

CHEMISTRY

# Module – III

# FUELS

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**What is Fuel?**

A fuel is a substance that produces useful energy either through combustion or through nuclear reaction. Energy should be released in a controlled manner and can be harnessed economically for domestic and industrial purposes. Fuels that produce heat energy by combustion are called as chemical fuels. Examples: wood, oil, natural gases, producer gas etc.

**Classification of Fuels**

On the basis of occurrence, fuels are of two types:

1. Primary or natural fuels- These are found in nature and are used as such, generally without processing. These are also known as fossil fuels. Examples include wood, peat, lignite, petroleum, natural gas etc.
2. Secondary or synthetic fuels- These are derived from the natural fuels by further chemical processing. Examples of this type are coke, charcoal, kerosene, producer gas, water gas etc.

Classification of the fuels can also be done on the basis of their physical states.

1. Solid fuels: wood, coal, charcoal, coke etc. are coming under this category.
2. Liquid fuels: petroleum, petrol, diesel, kerosene etc. are the examples of this category.
3. Gaseous fuels: Natural gas, coal gas, water gas, producer gas, bio gas etc. are the examples of this class of fuels.

**Characteristics of a good fuel**

- (i) High calorific value: The amount of heat energy released when a unity quantity of fuel is burnt completely is known as calorific value. Higher is the calorific value, the greater is the heat liberated per unit mass or volume of the fuel and the better is the fuel quality.
- (ii) Ignition temperature: It is the lowest temperature to which the fuel must be preheated so that it starts burning smoothly. An ideal fuel should have moderate ignition temperature. Fuels with low ignition temperature can burn spontaneously and cause explosion. High ignition temperature makes the fuel difficult to ignite.
- (iii) Moisture content: It should be low because the presence of moisture lowers the calorific value of the fuel.
- (iv) Non-combustible matter (Ash): Non-combustible matter reduces the calorific value of the fuel. It also needs additional investment for its storage, handling and disposal.

- (v) Velocity of combustion: Fuel must burn with a moderate rate. If the velocity is low, then a part of heat may get radiated instead of raising the temperature. If it is very high, then combustion may be uncontrollable.
- (vi) Combustion products should be harmless and non-polluting.
- (vii) Cost of the fuel: A good fuel should be readily available at low cost.
- (viii) Storage & transportation: A good fuel should be easy to handle, store & transport at low cost.

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

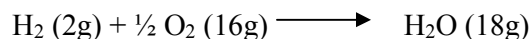
It is defined as the heat produced, when a unit quantity (mass or volume) of fuel is burnt completely and the hot combustion products are allowed to escape. In actual practice, when a fuel is burnt, the water vapour is allowed to escape along with the hot combustion gases.

### **Gross Calorific Value (GCV) or Higher Calorific Value (HCV)**

It is defined as the total amount of heat produced, when a unit quantity (mass or volume) of fuel is burnt completely and the products of combustion are cooled to room temperature.

**Relationship between GCV and NCV:** Usually, all fuels contain hydrogen. During the combustion, the hydrogen in the fuel is converted into steam. When the combustion products are cooled to room temperature, the steam gets condensed and heat equals to the latent heat of steam is evolved. This heat gets added in the measured heat and so GCV value is higher than NCV.

The combustion of hydrogen gives water as per the following chemical equation:



From the balanced chemical equation, it is indicated that 2 part by weight of hydrogen reacts with 16 parts by weight of oxygen to give 18 parts by weight of water

That means, 1 part by weight of hydrogen reacts with 8 parts by weight of oxygen to give 9 parts by weight of water.

If the amount of hydrogen in a given fuel is 'H',

Amount of heat produced will be  $\frac{1}{9} H \times \Delta H_v$

LCV or NCV = (HCV or GCV) – (Latent heat of water vapour formed)

or, LCV or NCV = (HCV or GCV) –  $(\frac{1}{9} H \times \Delta H_v)$

where,  $\Delta H_v$  = latent heat of steam, which is approximately 587 kcal/kg or cal/g

**Problem 1:** 2 kg of a coal was burnt in a bomb calorimeter. The heat liberated was found to be 14114 kcal. Calculate the calorific value of the coal sample. (Ans: 7057 kcal/kg )

**Problem 2:** GCV of a fuel containing 8% hydrogen was found to be 9226 Kcal/Kg. Find out NCV if the  $\Delta H_v = 587$  kcal/kg. (Ans: NCV= 8803.26 kcal/kg)

**Problem 3:** Calculate GCV of a coal sample if its NCV is 6767cal. Find the NCV if  $\Delta H_v = 587$  cal/g. (Ans: NCV= 7031.6 cal/g).

**Problem 4:** Calculate NCV of a fuel containing 6% hydrogen if its GCV is found to be 9804.6 kcal/kg.  $\Delta H_v = 587$  kcal/kg. (Ans: NCV= 9487.6 kcal/kg)

**Theoretical calculation of calorific value of a fuel**

If the composition of a fuel is known, the theoretical calculation of its calorific value can be done by using Dulong’s formula. Dulong assumed that the heat evolved comes from the combustion of C, H, & S present in the fuel and the calorific value of a fuel is the sum of the calorific values of these constituents. The higher calorific value of C, H & S are found to be 8080, 34500, & 2240 kcal/kg respectively.

Dulong’s formula can be written as:

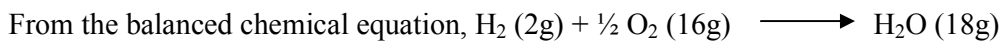
$$GCV = \left(\frac{1}{100}\right) \left[ 8080 C + 34500 \left(H - \frac{O}{8}\right) + 2240 S \right] kcal/kg \quad \dots \dots (3.1)$$

Where, C, H, S & O are the percentage of carbon, hydrogen, oxygen & sulphur respectively.

**Why the 2<sup>nd</sup> factor in equation 3.1 is  $\left(H - \frac{O}{8}\right)$  not H?**

Since some part of the hydrogen is fixed as water in the fuel and it is not available for combustion, it is required to subtract from the total amount of hydrogen available to calculate the amount of hydrogen available for combustion.

Thus, amount of hydrogen available for combustion = (Total mass of hydrogen) – (hydrogen combined with oxygen)



it is indicated that 1 part by weight of hydrogen reacts with 8 parts by weight of oxygen to give 9 parts by weight of water.

