are then separated by fractional distillation.
- ✓ This process is carried out in liquid phase at a temperature of 475 - 530° C and under pressure of 100 kg/cm^2 is called Liquid-phase thermal cracking
- ✓ or at a temperature of 600-650°C (heavy oil is vapourised) and under a low pressure of 10-20 kg/cm2, such process is called Vapour-phase thermal cracking.
- ✓ Petrol obtained from vapor phase cracking has better anti-knock properties but poor stability than petrol from liquid phase cracking.

Catalytic Cracking

In this process, cracking is carried out in presence of a catalyst at lower temperature (300° C to 450° C) and pressures (l to 5 kg/cm^2). The catalyst like aluminum silicate [$Al_2(SiO_3)$] or alumina [Al_2O_3] used in cracking gives higher yield and better quality of gasoline. There are two types of catalytic cracking in use

Advantages

i.   No external fuel is required. Heat required is derived from coal, embedded in the catalyst.

ii. Low pressure is required (1-5 kg/cm^2)

iii. Product contain very less amount of Sulphur (major part escapes out as H_2S gas)

iv. Catalytic cracking yields a higher quantity of branched-chain, unsaturated, aromatic hydrocarbons as compared to thermal cracking and hence have better anti-knock characteristics

There are two types of catalytic cracking in use
i) **Fixed-bed catalytic cracking**
ii) **Fluid (Moving)-bed catalytic cracking**

Fixed-bed catalytic cracking

➢ The heavy oil is passed through the heater, where the oil is vapourised and heated to 400 to 500°C and then forced through a catalytic champers containing the catalyst of silica alumina gel (SiO_2, Al_2O_3) or bauxite, is mixed with clay and zirconium oxide maintained at 400 to 500°C and 1.5 kg/cm^2 pressure. During their passage through the tower, cracking takes place about 30-40% of the charge is converted into gasoline and about 2- 4% carbon is formed which gets deposited on the catalytic bed.

➢ The vapours produced are then passed through a fractionating column, where heavy oil fractions condensed. The vapours are then admitted into a cooler, where some of the gaseous products are condensed along with gasoline and uncondensed gases move on. The gasoline containing some dissolved gases is then sent to a stabilizer, where the dissolved gases are removed and pure gasoline is obtained.

➢ When substantial amount of carbon is deposited on the catalyst bed, during cracking, the catalyst stops functioning. It is reactivated by burning off the deposited carbon in a stream of hot air. During the reactivation of catalyst, the vapours are diverted through another catalyst chamber.

Fixed-bed catalytic cracking
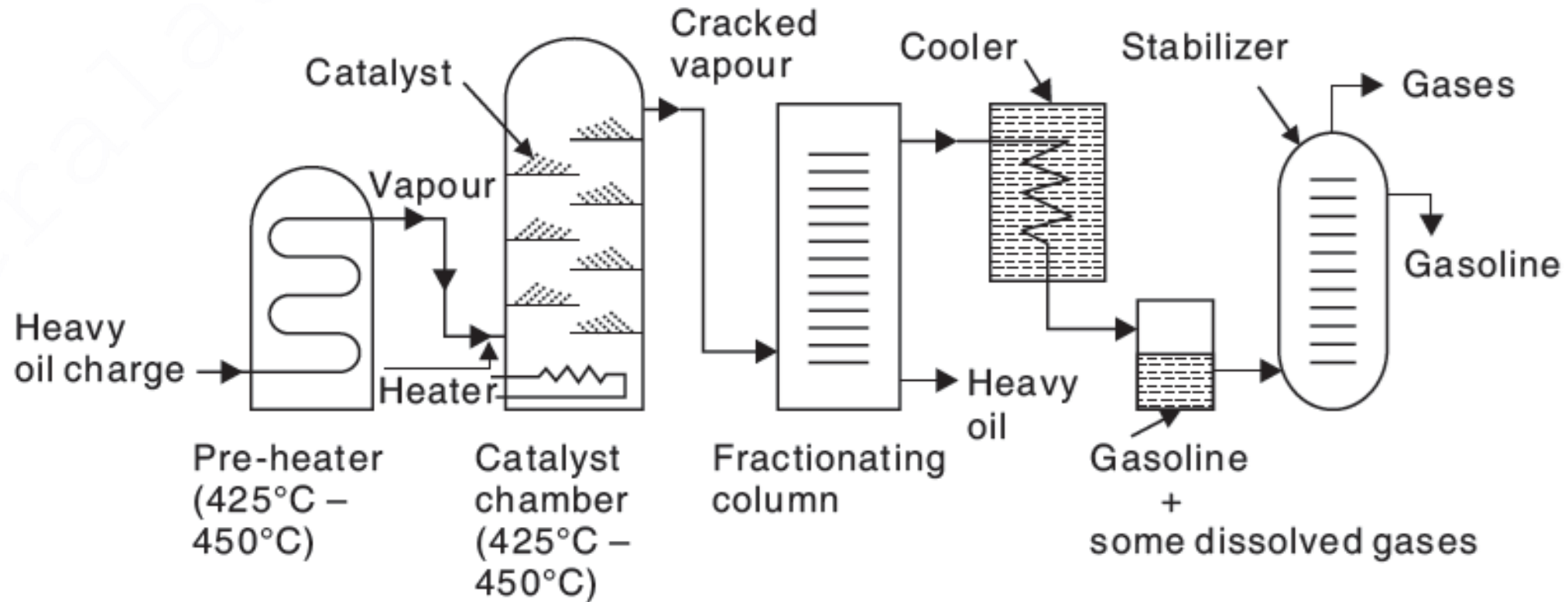
Fig. Fixed-bed catalytic cracking

Fluid (Moving)-bed catalytic cracking

❑ In this process, solid catalyst is finely powdered, so that it behaves almost as a fluid, which can be circulated in gas stream.

❑ The vapours of cracking stock (gas oil, heavy oil, etc.,) mixed with fluidized catalyst is forced up into a large reactor bed in which cracking of the heavier molecules into lighter molecules occurs at a temperature of 530°C and pressure of about 3 to 5 kg/cm^2.

❑ The top of the reactor, there is a centrifugal separator, which, allows the low boiling lighter molecules move up to the top of the reactor and enter into the fractionating column but retains all the catalyst powder in the reactor itself.

❑ The carbon deposited on the catalyst powder are burnt off in the regenerator and the temperature rises to about 590°C or more.

❑ The cracked gases and gasoline are removed from the top of the fractionating column and sent to a cooler, where gasoline is condensed. It is then sent to a stabilizer to recover pure gasoline.

❑ The product contains a higher proportion of aromatics and iso-paraffins.

