MODULE - 2

Chemical Energy Sources and Engineering Materials

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10 hours

Introduction:

Energy: Energy is an important aspect for human activity. large number of energy sources such as animal waste, coal, oil and gas are available. Out of these, coal, oil and gas are called Fossil fuels. As these sources are depleting in nature, after some years availability of fossil fuels may come to end. Hence these sources are called non-renewable sources. But wood, charcoal and animal wastes are renewable because they can be regenerated again in nature in short time.

Today we are facing many energy problems, because the sources of petroleum and natural gas are dwindling or depleting day by day. Hence, there is lot of research work going on to develop new sources of energy, alternative to fossil fuels.

Definition of Fuel: Chemical fuel is "**combustible substance, containing carbon as main constituent, which on proper burning gives large amount of heat, which can be used conveniently & economically for domestic and industrial purposes**".

Ex: Wood, coal, charcoal, oil, gas, petrol, diesel, producer gas, etc are some of the fuels.

CLASSIFICATION OF FUELS

The fuels are classified according to their

(a) Occurrence (Origin)
(b) The state of aggregation (Physical state)

According to **occurrence**, fuels are subdivided in to two types they are

(a) **Natural OR Primary fuels:** Primary fuels are those which are occur in nature as such.
Ex: Wood, peat, coal, petroleum, natural gas etc.

(b) **Artificial OR Secondary fuels:** Secondary fuels are those which are prepared from primary fuels. [In general all secondary fuels are prepared from primary fuels only].
Ex: petrol,diesel,kerosene, charcoal, etc.

According to **Physical state**, fuels are further divided in to three types they are

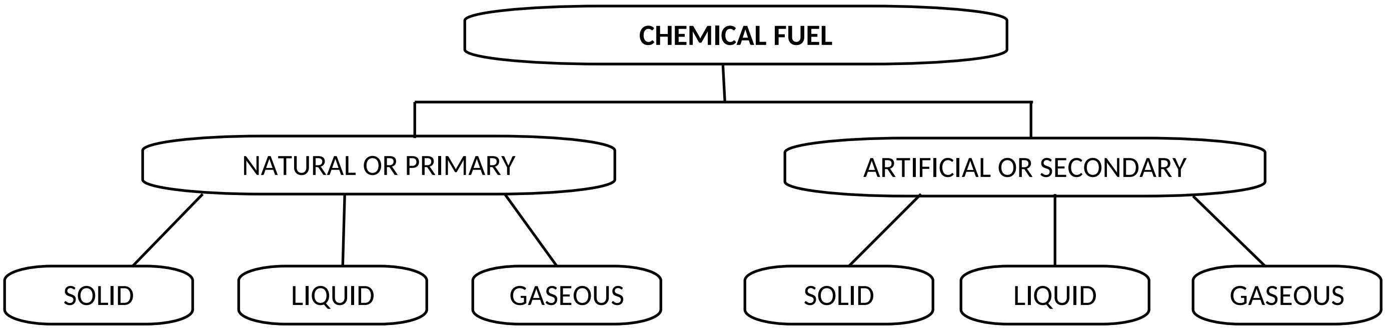
(a) **Solid fuel**: A fuel which exits in the solid state.
Ex; Coke, charcoal, etc

(b) **Liquid fuel:** A fuel which exits in the liquid state.
Ex; petrol, kerosene, etc

(c) **Gaseous fuel:** A fuel which exits in the gaseous state.

Ex; Biogas, water gas, etc

CLASSIFICATION OF FUELS ARE SUMMERISED AS



SOLID	LIQUID	GASEOUS	SOLID	LIQUID	GASEOUS
Wood	Crude oil	Natural gas	Coke	Petrol	Coal gas
Peat			Charcoal	Diesel	Water gas
Lignite			Briquette	Kerosene	Biogas
Coal					

CHARACTERSTICS OF A GOOD FUEL (OR) IDEAL FUEL

1. A good fuel should possess high calorific value.
2. A good fuel should have moderate ignition temperature. [If ignition temperature is low, the fuel can catch fire easily. Lower ignition temperature is dangareous for storage and transportation of fuel. If ignition temperature is high, it is difficult to ignite the fuel.]
3. Low moisture content. [moisture reduces the heating value].
4. A good fuel should contain low non-combustible matter. [after combustion, the non-combustible matter remains in the form of ash. or clinker. Storage, handling & disposal is problem.]
5. The products of combustion should not be harmful. [on heating, they should not give objectionable & harmful gases like CO_2, CO, SO_2, H_2S, etc].
6. A good fuel should be readily available in bulk at a cheap rate.
7. A good fuel should be easy to transport.
8. A good fuel combustion process should be easily controllable. [the combustion of the fuel should be easily start or stoped when required.]
9. Storage cost in bulk should be low.
10. A good fuel should burn in air with efficiency without much smoke.

Comparision between Solid, Liquid and Gaseous fuels

1. Solid fuels

Advantages

1. They are easy to transport.
2. They are convenient to store without any risk.
3. Their cost of production is low.
4. They posses moderate ignition temperature.

Disadvantages

1. Their ash content is high.
2. Their large proportion of heat is wasted during combustion.
3. They burn with clinker formation.
4. Their combustion operation cannot be controlled easily.
5. Their cost of handling is high.
6. Their calorific value is lower as compared to liquid fuels.
7. They cannot be used as I.C. engine fuels.
8. They require large excess of air for complete combustion.

2. Liquid fuels

Advantages

1. They posses higher calorific value.
2. They burn without forming ash, dust clinkers etc.
3. Their firing is easier and also fire can be extinguished easily by stopping the liquid fuel supply.
4. They are easy to transport through pipes.
5. They can be stored indefinitely without loss.
6. They requires less excess of air for complete combustion.
7. They can be used as I.C. engine fuels.

