



# Unit IV: Fuel

# Introduction

**Definition of Fuel:** Any carbon containing material, which on combustion gives large amount of heat that can be utilised domestically or industrially.

Or

Fuel is a material used to produce energy or heat that can be used domestically or industrially.

Chemically carbon containing fuel can be represented as carbon bonded to hydrogen by covalent bond (C-H). There may be presence of nitrogen, sulphur, oxygen along with hydrogen in a fuel.

# Classification



Fuels can be classified based on occurrence, state of fuel and based on chemical reaction.

- **Classification based on occurrence:**
  - Natural (Primary fuel): Wood, Coal , Crude oil
  - Artificial or Synthetic fuel (Secondary fuel): Charcoal, Petrol, Diesel
- **Classification based on state of fuel:**
  - Solid: Coal, Wood, coke
  - Liquid: Crude oil or petroleum, Petrol, Diesel
  - Gaseous: Natural gas, CNG, LPG

# Classification

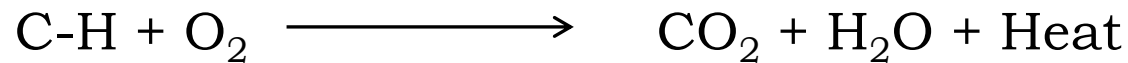


## **Classification of fuel based on chemical reaction**

1. Based on combustion reaction
  - a) In presence of excess of oxygen: Fossil fuel, wood
  - b) In presence of sufficient oxygen: IC engine fuel like diesel, petrol
  - c) In absence of oxygen: rocket fuel
2. Based on spontaneous oxidation reduction reaction: Fuel cell  
e.g. Hydrogen, ethanol, hydrocarbon
3. Based on nuclear reaction
  - a) Nuclear Fusion: deuterium, tritium, hydrogen
  - b) Nuclear Fission:  $U^{235}$ ,  $P^{239}$

# Combustion

- Fuel can be represented as C-H i.e. hydrocarbons
- Combustion is a chemical process in which the carbon and hydrogen from fuel reacts with oxygen to produce CO<sub>2</sub> and H<sub>2</sub>O along with liberation of heat.



- As in case of combustion there is a production of water molecule along with heat, some part of heat produced is taken away by water molecule.
- This amount of heat taken away by water molecule is called as latent heat (587 cal/g).

# Calorific Value of Fuel



**Calorific value:** Amount of heat liberated by complete combustion of unit mass or unit volume of a fuel at STP.

Calorific values are of two types:

1. **Gross calorific value (GCV)/Higher calorific value (HCV):** It is the total amount of heat liberated by complete combustion of unit mass or unit volume of a fuel and products of combustion are cooled to the room temperature( $15^{\circ}\text{C}$ )
2. **Net Calorific value (NCV)/Lower calorific value(LCV):** It is the net amount of heat liberated by complete combustion of unit mass or unit volume of a fuel and the products of combustion are allowed to escape.

# Calorific Value of Fuel



- Products of combustion is water produced during the combustion.

As water takes away heat of combustion in the form of latent heat, if this heat is considered for calculation of calorific value, then it is called as GCV or HCV. If latent heat is not considered for the calculation of calorific value it is called as NCV or LCV.

- Hence, relation between GCV and NCV can be given as follows:

$$\text{GCV} = \text{NCV} + \text{latent heat of water}$$

- If H is the % of hydrogen in given fuel sample, then amount of water produced by combustion will be  $(9 \cdot H / 100)$ . Therefore, the latent heat

taken away by water will be 
$$= \frac{9 \cdot H \cdot \text{latent heat of water}}{100}$$

Hence, 
$$\text{GCV} = \text{NCV} + \frac{9 \cdot H \cdot \text{latent heat of water}}{100}$$

# Calorific Value of Fuel



- Units of latent heat of water, NCV and GCV should be same
- Units of Calorific Values:

CGS: cal/g (or cal/litre for gaseous fuel)

MKS: kcal/kg (kcal/m<sup>3</sup> for gaseous fuel)

SI: J/kg (J/ m<sup>3</sup> for gaseous fuel)

$$1 \text{ cal/g} = 1 \text{ kcal/kg} = 4.18 \text{ kJ/kg}$$

**Latent heat of water is 587 cal/g or 587 kcal/kg or 2450 kJ/kg**

$$GCV = NCV + \frac{9 * H * 587}{100}$$



# Bomb Calorimeter

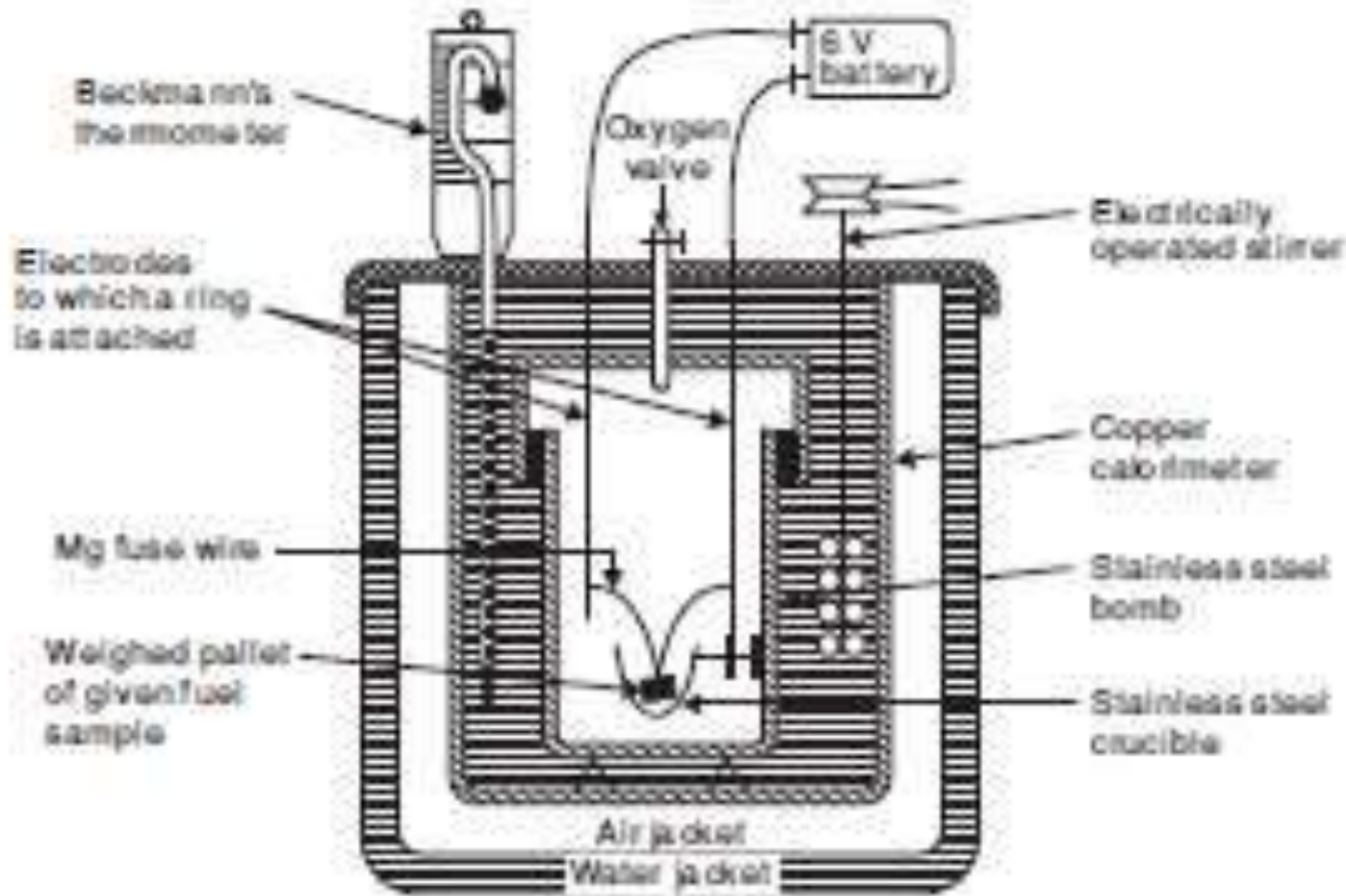


Fig 18.1 Bomb calorimeter.

# Bomb Calorimeter

Bomb Calorimeter is used to calculate Calorific value of Solid and Non-Volatile liquid fuels.

Principle: Known mass of solid or liquid fuel is burnt completely in presence of excess of oxygen and heat evolved is allowed to be absorbed by the water present in calorimeter. By knowing the mass of fuel burnt, mass of water in calorimeter and rise in temperature of water, calorific value of a solid or liquid fuel can be calculated.

# Bomb Calorimeter

## Construction:

Following are the components of bomb calorimeter

- 1) Stainless steel Bomb
- 2) Calorimeter
- 3) Air and water jacket
- 4) Other accessories
  - a) Oxygen cylinder
  - b) Pellet Press
  - c) D.C. battery

# Bomb Calorimeter

## Construction:

### 1) Stainless steel Bomb

- It is a stainless steel cylinder having capacity to withstand high pressure.
- It is provided with a stainless steel lid equipped with two stainless steel electrode.
- Out of the two electrode one electrode is attached to a ring, on which a crucible containing fuel can be mounted.
- A resistance wire is connected to these two electrode forming a loop and further inserted in fuel kept in crucible.

# Bomb Calorimeter



## Construction:

### 1) Stainless steel Bomb

- The stainless steel electrodes are externally connected to a 6 volt D. C. battery.
- The lid is also provided with a  $O_2$  inlet pipe, so that excess of oxygen can be made available for complete combustion of fuel.
- There is a valve present with lid, so as to release pressure generated after combustion of fuel.
- The lid can be fitted air tight to bomb with help of screws provided.

# Bomb Calorimeter



## Construction:

### 2) Copper Calorimeter

- The stainless steel bomb is kept inside a copper vessel called as copper calorimeter.
- The copper calorimeter contains a known mass of water, which will absorb the heat produced by combustion of fuel.
- It is provided with a electrically operated stirrer to uniformly distribute the heat of combustion.
- There is a thermometer called as Beckman's thermometer placed in the water to measure rise in temperature of water.

# Bomb Calorimeter



## Construction:

### 3) Air and water Jacket

- Copper calorimeter is placed on insulating stand in air jacket, surrounded by water jacket.
- The air and water jacket avoid the loss of heat from the calorimeter.

### 3) Other accessories

- a) O<sub>2</sub> cylinder: Provide excess oxygen for complete combustion of fuel.
- b) 6 V battery: Helps for ignition of fuel.
- c) Pellet press: Solid powdered fuel is converted to pellet by pellet press. Liquid fuel is taken in a polymer capsule.

# Bomb Calorimeter



Working: A solid fuel is powdered and air dried, further converted in pellet by pellet press. Liquid fuel is sealed in a capsule. Check the weight of crucible and keep the fuel inside crucible. Again check the weight of crucible containing fuel and calculate the weight of fuel say X g.

