UNIT III   FUELS AND COMBUSTION

Calorific value – classification – coal – proximate and ultimate analysis – metallurgical coke – manufacture by Otto-Hoffmann method – petroleum processing and fractions – cracking – catalytic crang and methods – knocking – octane number and cetane number – synthetic petrol – Fischer Tropsch and Bergium processes – gaseous fuels – water gas, producer gas, CNG and LPG – flue gas analysis – Orsat apparatus – theoretical air for combustion.

INTRODUCTION:

Fuel is a combustible substance, containing carbon as main constituent, which on proper burning gives large amount of heat, which can be used economically for domestic and industrial purposes. Eg., Wood, Charcoal, Coal, Kerosene, Petrol, Producer gas, Oil gas, LPG etc.,
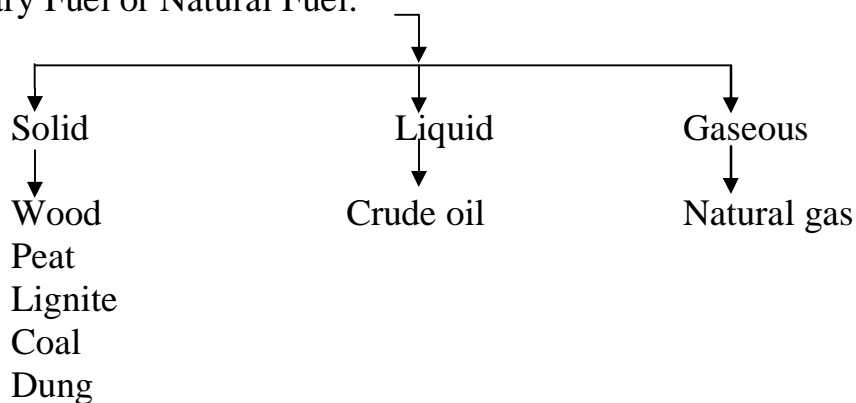
During the process of combustion of a fuel (like coal), the atoms of carbon, hydrogen, etc. combine with oxygen with the simultaneous liberation of heat at a rapid rate.
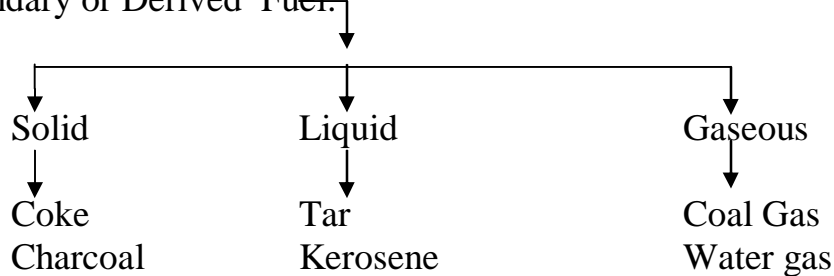
Fuel + Oxygen ---> Products + Heat
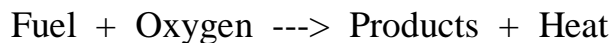
CLASSIFICATION OF FUELS:

Chemical Fuels: It is of two types viz., Primary or Natural Fuel and Secondary or Derived Fuel.

Primary Fuel or Natural Fuel:

Solid	Liquid	Gaseous
Wood	Crude oil	Natural gas
Peat		
Lignite		
Coal		
Dung		

Secondary or Derived Fuel:

Solid	Liquid	Gaseous
Coke	Tar	Coal Gas
Charcoal	Kerosene	Water gas

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Petroleum	Diesel	Oil gas
Coke	Petrol	Bio gas
Coal	Fuel oil	Blast furnace gas
Briquette	Synthetic Gasoline gas	Coke over gas

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. This is the unit of metric system and 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 calories.

(3) British Thermal Unit (BTU)- 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 BTU = 252 cal = 0.252 kcal and 1 kcal = 3.968 BTU

(4) Centigrade heat unit (CHU)-is "the quantity of heat required to raise the temperature of 1 pound of water through one degree centigrade". Thus,

1 kcal = 3.968 BTU = 2.2 CHU

HIGHER OR GROSS CALORIFIC VALUE:

It 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 (15° C or 60° F).

It is explained that 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, the latent heat of condensation of steam also gets included in the measured heat which is then called GCV.

LOWER OR NET CALORIFIC VALUE:

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

In actual practice 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.

DETERMINATION OF CALORIFIC VALUE USING BOMB CALORIMETER

The calorific value of solid or liquid fuels can be determined with the help of bomb calorimeter.

Description:

Bomb Calorimeter consists of a strong stainless steel bomb where the fuel sample is burnt. The bomb has oxygen inlet valve and two stainless steel electrodes. A small ring is attached to one of the electrodes. In this ring, a nickel or stainless steel crucible is placed.

The bomb is placed in a copper calorimeter containing a known weight of water sample. The copper calorimeter is provided with a Beckmann's thermometer and stirrer for stirring water. The copper calorimeter is covered by an air jacket and water jacket.

Functioning:

A known weight of the fuel sample is taken into the crucible. The fine magnesium wire is touching the fuel sample and then stretched across the electrodes. The bomb lid is tightly closed with the help of screw. The bomb is filled with oxygen at 25 atmospheric pressure.

The bomb is now placed in a copper calorimeter which containing known weight of water. Initial temperature of the water in the calorimeter is noted (t_1°C) after stirring. The electrodes are connected to a battery (6 v). The current is now supplied to the fuel sample which undergoes burning with the evolution of heat. The liberated heat increases the temperature of water in the calorimeter. The maximum temperature of the water during experiment is finally noted (t_2°C). From the temperature difference, calorific value of the fuel can be calculated as follows:

Calculation:

Weight of the fuel sample taken in the crucible	=	x g
Weight of water taken in the calorimeter	=	W g
Weight of calorimeter and stirrer in terms of water Equivalent	=	A g
Initial temperature of water in the calorimeter	=	t_1°C
Final temperature of water in the calorimeter	=	t_2°C
Heat absorbed by the water	=	W (t_2-t_1) cal ----(1)
Heat absorbed the calorimeter	=	A (t_2-t_1) cal ----(2)
Total heat absorbed by the water	=	W(t_2-t_1) + A(t_2-t_1) cal
	=	(W+A) (t_2-t_1) cal ----(3)

The relationship between heat liberated by the fuel and HCV is as follows:
Heat liberated by the fuel = x x (HCV) ----(4)

Therefore, heat liberated by the fuel = Heat absorbed by the water and calorimeter
X Weight of fuel

Compare equation (3) and (4), we get

$$x \times (HCV) = (W+A)(t_2-t_1)$$

$$HCV = \frac{(W+A)(t_2-t_1)}{X} \ cal/g$$

Calculation of Lower Calorific Value (LCV):

The percentage of hydrogen in the fuel = H
Weight of water produced 1 g of the fuel = $\frac{9H}{100}$ g = 0.09 g

Therefore, heat liberated during the
Condensation of steam = 0.09 H x 587 cal/g

Lower calorific value of the fuel = HCV – Latent heat of water
liberated by the fuel

$$LCV = HCV – (0.09 H \times 587) \ cal/g.$$

CHARACTERISTICS OF A GOOD FUEL:

High calorific value
Moderate ignition temperature
Low moisture content
Low non-combustible matter content
Moderate velocity of combustion
Products of combustion should not be harmful
Low cost
Easy to transport
Combustion should be easily controllable
Should not undergo spontaneous combustion
Storage cost in bulk should be low
Should burn in air with efficiency without much smoke
In case of solid fuel, the size should be uniform so that combustion is regular.

COAL:

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

The successive stages in the transformation of vegetable matter into coal are – wood, peat, lignite, bituminous coal, steam coal and anthracite. Anthracite is probably the purest form of coal and contains 95 % carbon.

ANALYSIS OF COAL:

The composition of coal varies widely and hence it is necessary to analyse and interpret the results from the points of view of commercial classification, price fixation and proper industrial utilization. The quality of a coal is ascertained by the following two types of analysis.

Proximate Analysis and Ultimate Analysis

PROXIMATE ANALYSIS:

It is called 'proximate' because the data collected vary with the procedure adopted. It is an empirical but important analysis dealing with the determination of

Moisture content
Volatile matter
Ash content
Fixed carbon.

(i) Determination of moisture content in coal:

It is the loss in weight of coal caused by heating a weighed quantity of coal sample for one hour at 105 C.

$$\% \text{ of moisture content} = \frac{\text{Loss in weight of coal}}{\text{Weight of coal taken initially}} \times 100$$

Significance of Moisture:

High moisture content of the coal is undesirable for the following reasons:
1) Reduces the calorific value of coal
2) Increases the consumption of coal for heating purpose.
3) Lengthens the time of heating.

(ii) Determination of volatile matter in coal:

It is the loss in weight of moisture free powdered coal when heated in a crucible fitted with cover in a muffle furnace at 950 C for seven minutes.

$$\% \text{ of volatile matter in coal} = \frac{\text{Loss in weight of moisture free coal}}{\text{Weight of coal taken}} \times 100$$

Significance of volatile matter:

During burning of coal, gases like CO, CO_2, CH_4, N_2, O_2, hydrocarbons etc. that come out are called volatile matter of the coal.

