ENERGY SOURCES

A **fuel** can be defined as a combustible substance containing carbon as the major constituent which gives large amount of heat on burning, which can be used for domestic and industrial purposes. The main sources of fuels are coal and petroleum oils etc.

During combustion of fuels, the atoms of carbon, hydrogen etc. combines with oxygen and liberates heat at a rapid rate. The energy is liberated due to the rearrangement of valency electrons in these atoms and results in the formation of CO_2, H_2O etc. The energy released during the combustion process is the difference in the energy of reactants and that of products.

$$\text{Fuel} + O_2 \longrightarrow \text{Products} + \text{Heat}$$

(More heat energy content) (Less heat energy content)

Characteristics of a good fuel:-

A good fuel should satisfy the following requirements

- It should have a high calorific value i.e., it should evolve a large amount of heat when it is burnt.
- Its moisture content should be low so that its heating value should be high.
- An ideal fuel should have moderate ignition temperature.
- It should not produce harmful products like CO_2, SO_2, H_2S and other poisonous gases on burning since they pollute the atmosphere.
- A fuel should have low content of non-combustible matter in the form of ash or clinker. Since the presence of on-combustible matter will enhance the cost of storage, handling and disposal of waste.
- The combustion of fuel should be controllable so that it can be started or stopped.
- It should not give any offensive odour.
- It should have moderate velocity of combustion.

Classification of fuels:-

Fuels have been classified according to their occurrence and state of aggregation

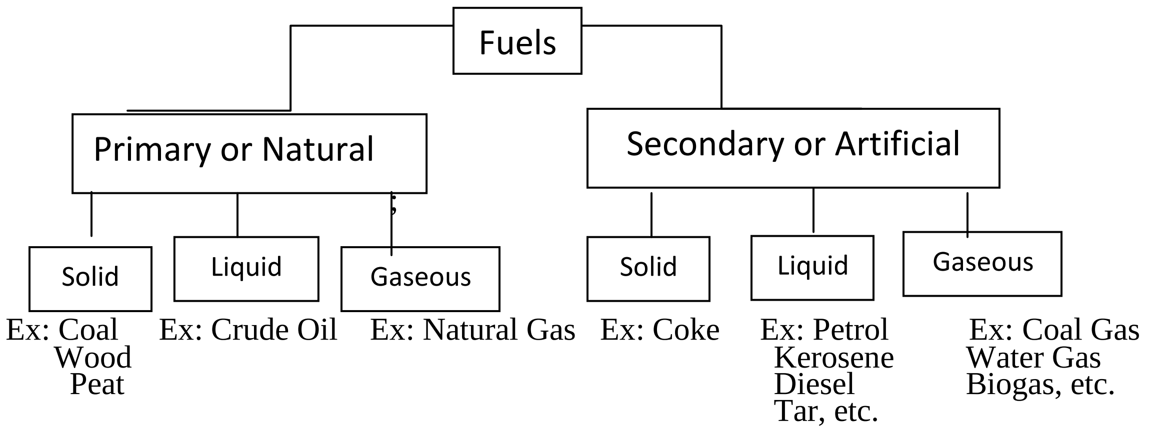
- Based on their occurrence, the fuels are of two types.
  (a) Natural or primary fuels, which are found in nature.

Ex:-wood, coal, peat, petroleum etc.

(b) Artificial or secondary fuels, which are prepared from primary fuels.

Ex:-kerosene, petrol, producer gas etc.

- Based on physical state of aggregation, the fuels are divided into solids, liquids and gases.



SOLID FUELS

The main solid fuels are wood, peat, lignite, coal and char coal. Certain agricultural and industrial wastes like rice husk, coconut and nut shells etc. are also employed as fuels.

COAL: Coal is a highly carbonaceous matter that is formed as a result of alteration of vegetable matter under certain favorable conditions. It is mainly composed of carbon, hydrogen, nitrogen and oxygen besides non-combustible organic matter.

Selection of coal: The following factors are considered for the selection of coal for different uses.