Disadvantages

1. The cost of liquid fuel is relatively much higher as compared to solid fuel.
2. Costly special storage tanks are required for storing liquid fuels.
3. There is a greater risk of fire hazards, particularly in case of highly inflammable & volatile liquid fuels.
4. They give bad odour.
5. For efficient burning of liquid fuels specially constructed burners & spraying apparatus are required.

3. Gaseous fuel

Advantages

1. They can be conveyed easily through pipe lines.
2. They can be lighted at moment notice.
3. They have high heat content and hence help us in having higher temperature.
4. Their combustion can readily be controlled for changes in demand like oxidising or reducing atmosphere, length of flame, temperature, etc.
5. They burn without any smoke & are ashless. So there is no labour involved in ash handling etc.
6. They donot require any special burners.
7. They burn in slight excess of air supply.
8. Complete combustion, without pollution is possible due to uniform mixing of air & fuel.
9. They have high calorific value.
10. They can also be used as IC engine fuels.

Disadvantages

1. Very large storage tanks are needed for them.
2. They are highly inflammable, so chance of fire hazards are high in their use.
3. They are more costly as compared to solid and liquid fuels.

CALORIFIC VALUE

An important parameter of fuel is Calorific value. It gives useful information about **fuel heating efficiency.** The performance of fuel is expressed in terms of Calorific value.

Hence, it can be defined as "**The total amount of heat is liberated, when a unit mass or volume of fuel is burnt completely in air (oxygen)**".

It is expressed in terms of ***cal per gm*** **(cal/g)**, ***kilocal per kg*** **(kcal/kg)*****, Joules per Kg*** (***J/Kg***) or ***KiloJoules per Kg*** **(*KJ/Kg*)** for Solid and liquid fuels.

1 Kcal/Kg = 4.187 KJ/Kg

For liquid and gas it is expressed in terms of ***Joules per cubic meter*** or **(J/m^3).**

TYPES OF CALORIFIC VALUE: There are two types of calorific values, they are

(a) Higher or Gross calorific value (HCV/GCV): Usually, all fuels contain some hydrogen and when the calorific value of hydrogen containing fuel is determined experimentally, the hydrogen is converted into steam. If the products of the combustion are condensed to room temperature (15 ^{0}C), the latent heat of condensation of steam also gets included in the measured heat, which is then called "higher or gross calorific value". Hence, Gross or Higher calorific value is "the total amount of heat produced when a unit mass or volume of the fuel has been burnt completely and the products of combustion have been cooled to room temperature".

(b) Lower or Net calorific value (LCV/NCV): In actual use of any fuel, the water vapour and moisture, etc, are not condensed and escape as such along with hot combustion gases. So, Net or Lower calorific value (**LCV**) can be defined as "the total amount of heat produced when unit mass or volume of the fuel has been burnt completely and the products are permitted to escape".

$$\text{Alternatively, LCV or NCV} = \text{GCV} - \frac{(9 \times \text{percentage of Hydrogen})}{100} \times \text{latent heat of steam} \times 4.187$$

$$\text{NCV} = \text{GCV} - 0.09 \times \%\ \text{Hydrogen} \times \text{latent heat of steam} \times 4.187$$

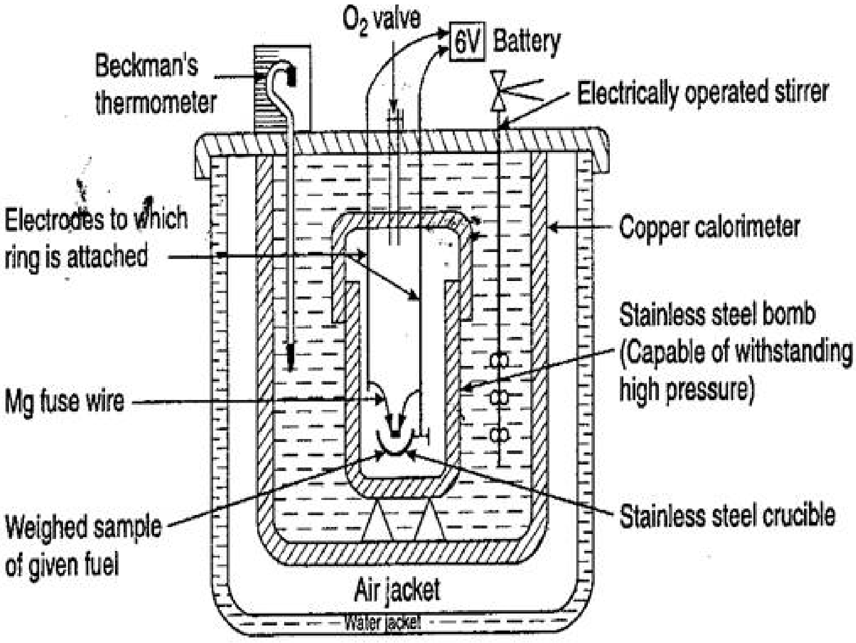
$$= \text{GCV} - 0.09 \times \%\ \text{Hydrogen} \times 587 \times 4.187$$

Because, 1 part by mass of Hydrogen produces 9 parts by mass of water and the latent heat of steam is 587 cal/gm or kcal/kg.

DETERMINATION OF CALORIFIC VALUE OF SOLID FUEL BY BOMB CALORIMETER

This apparatus is used to find the *calorific value* of solid or liquid fuel. The bomb calorimeter consists of a strong cyclindrical vessel made of stainless steel. The combustion of fuel is allowed to takeplace in this bomb. It is provided with a lid, which can make a perfect gas tight seal. The lid is also provided with two stainless steel electrodes and an inlet valve for entry of oxygen used for combustion. A small ring is also attached with one of the electrode. This bring supports a crucible made either of Ni or stainless steel.