It has been found that the coal with higher volatile matter content ignites easily has lower calorific value burns with long yellow smoky flame will evolve more coal gas when heated in the absence of air.

(iii) Determination of ash in coal:

It is the weight of residue obtained after burning a known weight of coal in an open crucible in the presence of air at 750 C for 30 minutes.

$$\% \text{ of ash in coal} = \frac{\text{Weight of residue ash formed}}{\text{Weight of coal taken}} \times 100$$

Significance of ash content:

1) Ash in the combination product of mineral matter in the coal. It consists mainly SiO_2, Al_2O_3 and Fe_2O_3 with varying amount of other oxides such as Na_2O, CaO, MgO etc.
2) Ash containing the oxides of Na, Ca and Mg melt easily.
3) High ash content in coal is undesirable because it
    i) increases transporting, handling and storage costs
    ii) is harder and stronger
    iii) has lower calorific value

(iv) Determination of fixed carbon:

It is determined indirectly by deducting the sum total of moisture, volatile matter and ash percentage from 100.

$$\% \text{ of fixed carbon in coal} = 100 - \% (\text{moisture} + \text{volatile matter} + \text{ash})$$

Significance of Fixed carbon:

It is the pure carbon present in coal. Higher the fixed carbon content of the coal, higher will be the calorific value of the sample.

The proximate analysis data of some Indian coal samples are presented here.

S. No.	Source of sample	Moisture (%)	VM (%)	Ash (%)	Fixed carbon (%)
1.	Assam	1.2 – 1.5	35-38	1.6-2	55-60
2.	Jharia	0.6-2.0	15-25	10-20	60-68
3.	Raniganj	4-6	30-35	9-15	50-60

ULTIMATE ANALYSIS

Ultimate analysis refers the determination of weight percentage of carbon, hydrogen, nitrogen, oxygen and sulphur of pure, dry coal.

This analysis gives the elementary, ultimate constituents of coal.

This analysis is essential for calculating heat balances in any process for which coal is employed as a fuel.

It is useful to the designing of coal burning equipments and auxillaries.

a) Determination of carbon and hydrogen in coal:

A known amount of coal is burnt in presence of oxygen thereby converting carbon and hydrogen of coal into-

(i) CO_2 ($C + O_2 \longrightarrow CO_2$) and (ii) H_2O ($H_2 + \frac{1}{2} O_2 \longrightarrow H_2O$) respectively. The products of combustion CO_2 and H_2O are passing over weighed tubes of anhydrous $CaCl_2$ and KOH which absorb H_2O and CO_2 respectively.

The increase in the weight of $CaCl_2$ tube represents the weight of water formed while the increase in the weight of KOH tube represents the weight of CO_2 formed.
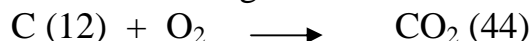
The percentage of carbon and hydrogen in coal can be calculated in the following way-

The weight of coal sample taken = x g
The increase in the weight of KOH tube = y g
The increase in the weight of $CaCl_2$ tube = z g

Consider the following reaction
$$C (12) + O_2 \longrightarrow CO_2 (44)$$

44 g of CO_2 contains 12 g of carbon

Therefore y g of CO_2 contains $= \dfrac{y \times 12}{44}$ g of carbon.

X g of coal contains $= \dfrac{12}{44} y$ g carbon

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% of carbon in coal $= \dfrac{12 \ y}{44x} \times 100$

Significance of Total Carbon: It is the sum total of fixed carbon and the carbon present in the volatile matters like CO, CO_2, hydrocarbons. Thus, total carbon is always more than fixed carbon in any coal. High total carbon containing coal will have higher calorific value.

(b) Determination of hydrogen:

Consider the following reaction.

$$H_2 \ (2) \ + \ \tfrac{1}{2} \ O_2 \longrightarrow H_2O(18)$$
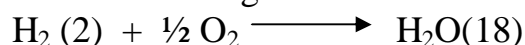
18 g of water contains 2 g of hydrogen.

Z g of water contains $= \dfrac{2}{18} \ z$ of hydrogen

X g of coal contains $= \dfrac{2}{18} \ z$ g of hydrogen

% of hydrogen in coal $= \dfrac{2 \ z}{18 \ x} \times 100$

Significance of Hydrogen: It increases the calorific value of the coal. It is associated with the volatile matter of the coal. When the coal containing more of hydrogen is heated, it combines with nitrogen present in coal forming ammonia. Ammonia is usually recovered as $(NH_4)_2SO_4$, a valuable fertilizer.

(c) Determination of nitrogen:

This is done by Kjeldhal's method.

A known amount of powdered coal is heated with concentrated sulphuric acid in the presence of K_2SO_4 and $CuSO_4$ in a long necked Kjeldhal's fask. This converts nitrogen of coal to ammonium sulphate. When the clear solution is obtained (ie., the whole of nitrogen is converted into ammonium sulphate), it is heated with 50 % NaOH solution and the following reaction occurs:

$$(NH_4)_2SO_4 \ + \ 2 \ NaOH \longrightarrow Na_2SO_4 \ + \ 2 \ NH_3 \ + \ H_2O$$

The ammonia thus formed is distilled over and is absorbed in a known quantity of standard 0.1 N H_2SO_4 solution. The volume of unused 0.1 N H_2SO_4 is then determined by titrating against standard NaOH solution. Thus, the amount of acid neutralized by liberated ammonia from coal is determined using the formula.

$$\% \text{ Nitrogen in coal } = \frac{14 \times \text{volume of acid used} \times \text{normality}}{1000 \ x} \times 100$$

Or $$= \frac{1.4 \times \text{voume of acid used} \times \text{normality}}{X}$$

Significance: Presence of nitrogen decreases the calorific value of the coal. However, when coal is carbonized, its N_2 and H_2 combine and form NH_3. Ammonia is recovered as $(NH_4)_2SO_4$, a valuable fertilizer.

(d) Determination of sulphur in coal:

A known amount of coal is burnt completely in Bomb calorimeter in presence of oxygen.

Ash thus obtained contains sulphur of coal as sulphate which is extracted with dil. HCl.

The acid extract is then treated with BaCl2 solution to precipitate sulphate as $BaSO_4$.

The precipitate is filtered, washed, dried and weighed. From the weight of $BaSO_4$, the percentage of sulphur in coal is calculated in the following way.

The weight of coal sample taken   = x g
The weight of BaSO4 precipitate   = y g
Consider the following equations

$$S (32) + 2O_2 \longrightarrow SO_4 \xrightarrow{BaCl_2} BaSO_4 (233)$$

233 g of $BaSO_4$ contains 32 g of sulphur.

Therefore, y g of $BaSO_4$ contains $= \dfrac{32}{233} y$ g sulphur.

Therefore x g of coal contains $= \dfrac{32 \ y}{233}$ g sulphur.

% of sulphur in the coal $= \dfrac{32 \ y}{233} \times 100.$

Significance:

It increases the calorific value of the coal, yet it has the following undesirable effect-

The oxidation products of sulphur (SO_2, SO_3) especially in presence of moisture forms sulphuric acid which corrodes the equipment and pollutes the atmosphere.

It is calculated indirectly in the following way-
% of oxygen in coal $= 100 - \% (C + H + N + S + ash)$.

Significance:
The less the oxygen content, the better is the coal. As the oxygen content increases, its moisture holding capacity also increases.

METALLURGICAL COKE:

When bituminous coal (coal containing about 90 % carbon) is heated strongly in absence of air, the volatile matter escapes out and a while, lustrous, dense, strong, porous and coherent mass is left which is called metallurgical coke.

Characteristics of metallurgical coke:

The most important industrial fuel is the metallurgical coke. This is used in the metallurgical industry, especially in the blast furnace. A good metallurgical coke must have following requirements:

Purity: Low moisture and ash content are desirable in metallurgical coke. It must contain minimum percentage of phosphorous and sulphur.
Porosity: High porosity is desirable in furnace coke to obtain high rate of combustion.
Strength: The coke should be hard and strong to withstand pressure of ore, flux etc. in the furnace.
Size: Metallurgical coke must be uniform and medium size.
Calorific value: This should be high.
Combustibility: It should burn easily.
Reactivity: It refers to its ability to react with O_2, CO_2, steam and air. The metallurgical coke must have low reactivity.
Cost: It must be cheap and readily available.

Metallurgical coke is superior to coal for the following reasons:
Coke is stronger and more porous than coal
Coke contains lesser amount of sulphur than coal
Coke does not contain much volatile matter.

Manufacture of Metallurgical coke by Otto Hoffmann's method:

In order to (i) save the fuel for heating purpose and (ii) recover valuable by-products like coal gas, ammonia, benzol oil, tar etc. Otto Hoffmann developed a modern by-product coke oven. Here, the heating is done externally by a portion of coal gas produced during the process itself. It also utilizes the waste flue gases for heating the checker work bricks.

