UNIT – 2 (Mrs. Samta Deshpande)

DEFINITION OF FUEL:-

Fuels can be defined as any combustible substance which during combustion gives **large amount of heat** which can be used economically for domestic and industrial purposes.

During combustion of a fuel the atom of carbon, hydrogen etc. combines with oxygen and liberates large amount of heat and also forms new compounds (like CO_2, H_2O etc.). These new compounds have less energy. The heat released during combustion is the **difference** in reactants (C, H, and O) and products (CO_2, H_2O) energy.

Fuel + O_2 $\longrightarrow$ Products + Heat

(More heat)
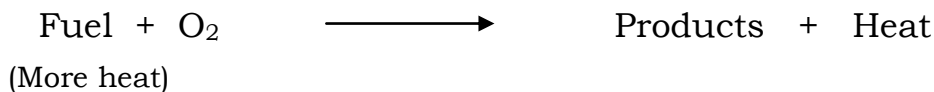
CLASSIFICATION OF FUEL:-

Fuels can be classified –

(A)   On the basis of their Occurrence -

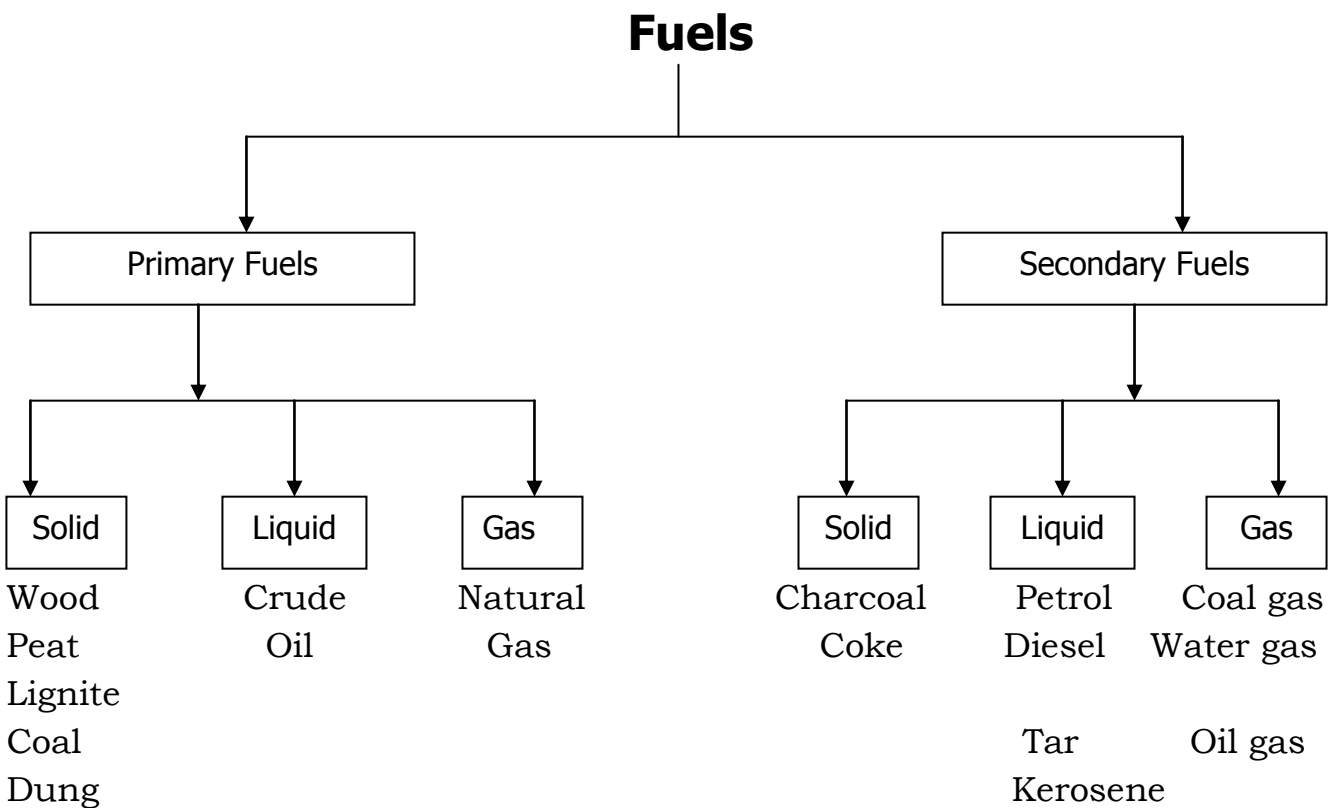(i)   **Natural or Primary fuel** – Fuels which are found in nature as such are called Natural fuels.

Ex. – Wood, Coal, Peat, Petroleum etc.

(ii)   **Artificial or Secondary fuel** – Fuels which are prepared form primary fuel are called secondary fuels.

Ex. – Coke, Petrol, Bio gas etc.

(B)   On the basis of Physical State of aggregation –

On this basis their physical state of aggregation fuels are classified in to three types - solid, liquid and gas.

Fuels

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                              Fuels
                 ┌──────────────┴──────────────┐
          ┌─────────────┐               ┌──────────────┐
          │ Primary Fuels│               │Secondary Fuels│
          └─────────────┘               └──────────────┘
        ┌──────┼──────┐              ┌───────┼───────┐
     ┌─────┐┌─────┐┌─────┐       ┌─────┐ ┌──────┐ ┌─────┐
     │Solid││Liquid││ Gas │       │Solid│ │Liquid│ │ Gas │
     └─────┘└─────┘└─────┘       └─────┘ └──────┘ └─────┘
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Solid	Liquid	Gas	Solid	Liquid	Gas
Wood	Crude	Natural	Charcoal	Petrol	Coal gas
Peat	Oil	Gas	Coke	Diesel	Water gas
Lignite					
Coal				Tar	Oil gas
Dung				Kerosene	

CHARACTERISTICS OF GOOD FUEL –

(1) **High Calorific Value: -** A fuel should have high calorific value, since the amount of heat liberated and temperature attained thereby depends upon the caloric value.

(2) **Moderate Ignition Temperature :-** A fuel should have Moderate Ignition Temperature .If a fuel has low ignition temperature it can causes fire hazards during storage and transport of fuel and if fuel have high ignition temperature then it is safe for storage and transport but their might be some difficulty during ignition.

(3) **Low Moisture Content: -** The moisture if present in the fuel reduces its heating value. Hence, fuel should have low moisture content.

(4) **Low Non-Combustible Matter: -** After combustion the non – combustible matter remains, generally in the form of ash or clinker. They reduce the heating value. Each % of non – combustible matter in fuel means a heat loss of about 1.5%. Hence, a fuel should have low non – combustible matter.

(5) **Moderate Rate of Combustion: -** If the rate of combustion is low then the required high temperature may not be possible. If the rate

of combustion is high then it gets out of control. So fuel must be burn with a Moderate Rate.

(6) **Harmless Combustion Products: -** They should not pollute the atmosphere by emitting CO, SO_2 & H_2S.

(7) **Low Cost: -** A good fuel should be readily available in bulk and at low cost.

(8) **Easy to Transport: -** Fuel must be easily handled either solid , liquid or gas. fuels can easily be transported from one place to another.

(9) **Uniform Size: -** In case of solid fuel, the size should be uniform so that combustion is regular.

(10) **Controllable Combustion: -** So that combustion can be started or stopped when required.
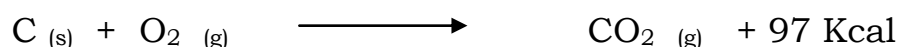
COMBUSTION:-

Combustion is an exothermic chemical reaction. It is followed by the release of heat & light at a rapid rate, thus the temperature rises. In combustion of fuel the atoms of carbon, hydrogen etc. 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 in them, thus the energy (heat) released during combustion process is the difference in energy of reactants and that of products generated.

$$\text{Fuel} + O_2 \longrightarrow \text{Products} + \text{Heat}$$
(more heat)　　　　　　　　　　　　　　(less heat)
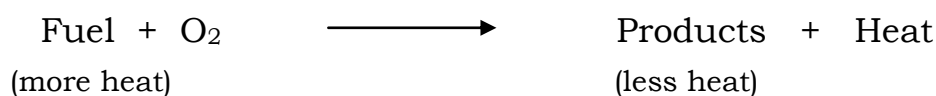
Ex. – Combustion of carbon in presence of oxygen; liberates 97 Kcal of heat

$$C_{(s)} + O_{2\,(g)} \longrightarrow CO_{2\,(g)} + 97 \text{ Kcal}$$

Ignition Temperature: - It is the minimum temperature at which a substance ignites and burns without further addition of heat from outside.

Calculation of Air Quantities: - To find out the amount of air required for the combustion of a unit quantity of a fuel, it is necessary to apply the following chemical principles –

(1) Substance always combines in **definite proportion**. These proportions are determined by their molecular masses.

