

Unit IV

ENERGY SOURCES

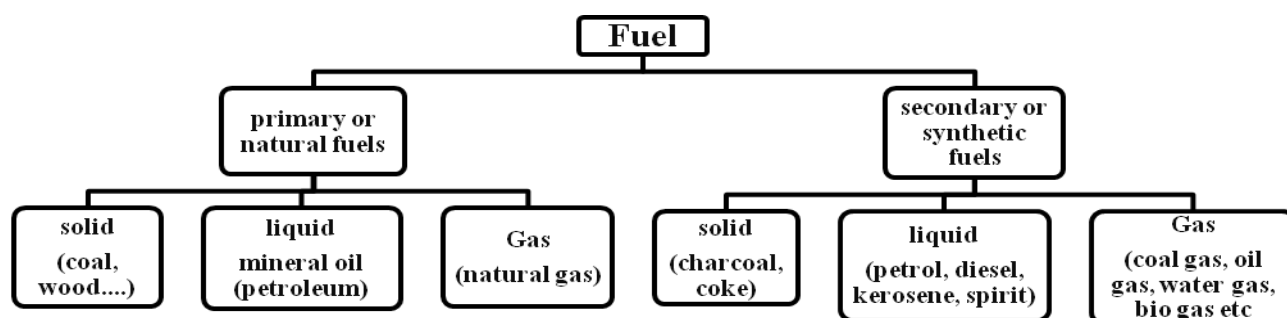
Introduction

Any substance which is a source of heat energy is called fuel. Fuel is a combustible substance which on burning in the presence of O₂/air produces a large amount of heat that can be used for domestic and industrial purposes. Eg: wood, charcoal, coal, kerosene, diesel, natural gas and LPG gas are some commonly used fuels. These substances contain carbon as the major constituent which is capable of releasing a large amount of heat energy during combustion. This energy is liberated due to the rearrangement of valence electrons in these atoms, resulting in the formation of products of lower energy compounds such as CO₂, H₂O, etc.,

Fuel (more energy content) + O₂ \longrightarrow products (less energy compounds) + Heat

Classification

Fuels are broadly classified as natural or primary fuels which are found in nature and secondary or artificial fuels which are prepared from primary fuels.



Characteristics of good fuel

A good fuel should satisfy the following requirements:

1. It should have high calorific value per unit weight, because the amount of heat liberated and temperature attained depends upon the calorific value of the fuel.
2. Its moisture content should be low, so that heating value will be high.
3. It should not produce toxic or poisonous gases like CO₂, SO₂, H₂S, etc. since they pollute atmosphere.
4. Should have low content of non-combustible matter in the form of ash or clinker. The non-combustible matter also reduces the calorific value of a fuel and disposal of waste product produced and storage of fuel will enhance the cost.
5. It should be readily available in bulk at low cost so that it will be economical.
6. An ideal fuel should have moderate ignition temperature, Lower ignition temperature is dangerous for storage and transport as it can catch fire and leads to fire hazards. Thus, a good fuel should have moderate ignition temperature. On the other hand, high ignition temperature is also not preferable as it causes difficulty in igniting the fuel.
7. The combustion of the fuel should be controllable so that it can be started or stopped as per requirement.
8. It should not give offensive odour.

9. It should not ignite spontaneously leading to fire accidents.

Solid fuels

The main solid fuels are wood, peat, lignite, coal and charcoal. In addition to these certain agriculture and industrial wastes such as rice husk, coconut and nut shells, bagasse, etc. are also employed as fuels.

Coal

Coal – is a fossil fuel which occurs in layers in the earth crust. It is formed by partial decay of plant materials accumulated millions of years ago and further altered by the action of heat and pressure.

The coals are classified based on the carbon content.

Features of solid fuels

S.No.	Fuel	% of carbon	Calorific value (k.cal/kg)	Main applications
1.	Wood	50	4000-4500	Domestic fuel
2.	Peat	57	4125-5400	Used in deficiency of high rank coal is prevailing
3.	Lignite	67	6500-7100	Used for steam generation in thermal power plants and for the production of producer gas.
4.	Bituminous	83	8000-8500	Used in making coal gas and metallurgical coke. Also used for steam generation in thermal plants and for domestic heating.
5.	Anthracite	93	8650-8700	Used for households and for steam raising. Also used in metallurgical purposes, where no smoke and high local heat is desired.

Analysis of Coal

To find out the quality of coal two methods are used for analysis:

- Proximate analysis
- Ultimate analysis

1. Proximate Analysis: It gives the information about the practical utility of coal. It determines the moisture, volatile matter, ash and fixed carbon contents of coal.

a. Moisture content: A known mass of powdered air-dried coal sample is heated in a crucible placed in electric hot air oven at 105-110°C for 1 hour, then it is cooled to room temperature in a dessicator and weighed. The loss of weight is reported as % of moisture content.

$$\% \text{ of moisture content} = \frac{\text{loss in weight}}{\text{initial wt of coal taken}} \times 100$$

Significance- Excess moisture is undesirable in coal. It lowers (the heating value of the coal) calorific value of coal. Lesser moisture means better quality but 10% moisture content may be present to produce a more uniform fuel bed and less of 'fly-ash'.

b. Volatile matter: The above sample from (1a) is heated in an electric furnace (muffle furnace) at 950 ± 20°C in a crucible covered with lid for about 7 minutes. It is then cooled to room temperature and weighed.

$$\% \text{ of volatile matter} = \frac{\text{Loss in wt due to volatile matter}}{\text{initial wt of coal taken}} \times 100$$

Significance: A high volatile matter content is undesirable because large proportion of fuel is burnt as vapor and may escape unburnt.