The oven consists of a number of narrow silica chambers, each about 10-12 m long, 3-4 m tall and 0.4-0.45 m wide, erected side by side with vertical flues between them to form a sort of battery. Each chamber has a hole at the top to introduce the charge, a gas off take and a refractory lined cast iron door at each end for coke discharge. The oven works on heat regenerative principle ie. the waste gas produced during carbonization is utilized for heating. The ovens are charged from the top and closed to restrict the entry of air.
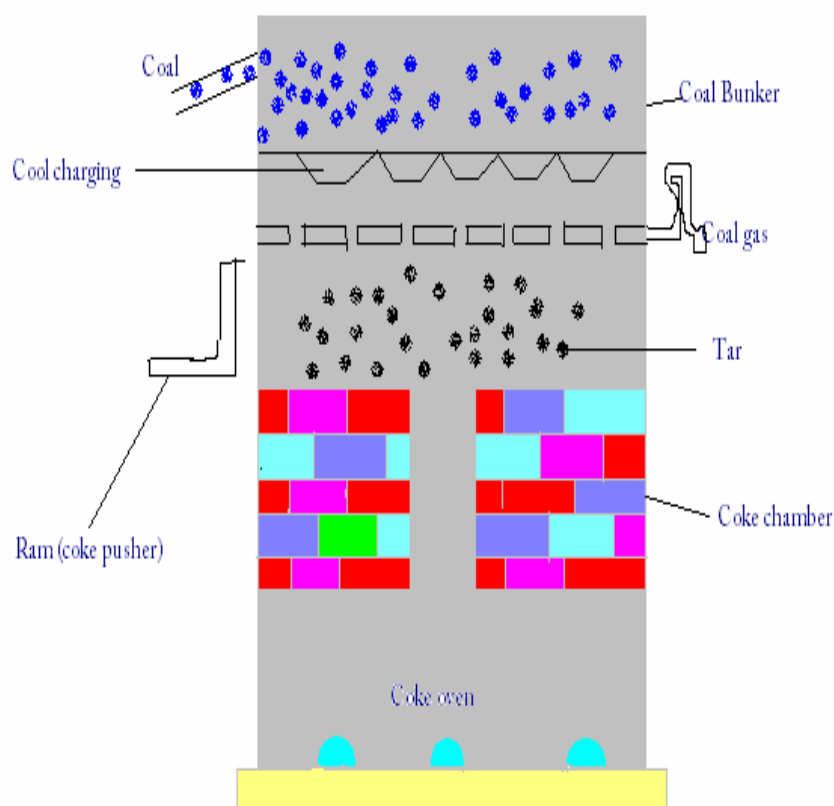
Finely powdered, crushed coal is introduced through the charging hole at the top of the chambers which are then tightly closed at both ends to cut off the supply of air. The ovens are heated to 1200° deg C by burning producer gas. The air required for the combustion of the fuel is preheated in regenerators flanking the retorts, while the flue gases leave their acquired heat to one generator; the other generator is used for preheating the

incoming air. The cycle goes on and the heating is continued until all the volatile matter has escaped. It takes nearly 18 hours for carbonization of a charge.

The heating of air-alone is required if the fuel gas is coal gas which has a high calorific value. If the fuel is producer gas or blast furnace gas, both air and fuel need to be preheated as they have low calorific value. When the carbonization is over, the red hot coke is pushed out into truck by a massive ram. It is then quenched by spraying water (wet quenching). Alternatively, the red hot coke may be placed in a chamber and cooled by sending in inert gases from boilers. The inert gases are then circulated to boilers where they generate steam. This method is known as dry quenching. The dry quenched coke is cleaner, drier and stronger and contains lesser dust than the wet quenched. The yield is about 70 %.

Recovery of by-products:

The gas coming out of the retort is known as coke oven gas. This consist of tar, ammonia, moisture, aromatic hydrocarbons (naphthalene, benzene), H_2S etc. It can be used as a fuel after removing coal tar and ammonia.

i) Recovery of tar: The coke oven gas is first passed through a tower in which liquid ammonia is sprayed. Tar and dust get collected in a tank below, which is heated by a steam coil to recover back the ammonia sprayed.

ii) Recovery of ammonia: The coke oven gas is passed through another tower in which water is sprayed. Gaseous ammonia goes into solution as NH_4OH.

iii) Recovery of naphthalene: After recovering ammonia, the remaining gases are led through another tower where water is sprayed at low temperature when naphthalene gets condensed.

iv) Recovery of benzene: The resultant gas from the previous step is sprayed with petroleum whereby benzene and its homologues can be recovered.

v) Recovery of H_2S: The gases are then passed through a purifier, packed with moist Fe_2O_3. Hydrogen sulphide is retained here.

$$Fe_2O_3 + 3\ H_2S \longrightarrow Fe_2S_3 + 3\ H_2O$$
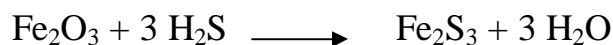
When all the Fe_2O_3 is converted into Fe_2S_3, the purifier on exposure to the atmosphere, regenerates Fe_2O_3 in the following manner.

$$Fe_2S_3 + 4\ O_2 \longrightarrow 2\ FeO + 3\ SO_2$$
$$4\ FeO + O_2 \longrightarrow 2\ Fe_2O_3$$

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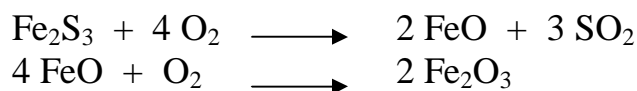
Petroleum or crude oil is a dark greenish-brown, viscous oil found deep in earth crust. It is composed mainly of various hydrocarbons (like straight-chain paraffins, cycloparaffins or naphthalenes, olefins and aromatics), together with small amounts of organic compounds containing oxygen, nitrogen and sulphur.

Mining of petroleum:

It is done by drilling holes in the earth's crust and sinking pipes upto the oil-bearing porous rocks.

Refining of crude oil:

The crude oil 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, are called the oil refineries. The refining involves

Step 1: Separation of water (Cottrell's process):

The crude oil from the oil well is an extremely stable emulsion of oil and salt water. The process of freeing oil from water consists in allowing the crude to flow between two highly charged electrodes. The colloidal water-droplets coalesce to form large drops, which separate out from the oil.

Step 2: Removal of harmful sulphur compounds:

This involves in treating oil with copper oxide. A reaction occurs with sulphur compounds, which results in the formation of copper sulphide (a solid), which is then removed by filtration.

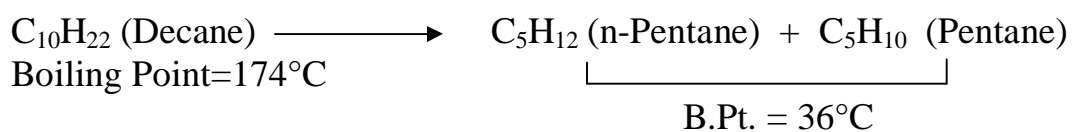### Step 3: Fractional distillation:

The crude oil is then heated to about 400 deg C in an iron retort whereby all volatile constituents, except the residue (asphalt or coke) are evaporated. The hot vapours are then passed up a fractionating colum, 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. As the vapours go up, they become gradually cooler and fractional condensation takes place at different heights of column. Higher boiling fraction condenses first, while the lower boiling fractions turn-by-turn.

Name of fraction	Boiling range	Approx. comp. hydrocarbon containing C-atoms	Uses
Uncondensed gas	Below 30 deg C	C1-C4	As domestic or industrial fuel under the name LPG.
Petroleum	30-70 deg C	C5-C7	As a solvent

ether			
Gasoline or petrol or motor spirit	40-120 deg C	C5-C9	As motor fuel, solvent and in dry cleaning
Naphtha or solvent spirit	120-180 deg C	C9-C10	As solvent and in dry cleaning
Kerosene oil	180-250 deg C	C10-C16	As an illuminant, jet engine fuel and for preparing laboratory gas.
Diesel oil or fuel oil or gas oil	250-320 deg C	C10-C18	Diesel engine fuel.
Heavy oil	320-400 deg C	C17-C30	For getting gasoline by cracking process
i) Lubricating oil			As lubricant
ii) Petroleum jelly			As lubricant and in cosmetics and medicines.
iii) Grease			As lubricant
iv) Paraffin wax			In candles, boot polishes, wax paper, tarpolin cloth etc.
Residue may be either i) Asphalt or ii) Petroleum coke	Above 400 deg C.	C30 and above	Water proofing of roofs and road making As a fuel and in moulding arc light rods.

CRACKING:

It is defined as the decomposition of bigger hydrocarbon molecules into simpler low boiling hydrocarbons of lower molecular weight. For example,

$C_{10}H_{22}$ (Decane) $\longrightarrow$ C_5H_{12} (n-Pentane) + C_5H_{10} (Pentane)
Boiling Point=174°C

B.Pt. = 36°C

There are two methods of cracking in use:

1. Thermal cracking   2. Catalytic cracking

Thermal cracking:

The heavy oils are subjected to high temperature and pressure, when the bigger hydrocarbon molecules break down to give smaller molecules of the paraffins, olefins plus some hydrogen. This process may be carried out either in liquid-phase or vapour-phase.

