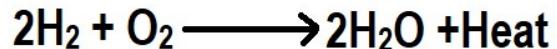


Introduction

- A fuel is a substance that produces large amount heat energy either through combustion or through nuclear reaction. This large amount of heat energy can be used economically for domestic and industrial purposes.
- Fuel that produces heat energy by combustion are termed as “chemical fuels”.. During the process of combustion of a chemical fuel the atoms of Carbon, Hydrogen, Sulphur etc combine with oxygen with simultaneous liberation of heat. In the process of combustion, the chemical energy of fuel is converted into heat energy. The concept generally applied to those materials which store energy in the form of chemical energy that could be released through combustion only when needed. For example **Wood, Coal , charcoal coke petrol etc.**



- However combustion is not always necessary for a fuel to produce heat. Energy can also be liberated by fission or fusion of nuclei. This energy is much greater than the energy released by chemical fuel and such type of fuel are known as nuclear fuel. For example plutonium, uranium etc.

CLASSIFICATION OF FUEL

Fuel can be classified on the basis of their (i) occurrence and (ii) Physical state

(i) On the basis of occurrence fuel are also classified in to two categories.

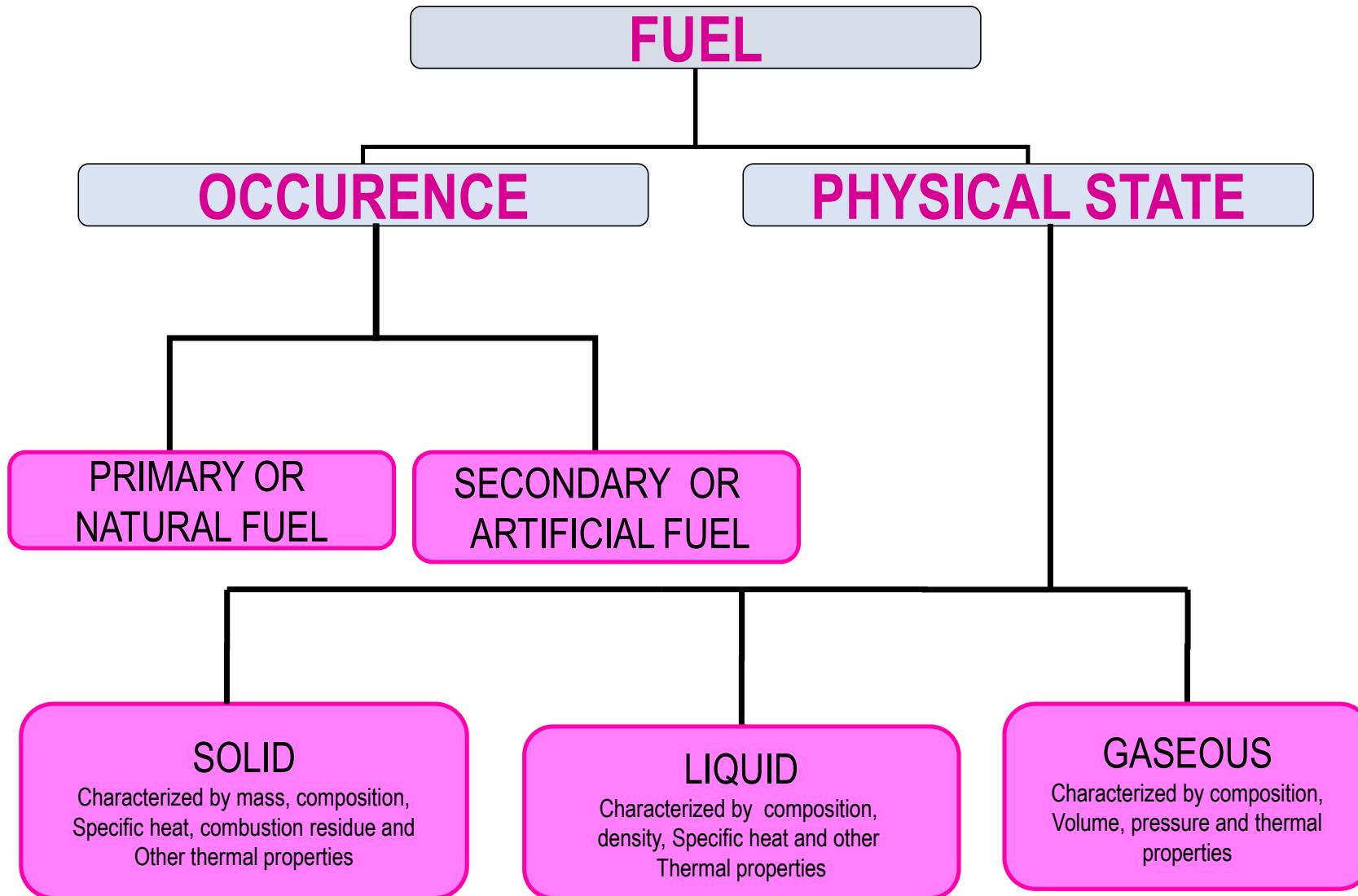
(a) **Primary Fuel or Natural Fuels:** These are found to occur in nature and are used either processing to a certain extent or without processing but the chemical comical constitution of fuel does not alter. These are also known as fossil fuels. For example: Wood, peat, lignite, coal, petroleum, natural gas etc.

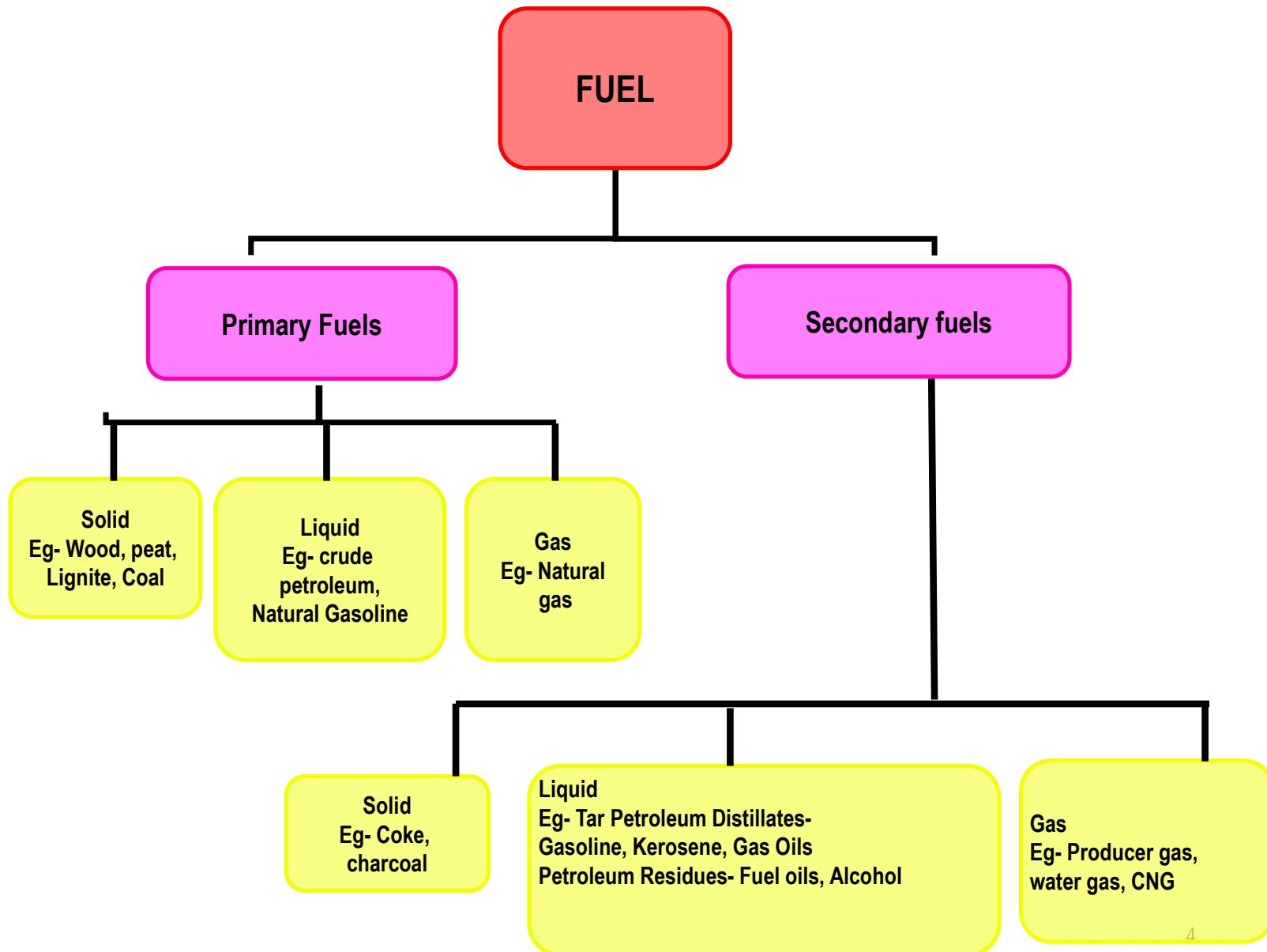
(b) **Secondary fuel or derived fuel:** These are the fuel that are derived from primary fuels by further chemical processing .
For example coke, kerosene, producer gas, water gas etc.

Both primary and secondary fuels may be further classified based upon their physical state as

- (a) Solid fuels.
- (b) Liquid fuels.
- (c) Gaseous fuels.

CLASSIFICATION OF FUEL





CHARACTERISTICS OF GOOD FUEL

1. HIGH CALORIFIC VALUE:

A good fuel should have high calorific value i.e. it should produce large amount of heat on burning.

2. MODERATE IGNITION TEMPERATURE:

Ignition temperature: the lowest temperature to which fuel must be pre-heated so that it starts burning smoothly. If ignition temp. is low, the fuel catches fire easily. Low ignition temperature is dangerous for storage and transportation of fuel. High temperature causes difficulty in handling. So ,a good fuel should have moderate ignition temperature.

3. LOW MOISTURE CONTENT:

A good fuel should have low moisture content as moisture content reduces the calorific value.

4. LOW NON-COMBUSTIBLE MATTER CONTENT:

A good fuel should have low contents of non-combustible material as non-combustible matter is left in form of ash which decreases the calorific value of fuel

5. MODERATE RATE OF COMBUSTION:

The temperature of combustion of fuel depends upon the rate of combustion. If the rate of combustion is low, then required high temperature may not be reached soon. On the other hand, too high combustion rate causes high temperature very quickly.

CHARACTERISTICS OF GOOD FUEL

6. MINIMUM SMOKE AND NON-POISONOUS GASES:

On burning, fuel should not give out objectionable and poisonous gases. In other words, gaseous products should not pollute the atmosphere. Gases like CO, SO₂, H₂S etc. are some of harmful gases.

7. CHEAP:

A good fuel should be cheap and readily available.

8. EASY TRANSPORTATION:

A good fuel should be easy to handle and transport at low cost

9. CONTROLLABLE COMBUSTION:

Combustion of fuel should be easy to start or stop when required.

10. NON SPONTANEOUS COMBUSTION:

Combustion of fuel should be non-spontaneous otherwise it can cause fire hazards.

11. LOW STORAGE COST:

A good fuel should be easily stored at low cost.

