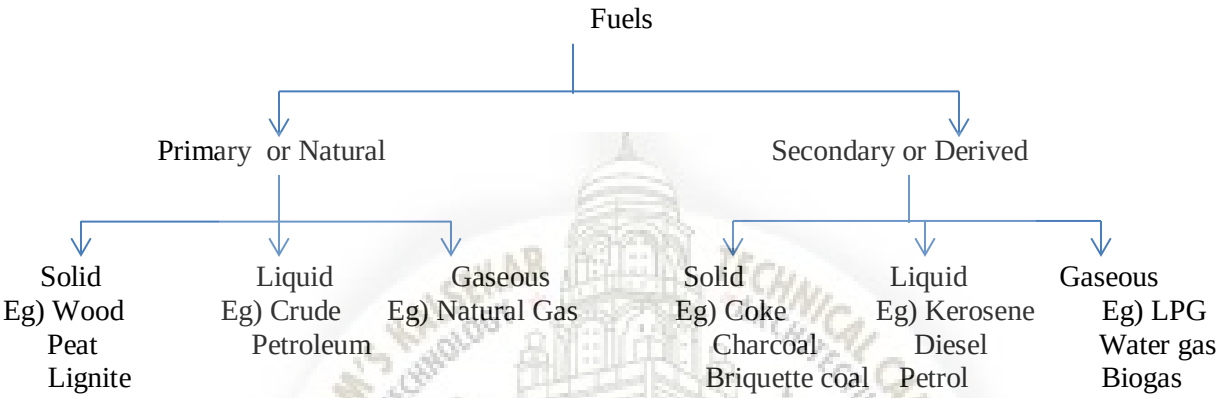
FUELS

Q1) Define Fuel and give its significance.

Ans) A fuel is a combustible substance containing carbon as the main constituent which on proper burning gives large amount of heat which can be used economically for domestic and industrial purpose.

Classification of Fuels:



Q2) Define the following terms:

Ans)1) **Calorific Value:** The total quantity of heat liberated when a unit mass of the fuel is burnt completely.

Units: Solid and Liquids - Cals/gm or Kcal/kg

Gases - Kcal/m^3

2) Ignition Temperature: The minimum temperature to which a substance must be heated before it burns spontaneously independently of the source of heat.

3) Calorie: A Calorie is defined as the amount of heat required to raise the temperature of one gram of water through 1^0c ie from 15.5^0c to 16.5 ^{0}c

4) Kilocalorie: A kilocalorie is defined as the amount of heat required to raise the temperature of one kilogram of water through 1^0c ie from 15.5^0c to 16.5 ^{0}c . 1Kcal= 1000Cal

5) British Thermal Unit: A B.Th.U is defined as the amount of heat required to raise the temperature of one pound of water through 1^0F. 1BThU = 256 Cals=0.256Kcal

Q3) What is Dulong's Formula.

Ans) The calorific value of a fuel can be calculated approximately from the ultimate analysis, which gives the % of elements like C,H,S,N and O.

According to Dulong, the calorific value of fuel is the sum of calorific values of all the elements present. The calorific values of different elements are given as under,

Calorific value of Carbon= 8080cal/gm

Calorific value of Sulphur = 2240 cal/gm

Thus, Dulong's formula is given as,

$$H.C.V = \frac{1}{100}[8080C + 34500(H - O/8) + 2240\,S]$$

where C,H,O and S are the % of C,H,O and S respectively.

In this formula, oxygen is assumed to be present in combination with hydrogen as water and,

$$L.C.V = H.C.V - \frac{9}{100} H \times 587$$

Q4) Define Gross Calorific Value (G.C.V) or Higher Calorific Value (H.C.V).

Ans) **G.C.V:** The total amount of heat produced when a unit mass of fuel is burnt completely and the products of combustion are cooled down to room temperature usually 60^0F or 15^0c

N.C.V: It is defined as the net amount of heat produced when a unit mass of fuel is burnt completely and the products of combustion are allowed to escape into the atmosphere.

Net Calorific Value = Gross Calorific Value – Latent heat of water vapour produced.

= G.C.V – Mass of Hydrogen per unit weight of fuel burnt x 9 x Latent heat of Steam

= G.C.V – H /100 x 9 x 587

N.C.V = G.C.V – 0.09H x 587

Q5) What are the characteristics of an ideal Fuel.

Ans) A good fuel should have the following characteristics:

1) Calorific Value : A good fuel should have high calorific value since the amount of heat liberated and temperature attained thereby depends upon the calorific value of fuel.

2) Low Moisture Content: The moisture content of the fuel should be low, because moisture reduces the heating value (calorific value) of fuel.

3) Moderate Ignition Temperature: A good fuel should have moderate ignition temperature. Low ignition temperature is dangerous for storage and transport of fuel, since it can cause fire hazards. On the other hand high ignition temperature causes difficulty in initiating a fire.

4) Low Non-Combustible matter: Higher the noncombustible matter lower will be the calorific value and it also causes disposal problems.

5) Moderate velocity of combustion: Fuel should have a moderate rate of combustion. If the rate of combustion is low, then the required temperature is not attained and high rate of combustion is not desirable.

6) Easy to transport: Fuel must be easy to handle, store and transport at a low cost. Transportation of gaseous fuel is costly and can cause fire hazards. Storage cost of fuel in bulk should be low.

7) Products of combustion : A good fuel should not release harmful combustion products like CO,SO2,NO,H_2S etc which have harmful effects on health of living beings. Therefore a good fuel should be environmentally friendly.

Q6) Explain in brief the various tests under proximate analysis of coal.

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

1) % Moisture: A known quantity of air dried coal sample is taken in a crucible and heated in an oven at 105^{o}c to 110^{o}c for 1 hour. Then the coal sample is taken out from the oven, cooled in a desiccator and weighed .The heating and cooling procedure is continued till constant weight.

% Moisture = Loss in weight of coal x 100

Weight of coal taken

Significance: Higher the moisture content, lower will be the calorific value and vice versa. Thus it reduces the efficiency of fuel and increases the transport cost.

2) % Volatile matter: A known quantity of coal sample is taken in a crucible with vented lid and kept in a muffle furnace maintained at 925+-20^{o}c for exactly 7 minutes. After that it is removed, cooled in a desiccator and weighed.

% Volatile matter = Loss in weight of Volatile matter x 100

Weight of coal taken

Significance:

a) High volatile matter.

b) Gives long smoky flame.

c) Escapes into the atmosphere and therefore decreases the calorific value.

d) Decreases the quality and hence affects the rank of coal.

3) Ash Content: A known quantity of dried sample is taken in an open silica crucible and heated at 700^{o}c to 750^{o}c in a muffle furnace until a constant weight is obtained .The weight of the residue is reported as Ash.

% Ash= Weight of residue x 100

Weight of dried coal

Significance :

1) Higher the ash content more will be the non combustible matter and lower will be the calorific value.

2) Increases disposal problems.

3) The presence of ash increases transporting, handling and storage cost.

4) It also causes early wear of furnace walls, burning of apparatus.

4) % Fixed Carbon: This can be determined as follows,

% Fixed Carbon = 100-(% Moisture + % Volatile Matter + % Ash)

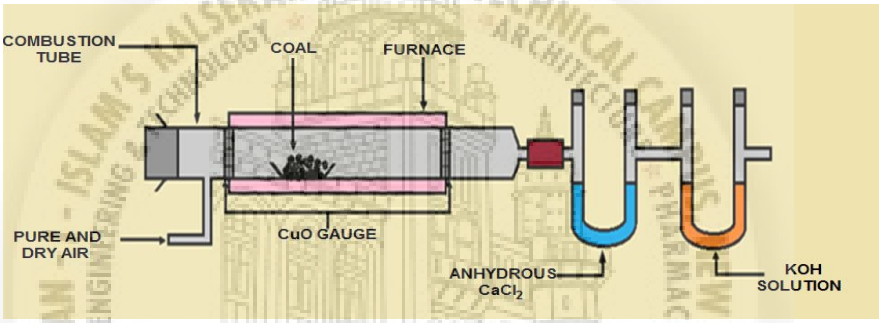
Significance:

1) Higher the % fixed carbon, more will be the calorific value.