If the amount of oxygen in the fuel is ‘O’, then

Fixed mass of hydrogen =  $(1/8) O = (\text{mass of oxygen in the fuel}) / 8$

So amount of hydrogen available for combustion =  $H - \frac{O}{8}$

$$LCV \text{ or } NCV = \left( HCV - 9 \times \frac{H}{100} \times 587 \right) kcal/kg$$

or,  $LCV \text{ or } NCV = (HCV - 0.09 H \times 587) kcal/kg \dots \dots \dots (3.2)$

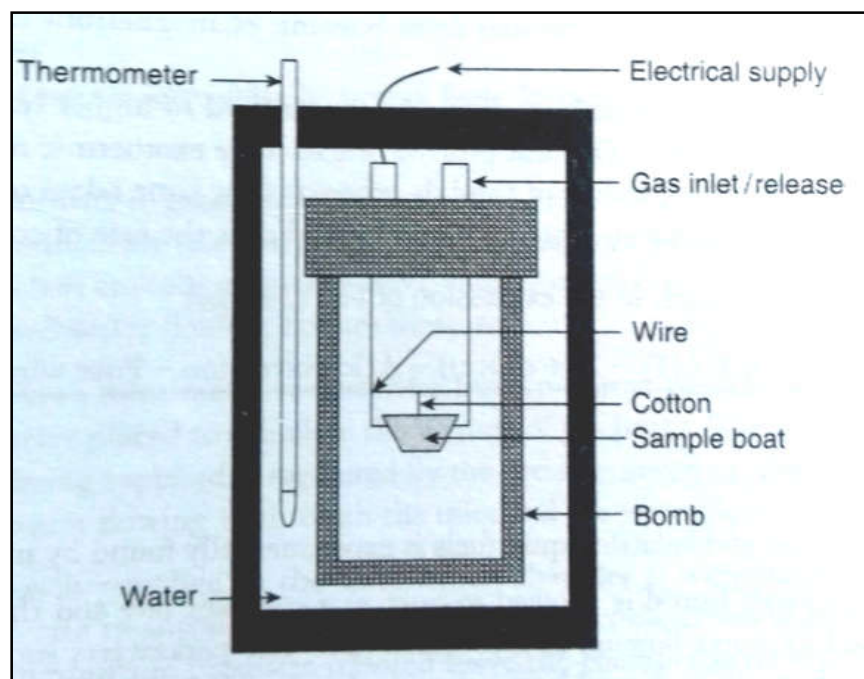
However, experimentally, HCV and LCV can be determined by using Bomb calorimeter. For solid and liquid fuels, Junker's calorimeter and for gaseous fuels, Boy's calorimeters are used.

### **Bomb Calorimeter**

**Principle:** In this method, a known amount of solid and liquid fuel is burnt in excess oxygen. The liberated heat is absorbed in a known quantity of surrounding water raising its temperature. The calorific value is then calculated from the relationship:

Heat produced by the fuel = heat absorbed by the water and calorimeter

**Construction:** It consists of a cylindrical bomb made of stainless steel. The bomb is provided with a lid to close it and make it air-tight. The combustion of the fuel is allowed to take place inside the bomb with the help of electricity. The electrodes are attached with a small ring which supports a crucible made of nickel or stainless steel. Supply of oxygen is carried out through an inlet. The bomb is placed in a copper calorimeter, which is surrounded by an air-jacket and water-jacket in order to prevent loss of heat owing to radiation. The calorimeter is also provided with a motor-driven stirrer and thermometer.



**Figure 3.1:** Diagram of Bomb calorimeter

**Working:** A known amount of the fuel is placed in the crucible supported over the ring. A fine magnesium wire touching the sample of the fuel is then stretched across the electrodes. The bomb lid is tightly screwed and filled with oxygen at about 25 atm pressure. The bomb is

then placed in the copper calorimeter containing a known amount of water. The stirrer is driven and the initial temperature of water is noted. The combustion of the fuel is then started by connecting the electrodes to a battery. Heat is liberated due to exothermic combustion of the fuel. The stirring of water is continued and the final temperature of water is recorded.

Calculation: Suppose,

Weight of the fuel sample taken =  $x$  g

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

Water equivalent of calorimeter =  $w$  g

Initial temperature of water in the calorimeter =  $T_1$  °C

Final temperature of water in the calorimeter =  $T_2$  °C

If higher calorific value of the fuel is HCV,

Heat liberated by the combustion of the fuel =  $x$  (HCV)

Heat absorbed by the water and the calorimeter =  $(W + w) S (T_2 - T_1)$

Where  $S$  is the specific heat of water.

But, heat liberated by the fuel = heat absorbed by the water and the calorimeter

Thus,  $x$  (HCV) =  $(W + w) S (T_2 - T_1)$

Therefore,  $HCV = (W + w) S (T_2 - T_1) / x$

And or,  $LCV$  or  $NCV = (HCV - 0.09 H \times 587) kcal/kg$

**Corrections:** For more accurate calculations, certain corrections are incorporated.

- Fuse wire correction- The heat liberated from burning of the magnesium fuse wire is taken into account
- Acid correction: when fuels containing S and N are oxidised at higher temperature, they form acids through exothermic reactions. The heat evolved is considered.
- Cooling correction: It is the product of  $t$  and  $dt$ , where  $t$  is the time taken to cool the temperature of water from high temperature to room temperature and  $dt$  is the rate of cooling per minute.

Incorporating all the corrections, we get

$HCV = [ \{ (W + w) S (T_2 - T_1 + t dt) \} - \text{acid correction} - \text{fuse wire correction} ] / x$

**Problem 5:** Calculate the gross and net calorific values of a coal sample having 85 % C, 8 % H, 1 % S, 2% N and 4% ash. Latent heat of steam = 587 kcal/kg.

(Ans: GCV=9650.4 kcal/kg and NCV= 9227.76 kcal/kg)

**Problem 6:** A sample of coal has the following composition: C = 82 %, H= 7.5 %, S = 1.5 %, N = 0.6 %, O = 8.4 %. Find GCV using Dulong's Formula. (Ans: GCV=8965.25 kcal/kg)

**Problem 7:** Calculate GCV and NCV of coal sample having the following composition:

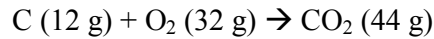
C = 80%, H = 7%, S= 3.5 %, N = 2.1%, ash = 4.4%.

(Ans: GCV=8828.02 kcal/kg and NCV= 8458.2 kcal/kg)

**Calculation of theoretical air for the combustion of a fuel**

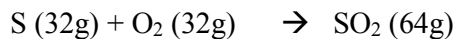
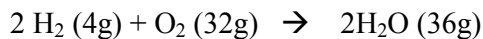
The volume and weight of the amount of air required for the complete combustion of certain amount of a fuel can be calculated theoretically using its composition data and the balanced combustion equation for each of the combustible composition of the fuel.

The stoichimetric equation involved in the combustion of carbon is:



Here, 12 parts by weight of carbon requires 32 parts by weight of oxygen to produce 44 parts by weight of CO<sub>2</sub>.

Similarly, for hydrogen and sulphur, we can write



Here, 4 parts by weight of hydrogen requires 32 parts by weight of oxygen to produce 36 parts by weight of H<sub>2</sub>O.

32 parts by weight of carbon requires 32 parts by weight of oxygen to produce 64 parts by weight of SO<sub>2</sub>.