Comparison of solid, liquid and gaseous fuel

PROPERTY	SOLID FUELS	LIQUID FUELS	GASEOUS FUELS
CALORIFIC VALUE	Less calorific value (CV) and thermal efficiency (TE) due to high ash and moisture content	High CV and TE than solid fuels	High CV and TE than solid fuels
CONTROL OF COMBUSTION	Not easily controlled. They possess moderate ignition temperature. Combustion is slow but it can not controlled.	Easily controlled by regulating liquid flow. For liquid fuel combustion takes place readily.	Easily controlled by temperature variation and air supply. Combustion is very fast for gaseous fuel.
APPLICATIONS	Not used in Internal combustion engine (ICE)	Used in ICE	Used in ICE
MERITS	<ul style="list-style-type: none"> 1. Have moderate ignition temperature 2. Low production cost as they are not easily explosive so easily transported and stored 	<ul style="list-style-type: none"> 1. Combustion products are clean and dust and soot free 2. Need less air for complete combustion 3. Easily fired and extinguished 	<ul style="list-style-type: none"> 1. Complete combustion occurs so no release of smoke or ash particles 2. Preheating can be done to overcome the heat of combustion

Comparison of solid, liquid and gaseous fuel

PROPERTY	SOLID FUELS	LIQUID FUELS	GASEOUS FUELS
DEMERITS	<ol style="list-style-type: none">1. Need excess air for combustion so uncontrollable2. They block air circulation during combustion thus accelerates corrosion3. Flue gases are released containing dust and soot particles	<ol style="list-style-type: none">1. High production cost so not stored easily2. Require special combustion burners thus releasing offensive odour	<ol style="list-style-type: none">1. High production cost so not stored easily2. Highly inflammable so risky

CALORIFIC VALUE

It is defined as the total amount of heat (expressed in calories or kilo calories) liberated when a unit mass (1gm or 1kg) or volume of the fuel is burnt completely.

It depends upon the *nature of the fuel* and the *relative proportions of the elements* present. If moisture is present there is considerable reduction the calorific value of a fuel. The calorific value may be theoretically calculated from the chemical composition of the fuel.

If both hydrogen and oxygen are present, it may be assumed that all the oxygen are already combined with 1/8 of its weight of hydrogen to form water. This fraction is then deducted from the hydrogen content of the fuel in the calculation. Thus for a fuel containing carbon, hydrogen, oxygen and sulphur, the calorific value of the fuel is given by **DULONG FORMULA**

Determination of calorific value from Dulong formula (Theoretically)

$$\text{Calorific value} = 1/100 [8080 C + 34500 \{H - O/8\} + 2240 S] \text{ kcal/kg}$$

Where, C = % of Carbon, CV = 8080

H = % of Hydrogen, CV = 34500

O = % of Oxygen, and

S = % of Sulphur, CV = 2240

UNITS FOR heat

BTU – The amount of heat needed to raise the temperature of 1 lb (pound) of water by 1°F .

$$1 \text{ BTU} = 252 \text{ Cal} = 1054.6 \text{ J} = 1054.6 \times 10^7 \text{ erg}$$

2. Calorie – The amount of heat needed to raise the temperature of 1 g of water by 1°C .

$$1 \text{ Calorie} = 4.815 \text{ J} = 4.815 \times 10^7 \text{ erg}$$

3. Kilocalories: The amount of heat needed to raise the temperature of 1 kg of water by 1°C .

$$1 \text{ Kcal} = 1000 \text{ Cal}$$

Units of calorific value

The units of calorific value for solid, liquid and gaseous fuels are given below.

System	Solid / Liquid fuels	Gaseous fuels
CGS	calories/gm	calories/ cm ³
MKS	Kcal/Kg	Kcal/m ³
BTU	B.T.U./lb	B.T.U./ ft ³

These units can be interconverted as follows

$$1 \text{ cal/g} = 1 \text{ Kcal/kg} = 1.8 \text{ B.T.U./lb}$$

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

$$1 \text{ B.T.U. /ft}^3 = 9.3 \text{ Kcal/m}^3$$

GROSS AND NET CALORIFIC VALUE

With fuels containing hydrogen, two calorific values are distinguished, **the gross and the net calorific value**

GROSS OR HIGH CALORIFIC VALUE (GCV OR HCV)

(Gross calorific value also known as higher calorific value).

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.

Usually all fuel contains hydrogen. During combustion, the hydrogen present in the fuel is converted into steam. When the combustion products are cooled to room temperature, the steam gets condensed into water and heat that equals to the latent heat of condensation of the steam evolved. This heat gets included in the measured heat and so its value is high.

Hence ,it is called higher calorific value.

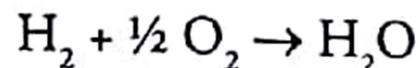
NET OR LOWER CALORIFIC VALUE (NCV OR LCV)

Net calorific value is the heat produced when unit quantity (mass/volume) of a fuel is burnt completely and the products of combustion are allowed to escape.

Under normal working conditions, when a fuel is burnt water vapour escape along with hot combustion gases. Hence heat available lesser than the gross calorific value. So net calorific value also known as low calorific value.

Thus $LCV = HCV - \text{Latent heat of water vapour formed.}$

As 1 part by weight of hydrogen gives 9 parts by weight of water,



$LCV = HCV - \text{Weight of hydrogen in fuel} \times 9 \times \text{latent heat of steam}$

GROSS CALORIFIC VALUE AND NET CALORIFIC VALUE

Dulong's formula for calorific value from the chemical composition of fuel is :

$$HCV = \frac{1}{100} [8,080 C + 34,500 (H - \frac{O}{8}) + 2,240 S] \text{ kcal/kg}$$

where C, H, O, and S are the percentages of carbon, hydrogen, oxygen and sulphur in the fuel respectively. In this formula, oxygen is assumed to be present in combination with hydrogen as water, and

$$LCV = [HCV - \frac{9H}{100} \times 587] \text{ kcal/kg}$$

$$LCV = [HCV - 0.09 H \times 587] \text{ kcal/kg}$$

This is based on the fact that 1 part of H by mass gives 9 parts of H₂O, and latent heat of steam is 587 kcal/kg.

Example 1: 2kg of coal sample was burnt in a bomb calorimeter. The heat liberated was estimated and found to be 14114 Kcal. Calculate the calorific value of the coal sample.

Ans: Heat liberated on burning of 2 kg coal = 14114 Kcal

Therefore, heat liberated on the combustion of 1Kg coal = $\frac{14114}{2} = 7057$ Kcal.

Example 2 : The gross calorific value of a fuel containing 8% of hydrogen was found to be 9230 Kcal/kg. calculate net calorific value.

Ans :

$$NCV = GCV - 0.09 \times H \times \text{Latent heat of steam}$$

[As we know latent heat of steam is 587 Kcal/kg]

$$NCV = [9230 - 0.09 \times 8 \times 587] \text{ Kcal/kg}$$

$$= 9230 - 422.64$$

$$= 8807.36 \text{ Kcal/kg}$$

Exmple3: Calculate the gross and net calorific values of a coal sample having the following composition

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

Solution

$$(I) \text{ G.C.V} = 1/100[8080 C + 34500(H - O/8) + 2240 S] \text{ Kcal/kg}$$

$$= 1/100[8080 \times 80 + 34500(7 - 3/8) + 2240 \times 3.5] \text{ Kcal/kg}$$

$$\sim 8828.0 \text{ Kcal/kg}$$

, ,

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

$$= 8828 - [0.09 \times 7 \times 587] \text{ Kcal/kg}$$

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

Bomb Calorimeter

It is used to calculate Calorific Value of solid and non-volatile liquid fuels experimentally.

Principle: A known mass of a fuel is burnt in presence of excess oxygen and the heat liberated is absorbed in a known amount of water. This heat liberated is measured by observing the change in temperature. The calorific value of the fuel can be calculated using following principle

Heat liberated by the fuel = Heat absorbed by water and the calorimeter.

Thus the quantity of heat produced by burning a unit mass of the fuel is calculated.

Generally Bomb calorimeter

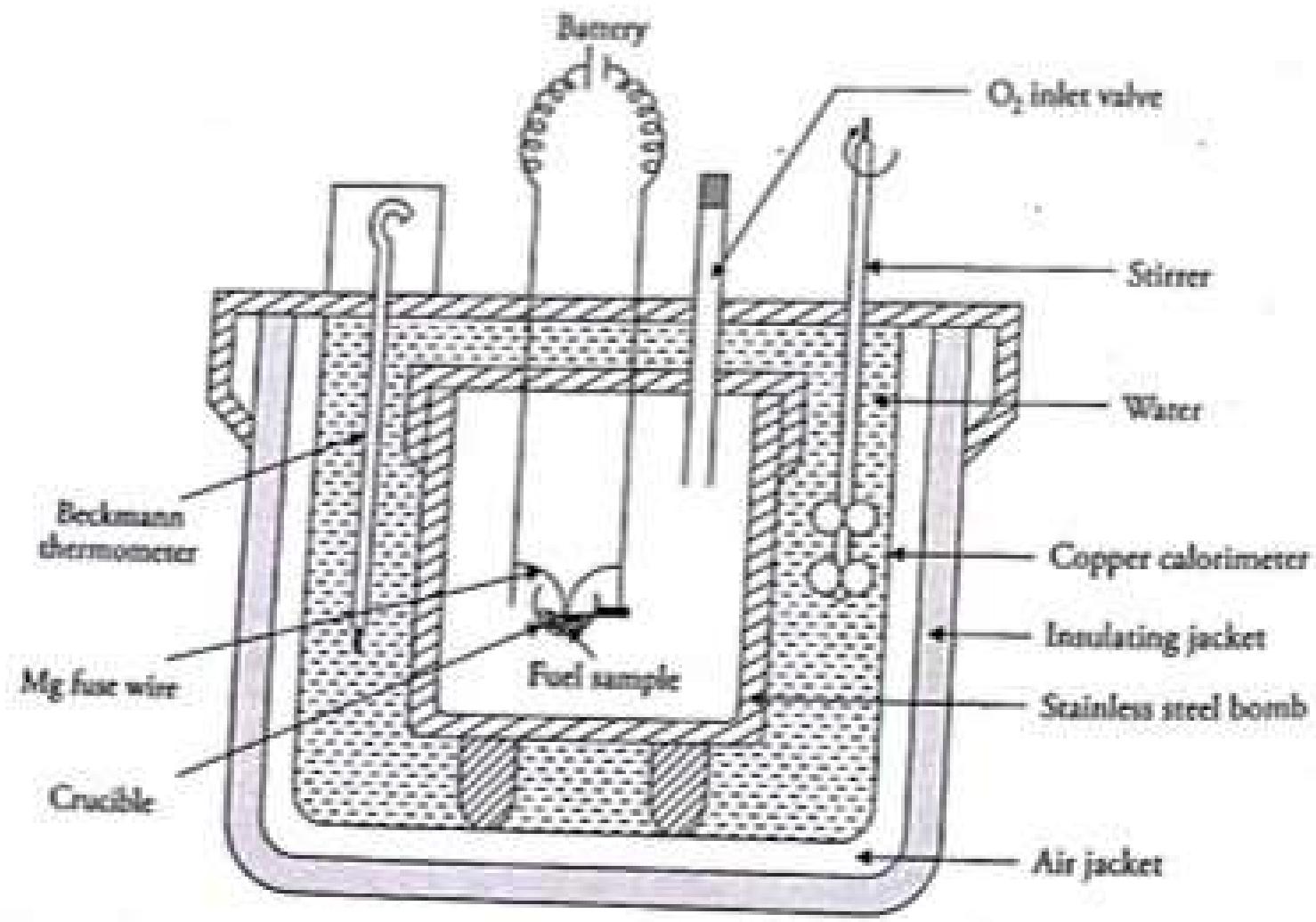
- Generally Bomb calorimeter used to measure enthalpy changes of combustion reactions at a constant volume
- In Bomb calorimeter there is tiny inner metal chamber which is known as a bomb
- The bomb contains pure oxygen, the reactants are ignited using an electric coil
- A known quantity of water surrounds the bomb and absorbs energy that is released by the reaction
- To obtain precise heat measurements, we must know or find out the heat capacity of the bomb calorimeter
- Heat capacity takes into account all the parts of the calorimeter that can lose or gain.

