

**FUEL**

Fuel is a combustible substance containing carbon as main constituent which on proper burning gives large amount of heat that can be used for domestic and industrial purposes.

Ex: Wood, Coal, Charcoal, Kerosene, Petrol.

**FOSSIL FUEL**

The primary and main sources of fuel are coal and Petroleum. These are stored fuel available in earth crust and are called fossil fuel.

**Classification:****1. On the basis of occurrence :**

Fuels are of two types on the basis of their occurrence, they are

- (a) Natural – Primary fuel
- (b) Artificial- Secondary fuel.

**(a) Natural – Primary fuel :**

The fuels which are found from nature are Natural or Primary fuel:

Ex : Wood, Petroleum, Coal, Natural Gas etc

**(b) Artificial- Secondary fuel :**

Fuels which are derived artificially from primary fuel are known as artificial fuel.

Ex: Kerosene, Coal Gas, LPG etc

**2. On the basis of physical state of aggregation**

Fuels are of 3 types depending upon the state of the fuel.

- a) Solid Fuel – Wood, Coal, Coke
- b) Liquid Fuel – Kerosene, Petrol, Diesel
- c) Gaseous Fuel – LPG, Coal Gas, Natural Gas.

**Units of Heat****CGS System**

**Calorie:** It is the amount of heat required to raise the temperature of 1 g of water through 1°C.

**MKS System**

**Kilo Calorie:** It is the amount of heat required to raise the temp. of 1 kg of water through 1°C.

1 Kcal = 1000 Cal.

**British Thermal Unit (BTU / BTHU)**

It is the amount of heat required to raise temperature of 1 pound of water through 1°F

1 BTHU = 252 cal. = 0.252K cal.

**Centigrade Heat Unit (CHU)**

It is the amount of heat required to raise the temperature of 1 pound of water through 1°C.

1 Kcal = 3.968 BTHU = 2.2 CHU

**Calorific Value. (CV)**

It is the total amount of heat liberated when a unit mass or volume of fuel is burnt completely in presence of Oxygen.

It is of two types. (i) Higher Calorific Value (HCV) or Gross Calorific Value (GCV)  
(ii) Lower Calorific Value (LCV) or Net Calorific Value (NCV)

**(i) Higher Calorific Value (HCV) / Gross Calorific Value (GCV)**

It is the total amount of heat liberated when unit mass or volume of the fuel is burnt completely and the product of combustion are cooled to room temperature.

**(ii) Lower Calorific Value (LCV) or Net Calorific Value (NCV)**

It is defined as the net heat produce when a unit mass or volume of fuel is burnt completely and the products of combustion are allowed to escape.

LCV = HCV - Latent Heat of Vaporisation.

= HCV - (Mass of  $H_2$  x 9 x Latent Heat of Vaporisation)

$\left[ \begin{array}{l} \because 2 \text{ parts by mass of } H_2 \text{ produces } 18 \text{ parts by mass of } H_2O \\ 1 \text{ part by mass of } H_2 \text{ produces } 9 \text{ parts by mass of } H_2O \end{array} \right]$

**Unit of Calorific Values**

For solid and liquid fuels unit is **Cal/g , KCal / Kg, BTHU/ lb**

For Gaseous Fuel is **Cal /Cm<sup>3</sup>, KCal/m<sup>3</sup>, BTHU/Ft<sup>3</sup>**

**Characteristics of Good Fuel**

A good fuel should have

- i. High calorific value.
- ii. Moderate ignition temperature because low ignition temperature is dangerous for storage & transportation of fuel since it can cause fire hazard and high ignition temperature can cause difficulty in kindling or ignition. But the fuel is safe during storage, handling & transport. Hence an ideal fuel should have moderate temp.
- iii. Low moisture content as moisture reduces the calorific value.
- iv. Low non-combustible matter content as it reduces the total heat by producing ash.
- v. Moderate velocity of combustion
- vi. Harmless combustion bi-product
- vii. Low cost
- viii. Easy Transportation – Solid & liquid fuels are easy for transportation but the transportation of gaseous fuel is very costly.
- ix. Combustion may be controllable
- x. Non-spontaneous combustion.
- xi. Burn in air with efficiency without muck smoke.

**Comparison of Solid , Liquid and Gaseous Fuel**

Characteristics	Solid Fuel	Liquid Fuel	Gaseous Fuel
Calorific value	Least	Higher	Highest
Cost	Cheap	More costly than solid fuel	Costly
Storage and Transportation	Convenient	Easy to transport through pipe lines but care must be taken to store them in closed container	Should be stored in voluminous storage tank & can be distributed through pipe line
Risk of fire hazard	Least	Greater risk than solid fuels	High risk full as they are highly inflammable.
Rate of Combustion	Slow process	Quick Process	Very rapid and efficient
Rate of control	Not easy	It can be controlled or stopped when needed	Possible by controlling air supply
Handling Cost	High because need more labour & space.	Low	Low
Ash Content	Ash is always a problem and its disposal is also a problem	No Ash	No Ash
Smoke	More Smoke	Less Smoke	No smoke
Use in IC Engine	Not Possible	Possible	Possible
Thermal Efficiency	Least	Higher	Highest

**Theoretical Calculation of calorific value by Dulong's Formula:**

Calorific Value of the fuel is the sum of Calorific Values due to all components present in the given fuel.

<u>Constituent</u>	<u>C</u>	<u>H</u>	<u>S</u>
GCV in KCal/ Kg	8080	34500	2240

$$GCV = \frac{1}{100} \left[ 8080 C + 34500 \left( H - \frac{O}{8} \right) + 2240 S \right] \text{ KCal/Kg}$$

$$NCV = GCV - 0.09H \times 587 \text{ KCal/Kg}$$

Where : C is the % of Carbon , H is the % of Hydrogen, S is the % of Sulphur

**Q- 1. Calculate gross & net calorific value of a sample having following composition.**

**C = 80%, H=7%, O=3%, S=3.5%, N=2.5%, Ash=4.44%.**

**Sol<sup>n</sup>.**

$$\begin{aligned}
 GCV \text{ or } HCV &= \frac{1}{100} \left[ 8080 C + 34500 \left( H - \frac{O}{8} \right) + 2240 S \right] \text{ KCal/Kg} \\
 &= \frac{1}{100} \left[ 8080 \times 80 + 34500 \left( 7 - \frac{3}{8} \right) + 2240 \times 3.5 \right] \\
 &= 8828.025 \text{ K Cal / Kg}
 \end{aligned}$$

$$\begin{aligned}
 NCV &= GCV - 0.09H \times 587 \text{ KCal/Kg} = 8828.025 - 0.09 \times 7 \times 587 \text{ KCal/Kg} \\
 &= 8458.215 \text{ KCal/Kg}
 \end{aligned}$$

**Q-2). Calculate HCV & NCV of a sample of Coal having the following composition by weight : C=75% , H=5.2% , O =12.1% , N=3.2%, Ash = 4.5% .**

**Sol<sup>n</sup>.**

$$GCV \text{ or } HCV = \frac{1}{100} \left[ 8080 C + 34500 \left( H - \frac{O}{8} \right) + 2240 S \right] \text{ KCal/Kg}$$

$$= \frac{1}{100} \left[ 8080 \times 75 + 34500 \left( 5.2 - \frac{12.1}{8} \right) + 2240 \times 0 \right]$$

$$= 7332.1825 \text{ K Cal / Kg}$$

$$NCV = GCV - 0.09H \times 587 \text{ KCal/Kg} = 7332.1825 - 0.09 \times 5.2 \times 587 \text{ KCal/Kg}$$

$$= 7057.4715 \text{ KCal/Kg}$$

### **Combustion Calculation**

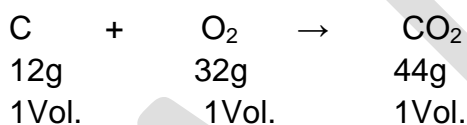
The process of oxidation of fuel producing heat & light at a rapid rate is called as combustion.

### **Calculation**

Combustion calculation is based on balance chemical equation of oxidation of constituents of fuel.

### **Combustion Equation**

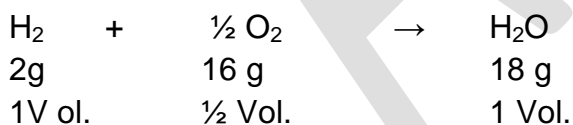
#### **1. Carbon (C)**



Mass O<sub>2</sub> required for combustion Carbon present in the fuel = 32/12 x mass of C

Vol. of O<sub>2</sub> required = Vol. of Carbon

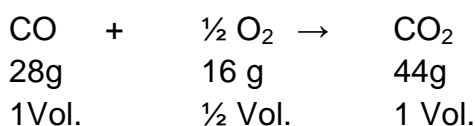
#### **2. Hydrogen (H)**



Mass of O<sub>2</sub> required for combustion of hydrogen present in fuel = 16/2 x mass of H

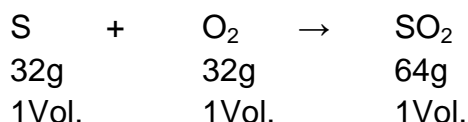
Vol. of O<sub>2</sub> required = ½ the Vol. of Hydrogen

#### **3. Carbon Monoxide (CO)**



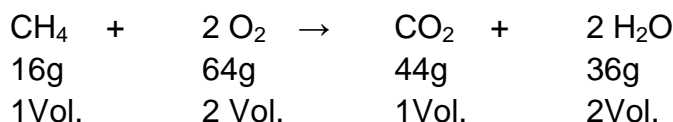
Mass of O<sub>2</sub> required for combustion of CO = 16/28 x mass of CO

