

Unit-I - Fuels

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1.1 Introduction

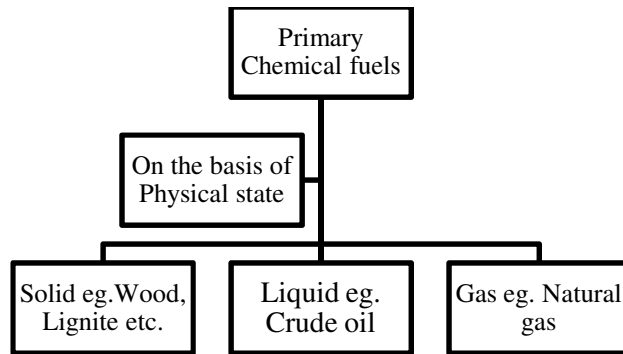
1.1.1 Fuel :- A fuel is any material that can be made to react with other substances so that it releases energy as thermal energy or to be used for work. The concept was originally applied solely to those materials capable of releasing chemical energy but has since also been applied to other sources of heat energy such as nuclear energy (via nuclear fission and nuclear fusion).

1.1.2 Classification of Fuels:- On the basis of requirement of combustion fuels are of two types:

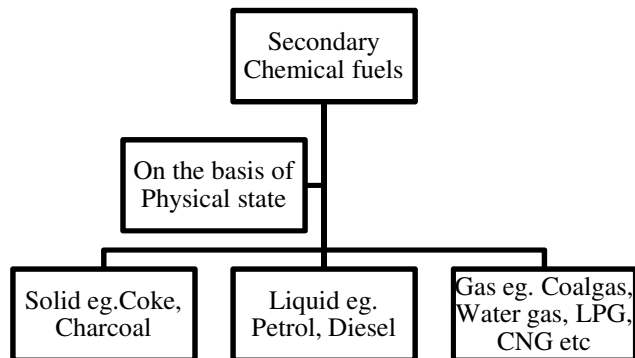
1. Chemical fuels (combustion required) eg. coal, gasoline, LPG etc.
2. Nuclear fuels (combustion not required) eg. Uranium, Plutonium etc.

1.1.3 Chemical fuels:- On the basis of occurrence chemical fuels are of two types:

(A) **Primary chemical fuels** : Fuels which occurs in nature as such and can be used with or without little modification(removal of moisture only) eg. Wood, Crude oil, Natural gas etc.



(B) **Secondary chemical fuels** : Fuels which are derived from primary fuels called secondary fuels eg. Coke, Charcoal, Petrol, diesel, Coal gas, Water gas, LPG, CNG etc.



1.2 Calorific Value (CV) :- It is defined as the total amount of heat energy liberated when unit Quantity (mass /volume) of a substance is completely burnt in presence of oxygen.

1.2.1 Units of Calorific Value (CV) :- Units for solid, liquid and gaseous fuels are :

Table 1:

S. No.	Unit Systems	Units for Solid/Liquid	Units for Gaseous fuels	Definition
1.	C.G.S	Calories/g	Calories/ cm ³	<u>Calorie</u> :- Heat required to raise temp. of 1g of water through 1 °C.
2.	M.K.S	Kilo Calories/Kg	Kilo Calories/ m ³	<u>Kilo Calorie</u> :- Heat required to raise temp. of 1kg of water through 1 °C.
3.	B.T.U	B.T.U/pound	B.T.U/ft ³	<u>B.T.U</u> :- Heat required to raise temp. of 1 Pound of water through 1 °F.
4.	C.H.U	C.H.U/ pound	C.H.U/ft ³	<u>C.H.U</u> :- Heat required to raise temp. of 1 Pound of water through 1 °C.

B.T.U – British Thermal Unit. , C.H.U- Centigrade Heat Unit.

Relationship among various units of Units of Calorific Value (CV):

$$1000 \text{ cal.} = 1 \text{ k.cal.} = 3.969 \text{ B.T.U} = 2.2 \text{ C.H.U}$$

1.2.2 Types of Calorific Value (CV) :- There are two types of Calorific Value (CV) :

- (1) Gross or Higher calorific value (GCV or HCV).
- (2) Net or Lower calorific value (NCV or LCV).

(1) **Gross or Higher calorific value (GCV or HCV) :-** It is defined as the total amount of heat energy liberated when unit quantity (mass /volume) of a substance is completely burnt in presence of oxygen and products of combustion are cooled down to room temperature (15 °C). It is called Gross or Higher calorific value (GCV or HCV) because usually all fuels contains hydrogen (H₂), which on combustion converted in to steam. As the products of combustion (mainly water vapours) are cooled down to room temperature latent heat of condensation is released, which is included in Gross or Higher calorific value(GCV or HCV).

(2) **Net or Lower calorific value (NCV or LCV) :-** It is defined as the net amount of heat energy liberated when unit quantity (mass /volume) of a substance is completely burnt in presence of oxygen and products of combustion are allowed to escape.

Relationship between (GCV or HCV) and (NCV or LCV):

$$\text{NCV or LCV} = \text{GCV or HCV} - \text{Weight of water} \times \text{Latent heat of steam}$$

$$\text{NCV or LCV} = \text{GCV or HCV} - 9 \times \text{H} \times 587$$

Where: **H** = Amount of hydrogen & **587 cal/g** = Latent heat of condensation of steam.

1.2.3 Determination of Calorific Value (C V):-

(1) **For solid and non- volatile liquid fuels:-** Calorific Value (CV) is determined using Bomb Calorimeter.

Principle: - Heat lost = Heat gained

Construction :- It consists of the following parts:

- (i) Central cylindrical bomb: - It is a cylindrical container made up of stainless steel provided with a cap or lid. The lid in turn is provided with two holes for electrodes and one for oxygen valve. The two electrodes are connected to a 6V battery via a key 'K'. A small ring is fitted to one of the electrodes which acts as support for stainless steel crucible.
- (ii) Central cylindrical bomb is placed in copper calorimeter containing known amount of water. The copper calorimeter is provided with electrical stirrer and Beckmann's thermometer.
- (iii) The copper calorimeter is surrounded with air jacket and water jacket to prevent or minimize heat losses.

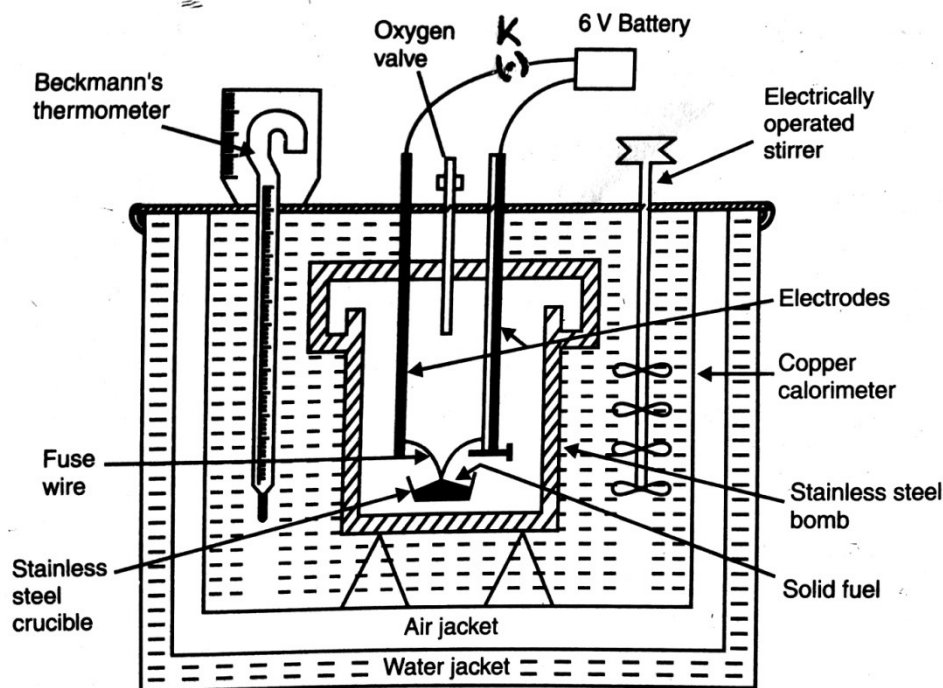


Fig.1

Working: - A known amount of fuel is placed in stainless steel crucible and magnesium (Mg) wires are stretched touching the fuel. The bomb is placed in copper calorimeter containing known amount of water. After thorough mixing with electrical stirrer, note the initial temperature of water. The key is inserted which produces a spark and fuel starts burning. Heat produced due to burning of fuel is transferred to water in calorimeter. After thorough mixing with electrical stirrer, note the final temperature of water.