The bomb is placed in a copper calorimeter, which is surrounded by air jacket and water jacket in order to avoid losses due to radiation. The calorimeter is provided with an electrically operated stirrer and Beckmann’s thermometer, which can read accurately temperature difference upto 1/100th of a degree.



BOMB CALORIMETER

A known amount (‘m’ gm)of the fuel whose calorific value is determined is placed in the Ni or stainless steel crucible, which is then supported over the ring. A ‘Mg’ fuse wire touching the fuel sample is then stretched across the electrodes. The bomb lid is tightly screwed and filled with oxygen at about 25 atm pressure. The bomb is then placed carefully in the copper calorimeter containing a known amount of water (‘w’gm). The stirrer is driven and initial temperature of water (‘t_1’^{0}C) is noted. The electrodes are then connected to a battery and circuit is completed. The combustion of the fuel sample takes place and heat is liberated because all combustion reactions are exothermic. Stirring of water is continued and final temperature (‘t_2’^{0}C) of water is recorded.

OBSERVATION AND CALCULATIONS:

(a) Mass of fuel = m gm = ‘m’ kg

(b) Initial temperature of water = $t_1{}^0C$
(c) Maximum temperature attained by water in the calorimeter = $t_2{}^0C$
(d) Rise in temperature of water =($t_2 - t_1$) = t^0 C
(e) Weight of water taken in calorimeter = w_1 kg
(f) Water equivalent of calorimeter = w_2 kg
(g) Specific heat of water (S) = 4.187 KJ/Kg/^{0}C

There fore,

$$\boxed{\textbf{HCV of fuel} = \frac{[w_1 + w_2] \text{ x } S \text{ x } (t_2 - t_1)}{m} \quad \textbf{KJ Kg}^{-1}}$$

Lower calorific value is calculated using the equation

LCV = HCV - Heat released by the condensation of steam

$$\text{LCV} = \text{GCV} - \frac{9}{100} \text{ x } \% H_2 \text{ x latent heat of steam}$$

$$\boxed{\textbf{LCV = GCV- 0.09 x \% } H_2 \textbf{ x 587 x 4.187} \quad \textbf{KJ kg}^{-1}}$$

(Note: If the mass of fuel is given in grams, convert that into kg. For example, 0.2 g = 0.2 ′ 10^{-3} kg. If specific heat of water is given in $J\ kg^{-1}\ {}^oC^{-1}$, calorific value will be in $J\ kg^{-1}$. If the specific heat is given in $kJ\ kg^{-1}\ {}^oC^{-1}$, then the calorific value will be in $kJ\ kg^{-1}$.) Specific heat of water is 1 *cal/gm*, but 1 cal = 4.187 *J*).

PROBLEMS

1. Calculate the calorific value of a sample of coal from the following data

Solution:

Mass of coal = 0.6gm
Water equivalent of calorimeter = 2200gm
Specific heat of water = 4.187 KJ Kg^{-1} C^{0-1}
Rise in temperature = 6.52^{0}C

$$\text{HCV} = \frac{(\text{w x s x t})}{\text{m}}$$

$$= \frac{(2.2\text{x}4.187\text{x}6.52)}{0.0006}$$

$$\boxed{\textbf{HCV = 1.0 x } 10^5 \textbf{ KJ /Kg}}$$

2. On burning 0.85 gm of coal sample (Carbon = 90%, Hydrogen = 5% and ash = 5%) was subjected to combustion in a Bomb calorimeter. Mass of water taken in the calorimeter was 2000 gm and water equivalent of calorimeter was 600 gm. The rise in temperature was found to be

3.5^0C. Calculate gross and net calorific value of the sample. (given latent heat of steam = 2457 KJ/Kg and specific heat of water = 4.187 KJ Kg^{-1} C^{0-1}

Solution:

Mass of the fuel = 0.85 g = 0.85 x 10^{-3} Kg
Weight of the water in copper calorimeter = 2000 gm = 2000 x 10^{-3} Kg
Water equivalent of calorimeter = 600 gm = 600 x 10^{-3} Kg
Specific heat of water = 4.187 KJ/Kg/C^0
Latent heat of steam = 2457 KJ/Kg
Raise in temperature = 3.5^0C
% of Hydrogen = 5 %

$$GCV = \frac{(W_1+W_2)\ S\ (t_2-t_1)}{m}$$

$$= \frac{(2000+600) \times 10^{-3} \times 4.187 \times (3.5)}{0.85 \times 10^{-3}}$$

GCV = 44,825 KJ/Kg

$$NCV = GCV - 0.09 \times \%\ H_2 \times 587 \times 4.187$$

$$= 44825 - 0.09 \times 5 \times 587 \times 4.187$$

NCV = 43,719 KJ/Kg

3. Calculate GCV and NCV from the following data

Mass of the fuel = 0.84 gm = 0.84 x 10^{-3} Kg
Weight of the water in copper calorimeter = 2800 gm = 2800 x 10^{-3} Kg
Water equivalent of calorimeter = 350 gm = 350 x 10^{-3} Kg
Specific heat of water =4.187 KJ Kg^{-1} C^{0-1}
Latent heat of steam = 2457 KJ/Kg
Raise in temperature = 3.5^0C
% of Hydrogen = 5.2%

Solution:

$$GCV = \frac{(W_1+W_2)\ S\ (t_2-t_1)}{m}$$

$$= \frac{(2800+350) \times 10^{-3} \times 4.187 \times (3.5)}{0.84 \times 10^{-3}}$$

GCV = 54,954.375 KJ/Kg

$\text{NCV} = \text{GCV} - 0.09 \times \%\,H_2 \times 587 \times 4.187$

$= 54{,}954.375 - 0.09 \times 5.2 \times 587 \times 4.187$

$\boxed{\textbf{NCV = 53,804.139 KJ/Kg}}$

4. Calculate the gross and net calorific value of a sample from the following data obtained from a bomb calorimeter experiment. Weight of coal = 0.73 g. Weight of water in the calorimeter is 1500g, water equivalent of calorimeter = 470 g. Initial temperature of water = 25^0C.
   Final temperature = 27.3^0C, percentage of hydrogen in coal sample = 2.5%. Latent heat of steam = 587x4.187 KJ/Kg. Specific heat of water = 4.187 KJ/Kg/^{0}C.