2) A good quality coal should have low moisture content, low volatile matter and low ash content which automatically leads to high % Fixed carbon.

Q7) How is Ultimate analysis is carried out? What is its significance?

Ans) It involves following determination,



1) % Carbon and % Hydrogen:

About 1-2gm of accurately weighed coal sample is burnt in a current of oxygen in a combustion apparatus, when C and H present in coal are oxidized to CO_2 and H_2O respectively. The gaseous products are absorbed respectively in KOH and $CaCl_2$ tubes of known weights .The increase in weights of these are determined.

Reactions:

$$2KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$$

$$CaCl_2 + 7\ H_2O \longrightarrow CaCl_2.7\ H_2O$$

$$C + O_2 \longrightarrow CO_2 \quad , \quad H_2 + 1/2O_2 \longrightarrow H_2O$$

12 32 44 2 16 18

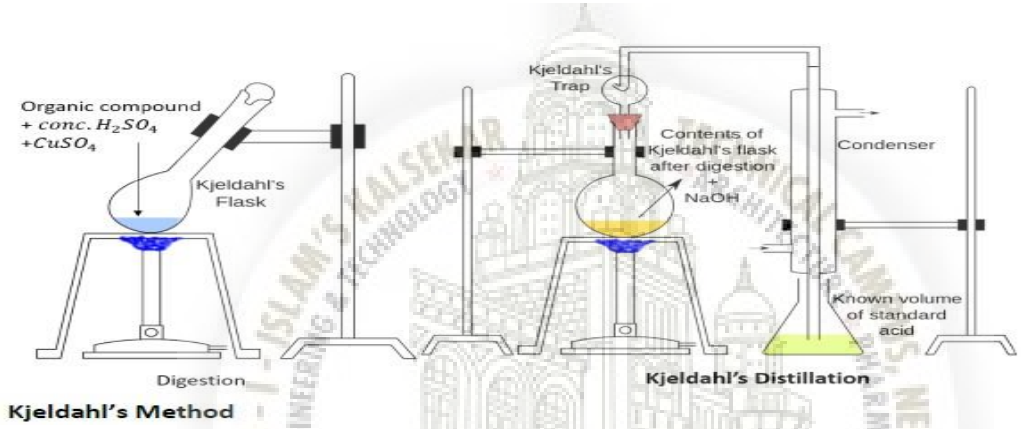
% Carbon = Increase in weight of KOH tube x 12 x 100
Weight of coal sample x 44

% Hydrogen = Increase in weight of $CaCl_2$ tube x 2 x 100
Weight of coal sample x 18

Significance:1)Higher the percentage of Carbon and Hydrogen ,higher is the calorific value and better is the quality of coal.

2) Hydrogen is mostly associated with volatile matter and present in the form of water. Hence, higher content of Hydrogen is undesirable.

2) % Nitrogen:



About 1gm of accurately weighed coal sample is digested in a Kjeldahl's flask with conc H_2SO_4, K_2SO_4, and $HgSO_4$ (acts as a catalyst) .The nitrogen present in the coal gets converted into ammonium sulphate. The contents of the Kjeldahl's flask are quantitatively transferred to a round bottomed flask, then NaOH is added and refluxed.

Liberated ammonia is collected in a flask containing known quantity of known normal H_2SO_4. The unreacted H_2SO_4 is titrated against std NaOH using phenolphthalein indicator till the colour changes from colourless to light pink. A blank titration of the same H_2SO_4 is carried out.

% Nitrogen = Volume of acid used x Normality of acid x 1.4
Weight of coal sample taken

$(NH_4)_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2\ NH_3 + 2H_2O$

Let weight of coal taken = W gms

Volume of N/10 NaOH required for Blank reading = Y ml

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

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

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

1000ml of 1N ammonia solution = 17gm of NH_3

1000ml of 1 N NH_3 solution = 14gm of Nitrogen

1000ml of 0. 1 N NH_3 solution = 1.4gm of Nitrogen

(y-x) ml of 0.1N NH_3 solution = $\frac{1.4\,(y-x)}{1000}$ gms of Nitrogen

W gm of coal contains $\frac{1.4\,(y-x)}{1000}$ gms of Nitrogen

100gm of coal contains = $\frac{1.4(y-x)}{1000} \times \frac{100}{W}$ gm of Nitrogen

% Nitrogen = $\frac{1.4\,(y-x)}{10 \times W}$

OR **% Nitrogen = $\frac{\text{Volume of acid used x Normality of acid x 1.4}}{\text{Weight of coal sample taken}}$**

Significance :

Since, Nitrogen is an inert and incombustible gas, it doesn't help in combustion and thus has no calorific value. Hence its presence is undesirable in good quality coal.

3) % Sulphur: A known weight of coal is burnt completely in Bomb calorimeter, in a current of oxygen .During burning, sulphur present in coal is oxidized to sulphate. Ash from bomb calorimeter is extracted with dil HCl and acid extract is treated with Barium Chloride solution to precipitate sulphate as Barium Sulphate. This precipitate is filtered , washed and heated to a constant weight and weighed.

$$S \xrightarrow{O_2} SO_4 \xrightarrow{BaCl_2} BaSO_4$$

32 233

% Sulphur = $\frac{\text{Weight of } BaSO_4 \text{ obtained x 32 x 100}}{\text{Weight of coal sample taken in bomb x 233}}$

Significance: Presence of Sulphur in coal contributes to the calorific value of coal ,but its combustion products,SO_2 and SO_3 are highly corrosive to the equipment's specially in presence of moisture.
Also ,the oxides of sulphur cause environmental pollution.

4) % Ash: Same as in Proximate Analysis

5) % Oxygen = 100 - (% C + % H + % N + % S + % Ash)

Liquid Fuels

Q8) Define crude petroleum oil and give its classification.

Ans) The crude petroleum obtained from earth's crust is the main source of other liquid fuels. Mainly it consists of a complex mixture of aliphatic hydrocarbons with small amount of other organic compounds containing nitrogen, oxygen and sulphur.

Classification of Crude Petroleum Oil

Based on the residue left after distillation, the crude petroleum is classified as,

1)Paraffinic Based Petroleum: These mainly consists of saturated paraffinic hydrocarbons together with smaller amounts of naphthenes and aromatic hydrocarbons. These oils on distillation leave a residue of solid paraffin wax.

2) Asphaltic Based Petroleum: These mainly consists of non-paraffinic hydrocarbons such as aromatic and naphthenic hydrocarbons. These oils on distillation leave a residue of solid paraffin wax.

3) Mixed Base Petroleum: These are intermediate between paraffinic and asphaltic based oils. These contain varying proportions of asphaltic, naphthenic and aromatic hydrocarbons.

Q9) Explain Mining of Petroleum.

