

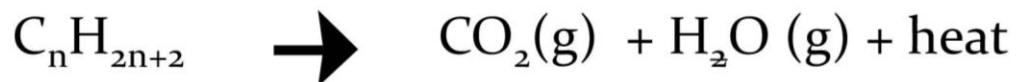
# Fuels

A fuel is a combustible substance containing carbon as the main constituent which on proper burning gives a large amount of heat that can be used economically.

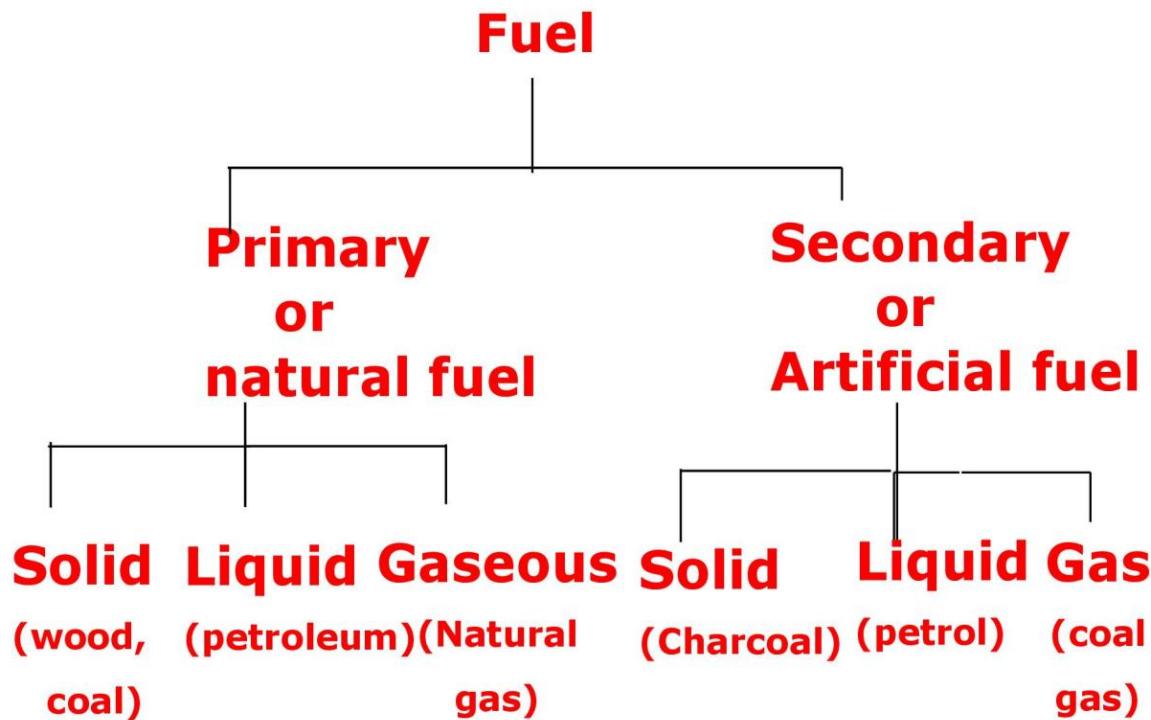
For example, wood, coal, kerosene, petrol, diesel and water gas.

Combustion is a chemical reaction in which a substance combines with oxygen producing heat, light and flame.

Combustion reaction of a fuel can be represented as follows



# Classification of Fuels



Primary fuels are found in nature whereas

Secondary fuel are prepared from primary fuel by processing them in a number of ways.

# **Characteristics of Good Fuel**

**A good fuel should have**

- high calorific value
- moderate ignition temperature
- low moisture content
- low non combustible matter content
- low cost and easy availability
- easy to transport and storage cost should be low
- products of combustion should not be harmful.
- burn in air without much smoke
- combustion should be easily controllable.

# **Calorific Value**

**Calorific value of a fuel** is the total quantity of heat liberated when one unit of fuel is burnt completely.

**Gross or Higher calorific value (G.C.V or H.C.V):** It is the total quantity of heat liberated when one unit of fuel is burnt completely and products of combustion has been cooled to room temperature.

**Net or Lower calorific value (N.C.V or L.C.V) :** It is the total quantity of heat liberated when one unit of fuel is burnt completely and products of combustion has been permitted to escape.

L.C.V= H.C.V – Latent heat of water vapour formed  
Latent heat of steam= 537 cal/gm

# Theoretical calculation of Calorific value using Dulong's Formula

$$H.C.V = [8080C + 34500(H-O/8) + 2240 S]/100 \text{ kcal/kg}$$

Where,

C= % of carbon in the fuel

H= % of hydrogen in the fuel

O= % of oxygen in the fuel

S= % of sulphur in the fuel

And

Calorific value of carbon= 8080 kcal/kg

Calorific value of hydrogen= 34500 kcal/kg

Calorific value of sulphur= 2240 kcal/kg

L.C.V= H.C.V – Latent heat of water vapour formed

$$=[H.C.V - 9H \times 537/100] \text{ kcal/kg}$$

$$=[H.C.V - 0.09H \times 537] \text{ kcal/kg}$$

# Units of Calorific Value

Units of calorific value	Solid fuel	Liquid fuel	Gaseous fuel
CGS method	cal/g	cal/g	cal/cm <sup>3</sup>
MKS method	Kcal/Kg	Kcal/Kg	Kcal/m <sup>3</sup>
FPS method	B.Th.U/lb	B.Th.U/lb	BTU/ft <sup>3</sup>
SI method	Joule/Kg	Joule/Kg	Joule/m <sup>3</sup>

$$1 \text{ Kcal/kg} = 1.8 \text{ B.Th.U/lb}$$

$$1 \text{ Kcal/m}^3 = 0.1077 \text{ B.Th.U/ft}^3$$

The Calorie, a unit of heat may be defined as, the heat required to raise the temperature of **1kg of water from 15°C to 16°C**.

A British Thermal Unit may be defined as, the heat required to raise the temperature of **one pound of water from 60°F to 61°F**.

$$1\text{BTU} = 2.252\text{Kcal} = 2252\text{cal}$$

$$1\text{kcal} = 1000\text{cal}$$

$$1\text{kcal} = 3.968\text{BTU}$$

Centigrade Heat unit is the heat required to raise the temperature of **1pound water through 1 degree centigrade**.

$$1\text{kcal} = 2.2\text{CHU} = 3.968\text{BTU}$$

$$1\text{kcal/kg} = 1.8\text{BTU/lb}$$

$$1\text{kcal/m}^3 = 0.1077\text{BTU/ft}^3$$

$$1\text{BTU/ft}^3 = 9.3\text{kcal/m}^3$$

## Numerical:

Solution

1. Convert 450cal/gm into a. kcal/kg b. BTU/lb c. kcal/m<sup>3</sup> d. BTU/ft<sup>3</sup> e. CHU/lb.  
(I)  $G.C.V = \frac{1}{100}[8080 * \frac{80}{8}C + 34500(\%H - \frac{O}{8}) + 2240 * \%S]$  kcal/kg

Solution: a. 450kcal/kg b. 810BTU/lb c. d. e. 449.09CHU/lb

- =  $\frac{1}{100}[8080 * 80 + 34500(7 - 3/8) + 2240 * 3.5]$  kcal/kg  
2. Calculate the gross and net calorific values of a coal sample having the following composition C = 80%; H = 7%; O = 3%; S = 3.5%; N = 2.5% and ash 4.4%

$$(II) N.C.V = G.C.V - [0.09H * 587] \text{ kcal/kg}$$

$$= 8828 - [0.09 * 7 * 587] \text{ kcal/kg}$$

$$= 8458.2 \text{ k cal/kg}$$

### Numerical:

3. A sample of coal contains: C= 60%, O= 33%, H= 6%, S= 0.5%, N= 0.3%, Ash= 0.2%. Calculate GCV and NCV.

Solution: GCV= 5506.075Kcal/kg, NCV= 5216.095Kcal/kg

4. A sample of coal contains C= 70%, O= 8%, N= 3%, S= 2%, Ash= 7%. If LCV is 8277.50Kcal/kg, find HCV and %H.

Solution: %H= 9.84    HCV= 8750.60 Kcal/kg

5. A sample of coal contains C= 61%, gH= 6%, S= 0.5%, N= 0.2%, Ash= 0.3%. Calculate GCV and NCV.

Solution: %O= 32 GCV= 4250 Kcal/kg    NCV= 3933.02 Kcal/kg

# Comparison of Solid, Liquid and Gaseous Fuels

Solid fuel	Liquid fuel	Gaseous fuel
<b>1. Calorific value:</b> Their calorific value is low.	Their calorific value is high	Their calorific value is highest.
<b>2. Pollution:</b> Their ash content is high and they produces lot of smoke on burning.	Their ash content is low and they burn without smoke.	They are almost pollution free; they burn without smoke and ash less.
<b>3. Ignition temp and fire hazard:</b> They possess moderate ignition temperature	Their ignition temp is low so there is a chance of fire hazard.	They have a very low ignition temp so they are highly inflammable and chances of fire hazard is highest.
<b>4. Cost:</b> Their production cost is low.	Cost is relatively higher than solid fuel.	They are more costly compare to solid and liquid fuel.

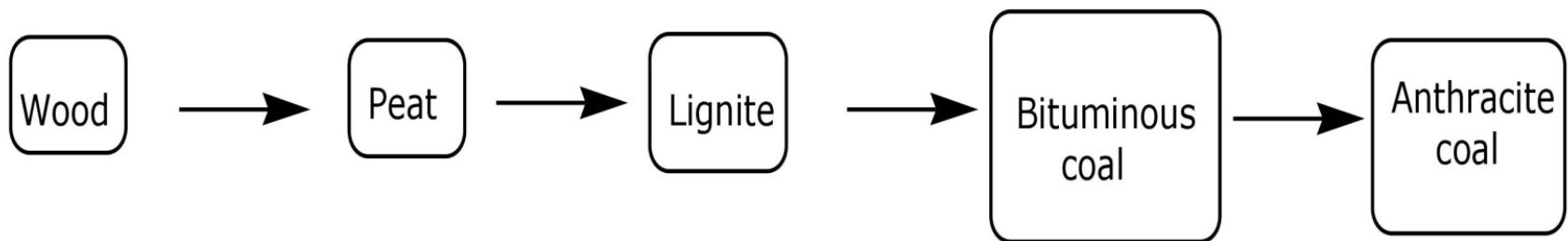
Solid fuel	Liquid fuel	Gaseous fuel
<p><b>5. Transportation:</b> They are easy to transport through normal carriage so cost is low.</p>	<p>They can be transported through pipelines hence it is more costly.</p>	<p>They can be conveyed through pipelines hence costly.</p>
<p><b>6. Storage</b> Their storage needs lot of space but there is no risk.</p>	<p>Costly special storage tank is required for storing and safety precaution has to be taken to prevent fire hazard as most of them are highly inflammable and volatile</p>	<p>They can be compressed in cylinder so storage does not need lot of space. Safety precaution has to be taken to prevent fire hazard as they are highly inflammable and volatile.</p>
<p><b>3. Mode of operation during combustion:</b> Their thermal efficiency is low and ignition temperature is high so large proportion of heat is wasted during combustion. They require a large excess of air for complete combustion. But the combustion operation cannot be controlled easily.</p>	<p>Their ignition temp is low so firing is easier and fire can be extinguished by stopping liquid fuel supply. The flame produced by burning can be easily controlled by adjusting fuel supply.</p>	<p>Their ignition temp is lowest so firing is very easy. The flame produced by burning can be easily controlled by adjusting fuel supply.</p>