- The calorific value of a fuel should be high, so that large quantities of heat can be obtained from a small quantity of coal.
- It should have low moisture content.
- It should have low ash content since the presence of ash reduces the heating value of coal.
- Coal should have high calorific intensity.
- The size of coal should be uniform to facilitate handling and regulation of combustion.

Analysis of coal:-

The coal should be analyzed to assess its quality. It is done by the following two methods.

Proximate analysis: - This analysis records moisture, volatile matter, ash and fixed carbon as percentages of original weight of coal sample. This analysis is of significant in commercial classification and industrial utilization of coal.

It is a quantitative analysis of following determinations.

(i)**Moisture content:-** About 1g of finely powdered air dried coal sample is weighed in a crucible and is placed inside an electric hot air oven maintained at 105-110^{o}c.It is kept for one hour and then taken out. It is cooled in a desiccator and weighed. The loss in weight is reported as the moisture content on percentage basis.

$$\% \text{ of moisture} = \frac{\text{Loss in weight due to loss in moisture}}{\text{Weight of coal sample taken}} \times 100$$

(ii) **volatile matter:-** The moisture free coal is taken in a silica crucible and heated for 7 minutes in a muffle furnace at 925^{o}C+-20^{o}C.The crucible is taken out and cooled first in air and then in desiccators. The loss in weight is reported as volatile matter on percentage basis.

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

(iii)**Ash content:-**It is the weight of residue obtained after burning a weighed amount of dry coal in an open crucible at 700-750^{o}C for half an hour in a muffle furnace. The weight of residue remaining in the crucible is reported as ash content on percentage basis.

$$\% \text{ of ash} = \frac{\text{Weight of the ash formed}}{\text{Weight of dry coal taken}} \times 100$$

(iv) **Fixed carbon: -** It is the quantity of carbon in coal that can be burnt by a primary current of air drawn through the hot bed of fuel.

The sum total of the percentages of moisture, volatile matter and ash subtracted from 100 gives percentage of fixed carbon.

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

Significance of proximate analysis:- It provides the following valuable information in assessing the quality of coal.

(i) **Moisture content:-**Moisture lowers the effective calorific value because considerable amount of heat is wasted in evaporating the moisture during combustion. Hence lesser the moisture content, better the quality of coal as a fuel.

(ii)**Volatile matter:-** It may be combustible gases (H_2,CO,CH_4 etc.) or non-combustible gases (CO_2,N_2).The presence of non-combustible gases is undesirable since they do not add to the heat value.

The volatile matter content of coal influences the furnace design. Higher the content, larger is the combustion space required. The % of volatile matter in coal denotes the proportion of coal which will be converted into gas and tar products by heat. Hence high volatile matter content is preferable in coal gas manufacture and carbonization plants. Low volatile matter and high fixed carbon is preferred for manufacture of metallurgical coke.

(iii)**Ash: -** It is the non-combustible, useless matter that is left behind when all the combustible matter s burnt off from coal. Hence lesser the ash content better is the quality of coal.

(iv)**Fixed carbon: -** Higher the percentage of fixed carbon, greater is its calorific value and better the quality of coal.

Ultimate analysis: - This is the elemental analysis. It involves the determination of carbon and hydrogen, nitrogen, sulphur and oxygen.

(i) **Carbon and hydrogen: -** About 1-2g of accurately weighed coal sample is burnt in a current of oxygen in a combustion apparatus. The carbon and hydrogen of the sample are converted into CO_2 and H_2O.These is absorbed by KOH and $CaCl_2$ tubes of known weights. The weights of $CaCl_2$ and KOH in the bulbs are determined.

$$C + O_2 \longrightarrow CO_2$$

$$H_2 + 1/2O_2 \longrightarrow H_2O$$

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

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

The increase in weight of $CaCl_2$ gives the weight of H_2O formed and increase in weight of KOH gives the weight of CO_2 formed.