Keep the crucible on the ring provided with electrode, a fine resistance magnesium wire is tied to electrodes in the form of a loop and further touched to the fuel in crucible. 10 ml of distilled water is added in bomb to absorb acidic gases produced during combustion. The bomb lid is tightly closed with the help of screw and is filled with oxygen at 25 atmospheric pressure.



# Bomb Calorimeter



## Working

Copper calorimeter is filled with known weight of water and bomb is immersed in the calorimeter containing water. Stirrer and Beckmann's thermometer is inserted in calorimeter. Started the stirring and initial temperature of the water in the calorimeter is noted ( $t_1^\circ\text{C}$ ). The electrodes are connected to a battery (6 v).

Fuel is combusted by using battery and resistance wire. Heat evolved is absorbed by the water present in calorimeter and leading to rise in temperature of water. Further maximum temperature attained by water is noted as ( $t_2^\circ\text{C}$ ). Now allow the water to reach room temperature and measure time required to reach room temperature note this time as  $t$  minutes.

# Bomb Calorimeter



## Calculations:

From above experiment we have

Weight of the fuel sample taken in the crucible =  $X$  g

Weight of water taken in the calorimeter =  $W$  g

Weight of calorimeter and stirrer in terms of water Equivalent =  $w$  g

Initial temperature of water in the calorimeter =  $t_1^\circ\text{C}$

Final temperature of water in the calorimeter =  $t_2^\circ\text{C}$

Specific heat of water =  $S$  cal /g  $^\circ\text{C}$  = 1 cal/g  $^\circ\text{C}$

Let Gross calorific value of the fuel is  $Q$  cal/g

# Bomb Calorimeter



## Calculations:

Heat produced by combustion of x g of fuel = Heat absorbed by the water and calorimeter

$$xQ = (W+w) (t_2-t_1).S$$

$$\text{Hence, } Q = (W+w) (t_2-t_1).S/x \text{ cal/g}$$

## Calculation of Lower Calorific Value (LCV):

If H is the percentage of hydrogen in the fuel

Then weight of water produced 1 g of the fuel =  $9 H \text{ g} = 0.09 \text{ g } 100$

Therefore, heat liberated during the Condensation of steam =  $0.09$

$H \times 587 \text{ cal/g}$

# Bomb Calorimeter



## Calculations:

Lower calorific value of the fuel = HCV – Latent heat of water liberated by the fuel

$$\text{LCV} = \text{HCV} - (0.09 \text{ H} \times 587) \text{ cal/g.}$$

## Corrections:

Acid Correction (A): If the fuel contains Sulfur and nitrogen then formation of  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  will take place and as formation of acid is an exothermic reaction, it adds to GCV hence heat of formation of acid should be subtracted from heat produced by combustion.

# Bomb Calorimeter



## Corrections:

Fuse wire correction (F): Heat produced by sparking of fuse wire adds to the calorific value hence it should be subtracted.

Cotton correction (C): Combustion of cotton used for tiding the fuse wire leads to increased calorific value hence cotton correction should be subtracted from GCV

Cooling correction ( $t_c$ ): If “t” is the time required to cool the water from  $t_2$  °C to room temperature and “dt” is the rate of cooling then  $t \cdot dt$  is the cooling correction and that has to be added to rise in temperature.

Hence the final formula for GCV with correction is

# Bomb Calorimeter



Corrected formula to calculate GCV by bomb calorimeter

$$Q = \frac{(W + w) \times (t_2 - t_1 + t_c) - (A + F + C)}{x}$$

# Bomb Calorimeter



Numerical:

In a bomb calorimeter experiment following data was obtained  
calculate GCV and NCV, if fuel consist of 5% H.

Weight of Fuel X= 1.1 g

Weight of water taken in calorimeter W = 1200 g

Water equivalent of calorimeter = w = 990 g

Rise in temperature of water =  $(t_2 - t_1) ^\circ\text{C} = 6.5 ^\circ\text{C}$

Acid correction = A= 64 cal

Fuse wire correction = 6 cal

Cooling correction = 0.04  $^\circ\text{C}$

# Bomb Calorimeter



Numerical solution:

$$Q = \frac{(W + w) \times (t_2 - t_1 + t_c) - (A + F + C)}{x}$$

$$Q = \frac{(1200 + 990)(6.5 + 0.04) - (64 + 6)}{1.1}$$

$$Q = 12956.90 \text{ cal/g}$$

$$NCV = Q - \left(\frac{9}{100} \times h \times 587\right)$$

$$NCV = 12692.75 \text{ cal/g}$$





# Boy's Gas Calorimeter

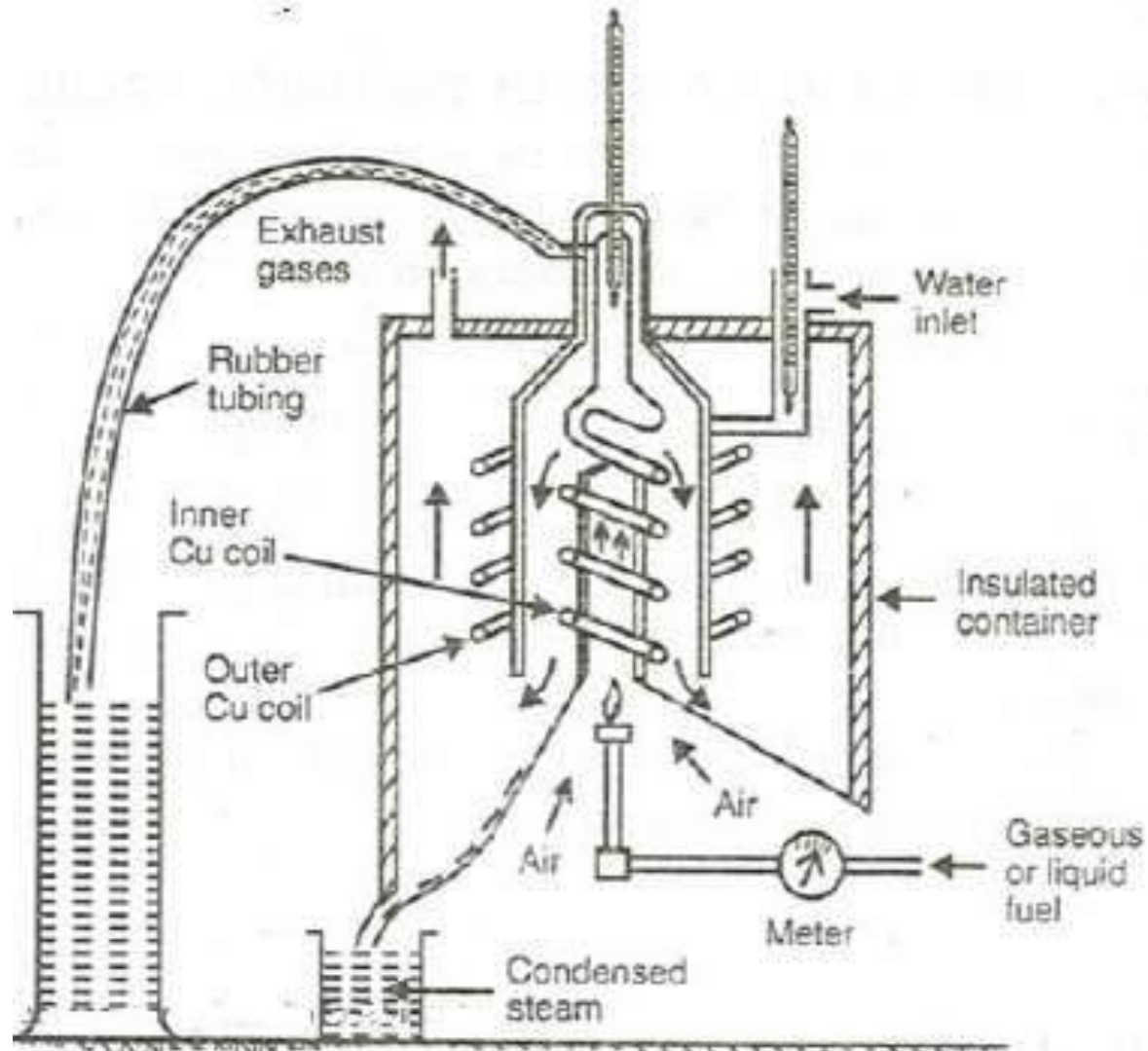
- This calorimeter is used to calculate calorific value of a gaseous or highly volatile liquid fuel
- **Principle:** A gaseous or volatile liquid fuel is combusted at known and constant rate, under such condition that the heat evolved is completely absorbed by the water flowing through calorimeter. By knowing the volume of fuel burnt, mass of water and rise in temp. of water calorific value of a gaseous or volatile liquid fuel can be calculated.

# Boy's Gas Calorimeter

- **Components:**
  - Gas burner assembly
  - Combustion chamber(calorimeter)
  - Thermometer
  - Insulating cover

# Boy's Gas Calorimeter

- Diagram:



# Boy's Gas Calorimeter

- **Components:**
  - Gas burner assembly: the gas burner assembly is situated at the middle of calorimeter. It is equipped with a stop cork and pressure regulator so as to maintain the flow rate of gaseous fuel. The gas is burnt at a rate of 3-4 lit per min.
  - Combustion chamber(calorimeter): the gas burner is surrounded by a chamber called as calorimeter or combustion chamber. It is provided with copper tubing coiled inside and out side of the chamber.

# Boy's Gas Calorimeter

- **Components:**

- Water enters from the top of outer coil and goes downward and enters in inner coil. Then it flows from down to up in the inner coil. The heat of combustion is absorbed by the water flowing at constant rate. The water from outlet is collected in a container. It is also provided with another outlet at the base of calorimeter, so as to collect condensed water formed during the combustion process.

# Boy's Gas Calorimeter

- **Components:**

- Thermometer: The calorimeter is provided with two thermometers one at the inlet of water and another is at outlet, so as to measure change in temperature of water.
- Insulating cover: The calorimeter is surrounded by the insulating cover to avoid contact between calorimeter and atmosphere. The cover is provided with an exhaust for exhaust gases.

# Boy's Gas Calorimeter

- **Working**

- Allow the gaseous fuel flow at constant rate and start the combustion of fuel. The rate of combustion should be 3-4 lit/ min.
- Allow the water flow through the copper coil at constant rate and adjust the flow rate such that temperature of water flowing through calorimeter remains constant i.e. thermometer  $T_2$  shows constant temperature.
- Allow the assembly to get stabilized.

# Boy's Gas Calorimeter

- **Working**

- As thermometer reading shows stable value note down temperature in thermometer  $T_1$  and  $T_2$
- Mass of water passed through coil in time  $t$  and volume of fuel burnt in time  $t$ .
- Mass of water condensed in time  $t$ .