$$C_{\text{total}} = C_{\text{water}} + C_{\text{thermometer}} + C_{\text{stirrer}} + C_{\text{container}}$$

$$\text{and } q_{\text{cal}} = C_{\text{total}} \Delta T$$

C_{total} = heat capacity of the calorimeter

CONSTRUCTION:



CONSTRUCTION:

- (i) **Stainless steel bomb:** It consists of a cylindrical vessel called bomb, made of stainless steel, in which the combustion of fuel occurs. The bomb is provided with lid, which can be screwed to the body of bomb so as to make a perfect gas tight seal. The lid is provided with electrodes and an oxygen inlet value. To one of the electrodes, a small ring is attached. This ring is utilized to support a nickel or stainless steel crucible in which fuel burnt. A small length of a platinum/ Mg wire is framed in a loop dipping in the fuel and connected to the electrodes which are joined to the terminal of a battery. The role of Pt is in bomb calorimeter is to resist corrosive action of HNO_3 and H_2SO_4 vapours formed because of burning of fuel So the inner side of bomb designed such a way that it resist high pressure and corrosion which may be caused during the combustion.
- (ii) **Copper calorimeter:** This bomb is placed in the copper calorimeter containing a known weight of water.. An accurate thermometer, which can read the accurate temperatures up to $1/100^\circ\text{C}$, is fitted to the lid. An electrified operating stirrer is provided to stir in the copper calorimeter thoroughly.
- (iii) **Air jacket and water jacket:** The copper calorimeter is surrounded by an air jacket along with a water jacket to prevent loss of heat due to radiation.

Working:

A known amount of the fuel (generally 0.5-1gm) is taken in the crucible. A fine Mg wire, touching the fuel sample is then stretched across the electrodes. About 10 mL of distilled water is introduced into the bomb to absorb vapors of sulfuric acid and nitric acid formed during combustion. The bomb lid is tightly screwed. The bomb is filled with oxygen at 25 atmospheric pressure and placed in a copper calorimeter containing a known weight of water. The initial temperature (T_1) of the water is noted after thorough stirring. The electrode then connected with 6-volt battery to complete the circuit. The sample burns and heat is liberated. This heat is absorbed by water. Maximum temperature of thermometer is recorded. Time taken to cool the water in the calorimeter from maximum temperature to room temperature is also noted.

CALCULATIONS:

Let,

Weight of fuel sample taken

$$= x \text{ gm}$$

Weight of water in the calorimeter

$$= W \text{ gm}$$

Water equivalent of calorimeter , stirrer, thermometer , bomb etc

$$= w \text{ gm}$$

Initial temperature of water in calorimeter

$$= t_1 {}^{\circ}\text{C.}$$

Final temperature of water in calorimeter

$$= t_2 {}^{\circ}\text{C.}$$

Higher calorific value of fuel

$$= H \text{ caloric/gm}$$

Heat liberated by burning of fuel

$$= x \times H$$

Heat gained by water

$$= W \times \Delta T \times \text{specific heat of water.}$$

$$= W \times (t_2 - t_1) \times S_{\text{water}}$$

$$= W \times (t_2 - t_1) \times 1 \quad = W \times (t_2 - t_1)$$

Heat gain by calorimeter

$$= w \times (t_2 - t_1)$$

Total heat gained

$$= W \times (t_2 - t_1) + w \times (t_2 - t_1)$$

$$= (W + w) \times (t_2 - t_1)$$

But

Heat liberated by the fuel = Heat absorbed by water and calorimeter

$$\text{So, } x \times H = (W + w) \times (t_2 - t_1)$$

CALCULATIONS:

$$x \times H = (W + w) \times (t_2 - t_1)$$

$$H = \frac{(W + w) \times (t_2 - t_1)}{x}$$

Generally H is known as gross calorific value (GCV) or high calorific value (HCV)

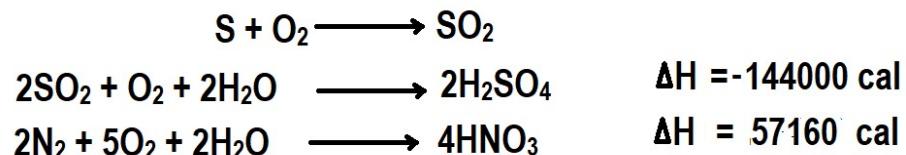
Now net calorific value (NCV) or lower calorific value (LCV) will be

$$LCV = HCV - 0.09 H \times 587 \text{ cal/gm}$$

Heat taken by water in converting steam = 587 cal/gm

CORRECTIONS:

1. **Fuse wire corrections (FWC):** The gross calorific value calculated above includes the heat liberated by the ignition of Mg fuse wire. Hence this amount of heat has to be subtracted from the total value.
2. **Acid corrections (AC):** when fuels containing S and N are oxidized to high temperatures they form H_2SO_4 and HNO_3 releasing energy (exothermic) that must be considered. The formation of acids is exothermic and this should be subtracted from the obtained value of GCV.



CORRECTIONS:

3.Cooling corrections: Heating and cooling are simultaneous process. As the temperature rises above the room temperature, the loss of heat occurs due to radiation and higher temperature recorded will be slightly less than the obtained if there was no heat loss. A temperature correction (cooling correction) is therefore necessary to get the correct rise in temperature.

If the time taken for the water in the calorimeter to cool from maximum temperature attained to room temperature is x minutes and the rate of cooling is dt/min , then the cooling correction is

$$= x \times dt$$

And this is added to the rise in temperature.

$$HCV \text{ of fuel } (H) = \frac{(W + w)(t_2 - t_1 + \text{cooling correction}) - (\text{Acid} + \text{fuse wire correction})}{\text{Mass of the fuel } (x)}$$

Numerical problem 3: A coal sample has the following composition by weight. C = 90%, O = 3%, S = 0.5%, N = 0.5 % and ash = 2.5%. Net calorific value of the fuel was found to be 8490 kcal/kg. Calculate the % of H and GCV.

Ans:- We know $Ncv = [Hcv - 0.09H \times 587] \text{ kcal/kg}$

$$\Rightarrow Hcv = [Ncv + 0.09H \times 587] \text{ kcal/kg}$$

$$\Rightarrow Hcv = [8490 + 52.8H] \text{ kcal/kg} \quad \textcircled{1}$$

According to Dulong formula Calorific value can be expressed as

$$Hcv = \frac{1}{100} [8080 \times C + 34500(H - \frac{O}{8}) + 2240 \times S] \text{ kcal/kg}$$

$$= \frac{1}{100} [8080 \times 90 + 34500(H - \frac{3}{8}) + 2240 \times 0.5] \text{ kcal/kg}$$

$$= \frac{1}{100} [727200 + 34500H - 12937.5 + 1120] \text{ kcal/kg}$$

$$= \frac{1}{100} [715382.5 + 34500H] \text{ kcal/kg}$$

$$Hcv = [7153.825 + 345H] \text{ kcal/kg} \quad \textcircled{2}$$

Comparing equation II with equation I we get:

$$[7153.825 + 345H] \text{ kcal/kg} = [8490 + 52.8H] \text{ kcal/kg}$$

$$\Rightarrow 345H - 52.8H = 8490 - 7153.825$$

$$\Rightarrow 292.2H = 1336.175$$

$$\Rightarrow H = \frac{1336.175}{292.2}$$

$$\simeq 4.5728 \%$$

$Hcv = [Ncv + 0.09H \times 587] \text{ kcal/kg}$

$$= 8490 + 52.8H$$

$$= [8490 + 52.8 \times 4.5728] \text{ kcal/kg}$$

$$= [8490 + 241.4438] \text{ kcal/kg}$$

$$= 8731.4438 \text{ kcal/kg}.$$

Solid fuel: Coal

Solid fuel: Solid fuel refers to several types of solid materials that are used to produce energy. For example wood, coal etc.

Coal: Coal is regarded as a fossil fuel produced from large accumulations of vegetable debris due to partial decay and alteration by the action of heat and pressure over millions of years. Coal is a highly carbonaceous matter that has been formed as a result of alteration of vegetable matter (e.g., plants) under certain favourable conditions. It is chiefly composed of C, H, N, S and O, besides non-combustible inorganic matter.

Types of Coal : Coals are classified on the basis of their rank. Rank is defined as the degree or extent of maturation and is therefore a qualitative measure of carbon contents. Peat, lignite and sub-bituminous coals are referred as low rank coals while bituminous coals and anthracites are classed as high rank. In European terminology, the lignite and sub-bituminous coals are called soft coals while bituminous coals and anthracite coals are termed as hard coals.

Analysis of Coal

There are two methods: proximate analysis and ultimate analysis.

1. Proximate Analysis: It includes the determination of moisture, volatile matter, ash and fixed carbon. This gives quick and valuable information regarding commercial classification and determination of suitability for a particular industrial use.

2. Ultimate Analysis: It includes the determination of carbon, hydrogen, nitrogen, sulphur and oxygen in coal. It is used for the determination of elements present in the coal and also known elemental analysis. This analysis gives exact results and are useful in calculating the calorific value of coal using Dulong's formula.

Proximate analysis

1. Moisture Content (MC) : 1gm of powdered and air-dried coal sample in crucible is heated at 105-110°C in an electric air oven for 1 hour. Then the sample is cooled to room temperature and weighed again. The loss in weight represents moisture. The loss in weight of the sample is found out and percentage of moisture is calculated as % of moisture.

Proximate analysis

Calculation:

Let the weight of coal sample = W gm

Weight after heating for 1 hour = W_1 gm

Loss in weight that is weight of moisture = $(W - W_1)$

$$\% \text{ of Moisture} = \frac{(W - W_1)}{W} \times 100\%$$

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

Significance of Moisture content

- (i) Moisture in coal evaporates during the burning of coal and it takes some of the burning of coal and it takes some of the liberated heat in the form of latent heat of evaporation. Therefore, moisture lowers the effective calorific value of coal.
- (ii) Moisture quenches the fire in the furnace. Hence, lesser the moisture content, better the quality of coal as a fuel.
- (iii) It increases the consumption of coal for heating purpose. So presence of higher amount of moisture in coal lengthens the time of heating.
- (iv) However, presence of moisture, up to 10%, produces a more uniform fuel-bed and less of "fly-ash".

Proximate analysis

2. Volatile matter: The volatile matter present in the coal may be combustible gases such as H₂, CO, CH₄, and other hydrocarbons or non combustible gases such as CO₂ and N₂. It does not include moisture of the coal.

