CHEMICAL FUELS

FUEL: A fuel is defined as any combustible substance, containing carbon as main constituent, which can liberate a large amount of useful heat on combustion.

$$\text{Fuel} + O_2 \longrightarrow \text{Products} + \text{Heat}$$

Heat evolved by burning fuel is mainly used for heating purposes. It can also be used for doing mechanical work.

Eg: coal is used in locomotive engines; petrol is used in combustion engines etc.

FOSSIL FUELS: The primary or main sources of fuels are coal & petroleum oils, the amounts of which are dwindling day-by-day and are available in the earth's crust are termed as 'fossil fuels'.

CLASSIFICATION OF FUELS: Fuels can be classified into two different ways (1) Basing on their occurrence (2) on the physical state of aggregation.

Chemical Fuels

Primary (or) **Natural**			**Secondary** (or) **Derived**		
Solid	**Liquid**	**Gaseous**	**Solid**	**Liquid**	**Gaseous**
Wood	Crude oil	Natural gas	Coke	Tar	Coal gas
Peat			Charcoal	Kerosene	Water gas
Coal			Coal briquette	diesel	Biogas
Dung				Petrol	Oil gas
				LPG	

Colloidal Fuel: Colloidal fuel is a suspension of finely powdered coal in fuel oil (or in liquid fuel) in the ratio 3:2, along with some stabilizing agent and possesses higher calorific values.

These fuels are used in industrial furnaces for cement manufacturing brick firing, ceramic firing, metal processing etc.

The quantity of a fuel is expressed in terms of calorific value.

CALORIFIC VALUE: The total quantity of heat liberated by combustion of unit mass (or volume) of the fuel in air or oxygen is called 'Calorific value' of the fuel.

Units : 1)**Calorie:** calorie is the amount of heat required to raise the temperature of 1gm of water through 1^0C (15-16^0C)

ii) **British Thermal Unit (B.Th.U):** It is defined as 'the quantity of heat required to raise the temperature of 1 pound of water through 1^0 F (60-61^0F)'. 1 B.Th.U = 252 cal (or) 1 Kcal = 3.968 B.Th.U.

iii) **Centigrade heat unit (C.H.U):** It is 'the quantity of heat required to raise the temperature of 1 pound of water through 1^0C.

1 K Cal= 3.968 B.Th.U = 2.2 C.H.U

CHARACTERISTICS (or REQUIREMENTS) of a GOOD FUEL:
A good fuel should possess the following characteristics:

1)**High Calorific Value:** A good fuel should possess high calorific value as the amount of heat liberated & temperature attained depends upon the calorific value of fuel.

CV of wood = 4000-5000 K Cal/kg; Coal = 8000-85000 K Cal/kg

2) **Moderate Ignition Temperature:** Ignition temperature is the minimum temperature to which the fuel must be pre-heated, so that it starts burning smoothly.

However low ignition temperature is dangerous for storage & transport of fuel and also high ignition temperature is difficult in igniting the fuel. Hence the ignition temperature should be moderate.

3) **Low moisture Content:** The presence of moisture reduces the heating value of the fuel. Hence moisture content should be low.

4) **Low Non-Combustible Matter content :** The presence of non-combustible matter like ash after combustion reduces the heating value. Hence for a good fuel it should be low.

5) **Moderate Rate of Combustion:** Low rate of combustion may radiate the heat liberated, instead of raising the temperature and also high rate of combustion may not be controlled. Hence a good fuel should have moderate rate of combustion.

6) **Harmless combustion products:** The fuel during combustion should not emit gasses like CO,SO_2, H_2S, etc, which pollute the atmosphere.

7) **Low Cost:** The fuel should be of low cost, easy to transport & low storage cost

8) Combustion should be easily controllable i.e., combustion of fuel should be easy to start or stop, when required.

9) The fuel should burn with efficiency without much smoke.

10) Fuel should have uniform size, so that combustion will be regular.

HIGHER CALORIFIC VALUE (or) **GROSS CALORIFIC VALUE (HCV):**

Hydrogen is present in all fuels. Burning of these fuels convert hydrogen into steam. If the products of combustion are condensed to room temperature, latent heat of condensation of steam is also included in the measured heat. It is called higher colorific value.

Def: Higher calorific value is defined as the total amount of heat liberated by burning unit mass or unit volume of the fuel & by condensing the products of combustion to room temperature (i.e., 15^0C or 60^0F)

LOWER CALORIFIC VALUE (or) **NET CALORIFIC VALUE (LCV):**

LCV is defined as 'the total amount of heat liberated by burning unit mass or unit volume of fuel & by allowing the products of combustion to escape.

LCV = HCV – Latent heat of water vapour formed.

Since 1 part of hydrogen by mass produces 9 parts of water by mass

LCV = HCV – mass of hydrogen x 9 x latent heat of steam

Latent heat of steam = 587 Cal/gm or K Cal/kg or 1060 B.Th.U/Lb

THEORETICAL CALCULATION OF CALORIFIC VALUE OF A FUEL BY DULONG'S FORMULA

Calorific value of the fuel is nothing but the sum of the calorific values of the chief constituents of the fuel.

