## UNIT- II: Fuels & Lubricants

Fuels - Classification, examples, relative merits, types of coal, determination of calorific value of solid fuels, Bomb calorimeter, theoretical oxygen requirement for combustion, proximate & ultimate analysis of coal, manufacture of metallurgical coke, flue gas analysis, problems.

Fuel Definition:

Fuels are the main energy sources for industry and domestic purposes. 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.

Ex: 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.

$$Fuel + Oxygen \rightarrow Products + Heat$$
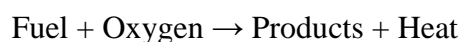
Classification of Fuels:

Classification of fuels is based on two factors.

1. *Occurrence (and preparation):* On the basis of occurrence, the fuels are further divided into,
   ➢ Natural or Primary fuels: These are found in nature.

   Ex: Wood, peat, coal, petroleum, natural gas etc.

   ➢ Artificial or Secondary fuels: These are prepared artificially from the primary fuels.

   Ex: Charcoal, coke, kerosene, diesel, petrol, coal gas, producer gas, blast furnace gas etc.

2. *The state of aggregation:* Each type of classification based on occurrence is again subdivided based upon their state of aggregation like:
   ➢ Solid fuels
   ➢ Liquid fuels
   ➢ Gaseous fuels

Sl. No.	State of fuel	Natural	Artificial
1	Solid	Wood, peat, lignite, coal	Wood charcoal, coke
2	Liquid	Crude petroleum	Kerosene, petrol, diesel, alcohol
3	Gaseous	Natural gas	Water gas, producer gas, biogas, coal gas, LPG

Characteristics of a good fuel:

- The fuel should be easily available.
- It should be dry and should have less moisture content.
- It should be cheap, easily transportable and has high calorific value.
- It must have moderate ignition temperature and should leave less ash after combustion.
- The combustion speed of a good fuel should be moderate.
- It should not burn spontaneously to avoid fire hazards.
- Its handling should be easy and should not give poisonous gases after combustion.
- The combustion of a good fuel should not be explosive.

Relative merits:

➤ *The various advantages of solid fuels are given below:*

o They are easy to transport.

o They are convenient to store without any risk of spontaneous explosion.

o Their cost of production is low.

o They possess moderate ignition temperature.

➤ *The advantages of liquid fuels can be summarized as follows:*

o They possess higher calorific value than solid fuels.

o They burn without dust, ash, clinkers, etc.

o They are easy to transport through pipes.

o Loss of heat in chimney is very low.

o They require less excess air for complete combustion.

o They require less furnace space for combustion.

➤ *The advantages of gaseous fuels are given below:*

o They can be conveyed easily through pipelines to the actual place of need, thereby eliminating manual labor in transportation.

o They have high heat contents and hence help us in having higher temperatures.

o They burn without any shoot, or smoke and ashes.

o They are free from impurities found in solid and liquid fuels.

➤ *Liquid and gaseous fuels are considered better fuels than the solid fuels because of:*

o Liquid and gaseous fuels are easier to handle than solid fuels.

o Liquid and gaseous fuels can be transported easily through pipelines.

- Liquid and gaseous fuels do not leave any residue after burning.
- Liquid and gaseous fuels have higher calorific values than the solid fuels.
- Liquid and gaseous fuels produce little or no smoke.
- Liquid and gaseous fuels have relatively low ignition temperature and hence they burn more easily than solid fuels.

➢ *The main disadvantages of gaseous fuels are:*
- Very large storage tanks are needed for storing gaseous fuels.
- They are highly inflammable, so chances of fire hazards are high in their use.
- They are costlier than solid or liquid fuels.

Solid fuels:

The main solid fuels are wood, peat, lignite, coal and charcoal.

Wood:

It is a low-grade fuel. Freshly cut wood contains 25-50% moisture. Moisture may be reduced to 25% on air-drying. The composition of moisture free wood is $C = 55\%$; $H_2 = 6\%$; $O_2 = 43\%$ and ash = 1%. The calorific value of dried wood is 3500 to 4500 kcal/kg. It burns with a long and non-smoky flame. It is used as a domestic fuel.

Types of Coal:

Coal is occurring in layers in the earth crust. Coal is a natural fuel formed by the slow carbonization of plant matter buried under the earth some thousands of years ago and further altered by action of heat and pressure. It is chiefly composed of C, H, N and O besides non-combustible inorganic matter. It is classified into four kinds based on the carbon content and the calorific value.

1. Peat

2. Lignite

3. Bituminous coal

4. Anthracite coal

The process of conversion of wood into coal can be represented as:

$$\text{Wood} — \text{Peat} — \text{Lignite} — \text{Bituminous Coal} — \text{Anthracite}$$

1. Peat: A brown deposit resembling soil, formed by the partial decomposition of plant matter in the wet and acidic conditions. It is the first stage of formation of coal from wood. It is brown, fibrous jelly-like mass. It contains 80-90% moisture. The composition of peat is $C = 57\%$; $H_2 =$

6%; O_2 = 35% and ash = 2.5%. The calorific value of peat is 5400 kcal/kg. It is a low-grade fuel due to high water content. Lowest rank coal.

Uses

1. It is used as fertilizer.

2. It is used in household cooking in some places.

2. Lignite: A soft brownish coal showing traces of plant structure, intermediate between bituminous coal and peat. Lignite is immature form of coal. It contains 20-60% moisture. Air-dried lignite contains C = 60-70% and O_2 = 20%. It burns with a long smoky flame. The calorific value of lignite is 6500-7100 kcal/kg.

Uses

1. It is used as a domestic fuel.

2. It is used as a boiler fuel for steam production.

3. It is used in the manufacture of producer gas ($CO+N_2$).

3. Bituminous coal:

These are pitch black to dark grey coal. It is a high quality fuel. Its moisture content is 4%. Its composition is C = 83%; O_2 = 10%; H_2 = 5% and N_2 = 2%. Its calorific value is 8500 kcal/kg.

Uses

1. It is used in metallurgy.

2. It is used in steam production.

3. It is used for making coal gas (a mixture of gases, chiefly hydrogen, methane, and carbon monoxide).

4. It is also used for domestic heating.

4. Anthracite coal:

It is the superior form of coal or a class of highest rank coal. It contains $C = 92\text{-}98\%$; $O_2 = 3\%$; $H_2 = 3\%$ and $N_2 = 0.7\%$. It burns without smoke. Its calorific value is 8700 kcal/kg.