It is determined by heating known weight of moisture free coal in a silica crucible covered with a vented lid at 950± 20°C for 7 min in a muffle furnace. The crucible is then taken out and cooled inside a desiccator and weighed again. Complete removal of volatile matter is judged by bubbling the gas through a water seal. Loss in weight give the weight of the volatile matter and **% of volatile** mater is calculated.

Let the weight of coal sample = W gm

Let the weight of coal sample after heating for 1 hr that is weight after removal of moisture is = W₂ g

Let the weight of sample after removal of volatile matter = W₂ gm

$$\text{So, \% of volatile matter} = \frac{(W_1 - W_2)}{W} \times 100$$

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

Proximate analysis

Significance of volatile matter:

- Volatile matters are the CH₄, Hydro carbons, and CO, and incombustible gases like CO₂ and NO₂ in coal. Thus the volatile matter is an index of the gaseous fuels present. Typical range of volatile matter is 20 to 35%.
- Coal containing high % of volatile matter burns with a long flame, high smoke and low calorific value
- A high % of volatile matter indicates that a large amount of fuel is burnt as gas.
- Presence of non-combustible gases is undesirable since they do not add to the heat value.
- For efficient use of fuel the outgoing combustible gas (volatile matter) has to be burnt by supplying secondary air. This requires a large combustion space.
- If the furnace volume is small or flame is short, a large amount of volatile matter will escape unburnt
- Coal with greater % of volatile matter (Say more than 40%) do not form coke well. Presence of low volatile matter (less than 10%) do not cake at all end and not form good quality coke. Coal having medium (20-30%) volatile matter are capable of forming hard and strong coke during carbonization.
- High volatile matter containing coal useful in coal gas manufacture because volatile matter in a coal denotes the proportion of coal that will be converted into gas and tar products by heat. Whereas for preparation of metallurgical coke, coal with low volatile matter is preferred.

Proximate analysis

3. Analysis of Ash:

After the removal of moisture and volatile matter the residual coal in the crucible is further heated without lid in a muffle furnace at $700 \pm 50^\circ \text{ C}$ for $\frac{1}{2} \text{ hour}$. The crucible is then taken out, cooled first in air, then in desiccator and weighed. The heating, cooling and weighing is to be repeat until a *constant weight* is obtained. The residue is reported as ash on percentage-basis. % of Ash can be calculated as

Let the weight of coal sample = W gm

Let the weight of ash formed = W_3 gm

$$\% \text{ of ash} = \frac{W_3}{W} \times 100$$

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

Proximate analysis

Significance of Ash

- (i) Ash is the combination product of mineral matter in the coal. It consists mainly SiO_2 , Al_2O_3 and Fe_2O_3 with varying amount of other oxides such as Na_2O , CaO , MgO etc. **High ash content in coal is undesirable because it has lower calorific value.**
- (ii) **Ash** is a useless, non-combustible matter, which reduces the calorific value of coal. Moreover, ash causes the hindrance to the flow of air and heat, thereby lowering the temperature. Presence of higher amount of ash in coal causes obstruction to air supply; thereby the burning of coal becomes *irregular*. **Hence, lower the ash content, better the quality of coal.**
- (ii) The presence of ash also increases transporting, handling and storage costs. The presence of ash also causes early wear of furnace walls, burning of apparatus and *feeding* mechanism.

4. Fixed Carbon (FC)

The amount of carbon left is burnt by a primary current of air from hot bed of the fuel.

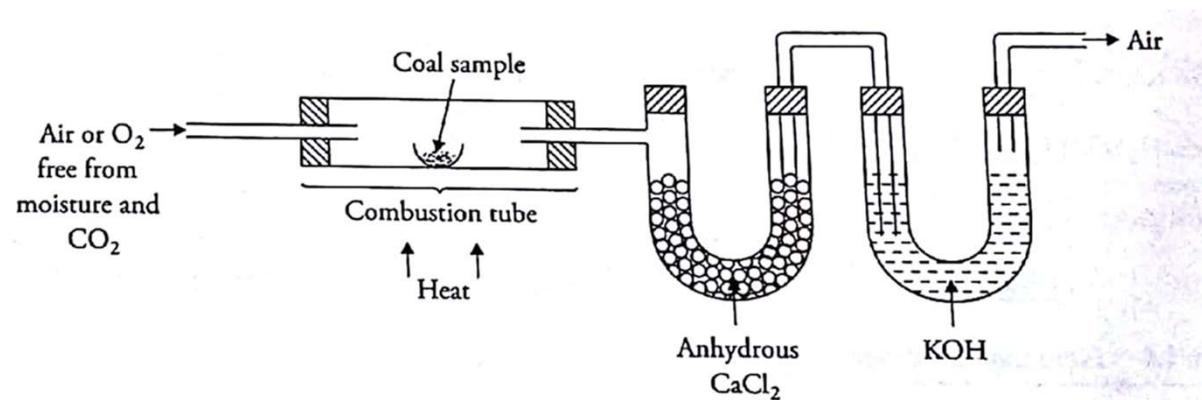
Fixed carbon: Percentage of fixed carbon = 100 - % of (moisture + volatile matter + ash)

Significance Fixed carbon: Higher the percentage of fixed carbon, greater is its calorific and better the quality coal. Greater the percentage of fixed carbon, smaller is the percentage of volatile matter. This also represents the quantity of carbon (in coal) that can be burnt by a primary current of air drawn through the hot bed of a fuel.

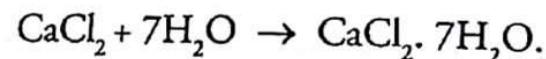
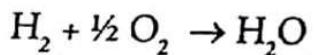
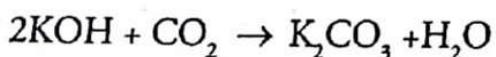
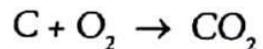
ULTIMATE ANALYSIS OF COAL

It includes the determination of carbon, hydrogen, nitrogen, sulphur and oxygen in coal. It is used for the determination of elements present in the coal and also known elemental analysis. This analysis gives exact results and are useful in calculating the calorific value of coal using Dulong's formula.

1. Carbon and hydrogen: About 1-2 g of accurately weighed coal sample is burnt in a current of oxygen in a combustion apparatus. C and H present in the coal sample are converted into CO_2 and H_2O respectively. The gaseous products of combustion are absorbed respectively in KOH and CaCl_2 tubes of known weights. The increase in weights of these are then determined.



Calculations:



Let the weight of coal sample taken = x gm.

Increase in weight of KOH tube = y gm.

Increase in weight of $CaCl_2$ tube = z gm.

Now,

44 gm of CO_2 contains 12 gm of C.

y gm of CO_2 contains $\frac{12}{44} \times y$ gm of C.

$$\% \text{ Carbon} = \frac{12}{44} \times \frac{y}{x} \times 100$$

$$\text{or, percentage of carbon} = \frac{12}{44} \times \frac{\text{Increase in weight of KOH tube}}{\text{weight of coal sample taken}} \times 100$$

ULTIMATE ANALYSIS OF COAL

Similarly

18 gm of H_2O contains 2 gm of H

z gm of H_2O contains $\frac{2 \times z}{18}$ gm of H

% of Hydrogen = $\frac{2}{18} \times \frac{z}{x} \times 100$

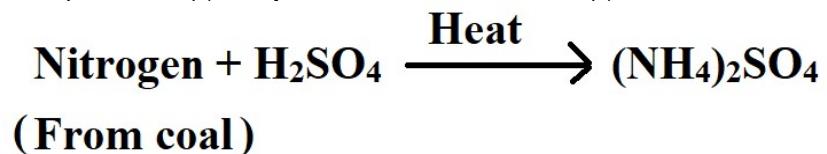
Percentage of hydrogen = $\frac{2}{18} \times \frac{\text{Increase in weight of } \text{CaCl}_2 \text{ tube}}{\text{Weight of coal sample taken}} \times 100$

Significance of Carbon and hydrogen: Greater the percentage of carbon and hydrogen better is the coal in quality and calorific value. However, hydrogen is mostly associated with the volatile matter and hence, it affects the use to which the coal is put. Also higher percentage of carbon in coal reduces the size of combustion chamber required. The amount of carbon, the major combustible constituent of coal, depends on the type of coal and its percentage increases with rank from lignite to anthracite. Thus, percentage of carbon forms the basis of classification of coal.

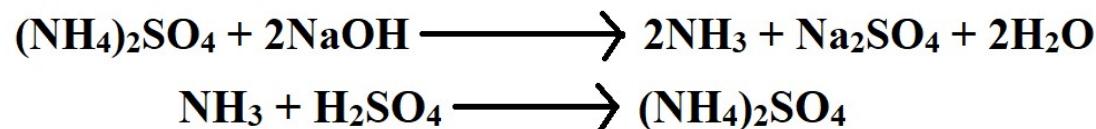
ULTIMATE ANALYSIS OF COAL

Analysis of Nitrogen: Nitrogen present in coal sample is estimated by *Kjeldahl's Method.*

About 1 g of accurately weighed powdered 'coal' is heated with concentrated H_2SO_4 along-with K_2SO_4 (catalyst) in a long-necked flask(called *Kjeldahl's flask*). Nitrogen present in the coal gets converted to $(\text{NH}_4)_2\text{SO}_4$ quantitatively.