Liquid-phase thermal cracking: The heavy oil or gas oil stock is cracked at a suitable temperature of 475-530°C and under pressure of 100 kg/cm2. The cracked products are then separated in a fractionating column. The yield is 50-60 % and octane rating of the petrol produced is 65-75.

Vapour-phase thermal cracking: The cracking oil is first vapourised and then cracked at about 600-650°C and under a low pressure of 10-20 kg/cm2. This process is suitable only for those oils, which may be readily vaporized. It requires less time than the liquid-phase method. Petrol obtained from vapour-phase cracking has better anti-knock properties, but poorer stability than petrol from liquid-phase cracking.
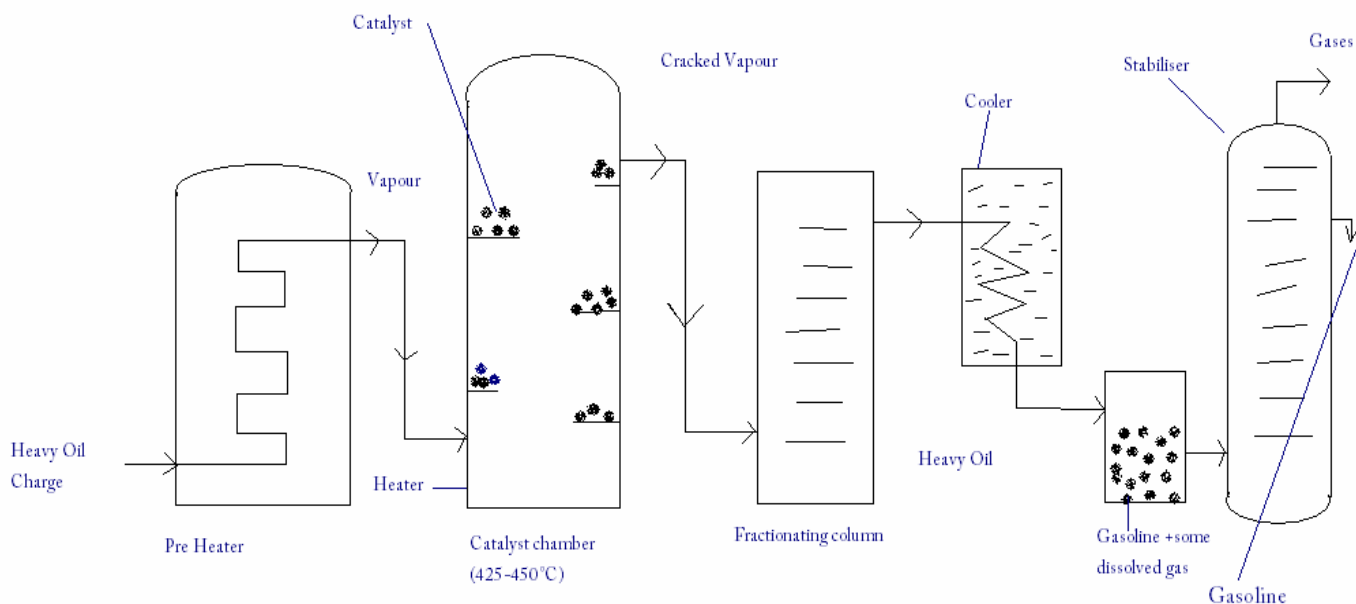
Catalytic cracking:

The quality and yield of gasoline produced by cracking can be greatly improved by using a suitable catalyst like aluminium silicate $[Al_2(SiO_3)_3]$ or alumina $[Al_2O_3]$.

There are two methods of catalytic cracking in use:

(a) Fixed-bed catalytic cracking:

The oil vapours are heated in a pre-heater to cracking temperatures (420-450°C) and then forced through a catalytic chamber maintained at 425-450°C and 1.5 kg/cm2 pressure. During the passage through the tower, about 40 % of the charge is converted into gasoline and about 2-4 % carbon is formed. The later gets adsorbed on the catalyst bed. The vapours produced are then passed through a fractionating column, where heavy oil fractions condense. The vapours are then led through a cooler, where someof the gases 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.

The catalyst, after 8-10 hours, stops functioning, due to the deposition of black layer of carbon, formed during cracking. This is re-activated by burning off the deposited carbon. During the re-activation interval, the vapours are diverted through another catalyst chamber.
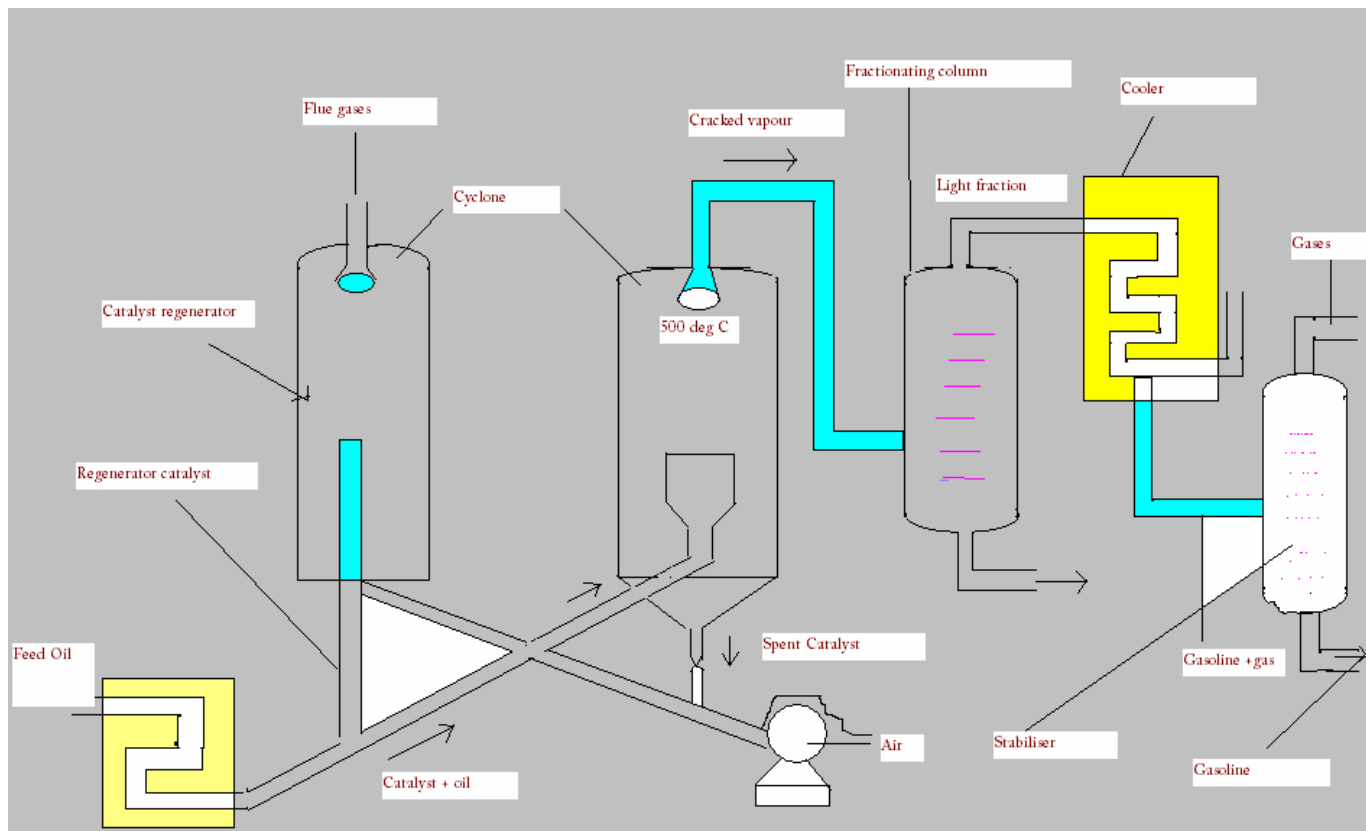
Fixed bed catalytic cracking

(b) Moving-bed catalytic cracking:

The solid catalyst is very 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 into lighter molecules occurs. Near the top of the reactor, there is a centrifugal separator (called cyclone), which allows only the cracked oil vapours to pass on to fractionating column, but retains all the catalyst powder in the reactor itself. The catalyst powder gradually becomes heavier, due to coating with carbon, and settles to the bottom, from where it is forced by an air blast to regenerator maintained at 600°C.

In regenerator, carbon is burnt and the regenerated catalyst then flows through a stand pipe for mixing with fresh batch of incoming cracking oil. At the top of the regenerator, there is a separator, which permits only gases (CO_2, etc.) to pass out, but holds back catalyst particles.