Uses:

1. It is used for steam production and house hold purposes.

2. It is used for direct burning in boilers and in metallurgy.

3. It is used in thermal power plant.

4. It is used in coal tar distillation.

Calorific value:

- The prime property of a fuel is its capacity to supply heat.
- Normally when a combustible substance burns the total heat depends upon the quantity of fuel burnt, its nature, air supplied for combustion and certain other conditions leading the combustion.
- Further the heat produced is different for different fuels and is termed as its calorific value.

Definition:

Calorific value is the amount of heat liberated by the complete combustion of a unit weight of the fuel and in usually expressed as cal/g or kcal/g.

Higher or Gross Calorific Value (HCV/GCV):

It is the total amount of heat produced, when unit mass 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.

(Latent heat of condensation is energy released when water vapor condenses to form liquid droplets.)

Lower or Net Calorific Value (LCV/NCV):

It is the net heat produced, when unit mass of the fuel is burnt completely and the products are permitted to escape. In actual practice of any fuel, the water vapor and moisture, etc., are not condensed and escape as such along with hot combustion gases. Hence, a lesser amount of heat is available. Net calorific value is the gross calorific value excluding the latent heat of condensation of water. Therefore,

$$\text{LCV or NCV} = \text{HCV} - \text{Latent heat of water vapor formed}$$

Determination of calorific value of solid fuels:

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.
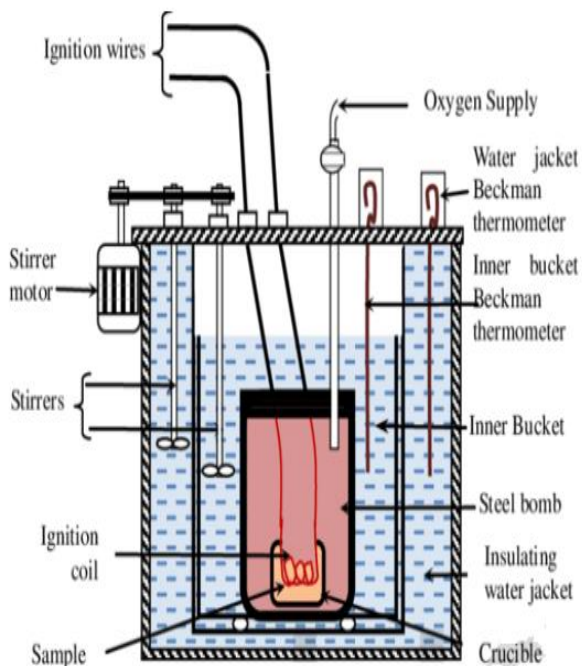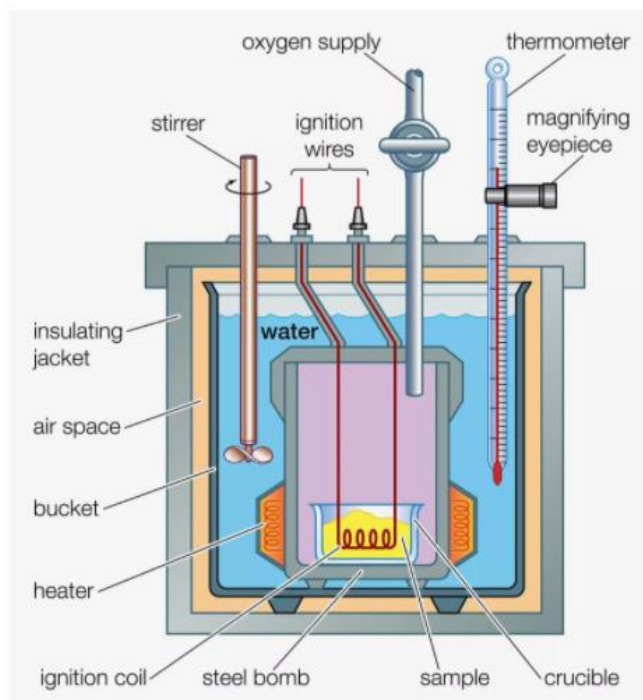
Functioning:

o   A known weight of the fuel sample is taken into the crucible.

o   The fine magnesium wire is touching the fuel sample and then stretched across the electrodes.

o   The bomb lid is tightly closed with the help of screw.

o   The bomb is filled with oxygen at 25 atmospheric pressure.

o   The bomb is now placed in a copper calorimeter which containing known weight of water.

o   Initial temperature of the water in the calorimeter is noted (t_1°C) after stirring.

o   The electrodes are connected to a battery.

o   The current is now supplied to the sample which undergoes burning with the evolution of heat.

o   The liberated heat increases the temperature of water in the calorimeter.

o   The maximum temperature of the water during experiment is finally noted (t_2°C).

o   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 = w 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 -----------------(i)

Heat absorbed the calorimeter = w (t_2-t_1) cal --------------(ii)

Total heat absorbed = W (t_2-t_1) + w (t_2-t_1) cal

$\qquad\qquad\qquad$ = (W+w) (t_2-t_1) cal -------------------(iii)

The relationship between heat liberated by the fuel and HCV is as follows:

Heat liberated by the fuel = x x (HCV) --------------------(iv)

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

From equations (iii) and (iv), x x (HCV) = (W+ w) (t_2-t_1)

$$HCV = \frac{(W+w)(t2-t1)}{x} \text{ cal/g}$$

Corrections: For accurate results the following corrections are also incorporated.

Fuse wire correction: The heat liberated during the determination of calorific value, includes the

heat given out by ignition of the fuse wire used. Hence, it must be subtracted from the total value.

Acid correction: The fuels containing S and N are oxidized, under high pressure and temperature of ignition, of sulphuric acid and nitric acid respectively. The above reactions are exothermic in nature. Thus, the measured amount of heat also given out during the acid formation.

$$S + H_2 + 2O_2 \longrightarrow H_2SO_4 + \text{heat}$$
$$2N + H_2 + 3O_2 \longrightarrow 2HNO_3 + \text{heat}$$
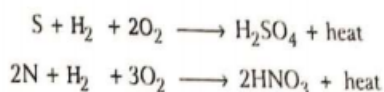
Cooling correction: As the temperature rises above the room temperature, the loss of heat does occur due to radiation, and the highest temperature recorded will be slightly less than that obtained. A temperature correction is therefore necessary to get the correct rise in temperature.

The time taken to cool the water in copper calorimeter from maximum temperature to room temperature is recorded. From the rate of cooling (dt°/min) and the actual time taken for cooling (t min), the cooling correction (dt X t) is added to the increase the temperature.

$$HCV = \frac{[(W + w)(t_2 - t_1 + \text{cooling correction})] - (ACID + FUSE \text{ correction})}{\text{Mass of fuel sample } (x)}$$
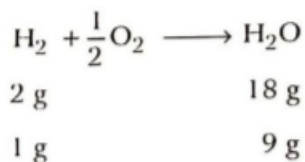
Calculation of Lower Calorific Value (LCV):

LCV or NCV = HCV – Latent heat of water vapor formed

Let H = % of hydrogen in fuel, then:

$1 \times \dfrac{H}{100}$ g = g of hydrogen present in 1 g fuel.