Volume of O<sub>2</sub> required = ½ x Vol. of CO

**4. Sulphur (S)**

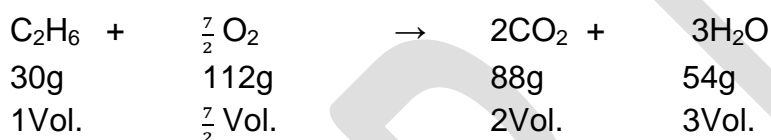
Mass of O<sub>2</sub> required for combustion of sulphur = Mass of S

Vol. of O<sub>2</sub> required = Vol. of Sulphur

**5. Methane (CH<sub>4</sub>)**

Mass of O<sub>2</sub> required for combustion of CH<sub>4</sub> = 64/16 x mass of CH<sub>4</sub>

Vol. of O<sub>2</sub> = 2 x Vol. of CH<sub>4</sub>

**6. Ethane (C<sub>2</sub>H<sub>6</sub>)**

Mass of O<sub>2</sub> required for combustion of Ethane = 112/30 x mass of C<sub>2</sub>H<sub>6</sub>

Vol. of O<sub>2</sub> required =  $\frac{7}{2}$  x Vol. of C<sub>2</sub>H<sub>6</sub>

**7. Ethyne or Acetylene (C<sub>2</sub>H<sub>2</sub>)**

Mass of O<sub>2</sub> required for combustion of Ethane = 80/26 x mass of C<sub>2</sub>H<sub>2</sub>

Vol. of O<sub>2</sub> required =  $\frac{5}{2}$  x Vol. of C<sub>2</sub>H<sub>2</sub>

Total mass of theoretical O<sub>2</sub> required for combustion of fuel = (Sum of the O<sub>2</sub> required for combustion of individual components of the fuel – O<sub>2</sub> Present in the fuel).

Mass of the air required = (Mass of O<sub>2</sub> required x 100 / 23)

[Because 23 % by mass of O<sub>2</sub> Present in the air ]

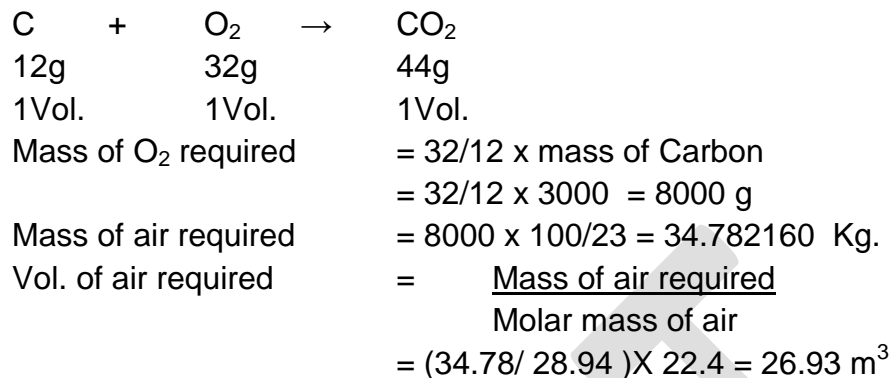
Vol. of air required = (Vol. of O<sub>2</sub> required x 100/21)

[As 21% by volume of O<sub>2</sub> present in air]

28.94 g/mol is taken as molar mass of Air. [1 mole of any gas at STP has volume 22.4 ltr.]

**Q-1). Calculate the Weight & Volume of air required for combustion of 3 Kg of Carbon.**

**Sol<sup>n</sup>.**



**Alternatively :**

32 g of O<sub>2</sub> occupied = 22.4 Lt.

01 g of O<sub>2</sub> occupied =  $22.4/32$

8000 g of O<sub>2</sub> occupied =  $22.4/32 \times 8000$   
 = 5600 Lt.

Volume of O<sub>2</sub> required =  $1/1 \times 5600 \text{ Lt}$

Volume of air required =  $5600 \times (100/21) = 26.66 \text{ m}^3$

**Q-2). The % composition of coal sample is C=80%, H=4%, O<sub>2</sub> =3%, N=3%, S=2%, Ash=5%, Moisture =3%.**

**(a) Calculate the quantity of O<sub>2</sub> & air required for complete combustion of 1Kg. coal.**

**(b) Calculate the quantity of air needed for complete combustion of 1 Kg. of Coal, if 60 % of excess air is supplied**

**Sol<sup>n</sup>. (a)**

1Kg. = 1000 g of coal

Mass of C =  $80/100 \times 1000 = 800 \text{ g}$

Mass of H =  $04/100 \times 1000 = 40 \text{ g}$

Mass of O<sub>2</sub> =  $03/100 \times 1000 = 30 \text{ g}$

Mass of N<sub>2</sub> =  $03/100 \times 1000 = 30 \text{ g}$

Mass of S =  $02/100 \times 1000 = 20 \text{ g}$

Mass of ash =  $05/100 \times 1000 = 50 \text{ g}$

Mass of Moisture =  $03/100 \times 1000 = 30 \text{ g}$

Mass of O<sub>2</sub> required =  $[(32/12 \times 800) + (16/2 \times 40) + (32/32 \times 20)] - 30 \text{ g}$   
 =  $\{(2133.34 + 320 + 20) - 30\} \text{ g} = 2443.33 \text{ g}$

Mass of air required =  $2443.33 \times 100/23 = 10623.18 \text{ g} = 10.623 \text{ Kg.}$

**Sol<sup>n</sup>. (b)** If 60% of excess air is supplied then mass of air need is  $10.623.18 \times 160/100$   
 = 16997.088g = 16.997 Kg.

**Q-3). Calculate the volume of air required for complete combustion of 1 ltr of gaseous fuel having composition CO = 46%, CH<sub>4</sub> = 10%, C<sub>2</sub>H<sub>2</sub> = 4%, H<sub>2</sub> = 4%, N<sub>2</sub> = 1%.**

**Sol<sup>n</sup>.** 1 Lt. = 1000 cm<sup>3</sup> = 1000 ml

$$\text{Vol. of CO} = 46/100 \times 1000 = 460 \text{ ml}$$

$$\text{Vol. of CH}_4 = 10/100 \times 1000 = 100 \text{ ml}$$

$$\text{Vol. of C}_2\text{H}_2 = 04/100 \times 1000 = 40 \text{ ml}$$

$$\text{Vol. of H}_2 = 04/100 \times 1000 = 40 \text{ ml}$$

$$\begin{aligned} \text{Vol. of O}_2 \text{ required} &= [(1/2 \times 460) + (5/2 \times 40) + (2 \times 100) + (1/2 \times 40)] \text{ ml} \\ &= 230 + 100 + 200 + 20 = 550 \text{ ml} \end{aligned}$$

$$\text{Vol. of air required} = 550 \times 100/21 = 2619.04 \text{ ml} = 2.62 \text{ ltr.}$$

**Q-4). Calculate wt. & vol. of air required for complete combustion of 1 Kg. of Coal having the composition of C=80 %, H=7%, O= 3%, S=3.5%, N=2.5%, ash=4.4%.**

**Sol<sup>n</sup>.**

C=80 %, H=7%, O=3%, S=3.5%, N=2.5%, ash=4.4%

1Kg. = 1000 g

$$\text{Mass of C} = 80/100 \times 1000 = 800 \text{ g}$$

$$\text{Mass of H} = 07/100 \times 1000 = 70 \text{ g}$$

$$\text{Mass of O}_2 = 03/100 \times 1000 = 30 \text{ g}$$

$$\text{Mass of N}_2 = 2.5/100 \times 1000 = 25 \text{ g}$$

$$\text{Mass of S} = 3.5/100 \times 1000 = 35 \text{ g}$$

$$\text{Mass of ash} = 4.4/100 \times 1000 = 44 \text{ g}$$

$$\begin{aligned} \text{Mass of O}_2 \text{ required} &= [(32/12 \times 800) + (16/12 \times 70) + (1 \times 35)] - 30 \text{ g} \\ &= 2698.33 \text{ g} \end{aligned}$$

$$\text{Mass of Air required} = (2698.33 \times 100 / 23) \text{ g} = 11731.86 \text{ g} = 11.731 \text{ Kg}$$

$$\begin{aligned} \text{Volume of Air required} &= \frac{\text{Mass of air required} \times 22.4}{\text{Molar mass of Air}} \\ &= \frac{11731.86 \times 22.4}{28.94} = 9080.64 \text{ ltr} = 9.081 \text{ m}^3 \end{aligned}$$

**SOLID FUEL**

Solid fuel refers to various types of solid material that are used as fuel to produce energy and provide heating, usually released through combustion. Solid fuels include wood, charcoal, peat, coal, hexamine fuel tablets, and pellets made from wood, corn, wheat, rye and other grains.

Solid fuels are mainly classified into two categories

1. Natural Solid Fuel : wood, Coal etc obtained from nature.
2. Manufactured Fuel : Charcoal, Coke, Briquettes etc it is also called as derived fuel.

**WOOD**

Wood is a vegetable tissue of trees and bushes it consists of cellulose, lignin, resins, inorganic materials and water. It is kindled and gives maximum intensity of very quickly. It burns with long non smoky flame.

**Composition:**

C-55%, H<sub>2</sub>- 6% , O<sub>2</sub>- 43%, Water and non combustible mater – 1%

**Calorific Value:** 3500 to 4500 Kcal/Kg

**COAL**

Coal is a hard rock which can be burned as a solid fossil fuel. It is mostly carbon but also contains hydrogen, sulphur, oxygen and nitrogen. It is a sedimentary rock formed from peat by the pressure of rocks.

**Types of Coal****PEAT**

It is the first stage of coal formation from cellulose. It is formed by gradual decaying of vegetable mater in moist places in low lands.