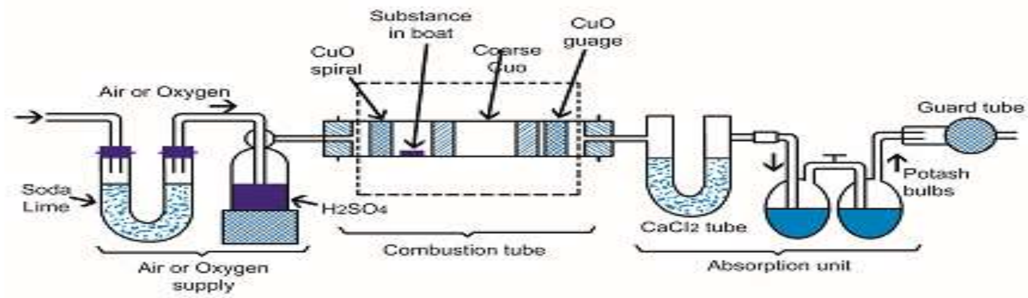


Fig. 6.1 : Carbon and hydrogen determination

$$\% \text{ of carbon} = \frac{\text{Increase in weight of KOH} \times 12}{\text{Weight of coal sample taken} \times 44} \times 100$$

Where 12 represent the atomic weight of carbon and 44 represents the mol.wt. of CO_2.

$$\% \text{ of hydrogen} = \frac{\text{Increase in weight of } CaCl_2 \times 2}{\text{Weight of coal sample} \times 18} \times 100$$

Where 2 is the mol.wt. of H_2 and 18 is the mol.wt. of H_2O.

(ii) **Nitrogen: -** The nitrogen in coal is determined by kjeldahl's method. About 1g of accurately weighed powdered coal is heated with conc.H_2SO_4 along with K_2SO_4 and $CuSO_4$ in a long necked flask called kjeldahl's flask.

After the solution becomes clear i.e., when whole nitrogen is converted into ammonium sulphate, it is treated with excess of NaOH to liberate NH_3. The liberated ammonia is distilled into a measured amount of standard acid solution. The unused acid is then determined by titrating with standard NaOH solution. Thus the amount of acid neutralized by liberated NH_3 is determined. From this, the nitrogen present in the sample is calculated.

$$\% \text{ of nitrogen} = \frac{\text{Volume of acid used} \times \text{normality of acid} \times 14}{\text{Weight of coal sample taken} \times 1000} \times 100$$

(iii) **Sulphur: -** It is determined from the washings obtained from the known mass of coal used in a bomb calorimeter for determination of calorific value. During this, sulphur is converted into sulphate. The washings are treated with barium chloride solution and thus barium sulphate is precipitated. The precipitate is filtered, washed and heated to constant weight.

$$S \xrightarrow{O_2} SO_4^{-2} \xrightarrow{BaCl_2} BaSO_4$$

$$\% \text{ of sulphur} = \frac{\text{Weight of } BaSO_4 \text{ obtained X 32}}{\text{Weight of coal sample taken X 233}} \text{ X 100}$$

Where 32 is the atomic weight of sulphur and 233 is the molecular weight of $BaSO_4$.

(iv) **Oxygen: -** It is determined indirectly by deducting the combined % of carbon, hydrogen, nitrogen and sulphur from 100.

% of oxygen = 100 - % of (C +H +N+ S)

Significance of ultimate analysis: - It gives the following information.

(i) Carbon &hydrogen: - Greater the percentage of carbon and hydrogen better is the coal in quality and calorific value.

The hydrogen is combustible and present in combination with oxygen in water. On heating, it changes into steam. The calorific value of any fuel containing hydrogen is only due to hydrogen present in free state and not in combined form as water. So lesser the percentage of hydrogen better is the quality of coal.

(ii) Nitrogen: - It has no calorific value and hence its presence is not desirable.

(iii) Sulphur: - Sulphur adds to the calorific value of coal since the oxidation of sulphur is an exothermic process.

$$S + O_2 \longrightarrow SO_2 + \text{heat}$$

But SO_2 is harmful. Because it gets oxidized to SO_3, which forms H_2SO_4 leading to corrosion.

$$2\,SO_2 + O_2 \longrightarrow 2SO_3$$

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

(iv) Oxygen:-The oxygen content in coal decreases the calorific value. Hence a good quality coal should have low percentage of oxygen.