Fluid (Moving)-bed catalytic cracking
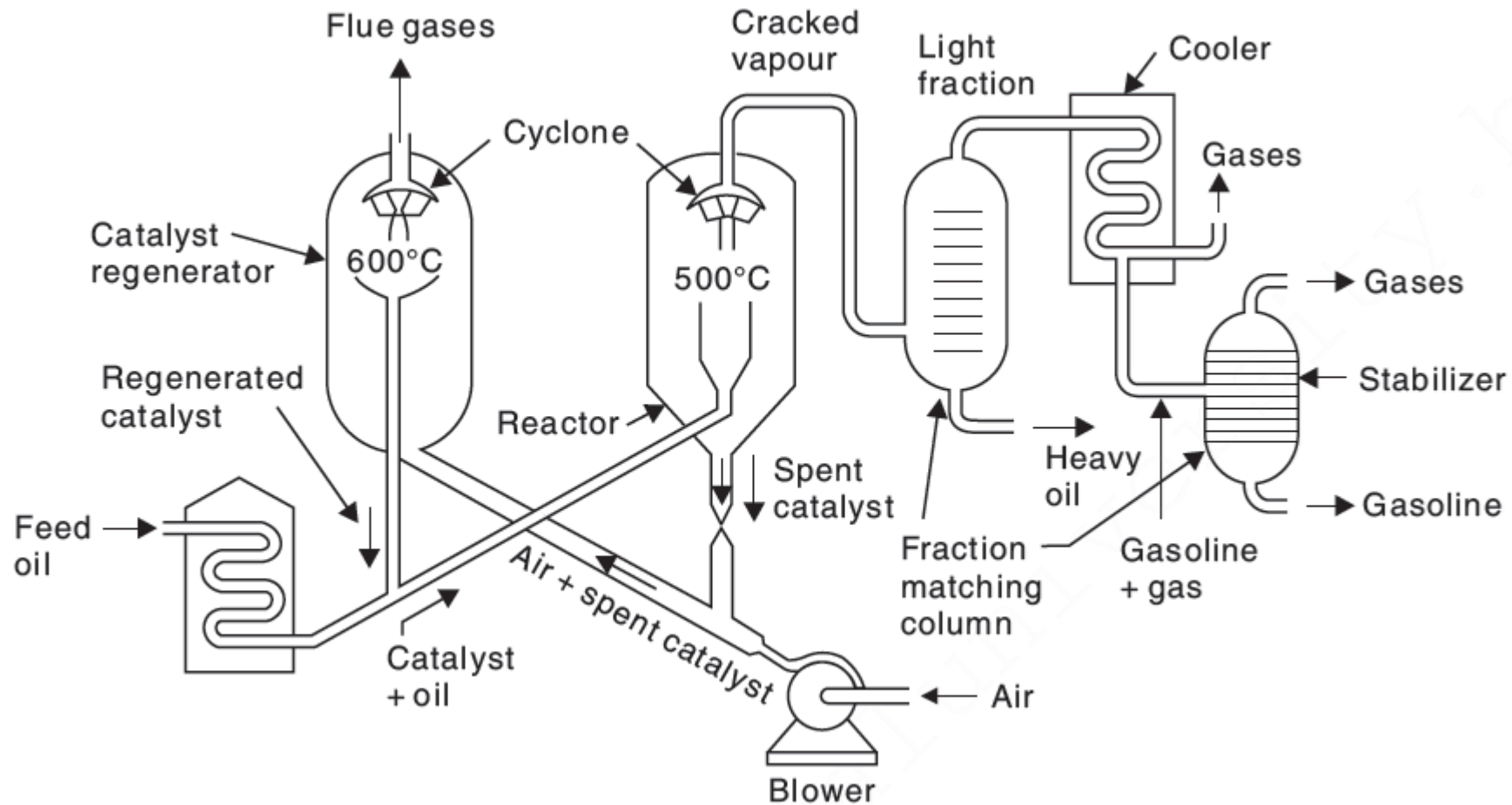
Fig: Moving-bed type catalytic cracking

Synthetic Petrol

(1) Polymerization

(2) Fishcher-Tropsch method

(3) Bergius process

Polymerization

❖ Gases obtained as a by-product from cracking of heavy oils, etc., contains olefins (like ethylene, propene and butenes) and alkanes (such as methane, ethane, propane and butane).

❖ This gaseous mixture when subjected to high pressure and high temperature with or without catalyst, it polymerize to form bigger hydrocarbons called **polymer gasoline**.

prop-1-ene   +   but-1-ene   → (Pressure, Heat and/or Catalyst) → 5-methylhex-1-ene
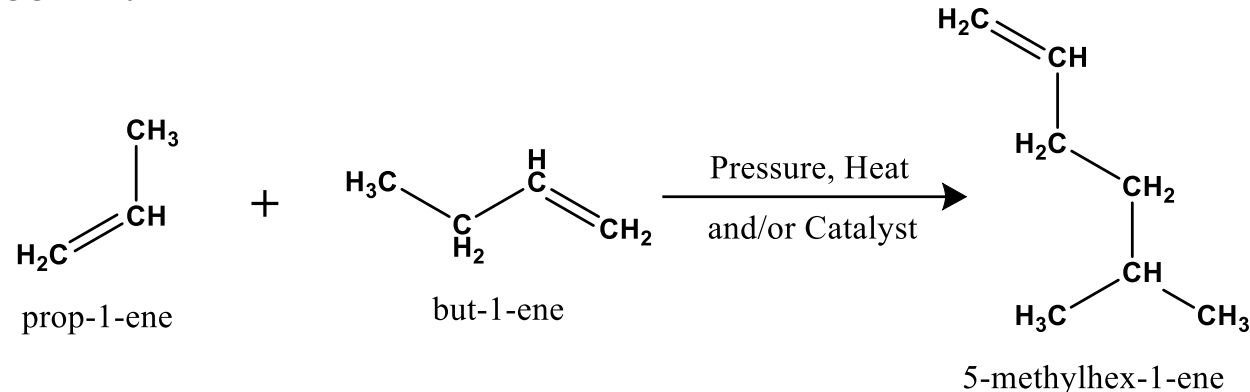
Types of polymerization

➢ **Thermal Polymerization:** at temperature 500-600°C and 70-350 kg/cm^2. Product is gasoline and gas oil mixture

➢ **Catalytic Polymerization:** at 150-200°C and in presence of catalyst like phosphoric acid. Products are gasoline and unpolymerized gas which is separated and recycled for polymerization

Fishcher-Tropsch method

➢ In this process, coal is first converted into coke. Then water gas ($CO + H_2$) is produced by the action of steam over red hot coke.

➢ The gas is purified by passing through Fe_2O_3 (to remove H_2S) and then into a mixture of $Fe_2O_3.Na_2CO_3$ (to remove organic Sulphur compounds).

➢ The purified gas is compressed to 5 to 25 atm and then led through a converter (containing a catalyst, consisting of a mixture of *100 parts cobalt, 5 parts thoria, 8 parts magnesia and 200 parts kieselguhr earth*) maintained at ~200-300°C.

$$n\ CO\ +\ 2n\ H_2\ \longrightarrow\ C_nH_{2n}\ +\ n\ H_2O$$

$$n\ CO\ +\ (2n+1)\ H_2\ \longrightarrow\ C_nH_{2n+2}\ +\ n\ H_2O$$

➢ Reaction is exothermic, so outcoming hot mixture is led to a cooler, where a liquid is resembling crude oil is obtained

➢ Crude oil then fractionated to get gasoline and high boiling point heavy oil

➢ Heavy oil then recycled for cracking to get more gasoline.

Fishcher-Tropsch method
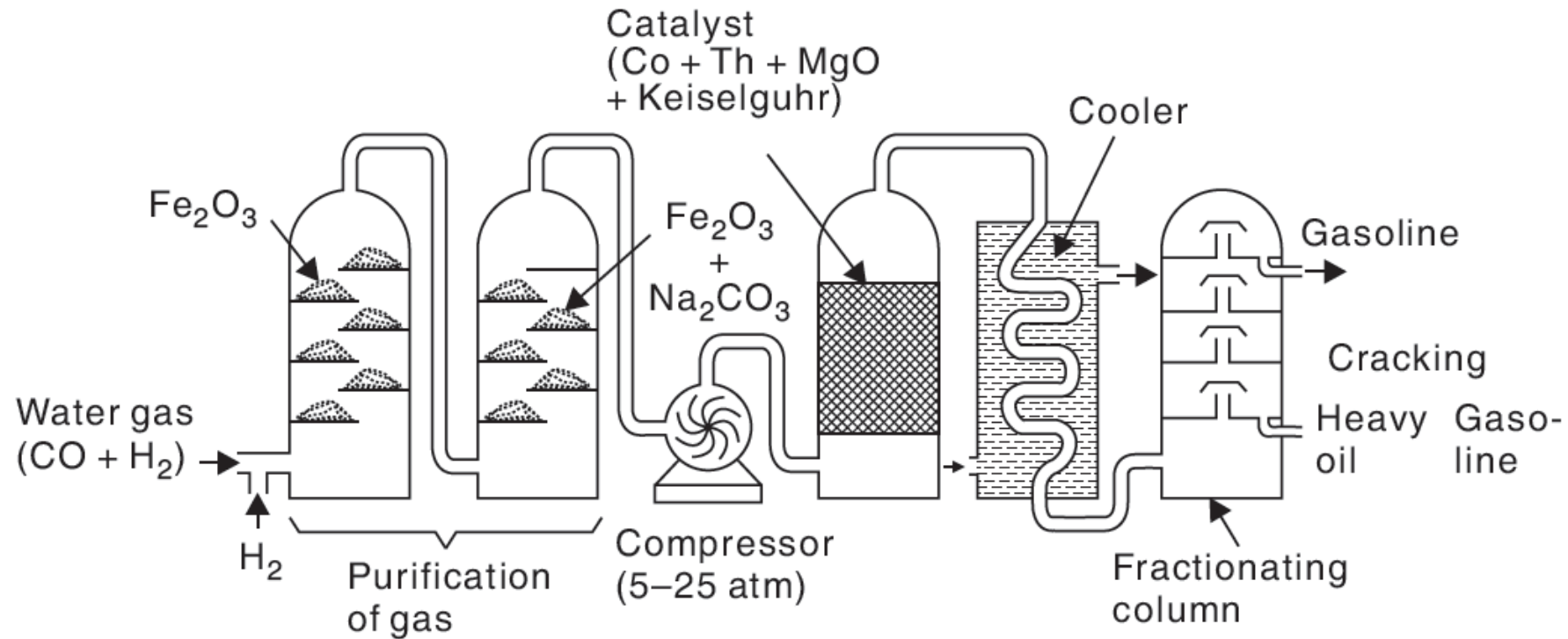
Fig: Fischer-Tropsch method

Bergius Process

- This method was developed by Bergius in Germany during the First World War.