# Boy's Gas Calorimeter



## Observations:

From experiment,

- Volume of gas burnt in time  $t$  at STP =  $V$  lit ( or  $V$   $m^3$ )
- Mass of water passed through copper coil in time  $t$  =  $W$  kg
- Mass of water produced during combustion of fuel in time  $t$  =  $m$  kg
- Temperature of incoming water =  $t_1$  °C
- Temperature of out going water =  $t_2$  °C

# Boy's Gas Calorimeter



## Calculations:

Let “L” be the GCV of fuel

Amount of heat produced by combustion of fuel =  
amount of heat absorbed by cooling water

Hence,  $L \cdot V = W \cdot (t_2 - t_1)$

$$L = \frac{W(t_2 - t_1)}{V} \text{ Kcal/m}^3$$

# Boy's Gas Calorimeter



## Calculations:

- If  $m$  is the mass of water produced by combustion of  $V$  lit of fuel, then mass of water produced per unit fuel combusted will be  $m/V$  Kg/ $m^3$
- Latent heat of water is  $587$  kcal/ $m^3$
- $\therefore$  The latent heat of  $m/V$  water =  $m/V \times 587$  kcal/ $m^3$ 
  - As  $LCV$  of Fuel =  $GCV$  - Latent heat of water

$$LCV = \left[ \frac{W(t_2 - t_1)}{V} - \frac{m}{V} \times 587 \right] Kcal/m^3$$

# Boy's Gas Calorimeter

## Numerical:

Following observations were noted in the Boy's gas calorimeter experiment

- Volume of gas burnt at STP =  $0.1 \text{ m}^3$
- Mass of cooling water used = 25 kg
- Rise in temperature of water =  $9.1^\circ\text{C}$
- Mass of steam condensed = 0.04 kg

Find the GCV and NCV of the fuel

# Boy's Gas Calorimeter

Numerical:

Solution: As  $GCV = L = \frac{W(t_2 - t_1)}{V} \text{ Kcal/m}^3$

$$L = \frac{25(9.1)}{0.1}$$

$$L = 2275 \text{ Kcal/m}^3$$

$$LCV = \left[ \frac{W(t_2 - t_1)}{V} - \frac{m}{V} \times 587 \right] \text{ Kcal/m}^3$$

$$LCV = 2275 - \frac{0.04}{0.1} \times 587$$

$$LCV = 2040.2 \text{ Kcal/m}^3$$

# Characteristics of Good Fuels



- 1. High calorific value:** Amount of heat liberated on complete combustion of 1gm of substance.
- 2. Moderate Ignition point:** Minimum temperature at which fuel catches fire. If it is low, then there are chances of fire hazards during storage and transportation and if it high there will be difficulty in the ignition.
- 3. Moderate velocity of combustion:** If it is low then the required temperature will not be attained quickly and if it is high then liberated heat is not utilized properly
- 4. Combustion rate should be easily controllable**  
combustion of good fuel should be easy to start and stop whenever required
- 5. Low ash content:** More ash will cause pollution
- 6. Harmless Products of combustion**
- 7. Low cost**
- 8. Occupies low volume and has high density**
- 9. Easy storage and transportation**
- 10. Low moisture content:** Will cause pollution

Sr. No.	Criteria	Solid Fuel	Liquid Fuel	Gaseous Fuel
1	Calorific Value (C.V.)	Low	<b>Higher</b>	<b>Highest</b>
2	Ignition Point (I.P.)	Very high	<b>Moderate</b>	Very low
3	Cost	<b>Very cheap</b>	costly	Costly
4	Noncombustible matter (ash)	High	<b>Negligible</b>	<b>Nil</b>
5	Rate of Combustion	Not controllable	<b>Controllable</b>	<b>Controllable</b>
6	Transportation	Laborious but <b>hazard free</b>	<b>Easy</b> (piping)	<b>Easy</b> but risk of hazard
7	Air requirement for complete combustion	Large excess	<b>Small excess</b>	<b>Just sufficient</b>
8	Use in I.C. engine	Cannot be used	<b>Convenient</b>	<b>Can be used</b>
9	Volatile matter	Large	<b>Negligible</b>	<b>Nil</b>
10	Space for storage	Small	<b>Smaller</b>	Very large
11	Moisture	High	Nil	<b>Nil</b>
12	Smoke (pollution)	Considerable	<b>Lower</b>	<b>Nil</b>
13	Thermal efficiency	Low	<b>High</b>	<b>High</b>

# Solid Fuels: Coal

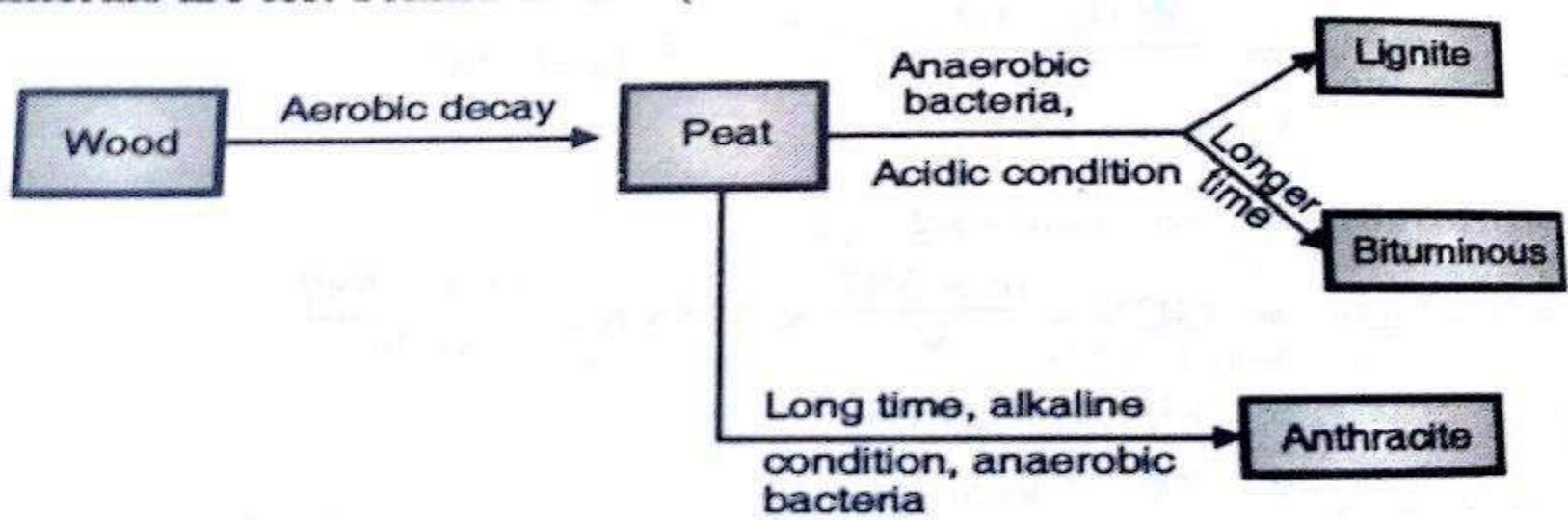
**Coal:** highly **carbonaceous** material, regarded as a fossil fuel produced from the vegetable debris under conditions of high temperature and pressure over million of years.

The process of conversion of **wood into coal** is known as **coalification**.

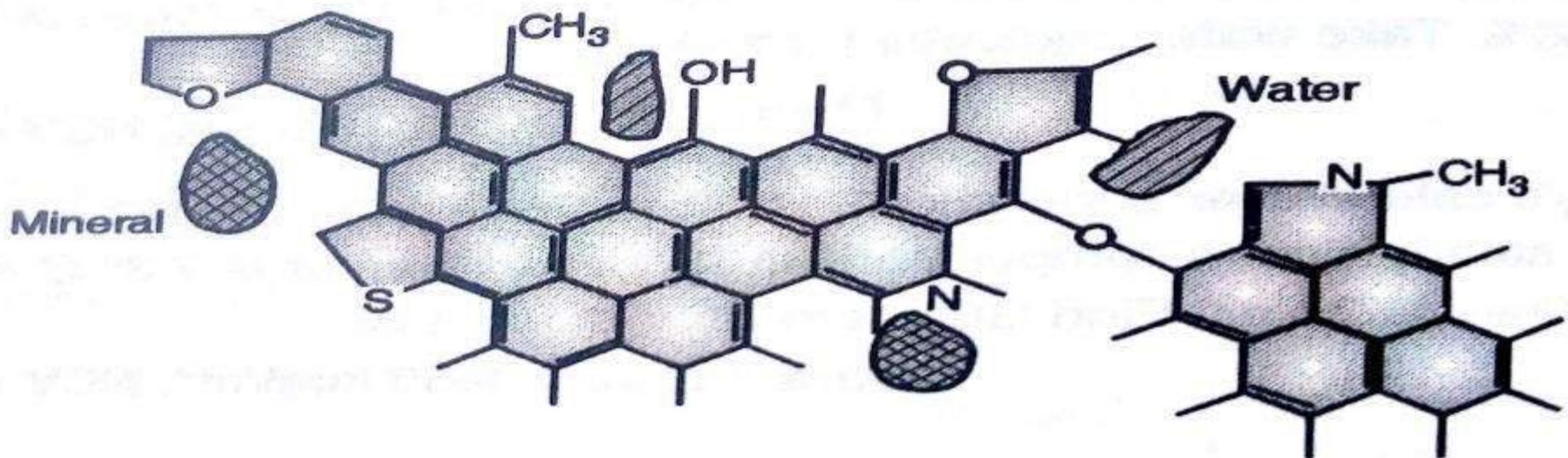
**Coalification** is a very **slow process** and takes millions of years for formation.

- Main constitute of coal is C atom – mostly **sp<sup>2</sup> hybridized**
- Atoms **like H,O,N,S** are **covalently bonded** to C atom
- Coal molecules are huge with **indefinite number of carbon atom**.
- Coal contains **water and minerals particles entrapped**



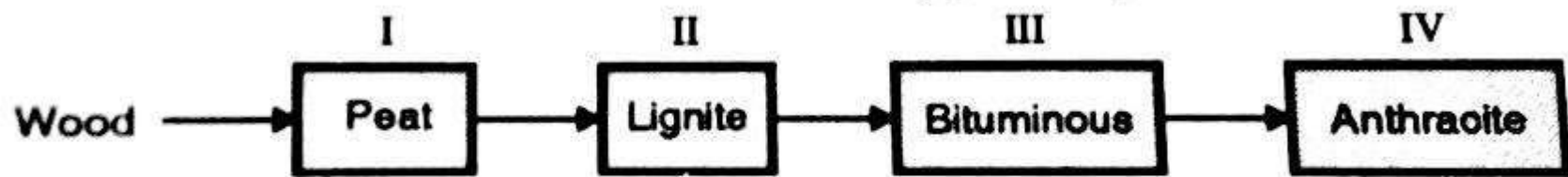


**Fig. 4.6.1**



**Fig. 4.6.2 : Schematic coal structure**





**Fig. 4.7.1 : Schematic coal structure**

**Table 4.7.1**

Type of coal	Moisture	C	H	N	O	Ash	Volatile matter	Calorific value
Peat	25	57	6	2	35	10	50	~ 5400 cal/gm
Lignite	20	65	5	2	25	15	45	~ 6700 cal/gm
Sub-bituminous	11	75	5	1.8	16	20	35	~ 7000 cal/gm
Bituminous	4	80	5	2.0	10	15	20 – 30	~ 8000 cal/gm
Semibituminous	2.5	85	4	1.0	5	10	15	~ 8400 cal/gm
Anthracite	1.5	95	3	0.7	3	3	2	~ 8700 cal/gm