High volatile matter content gives high smoke, long flames and relatively low heating value or calorific value.

c. Ash content: The residual coal in the crucible free from moisture and volatile matter (of process b) is heated in a muffle furnace without lid at $700 \pm 50^\circ\text{C}$ in the presence of air for $\frac{1}{2}$ hour. It undergoes combustion and results in the formation of ash. It is cooled and weighed

$$\% \text{ of ash} = \frac{\text{wt of ash left}}{\text{initial wt of coal taken}} \times 100$$

Significance: High ash content is not desirable as it does not contribute to the calorific value. Formation of ash lumps due to clinkering may restrict the passage of air in the furnace and thereby reducing the temperature or lower the rate of combustion.

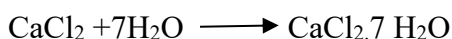
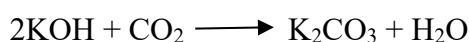
d. Fixed carbon: % of fixed carbon is determined by subtracting the sum of moisture, volatile matter and ash content from 100.

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

Significance: Higher the % of fixed C higher the calorific value and better the quality of coal.

2. Ultimate analysis: In this method C, H, N, S, ash and O_2 are determined.

a. C and H: Known weight of coal sample is burnt in a stream of pure O_2 in a combustible tube. C is converted to CO_2 and H to H_2O . They are absorbed separately in KOH bulb and anhydrous CaCl_2 tubes of known weight. On absorption of these gases CO_2 and H_2O , the KOH bulb and CaCl_2 tubes weight will be increased due to the contribution by CO_2 and H_2O .



$$\% \text{ C} = \frac{\text{increase in wt of KOH tube}}{\text{wt of coal taken}} \times \frac{12}{44} \times 100$$

$$\% \text{ H}_2 = \frac{\text{increase in wt of CaCl}_2 \text{ bulb}}{\text{wt of coal taken}} \times \frac{2}{18} \times 100$$

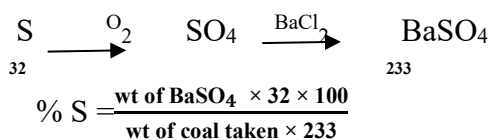
Significance: Greater the % of C and H, better is the quality of Coal with high calorific value. However, presence of excess H indicates presence of high volatile matter and hence affects the coal to which it is put to use.

b. Nitrogen: A known weight of powdered coal is oxidized by heating with Conc. H_2SO_4 along with K_2SO_4 and HgSO_4 in a kjeldahl flask. After the solution has become clear it is treated with KOH. Ammonia is liberated and is allowed to absorb by known excess volume of standard acid. The unused acid is determined by titrating with standard NaOH. From this the Volume of NH_3 liberated is obtained.

$$\% \text{ Nitrogen} = \frac{\text{vol of acid used} \times \text{normality of acid} \times 14 \times 100}{\text{wt of coal taken} \times 1000}$$

Significance: N_2 has no calorific value and hence its presence in coal is undesirable. Thus a good quality of coal should have a very little N_2 content.

c. Sulphur: A known wt. of coal is burnt completely in bomb calorimeter in O_2 which converts S to sulphates. The ash from bomb calorimeter is extracted with dilute HCl. The acid extract is then treated with BaCl_2 to precipitate SO_4 of acid as BaSO_4 . The ppt. is filtered, washed, dried and weighed.



Significance of S: S contributes to calorific value but its combustion products SO₂ and SO₃ corrode the equipment and also cause atmospheric pollution. So S is highly undesirable in coal to be used for making coke for iron and steel industry.

- d. Ash determination is carried out as in proximate analysis

Significance of Ash: Ash is not useful or useless and requires extra cost for its disposal as well as transportation, handling and storage costs. It lowers calorific value, obstruct the flow of heat and causes clinker formation.

- e. **Oxygen:** O₂ is determined by subtracting the total % of C, H, N, S and ash from 100.

$$\% \text{ O}_2 = 100 - \% (\text{C} + \text{H} + \text{N} + \text{S} + \text{ash})$$

Significance of O₂: O₂ content decreases calorific value of coal. An increase of 1% O₂ content decreases the calorific value by about 1.7% and hence O₂ is undesirable. So, a good quality of coke should have lower % of O₂.

Liquid Fuels

The thermal efficiency of liquid fuels is higher than solid fuels. Hence liquid fuels are the important commercial and domestic fuels used these days. Most of these fuels are obtained from the naturally occurring petroleum or crude oil through a process called as Fractional distillation.

Crude Oil or Petroleum

Petroleum or crude oil is the main source of liquid fuels. 60% of the world reserves of petroleum are in the Middle East while 15% are in the Western hemisphere.

The word petroleum is derived from the two Latin words, Petra (=rock) and Oleum (=oil). So, it is also known as crude oil or rock oil or mineral oil. It is a dark coloured viscous liquid found deep in the earth's crust. It is a complex mixture of hydrocarbons (eg. paraffinic, olefinic and aromatic) with small quantity of optically active organic compounds containing O, N and S and traces of metallic constituents.

The average composition of crude oil is

C - 80 to 87%

H - 11.1 to 15.0%

S - 0.1 to 3.5%

O - 0.1 to 0.9 %

N - 0.4 to 0.9%

Besides these, some heavier grades of petroleum may contain compounds of heavy metals like Fe, Ni, V, etc.

Classification of petroleum oil or crude oils

The proportions in which the paraffinic, olefinic and aromatic hydrocarbons are present mainly define the character of the crude oil. On the basis of residues left behind on distillation, crude oil can be classified as 1. Paraffin base oils, 2. Asphaltic base oils and 3. Mixed base oils.

Residue obtained after distillation	Name	Contents	Remarks
Paraffin-Wax	Paraffin-base	Straight chain hydrocarbons and small amounts of naphthenes and aromatic hydrocarbons.	Furnish low octane number straight run gasoline.
Asphalt	Asphaltic-base	Aromatic and naphthenic (cycloparaffins) hydrocarbons.	Furnish high octane number straight run gasoline.
Paraffin wax & Asphalt	Mixed base	Paraffins, naphthenes and aromatic hydrocarbons.	Furnish medium grade straight run gasoline.