As all fuels contain some hydrogen and when the calorific value of hydrogen containing fuel is determined experimentally, hydrogen is converted into steam according to

$$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$$

2 g	18 g
1 g	9 g

Weight of H_2O produced from $\dfrac{H}{100}$ g H_2 (or 1 g fuel) $= \dfrac{9H}{100}$ g $= 0.09$ Hg

So, heat taken by H_2O in forming steam $= 0.09\ H \times 587$ cal   (Latent heat of steam $= 587$ cal/g)

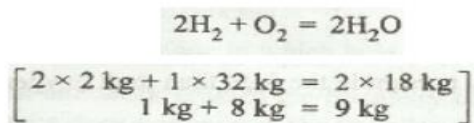LCV of the fuel = HCV – Latent heat of water formed by the fuel

LCV = HCV – (0.09 H x 587) cal/g.

**Theoretical oxygen requirement for combustion:**

- The minimum amount of air which supplies the required amount of oxygen for complete combustion of a fuel is called the theoretical air.

- In order to obtain maximum amount of heat from a fuel, the sufficient supply of oxygen is very essential for the complete combustion of a fuel.

- The theoretical or minimum amount of oxygen required for complete combustion of 1 kg of fuel may be calculated from the chemical analysis of the fuel.

- Let us consider 1 kg of a fuel, the ultimate analysis of which shows that carbon is C kg, hydrogen H kg, oxygen O kg and sulphur S kg.

- 1 kg of carbon requires 8/3 kg of oxygen for its complete combustion; therefore, C kg of carbon will require C x 8/3 kg of oxygen which is equivalent to 2.66C kg of oxygen.

$$C + O_2 = CO_2$$
$$12 \text{ kg} + 32 \text{ kg} = 44 \text{ kg}$$
$$1 \text{ kg} + \frac{8}{3} \text{ kg} = \frac{11}{3} \text{ kg}$$
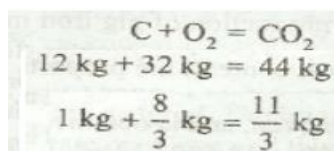
- 1 kg of hydrogen requires 8 kg of oxygen; therefore, H kg of hydrogen requires 8H kg of oxygen.

$$2H_2 + O_2 = 2H_2O$$
$$\left[\begin{array}{c} 2 \times 2 \text{ kg} + 1 \times 32 \text{ kg} = 2 \times 18 \text{ kg} \\ 1 \text{ kg} + 8 \text{ kg} = 9 \text{ kg} \end{array} \right]$$

- 1 kg of sulphur requires 1 kg of oxygen; therefore, S kg of sulphur requires S kg of oxygen.

$$S + O_2 = SO_2$$
$$32 \text{ kg} + 32 \text{ kg} = 64 \text{ kg}$$
$$1 \text{ kg} + 1 \text{ kg} = 2 \text{ kg}$$
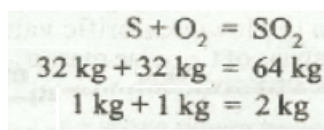
∴ The quantity of oxygen required for combustion of 1 kg of the fuel = (2.66C + 8H + S) kg.

- If the fuel contains O kg of oxygen, then it is taken into account.

∴ Oxygen required for the complete combustion of 1 kg fuel is: (2.66C + 8H + S – O) kg.

- The composition of air is taken as: Nitrogen (N_2) = 77%; Oxygen (O_2) = 23% (by mass) and Nitrogen (N_2) = 79%; Oxygen (O_2) = 21% (by volume).

- Thus, for obtaining 1 kg of oxygen, amount of air required: $\frac{100}{23} = 4.35$ kg.

- Theoretical or minimum air required for complete combustion of 1 kg of fuel is:

$$= 4.35 \, [(2.66C + 8H + S) – O] \text{ kg.}$$

Analysis of Coal:

The composition of coal varies widely and hence it is necessary to analyze the coal. The analysis of coal is helpful in its ranking. The assessment of the quality of coal is carried out by these two types of analyses.
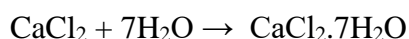
(A) Proximate analysis

(B) Ultimate analysis

(A). Proximate analysis:

In this analysis, the percentage of carbon is indirectly determined. It is a quantitative analysis of the following parameters.

    (i) Moisture content   (ii) Volatile matter

    (iii) Ash   (v) 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^oC.

% of moisture content $= \frac{Loss\ in\ weight\ of\ coal}{weight\ of\ coal\ taken}$ X 100

High moisture content of the coal is undesirable due to:

- Reduces the calorific value of coal
- Increases the consumption of coal for heating purpose.

(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 furnace at 950^oC for seven minutes.

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

- It has been found that the coal with higher volatile matter content ignites easily.

(iii) Determination of ash in coal:

Coal sample of accurate weight in a crucible is heated in a furnace at 750^0C for 30 min. Crucible is taken out, cooled in desiccators and weighed. Heating, cooling and weighing is repeated, till a constant weight is obtained. The residue is reported as ash.

% of ash $= \frac{weight\ of\ residue\ ash\ formed}{weight\ of\ coal\ taken}$ X 100

- Ash is the mineral matter in the coal. It consists mainly SiO_2, Al_2O_3 and Fe_2O_3 with varying amounts of other oxides such as Na_2O, CaO, MgO etc.
- High ash content in coal is undesirable due to increases transporting & storage costs and has lower calorific value.