- The low ash coal is finely powdered and made into a paste with heavy oil and then a catalyst (composed of tin or nickel oleate) is incorporated.

- The whole is heated with hydrogen at 450°C and under a pressure 200-250 atm for about 1.5 hours, during which hydrogen combines with coal to form saturated hydrocarbons, which decompose at prevailing high temperature and pressure to yield low-boiling liquid hydrocarbons.

- The issuing gases (from the reaction vessel) are led to condenser, where a liquid resembling crude oil is obtained, which is then fractionated to get: (i) gasoline, (ii) middle oil, and (iii) heavy oil.

- The latter is used again for making paste with fresh coal dust. The middle oil is hydrogenated in vapour-phase in presence of a solid catalyst to yields more gasoline. The yields of gasoline in about 60% of the coal dust used.

Bergius Process
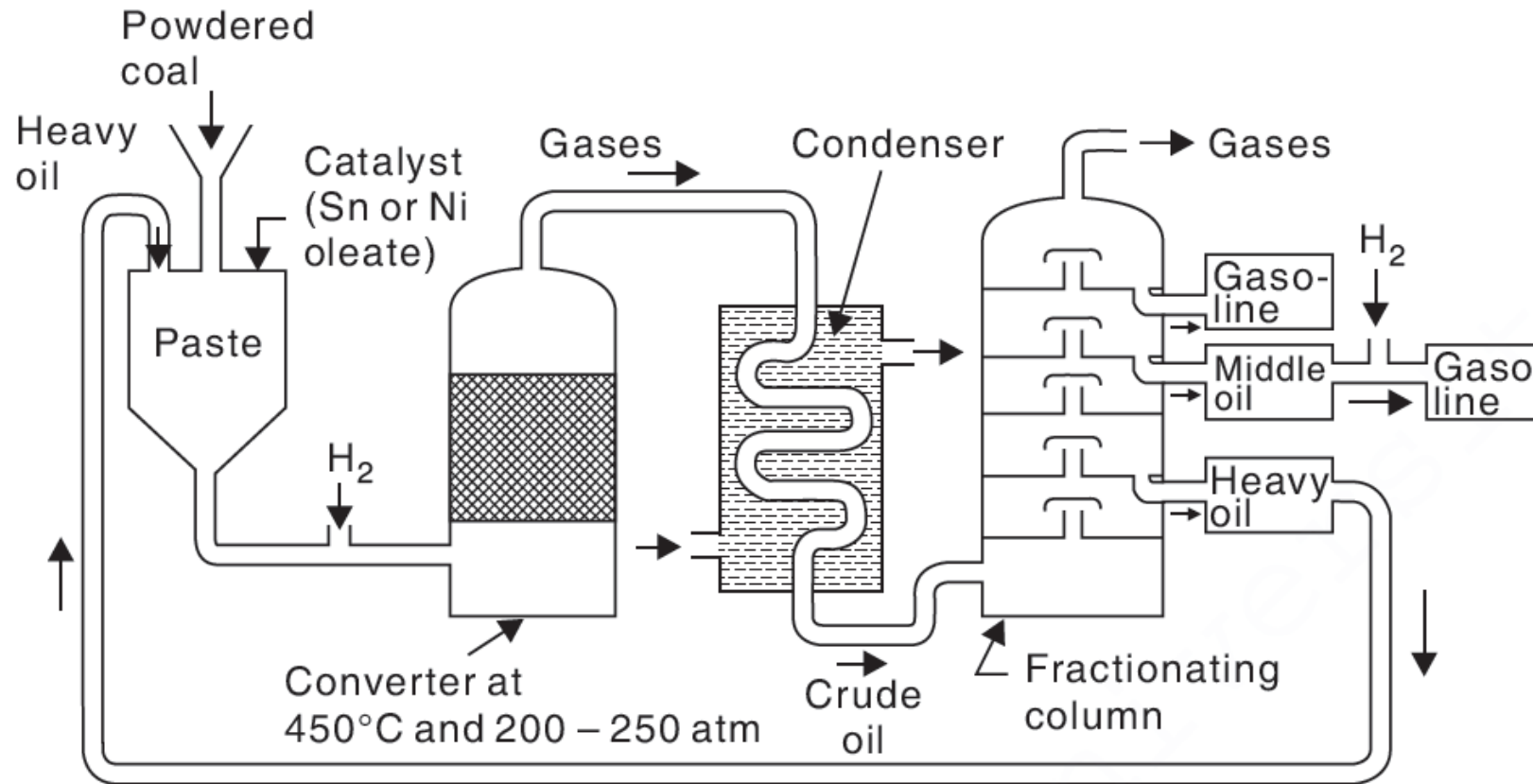
Fig: Bergius process of hydrogenation of coal to gasoline

Refining of Gasoline

❑ Gasoline obtained from fractionation of crude petroleum contains some undesirable unsaturated straight chain hydrocarbons and Sulphur compounds

❑ These hydrocarbons gets oxidized and polymerized to form gum and sludge on storing

❑ Also Sulphur compounds lead to corrosion of internal combustion engine

<u>Characteristics of an ideal gasoline</u>

1. It must be cheap and readily available
2. It must burn clean and produce no corrosion , etc., on combustion
3. It should mix readily with air and afford uniform manifold distribution, i.e., it should easily vaporize
4. It must be knock resistant
5. It should not pre-ignite easily
6. It should not tend to decrease the volumetric efficiency of the engine
7. It must have high calorific value

Refining

❑ The sulphur compounds are, generally, removed by treating gasoline with an alkaline solution of sodium plumbite with controlled addition of S. This refining process (called 'sweetening') converts sulphur compounds into disulphides (Doctor's process).

$$2RSH \;+\; Na_2PbO_2 \longrightarrow Pb(SR)_2 \;+\; 2NaOH$$

Sodium Plumbite

$$Pb(SR)_2 \;+\; S \longrightarrow PbS \;(s) \;+\; RSSR$$
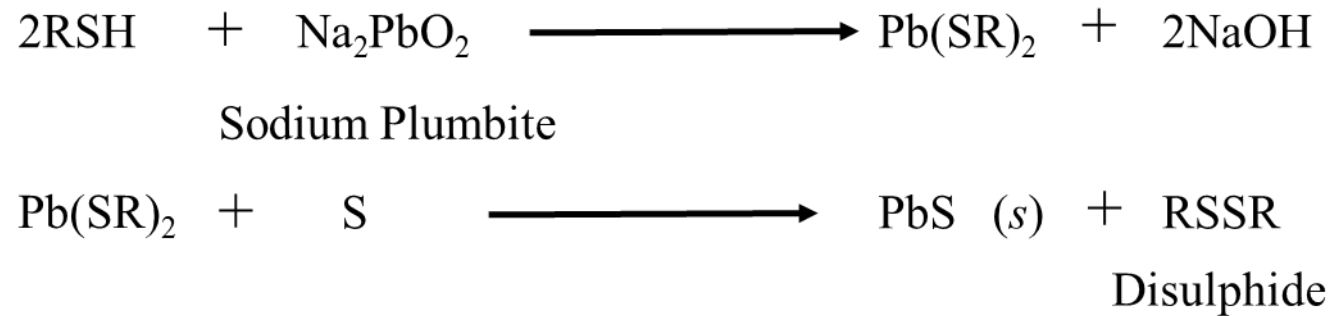
Disulphide

❑ PbS is removed by filtration
❑ Disulphides are extracted with a suitable solvents
❑ After the refining of gasoline, some inhibitors are added. These retard the oxidation reactions, thereby improving storing qualities of gasoline.