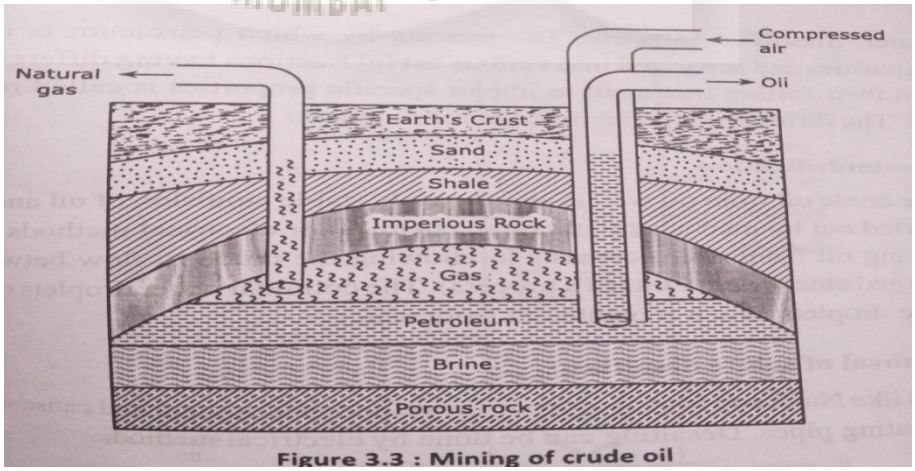


Figure 3.3 : Mining of crude oil

Ans) Petroleum is found underneath the earth's surface at different depths (at about 5000feet or more) varying from place to place. The oil is found below the impervious rock floating over salt water of brine. It is often accompanied with natural gas (mainly methane) which exerts pressure on the oil surface and drive out oil through natural openings, the method of pumping is called as **Pressure drive,** but when the pressure is low, the oil has to be removed by lift pump.

Mining of oil is done by drilling holes in the earth's crust and sinking two coaxial pipes into the oil bearing strata.

The compressed air is forced through the outer pipe when oil comes out through the inner pipe ,this method is called as **Water drive.**

Q10) Explain the refining of petroleum with reference to bubble tower diagram.

Ans) **Refining of Petroleum:**

The process by which the crude oil is freed from its impurities, separated into various fractions having different boiling points, and further treated to remove undesirable tendencies and to impart specific properties in them is broadly known as **Refining of Petroleum**.

The following are the steps involved in refining of petroleum.

1)Removal of Water/ De-emulsification: The emulsified oil along with salts dissolved is removed by subjecting the crude oil to an electric field formed by a high voltage alternating current which destroys the emulsion films. The colloidal water droplets unite to form large drops which separate from oil.

2) Removal of salts : The emulsion free crude oil is then subjected to electrical desalting to remove NaCl and $MgCl_2$ which may corrode the refining equipment and cause scale formation in the heating pipes.

3) Removal of Sulphur: The oil is treated with copper oxide to remove sulphur compunds as copper sulphide which is removed by filtration.

4) Fractional Distillation:

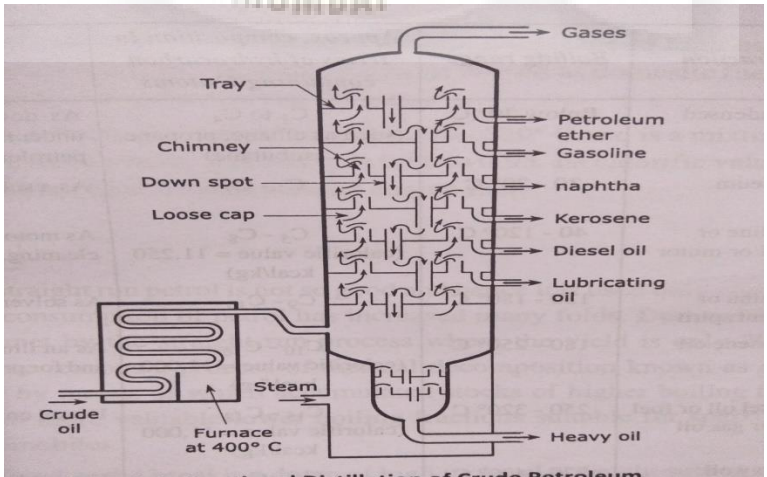


Figure 3.4 : Fractional Distillation of Crude Petroleum

The fractionating column is about 30m in height and 3m in diameter. It consists of around 50-60 horizontal trays and each tray is provided with 4 to 5 bubble cups with loose caps.

The crude oil is heated to about 300-400^{0}c in the pipe still and the hot vapours are allowed to pass through the bubble towers .

The vapours travel upwards through the bubble cups and gets cooled.

Higher boiling point organic compounds get condensed in bubble cups and liquid deposits on the trays.

The uncondensed vapours rises up and get condensed turn by turn on upper bubble trays. The extra liquid on tray flows down through the downspout pipe to the next lower plate. Higher boiling fractions condense at lower plates and lower boiling fractions condense at plates at higher level.

Thus the crude oil gets fractionated into different fractions in order of their boiling ranges and are collected at different heights in the columns with the help of condensers.

This fractionation gives uncondensed gases, straight run petrol, kerosene and gas oil fractions.

A brief description of three most important liquid fuels derived from petroleum is given below.

Sr No	**Name of fraction**	**Boiling range**	**Approximate Hydrocarbon range**	**Uses**
1.	Uncondensed Gases	Below 30^{0}c	C1 to C4	As domestic or industrial fuel .(LPG)
2.	Petroleum ether	30^{0}c - 70^{0}c	C3-C7	As a solvent.
3.	Gasoline or petrol or motor spirit	40^{0}c-120^{0}c	C5-C8	As a motor fuel, solvent and in dry cleaning
4.	Naphtha or solvent spirit	120^{0}c-180^{0}c	C9-C10	As a solvent in dry cleaning.
5.	Kerosene oil	180^{0}c-250^{0}c	C10-C16	As an illuminant, jet engine fuel and for preparing laboratory gases.
6.	Diesel oil or fuel oil or gas oil	250^{0}c-320^{0}c	C15-C18	Diesel engine fuel.
7.	Heavy oil	320^{0}c-400^{0}c	C17-C30	For getting gasoline by cracking process.
8.	Residue of Asphalt or Petroleum coke	Above 400^{0}c	C30 and Above	Water –proofing of roofs and road making. As a fuel and in moulding arc light rods.

i) Gasoline or petrol is obtained between 40^0c -120^0c and is a mixture of hydrocarbons such as C5-C12 (Pentane) to C8-H18(Octane).Its approximate composition is C= 84%,H=15%,N+S+O = 1%.Its calorific value is about 11,230 kcal/kg. It is highly volatile, inflammable and used as fuel for internal combustion engines of automobiles and aeroplanes.

ii)Kerosene oil is a fraction obtained between 180^0c - 250^0c and is a mixture of hydrocarbons such as C10H22 (Decane) to C16H34(Hexadecane).Its approximate composition is C= 84%,H=16% with less than 0.1%S.Its specific gravity is 0.75-0.85.Its calorific value is 11,100kcal/kg. Due to high boiling point range, kerosene does not vapourises easily. It is used as a domestic fuel in stoves, as jet engine fuel and for making oil gas.

iii) Diesel oil is a fraction obtained between 250^0c -320^0c and is a mixture C15H32 to C18H38 hydrocarbons. Its density is 0.86 to 0.95.Its calorific value is about 11,000kcal/kg. It is used as a diesel engine.

Q11) Define Cracking. Explain Thermal Cracking in detail.

Ans**) Defination:** The process of thermal decomposition of high boiling fractions of high molecular weight hydrocarbons to low boiling fractions of low molecular weight hydrocarbons is called as **Cracking.**

Eg) $C_{10}H_{22} \rightarrow C_5H_{12} + C_5H_{10}$, $C_{16}H_{34} \rightarrow C_8H_{18} + C_8H_{16}$

Decane Pentane Pentene Cetane Octane Octene

Types of Cracking:

1) Thermal Cracking

2) Catalytic Cracking

1) Thermal Cracking:

a) Liquid Phase Cracking: In this method ,oil is pumped into the coil kept at 420^0c to 550^0c under a pressure of 15 to 100kg/cm^2 .Octane value of gasoline obtained after cracking is low ,ie 65 to70 and therefore mixed with higher octane value gasoline.

b) Vapour Phase Thermal Cracking: In this method, oil is first converted into vapours by heating it in an heater at 400^0c. The vapours are then passed to the reaction chamber which is maintained at 600^0c to 650^0c and under a pressure of 10 to 20kg/cm^2. Octane value of gasoline obtained is 70 to 80.