Constituent	:	Hydrogen	Carbon	Sulphur
HCV(k Cal/kg)	:	34,500	8080	2240

$2H_2 + O_2 \longrightarrow 2H_2O$ ie, 8 parts of oxygen combines with 1 part of 4

32 36 or hydrogen to form H_2O

1 8 9

Fixed hydrogen = $\frac{\text{mass of oxygen}}{8}$

Amount of hydrogen available for combustion =

Total mass of hydrogen in fuel – fixed hydrogen = $H - \frac{O}{8}$

Dulong's formula for calorific value from chemical composition of fuel is given by

$$\mathbf{HCV} = \frac{1}{100}\left[8080\,C + 34{,}500\left(H - \frac{O}{8}\right) + 2240\,S\right] \text{ Kcal/kg (or) Cal/gm}$$

$$\mathbf{LCV} = \left[\text{HCV} - \left(\frac{H}{100} X\, 9\right) \times 587\right] = \left[\text{HCV} - 0.09H \times 587\right] \text{ K cal/kg (or) Cal/gm}$$

Here C = % of Carbon; H = % of hydrogen; O = % of oxygen

S = % of Sulphur & where $\frac{H}{100}$ x 9 = mass of water from 1gm of fuel

1) Calculate the gross (HCV) and net (LCV) colorific values of coal having the following compositions C – 85%, H = 8%, S = 1% , N = 2%, and ash 4% . Latent heat of steam = 587 Kcal/kg.

Sol : We know that Dulong's formula for HCV of fuel is given by

HCV = 1/100 (8080 C + 34500 (H - O/8) + 2240 S)

Given C = 85% ; H = 8% ; S=1% ; N=2% ; Ash = 4% ;O= 0;

Latent heat of steam = 587 Kcal/Kg

HCV = 1/100 (8080 x 85 + 34500 x 8 + 2240 x 1)

= 1/100 (686800 + 276000 + 2240) = **9650.4** Kcal/kg

LCV = (HCV – 0.09H x 587)

= (9650.4 – 0.09 x 8 x 587) = **9227.76** Kcal/Kg

2) Calculate the Gross and Net calorific values of coal sample having the following compositions

C = 80%, H = 7%, O = 3% , S = 3.5%, N = 2%, and ash = 5%

Sol : Given that C = 80% , H = 7% , O = 3% , S = 3.5% , N = 2%, and ash = 5%

From Dulong's formula for HCV = 1/100 (8080C + 34500 (H- O/8) + 2240 S)

HCV = 1/100 (8080 x 80 + 34500 (7- 3/8) + 2240 x 3.5)

= 1/100 (646400 + 228562.5 + 7840) = **8828.03** Kcal/kg

LCV = (HCV – 0.09H x 587)

= (8828.03 - 0.09 x 7 x 587) = **8458.22** Kcal/Kg

A) SOLID FUELS:

(a)Advantages :

1) They are easy to transport
2) They are convenient to store, without risk of explosion.
3) Their cost of production is low
4) They possess moderate ignition temperatures

(b)Disadvantages :

1) Their ash content is high
2) Their thermal efficiency is low
3) Their calorific value is lower as compared to that of liquid fuels.
4) They cannot be used as internal combustion engines.
5) They require large excess of air for complete combustion.

B) LIQUID FUELS:

(a)Advantages :

1) They possess higher calorific value than solid fuels
2) They burn without forming dust, ash, clinkers etc
3) They are easy to transport through pipes.
4) They can be used as internal combustion fuels.
5) They require less excess of air for complete combustion.
6) They require less furnace space for combustion.

(b)Disadvantages :

1) The cost of liquid fuel is higher as compared to solid fuels.

2) Costly special storage tanks are required for storing liquid fuels
3) There is risk of fire hazards in case of highly inflammable & volatile liquid fuel.
4) They give bad odour
5) Special burners and spraying apparatus required for efficient burning.

C) GASEOUS FUELS:

(a)Advantages :

1) They can be lighted at moments notice
2) They have high calorific values
3) They burn without any soot (or smoke) and are ash less.
4) They burn in slight excess of air.
5) Their combustion can readily be controlled
6) They can also be used as internal combustion engine fuels.

(b)Disadvantages :

1) Very large storage tanks are needed for them
2) They are highly inflammable, so chances of fire hazards are high in their use.
3) They are more costly as compared to the solid & liquid fuels.

COMBUSTION: Combustion is an exothermic chemical reaction, which is accompanied by development of heat and light at a rapid rate, so that temperature rises considerably.

$$\text{Fuel} + O_2 \longrightarrow \text{Products} + \text{Heat}$$

Eg: Combustion of carbon in oxygen. ($C_{(s)} + O_{2\ (g)} \rightarrow CO_{2\ (g)} + 97$ Kcal)

IGNITION TEMPERATURE: The minimum temperature at which the substance ignites and burns without further addition of heat from outside is termed as 'Ignition temperature'.

Calculation of Air Quantities:

To find the amount of oxygen and hence amount of air required for combustion of unit quantity of fuel, the following elementary principles are to be considered.

1) Substances always combine in definite proportions which are determined by molecular masses of reactants & products formed.

Eg: $C + O_2 \rightarrow CO_2$ $\qquad$ $2H_2 + O_2 \rightarrow 2H_2O$

12 $\quad$ 32 $\quad$ 44 $\qquad\qquad$ 4 $\quad$ 32 $\quad$ 36

2) The volume occupied by one mole of any gas at STP (0^0 C & 760 mm pressure) is 22.4 litres.

3) Mass percent of O_2 in air is 23% i.e, 1 kg of O_2 is supplied by 100/23 kgs of air & volume percent of O_2 in air is 21% i.e, $1m^3$ (1000 lts) of oxygen is supplied by 100/21 m^3 of air.