Reforming

Reforming is a process of bringing about structural modifications in the components of straight run gasoline (prepared by the fractional distillation of the crude oil), with the primary object of imtproving its anti-knock characteristics.

Thermal Reforming:

Catalytic Reforming:

cyclohexane   Pt (0.75 %) / $-3H_2$ benzene
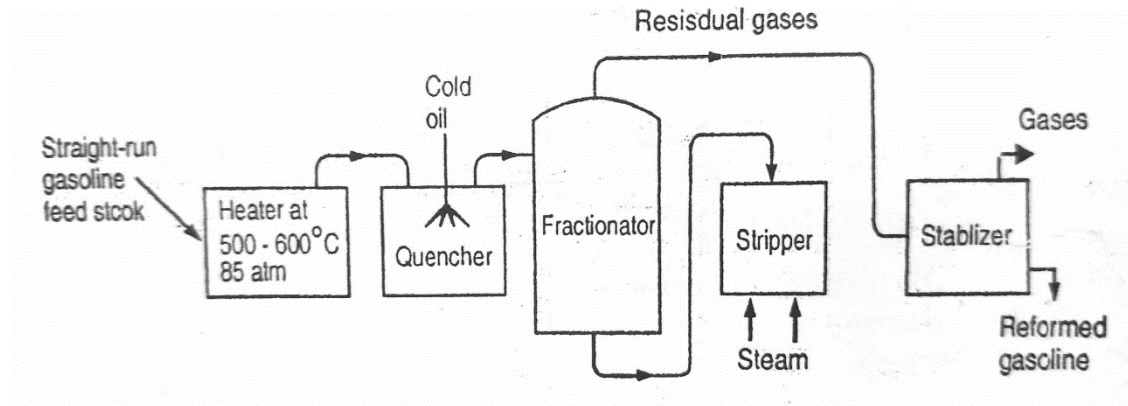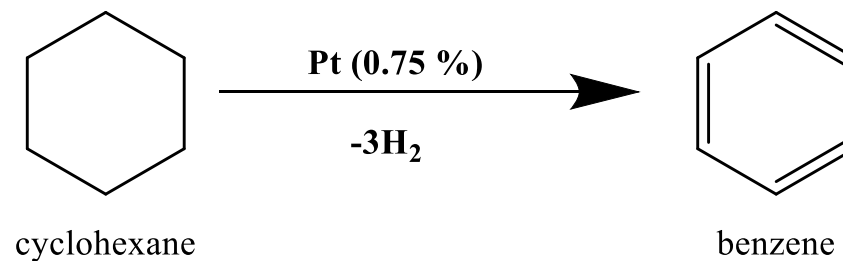
Knocking

Knocking is a kind of explosion due to rapid pressure rise occurring in an IC engine

In a petrol engine, a mixture of gasoline vapour and air at 1: 17 ratio is used as fuel. This mixture is compressed and ignited by an electric spark. The products of oxidation reaction (combustion) increases the pressure and pushes the piston down the cylinder. If the combustion proceeds in a regular way, there is no problem in knocking. But in some cases, the rate of combustion (oxidation) will not be uniform due to unwanted chemical constituents of gasoline. The rate of ignition of the fuel gradually increases and the final portion of the fuel-air mixture gets ignited instantaneously producing an explosive sound known as "**Knocking**". Knocking property of the fuel reduces the efficiency of engine. So a good gasoline should resist knocking.

❑ **Chemical structure and knocking**
- The knocking tendency of fuel hydrocarbons mainly depends on their chemical structures. The knocking tendency decreases in the following order.
- Straight chain paraffins> Branched chain paraffins> Cycloparaffins > Olefins > Aromatics.

❑ **Improvement of antiknock characteristics**
- The octane number of fuel can be improved by
- (i) blending petrol of high octane number with petrol of low octane number, so that the octane number of the latter can be improved.
  (ii) the addition of anti-knock agents like Tetra-Ethyl Lead (TEL).

Octane rating (introduced by Edger in 1872)

➤ It has been found that n-heptane knocks very badly and hence, its anti-knock value has arbitrarily been given zero
➤ On the other hand, isooctane (2,2,4-trimethyl pentane)is having very good anti-knocking properties. Thus octane number is given 100.
➤ In this way, "80-octane" fuel is one which has the same combustion characteristics as a 80:20 mixture of isooctane and n-heptane.
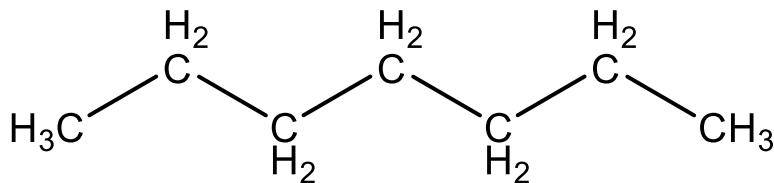
heptane, octane no. = 0
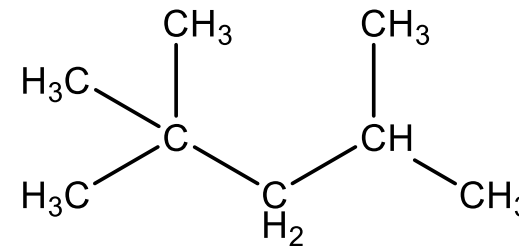
2,2,4-trimethylpentane, octane no. = 100

Anti-Knocking agent

LEADED PETROL (ANTI-KNOCK AGENT)

➢ The anti-knock properties of a gasoline can be improved by the addition of suitable additives. Tetraethyl lead (TEL) or $Pb(C_2H_5)_4$ is an important additive added to petrol. Thus the petrol containing tetra ethyl lead is called leaded petrol.

➢ TEL reduces the knocking tendency of hydrocarbon.

➢ Knocking follows a free radical mechanism, leading to a chain growth which results in an explosion. If the chains are terminated before their growth, knocking will cease.

➢ TEL decomposes thermally to form ethyl free radicals which combine with the growing free radicals of knocking process and thus the chain growth is stopped.

Anti-Knocking agent

Disadvantages of using TEL

I.   When the leaded petrol is used as a fuel, the TEL is converted to lead oxide and metallic lead. This lead deposits on the spark plug and on cylinder walls which is harmful to engine life. To avoid this, small amount of ethylene dibromide is added along with TEL. This ethylene dibromide reacts with Pb and PbO to give volatile lead bromide, which goes out along with exhaust gases.

II. But this creates atmospheric pollution. So nowadays aromatic phosphates are used instead of TEL

III. Nowadays aromatic phosphates are used as antiknock agent because it avoids lead pollution.

Unleaded Petrol

➤ Octane rating of petrol is in leaded petrol is increased by adding tetra ethyl lead or tetramethyl lead

➤ However, combustion of lead petrol leads to formation of litharge (PbO), which deposition the inner wall of cylinder and jams the piston.

➤ Also leaded petrol cannot be used in automobiles equipped cost catalytic converter, because lead present in exhaust gas poisons the catalyst, thereby destroying the active sites

➤ Alternative method of increasing octane number of petrol is to add high octane compounds like isopentane, isooctane, ethyl benzene, isopropyl benzene, methyl tertiary butyl ether (MTBE). Out of these MTBE is preferred, because it contains oxygen in the form of ether group and supplies oxygen for the combustion of petrol in internal combustion engines, thereby reducing the extent of peroxy compound formation

➤ "Unleaded petrol" is one where in the enhancement of octane rating is accomplished without the addition of lead compounds

➤ major advantage of unleaded petrol is that it permits 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 harmless gases (CO, and N, respectively). Moreover, it oxidizes unburnt hydrocarbon into CO, and H_2O.