Flue gases | Fractionating column | Cooler

Cracked vapour

Cyclone | Light fraction | Gases

Catalyst regenerator

500 deg C

Regenerator catalyst

Feed Oil

Spent Catalyst

Gasoline + gas

Air

Stabiliser

Gasoline

Catalyst + oil

KNOCKING:

In an internal combustion engine, a mixture of gasoline (petroleum) vapour and air is used as a fuel. After the initiation of the combustion reaction by spark in the cylinder, the flame should spread rapidly and smoothly through the gaseous mixture; thereby the expanding gas drives the piston down the cylinder. The ratio of the gaseous volume in the cylinder at the end of the suction stroke to the volume at the end of compression stroke of the piston is known as the compression ratio. The efficiency of an internal combustion engine increases with the compression ratio.

However, successful high compression ratio is dependent on the nature of the constituents present in the gasoline used. In certain circumstances, due to the presence of some constituents in the gasoline used, the rate of oxidation becomes so great that the last portion of the fuel air mixture gets ignited instantaneously producing an explosive violence known as knocking. The knocking results in loss of efficiency, since this ultimately decreases the compression ratio.

The phenomenon of knocking is not yet fully understood. However, it is noted that the tendency of fuel constituents to knock is in the following order:
Straight chain paraffins (n-paraffins)>branched chain paraffins (iso paraffins)>olefins>cycloparaffins (naphthalenes)>aromatics.

Thus, olefins of the same carbon chain length possess better antiknock properties than the corresponding paraffins and so on.

OCTANE NUMBER:

The most common way of expressing the knocking characteristics of a combustion engine fuel is by octane number introduced by Edger in 1972. It has been found that n-heptane, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3, knocks very badly and hence, its antiknock value has been arbitrarily given zero. On the other hand, iso-octane (2,2,4 – trimethylpentane) gives very little knocking, so its antiknock value has been given as 100.

Thus, Octane number (or rating) of a gasoline (or any other internal combustion engine fuel) is the percentage of iso-octane in a mixture of iso-octane and n-heptane, which matches the fuel under test in knocking characteristics.

Thus, if a sample of petrol gives as much of knocking as a mixture of 75 parts of iso-octane and 25 parts of n-heptane, then its octane number is taken as 75. The octane ratings of some common hydrocarbons are given in the table.

Sl. No.	Hydrocarbon	Octane number
1.	Benzene	100 +
2.	Isopentane	90
3.	Cyclohexane	77
4.	2-methyl pentane	71
5.	n-pentane	62

Fuels with octane rating greater than 100 are quite common nowadays and they are rated by comparison with a blend of iso-octane with tetra ethyl lead (TEL) which greatly diminishes the knocking tendency of any hydrocarbon with which it is mixed. The value of octane number in such cases is determined by extrapolation.

CETANE NUMBER:

In a diesel engine, the fuel is exploded not by a spark but by the application of heat and pressure. Diesel engine fuels consist of longer chain hydrocarbons than internal combustion engine fuels. In other words, hydrocarbon molecules in a diesel fuel should be as far as possible the straight chain ones, with a minimum admixture of aromatics and side chain hydrocarbon molecules.

The suitability of a diesel fuel is determined by its cetane value which is the percentage of hexadecane in a mixture of hexadecane and 2-methyl naphthalene, which has the same ignition characteristics as the diesel fuel in question.
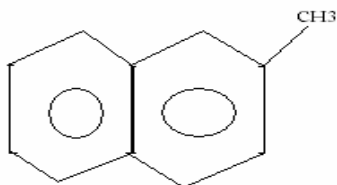
2-methyl naphthalene
Cetane number=0

CH_3-(-CH_2-)$_{14}$-CH_3
n-hexadecane
Cetane number=100

The cetane number of a diesel fuel can be raised by the addition of small quantity of certain pre-ignition dopes like ethyl nitrite, isoamyl nitrite, acetone peroxide.

An oil of high octane number has a low cetane number and vice-versa. Consequently, petroleum crude gives petrol of high octane number and diesel of low cetane number.
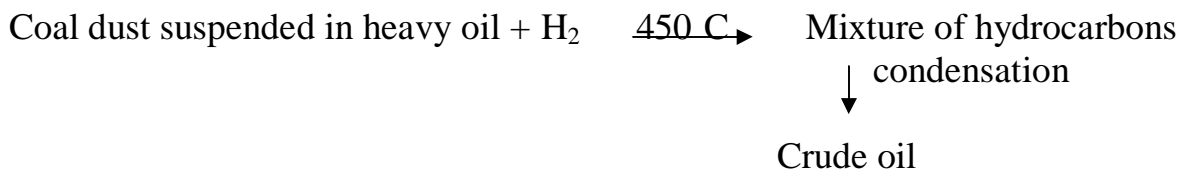
SYNTHETIC PETROL :

In countries like Germany and South Africa which do not have extensive petroleum deposits, motor fuels are derived from non-petroleum sources. Petroleum can be produced from coal by the following two methods.

BERGIUS PROCESS: (HYDROGENATION OF COAL)

This method was first proposed by Bergius in Germany. It consists of converting low grade coals such as bitminuous coal into liquid and gaseous fuels by hydrogenating them in presence of iron oxide as catalyst.

The raw materials used in the process are coal dust, heavy oil and nickel oleate or tin oleate. A coal paste is prepared by mixing coal dust with heavy oil and catalyst. It is then pumped into the converter where the paste is heated to 450 C under 200-250 atmosphere in pressure of hydrogen.

The reaction products mainly contain mixture of petroleum hydrocarbons

Coal dust suspended in heavy oil + H_2 $\xrightarrow{\text{450 C}}$ Mixture of hydrocarbons

$\downarrow$ condensation

Crude oil

Since the reaction is exothermic, the vapours leaving the converters are condensed in the condenser to give synthetic petroleum or crude oil. The oil is then fractionally distilled to give (i) petrol (ii) middle oil (iii) heavy oil.

Middle oil is again hydrogenated in presence of solid catalyst to produce more amount of petroleum

Heavy oil is used for making paste with fresh coal dust which is required for this process.
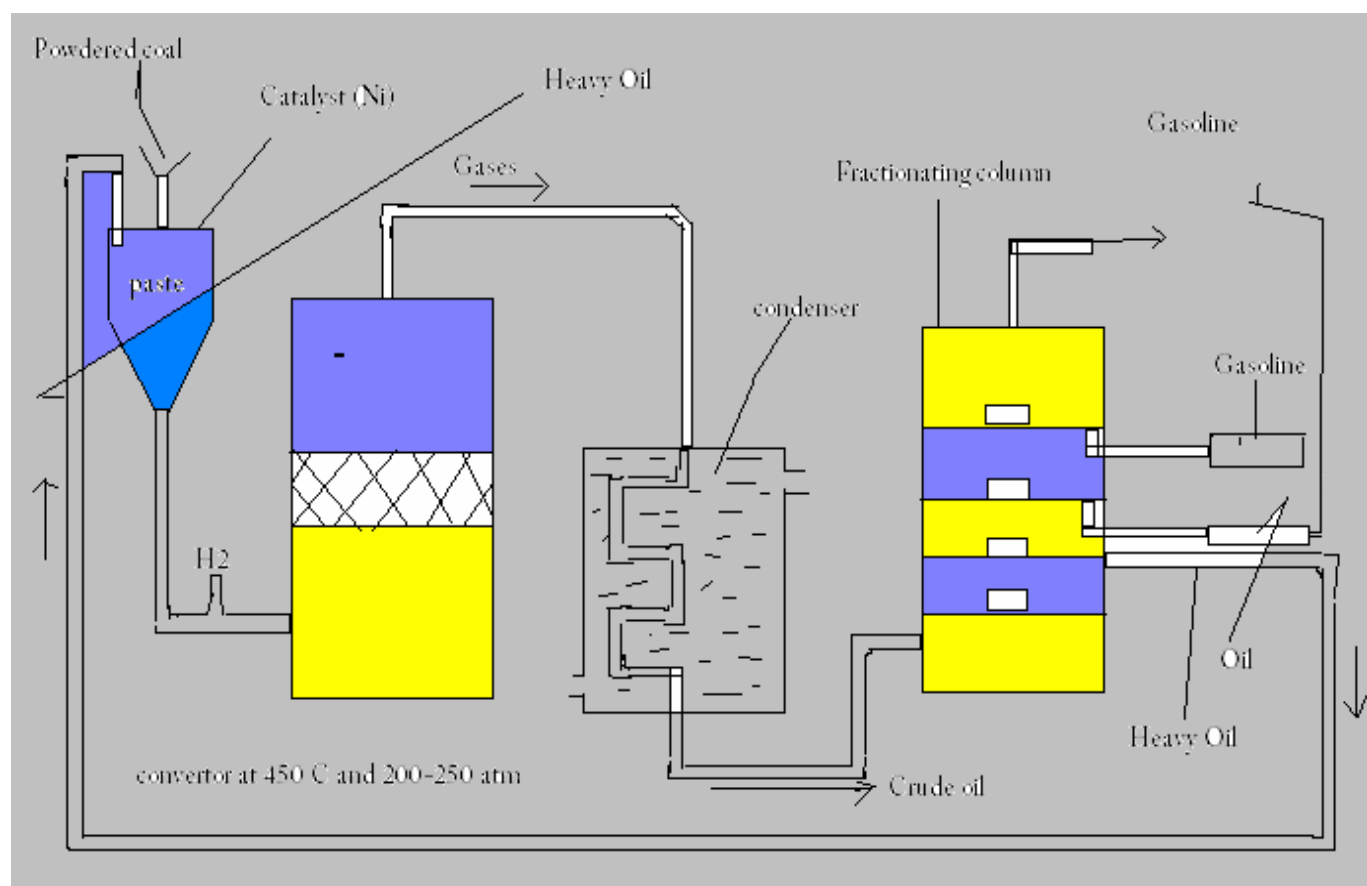

FISHER-TROPSCH PROCESS:

This method was first developed by Fischer and Tropsch in 1962 in Germany. The raw materials used in this process are hard coke, steam to produce water gas (a mixture of $CO+H_2$). Water gas is obtained by passing steam over red hot coke as below:

$C + H_2O \longrightarrow CO + H_2$
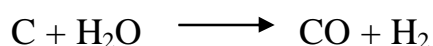
The first step in this process is the purification of gas. The water gas is passed through Fe_2O_3 to remove H_2S and organic sulphur compounds. The gas is again passed through a mixture of Fe_2O_3 and Na_2CO_3.