Calculations: - Let:

Weight of fuel taken = X g

Weight of water in calorimeter = W g

Water equivalent of calorimeter = w_{eq} g

Initial temperature of water = T_1 °C

Final temperature of water = T_2 °C

$$\Delta t = (T_2 - T_1)$$

$$\text{GCV or HCV of fuel} = C \text{ cal/g}$$

Now applying the principle of calorimeter :

$$\text{Heat lost} = \text{Heat gained}$$

$$C \cdot X = \text{Heat gained by water in calorimeter} + \text{Heat gained by calorimeter}$$

$$C \cdot X = W \cdot S_w \cdot \Delta t + M \cdot S_{cal} \cdot \Delta t$$

[where: S_w = specific heat of water, S_{cal} and, M = mean specific heat and mass of calorimeter]

$$C \cdot X = W (T_2 - T_1) + w_{eq} (T_2 - T_1)$$

[where: $S_w = 1$, $M \cdot S_{cal} = w_{eq}$ (Water equivalent of calorimeter)]

$$C \cdot X = (W + w_{eq}) (T_2 - T_1)$$

$$C = \frac{(W + w_{eq})(T_2 - T_1)}{X} \text{ Cal/g} \dots\dots\dots (1)$$

The calorific value obtained by bomb calorimeter is Gross or Higher calorific value(GCV or HCV) because combustion is taking place under closed conditions and products of combustion are not allowed to escape:

$$\text{GCV or HCV} = \frac{(W + w_{eq})(T_2 - T_1)}{X} \text{ Cal/g} \dots\dots\dots (2)$$

$$\text{NCV or LCV} = \frac{(W + w_{eq})(T_2 - T_1)}{X} - 9 \times H \times 587 \text{ Cal/g} \dots\dots\dots (3)$$

Corrections:- For obtaining accurate results following corrections are made:

- (i) Fuse/Mg wire Correction (F.W.C) :- fuel is ignited using fuse/Mg wire so the heat produced by burning of fuse/Mg wire is also included in GCV measured above. Hence this heat is to be subtracted from final formula.
- (ii) Acid Correction (A.C) :- Sulphur and Nitrogen present in the fuel produce H_2SO_4 and HNO_3 . The process of formation of these acids is exothermic and heat evolved is also included in GCV measured above. Hence this heat is to be subtracted from final formula.
- (iii) Cooling Correction (C.C) :- Heating and cooling are simultaneous processes so when temp. rises above room temp. loss of heat occurs due to radiation etc. So highest temp. attained is somewhat less and correction is required.

After applying correction (i),(ii) and (iii) eqn. (3) becomes:

$$\text{GCV} = \frac{(W + w_{eq})[(T_2 - T_1) + C.C] - [(A.C) + (F.W.C)]}{X} \text{ Cal/g} \dots\dots\dots (4)$$

Example 1. The following data were obtained in bomb calorimeter experiment:

Weight of coal burnt = 0.996 g
 Weight of water in calorimeter = 2490 g
 Weight of calorimeter = 3900 g
 Mean specific heat of apparatus = 0.099
 Initial temperature of water = 25°C
 Final temperature of water = 27.592°C

$$\text{GCV or HCV of fuel} = C \text{ cal/g}$$

Solution:

$$T_2 - T_1 = 2.592$$

$$C = \frac{[W + w_{\text{eq.}}](T_2 - T_1)}{X} \text{ Cal/g}$$

$$C = \frac{[2490 + (3900 \times 0.099)](2.592)}{0.996} \text{ Cal/g} = 7484.8 \text{ Cal/g (GCV or HCV)}$$

$$\text{NCV or LCV} = 7484.8 - 0.09 \times 6 \times 587 = 7167.82 \text{ Cal/g}$$

(2) **For volatile liquid and gaseous fuels:-** Calorific Value (CV) is determined using Boy's gas Calorimeter.

Principle: -

$$\text{Heat lost} = \text{Heat gained}$$

Construction: - It consists of following parts:

- (i) A gas burner provided with a meter.
- (ii) The burner is surrounded by a combustion chamber, which has copper tubing inside as well as outside. Through the copper coil, water at constant rate is flown. Water enters from the top of the outer coil, passes through outer coils, moves to bottom of combustion chamber and then moves upwards through inner coils, and exit from the top.
- (iii) Thermometers t_1 and t_2 at water inlet and outlet respectively.
- (iv) A container is provided for collecting water which is formed due to the condensation of steam. The whole assembly is enclosed in an insulated chamber.

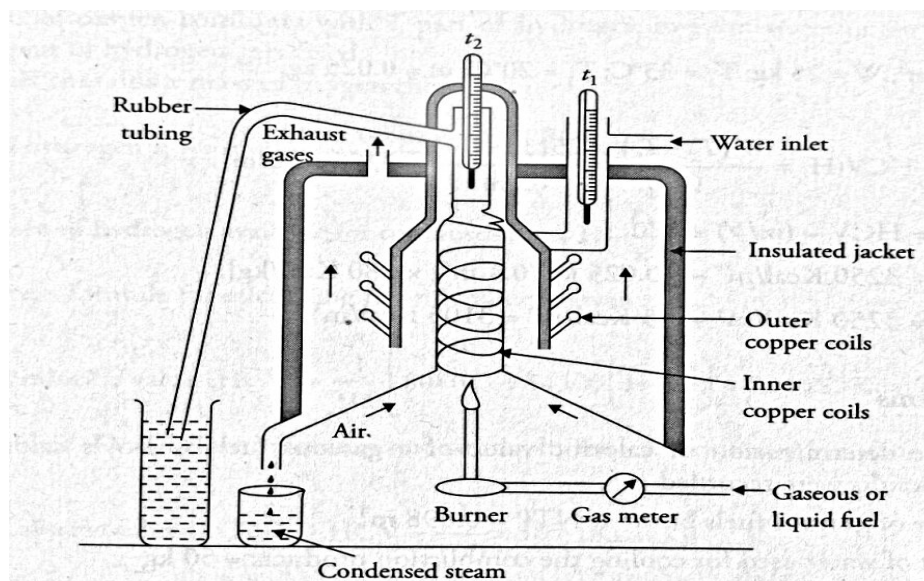


Fig.2

Working:- The calorimeter is pre-heated for 15 minutes. When the calorimeter gets warmed, the rate of flow of water is so adjusted that water leaves the apparatus nearly atmospheric pressure. Heat produced by burning of fuel is transferred to water in copper coils. The steam formed due to combustion of fuel gets condensed to water which is collected. The following readings are noted :

- (i) Volume of gas burnt in time t .
- (ii) Weight of water passed through the copper coil in time t .
- (iii) Temp. of incoming and outgoing water.
- (iv) Weight of water condensed in time t .

Calculations:- Let:

$$\text{Volume of gas burnt in time } t = V \text{ m}^3$$

$$\text{Weight of water passed through the copper coil in time } t = W \text{ Kg}$$

$$\text{Temperature of incoming water} = t_1^{\circ}\text{C}$$

$$\text{Temperature of outgoing water} = t_2^{\circ}\text{C}$$

$$\Delta t = (t_2 - t_1)$$

$$\text{Weight of water condensed in time } t = m \text{ Kg}$$

$$\text{GCV or HCV of fuel} = 'C' \text{ K.cal/ m}^3$$

Now applying the principle of calorimetry:

$$\text{Heat lost} = \text{Heat gained}$$

$$C \cdot V = \text{Heat gained by water circulating in copper coils.}$$

$$C \cdot V = W (t_2 - t_1)$$

$$C = \frac{W (t_2 - t_1)}{V}$$

$$\text{GCV} = \frac{W (t_2 - t_1)}{V}$$

NCV:-

$$\text{Weight of water condensed per m}^3 \text{ of gas} = m/V \text{ Kg}$$

$$\text{Latent heat of steam per m}^3 \text{ of gas} = m \cdot 587/V \text{ K.cal}$$

$$\text{NCV or LCV} = \text{GCV or HCV} - m \cdot 587/V \text{ K.cal/ m}^3$$

Example 2. The following data were obtained in Boy's gas calorimeter experiment:

$$\text{Volume of gas burnt} = 0.09 \text{ m}^3$$

$$\text{Weight of water passed calorimeter} = 25 \text{ kg}$$

$$\text{Weight of water condensed calorimeter} = 0.02 \text{ kg}$$

$$\text{Weight of calorimeter} = 3900 \text{ g}$$

$$\text{Mean specific heat of apparatus} = 0.099$$

$$\text{Temperature of incoming water} = 25^{\circ}\text{C}$$

$$\text{Temperature of outgoing water} = 30^{\circ}\text{C}$$

$$\text{GCV or HCV of fuel} = C \text{ K .cal/m}^3$$

Solution:-

$$T_2 - T_1 = 5$$

$$C = \frac{W (T_2 - T_1)}{V} \text{ K .cal/m}^3$$

$$C = \frac{25 \times 5}{0.09} \text{ Cal/g} = 1388.9 \text{ K .cal/g (GCV or HCV)}$$

$$\text{NCV or LCV} = 1388.9 - \frac{0.02 \times 587}{0.09} = 1258.5 \text{ K .cal/g}$$

1.2.4 Theoretical calculation of Calorific Value (CV) - Dulong's formula:- Calorific Value (CV) can be calculated theoretically if amount or percentage of the constituent elements of the fuel are known. According to Dulong Calorific Value of a fuel is the sum of calorific value of its constituents.

Table 2:

S. No.	Substance	Calorific Value
1.	Carbon	8080
2.	Hydrogen	34500
3.	Sulphur	2240

Dulong's formula: $\text{GCV or HCV} = [C \cdot 8080 + 34500 (H - O_{xy}/8) + S \cdot 2240]$

(where: C, H, O_{xy} & S are the amounts of Carbon, Hydrogen, Oxygen & Sulphur respectively)

or

$$\text{GCV or HCV} = 1/100 [C \cdot 8080 + 34500 (H - O_{xy}/8) + S \cdot 2240]$$

(where: C ,H, O_{xy} & S are the % of Carbon, Hydrogen, Oxygen & Sulphur respectively)

$$\text{NCV or LCV} = \text{GCV or HCV} - 0.09 \cdot H\% \cdot 587 \text{ Cal/g}$$

Example 3 Calculate GCV and NCV of coal sample having following composition:

$$C = 80\% \quad H_2 = 8\% \quad O_2 = 5\% \quad S = 3.4 \quad N_2 = 1.3\% \quad \text{Ash} = 2.3\%$$

Solution: $\text{GCV or HCV} = 1/100 [C \cdot 8080 + 34500 (H - O_{xy}/8) + S \cdot 2240]$

$$\text{GCV or HCV} = 1/100 [80 \cdot 8080 + 34500 (8 - 5/8) + 3.4 \cdot 2240]$$

$$\text{GCV or HCV} = 1/100 [646400 + 254437.5 + 7616] = 9084.5 \text{ K . cal/kg}$$

$$\text{NCV or LCV} = \text{GCV or HCV} - 0.09 \cdot H\% \cdot 587 \text{ K .cal/kg}$$

$$\text{NCV or LCV} = 9084.5 - 0.09 \cdot 8 \cdot 587 \text{ K .cal/kg}$$

$$\text{NCV or LCV} = 9084.5 - 422.64 = 8661.86 \text{ K .cal}$$

1.3 Coal Analysis:- Coal is a widely used solid fuel. The quality of coal is composition dependent so in order to compare the coals the analysis is carried out. Coal is analysed in two ways:

- (1) Proximate analysis.
- (2) Ultimate analysis.