(iv) Determination of fixed carbon:

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

% of fixed carbon in coal = 100 - % (moisture + volatile matter + ash)

- It is the pure carbon present in coal.
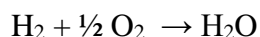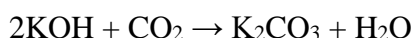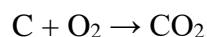- Higher the fixed carbon content of the coal, higher will be the calorific value of the sample.
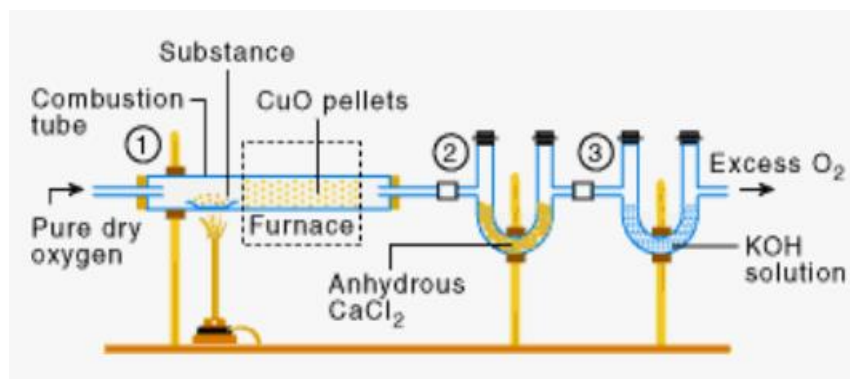
(B). Ultimate Analysis:

This analysis involves the determination of carbon, hydrogen, nitrogen, oxygen and sulphur of pure, dry coal. This analysis gives the elementary, ultimate constituents of coal.

(i) Determination of carbon and hydrogen in coal

(ii) Determination of nitrogen in coal

(iii) Determination of sulphur in coal

(iv) Determination of oxygen in coal

(i) 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 CO_2 and H_2O respectively. The CuO serves to oxidize traces of carbon, C, and carbon monoxide, CO, formed during the combustion process to carbon dioxide, CO_2. It also confirms that all of the hydrogen is oxidized completely to form water, H_2O. The gaseous 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 weights of these are then determined. 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.

$$C + O_2 \rightarrow CO_2$$

$$2KOH + CO_2 \rightarrow K_2CO_3 + H_2O$$

$$H_2 + \tfrac{1}{2} O_2 \rightarrow H_2O$$

$$CaCl_2 + 7H_2O \rightarrow CaCl_2.7H_2O$$

The percentage of carbon and hydrogen in coal can be calculated in the following way.

$$\% \ C = \frac{Increase \ in \ weight \ of \ KOH \ tube \ X \ 12}{weight \ of \ coal \ sample \ taken \ X \ 44} \ X \ 100$$

$$\% \ H = \frac{Increase \ in \ weight \ of \ CaCl2 \ tube \ X \ 2}{weight \ of \ coal \ sample \ taken \ X \ 18} \ X \ 100$$

- High total carbon containing coal will have higher calorific value.
- Hydrogen: It increases the calorific value of the coal.

    It is associated with the volatile matter of the coal.
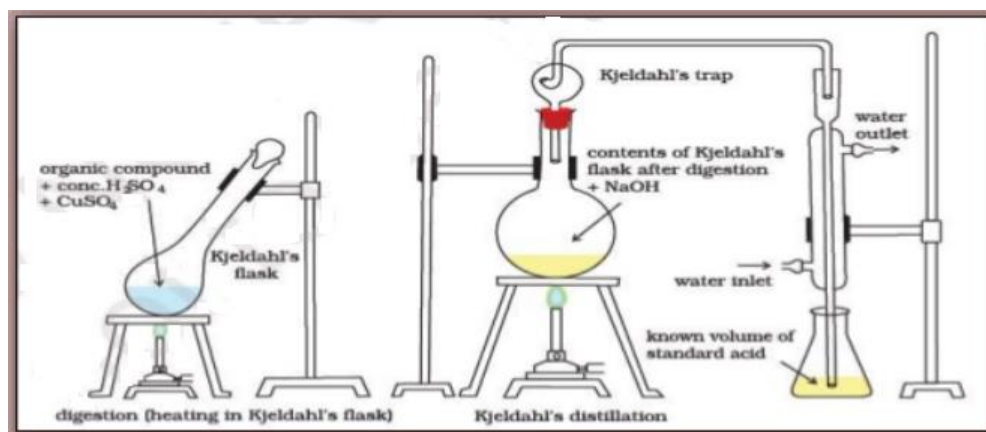
(ii) Determination of nitrogen:

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 flask. 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 treated with excess NaOH solution and the following reaction occurs:

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

The liberated ammonia is distilled over and absorbed in a known volume of standard 0.1 N H_2SO_4 solution. The volume of unused 0.1 N H_2SO_4 is then determined by back titration with standard NaOH solution. From the volume of acid used by ammonia liberated, the % of nitrogen in coal is calculated as follows:

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

$$\% \ Nitrogen \ in \ coal \ = \frac{1.4 \ x \ voume \ of \ acid \ used \ x \ normality}{Weight \ of \ coal \ taken}$$

Kjeldahl's trap

water outlet

contents of Kjeldahl's flask after digestion + NaOH

organic compound + conc. H₂SO₄ + CuSO₄

Kjeldahl's flask

water inlet

known volume of standard acid

digestion (heating in Kjeldahl's flask)

Kjeldahl's distillation

- ▪ Presence of nitrogen decreases the calorific value of the coal.
- ▪ Ammonia is recovered as $(NH_4)_2SO_4$, a valuable fertilizer.

(iii) 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 $BaCl_2$ 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 $BaSO_4$ precipitate = y g

Consider the following equations

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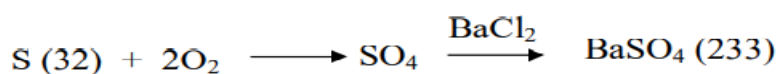
233 g of $BaSO_4$ contains 32 g of sulphur

$$\% \text{ of Sulphur} = \frac{\text{Weight of BaSO4 obtained} \times 32}{\text{Weight of coal taken} \times 233} \times 100$$

$$\text{(OR)} \quad \% \text{ of Sulphur} = \frac{y \times 32}{x \times 233} \times 100$$

- ● 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.

(iv) **Determination of oxygen:**

Coal sample of accurate weight in a crucible is heated in a furnace at 750^0C for 30 min. Crucible is taken out and cooled first in air and then in desiccators and weighed. Heating, cooling and weighing is repeated, till a constant weight is obtained. The residue is reported as ash.

$$\% \text{ of ash} = \frac{weight\ of\ residue\ ash\ formed}{weight\ of\ coal\ taken}\ X\ 100$$

% of oxygen is determined by deducting the combined percentage of carbon, hydrogen, nitrogen, sulphur and ash from 100.

$$\% \text{ of oxygen in coal} = 100 - \% (C + H + N + S + ash).$$

▪ As the oxygen content increases, its moisture holding capacity also increases.

▪ The less the oxygen content, the better is the coal.

Manufacture of 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 (sticking together) is left which is called metallurgical coke.

Manufacture of metallurgical coke by Otto Hoffmann's method:

• Here, the heating is done externally by a portion of coal gas produced during the process itself or by producer gas ($CO+N_2$) or by blast furnace gas.

• Moreover, the heating is done on the basis of "regenerative system" i.e., utilizing the waste flue gases for heating the checker-work of bricks.