Mining of Petroleum:

In order to bring the crude oil to the surface, pipes are sent through the drilled holes in to the oil wells or pumped out with the help of air – lift pumps.

Refining of Petroleum/Processing of petroleum

Crude oil coming out from the well generally consists of a frothing mixture of solid, liquid and gaseous hydrocarbons containing sand and water in suspension. Hence it is not water, S and other impurities; the crude oil is subjected to fractional distillation to recover the various saleable products.

The process by which the crude oil is freed from its impurities, separation into various fractions having different boiling points, and further heated to remove undesirable tendencies and to impart specific properties in them is broadly known as ‘refining of petroleum’. This is done in the following steps:

1. De-emulsification
2. Removal of harmful impurities
3. Fractional distillation

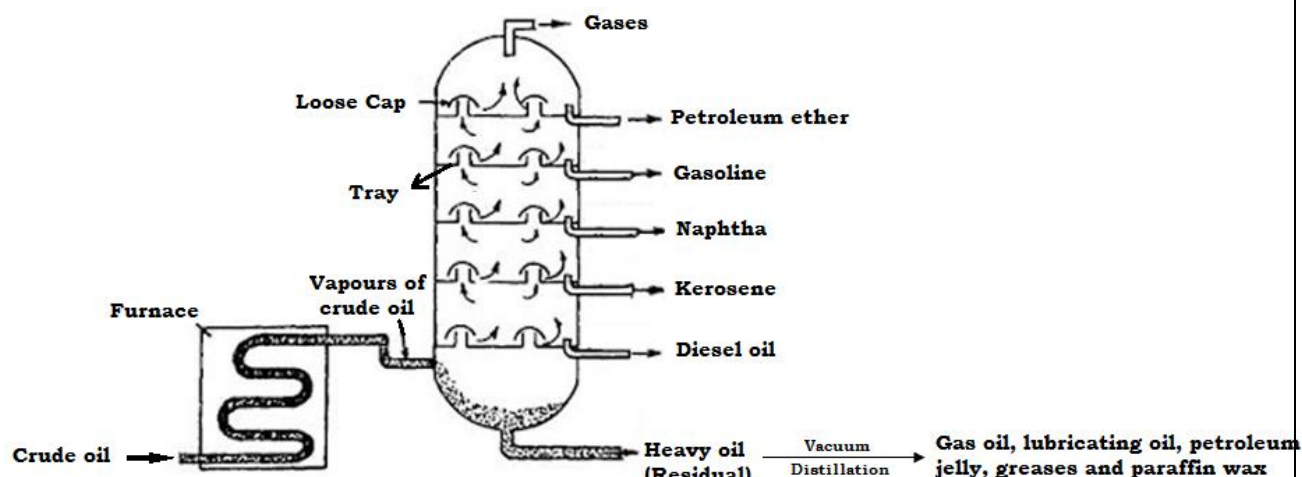
1. De-emulsification: As the crude oil is pumped out it is in the form of stable emulsions of oil-in-water type (hydrophilic) and water-in-oil type (hydrophobic) which are yellow to dark brown in colour.

The electrical method is widely used at oil wells and petroleum-processing plants. In this method, the crude oil is subjected to an electrical field formed by a high-voltage alternating current (A/C) which destroys the emulsion films. Droplets of the dispersed phase coalesce to form bigger drops which separate out from the oil.

2. Removal of harmful impurities: In order to remove sulphur compounds, the oil is treated with copper oxide and the copper sulphide formed is separated by filtration.

3. Fractional distillation: Petroleum is a mixture of group of hydrocarbons with specific boiling ranges called fractions. Different fractions have different numbers of carbon atoms. (eg: Kerosene fraction has carbon atom composition C_{10} to C_{16} and boil in the range of 180-250°C). The fractions with few carbon atoms (C_5 - C_7 B.P. 30-70°C) have low boiling points, while the fractions with many carbon atoms have high boiling points. (C_{17} – C_{30} B.P. 320-400°C).

The fractional distillation is carried out in a specially designed tall fractionating tower or column made up of steel. It is provided with a large number of horizontal stainless steel trays. Each tray is provided with a small chimney covered with a loose cap.



Petroleum is heated in a furnace to about 400°C . The oil vaporizes and passes into fractionating column. As the vapour of the oil rise up in the fractionating tower they become cooler and get condensed at the trays. The fractions come out of the column at different heights depending on their B.P. Thus the petroleum gas fraction comes out at the top of the column as its hydrocarbon molecules have the lowest B.P. The residue from the bottom of fractionating column is vacuum distilled to recover various fractions.

Properties and uses of the fractions

The various important fractions collected from the fractionating column, their approximate B.P. ranges, position and uses are listed here.

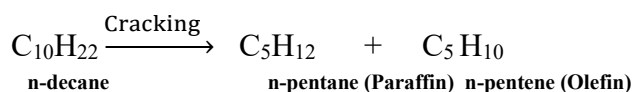
Fraction	Approximate B.P. Range ($^{\circ}\text{C}$)	Composition Carbon range	Uses
Uncondensed gases	0-30	$\text{C}_1\text{-C}_4$	Domestic fuel (LPG).
Petroleum ether	30-70	$\text{C}_5\text{-C}_7$	As a solvent.
Gasoline or petrol	40-120	$\text{C}_5\text{-C}_9$	As fuel of IC engine, solvent & in dry cleaning.
Naphtha or solvent spirit	120-180	$\text{C}_9\text{-C}_{10}$	As a solvent, for paints and varnishes & in dry cleaning.
Kerosene oil	180-250	$\text{C}_{10}\text{-C}_{16}$	As an illuminant, jet engine fuel and for making oil gas.
Diesel oil	250-320	$\text{C}_{10}\text{-C}_{19}$	Diesel engine fuel, carbureting of water gas.
Heavy oil	320-400	$\text{C}_{17}\text{-C}_{30}$	Used for getting gasoline by cracking.
Re-fractionation of Heavy Oil gives- • Lubricating oil • Petroleum jelly • Grease • Paraffin wax	- - - -	$\text{C}_{17}\text{-C}_{20}$ - - -	As lubricant, In cosmetics and medicine As lubricant Used in making wax paper, candles, boot polish, etc.
Residue • Asphalt • Petroleum coke	> 400	C_{30} and above	Used for making roads and water proofing roofs. As fuel