LIQUID FUELS

- Liquid fuels are the important commercial and domestic fuels.
- These are obtained from the naturally occurring petroleum or crude oil called as primary fuel.
- Apart of liquid fuels are obtained from hydrogenation of coal.

Advantages of liquid fuels:-

- They require less room for storage.
- Liquid fuels leave very little ash after burning.
- Maximum temperature is achieved in a short period of time.
- They exhibit uniform rate of combustion.
- The furnace space required is lesser than the solid fuels.

Disadvantages of liquid fuels:-

- They are more expensive than solid fuels.
- They give unpleasant odours.
- Special type of burners is needed for their burning.
- Careful supervision is necessary to avoid difficulties.

Crude oil or petroleum:-

- It is also called as rock oil or mineral oil.
- It is dark, greenish brown, viscous oil found deep in earth's crust.
- It is mainly composed of various hydrocarbons small amounts of organic compounds containing oxygen, nitrogen and sulphur.
- The average composition of crude oil is

  C = 79.5 to 87.1%

  H = 11.5 to 14.8%

  S = 0.1 to 3.5%

  N+O = 0.1 to 0.5%

Classification: - There are three principle varieties of petroleum.

(a)Paraffinic- base type crude mainly composed of saturated hydrocarbons from CH_4 to $C_{35}H_{72}$ and a little of naphthalenes &aromatics.

(b)Asphaltic- base type crude mainly contains cycloparaffins or naphthalenes with small amount of paraffins &aromatic hydrocarbons.

(c)Mixed-base type crude contains both paraffinic &asphaltic hydrocarbons.

Origin of petroleum:-

According to modern theory, petroleum has resulted from the partial decomposition of marine animals and vegetables, organisms of pre-historic forests.

REFINING OF PETROLEUM:-

- Refining is defined as "the process by which petroleum is made free of impurities, division of petroleum into different fractions having different boiling points and their further treatment to impart specific properties."

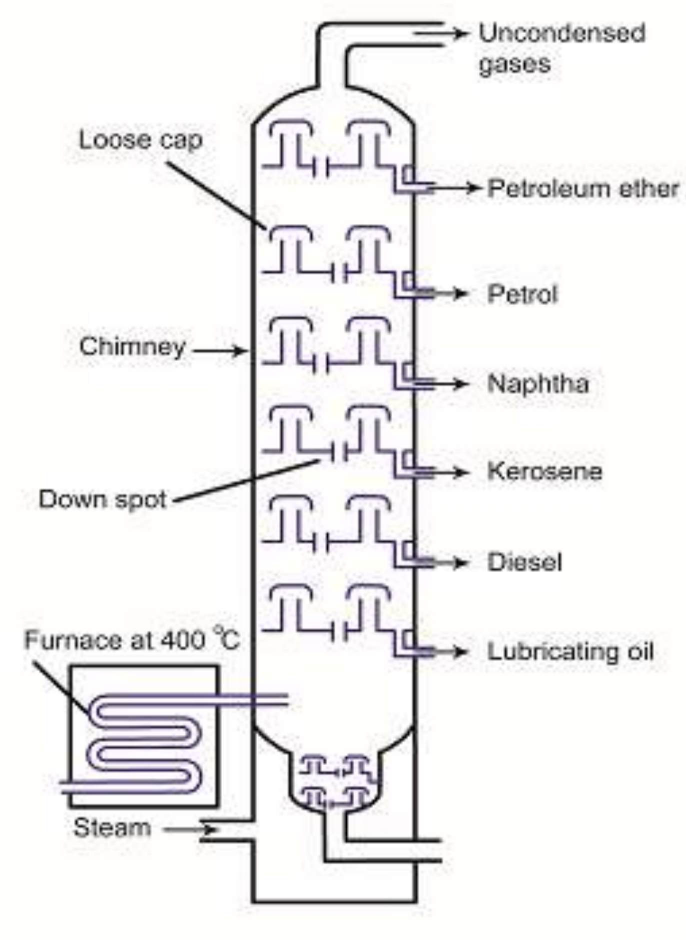


Fig. 6.4 : Refining of petroleum

- In refining of petroleum, the crude oil is separated into various useful fractions by fractional distillation and finally converted into desired specific products.
- The plants used for refining of petroleum are called oil refineries.