So the weight of oxygen required to burn (oxidise) *W* kg of a fuel sample containing C % of carbon, H % of hydrogen, and S % of sulphur is

$$\left[ \left(\frac{32}{12}\right)C + \left(\frac{32}{4}\right)H + \left(\frac{32}{32}\right)S \right] \times \frac{W}{100} \text{ kg} \dots\dots\dots (3.3)$$

Nitrogen is incombustible and hence is not included in the equation. However, if the fuel sample contains O % of oxygen, then that amount must be subtracted from the equation (3.3) and the equation takes the following form (equation (3.4)).

$$\left[ \left(\frac{32}{12}\right)C + 8 H + S - O \right] \times \frac{W}{100} \text{ kg} \dots\dots\dots(3.4)$$

Since the percentage of oxygen in air by volume is 21 % and 23.2 % by weight, the weight of air required for the complete combustion of the above fuel sample is

$$\left[ \left( \frac{32}{12} \right) C + 8 H + S - O \right] \times \frac{W}{100} \times \left( \frac{100}{23.2} \right) \text{kg} \dots\dots\dots(3.5)$$

Again, the average molecular weight of air is 28.94 g.

Thus, we can write, 28.94 g of air occupies 22.4 L.

This relationship can be used in order to calculate the volume of air required for the complete combustion of the above fuel sample.

**Problem 8:** Calculate the weight and volume of air required in combustion of 4 kg of carbon. (Ans. 69.56 kg, 48695.6 L)

**Problem 9:** The percentage composition of a coal sample is: C = 85 %, H = 5 %, O = 6 %, N = 4 %, S = 2 %, ash = 5 % and moisture = 3 %. (i) Calculate the minimum amount of air needed in combustion of 1 kg of coal. (ii) Calculate the weight and volume of air required in combustion of 1 kg of coal if it is supplied 40 % in excess. (Ans. (i) 11.68 kg, (ii) 16.35 kg, 11447.6 L)

**Problem 10:** Calculate the volume of air required for the complete combustion of 1 m<sup>3</sup> of the gaseous fuel having the following composition by volume: H<sub>2</sub> = 50 %, CH<sub>4</sub> = 36 %, CO = 6 %, C<sub>2</sub>H<sub>4</sub> = 4 %, H<sub>2</sub>O vapour = 2.5 %, N<sub>2</sub> = 1.5 %. (Ans. 5.33 m<sup>3</sup>)

### **Solid Fuels - Coal:**

Coal is a complex organic compound derived from the dead plants buried under the ground for several years. The degraded matter was converted into various types of coal: Peat, lignite, bituminous and anthracite. This classification is made based on the carbon content. The highest ranking of coal, which has largest carbon content, is anthracite. The lowest rank of the coal is peat, which is formed at the first stage of the coalification. The next rank is lignite (also called as brown coal) and then bituminous coal. Thus the order of ranking of coals is: Anthracite > Bituminous > Sub-bituminous > Lignite > Peat

In order to know the calorific values of the varieties of coal with varying composition of carbon, moisture, volatile matters, analysis of coal is very much important. There are two types of analyses for determination of the quality of the coal.

### **Proximate Analysis**

It includes the determination of moisture content, volatile matter, ash and fixed carbon content. In this analysis, the data varies with the procedure adopted for study.



Moisture content: About 1g of finely divided powder of air-dried coal sample is weighed in a crucible and placed inside an electric hot air oven, maintained at 105 – 110 °C. The crucible is allowed to remain in the oven for an hour and then taken out, cooled in desiccators and weighed. The loss of weight is reported as moisture percentage.

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

Volatile matter: The dried sample of coal left in the crucible after analysis of moisture content is then covered with a lid and placed in an electric furnace maintained at 925 °C. The crucible taken out after 7 min of heating and then cooled in air and then in desiccators. After taking weight, the loss in weight is reported as volatile matter in percentage terms.

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

Ash content: The residual coal in the crucible after analysis of volatile matter is then heated without lid in muffle furnace at 700 ±5 °C. After 0.5h, the crucible is taken out, cooled first in air, then in a desiccators and weighed. Heating, cooling, weighed is repeated till a constant weight is obtained. The residue is reported as ash in percentage term.

$$\text{Ash \%} = \frac{\text{Weight of ash left in the crucible}}{\text{Weight of coal taken}} \times 100$$

Fixed carbon: this refers to the amount of carbon present in the coal sample. This is calculated by deducting the percentage amount of moisture, volatile matter and ash from 100.

$$\text{Fixed carbon \%} = 100 (\text{Moisture \%} + \text{Volatile matter \%} + \text{Ash\%})$$

### **Significance of Proximate Analysis:**

1. Moisture lowers the calorific value of coal and it quenches the fire in the furnace. So lesser is the moisture content, better is the quality of coal as fuel.
2. High volatile matter content means that a large proportion of the matter escapes unburnt. This matter may be combustible gasses or non-combustible matter. The presence of non-combustible matters do not add calorific value, but it increases the volume of the furnace required. Hence, higher volatile content in coal is undesirable.
3. Ash is a useless non-combustible matter, which reduces the calorific value of coal. Ash causes the hindrance of flow of air and heat, thereby, lowering the temperature. It also causes wear of furnace walls, burning of apparatus and feeding mechanism. Hence, lower is the ash content; better is the quality of coal. The presence of ash also increases the transport, handling, storage and disposal cost.
4. Higher is the fixed carbon content, better is the quality of coal. It is useful for designing the furnace and firebox.

### **Ultimate Analysis**

This analysis involves the determination of content of carbon, hydrogen, nitrogen, sulphur, oxygen and ash present in a coal sample. The content of carbon, hydrogen, nitrogen, sulphur

and ash are determined experimentally, whereas that of oxygen is determined theoretically. Greater is the percentage of carbon and hydrogen, better is the quality of the coal and calorific value. Nitrogen has no calorific value, hence its presence is undesirable. Sulphur is present to the extent of 0.5- 3.0 % and its burning has harmful effects in terms of corrosion of equipments and the atmospheric pollution. So presence of sulphur is undesirable even though it contributes to the heating value of coal on combustion. Oxygen content decreases the calorific value of coal. High oxygen content coals are characterized by high inherent moisture content, low calorific value and low cooking power. Thus, a good quality coal should have low percentage of oxygen.