Mass Proportion

$$C_{(s)} + O_{2\ (g)} \longrightarrow CO_{2\ (g)}$$
$$12 \quad + \quad 32 \qquad\qquad\qquad 44$$
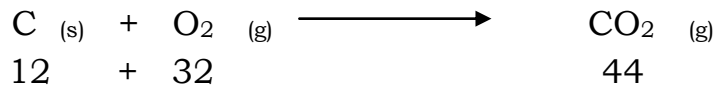
This indicates that mass proportion of C and O_2 and CO_2 are (12:32:44). This means 12 gm of carbon requires 32 gm of oxygen and 44 gm of CO_2 formed.

(2) 22.4L of any gas at 0^0C and 760 mm pressure 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 **S. T. P.** will have a mass of 32 gm.

(3) **Air contains 21% of oxygen by volume and 23% of oxygen by mass.** Hence, the amount of oxygen required by the fuel, & the amount of air, can be calculated.

∵ 23 Kg of oxygen is supplied by 100 Kg of air

∴ 1 Kg of oxygen is supplied by 100 Kg of air = $\dfrac{1 \times 100}{23} = 4.23$ Kg.

∵ 21 m³ of oxygen is supplied by 100 m³ of air

∴ 1 m³ of oxygen is supplied by 100 m³ of air = $\dfrac{1 \times 100}{21} = 4.76$ m³ of air

(4) 28.94 g mol^{-1} is taken as **molar mass of air.**

(5) **Minimum oxygen required** for combustion **=** Theoretical oxygen required – O_2 present in fuel.

(6) 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.

(7) The mass of any gas can be converted to its volume by assuming that gas behaves ideally

PV = nRT

P = Pressure (atm) V = Volume (liters)
n = No. of moles   T = Temp. (Kelvin)

(8) Total amount of hydrogen is either present in the combined form (H_2O) or free form. Combined form is not combustible. Rest of hydrogen is called available hydrogen, takes part in combustion.

$$2H_2 + O_2 \longrightarrow 2H_2O + \text{Heat}$$

Mass- 4   32
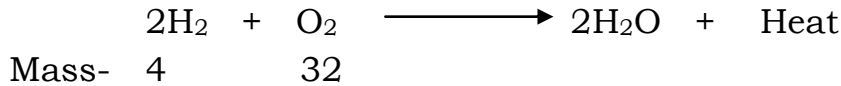
Now 1 part of hydrogen combines 8 parts by mass of oxygen, so available oxygen.

$$\left[\text{Mass of hydrogen} - \left\{ \frac{\text{Mass of oxygen}}{8} \right\} \right]$$

(9) Nitrogen, ash and CO_2 present in fuel are non combustible matters. Hence they do not take oxygen during combustion process.

(10) Total amount of oxygen consumed by the fuel will thus be given by the sum of the amount of oxygen required by the individual combustible constituents present in the fuel.

Since air has 23% by wt. of oxygen or 21% by volume of oxygen.

For complete combustion.

(i)   Wt. = Net $O_2 \times \dfrac{100}{23}$ gm.

(ii)   Vol. = Net $O_2 \times \dfrac{100}{21}$ gm.

Conversion of volume into weight

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

And for air $1L \times \left(\dfrac{\text{mol}}{22.42} \right) \times \left(\dfrac{28.95 \text{ g}}{\text{mol}} \right)$
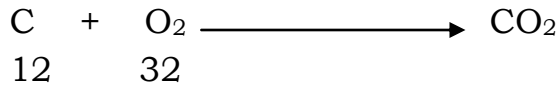
Thus $1L = \dfrac{28.94}{22.4}$ gm

Most commonly combustion reactions are –

(i) $H_2 + \dfrac{1}{2} O_2 \longrightarrow H_2O$

(ii) $S + O_2 \longrightarrow SO_2$

(iii) $CO + \frac{1}{2} O_2 \longrightarrow CO_2$

(iv) $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

(v) $C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$

Numerical No. – 1

Calculate the weight and volume of air required for the combustion of one Kg of carbon.

Solution: - carbon undergoes combustion by this –

$$C \ + \ O_2 \longrightarrow CO_2$$
$$12 \quad 32$$

Thus wt. of O_2 required for combustion of 12g. of carbon = 32 gm.

$\because$ 12 Kg of carbon require = 32 Kg of O_2

$\therefore$ 1 Kg of carbon = $\dfrac{32}{12} \times 1$ = 2.667 Kg of O_2

$\therefore$ Wt of air required = 2.667 $\times \dfrac{100}{23}$ = 11.59

Now since 32 gm of oxygen occupies 22.4 ℓ at NTP

$\therefore$ 1 gm of O_2 of oxygen occupies = $\dfrac{22.4}{32}$ L

$\therefore$ 2.667 × 1000 gm O_2 will occupy = $\dfrac{22.4}{32}$ × 2.667 × 1000 = 1866.9 L

$\therefore$ Volume of air required = 1866.9 × $\dfrac{100}{21}$ = **8890 Liters or 8.890 m³**

Numerical No. – 2

Calculate the volume of air required for complete combustion of five liters of CO, given percentage of oxygen in air = 21.

Solution: - Combustion reaction

$$CO \ + \ 0.5O_2 \longrightarrow CO_2$$
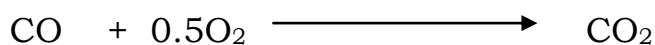
Vol. of O_2 needed

5 liter × 0.5 = 2.5 liter

Hence,

$$\text{Volume of air required} = 2.5 \times \frac{100}{21} = \textbf{11.9 liter}$$

Numerical No. – 3

A gas has the following composition by volume H_2 = 30%, CH_4 = 5%, CO = 20%, CO_2 = 6%, O_2 = 5% and N_2 = 34%.

If 50% excess air is used find the weight of air actually supplied per m^3 of this gas, molecular weight of air = 28.97.

Solution: - In one m^3 of the gas

Composition (%/100)	**Volume of O_2 needed**
H_2 (30%) = 0.3 m^3	0.3 × 0.5 = 0.15 m^3
CH_4 (5%) = 0.05 m^3	0.05 × 2 = 0.1 m^3
CO (20%) = 0.2 m^3	0.2 × 0.5 = 0.1 m^3
	Total = 0.35 m^3
O_2(5%) = 0.05 m^3	Less O_2 in fuel gas = - 0.05 m^3
	Net O_2 needed = 0.3 m^3 = 300 L

$\because$ 1 m^3 ——— 1000 L

$\therefore$ .3 m^3 ——— 1000 × .3 = 300 L

Volume of air required for 1 m^3 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 m^3 of the gas

$$= 2142.8 \text{ L} \left(\frac{1 \text{ mol}}{22.41}\right) \times \left(\frac{28.97 \text{ gm}}{\text{mol}}\right) = \textbf{2771 gm.}$$
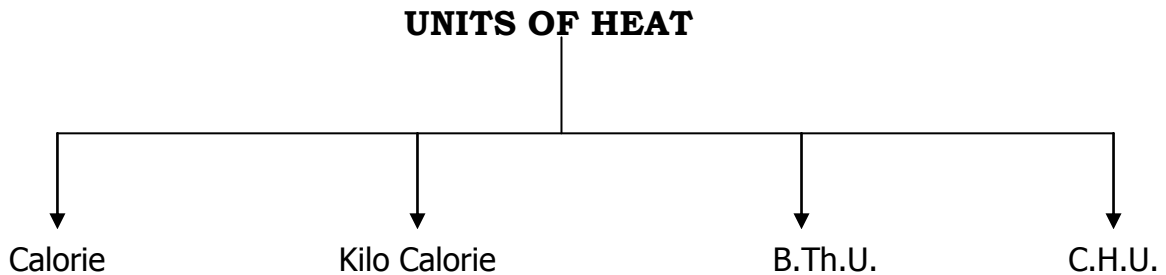
Dulong's formula for calculation of H. C. V. –

Gross Calorific Value (G. C. V.) = $\frac{1}{100}\left[8{,}080 \times C + 34{,}500\left(H - \frac{0}{8}\right) + 2{,}240 \times S\right]$

Kcal/Kg.

Net Calorific Value (N. C. V.) = NCV = (GCV – 0.09 H × 587) Kcal/Kg.

CALORIFIC VALUE

Calorific value of a fuel is defined as "the total quantity of heat liberated from the combustion of a unit mass of the fuel in air or oxygen."

UNITS OF HEAT

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                    UNITS OF HEAT
                         |
      ┌──────────┬───────┴───────┬──────────┐
      ↓          ↓               ↓          ↓
   Calorie   Kilo Calorie     B.Th.U.     C.H.U.
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1) **Calorie: -** Calorie is the amount of heat required to increase the temperature of 1 gm of water through one degree centigrade.

2) **Kilo Calorie (Or Kilogram Centigrade Units):-** It is equal to 1000 calorie, "The quantity of heat required to increase the temperature of one kilogram of water through one degree centigrade".