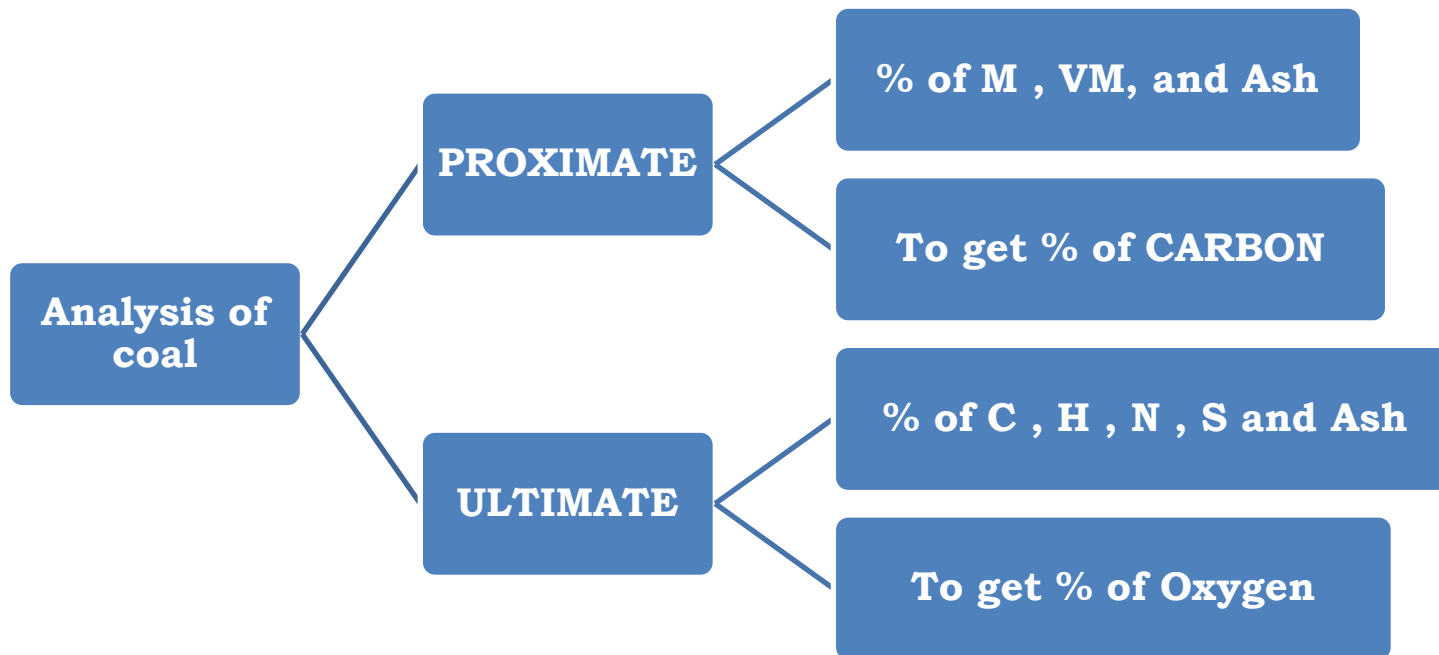
# Analysis of Coal

To fix price and use of coal

To calculate CV of coal

To calculate air and oxygen requirement for complete combustion of coal

**Analysis of coal:** 1) Proximate analysis  
2) Ultimate analysis





# Analysis of Coal



## Analysis of Coal

The results of analysis are generally reported in the following ways:

- As received basis
- Air dried basis
- Moisture free basis (oven dried)
- Moisture and ash free basis

**Proximate Analysis:** Determination of % Moisture, % Volatile Matter, % Ash and % Fixed Carbon.

## Proximate Analysis:

### 1) Moisture % :

Porcelain crucible,

**110°C in oven**

**for 1 hr**

Initial weight of coal = m g,

Final weight is  $m_1$  gm

Loss in weight =  $m - m_1$

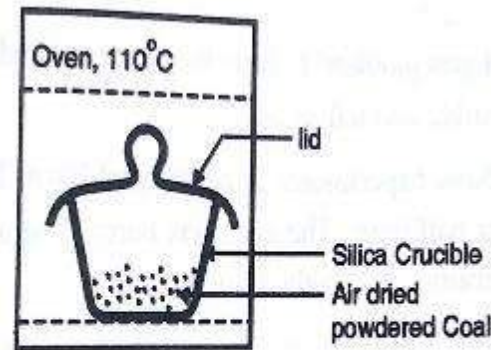


Fig 4.8.1(a) : Silica crucible

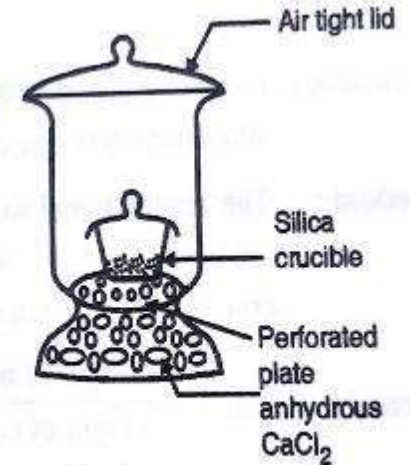


Fig. 4.8.1(b): Desiccator

$$\text{Moisture \%} = \frac{\text{loss in weight}}{\text{weight of coal sample}} \times 100 = \frac{m - m_1}{m} \times 100$$

## 2) % Volatile matter (V.M.)

- At 925° C coal molecules under go thermal degradation to produce volatile matter.
- V.M. is the thermally decomposed coal during burning of coal, that escapes without combustion, in the form of smoke.
- Muffle furnace, 925° C for 7 min.

$$\text{V.M. \%} = \frac{\text{weight of volatile matter}}{\text{weight of air dried coal}} \times 100 = \frac{m_1 - m_2}{m} \times 100$$

- **1.0 gm of a coal sample is heated to remove all moisutre. Then the residual coal looses 0.21 gm weight when heated in muffles furnace at 950 °C calculate % volatile matter.**

# V.M. %

- For fresh coal sample

$$\text{V.M. \%} = \frac{\text{loss in weight due to moisture, V.M.}}{\text{weight of coal sample}} \times 100 - \text{moisture \%}$$

$$\text{V.M. \%} = \frac{(W - W_1) \times 100}{W} - \text{moisture \%}$$

- A coal contains 10 % moisture and 1 gm of coal loses 0.3 gm weight on heating at 925 °C in the absence of air. Calculate % volatile matter.



- **3) Ash %**
- Inorganic matter in coal gets oxidized to form metal oxide and silica which is non-combustible and left as ash
- Open silica crucible
- **At 750° C for half hour in muffle furnace**
- coal get burnt and ash left in crucible

$$\text{Ash \%} = \frac{\text{weight of ash}}{\text{weight of coal}} \times 100 = \frac{m_3}{m} \times 100$$

- 1 gm of coal sample is ignited at 750 °C in a muffle furnace the residue weighed is 0.15 gm. Calculate the % ash

- 4) Fixed carbon %

$$\text{F.C. \%} = 100 - (\text{moisture\%} + \text{V.M.\%} + \text{Ash\%})$$

Exactly 2.2 gm of the sample on heating in a silica crucible for about an hour at 110 °C gave a residue of 1.98 gm. The crucible was then covered with a vented lid and strongly heated for exactly 7 minutes at  $950 \pm 20$  °C. 1.2 gm of residue was left behind. The crucible was then heated without the lid until constant weight was reached. The final residue weighed 0.240 gm. Calculate the percentage results of the above data.

[Ans. : % moisture = 10 %

% VM = 35.45 %

% ash = 10.91 %

% Fixed carbon = 43.64 %]

A sample of coal (2.7 gm) was weighed in a silica crucible. After heating for one hour at 110 °C, the residue weighed 2.625 gm. The crucible is next covered with vented lid and strongly heated at 950 °C. After cooling, the residue weighed 2.5 gm. The crucible is then heated without lid to get a constant weight of 0.240 gm. Calculate percentage results of the above analysis.

[Ans. : % moisture = 2.78 %

% VM = 4.63 %

% ash = 8.89 %

% Fixed carbon = 83.7 %]

# Significance of Proximate Analysis

## **Moisture**

- decreases calorific value, increases ignition temperature
- Lower the % moisture, better the quality of coal .

## **Volatile matter**

- Decreases calorific value, increases pollution, elongates flame
- Lesser the % V.M., better the quality of coal.
- 25- 30 % volatile matter content is desirable or suitable for making hard and strong coke .

## **Ash**

- Reduces calorific value, disposal is a problem, fuses to form clinker that blocks air supply
- Lesser the % ash, better the quality of coal .

# Ultimate Analysis of Coal

To determine % of elements present in coal

% C, % H – by [combustion method](#)

% N – by [Kjeldahl's Method](#)

% S – by [Eschka method](#)

% O and

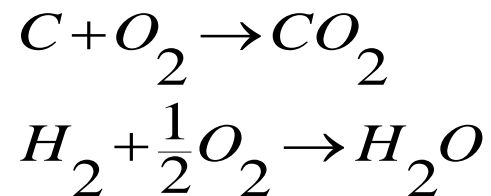
% ash (as in proximate analysis)

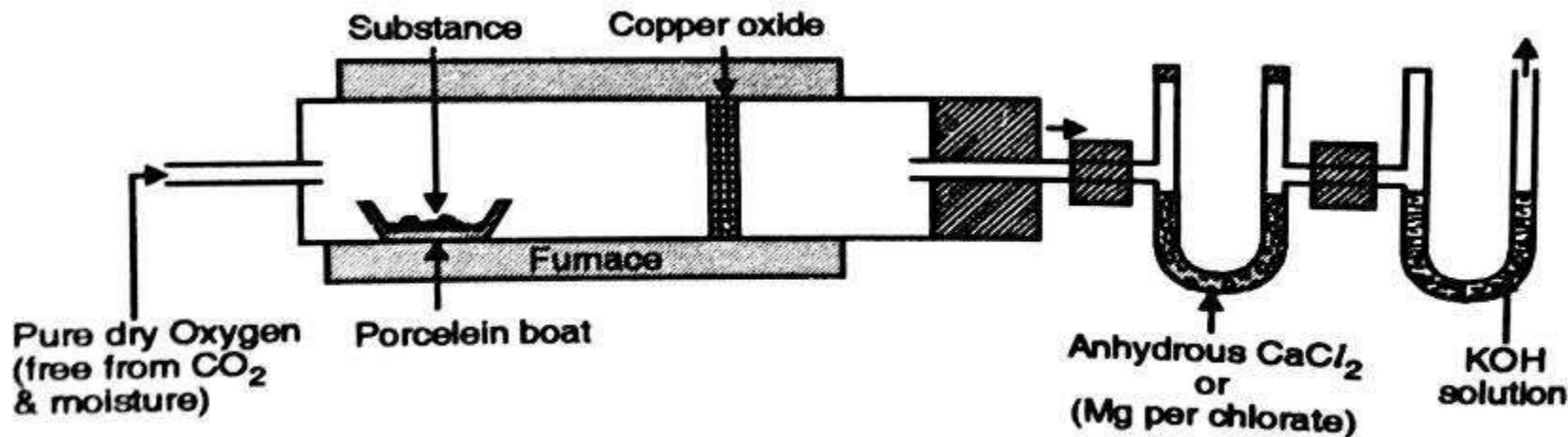
# Ultimate Analysis of Coal

## % C, % H – by Combustion Method

- The percentage of fixed carbon helps in designing the furnace and shape of the fire-box because it is the fixed carbon that burns in the solid state.