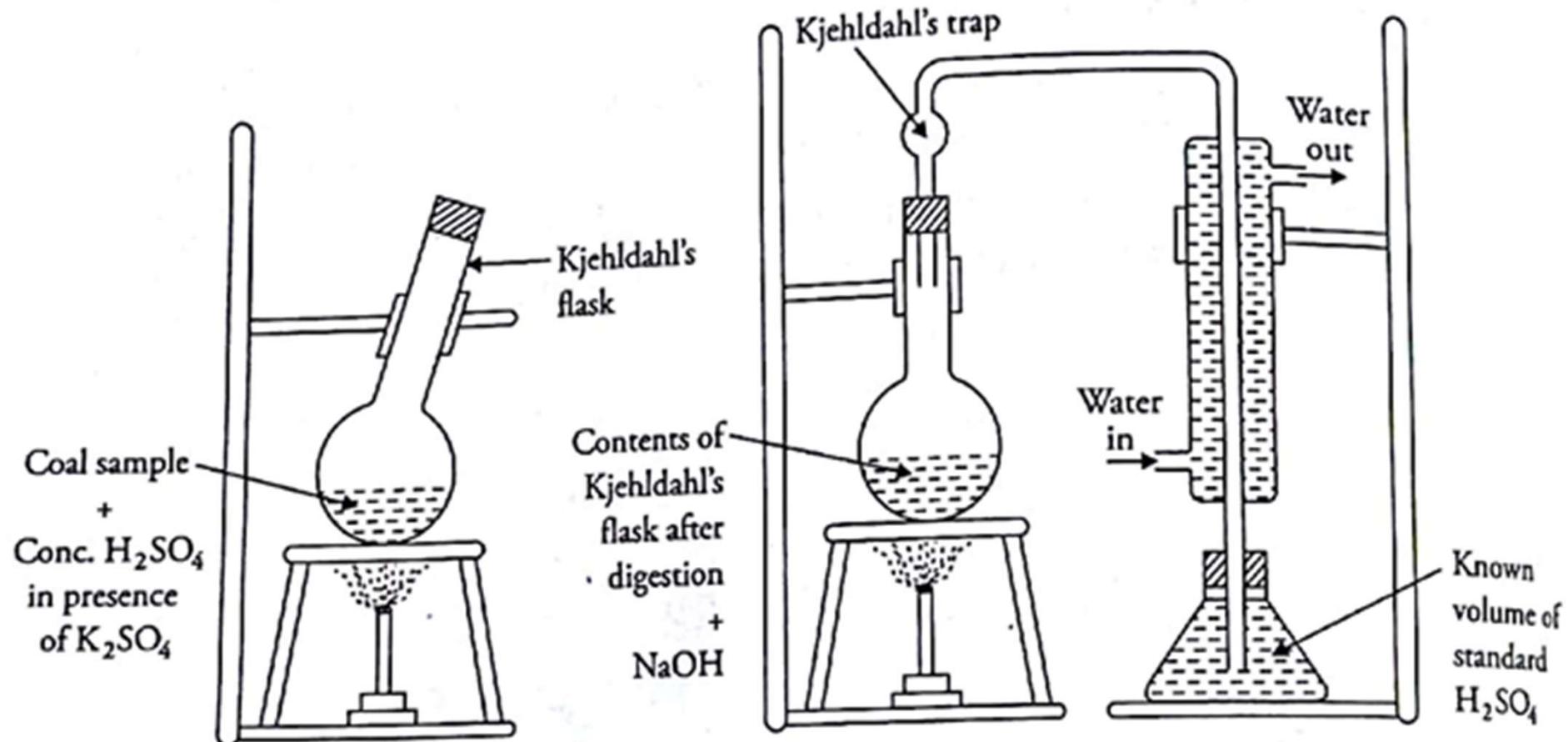


After the solution becomes clear, it is treated with excess of NaOH or KOH and the liberated ammonia is distilled over and absorbed in a known volume of standard H_2SO_4 (say $\sim \frac{N}{10}$) solution. The unused acid is then determined by back titration with standard NaOH solution. From the volume of acid used by ammonia liberated, the percentage of N in coal is calculated.



ULTIMATE ANALYSIS OF COAL

Analysis of Nitrogen:



ULTIMATE ANALYSIS OF COAL

Analysis of Nitrogen calculation:

Let the weight of the coal sample = Wgm

Volume of H_2SO_4 is = V_1 mL

Normality of acid = N_1

As we know, Equivalents of H_2SO_4 used = Equivalent of NH_3 formed.

Equivalents of H_2SO_4 used = $N_1 V_1$.

Equivalents of NH_3 formed. = $N_1 V_1$.

Generally 1N solution of NH_3 mean 1 gm equivalent NH_3 in 1 Litre

Since, 1000 mL 1 N solution of NH_3 contains 17 gm NH_3 = 14 gm of N

$$N_1 V_1 \text{ of } \text{NH}_3 \text{ will contain} = \frac{14}{1000} \times N_1 V_1$$

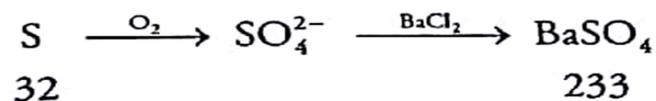
$$\% \text{ of N} = \frac{14}{1000} \times \frac{N_1 V_1}{W} \times 100$$

$$\% \text{ of nitrogen} = \frac{\text{Volume of } \text{H}_2\text{SO}_4 \times \text{Normality of } \text{H}_2\text{SO}_4 \times 1.4}{\text{Weight of coal sample taken}}$$

Significance of Nitrogen: Nitrogen has no calorific value and hence its presence in coal is undesirable. Thus, a good quality coal has very little nitrogen content.

ULTIMATE ANALYSIS OF COAL

3. Analysis of Sulphur: A known amount of coal is burnt completely in a bomb calorimeter in a current of oxygen. Sulphur in the coal is oxidized to sulphates. The ash form of the bomb calorimeter is extracted with dilute HCl. The acid extract is treated with BaCl₂ solution to precipitate sulphate as BaSO₄. This precipitate is filtered, washed and heated to constant weight. From the weight of BaSO₄ formed, S is estimated as follows,



Let the weight of coal sample = W gm

Weight of BaSO₄ = x gm

∴ 233 gm of BaSO₄ = 32 g of S

$$\therefore x \text{ gm of BaSO}_4 = \frac{32}{233} \times x$$

$$\% \text{ S} = \frac{32}{233} \times \frac{x}{W} \times 100$$

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

ULTIMATE ANALYSIS OF COAL

Significance of S:

- Although Sulphur increases the calorific value of fuel, yet its presence is undesirable because it gets oxidized to SO_2 and SO_3 which causes environmental pollution.
- Sulphur containing coal is not suitable for preparing metallurgical coke. Presence of Sulphur in coke used in the iron industry affects the quality and properties of steel.

4. Determination of Ash: determination is carried out as in proximate analysis.

5. Determination of Oxygen: Percentage of O = 100 - Percentage of (C + H + S + N + ash)

Significance of Oxygen:

- Oxygen content decreases the calorific value of coal. High oxygen-content coals are characterized by high inherent moisture, low calorific value, and low coking power.
- Moreover, oxygen is in combined form with hydrogen in coal and thus, hydrogen available for combustion is lesser than actual one. An increase in 1% oxygen content decreases the calorific value by about 1. 7% and hence, oxygen is undesirable. Thus, a good quality coal should have low percentage of oxygen

Example 2. A sample of coal was analysed as follows:

Exactly 2.5 g was weighed in a silica crucible, after heating for 1 hr. at 110°C the residue was weighed to be 2.415 g. Next the crucible was covered with a rented lid and strongly heated for exactly 7 mins. at 1000°C. The residue was weighed to be 1.528 g. Then the crucible was heated without cover until a constant weight to 0.245 g was obtained. From the above data calculate the proximate analysis of coal.

(i) *Percentage of moisture*

$$\text{Weight of coal sample taken} = 2.500 \text{ g}$$

$$\text{Weight after heating at } 110^\circ\text{C} = 2.415 \text{ g}$$

$$\text{Loss of weight} = \text{weight of moisture} = 2.500 - 2.415 = 0.085 \text{ g}$$

$$\begin{aligned}\% \text{ moisture} &= \frac{\text{weight of moisture}}{\text{weight of coal taken}} \times 100 \\ &= \frac{0.085}{2.500} \times 100 = 3.4\%\end{aligned}$$

$$\% \text{ moisture} = 3.4\%$$

(ii) *Percentage of volatile matter*

$$\text{Weight of residue after heating at } 950^\circ\text{C} = 1.528 \text{ g}$$

$$\text{Loss of weight} = \text{weight of volatile matter} = 2.415 - 1.528 = 0.887 \text{ g.}$$

$$\begin{aligned}\% \text{ volatile matter} &= \frac{\text{weight of volatile matter}}{\text{weight of coal sample taken}} \times 100 \\ &= \frac{0.887}{2.500} \times 100 = 35.48\end{aligned}$$

$$\% \text{ volatile matter} = 35.48\%$$

(iii) *Percentage of ash*

$$\begin{aligned}\frac{\text{weight of residue left}}{\text{weight of coal sample taken}} \times 100 \\ \frac{0.245}{2.5} \times 100 = 9.8\%\end{aligned}$$

$$\% \text{ ash} = 9.8\%$$

(iv) *Percentage of fixed carbon* = $100 - \% \text{ of } (\text{moisture} + \text{volatile matter} + \text{ash})$

$$= 100 - (3.4 + 35.48 + 9.8)$$

$$= 100 - 48.68 = 51.32\%$$

$$\% \text{ fixed carbon} = 51.32\%$$

Liquid fuel: petroleum

- Liquid fuels are used extensively in industrial and domestic purpose. Application of liquid fuel in internal combustion engines makes them very essential fuels. The main source of liquid fuel is petroleum fuel. The term petroleum means rock oil. (In Latin *Perra* means *rock* and *oleum* means *oil*).
- Petroleum is a fossil fuel because it is made from the remains of plants and animals buried millions of years ago. Petroleum is a dark, greenish brown, viscous liquid that is found underground. It comprises hydrocarbons such as:
 1. It contains straight paraffins or cycloparaffins like methane, ethane, propane, butane, isobutane, pentane, hexane Olefins like ethene, butene etc
 2. Aromatics like benzene etc
 3. Other organic compounds containing N, O, S
- Due to the presence of sulphur, it has an unpleasant smell. It also contains impurities of sand, brine or sea water. Hence it is called crude oil.

Element	Carbon	Hydrogen	Sulphur	Nitrogen	Oxygen
%	~75.5 -87.1	~11.5- 14.8	~01 -3.5	~04-3.5	~0.1-0.9

Classification of petroleum

Petroleum is classified into **three** categories according to its composition.

- 1. Paraffinic base petroleum:** It is mainly composed of straight chain saturated hydrocarbons from CH_4 to $\text{C}_{35}\text{H}_{72}$ along with small amount of naphthene's and aromatic hydrocarbons.
- 2. Naphthenic or asphaltic base petroleum:** It contains mainly cycloparaffins or naphthenes as main constituent along with smaller amount of paraffins and aromatic hydrocarbons.
- 3. Mixed base petroleum:** It contains both paraffins and asphaltic hydrocarbons.

Mining and Refining of Petroleum

The crude oil obtained from the earth crust contains water, sulphur and some unwanted impurities. After removal of water, sulphur and these impurities, the crude oil is separated into various useful fractions by fractional distillation and finally converted into desired specific products having different boiling points. The process is called "Refining of Petroleum" and the refining plants are called "Oil refineries". The process of refining involves the following steps.

Step -I: Separation of water or demulsification (Cottrell's process)

The crude oil from the oil well is an extremely stable emulsion of oil and salt water. The crude oil is allowed to flow between two highly charged electrodes, where colloidal water droplets coalesce to form large drops, which is then separated out from the oil.

Step - II: Removal of harmful impurities

- (a) The presence of NaCl and MgCl_2 in the crude oil can corrode the refining equipment, hence these salts are removed by electrical desalting and dehydration methods.
- (b) The sulphur compounds present in the crude oil is removed by treating oil with copper oxide, which results in the formation of copper sulphide (solid), which is then removed by filtration.