4) Molecular mass of air is 28.94 gm/mole.

5) As it is known that oxygen present in the fuel is associated in the form of H_2O. Hence available hydrogen is given by

$$\left(\text{Mass of Hydrogen} - \frac{\text{Mass of oxygen}}{8} \right)$$

6) Mass of any gas can be converted into its volume at a certain temperature & pressure by assuming the gas to be ideal PV = nRT

7) Nitrogen, Ash, CO_2 present in the fuel or air are in combustible matter and hence they do not take any oxygen during combustion.

8) The total amount of oxygen consumed by the fuel will be given by the sum of amounts of oxygen required by individual combustion of constituents present in the fuel.

9) If oxygen is present as one of the constituents in the fuel then its amount should be subtracted from the total amount of oxygen required.

10) Conversion of volume into weight

28.94 gm of air occupies ------ 22.4 lts
? of air occupies ------- 1lt of air

$$\Rightarrow 1 \times \frac{28.94}{22.4} = \quad \text{gms.}$$

*Theoretical amount of O_2 required for the complete combustion of 1 kg solid or liquid fuel

$$= \left(\frac{32}{12} \times C + 8\left(H - \frac{O}{8} \right) + S \right) \text{Kg}$$

Where C, H, S, & O represents the masses of carbon, hydrogen, sulphur & oxygen respectively per kg of the fuel.

Since the percentage of oxygen in air by mass is 23, so the amount of air require theoretically for combustion of 1 kg of fuel.

$$\left(\quad \left(\quad \right) \quad \right)$$

$$= \frac{100}{23}\ \frac{32}{12} \times C + 8\ H - \frac{O}{8} + S \quad Kg$$

NUMERICALS :

1) Calculate the weight and volume of air required for the combustion of 3kgs of carbon.

Sol : Combustion equation is

$$C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g)$$

1mol = 12g; 1mole = 32g

1mol (or 12gm) of C requires = 1mole (or 32gm) of O_2

Or 3000gm (3kgs) $= \frac{32}{12} \times 3000$ = 8000 gm (or) 8 kg of O_2

Wt.of air require for combustion of 3 kg of carbon is

$$8 \times \frac{100}{23} = 34.783 \text{ kg}$$

Volume of air required is given by

28.94 gm ⟶ 22.4 lts

34.783 x 1000gm ⟶ ?

$$\frac{34.783 \times 1000 \times 22.4}{28.94} = \mathbf{26922.5\ litres}$$

2) A sample of coal was found to have the following percentage composition by weight. C = 75% H = 5.2% O = 12.1% N = 3.2% & Ash = 4.5% calculate the minimum amount of oxygen & air by weight necessary for complete combustion of 1 kg of coal.

Sol: Given that C = 75% ⇒ For 1kg = 750 gm
H = 5.2% ⇒ For 1kg = 52 gm
O = 121% ⇒ For 1kg = 121 gm
N = 3.2% ⇒ For 1kg = 32 gm
Ash =4.5% ⇒ For 1kg = 45 gm

Wt.of O_2 required for the combustion of fuel

$$= \left(\left(C \times \frac{32}{12} \right) + \left(H \times \frac{16}{2} \right) + \left(S \times \frac{32}{32} \right) - O \right)$$

$$= \left\{ \left(750 \times \frac{32}{12} + 52 \times \frac{16}{2} + 0 \right) - 121 \right\} = (2000 + 416 - 121)$$

Minimum weight of air required = 2295 x $\frac{100}{23}$ = 9,978 gm or **9.978 kg**

3) A fuel gas has the following composition by volume:
Hydrogen-24% ; methane-30% ; ethane-11%; ethylene-4.5% ; butene-2.5%; carbon monoxide-6.0% ; carbon dioxide-8% ; oxygen-3% ; nitrogen-12% . Calculate the theoretical amount of air required at 25°C & 750 mm pressure for complete combustion of 1 m^3.

Sol.

1 m^3 of fuel gas contains :

H_2 = 0.24 m^3 ; CH_4 = 0.30 m^3 ; C_2H_6 = 0.11 m^3 ; C_2H_4 = 0.045 m^3 ; C_4H_8 = 0.025 m^3 ; CO = 0.06 m^3 ; CO_2 = 0.08 m^3 ; O_2 = 0.03 m^3 ; N_2 = 0.12 m^3 ;

Combustion Reaction	Volume of O_2 required
$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	$0.240\ m^3 \times \frac{1}{2} = 0.120\ m^3$
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	$0.300\ m^3 \times 2 = 0.600\ m^3$
$C_2H_6 + \frac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O$	$0.110\ m^3 \times \frac{7}{2} = 0.385\ m^3$
$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$	$0.045\ m^3 \times 3 = 0.135\ m^3$
$C_4H_8 + 6O_2 \rightarrow 4CO_2 + 4H_2O$	$0.025\ m^3 \times 6 = 0.150\ m^3$
$CO + \frac{1}{2}O_2 \rightarrow CO_2$	$0.060\ m^3 \times \frac{1}{2} = 0.030\ m^3$
$-\ O_2$	$-\ 0.03\ m^3 = 0.030\ m^3$
	Total = $1.390\ m^3$

Calculation of volume of O_2 at 25°C & 750 mm pressure

Given data (STP)	At 25°C & 750 mm
P_1 = 760 mm	P_2 = 750 mm
V_1 = 1.390 m^3	V_2 = ?
T_1 = 273 K	T_2 = 298 K

$$\therefore \quad \frac{760 \text{ X } 1.39\ m^3}{273} = \frac{750 \text{ X } V_2}{298}$$

$$\Rightarrow \quad V_2 = \frac{760 \text{ X } 1.39 \text{ X } 298}{273 \text{ X } 750} = \underline{\mathbf{1.538\ m^3}}$$

Volume of air required = $1.538\ m^3 \times \frac{100}{21}$ = **$7.324\ m^3$**

SOLID FUELS:

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

Various types of coal are commonly recognized on the basis of Rank.