# Solid Fuel

## Classification of Coal

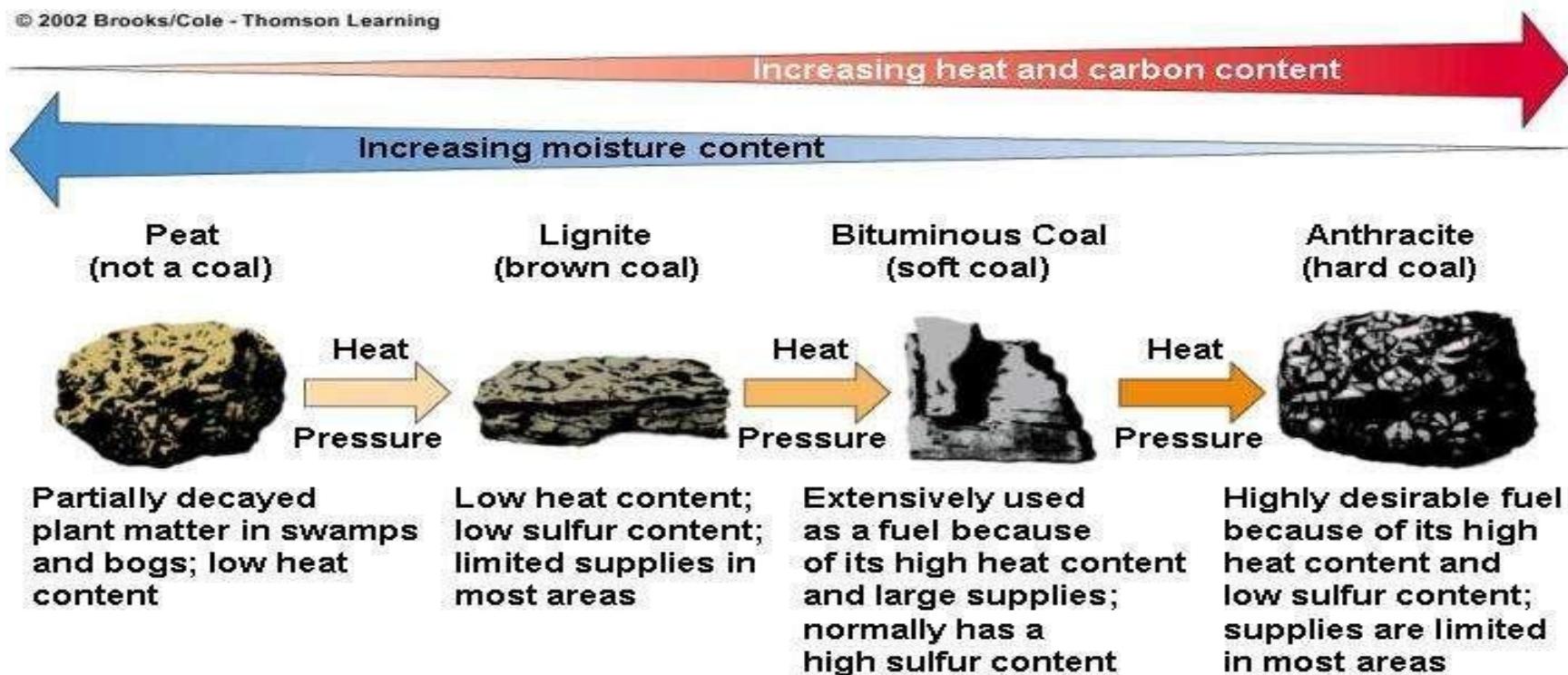
Coal is a primary solid fuel which occurs in nature in very impure form of carbon. It is a fossil fuel.

Wood, peat, lignite, bituminous and anthracite are the different stages in the conversion of wood to coal. Carbon content is highest in anthracite coal.



# Coal formation process

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# Classification of Coal

	Wood	Peat	Lignite	Bituminous coal	Anthracite coal
% of Moisture content	25	25	20	4	1.5
% of Carbon content	50	57	60-80	83	93.3
% of Hydrogen content	6	5.7	5	5	3
Calorific value (Kcal/kg)	4000- 4500	4500- 5000	6500- 7000	8100- 8600	8650- 8700

## **Analysis of coal:**

The purpose is to-

1. To decide the price of coal.
2. To determine the quality of coal.
3. To specify the use of coal for a particular purpose.
4. To calculate the theoretical calorific value of coal.
5. To calculate the air requirement for complete combustion of coal and design the furnace fir box suitably.

Analysis of coal sample is required to access the quality of coal.

**(A) Proximate analysis (PA):** It is the process of determination of moisture, volatile matter, ash and fixed carbon content.

**(B) Ultimate analysis (UA):** It is the process of determination of composition of various components of coal which includes the determination of % of C, H, S, N, O and ash content. It is necessary for utilization of coal for industrial purpose.

The **significance** of various parameters of proximate coal analysis:

**Moisture :**

Moisture increases transportation, handling, storage cost

Moisture decreases the heat content per kg of power plant coal

Moisture increases heat loss due to evaporation and superheating of vapor

Moisture helps in binding the fines

Moisture helps in radiation heat transfer

**Volatile matter:**

Volatile matter also contributes to the heating value of coal

Increase in percentage of volatile matter in coal proportionately increases flame length (smoky flame) and helps in easier ignition of coal

Sets of minimum limit of furnace height and volume

Influences secondary oil support

**Ash:**

Ash is an impurity which will not burn

Ash content is important in design of furnace grate, combustion volume, pollution control equipment (ESP) and Ash handling plant

Ash increases transportation, handling, storage cost

Ash affects combustion efficiency and boiler efficiency

Ash causes clinkering and slagging problems in boiler

**Fix carbon:**

Fix carbon acts as a main heat generator during burning.

Fix carbon gives a rough estimate of heating value of coal

## PROXIMATE ANALYSIS OF COAL :

### Procedure:

**Determination of Inherent Moisture:** Transfer about 1g ( $W_{coal}$ ) of powdered air-dried coal sample into a previously weighed silica crucible. Place the open crucible with sample in an ***electric oven*** and heat it at about ***105 - 110°C*** for an **hour**. Take out the crucible after one hour from the oven and cool it in a **desiccator** (containing moisture absorbing anhydrous calcium chloride). Then weigh the crucible with sample. Calculate the loss in weight.

$$\text{Weight before heating} - \text{Weight after heating} = \text{Loss in weight of coal}$$

$$\% \text{Moisture} = \frac{\text{Loss in weight}}{\text{Weight of Coal}} \times 100$$

**ii) Volatile matter:** The dried sample of coal left in the crucible in step (i) is then covered with a lid and placed in a muffle furnace, maintained at  $950^{\circ}\text{C}$ . The crucible is taken out after 7 minutes of heating. It is cooled first in air then in a desiccator and finally weighed.

$$\% \text{ Volatile matter} = \frac{\text{Loss in weight}}{\text{Wt. of coal taken}} \times 100$$

### Determination of ash

- Coal sample of accurate weight in a crucible is heated in muffle furnace at **700+50 degree Celsius** for  $\frac{1}{2}$  an hour. Crucible is taken out and cooled first in air and then in **desiccators** and **weighed**.
- **% of ash** = 
$$\frac{\text{weight of ash left} * 100}{\text{weight of coal taken}}$$

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

$$\%FC = 100 - (\%M + \%VM + \%Ash)$$

### Numerical:

A sample of coal is analyzed as follows: Exactly 2.5 g was weighted into silica crucible. After heating for an hour at 110°C, the residue weighed 2.415g. The crucible next was covered with a vented lid and strongly heated for exactly seven minutes at 950°C. 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 weigh 0.245g. calculate the percentage result of above analysis.

## ***Significance of Ultimate Analysis***

1. Greater the percentage of carbon and hydrogen, better is the coal in quality and calorific value. However, hydrogen is mostly associated with the volatile matter and hence, it affects the use to which the coal is put to.
2. Nitrogen has no calorific value and hence its presence in coal is undesirable. Thus, a good quality coal has very little nitrogen content.
3. Sulphur is usually present to the extent of 0.5–3.0% and is derived from ores like iron pyrite and gypsum, etc., mines along with the coal. Sulphur, although contributes to the heating value of coal, on combustion it produces acids which have harmful effects of corroding the equipment and also causes atmospheric pollution.
4. Oxygen content decreases the calorific value of coal. High oxygen content coals are characterized by high inherent moisture content, low calorific value and low coking power. Moreover, oxygen is in combined form with hydrogen in coal and thus, hydrogen available for combustion is lesser than actually present.

# Ultimate Analysis

## i) Carbon and Hydrogen (Combustion Method):

An accurately weighed coal sample (1-2g) is burnt in a current of oxygen in combustion apparatus. As a result C and H of the coal are converted into  $\text{CO}_2$  and  $\text{H}_2\text{O}$  respectively. These are absorbed respectively in KOH and  $\text{CaCl}_2$  tubes of known weights. The increase in the weights of KOH and  $\text{CaCl}_2$  tubes corresponds to the amount of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  formed respectively.

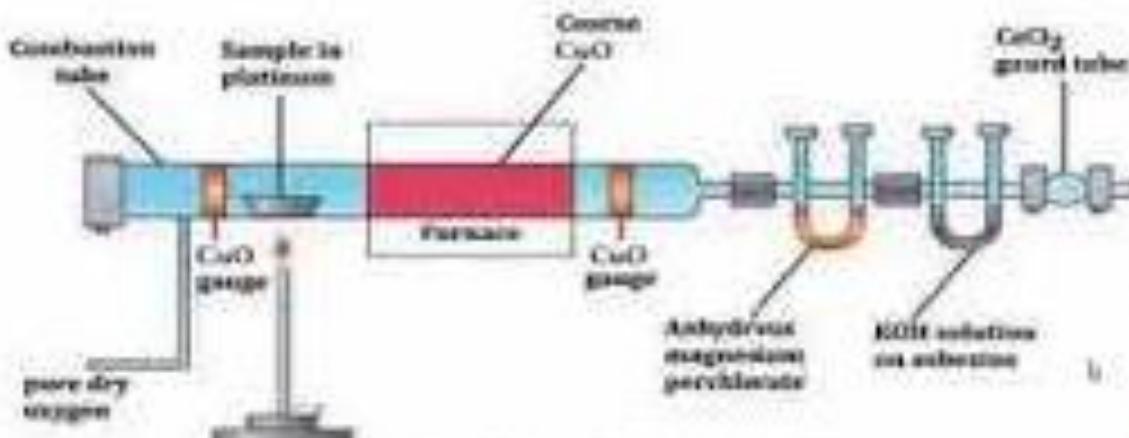
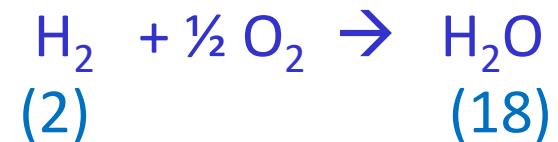
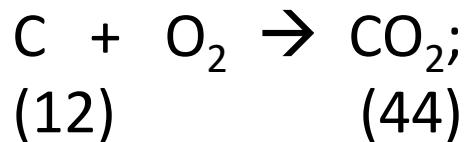


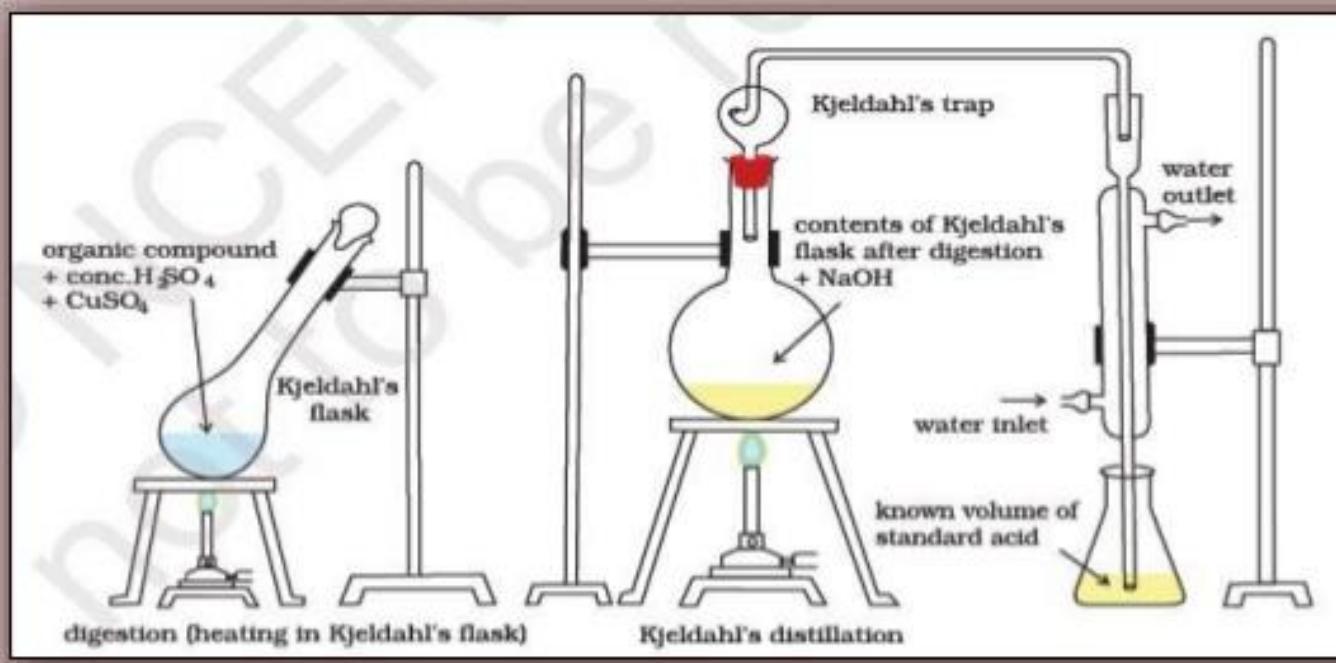
Fig 11.2 Estimation of Carbon and Hydrogen



$$\text{So, \%C} = \frac{\text{Increase in wt. of KOH tube} \times 12 \times 100}{\text{Wt. of coal sample} \times 44}$$

$$\text{\%H} = \frac{\text{Increase in wt. of CaCl}_2\text{ tube} \times 2 \times 100}{\text{Wt. of coal sample} \times 18}$$

# Determination of Nitrogen



- 1g of accurately weighed powdered coal is heated with conc. $\text{H}_2\text{SO}_4$  in kjeldahl flask.
- It is treated with excess KOH.