The process of refining involves the following steps.

(i)Removal of solid impurities: - The crude o

il is a mixture of solid, liquid and gaseous substances. This is allowed to stand for some time so that the heavy solid particles settle down and the gases evaporate. The supernatant liquid is then centrifuged and all the solids get removed.

(ii)Removal of water (Cottrell's process):- The crude oil from the oil well is a stable emulsion of oil and salt water. This mixture is passed between two highly charged electrodes so that emulsion films are destroyed and the colloidal water droplets combine into bigger drops and separates out from the oil.

(iii)Removal of harmful sulphur impurities: - It involves in treating in oil with copper oxide. The sulphur compounds get converted into insoluble copper sulphide and are removed by filtration.

(iv)Fractional distillation: - The crude oil is then heated to about 400^o C in an iron retort in which all the volatile constituents are evaporated. The hot vapors are then passed into a fractionating column. It is a tall, cylindrical tower containing a number of horizontal stainless steel trays at short distances. Each tray is provided with a small chimney covered with a loose cap.

As the vapors go up, they become cool and fractional condensation takes place at different heights of column. Higher boiling fractions condense first and the lower boiling fractions later.

The following are the various principal fractionation products obtained from crude.

(i) Uncondensed gases: - They are lower hydrocarbons and obtained below 30^oC.

They are highly combustible. They are used as domestic fuel.

(ii)Gasoline or petrol: - It is obtained between $40\text{-}120^o$c and is a mixture of hydro-

Carbons like pentane to octane.

Its calorific value is 11,250 k.cal/kg.

It is highly volatile and inflammable.

It is used as a fuel for internal combustion engines of automobiles and aeroplanes.

(iii)Kerosene oil: - It is obtained between 180^oc-250^oc and consists of paraffin's, Naphthalene and aromatic compounds.

Its calorific value is 11,000 k.cal/kg.

Kerosene oil is used as domestic fuel in stoves, tractor fuel, and illuminant, as jet engine fuel and for making oil gas.

(iv) Gas oil or diesel oil:- It is obtained between 250^oC-320^oC.

Its calorific value is 11,000k.cal/kg

It is used as diesel engine fuel.

(v)Residual oil: - It is the heaviest fraction of distillation

On cooling, it gives paraffin wax which is used in the manufacture of candle, polishes, paper etc.

It also gives greases and lubricating oil which are used as lubricants.

The asphalt is used as preservative for wood water proofing and laying down the roads.

FRACTIONS BY DISTILLATION OF CRUDE

Name of fraction	Boiling range	Approx. composition in terms of hydrocarbon containing C atoms	Uses
1. Uncondensed gas.	Below 30°C	C_1 to C_4 (such as ethane, propane, *iso*butane)	As domestic or industrial fuel under the name L.P.G. (liquefied petroleum gas).
2. Petroleum ether.	30 – 70°C	$C_5 - C_7$	As a solvent.
3. Gasoline or petrol or motor spirit.	40 – 120°C	$C_5 - C_9$ (calorific value = 11,250 kcal/kg)	As motor fuel, solvent and in dry cleaning.
4. Naphtha or solvent spirit.	120 – 180°C	$C_9 - C_{10}$	As solvent and in dry cleaning.
5. Kerosene oil.	180 – 250°C	$C_{10} - C_{16}$ (calorific value = 11,000 kcal/kg)	As an illuminant, jet engine fuel and for preparing laboratory gas.
6. Diesel oil or fuel oil or gas oil.	250 – 320°C	$C_{10} - C_{18}$ (calorific value = 11,000 kcal/kg)	Diesel engine fuel.
7. Heavy oil.	320 – 400°C	$C_{17} - C_{30}$	For getting gaso-line by cracking process.
This on *refrac-tionation* gives :			
(*a*) Lubricating oil.	-	-	As lubricant.
(*b*) Petroleum jelly. (vaseline)	-	-	As lubricant and in cosmetics and medicines.
(*c*) Grease.	-	-	As lubricant.
(*d*) Paraffin wax.			In candles, boot polishes, wax paper, tarpolin cloth, etc.
8. Residue may be either :	Above 400°C	C_{30} and above.	
(*a*) Asphalt. or	-	-	Water-proofing of roofs and road making.
(*b*) Petroleum coke.	-	-	As a fuel and in moulding arc light rods.