The purified gas is compressed to 5-25 atmosphere over a catalyst containing oxides of Th, Co and Mg on Kieselguhr at 250 C. The reaction products mainly contain straight chain paraffins and olefins:

$$n\ CO + 2\ n\ H_2 \longrightarrow C_n\ H_{2n} + n\ H_2O$$

$$n\ CO + (2n+1) \longrightarrow C_nH_{2n+2} + n\ H_2O$$
$$n\text{-paraffins}$$
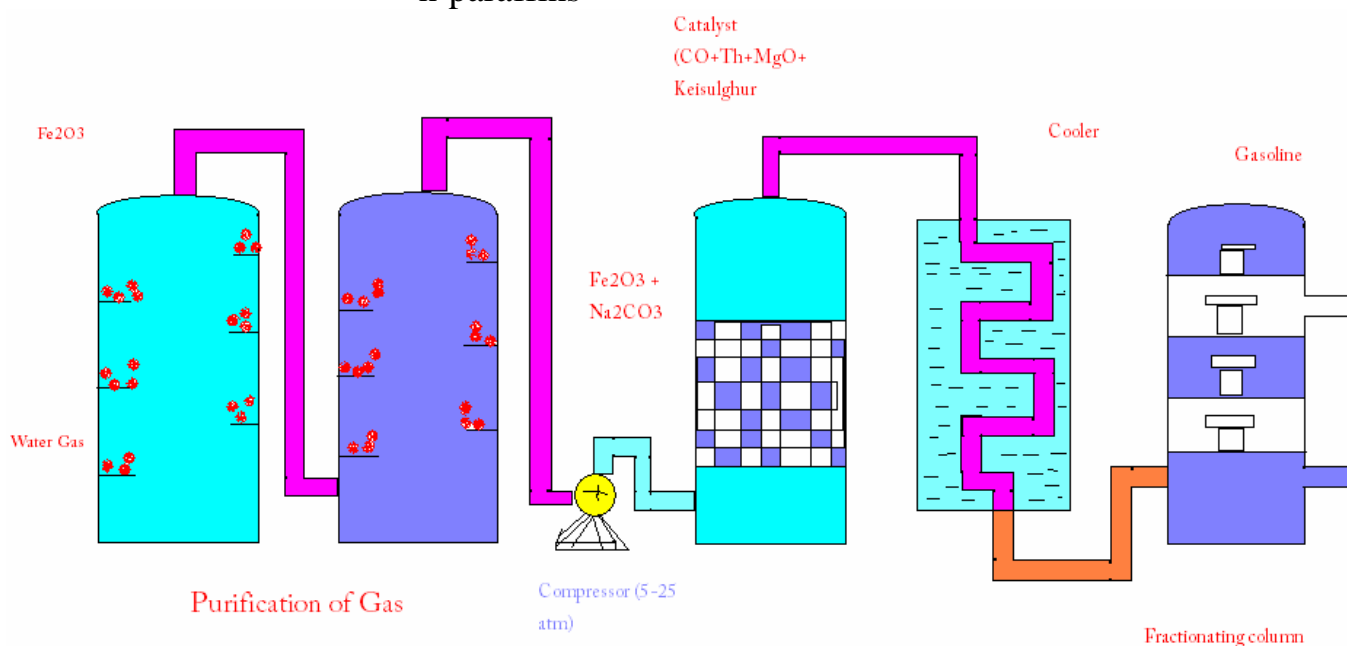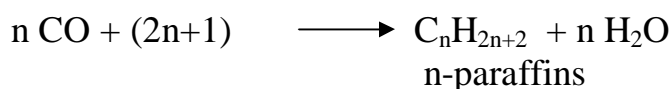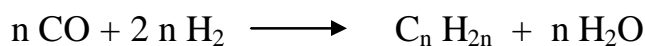
GASEOUS FUELS

WATER GAS:

It is essentially a mixture of CO and H_2. Its calorific value is 2800 kcal/m3. The average composition of water gas is H_2 (51 %); CO (41 %); N_2 (4 %); CO_2 (4 %).

Manufacture:

A water gas generator is a steel cylindrical vessel. At the top, it is provided with a hopper for adding coke. Water gas outlet is provided near the top. At the bottom, it is provided with an arrangement of taking out ash formed.

Water gas is obtained by the action of steam on a bed of coal heated to 1000 C.

$$C + H_2O \longrightarrow CO + H_2 - 28 \text{ kcal.}$$

Since the above reaction is endothermic, the coal cools down after a few minutes and the reaction proceeds in a different way to form CO_2 and H_2, instead of water gas ($CO + H_2$).

$$C + 2 H_2O \longrightarrow CO_2 + 2 H_2 - 19 \text{ kcal.}$$
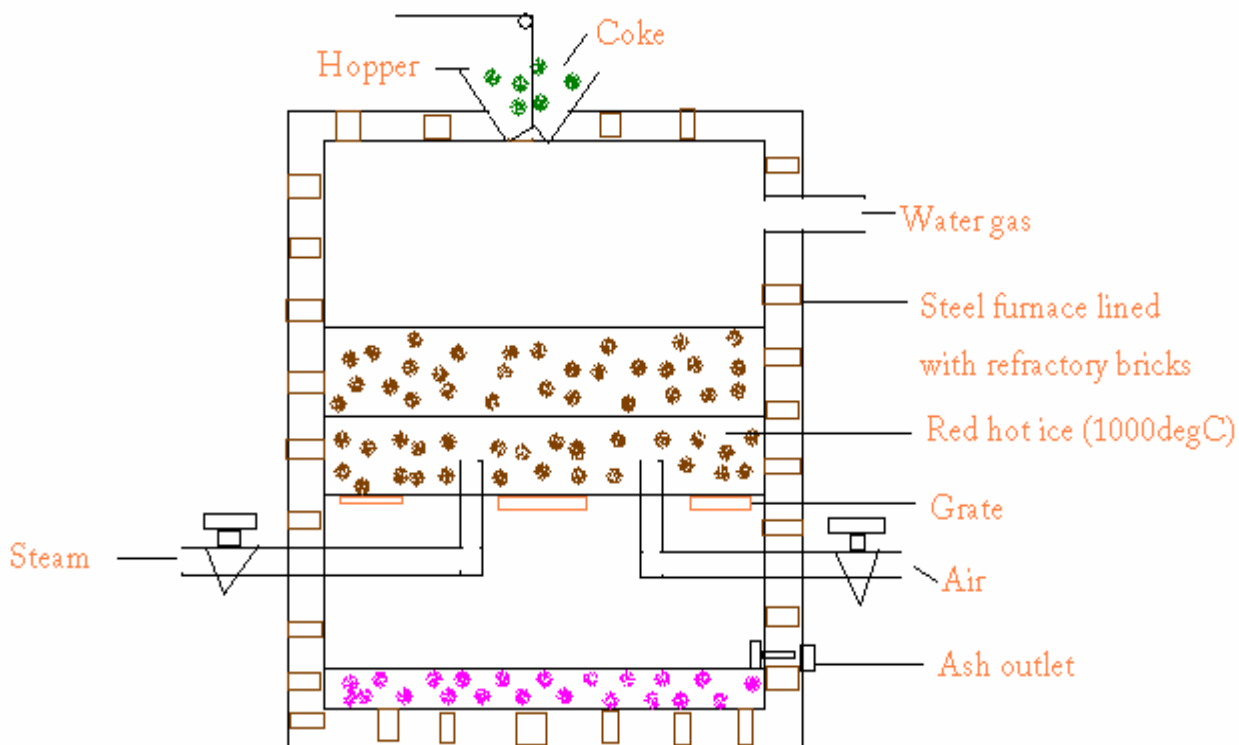
In order to avoid the above undesirable reaction, the blow of air replaces the blow of steam. The following reactions now occur.

$$C + O_2 \longrightarrow CO_2 + 97 \text{ kcal.}$$

$$2C + O_2 \longrightarrow 2CO + 59 \text{ kcal.}$$
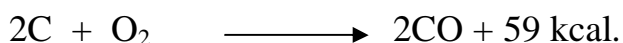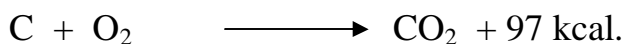
Due to exothermic reactions, the temperature of the bed rises and when the temperature increases to 1000 C, air entry is stopped and steam is again passed. Thus, steam and air are blown alternatively. Therefore, the manufacture of water gas is intermittent.