- Liberated ammonia is distilled over and absorbed in a known **volume of standard** solution of acid.
- Unused acid is determined by back titration with standard **NaOH**.

**% of N is**  
volume of acid used\*normality\*1.4  
weight of coal sample taken

$$\% \text{ of N} = \frac{\text{Volume of acid used} \times \text{Normality} \times 1.4}{\text{weight of coal taken}}$$



Let weight of coal taken = W gm.

Vol of N/10 NaOH required for blank Rdg = Y ml.

Vol. of N/10 NaOH required = x ml (to titrate unreacted acid)

Vol. of N/10 acid reacted with ammonia = (y-x) ml.

Vol. of N/10 ammonia = (y-x) ml.

1000 ml of 1N ammonia solution = 17 gm of NH<sub>3</sub>

1000 ml of 1N NH<sub>3</sub> Solution = 14 gm of N.

1000 ml of 0.1N NH<sub>3</sub> solution = 1.4 gm of N.

$$\therefore (\text{y}-\text{x}) \text{ ml of } 0.1\text{N NH}_3 \text{ solution} = \frac{1.4(\text{y}-\text{x})}{1000} \text{ gm of N}$$

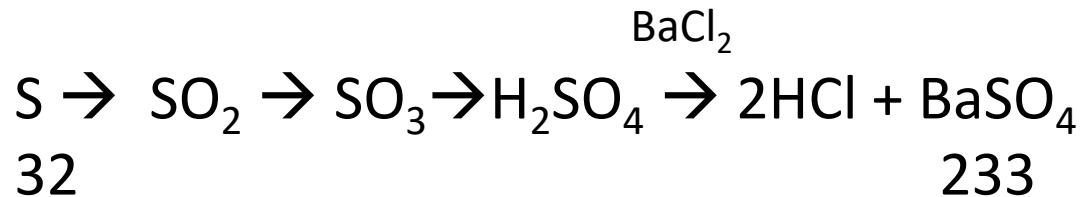
$$\text{W gm of coal contains } \frac{1.4(\text{y}-\text{x})}{1000} \text{ gm of N.}$$

$$\therefore 100 \text{ gm of coal contains} = \frac{1.4(\text{y}-\text{x})}{1000} \times \frac{100}{\text{w}} = \% \text{ N} = \frac{1.4(\text{y}-\text{x})}{10 \times \text{w}}$$

$$\text{OR} \quad \% \text{ of N} = \frac{\text{vol. of acid used} \times \text{normality} \times 1.4}{\text{weight of coal taken}}$$

## Determination of Sulphur:

Take 10ml of distilled water in a bomb calorimeter. Burn the known weight of powdered and air dried coal sample in it. Collect the washings in a beaker and add barium chloride solution to it. Filter the precipitate of barium sulphate formed. Dry it and weigh it. Calculate the %S as-



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

## Determination of ash and oxygen

- Coal sample of accurate weight in a crucible is heated in muffle furnace at **700+50 degree Celsius** for  $\frac{1}{2}$  an hour. Crucible is taken out and cooled first in air and then in **desiccators** and **weighed**.
  - **% of ash** =  $\frac{\text{weight of ash left} * 100}{\text{weight of coal taken}}$
  - **% of oxygen** is  
100-percentage of (**C+H+S+N+Ash**)

## Numerical:

1. 0.2g of coal sample is burnt. The gaseous products are absorbed in potash bulb and calcium chloride tube of known weight. The increase in weight of potash bulb and calcium chloride tube are 0.66gm and 0.08gm respectively. Calculate %C and %H. (Solution: C= 90%; H= 4.44%)
2. 3gm of coal was heated in Kjeldahl's flask and ammonia formed was absorbed in 40ml of 0.5N acid. After absorption, the excess acid required 18.5ml of 0.5N KOH for neutralization. 2.3gm of same coal sample gave 0.35gm BaSO<sub>4</sub> ppt. Calculate %N and %S. (N= 5.01%; S= 2.089%)

# Liquid Fuel

## PETROLEUM

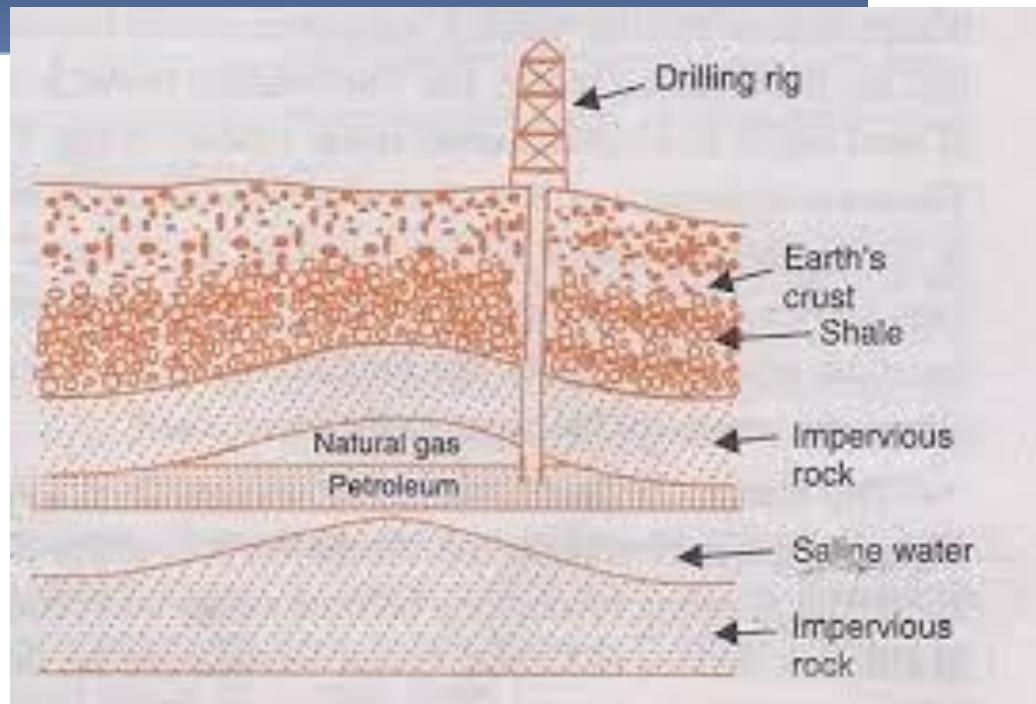
- The single largest source of **liquid fuel is petroleum**.
- Petroleum (petra=rock;olium=oil) is also known as **rock oil or mineral oil**.
- Crude oil (petroleum) is a viscous liquid containing hydrocarbons , petroleum also contains small amounts of non-hydrocarbons mineral impurities that we extract from underground deposits at a depth of **500-1500 ft** at various places.
- It is mainly composed of various hydrocarbons (like straight chain paraffins, cycloparaffins or napthenes, olefins, and aromatics) together with small amount of organic compounds containing oxygen nitrogen and sulphur

## Occurrence of petroleum

Petroleum occurs deep under the surface of the earth between two layers of impervious rocks (non-porous rocks). Petroleum being lighter than water, floats over water. Petroleum deposits are usually found mixed with water, salt, silt, and earth particles such as sand, clay, etc..

Petroleum does not occur in all the places of earth. It is found only in certain places of earth. Natural gas occurs just above the petroleum oil trapped under the rocks.

**Mining** is done by drilling holes in the earth's crust and sinking pipe upto the oil bearing rock. The hydrostatic pressure exerted by the natural gas helps to get petroleum piped out with pressure. When this pressure falls, oil can be pumped out by forcing air (airlift process) or water (hydro process) through another pipe sinked in the earth's crust.



# Composition of typical crude oil

Carbon:	83-87%
Hydrogen:	11-14%
Nitrogen:	0-0.5%
Sulfur:	0-6%
Oxygen:	0-3.5%

Plus oxygenated compounds like phenols, fatty acids, ketones and metallic elements like vanadium and nickel.

## Classification of Petroleum

### ➤ Paraffinic Base Type Crude Petroleum

This type of petroleum is mainly composed of the saturated hydrocarbons from  $\text{CH}_4$  to  $\text{C}_{35}\text{H}_{72}$  and a little of the napthenes and aromatics. The hydrocarbons from  $\text{C}_{18}\text{H}_{38}$  to  $\text{C}_{35}\text{H}_{72}$  are sometimes called Waxes.

### ➤ Asphalitic Base Type Crude Petroleum

It contains mainly cycloparaffins or napthenes with smaller amount of parffins and aromatic hydrocarbons.

### ➤ Mixed Base Type Crude Petroleum

It contains both paraffinic and asphaltic hydrocarbons and are generally rich in semi-solid waxes.

# Refining of Petroleum

- Crude oil must undergo several separation processes so that its components can be obtained and used as fuels or converted to more valuable products. The process of transforming crude oil into finished petroleum products (that the market demands) is called crude oil refining/ refining of petroleum.
- 1. **Separation of water and Desalting:** The emulsified water alongwith the dissolved salts is removed by passing the crude oil through highly charged electrodes when the colloidal water droplets unite to form large drops which separate from the oil.
- 2. **Removal of Sulphur:** The crude oil is then heated with CuO to remove sulphur as CuS.
- 3. **Fractional distillation:** The principle of fractional distillation is that vapours of higher boiling point compounds get condensed into liquid during stepwise cooling.

# EQUIPMENT

The main equipment is a tall cylinder called a fractionator (or fractional distillation column)

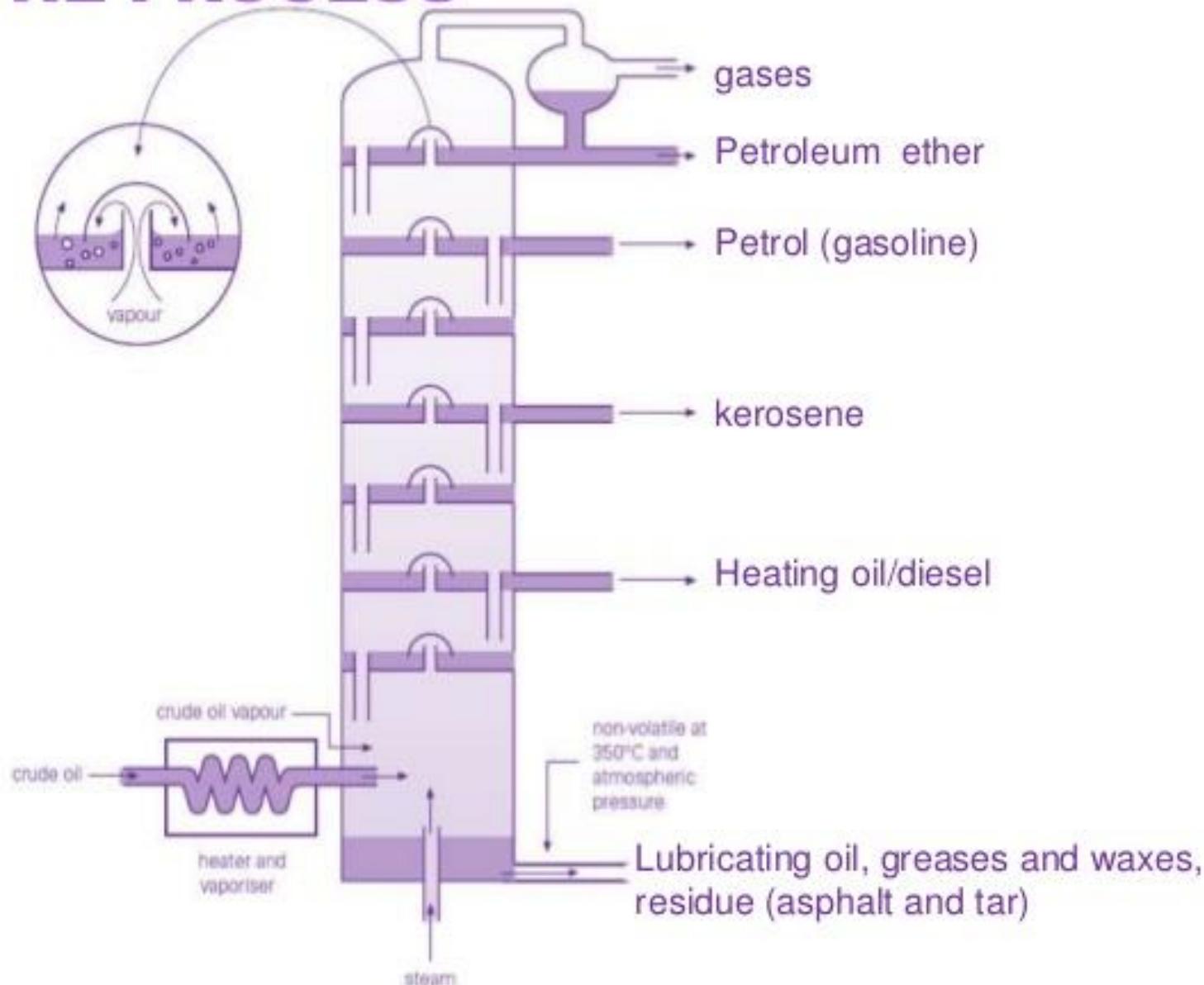
Inside this column there are many trays, or horizontal plates, all located at different heights.