A New Form of Carbon
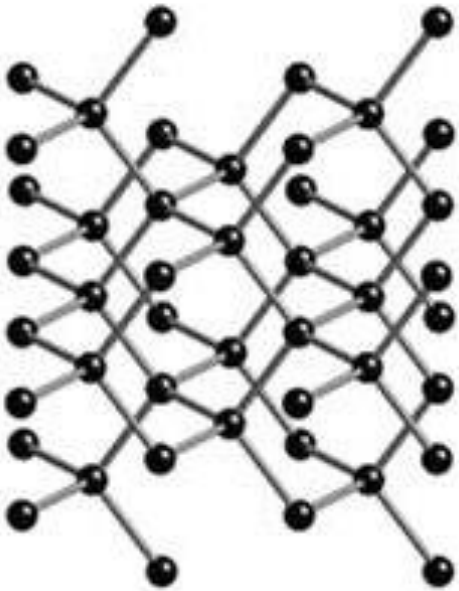
Diamond
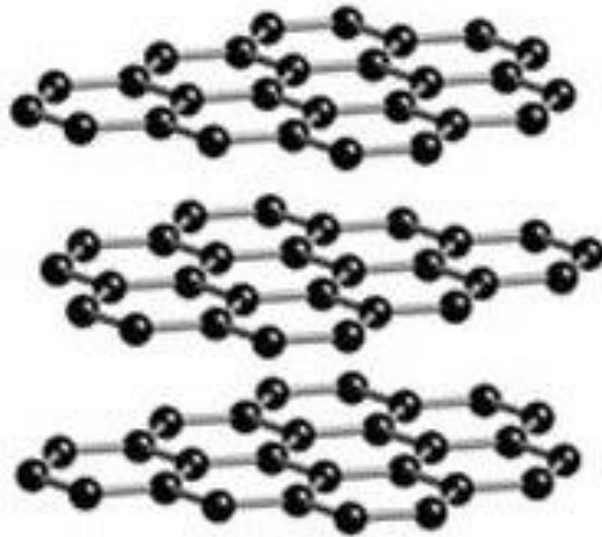
Graphite
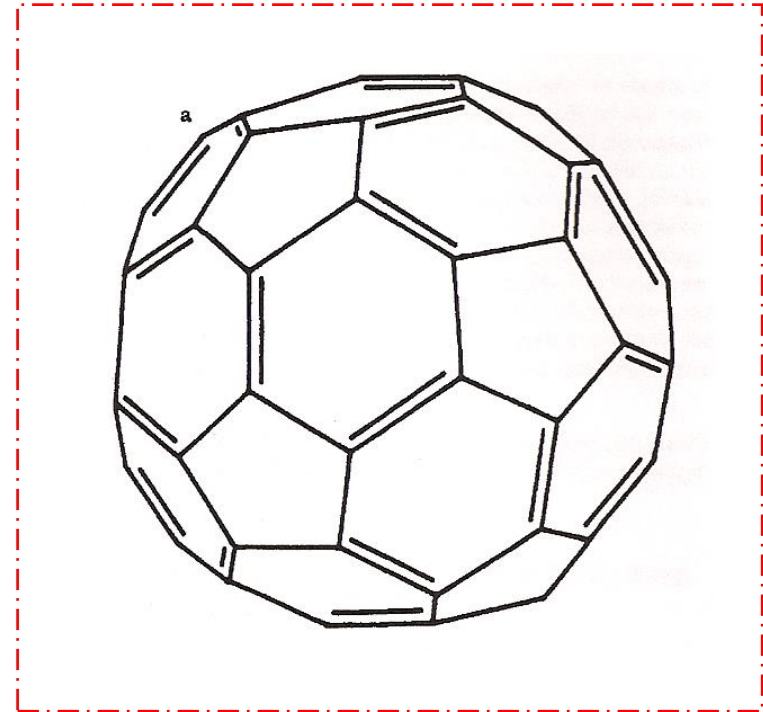
C_{60} Buckyball

Fullerene

➢ A Fullerene is any molecule composed entirely of carbon, in the form of a hollow sphere, ellipsoid, or tube.

➢ Spherical fullerenes are also called buckyballs, and cylindrical ones are called carbon nanotubes or buckytubes
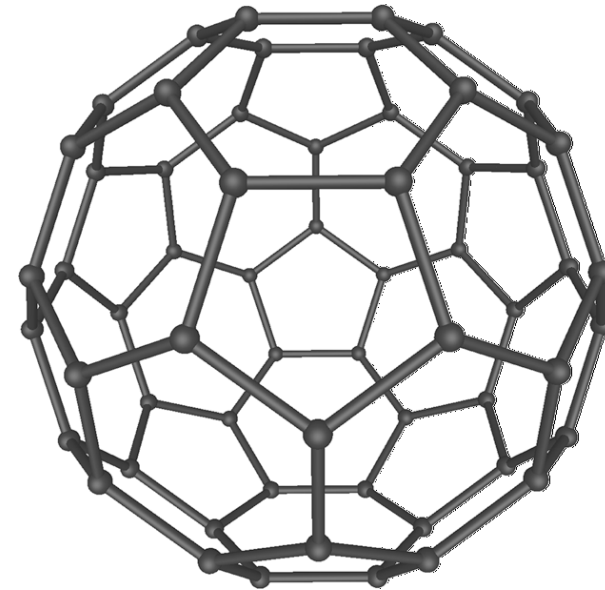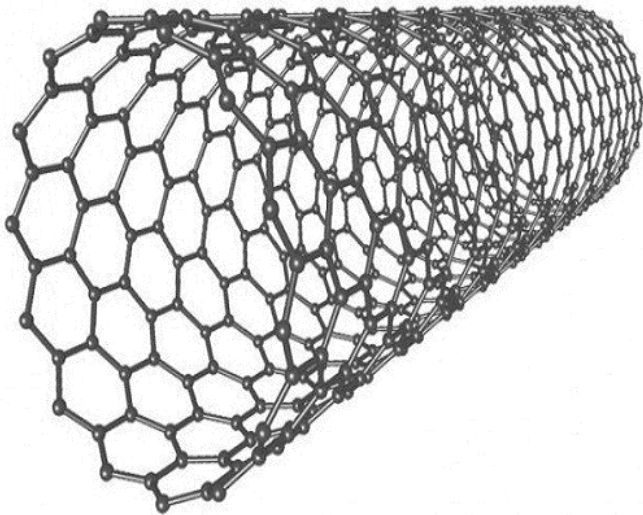
History

➤ The existence of C60 was predicted by Eiji Osawa of Toyohashi University of Technology in a Japanese magazine in 1970

➤ With mass spectrometry, discrete peaks were observed corresponding to molecules with the exact mass of sixty or seventy or more carbon atoms. In 1985, James R. Heath, Robert Curl and Richard Smalley, from Rice University discovered C60, and shortly thereafter came to discover the fullerenes.

➤ Kroto, Curl, and Smalley were awarded the 1996 Nobel Prize in Chemistry for their roles in the discovery of this class of compounds.

➤ Minute quantities of the fullerenes, in the form of C60, C70, C76, and C84 molecules, are produced in nature, hidden in soot and formed by lightning discharges in the atmosphere.
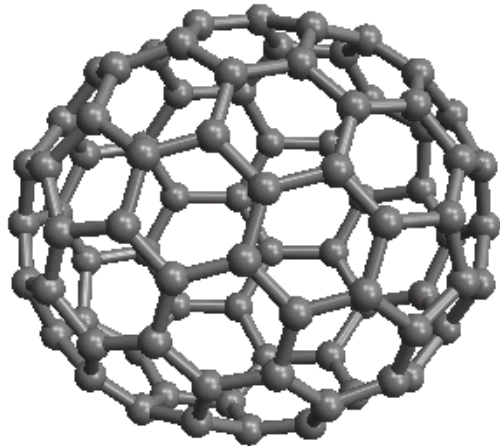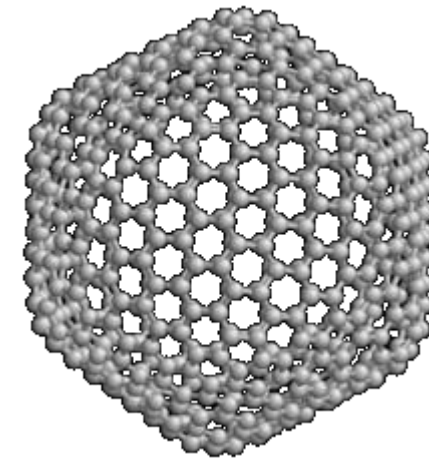
C84 Fullerene   The Icosahedral Fullerene C540

Naming

➢ Buckminsterfullerene (C60) was named after Richard Buckminster Fuller, a noted architectural modeler who popularized the geodesic dome.