**Composition** : C – 4 to 6 % , Moisture – 85%, Volatile mater – 10 %.

**Calorific Value** : 3400 Kcal/Kg.

**LIGNITE**

Lignite, often referred to as brown coal, is a soft, brown, combustible, sedimentary rock formed from naturally compressed peat. It is considered the lowest rank of coal due to its relatively low heat content. It is used for manufacturing producer gas.

**Composition** : Carbon - 60–70 % , Ash Content : 6 – 19% , H- 4- 5%.

**Calorific Value** : 6500 to 7000 KCal/ Kg

**BITUMINOUS**

Bituminous coal or black coal is a relatively soft coal containing a tarlike substance called bitumen or asphalt. It is of higher quality than lignite coal but of poorer quality than anthracite. Formation is usually the result of high pressure being exerted on lignite. They appear in three varieties such as Sub Bituminous, Bituminous and Super Bituminous. These are used for gas industry, coal tar distillation and for

**Composition** : Carbon - 60–80 % , Ash Content- 2 – 10% , H- 4.5- 5.5%, N-1%, O-5%

**Calorific Value:** 7000 to 8500 KCal/ Kg

**ANTHRACITE**

Anthracite, often referred to as hard coal, is a hard, compact variety of coal that has a sub- metallic lustre. It has the highest carbon content, the fewest impurities and the highest energy density of all types of coal and is the highest ranking of coals. It is used as Domestic fuel, Automatic stoker furnaces, Hand-fired stoves, Charcoal briquettes and Power generation.

**Composition** : Carbon - 92–98 % , Ash Content- 2 – 8% and rest are moisture, H, N,O etc

**Calorific Value** : 8500 to 8700 KCal/ Kg



## COKE

Coke is a grey, hard and porous fuel with high carbon content with low impurities, made by heating coal in the absence of air (destructive distillation process). It is an important industrial product used mainly in iron ore smelting. "Coke" usually refers to the product derived from low-ash and low-sulphur bituminous coal by a process called coking.

Coke Can be classified into two categories such as Soft coke and Hard coke

**Soft coke:** It is obtained as the solid residue from the destructive distillation of coal in the temperature range of 600-650°C (Low temperature carbonisation). It contains 5-10% of volatile mater. It burns without smoke. It is extensively used as domestic fuel.

**Hard coke:** It is obtained as the solid residue from the destructive distillation of coal in the temperature range of 1200-1400°C (High temperature carbonisation). It burns with smoke. It is useful for metallurgical purposes.

## ANALYSIS OF COAL

Analysis of coal is of two kinds, Proximate Analysis and Ultimate Analysis

**Proximate Analysis:** It is determination of moisture, volatile matter, ash, fixed carbon and sometimes sulphur. The proximate analysis gives information about the practical utility of coal. The determination for proximate analysis is made in the following manner:

- (i) **Moisture Content:** Loss in weight caused by heating of weighed quantity of sample for 1hr. in air oven at a temperature of 105 to 107°C is the moisture content.

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

- (ii) **Volatile matter:** It is the loss in weight of moisture –free coal when heated in a crucible fitted with cover, in a furnace at 950°C for 7 mins. It is then taken out and cooled in a desiccator. The loss of weight is reported as volatile on % basis

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

- (iii) **Ash :** It is the weight of residue obtained after burning a weighed quantity of coal in a muffle furnace in a current of air, till a constant weight is obtained.

$$\% \text{ of ash} = \frac{\text{weight of Ash}}{\text{Weight of coal take}} \times 100$$

- (iv) **Fixed Carbon:** It is determined indirectly by deducting the sum total of moisture, ash and volatile matter from 100.

$$\% \text{ of caron} = 100 - (\% \text{ moisture} + \% \text{ volatile matter} + \% \text{ ash})$$

### **Important of proximate analysis:**

- Moisture content of coal should be less as it reduces the calorific value of the coal and high moisture content adds to the transportation cost also.
- The rank of the coal increase as the volatile matter content decreases.
- Ash also reduces calorific value of the coal, so it is undesirable.
- Higher is the fixed carbon content higher is the calorific value of the coal.
- This process helps to select the good quality of coal for carbonisation.

**Ultimate Analysis:** It is the determination of carbon, hydrogen, nitrogen, oxygen, sulphur and ash in coal. Oxygen is determined by difference. It involves the following steps :

- i. **Determination of Carbon and Hydrogen:** About 1gm of coal is burnt in a combustion apparatus in presence of oxygen and the gaseous products are made to pass through a tube containing pre weighed KOH and anhydrous  $\text{CaCl}_2$ . KOH absorbs  $\text{CO}_2$  formed and  $\text{CaCl}_2$  absorbs moistures formed. So the increase in the weight of KOH represents the weight of  $\text{CO}_2$  the increase in the weight of  $\text{CaCl}_2$  represents the weight of moisture content.



$$\% \text{ of Carbon} = \frac{\text{Increase in weight of KOH} \times 12 \times 100}{\text{Weight of sample} \times 44}$$

$$\% \text{ of Hydrogen} = \frac{\text{Increase in weight of CaCl}_2 \times 4 \times 100}{\text{Weight of sample} \times 36}$$

- ii. **Determination of Nitrogen:** About 1g of powdered coal sample is heated with  $\text{H}_2\text{SO}_4$  along with  $\text{KHSO}_4$  as catalyst in a long necked flask ( Kjeldahl's Flask). After the solution become clear , it is treated with excess KOH and liberated  $\text{NH}_3$  is distilled over and absorbed in known volume of standard acid solution and the unused acid is determined by back titration with NaOH. From the volume of unused acid ammonia liberated and the % nitrogen in sample is calculated.

$$\% \text{ of Nitrogen} = \frac{\text{Volume of acid} \times \text{Normality} \times 1.4}{\text{Weight of coal taken}}$$

**Note :** 1 ltr of N/10  $\text{H}_2\text{SO}_4$  is consumed is equivalent to 0.1 gm mol of  $\text{NH}_3$  or 1.4 g of  $\text{N}_2$

- iii. **Determination of Sulphur:** It is determined by Bomb Calorimeter by using 1g of powdered coal sample. During this process sulphur is converted to sulphates. The sulphates are precipitated by treating it with  $\text{BaCl}_2$  and then filtered and weighed.

$$\% \text{ of Sulphur} = \frac{\text{Weight of BaSO}_4 \times 32 \times 100}{\text{Weight of coal} \times 233}$$

- iv. **Determination of ash Content:** It is the weight of residue obtained after burning a weighed quantity of coal in a muffle furnace in a current of air, till a constant weight is obtained.

$$\% \text{ of ash} = \frac{\text{weight of Ash}}{\text{Weight of coal take}} \times 100$$

- v. **Determination of Oxygen :** It is determined indirectly by deducting the combined % of carbon, hydrogen, nitrogen, sulphur and ash from 100.

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

#### Importance of Ultimate Analysis :

- Greater is the % of carbon better is the quality of coal as it increases the calorific value of the coal.
- Nitrogen has low calorific value, hence it is not desirable and also it leads to air pollution.
- Sulphur is also not desirable as it leads to air pollution by forming oxides of sulphur.
- Oxygen decreases the calorific value by combining with hydrogen and reduces the available hydrogen for combustion.

## **LIQUID FUEL**

**Liquid fuels** are combustible liquid molecules that can be harnessed to create mechanical energy, usually producing kinetic energy; they also must take the shape of their container. It is the fumes of liquid fuels that are flammable instead of the fluid. Most liquid fuels in widespread use are derived from fossil fuels; however, there are several types, such as hydrogen fuel (for automotive uses), ethanol, and biodiesel, which are also categorized as a liquid fuel. Many liquid fuels play a primary role in transportation and the economy.

### **Petroleum**

- These are used extensively in industrial and domestic field.
- The single largest source of liquid fuel is petroleum / crude oil.
- It is dark, greenish, brown viscous oil found deep inside the earth crust.
- It is a mixture of hydrocarbons such as straight chain paraffin, cyclo-paraffin, naphthalene, poly-phenes, aromatics along with small amount of organic compound containing  $N_2$ ,  $O_2$  & S.

**Composition –**

C =	79.5 -87.1 %
H <sub>2</sub> =	11.5 – 14.8 %
S =	0.1 - 3.5 %
N <sub>2</sub> =	0.4 - 0.9 %
O <sub>2</sub> =	0.1-0.9 %

### **Physical / Chemical Properties**

Petroleum is graded according to the following physico-chemical property.

1. Specific gravity
2. Calorific value
3. Flash pt. or ignition pt.
4. Viscosity
5. Sulphur Content
6. Moisture and sediment Content
7. Specific Heat and coefficient of Expansion

### **Classification of petroleum**

The chemical nature of the crude petroleum varies with the part of the world in which it is found. They appear in three varieties.

#### **i. Paraffinic base type crude:**

It is mainly composed of saturated hydrocarbon from  $CH_4$  to  $C_{35}H_{72}$  and a little of naphthalene & aromatic compound. The hydrocarbons from  $C_{18}H_{38}$  to  $C_{35}H_{72}$  are semi solid and are called as wax.

#### **ii. Asphaltic base type crude**

It contains mainly cyclo- paraffin or naphthalene with smaller amount of paraffin and aromatic hydro-carbons. These are called bitumen's.

#### **iii. Mixed base type crude**

It contains both paraffinic and asphaltic hydrocarbons & is generally rich in semisolid waxes. Furnish medium grade straight run gasoline.

## **REFINING OF PETROLEUM**

The crude oil is separated into various fractions having different boiling ranges by fractional distillation and finally converted into desired specific product by removing undesirable impurities and the process is known as refining of crude oil. This process involves three steps.