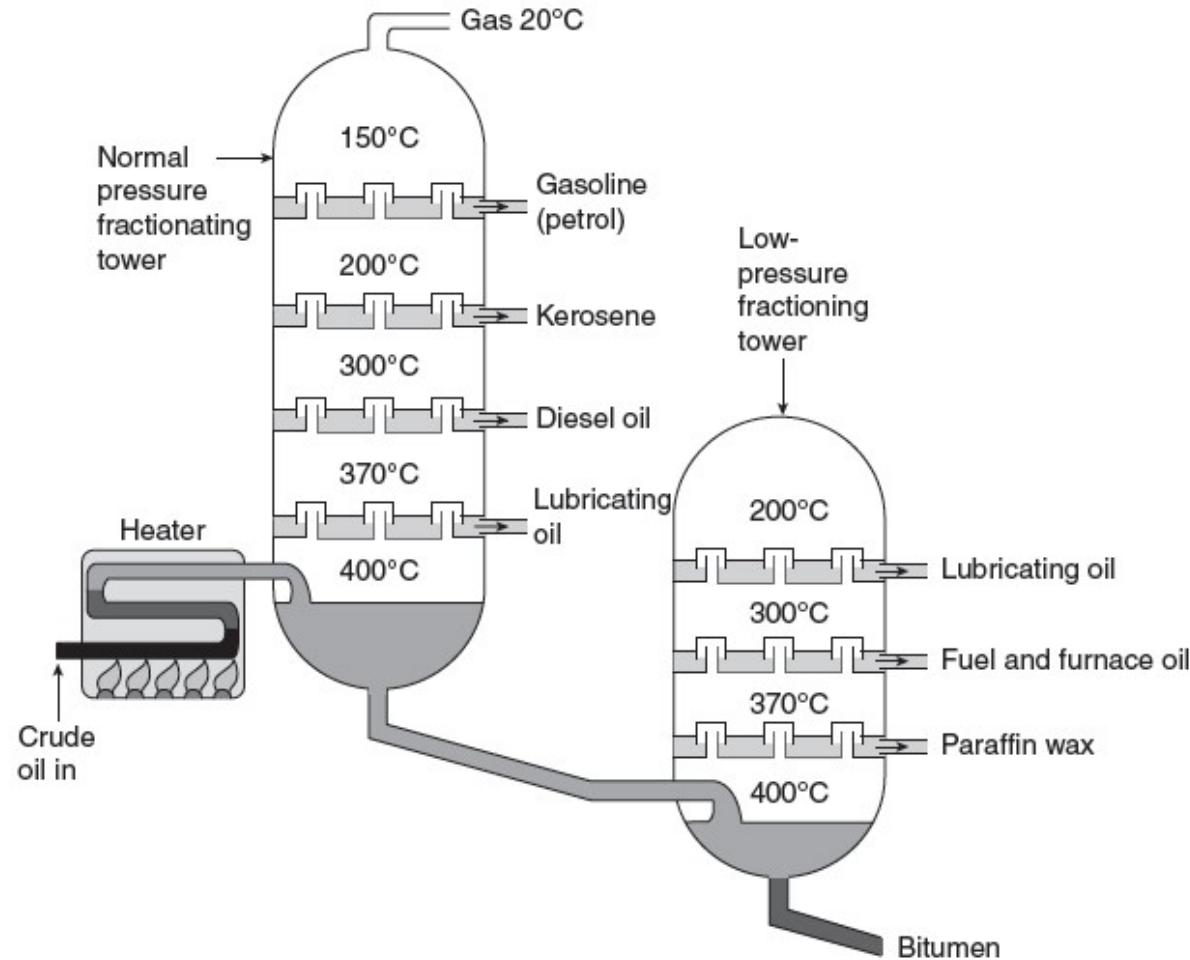
Mining and Refining of Petroleum

Step - III: Fractional distillation

The crude oil is then heated to about 400°C in an iron retort, whereby all volatile substances (except asphalt or coke) are evaporated. The hot vapors are then passed up a fractionating column, which is a tall cylindrical tower containing a number of horizontal stainless steel trays at short distances. Each tray is provided with small chimney covered with a loose cap.

When the vapours of the oil go up in the fractionating column, they become gradually cooler and get condensed at different heights of column. The fractions having higher boiling points condense at lower trays whereas the fractions having lower boiling points condense at higher trays.

Fractional Distillation



Various fractions of crude oil and their composition and uses

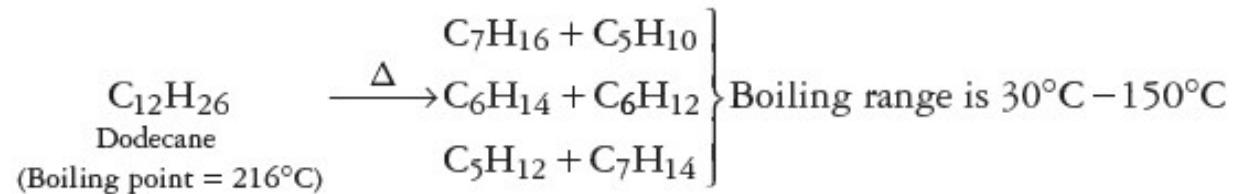
	Name of the fractions	Boiling range (°C)	Composition of hydrocarbon	Uses
1.	Uncondensed gases	Below 30°C	C ₁ to C ₄	As domestic and industrial fuel under the name LPG
2.	Petroleum ether	30 - 70 °C	C ₅ to C ₇	As a solvent.
3.	Gasoline (or) petrol.	40 - 120 °C	C ₅ to C ₉	As motor fuel, solvent and in dry cleaning.
4.	Naphtha(or} solvent spirit	120. - 180 °C	C ₉ to C ₁₀	As solvent and in dry cleaning.
5.	Kerosene oil.	180 - 250 °C	C ₁₀ to C ₁₆	As fuel for jet engines and an illuminant.
6.	Diesel oil (or) gas oil	250-320 °C	C ₁₀ to C ₁₈	As Diesel engine fuel.
7.	Heavy oil.	320 - 400 °C	C ₁₇ to C ₃₀	Production of gasoline by cracking process.

Various fractions recovered from Heavy Oil

S1 No.	Name of the fractions	Boiling range ($^{\circ}\text{C}$)	Composition of Hydrocarbons	Uses
1.	Lubricating oil	-	C_{17} to C_{20}	Used as lubricants
2.	Petroleum jelly (Vaseline)	-	-	Used in medicines and cosmetics
3.	Paraffin wax	-	C_{20} to C_{28}	Used in candles, wax paper, boot polish, etc
		-		
4.	Grease	-	-	Used as lubricants.
5.	Asphalt or bitumen	Above 400°C	C_{30} and above	Used for making roads, water proof roofing, etc

Cracking

Cracking is decomposition of high molecular weight hydrocarbon (with high boiling points) to low molecular weight hydrocarbon with low boiling points). The lower boiling fractions are suitable for internal combustion engines of automobiles.



The gasoline obtained from the fractional distillation of petroleum, has the highest demand as a motor fuel, but the yield of this fractions is only 20-30% (Crude oil) and also quality as straight-run gasoline which is not good enough to use in automobile industry hence is used only after proper blending. To overcome these difficulties, the higher boiling fractions (e.g. fuel oil and gas oil) are converted into lower boiling fractions gasoline (petrol) by cracking process.

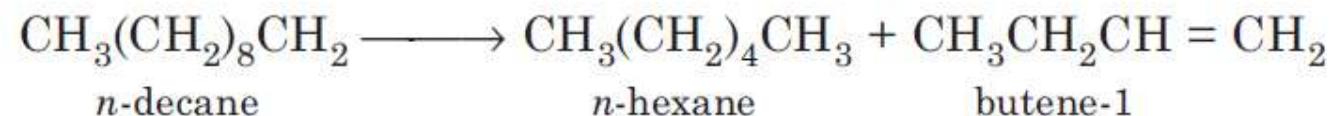
The cracked gasoline gives better engine performance i.e., they are suitable for spark -ignition engines of automobiles. In cracking process, higher saturated hydrocarbon molecules are converted into simpler molecules such as paraffinic and olefinic hydrocarbons,

There are two methods of cracking in use

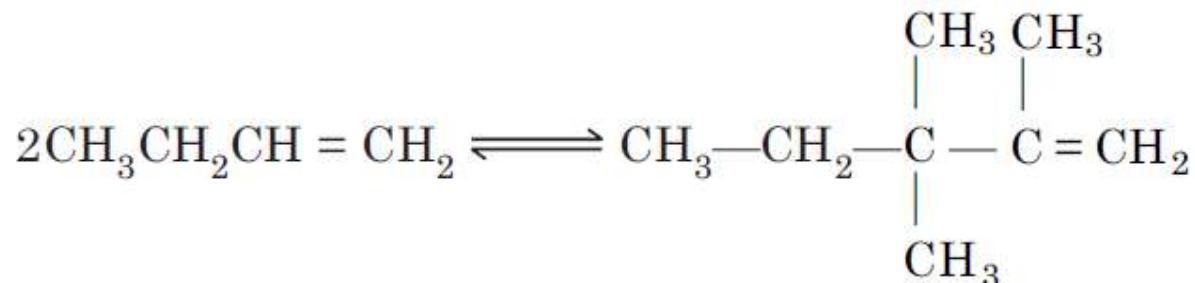
1. Thermal cracking 2. Catalytic cracking

Thermal cracking

When the cracking process is carried out without any catalyst at high temperature ($\sim 450^{\circ}\text{C} - 750^{\circ}\text{C}$) at high pressure ($\sim 10\text{-}100 \text{ kg/cm}^2$) is known as thermal cracking. In thermal cracking the bigger hydrocarbons breakdown to give smaller molecules of paraffins, olefins and some hydrogen. This process may be carried out either in liquid phase or in vapour phase. The important reactions of thermal cracking are decomposition, dehydrogenation, isomerization and polymerization.



The olefins formed isomerizes and polymerizes.



Thermal cracking:

Thermal cracking also classified into two categories

(a)Liquid phase thermal cracking: By this method any type of oil (residue, fuel oil or gasoline) can be cracked. The charge is kept in liquid form by applying high pressure ($\sim 100 \text{ kg/cm}^2$) at a suitable temperature $\sim 450^\circ\text{C} - 530^\circ\text{C}$. The cracked product are separated in a fractional column. The octane rating of the product is 65-70.

(b)Vapour phase thermal cracking: This method is suitable for oil which can be readily vaporized. The oil is first vaporized and then cracked at about $\sim 600^\circ\text{C} - 650^\circ\text{C}$ and under comparatively low pressure $\sim 10 - 20 \text{ kg/cm}^2$. It required less time than the liquid phase method. Petrol obtained from vapour phase cracking has better antiknock properties but very poor stability as compared to petrol obtained from liquid phase cracking.

Comparison of liquid phase and vapour phase thermal cracking:

Characteristic	Liquid phase thermal cracking	Vapour phase thermal cracking
Cracking temperature	$\sim 450 - 530^\circ\text{C}$	$\sim 600 - 650^\circ\text{C}$
Pressure	$\sim 100 \text{ kg/cm}^2$	$\sim 10 - 20 \text{ kg/cm}^2$
Octane rating of petrol	65-70	Greater than 70
Type of oil used under cracking	Any heavy oil can be cracked	Oil should be readily vaporized

Catalytic cracking

In this process, cracking is carried out in presence of a catalyst at lower temperature (300°C to 450°C) and pressures (1 to 5 kg/cm²). The use of catalyst during cracking accelerates the reaction at the same time modifies the yield and the nature of products. The catalyst like aluminum silicate [Al₂(SiO₃)₂] or alumina [Al₂O₃] used in cracking gives higher yield and better quality of gasoline.

There are mainly two types of catalytic cracking.