Solution:

Mass of the coal fuel = 0.73 gm = 0.73 x 10^{-3} Kg
Weight of the water in copper calorimeter = 1500 gm = 1500 x 10^{-3} Kg
Water equivalent of calorimeter = 470 gm = 470 x 10^{-3} Kg
Specific heat of water = 4.187 KJ Kg^{-1} C^{0-1}
Latent heat of steam = 587x4.187 KJ/Kg
Raise in temperature = 2.3^0C
% of Hydrogen = 2.5%

$$\text{GCV} = \frac{(W_1+W_2)\ S\ (t_2-t_1)}{m}$$

$$= \frac{(1500+470) \times 10^{-3} \times 4.187 \times (2.3)}{0.73 \times 10^{-3}}$$

$\boxed{\textbf{GCV = 25,988.078 KJ/Kg}}$

$\text{NCV} = \text{GCV} - 0.09 \times \%\,H_2 \times 587 \times 4.187$

$= 25{,}988.078 - 0.09 \times 2.5 \times 587 \times 4.187$

$\boxed{\textbf{NCV = 25,435.08 KJ/Kg}}$

PETROLEUM CRACKING

Petroleum is a dark viscous liquid which consists of a complex mixture of many hydrocarbons. The word petroleum is derived from Greek word:(Petra = rock, oleum = oil) or crude oil.

Crude petroleum is a dark brown or greenish viscous liquid possessing usually an offensive odour. Petroleum is essentially a mixture of alkane hydrocarbons which are present in it, right from methane up to the higher members containing as many as thirty five carbon atoms. It is also containing varying amounts of aromatic hydrocarbons & cycloalkanes. Besides the various types of hydrocarbons petroleum organic compound containing Nitrogen & Sulphur. [Average composition of crude petroleum is C = 75 - 85%, H = 11-14%, S = 0.1- 4%, N + O = 0.1 - 0.5%].

WHY CRACKING: of all the fractions obtained by fractionation of petroleum, gasoline or petrol has the largest demand as MOTOR FUEL., but the yield of this fraction is only about 20-30% of the crude. Also, the quality of so-called “**Straight-run**” gasoline is not high. It has to be properly treated or blended. Moreover, there is surplus of heavier fractions. To overcome these difficulties, the middle and heavier fractions are subjected to cracking to get petrol. The petrol obtained from cracking has far better than “straight-run” petrol. So, inorder to improve the quality and quantity i.e to produce more petrol having high octane number. Heavier fractions are converted in to smaller fractions suitable for automobile by 2 important chemical methods. They are, (a) Cracking (b) Reforming

Cracking is defined as “The process of breaking higher hydrocarbon molecules of higher molecular weight (high boiling point) into lower hydrocarbons of lower molecular weight (High boiling hydrocarbons into low boiling hydrocarbons) with the intention of increasing the quality and high yeild of petrol”.

Eg:-

$$\underset{\textbf{Decane}}{C_{10}H_{22}} \longrightarrow \underset{\textbf{Octane}}{C_8H_{18}} + \underset{\textbf{Ethylene}}{C_2H_4}$$

There are two types of cracking

1. Thermal cracking

2. Catalytic cracking

1. Thermal cracking:- it is the older technique, where temperature is used to break the molecules. The heavy oil fraction is heated to around 600^0C maintaining it either in liquid phase (liquid phase cracking, yield is abou 45%) or in vapour phase (vapour phase cracking, yielld is about 50%) under pressure. In this process, time taken for cracking is more, and percentage of gasoline is less (< 50%).