The refining of petroleum into commercial fuels is an immense industry upon which almost every aspect of modern society depends. A large part of refining process consists of partially separating the different chemical constituents of petroleum by distillation.

Cracking

The mixture of light hydrocarbons which is obtained by distillation is called “straight run gasoline” and consists mainly of straight chain molecules. However, the gasoline obtained by fractional distillation is not of very good quality. So to get improved gasoline a process of thermal decomposition known as cracking is used. Thus **cracking may be defined as a process by which the higher hydrocarbons (having higher M.Wt. and high B.P.) are decomposed into lower M.Wt. hydrocarbons having low B.P. by the application of heat.**

Eg: $C_{10}H_{22}$ (higher saturated hydrocarbon) cracks into paraffinic and olefinic hydrocarbons.



There are three methods of cracking

1. Thermal cracking
2. Catalytic cracking
3. Hydrogenation cracking

1. Thermal cracking: Cracking takes place by the application of temperature (heat) and pressure. It takes place by two ways

a) Liquid phase cracking: The heavy oil or the gas oil stock is maintained at 420-550°C and under high pressure 7-10 atm. so that the reaction products are in the liquid state. The cracked products are separated in a fractionating column. The important fractions are cracked gasoline (30-35%), cracking gases (10-45%) and cracked fuel oil (50-55%). The octane rating of the products is about 70.

b) Vapour phase thermal cracking: In this process only those oils (kerosene oil), which can be vaporized at about 600°C are cracked under atmospheric pressure. Gasoline obtained by this process has better antiknock properties. However, its stability is low when compared to liquid phase cracking.

2. Catalytic cracking: A better quality and yield is obtained by this process compared to thermal cracking. The cracking is carried out in the presence of a catalyst - Aluminium silicate [$Al_2(SiO_3)_3$] or alumina [Al_2O_3]

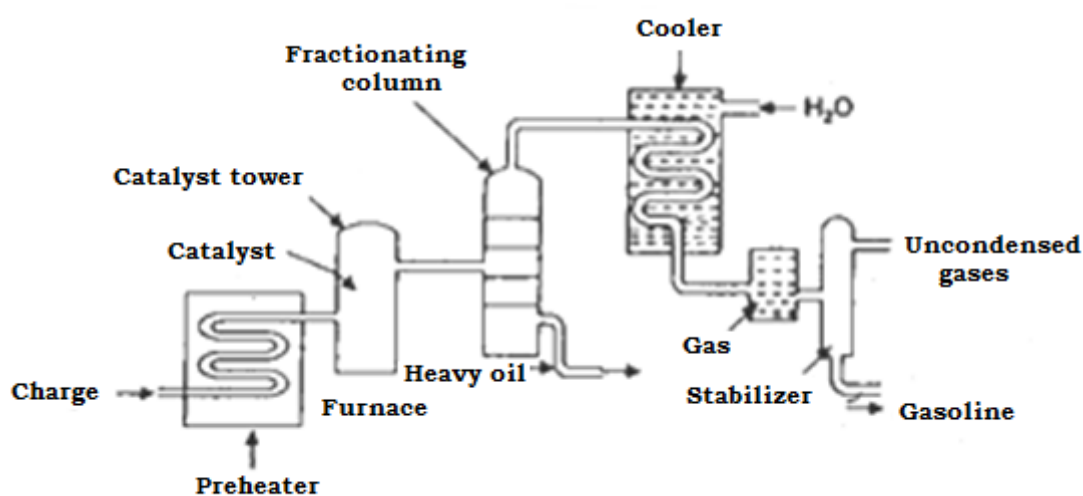
The catalytic cracking has some advantages over thermal cracking. They are -

- The yield of gasoline is higher.
- The quality of the gasoline produced is better.
- No external fuel is necessary for burning. The heat required for burning is derived from the coal embedded in the catalyst, during regeneration process.
- Pressure required for cracking is low.
- Gasoline obtained contains high percentage of iso-paraffins and aromatic hydrocarbons and low percentage of olefins. This increases its antiknock properties (octane number 80)
- The product contains very little amount of S, as a major portion of which escapes as H_2S .

Depending upon how the catalyst is used, the catalytic cracking is of two types.

- a) **Fixed bed catalytic cracking:** The catalyst silica alumina gel or bauxite mixed with clay and Zirconium oxide is in the form of fixed beds in the catalytic tower. The heavy oil charge is passed through a heater and heated to a cracking temperature (420-450°C) and pressure of 1 to 5 kg cm⁻².