**Carbon and Hydrogen:** A known amount of coal is taken in a combustion tube and is burnt in excess of pure oxygen.

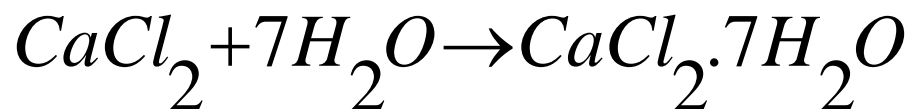
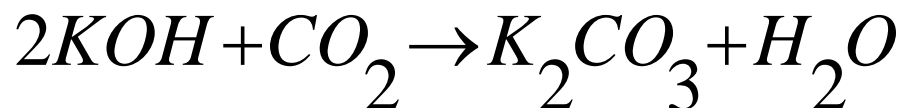




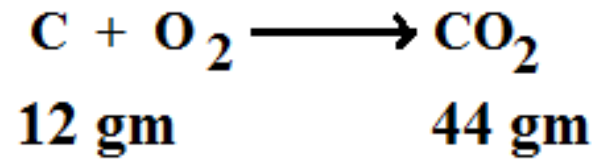
**Fig. 4.8.2 : Combustion apparatus**

## Estimation of carbon and hydrogen

- The moisture and  $\text{CO}_2$  liberated by heating the coal sample are absorbed by pre-weighed anhydrous  $\text{CaCl}_2$  and  $\text{KOH}$  placed in U-tubes. Increase in weight in each case is recorded.



**%C:**



44 gm of CO<sub>2</sub> contains = 12 gm of C

$$y \text{ gm of CO}_2 \text{ contain} = \frac{12}{44} \times y \text{ gm of C}$$

$$W \text{ gm of coal contain} = \frac{12}{44} \times y \text{ gm of C}$$

$$100 \text{ gm of coal contain} = \frac{12}{44} \times \frac{y}{w} \times 100$$

$$\%C = \frac{12}{44} \times \frac{\text{weight of CO}_2}{\text{weight of coal}} \times 100$$

**%H:**

18 gm of H<sub>2</sub>O = 2 gm of H

$$y \text{ gm of H}_2\text{O} = \frac{2}{18} \times y \text{ gm of H}$$

$$W \text{ gm of coal contain} = \frac{2}{18} \times y \text{ gm of H}$$

$$100 \text{ gm of coal contain} = \frac{y \times 2}{18} \times \frac{100}{W} \text{ gm of H}$$

$$\% \text{ H} = \frac{2}{18} \times \frac{\text{Weight of H}_2\text{O}}{\text{weight of coal}} \times 100$$



$$\% C = \frac{\text{Increase in weight of KOH} \times 12 \times 100}{\text{weight of coal} \times 44}$$

$$\% C = \frac{\text{Weight of CO}_2 \text{ formed} \times 12 \times 100}{\text{weight of coal} \times 44}$$

Similarly,

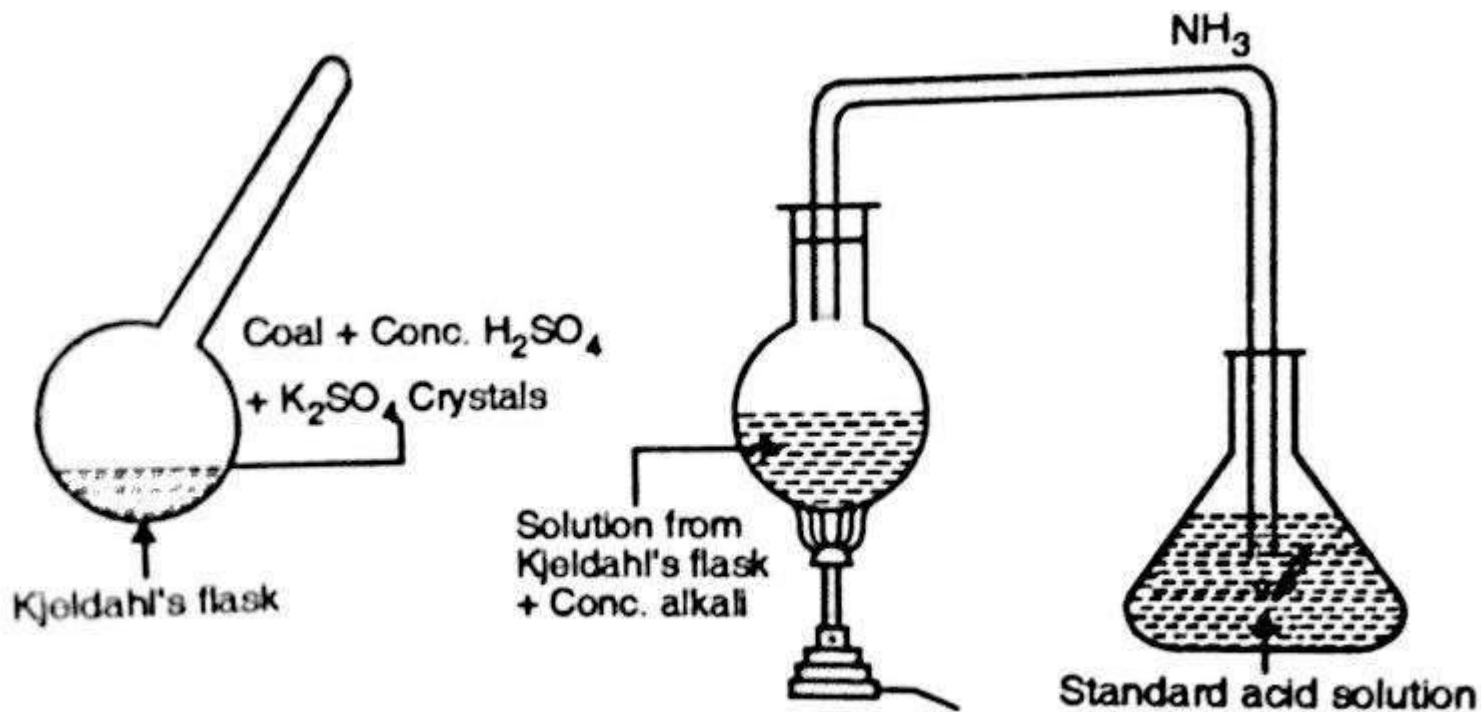
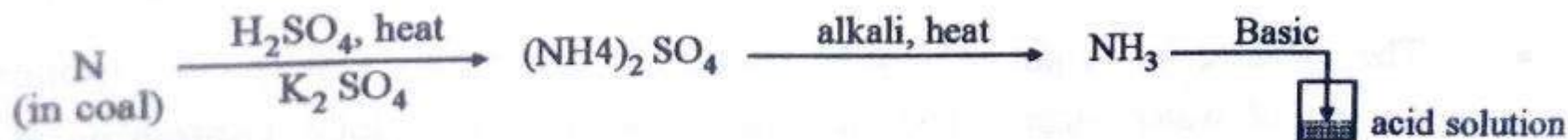
$$\% H = \frac{\text{Increase in wt of CaCl}_2 \times 2 \times 100}{\text{weight of coal} \times 18}$$

$$\% H = \frac{\text{weight of H}_2\text{O formed} \times 2 \times 100}{\text{weight of coal} \times 18}$$

0.25 gm of coal sample on burning in combustion chamber in the current of pure O<sub>2</sub> was found to increase of CaCl<sub>2</sub> U tube by 0.08 gm. hence % H present in the coal is.....

2.02 gm of the coal is burnt in combustion tube. On passing the O<sub>2</sub> increases the weight of KOH tube by 5.88 gm. Hence % C present in the coal is .....

# **% Nitrogen by Kjeldahl's method**



**Fig. 4.8.3 : Estimation of nitrogen in coal**

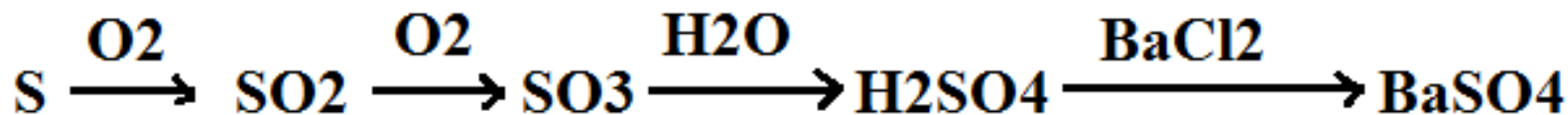
- The unused acid is then determined by titrating with NaOH. From the volume of acid used by  $\text{NH}_3$  liberated, the percentage of nitrogen can be calculated. The volume of NaOH required is same as the volume of unreacted acid in the conical flask. Thus volume of acid can be determine.
- Mass of coal = m gm
- $V_2$  ml = Blank titration reading
- $V_1$  ml = Back titration reading
- Volume of acid consumed by  $\text{NH}_3 = (V_2 - V_1)$  ml

$$\text{N \%} = \frac{\text{volume of acid consumed} \times \text{normality} \times 1.4}{\text{Weight of coal sample}}$$

- **1 gm of a coal sample in Kjeldahl's experiment liberated ammonia which was absorbed in 50 ml  $\text{H}_2\text{SO}_4$ . the resultant solution required 14 ml of 0.1 N NaOH for the complete neutralization of  $\text{H}_2\text{SO}_4$  in back titration. The reading of blank titration was 25 ml. hence the % N in coal was.....**

## % Sulphur by Eschka method

- Sulphur present in coal first converted into  $\text{SO}_3$ , which is soluble in water forming  $\text{H}_2\text{SO}_4$ .



- $\text{H}_2\text{SO}_4 + \text{BaCl}_2 \rightarrow \text{BaSO}_4 \downarrow$
- A white precipitate of  $\text{BaSO}_4$  is obtained
- Filter the precipitate of  $\text{BaSO}_4$ , dry it and weigh the precipitate of  $\text{BaSO}_4$ , from the weight of  $\text{BaSO}_4$  ppt, S% can be calculated.

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

- 0.55 gm of coal is combusted in bomb calorimeter on combustion the solution from the bomb on treatment with  $\text{BaCl}_2$  forms 0.025 gm  $\text{BaSO}_4$  therefore % S in the coal is....