(a)Fixed bed catalytic cracking

(b)Moving bed or Fluidized-bed catalytic cracking

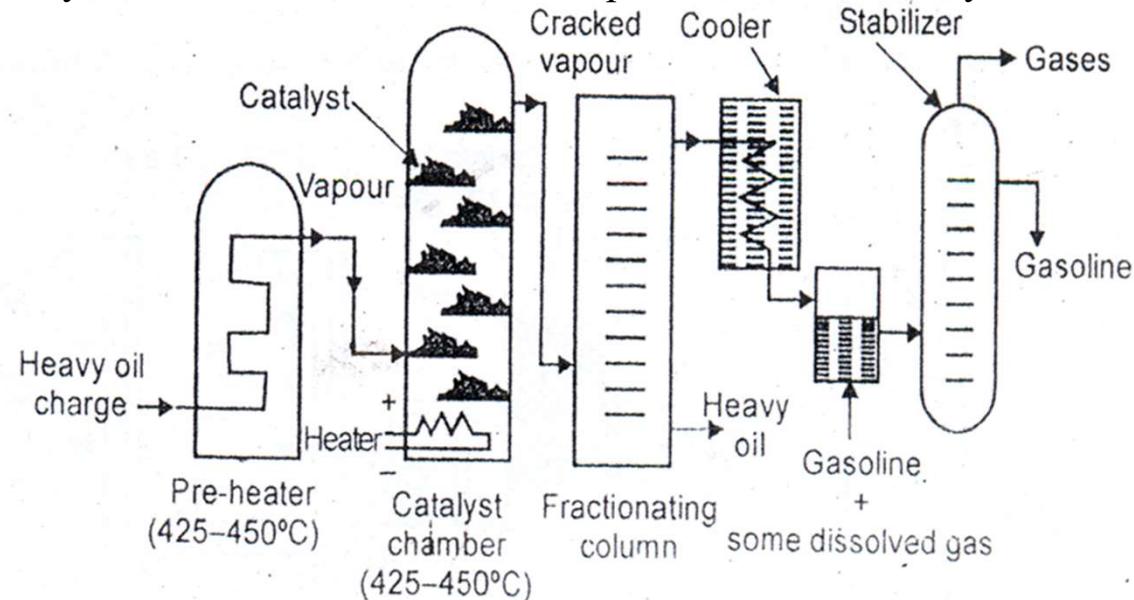
Fixed bed catalytic cracking

In fixed bed catalytic cracking the heavy oil is passed through the heater, where the oil is vaporized and heated to 420 to 450°C and then passed through a catalytic chambers containing the catalyst of silica alumina gel (SiO₂, Al₂O₃) or bauxite mixed with clay and zirconium oxide maintained at 425 to 450°C and 1.5 kg/cm² pressure. During their passage through the tower, cracking takes place about 30-40% of the charge is converted into gasoline and about 3- 4% carbon is formed which gets deposited on the catalytic bed.

Fixed bed catalytic cracking

The vapours produced are then passed through a fractionating column, where heavy oil fractions condensed. The vapours are then admitted into a cooler, where some of the gaseous products are condensed along with gasoline and uncondensed gases move on. The gasoline containing some dissolved gases is then sent to a stabilizer, where the dissolved gases are removed and pure gasoline is obtained.

When substantial amount of carbon is deposited on the catalyst bed, during cracking, the catalyst stops functioning. It is reactivated by burning off the deposited carbon in a stream of hot air. During the reactivation of catalyst, the vapours are diverted through another catalyst chamber so that the reaction proceeds continuously .



Moving bed or Fluidized-bed catalytic cracking

In this process, solid catalyst is finely powdered, so that it behaves almost as a fluid, which can be circulated in gas stream. The vapours of cracking stock (gas oil, heavy oil, etc.,) mixed with fluidized catalyst is forced up into a large reactor bed in which cracking of the heavier molecules into lighter molecules occurs at a temperature of $\sim 500^{\circ}\text{C}$ and pressure of about $\sim 5 \text{ kg/cm}^2$. The top of the reactor, there is a centrifugal separator, which, allows the low boiling lighter molecules move up to the top of the reactor and enter into the fractionating column but retains all the catalyst powder in the reactor itself. The catalyst powder gradually becomes heavier due to coating with carbon formed and settles at the bottom. This is called spent catalysis and is forced by a blast of air to the regenerator maintained at 600°C . The carbon deposited on the catalyst powder are burnt off in the regenerator and the catalyst is reactivated. The regenerated catalyst is then flows through a standpipe to get mixed with fresh charge. The cyclone at the top of the regenerator allows to escape CO_2 along with other gases to escape retaining the catalyst particles. The cracked gases and gasoline are removed from the top of the fractionating column and sent to a cooler, where gasoline is condensed. It is then sent to a stabilizer to recover pure gasoline. The product contains a higher proportion of aromatics and iso-paraffins.

Advantage of catalytic cracking over thermal cracking

- (i) The quality and yield of petrol is better
- (ii) External fuel is not necessary since the coal embedded in the catalyst supplies the heat.
- (iii) Operating pressure is lower
- (iv) Byproduct gas evolution being low, yield of petrol is higher
- (v) Due to higher aromatics content, the anti-knocking properties are higher.
- (vi) Greater portion of S escape as H_2S , so residual S content of the oil is low.
- (vii) Gum-forming compound are very low.
- (viii) In presence of specific catalyst preferentially the cracking of naphthenic materials takes place. So it becomes richer in paraffinic compounds.
- (ix) Only the high-boiling hydrocarbons and the side chain of the aromatics are decomposed preferentially.

Petroleum Processing

1. Polymerisation: In this method small molecule of hydrocarbon are combine to larger molecules like gasoline. During cracking large quantities of olefins or unsaturated hydrocarbon (like ethylene, propane, and butane) and alkanes (Such as methane, ethane and butane) are obtained as by products. The gasoline obtained by polymerisation reaction known as polymer gasoline. It has high octane number.

Polymerisation is carried out in two ways.

i. **Thermal Polymerization:** In this polymerization of cracked gases is carried out at $500\text{-}600^{\circ}\text{C}$ at $70\text{-}350 \text{ kg/cm}^2$ pressure. The product is gasoline and gas oil which are separated by fraction distillation.

ii. **Catalytic Polymerization:** It is carried out in the presence of catalyst like phosphoric acid and sulphuric acid. The process carried out at low temperature ($150\text{-}200^{\circ}\text{C}$).

2. Alkylation: This method used to convert olefins to gasoline. In this process, alkane and alkene are combined together in the presence of a catalyst under proper temperature and pressure. The most important example is the reaction of isobutane and isobutene in the presence of anhydrous HF at room temperature to give iso-octane. This process is used to produce gasoline of improved quality.

Synthesis of Gasoline

The gasoline obtained from the fractional distillation of crude petroleum oil is not enough to meet the requirement of the present community due to vast increase of automobiles. Hence an alternate source need of finding out to manufacture synthetic petrol. Synthetic petrol can be manufactured by the process of hydrogenation of coal. The preparation of liquid fuels from solid coal is called hydrogenation of coal.

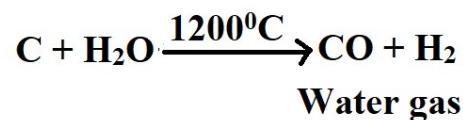
- Gasoline is synthesized by the following methods.

- **1. Fischer- Tropsch process.**

- **2. Bergius process.**

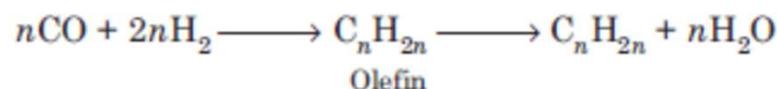
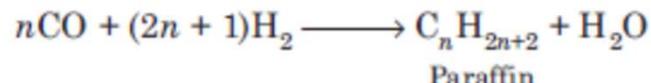
Fischer- Tropsch process

This process is based on the catalytic hydrogenation of carbon monoxide. In this process, coal is first converted into coke. Then water gas is produced by the action of steam over red hot coke.

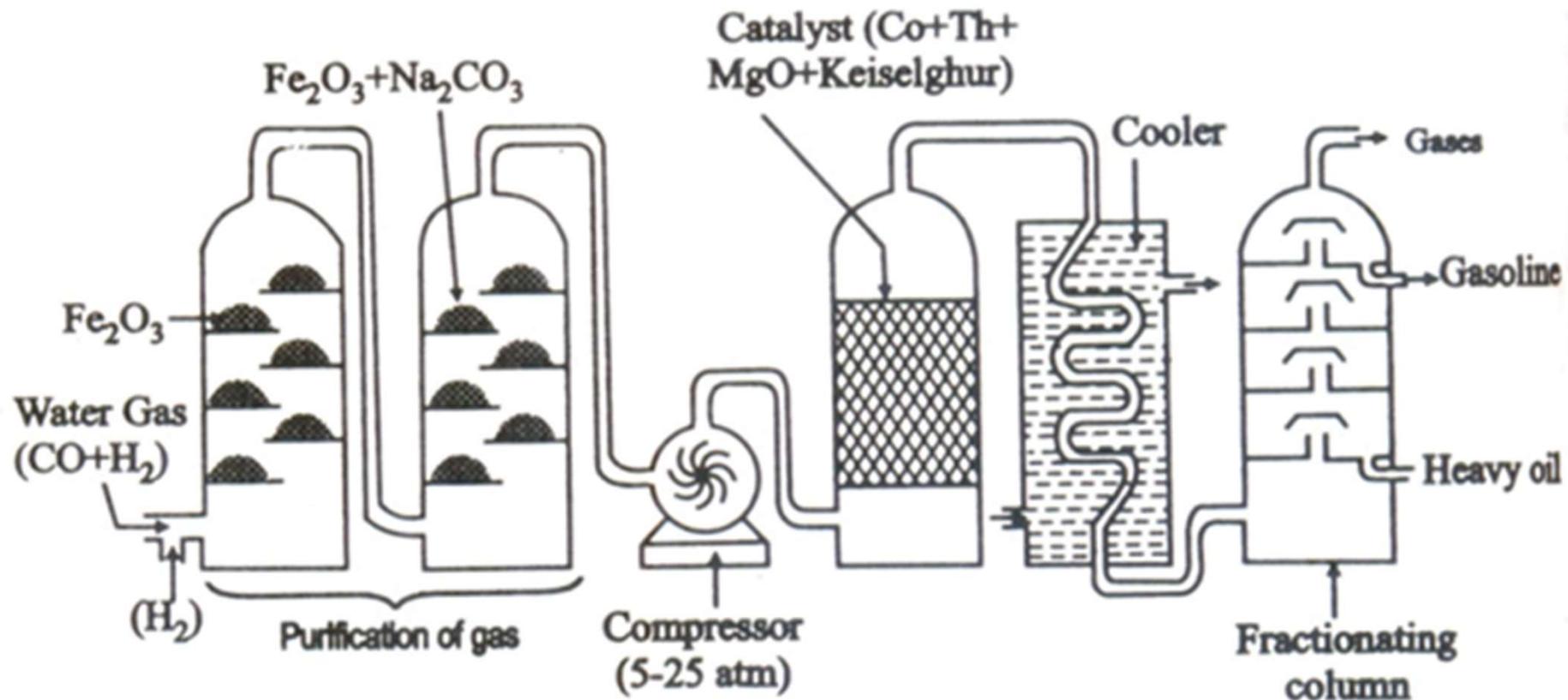


Water gas is purified by passing over Fe_2O_3 to remove H_2S , then passing over a mixture of Fe_2O_3 , Na_2CO_3 to remove organic S compounds. The purified gas is compressed to 5 to 25 atmosphere at $200^{\circ} - 300^{\circ}\text{C}$ passed through a converter containing catalyst which is a mixture 100 parts cobalt, 5 parts thorium, 8 parts magnesium and 200 parts kieselguhr.

The reactions are strongly exothermic. Hence, the hot out coming gaseous mixture is led to a cooler where a liquid resembling crude oil is obtained. This is then subjected to fractional distillation to yield gasoline, diesel oil and heavy oil. The heavy oil can be reuse for cracking to obtain more gasoline. The gasoline formed by Fischer – Tropsch process is rich in straight chain hydrocarbons, and hence its octane number is only 40. However, the diesel oil obtained is excellent quality.