• The by-product coke oven consists of number of narrow silica chambers (each about 10 to 12 m long, 3 to 4 m high and 0.40 to 0.45 m wide) established side-by-side with vertical flues in-between them to form a kind of battery.

• Each chamber is provided with a charging hole at the top, a gas off-take and a refractory-lined cast iron door at each ends for discharging coke.

• The oven works on heat regenerative principle i.e., 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.

Otto Hoffmann's byproduct coke oven
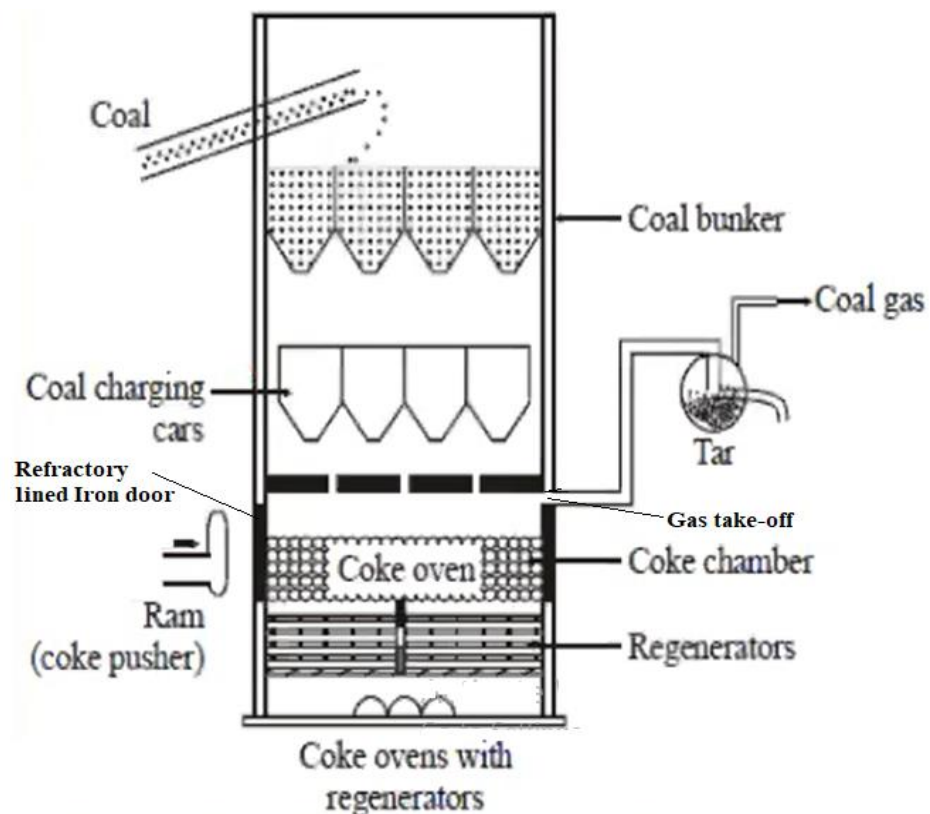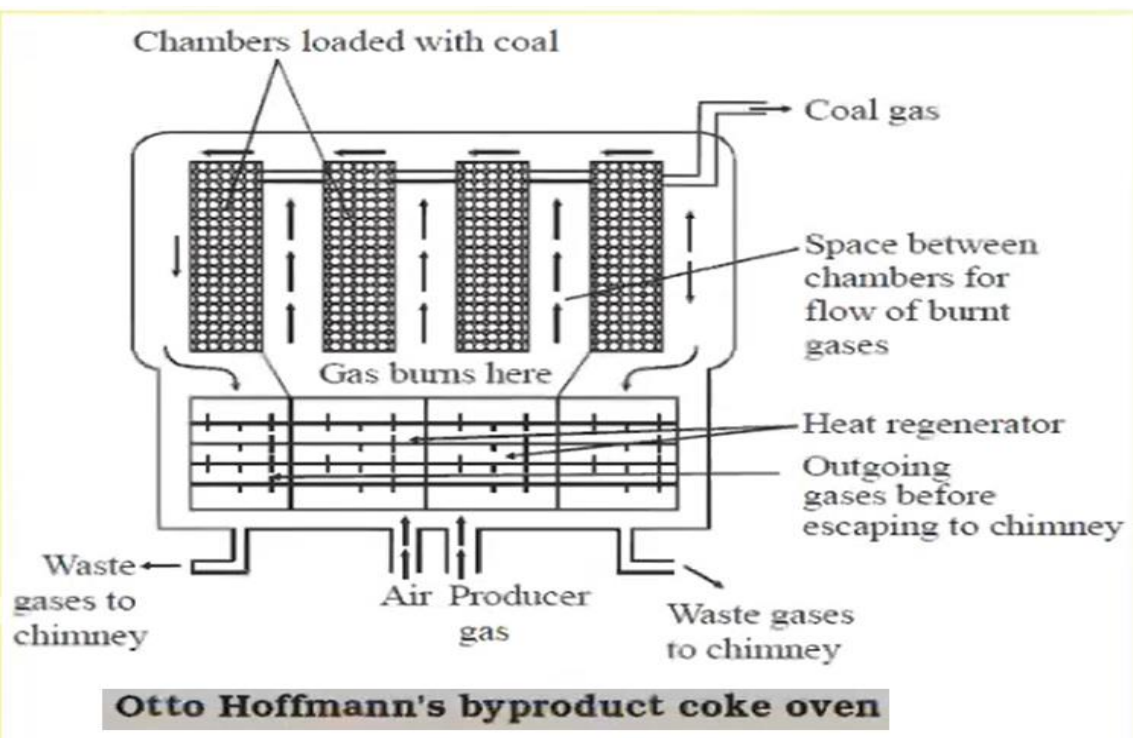
Schematic representation of a single chamber of Otto Hoffmann's oven

- A charge consisting of finely crushed coal is introduced through the charging holes at the top of chambers, which are then closed tightly at both ends to prevent any access of air.
- The coke ovens are heated to 1, 200°C by burning gaseous fuel (like producer gas) and usually employing a regenerative principle.
- The ovens are heated to 1200°C by burning the preheated air and producer gas mixture in the interspaces between the chambers.
- Hot flue gases produced during combustion, before escaping to chimney, are allowed to pass through the checker brick work in the regenerators of the next oven to preheat it until the temperature raised to 1000^0C.
- The air and fuel gas are pass through other preheated regenerators.
- The cycle goes on and the heating is continued until all the volatile matter has escaped.
- Carbonization of a charge of coal takes about between 11 to 18 hours.
- For economical heating, the direction of inlet gases and flue gases are changed frequently.
- 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. 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 %.