➢ The shortened name 'fullerene' is used to refer to the family of fullerenes.

➢ The suffix "ene" indicates that each C atom is covalently bonded to three others.

The Montreal Biosphère by Buckminster Fuller, 1967

Types of Fullerenes

➢ **BUCKYBALL CLUSTERS**: smallest member is C20 (unsaturated version of dodecahedrane) and the most common is C60.

➢ **NANOTUBES**: hollow tubes of very small dimensions, having single or multiple walls; potential applications in electronics industry.

➢ **MEGATUBES**: larger in diameter than nanotubes and prepared with walls of different thickness; potentially used for the transport of a variety of molecules of different sizes.

➢ **POLYMERS**: chain, two-dimensional and three-dimensional polymers are formed under high-pressure high-temperature conditions; single-strand polymers are formed using the Atom Transfer Radical Addition Polymerization (ATRAP) route.

➢ **NANO"ONIONS**": spherical particles based on multiple carbon layers surrounding a buckyball core; proposed for lubricants.

➢ **LINKED "BALL-AND-CHAIN" DIMERS**: two buckyballs linked by a carbon chain.

Synthesis of C60

➢ The experimental set-up used to discover C60.
➢ The graphite disk is evaporated with a Nd:YAG laser and the evaporated carbon plasma is cooled by a stream of helium coming from a pulsed valve.
➢ The clusters of carbon are produced in the integration cup and are expanded into vacuum. The ions are detected by time of flight mass spectrometry
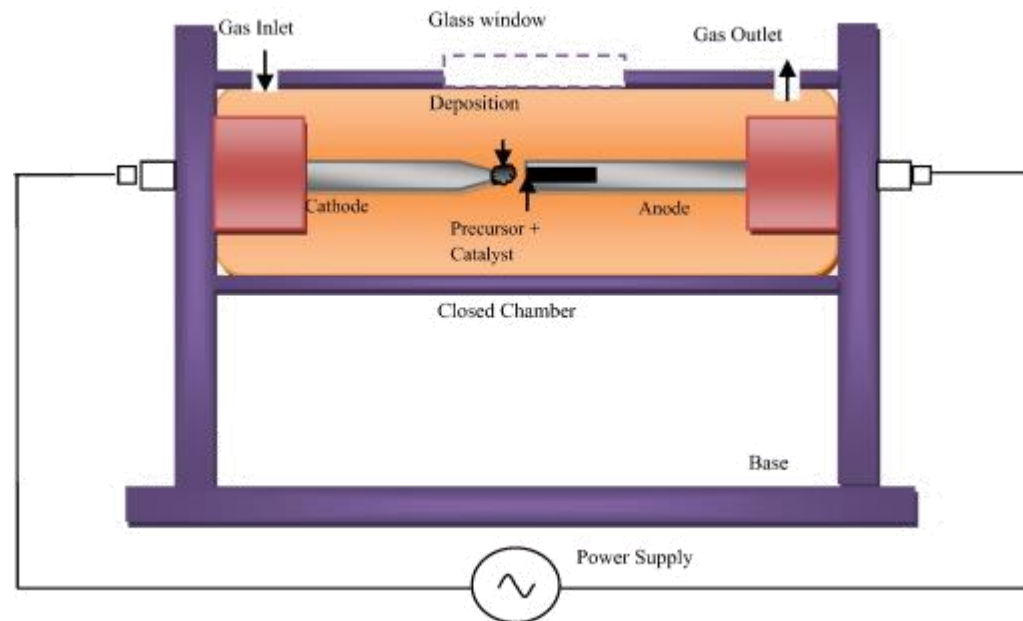
Arc Discharge Method

Properties of Fullerene

➢ **AROMATICITY**

- Researchers have been able to increase the reactivity of fullerenes by attaching active groups to their surfaces.
- Buckminsterfullerene does not exhibit "superaromaticity": that is, the electrons in the hexagonal rings do not delocalize over the whole molecule.

➢ **CHEMISTRY**

- Fullerenes are stable, but not totally unreactive.
- Other atoms can be trapped inside fullerenes to form inclusion compounds known as endohedral fullerenes.

The few of the applications of fullerenes are-

A. Artificial photosynthesis

B. Non-linear optics

C. In cosmetics.

D. In surface coatings

E. Bio logical applications

Application of Fullerene

The few of the applications of fullerenes are-

A. Artificial photosynthesis

B. Non-linear optics

C. In cosmetics.

D. In surface coatings

E. Bio logical applications

It is a powerful antioxidant, reacting readily and at a high rate with free radicals, which are often the cause of cell damage or death.
 It behaves like a "radical sponge," as it can sponge-up and neutralize 20 or more free radicals per fullerene molecule.
 It possess a novel ability of selectively entering oxidation-damaged cerebral endothelial cells rather than normal endothelial cells and then protecting them from apoptosis.

Polymers

❑ Polymers are known to have good insulating properties. (they are used in electrical and electronic applications as insulators)

❑ Polymers are one of the most used materials in the modern world. Their uses and application range from containers to clothing.

❑ They are used to coat metal wires to prevent electric shocks.

Properties

❑ Lightness

❑ Strength

❑ Flexibility

❑ Resistance to Corrosion and chemical attack

❑ Elasticity

❑ Mouldability

❑ Ease of handling

Uses

❖ In space

❖ Aeronautics

❖ Electronics

❖ Non-linear Optics

What is conductivity?

Conductivity is the ability of a material to pass an electric current. In a metal the outer electrons are free to carry charge and the impedance to flow of charge is mainly due to the electrons "bumping" in to each other.

Conducting Polymer: History

➢ Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa have changed this view with their discovery that a polymer, polyacetylene (PA), can be made conductive almost like a metal.

➢ They found that organic conjugated polymers, exhibits dramatic increase in electrical conductivity on treatment with oxidizing (electron-accepting) or reducing (electron donating) agents.

➢ These oxidation and reduction reactions, which induce high conductivity in PA are termed as p-doping and n-doping.

Alan G. MacDiarmid
Professor at the University of Pennsylvania, Philadelphia. USA.

Hideki Shirakawa
Professor Emeritus, University of Tsukuba. Japan.

Alan J. Heeger
Professor at the University of California at Santa Barbara. USA.

Instability of PA in air

➢ The discovery of highly conducting PA led to sudden research activity directed towards the study of new conducting polymeric systems as PA was found to be less stable in air

➢ PA get oxidized in presence of air forming new covalent bonds in the form of O_2 and CO_2 interrupting double bond conjugation.

➢ Hence less conjugation leads to lowering in conductivity.
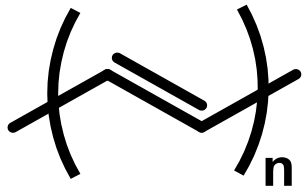
Polyacetylene (PA)
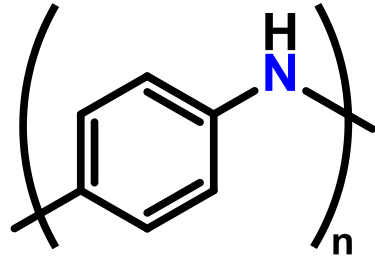
Polyaniline (PANI)
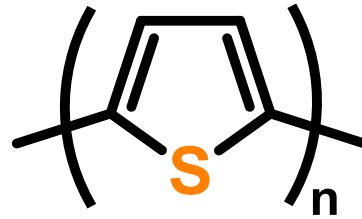
Polythiophene (PT)
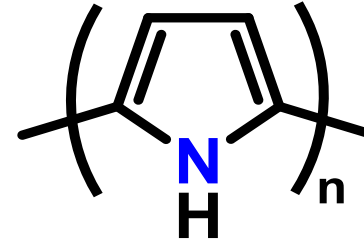
Polypyrrole (PPy)
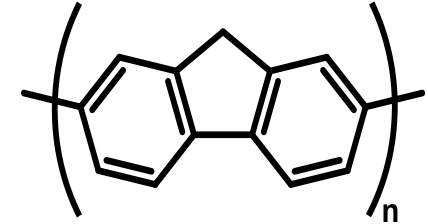
Polyfluorenes (PF)
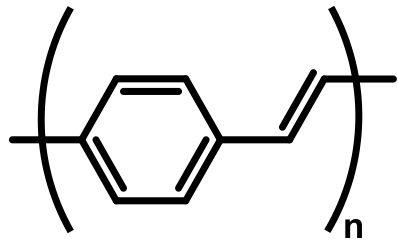
Poly(*p*-phenylene vinylene) (PPV)
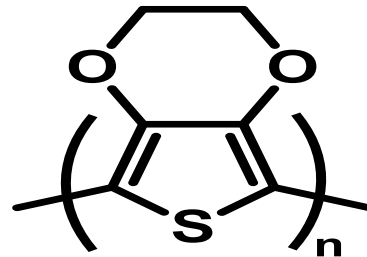
Poly(3,4-ethylenedioxythiophene) (PEDOT)
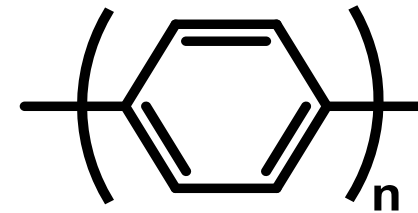
Poly(*p*-phenylene) (PPP)
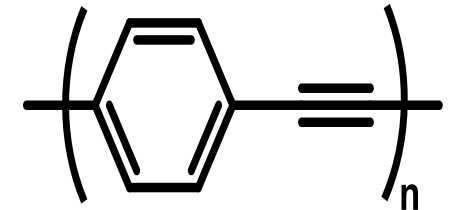
Poly(*p*-phenylene ethynylene) (PPE)