RANK: The qualitative measure of carbon content in coal (or the degree or extent of maturation of coal) is called "Rank'.

The progressive transformation of wood is as follows:

Wood ⟶ peat ⟶ Lignite ⟶ Bituminous coal ⟶ Anthracite

Rank	Type of Coals	Qualities
Low rank coals	peat, lignite & sub Bituminous	Soft, low % of carbon, low calorific value, High moisture content, H,O,S,N Content is more.
High rank coals	Bituminous, Anthracite	Hard, higher % of carbon, high calorific value, low moisture content, H,O,S,N Contents are less.

AVERAGE COMPOSITION:

FUEL	Moisture of air – dried sample at 40^0C (%)	C (%)	H (%)	N (%)	O (%)	Calorific value (Kcal/Kg)
Wood	25	50.0	6.0	0.5	43.5	4000 – 4500
Peat	25	57.0	5.7	2.0	35.3	4125 – 5400
Lignite	20	67.0	5.0	1.5	26.5	6500 – 7100
Sub-bituminous coal	11	77.0	5.0	1.8	16.2	7000 – 7500
Bituminous coal	4	83.0	5.0	2.0	10.0	8000 – 8500

Semi – Bituminous coal Anthracite	1 1.5	90.0 93.3	4.5 3.0	1.5 0.7	4.0 3.0	8350 – 8500 8650 – 8700

ANALYSIS OF COAL: To ascertain the quality of coal it is subjected to two types of analysis : **(1)**Proximate analysis **(2)** Ultimate analysis

1) PROXIMATE ANALYSIS :

It includes the determination of **(a)** moisture content **(b)** volatile matter **(c)** Ash **(d)** Fixed carbon.

(a) Moisture Content : About 1gm of finely powdered dry coal sample is weighed in a silica crucible & then placed in an electric hot air oven maintained at a temperature of 105^0 to 110^0 C. The crucible is allowed to remain in the oven for 1 hour. It is then cooled in a desiccator and weighed. % of loss in weight is reported as moisture

$$\textbf{\% of Moisture} = \frac{\textbf{Loss in weight}}{\textbf{Wt.of coal taken}} \times 100$$

(b) Volatile Matter : The dried of coal left in crucible after evaporation of Moisture is then covered with lid and placed in muffle furnace maintained at $925^0 \pm 20\ ^0$C. The crucible is taken out after 7 minutes of heating. It is cooled first in air and then in a desiccators and weighed again. The loss in weight is reported as volatile matter.

$$\textbf{\% of volatile matter} = \frac{\textbf{loss in weight due to the removal of volatile matter}}{\textbf{Wt. of coal sample taken}} \times 100$$

(c) Ash : The residual coal is then heated without lid in a muffle furnace at $700^0 \pm 50^0$C for about half an hour. The crucible is then taken out, cooled first in air and then in a desiccators & weighed. Heating, cooling & weighing is repeated till constant weight is obtained. The residue reported is ash.

$$\textbf{\% of Ash} = \frac{\textbf{Weight of Ash left}}{\textbf{Weight of coal taken}} \times 100$$

(d) Fixed Carbon :

% of Fixed Carbon = 100 - % of (Moisture + Volatile matter + ash)

SIGNIFICANCE of PROXIMATE ANALYSIS :

1) Moisture Content: Moisture lowers the calorific value of the coal due to latent heat of evaporation. Also it quenches the fire in the furnace. Hence lesser the Moisture content better is the quality of coal as fuel.

2) <u>Volatile Matter:</u> Coal with high volatile matter is undesirable. A high volatile matter containing coal burns with **(i)** long flame **(ii)** high smoke and **(iii)** low calorific value. Hence lesser the volatile matter better is the rank of Coal.

3) <u>Ash:</u> Ash is the next combustible useless matter, which is left behind when all the combustible substances have burnt from coal. The presence of ash reduces the calorific value of coal and hinders the flow of air and heat thereby decreasing the efficiency of coal. Hence lower the ash content better is the quality of coal.

4) <u>Fixed Carbon:</u> It represents the quantity of carbon that burns in solid state by a primary current of air drawn through hot bed of fuel.
Higher the % of fixed carbon, greater is the calorific value and better is the quality of coal.