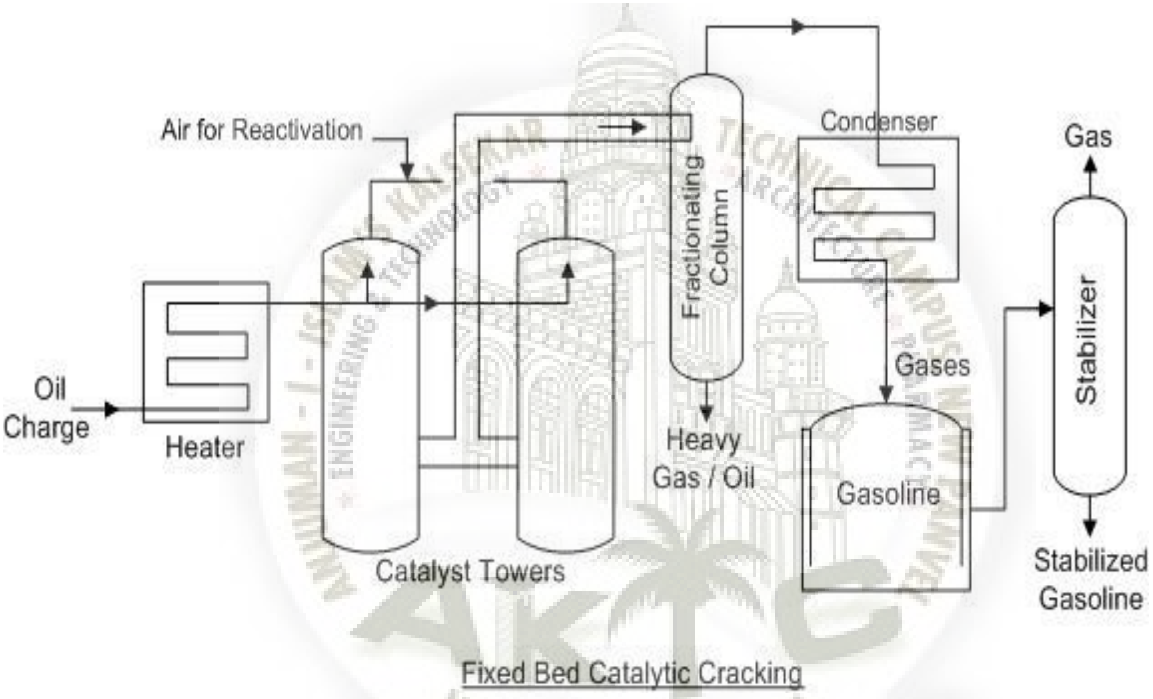
2) Catalytic Cracking: When cracking is done in presence of a catalyst, usually a mixture of silica and alumina or aluminium silicate, it is known as **Catalytic Cracking.**

Types of Catalytic Cracking:

a) Fixed Bed Catalytic Cracking

b) Fluid Bed or Moving Bed Catalytic Cracking

a) Fixed Bed Catalytic Cracking

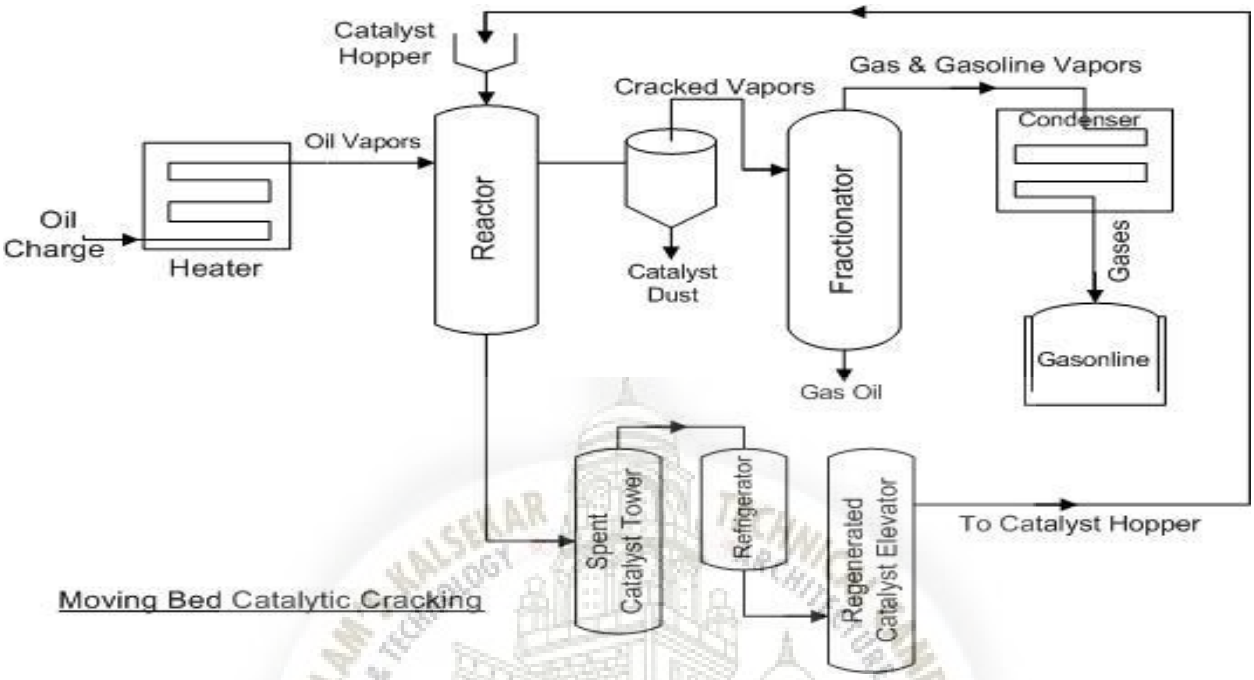


Fixed Bed Catalytic Cracking

In this method the heavy oil is passed through a preheater maintained at 420^0c to 560^0c to convert into vapour state. The vapours are passed through a fixed bed of catalyst (artificial clay mixed with zirconium oxide)maintained at 425^0c to 450^0c and pressure of 1.5kg/cm^2,undergoes cracking and then fractioned to get gasoline and some gases are condensed and the uncondensed gases move on.

The condensate is now sent into stabilizer where the dissolved gases are removed and pure gasoline is recovered with octane value 80 to 85. After sometime, the catalyst gets deactivated because of deposition of carbon on it. Hence, it is taken out and heated in open to get rid of deposited carbon as CO_2.

b) Fluid Bed or Moving Bed Catalytic Cracking:



In this process, the catalyst is in the form of a very fine powder so that it behaves like a fluid. Heated heavy oil vapours enter at the bottom of catalyst chamber and catalyst is introduced from top of hopper and meets the upcoming stream of oil vapours. The cracked vapors enter the fractionating column where heavy oil is separated from gas and gasoline.

The heavy oil is withdrawn from the bottom and vapours are sent to a cooler where it is condensed and sent to stabilizer to recover pure gasoline. The spent catalyst is withdrawn from bottom and is reactivated (maintained at 600^0c) were the deposits of carbon on the catalyst are burnt off. The reactivated catalyst is reused.

Q12) What are the advantages of catalytic cracking over the thermal cracking?

Ans) i) Gasoline produced has higher octane rating and is of better quality.

ii) Yield of petrol is higher.

iii) The process can be better controlled than the thermal process. The product contains has sulphur compounds is much lower pressure (about 1-5 kg/m) is needed.

iv) The presence of isoparaffines and aromatics, improve antiknocking quality of gasoline. The percentage of gum forming compounds is very low.

Q13) Distinguish between Thermal Cracking and Catalytic Cracking.