1.3.1 Proximate analysis:- Proximate analysis is an empirical analysis and the results varies with the procedure adopted. The following parameters are determined under proximate analysis:

- (i) **Moisture content :-** It is determined by heating a known amount of air dried coal to 105-110 °C in an electric oven for one hour, cooled in desiccator and weighed. Loss of weight is reported as moisture percentage:

$$\% \text{ of Moisture} = \frac{\text{Loss in weight} * 100}{\text{Weight of coal taken}}$$

Significance:- High moisture content is undesirable in coal because:

- (a) Creates ignition problems.
- (b) Lowers the calorific value.
- (c) Quenches fire in furnace

- (ii) **Volatile Matter content: -** It is determined by heating a known amount of moisture free coal in a covered platinum crucible at 930-970°C for 7 minutes, cooled in dessicator and weighed. Loss of weight is reported as volatile matter percentage:

$$\% \text{ of volatile matter} = \frac{\text{Loss in weight due to volatile matter} * 100}{\text{Weight of coal sample taken}}$$

Significance:- High volatile matter content is undesirable in coal because:

- (a) Fuel burns with smoke, high flames & gives low heating value.
- (b) Lowers the calorific value.

- (iii) **Ash or Residue content: -** It is determined by heating a known amount of moisture & volatile matter free coal in a platinum crucible without covering at 650-750°C for 30 minutes. The residue left after complete combustion is cooled in dessicator and weighed. From the weight of residue percentage is calculated:

$$\% \text{ of Ash or Residue content} = \frac{\text{Weight of residue left} * 100}{\text{Weight of coal sample taken}}$$

Significance:- High Ash or Residue content is undesirable in coal because:

- (a) Lowers the calorific value.
- (b) High amount of ash or residue may restrict the air flow in furnace
- (c) Ash or residue may form clinkers at high temperature.

- (iv) **Fixed Carbon content: -** It simply determined as:

$$\% \text{ of Fixed Carbon} = 100 - [\% \text{ of Moisture} + \% \text{ of volatile matter} + \% \text{ of Ash or Residue}]$$

Significance:- High Carbon content is desirable in coal because:

- (a) Increases the calorific value.
- (b) Helps to reduce size of combustion chamber.

Example 4 A coal sample was analyzed as follows: Exactly 3.0 g was weighed in to a silica crucible. After heating for one hour at 110 °C, the residue weighed 2.925g. The sample was transferred to platinum crucible and

heated covered for exactly 7 minutes at 930-970 °C, the residue weighed 2.252g. The sample was heated uncovered in platinum crucible and for 30 minutes at 650-750 °C, the residue weighed 0.255g.

Solution: Mass of moisture in coal = 3.0 – 2.925 = 0.075g

Mass of volatile matter in coal = 2.925 – 2.252 = 0.673g

Mass of residue = 0.255g

$$\% \text{ of Moisture} = \frac{0.075 \times 100}{3} = 2.5\%$$

$$\% \text{ of Volatile matter} = \frac{0.673 \times 100}{3} = 22.43\%$$

$$\% \text{ of Ash content} = \frac{0.255 \times 100}{3} = 8.5\%$$

$$\% \text{ of Fixed Carbon} = 100 - [2.5 + 22.43 + 8.5]$$

$$\% \text{ of Fixed Carbon} = 100 - 33.43 = 66.57\%$$

1.3.2 Ultimate analysis:- Ultimate analysis is carried out to ascertain the composition of coal which includes estimation of carbon, Hydrogen, Nitrogen, Sulphur & Oxygen etc.

- (i) **Estimation of Carbon & Hydrogen:-** A known amount of coal is taken in combustion tube & burnt in excess of oxygen:



The gaseous products of combustion are passed through bulbs 'A' & 'B' containing known amount of anhydrous CaCl_2 & KOH respectively. The increase in weights of bulbs A & B are weights of H_2O & CO_2 respectively.

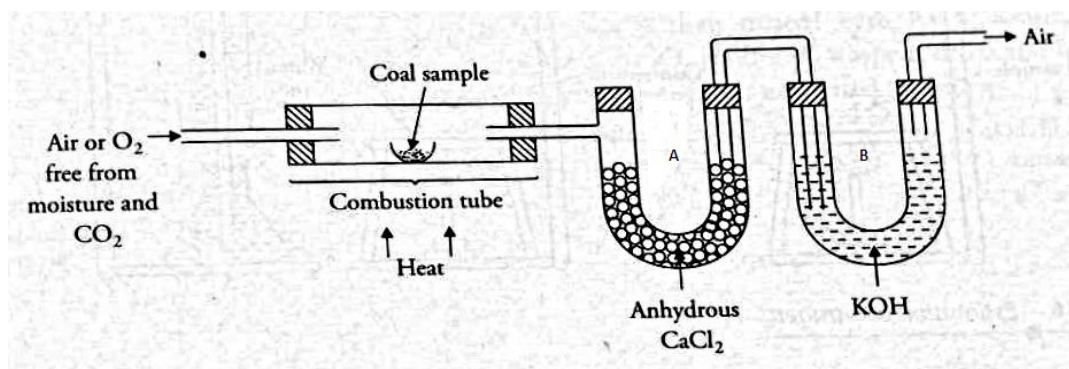


Fig.3



Calculations:-

Let, weight of coal sample taken = Z g

Increase in weight of CaCl_2 bulb 'A' = X g

Increase in weight of KOH bulb 'B' = Y g

Percentage of Carbon:-

$$\% \text{ C} = \frac{12}{44} * \frac{Y * 100}{\text{Weight of coal sample taken}}$$

Percentage of Hydrogen:-

$$\% \text{ H}_2 = \frac{2}{18} * \frac{X * 100}{\text{Weight of coal sample taken}}$$

Significance:- High Carbon & Hydrogen content is desirable in coal because:

- (a) Increases the calorific value.
- (b) Helps to reduce size of combustion.

(ii) **Estimation of Nitrogen (Kjeldhal's Method):-** It is determined by Kjeldhal's method:

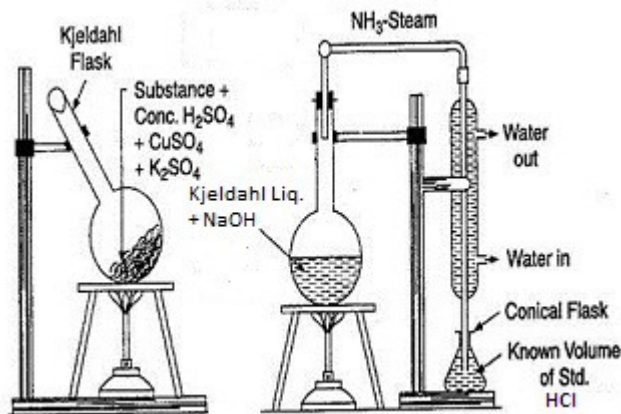


Fig.4

- (a) A known amount of coal sample is heated with conc. H_2SO_4 in presence of K_2SO_4 & CuSO_4 to convert the Nitrogen of fuel in to $(\text{NH}_4)_2\text{SO}_4$.



- (b) The content is then transferred to round bottom flask & heated with NaOH to liberate NH_3 .



- (c) The NH_3 gas thus liberated is absorbed in known volume of standard acid:



The unused acid is then determined by titrating with standard NaOH .

Amount of acid used = Volume of acid taken for absorption – Unused acid

From the volume of acid used % of N₂ can be calculated as:

(d) Calculations:

Let, the weight of coal taken = W g
 Volume of acid used = V₁ mL
 Normality of acid = N₁
 Volume of ammonia formed = V₂ mL
 Normality of ammonia formed = N₂

Applying Normality equation, we have:

$$\begin{array}{ccccccc} \text{N}_1 & \text{V}_1 & = & \text{N}_2 & \text{V}_2 & \dots\dots\dots(1) \\ \text{Acid} & & & \text{NH}_3 & & \end{array}$$

Let's assume ammonia formed in the experiment is unity (N₂ = 1), then equation (1) becomes:

$$\text{N}_1 \text{V}_1 = 1 \times \text{V}_2 \dots\dots\dots(2)$$

$$\text{N}_1 \text{V}_1 = \text{V}_2 \dots\dots\dots(3)$$

As 1000 mL of 1N solution of NH₃ contains NH₃ = 17g and Nitrogen = 14g

$$1\text{mL of } 1\text{N solution of NH}_3 \text{ contains Nitrogen} = \frac{14}{1000} \text{ g}$$

$$\text{V}_2\text{mL of } 1\text{N solution of NH}_3 \text{ contains Nitrogen} = \frac{14}{1000} * \text{V}_2 = \frac{14}{1000} * \text{N}_1\text{V}_1$$

$$\% \text{ N}_2 = \frac{14}{1000} * \frac{\text{N}_1\text{V}_1}{\text{W}} * 100$$

(iii) **Estimation of Sulfur (BaCl₂ Method):-**

(a) A known amount of coal sample is heated with conc. HNO₃ to convert all sulphur of the fuel in to sulfuric acid (H₂SO₄).