# % Oxygen and % Ash

- **% Ash is determined by proximate analysis**
- **Ash:** Coal contains inorganic mineral substances which are converted into ash by chemical reactions during the combustion of coal.
- Ash usually consists of silica, alumina, iron oxide and small quantities of lime, magnesia etc.
- Ash content is determined by heating the residue left after the removal of volatile matter at  $700 \pm 50^{\circ}\text{C}$  for  $\frac{1}{2}$  an hour without covering
- **$\% \text{ O}_2 = 100 - (\% \text{ C} + \% \text{ H} + \% \text{ S} + \% \text{ N} + \% \text{ Ash})$**

# Unit 4: Fuels

## Content:

- **Liquid Fuels: Petroleum**
- **Gaseous Fuel: CNG**
- **Alternative Fuel:**
  - 1) Power Alcohol**
  - 2) Biodiesel**
- **Hydrogen as a Future Fuel**



# Liquid Fuels: Petroleum

## **Petroleum/Crude Oil:**

Dark greenish-brownish viscous oil found deep in earth crust, mainly composed of different hydrocarbons like paraffins, cycloparaffins or naphthalenes, aromatic hydrocarbon with small amount of compounds containing oxygen, nitrogen and sulphur.

**Average composition of Petroleum** in terms of it's constituent C= 80-87%; H= 11-15%; S=0.1-3%; O: 0.1-0.9% and N= 0.4-0.9%

# Liquid Fuels: Petroleum



**Types of Petroleum: Based on type of HC present**

- 1) Paraffinic Base Type:** Mainly contain saturated hydrocarbon (HC)
- 2) Ashphaltic:** Mainly contain cyclo-paraffins (naphthenes)
- 3) Mixed Base Type:** Contains both paraffinic and ashphaltic hydrocarbon



# Refining of Petroleum



- Crude Oil is a complex mixture of HCs in different forms, hence cannot be used directly as a fuel or feed for manufacturing chemicals
- Therefore, it has to be refined

**Refining:** Process in which the petroleum is separated into its components by fractional distillation along with the separation of impurities

Process is carried out in 3 steps in Refinery.

## **Step 1: Separation of water (by Cottrell's Process)**

Crude oil (stable emulsion) is passed through highly charged electrodes. Colloidal water droplets coalesce to form a big drop which is then separated from oil

# Refining of Petroleum



## **Step 2: Removal of Sulphur compounds (Harmful)**

Crude oil is treated with hot copper oxide, which results in formation of copper sulphides precipitate which is then removed by filtration. Thus, harmful sulphur compounds are removed.

## **Step 3: Fractional Distillation**

**Principle:** The vapours of higher **boiling point** fractions (components) first gets condensed into liquid, during the stepwise cooling. Various useful fractions are obtained by fractionation like petrol, diesel, kerosene etc.

# Refining of Petroleum



## Construction of Fractionating Column:

- Refining is carried out in a long cylindrical tower, called as fractionating column
- Fractionating column is a tall Stainless steel tower of about 30 m in height and 3 m in diameter
- There are 50-60 horizontal stainless steel trays at about half meter distance in tower. Each tray is provided with 4-5 bubble cups with loosely held caps so that rising vapours through the cups bubble in liquid deposited on tray
- Fractions are taken out from some bubble trays only (draw off plates) and not from all
- Temperature of the tower is  $400^{\circ}\text{C}$  near bottom and it decreases gradually to  $40^{\circ}\text{C}$  at top. Tower is cooled by open air.

# Refining of Petroleum



## Working of Fractionating Column:

- Crude oil is heated at about  $400^{\circ}\text{C}$  in a furnace or pipe still to convert it into vapours which enters from the bottom of tower
- Vapours travel upwards through the bubble cups and gradually gets cooled. Vapours of less volatile components with higher boiling point gets condensed and liquid gets deposited on the tray
- Uncondensed vapours rise up and gets condensed turn by turn on upper bubble trays. There is vigorous bubbling action on each tray. In case, large part of the vapours get condensed on a tray, then the extra liquid flows down to higher temperature lower trays and gets evaporated

# Refining of Petroleum

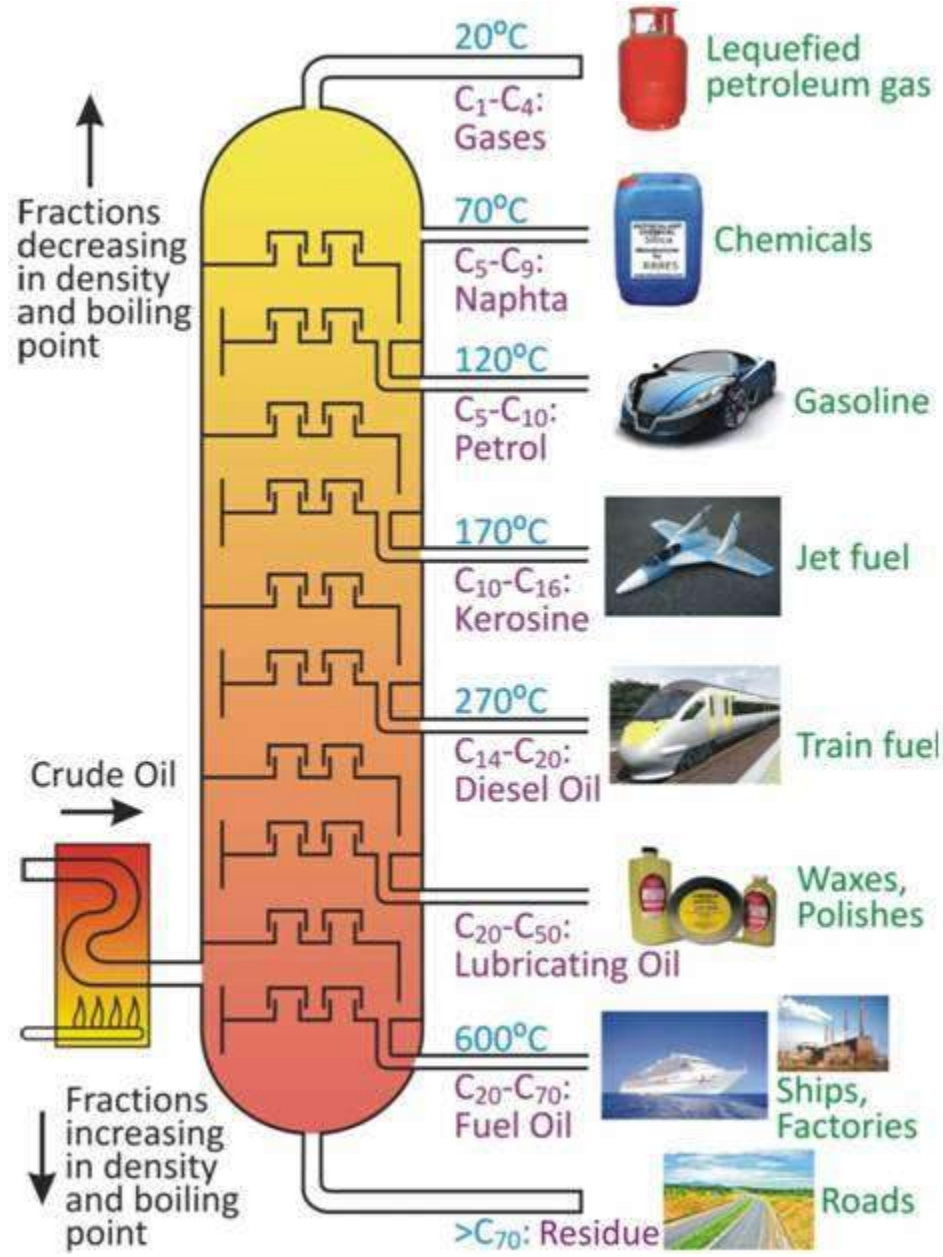


## Working of Fractionating Column:

- From some trays fractions like petrol, diesel, naphtha, heavy oil etc. are taken out while small part of vapours comes out as uncondensed gases from the top where temperature is about  $40^{\circ}\text{C}$
- Heavy oil fraction can be further fractionated to get lubricating oils, vaseline, greases, wax etc. It is possible to convert any higher boiling fraction into LPG or petrol by the process called as Cracking.
- Various products are obtained during fractional distillation which are as follows in the table:

# Refining of Petroleum

## Fractionating Column for Crude Oil



Sr No	Name of Fraction	Boiling Range	Approximate hydrocarbon composition	Uses
1	Uncondensed Gases	Below 30 <sup>0</sup> C	C <sub>1</sub> to C <sub>4</sub>	Domestic/Industrial (LPG)
2	Petroleum ether	30 - 70 <sup>0</sup> C	C <sub>5</sub> to C <sub>7</sub>	As a solvent
3	Gasoline/Petrol	40 - 120 <sup>0</sup> C	C <sub>5</sub> to C <sub>9</sub>	As motor fuel, solvent, dry cleaning agent
4	Naphtha/Solvent spirit	120 - 180 <sup>0</sup> C	C <sub>9</sub> to C <sub>10</sub>	As solvent, in Dry cleaning
5	Kerosene oil	180 - 250 <sup>0</sup> C	C <sub>10</sub> to C <sub>16</sub>	For illumination, domestic fuel
6	Diesel	250 - 320 <sup>0</sup> C	C <sub>16</sub> to C <sub>18</sub>	Fuel for diesel engine
7	Heavy oil: a) Lubricating oils b) Petroleum jelly c) Grease d) Paraffin wax	320 - 400 <sup>0</sup> C	C <sub>17</sub> to C <sub>30</sub>	For Petrol from Cracking As lubricant In Cosmetics, medicine Lubricant Candles, boot polish, wax paper
8	Residue: a) Asphalt b) Petroleum coke	Above 400 <sup>0</sup> C	Above C <sub>30</sub>	Water proofing of roofs, roads As fuel, moulding arc light rods

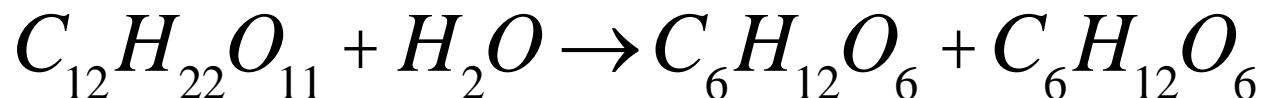
# Alternative Fuels: Power Alcohol



**Power Alcohol: When ethanol is blended with petrol (about 20-25%) and is used as fuel for IC engines, it is known as Power Alcohol.**

## **Preparation of Ethanol:**

- It can be obtained from Molasses which contains sucrose. Sucrose is converted into Glucose and Fructose by means of enzyme invertase from yeast at 30°C





# Alternative Fuels: Power Alcohol



## Preparation of Ethanol:

- The enzyme Zymase (from yeast) converts glucose and fructose into ethyl alcohol and  $\text{CO}_2$  by fermentation



- Fermented liquid (containing 18-20% of alcohol) is then subjected to fractional distillation to give 90-95% alcohol (also called as rectified spirit)
- For getting 100% alcohol (absolute alcohol) rectified spirit is treated with lime and distilled