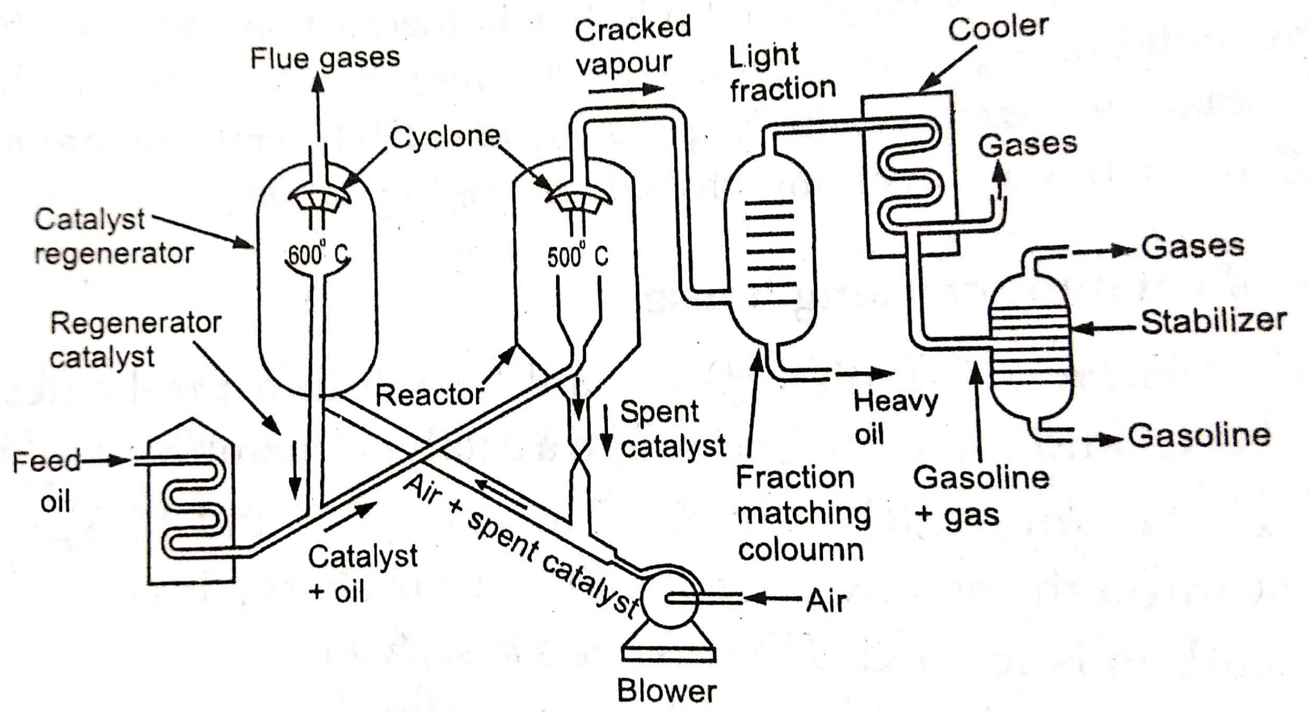
2. Catalytic cracking:- This is widely used technique where cracking is done in presence of catalyst. Use of catalyst not only decreases the temperature (about 500^0C) and time, but also increases the yield (about 60 - 70%). The important catalyst used during catalytic cracking process are, Alumina (Al_2O_3), SiO_2, mixture of synthetic alumina and silica, Natural clays,etc.

There are two types of catalytic cracking :-

(a) Fixed-bed catalytic cracking:- In this method, vapours of heavy oils are passed through a bed of porous catalyst. The cracked vapours are separated to get gasoline or petrol.(not included in our syllabus).

(b) Moving bed or Fluidised-bed catalytic cracking (FCC) :-

This is the most common and widely used method for catalytic cracking.



In this process the solid catalyst (Alumina – Al_2O_3, a white crystalline substance M.P. 2015^{0}C or natural clays or mixtures of synthetic alumina – Silica) is finely powdered so that it behaves almost as a fluid, which can be circulated in gass stream.

The vapours of gas oil, heavy oil etc is mixed with fluidised catalyst and this mixture is forced up into a large reactor maintained at 500^{0}C. Here, the mixture forms floating terbulent bed in which cracking of oil vapours occurs(heavier into lighter molecules occurs). Near the top of the reacrtor there is a centrifugal separator (called cyclone), which allows only the cracked oil vapours to pass on to the fractionating column, but retains all the catalyst powder in the reactor itself. The catalyst powder gradually becomes heavier due coating with carbon and it settles to the bottom of the reactor. The catalyst powder is forced up by using an air blast to regenarator maintained at 600^{0}C temperature. The carbon is burnt in the regenator and the regenerated catalyst flows through a stand pipe for mixing with fresh incoming cracking oil. At the top of the regenerator, there is a separator, which permits only gasess (CO_2, etc) to pass out, but holds back catalyst particles. The cracked products are passed through fractionating coloumn and different fractions are separated.

Advantages of Fluidised catalytic cracking:-

1. Good quality of petrol with high yield is obtained.
2. Catalyst can be regenerated and reused.
3. Very efficient and almost 70% cracking occurs in one stage in 3-4 sec.
4. Can be carried out at lower temperature and pressure.
5. Minimum amount of gaseous products are formed as by-products.
6. The process is continuous and controllable. So that the desired products can be obtained.

REFORMATION OF PETROL

In order to increase the anti-knock properties (octane nuber) of petrol or gasoline obtained by distillation of crude petroleum. It is subjected to a special type of cracking called reforming. Reforming process is important in the production of high octane petrol. **"The process involves a molecular rearrangement of hydrocarbons without any change in the number of carbon atoms to form new compounds"**. Reforming is usually brought about by passing the petroleum fraction at about 600^0C over anhydrous aluminium chloride or platinum catalyst in the presence of hydrogen.

The main reactions during reforming are

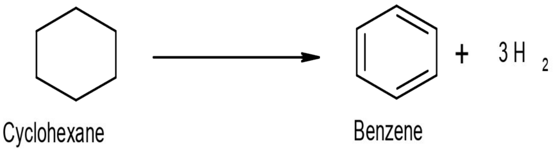
(a) Isomerization:- The straight chain HCs are converted into branched chain hydrocarbons.

Example: n – Hexane ® 2 - Methyl pentane

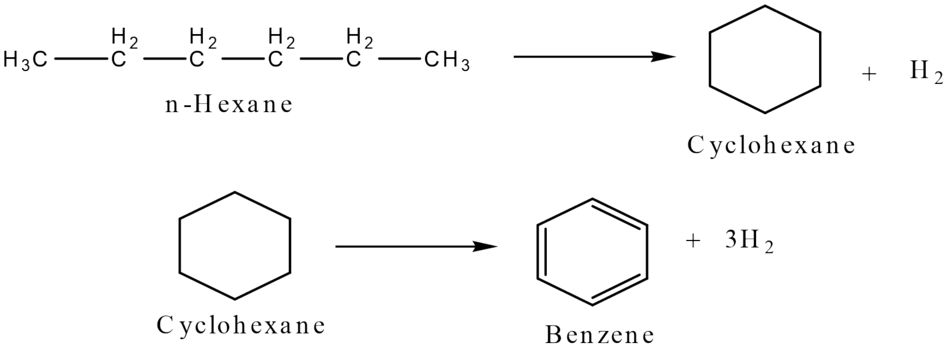
$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3 \longrightarrow CH_3\text{-}\underset{\underset{CH_3}{|}}{CH}\text{-}CH_2\text{-}CH_2\text{-}CH_3$$

(b) Dehydrogenation:- Cycloalkanes undergo dehydrogenation to form aromatic compounds.