Ans)

Sr NO	Thermal Cracking	Catalytic Cracking
1.	In this method heavy oils are subjected to high temperature and pressure when bigger hydrocarbons break down to give smaller molecules.	Heavy oils are cracked in presence of catalysts like Al2(SiO3)3 or alumina at comparatively low temperature and pressure.
2.	High temperatures of 475^0c to 650^0c and pressures of 15 to 100kg/cm2 are required for cracking.	Temperatures of 425^0c to 570^0c and low pressures of 1.5kg/cm2 are required for cracking.
3.	There are two types of Thermal cracking a)Liquid Phase b) Vapour Phase	There are two types of Thermal cracking a)Fixed Bed b) Moving Bed
4.	Octane value is 65 to 70	Octane value is 85 to 90
5.	Yield of gasoline is less	Yield of gasoline is more.
6.	External fuel is necessary for cracking.	No external fluid is required.
7.	Cracking can't be easily controlled.	Cracking can be easily controlled
8.	The percentage of gum or gum forming compound is more.	The percentage of gum or gum forming compound is less.
9.	The product contains more amount of sulphur.	The product contains less amount of sulphur.
10.	Product possess less antiknock properties than catalytic cracking.	Product possess better antiknock properties than thermal cracking.

Q14) Distinguish between Fixed Bed Catalytic Cracking and Fluid Bed Catalytic Cracking.

Ans)

Sr NO	Fixed Bed Catalytic Cracking	Fluid Bed Catalytic Cracking
1.	In this process the oil vapours are passed on to fixed bed of catalyst.	In this process the mixture of oil vapours and finely divided catalyst behaves in many respect as fluid.
2.	Temperature in the reactor is maintained at 425^0c to 450^0c and pressure of 1.5 kg/cm2	Temperature in the reactor is maintained at 500^0c and pressure of 3 to 5 kg/cm2
3.	Catalyst is not used.	Catalyst is used.
4.	The fixed bed is regenerated by burning of deposited carbon in a stream of hot air.	A regenerator is used to regenerate the fluid bed.
5.	Cracked vapours are passed into fractionating column.	Cracked vapours are first passed through internal cyclone separator and then into a fractionating column.

Q15) Explain the various methods involved in Refining of Gasoline.

Ans) The gasoline obtained by fractional distillation consists of undesirable, unsaturated straight chain hydrocarbons which gets oxidized and polymerized thus causing gum formation . Sulfur compounds forms sludge on storing, hence refining is required.

i) Removal of Sulphur compounds(Sweetening) : Sweetening means the removal of mercaptons,H_2S and dissolved free S so that the products has no bad smell and has no tendency to corrode. They can be removed by following methods.

1) Oxidation Processes:

i) H_2SO_4 treatment : In this oxidation of mercaptons occur so that it is converted to disulphides.

$$R\text{-}SH + H_2SO_4 \longrightarrow RS\text{-}SO_3H + H_2O$$

$$R\text{-}SH + RS\text{-}SO_3H \longrightarrow (RS)_2\,SO_2 + H_2O$$

$$(RS)_2\,SO_2 \longrightarrow R_2S_2 + SO_2$$

ii) Doctor's Treatment: In this method, alkaline solution of sodium plumbite with controlled addition of sulphur is used.

$$2R\text{-}SH + Na_2PbO_2 \longrightarrow (RS)_2\,Pb + 2NaOH$$

$$(RS)_2Pb + S \longrightarrow R_2S_2 + PbS\ (s)$$

The PbS formed is removed by filtration

iii) Catalytic removal: PbS act as a catalyst when oil is treated with NaOH

$$2R\text{-}SH + S + 2NaOH \longrightarrow R_2S_2 + Na_2S + H_2O$$

In this method, disulphide are formed which can lower the octane number and it forms SO_2 in exhaust pipes. So other methods are preferred.

2) Solvent processes:

i**) Caustic washing:** 5 – 15% caustic solution reacts with H_2S and low molecular weight mercaptons and removes them.

ii) Solutiser process: 25% caustic alkali with solutiser agent like potassium iso butyrate is used.

3) Catalytic desulphurization: In this method all sulphur compounds except heterocyclic sulphur compounds are removed. The sulphur compounds are decomposed at high temperature and produce H_2S which is removed by fractionation. The catalyst used can be bauxite or Fuller's earth.

ii) Removal of colour: Presence of Sulphur compounds, high boiling molecules, gum etc result in colour formation which can be removed by passing the gasoline vapours through Fuller's earth or by giving cold sulphuric acid treatment.

iii) Removal of gum: Gum is a dark coloured polymer formed due to the oxidation and polymerization of diolefins. To prevent it , inhibitors like cresol, phenylene diamine are added. In natural gasoline there are no diolefins so no gum is formed whereas gasoline formed by thermal cracking contains diolefins.

Stabilisation: Gasoline is stabilized by removing gases like CH_4, C_2H_6, C_3H_8,and C_4H_{10} by passing into a fractionating tower.

Q16) Explain knocking in Petrol engine.

Ans) **Knocking:** It is defined as sharp metallic sound produced in the internal combustion engine and results into a loss of energy.

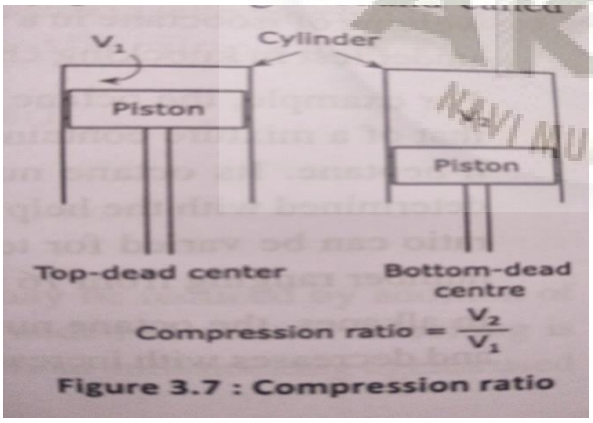
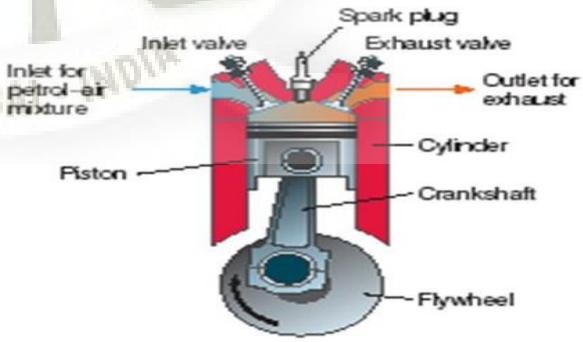


Figure 3.7 : Compression ratio



Petrol Engine:

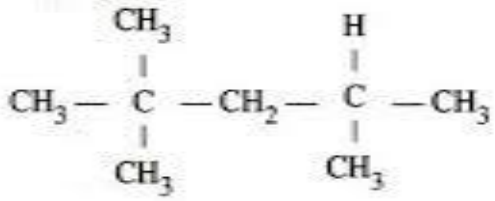
- The petrol engine is a spark ignition type of internal combustion engine.
- In this a mixture of air and fuel (petrol) is compressed and ignited by an electric spark.

- Generally, this combustion of fuel proceeds in a regular and uniform way. But in certain circumstances, the rate of oxidation is so great that the mixture detonates producing the sound called **"Engine Knock'.**
- The rate of oxidation of a hydrocarbon molecule depends on the number of carbon atoms in the molecule, structure and temperature.
- The temperature in turn depends upon the compression ratio.
- The ratio of the cylinder volume at the end of the suction stroke to that at the end of the compression stroke of the piston. Theoretically the power output and efficiency of an IC engine should increase with the increase in the compression ratio (CR).But in actual practice ,the power increases to a maximum and then falls rapidly with further increase in CR, knocking becomes more pronounced and heavy as the CR is increased above the optimum value and finally pre-ignition occurs.
- The tendency to knock depends upon the type of fuel, engine design, plug location etc.