(b) The sulfuric acid so formed is treated with BaCl₂ to get white precipitates of BaSO₄.



(c) The reaction mixture is filtered and dry precipitates of BaSO₄ are weighed.

(d) Calculations:

Let, the weight of coal taken = W g
 Weight of BaSO₄ precipitates = X g

233g of BaSO₄ contains Sulphur = 32g (m.wt. of BaSO₄ = 233, Atomic wt. of S = 32)

$$\% S = \frac{32}{233} * \frac{X}{W} * 100$$

- (iv) **Ash or residue content:-** It is determined by the same procedure as used in proximate analysis i.e. by heating a known amount of moisture & volatile matter free coal in a platinum crucible without covering at 650-750°C for 30 minutes. The residue left after complete combustion is cooled in dessicator and weighed. From the weight of residue percentage is calculated:

$$\% \text{ of Ash or Residue content} = \frac{\text{Weight of residue left} * 100}{\text{Weight of coal sample taken}}$$

- (v) **Oxygen :-** It is generally calculated by difference method:

$$\% \text{ of Oxygen} = 100 - [\% C + \% \text{ of H}_2 + \% \text{ of N}_2 + \% \text{ of Ash or Residue}]$$

Example 5 1.56g of coal sample was kjeldahlized and NH₃ gas thus evolved was absorbed in 50 mL of 0.1 N sulphuric acid. After absorption, the excess(residual) of acid required 6.25mL of 0.1 N sodium hydroxide for complete neutralization. 2.60g of the same sample in quantitative analysis gave 0.1755g of BaSO₄. Calculate % of N and S in the sample.

Solution:-

$$\begin{aligned} 6.25 \text{ ml of } 0.1 \text{ N NaOH} &= 6.25 \text{ ml of } 0.1 \text{ N H}_2\text{SO}_4 \\ \therefore \text{ Volume of H}_2\text{SO}_4 \text{ used to} & \\ \text{neutralize NH}_3 \text{ evolved} &= 50 \text{ ml of } .1 \text{ N} - 6.25 \text{ ml of } .1 \text{ N H}_2\text{SO}_4 \\ &= 43.75 \text{ ml of } .1 \text{ N H}_2\text{SO}_4 \\ \text{Percentage of Nitrogen} &= \frac{\text{Vol. of H}_2\text{SO}_4 \text{ used} \times \text{Normality} \times 1.4}{\text{Weight of coal sample taken}} \\ &= \frac{43.75 \times .1 \times 1.4}{1.56} = 3.926\% \\ \text{Percentage of sulphur} &= \frac{\text{wt. of BaSO}_4 \text{ ppt. obtained} \times 32 \times 100}{233 \times \text{wt. of coal sample taken}} \\ &= \frac{0.1755 \times 32 \times 100}{233 \times 2.60} = 0.927\% \end{aligned}$$

1.4 Carbonization:- It is the process of heating of coal in absence of air to sufficiently high temperature to obtain a coherent mass which is hard, rich in carbon, porous & lustrous called coke.

1.4.1 Process of carbonization of coal:-The coal to coke transformation takes place as the coal is heated at sufficient high temperature in absence of oxygen. When the state of fusing is reached, the layer of heated coal softens and fuses. From about 375 C° to 475 C°, the coal decomposes to form plastic layer. Destructive distillation reactions proceed rapidly in the plastic layer with evolution of volatile products. At about 475 C° to 600C°, there is a marked evolution of tar, and aromatic hydrocarbon compounds. The gas and condensable vapour are entrapped in the plastic mass and, as they expand tend to swell it. As the reactions proceed and as the temperature of the fused zone increases, the plasticity of the coal decreases. With continued heating and evolution of the gas the fused layer gradually resolidifies into semi coke having typical, cellular coke structure. The coke at this stage still contains substantial volatile matter. As the temperature increases further beyond 600C°, the destructive distillation reaction continues with the evolution of gas and a little tar. The coke stabilization takes place as the temperature increases from 600C° to 1100C°.

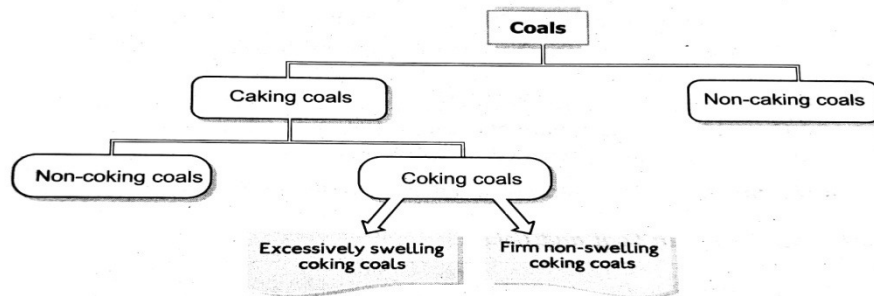


Fig.5

The coal can be classified on basis of carbonization as:

- Caking coals: Those which can be easily converted to coke. These contain sufficient amount of volatile matter i.e. 15-30 %. The caking coals having volatile matter more than 20% are called coking coals and less than 20% are known as non-caking coals.
- Non-Caking coals: Those which can't be converted to coke. These doesn't contain sufficient amount of volatile matter.

1.4.2 Types of Carbonization:- It is mainly of two types:

- Low temperature carbonization (LTC).
- High temperature carbonization (HTC).

Table 3:

S.No.	Characteristic Features	LTC	HTC
A. Process			
1.	Temperature	500-700 C°	1000-1200 C°
2.	Yield	75-80%	65-75%
B. Product(Coke)			
1.	Mechanical Strength	Low	High
2.	Residual volatile matter	5-15%	1-3%
3.	% of Aliphatic hydrocarbons	High	Low
4.	% of Aromatic hydrocarbons	Low	High
5.	Combustion properties	Burns with smokeless flame	Burns with smoky flame
6.	Uses	Used as domestic fuel	Used as metallurgical purpose (as reducing agent & fuel)
C. By-Products (Gases)			
1.	Yield of gases	130-150m ³	300-390m ³
2.	Calorific value of gases	6500-9500 k.Cal/m ³	5400-6000 k.Cal/m ³

1.4.3 Manufacturing of metallurgical coke- Otto Hoffmanns Oven:- It is a chamber oven in which coke is manufactured with number of gaseous by-products. In order to save the fuel for heating purpose and 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.

Principle:- It works on the principle of heat economy or regenerative principle i.e. utilization of heat of flue gases for heating of checker work system of silica bricks. The heat economy is achieved by changing the direction of flow of gases in each and every 30 minutes.

Construction:- The oven consists of a number of narrow rectangular chambers made up of silica bricks, each about 12 -14 m long, 4-5 m tall and 0.45-0.5 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 (Coal), a gas off take and a refractory lined cast iron door at bottom for coke discharge. The chambers are then surrounded by an insulating boundary wall provided with a checker work system of silica bricks for inlet of fuel gases and outlet of flue gases (exhaust gases).

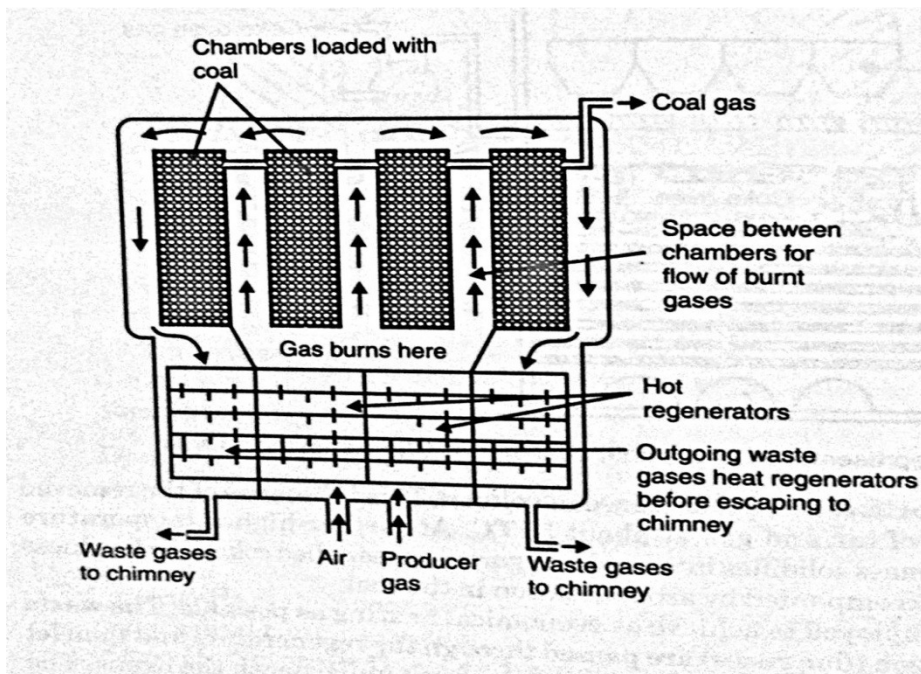


Fig.6

Working:- 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 checker work system of ovens is preheated to $1200\text{ }^{\circ}\text{C}$ then mixture of air and producer gas ($\text{CO} + \text{N}_2$) is allowed to enter. The preheated checker work system ignites the mixture of air and producer gas ($\text{CO} + \text{N}_2$) and generates a lot of heat and flue gases. The hot flue gases heats up coal in the chambers & outlet checker work system before escaping. The process of carbonization starts at walls, takes place layer by layer and proceeds towards centre. 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:-

- (i) Recovery of tar: The coke oven gas is first passed through a tower in which liquar ammonia is sprayed. Tar and dust are soluble in ammonia and hence get collected in a tank.