### **(I) Separation of H<sub>2</sub>O :**

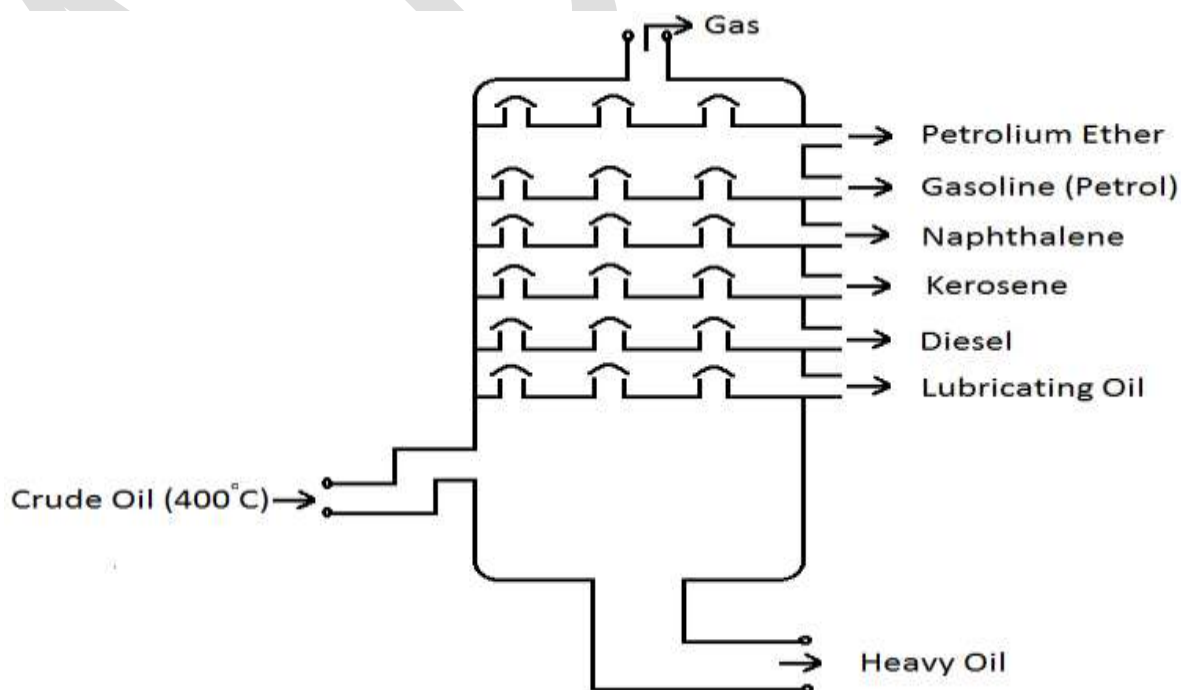
The crude oil is separated from H<sub>2</sub>O by allowing the crude to flow between highly charged electrodes. The colloidal water droplets combine to form large drop and separated from the oil.

### **(II) Removal of Sulphur Compound:**

Sulphur compounds are removed by treating the crude oil with CuO and the treatment results in the formation of CuS in solid form which can be easily removed by filtration.

### **(III) Fractional Distillation:**

- The crude oil is heated to about 400°C in a pipe till all the volatile constituent are evaporated.
- The hot vapour then passed through a tall cylindrical tower known as fractionating column containing number of horizontal stainless steel trays at short distance. Each tray is provided with a chimney with loose caps.
- As the vapour goes up they become gradually cooler and fractional condensation takes place at different heights of the column.
- Higher boiling fractions are condensed first while lower boiling fractions are condensed afterwards.



Fraction	Composition	Boiling Point
Gas	C <sub>1</sub> to C <sub>4</sub>	Less than 30°C
Petroleum Ether	C <sub>5</sub> to C <sub>7</sub>	30 - 70°C
Petrol	C <sub>5</sub> to C <sub>9</sub>	70 - 90°C
Light Petroleum	C <sub>6</sub> to C <sub>8</sub>	90 - 120°C
Naphthalene	C <sub>9</sub> to C <sub>10</sub>	120 - 180°C
Kerosene	C <sub>10</sub> to C <sub>16</sub>	180 - 250°C
Diesel	C <sub>15</sub> to C <sub>18</sub>	250 - 320°C
Heavy Oil	C <sub>18</sub> -C <sub>30</sub>	320 - 400°C

### **PETROL /GASOLINE / MOTOR SPIRIT**

- The composition of petrol is a mixture of hydro carbon from C<sub>5</sub>H<sub>12</sub>→C<sub>8</sub>H<sub>18</sub>.
- The straight run fraction is collected between 40°C - 120°C.
- It is highly volatile and inflammable in nature.
- Its calorific value is 11250 Kcal/Kg.
- It is used in IC Engine.
- The consumption per unit is more.
- Its thermal efficiency is low.
- Its combustion process is simple and required IC engine.
- It is costlier than diesel.
- No compression is needed during combustion of gasoline.
- Its exhaust gasses contain higher amount of pollutants.

### **Diesel**

- The composition of diesel is C<sub>15</sub>H<sub>32</sub> to C<sub>18</sub>H<sub>38</sub>.
- This fraction obtained between 250°C to 320°C.
- Its density is 0.86-0.95 g/CC.
- Its calorific value is about 11000 KCal/Kg.
- It is used as fuel in diesel engine.
- Its consumption per unit is less.
- Its thermal efficiency is high.
- Its combustion process is complex and requires a more expensive fuel injection device.
- Its combustion requires heavy equipments to compress air.
- Its exhaust gasses contain lesser amount of pollutant.

### **KEROSENE**

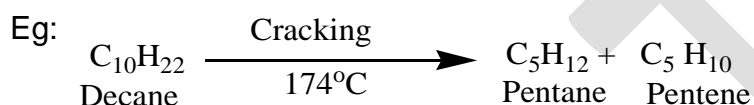
- It is obtained between 180°C-250°C during fractional distillation of crude petroleum.
- Its composition of kerosene is a mixture of hydrocarbon from C<sub>10</sub>H<sub>22</sub> - C<sub>16</sub>H<sub>34</sub>.
- Its specific gravity 0.75 to 0.85 g/cc
- Its CV is 11100 Kcal/Kg.
- Due to boiling point range kerosene doesn't vaporise easily.
- It is used as domestic fuel in stove and as jet engine fuel and for making oil gas.

**HEAVY OIL:**

- It is obtained between 320°C-400°C during fractional distillation of crude petroleum.
- Lubricating oil is used as lubricants.
- Petroleum jelly (Vaseline) which is used as lubricants in medicine and cosmetics.
- Paraffin wax used in candle, boot polish, wax paper, tarpaulin cloth for electrical insulation.

**CRACKING**

It is defined as decomposition of high molecular weight hydrocarbons of high boiling point ranges into simpler and lower molecular weight hydrocarbons of low boiling point ranges.



It is of 2 type's i.e.

1. Thermal Cracking
2. Catalytic Cracking

**THEMAL CRACKING**

When cracking takes place simply by the application of heat and pressure in absence of catalyst, the process is called thermal cracking. In this process long chain hydrocarbons break down to give smaller molecules of paraffin's, olefins etc. Thermal cracking may be carried out either in liquid phase or in vapour phase.

**a. Liquid phase thermal cracking.**

In this method any type of oil (residues / heavy oil) can be cracked. The charge is kept in the liquid form by applying high pressures of the range 30 kg /cm<sup>2</sup> to 100 kg /cm<sup>2</sup> at a suitable temperature of 476 - 530°C. The cracked products are separated in a fractionating column. The important fractions are:

Cracked gasoline (30-35%);

Crackling gases (10-45%);

Cracked fuel oil (50-55%).

The cracked gasoline has an octane number of about 70. The cracking gases constitute raw materials for petrochemicals. The cracking residue is used as a fuel.

**b. Vapour phase thermal cracking**

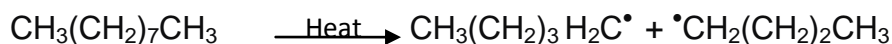
In this method only those oils which can vaporize at low temperatures can be cracked. The petroleum fractions of low boiling range like kerosene oil are heated at a temperature of 670-720°C under low pressure of 10-20 kg/cm<sup>2</sup>. The time required for cracking is much less as compared to liquid phase thermal cracking. Petrol obtained from vapour phase cracking has better antiknock properties but poorer stability.

## MECHANISM OF THERMAL CRACKING

Thermal cracking is generally carried out in free radical mechanism. The mechanism can be illustrated by taking the example of n-nonane.

### Initiation:

Formation of Free radical by heat



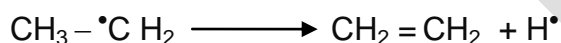
### Propagation

The free radicals formed are thermally unstable and undergo fission at the  $\beta$  position to yield a new radical and an olefin.



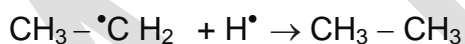
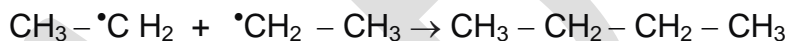
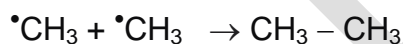
This  $\beta$  fission continues, till a thermally more stable radical is formed.

The radicals having no C-C bond in the  $\beta$  position give rise to hydrogen free radicals.



### Termination:

Free radicals formed in the propagation stage combine to form stable compounds



## CATALYTIC CRACKING

The breaking up large hydrocarbon molecules to smaller and more useful bits at lower temperature and pressure in the presence of a catalyst is called as catalytic Cracking.

Modern cracking uses **zeolites** as the catalyst. These are complex aluminosilicates, and are large lattices of aluminium, silicon and oxygen atoms carrying a negative charge. They are, of course, associated with positive ions such as sodium ions.