## **Liquid Fuel:**

### **Petroleum:**

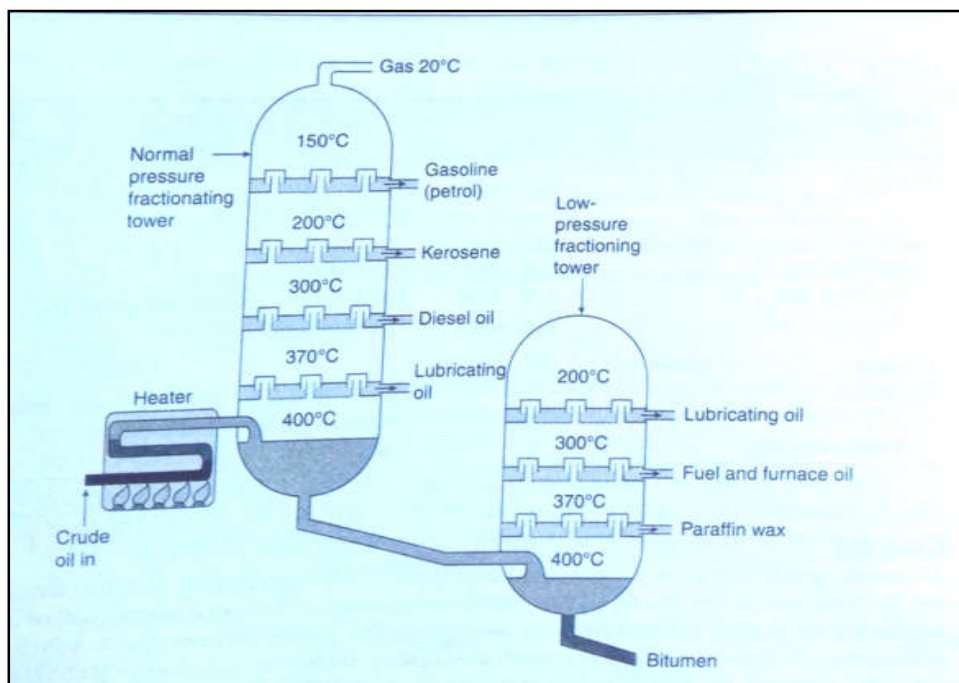
Petroleum is a fossil fuel and can be classified into three categories based on the composition.

- (a) Paraffinic base petroleum: straight chain paraffin main compound.
- (b) Asphaltic or Naphthalic base petroleum: cycloparaffin is the main compound.
- (c) Mixed base petroleum: Both straight chain and cycloparaffin are present.

Petroleum is buried underground in tiny pockets in rocks, which is pumped to the surface and it is sent to refinery to refining for separation into different types of product and fuels. The petroleum obtained by mining is viscous and dark colour liquid contains hydrocarbons (straight and cycloparaffins, olefins, aromatics and some organic compounds containing S, N, O). In addition it also contains, sand, brine, and sulphur. After removal of the above impurities, the oil is subjected to fractional distillation in a refinery. The process of converting crude oil into several useful fractions is referred to as refining of petroleum. The important steps involved are:

- (i) Fractional distillation to give various fractions
- (ii) Conversion of less desirable fraction to valuable products by processes like cracking.
- (iii) Treatment of fraction to remove undesirable substances.

Fractional distillation of crude oil is performed to separate into a number of fractions having different and definite boiling ranges. The crude oil is preheated in a furnace to about 400°C and introduced in the fractionating tower. The tower is not towards the lower end and comparatively cooler at the upper end. As the vapour of oil rises up the column, they get cooled and condensed in the trays. The highest boiling fraction condenses first at the bottom and the lowest boiling fraction at the top. Outlets are provided in the side of the column at suitable height to withdraw the fraction. The uncondensed gases are liquefied to give the LPG, which consists of a mix of methane, ethane, propane and butane. The black, tarry residue left in the retort is called asphalt.



**Figure 3.2:** Diagram of Fractional distillation column.

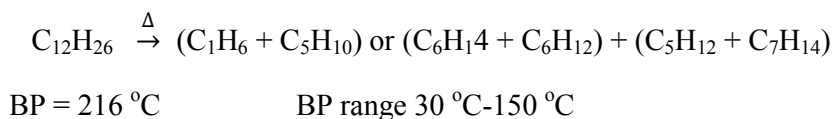
**Table 3.1:** Major fractions of distillation of crude oil and their uses.

S. No	Fraction's name	Boiling Temperature range	Approximate Composition	Uses
1	Uncondensed gas	Bellow 300 °C	C <sub>1</sub> -C <sub>4</sub>	Used as domestic fuel and synthesis of organic compounds
2	Petroleum Ether	30-70 °C	C <sub>5</sub> -C <sub>7</sub>	Solvents for fats and oils, used in dry cleaning
3	Gasoline or petrol	70-120 °C	C <sub>5</sub> -C <sub>9</sub>	Fuels for IC engines of automobiles and dry cleaning
4	Naphtha or solvent spirit	120-180 °C	C <sub>9</sub> -C <sub>10</sub>	Solvent for paints and varnishes and in dry cleaning
5	Kerosene oil	180-250 °C	C <sub>10</sub> -C <sub>16</sub>	Illuminants, Fuels for stoves, for making oil gas
6	Diesel	250-320 °C	C <sub>15</sub> -C <sub>18</sub>	Diesel engine fuel, synthesis of gasoline by cracking
7	Heavy oil On vacuum distillation gives (i)Lubricating oil (ii)Petroleum jelly (iii)Greases (iv)Paraffin wax	320-400 °C	C <sub>17</sub> -C <sub>40</sub>	Fuel for ships, synthesis of gasoline by cracking  (i)As Lubricants (ii)In cosmetics and medicines (iii)As lubricant (iv)In candles, boot polishes, wax paper

7	Residue: (i)Pitch (ii)Petroleum cokes	>400 °C	Above C <sub>40</sub>	Road making, water proofing of roofs As solid fuel in moulding electrodes rods for cells
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## **Cracking:**

Of all the hydrocarbons obtained in different fraction, gasoline fraction has the highest demand due to its use in automobiles. The gasoline obtained straight from fractionation tower is not of good quality and is obtained in poor yield (20%). Hence, a process of thermal decomposition of high boiling fraction is converted into more valuable lower boiling fractions. This process is called as cracking.



Two methods of cracking are:

### **(1) Thermal cracking:**

In this method, heavier oils are subjected to high temperature and pressure, so that bigger hydrocarbons break into smaller molecules of paraffin, and some hydrogen. This process is carried out either in liquid or vapour phase.

In liquid phase thermal cracking, the cracking heavy oils is done at a temperature 475-530 °C or 'P' of 7-70atm to keep the product in liquid phase. The yield is approx 60-65%.