    1 Kcal = 1000 cal.

3) **British thermal unit (B.Th.U.): -** "The quantity of heat required to increase the temperature of one pound of water through one degree Fahrenheit."

    1 Kcal = 3.968 B.Th.U.

4) **Centigrade Heat Unit (C.H.U.): -** "The quantity of heat required to raise the temperature of 1 pound of water through one degree centigrade."

    1 Kcal = 3.968 B.Th.U. = 2.2 C. H. U.

Higher or Gross Calorific Value: - Hydrogen is present in almost all fuels when calorific value of such fuel is determined; hydrogen present is converted into steam. If the products are brought to room temperature the latent heat of condensation of steam also gets included in the measurement of heat, then it is called Higher or Gross Calorific Value.

Definition of H. C. V.: - It is total amount of heat liberated when a unit mass or unit volume of fuel has been burnt completely and the products are cooled to room temperature.

Lower or Net Calorific Value :- In practice in any fuel when burnt, the water vapor and moisture etc. escapes along with hot combustion gases. Since they are not condensed the lesser amount of heat is available so –

Definition of L. C. V.: - "The net heat produced, when a unit mass or unit volume of the fuel is burnt completely and the combustion products are allowed to escape."

Net calorific value = Gross calorific value – Latent heat of water vapor formed.

L.C.V. = H. C. V. – Mass of hydrogen × 9 × Latent heat of steam.

1 part by weight of hydrogen gives 9 parts by weight of water as follows:-

$$H_2 + O \longrightarrow H_2O$$

2g	16g	18g
1g	8g	9g
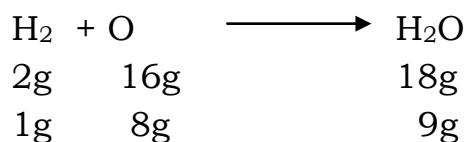
Latent heat of steam is 587 Kcal/Kg.

Determination of Calorific Value (By Bomb Calorimeter)

Principle: - A known amount of fuel is burnt and the quantity of heat produced is absorbed in water and measured. Then the quantity of heat produce by burning a unit mass of the fuel is calculated.

This apparatus is used to find the calorific value of solid and liquid fuels.

Construction:-

➢ It consists of a strong cylindrical stainless steel Bomb.
➢ In which combustion of fuel is made to takes place.
➢ The Bomb is provided with two electrical lids made up of platinum are fixed.

➢ A silica crucible is kept inside the apparatus, in which weighed quantity of fuel is taken.

➢ A fuse wire of platinum is dipped in the fuel taken in the crucible. Its ends are connected to the battery.

➢ The Bomb is placed in the copper calorimeter, containing known quantity of water.

➢ The copper calorimeter is surrounded by an air jacket, which is further enclosed in a vessel containing water.

➢ The calorimeter is provided with an electrically operated stirrer and Beckmann's thermometer. Which can read accurately temperature difference upto $1/100^{th}$ of a degree

Working:-

➢ A known mass of fuel is taken in crucible.

➢ A fine mg wire touching the fuel sample.

➢ Bomb filled with oxygen to 25- 20 atmospheric pressure.

➢ The Bomb is then lowered into copper calorimeter, having a known mass of water.

➢ The stirrer is worked and initial temperature of water is noted.

➢ The electrodes are then connected to 6-volt battery.

➢ The sample burns and heat is liberated.

➢ The maximum temperature is recorded.

Calculation:-

Let -X = Mass of fuel (in gm.)

W = Mass of water in calorimeter.

w = Water equivalent of calorimeter, stirrer, thermometer etc.

t_1 = Initial temperature of water in calorimeter.

t_2 = Final temperature of water in calorimeter.

L = Higher calorific value of fuel (in cal/gm).

∴   Heat liberated by burning of fuel = **XL**

Heat absorbed by water and apparatus, etc. = **(W+w) (t_2 – t_1)**.

But
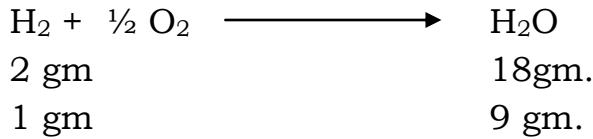
Heat liberated by fuel = Heat absorbed by water

XL = (W + w) (t_2 – t_1)

HCV of fuel (L) = $\dfrac{(W+w)(t_2 - t_1)}{x}$ **cal/g.**

Let H = % of hydrogen in the fuel.

Then gms of hydrogen present in 1 gm fuel = $\dfrac{H}{100}$ gm.

As all fuels have hydrogen when the calorific value of hydrogen fuel is determined, H is converted into steam.

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

2 gm   18gm.

1 gm   9 gm.

Wt. of water produced from 1 gm H_2 = 9 gm.

Wt. of water produced from $\dfrac{H}{100}$ gm H_2 = 9 × $\dfrac{H}{100}$ gm = 0.09 H gm.

Latent heat of steam = 587 cal/gm.

∴   Latent heat of water vapour = 0.09 H × 587 cal
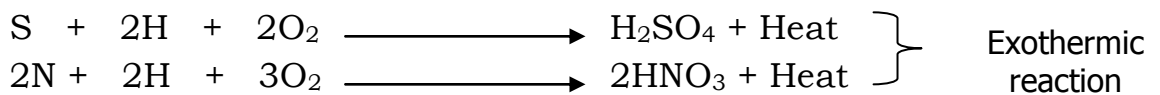
∴   LCV = (HCV – 0.09 H × 587) cal/gm.

Correction:-

To get more accurate results, the following corrections are applied: -

(i) Fuse Wire Correction: - The heat liberated as measured above, includes the heat given out by ignition of fuse wire used, hence it must be subtracted from the total value.

BOMB CALORIMETER DIAGRAM

(ii) Acid Correction: - Fuels having S and N are oxidized into H_2SO_4 and HNO_3.

S + 2H + 2O$_2$ $\longrightarrow$ H_2SO_4 + Heat   ⎤ Exothermic

2N + 2H + 3O$_2$ $\longrightarrow$ 2HNO$_3$ + Heat   ⎦ reaction

Formation of acid is "exothermic reaction". So the measured heat also includes the heat given out during the acid formation. Hence it has to be subtracted from the total value.

(iii) Cooling Correction L =

Correction = dT x t is added to the rise in temperature.

$$\therefore \; L = \dfrac{(W+w)\;\left(t_2 - t_1 + \text{cooling correction}\right) - (\text{Acid} + \text{fuse correction})}{\text{Mass of fuel}(x)}$$

NUMERICAL NO. – 1

0.72 gm of a fuel containing 80% carbon, when burn in a bomb, increased the temperature of water from 27.3⁰ to 29.1⁰ C. If the calorimeter contains 250 gm of water and its water equivalent is 150 gm. Calculate HCV.

Solution: - Here, x = 0.72 gm,   W = 250 g, w = 150 g,

t_1 = 27.3⁰C, t_2 = 29.1⁰ C

$\therefore$ **HCV = L** = $\dfrac{(W + w)(t_2 - t_1)}{x}$ K cal/Kg.

$$L = \dfrac{(250 + 150)(29.1 - 27.3)}{0.72}$$

L = 1,000 K cal/Kg.

NUMERICAL NO. – 2

On burning 0.83 g of a solid fuel in a bomb the temperature of 3,500 g of water increased from 2.5⁰C to 29.2⁰C. Water equivalent of calorimeter and latent heat of steam are 385.0 g and 587.0 cal/g. If the fuel contains   0.7% H, calculate its gross and net calorific value.

Solution: - Here, x = 0.83 gm,   W = 3,500 g,   w = 385.0 g,

t_1 = 26.5⁰C, t_2 = 29.2⁰ C   H = 0.7% Latent

Heat = 587 cal/g.

$\therefore$ HCV = L = $\dfrac{(W + w)(t_2 - t_1)}{x}$ K cal/Kg.

$$L = \dfrac{(3,500 + 385)(29.2 - 26.5)}{0.83}$$

L = 12,638 cal/Kg.

Net calorific value = GCV – 0.09H × 587

= 12,638 – 0.09 × .7 × 587

$$= 12,638 - 37$$

$$\textbf{= 12,601 cal/g.}$$

NUMERICAL NO. – 3

A sample of coal contains C = 93%, H = 6%, and ash = 1%. The following data were obtained when the above coal was tested in bomb calorimeter.

- (i) **Wt. of coal burnt = 0.92 g.**
- (ii) **Wt. of water taken = 550 g.**
- (iii) **Water eq. in bomb calorimeter = 2,200 g.**
- (iv) **Rise in temp. = 2.42^0 C.**
- (v) **Fuse wire correction = 10.0 cal.**
- (vi) **Acid correction = 50.0 cal.**

Calculate gross and net calorific value of the coal, assuming the latent heat of condensation of steam as 580 cal/g.