2 ULTIMATE ANALYSIS:

It involves the following determinations **(1)** Carbon & Hydrogen **(2)** Nitrogen **(3)** Sulphur **(4)**Ash **(5)** Oxygen

1) <u>Carbon & Hydrogen:</u> About 1-2 gms of coal powder is weighed and burnt in excess of oxygen in a combustion apparatus. Carbon & Hydrogen are converted to CO_2 and H_2O respectively. The gaseous products are passed through weighed tubes of anhydrous $CaCl_2$ which absorbs all the H_2O and through weighed tubes of KOH where CO_2 is absorbed.

$$H_2 + \tfrac{1}{2} O_2 \longrightarrow H_2O \qquad C + O_2 \longrightarrow CO_2$$

$$CaCl_2 + 7H_2O \longrightarrow CaCl_2.\,7H_2O \qquad 2KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$$

$$\%\text{ of Hydrogen} = \frac{\text{Increase in Wt.of } CaCl_2 \text{ tube}}{\text{Wt of Coal Sample taken}} \times \frac{2}{18} \times 100$$

$$\%\text{ of Carbon} = \frac{\text{Increase in Wt.of KOH tube}}{\text{Wt of Coal Sample taken}} \times \frac{12}{44} \times 100$$

2) <u>Nitrogen :</u> About 1gm of accurately weighed coal powder is treated with Conc.H_2SO_4 along with K_2SO_4 catalyst in a KJeldahl flask & heated. Nitrogen is converted to ammonium Sulphate $(NH_4)_2SO_4$. After solution becomes clear, it is then treated with excess of KOH to liberate NH_3. NH_3 so produced is distilled over & absorbed in a known volume of standard H_2SO_4 soln.(N/10). The unused H_2SO_4 solution is determined by titration with standard NaOH solution.(N/10).

$$\%\text{of Nitrogen} = \frac{\text{Vol. of acid used} \times \text{Normality of acid} \times 1.4}{\text{Weight of Coal taken}}$$

- Coal Contain Nitrogen $\xrightarrow[K_2SO_4]{Conc.H_2SO_4}$ $(NH_4)_2SO_4$ $\xrightarrow{\text{Excess KOH}}$ NH_3 $\xrightarrow{\text{Distilled}}$ Absorbed in known Vol.of 0.1N H_2SO_4 $\rightarrow$ Unused H_2SO_4 is Titrated c 0.1 N NaOH

3) <u>Sulphur :</u> A known mass of Sulphur containing coal is burnt in bomb colorimeter. Sulphur is oxidized to sulphate, which is washed. Washings contain Sulphate are treated with $BaCl_2$ solution which precipitates out as $BaSO_4$.

$$BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HCl$$

The precipitate is filtered, washed and heated to constant weight.

$$\%\text{ of Sulphur} = \frac{\text{Wt of } BaSO_4 \text{ obtained} \times 32 \times 100}{\text{Wt of coal sample taken} \times 233}$$ where mol.wt. of $BaSO_4$ = 233

4) <u>Ash :</u> As determined by proximate analysis

5) <u>Oxygen :</u>

$$\%\text{ of Oxygen} = 100 - \%\ (C + H + N + S + \text{ash})$$

<u>SIGNIFICANCE of ULTIMATE ANALYSIS :</u>

It is useful in combustion calculations.

<u>Carbon:</u> Greater the % of carbon, better is the quality of coal and higher will be the calorific value .

<u>Hydrogen:</u> Hydrogen is mostly associated with volatile matter & affects the use of coal.

<u>Nitrogen:</u> A good quality coal should contain very little nitrogen content as it has no calorific value .

<u>Sulphur:</u> Although sulphur contributes to heating value of coal, its combustion products produce corrosive acidic gases like SO_2, SO_3 etc which pollutes atmosphere. Hence the presence of sulphur is highly undesirable in coal. Usually 0.5 to 3% of sulphur is present in coal.

<u>Oxygen:</u> A good quality coal should contain low % of oxygen. It is associated with H_2 as water which reduces the available hydrogen for combustion.

Higher the oxygen content higher will be the moisture. As a result calorific value will be low. Increase of 1% of oxygen, decreases the calorific value by 1.7%.

1) A sample of coal was analyzed as follows: Exactly 2.500g was weighed into a silica crucible. After heating for 1 hour at 110^0 C, the residue weighed 2.415g. The crucible was then covered with a vented lid and strongly heated for exactly 7 minutes at 950 ± 20^0C. The residue weighed 1.528g. The crucible was then heated without the cover, until a constant weight was obtained. The last residue was found to weight 0.245g **(i)** calculate the percentage results of the above analysis (**ii)** To which type of analysis does the above description belong? Why is the analysis so named?

Sol : (i) a) Moisture (%) $= \dfrac{\text{loss in weight}}{\text{Wt. of coal taken}} \times 100$

$$= \frac{2.5 - 2.415}{2.5} \times 100 = \mathbf{3.40\ \%}$$

b) Volatile matter (%) $= \dfrac{\text{loss in wt.due to removal of volatile matter}}{\text{Wt. of coal Spl taken}} \times 100$

$$= \frac{2.415 - 1.528}{2.5} \times 100 = \mathbf{35.48\ \%}$$

c) Ash (%) $= \dfrac{\text{Wt. of ash left}}{\text{Wt. of coal taken}} \times 100$

$$= \frac{0.245}{2.5} \times 100 = \mathbf{9.80\ \%}$$

d) Fixed carbon (%) = 100 - % of (Moisture + Volatile matter + ash)

$$= 100 - (3.40 + 35.48 + 9.80) = \mathbf{51.32\ \%}$$

ii) This type of analysis is known as proximate analysis because the data collected vary with the procedures adopted.

2) 1.56gm of the coal was KJeldalized and NH_3 gas thus evolved was absorbed in 50ml of 0.1N H_2SO_4. After absorption, the excess (residual) acid – required 6.25ml of 0.1N NaOH for exact neutralization. 2.60g of the coal sample in a quantitative analysis gave 0.1755g of $BaSO_4$. Calculate the percentage of N and S in the coal sample.