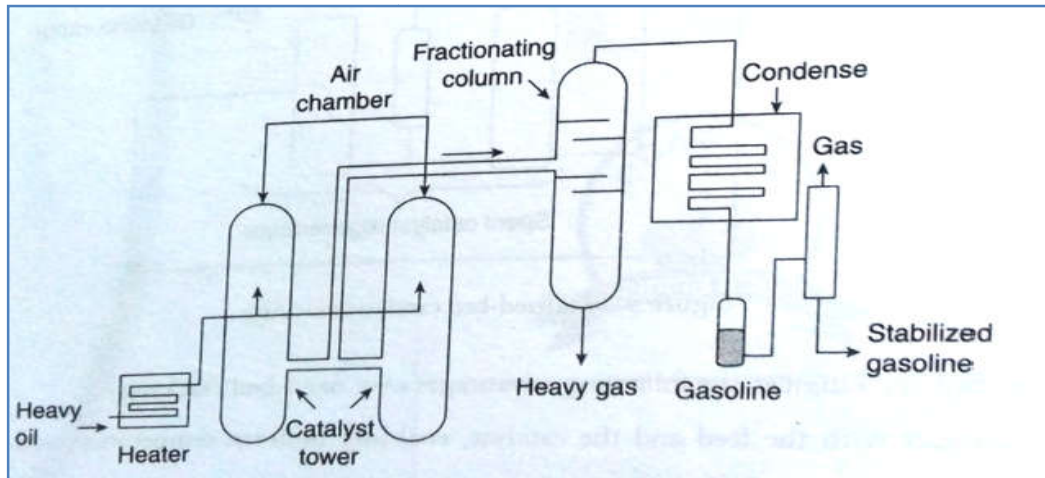
In vapour phase thermal cracking, the oil is first vaporized and then heated at 600-650 °C and subjected to a 'P' of 3.5-10.5atm for a short time for cracking.

### **(2) Catalytic cracking:**

Here high temperature and pressures are not necessary and cracking takes place in presence of a catalyst, which is generally a mixture of silica and alumina and aluminium silicate, bauxite etc. It may of two types:

#### **(i) Fixed bed cracking:**

Cracking is carried out around 500<sup>0</sup>C over the catalyst, which is used in the form of a fixed bed. A number of cracking furnaces are used, so that if the catalyst is sent in one furnace, the other one is used. The spent catalyst which is deposited by carbon can be regenerated by burning the carbon in a current of air.

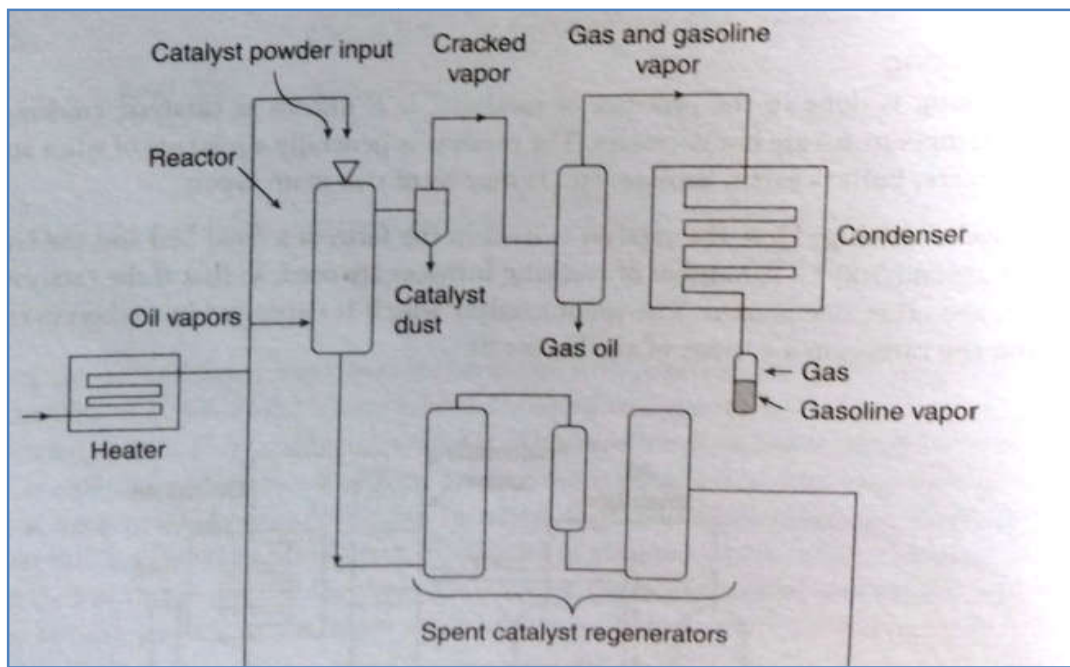


**Figure 3.3:** Fixed bed catalytic cracking

**(ii) Fluidized (moving) bed catalytic cracking:**

Fluidized catalyst is used to perform cracking continuously. The catalyst is suspended in a stream of oil vapour. The spent catalyst continuously flows out of the bottom of the furnace and can be regenerated, while fresh catalyst is added from the top. The temperature is maintained at 450-550 °C and pressure at 1-2 atm.

The cracked pooch rise up to the top of the reactor and enter the fractionating column and passed through a cooler, where some grazes condensed.



**Figure 3.4:** Fluidised bed catalytic cracking

## **Knocking:**

It is defined as metallic sound similar to rattling of hammer produced in internal combustion (IC) engine due to immature ignition of fuel oil-air mixture.

An IC engine uses either gasoline or diesel as fuel and a mixture of fuel-air is ignited inside the IC. The ignition is brought about by means of an electric spark (in petrol engines) or by compressing the air (in diesel engine).

In petrol engine, the whole process comprises of four strokes:

- (i) Suction stroke: The downward moving piston sucks a mixture of air and fuel (petrol) vapours in the carburettor into the cylinder.
- (ii) Compression stroke: The piston moves up, compressing the gas mixture. The ratio of initial volume (at the end of suction stroke) to the final volume (at the end of compression stroke) is known as compression ratio (CR).
- (iii) Power stroke: Just before the piston reaches the top centre of the cylinder, a spark from the spark plug ignites the gas mixture. The hot gases produced due to combustion increase the pressure and push the piston down.
- (iv) Exhaust stroke: This is the last stroke, in which the piston rises up and expels the exhaust gases from the cylinder.

The cycle then repeats itself. After the initiated by a spark, the fuel air mixture should burn smoothly and rapidly so that the expanding gas drives the piston down the cylinder smoothly.

The efficiency of IC engine depends on compression ratio (CR). Higher is the CR, greater is the efficiency of the engine. To achieve maximum efficiency a CR of 7-8 is required. However, if the compression ratio exceeds certain limit, the fuel air-mixture may get heated to a temperature, greater than its ignition temperature leading to spontaneous ignition and explosive combustion of fuel, even before sparking. This results in the thermal shock wave, which hits the cylinder and piston, causing a characteristic metallic or rattling sound, called as knocking.

Knocking increases the fuel consumption, decreases the efficiency of engine, causes mechanical damages to piston and cylinder due to overheating. Knocking depends on the chemical composition of the fuel, engine design, and shape of piston, location of plug etc. and also on running condition.

## **Relationship between chemical structure and knocking:**

Knocking tendency decreases with increases in compactness of the molecule.