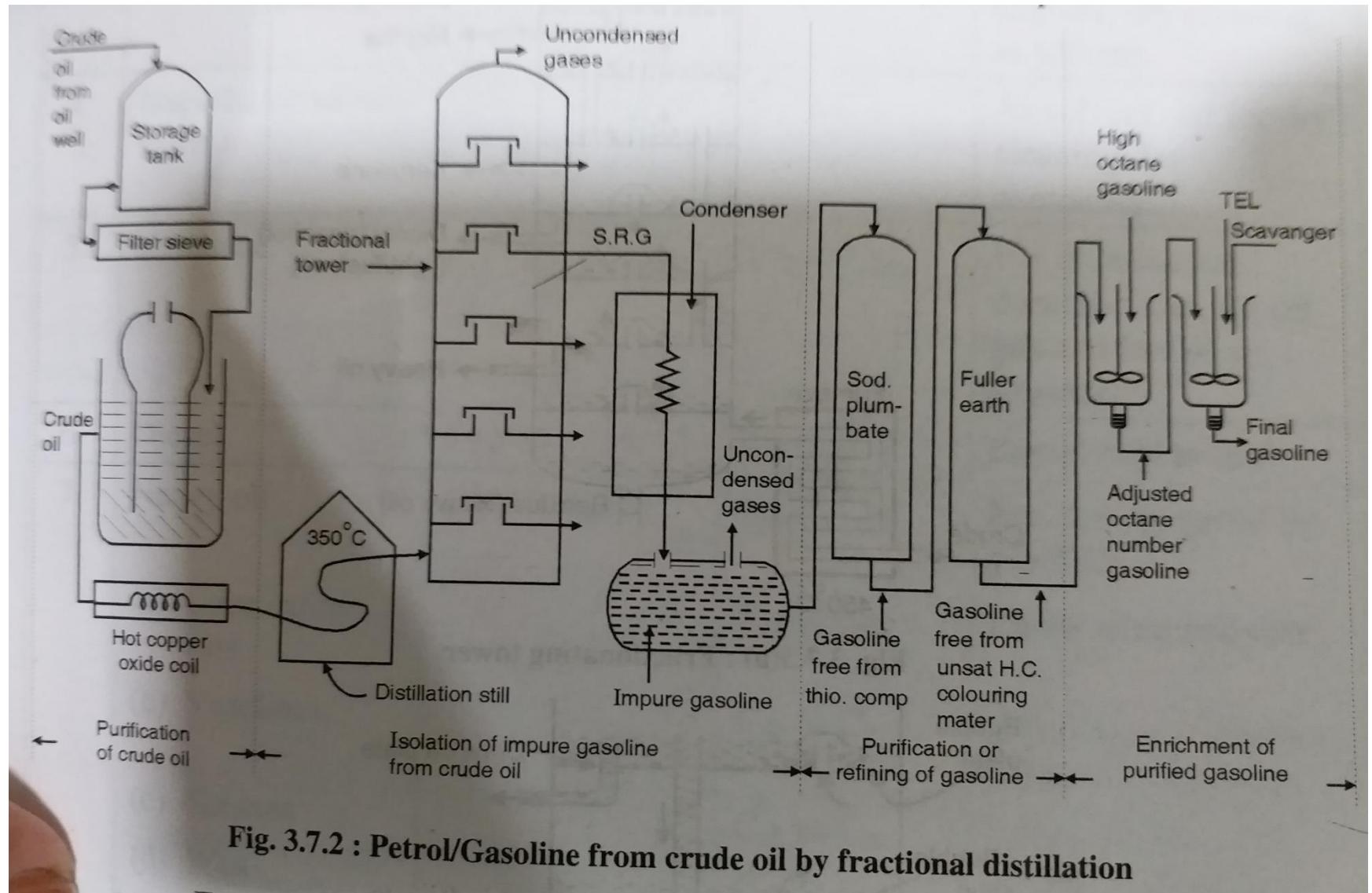
Each tray collects a different fraction when it cools to its own boiling point and condenses.

## Process

Generally crude oil contains compounds having boiling points upto 400 °C. In this process, crude oil is heated to above 400 °C in a pipe. Its vapors are allowed to enter into a fractionating tower having different compartment to collect different volatilities. These are now condensed to liquid and are separated.

# THE PROCESS





**Fig. 3.7.2 : Petrol/Gasoline from crude oil by fractional distillation**

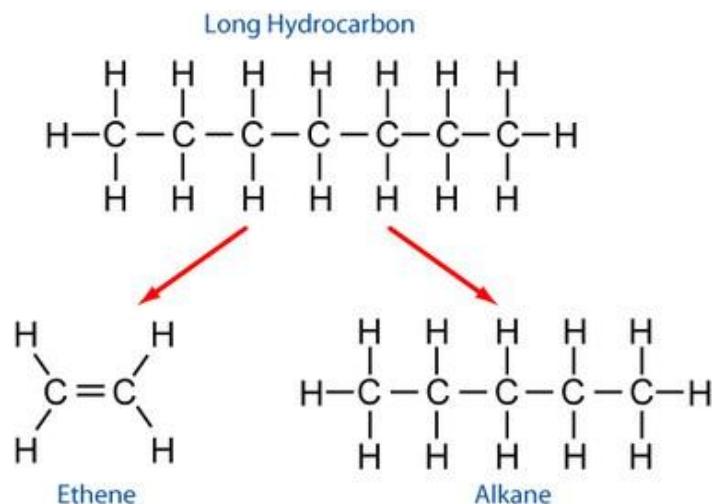
Table 3.7.1 : Products of fractional distillation of crude oil

Sr. No.	Name of fraction	Boiling range	Composition of hydrocarbon	[ May 2006 ] Uses
1.	Uncondensed gases	Below 40° C	C <sub>1</sub> to C <sub>4</sub>	Domestic and industrial fuel under 'LPG' name.
2.	Aviation fuel or petroleum other	40-70° C	C <sub>5</sub> to C <sub>7</sub>	Fuel for aeroplane, helicopters, as solvent.
3.	Petrol or gasoline	60° C - 120° C	C <sub>5</sub> to C <sub>8</sub>	Fuel for petrol engines, dry cleaning, as solvent.
4.	Naphtha or solvent spirit	120° C - 180° C	C <sub>7</sub> to C <sub>10</sub>	As solvent and for dry cleaning, for chemicals.
5.	Kerosene	180° C - 250° C	C <sub>10</sub> to C <sub>16</sub>	For illumination, domestic fuel, for oil gas and fuel of jet engines.
6.	Diesel	250° C - 320° C	C <sub>15</sub> to C <sub>18</sub>	Diesel engine fuel.
7.	Heavy oil	320° C-400° C	C <sub>17</sub> to C <sub>30</sub>	For making petrol by cracking.
	(a) Lubricating oils	—	C <sub>18</sub> to C <sub>20</sub>	Lubricating purposes,
	(b) Vaseline	—	C <sub>20</sub> to C <sub>22</sub>	Cosmetics, medicines, ointments, lubricant.
	(c) Greases	—	C <sub>22</sub> to C <sub>26</sub>	Lubrication.
	(d) Wax	—	C <sub>26</sub> to C <sub>30</sub>	Candles, boot polish, tarpaulin cloth, wax paper, etc.
8.	Residue (a) asphalt (b) petroleum coke	—	above C <sub>30</sub>	Road making, water proofing of roofs. As fuel, for arc light rods.

The petrol obtained after fractional distillation is also known as straight run petrol. The yield of petrol is very low. Also, the quality (octane number) is poor. Thus, various other fractions obtained in the fractional distillation are further subjected to cracking to increase the overall yield and quality of petrol. The quality of petrol can also be improved by adding various additives to it; like TEL, TML, etc.

### Cracking:

Cracking is defined as a process, wherein complex organic molecules namely long chain hydrocarbons or kerogens with high molecular weight are broken down into smaller molecules namely light hydrocarbons with low molecular weight. It is caused by the breaking of carbon-carbon bonds.



# CRACKING

Involves the breaking of C-C bonds in alkanes

Converts heavy fractions into higher value products

- THERMAL

proceeds via a free radical mechanism

- CATALYTIC

proceeds via a carbocation (carbonium ion) mechanism

# **THERMAL CRACKING**

- **High Pressure** ... 7000 kPa
- **High Temperature** ... 400°C to 900°C
- **Free Radical Mechanism**
- **Homolytic fission**
- **Produces mostly alkenes** ...e.g. ethene for making polymers and ethanol
- **Produces Hydrogen** ... used in the Haber Process and in margarine manufacture
- Bonds can be broken anywhere in the molecule by C-C bond fission or C-H bond fission

### 3.8.2.1 Thermal Cracking

#### (a) Liquid phase thermal cracking

- By this method, any type of oil can be cracked. In this method, the oil is pumped into the coil kept at 420° C to 550° C under a pressure of 15 to 100 kg/cm<sup>2</sup>. As the temperature increases, a better quality of gasoline is produced.
- The octane value of this gasoline is low, i.e. 65 to 70. Therefore, it is mixed with higher octane value gasoline and then used in engine.