# Alternative Fuels: Power Alcohol



## Advantages:

- 1) High Octane number (ON) about 90 as compared to conventional petrol with ON:60-70 (provide better antiknocking properties)
- 2) Ethanol renewable source of energy; reduces foreign dependency
- 3) Reduced emission of harmful gases as alcohol blended with petrol burns clean
- 4) Reduces the overheating of engine; extending engine life
- 5) Reduces deposition of Carbon and the gummy products on internal parts of engine when alcohol is blended
- 6) Removes all traces of moisture in the petrol as Alcohol capable to absorb

# Alternative Fuels: Power Alcohol



## Disadvantages:

- 1) Ethanol lowers the calorific value of petrol
- 2) Alcohol may get oxidized to acetic acid which may cause corrosion of engine parts
- 3) Air required for complete combustion is less as ethanol contains Oxygen atoms; hence needed modification of air inlet or operation of choke
- 4) Alcohol has high surface tension, hence difficult to atomize, particularly at low temperatures, causes starting trouble; hence carburetor needs special arrangements in the vehicle

# Alternative Fuels: Biodiesel



**Biodiesel: Also called as Biofuel obtained from renewable sources of energy such as vegetable oils or animal oils by transesterification**

- Mainly used as a fuel for diesel engines (compression Ignition engine)
- Vegetable oils like sunflower oil, peanut oil, palm oil, soyabean oil, rapeseed oil etc. used for biodiesel.  
(Normally non edible vegetable oils are preferred)

# Alternative Fuels: Biodiesel

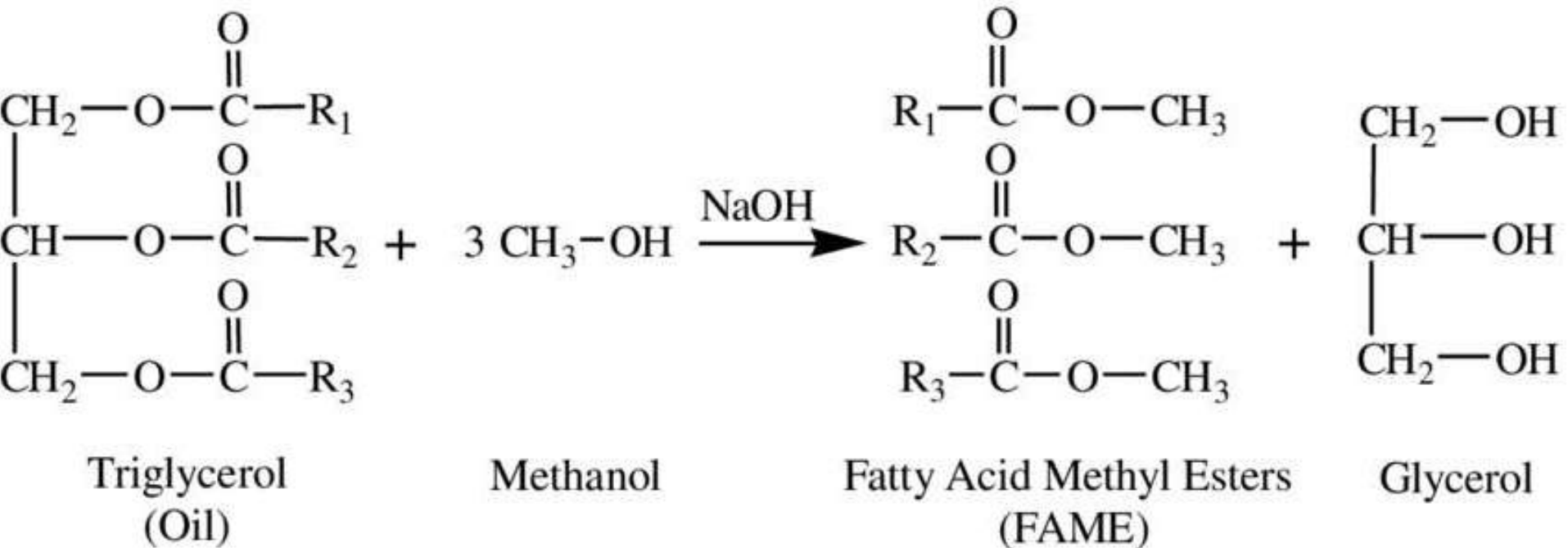


## Chemical Nature of Biodiesel:

- Vegetable oils are mainly triglycerides of fatty acids (ester of glycerol and 3 fatty acids) with High Viscosity, High Flash point and Low calorific value
- Vegetable oils can be converted into Biodiesel by the process called **Transesterification**.
- Transesterification: Conversion of one type of ester to other. In this process, animal/vegetable oils are heated with excess of methanol in presence of catalysts like sodium methoxide, potassium methoxide, NaOH/KOH. Catalysts should be free from moisture (otherwise it promotes the saponification and not transesterification)

# Alternative Fuels: Biodiesel

## Chemical Nature of Biodiesel:



$\text{R}_1, \text{R}_2, \text{R}_3$  – fatty acid alkyl groups (same or different)

Biodiesel (FAME) may contain compound like:

Methyl Stearate ( $\text{C}_{17}\text{H}_{35}\text{COOH CH}_3$ ),

Methyl Palmitate ( $\text{C}_{15}\text{H}_{31}\text{COOH CH}_3$ )

# Alternative Fuels: Biodiesel



## Chemical Nature of Biodiesel:

- Biodiesel (also called as **B100**) used as an alternative fuel for diesel engine or it can be blended with petroleum diesel
- Most commonly used blends are **B5 (5% of Biodiesel mixed with 95% of petroleum diesel)** and **B20**
- Blended Biodiesel can be used directly into diesel engine (designed for conventional diesel) while B100 needs modification in engine
- Jatropa and Karanja oil seeds are used in India for Biodiesel

# Alternative Fuels: Biodiesel



## Preparation of Biodiesel:

- Filtered non edible vegetable/animal oil(free from moisture) taken in Reaction vessel and heated to about  $110^{\circ}\text{C}$ . About 2% sodium methoxide (Na metal + Methanol) and 20% methanol added to reaction vessel
- Mixture is refluxed at  $60-70^{\circ}\text{C}$  for about 1 to 7 hours depending on the type of oil used
- Mixture is cooled and mixed with water to dissolve glycerine formed in the reaction
- Water insoluble Biodiesel phase is then separated from water phase through a separating funnel
- Suitable antioxidants are added to avoid oxidation & increase stability



# Alternative Fuels: Biodiesel



## Advantages:

- 1) Non conventional and renewable source of energy obtained from domestic sources.
- 2) High Cetane Numbers 46 to 54 and high Calorific Value of about 40 kJ/gm than that of conventional diesels
- 3) Clean fuel as Oxygen present in fuel helps for complete combustion and thus no particulates/CO pollutants
- 4) Reduces dependency on foreign countries for diesel
- 5) Non toxic, free from Sulphur
- 6) Better Lubricity
- 7) Higher Flash point and thus safer for storage

# Alternative Fuels: Biodiesel



## Limitations:

- 1) Higher Cloud Point and Pour point than conventional diesel (cause problem in fuel flow line, hence cannot be used in cold countries)
- 2) Strongly adheres on some metals and can become gummy
- 3) Not compatible with some rubber hoses and gaskets as it's dissolving action
- 4) Costly in the regions where there is shortage of vegetable oils (costly starting material)



# Gaseous Fuels

## **Compressed Natural Gas (CNG):**

It is simply **natural gas mainly comprised of Methane** that is stored under high pressure in gaseous form which remains **clear, odourless** and **non corrosive**. It is greener, cheaper and more efficient alternative to the traditional petrol and diesel fuels for vehicles.

**Composition:** CNG is a mixture of hydrocarbons, the average composition is: **Methane: 80-90%**, Ethane: 5-10%, Propane: 2-5 % and very small quantity of Butane (@0.58%) and Pentane (@0.37%)

# Compressed Natural Gas (CNG)



## Properties:

- 1) High Ignition point (about  $550^{\circ}\text{C}$ ) and requires more air
- 2) Mixes better with air than liquid fuels
- 3) Undergoes complete combustion and no evolution of  $\text{CO}$  and  $\text{SO}_x$  emissions
- 4) No pollutants like S, N, C particles hence greener or clean
- 5) Calorific Value is about  $13000 \text{ Kcal/m}^3$

## Applications:

- 1) Automobile Fuel (As a substitute for petrol and diesel)
- 2) Industrial Fuel
- 3) For production of Hydrogen and Carbon Black

# HYDROGEN AS A FUTURE FUEL



- Its availability from fully renewable resources  
( water and sunlight)
- It is nontoxic
- It's a clean fuel
- It has high calorific value
- It is used as a rocket fuel
- Can be used as a fuel for vehicles
- In a fuel cell, directly Hydrogen gas or by using  $\text{CH}_3\text{OH}$  as  $\text{H}_2$  carrier which avoids the need to store  $\text{H}_2$  under pressure, constant source of energy

# PROPERTIES OF HYDROGEN



- Colorless, odorless and insoluble in water
- Diatomic molecule in which two H atoms are joined by strong covalent bond with bond energy 435.9 KJ/mole
- Density is 0.08987 gm/cc at 0° C and 1 atm.  
Pressure, it is 14 times lighter than air
- It burns in air forming water and liberates a large amount of energy. This reaction is often explosive
- It reacts with halogen, many metals, with N<sub>2</sub>
- **Clean source of energy hence it can replace coal and oil as major source of energy in future**
- Liquid hydrogen is used as a fuel in space rockets

# Production of Hydrogen



## **1) Industrial Method:**

**a) Steam reforming of Methane  
/Natural gas**

**b) Steam reforming of coal/coke**

2) Electrolysis of water

3) Lab scale: by acids or alkalies.