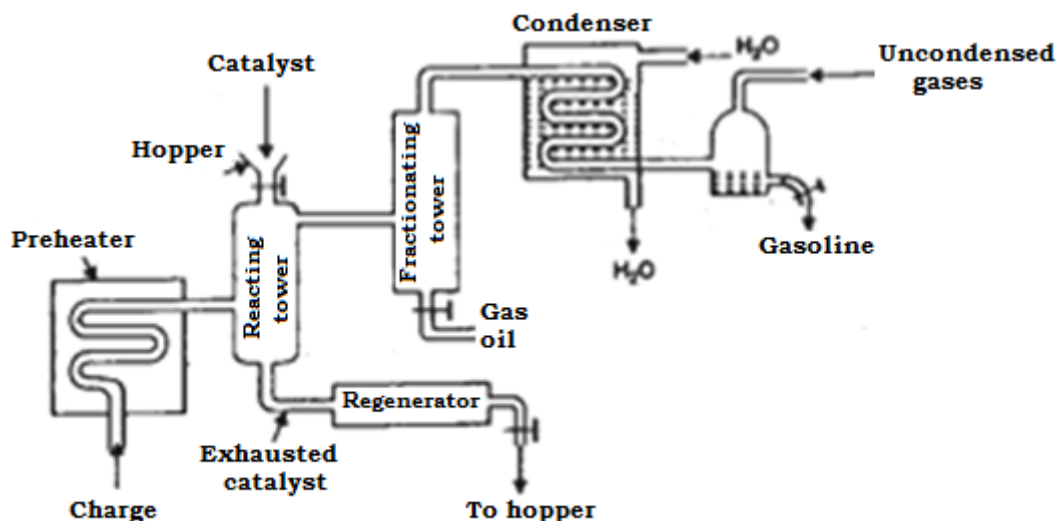
Cracking takes place and products move through the fractionating column where fractional distillation takes place. The vapors of the mixture are then led to pass through a cooler where gasoline along with some other gases gets condensed. The uncondensed gases move on. The gasoline then moves to a stabilizer where the dissolved gases are removed and the gasoline gas gets stabilized or recovered. The catalyst stops functioning after a period of time due to deposition of a black layer of carbon formed during cracking. A stream of hot air is passed over the catalyst when carbon gets burnt off, thereby reactivating the catalyst.



Fixed Bed Catalytic Cracking

- b) Fluid Bed Cracking or Moving Bed Cracking:** In this process, the solid catalyst is very finely powdered and circulated in the gas stream. The heavy oil is pre heated and the vapours or charge are allowed to mix with hot catalyst in the reacting tower which is maintained at 500°C, due to this high temperature of catalyst, the cracking of heavy oil takes place. The cracked vapours are passed through fractionating column. The catalyst powder gradually becomes heavier due to the deposition of carbon and settles at bottom. This is forced into the regenerator. In this regenerator carbon is burnt off and catalyst is regenerated or reactivated and again sent into reacting tower through hopper.

The gases from the fractionating towers are sent into condenser and then to stabilizer to recover gasoline.



Fluid Bed or Moving Bed Cracking

- c) **Hydrogenation cracking:** In presence of hydrogen the heavy oils crack under high temperature and pressure. This process is known as hydrogenation cracking. By recycling the oil, complete cracking can be affected at temperature of $450 - 525^{\circ}\text{C}$ and a pressure of 25 kg cm^{-2} . This method is very costly and technically intricate and needs large quantity of hydrogen. It is due to these reasons this method is used less but the cracking complete.

Knocking

In a petrol engine a mixture of gasoline vapour and air in a fixed ratio (1:17) is used as a fuel. This mixture is compressed and ignited by an electric spark. After initiation of the combustion reaction by spark in the cylinder the flame should spread rapidly and smoothly through the gasoline mixture, thereby the expanding gas drives the piston down the cylinder. The fuel-air mixture is compressed. The efficiency of an integral combustion engine increases with the compression ratio [ratio of gasoline volume in the cylinder at the end of the suction stroke to the volume at the end of compression stroke of the piston].

But in certain circumstances the rate of oxidation of hydrocarbons is so great that the last portion of the oil and air mixture detonates producing an explosive sound called Knocking or Engine knock. The knocking results in loss of efficiency. So knocking not only results in decreased power output but can also cause mechanical damage by overheating of the cylinder parts. Knocking is also termed as pinking or auto ignition.

A good gasoline should resist knocking. It was recognized that chemical structures of the fuel hydrocarbon largely determine their knocking tendency. The tendency to knock decreases in the following order:

Straight chain paraffins > branched chain paraffins > cycloparaffins > olefins > aromatics.

Adverse effects of Knocking

- Knocking produces an undesirable rattling sound.
- It results in decrease in efficiency.
- Driving and travelling become unpleasant.
- It increases fuel consumption.
- It causes mechanical damage to the engine parts and spark plug.

Prevention of Knocking:

Knocking in petroleum may be minimized by the following methods:

- A suitable change in engine design may be made to have optimum combustion ratio.
- High octane number fuel may be used.
- Anti-knocking agents may be used.

Anti-knocking agents :

Knocking of petrol may be reduced by the addition of some organo-lead compounds into it. The substance added to control knocking is called as Anti-knocking agent. The commonly employed anti-knocking agents are –

- Tetra ethyl lead Pb (C₂H₅)₄ (TEL)
- Tetra methyl lead Pb (CH₃)₄ (TML)
- A mixture of TEL and TML.

They are used along with ethylene dichloride or dibromide. The anti-knocking agents produce ethyl and methyl free radicals by dissociation. These radicals combine with free-radicals formed by branching chain reaction during the combustion of gasoline and form stable hydrocarbons. Thus, the population of chain carriers is kept under control thereby reducing knocking greatly even with the use of small quantities of TEL and TML.

Disadvantages of TEL and TML

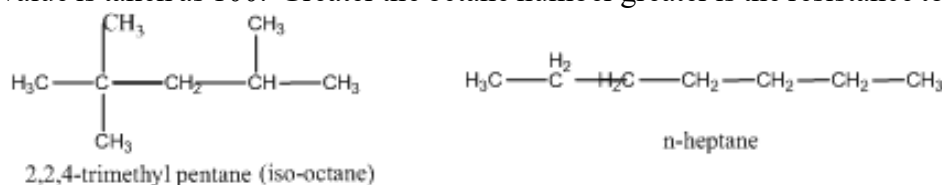
- They get converted to lead or lead oxide (PbO) and get deposited on the engine parts or the exhaust pipes causing damage.
- If they are used along with ethylene dibromide or dichloride, lead and lead oxide are converted to volatile lead halides.
- These halides escape into the atmosphere, which are poisonous to animals and human beings. Hence, the use of organolead compounds should be discouraged.