Uses: Water gas is used

1) As a source of hydrogen gas
2) In the manufacture of NH_3 by Haber's process.
3) As an illuminating gas.
4) As a fuel gas
5) For welding purposes

PRODUCER GAS:

Producer gas is essentially a mixture of combustible gases (CO and H_2) associated with larger percentage of non combustible gases (N_2 and CO_2). The calorific value is only 1800 k cal/m^3. The average composition of producer gas is 50 % N_2; 30 % CO; 10 % H_2 and rest CO_2 and CH_4.

Manufacture:

The reactor (furnace used for the manufacture of producer gas is known as producer. It consists of large airtight mild steel cylindrical towers lined inside with refractory bricks. At the bottom, it is provided with pipe for blowing air and an arrangement for removing air. Coal is added through a hopper at the top and producer gas comes out from an exit near the top.
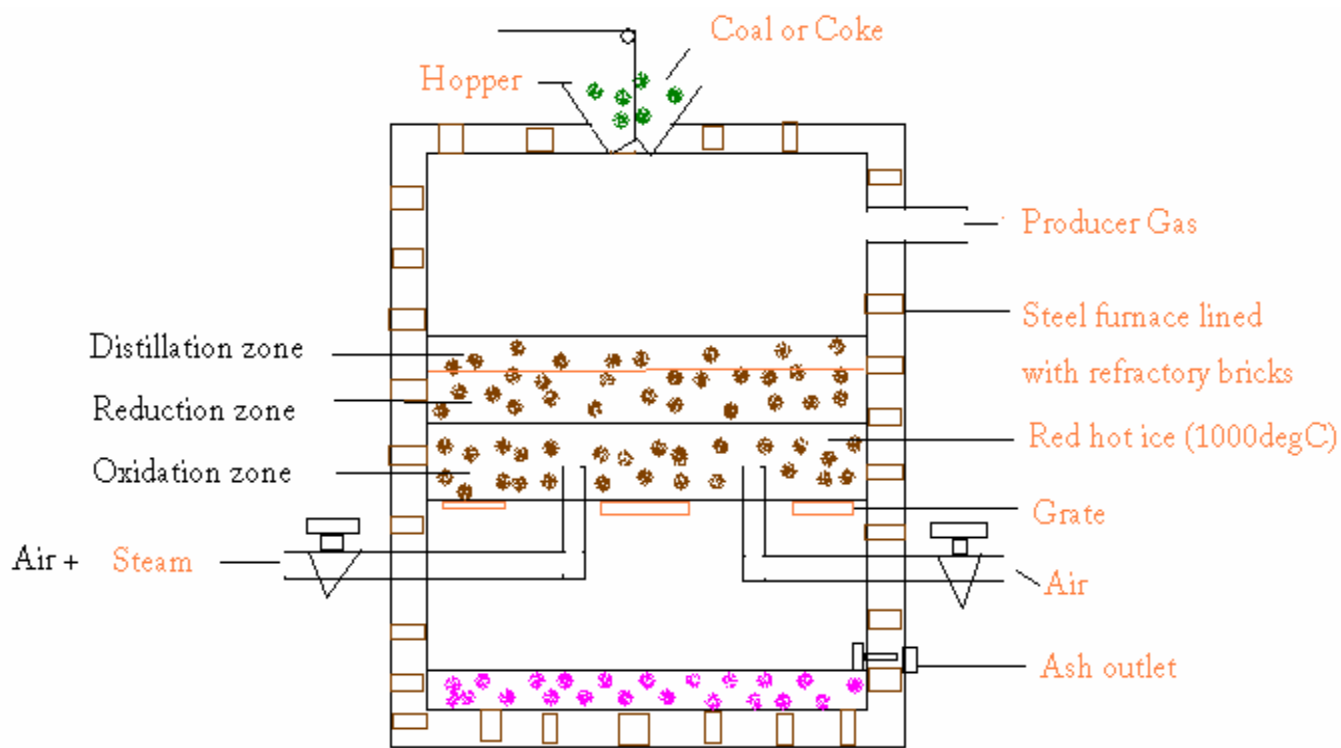
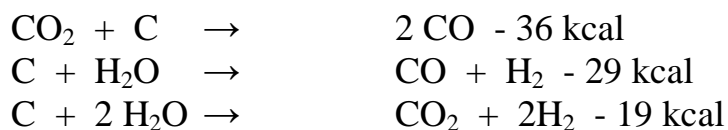The formation of producer gas involves the following:

(a) Combustion or oxidation zone:

When a mixture of air and little steam is passed through a bed of red hot coal, carbon (of the coal) combines with oxygen (of the air) in the lower part of the furnace to form CO_2.

$$C + O_2 \rightarrow CO_2 + 97 \text{ kcal.}$$

(b) Reduction zone:

Here, carbon dioxide and steam combines with the red hot coke and liberates free hydrogen and carbon monoxide.

$$CO_2 + C \rightarrow 2\,CO - 36 \text{ kcal}$$
$$C + H_2O \rightarrow CO + H_2 - 29 \text{ kcal}$$
$$C + 2\,H_2O \rightarrow CO_2 + 2H_2 - 19 \text{ kcal}$$

Nitrogen of the air remain unaffected throughout the process. Thus, a mixture of CO and N_2 with traces of CO_2 and hydrocarbons comes out through the exit at the upper side of the producer.

Producer gas is a poisonous gas; insoluble in water and heavier than air.

Uses:

1) It is a cheap, clean and easily producible gas and is used for heating open hearth furnaces (in steel and glass manufacture); muffle furnaces, retorts etc.,
2) As a reducing agent in metallurgical operations.

COMPRESSED NATURAL GAS (CNG)

CNG is natural gas compressed to a high pressure of about 1000 atmospheres. A steel cylinder containing 15 kg of CNG contains about 2 x 104 L or 20 m3 of natural gas at 1 atmospheric pressure. It is derived from natural gas and the main constituent of CNG is methane.

Properties:

1) CNG is comparatively much less pollution causing fuel as it produces less CO, ozone and hydrocarbons during combustion.
2) During it s combustion, no sulphur and nitrogen gases are evolved.
3) No carbon particles are ejected during combustion.

4) It is less expensive than petrol and diesel.
5) The ignition temperature of CNG is 550 C.
6) CNG is a better fuel than petrol/diesel for automobiles.
7) CNG requires more air for ignition.

Uses:

   As CNG is the cheapest, cleanest and least environmentally impacting alternative fuel. In Delhi, it is mandatory for all buses, taxis and auto to use CNG as a fuel.

LIQUIFIED PETROLEUM GAS (LPG)

   LPG or bottled gas or refinery gas is obtained as a by-product during the cracking of heavy oils or from natural gas. LPG is dehydrated, desulphurised and traces of odorous organic sulphides (mercaptans) are added to give warning of gas leak. LPG is supplied under pressure in containers under the trade name like Indane, Bharat gas, etc. Its calorific value is about 27,800 kcal/m^3.

   It consists of hydrocarbons of such volatility that they can exist as gas under atmospheric pressure, but can be readily liquefied under pressure. The main constituents of LPG are n-butane, isobutene, butylenes and propane, with little or no propylene and ethane.

Uses: Use as a domestic fuel and industrial fuel. Nowadays used as motor fuel.

Assignment:
1. What are all the advantages of LPG over gaseous fuel?
2. What are all the advantages of LPG over gasoline as a motor fuel?
3. What are all the disadvantages of LPG over gasoline gas a motor fuel?

FLUE GAS ANALYSIS – ORSAT'S APPARATUS

   The mixture of gases like SO_2, CO_2, O_2, CO etc. coming out from the combustion chamber is called flue gas.

Importance of Flue Gas Analysis:

(i)   The analysis gives the idea of whether a combustion process is complete or not.
(ii)   The C and H present in a fuel undergo combustion forming CO_2 and H_2O respectively. Any N present is not at all involved in the combustion. ie., the products of combustion are CO_2, H_2O and N_2.
(iii)   If analysis of a flue gas indicates the presence of CO; it is suggestive of incomplete combustion. (wastage of heat is inferred)

(iv)   If there is considerable amount of oxygen, it shows that there is excess supply of O_2 although combustion would have been complete.