Knocking tendency decreases with increases in double bonds, rings (cyclic structure).

Knocking tendency is higher, when straight chain hydrocarbons are used in IC engine, whereas branched chain hydrocarbons, aromatics (benzene, toluene), cycloalkane have lesser tendency to knock. The knocking tendency follows the order:

Aromatic < Cycloalkane < Olefins < Branched chain alkane < Straight chain alkane  
*Knocking increases*  
→

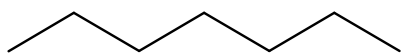
For straight chain alkane:

n-butane < n-pentane < n-hexane < n-heptane  
*Knocking increases*  
→

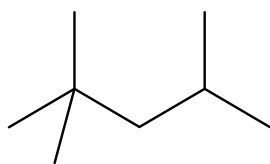
### **Octane Number:**

In order to express the knocking (anti-knocking) property of fuel, an arbitrary scale, octane rating or octane number is provided by G. Edger in 1926. It is determined by matching the knocking characteristic of the fuel being tested with those of the mixtures of n-heptane and iso-octane (2, 2, 4- tri-methyl pentane) in a standard cylinder engine of variable CR and under the same set of conditions.

It is observed that n-heptanes have the poorest anti-knock properties of all pure compounds suitable as fuels for IC engines. On the other hand, iso-octane has very good antiknock properties (high resistance to knocking). So octane number of n-heptane and iso-octane are arbitrary assigned as zero and 100 respectively.



(n-heptane) (Octane no. Zero)



iso-octane) (octane no. 100)

Thus, the octane number of a fuel can be defined as the percentage (by volume) of iso-octane in the iso-octane and n-heptanes mixture that has same knocking characteristics as the fuel under examination, under same set of conditions.

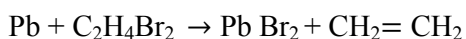
Thus, a fuel with octane number 80 is one which has the same combustion characteristics to that of 80:20 mixture of iso-octane and n-heptane.

### **Anti-knocking agents:**

The petrol from fractional distillation has low octane number and is called as unleaded petrol. The octane number of gasoline (petrol) can be increased by adding additives like benzol and alcohol. This process is called blending. Benzol is a mixture of 70% benzene, 18% toluene and 6% xylene and rest other hydrocarbons and it is obtained during fractional distillation of light oil in the temperature range 80-170 °C.

The generally used anti-knocking agent, tetraethyl lead ( $\text{Pb}(\text{C}_2\text{H}_5)_4$ ) (TEL). The process of addition of TEL to gasoline to increase its octane number is known as doping. TEL is a colourless liquid with a sweet odour but it is highly poisonous. About 0.5ml TEL per litre is added for motor fuels and about 1mL of TEL per litres is added for aviation fuels. Gasoline

containing TEL is coloured with 2% red dye to indicate its poisonous nature and this variety of petrol is called leaded petrol. It is believed that during combustion of gasoline, TEL forms Pb and PbO particles, which acts as free radicals chain inhibitors and thus curtail the propagation of explosive chain reaction and thereby, minimises the knocking (It is believed that knocking is a free radical mechanism). However lead and PbO vapours so formed contaminate the atmosphere. PbO is rapidly reduced to Pb which deposited on the spark plug, cylinder walls and piston heads. Hence, it is harmful to engine. To overcome these disadvantages of leaded petrol and to improve the octane number of fuels, ethylene dibromide (C<sub>2</sub>H<sub>4</sub>Br<sub>2</sub>) is also added, so that lead formed is converted into lead bromide, which is volatile and escapes into the atmosphere.



### **Unleaded petrol:**

Owing to the harmful effect of lead, unleaded petrol is being used. It is the one, where octane number is increased without the addition of lead compounds. In this case, high octane number compounds such as isopentane, iso octane, ethyl benzene, isopropyl benzene, methyl tertiary butyl ether (MTBE) are used. Out of these, MTBE is preferred because it contains oxygen in the form of ether group and supplies oxygen for the combustion of petrol in internal combustion engines, thereby reducing peroxy compound formation.

Use of unleaded petrol requires use of catalytic converter. A catalytic converter contains a catalyst (Rhodium), which converts toxic gases (CO and NO) into harmless gases (CO<sub>2</sub> and N<sub>2</sub>). Moreover it oxidised un-burnt hydrocarbons to CO<sub>2</sub> and H<sub>2</sub>O.

### **Knocking in Compression Ignition (diesel) engine:**

In diesel engine, the fuel is ignited with help of heat generated by the compression of air inside the combustion chamber and not by spark, as in case of petrol engine. The injected diesel droplet gets ignited by absorption of heat in the cylinder. However, the combustion of fuel in diesel engine is not spontaneous of that of petrol engine. There is a time lag between fuel injection and its ignition. It is called as ignition delay or ignition lag. For the efficient functioning of the diesel engine, this induction lag should be as brief as possible.

When a fuel has long induction lag, a portion of the injected fuel gets accumulated in the cylinder before ignition and when ignition takes place, the accumulated fuel burns violently leading to sudden increase in temperature and pressure. This non-uniform burning of the fuel is known as diesel knocking. The greater is the induction lag, higher in the diesel knock.

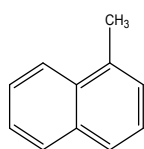
Chemically, the diesel engine fuel consists of straight long chain hydrocarbons with minimum amount of branched chain and aromatic hydrocarbons. Thus, in contrast to gasoline, the diesel engine fuel should have low spontaneous ignition temperature so as to minimize the induction lag.



## **Cetane Number or Cetane Rating:**

It is used for rating diesel oil. Cetane number is a measure of fuel's ignition delay. It represents the spontaneous ignition temperature of a particular diesel fuel. It is the measure of the ease, with which the fuel will ignite under compression. The hydrocarbon, cetane (n-hexadecane) has a very short ignition delay (ignite rapidly) than any other diesel fuel and is assigned arbitrarily cetane no. 100. On the other hand,  $\alpha$ -methyl naphthalene has a long ignition delay (ignites slowly) compared to any other diesel fuel and hence, is assigned cetane no. of zero.

$\text{CH}_3(\text{CH}_2)_{14}\text{CH}_3$  (Cetane) (cetane no.100)



( $\alpha$ -methyl naphthalene) (Cetane No. Zero)

Thus, cetane number of a diesel fuel can be defined as the percentage of cetane and  $\alpha$ -methyl naphthalene, which has the same ignition properties as that of the fuel under examination at the same set of conditions. For example, a diesel fuel will have a cetane number of 60, if it has the same ignition characteristics as that of a mixture of 60% cetane and 40%  $\alpha$ -methyl naphthalene.

The cetane number of a fuel depends on the nature and composition of hydrocarbons. The straight chain hydrocarbons ignite quite readily and have higher cetane number compared to aromatics, which have lower cetane number. The decreasing order of cetane number is as follows.

n-alkanes > naphthalene > alkenes > branched alkanes > aromatics

Thus, hydrocarbons which are poor gasoline fuels are quite good diesel fuels.