- (i) Recovery of ammonia: The coke oven gas is passed through another tower in which water at room temperature is sprayed. Gaseous ammonia goes into solution as NH_4OH .
- (ii) Recovery of naphthalene: After recovering ammonia, the remaining gases are led through another tower where water at low temperature is sprayed and naphthalene gets condensed.
- (iii) Recovery of benzene: The resultant gas from the previous step is sprayed with petroleum whereby benzene and its homologues can be recovered.
- (iv) Recovery of H_2S : The gases are then passed through a purifier, packed with moist Fe_2O_3 . Hydrogen sulphide is retained here.

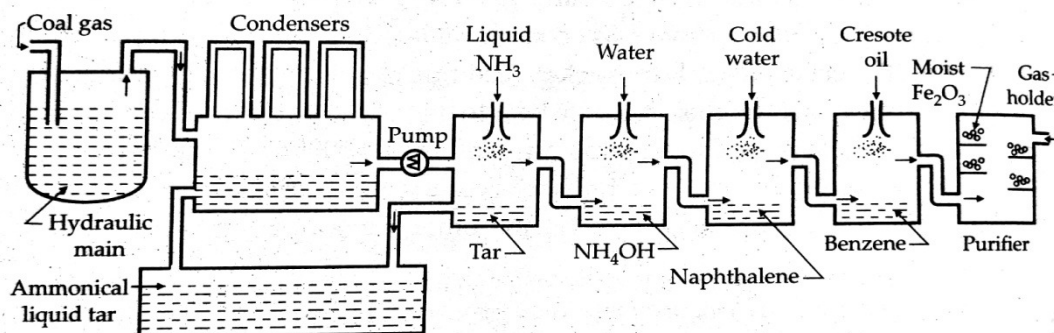


Fig.7

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



There are two methods of cracking in use:

1. Thermal cracking
2. Catalytic cracking

1. 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.

- (a) **Liquid-phase thermal cracking**: The heavy oil or gas oil stock is cracked at a suitable temperature of $475\text{--}530^\circ\text{C}$ and under pressure of 100 kg/cm^2 . 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.
- (b) **Vapour-phase thermal cracking**: The cracking oil is first vapourised and then cracked at about $600\text{--}650^\circ\text{C}$ and under a low pressure of $10\text{--}20 \text{ kg/cm}^2$. 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.

2. **Catalytic cracking**:-The quality and yield of gasoline produced by cracking can be greatly improved by using a suitable catalyst like aluminum silicate $[\text{Al}_2(\text{SiO}_3)_3]$ or alumina $[\text{Al}_2\text{O}_3]$.

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 some of 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.

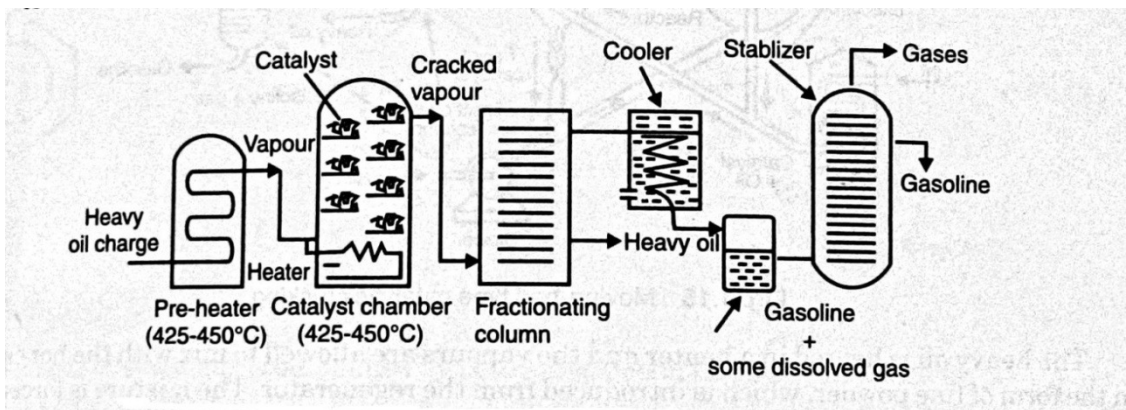


Fig.8

- (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.

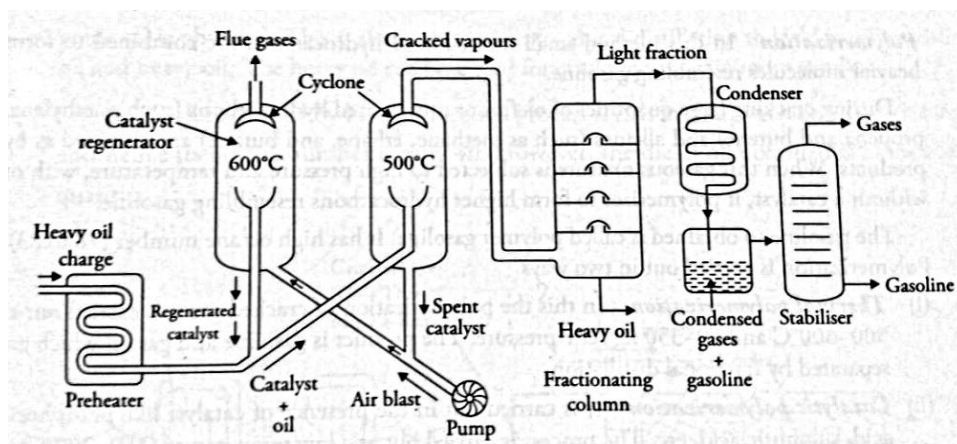


Fig.9

1.6 Knocking:- In an internal combustion engine, a mixture of gasoline (petroleum) vapours 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.

1.6.1 Octane Ratings:- 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, $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$, 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.

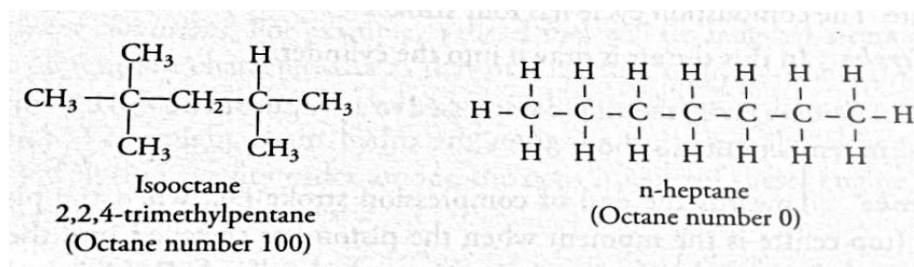
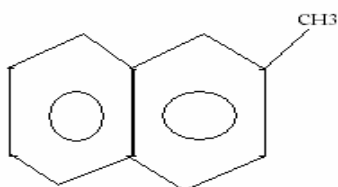


Table 4:

S.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.

1.6.2 Cetane Ratings:-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.



α - methyl naphthalene
Cetane number=0



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.

1.7 Combustion

Combustion is an exothermic chemical reaction, which is accompanied by development of heat and light at a rapid rate, temperature rises considerably. During the process of combustion of a fuel, the atoms of hydrocarbons combine with oxygen with the simultaneous liberation of heat at a rapid rate. This energy is liberated due to the formation of new compounds having less energy and the energy released during the combustion process is the difference in the energy of the reactants and that of the product formed.



For example, combustion of carbon in oxygen:



For proper combustion, the substance must be brought to its kindling (or) ignition temperature, which may be defined as the minimum temperature at which the substance ignites and burns without further addition of heat from outside.

1.7.1 Factors affecting the rate of combustion

The rate of combustion depends on the following factors:

1. The concentration of the fuel and air.
2. The nature of the combustible substance
3. The temperature
4. With increase in pressure or surface area of the fuel the rate of combustion can be increased.
5. It increases within increase in pressure of air.
6. It Increases with preheating of fuel and air

1.7.2 Theoretical Calculation of Minimum Air required for Combustion

In order of achieve efficient combustion of fuel, it is essential that the fuel is brought into intimate contact with sufficient quantity of air to burn all the combustible matter under appropriate conditions.

The correct conditions are:

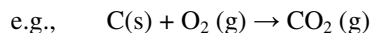
- I. Intimate mixing of air with combustible matter, and
- II. Sufficient time to allow the combustion process to be completed.

If these factors are inappropriate, inefficient combustion occurs.

The elements usually present in common fuels which enter into the process of combustion are mainly **C, H, S and O**. Whereas, nitrogen, ash and CO₂ (if any) present in the fuel are incombustible matters and hence they do not take any oxygen during combustion.

To find the amount of oxygen and hence, the amount of air required for the combustion of a unit quantity of a fuel, it is necessary to apply the following chemical principles:

- "Substances always combine in definite proportions. These proportions are determined by their molecular masses." For example, for the combustion of carbon, the combustion equation is:



Mass proportions 12 32 44

This indicates that mass proportions of carbon, oxygen and carbon dioxide are (12: 32: 44). This means 12 gm of carbon requires 32 gm of oxygen and 44 gm of CO_2 is formed after combustion.

- 22.4 L of any gas at 0°C and 760 mm pressure (i.e., at STP) has a mass equal to its 1 mol. Since the molar mass of O_2 is 32 gm thus, 22.4 L of O_2 at STP will have a mass of 32 gm.
- Air contains 21 % of oxygen by volume; and 23 % of oxygen by mass. Hence from the amount of oxygen required by the fuel the amount of air can be calculated. For instance,

$$1 \text{ Kg of oxygen is supplied by } \frac{1 \times 100}{23} = 4.35 \text{ Kg of air}$$

$$1 \text{ m}^3 \text{ of oxygen is supplied by } \frac{1 \times 100}{21} = 4.76 \text{ m}^3 \text{ of air}$$

- 28.94 gmol^{-1} is taken as molar mass of air.
- Minimum oxygen required for combustion = Theoretical oxygen required — oxygen present in the fuel
- Minimum O_2 required should be calculated on the basis of complete combustion. If the combustion products contain CO and O_2 , then excess O_2 is found by subtracting the amount of O_2 required to burn CO to CO_2 .
- The mass of any gas can be converted to its volume at certain temperature and pressure by assuming that the gas behaves ideally and using the gas equation:

$$PV = nRT$$

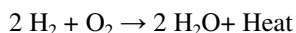
where P = Pressure of gas in atmosphere;

V = volume of gas in Litres;

N = number of moles of the gas and

T = Temperature on Kelvin scale

- The total amount of hydrogen is either present in the combined form (i.e., as H_2O) or free form. Combined hydrogen is a non-combustible substance. Hence it does not take part in combustion. The rest of hydrogen called available hydrogen only take part in combustion reaction.