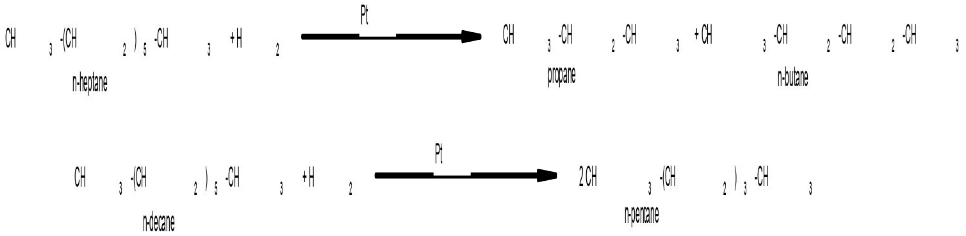
Example: Cyclo hexane ® Benzene + Hydrogen



(c) Dehydrocyclisation:- Straight chain HC undergo cyclisation followed by dehydrogenation to produce aromatic hydrocarbon.



(d) Hydro-cracking: - n-paraffin's undergo hydro-cracking (in presence of H_2 and catalyst) to produce light gases, that are removed from gasoline to improve ON.



$$\underset{\text{n-heptane}}{CH_3\text{-}(CH_2)_5\text{-}CH_3} + H_2 \xrightarrow{Pt} \underset{\text{propane}}{CH_3\text{-}CH_2\text{-}CH_3} + \underset{\text{n-butane}}{CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3}$$

$$\underset{\text{n-decane}}{CH_3\text{-}(CH_2)_5\text{-}CH_3} + H_2 \xrightarrow{Pt} 2\,\underset{\text{n-pentane}}{CH_3\text{-}(CH_2)_3\text{-}CH_3}$$

KNOCKING IN IC ENGINE

In an internal combustion engine, a mixture of gasoline or petrol vapour and air is used as a fuel. This mixture is compressed and ignited by a spark in the cylinder. The ratio of original volume of the fuel mixture to that of the final volume obtained after compression is called compression ratio. The efficiency of internal combustion engine depends upon this compression ratio and higher the compression ratio, higher is the efficiency of the engine. However, there is a limit to this, beyond particular compression ratio the petrol-air mixture suddenly bursts in to flames (pre-ignition) and flame propagation increases nearly 200 times more. This process is accompanied by a sharp knock in the engine (metallic sound) & a black smoke issues out from the exhaust. The knocking increases fuel consumption and engine wear & reduces engine power.

Chemical structure and knocking: The tendency of fuel constituents to knock is in the following order:

Straight-chain alkane hydrocarbons > branched-chain alkanes (iso-alkanes) > alkenes > cycloalkanes > aromatics.

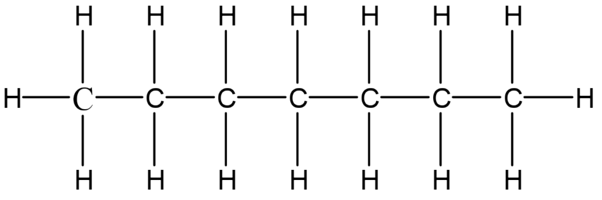
Definition: Explosive combustion of air-petrol vapour mixture produces shock waves which hit the cylinder wall and piston of IC engine, creating rattling sound is known as Knocking in IC engine.

NOTE

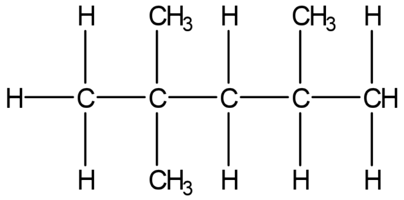
1. Knocking increases with increasing compression ratio.
2. Knocking tendency of alkanes increases with increase in the length of the carbon chain.
3. Branched chain alkanes have lower tendency to knock and so have higher octane number.
4. Knocking property decreases with increase in the number of C=C & rings.
5. The aromatic hydrocarbons have less knocking tendency than alkanes.
6. Straight run gasolines (petrol obtained from crude petroleum) have higher knocking properties.
7. Reformed gasoline have low knocking properties as in evident from their octane number.

Octane Number (ON)

For modern high speed petrol engines a high compression is essential for efficiency. But a straight run air gasoline mixture ignites prematurely under high compression and burns in an explosive and disorderly fashion producing a sharp metallic sound called knocking. Knocking causes a great loss of power, a part of energy is converted in to metallic rattle. High fuel is consumed in this manner and also causes damages to the engines. In order to classify fuels according to the knocking property the scientist Edger (1927) introduced an orbitrary scale for rating the fuels called octane number. It has been found that n-heptane knocks very badly and hence its anti-knock value has been given zero and on the other hand iso-octane (2,2,4-trimethyl pentane) gives very little knocking. So its anti-knock value has been given as 100. Thus octane number (or rating) of a fuel (or any other internal combustion fuel), may be defined as the percentage of iso-octane in a mixture of iso-octane and n-heptane, which matches the fuel under test in knocking characteristics. For example, the fuel with octane number 75 would give the same knocking as a mixture by volume of 75% iso-octane and 25% n-heptane. In other words, the gasoline having an octane number of 75, behaves like a mixture of 75% iso-octane and 25% n-heptane.



n-heptane

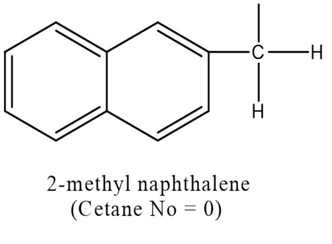


iso-octane

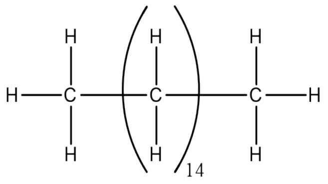
Now a days gasoline with octane number rating as high as 135 & even more have been produced and they are used for aviation purpose.