The cetane rating of a diesel fuel can be raised by addition of small quantity of certain pre-ignition drops, such as ethyl nitrite, isoamyl nitrite, acetone peroxide, nitronaphthalene etc.

## **Power alcohols (non-petrol fuels):**

Power alcohol is a mixture of 5-25% ethyl alcohol with petrol and is used as a fuel in IC engines.

### **Advantages of power alcohol:**

- Ethyl alcohol has an octane number 90 and has good anti-knocking properties, where as that of petrol is 60-70. Thus, blending petrol with ethyl alcohol improves the anti-knocking properties and octane number of the petrol,
- Use of power alcohol reduces the carbon monoxide emission from the engine.

➤ Ethyl alcohol absorbs traces of moisture. The petrol power alcohol is cheaper than alcohol.

**Disadvantages of power alcohol:**

- Ethyl alcohol lap calorific value is (7000 kcal/kg) is much lesser than that of petrol (11,500kcal/kg). Hence addition of ethyl alcohol to petrol reduces its calorific value by 35%.
- Its surface tension is high and its atomization is difficult at lower temperature. This leads to starting trouble in a vehicle and the vehicle remain sluggish for quite some time after starting.
- It may undergo oxidation reaction to form acetic acid which corrodes engine parts.
- The output power generated is reduced to 35%.
- As it contains oxygen atom, the amount of air required for complete combustion is less. Therefore, the carburettor and engine need to be modified.

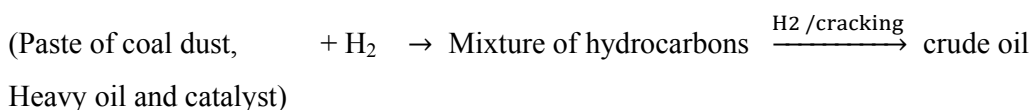
**Synthetic petrol:**

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

**Bergius process:**

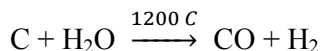
This process, developed by Bergius of Germany involves the conversion of low grade coals, such as bituminous or brown coals into liquid and gaseous fuels by hydrogenating them in the presence of catalyst. In process, low ash coal is powdered and mixture with heavy oil and catalyst (tin or Ni) to make a paste. This paste is heated in a converter with hydrogen at 450 °C and 200-250 atm pressure for 2h.

The coal undergoes hydrogenation to form saturated hydrocarbons that decompose at prevailing high temperature and pressure to yield low boiling liquid hydrocarbons. The vapour leaving the chamber is condensed to get a liquid resembling crude oil. This is subjected to fractional distillation to give gasoline, middle oil and heavy oil. Middle oil is again hydrogenated to obtained gasoline. The gasoline so obtained contains 74% power alcohol, 22% aromatics and 4% olefins. Yield is 60%.



### **Fischer-Tropsch method:**

In this method, coke is converted into water gas (CO + H<sub>2</sub>) by passing steam over red hot coke.



A mixture of water gas and hydrogen is purified by passing through Fe<sub>2</sub>O<sub>3</sub> (to remove H<sub>2</sub>S) and then through a mixture of Fe<sub>2</sub>O<sub>3</sub> + Na<sub>2</sub>CO<sub>3</sub> to remove organic Sulphur compound.

The purified gas is compressed to 5.25 atm and then passed through a catalytic converter maintained at about 200-300 °C. The catalyst consists of a mixture of cobalt (100 parts) Thorium (5parts), Magnesia (8 parts) and Keiselghur earth (is a soft, porous, silicious sedimentary rock, that easily crumbled to powder). A mixture of saturated and unsaturated hydrocarbons is formed. All the reactions are exothermic.

The vapours formed are passed through a cooler, where liquid resembling crude oil is obtained. This is then subjected to fractional distillation to yield gasoline, diesel and heavy oil. The heavy oil is reused for cracking to obtained more gasoline.

## **Gaseous Fuels**

### **Natural gas:**

It is associated with petroleum in nature and occurs near coal mines and oil fields. It is a mixture of methane and higher hydrocarbons such as n-propane, n-butane, isobutene, iso-pentane etc. Natural gas associated with crude oil, is termed as dry gas. Wet gas has higher calorific value than dry gas.

### **Composition of Natural gas:**

CH<sub>4</sub>= 70-90%,      C<sub>2</sub>H<sub>6</sub>= 5-10%,      H<sub>2</sub>= 3%,      Remaining CO and CO<sub>2</sub>

**Calorific value** = 12000-14000 kcal / m<sup>3</sup>

**Application:** As fuel in domestic and industrial sector as well as in motor vehicles.

As important ingredient in manufacture of various fertilizers, plastics, pharmaceuticals, fabrics and antifreeze agents.

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

It is obtained by compressing natural gas to a high pressure of about 1000 atm. It is used as substitute for petrol and diesel. It is a very clean and economical fuel. It is better than LPG because it is safer than gasoline and has high ignition temperature than gasoline and diesel.

Lighter than air and disperses easily in air and minimize the risk of ignition. LPG is heavier than air and settle at the ground and hence, risky.

CNG produces lesser CO on combustion and do not emit forbidden pollutants such as SO<sub>2</sub>, SO<sub>3</sub>, HCHO etc.

### **LPG (Liquefied Petroleum Gas):**

LPG is used as fuel in domestic, industrial vehicles. It is obtained as a by-product during cracking of heavy oils or from natural gas. It is bottled in cylinders under high pressure and ethyl mercaptan is added to detect leakage.

**Composition:** n-butane, i-butane, butylenes and propane

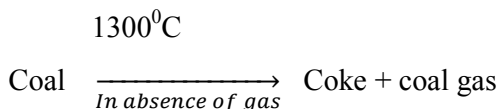
**Properties:** Colourless, 1.5-2 times heavier than air, Non toxic and non poisonous gas

High **calorific value** of about 27800 kcal / m<sup>3</sup>

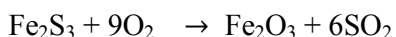
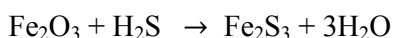
It is nearly three times the calorific value of natural gas and 7 times greater than that of coal gas.

### **Coal gas:**

It is obtained when coal is heated in absence of air at about 1300 °C in coke. The fuel used for the purpose is a mixture of producer gas and air.



Tar, NH<sub>3</sub>, naphthalene and benzene are removed by passing through water, cold water, petroleum respectively. H<sub>2</sub>S is removed by passing it over moist ferric oxide.



Coal gas is a colourless gas having characteristic odour is lighter than air and burns with long smoky flame.