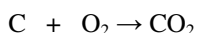
Mass proportions 4 32

Now 1 part of hydrogen combines chemically with 8 parts by mass of oxygen so the available hydrogen

$$= [\text{Mass of hydrogen} - (\frac{\text{Mass of oxygen}}{8})]$$

The most commonly involved combustion reactions are as follows:

a) Combustion of Carbon



12 32 44 (by weight)

12 parts by weight of carbon require 32 parts by weight of oxygen for complete combustion.

(or)

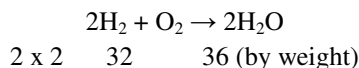
1 part by volume of carbon requires 1 part by volume of oxygen for complete combustion.

∴ **X** parts by weight of carbon require $= \frac{32X}{12}$ parts by weight of O₂

b) Combustion of Hydrogen

Oxygen when present in the fuel is always in combination with hydrogen. So, the quantity of hydrogen in combination with oxygen, which is present in the fuel, will not take part in the combustion reaction. Therefore, the quantity of hydrogen in combination with oxygen is deduced from the total hydrogen in the fuel.

Now, the quantity of hydrogen available for combustion reaction will be, $H - \frac{O}{8}$ where H is the total quantity of hydrogen and O is the total quantity of oxygen in the fuel. (In water the quantity of hydrogen in combination with oxygen is one-eighth of the weight of oxygen).



4 parts by weight of hydrogen require 32 parts by weight of oxygen for complete combustion.

(or)

2 parts by volume of hydrogen require 1 part by volume of oxygen for complete combustion.

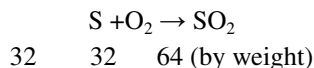
∴ **H** parts by weight of hydrogen requires $= \frac{32H}{4}$ parts by weight of O₂

But, some of the hydrogen is present in the combined form with oxygen (i.e. as H₂O). This combined hydrogen does not take part in the combustion reaction. Therefore, the quantity of combined hydrogen must be deduced from the total hydrogen in the fuel.

∴ $H - \frac{O}{8}$ part by weight of hydrogen requires

$$\frac{[H - \frac{O}{8}] \times 32}{4} = 8[H - \frac{O}{8}] \text{ parts by weight of O}_2$$

c) Combustion of Sulphur



32 parts by weight of sulphur requires 32 parts by weight of oxygen for complete combustion.

(or)

1 part by volume of sulphur requires 1 part by volume of oxygen for complete combustion.

$\therefore S$ parts by weight of sulphur requires = $\frac{32 \times S}{32} = S$ parts by weight of O_2

Consequently, theoretical amount of oxygen required for the complete combustion of 1 kg of solid or liquid fuel.

Theoretical minimum O_2 = $\left[\frac{32}{12} \times C + 8\left(H - \frac{O}{8}\right) + S \right]$ kg

Since mass % of O_2 in air is 23, the amount of air required theoretically for combustion of 1 kg of the fuel is,

Air (theoretical) = $\frac{100}{23} \left[\frac{32}{12} \times C + 8\left(H - \frac{O}{8}\right) + S \right]$ kg

Volume of Air Required for Complete Combustion of Gaseous Combustible Matters

a) $H_2(g) + 1/2O_2 \rightarrow H_2O$

1 vol 0.5 vol

1 volume of H_2 (g) requires 0.5 volume of oxygen

b) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

1 vol 2 vol

1 volume of CH_4 requires 2.0 volume of oxygen

c) $CO(g) + 1/2O_2 \rightarrow CO_2$

1 vol 0.5 vol

1 volume of CO requires 0.5 volume of oxygen

d) $C_2H_4(g) + 3O_2 \rightarrow 2CO_2 + 2H_2O$

1 vol 3 vol

1 volume of C_2H_4 (g) requires 3.0 volume of oxygen

Amount of O_2 required by the fuel will be given by subtracting the amount of O_2 already present in the fuel from the total or theoretical amount of O_2 required by the fuel.

1.3 Excess

air for
combustion

It is
necessary

Net amount of O_2 required = Total amount of O_2 required $- O_2$ already present in the fuel

Total amount of O_2 required = Sum of the amounts of oxygen required by the individual combustible constituent present in the fuel

to supply excess air for complete combustion of the fuel. It is found out from the theoretical amount of air as follows.

The amount of air required if excess air is supplied =

$$\frac{\text{Theoretical amount of air}}{100} \times [100 + \% \text{ of excess air}]$$

Table 5: Procedure of combustible calculations

Fuel Constituent	Amount	Combustion reaction	Wt. of O_2 needed (gm)	Volume of O_2 needed
C	(x gm or m^3)	$C + O_2 \rightarrow CO_2$	$x \times \frac{32}{12} = a$	$x \times 1 = A$
H_2	(y gm or m^3)	$H_2 + 0.5O_2 \rightarrow H_2O$	$y \times \frac{16}{2} = b$	$y \times 0.5 = B$
CO	(z gm or m^3)	$CO + 0.5O_2 \rightarrow CO_2$	$z \times \frac{16}{28} = c$	$z \times 0.5 = C$
S	(p gm or m^3)	$S + O_2 \rightarrow SO_2$	$p \times \frac{32}{32} = d$	$p \times 1 = D$
CH_4	(q gm or m^3)	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	$q \times \frac{2 \times 32}{16} = e$	$q \times 2 = E$
Total O_2 needed			$t = a + b + c + d + e$	$T = A + B + C + D + E$
Less O_2 in fuel			$= - w \text{ gm}$	$= - w \text{ m}^3$
Net O_2 needed			$= t - w$	$= T - w$

(i) Since air has 23% by weight O_2

Minimum weight of air needed for complete combustion

$$\text{Net } O_2 \times \frac{100}{23} \text{ gm}$$

(ii) As air has 21% by volume O_2 ,

so, minimum volume of air needed for complete combustion

$$\text{Net } O_2 \times \frac{100}{21} \text{ m}^3$$

(iii) Conversion of volume into weight

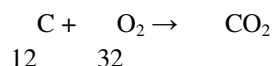
$$1\text{m}^3 = 1000 \text{ L}$$

And for air $1\text{L} \times \left(\frac{\text{mol}}{22.4 \text{ L}}\right) \times \left(\frac{28.94 \text{ g}}{\text{mol}}\right)$

Thus $1\text{L} = \frac{28.94}{22.4} \text{ gm}$

Example 6 Calculate the weight and volume of air required for combustion of 1 kg of carbon.

Carbon undergoes combustion according to the equation



Thus, weight of O₂ required for combustion of 12 gm of carbon = 32 gm

weight of oxygen required by 1 kg of carbon = $\frac{32}{12} \text{ kg}$

weight of air (containing 23% O₂) required = $\frac{100}{23} \times \frac{32}{12} = 11.59 \text{ kg}$

Now, since 32 gm (1 mole) of oxygen occupies 22.4 litres at NTP

$\therefore \frac{32}{12} \times 1000 \text{ gm O}_2 \text{ will occupy} = \frac{22.4}{32} \times \frac{32}{12} \times 1000 = 1866.67 \text{ L}$

So, volume of air (containing 21% oxygen) required

$= \frac{100}{21} \times 1866.67 = 8888.89 \text{ Litres}$

$= 8888.89 \text{ L} \times \frac{1 \text{ m}^3}{1000 \text{ L}} = 8.88 \text{ m}^3$

Example 7 A gas has the following composition by volume:

H₂ = 30%; CH₄ = 5%; CO = 20%; CO₂ = 6%; O₂ = 5% and N₂ = 34%.

If 50% excess air is used, find the weight of air actually supplied per m³ of this gas. Given molecular weight of air = 28.97.

Solution: In one m³ of the gas

Composition of components	Combustion reactions	Volume of O ₂ needed
H ₂ (30%) = 0.3 m ³	H ₂ + 0.5O ₂ → H ₂ O	0.3 x 0.5 = 0.15 m ³
CH ₄ (5%) = 0.05 m ³	CH ₄ + 2O ₂ → CO ₂ + 2 H ₂ O	0.05 x 2 = 0.1 m ³
CO (20%) = 0.2 m ³	CO + 0.5O ₂ → CO ₂	0.2 x 0.5 = 0.1 m ³
O ₂ (5%) = 0.05 m ³		Total = 0.35 m ³
		Less O ₂ in fuel gas = - 0.05 m ³
		Net O ₂ needed = 0.3 m ³ = 300 L

Volume of air required for 1 m³ of gas using 50% excess air

$$= 300 \times \frac{100}{21} \times \frac{150}{100} = 2142.8\text{L}$$

Hence, weight of air actually supplied per m³ of the gas

$$= 2142.8\text{L} \times \left(\frac{1 \text{ mol}}{22.4\text{L}}\right) \times \left(\frac{28.97\text{gm}}{\text{mol}}\right) = 2771 \text{ gm}$$

Example 8 The % analysis by volume of producer gas is H₂=18.3%, CH₄=3.4%, CO=25.4%, CO₂=5.1%, N₂=47.8%. Calculate the volume of air required per m³ of the gas.