Unleaded petrol does not contain TEL or TML. To avoid knocking various other substances (ethyl t-butyl ether or methyl t-butyl ether) are mixed with gasoline which are having high octane number.

Octane Number

Edger introduced the term Octane Number to explain the knocking characteristics of combustion engine fuel. The Octane Number of a fuel is a measure of its ability to resist knocking. A fuel with high octane number has a greatest resistance to spontaneous combustion/ignition.

The octane number of gasoline is defined as the percentage of iso-octane present in a mix of iso-octane and n-heptane. n-Heptane knocks very badly and hence its anti-knocking value is arbitrarily given as zero. Whereas iso-octane gives very little knocking and so its anti-knocking value is taken as 100. Greater the octane number greater is the resistance to knocking.

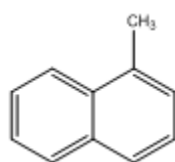


Thus if a sample of petrol gives as much of knocking as a mix of 75 parts of iso-octane and 25 parts of n-heptane, then its octane number is 75. Olefins have higher antiknock property than the corresponding paraffins. Aromatic hydrocarbons such as benzene and toluene have

high octane numbers. The octane number of fuels may be improved by adding alcohols and ethers.

Cetane Number

In diesel engines the fuel is exploded by the application of heat and pressure and not a spark. The interval between the start of fuel injection and the ignition is called ignition delay and is an important quality of diesel fuel. If the ignition delay is long, it is responsible for diesel knocking. In order to avoid diesel knock, the ignition delay period should be as short as possible and these diesel fuels are graded by means of cetane ratings. So the knocking characteristics are referred as cetane number. Cetane number of diesel oil is defined as the percent by volume of cetane in a mix of cetane and α – methyl naphthalene. Cetane (n-hexadecane) $[\text{CH}_3-(\text{CH}_2)_{14}-\text{CH}_3]$ having a very short ignition delay is given the value of 100 in the rating scale. α – methyl naphthalene having a longer ignition delay represents zero of the scale.



High cetane number fuels eliminate diesel knock and can be increased by adding certain organic additives such as ethyl nitrate ($\text{C}_2\text{H}_5\text{ONO}_2$), amyl nitrate ($\text{C}_5\text{H}_{11}\text{ONO}_2$) and acetone peroxide. So diesel knocking may be minimized.

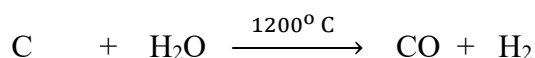
Synthetic Petrol

Due to heavy demand for petrol or gasoline, synthetic methods for the preparation of petrol are designed. The important methods commonly used are

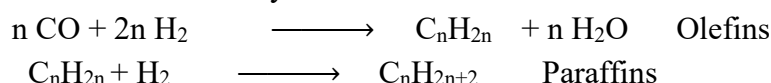
1. Polymerisation
2. Fischer – Tropsch process
3. Bergius process

1. Fischer- Tropsch Process

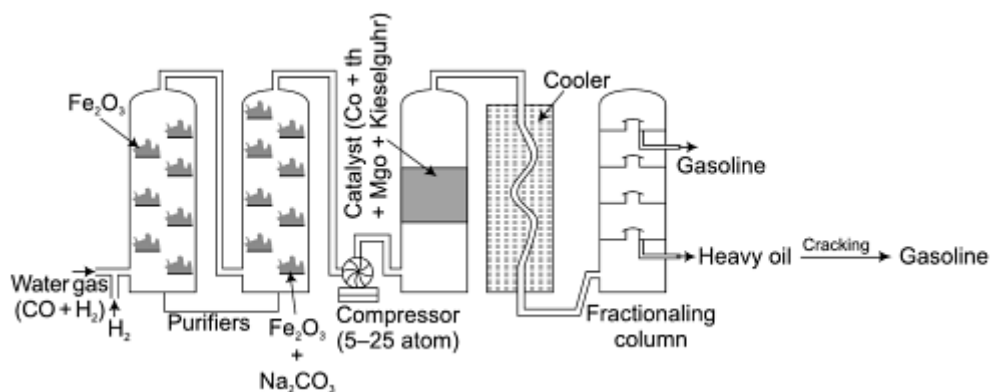
This method was developed by two German scientists Franz Fischer and Hans Tropsch. The raw material is the hard coke which is converted into water gas ($\text{CO} + \text{H}_2$) by passing steam over red hot coke.



Water gas so produced is mixed with hydrogen and is purified by passing through Fe_2O_3 to remove H_2S and then into a mixture of $\text{Fe}_2\text{O}_3 + \text{Na}_2\text{CO}_3$ to remove organic sulphur compounds. The purified gas is compressed at 5 to 25 atmospheres. The compressed gas is then led through a converter containing a catalyst (A mixture of 100 parts cobalt + 5 parts thorium + 8 parts magnesia + 200 parts keiselguhar earth) maintained at about $200-300^\circ\text{C}$. A mixture of saturated and unsaturated hydrocarbons is formed.



The reaction is exothermic. So, out coming hot gaseous mixture is led to a cooler, where a liquid resembling crude oil is obtained. Thus the crude oil obtained is then fractionated to yield gasoline and high boiling heavy oil. The heavy oil is reused for cracking to get more gasoline.



Gaseous Fuels

There are some fuels which are in gaseous state and are called gaseous fuels. Natural gas, coal gas, coke oven gas, producer gas, water gas, liquefied petroleum gas are some examples of gaseous fuels. The usage of gaseous fuels is on increase over the years due to the following advantages.