<u>Cetane number (CN): Diesel engine fuel</u>

In a diesel engine, the fuel is exploded not by a spark, but by the application of heat and pressure. Deisel engine fuels consists of longer chain hydrocarbons than IC engine fuel. The suitability of a diesel fuel is determined by its cetane value(CN), which is the percentage of hexadecane (Cetane) in a mixture of hexadecane and 2-methyl naphthalene which knocks at the some compression ratio as the fuel under examination. Diesel engine normally requires a fuel of cetane number greater than 50.



2-methyl naphthalene
(Cetane No = 0)



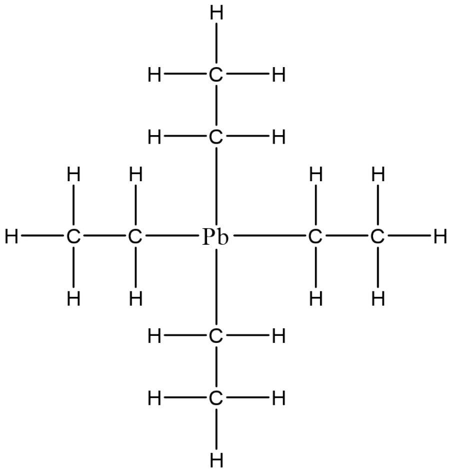
n-hexadecane
(Cetane No = 100)

Prevention of knockinge

Knocking of gasoline can be decreased by adding certain compounds and these compounds are known as anti-knocking compounds/ agents. This anti knocking agent increases the octane number and decreases knocking. Tetra ethyl lead (TEL) is $Pb(C_2H_5)_4$ a very important alkylated compound and is mainly used as anti knocking agents for gasoline. According to the most accepted theory, TEL is converted in to a cloud of finely divided lead oxide particles in the cylinder and these particles react with any hydrocarbon peroxide molecules formed, thereby slowing down the chain oxidation reaction and thus decreases the knocking. However, the deposit of lead oxide is harmful to the engine life. Consequently, in order to stop this small amount of ethylene di bromide is also added to petrol. The added ethylene di bromide removes lead oxide as volatile lead bromide along with the exhaust gases.

Now a days, Tetra methyl lead (TML) has been used instead of TEL, because of higher anti knocking qualities and stability at higher temperature.

Tetra Ethyl Lead(TEL)



Unleaded petrol

Octane value may also be increased by mixing straight chain hydrocarbons with the high octane components such as iso-pentene, iso-octane, ethyl benzene and iso propyl benzene. Methyl tertiary butyl ether (MTBE) is also used to increase the octane value. MTBE contains oxygen in the form of ether group and supplies oxygen for the combustion of the petrol in IC engine. Thus reducing the formation of peroxide compounds. Petrol where in the knocking tendency can be reduced without the addition of lead compounds is called as unleaded petrol.

POWER ALCOHOL

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

The importances of power alcohol as fuel are

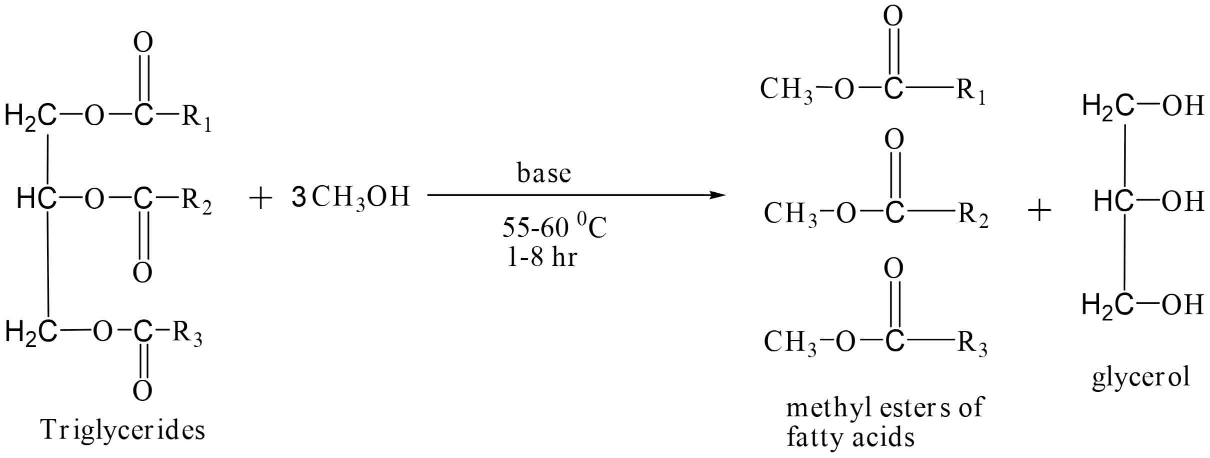
1. Alcohol has an octane number of 90; while petrol has octane number of 60-70. Addition of power alcohol to petrol increases the octane number. Hence alcohol blended petrol possesses better anti-knock properties.
2. Because of the higher octane number, alcohol-blended petrol can be used in engines with
3. higher compression ratio. This compensates for the lower heating value of value of alcohol in the blend.
4. There are no starting difficulties with alcohol-petrol blend.
5. Lubrication in case of alcohol-petrol blend and pure petrol is the same.
6. Ethanol is biodegradable.