% of Nitrogen $= \dfrac{\text{Vol.of acid used} \times \text{normality of acid} \times 1.4}{\text{Wt. of coal taken}}$

$$= \underline{(50-6.25) \times 0.1 \times 1.4} = \underline{43.75 \times 0.1 \times 1.4} = \mathbf{3.926\ \%}$$

1.56 1.56

$$\% \text{ of Sulphur} = \frac{\text{Wt.of } BaSO_4 \text{ obtained } \times 32}{\text{Wt.of coal Spl taken in bomb} \times 233} \times 100$$

$$= \frac{0.1755 \times 32}{2.60 \times 233} \times 100 = \mathbf{0.927\ \%}$$

LIQUID FUELS:

The main source of liquid fuels is petroleum (petra = rock, oleum = oil).It is also called as 'Crude oil'. It is dark greenish – brown viscous oil present deep in earth crust.

Petroleum consists of liquid fuels like gasoline, diesel, kerosene etc. paraffins, cyclo paraffins, olefins, aromatic compounds etc. The average composition of crude petroleum is C = 80-87% ; H = 11.1 – 15% S = 0.1 – 3.5%; 0= 0.1 – 0.9%; N = 0.4 – 0.9%.

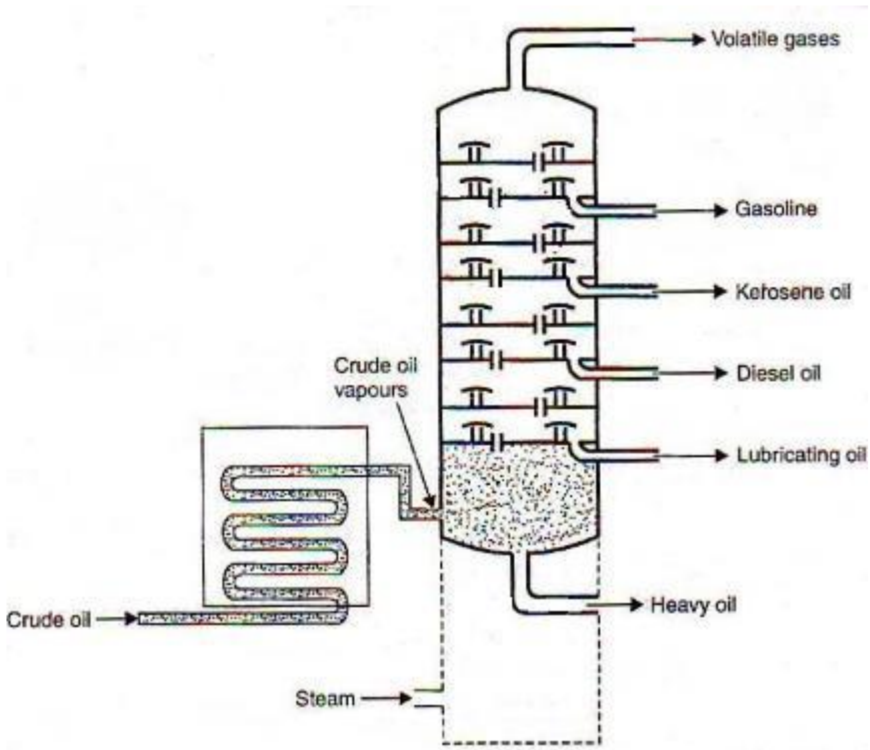
FRACTIONATION OF PETROLEUM CRUDE (OR) REFINING OF CRUDE OIL:

Crude oil is separated into various useful fractions by fractional distillation. The process is called 'Refining of crude oil'. Refining involves the following steps:

Step:1 ***Separation of water by Cottrell's process*** **:** The crude oil from the oil well is an extremely stable emulsion of oil & salt water. When this emulsion is allowed to flow between two highly charged electrodes. The colloidal water droplets coalesce to form large drops which separates out from the oil.

Step:2 ***Removal of Harmful Sulphur compounds*** **:** The oil may contain harmful sulphur compounds, hence they must be removed. Oil is treated with copper oxide, sulphur compounds present in oil are converted into solid copper sulphide which are then removed by filtration.

Step:3 ***Fractional Distillation*** **:** The crude oil is heated to about 400^0C in an iron retort & hot vapours formed are passed through fractionating column, which is a tall cylindrical tower containing a number of horizontal stainless steel trays at short distances. Each tray is provided with small chimney covered with a loose cap. As the vapours go up they become gradually cooler & fractional condensation takes place at different heights of column. Higher boiling fraction condenses first while the lower boiling fraction later.



1.Gasoline (or) Petrol (or) Motor Spirit : It is a mixture of hydro carbons such as pentane to octane and is obtained between **40 ^{0}C – 120 ^{0}C**. This fraction is highly volatile & inflammable. It is used as fuel for internal combustion engines of automobiles & aero planes etc. Its calorific value is **11,250 cal/gm**. The approximate composition is **C = 84% ; H = 15% ; N+S+O = 1.0%**

2.Kerosene Oil: It is a mixture of hydrocarbons from decane to hexa decane. It is obtained between **180 ^{0}C – 250 ^{0}C**. It does not vaporize easily. It is used as domestic fuel in stoves, as jet engine fuel and for making oil gas. Its calorific value is **11,100 cal/gm**. The approximate composition is **C = 83%; H = 16% with less than 0.1% of Sulphur**. Its density is **0.75 – 0.85**.