Solution: - GCV = $\dfrac{(W + w)(t_2 - t_1) - [Acid + fuse\,correction]}{x}$

$$GCV = \dfrac{(550 + 2,200) \times 2.42 - [50 + 10]}{0.92\ g}$$

GCV = 7,168.5 cal/g.

$\therefore$ NCV = [GCV – 0.9 H × Latent heat of steam]

NCV = 7,168.5 – 0.09 × 6 × 580.

NCV = 6,855.3 cal/g.

NUMERICAL NO. – 4

The % analysis by volume of producer gas is H_2 – 18.3%, CH_4 – 3.4%, CO – 25.4%, CO_2 – 5.1%, N_2 – 47.8%, calculate the volume of air required m^3 as the gas.

Composition	Equation	O₂ needed
$H_2 \rightarrow$ (18.3%) = 0.183 m³	$H_2 + .05 \rightarrow H_2O$	$0.183 \times .5 = 0.0915$
$CH_4 \rightarrow$ (3.4%) = 0.034 m³	$CH_4 + 2O_2 \rightarrow CO_2$	$0.034 \times 2 = 0.068$
$CO \rightarrow$ (25.4%) = 0.254 m³	$CO + .5O_2 \rightarrow CO_2$	$0.254 \times .5 = 0.127$
CO_2		
N_2		
Total O₂ =		0.2865 m³

$\therefore$ Air required per m³ or volume of air = $0.2865 \times \dfrac{100}{21}$ 1.3642 m³

Ans.   Volume of air = 1.3642 m³

NUMERICAL NO. – 5

A gas has the following composition by volume H_2 – 22%, CH_2 – 4%, CO - 20%, CO_2 – 6%, O_2 – 3% and N_2 – 45%. If 25% excess air is used. Find the weight of air actually supplied per m^3 of this gas

In one m^3 of the gas –

Composition	Equation	O_2 needed
$H_2 \rightarrow$ (22%) = 0.22 m^3	$H_2 + .5 O_2 \rightarrow H_2O$	0.22 × .5 = 0.11 m^3
$CH_4 \rightarrow$ (4%) = 0.04 m^3	$CH_4 + 2O_2 \rightarrow CO_2$	0.04 × 2 = 0.08 m^3
$CO \rightarrow$ (20%) = 0.20 m^3	$CO + .5O_2 \rightarrow CO_2$	0.20 × .5 = 0.1 m^3
CO_2		
$O_2 \rightarrow$ (3%) = 0.03 m^3		(- .03 m^3)
N_2		
	Total O_2 =	0.26 m^3

0.26 m^3 = 260 L

$\because$ $1m^3$ ——— 1000 L

$\therefore$ .26 m^3 ——— 1000 × .26   =   **260 L**

Volume of air required for 1 m^3 of gas using 25% excess air = $260 \times \dfrac{100}{21} \times \dfrac{125}{100}$

= 1547.61 L

Hence, weight of air actually supplied per m^3 of the gas $= 1547.61 \times \dfrac{28.97 \, gm}{22.4}$

= 2001.54 gm.

Or

Ans.= 2 Kg.

$\therefore$ Net weight of oxygen required for combustion =

$$\left[\frac{32}{12}C + \frac{16}{2}H + \frac{32}{32}S \right] - O_2 \text{ Present in fuel}$$

Significance of Proximate Analysis:-

Proximate analysis, which includes the determination of moisture, volatile matter, ash and fixed carbon. Proximate analysis gives valuable information about the practical utility of coal.

It involves the following determination-

(i) **Moisture Content :-** High % of moisture is not good because –

(a) It increases the cost of coal as well as transportation charges. Hence lesser the moisture content better will be the quality of coal.

(b) It quenches the fire in the furnace, but presence of moisture up to 10% produces a more uniform fuel bed and less of fly ash.

(c) Moisture in coal evaporates during the burning. The moisture losses the calorific value of fuel.

Determination: - By heating a small amount of coal powder in crucible at $100 - 110^0$ C and then cool, weighing till the weight becomes constant.

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

(ii) **Volatile Matter :-**

(a) The volatile matters will combustible or non-combustible gases. The presence of non combustible gases is always undesirable.

(b) When coal has high volatile matters then high proportion of fuel distill over as gas. So higher volatile matter in coal is undesirable.

(c) Coal having higher volatile matter burns with long flame, high smoke and low calorific value

(d) When by product recovery is the main object, volatile matter has special significance. In coal gas plant and carbonization plants.

(e) Medium volatile matter containing coal give hard and strong coke on carbonization.

Determination: - By heating moisture free coal in silica crucible at 925^0C $\pm$ 20^0C for 7 minutes and cooled at desiccators and weighted again.

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

(iii) Ash: - When all combustible substances have been burnt only ash is left in coal. It is not needed because.

(a) It causes hindrance to the flow of air and heat.
(b) It increases cost of storage. It reduces calorific value of fuel.
(c) Burning of coal becomes irregular due to formation of clinkers. (Fused lumps of ash).

Determination: - Weighted amount of dry coal is burnt at 750^0C. So ash is left only.

$$\% \text{ of ash } = \frac{\text{wt. of ash formed}}{\text{wt. of dry coal}} \times 100$$

(iv) Fixed Carbon: - After determination of moisture, volatile matter, and ash, the remaining part is fixed carbon higher the % of fixed carbon greater the calorific value.

Determination: - By deducting the sum total of moisture, volatile matter and ash from 100%

% of fixed carbon = 100 - % (Moisture + Volatile matter + Ash)

Ultimate Analysis:-

It is useful for combustion calculation. It includes the H, N, S, ash and oxygen.

(i) Carbon and Hydrogen : -

Significance: -
⚲ Greater the % of C and H, better is the coal and give high calorific value.
⚲ Carbon % is the basis of classification of coal.
⚲ Hydrogen is mostly associated with volatile matter and moisture hence it effects the calorific value of coal .Higher % is undesirable.

Determination: - About $1 - 2$ gm of coal sample is burnt. C and H are converted in to CO_2 and H_2O. They passed in two bulbs. One bulb contain weighted amount of anhydrous $CaCl_2$ which absorb water.

$$CaCl_2 + 7H_2O \longrightarrow CaCl_2. 7H_2O$$
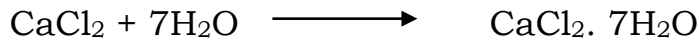
Second bulb contain weighted amount of KOH which absorb CO_2.
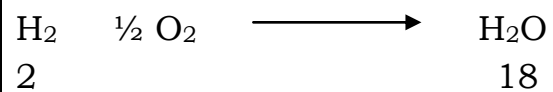
$$2KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$$
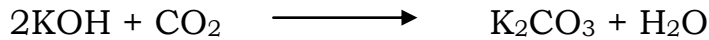
Wt. of $CaCl_2$ and KOH bulbs are measured. Increase weight of $CaCl_2$ bulb shows wt. of H_2O and increase weight of KOH bulb is wt. of CO_2.

$C + O_2 \longrightarrow CO_2$	$H_2 \quad \frac{1}{2} O_2 \longrightarrow H_2O$
12 $\qquad\qquad$ 44	2 $\qquad\qquad$ 18
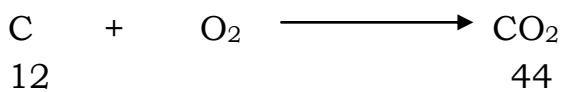
$$\frac{\text{wt.of C}}{\text{wt.of CO}_2} = \frac{\text{At.wt.}=12}{\text{mol.wt}=44} \qquad \frac{\text{wt.of H}_2}{\text{wt.of H}_2O} = \frac{\text{At.wt.}=12}{\text{mol.wt}=18}$$

$$\% \text{ of C} = \frac{\text{wt.of carbon}}{\text{coal taken}} \times 100 \qquad \% \text{ of H} = \frac{\text{wt.of hydrogen}}{\text{wt.of coal}} \times 100$$

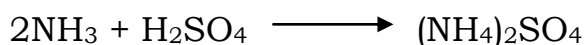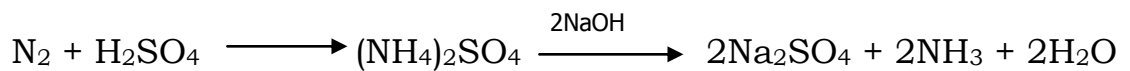$$\therefore \% \text{ of C} = \frac{\text{Increase in wt.of KOH} \times 12}{\text{wt.of coal taken} \times 44} \times 100 \qquad \% \text{ of H} = \frac{\text{Increase in wt.of CaCl}_2 \times 2}{\text{wt.of coal taken} \times 18} \times 100$$

(ii) **Nitrogen: -** N_2 in non combustible, having no C.V. hence a good quality coal have little amount of N.