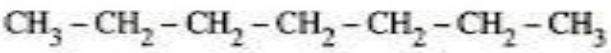
Q17) Define and Explain Octane Number.

Ans)

- The knocking characteristics of petrol sample are described by the octane number or antiknock value. Higher the octane number, lower is the tendency to knock and better is the quality of petrol.
- Isooctane (2,2,4-trimethyl pentane) has the least knocking tendency and its octane number is arbitrarily fixed as 100.
- n-Heptane ,a straight chain hydrocarbon, has highest tendency to knock and is assigned an octane number zero. In general, straight chain hydrocarbons have low octane numbers and those with branched chain have high values. The petrol whose octane number is to be determined is compared with reference mixtures of isooctane and n-heptane.
- **Octane Number is defined** as the percentage by volume of Iso-Octane in a mixture of Iso-octane and n-heptane which has the same knocking characteristics as that of fuel under test.



Iso octane 2, 2, 4-trimethyl pentane
Octane number = 100



n-Heptane
Octane number = 0

- For example, the octane number of automobile petrol is found to be equivalent to that of a mixture containing 70% by volume of Isooctane and 30% by volume of n-heptane. Its octane number is said to be 70.
- The octane number of petrol is determined with the help of a special single cylinder engine where the compression ratio can be varied for testing the octane. Automobiles petrol have octane number ranging from 76 to 95.
- In alkanes, the octane number increases with the number of branches in the chain and decreases with increase in chain length. Alkenes have higher octane number than alkanes containing same number of carbon atoms.
- Among alkenes, the octane number increases with a shift in the position of double bond to the center of the molecules.
- Cycloalkanes have a higher octane rating than alkanes with the same number of carbon atoms. The highest octane numbers are associated with the aromatic hydrocarbons.

The octane number of some common hydrocarbons is given below

Hydrocarbon	Octane number
Benzene	100+
Isopentane	90
Cyclopentane	77
2-methyl pentane	71
n-pentane	62
n-hexane	26

- Fuels with octane number greater than 100 are quite common now-a-days. They are rated by comparison with a blend of iso-octane with Tetra Ethyl Lead (TEL) which greatly diminishes the knocking tendency of any hydrocarbon with which it is mixed. The value of octane number in such cases is determined by extrapolation.

Q18) Explain knocking in Diesel Engines.

Ans)

- The diesel engine is a compression ignition engine that uses long straight chain hydrocarbons having boiling range 180^0c to 360^0c.
- Here air is passed into the cylinder and compressed to about 500psi (upstroke).
- Due to compression, the temperature of air rises to about 500^0c.
- The diesel oil is injected towards the end of compression stroke in the form of fine droplets into the hot compressed air.
- The injected oil droplets absorb the heat from the compressed air and get vaporized, attain self ignition temperature and burn spontaneously during the downward stroke.
- However the combustion of fuel in the diesel engines is not instantaneous but there exists a time lag between fuel injection and ignition.
- This time lag or ignition delay is a measure of knocking in diesel fuels.
- If the fuel has a short ignition delay, the fuel injected into the burning mixture continues to burn at the rate at which it is injected.
- On the other hand , if the fuel has a long ignition delay, then the fuel accumulation occurs in the engine even before ignition.
- When ignited, an explosive combustion occurs with sudden increase in pressure.
- This is called **'Diesel Knock'.**
- Longer the ignition delay, greater is the diesel knock.

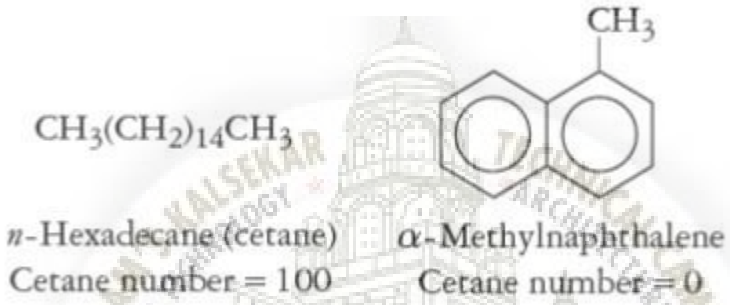
Q19) Explain Cetane Number.

Ans)

- The knocking characteristics of a diesel oil are expressed in terms of cetane number. Cetane ($C_{16}H_{34}$) is a saturated hydrocarbon, ignites very quickly and thus has very short ignition delay.

- Its Cetane number is 100. On the contrary α- methyl napthalene has very long ignition delay as compared to any other diesel fuel. Hence its Cetane Number is zero.
- **Defination:** The percentage by volume of cetane in a mixture of Cetane and α- methy napthalene which just matches the knocking characteristics of diesel oil under test.
- Oils having high octane no are good diesel fuels (least ignition delay) but are poor gasoline fuels (have low octane no) and vice versa.
- The Cetane no of diesel oil can be increased by addition of certain compounds called Dopes

or Ignition accelerators like ethyl nitrite ($C_2H_5NO_2$) ,ethyl nitrate ($C_2H_5NO_3$), Isoamyl nitrate ($(CH_3)_2CHCH_2CH_2NO_3$) etc



Q20) Write a short note on Anti-knocking agent.

Ans)

- The octane number of many poor fuels can be raised by the addition of Tetra Ethyl Lead(TEL)or (C2H5)4Pb or diethyl telluride (C2H5)2Te. About 0.5ml of TEL is added to 1 litre of motor fuel and 1ml of TEL is added to 1 litre of aviation fuel.
- Knocking in a petrol engine is due to the spontaneous ignition of the last portion of compressed mixture of petrol and air .The process of preignition is due to the production of hydroxyl and other free radicals which lead to explosive combustion .Addition of TEL react with free radicals and lead oxide is produced which decreases the chances of early denotation.
- The deposit of lead oxide is harmful to engine life. Therefore, ethylene dibromide (C 2H4Br2) is added to dope to convert the lead formed by the combustion into more volatile lead bromide which is swept out with the exhaust gases.
- But this also leads to atmospheric pollution allowed to settle down and the lower glycerine layer is drawn off. The upper layer of the methyl esters is washed and purified further. The unreacted methanol is recovered in a condenser, purified in a rectifying column and recycled.

Advantages:

- It can be prepared from renewable resources. Biodiesel is biodegradable. The exhaust gas emissions are lesser as compared to the conventional diesel fuels. Since the organic carbon

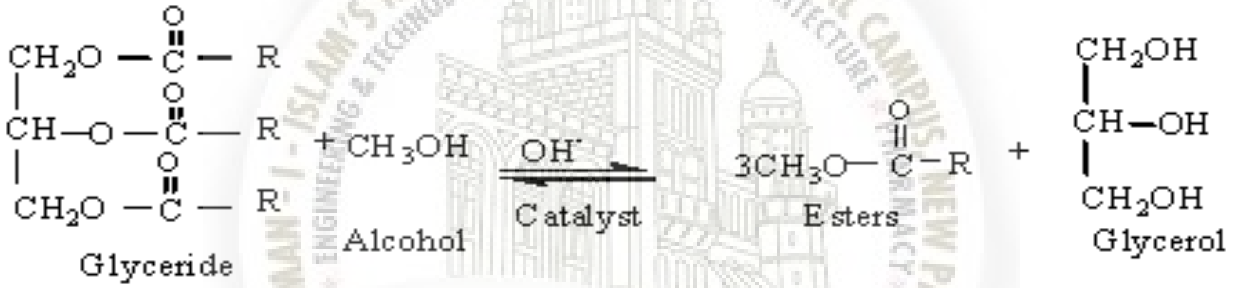
present in biodiesel is photosynthetic in origin, it does not contribute to rise the level of environmental CO_2 and the subsequent greenhouse effect.