Fischer- Tropsch process



Bergius process.

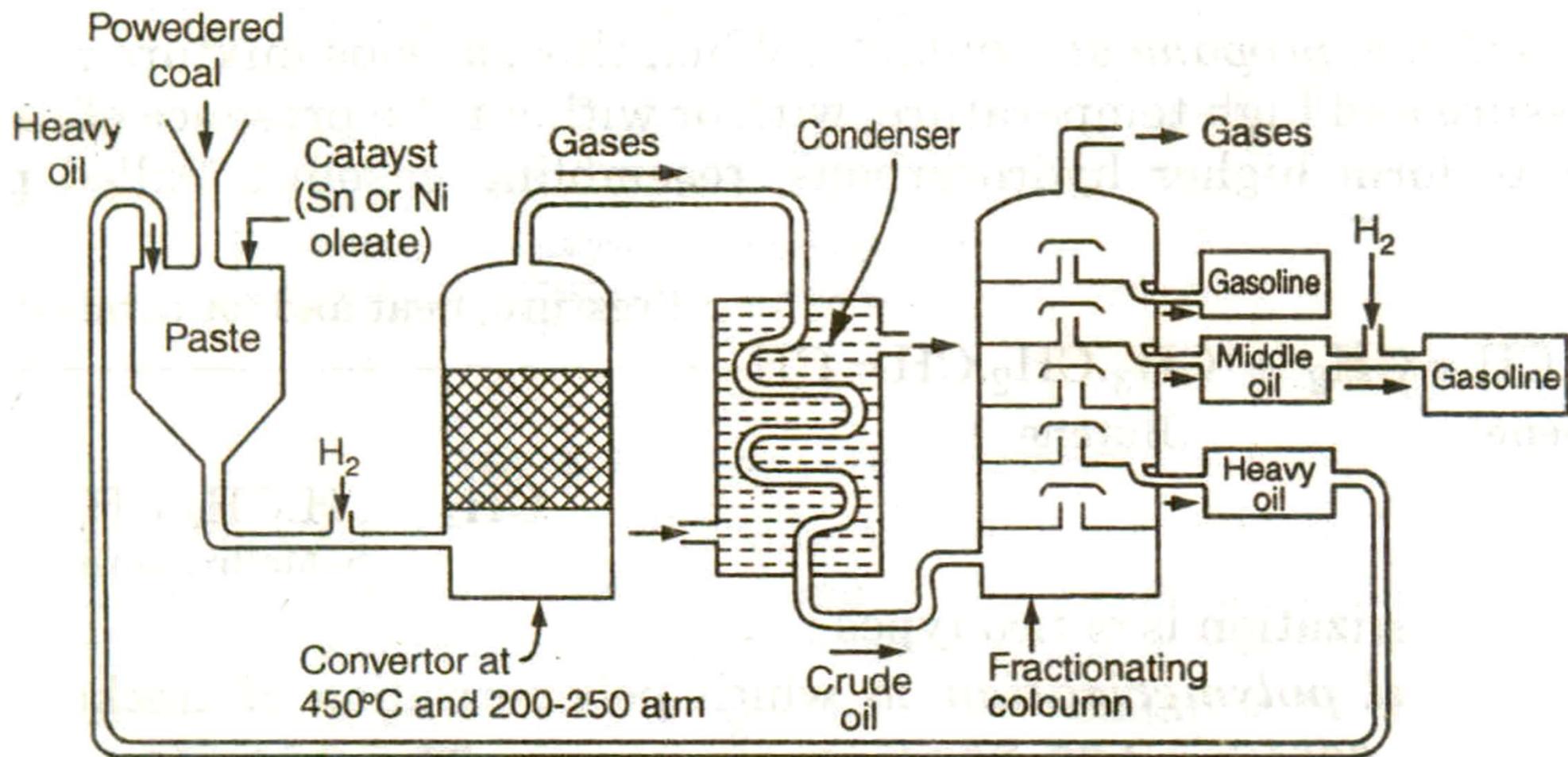
This process developed by Bergius of Germany involves the conversion of low-grade coals, such as bituminous coals or brown coals, into liquid and gaseous fuels by hydrogenating them in the presence of catalyst.

In this process, the low ash coal is powdered and mixed with heavy oil and catalyst (tin and Ni oleate) to make a paste. This paste is heated with hydrogen at 450°C and 200–250 atm pressure for about 2 hrs. The coal undergoes hydrogenation to form saturated hydrocarbons that decompose at prevailing high temperature and pressure to yield low-boiling liquid hydrocarbons. The vapors leaving the catalytic chamber are condensed, where a liquid resembling crude oil is obtained. This is subjected to fractional distillation to give (i) gasoline, (ii) middle oil and (iii) heavy oil.

The middle oil is again hydrogenated to obtain gasoline. Heavy oil is reused for making a paste with fresh coal dust.

The gasoline so obtained contains 74% paraffins, 22% aromatics and 4% olefins. Yield of gasoline is about 60% of the coal dust used.

Bergius process.



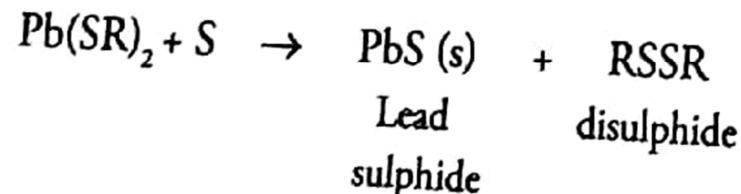
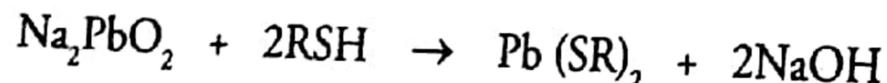
Refining of gasoline

The straight run gasoline obtained from fractional of crude petroleum or by synthesis contains substance such as

(i) Unsaturated olefines (ii) Sulphur. These substances are undesirable because

- Olefines undergoes oxidation and polymerization leading to gum and sludge formation which stop the function of engine.
- The Sulphur compounds lead to corrosion of internal combustion engine and H_2S gives bad order and make oil sour.

Removal of S related compound (Desulfurization): The S containing gasoline is termed as sour gasoline and the process of removal of S is known as “ sweetening”. It is accomplished by treating gasoline with sodium plumbite with controlled addition of S. The S compound are converted into PbS and disulfides. The above process is termed as “Doctors process”.



Knocking

Knocking is a kind of explosion due to rapid pressure rise occurring in an IC engine.

In a petrol engine, a mixture of gasoline vapour and air at 1: 17 ratio is used as fuel. This mixture is compressed and ignited by an electric spark. The products of oxidation reaction (combustion) increases the pressure and pushes the piston down the cylinder. If the combustion proceeds in a regular way, there is no problem in knocking. But in some cases, the rate of combustion (oxidation) will not be uniform due to unwanted chemical constituents of gasoline. The rate of ignition of the fuel gradually increases and the final portion of the fuel-air mixture gets ignited instantaneously producing an explosive sound known as "Knocking". Knocking property of the fuel reduces the efficiency of engine. So a good gasoline should resist knocking.

Knocking

Knocking in Spark Ignition Engines

Petrol is used in spark ignition engines. The rapid compression of the fuel-air mixture heats the engine, and it detonates without the spark being passed. This causes a violent jerk to the piston giving a metallic sound called knocking.

- **Chemical structure and knocking**
- The knocking tendency of fuel hydrocarbons mainly depends on their chemical structures. The knocking tendency decreases in the following order.
 - Straight chain paraffins > Branched chain paraffins > Cycloparaffins > Olefins > Aromatics.
- **Improvement of antiknock characteristics**
- The octane number of fuel can be improved by
 - (i) blending petrol of high octane number with petrol of low octane number, so that the octane number of the latter can be improved.
 - (ii) the addition of anti-knock agents like Tetra-Ethyl Lead (TEL).

Anti-Knocking agent

LEADED PETROL (ANTI-KNOCK AGENT)

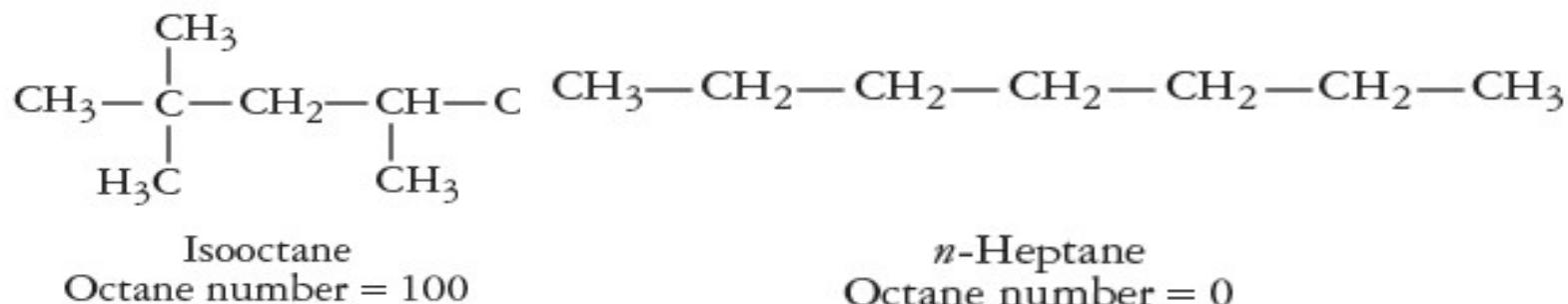
The anti-knock properties of a gasoline can be improved by the addition of suitable additives.

Tetraethyl lead (TEL) or $(C_2H_5)_4 Pb$ is an important additive added to petrol. Thus the petrol containing tetra ethyl lead is called leaded petrol.

TEL reduces the knocking tendency of hydrocarbon. Knocking follows a free radical mechanism, leading to a chain growth which results in an explosion. If the chains are terminated before their growth, knocking will cease. TEL decomposes thermally to form ethyl free radicals which combine with the growing free radicals of knocking process and thus the chain growth is stopped.

OCTANE NUMBER (or) OCTANE RATING

- Octane number is introduced to express the knocking characteristics of petrol. It has been found that n-heptane knocks very badly and hence, its anti-knock value has been given zero. On the other hand, iso-octane gives very little knocking and so, its anti-knock value has been given 100.
- Thus octane number is defined as 'the percentage of iso-octane present in a mixture of iso-octane and n-heptane.'



CETANE NUMBER (or) CETANE RATING

Cetane number is introduced to express the knocking characteristics of diesel. Cetane has a very short ignition lag and hence its cetane number is taken as 100. On the other hand α -methyl naphthalene has a long ignition lag and hence its cetane number is taken as zero.

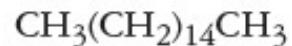
Thus the cetane number is defined as "the percentage of hexa decane present in a mixture of hexa decane and α -methyl napthalene, which has the same ignition lag as the fuel under test".

The cetane number decreases in the following order.

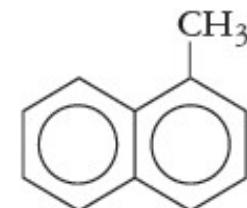
n-alkanes > Cycloalkanes > alkenes >branched alkanes >aromatics

The cetane number of a diesel oil can be increased by adding additives called dopes.

Important dopes: *Ethyl nitrate, Iso-amyl nitrate.*



n-Hexadecane (cetane)
Cetane number = 100



α -Methylnaphthalene
Cetane number = 0