3.Diesel oil (or) Fuel oil (or) Gas oil: It is a mixture of $C_{15}H_{32}$ to $C_{18}H_{38}$ and is obtained between **250 ^{0}C – 320 ^{0}C**. It is used as diesel engine fuel. Its calorific value is **11,000 cal/gm**. Its density is **0.86 – 0.95**. The oil contains **C = 85%; H = 12%.**

CRACKING: The decomposition of high molecular weight hydro carbons of high boiling point into simpler low molecular weight hydro carbons of low boiling point is called 'cracking'.

Eg: $C_{10}H_{22}$ (Decane) $\xrightarrow{\text{Cracking}}$ C_5H_{12} (n – pentane) + C_5H_{10} (pentene)

B.P = 174 ^{0}C → B.P = 36 ^{0}C

Significance of cracking: Of all fractions obtained by fractionation of petroleum, gasoline has the largest demand as a motor fuel but its yield is only 20%. Also the quality of motor fuel is not high. Hence it should be properly blended. To overcome the difficulties, the middle and heavier petroleum fractions are cracked to get petrol.

Petrol so obtained has better characteristics than straight run petrol.

Types of cracking

- **Thermal Cracking**
  - **Liquid phase Thermal cracking**
  - **Vapour Phase Thermal cracking**
- **Catalytic Cracking**
  - **Fixed bed catalytic cracking**
  - **Moving bed catalytic cracking**

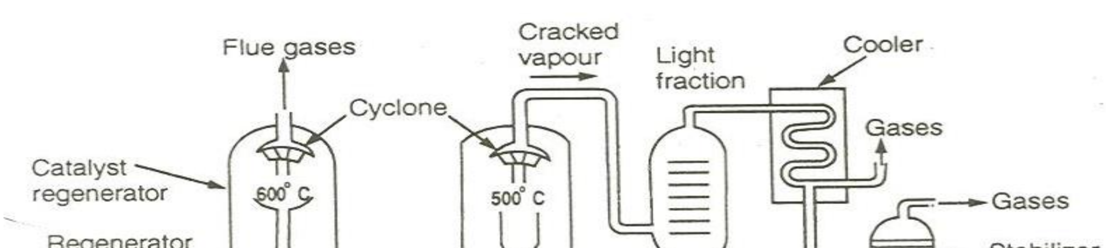
***Thermal Cracking*:** When heavy oils are subjected to high temperature and pressure in the absence of catalyst. It is called 'thermal cracking'. In this cracking, bigger hydrocarbon molecules break down to give smaller paraffins, olefins & some hydrogen.

***Catalytic cracking*:** The quality and quantity of gasoline produced by cracking can be greatly improved by using suitable catalyst like aluminum Silicate $Al_2(SiO_3)_3$ or Alumina (Al_2O_3).

Lower temperature & pressures are required for catalytic cracking comparative to thermal cracking.

Moving Bed Catalytic Cracking: In moving bed catalytic cracking, the feed oil is first passed through a pre-heater. The pre-heated oil vapours along with very finely powdered catalyst are then passed in a reactor which is maintained at 500°C for catalytic cracking. The cracked oil vapours are then passed to the fractionating column through a centrifugal separator, called cyclone (which allows only the cracked oil vapours, but retains the catalyst powder in the reactor), where heavy oil is separated. The vapours are then passed through the cooler, where gasoline condenses along with some gases and is then sent to a stabilizer to remove the dissolved gases and pure gasoline is recovered.

The catalyst powder gradually becomes heavier, due to the coating with carbon and settles to the bottom from where it is forced by an air



blower to regenerator (maintained at 600°C).In regenerator, carbon is burnt and the regenerated catalyst then flows through stand-pipe for mixing with fresh batch of the 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 the catalyst.

KNOCKING: In internal combustion engine, mixture of gasoline vapours and air is used as fuel. Combustion reaction is initiated by spark in the cylinder. The flame spreads throughout the gaseous mixture smoothly & rapidly, there by the expanding gas drives the piston down the cylinder.

But in certain circumstances the fuel – air mixture gets heated up to a temperature greater than ignition temperature during compression & the rate of oxidation becomes so great that the last portion of fuel – air mixture gets ignited spontaneously.

The resultant shock wave dissipates its energy by hitting the cylinder walls & piston emits the characteristic rattling sound called knocking.

Def: The rattling sound produced in an internal combustion engine as a result of spontaneous premature combustion of fuel – air mixture is called 'Knocking'.

Knocking depends upon **i)** Engine design **(ii)** Running conditions of engine **(iii)** chemical structure of fuel hydro carbons.

Consequences:

1) Decreased power output
2) Mechanical damage by overheating of cylinder

knocking characteristics is expressed in terms of octane number.

OCTANE NUMBER (or RATING): The percentage of iso-octane in a mixture of iso-octane & n-heptane mixture which has the same knocking characteristics as that of gasoline sample under the same conditions is known as **'Octane number'**.

For example, a fuel with octane number 60 will give the same knocking as the mixture by volume of 60% iso - octane and 40% n – heptane.

Higher is the octane number (anti knocking nature), better is the quality of fuel. n-heptane knocks severely & hence its antiknock value is arbitrarily given zero and iso - octane (2,2,4 - tri methyl pentane) gives very little knocking, and hence its anti-knock value is given as 100.