1. Combustion is under better control and burn instantaneously with rate of burning changes very easily. Gases are miscible with air and excess air needed is much less than for other forms of fuel. Oxidising and reducing atmosphere can be very easily created. These contribute to the fuel economy.
2. Heat from hot flue gases can be recovered and gaseous fuel can be pre-heated in regenerative furnaces, which gives much economy of heat and at the same time a high temperature is generated.
3. Gaseous fuels can be prepared at a central place and distributed over a wide area through pipelines. If direct usage of solid fuels are unsuitable, they can be converted to gaseous fuel and valuable by-products are recovered.
4. Neither smoke nor ash is produced. Thus gaseous fuels are very clean.
5. If the supply is from a public source, there is no problem of storage.

The major disadvantage of these fuels is storage as they occupy large storage area, which is difficult.

Natural Gas

Natural gas is obtained from wells dug in the oil-bearing regions. When natural gas occurs along-with petroleum in oil-wells, it is called 'Wet gas'. The wet gas is treated to remove propane, propene, butene and butane, which are used as LPG. On the other hand, when the gas is associated with crude oil, it is called 'Dry gas'. Before use, the natural gas is purified to remove objectionable ingredients such as water, gas, grit, H_2S , CO_2 , N_2 and heavier liquefiable hydrocarbons (propane, butane, butene, etc.).

The approximate composition of natural gas is: $\text{CH}_4 = 70\text{-}90\%$; $\text{C}_2\text{H}_6 = 5\text{-}10\%$; $\text{H}_2 = 3\%$; $\text{CO} + \text{CO}_2 = \text{rest}$. The calorific value varies from $12,000\text{-}14,000 \text{ kcal/m}^3$.

Uses:

1. It is an excellent domestic fuel and can be conveyed over very large distances in pipelines.
2. Synthetic proteins are obtained by microbiological fermentation of methane.
3. It has recently been used in the manufacture of a number of chemicals by synthetic processes.
4. It is also used as raw material for the manufacture of carbon black and hydrogen.

CNG as a fuel

Compressed natural gas (CNG) is natural gas compressed to a high pressure of about 1,000 atmospheres. A steel cylinder containing 15 Kg of CNG contains about 2×10^4 L or 20 m^3 of natural gas at 1 atmospheric pressure. CNG is now being used as a substitute for petrol and diesel, since it is comparatively much less pollution causing fuel. During its combustion, no sulphur and nitrogen gases are evolved. Moreover, no carbon particles are ejected. Hence, it is a better fuel than petrol/diesel for automobiles. However, initial cost of engine designed to use CNG as a fuel is comparatively higher than that of engine designed to use petrol/diesel.

In Delhi, it is mandatory to use CNG as a fuel for all buses, taxis and auto to use CNG as a fuel.

Advantages of CNG

1. CNG is a much safer fuel, since it ignites at a higher temperature than gasoline and diesel.
2. The conversion of gasoline operated automobiles into CNG operated vehicle is very easy.
3. The operating cost of CNG fuel is much lower compared to gasoline operation.
4. Combustion of CNG leads to lesser CO emissions than gasoline.
5. CNG mixes better with air than liquid fuels.
6. Emissions from CNG operated vehicle contain no unregulated pollutants like smoke, SO_2 , SO_3 , C_6H_6 , HCHO, etc.

LPG as a fuel

Liquefied petroleum gas (LPG) or bottled gas or refinery gas is obtained as a by-product, during the cracking of heavy oils or from natural gas. LPG is dehydrated, desulphurised and traces of odorous organic sulphides (mercaptans) are added to give warning of gas leak. LPG is supplied under pressure in containers under the trade name like Indane, Bharat gas, etc. Its calorific value is about $27,800 \text{ K. Cal/m}^3$.

LPG consists of hydrocarbons of such volatility that they can exist as gas under atmospheric pressure, but can be readily liquefied under pressure. The main constituents of LPG are n-butane, isobutene, butylene and propane, with little or no propylene and ethane.

Uses

1. The largest use of LPG at present is as domestic fuel and industrial fuel.
2. There is an increasing trend to use LPG as motor fuel.

Advantages (Domestic and industrial fuel)

1. High efficiency and heating rate. The calorific value is roughly 3 times that of natural gas and 7 times that of coal gas.
2. Use of well designed, durable and neatly constructed burners ensure complete combustion with no smoke.
3. Needs little care for maintenance purpose.
4. Cleanliness in storage, handling and use.
5. Flexibility and easy control.
6. Easy to manipulate.
7. Portability in cylinders/containers makes its use possible in remote/isolated places.
8. Comparatively less health hazard, even in case of leakage, since it contains no carbon monoxide.

Disadvantages

1. Fire hazards are as great as with any other gaseous fuel.

Advantages (Motor fuel)

1. It is cheaper than gasoline.
2. It gives better manifold distribution and mixes easily with air.
3. It is highly knock-resistant.
4. Residue and oil contamination is small, as it burns cleanly.

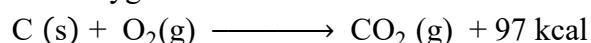
Disadvantages

1. Due to its faint odour, leakage cannot be easily detected.
2. Handling has to be done under pressure.
3. LPG is advantageous only in engines working under high compression ratios.
4. Its octane number is quite low.
5. Its response to blending is very poor.
6. Use of LPG is limited only to certain classes of vehicles like trucks and tractors.

Combustion

Combustion is an exothermic chemical reaction, which is accompanied by development of heat and light at a rapid rate, so that temperature rises considerably.

Eg: Combustion of carbon in oxygen.



For proper combustion, the substance must be brought to its kindling or ignition temperature, which may be defined as “the minimum temperature at which the substance ignites and burns without further addition of heat from outside”.