Q21) What is Bio-Diesel? Explain the method to obtain Bio-diesel from vegetable oil. Give advantages of Bio-diesel.

Ans)

- Biodiesel is defined as the mono-alkyl esters of fatty acids derived from vegetable oil or animal fats.
- This reaction requires a catalyst such as sodium or potassium hydroxide and is called as 'Trans esterification'
- This is nothing but displacement of alcohol from an ester by another alcohol. The trans-esterification reaction of triglycerides present in vegetable oils using methanol may be represented as follows,

Reaction:



- Triglycerides can readily be trans esterified batch wise at atmospheric pressure and at temperature of about 60 to 70°c with an excess of methanol in presence of alkaline catalyst.
- After the reaction is complete, the mixture is allowed to settle down and the lower glycerine layer is drawn off.
- The upper layer of the methyl esters is washed and purified further. The unreacted methanol is recovered in a condenser, purified in a rectifying column and recycled.

Advantages:

1)It can be prepared from renewable resources.

2) Biodiesel is biodegradable.

3) The exhaust gas emissions are lesser as compared to the conventional diesel fuels.

4) Since the organic compound present in biodiesel is photosynthetic in origin, it does not contribute to rise the level of environmental CO_2 and the subsequent greenhouse effect.

Q22) Explain production of hydrocarbons from Petrocrops.

Ans)

- The latex of some plants contain petroleum like hydrocarbons which can be extracted by organic solvents as a biocrude analogus to crude petroleum.
- Biocrude can be hydrocracked (Cracked with hydrogen) to yield oil. Such plants are called Petrocrops. These are lactiferous plants (plants belonging to Euphorbiaces, asclepiadaceae families)growing in arid and semiarid regions specially in uncultivated lands.
- These plants secrete milky latex. The latex can be collected and stored or it can be extracted from the biomass using organic solvents.
- This latex is a rich source of hydrocrackable hydrocarbons and is called 'Biocrude'. This can be converted into petroleum products using metal oxide catalysts.
- More than 400 species of petroleum plants belonging to different families are known .

Q23) Define Power alcohol. Give advantages of power alcohol.

Ans)

- Power alcohol is a gasoline blend containing ethanol which can be used as a fuel in internal combustion engines.
- Blend containing up to 25% of alcohol with petrol are used. Its objective is to reduce oil imports and provide an alternative to non- renewable energy source, gasoline.

Advantages:

1) Alcohol has an octane number of 90,while petrol has octane number of 60-70.Addition of power alcohol to petrol increases the octane number. Hence alcohol blended petrol possesses better anti-knock properties.

2) Because of the higher octane number, alcohol-blended petrol can be used in engines with higher compression ratio. This compensates for the lower heating value of alcohol in the blend.

3) There are no starting difficulties with alcohol-petrol blend.

4) Lubrication in case of alcohol-petrol blend and pure petrol is the same.

5) Ethanol is biodegradable.

Q24) Explain the production of Ethanol from molasses.

Ans)

- Ethanol can be produced by fermentation and can be used as fuel. Two major energy crops are sugarcane and sugar beet.
- Along with sugar these plants give valuable byproducts such as bagasse which is a fibrous residue left after extraction of sugar juice.

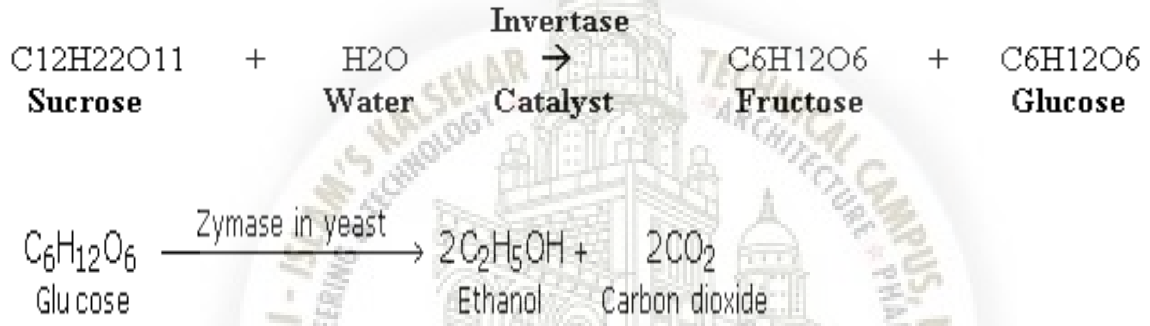
- It can be converted into microbial protein which is used as animal feed. It is also used for manufacture of ethanol and paper.
- After isolation of sugar the mother liquor is known as **Molasses.** It is used to manufacture ethanol by fermentation as follows:

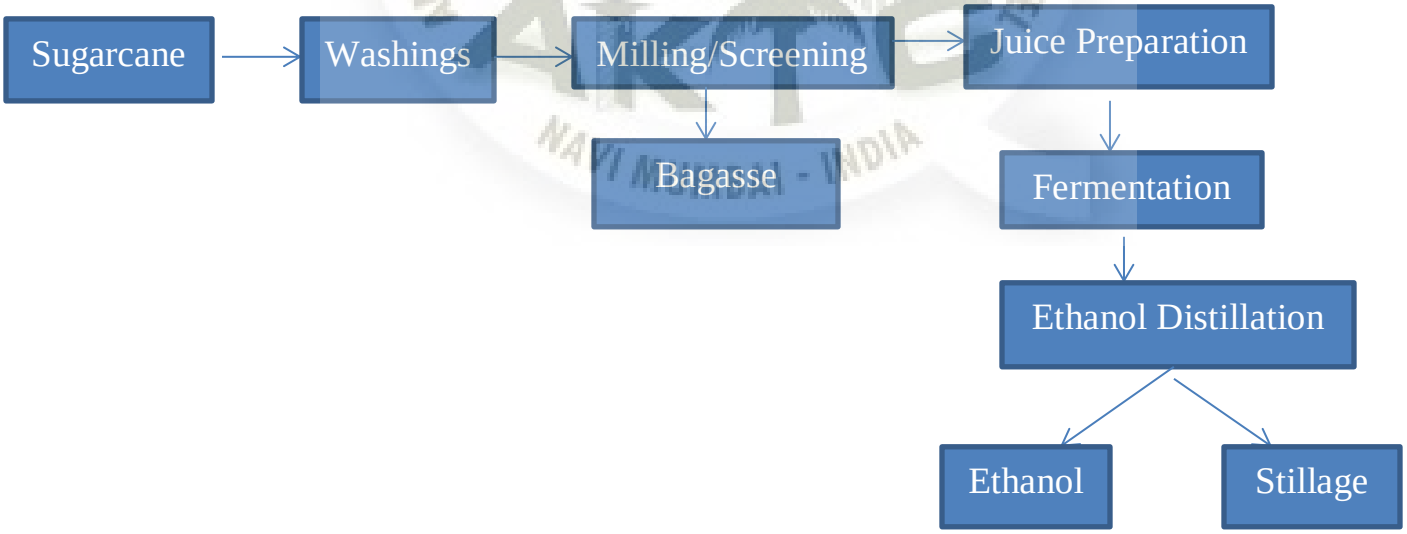
This fermentation is carried out by yeasts.

Fermentation by yeasts: The yeast cell produces an enzyme called as Zymase which acts only on monosaccharides.

It contains another enzyme invertase which hydrolyses sucrose (cane sugar) into glucose and fructose (Invert sugar).Then they can be converted into ethyl alcohol and carbondioxide by action of zymase.

Reactions:





Eg) i) Some fermentation produce acids such as acetic acid in the preparation of vinegar from apple juice.