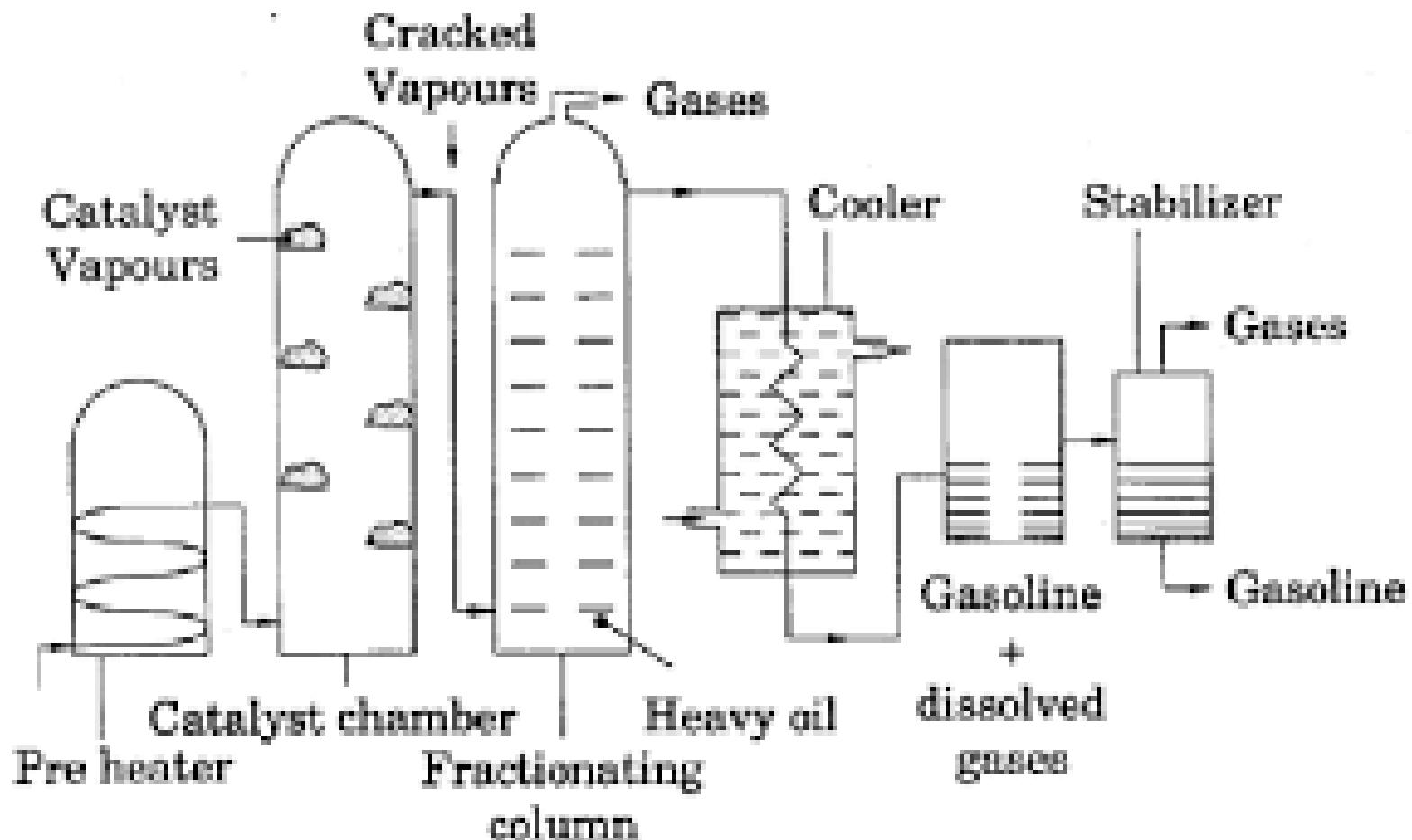
#### (b) Vapour phase thermal cracking

- In this method, the heavy oil is heated in the heater at 400°C to convert it into the vapours and then these vapours are passed to the reaction chamber which is maintained at 600°C to 650°C and under a pressure of 10 to 20 kg/cm<sup>2</sup>.
- At this stage, the higher hydrocarbons are converted into lower hydrocarbons easily and the octane value of petrol is usually 75 to 80.

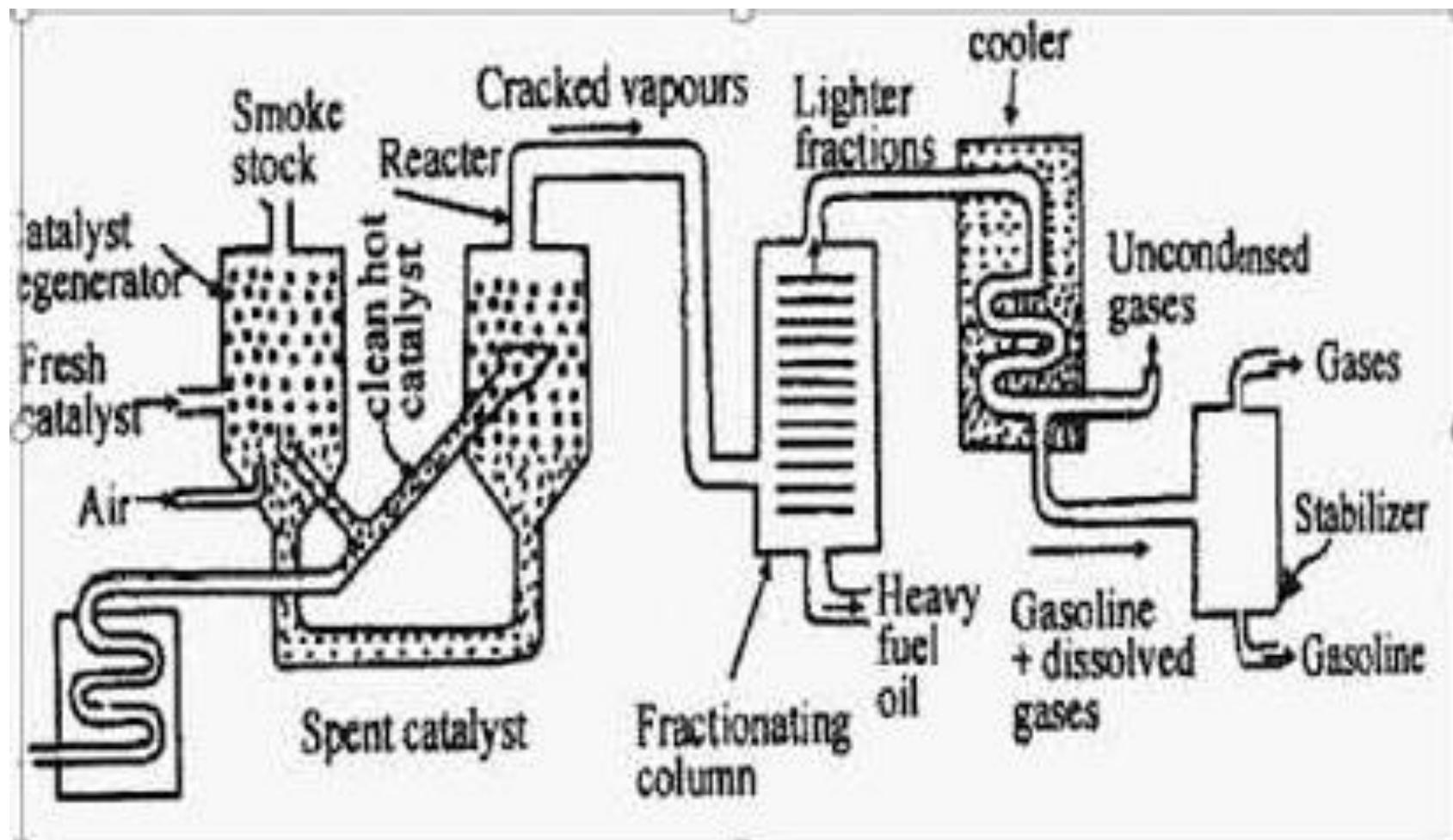
#### Comparison of liquid phase and vapour phase thermal cracking

Sr. No.	Characteristic	Liquid Phase Thermal Cracking	Vapour Phase Thermal Cracking
1.	Cracking temperature	Moderate i.e. 420°C – 550°C	600°C – 650°C
2.	Pressure	High = 15 to 100 kg/cm <sup>2</sup>	Low = 15 – 20 kg/cm <sup>2</sup>
3.	Yield percentages	50 – 60%	—
4.	Octane rating	65 – 70	> 70 (75 – 80)
5.	Pre-requirement for process	Any type of heavy oil can be used	Oil has to be vaporised readily
6.	Time required	Comparatively more	Comparatively less

# Fixed bed catalytic cracking



# Fluidized bed catalytic cracking



### **Regeneration of exhausted catalyst**

- Catalyst gets deactivated due to the deposition of free carbon on catalyst.
- The deactivated catalyst is taken from the bottom of the cracker and brought into regenerator where it is heated to about 500°C in the presence of hot air to burn carbon dioxide which is taken out from the top of the regenerator.
- The regenerated catalyst in hot condition is taken down to the vapours of heavy oil and recirculated in the cracker.

#### **3.8.2.3 Advantages of Catalytic Process**

- i) The cracking reaction can be carried out at lower temperature and pressure.
- ii) The cracking is specific in nature and can give proper quality of gasoline.
- iii) The octane value of gasoline is higher by catalytic process, hence better for petrol engine.

#### **Comparison of fixed bed and moving bed catalytic cracking**

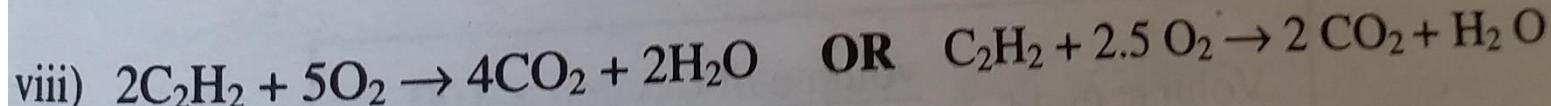
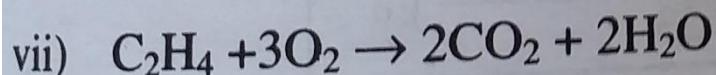
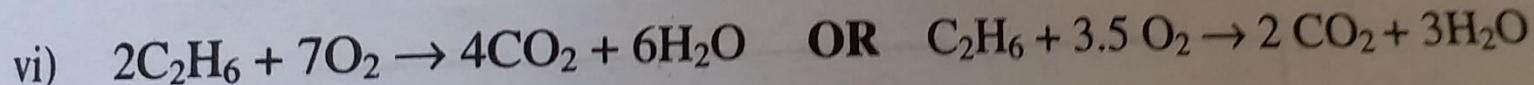
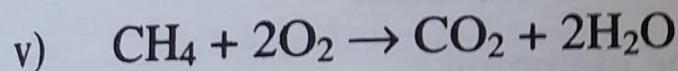
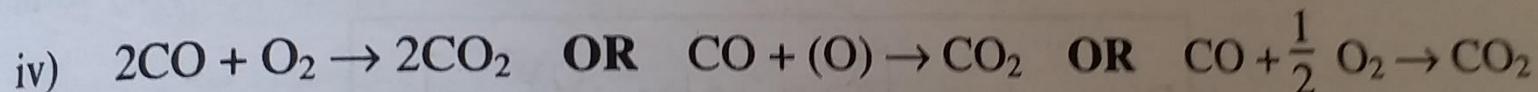
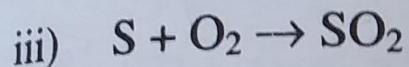
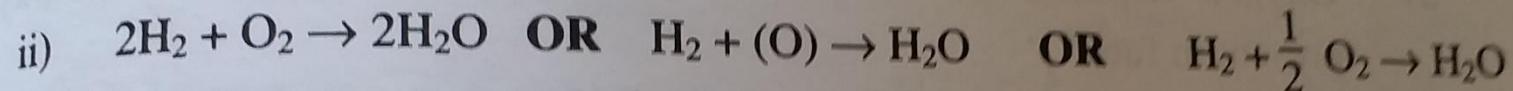
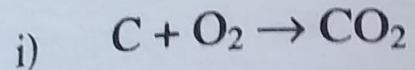
[ Dec. 2009 ]

Sr. No	Characteristic	Fixed Bed Catalytic Cracking	Moving Bed or Fluidised Bed Catalytic Cracking
1.	Chamber Reaction temperature	i.e. 425°C – 540°C	550°C – 570°C
2.	Pressure	1.5 kg/cm <sup>2</sup>	Around 1 kg/cm <sup>2</sup>
3.	Octane value	80 – 85	85 – 90

# Combustion

- Combustion is the process of burning any combustible substance in the presence of oxygen, which liberates energy in the form of heat and light. For efficient combustion, it is essential that the fuel must be brought into intimate contact with sufficient quantity of air or oxygen.
- The combustible substance usually present in fuels, which enter into the combustion, are mainly C, H, S and O. But N, CO<sub>2</sub> and ash are incombustible matters present in the fuel, they do not take any oxygen during combustion.
- For the complete combustion of a given quantity of fuel, the quantity of oxygen and thus the quantity of air required can be calculated by considering the following point- Substances always combine in definite proportions, which are determined by the molecular weights of the substances.

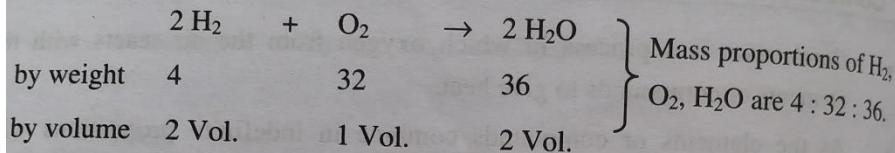
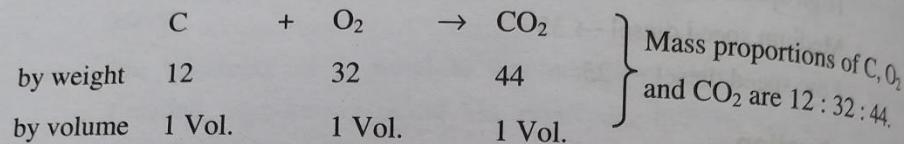
The commonly involved combustion reactions are:



### 3.10.1 Calculation of Quantity of Air Required for Combustion of Fuel

#### By weight and volume

- 1) A substance and oxygen combine in definite proportion as per concept.