Determination: - Nitrogen estimation is carried out by Kjeldahal's method. About 1 gm of coal is heated with con. H_2SO_4.upto clear solution obtained which is of ammonium sulphate $((NH_4)_2 SO_4)$. It is treated with NaOH to liberate ammonia. This ammonia absorbs in known volume of standard H_2SO_4. And unused H_2SO_4 is then determined from the volume of acid used by ammonia liberated, the % of N in coal is calculated as follows –

$$N_2 + H_2SO_4 \longrightarrow (NH_4)_2SO_4 \xrightarrow{2NaOH} 2Na_2SO_4 + 2NH_3 + 2H_2O$$

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

$$\% \text{ of N} = \frac{\text{wt.of nitrogen}}{\text{wt.of coal taken (1gtm)}} \times 100$$

$$\% \text{ of N} = \frac{0.1(v_1 - v_2)/100}{1} \times 14 \times 100$$

$$\underline{\textbf{\% \quad of N = 0.1 (v}_1\textbf{ – v}_2\textbf{) x 1.4}}$$

(iii) **Sulphur : -**

Significance : - It contributes to the heating value of coal but on combustion gives acids SO_2 and SO_3, which have harmful effect of corroding the equipments. And cause air pollution.

Presence of sulphur is highly undesirable in coal.

Determination: - Known amount of sulphur is burnt in bomb calorimeter sulphur is convert into sulphates they will treated with Barium chloride to precipitate sulphate $BaSO_4$. The ppt. of $BaSO_4$ is filtered, washed dried and heated to constant weight.

$$S \xrightarrow{\quad O_2 \quad} \overset{--}{SO_4} \xrightarrow{\quad BaCl_2 \quad} BaSO_4$$
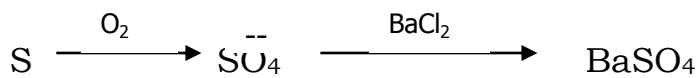
$$\frac{\text{wt.of sulphur}}{\text{wt.of BaSO}_4} = \frac{\text{At.wt s} = 32}{\text{mole wt.BaSO}_4 (233)}$$

Let wt. of $BaSO_4$ precipitate is W_2 gm.

Hence, wt. of S = $\dfrac{32}{233} \times W_2$ gm

Let wt. of coal taken W_1 gm.

$$\underline{\textbf{\% of S =}} \ \frac{\text{wt.of BaSO}_4 \text{ obtained} \times 32}{\text{wt.of coal taken} \times 233} \times 100$$

$$\therefore \ \textbf{\% S =} \ \frac{W_1}{W_2} \times \frac{32}{233} \times \frac{100}{1}$$

(iv) **Ash: - Same** as "Proximate Analysis".

(v) **Oxygen -** High oxygen content in coals have high inherent moisture and low calorific value. An increase in 1% oxygen content decreases the calorific value about 1.7%. Thus good quality coal should have low % of O_2.

Determination: - It is determined indirectly by deducting the combined % of (C, H, N, S and Ash) from 100.

% of oxygen = 100 (% of C + H + N + S + ash).

NUMERICAL NO. – 1

0.5 g of a sample of coal was used in a bomb for the determination of G.C.V., Calorific value of coal has to be 8,600 cal/g. The ash formed in the bomb calorimeter was extracted with acid and acid was treated with barium chloride solution and a precipitate of $BaSO_4$ was obtained. Precipitate was filtered, dried and weighted. The weight of precipitate was found to be 0.05g. Calculate the % of sulphur in the coal sample.

Solution: - % of sulphur = $\dfrac{\text{wt.of } BaSO_4 \text{ ppt} \times 32}{\text{wt.of coal taken} \times 233} \times 100$

% of S = $\dfrac{0.05 \times 32 \times 100}{0.5 \times 233} = 1.373\%$

% of S = 1.373%

NUMERICAL NO. – 2

1.0 g of a sample of coal was used for nitrogen estimation by Kjeldahl method. The evolved ammonia was collected in 25 ml N/10 H_2SO_4. To neutralize excess acid, 15 ml of 0.1 N NaOH was required. Determine the % of N.

Solution: 15 ml of 0.1 N NaOH = excess of 0.1 NH_2SO_4

% vol. of H_2SO_4 used to neutralize the ammonia evolved.

= 25 ml. of 0.1 N H_2SO_4 – 15 ml of 0.1 N NaOH
= 10 ml of 0.1 N.

% of N = $\dfrac{\text{vol. of } H_2SO_4 \text{ used} \times \text{normality} \times 1.4}{\text{wt.of coal taken}}$

% of N = $\dfrac{10 \times 0.1 \times 1.4}{1.0} = 1.4$

% of N = 1.4 Ans.

BASED ON PROXIMATE ULTIMATE ANALYSIS

NUMERICAL NO. – 3

A sample of Gondwana coal of Jharia was analyzed as follows; exactly 2.500 gm was weighted into silica crucible. After heating for 1 hour at 110⁰C, the residue weighted 2.415 gm. The crucible was then covered with a vented lid and strongly heated for exactly 7 minutes at 950⁰C ± 20⁰C. The residue weighted 1.528 gm. The crucible was then heated without the cover until constant weighted was obtained. The last residue was found to weight 0.245 gm. (i) Calculate the % of result of above analysis (ii) To which type does the above description belong.

Solution: - Mass of coal sample = 2.5 gm.

Mass of moisture in coal sample = 2.5 – 2.415 = 0.085 gm.

Mass of volatile matter = 2.415 – 1.528 = 0.887 gm.

Mass of ash = 0.245 gm.

Analysis of coal

% of moisture = $\frac{0.085 \times 100}{2.5}$ = **3.4% Ans.**

% of volatile matter = $\frac{0.887 \times 100}{2.5}$ = **35.48% Ans.**

% of ash = $\frac{0.245 \times 100}{2.5}$ = **9.8% Ans.**

% of fixed carbon = 100 – (3.4 + 35.48 + 9.8)

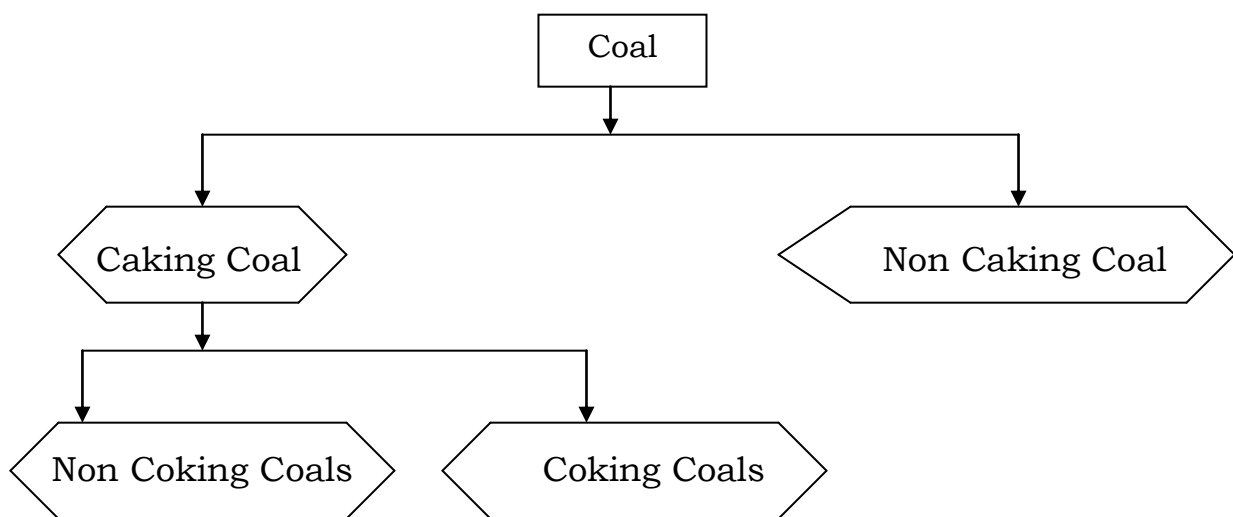**= 51.32 Ans.**

The above description belongs to proximate analysis.

Carbonization:-

The process of converting coal into coke is called carbonization. When a coking coal is heated in the absence of air, the porous, hard and strong residue left is called Coke. Coal can be classify in to two types –

(i) **Non Coking Coals: -** Which has no fusing effect. They are known as 'free burning coals'.