$C_6H_{12}O_6 \longrightarrow 2\ C_2H_5\ OH + 2CO_2$ (Alcoholic Fermentation)

Glucose in Apple juice — Ethyl alcohol

$C_2H_5\ OH + O_2 \longrightarrow CH_3COOH + H_2O$ (Acetic Fermentation)

ii) Koumiss and cheese are made by acid fermentation of milk.

Q25) Write a short note on Catalytic Converter and Unleaded Gasoline.

Ans)

- Mixing 0.1% TEL per gallon of gasoline increases the octane rating by 10 to 15 points. Since lead is toxic and causes environmental pollution, slowly it has been phased out from gasoline.
- Unleaded gasoline is supplied in India to minimize undesirable lead emissions on one hand and to enable incorporation of catalytic converters with the internal combustion engines.
- Catalytic converter is fitted in the exhaust system after the exhaust manifold of petrol driven/vehicles.
- When the exhaust gases containing partially oxidized carbon, unoxidized hydrocarbons, and NO_x come into contact with the coated catalyst surface, they get catalytically converted into CO_2 and H_2O.Under suitable conditions of engine operation NO_x come gets reduced to N_2.

- $CO + 0.5O_2 \rightarrow CO_2$
- $C_3H_6 + 4.5O_2 \rightarrow 3CO_2 + 3H_2O$
- $NO + CO \rightarrow N_2 + CO_2$

- Catalysts made of noble metals like Platinum (Pt) and Palladium (Pd) are susceptible to get poisoned by lead and they are very expensive.
- Hence leaded petrol cannot be used in engines with catalytic converters. The newly developed catalytic converter technology consists of a ceramic or metallic honeycomb support coated with a low cost catalyst placed in a suitably designed non- corrosive metallic housing.

Q26) Define and Explain Fuel cell. What are its types?

Ans)

- A fuel cell is a device that converts the chemical energy from a fuel into electrical energy through a chemical reaction of positively charged hydrogen ions with oxygen or another oxidizing agent .
- It consists of two electrodes and an electrolyte that converts chemical energy of a fuel (Hydrogen, methanol etc) and an oxidant (air, oxygen) into electricity.

- Fuel cell can be represented as : Fuel/Electrode/Electrolyte/Electrode/Oxidant
- Fuel and oxidizing agents are continuously and separately fed into the respective electrode at which they undergo redox reaction generating electrical energy.

At Anode: Fuel undergoes oxidation

Fuel $\longrightarrow$ Oxidized Product + ne^-

At Cathode: The oxidant gets reduced

Oxidant + ne^- $\longrightarrow$ Reduced product

Types of Fuel Cell:

On the basis of type of electrolyte they are classified as follows:

1) Alkaline Fuel Cell: It consists of KOH as an electrolyte with porous electrodes of carbon having Nickel or platinum as the electro-catalyst. Hydrogen is used as fuel and oxygen as oxidant.

2) Molten Carbonate Fuel Cell: It consists of molten mixture of high temperature alkali carbonate like Na,K or Li to be used as an electrolyte.

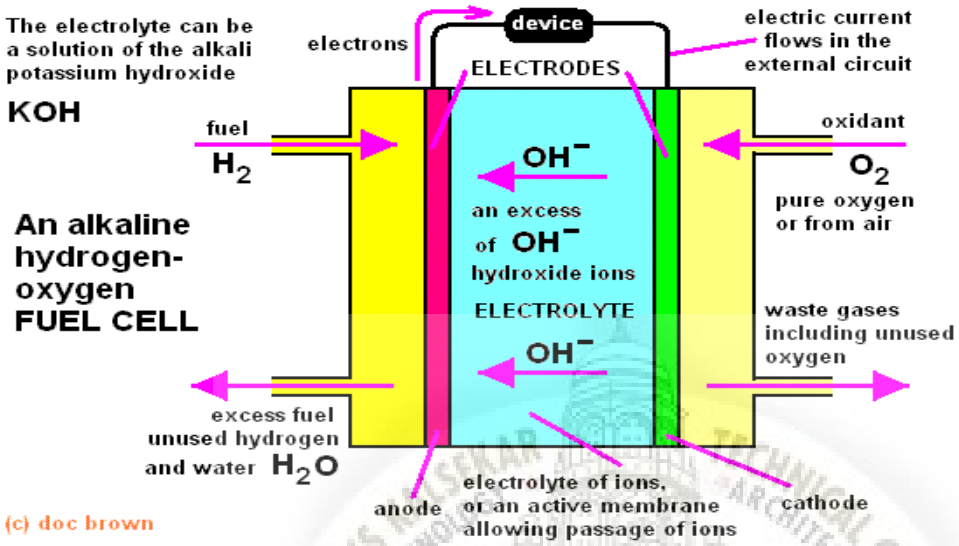
3) Phosphoric Acid Fuel Cells: It consists of anode of porous graphite substrate with platinum alloy as the catalyst, cathode is similar to the anode but made with a noble metal catalyst, and concentrated phosphoric acid as an electrolyte.

4) Polymer Electrolyte Membrane Fuel Cells or Proton Exchange Membrane Fuel Cells: In this cell a proton-conducting polymer membrane containing the electrolyte solution that allows H+ ions to pass through it is used as an electrolyte. Finely divided platinum deposited on each surface of membrane serves as a catalyst and current collector.

5) Solid Oxide Fuel Cells: It consists of hard ceramic compound of metal (like calcium or Zirconium) oxides as Electrolyte .It allows ionic conductivity of oxygen ions from cathode to anode.

Q27) Explain Hydrogen Oxygen Fuel Cell with neat labeled diagram.

Ans)



- It is the simplest type of alkaline Fuel cell in which Hydrogen is used as the fuel and oxygen gas is the oxidant.
- The cell consists of a porous carbon electrode impregnated with catalyst such as finely divided Platinum or Palladium as anode.
- The cathode is also a porous carbon electrode impregnated with Pt or Ag as a catalyst.
- The electrolyte is an aqueous solution of KOH. The hydrogen gas fuel is continuously supplied at anode and oxygen gas at the cathode.
- As the hydrogen gas diffuses through the anode, it is adsorbed at the electrode surface and reacts with hydrogen ions to form water. At the cathode oxygen diffusing through the cathode is adsorbed and reduced to hydroxyl ions.
- The electrode reaction are as follows:

At Anode: $2\,H_{2(g)} + 4OH\,(aq) \longrightarrow 4\,H_2O + 4e^-$

At Cathode: $O_{2(g)} + 2\,H_2O(l) \longrightarrow 4OH^-$

Net Reaction : $2\,H_{2(g)} + O_{2(g)} \longrightarrow 2\,H_2O(l)$

The hydrogen and oxygen are converted to water, which is the waste product of the cell. This cell generates a voltage of 105V as long as continuous supply of hydrogen and oxygen is maintained.

Advantages:

1)High efficiency of the conversion process.

2) No moving parts and hence operates silently and requires less maintenance.

3) Absence of harmful waste products.

4) Can be installed near the use point, thus reducing electrical transmission requirements and accompanying losses.

Disadvantages:

1)High initial cost.

2) Fuel in the form of gases and oxygen need to be stored in tanks under high pressure .

3) Power output is moderate.

4) Most alkaline cells suffers from CO_2 degradation and hence CO_2 should be removed from fuels and air.

Applications:

1)Fuel cells can be located near the load center, to meet the demand of isolated sites such as construction sites ,military caps and small villages. Emergency or auxiliary supply to critical loads such as hospitals, educational institutions etc can be met using fuel cells.

2) It can be used as a mobile power source in vehicles , submarines and spacecraft's. A Hydrogen – Oxygen alkali fuel cell has been used successfully to provide power in shuttle spacecraft's.

3)It is also being tested as a power source for propulsion of electric vehicles like car, buses etc.