4) Solar Energy Method:

Water Splitting (Thermal Processes)

Photolysis of water using coordination

catalyst i.e. Photosensitizer, e.g.  $[\text{Ru}(\text{bPy})_3]^{+2}$

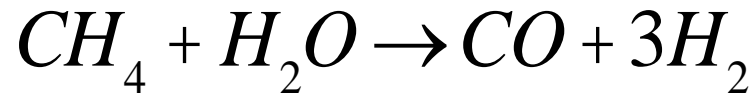
# Production of Hydrogen



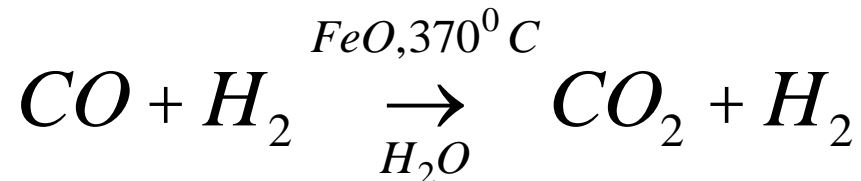
## 1) Steam Reforming of Methane:

### 3 Steps process

- i) **Steam reforming reaction:** Methane with steam at  $800^{\circ}\text{C}$  in presence of Ni catalyst to produce water gas ( $\text{CO} + \text{H}_2$ )



- ii) **Water Gas Shift reaction:** At  $370^{\circ}\text{C}$  in presence of FeO catalyst to produce  $\text{CO}_2$  &  $\text{H}_2$  with steam

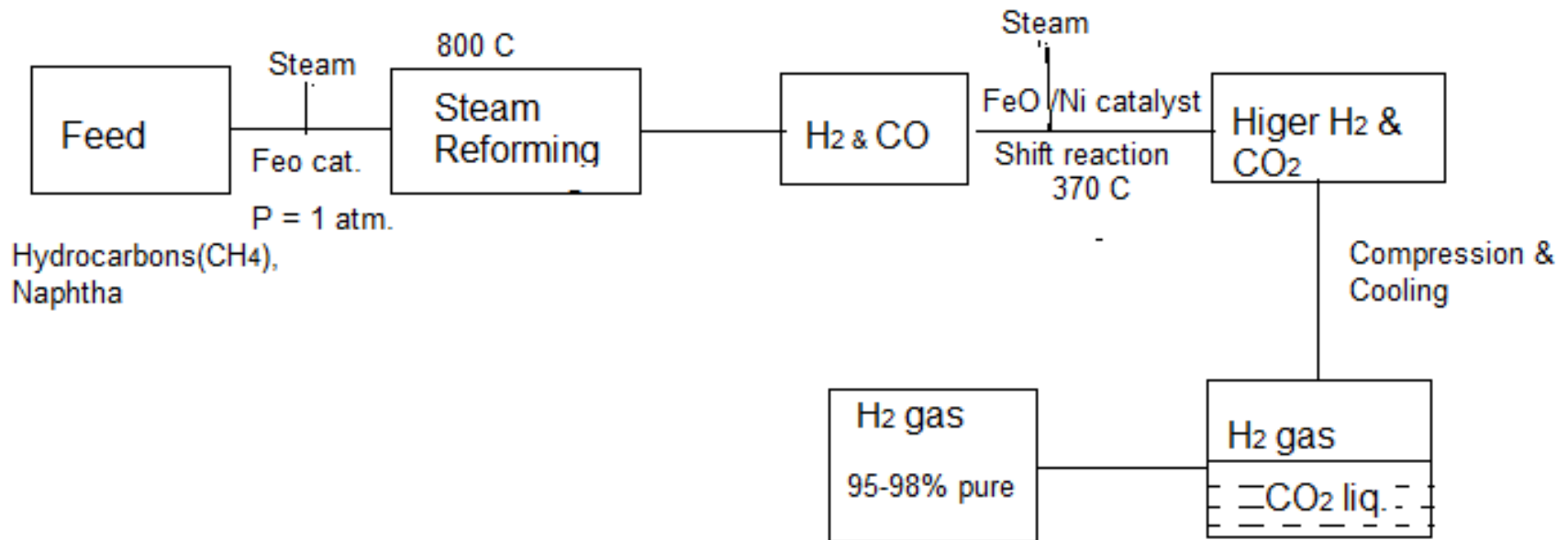




# Production of Hydrogen



**iii) Removal of  $\text{CO}_2$**  : Compression & liquefaction of mixture (obtained from Water Gas Shift reaction) to separate Hydrogen gas



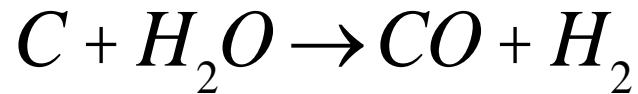
# Production of Hydrogen



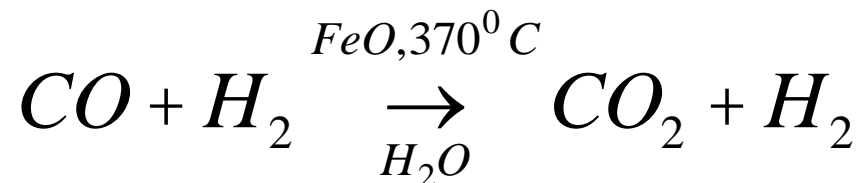
## 1) Steam Reforming of coal/coke

### 3 Steps process

- i) **Steam reforming reaction:** Coal/Coke with steam at  $1000^{\circ}\text{C}$  in presence of Ni/FeO catalyst to produce water gas ( $\text{CO} + \text{H}_2$ )



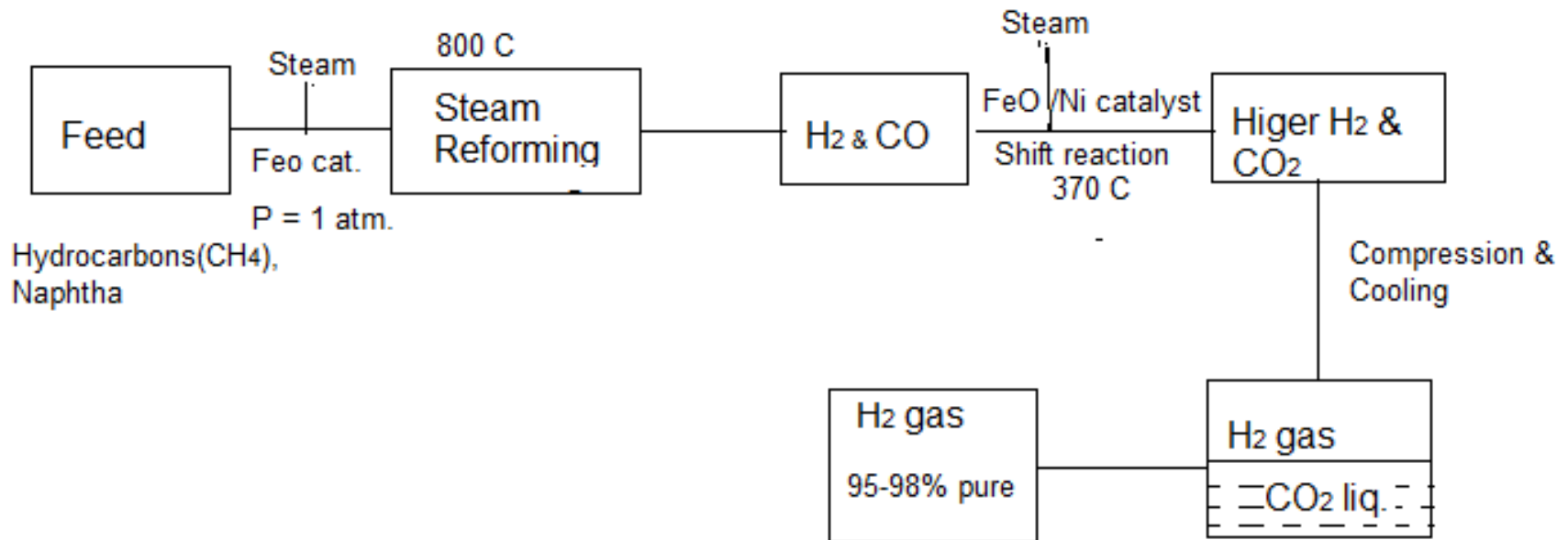
- ii) **Water Gas Shift reaction:** At  $370^{\circ}\text{C}$  in presence of FeO catalyst to produce  $\text{CO}_2$  &  $\text{H}_2$  with steam



# Production of Hydrogen



**iii) Removal of  $\text{CO}_2$**  : Compression & liquefaction of mixture (obtained from Water Gas Shift reaction) to separate Hydrogen gas



$\text{H}_2$  obtained from coal is less & with impurities like  $\text{H}_2\text{S}$ ,  $\text{SO}_2$  hence less preferred although cheap

# Storage of Hydrogen



## Difficulties:

- Decarburization
- Lightest gas (MW:2); Quantity stored less
- High cost of compression & energy
- Very low Boiling Point  $-252.6^{\circ}\text{C}$ , difficult to liquefy; high cost of cooling & insulation
- Very low Ignition Temp., highly inflammable
- Mixture of  $2:1\text{H}_2\text{-O}_2$  highly explosive
- Storage in hydrides requires longer duration & Decomposition requires high Temp

# Storage of Hydrogen



## Physical Storage:

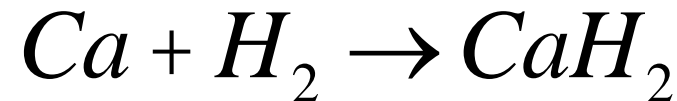
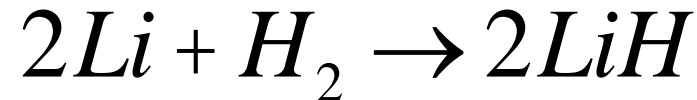
- Compression – Tanks & cylinders at high pressure
- Liquefaction – Cryogenic storage
- Adsorption on Carbon nanomaterials – small size, porous structure(pores of molecular dimension), low density, high surface area
- Metal Organic framework (MOF) – crystalline, porous, inorganic-organic hybrid materials

# Storage of Hydrogen

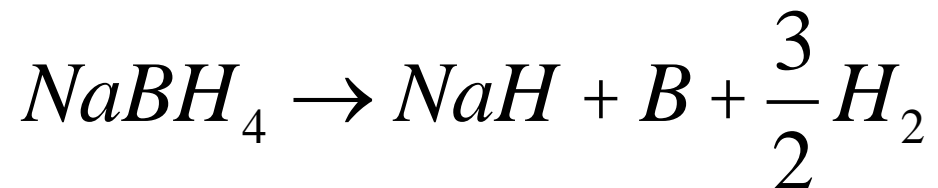


## Chemical Storage:

- **Metal Hydrides** –prepared by heating metal &  $H_2$  at  $300^{\circ}C$ - $700^{\circ}C$ , can be released after heating at high temp. eg:  $LiH$ ,  $CaH_2$ ,  $NaBH_4$ ,  $LiAlH_4$ ,  $TiFeH_2$ ,  $LaNi_5S_6$



- Release of  $H_2$



# Storage of Hydrogen



## Chemical Storage:

- **Alanates** – Metal Aluminohydrides (H atoms get adsorbed or occupy interstitial position of solid network lattice) Eg: Sodium Alanate -  $\text{NaAlH}_4$  (store about 7.4%  $\text{H}_2$ ): Highly Inflammable, does not react in dry air but ignites or explodes with water or moist air
- Release of  $\text{H}_2$   
$$3\text{NaAlH}_4 \rightarrow \text{Na}_3\text{AlH}_6 + 2\text{Al} + 3\text{H}_2 \left( 3.3\% \text{H}_2 \text{ at } 35^\circ \text{C} \right)$$
$$2\text{Na}_3\text{AlH}_6 \rightarrow 6\text{NaH} + 2\text{Al} + 3\text{H}_2 \left( 1.7\% \text{H}_2 \text{ at } 110^\circ \text{C} \right)$$
$$\text{LaNi}_5\text{H}_6 \text{ stores } 1.3\% \text{H}_2 \text{ \& } \text{LiAlH}_4 \text{ stores } 5.5\% \text{H}_2$$

# Applications of hydrogen



- 1) As a fuel in Internal combustion engine of vehicles
- 2) For preparation of ammonia (Haber's process)
- 3) As a Rocket propellant
- 4) As a fuel for fuel cells
- 5) Used in industries:
  - annealing of metal,
  - cutting metals,
  - oxy-hydrogen flame for fabrication