(ii) **Coking Coals: -** Such coals give porous, hard and strong residue after heating in absence of air. They are used in 'Metallurgical Purposes' because they are quite strong.

```
                          ┌──────────┐
                          │   Coal   │
                          └──────────┘
                               │
              ┌────────────────┴────────────────┐
              ▼                                  ▼
    ┌──────────────────┐              ┌──────────────────────┐
    │   Caking Coal    │              │   Non Caking Coal    │
    └──────────────────┘              └──────────────────────┘
              │
      ┌───────┴────────┐
      ▼                ▼
┌──────────────────┐  ┌──────────────────┐
│ Non Coking Coals │  │   Coking Coals   │
└──────────────────┘  └──────────────────┘
```

Carbonization:-

Depending upon the temperature, carbonization is of two types –

(i) **Low Temperature Carbonization (L.T.C.) (500 – 750⁰C): -** In this process, the heating of coal is carried at 500 – 750⁰C. The yield of coke is about 75 – 80% and it contain about 5 – 15% volatile matter. It is not very strong so can't be used as a metallurgical coke. Since it is easily ignited, it is a valuable, smokeless fuel for domestic use. The by – product gas produced by this process is richer in heating value. Hence it is more useful fuel. This process is carried out both with coking and non coking coals.

(ii) **High Temperature Carbonization (H.T.C.) (> 900⁰C): -** In this process, the heating of coal is carried out at 900⁰C – 1200⁰C. The yield of coke is about 65 to 75% volatile matter is 1 – 3%. It is very hard, strong pure, porous so it is used in Metallurgical coke. The

by product gas produced by this process is high in volume but has low calorific value.

Table: Low and High Temperature Carbonization

Low Temperature Carbonization	High Temperature Carbonization
1. **Heating temp;** About 500 – 750⁰C	About 900 – 1200⁰c
2. **Yield of coke**; 75-80%	65 to 75%
3. **Volatile matter**; 5-15%	1 – 3%
4. **Mechanical strength;** Not strong	Mechanical strength
5. **Calorific value;** High about 6500- 9500 Kcal/m³	Low about 5400-6000 Kcal/m³
6. **Quantity of by product;** About 130-150 m³/tonne	About 300-390 m³/tonne
7. **Coke produced;** is soft	Is hard
8. **Use of coke**; Domestic	Metallurgical purpose
9. **% of aromatic hydrocarbon;** Lower	Higher
10. **Smoke produced;** Smokeless	Smoky

Manufacture of Metallurgical Coke; By Otto Hoffmann's By – Product Oven Method.

"Regenerative Principle of Heat Economy

Introduction: - Otto Hoffmann develops modern method for manufacturing metallurgical coke. In order to

(i)   Increase the thermal efficiency of carbonization process,

(ii)   Recovery of by products.

Construction :- The by product coke oven consists of a number of narrow silica chambers each chambers is about 10 -12 meter long, 3 – 4m high and 0.40 – 0.45 m wide. These chambers are erected side by side with Vertical Flues in between them to form a sort a battery. Each chamber has Charging Hole at the top for charging the coal and removal of volatile matter *gas takes off). More over heating is done on the basis of 'Regenerative System of heat economy', so utilizing the waste flue gases for heating the checker work of bricks.

Theory: -   Coking process is done in narrow ovens, which are heated from both sides because coal is poor conductor of heat. The coals adjacent to oven walls get heated first and the plastic zone formed in the case of caking coals moves away from the walls towards the central zone. The plastic zone though mobile is such a bad conductor of heat that while the inner zones are getting heated, the semi – coke at the outer zones would have been converted into coke.

Working: -   Finely crushed coal is introduced in the charging holes at the top of chamber. And cut the supply of air. The ovens are heated to 1200^0C by burning gas (producer gas). Each oven is separated from another oven by a vertical flue in which the fuel gas burns.

These ovens work on the Regenerative principle of heat economy. The flue gases produced during combustion, before escaping to chimney, pass on their heat to one or two sets of checker brick, until this brick has been raised to temp. about 1000^0C. The inlet gas are passed through the heated checker brick, which get preheated, while the flue gases leave their acquired heat to one generator the other generator is used for preheating the incoming air. Heating is continued, until all the volatile matter has escaped. It takes about 11 – 18 hrs for carbonization of a charge of coal.

Quenching: -   After the completion of carbonization, the discharging doors are lifted by a crane and the red hot coke is pushed out into a coke car. The car carries it to quenching station where the coke comes into contact with a spray of cooling water. Then it is supplied for different purposes. In place of wet quenching, 'dry quenching' can also be done. It has many advantages, because the coke produced is more strong, dense, non reactive. Coke is cheaper also and contains lesser dust then 'wet quenching'.

Diagram

Recovery of By Products: - The gas coming out from the oven is known as 'Coke Oven Gas'. It is mainly consist of NH_3, H_2S, C_6H_6, Tar, Naphthalene etc.

(i) Recovery of Tar: - The gas passed through a tower in which liquid ammonia is sprayed. Here dust and tar get collected in a tank below, which is heated by steam coils to recover back ammonia. The ammonia is used again.

(ii) Recovery of Ammonia: - The gas from the chamber is then passed a tower in which water is sprayed. Here ammonia goes into solution as NH_4OH.

(iii) Recovery of Naphthalene: - The gas then passed a tower in which water is sprayed at low temp. When naphthalene gets condensed.

(iv) Recovery of Benzene: - The gas is then sprayed with petroleum when benzene and its homologous can be recovered.

(v) Recovery of H₂S :- The gas is then passed to a purifier, packed with moist Fe_2O_3.
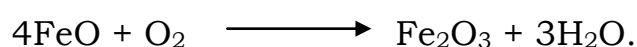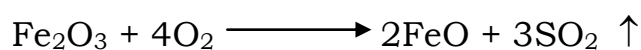
$$Fe_2O_3 + 3H_2S \longrightarrow Fe_2S_3 + 3H_2O.$$

Significance of Recovery of By Product

Coke oven gas contains large no. of valuable impurities.

(i) Tar: - Tar is used for road making; it gives on fractional distillation benzene, toluene, naphthalene etc.

(ii) Ammonia: - The removal of ammonia from the gas is necessary to avoid the blockage of gas pipes by ammonium carbonate.

(iii) Naphthalene: - Naphthalene and other higher aromatics present in vapours, may cause blocking of the gas pipes.

(iv) Benzene: - Is an important solvents and raw materials for plastic.

(v) H₂S :- Sulphur compounds may get oxidized to SO_2 and finally to H_2SO_4 obtained.

$$Fe_2O_3 + 3H_2S \longrightarrow Fe_2S_3 + 3H_2O$$
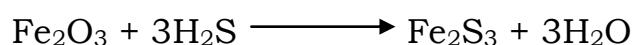
After time, when all Fe_2O_3 is changed into Fe_2S_3

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

$$4FeO + O_2 \longrightarrow Fe_2O_3 + 3H_2O.$$

Liquid Fuel; Petroleum (Its Chemical Composition)

Petroleum or crude oil is dark greenish – brown viscous oil found deep in earth's crust.

Petra = Rock and Oleum = Oil

Petroleum is also called mineral oil because it occurs beneath the earth. The composition (Average) of petroleum is –

C = 80 to 87 %
H = 11.1 to 15 %
S = 0.1 to 3.5 %
O = 0.1 to 0.9 %
N = 0.4 to 0.9 %

Petroleum is a complex mixture of paraffin, olefin and aromatic hydrocarbons. The common constituents present in petroleum are-

Composition		Remarks
Hydrocarbons	-	Present about 70% Normal branched, cycloalkanes present.
Sulphur containing compounds	-	Sulphur is present in either free form or compound form like H_2S, Thiols, Thiophene, and Thioalkanes.
Oxygen containing compounds	-	(C_4 – C_9) carboxylic acids occur in low boiling fractions while Naphthenic acid occur in high boiling fraction.
Nitrogen containing compound	-	Mainly in form of pyrrole, indole pyridine, quinoline etc.
Inorganic compounds	-	These are organo metallic compounds of Cu, Fe, Ni and V.

Fractional Distillation

Introduction: - The crude oil is separated into various fractions (having different boiling points) with the help of fractional distillation. These fractions are finally converted into desired specific products by removing impurities. The process is called 'refining of crude oil'.

Process: - The crude oil is heated to about 400⁰C in a pipe, where all volatile matter are evaporated. The hot vapors are then passed through a tall

cylindrical tower, known as 'Fractionating Column' containing a number of horizontal stainless steel trays at short distances. These trays are provided with individual Chimney which are covered with a loose cap.

As the vapors go up, they become gradually cooler and fractional condensation takes place at different heights of column. Higher boiling fraction condenses first while the lower boiling fractions turn-by-turn.

Diagram

Various Fractions by Distillation of Crude Oil

Name of fraction	Boiling Temp.	Approximate Composition in terms of HC	Uses
1. Uncondensed gas	$< 30^0C$	C_1 to C_4 ethane, propane	Used as L.P.G.
2. Petroleum ether	$30 - 70^0C$	C_5 to C_7	Used as solvent
3. Gasoline or petrol	40 to 120^0C	C_5 to C_8	Used as fuel for IC engines solvent
4. Naphtha	120 to 180^0C	C_8 to C_{10}	Solvent, in dry cleaning
5. Kerosene Oil	180^0 to 250^0C	C_{10} to C_{16}	Fuel, in preparing laboratory gas
6. Diesel Oil	250 to 320^0C	C_{10} to C_{18}	Used as diesel engine fuel
7. Heavy Oil	320 to 400^0C	C_{17} to C_{30}	For getting gasoline by cracking
This on re fractionation gives Lubricating oil Vaseline Grease			As lubricants In cosmetics As lubricants
8. Residue may	$> 400^0C$	C_{30} and above	Water proofing of roofs.
(i) Asphalt			
(ii) Petroleum coke			As a fuel and in moulding arc light rods

A brief description of three major important liquids.