Nitrogen, ash (mineral matter) and CO<sub>2</sub> are not combustible.

- 2) At STP conditions, 22.4 litres of a gas is one gram-mole.
- 3) Air contains 21% oxygen by volume and 23% oxygen by mass.
- 4) Molar mass of air is taken as 28.94 gm/mole.
- 5) Oxygen required for combustion = theoretical O<sub>2</sub> required - Oxygen present in fuel.
- 6) Out of the total % of hydrogen in fuel, if some part is in the form of H<sub>2</sub>O, then only the rest of the part combines with O<sub>2</sub>.
- 7) When % of elements in a fuel is given, then calculate quantity by formula:

$$\boxed{\text{O}_2 \text{ quantity} = \left[ \frac{32}{12} \text{C} + 8 \left( \text{H} - \frac{\text{O}}{8} \right) + \text{S} \right] \text{kg}}$$

where C, H, S, O are masses of the elements.

$$\boxed{\text{Quantity of air} = \frac{\text{Oxygen quantity} \times 100}{23} \text{ kg}}$$

$$\boxed{\text{Volume of air} = \frac{\text{volume of oxygen} \times 100}{21} \text{ m}^3}$$

STP 22.4 lit = gram mol wt

Mol mass of air= 28.94gm/mol

22.4 **lit** of air= 28.94**gm** of air  
or 22.4**m<sup>3</sup>** of air = 28.94**kg** air

$$PV = nRT$$

(By Boyles & Charles Law)

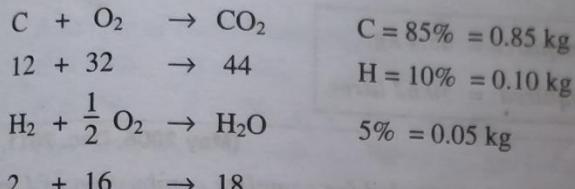
$$P_0V_0/T_0 = P_1V_1/T_1$$

Example

Calculate the weight and volume of air required for complete combustion of 5 kg. coal with following compositions, C = 85%; H = 10%; O = 5%.

Solution

Combustion reactions :



Calculation of  $\text{O}_2$  needed for 1 kg coal

Elements = Weight in kg	Weight of $\text{O}_2$ required for complete combustion in kg.
C = 0.85	$0.85 \times \frac{32}{12} = 2.26 \text{ kg.}$
H = 0.1	$0.1 \times 8 = 0.8 \text{ kg.}$
O = 0.05	-
	Total oxygen = 3.06 kg.

Weight of oxygen required

$$\begin{aligned} &= \text{Weight of oxygen needed} - \text{weight of oxygen present} \\ &= 3.06 - 0.05 = [3.01 \text{ kg}] \end{aligned}$$

∴ Weight of Air required for complete combustion

[∴ Air contains 23%  $\text{O}_2$  by weight]

$$= 3.01 \times \frac{100}{23} = [13.08 \text{ kg. per 1 kg. coal.}]$$

∴ Air required for 5 kg. of coal

$$= 13.08 \times 5 = [65.40 \text{ kg.}]$$

### Volume of Air

$$\therefore 28.94 \text{ kg. of air} = 22,400 \text{ ml volume at NTP}$$

$$\begin{aligned} \therefore 65.4 \text{ kg. of air} &= \frac{22400 \times 65.4}{28.94} = 50620.6 \text{ ml. air} \\ &= [50.6206 \text{ litres of air}] \end{aligned}$$

Ans. : Weight of air required = 65.4 kg.  
 Volume of air required = 50.62 litres.

**Example 3.14.\***

Calculate the volume of air containing 25 % oxygen by volume at 27°C and 760 mm pressure which will be required for complete combustion of 3 kg fuel containing, C = 75%; H = 23%; and Ash = 2%.

**Solution :** Calculation of O<sub>2</sub> needed for 1 kg coal.

Components	% Composition	Weight of elements per kg. of fuel	Weight of O <sub>2</sub> in kg for 1 kg fuel
Carbon	75	0.75	$\frac{32}{12} \times 0.75 = 2.00$
Hydrogen	23	0.23	$\frac{16}{2} \times 0.23 = 1.84$
Ash	2	—	—
			—
		Total O <sub>2</sub>	3.84 kg

∴ Weight of O<sub>2</sub> required per 3 kg of fuel = 11.5275 kg.

Volume of oxygen at NTP

∴ 32 kg. of O<sub>2</sub> → 22.4 cu.m. of O<sub>2</sub>

$$\therefore 11.5275 \text{ kg of O}_2 = \frac{22.4 \times 11.5275}{32} = 8.06 \text{ cu.m.}$$

$$\text{Now } \therefore \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\frac{760 \times 8.06}{273} = \frac{760 \times V_2}{300}$$

$$V_2 = \frac{1837680}{207480}$$

$$\therefore V_2 = 8.857 \text{ cu.m. O}_2$$

But, air contains 25% O<sub>2</sub> by volume.

∴ 25 cu.m. of O<sub>2</sub> is present in 100 cu.m. of air.

$$\therefore 8.857 \text{ cu.m. of O}_2 \text{ is present in } \frac{8.857 \times 100}{25} = [35.43 \text{ cu.m. of air.}]$$

**Ans. : Volume of air = 35.43 cu.m**

A sample of coal requires 20% excess air for complete combustion.  
 Calculate weight of air for 250 gm of the coal, if its composition is,  
 $C = 81\%$ ,  $H = 4\%$ ,  $N = 1.5\%$ ,  $S = 1.2\%$ ,  $O = 3\%$ , ash = 9.3%.

Let us calculate the  $O_2$  required for 1 kg of coal first.

$$\text{Weight of carbon} = \frac{81}{100} \times 1 = 0.81 \text{ kg}$$

$$\text{Weight of hydrogen} = \frac{4}{100} \times 1 = 0.04 \text{ kg}$$

$$\text{Weight of sulphur} = \frac{1.2}{100} \times 1 = 0.012 \text{ kg}$$

$$\text{Weight of oxygen} = \frac{3}{100} \times 1 = 0.03 \text{ kg}$$

**Calculation of  $O_2$  needed for 1 kg coal.**

Reactions	Weight of $O_2$ required
$C + O_2 \rightarrow CO_2$ 12 32	$0.81 \times \frac{32}{12} = 2.16 \text{ kg}$
$2 H_2 + O_2 \rightarrow 2 H_2O$ 4 32	$0.04 \times \frac{32}{4} = 0.32 \text{ kg}$
$S + O_2 \rightarrow SO_2$ 32 32	$0.012 \times \frac{32}{32} = 0.012 \text{ kg}$
	Total $O_2$ required = 2.492 kg
	Less $O_2$ available = - 0.03
	Net $O_2$ required = 2.462 kg

$$\text{Weight of air required} = \frac{\text{weight of } O_2 \times 100}{23} = 10.7 \text{ kg air.}$$

As 20% excess is required for complete combustion, then practically required weight of air

$$= \frac{10.7 \times 120}{100} = 12.845 \text{ kg air.}$$

As 1000 gm of coal requires 12.845 kg air.

$$\therefore 250 \text{ gm of coal requires} = \frac{250}{1000} \times 12.845 = 3.211 \text{ kg air.}$$

**Example 3.14.6**

A petrol sample contains 14% H and 86% C. Calculate volumes of oxygen and air required for complete combustion of 1 kg of the petrol, at STP conditions.

tion

Given data : Weight of petrol = 1 kg, weight of C =  $\frac{86}{100} \times 1 = 0.86$  kg.

$$\text{Weight of H} = \frac{14}{100} \times 1 = 0.14 \text{ kg}, \quad \text{O \%} = 0$$

**Calculation of O<sub>2</sub> needed for 1 kg coal**

Reactions	Weight of oxygen required
C + O <sub>2</sub> → CO <sub>2</sub>	$\frac{32}{12} \times 0.86 = 2.293$ kg
2 H <sub>2</sub> + O <sub>2</sub> → 2 H <sub>2</sub> O	$\frac{32}{4} \times 0.14 = 1.12$ kg
	Total O <sub>2</sub> = 3.413 kg

As 32 gm O<sub>2</sub> at STP occupies 22.4 lit.

$$\therefore 3.413 \times 1000 \text{ gm O}_2 \text{ at STP will occupy } \frac{3.413 \times 1000 \times 22.4}{32} \text{ lit.}$$

$$= [2389.3 \text{ litres oxygen gas.}]$$

$$\text{Volume of air at STP} = \text{Volume of O}_2 \times \frac{100}{21} = [11377.8 \text{ litres air.}]$$

**Ans. :** Volume of O<sub>2</sub> = 2389.3 liters

Volume of air = 11377.8 liters

ample 3.15.1

A gaseous fuel has following composition by volume -  $CH_4 = 35\%$ ,  $CO = 10\%$ ,  $H_2 = 6\%$ ,  $C_3H_8 = 10\%$ . Calculate the weight of air required for complete combustion. (Given : Molecular weight of air = 28.94)

ution

en data :

$$\text{Volume of gas fuel} = 1 \text{ m}^3,$$

$$\text{Volume of } H_2 = 0.06 \text{ m}^3$$

$$\text{Volume of } CH_4 = 0.35 \text{ m}^3,$$

$$\text{Volume of } CO = 0.1 \text{ m}^3$$

$$\text{Volume of } C_3H_8 = 0.1 \text{ m}^3$$

### Calculation of Volume of $O_2$ needed for $1m^3$ of fuel

Reactions	Volume of $O_2$ required
$2 H_2 + O_2 \rightarrow 2 H_2O$ 2 vol. 1 vol.	$1/2 \times 0.06 = 0.03 \text{ m}^3$
$CH_4 + 2 O_2 \rightarrow CO_2 + 2 H_2O$ 1 vol. 2 vol.	$2/1 \times 0.35 = 0.7 \text{ m}^3$
$CO + 0.5 O_2 \rightarrow CO_2$	$0.5 \times 0.1 = 0.05 \text{ m}^3$
$C_3H_8 + 5 O_2 \rightarrow 3CO_2 + 4 H_2O$	$5 \times 0.1 = 0.5 \text{ m}^3$
Total $O_2$ required	$= 1.28 \text{ m}^3$
$O_2$ present in sample	nil

$$\text{Total } O_2 \text{ required} = 1.28 \text{ m}^3$$

$$\begin{aligned} \text{Volume of air} &= \text{Volume of } O_2 \times \frac{100}{21} = 1.28 \times \frac{100}{21} \\ &= 6.095 \text{ m}^3 \text{ of air} = 6.095 \text{ litres air} \end{aligned}$$

$\therefore$  weight of air

$$\because 22.4 \text{ litres} = 28.94 \text{ kg air}$$

$$\therefore 6.095 \text{ litres} = \left( \frac{6.095 \times 28.94}{22.4} \right) \text{ kg of air} = 7.874 \text{ kg of air}$$

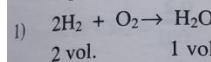
Ans. : Volume of air =  $6.095 \text{ m}^3$  or 6095 litres air

Weight of air = 7.874 kg

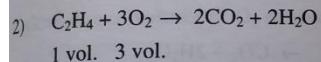
*Calculate volume of air required for complete combustion of 1 cu.m. of gaseous fuel having following compositions by volume.  $H_2 = 25\%$ ;  $C_2H_4 = 10\%$ ;  $CH_4 = 30\%$ ;  $CO = 32\%$ ;  $N_2 = 2\%$  and water vapour = 1%.*

Compounds	% By volume	Per cu.m.
$H_2$	25	0.25
$C_2H_4$	10	0.10
$CH_4$	30	0.30
CO	32	0.32
$N_2$	2	0.02
Water Vapour	1	0.01

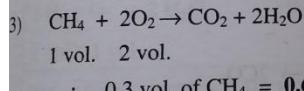
Equation involved



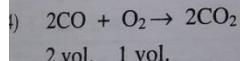
$$\therefore 0.25 \text{ vol. of } H_2 \text{ required } \frac{0.25}{2} = 0.125 \text{ cu.m. of } O_2.$$



$$\therefore 0.1 \text{ vol. of } C_2H_4 = 0.3 \text{ cu.m. of } O_2.$$



$$\therefore 0.3 \text{ vol. of } CH_4 = 0.6 \text{ cu.m. of } O_2.$$



$$\therefore 0.32 \text{ vol. of } CO = \frac{0.25}{2} = 0.3 \text{ cu.m. of } O_2.$$

$$\begin{aligned}\therefore \text{Total } O_2 &= 0.125 + 0.3 + 0.6 + 0.16 \\ &= 1.185 \text{ cu.m. of oxygen.}\end{aligned}$$

Air contains 21 percentage  $O_2$  by volume.

$$\therefore 21 \text{ cu.m. of } O_2 = 100 \text{ cu.m. of air}$$

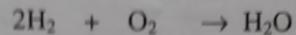
$$\begin{aligned}\therefore 1.185 \text{ cu.m. of } O_2 &= \frac{100}{21} (1.185) \\ &= 5.64 \text{ cu.m.}\end{aligned}$$

*Ans. : Volume of air required = 5.64 cu.m.*

3.15.6

A gas has following compounds by volume.  $H_2 = 20\%$ ;  $CH_4 = 10\%$ ,  $CO = 25\%$ ;  $O_2 = 5\%$ ;  $CO_2 = 15\%$ ;  $N_2 = 20\%$ . Calculate volume of air at  $25^\circ C$  and 750 mm. Pressure for complete combustion of 1 cu.m of fuel.