CRACKING:-

- During distillation of crude oil, the gasoline obtained is of very important in automobile industry.
- The yield and quality of gasoline is improved by cracking.
- It involves thermal decomposition of heavier fractions.

Cracking is defined as the process by which the higher hydrocarbons are decomposed into lower hydrocarbons by the application of heat.

E.g.:- $C_{10}H_{22}$ cracks into paraffinic and olefinic hydrocarbons.

$$C_{10}H_{22} \longrightarrow C_5H_{12} + C_5H_{10}$$

Paraffin olefin

The simpler molecules decompose into end product C and H_2.

$$CH_4 \longrightarrow C + 2H_2$$

There are three methods of cracking. They are

A) Thermal cracking
B) Catalytic cracking
c) Hydrogenation cracking

Significance:-

- The yield of gasoline is high.
- The quality of gasoline is better.
- The heat required for burning is derived from the coal embedded in the catalyst. So no eternal catalyst is required.
- Requirement of low pressure for cracking.
- The process can be controlled easily and so desired products are obtained.
- The product of cracking contains a higher amount of aromatics. So it possesses anti-knock properties.
- The gasoline produced as a high octane rating.

Synthetic Petrol:-

The important methods commonly used for synthesis of petrol are:-

- Fischer-Tropsch method
- Bergius process

(i)Fischer-Tropsch method:-

- In this method, the raw material is the hard coke. The red hot coke is converted into water gas by passing steam over it.

$$C + H_2O \longrightarrow CO + H_2$$
(Water gas)

- The water gas is then mixed with hydrogen. The gas is purified by passing through Fe_2O_3 to remove H_2S and then into mixture of Fe_2O_3 and Na_2CO_3 to remove organic sulphur compounds.
- The purified gas is then compressed to 5-25atm and then led through a convertor containing the catalyst consisting of Fe, Ni or Co.
- The product formed depends upon the catalyst.
- A Cobalt catalyst gives more olefins.
- Iron oxide with K_2CO_3 as promoter gives heavier hydrocarbons.
- Mixed catalysts like Cobalt magnesia are used to produce high grade diesel fuel from the enriched water gas.

$$n\,CO + 2n\,H_2 \longrightarrow C_nH_{2n} + n\,H_2O$$
$$n\,CO + (2n+1)H_2 \longrightarrow C_nH_{2n+2} + nH_2O$$

- The reactions are exothermic. So the outgoing hot gaseous mixture is led to a cooler, where crude oil is obtained.