Solution: Volume of constituents in 1 m³ of producer gas and oxygen needed combustion can be calculated as:

Composition (m ³)	Combustion equation	Volume of O ₂ needed (m ³)
H ₂ = $1 \times \frac{18.3}{100} = 0.183$	H ₂ + 0.5O ₂ → H ₂ O	0.183 x 0.5 = 0.0915
CH ₄ = $1 \times \frac{3.4}{100} = 0.034$	CH ₄ + 2O ₂ → CO ₂ + 2 H ₂ O	0.034 x 2 = 0.068
CO = $1 \times \frac{25.4}{100} = 0.254$	CO + 0.5O ₂ → CO ₂	0.254 x 0.5 = 0.127
Total volume of O ₂ needed		0.0915+ 0.068 + 0.127 =0.2865 m ³

The volume of air required per m³ of producer gas

$$= 0.2865 \times \frac{100}{21} \text{m}^3 = \mathbf{1.364 \text{ m}^3}$$

Example 9 A Petroleum gas has the following composition:

Ethane = 5%, propane = 10%, butane = 40%, Butene = 10%, Isobutane = 30%, propene = 5%.

Calculate the volume of air required for complete combustion of 100 m³ of the gas and the percentage composition of the dry flue gases if 35% excess air is supplied.

Solution:

Fuel Constituent	Amount in 100 m ³	Combustion reaction	Volume of O ₂ needed for combustion (m ³)	Volume of dry product (CO ₂) of combustion
1. Ethane (C ₂ H ₆)	$100 \times \frac{5}{100} = 5$	C ₂ H ₆ + $\frac{7}{2}$ O ₂ → 2CO ₂ + 3H ₂ O 1m ³ 3.5m ³	5 × 3.5 = 17.5	5 × 2 = 10
2. Propane (C ₃ H ₈)	$100 \times \frac{10}{100} = 10$	C ₃ H ₈ + 5O ₂ → 3CO ₂ + 4H ₂ O 1m ³ 5m ³	10 × 5 = 50	10 × 3 = 30

3.	Butane (C ₄ H ₁₀)	$100 \times \frac{40}{100} = 40$	$\text{C}_4\text{H}_{10} + \frac{13}{2}\text{O}_2 \rightarrow 4\text{CO}_2 + 5\text{H}_2\text{O}$ $1\text{m}^3 \quad 6.5\text{m}^3$	$40 \times 6.5 = 260$	$40 \times 4 = 160$
4.	Butene (C ₄ H ₈)	$100 \times \frac{10}{100} = 10$	$\text{C}_4\text{H}_8 + 6\text{O}_2 \rightarrow 4\text{CO}_2 + 4\text{H}_2\text{O}$ $1\text{m}^3 \quad 6\text{m}^3$	$10 \times 6 = 60$	$10 \times 4 = 40$
5.	Isobutane (C ₄ H ₁₀)	$100 \times \frac{30}{100} = 30$	$\text{C}_4\text{H}_{10} + \frac{13}{2}\text{O}_2 \rightarrow 4\text{CO}_2 + 5\text{H}_2\text{O}$ $1\text{m}^3 \quad 6.5\text{m}^3$	$30 \times 6.5 = 195$	$30 \times 4 = 120$
6.	Propene (C ₃ H ₆)	$100 \times \frac{5}{100} = 5$	$\text{C}_3\text{H}_6 + \frac{9}{2}\text{O}_2 \rightarrow 3\text{CO}_2 + 3\text{H}_2\text{O}$ $1\text{m}^3 \quad 4.5\text{m}^3$	$5 \times 4.5 = 22.5$	$5 \times 3 = 15$
			Net = Total	x = 605 m ³	z = 375

Net Vol. of air required for combustion = $605 \times \frac{100}{21} = 2880.95 \text{ m}^3$

Total Vol. of air required for combustion, if 35% excess air is supplied

$$y = 2880.95 \times \frac{135}{100} = 3889.29 \text{ m}^3$$

Dry flue gas analysis:

(i) $\text{O}_2 = 35\% \text{ of } x = \frac{35}{100} \times 605 = 211.75 \text{ m}^3$

(ii) $\text{N}_2 = 79\% \text{ of } y = \frac{79}{100} \times 3889.29 = 3072.54 \text{ m}^3$

(iii) $\text{CO}_2 = 375 \text{ m}^3$

(iv) Total Vol. of dry products of combustion = $\text{O}_2 + \text{N}_2 + \text{CO}_2 = 3659.29 \text{ m}^3$

$$\% \text{O}_2 = \frac{211.75}{3659.29} \times 100 = 5.79$$

$$\% \text{N}_2 = \frac{3072.54}{3659.29} \times 100 = 83.97$$

$$\% \text{CO}_2 = \frac{375}{3659.29} \times 100 = 10.25$$

Applications of Chemical Fuels:-

Solid fuel:- Solid fuel refers to various types of solid material that are used as fuel to produce energy and provide heating, usually released through combustion. Solid fuels include wood, charcoal, peat, coal, hexamine fuel tablets, and pellets made from wood (see wood pellets), corn, wheat, rye and other grains. Solid-fuel rocket technology also uses solid fuel (see solid propellants). Solid fuels have been used by humanity for many years to create fire. Coal was the fuel source which enabled the industrial revolution, from firing furnaces, to running steam engines and most widely used solid fuel.. Wood was also extensively used to run steam locomotives. Both peat and coal are still used in electricity generation today. The use of some solid fuels (e.g. coal) is restricted or prohibited in some urban areas, due to unsafe levels of toxic emissions. The use of other solid fuels as wood is decreasing as heating technology and the availability of good quality fuel improves. In some areas, smokeless coal is

often the only solid fuel used. In Ireland, peat briquettes are used as smokeless fuel. They are also used to start a coal fire.

Liquid fuels:- Liquid fuels are combustible or energy-generating molecules that can be harnessed to create mechanical energy, usually producing kinetic energy. They must also take the shape of their container; the fumes of liquid fuels are flammable, not the fluids. Most liquid fuels in widespread use are derived from the fossilized remains of dead plants and animals by exposure to heat and pressure inside the Earth's crust. However, there are several types, such as hydrogen fuel (for automotive uses), ethanol, jet fuel and bio-diesel, which are all categorized as liquid fuels. Emulsified fuels of oil in water, such as orimulsion, have been developed as a way to make heavy oil fractions usable as liquid fuels. Many liquid fuels play a primary role in transportation and the economy.

Some common properties of liquid fuels are that they are easy to transport and can be handled easily. They are also relatively easy to use for all engineering applications and in home use. Fuels like kerosene are rationed in some countries, for example in government-subsidized shops in India for home use.

Conventional diesel is similar to gasoline in that it is a mixture of aliphatic hydrocarbons extracted from petroleum. Kerosene is used in kerosene lamps and as a fuel for cooking, heating, and small engines. Natural gas, composed chiefly of methane, can only exist as a liquid at very low temperatures (regardless of pressure), which limits its direct use as a liquid fuel in most applications. LP gas is a mixture of propane and butane, both of which are easily compressible gases under standard atmospheric conditions. It offers many of the advantages of compressed natural gas (CNG) but is denser than air, does not burn as cleanly, and is much more easily compressed. Commonly used for cooking and space heating, LP gas and compressed propane are seeing increased use in motorized vehicles. Propane is the third most commonly used motor fuel globally.

Fuel gas:- Fuel gas is any one of a number of fuels that are gaseous under ordinary conditions. Many fuel gases are composed of hydrocarbons (such as methane or propane), hydrogen, carbon monoxide, or mixtures thereof. Such gases are sources of potential heat energy or light energy that can be readily transmitted and distributed through pipes from the point of origin directly to the place of consumption. Fuel gas is contrasted with liquid fuels and from solid fuels, though some fuel gases are liquefied for storage or transport. While their gaseous nature can be advantageous, avoiding the difficulty of transporting solid fuel and the dangers of spillage inherent in liquid fuels, it can also be dangerous. It is possible for a fuel gas to be undetected and collect in certain areas, leading to the risk of a gas explosion. For this reason, odorizers are added to most fuel gases so that they may be detected by a distinct smell. The most common type of fuel gas in current use is natural gas.

Biofuels:- Biofuel can be broadly defined as solid, liquid, or gas fuel consisting of, or derived from biomass. Biomass can also be used directly for heating or power—known as biomass fuel. Biofuel can be produced from any carbon source that can be replenished rapidly e.g. plants. Many different plants and plant-derived materials are used for biofuel manufacture.

Perhaps the earliest fuel employed by humans is wood. Evidence shows controlled fire was used up to 1.5 million years ago at Swartkrans, South Africa. It is unknown which hominid species first used fire, as both *Australopithecus* and an early species of *Homo* were present at the sites. As a fuel, wood has remained in use up until the present day, although it has been superseded for many purposes by other sources. Wood has an energy density of 10–20 MJ/kg.

Recently biofuels have been developed for use in automotive transport (for example Bioethanol and Biodiesel), but there is widespread public debate about how carbon efficient these fuels are.

Fossil fuels:- Fossil fuels are hydrocarbons, primarily coal and petroleum (liquid petroleum or natural gas), formed from the fossilized remains of ancient plants and animals^[12] by exposure to high heat and pressure in the absence of oxygen in the Earth's crust over hundreds of millions of years. Commonly, the term fossil fuel also includes hydrocarbon-containing natural resources that are not derived entirely from biological sources, such as tar sands. These latter sources are properly known as *mineral fuels*.