## CATALYTIC CRACKING METHODS

### 1. FIXED-BED CATALYTIC CRACKING

The catalyst ( $\text{Al}_2\text{O}_3 + \text{SiO}_2$ ) in the form of powder or pellets is placed on the grid in the catalytic chamber; the vapours of the feed stocks (Heavy oil, gas oil, etc.) are passed through the bed of catalyst maintained at 450- 500°C. About 50% of the feed stock is converted into gasoline together with elemental carbon which gets deposited on the surface of the catalyst. Cracked vapours are next subjected to fractionation in a fractionating column wherein gasoline is separated from uncracked heavy oil. The catalyst loses its activity because of the deposition of carbon and also due to the

adsorption of oil vapours. Accordingly, the catalyst requires regeneration after 8- 10 hours. During regeneration time, the cracking process is interrupted and the adsorbed oil is stripped off by passing steam while deposited carbon is burnt off by a hot air blast. The finely divided catalyst bed ( $\text{Al}_2\text{O}_3 + \text{SiO}_2$ ) is fluidized by the upward passage of feed stock vapours (Heavy oil, gas oil, etc.) in a cracking chamber (called Reactor) maintained at  $550^\circ\text{C}$ . Near the top of the reactor, there is a centrifugal separator (called cyclone), which allows only the cracked oil vapours to pass onto the fractionating column but retains the catalyst powder in the reactor itself. The catalyst powder gradually becomes heavier due to the deposition of carbon and settles to the bottom, from where it is forced by an air blast to the regenerator (maintained at  $600^\circ\text{C}$ ). After cracking, the products are fractionated into gases, gasoline, gas oils and residual oils. The heavier oil fractions may be cracked in a second-stage cracking. In regenerator, the spent catalyst is stripped of the adsorbed oil by passing steam and then decarbonised by a hot air blast.

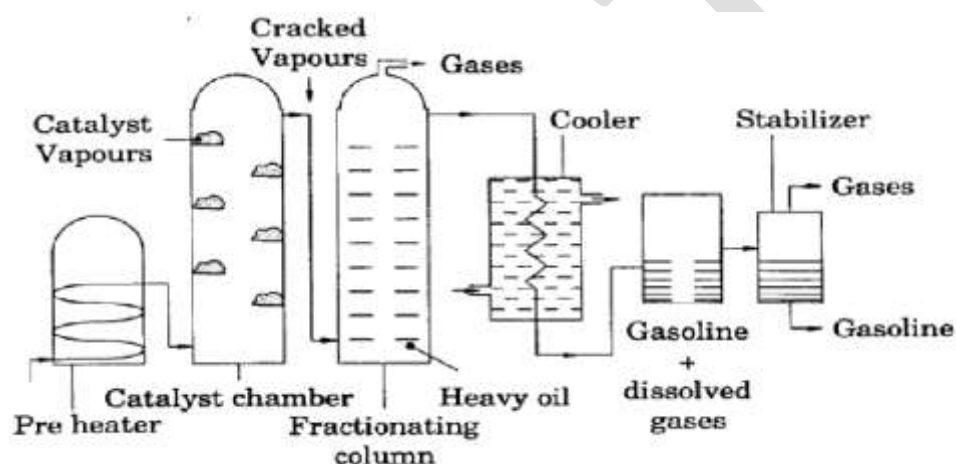


FIG. FIXED BED CATALYTIC CRACKING

## 2. FLUIDIZED (MOVING) BED CATALYTIC CRACKING

The finely divided catalyst bed ( $\text{Al}_2\text{O}_3 + \text{SiO}_2$ ) is fluidized by the upward passage of feed stock vapours (heavy oil, gas oil, etc.) in a cracking chamber (called Reactor) maintained at  $550^\circ\text{C}$ . Near the top of the reactor, there is a centrifugal separator (called Cyclone), which allows only the cracked oil vapours to pass onto the fractionating column but retains the catalyst powder in the reactor itself. The catalyst powder gradually becomes heavier due to the deposition of carbon and settles to the bottom. From where it is forced by an air blast to the regenerator (maintained at  $600^\circ\text{C}$ ). After cracking the products are fractionate into gases, gasoline, gas oils and residual oils. The heavier oil fractions may be cracked in a second stage cracking. In regenerator, the spent catalyst is stripped of the adsorbed oil by passing steam and then decarbonised by a hot air blast, under controlled conditions. The heat liberated during this regeneration is used to raise steam and to preheat the catalyst under controlled conditions.



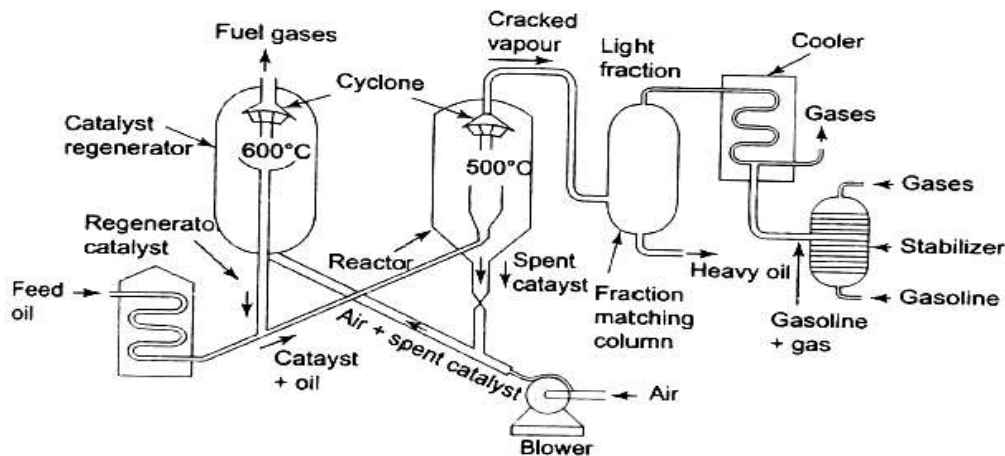


FIG : FLUIDIZED (MOVING) BED CATALYTIC CRACKING

### Advantages of Fluidized-bed cracking over Fixed bed cracking

- A high degree of mixing is achieved and consequently a good contact is established between the Catalyst and the feed stock vapours. This results in a higher yield.
- The regeneration of the inactive catalyst can be carried out continuously without interrupting the production of gasoline unlike in fixed-bed catalytic cracking.

### ADVANTAGES OF CATALYTIC CRACKING

- The octane number of gasoline produced is high.
- The yield of gasoline is also high.
- The process can be better controlled.
- The product contains a very little amount of undesirable sulphur.
- There is a saving in production costs since high temperatures and high pressures are not needed.
- In catalytic cracking, external fuel is not required. The necessary heat is obtained by burning off the coke deposited on the catalyst itself during the regeneration process.
- The gasoline formed contains much less gum and gum forming compounds.
- Catalysts are selective in their action and therefore they permit cracking of only high boiling hydrocarbons.

### Comparison between Thermal and Catalytic Cracking

Catalytic cracking differs with thermal cracking in

- ❖ Uses a catalyst
- ❖ Lower temperature
- ❖ Lower pressure
- ❖ More flexible
- ❖ Different reaction mechanisms (ionic vs. free radical)
- ❖ High thermal efficiency
- ❖ Good integration of cracking and regeneration
- ❖ High yields of gasoline and other distillates
- ❖ Low gas yields
- ❖ High product selectivity
- ❖ Low n-alkaline yields
- ❖ High, octane number
- ❖ Chain-branching and high yield of C4 olefins.
- ❖ High yields of aromatics.

**KNOCKING:**

Due to premature instantaneous ignition of fuel - air mixture in Internal Combustion (IC) engine, leading to production of an explosive sharp metallic sound is known as knocking.

**Causes of knocking:**

- i) Chemical structure of the fuel hydrocarbon.
- ii) Presence of some constituents having high rate of combustion in fuel.
- iii) Designs of the engine i.e. shape of the head and location of the plug.
- iv) Running condition of the vehicle.
- v) Compression ratio i.e.  $C.R = V_1/V_2$

Where :  $V_1$  is the volume of the fuel at the end of stroke.

$V_2$  is the Volume of the fuel at the end of compression.

**Note:**

With increase in compression ratio the efficiency of IC engine also increases but after critical compression ratio the tendency to knock also increases.

**Critical compression ratio** –The compression ratio at which fuel tends to knock is called as critical compression ratio.

**FOR PETROL FUEL**

The knocking tendency decreases in the order n-alkane > mono-substituted alkane > alkene > poly-substituted alkanes > aromatics. For straight chain hydrocarbons knocking increases with molecular weight and boiling point. e.g. n-hexane > n-pentane > n-butane.

**Probable Mechanism of Chemical Reaction that Leads to Knocking**

Free radical chain reaction leading to cracking and oxidation of hydrocarbon is probably the mechanism of chemical reaction that leads to knocking.

**Effect of knocking**

- It increases the fuel consumption.
- It results in decreased power output.
- It causes mechanical damage by overheating the cylinder parts or piston.
- Loss of energy.
- Increase in cost of maintenance.
- The driving being un-pleasant

**Prevention (Reduction / minimisation of knocking)**

- \* By suitable change in engine design.
- \* By using critical compression ratio
- \* By using high rating fuel
- \* By using anti-knock agents such as TEL ( Tetra Ethyl Lead) , TML(Tetra Methyl Lead) , BTX ( Benzene Toluene Xylene ).

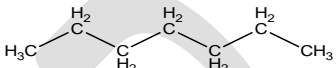
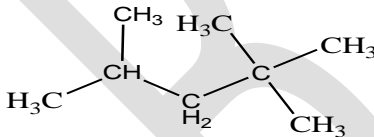
**OCTANE NUMBER (FOR PETROL FUEL)**

The resistance offered by gasoline for knocking cannot be defined in absolute terms.