(i)   **Gasoline or Petrol Fraction: -** It is a mixture of hydrocarbon from pentane to Octane. This fraction is obtained between 40 to 120⁰C. This fraction is highly volatile and inflammable and used as fuel for internal combustion (IC) engines. It's C. V. = 11,250 cal/gm.

(ii)   **Diesel Oil: -** It is mixture of hydrocarbon from C_{10} to C_{18}. This fraction is obtained between 250 to 320⁰C. It is used as a fuel for diesel engine. It's C. V. = 11,000 cal/gm.

(iii)   **Kerosene Oil: -** It is mixture of hydrocarbons from C_{10} to C_{16}. It does not vaporize easily. It is used as a domestic fuel, jet engine fuel. It's C. V. 11,100 cal/gm.

Knocking and Chemical Structure -

Two main terminology used in knocking is -

(i)   **Ignition Temperature: -** It is the minimum temperature at which the combustion is self start.

(ii)   **Compression Ratio: -** The power and efficiency of IC engine depends upon compression ratio (C.R.).

The ratio of gaseous volume (V_1) in cylinder at the end of suction stroke to the volume (V_2) at the end of compression stroke of the piston.

As $V_1 > V_2$ $\longrightarrow$ **CR = $\dfrac{V_1}{V_2} > 1$**

'CR indicates the extent of compression of fuel air mixture by piston'.

$$C. R. = \frac{V_1}{V_2}$$
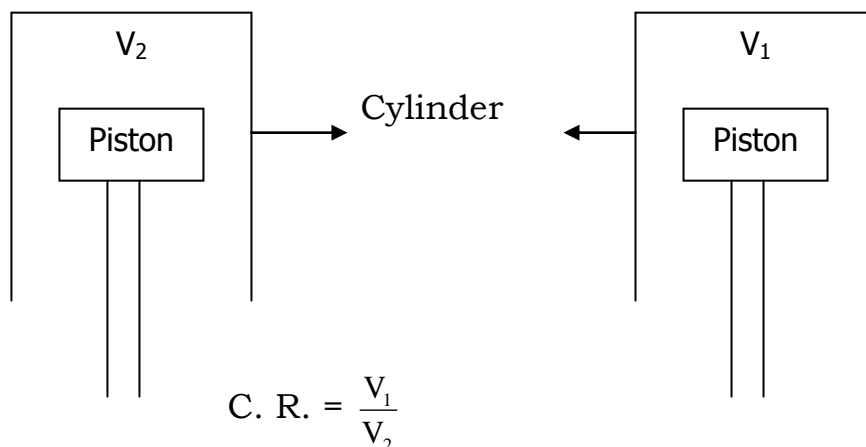
What is Knocking: - The fuel air mixture gets heated to a temperature greater than its ignition temp due to compression ratio. This leads to spontaneous combustion even before sparking.

It is also possible that the last portion of the fuel – air – mixture undergoes self – ignition after sparking and give detonating shock wave (explosion). The resulting shock wave dissipates its energy by hitting the cylinder walls and piston, and emitted sound is Knocking.

IC engine = Internal Combustion Engine.

The uneven burning of fuel is knocking.

Knocking is depending on: - fuel taken, engine design, shape of head, location of plug, chemical structure of fuel, running conditions.

Consequence of Knocking -

♣ Decreased power output.
♣ Mechanical damage by over heating of the cylinder parts.

With increase in C.R., efficiency of IC engine also increases but after critical C.R., tendency to knock also increases.

Chemical Structures

♣ Knocking tendency decreases with increase in the compactness of the molecules.
♣ Double bonds and cyclic compound.
♣ Knocking decrease with increase in length of hydrocarbon chain. Thus Octane no. of
   n – Butane, n – pentane, n – hexane and n – heptanes
   n - Hexane > n – pentane > n – butane are 90, 60, 20 and 0
   Respectively.
♣ Branched chain paraffin's have higher anti knocking properties. Ex. Thus 2 – Methyl hexane has an octane no. of 55 while 2:2 dimethyl pentane has an octane no. of 80.
♣ Aromatic hydrocarbon such as benzene and toluene has high octane number.
♣ Olefins have higher anti – knock properties.

Anti – Knocking Agents: - Tetra ethyl lead (TEL) and diethyl telluride $[(C_2H_5)_2$ Te] are anti knocking agents.

TEL gives Pb and PbO_2 during combustion. Pb and PbO_2 decreases engine life, hence they must removed by adding ethylene dibromide.
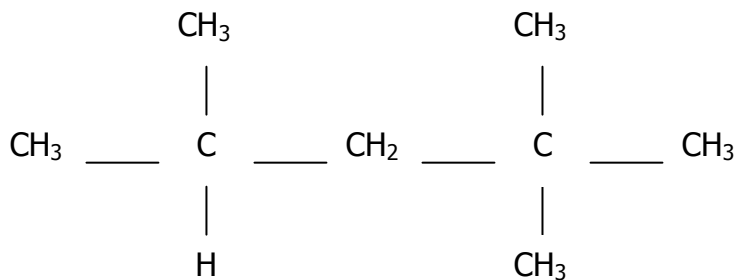
Pb , PbO$_2$ + C$_2$H$_4$Br$_2$ $\longrightarrow$ **PbBr$_2$**

PbBr$_2$ is volatile and escapes in atmosphere but creates pollution problem.

The adding of TEL in fuel is called 'Doping'.

Octane Number

The knocking tendencies of a fuel are expressed by 'Octane Number'. It is found that the hydrocarbon iso- octane (C$_8$H$_{18}$) having formula –

$$
\begin{array}{ccccccc}
& \text{CH}_3 & & & & \text{CH}_3 & \\
& | & & & & | & \\
\text{CH}_3 - & \text{C} & - \text{CH}_2 - & & \text{C} & - \text{CH}_3 \\
& | & & & & | & \\
& \text{H} & & & & \text{CH}_3 &
\end{array}
$$

This shows very little tendency to detonate (explosion) when mixed with air. Hence Octane number is 100.

On the other hand the straight chain hydrocarbon, n – heptane (C$_7$H$_{16}$) having formula –

CH$_3$ - CH$_2$ - CH$_2$ - CH$_2$ - CH$_2$ - CH$_2$ - CH$_3$

Knock very readily and hence its octane number is Zero (0). Octane rating is given by Graham Edgar in 1926.

Fuel	Octane Number	Character
N – heptane	0	Knocks severely
Iso – Octane	100	High resistance to knocking

The % of isooctane in the n – heptane – iso octane which just matches with the knocking character of the fuel. Thus if a fuel has octane number 70, it shows that it has same anti – knock quality as the mixture of 70 parts iso

octane and 30 parts n – heptane. The octane ratings of some common hydrocarbon are give below.

Hydrocarbon	Octane Number
Benzene	100^+
Isopentane	90
Cyclohexane	77
2 – methyl pentane	71
n – pentane	62
n – hexane	26

Additives for improving anti knock properties. : -

♣ TEL and Diethyl telluride $(C_2H_5)_2$ Te is added.

TEL gives Pb, PbO_2 during combustion. Pb and PbO_2 decreases engine life, hence they must removed by adding c_2H_4Br.

$$Pb, PbO_2 + C_2H_4Br \longrightarrow PbBr_2$$
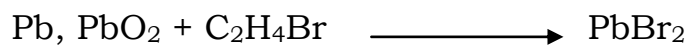
♣ Unleaded petrol.
♣ Benzene
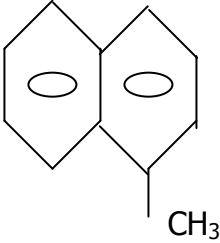Addition of TEL is called as "Doping"

Cetane Number – Diesel Engine Fuel: - The knocking tendency of diesel oil are expressed in terms of cetane number. Diesel engine fuels have a long chain hydrocarbon, which has a very short ignition log. This means that it is essential that the hydrocarbon molecules in a diesel fuel should be '**Straight Chain'.**

- ♣ In the diesel engine, air is first drawn into cylinder, and compressed temp. is 500^0C.
- ♣ End of compression stroke, diesel is injected.
- ♣ The Oil (Diesel) absorbs the heat from the air and it ignites spontaneously as it attains ignition temp.
- ♣ The combustion of fuel in a diesel engine is not instantaneous, the "interval between the start of fuel injection and its ignition is called the 'ignition delay' "

Ignition delay is due to (a) Engine Design (b) Mixing of spray (fuel) and air (c) Chemical nature of fuel.