Calorific value

The efficiency of a fuel is measured by its calorific value and it is defined as “the total quantity of heat liberated when a unit mass of the fuel is completely burnt in air or oxygen”. There are different units for measuring it:

1. **Calorie:** It is the amount of heat required to increase the temperature of 1gm of water through 1°centigrade.
2. **Kilocalorie:** Quantity of heat required to raise the temperature of one kilogram of water through one degree centigrade.
3. **British thermal unit (B.T.U):** The quantity of heat required to increase the temperature of one pound of water through one degree Fahrenheit. $1 \text{ B.T.U} = 252 \text{ cal} = 0.252 \text{ Kcal}$.
4. **Centigrade heat unit (C.H.U):** Quantity of heat required to raise the temperature of one pound of water through one degree centigrade

$$1 \text{ K.cal} = 3.968 \text{ B.T.U} = 2.2 \text{ C.H.U}$$

Generally a fuel is evaluated from its total calorific value i.e. higher calorific value (H.C.V) and lower calorific value (L.C.V).

Higher or gross calorific value (HCV)

The total amount of heat produced when unit mass of the fuel has been burnt completely and the products of combustion have been cooled to room temperature.

The fuel, which containing H_2 is burnt the hydrogen present undergoes combustion and is converted into steam. When this product is cooled to room temperature the steam gas

condensed into water and latent heat is evolved. This latent heat also is included in the gross calorific value. A bomb calorimeter is used to give gross or higher calorific value.

Net or Lower calorific value (LCV)

It is defined as the total amount of heat generated when a unit mass of fuel is completely burnt and hot combustion products (water vapour, moisture, combustion gases etc) are allowed to escape.

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

The calorific values of the components of fuels are

<u>Constituent</u>	<u>Calorific value (K cal/Kg)</u>
Hydrogen	34,500
Carbon	8,080
Sulphur	2,240

Theoretical determination of calorific value

Dulong's Formula:

In this formula the higher calorific value (HCV) of a fuel is the total of the calorific value of each of the components. Secondly 8 parts by weight of O₂ combine with one part by weight of hydrogen. So if oxygen is present, it must be present in the combined form with hydrogen as water thereby decreasing the amount of hydrogen available for combustion by O/8. The formula is then from that the percentage by mass of each gas is determined.

Dulong's formula:

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

Where C, H, O, S are the percentages of carbon, hydrogen, oxygen and sulphur respectively, as determined by the ultimate analysis of fuels

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

BIO DIESEL:

_Vegetable oils comprise of 90-95% triglycerides with small amount of diglycerides, free fatty acids, phospholipids, etc. Triglycerides are esters of long chain fatty acids, like stearic acid and palmitic acid. The viscosity of vegetable oils are higher and their molecular weights are in the range of 600 to 900, which are about 3 times higher than those of the diesel fuels.

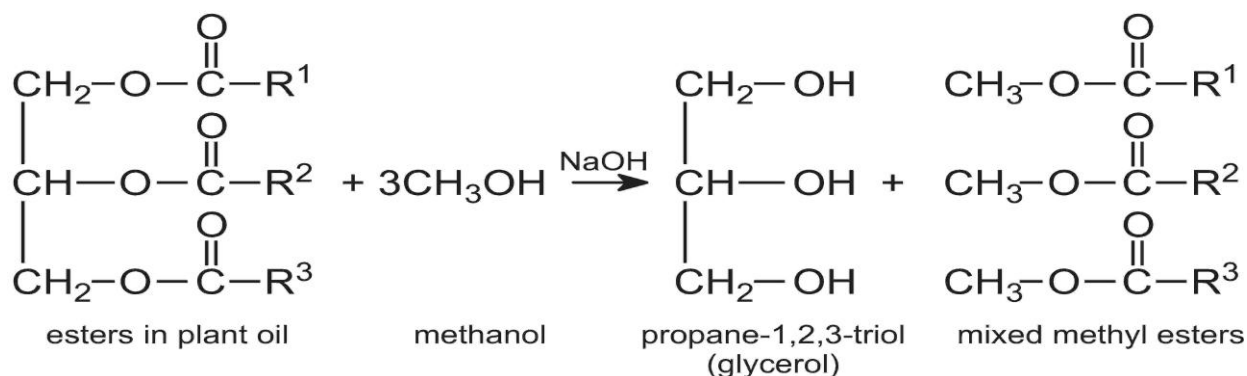
PROBLEMS IN USING VEGETABLE OILS DIRECTLY:

- 1.As the viscosity of vegetable oils are high, atomization is very poor and hence inefficient mixing of oil with air leads to incomplete combustion.
- 2.Oxidation and thermal polymerization of vegetable oils cause deposit formation.
- 3.Their high viscosity causes misfire and ignition delay.
- 4.Their high volatility and consequent high flash point lead to more deposit formation.

MANUFACTURE: TRANSESTERIFICATION (OR) ALCOHOLYSIS :

The above problems are overcome by reducing the viscosity of the vegetable oils by the process known as trans-esterification or alcoholysis.

- Alcoholysis is nothing but displacement of alcohol from ester by another alcohol.
- It involves treatment of vegetable oil with excess of methanol in presence of catalyst to give mono ethyl esters of long chain fatty acid and glycerine. It is allowed to stand for some time and glycerine is separated.



- Methyl esters of fatty acids, thus formed are called Bio-Diesel is defined as mono-alkyl esters of long chain fatty acids derived from vegetable oils or fats.
- It is a pure fuel before blending with conventional diesel fuel. Bio-Diesel can be blended with petroleum diesel.

ADVANTAGES OF BIO-DIESEL:

1. Bio-Diesel is bio-degradable.
2. It is prepared from renewable resources.
3. The gaseous pollutants are lesser as compared to the conventional diesel fuel.
4. Best engine performance and less smoke emission are achieved.