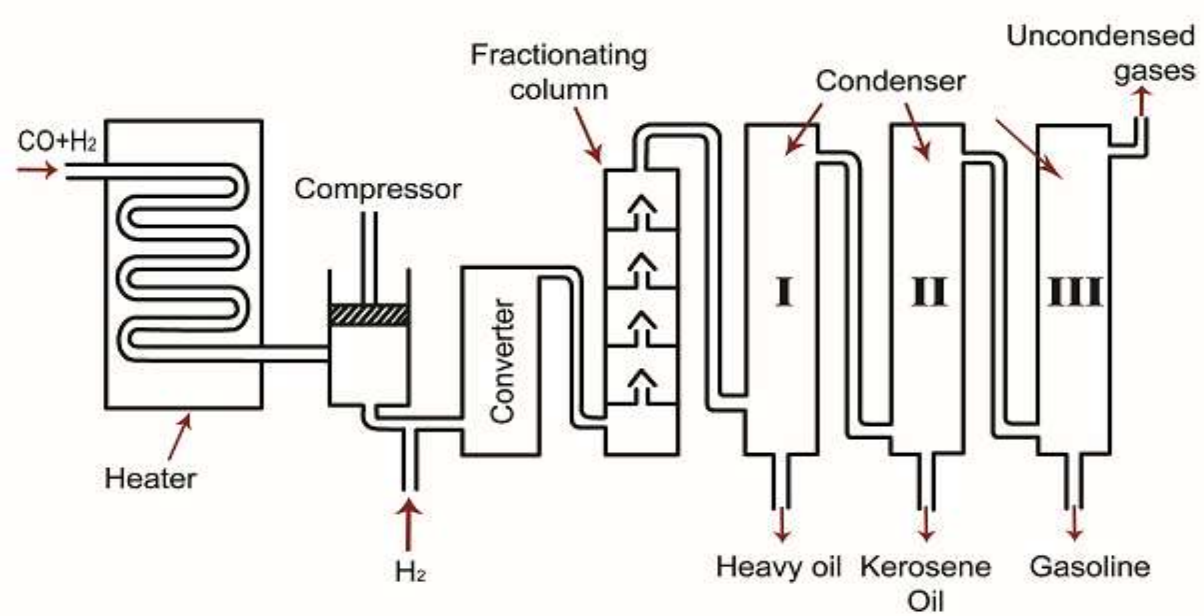
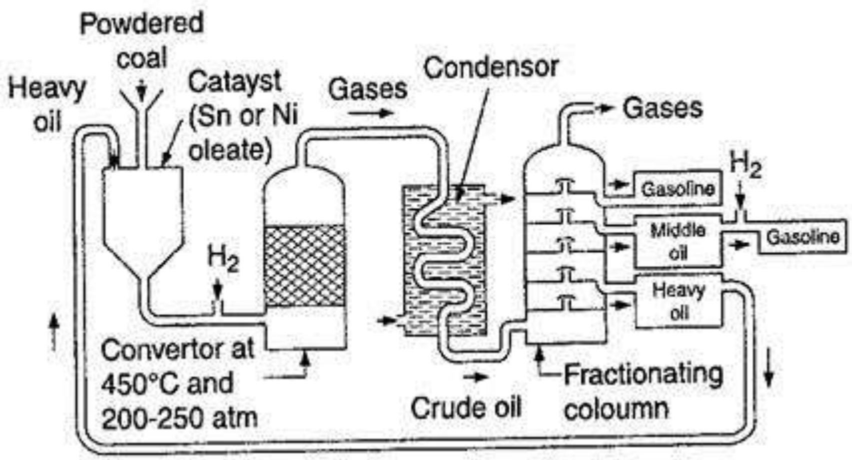


Fig. 6.9 : Fischer Tropsch method

- The crude oil is then passed into a fractionating column and separated into different fractions like heavy oil, kerosene oil and gasoline.
- Then heavy oil is reused for cracking to get more gasoline.

(ii) Bergius process (Hydrogenation of oil):-In this process, the low ash coal is finely powdered and made into a paste with heavy oil. A catalyst composed of tin or nickel oleate is mixed with it.



Bergius process

- The paste is then heated with hydrogen at $450^{o}c$ under a pressure of 200-250 atm for about 1.5 hours.
- The hydrogen combines with coal to form saturated hydrocarbons which decompose to yield lower hydrocarbons.
- The gases are led to a condenser to give crude oil. It is fractionated which results in the formation of gasoline, middle oil and heavy oil.
  (i) The top fraction is condensed and synthetic gasoline is recovered.
  (ii) The middle oil is hydrogenated in presence of solid catalyst to give more gasoline.
  (iii) The heavy oil fraction is recycled t make a paste with coal powder.
- The yield of gasoline is about 60% of coal dust used.

Knocking:-

- In an internal combustion engine, a mixture of gasoline vapour and air is used as a fuel.
- After initiating the combustion reaction, the flame should spread rapidly and smoothly through the gaseous mixture. Thus the expanding gas drives the piston down the cylinder.
- The ratio of gaseous volume in the cylinder at the end of suction stroke to the volume at the end of compression stroke of the piston is called compression ratio. It indicates the extent of compression of fuel-air mixture by piston.