If ignition delay is long, it will lead to fuel accumulation in the engine even before the ignition. When ignites creates explosion. This is diesel knock. It is shown in 'Cetane number'.

Cetane number: - Saturated hydrocarbon has a short ignition lag so its cetane no. is 100 and aromatic hydrocarbon has very long ignition lag so its cetane no. is zero (0).

Diesel fuel	Cetane no.	Remarks
Cetane $C_{16}H_{34}$	100	Very short ignition delay
α-methyl naphthalene CH₃	0	Longer ignition delay

"The % of cetane and α - methyl naphthalene is give by cetane number"
Consider the following series –
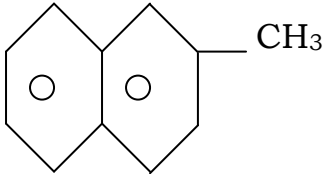n alkanes > naphthalenes > alkanes > branched-alkanes >aromatics

- ♣ Ignition delay increases from left to right.
- ♣ Ignition quality increases from right to left.

♣ Cetane no. increase from right to left.

Additives: - Cetane no. can be increased by adding substances like ethyl nitrite, isoamyl nitrate. These substances are called as "dopes".

Difference between Octane no. and Cetane no.

Octane No.	Cetane No.
Is the % of iso-octane in a mixture of isooctane and n-heptane. $CH_3 - (CH_2)_5 - CH_3$ n – heptane Knocks badly (Octane no. – 0) Iso – Octane (Octane no = 100) Give little knocking.	Is the % of cetane in a mixture of cetane and α-methyl naphthalene. α - methyl naphthalene (Cetane No. = 0) $CH_3 — (CH_2)_{14} — CH_3$ (Cetane No. = 100)
It is used for internal combustion engine	It is used for diesel fuel.
Octane no. can be raised by addition of TEL or (C_2H_5) Te.	Cetane no. can be raised by addition of dopes like ethyl nitrite.
Hydrocarbons which are poor diesel fuel are good gasoline fuel.	Hydrocarbon which are poor gasoline are good diesel fuel.
Straight chain fuels are worst fuels. They give low octane no.	Straight chain fuels are best. They give high cetane no.

FLUE GAS ANALYSIS:-

An idea about the complete or incomplete combustion of fuel is given by 'Flue Gas Analysis'. Thus –

(i) If the flue gases contain considerable amount of carbon monoxide, it shows incomplete combustion means short supply of oxygen.

(ii) If the flue gases contain considerable amount of oxygen, it shows complete combustion means or excess supply of oxygen.

The analysis of flue gases is carried by Orsat's Apparatus.

CONSTRUCTION:-

♣   It consists of horizontal tube at the one end of this tube is three way stop cock and the other end is connected with burette.

♣   Burette is surrounded with a water jacket to keep the temperature constant of gas.

♣   The burette is connected in series to a set of three absorption bulbs, each through a separate stop cock.

♣   The lower end of the jacket burette is further connected to a water reservoir with the help of rubber tube. The water level in the burette can be raised or lowered by raising or lowering.

♣   The other end of horizontal tube is connected to a U – tube.

♣   U – tube is packed with fused $CaCl_2$ and glass wool for drying flue gas and avoiding for smoke particles.

♣   Three absorption bulbs apart from having solution for absorbing CO_2, O_2 and CO.

♣   The first bulb has KOH solution and it absorbs only CO_2.

♣   The second bulb has alkaline pyrogallic acid and it can absorb O_2 and CO_2.

♣   For proper analysis it is necessary that the flue gas is passed through first bulb having KOH, where CO_2 is absorbed.

♣   Then it is passed through second bulb having acid, where only O_2 will be absorbed.

♣   Finally flue gases are passed through third bulb having $CuCl_2$ where only CO will be absorbed.

WORKING STEP – 1

♣   The whole apparatus is thoroughly cleaned.

♣   The absorption bulbs are filled with their respective solution and stop clock are closed. The water reservoir and jacket are filled with water.

♣   For the exclusion of air, the three way stop cock should be opened to the atmosphere.

♣   Flue gas is analyzed by lowering the water reservoir and connecting the three way stop cock to flue gas supply.

♣   Air should be expelled by repeating the above process of sucking and expelling the flue gas by lowering and raising the water reservoir.

STEP – 2

♣ 100 ml of flue gas is carefully sucked in the burette for analysis. The three way stop cock is closed then. The flue gas is forced in the bulb 1 by opening its stop cock and raising the water reservoir. Bulb 1 have KOH which absorbs CO_2 for complete absorption of CO_2 the flue gas is sent 2 or 3 times, again and again in bulb 1.

STEP – 3

♣ The unabsorbed gas is finally taken back in the burette and then stop cock for CO_2 absorption bulb is closed.

♣ The levels of water in the reservoir and burette are equalized and the value of residual gas is noted. The decrease in volume gives the volume of CO_2 in 100 ml of the flue gas sample.

♣ The volumes of O_2 and CO are similarly determined by passing the flue gas through absorption bulbs 2 and 3.

Diagram

Using Dulong's Formula

Q. 1. Calculate the gross and net calorific value of coal having the following composition. C = 85%, H = 8%, S = 1%, n = 2%, ash = 4% latent heat of steam = 587 cal/g.

Solution: - Gross calorific value (GCV) –

$$= \frac{1}{100} \left[8,080 \times C + 34,500 \left(H - \frac{0}{8} \right) + 2,240 \times s \right] Kcal / Kg.$$

$$= \frac{1}{100} \left[8,080 \times 85 + 34,500 \left(8 - \frac{0}{8} \right) + 2,240 \times 1 \right] Kcal / Kg.$$

$$= \frac{1}{100}\left[686{,}800 + 276{,}000 + 2{,}240\right] Kcal/Kg.$$

$$= \frac{1}{100}\left[965{,}040\right] Kcal/Kg.$$

$$= 9{,}650.4 \ Kcal/Kg.$$

Net calorific value.

NCV = (GCV – 0.09 H × 587) Kcal/Kg.

NCV = (9,650.4 – 0.09 × 8 × 587) Kcal/Kg.

NCV = 9,227.8 Kcal/Kg.

Q. 2. Calculate GCV and NCV of a coal having the following composition C = 80%, H = 7%, O = 3%, S = 3.5%, N = 2.1%, ash = 4.4%.

Solution: - Gross calorific value (GCV) –

$$GCV = \frac{1}{100}\left[8{,}080 \times C + 34{,}500\left(H - \frac{0}{8}\right) + 2{,}240 \times s\right] Kcal/Kg.$$

$$GCV = \frac{1}{100}\left[8{,}080 \times 80 + 34{,}500\left(7 - \frac{3}{8}\right) + 2{,}240 \times 3.5\right] Kcal/Kg.$$

$$GCV = \frac{1}{100}\left[8828\right] Kcal/Kg.$$

NCV = GCV – 0.09H × 587

NCV = 8828 – 0.09 × 7 × 587 Kcal/Kg.

NCV = 8458 Kcal/Kg.

Q. 3. The % composition by weight of a sample of cool was found to be - C = 81%, H = 5%, O = 8.5%, S = 1%, N = 17%, ash = 3.5%. calculate
(i) Calculate the minimum amount of O_2 and air required for complete
Combustion of 1 Kg of this coal.
(ii) % composition by weight of the by products of combustion.

Solution: - (i)   1 Kg of coal contains;

C = 810 gm, H = 50 gm, O = 85 gm, S = 10 gm, N = 10 gm.

Net O_2 = $\left[\dfrac{32}{12} \times C + \dfrac{16}{2} \times H + \dfrac{32}{32} \times S\right]$ − oxy. present in fuel

Net O_2 = $\left[\dfrac{32}{12} \times 810 + \dfrac{16}{2} \times 50 + \dfrac{32}{32} \times 10\right] - 85$

Net O_2 = $[2160 + 400 + 10] - 85$

Net O_2 = 2570 − 85

Net O_2 = 2485.

Minimum amount of air = Net O_2 × $\dfrac{100}{23}$

Minimum amount of air = 2485 × $\dfrac{100}{23}$ gm.

= 10804.34 gm or 10.8 Kg.

(ii)

Dry products	Amounts
CO_2	$\dfrac{44}{12} \times 810 = 2970\,gm.$
SO_2	$\dfrac{64}{23} \times 10 = 20\,gm.$
N_2	10 gm in fuel + $\dfrac{77}{100} \times 1080.4 = 8329.4\,gm.$

Total weight of dry product =

2970 + 20 + 8329.4 gm = 11319.4 gm.

% of CO_2 = $\dfrac{2970}{11319.4} \times 100$ = 26.2%

% of SO_2 = $\dfrac{20}{11319.4} \times 100$ = 0.177%

% of N_2 = $\dfrac{8329.4}{11319.4} \times 100$ = 73.6%