Compounds	% By volume	Per cu.m
$H_2$	20	0.2
$CH_4$	10	0.1
$CO$	25	0.25
$CO_2$	15	0.15
$O_2$	5	0.05
$N_2$	20	0.2



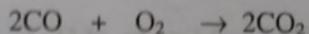
2 Vol. 1 Vol.

$\therefore 0.2 \text{ cu.m } H_2 = 0.1 \text{ cu.m of } O_2$ .



1 Vol. 2 Vol.

$\therefore 0.1 \text{ cu.m } CH_4 = 0.2 \text{ cu.m of } O_2$



2 Vol. 1 Vol.

$\therefore 0.25 \text{ cu.m } CO = 0.125 \text{ cu.m of } O_2$ .

$$\text{Total } O_2 = [(0.1 + 0.2 + 0.125) - 0.05] \text{ Cu.m}$$

$$= 0.375 \text{ cu.m}$$

$$\frac{P_0 V_0}{T_0} = \frac{P_1 V_1}{T_1}$$

$$\therefore \frac{760 \times 0.375}{273} = \frac{750 \times V_1}{298}$$

$$\therefore V_1 = 0.414 \text{ cu.m}$$

Volume of  $O_2$  in air = 21%

21 cu.m  $O_2 \rightarrow 100 \text{ cu.m air}$

$$0.414 \text{ cu.m } O_2 = \frac{100 \times 0.414}{21} = 1.975 \text{ cu.m}$$

$\therefore \text{Volume of air} = 1.975 \text{ cu.m}$

(May 2012, 4 Marks)

A gaseous fuel has the following composition by volume :  $H_2 = 35\%$ ,  $CH_4 = 45\%$ ,  $C_2H_6 = 6\%$ ,  $CO = 12\%$  and remaining  $N_2$ . Calculate the minimum amount of air required at  $27^\circ C$  and  $760 \text{ mm Hg}$  pressure for the complete combustion of 1 cu.m of the fuel.

ion :

$$H_2 = 0.35 \text{ m}^3, C_2H_6 = 0.06 \text{ m}^3$$

$$CH_4 = 0.45 \text{ m}^3, CO = 0.12 \text{ m}^3$$

Volume of  $O_2$  required

No.	Reaction	Volume of $O_2$ required
1.	$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$	$0.35 \times 0.5 = 0.175 \text{ m}^3$
	1 vol. 0.5 vol.	
2.	$CH_4 + 2 O_2 \rightarrow CO_2 + 2 H_2O$	$0.45 \times 2 = 0.90 \text{ m}^3$
	1 vol. 2 vol.	
.	$C_2H_6 + 3.5 O_2 \rightarrow 2CO_2 + 3 H_2O$	$0.06 \times 3.5 = 0.210 \text{ m}^3$
	1 vol. 3.5 vol.	
.	$CO + \frac{1}{2} O_2 \rightarrow CO_2$	$0.12 \times 0.5 = 0.06 \text{ m}^3$
	1 vol. 0.5 vol.	
.	$N_2$ No reaction.	-
	$\therefore$ Total $O_2$ required	$= 1.345 \text{ m}^3$
	$O_2$ present in fuel.	Nil

$$\therefore \text{Volume of air required} = \text{Volume of } O_2 \times \frac{100}{21}$$

$$= \left(1.345 \times \frac{100}{21}\right) \text{ m}^3$$

$$= 6.4048 \text{ m}^3$$

$$= 6.4048 \text{ litres of air}$$

$$\therefore \text{Weight of air} = \because 22.4 \text{ litres air} \equiv 28.94 \text{ kg}$$

$$\therefore 6.4048 \text{ litres air} \equiv$$

$$= 8.274 \text{ kg}$$

$$\text{Now, } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\therefore \frac{760 \times 6.4048}{273} = \frac{760 \times V_2}{273}$$

$$\therefore V_2 = \frac{6.4048 \times 300}{273} = 7.038 \text{ litres air}$$

Weight of air at 760 mm and  $27^\circ C$ :

$$\because 22.4 \text{ litres air} \equiv 28.94 \text{ kg}$$

$$\therefore 7.038 \text{ litres air} \equiv 9.092 \text{ kg}$$

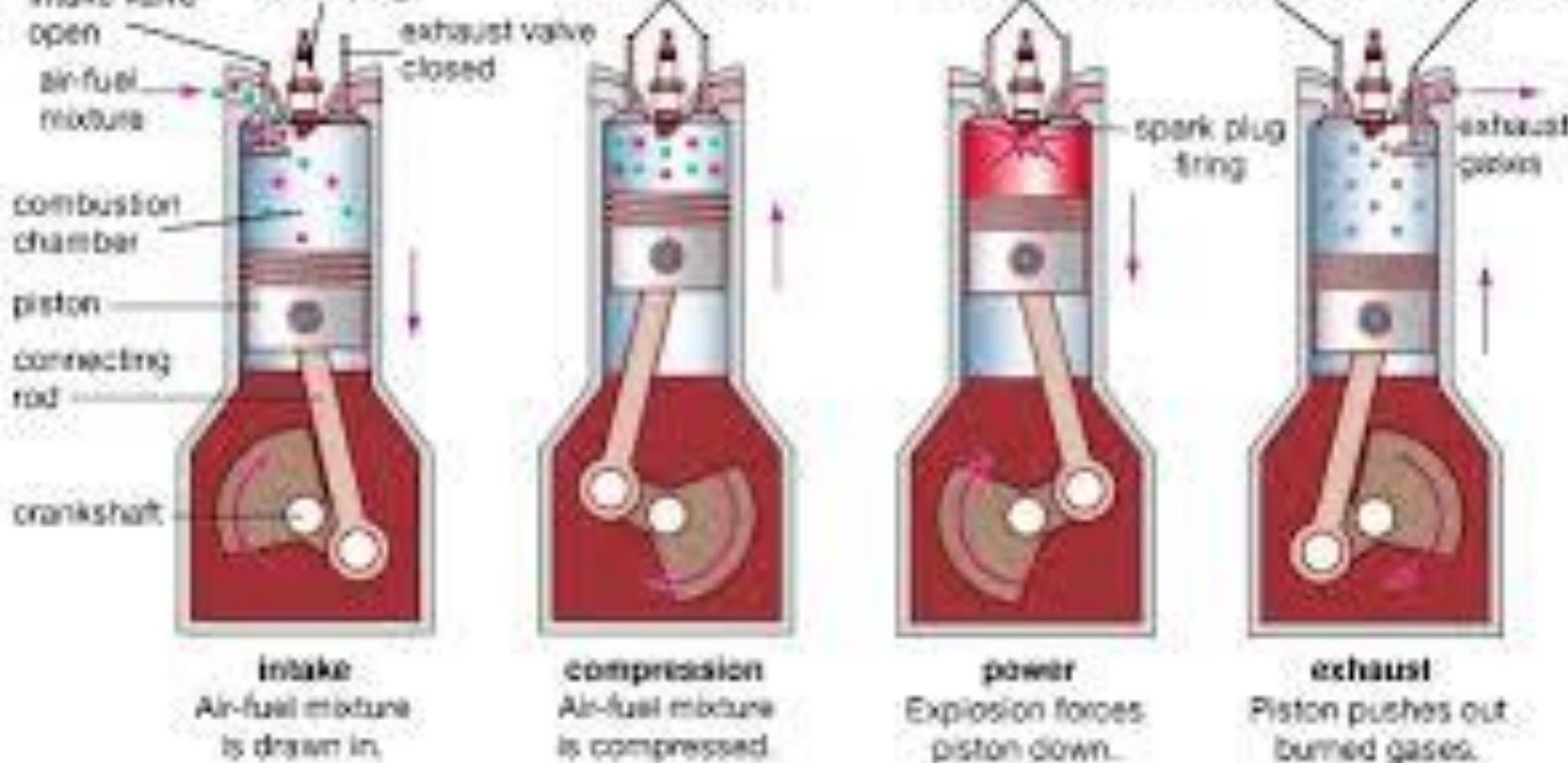
Ans. : Volume of air = 7.038 Litres

Weight of air = 9.092 kg

## **Knocking :**

### **Knocking in Internal Combustion (I.C.) Engines**

In an internal combustion engine, a mixture of air and petrol vapour is compressed and ignited by an electric spark from spark plug in the cylinder. The expanding gas drives the piston downward in the cylinder. The chemical reaction involved is the oxidation of hydrocarbon molecules. Sometimes, the rate of oxidation is so high that the last un-burnt portion of the fuel – air mixture gets ignited instantaneously. This produces a violent sound in the engine known as knocking. Thus **knocking** is due to the spontaneous ignition of the last un-burnt portion of the fuel-air mixture giving a metallic sound. The knocking lowers the efficiency of the engine, wastes the fuels and reduces the life of engine.

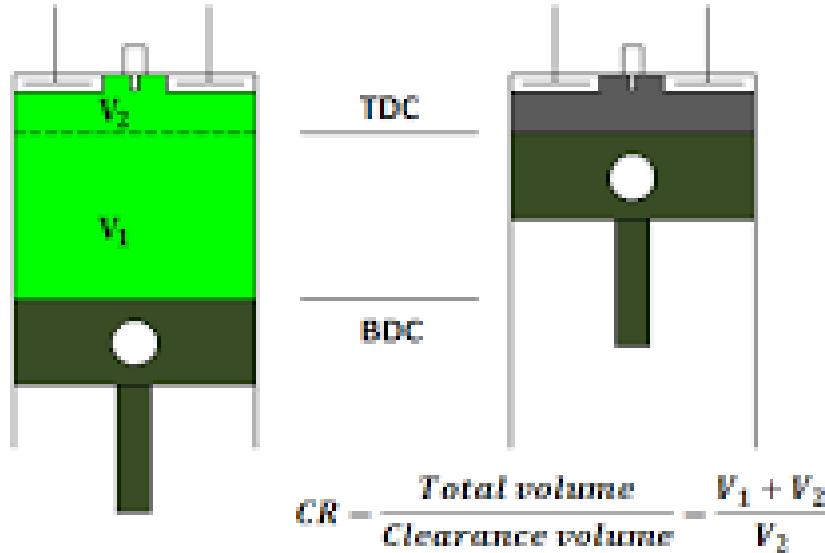


The rate of oxidation of a hydrocarbon molecule depends on the number of C-atoms in the molecule, on the structure and on the temperature.

The temperature depends on the compression ratio. It is the ratio of the cylinder volume at the end of the suction stroke to that at the end of compression stroke of the piston.

Higher the compression ratio (C.R.), higher is the efficiency and power output. But, the power increases to a maximum and then falls rapidly with further increase in compression ratio. The C.R. corresponding to the maximum power output is known as highest useful compression ratio (HUCR) at which a slight metallic knock can be heard.

The tendency to knock depends not only on the fuel but also on the engine design, shape of head, location of plug & ports etc and also upon the running conditions.



## Disadvantages of knocking:

- i) Knocking increases the engine noise and engine runs roughly, due to crank shaft vibrations.
- ii) If knocking is high, it may break the piston.
- iii) It decreases power output and efficiency of the machine.
- iv) Deposition of unburnt carbon increases in the engine increases due to knocking.