Fossil fuels contain high percentages of carbon and include coal, petroleum, and natural gas. They range from volatile materials with low carbon:hydrogen ratios like methane, to liquid petroleum to nonvolatile materials composed of almost pure carbon, like anthracite coal. Methane can be found in hydrocarbon fields, alone, associated with oil, or in the form of methane clathrates. Fossil fuels formed from the fossilized remains of dead plants^[12] by exposure to heat and pressure in the Earth's crust over millions of years. This biogenic theory was first introduced by German scholar Georg Agricola in 1556 and later by Mikhail Lomonosov in the 18th century.

It was estimated by the Energy Information Administration that in 2007 primary sources of energy consisted of petroleum 36.0%, coal 27.4%, natural gas 23.0%, amounting to an 86.4% share for fossil fuels in primary energy consumption in the world. Non-fossil sources in 2006 included hydroelectric 6.3%, nuclear 8.5%, and others (geothermal, solar, tidal, wind, wood, waste) amounting to 0.9%. World energy consumption was growing about 2.3% per year.

Fossil fuels are non-renewable resources because they take millions of years to form, and reserves are being depleted much faster than new ones are being made. So we must conserve these fuels and use them judiciously. The production and use of fossil fuels raise environmental concerns. A global movement toward the generation of renewable energy is therefore under way to help meet increased energy needs. The burning of fossil fuels produces around 21.3 billion tonnes (21.3 gigatonnes) of carbon dioxide (CO₂) per year, but it is estimated that natural processes can only absorb about half of that amount, so there is a net increase of 10.65 billion tonnes of atmospheric carbon dioxide per year (one tonne of atmospheric carbon is equivalent to 44/12 or 3.7 tonnes of carbon dioxide). Carbon dioxide is one of the greenhouse gases that enhances radiative forcing and contributes to global warming, causing the average surface temperature of the Earth to rise in response, which the vast majority of climate scientists agree will cause major adverse effects.

Questions:-

Short answer type questions

1. Define a fuel.
2. What are the advantages and disadvantages of solid fuels?
3. What are the requirements of good fuel?
4. What are GCV and NCV of a fuel?
5. What is carbonization?
6. How is coke superior to coal?
7. What is cracking?
8. What is knocking? How is it rectified?
9. What is octane number? How is it improved?
10. What is water gas? Mention its chemical composition.
11. Define cetane number.
12. What is meant proximate and ultimate analysis?

Long answer type questions

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 byproducts.
3. Describe the proximate and ultimate analysis of coal and their significance.
4. What is cracking? How is it useful in the preparation of synthetic petrol?
5. What are the characteristics of good metallurgical coke?
6. How will you determine the calorific value of fuel by using Bomb calorimeter?
7. Discuss the calculation of minimum air requirement for the complete combustion.
8. Explain the theoretical principles of combustion of fuel.

9. The percentage composition of a sample of bituminous coal, by weight was found to be C=76%, H=5.2%, O=12.8%, N=2.7%, S=1.2%, ash=2.1%. Calculate the minimum (a) weight and (b) volume at NTP of air necessary for complete combustion of 1 Kg coal and percentage composition by weight of dry products.
10. The percentage composition of a sample of anthracite coal, by weight was found to be C=90%, H=3.5%, O=3%, N=1%, S=0.5%, and the remaining being ash. Estimate the minimum weight of air required for complete combustion of 1 Kg of this fuel and the composition of dry products of combustion, by volume, if 50% excess air is supplied.

Assignments:-

Assignment-1

1. Calculate the gross and net calorific value of a coal sample from the following data obtained from bomb calorimeter. Weight of coal 0.73 g, weight of water in the calorimeter 1500 g, water equivalent in calorimeter 470 g, initial temp 25 °C and final temp 28°C, percentage of hydrogen in coal 2.5% and latent heat of steam 587 cal/g.
2. On burning 0.83 g of a solid fuel in a bomb calorimeter, the temperature of 3500 g of water increased from 25.50°C to 29.20°C. Water equivalent of calorimeter is 385 g and latent heat of steam is 587 cal/g. Calculate the gross and net calorific values if Acid correction is 60 cal, fuse wire correction is 10 cal, cooling correction 0.02°C and percentage of hydrogen in fuel is 0.7%.
3. A sample of coal has following composition by mass C = 70 %, O = 8 %, H = 10 %, N = 3 %, S = 2%, Ash = 7 %. Calculate H.C.V. and L.C.V. using Dulong's formula.
4. Calculate the gross and net calorific value of a coal sample from the following data obtained from Boy's gas calorimeter. Volume of gas used 0.1 m³, weight of water passed 24 kg, temperature of incoming water 25 °C, temperature of outgoing water 35 °C, weight of water condensed 0.030 kg and latent heat of steam 587 cal/g.
5. Calculate the gross and net calorific value of a coal using Dulong's formula which analyses: C 74%, H 6%, N 1%, O 9%, S 0.8%, moisture 2.2% and ash 8%.
6. The proximate analysis of coal is: Moisture 2.4%, Volatile Matter 29.4%, Fixed Carbon 58%, Ash 9.7% and Sulphur 0.5%. Its gross calorific value is 7650 Kcal/Kg. Calculate proximate analysis and calorific value on a) Moisture free basis b) Dry ash free basis.
7. The ultimate analysis of bituminous coal (dry basis %) is : C 77, H 5.8, N 1.7, O 4.8, S 2.5 and ash 9. The moisture content is 5 %. The gross calorific power is 7650 Kcal/Kg on dry basis. Calculate a) Gross calorific value, moist basis b) Net calorific value, dry basis c) Net calorific value, moist basis d) Gross calorific value, dry basis using Dulong formula.

Assignment-2

1. What is combustion? Discuss the fundamental principles of combustion calculations

- Calculate the volume of air required for complete combustion of 1 m^3 of a gaseous fuel having the composition- $\text{CO} = 46\%$, $\text{CH}_4 = 10\%$, $\text{H}_2 = 40\%$, $\text{C}_2\text{H}_2 = 2\%$, $\text{N}_2 = 1\%$ and the remaining being CO_2 .
- A sample of coal contains the following composition: $\text{C} = 72\%$, $\text{H}_2 = 6.2\%$, $\text{O}_2 = 14.8\%$, $\text{S} = 1.6\%$, $\text{N}_2 = 2.8\%$ and ash is 2.6% . Calculate the minimum amount of air required for complete combustion of 1 kg of coal and give the percentage composition of dry products of combustion.
- The composition by volume of a certain fuel sample is $\text{H}_2 = 24\%$, $\text{CO} = 6\%$, $\text{CO}_2 = 8\%$, $\text{CH}_4 = 30\%$, $\text{C}_2\text{H}_6 = 11\%$, $\text{C}_2\text{H}_4 = 4.5\%$, $\text{C}_4\text{H}_8 = 25\%$, $\text{O}_2 = 2\%$ and $\text{N}_2 = 12\%$. What theoretical amount of air would be required at 25°C and 750 mm pressure for complete combustion of 1 m^3 of the fuel.
- A petroleum gas has the following composition- Ethane= 5% , Propane= 10% , Butane= 40% , Butene= 10% , Isobutane= 30% and Propene= 5% . Calculate the volume of air required for complete combustion of 100 m^3 of the gas and the percentage composition of the dry flue gases if 35% excess air is supplied.
- A sample of coal was found to have the following percentage composition by weight- $\text{C} = 70\%$, $\text{H} = 6\%$, $\text{O} = 16\%$, $\text{N} = 3.5\%$ and ash= 4.5% . Calculate minimum amount of oxygen and air required for complete combustion of 1 kg of coal.
- A gas has the following composition by volume: $\text{H}_2 = 22\%$, $\text{CH}_4 = 4\%$, $\text{CO} = 20\%$, $\text{CO}_2 = 6\%$, $\text{O}_2 = 3\%$, $\text{N}_2 = 45\%$. If 25% excess air is used, find the weight of air actually supplied per m^3 of this gas.
- The composition by weight of a coal sample is $\text{C} = 82\%$, $\text{H} = 6\%$, $\text{O} = 6\%$, $\text{S} = 1\%$, $\text{N} = 2\%$ and ash= 3% . Calculate the minimum air required for complete combustion of 1 Kg of coal.
- The analysis of the coal in a boiler trial was $\text{C} = 88\%$, $\text{H} = 3.6\%$, $\text{O} = 4.8\%$, other matters= 3.6% and the flue gas analysis by volume was $\text{CO}_2 = 10.9\%$, $\text{CO} = 1\%$, $\text{O}_2 = 7.1\%$, $\text{N}_2 = 81\%$. Find the proportion of carbon burned to CO , and the air required per Kg of fuel for the combustion as it actually occurred and also the weight of flue gas per kg of fuel burned.
- A sample of petrol was found to contain 15.2% H and 84.8% C by weight. Calculate (a) the weight of air needed for the combustion of 1 Kg of the fuel; (b) the volumetric composition of the products of combustion if 15% excess air is supplied.
- A boiler is fired with coal having the following percentage composition by weight: $\text{C} = 74$, $\text{H}_2 = 6.8$, $\text{O}_2 = 13.2$, $\text{N}_2 = 2.1$, $\text{S} = 1.0$ and ash= 2.9 . Calculate the minimum quantity of air required for the complete combustion of 1 kg coal and the percentage composition by weight of the dry products of combustion if 20% excess air is supplied.
- A gaseous fuel has the following percentage composition $\text{CH}_4 = 22\%$, $\text{H}_2 = 10\%$, $\text{CO} = 26\%$, $\text{O}_2 = 2\%$, the remainder being N_2 . Calculate the volume of air required for the complete combustion of 100 m^3 of fuel.
- Calculate the minimum weight of air required for complete combustion of 1 kg of fuel containing: $\text{C} = 85\%$, $\text{H} = 4.5\%$, $\text{O} = 4\%$, $\text{S} = 1\%$, $\text{H}_2\text{O} = 1\%$, $\text{N} = 0.5\%$ and the rest is ash.

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