Flue gas analysis:

The mixture of gases like SO_2, CO_2, O_2, CO etc. coming out from the combustion chamber is called as flue gas. The flue gas analysis is carried out by using Orsat's apparatus.

Construction of Orsat's apparatus:

- Orsat's apparatus consists of a water-jacketed measuring burette, connected in series to a set of three absorption bulbs, each through a stop-cock.

- The other end is provided with a three-way stop-cock.
- The graduated burette is surrounded by a water-jacket to keep the temperature of the gas constant during the experiment.
- The lower end of the burette is connected to a water reservoir by means of a long rubber tubing.
- The level of water in the water reservoir can be raised or lowered by raising or lowering the water reservoir.
- The absorption bulbs have solutions for the absorption of CO_2, O_2 and CO respectively.
- First bulb has 'potassium hydroxide' solution (250g KOH in 500mL of boiled distilled water), and it absorbs only CO_2.
- Second bulb has a solution of 'alkaline pyrogallol (25g pyrogallol +200g KOH in 500 mL of distilled water) and it can absorb CO_2 and O_2.
- Third bulb contains 'ammonical cuprous chloride' (100g cuprous chloride + 125 mL liquor ammonia+375 mL of water) and it can absorb CO_2, O_2 and CO.
- Hence, it is necessary that the flue gas is passed first through potassium hydroxide bulb, where CO_2 is absorbed, then through alkaline pyrogallol bulb, when only O_2 will be absorbed and finally through ammonical cuprous chloride bulb, where only CO will be absorbed.
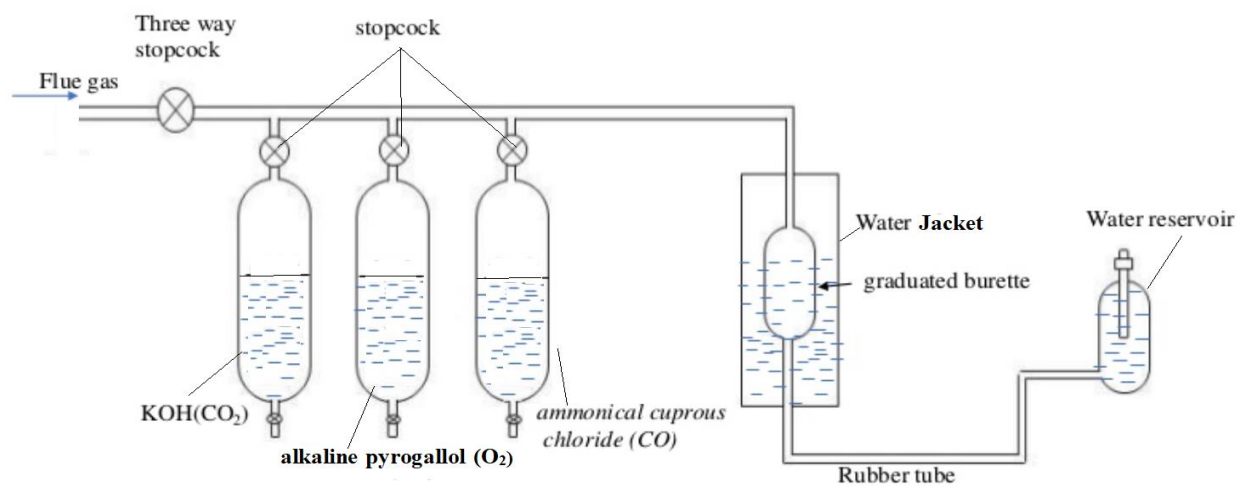
Working:
- Three-way stopcock is opened and the flue gas is filled in the graduated burette.
- The whole set up is water jacketed to maintain a constant temperature.
- The stopcock of the KOH reservoir is opened and the water reservoir is moved up.
- Water inflows in the graduated burette and pushes the gas to flow in the KOH reservoir.

- In that reservoir carbon dioxide is absorbed. The whole CO_2 in the sample is absorbed.
- The water reservoir is brought down so that the air again can rush to the burette.
- Again the stopcock of the alkaline pyrogallol reservoir is opened and the water reservoir is moved up.
- Water inflows in the graduated burette and pushes the gas to flow in the alkaline pyrogallol reservoir where the absorption of oxygen takes place.
- The same process is repeated with the ammonical cuprous chloride reservoir.
- The volume increase of all the reservoirs is measured and the amount of carbon dioxide, carbon monoxide and oxygen are determined.

Precautions:
- All the air in the reservoir bottle is expelled to atmosphere by lifting the reservoir bottle and opening the three-way to atmosphere.
- It is quite necessary to follow the order of absorbing gases: CO_2 first, O_2 second and CO last.

Problems:

Bomb Calorimeter:

1.

On burning 0.72 g of a solid fuel in a Bomb calorimeter, the temperature of 250 g of water is increased from 27.3°C to 29.1°C. If the water equivalent is 150 g, calculate the HCV of the fuel.

Sol:

x = 0.72 g

W = 250 g

T_1 = 27.3°C

T_2 = 29.1°C

w = 150 g

HCV of fuel = (W + w) (T_2- T_1) ÷ x cal/g

= (250 + 150) (29.1- 27.3) ÷ 0.72

= 1000 cal/g

2.

In an experiment in a Bomb calorimeter, a solid fuel of 0.90 g is burnt. It is observed that increase of temperature is 3.8°C of 4000 g of water. The fuel contains 1% of H. calculate the HCV and LCV value (equivalent weight of water = 385 g and latent heat of steam = 587 cal/g).

Sol:

Weight of fuel (x) = 0.90 g

Weight of water (W) = 4000 g

Equivalent weight of water (w) = 385 g

Rise in temperature (T_2-T_1) = 3.8°C

Percentage of carbon = 1%

Latent heat of steam = 587 cal/g

HCV = (W + w) $(T_2- T_1)$ ÷ cal/g

   = (4000 + 385) (3.8) ÷ 0.90 cal/g

   = **18514.5 cal/g**

LCV = (HCV − 0.09 H × 587)

   = 18514.5 − 0.09 × 1 × 587

   = **18461.6 cal/g**

3.

A sample of coal contains: C = 83%, H = 6% and ash 1%.

The following data were obtained when the above coal was tested in a bomb calorimeter:

Weight of coal burnt = 0.92 g

Weight of water taken = 550 g

Water equivalent of calorimeter = 2,200 g

Rise in temperature = 2.42°C

Fuse wire correction = 10.0 cal

Acid correction = 50.0 cal

Calculate the gross and net calorific values of coal, assuming that the latent heat of condensation of steam is 580 cal/g.