# **Chemical Structure of Fuel and Knocking Tendency in I.C. Engines**

The knocking tendency of fuel in I.C. engine **decreases** with increase in compactness of molecule, double bonds and cyclic structure as follows:

1. In normal paraffins (alkanes), the anti-knocking property decreases with increase in **length of hydrocarbon chain**.

E.g. The octane number of n–butane, n–pentane, n–hexane and n–heptane are 90, 60, 29 and 0 respectively.

2. **Branched chain** paraffins have higher anti-knock values than their normal isomers. Also, the antiknock values increases with the **number of branches and their position**.
3. **Olefins** (alkenes) have higher anti-knocking properties than the corresponding paraffins.

Also, the anti-knocking values increases as the **position of double bond** reaches the centre of chain.

4. **Aromatic hydrocarbons** such as benzene and toluene have high octane numbers and therefore high anti-knocking properties.
5. Cracked and reformed gasolines have higher octane numbers than the straight run gasolines.

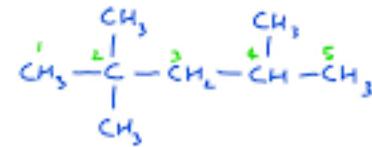
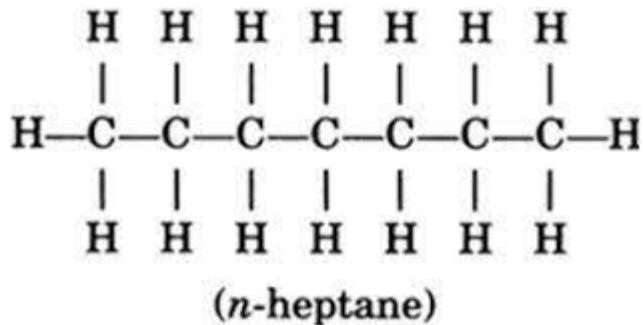
In general, the tendency to knock decreases with change in the nature of fuel as follows:

**Straight chain paraffins > branched chain paraffins > olefins > naphthalenes (alkynes) > aromatic hydrocarbons**

<https://www.youtube.com/watch?v=4ZysyokEU60>

## Octane Number

The knocking characteristics of a fuel (gasoline) are usually expressed by “octane number”. It was found that the hydrocarbon **iso-octane** ( $C_8H_{18}$ ) has very good combustion characteristics and has very little tendency to knock in an I.C. engine. Hence its octane number is taken as **100**. On the other hand, **n-heptane** ( $C_7H_{16}$ ) knocks very readily and hence its octane number is taken as **zero**.



2,2,4-Trimethyl pentane  
Iso-octane

The octane number of a fuel may be **defined** as the percentage of iso-octane in a mixture of iso-octane and n-heptane which just matches with the knocking tendency of the fuel under test.

E.g. A sample of petrol gives same knocking as a mixture of 70% iso-octane and 30% n-heptane then its octane number will be 70.

**So, the octane number-**

**Straight chain paraffins < branched chain paraffins < olefins < naphthalenes (alkynes) < aromatic hydrocarbons**

### **Anti-knocking Agents or Doping Agents**

The anti-knocking properties of a gasoline can be increased by adding some chemicals called as doping agents or anti-knocking agents and the process is called as doping.

Most commonly used doping agent is Tetra-Ethyl Lead (TEL),  $[\text{Pb}(\text{C}_2\text{H}_5)_4]$ . The addition of very small amount of TEL to gasoline of low anti-knock value increases its octane number to a great extent. In I.C. engines, **TEL react with the free radicals** formed during combustion and **lead oxide** is produced. As soon as the explosive combustion occurs, the lead oxide is **reduced to metallic lead** which is **deposited on the spark plug points, the cylinder walls and piston head**. This requires more frequent cleaning of these parts.

To overcome this difficulty, **ethylene dibromide ( $\text{C}_2\text{H}_4\text{Br}_2$ )** is also added to dope to convert the metallic lead into **volatile lead bromide**, which is removed with the **exhaust gases**.

Lead in exhaust gases creates environmental pollution hence now a days oxygenates are used like ethanol, methyl tertiary butyl ether (MTBE) or ethyl tertiary butyl ether (ETBE), which have octane number above 100. The oxygen of these compounds brings about complete combustion of petrol preventing peroxide formation and hence knocking is prevented. ETBE and MTBE are close relatives with similar characteristics. MTBE is derived from methanol and iso-butylene while ETBE is derived from ethanol and iso-butylene from same source. MTBE may contaminate ground water through gasoline leaks. ETBE has slightly high octane number and low vapour pressure but it is expensive than MTBE.

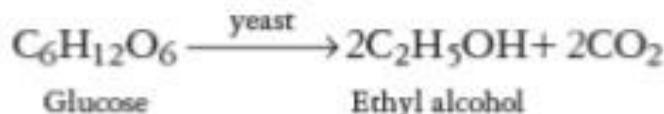
## **Power Alcohol and Synthetic Petrol**

## *Power Alcohol*

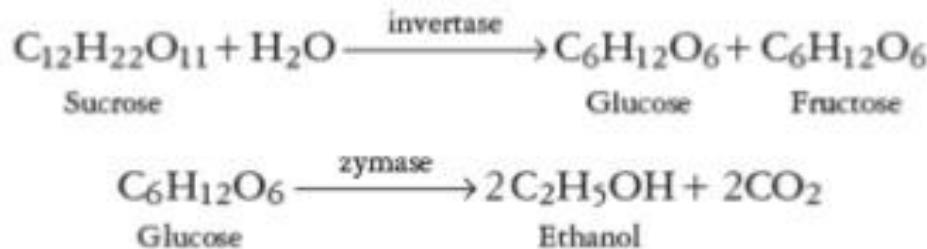
Ethyl alcohol is used as additive to motor fuels. When blended with petrol at concentrations of 5–10%, it is called power alcohol. The addition of alcohol to petrol increases its octane number.

## **Manufacture of Ethanol**

### 1. By fermentation



## 2. Using Molasses as raw material



The advantages of power alcohol are as follows:

1. Ethyl alcohol is a good antiknocking agent and power alcohol has octane number 90, while that of petrol is 65.
2. Any moisture content present is absorbed by alcohol.
3. Ethyl alcohol contains oxygen atoms, which help for complete combustion of power alcohol and the polluting emissions of CO, hydrocarbon, particulates are largely reduced.
4. Power alcohol is cheaper than petrol.

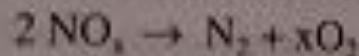
The disadvantages of power alcohol are as follows:

1. Ethyl alcohol has calorific value 7000 cal/g much lower than that of petrol which has 11500 cal/g. However, this problem could be overcome by using a specially designed engine with higher compression ratio.
2. The output of the power generated is reduced up to 35%.
3. It has high surface tension and its atomization is difficult, especially at lower temperature, thereby causing starting trouble.
4. It may undergo oxidation reaction to form acetic acid, which corrodes engine parts.
5. As it contains oxygen atoms, the amount of air required for complete combustion is less, therefore, the carburetor and engine need to be modified.

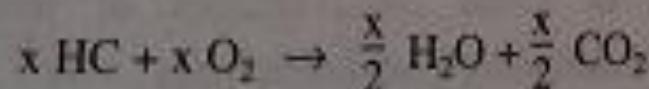
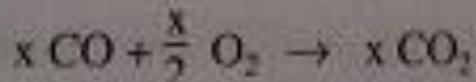
## 9.2 Unleaded Petrol

[ May 2012 ]

- In car exhaust, if catalytic converter is connected, leaded petrol can not be used; because, lead destroys the active sites of catalyst.
- In catalytic converter, two types of catalysts are used as,
  - (a) Reduction catalyst
  - (b) Oxidation catalyst
- Catalyst helps to reduce emissions of harmful gases by following reactions.
- Reduction catalyst contains Pt or Rh, which can reduce  $\text{NO}_x$  as,



Oxidation catalyst helps treating unburnt hydro carbons oxidation catalyst unburnt hydrocarbons and carbon monoxide, due to presence of Pd or Pt.



- Engine is connected with computerised oxygen sensors, and signals are indicated to adjust the requirement of oxygen which is adjusted.

### **9.2.1 Advantages of Unleaded Petrol (ULP)**

1. It is fuel without Lead which is a heavy metal and very harmful.
2. The use of ULP helps in controlling knocking in engines as it supports the use catalytic converters attached to exhaust in automobiles.
3. Octane Rating can be further improved by adding small amount of MTBE which supports combustion also.
4. ULP also allows use of catalysts like Rhodium which converts exhaust gases like CO and NO to  $\text{CO}_2$  and  $\text{N}_2$ . Rhodium also converts unburnt hydrocarbons to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

In a compression ignition (diesel) engine, only air is first forced into the cylinder and compressed to about 30– 50 kg/cm<sup>2</sup> pressure and temperature is increase to 500– 600 °C.

At this stage, fuel is injected in the form of spray into the very hot air. The fuel droplets vaporise and get heated to the temperature at which spontaneous ignition takes place and pressure is further increased to about 70 kg/cm<sup>2</sup>.

The time interval between the beginning of injection and the start of combustion is known as the period of ignition lag. It should be as small as possible.

**Knocking in diesel engine is due to long ignition lag.** When a fuel has long ignition lag, a large portion of the oil gets injected and deposited into the cylinder even before the ignition is started. This results in a violent combustion and a sudden increase in pressure which causes rough and bumpy running and is responsible for diesel knock. The greater the ignition lag, the higher is the diesel knock.

Thus knocking in a diesel engine is due to the **delay in spontaneous combustion of the first part of the fuel**. The ignition lag and diesel knock depend upon the following factors:

The **engine design**.

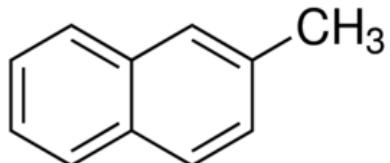
The **type of the injector**.

The **size of the oil droplets**.

The **chemical nature of fuel**.

## Cetane Number

The knocking characteristics of diesel oil are expressed in terms of **cetane number**. Cetane,  $\text{C}_{16}\text{H}_{34}$ , is a saturated hydrocarbon which has a very short ignition lag as compared to any commercial diesel oil. Hence its cetane number is taken as **100**. On the other hand,  **$\alpha$ -methyl naphthalene**,  $\text{C}_{11}\text{H}_{10}$ , has a very long ignition lag as compared to any commercial diesel oil. Hence its cetane number is taken as **zero**.



2-Methylnaphthalene



Cetane

Now, the cetane number of diesel oil is defined as the percentage by volume of cetane in a mixture of cetane and  $\alpha$ -methyl naphthalene which exactly matches in its knocking characteristics with the oil under test.

It is found that cetane number decreases as branching and aromaticity of the Hydrocarbon increases whereas it increases as length of saturated hydrocarbons increases. The cetane number can also be increased by adding 2% dopes like ethyl nitrate, acetone peroxide, ethyl nitrite etc.

In general, cetane , number of various hydrocarbons is in the order as follows:  
**n-alkane > cycloalkane > alkenes > branched alkanes > aromatic hydrocarbon**

## Distinguish between Cetane Number and Octane Number

Octane number	Cetane number
The octane number of a fuel may be defined as the percentage of iso-octane in a mixture of iso-octane and n-heptane which just matches with the knocking tendency of the fuel under test.	The cetane number of diesel oil is defined as the percentage by volume of cetane in a mixture of cetane and $\alpha$ -methyl naphthalene which exactly matches in its knocking characteristics with the oil under test.
The <b>octane Number</b> is a measure of the auto ignition resistance of gasoline (petrol) and other fuels used in spark-ignition internal combustion engines.	The <b>Cetane Number</b> is a measure of the combustion quality of diesel fuel under compression.
The higher the octane number, the better is the resistance of Gasoline to combustion prematurely, known as <b>Knocking</b> .	The Higher Cetane number means that the Diesel will ignite readily and, therefore, perform better in a diesel engine
Isooctane is given a maximum octane number, i.e. <b>100</b> . n-heptane is given a minimum octane number, i.e. <b>0</b> .	Cetane is given a maximum cetane number, i.e. <b>100</b> while $\alpha$ -methylnaphthalene is given a minimum cetane number, i.e. <b>0</b> .
Octane numbers are only used between 0 and 100. The fuels having better anti-knocking property than iso-octane are rated in other scales like octane Performance.	Cetane numbers are only used for the relatively light distillate diesel oils. For heavy (residual) fuel oil two other scales are used CCAI and CII