Disadvantages

1. It lowers the calorific value of petrol (7000 Kcal/Kg, petrol 10,000kCal/Kg)
2. Due to considerable surface tension, alcohol does not atomize at low temperature.
3. Due to oxidation of alcohol in storage tanks ,corrosion can occur.

BIO-DIESEL

Biodiesel is prepared from the process of transesterification of vegetable oils such as soyabean, jatropha, sunflower, peanut, rope seeds, mustard, rice bran, cotton seed, palmoil etc, that contain triglycerides. The transesterification process involves treatment of the triglycerides in these oils with excess of methanol in the presence of NaOH (Catalyst) to give monomethylesters of long chain fatty acids and glycerine [used cooking oil, rendered animal fat etc could also be converted to biodiesel].



Where R_1, R_2 and R_3 are long chain fatty acids. Transesterification is carried out above the boiling point of alcohol i.e. 55-60^{0}C for 1-8 hr. The mixture of methyl esters are called biodiesel and have desired characteristics of diesel fuel with cetane number in the range of 50-62. So, this biodiesel can be used as alternative fuel for compression ignition engines or can be blended with petro-diesel and used.

Advantages

1. It is made using renewable sources.
2. Readily undergoes bio degradation .
3. Biodiesel has a higher cetane number (50-60) compare to diesel (40 – 55).
4. Use of biodiesel reduces green house gases.

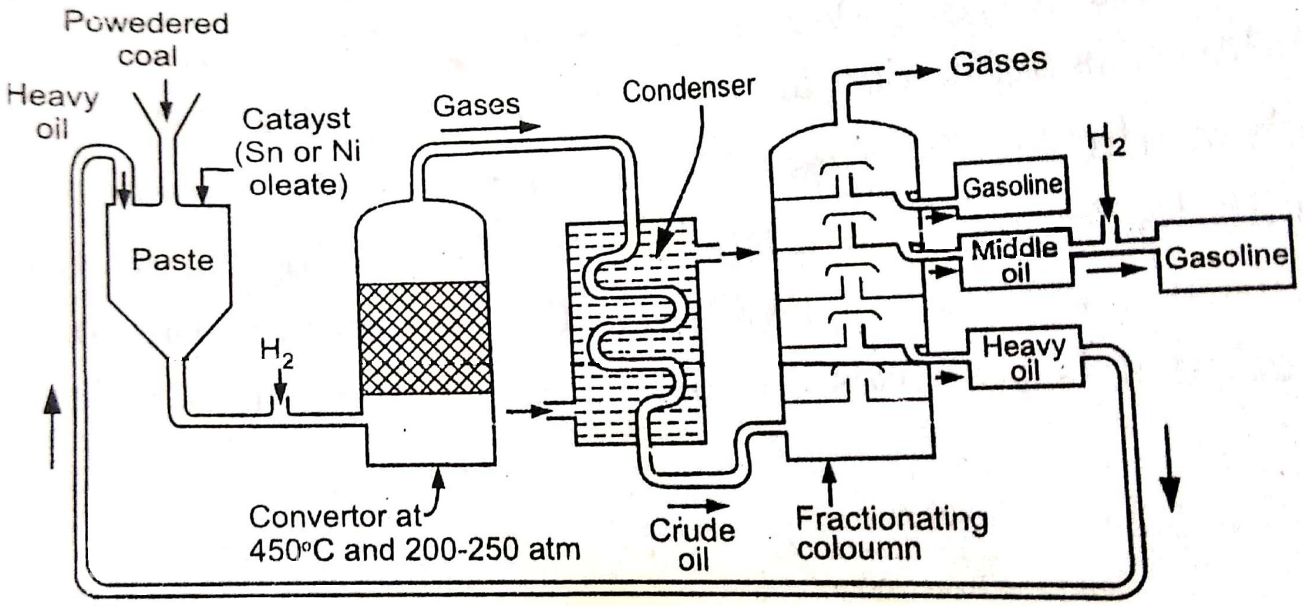
5. It is non toxic.

SYNTHETIC PETROL

During World War II, US govt stopped the supply of petrol and petroleum products to Germany. As a result of it, the scientist was asked to come up with some methods to prepare or produce synthetic petrol by the great dictator Hitler. In this context, two scientists came up with two different methods to synthesize petrol starting from coal. They are:-

(1) BERGIUS PROCESS
(2) FISCHER-TROPSCH PROCESS (not included in our syllabus).

SYNTHETIC PETROL BY BERGIUS METHOD



In this process, the low grade coal is finely powdered and made into a paste with heavy oil. A catalyst composed of Tin oleate or Ni oleate is mixed with it. It is then pumped along with hydrogen into the converter where the paste is heated to 450^0 C under 200-250 atm pressure for about 1.5 hr. The hydrogen combines with coal to form saturated hydrocarbons which decompose to yield mixture of lower hydrocarbons. Since the reaction is exothermic, the vapours leaving the converters are condensed in the condenser to give synthetic petroleum or crude oil. The crude oil is then fractionated to get (a) Gasoline or Petrol, (b) Middle oil and (c) heavy oil.

The top fraction is condensed and synthetic gasoline or petrol is recovered. The middle oil is hydrogenated in presence of a solid catalyst to give more gasoline. The heavy oil is recycled for making a paste with fresh coal powder which is required for this process. The yield of gasoline is about 60% of coal used.

TEXT BOOKS

1. Engineering Chemistry by M.M.Uppal, Khanna Publishers (2001 edition).

2. A text Book of Engineering Chemistry- by P C Jain and Monica Jain, Dhanapatrai Publications, New Delhi.(2015 edition)