Sol: Weight of coal sample (x) = 0.92 g

   Weight of water (W) = 550 g

   Water equation of calorimeter (w) = 2200 g

   Rise in temperature (T_2-T_1) = 2.42°C

   Fuse wire correction = 10.0 cal

   Acid correction = 50.0 cal

   Latent heat of steam = 580 cal/g.

   % of H = 6 %

   $$H.C.V. = \frac{(W+w)\ (T_2-T_1) - [Acid + Fuse\ corrections]}{x}$$

      = (550 + 2200) × 2.42 − [50 +10] ÷ 0.92 g

      = **7,168.5 cal/g**

   N.C.V. = (G.C.V. − 0.09 H × latent heat of steam)

      = (7,168.5 − 0.09 × 6 × 580) cal/g

      = **6,855.3 cal/g**

4.

A sample of coal containing 80% C, 15% H and 5% ash is tested in bomb calorimeter. The following results were obtained.

Weight of coal burnt	= 0.98 gm.
Weight of water taken	= 1000 gm.
Water equivalent of bomb and calorimeter	= 2500 gm.
Rise in temperature	= 2.5 °C.
Cooling correction	= 0.02°C.
Fuse wire correction	= 8.0 calories.
Acid correction	= 50.0 calories.

suming the latent heat of condensation of steam as 580 cal/gm, calculate the
er (ii) Lower calorific value of the fuel.

ion:

$$HCV = \frac{(W+w)(t_2 - t_1 + C_C) - (C_A + C_F)}{m}$$

$$HCV = \frac{(1000 + 2500)(2.5 + 0.02) - (50 + 8)}{0.98} \, cal/gm$$

$$= 8940.82 \, cal/gm$$

$$LCV = HCV - 0.09 \times H \times 580$$

$$= 8940.82 - 0.09 \times 15 \times 580 \, cal/gm$$

$$= 8940.82 - 783$$

$$LCV = 8157.82 \, cal/gm.$$

Analysis of coal:

(a)Proximate analysis:

1) 2.3 gm of air-dried coal sample was taken in a silica crucible. After heating it in an electric oven at 105- 110 ^{0}C for 1 hour, the residue weighed 2.2 gm. The residue was then ignited at 700-750^{0}C to a constant weight of 0.245 gm.

   In another experiment 1.1 gm of the same coal sample was heated in a silica crucible covered with a vented lid at a temperature 925 ± 25 ^{0}C for exactly 7 minutes. After cooling, the weight of residue was found to be 0.725 gm. Calculate % of fixed carbon.

Given:

(i)   Initial weight of coal sample = W_{coal} = 2.3 gm

   Weight of coal after heating at 105- 110 ^{0}C for 1 hour = 2.2 gm

   Loss in weight of coal after heating at 105- 110 ^{0}C for 1 hour = $W_{Moisture}$

   Constant weight of the residue left after igniting at 700-750^{0}C = W_{Ash}

   Hence, $W_{moisture}$ = 2.3 – 2.2 = 0.1 gm

   W_{Ash} = 0.245 gm

Therefore,

% of Moisture in coal = $\dfrac{W_{moisture} \times 100}{W_{Coal} \text{ (before heating)}}$ = $\dfrac{0.1 \times 100}{2.3}$ = **4.35 %**

% of Ash in coal = $\dfrac{W_{Ash} \times 100}{W_{Coal} \text{ (before heating)}}$ = $\dfrac{0.245 \times 100}{2.3}$ = **10. 65 %**

Given:

(ii) Initial weight of coal sample = W_{coal} = 1.1 gm

   Weight of coal after heating at 900 - 950 ^{0}C for 7 minutes = 0.725 gm

   Loss in weight of coal after heating at 925 ± 25 ^{0}C for 7 minutes =

   W_{coal} – W_{VM} = 1.1 – 0.725 = 0.375 gm

Therefore,

% of Volatile matter in coal = $\dfrac{W_{Lost} \times 100}{W_{Coal} \text{ (before heating)}}$ = $\dfrac{0.375 \times 100}{1.1}$

= **34.09 – %Moisture = 34.09 – 4.35 = 29.74%**

% of Fixed Carbon = 100 – (% Moisture + % Volatile matter + % Ash)

= 100 – (4.35 + 29.74 + 10.65) = 100 – 44.74 = **55.26 %**

2) A sample of coal was analysed as follows:

Exactly 2.25 gm was weighed into a silica crucible. After heating for one hour at 110 ^{0}C, the residue weighed, 2.13 gm. The crucible next was covered with a vented lid and strongly heated for 7 mins. at 950 $\pm$ 20 ^{0}C. The residue weighed 1.55g. The crucible was then heated without the cover, until a constant weight was obtained. The last residue was found to be 0.215g. Calculate the percentage results of above analysis.

Given:

Initial weight of coal sample = W_{coal} = 2.25 gm

Weight of coal after heating at 105- 110 ^{0}C for 1 hour = 2.13 gm

Weight of coal after heating at 925 $\pm$ 25 ^{0}C for 7 minutes = 1.55 gm

Constant weight of the residue left after igniting = 0.215 gm

W_{coal} = 2.25 gm

Loss in weight of coal after heating at 110 ^{0}C for 1 hour = **$W_{moisture}$** = 2.25 – 2.13
$$= 0.12 \text{ gm}$$

Loss in weight of coal after heating at 925 $\pm$ 25 ^{0}C for 7 minutes = Wt. of volatile matter = **W_{VM}** = 2.13 – 1.55 = 0.58 gm

Constant weight of the residue left after igniting = **W_{Ash}** = 0.215 gm

Therefore,

% of Moisture in coal = $\dfrac{W_{moisture} \times 100}{W_{Coal} \text{ (before heating)}}$ = $\dfrac{0.12 \times 100}{2.25}$ = **5.33 %**

% of volatile matter in coal = $\dfrac{W_{VM} \times 100}{W_{Coal} \text{ (Initial weight)}}$ = $\dfrac{0.58 \times 100}{2.25}$ = **25.77%**

$$\% \text{ of Ash in coal} = \frac{W_{Ash} \times 100}{W_{Coal} \text{ (Initial weight)}} = \frac{0.215 \times 100}{2.25} = 9.55\%$$

% of Fixed Carbon = 100 – (% Moisture + % Volatile matter + % Ash)

= 100 – (5.33 + 25.77 + 9.55) = 100 – 40.65 = **59.35 %**

Results:

% Moisture = 5.33

% Volatile matter = 25.77

% Ash = 9.55

% Fixed carbon = 59.35

Conclusion: Fixed carbon is more than 55 %, hence it is very good quality coal

(b)Ultimate analysis:

1) A 0.5 g of Coal sample on ultimate analysis produced 1.60g of CO_2 & 0.225g of H_2O. Find out the % of C & H of sample.

$$\to \% C = \frac{\text{weight of } CO_2 \times 12}{\text{Initial Weight of Coal Taken} \times 44} \times 100$$

Given,

$$\% C = \frac{1.60 \times 12}{0.5 \times 44} \times 100 = 87.27\%$$

$$\% H = \frac{0.225 \times 2}{0.5 \times 18} \times 100 = 5\%$$

2) 0.2 g of Coal sample was taken & burned in a combustion Appartus & the gaseous products of combustion were ~~approached~~ absorbed in a potash bulb & $CaCl_2$ tube ~~tt~~ which were previously weighted. There was increase in weight of calcium chloride tube by 0.06 g & that of potash bulb by 0.64 g after combustion. Find out the % of C & H of sample.

$$\rightarrow \%C = \frac{Incr.\ in\ KOH \times 12}{weight\ of\ initial\ coal \times 44} \times 100$$

$$\%C = \frac{0.64 \times 12}{0.2 \times 44} \times 100 = 87.27\%.$$

$$\%H = \frac{Incr.\ in\ CaCl_2 \times 2}{Initial\ weight \times 18} \times 100$$

$$= \frac{0.06 \times 2}{0.2 \times 18} \times 100$$

$$\%H = 3.33\%.$$

3.

1 g of coal sample in Kjeldhal's experiment liberated Ammonia which was absorbed in 25 m' of $\frac{N}{5}$ H_2SO_4. The excess of acid required 40ml of $\frac{N}{10}$ NaOH solution for back titration. Find out % of Nitrogen.

$\rightarrow$

$$\underset{Acid}{N_1 V_1} = \underset{Base}{N_2 V_2}$$

$$0.2 \times x = 0.1 \times 40$$

$$x = \frac{4}{0.2} = 20ml$$

Used = 25 − 20 = 5ml

$$\frac{Acid}{Normality} = \frac{1}{5} = 0.2\ N$$

$$\frac{Base}{Normality} = \frac{1}{10} = 0.1 N$$

$$\% N = \frac{\text{volume of Acid used} \times \text{Normality of Acid} \times 1.4}{\text{weight of Coal taken}}$$

$$= \frac{5 \times 0.2 \times 1.4}{1}$$

$$\% N = 1.4\%.$$

4.

0.5g of coal sample was burned completely in a bomb calorimeter. The ash formed was extracted with acid & the extract obtained was treated with barium chloride solution to get barium sulphate precipitate. The weight of dry precipitate was 0.025 g. Calculate the % S in the coal sample.

$$\% S = \frac{0.025 \times 32 \times 100}{0.5 \times 233} = 0.686\%$$

5.

***A coal sample on ultimate analysis gave following results:-

a) 0.5g coal produces 1.35g CO_2 & 0.225g H_2O

b) 0.4g coal in Kjeldhal's experiment liberated ammonia which was absorbed in 50 ml 0.5N H_2SO_4. The resultant solution required 22ml of 1N NaOH solution for complete neutralization.

c) 0.5g on combustion in bomb calorimeter followed by the treatment with $BaCl_2$ produces 0.06g $BaSO_4$ Calculate % of C, H, N, S & O assuming coal. contents 4.5% ash

a) Initial = 0.5
   1.35 = CO_2 & 0.225g H_2O.

$\%C = \dfrac{\text{weight of } CO_2 \text{ formed} \times 12 \times 100}{\text{weight of coal taken} \times 44}$

$= \dfrac{1.35 \times 100}{0.5 \times 44}$

$\%C = 6.136\%.$

$\%H = \dfrac{\text{weight of } H_2O \text{ formed} \times 2 \times 100}{\text{weight of coal taken} \times 18}$

$= \dfrac{0.225 \times 2 \times 100}{0.5 \times 18}$

$\%H = 5\%.$

b) Initial = 0.4 g.

Normal(A) Acid = 0.5
=ity
   Total Vol (A) = 50 ml
   Base NaOH = 22 ml
   Normality (NaOH) = 1 N

$\overset{(A)}{N_1 V_1} = \overset{(B)}{N_2 V_2}$

$0.5 \times x = 1 \times 22$

(unused) $x = \dfrac{22}{0.5} = 44\ ml$

Used = (50 − 44) = 6 ml.

$\%N = \dfrac{\text{Vol. of Acid used} \times \text{Normality} \times 1.4}{\text{weight of coal taken}}$

$= \dfrac{6 \times 0.5 \times 1.4}{0.4}$

$\%N = 10.5\%.$

$\%S = \dfrac{\text{weight of } BaSO_4 \times 32 \times 100}{\text{weight of coal taken} \times 233}$

$= \dfrac{0.06 \times 32 \times 100}{0.5 \times 233}$

$\%S = 1.64\%.$

$\%O = 100 - (\%C + \%H + \%N + \%S + \%ash)$

$= 100 - (6.136 + 5 + 10.5 + 1.64 + 4.5)$

$= 100 - (27.776)$

$\%O = 72.224\%.$

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Oxygen/Air requirement for combustion:

Combustion.

$$\text{Weight of Air Needed} = \left[\frac{32}{12}C + \frac{16}{2}H + S - O\right] \times \frac{100}{23}$$

OR

$$= \left[2.67C + 8H + S - O\right] \times \frac{100}{23}$$

$$\text{Volume of air required} = \frac{\text{weight of air} \times 22.4}{28.94} \; m^3$$

1.

Calculate weight & volume of air required for complete combustion of 5kg of coal with following composition:- C=54% ; H=6.5% ; O_2=3% ; N=1.8%; moisture = 17.3% ; ash = 17.4% (Molecular weight of air = 28.949).

＊＊ when Sulphur is not given in question Take its Value = 0 ＊＊

$$\text{wt of Air Needed} = \left[2.67C + 8H + S - O\right] \times \frac{100}{23}$$

$$= \left[2.67 \times 0.54 + 8 \times 0.065 + 0 - 0.03\right] \times \frac{100}{23}$$

$$= 1.9318 \times \frac{100}{23}$$

$$\text{wt of Air needed} = 8.399 \, kg \; *$$

$$\text{For } 5kg = 8.399 \times 5 = 41.995 \, kg$$

$$\text{volume} = \frac{\text{wt. of Air needed} \times 22.4}{28.949} = \frac{41.995 \times 22.4}{28.94}$$

$$\text{volum of Air} = 32.494 \, m^3$$