60

Conditions for Electrical Conductivity

❑ All the previous examples share many structural features like
i. Conjugated backbones
ii. Planarity
iii. Large anisotropy Ratio (i.e. intrachain conductivity is much larger than that of interchain conductivity)

❑ While the enhanced conductivity can be related to the
i. The alignment of polymer chains
ii. The conjugation length
iii. The doping percentage
iv. The purity of sample

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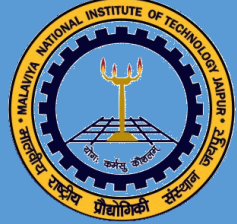
(1) The polymer consists of alternating single and double bonds, called conjugated double bonds.
In conjugation, the bonds between the carbon atoms are alternately single and double. Every bond contains a localised "sigma" (σ) bond which forms a strong chemical bond. In addition, every double bond also contains a less strongly localised "pi" (π) bond which is weaker.
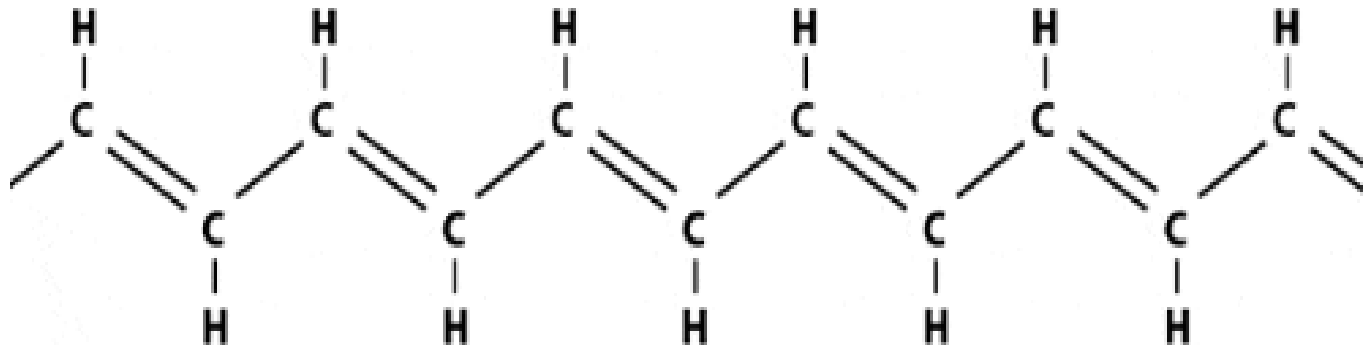
(2) Polymer has to be disturbed - either by removing electrons from (oxidation), or inserting them into (reduction), the material. (Doping; the role of the dopant is either to remove or to add electrons to the polymer.)

There are two types of doping:

Oxidation with halogen

Polymer + X $\longrightarrow$ (polymer)$^{n+}$ + X^{n-}

Reduction with alkali metal

Polymer + M $\longrightarrow$ (polymer)$^{n-}$ + M^{n+}

X= I$_2$, Br$_2$, AsF$_5$…….   M = Na, Li……….

❖ The iodine molecule attracts an electron from the polyacetylene chain and becomes I^{3-}. The polyacetylene molecule, now positively charged, is termed a radical cation, or polaron.

❖ The lonely electron of the double bond, from which an electron was removed, can move easily. As a consequence, the double bond **successively moves along the molecule**. This movement of charge is what is actually responsible for electrical conductivity.

❖ The positive charge, on the other hand, is fixed by electrostatic attraction to the iodide ion, which does not move so readily.
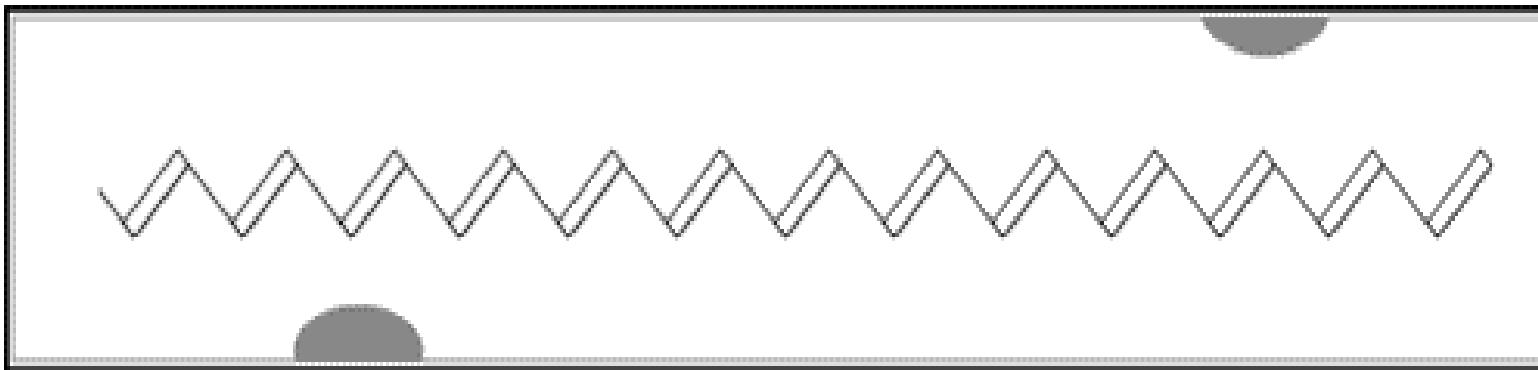
Conductivity Responsible Species

❖ Earlier increase in conductivity observed was initially thought to result from the formation of unfilled electronic bands.

❖ But this assumption was challenged as in PA and PPP, conductivity is associated with **spinless charge carriers** not unpaired electrons

❖ After doping, these polymers are associated with formnation of self-localized excitations such as solitons, polarons, bypolarons as they move throughout the material freely.

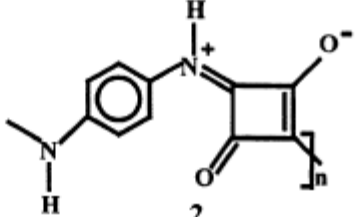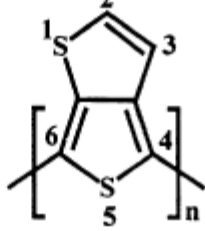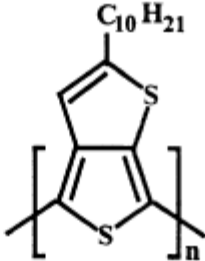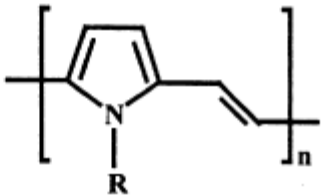❖ As a result of doping, strong electron-phonon interactions present in these quasi- one dimensional polymers.
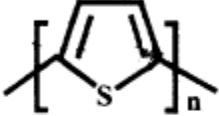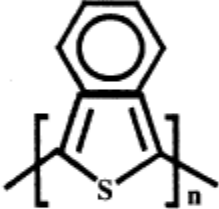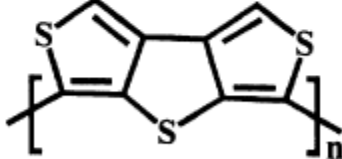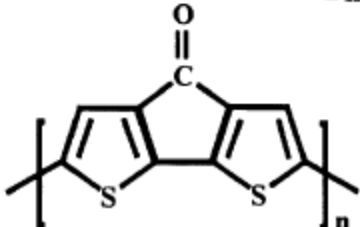
Engineering of small band gap polymers

❖ The process of doping enhance conductivity but it leads to chemical instability and poor processibility in them.