**Composition:** H<sub>2</sub>=40%, CH<sub>4</sub>=32%, CO=7%, C<sub>2</sub>H<sub>2</sub>=2%, C<sub>2</sub>H<sub>4</sub>=3%, N<sub>2</sub>=4%, CO<sub>2</sub>=1%

**Calorific value:** 4900 kcal / m<sup>3</sup>

**Uses:** As illuminants in cities and towns. As Fuel. As raw material for NH<sub>3</sub> production.

### **Producer gas:**

Composition: CO = 22-30%, H<sub>2</sub> = 8-12%, N<sub>2</sub> = 52-55%, CO<sub>2</sub> = 3%

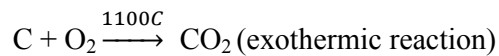
Calorific value: 900-1300 kcal / m<sup>3</sup>

It is insoluble in water and poisonous in nature.

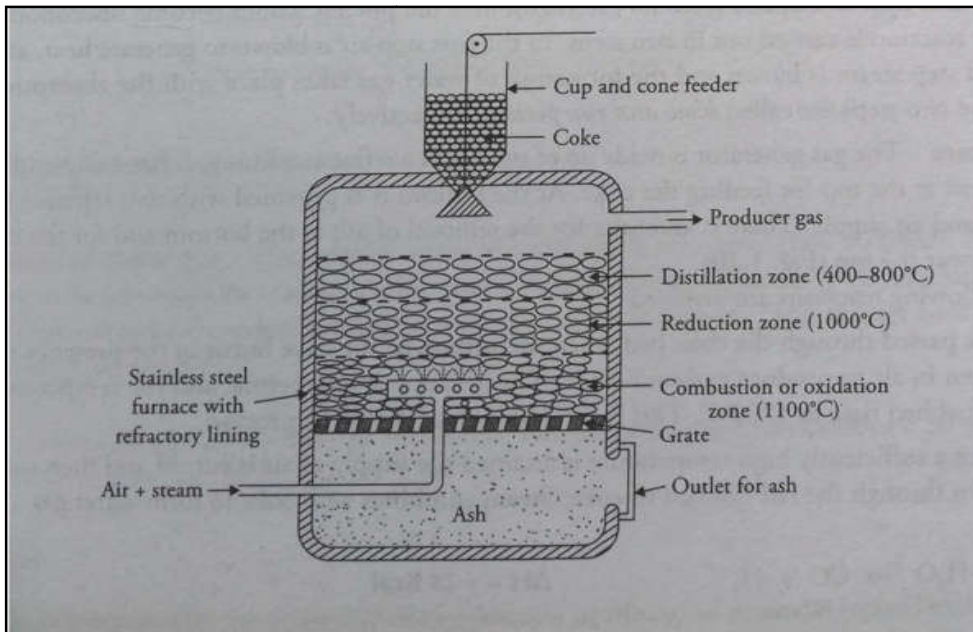
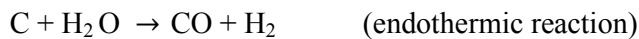
**Uses:** As reducing agent in metallurgical operations. used as fuel in the muffle furnace and retorts.

### **Production:**

It is resulted from the incomplete combustion of coal or coke in a partly closed generator, called gas producer. It is made by admitting a mixture of air and steam to the bottom of the gas producer. Upon reaching the combustion zone, the reaction occurs as:



The hot gases from the combustion zone heat the fuel in the reduction zone and the following reaction takes place:



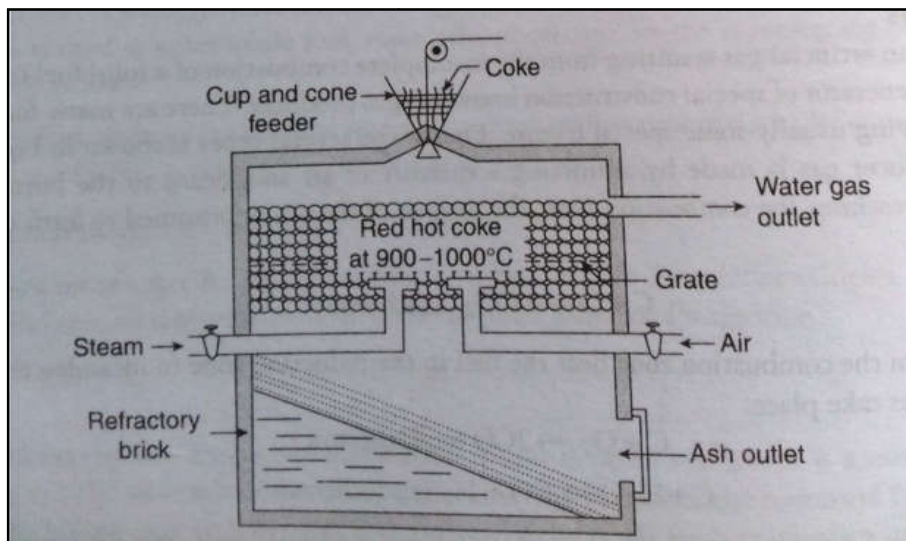
**Figure 3.5:** Gas producer for manufacture of producer gas.

## Water gas:

**Production:** The principle involved is same as in making producer gas, except in water gas, the air and steam are blown in an alternate intervals over a red hot coke at about 1000°C.



(Water gas)



**Figure 3.6:** Water gas plant.

Composition:  $\text{H}_2 = 51\%$ ,  $\text{CO} = 41\%$ ,  $\text{N}_2 = 4\%$ ,  $\text{CO}_2 = 4\%$

Calorific value:  $2800 \text{ kcal / m}^3$

Water gas burns with blue flame, hence it is termed as blue gas.

**Uses:** As fuel is Fischer-Tropsch process for manufacture of synthetic petrol.

Also used for the manufacture of methanol.

## Kerosene gas:

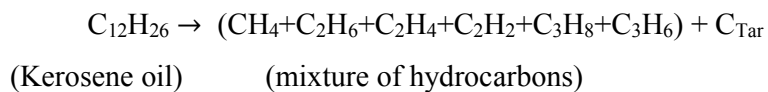
It is obtained by cracking kerosene oil.

Composition:  $\text{CH}_4 = 25\text{-}30\%$ ,  $\text{H}_2 = 50\text{-}55\%$ ,  $\text{CO} = 10\text{-}15\%$ ,  $\text{CO}_2 = 3\%$

Calorific value:  $4500 \text{ kcal / m}^3$

**Uses:** As laboratory gas, used to improve calorific value of water gas and these two gases are called carburetted water gas.

**Production:** A stream of kerosene oil is continuously allowed to fall in a red hot bottom of the retort resulting in cracking of the oil into a number of lower gaseous hydrocarbons.



Tar is removed by passing through water tank.

**References:**

1. Wiley Engineering Chemistry, second edition, Wiley India Pvt. Ltd.
2. Engineering Chemistry- Fundamentals and applications, by Shikha Agarwal, Cambridge University Press