In 1927 the knock rating was introduced by Graham Edgar as a measure for the knock resistance of a fuel. He suggested using the ratio of two hydrocarbons that could be produced in sufficient purity and quantity for reference purposes. He also defined the knock ratings of these two standard substances: **0 for the unbranched (n-heptane)** and **100 for the branched-chain hydrocarbon (2, 2, 4- trimethyl pentane, iso-octane)**. By this method the knock proneness of gasoline with different compositions became measurable by their comparison to corresponding standard mixtures with the same knock resistance. Simultaneously a quantitative result of the measurement was produced in form of the “octane number” (ON). The octane rating is a measure of the resistance of fuels to auto ignition.

**Definition:**

Octane number of petrol fuel is defined as the % of iso-octane in a mixture of iso-octane and n-heptanes that produce the same knocking characteristics as the fuel under same set of conditions.

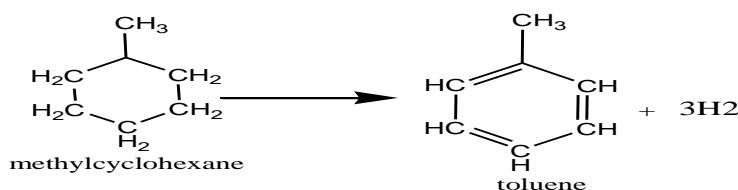
<u>Fuel</u>	<u>Structure</u>	<u>Octane Number</u>	<u>Knocking</u>
n-heptane		0	100
Iso- Octane (2,2,4-trimethyl pentane)		100	0

For Example: 91-Octane petrol is a mixture of 91% iso-octane and 9 % of n-heptane

- Automobile gasolines have octane no. ranging from 75 - 95.
- Aviation gasolines have greater knock resistance & their octane no. is greater than 100.
- In case of alkenes the octane no. increases with the no. of branches in the chain and decreases with increase in chain length.
- Alkenes have higher octane no. than alkenes containing same no. of carbon-atoms.
- Cycloalkanes have higher octane rating than alkane with same no. of carbon atom.
- The highest no. is associated with the aromatic hydrocarbon.

**How octane number of fuel can be increased?**

- \* By isomerisation : Straight Chain hydrocarbons are converted to branched chain.
- \* By aromatisation : Aliphatic compound are converted aromatic compound.



- \* By adding anti knock agent – TEL (Tetra Ethyl Lead), TML(Tetra Methyl Lead) , BTX( Benzene Toluene Xylene ).

**Function of TEL as anti- knocking agent.**

TEL gives rise to Pb. & PbO during combustion. These particles act as free radical chain inhibitors as they arrest the propagation of the explosive chain reaction responsible for knocking.

**Function of Ethylene Bromide as additive to petrol along with anti- knocking agent.**

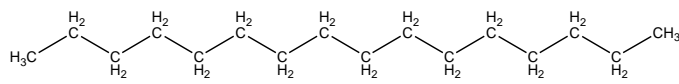
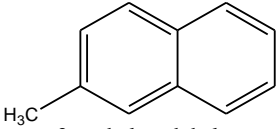
If TEL alone is used, the species Pb & PbO may get deposited on engine parts which causes mechanical damage, decrease the engine life's and also the vapours of Pb & PbO may pollute the air. So, in order to minimize the air pollution and damaged to engine parts TEL is used along with ethylene bromide ( $C_2H_3Br$ ). The function of the ethylene bromides is to convert the less volatile Pb & PbO into more volatile  $PbBr_2$  which escapes into air along with the exhaust gasses but pollution problem still exist.

**KNOCKING IN DIESEL ENGINE**

- \* The basic difference between petrol engine and diesel engine is that in case of diesel engine the fuel is ignited with the help of heat generated by the compression of air inside the combustion chamber and not by spark.
- \* The combustion of fuel in diesel engine is not instantaneous as that of petrol engine. There is a time lag between fuel injection and its ignition. This is called as ignition delay or igniting lag.
- \* Ignition delay is due to time taken for the vaporisation of the individual droplets and rising of the vapour to its ignition temperature.
- \* It depends on Engine design, Efficiency of the mixing of the spray and air, Injector design and Chemical nature of the fuel.
- \* If the ignition delay is long, it will lead to fuel accumulation in the engine even before the ignition. When ignited an explosion results as the combine effect of increased temperature and pressure, this is responsible for diesel knock.
- \* In order to grade the diesel fuel cetane rating is employed.
- \*

**CETANE NUMBER:**

- Cetane number is a measure of ease at which the fuel ignites under compression.
- Cetane number is defined as the % of n-hexadecane ( $C_{16}H_{34}$ ) in a mixture of hexadecane and 2-methyl naphthalene that has same knocking characteristic of fuel under consideration at the same set of conditions.

<u>Fuel</u>	<u>Structure</u>	<u>cetane Number</u>	<u>Knocking</u>
n-hexadecane		100	0
2-methyl naphthalene		0	100

Straight chain hydrocarbons get ignited readily and have higher cetane rating so the order of cetane number is : n-alkane > naphthalene > alkene > branched alkene > aromatics

**ADDITIVES TO INCREASE CETANE NUMBER**

The cetane no. of fuel can be increased by addition of very small amount of compound called as pre-ignition dopes such as alkali nitrates, ethyl nitrates, ethyl-nitrites, acetone peroxide etc.

Diesel fuels can be classified into 3 types

- High speed diesel (Cetane no. > 45)
- Medium speed diesel (Cetane no between 35 – 45 )
- Low speed diesel (Cetane no ≤ 25)

	<b>PETROL ENGINE</b>	<b>DIESEL ENGINE</b>
Fuel used	Petrol and air mixture	Diesel and air mixture
Ignition	By sparking	By compression of air
Cause of knocking	Due to pre-ignition	Due to delayed ignition
Knocking characteristics	Characterised by octane rating	Characterised by cetane (C <sub>16</sub> ) rating
Additive to reduce knocking	TEL (Tetra Ethyl Lead), TML (Tetra Methyl Lead), BTX (Benzene + Toluene + Xylene) is added to petrol to reduce knocking and increases octane number.	Alkali nitrite, acetone peroxides is used to reduce knocking and increases cetane number.

**UNLEADED PETROL:**

The petrol in which octane no. can be increased without the addition of lead compound is refers to as unleaded petrol. To improve the octane no. of the petrol concentration of high octane components like iso-pentane, iso-octane, ethyl benzene, iso-propyl benzene are increased by the process molecular reforming. This process increases the contents of molecules having branched and aromatic structure. **Methyl tertiary butyl ether (MTBE)** can also be added to petrol to improve the octane rating of the fuel. MTBE has O<sub>2</sub> in the form of ether group and supplies O<sub>2</sub> for the combustion of the petrol in IC engine reducing the formation of peroxy compounds.

**Advantages of unleaded petrol:**

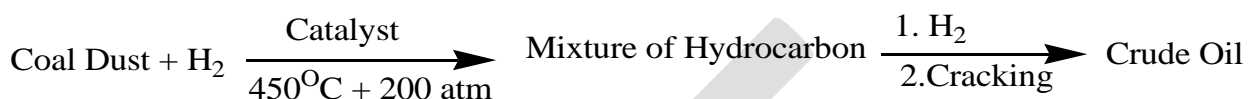
- It reduces lead pollution.
- It permits the attachment of catalytic converter to the exhaust pipe in the automobile. Catalytic converter contains Rhodium (R<sub>h</sub>) catalyst which converts toxic gasses like CO, NO into harmless gasses like CO<sub>2</sub> and N<sub>2</sub>. It also oxidises un burnt hydrocarbon into CO<sub>2</sub> and H<sub>2</sub>O.

**SYNTHETIC PETROL**

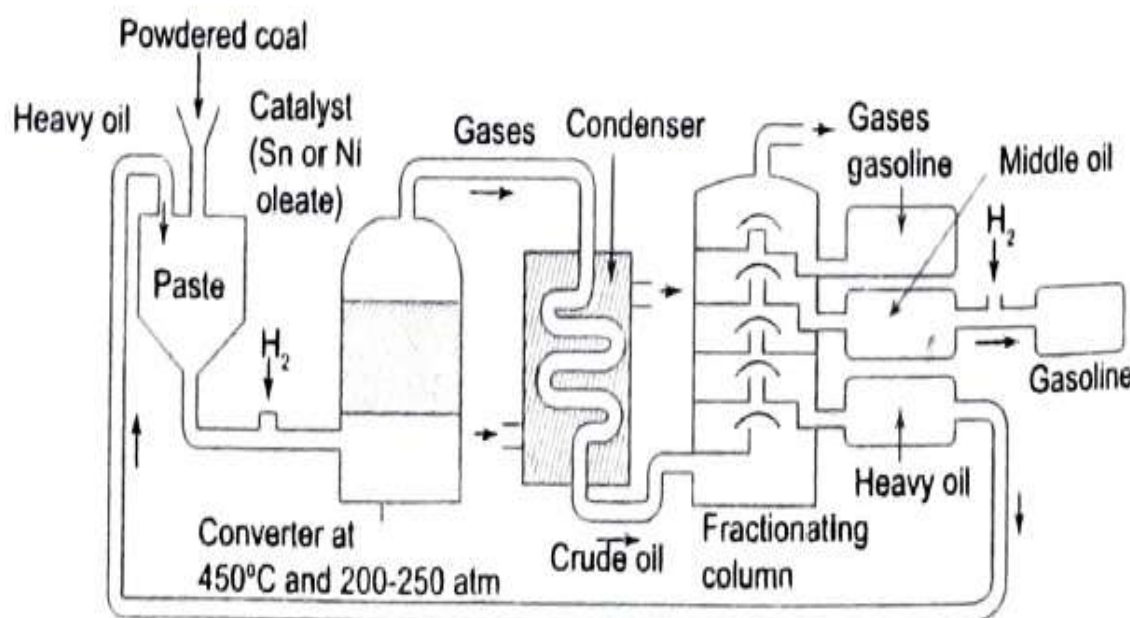
Synthetic petrol is a mixture of alkanes with composition resembling that of petrol, obtained artificially. The two important methods for preparation are: Bergius Process and Fischer-Tropsch Process.