❖ So achieving small band gap without using dopant is a challenging process but can be done by applying following strategies

1. Substitution/Fusion
2. Ladder polymerization
3. Topological methods
4. Copolymerization
5. Donor-Acceptor polymerization

| Name	Structure	Band-gap (eV)
1. Trans-PA		1.5
2. Polythiophene		2.1
3. Polyisothian-aphthene		1.0
4. Poly(dithieno-(3,4-b:3',4'-d)-thiophene		1.0
5. Poly –4H-cyclo-pentadithiophene		1.2
6. Polysquaraines		0.5
7. Poly(thieno[3,4-b] thiophene		0.85
8. Poly (2-decyl thieno(3,4-thiophene-4,6-dicyl)		0.92
9. Poly (1-alkyl-2,5-pyrrylene vinylene)		1.67

Conductivity of typical materials

❖ Doped polyacetylene is, e.g., comparable to good conductors such as copper and silver, whereas in its original form it is a semiconductor.
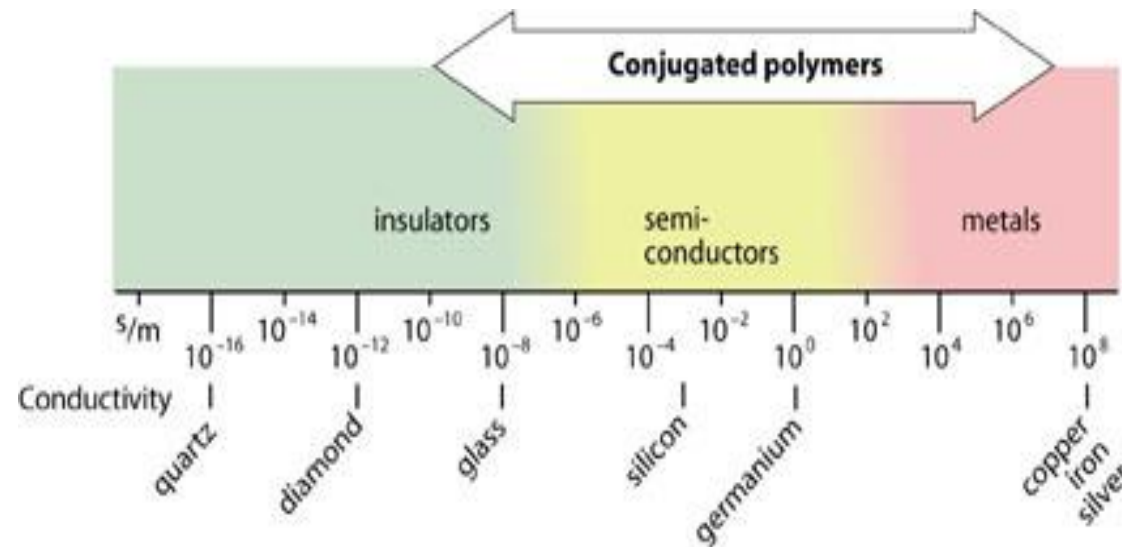
Conductivity of Polymers
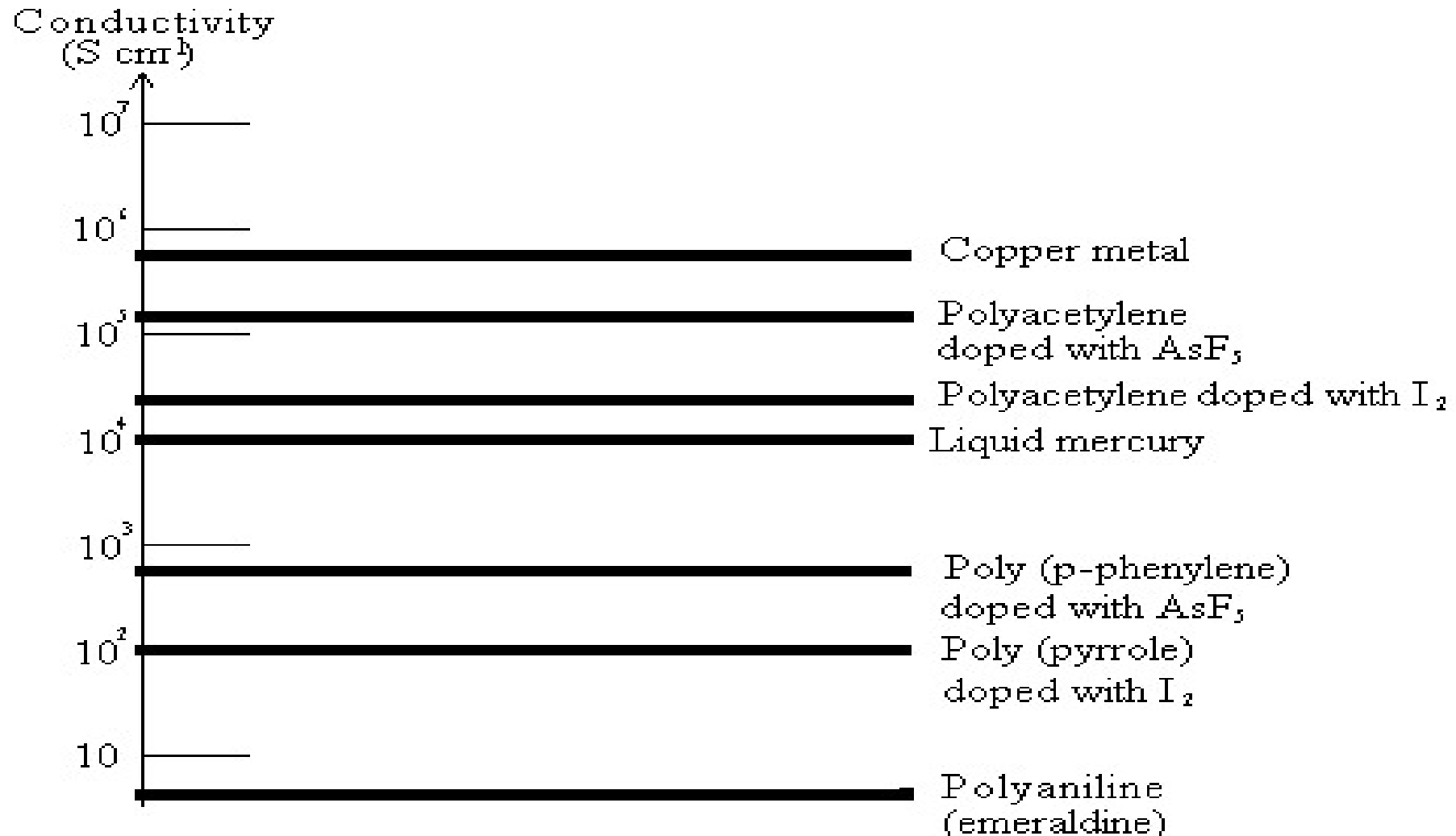
Logarithmic conductivity ladder locating some metals and conducting polymers

Applications of conductive Polymers

Conducting Polymers have many uses. The most documented are as follows:

❖ anti-static substances for photographic film
❖ Corrosion Inhibitors
❖ Compact Capacitors
❖ Anti Static Coating
❖ Electromagnetic shielding for computers "Smart Windows"
❖ Transistors
❖ Light Emitting Diodes (LEDs)
❖ Lasers used in flat televisions
❖ Solar cells
❖ Displays in mobile telephones and mini-format television screens