Analysis:

The flue gas analysis is carried out by using Orsat's apparatus. The analysis of flue gas generally deals with the determination of CO_2, O_2 and CO by absorbing them in the respective solution of KOH, alkaline pyrogallol and ammonium cuprous chloride.
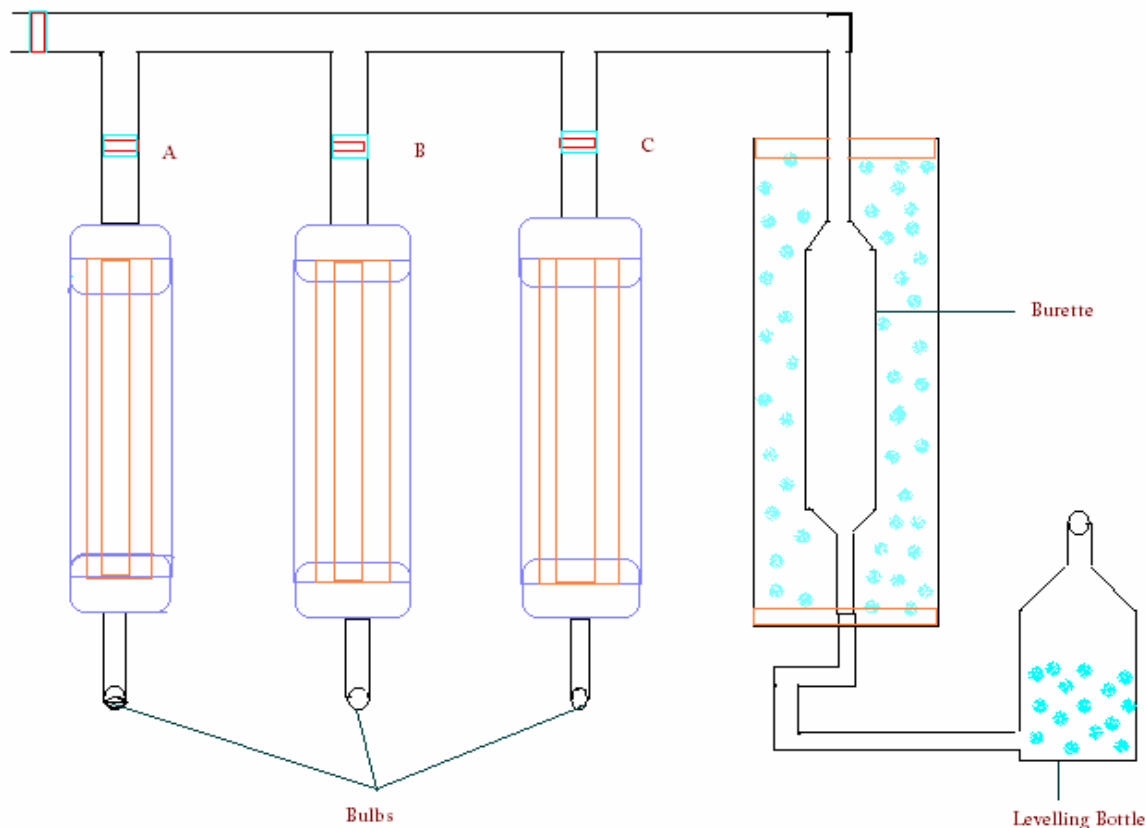
Description of Orsat's apparatus:

Orsat's apparatus consists of a horizontal tube having 3 way stopcock at one end and a water jacketed measuring burette at the other end. The horizontal tube is connected to three different absorption bulbs for the absorption of CO_2, O_2 and CO respectively. The lower end of the burette is connected to the leveling bottle by means of rubber tube.

The level of water in the leveling bottle (water reservoir) can be raised or lowered by raising or lowering the water reservoir. By changing the level of water, the flue gas can be moved into various parts of the apparatus during analysis.

It is essential to follow the order of absorbing the gases- CO_2 first; O_2 second and CO last.

This is because the absorbent used for O_2 (ie., alkaline pyrogallol) can also absorb some amount of CO_2 and the percentage of CO_2 left would be less.

a) Absorption of CO_2

Flue gas is passed into the bulb A via its stopcock by raising the water reservoir. CO2 present in the flue gas is absorbed by KOH (usually 250 g KOH in 500 mL distilled water). The gas is again sent to the burette and then again sent to bulb A. This process is repeated several times, by raising or lowering of water reservoir so as to ensure complete absorption of CO_2 in KOH. Now, the stopcock of bulb A is closed. The volume of residual gases in the burette is taken by equalizing the water level both in the burette and in the water reservoir. The difference between original volume and the volume of the gases after CO_2 absorption gives the volume of CO_2 absorbed.

b) Absorption of O_2

Stopcock of bulb A is closed and bulb B is opened. Oxygen present in the flue gas is absorbed by alkaline pyrogallol (25 g pyrogallol +200 g KOH in 500 mL distilled water). The absorption process is same as in bulb A.

c) Absorption of CO

Now the stopcock of bulb B is closed and stopcock of bulb C is opened. Carbon monoxide present in the flue gas is absorbed by ammoniacal cuprous chloride (100 g Cu_2Cl_2 + 125 mL liquid NH_3 + 375 mL water). Here also absorption process is same as in bulb A.

Since the total volume of the gas taken for analysis is 100 mL, the volume of the constituents are their percentage.

The residual gas after the above three determinations is taken as nitrogen.

Further, as the content of CO in the flue gas would be very low, it should be measured quite carefully.

Theoretical Air for Combustion:

Combustion is a process of rapid oxidation in which a fuel burns with the evolution of heat and light. The rate of combustion depends on

(i)   Nature of the fuel
(ii)   Temperature
(iii)   Concentration of the fuel and air or oxygen

Thus the combustion rate is increased by

(i)   Preheating the fuel and air
(ii)   Increasing the surface area of the fuel, and
(iii)   Increasing the pressure of air or oxygen used for combustion

The aim of combustion is to get the maximum amount of heat from a fuel in the shortest time and utilize the heat for various purposes. During the combustion, a fuel may undergo thermal decomposition to give simple products such as CO_2, H_2O etc. For efficient combustion, it is essential that the fuel must be mixed with sufficient quantity of air. The combustible constituents present in a fuel are C, H, S and O. But, non-combustible constituents N_2, CO_2 and ash present in the fuel do not take any oxygen during combustion.

Assignment:

1) Calculation of air for combustion of fuel with respect to
        (i)   Combustion of carbon
        (ii)   Combustion of hydrogen
        (iii)   Combustion of sulphur
        (iv)   Excess air for combustion

Fuels - Combustion Air and Flue Gases

Combustion air and flue gas for some common fuel gases, solids and fluids are indicated in the table below:

Fuel	Theoretical air for combustion Volume at standard pressure		Theoretical flue gas Volume at standard pressure	
Solids	(m^3/kg)	(ft^3/lb)	(m^3/kg)	(ft^3/lb)
Anthracite	9.4	150	9.5	152

Bituminous coal	6.9	110	7	112
Charcoal	8.4	134	8.4	135
Coke	8.4	134	8	135
Lignite	5.7	92	8.4	93
Peat	5.7	92	5.9	94
Semi anthracite	8.4	135	8.6	137
Wood (dry)	4.4	70	5	80
Gas	(m^3air/m^3 fuel)	(ft^3air/ft^3 fuel)	(m^3air/m^3 fuel)	(ft^3air/ft^3 fuel)
Butane C_4H_{10}	31	31	27	27
Natural gas	9.5	9.5	8.5	8.5
Propane C_3H_8	24	24	22	22
Town gas	4	4	3.8	3.8
Fluids	(m^3air/liter fuel)	(ft^3air/gal fuel)	(m^3air/liter fuel)	(ft^3air/gal fuel)
Gas oil	9.8	1570	10.4	1670
Heavy fuel oil	10.8	1730	11.6	1860

Questions review: (2 marks)

1. Define a fuel.
2. What are the advantages and disadvantages of solid fuels?
3. How the gaseous fuels are superior to all other fuels?
4. What are the requirements of good fuel?
5. What are GCV and NCV of a fuel?
6. How will you increase the rate of combustion?
7. What is carbonization?
8. What is metallurgical coke?
9. How the coke is superior to coal?
10. What is meant by refining of petroleum?
11. What is cracking?
12. What is knocking? How is it rectified?
13. What is octane number? How is it improved?
14. What is water gas? Mention its chemical composition.
15. Define cetane number.
16. Distinguish between petrol and diesel.
17. What is LPG? Mention its chemical composition and calorific value.
18. What is meant proximate and ultimate analysis?
19. Give the composition and use of producer gas.
20. Mention the significane of flue gas analysis.

Questions review: (6 marks)

1. Explain the gross and net calorific value. How they are related.
2. What is metallurgical coke? Explain the manufacture of metallurgical coke by Otto-Hoffmann method and the recovery of various by products.
3. How synthetic petrol is obtained by Bergius and Fischer-Tropsch method?
4. With a neat diagram, describe the manufacture of water gas.
5. What is producer gas? How is it manufactured?
6. Describe the proximate and ultimate analysis of coal and their significance.'
7. What is cracking? How is it useful of the preparation of synthetic petrol?
8. What are the good characteristics of good metallurgical coke?
9. What is crude oil? What are the various fractions obtained by the fractional distillation of crude oil? Mention the composition and uses?
10. How will you determine the calorific value of fuel by using Bomb calorimeter?
11. How the flue gas analysis is carried out? Explain with neat diagram.
12. With a neat diagram, describe the manufacture of producer gas.