**BERGIUS PROCESS**

In this method coal is used as a raw material. The method was developed by Bergius in Germany and hence the name. Coal is a mixture of high molecular complex organic compounds with low content of hydrogen. The finely divided coal is made into a paste with heavy oil or coal tar and then a catalyst composed of organic compound of tin is added. The coal paste along with the catalyst is prepared and then pumped in to the converter where it is heated to 400-500°C under 200-250 atm pressure in presence of hydrogen.



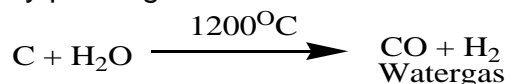
Hydrogenation takes place to form higher saturated compounds, which undergo cracking and hydrogenation process to yield mixture of alkanes. Thus, the vapours leaving the converter upon condensation give crude oil or synthetic petroleum. Crude oil is fractionally distilled to give petrol, middle oil and heavy oil. The middle oil is again hydrogenated in the vapour phase in the presence of a solid catalyst to give more gasoline. Actually the processing of middle oil gives four times the gasoline obtained by the primary hydrogenation of coal. Heavy oil is again used for making a paste with fresh coal dust.



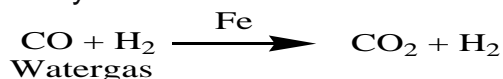
**FIG : BERGIUS PROCESS**

**FISCHER-TROPSCH PROCESS**

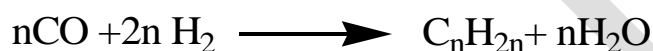
In this method, hard coke is converted in to mixture of carbon monoxide and hydrogen by passing stream over red hot coke.



From a part of the water gas, Carbon, monoxide is removed by converting it in to  $\text{CO}_2$ , which is obtained by passing the water gas with extra steam over a promoter iron oxide catalyst at  $450^\circ\text{C}$ .

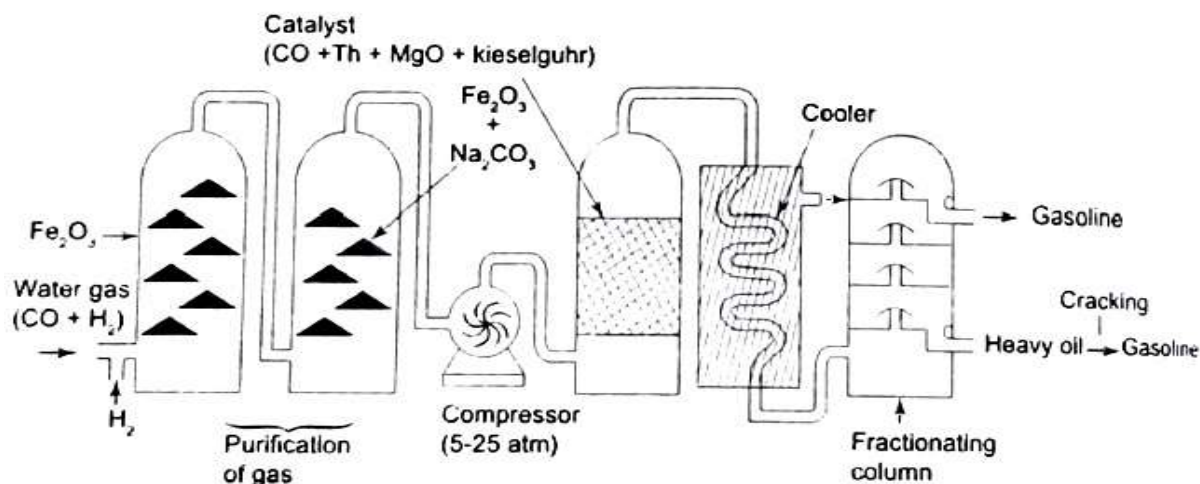


The residual  $\text{CO}_2$  is again removed by absorption in ammonia cuprous formate solution. Hydrogen so obtained is mixed with the rest of watergas in a ratio of synthetic gas i.e  $\text{H}_2$  and  $\text{CO}$  in a ratio of 2:1. The synthesized gas is passed at atmospheric pressure or at  $150 \text{ lb/in}^2$  pressure over a cobalt thorium oxide catalyst on Kieselguhr at  $180 - 200^\circ\text{C}$ . The reaction production is predominantly straight chain paraffins and olefins, the formation may be represented by the following equation:



The gas and vapours leaving the reaction vessel are passed through water-cooled condenser to condense. From the residual gaseous mixture, propane, butanes are obtained by absorbing activated carbon. The liquid on fractional distillation produces low grade motor spirit, high grade diesel oil, heavy oil and soft & hard waxes. A large amount of the heavy-oil after hydrogenation is used for the production of sodium alkyl-sulfonate. The soft wax is mainly oxidized to a fatty acid by air at  $100-120^\circ\text{C}$  in the presence of small amount of  $\text{KMnO}_4$  as a catalyst. Higher fatty acids are used for soap manufacturing and also for the production of synthetic fats. The hard wax is used for the conventional uses.

Although Fischer-Tropsch process requires a cheap raw material, it can't compete economically with petroleum as a source of gasoline. Hence, generally this process is used for the production of a number of hydrocarbons. The gaseous mixture is cooled and then passed under pressure through a fluid bed of finely divided iron at  $350-450^\circ\text{C}$ . The products obtained are gasoline, diesel fuel and an aqueous solution of oxygenated organic compounds, namely alcohols, aldehydes, acids and ketones.



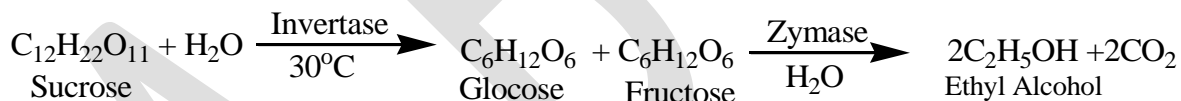
**Fig : FISCHER - TROPSCH PROCESS**

**POWER ALCOHOL:**

Power Alcohol is a mixture 75-80% petrol, 20-25% ethanol and minute amount of aromatic compounds such as benzene. It is used to generate power as an additive to motor fuels for internal combustion engine, hence is called as power alcohol. It has generally 80% petrol and 20% alcohol. The first four aliphatic alcohols are methanol, ethanol, propanol and butanol can be used for power alcohol.

**Manufacturing:**

Ethanol is commonly prepared from various biological organic substances through fermentation process. However widely it is manufactured from molasses. It is a viscous semi –solid material left after crystallisation of sugarcane juice. It is a mixture of sucrose, glucose and fructose. The molasses are diluted with H<sub>2</sub>O to reduce sugar concentration from 50-60 % to 10-12 %. Nutrients like ammonium sulphate, ammonium phosphate and some amount of H<sub>2</sub>SO<sub>4</sub> is added to maintain the pH value around 4-5. Right proportion of yeast are added and maintain in the temperature is about 30°C. The invertase enzyme of yeast converts entire sucrose into glucose and fructose. The zymase enzyme of yeast converts entire glucose and fructose into ethyl alcohol and release CO<sub>2</sub>. During this process more CO<sub>2</sub> is produced. Hence this process is known as fermentation process. The fermentation process may be complete at about 36-38 hours. Depending on the concentration of alcohol, it is named as wash, rectified spirit or absolute alcohol.

**Advantage:**

- These are prepared from waste, hence it reduce the pollution.
- It can burn completely thereby increasing combustion efficiency.
- It has an octane value of 90 but the petrol is having 60-70. When alcohol is mixed with petrol, increases the octane rating and this blended petrol possess better anti-knock property and reduces CO emission.
- Alcohol blended with petrol can absorb traces of moisture and increase calorific value.

**Disadvantages:**

- Alcohol may cause corrosion due to easy oxidation with acids.
- Due to low calorific value of alcohol more fuel is required.
- Particularly at low temperature alcohol is difficult to get atomized due to its considerable surface tension.



**GASEOUS FUEL:**

**Gaseous fuels** are hydrocarbons, hydrogen and carbon monoxide mixtures present in **gaseous** state which forms the basis of potential heat energy or light energy that can be readily disseminated by means of pipes from the origin to the place of consumption.

Gaseous fuels can be obtained in many ways

- From nature: example- natural gas, methane from coal mines.
- From solid fuels: example – producer gas, water gas, coal gas and blast furnace gas.
- From petroleum: example – refinery gases, LPG and gases from oil gasification.
- By fermentation of organic wastes: example – LPG → Composition include biogas, n-butane + isobutene + butylenes + propane C.V – 27800 Kcal/m<sup>3</sup>.

**NATURAL GAS:**

It is generally found in associated with petroleum in nature and occurs near coal mine or oil field. It is used not only as fuels for domestic and industrial purpose but also a raw material in various chemical syntheses. Natural gas i.e. derived from oil well is dry or wet. When natural gas found to be associated with petroleum in oil well is known as wet gas. It is obtained from the oil producing well and is a mixture of CH<sub>4</sub> and higher hydrocarbons such as n-propane, n-butane, iso-butane, iso-pentane etc. When natural gas is found to be associated with crude oil it is termed as dry gas. It contains mainly CH<sub>4</sub> and ethane (C<sub>2</sub>H<sub>6</sub>) with small amount of CO, H<sub>2</sub>, H<sub>2</sub>S, N<sub>2</sub> and inert gases. Wet natural gas has a higher CV than dry gas because of higher % of heavier unsaturated molecules.