Anti knock characteristics of a fuel can be improved by the addition of anti knocking agents like TEL (Tetra ethyl lead $(C_2H_5)_4Pb$) and diethyl telluride, $(C_2H_5)_2$ Te etc. During the combustion TEL produce Pb & PbO. These particles arrest the propagation of explosive chain reaction responsible for knocking.

Pb & PbO reduces the life of engine and also causes pollution. Hence should be removed by adding ethylene di bromide

$$Pb + C_2H_4Br_2 \longrightarrow PbBr_2 + C_2H_4$$

CETANE NUMBER: In diesel engine the fuel used is the mixture of diesel and air. In these engines ignition is carried out by compression of air. In this case also knocking arise due to delayed ignition. Knocking characteristics in diesel engine is expressed in terms of cetane number.

The percentage of n-hexadecane (cetane) in a mixture of hexa decane and 2 – methyl naphthalene which has the same characteristics as that of diesel fuel is called 'cetane number'.

n-hexadecane has high resistance to knocking hence its anti knock value is given as 100 and 2-methyl naphthalene has severe knocking value hence its anti knock value is given as zero.

Cetane number of the fuel can be improved by adding small amounts of pre-ignition dopes like ethyl nitrites, iso amyl nitrites etc. Diesel engines require a fuel of cetane number greater than 45.

GASEOUS FUELS :

LIQUEFIED PETROLEUM GAS (LPG): LPG or bottled gas or refinery gas is obtained as a by–product, during the cracking of heavy oils or from natural gas. LPG is dehydrated, desulphurised & traces of odorous organic sulphides (mercaptans) are added to give warning of gas leak. LPG is supplied under pressure in containers. Its calorific value is about **27,800 kcal/m^3**

LPG consists of hydro carbons of such volatility that they can exist as gas under atmospheric pressure, but can be readily liquefied under pressure. The main constituents of LPG are n-butane, iso butane, butylenes & propane with little or no propylene & ethane. It is highly knock resistant with high calorific values and burns cleanly.

USES: It is used as a domestic fuel and industrial fuel. However there is a increasing trend to use LPG as a motor fuel.

COMPRESSED NATURAL GAS (CNG): Natural gas is obtained with petroleum in large amounts from oil wells.

The main constituents of natural gas are methane (70-90%), ethane (5-10%), H_2(3%) and the rest other hydro carbons, CO & CO_2. The calorific value varies from **12,000 to 14,000 kcal/m^3.**

Compressed natural gas (CNG) is a natural gas compressed to a high pressure of **1000 atmospheres**. A steel cylinder containing 15kg of CNG contains about 2×10^4 L or 20m^3 of natural gas at 1atm pressure. As it causes less pollution, it is used as a substitute for petrol and diesel. During its combustion Sulphur & Nitrogen gases are not evolved. Carbon particles are also not ejected. But the cost of engine designed to use CNG as a fuel is more compared to the engine designed to use petrol or diesel.

Advantages of CNG:

i)It causes less pollution **(ii)** Products of combustion are free from sulphur & Nitrogen gases **(iii)** It undergoes regular combustion **(iv)** It is better fuel than petrol & diesel.

Block diagram of Moving bed catalytic cracking

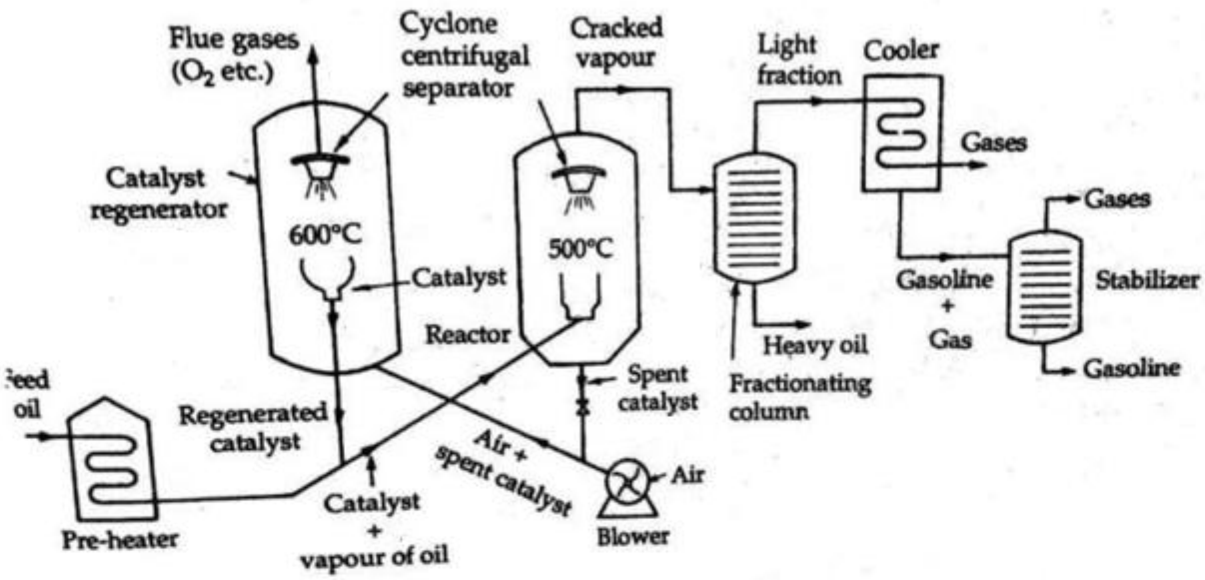


Fig. 4. Moving bed catalytic cracking.