**Composition:**

CH<sub>4</sub> → 70-90% , C<sub>2</sub>H<sub>6</sub> → 5-10%, H<sub>2</sub> → 3% , CO & CO<sub>2</sub> → rest

**Calorific Value** = 12000 to 14000 KCal/m<sup>3</sup>

**Application of Natural Gas:**

- Natural gas has wide range of application
- It is used as a fuel in domestic and in industrial sectors as well as in motor vehicles.
- It is also used to prepare ethane, prepare butanes, acetic acid etc.
- It serves as an important ingredient in the manufacture of various fertilizer, fabrics and antifreeze agents.

**CNG (Compressed Natural Gas):**

- It is obtained by compressing natural gas to a high pressure of about 1000 atm.
- CNG is used as substitute for petrol and diesel.
- It is very economical and clean fuel.
- It is better than LPG and is preferred over gasoline **Because**
  - Its ignition temperature is higher than gasoline or diesel, so it is safer.
  - It is lighter than air and disperses easily in air minimizing the risk of ignition but LPG being heavier than air settled at the ground level and hence is risky.
  - As compared to gasoline CNG produces lesser CO on combustion.
  - CNG operated vehicle don't emit the forbidden pollutant such as SO<sub>2</sub>, SO<sub>3</sub>, C<sub>6</sub>H<sub>6</sub> and HCHO

LIQUEFIED PETROLEUM GAS (LPG)

**Liquefied petroleum gas (LPG)**, also called **LP gas** is a flammable mixture of the volatile hydrocarbons propene, propane, butene, and butane. It was used as for a portable fuel source and its production and consumption for both domestic and industrial use have expanded ever since. A typical commercial mixture may also contain ethane and ethylene, as well as a volatile mercaptan, an odorant added as a safety precaution.

**Composition:**

Propane - about 48 %

Butane - about 50 %

Pentane - about 02%

**Calorific Value : 27800 Kcal/m<sup>3</sup>**

**Advantages of LPG over gaseous fuel:**

- High efficiency and heating rate. Its CV is 3 times that of natural gas and 7 times that of coal gas.
- Need little care for maintenance, cleanliness in storage, handling and use.
- Flexibility and easy control.
- Portability in steel cylinder makes its use possible in remote places.
- Less health hazard even in case of leakage since it contains no CO but risk of fire hazard is more.
- Use of well designed and heavily constructed burners ensures complete combustion with no smoke.

**Advantages of LPG over motor fuel :**

- It is cheaper than petrol.
- It can easily mix with air.
- Burning is smokeless and high knock resistant.
- Increases the engine life.

**Disadvantages of LPG over motor fuel :**

- Handling has to be done under pressure.
- Leakage cannot be easily detected.
- LPG is advantages only in engine working under high compression ratio.
- Its response to blending is very poor.

**OIL GAS:**

It is obtained by cracking of kerosene oil. It is used as laboratory gas.

**Composition**

CH<sub>4</sub> - 25 – 30 %

H<sub>2</sub> - 50 – 55 %

CO - 10-12 %

CO<sub>2</sub>- 2 – 3%

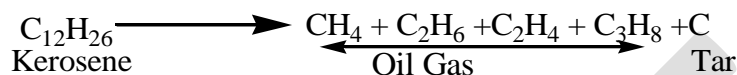
**Calorific Value : 6600 Kcal/m<sup>3</sup>**

**Production:**

The plant used for the purpose consists of a strong cast iron retort enclosed in a coal fired furnace. A burner is fitted at the mouth of retort through a water seal. A pipe from the hydraulic main leads to the gas holder. This pipe has a testing tap from where the sample of gas taken for testing.

**Working**

The retort is heated to red hot and a stream of oil is continuously allowed to fall on the red hot bottom of the retort. The oil on coming in contact with red hot retort immediately get crack into the number of lower gaseous hydrocarbons.



The gaseous mixture so obtained passes through the burner to a hydraulics tank, where tar get condensed. Then at the testing tap, proper colour of gas is tested. A good oil gas has golden colour. By properly adjusting the supply of air golden colour is obtained. The gas is properly stored in gas holder. Yield of the gas is 40-50%.

**WATER GAS:**

- It is essentially a mix of combustible gases like CO & H<sub>2</sub>.
- It is also known as blue gas because it burns with a blue flame due to combustion of CO.
- The average composition of water gas is as follows.

CO → 40 – 45 %

H<sub>2</sub> → 45 – 50 %

CO<sub>2</sub> → 4 %

N<sub>2</sub> → 4 %

**Calorific Value:** 10000 to 11000 Kcal/m<sup>3</sup>

**Manufacture :**

It is produced by passing steam and little air alternatively through a bed of red hot coke maintained at 1000 °C.

**Principle:**

When steam is blown through a bed of red hot coke at 1000°C water gas is formed

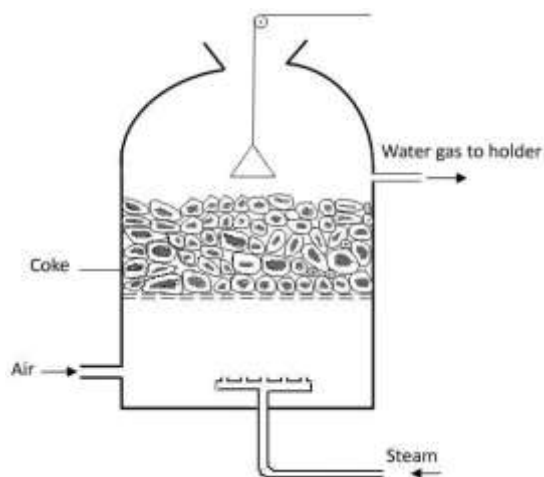
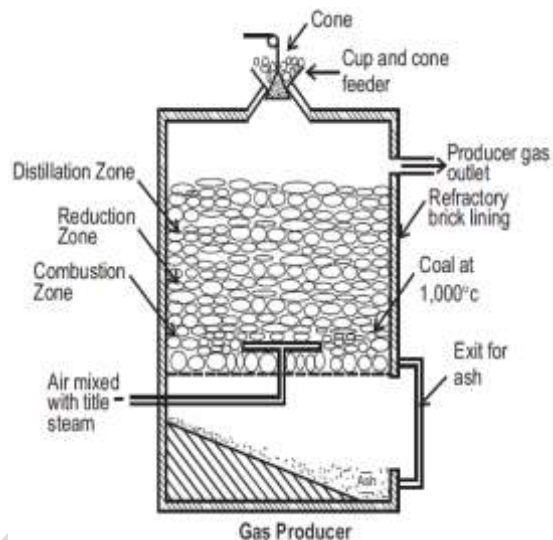


The reaction being endothermic in nature, the temperature of coke bed gradually decreases with continuous passes of steam and the drop in temperature must be prevented. For this the steam supply is temporarily cut off and air blown in. The overall reaction during air blow is the formation of CO.  $2\text{C} + \text{O}_2 \longrightarrow 2\text{CO} ; \Delta H = -221.9 \text{ KJ}$

The reaction being exothermic increases the temperature of the coke bed to about 1000°C. Thus by blowing steam and air alternatively the temperature of coke bed can be maintained at 1000°C.

**Uses:**

- It is used for the production of H<sub>2</sub>
- It is extensively used for the manufacture of methyl alcohol and synthetic petrol
- It is used as a fuel in a glass & ceramic industry.
- Enriched water gas mixed with hydrocarbons which burns with luminous flame is used as illuminating agent.

**WATER GAS PRODUCTION****PRODUCER GAS PRODUCTION****PRODUCER GAS:**

- It is essentially a mixture of CO and N<sub>2</sub>.
- It is prepared by passing air mixed with little steam over a red hot coal bed maintained at 1100°C.
- The avg. Composition of producer gas is as follows.  
CO = 25-30 % ; N<sub>2</sub> = 50-55 % ; H<sub>2</sub> = 10 % ; CO<sub>2</sub> = 5 % ; Hydrocarbon = 2-3 %

**Calorific Value:** 4000 -5000 KCal/m<sup>3</sup>**Manufacture:**

The producer is charged with coal from the top and the charge is heated at about 1100°C. A mix of air and steam is passed over red hot coal through inlet at the bottom. The producer gas goes out through the outlet at the top.

Reaction taking place in different zone of the fuel bed.

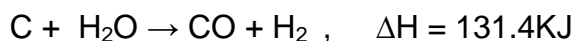
**Oxidation Zone :**

This is the lowest part of the coal bed. Here the carbon burns in presence of excess air to give CO<sub>2</sub>.  $2C + 2O_2 \rightarrow 2CO_2 \quad \Delta H = - 393.5 \text{ KJ}$ .

**Reduction Zone:**

CO<sub>2</sub> produced in the Oxidation zone then rises through the hot bed and is reduced by the coal to CO.  $CO_2 + C \rightarrow 2CO \quad \Delta H = -103.5 \text{ KJ}$

The overall reaction in the formation of CO being exothermic the fuel bed gets heated up beyond 1100°C at high temperature the ash form clinkers or slags which are difficult to remove. So the grate bar and the refractory line gets distorted. In order to avoid these problems in the producer a reduction in temperature is achieved by passing air with steam instead of air alone. So in the red<sup>n</sup> zone steam gets reduced to water gas.



This endothermic reaction brings down the temperature to the optimum level.

**Distillation Zone:**

This is the upper most part of the fuel bed where the distillation of volatile matter of coal occurs.

**Uses:**

- It is used as a fuel in manufacture of steel, glass, coal gas.
- It is used as reducing agent in metallurgical operation.