- The efficiency of an internal combustion engine increases with increase in compression ratio and this depends upon the nature of constituents in gasoline that is used.
- In some cases, the rate of oxidation is so great that the last portion of fuel-air mixture gets ignited instantaneously and produces sound in the engine called as knock. This rattling noise produced in the internal combustion engine is called knocking.
- This defect is due to the faulty design of engine, which results in loss of efficiency. It is also due to unfavorable conditions due to defective ignition of fuel-air mixture.
- The tendency of fuel constituents to knock is in the following order
  Straight chain paraffins>branched chain paraffins>olefins>cycloparaffins>aromatics
- Thus olefins possess better anti-knock properties than the corresponding paraffins and so on.
- Hence the fuel with least knocking is a good fuel.
- The knocking is decreased by adding a little of tetra ethyl lead (TEL).It is a colourless, sweet smelling and highly poisonous liquid.

Octane number:-

- The performance of gasoline in an internal combustion engine is rated based on octane number. Higher the octane number of fuel better is its performance and lower is the knocking engines.
- The octane number of gasoline is defined as the percentage of iso-octane present in a mixture of iso-octane and n-heptane.
  Eg:-The octane number of a motor fuel is 80.It means that the gasoline will produce knocking by the mixture of 80 parts of iso-octane and 20 parts of heptane.
- n-heptane knocks very badly and its anti-knock value is arbitrarily fixed as zero and iso-octane has the highest anti-knocking value i.e., 100.

```
        CH3        CH3
         |          |
H3C─CH─CH2─C─CH3
                    |
                   CH3
```

$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$

n-heptane

Octane number = 0

Iso octane (2,2,4-tri methyl pentane)

Octane number = 100

So the octane number shows the anti-knocking property of any fuel.

Improvement of anti-knock characteristic of a fuel:-

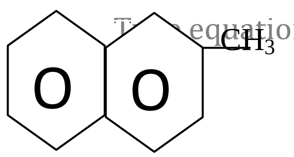
The octane number of fuels can be raised by the addition of certain compounds like tetra ethyl lead [$(C_2H_5)_4$Pb orTEL], diethyl telluride [$(C_2H_5)_2$Te].

Such compounds are called anti-knock compounds and the process is called doping.

Cetane number:-

- In diesel engines, the fuel is exploded by the application of heat and pressure.
- Diesel engine fuels consist of longer chain hydrocarbons than internal combustion engine fuels.
- The main characteristic of a diesel engine fuel is that it should easily ignite below compression temperature and there should be as short an induction lag as possible.
- It is essential that the hydrocarbon molecules in a diesel fuel should be straight chain ones with a minimum admixture of aromatic and side chain hydrocarbon molecules.
- The knocking characteristics of diesel oil are given by **cetane number** which is defined as the percentage of hexadecane in a mixture of hexadecane and 2-methyl naphthalene.

  Cetane is a saturated hydrocarbon ($C_{16}H_{34}$) having a short ignition delay and hence its cetane number is 100.



$$H_3C-(CH_2)_{14}-CH_3$$

2- Methyl naphthalene
Cetane number = 0

n-hexa decane (cetane)
cetane number = 100

- 2- Methyl naphthalene has a long ignition delay and hence its cetane number is taken as zero.
- The cetane number can be improved by adding certain additives like ethyl nitrite, iso amyl nitrite, acetone peroxide etc., which are called pre-ignition dopes.
- Cetane number of a fuel depends on the nature and composition of its hydrocarbon.
- The order of cetane number for the following in the order
  n-alkanes > naphthalenes>alkenes>branched alkanes>aromatics
  Thus hydrocarbons which are poor gaoline fuels are good diesel fuels.

GASEOUS FUELS:-

The gaseous fuels are the most preferred fuels because of their ease of storage, transport, handling and ignition.

Advantages of gaseous fuels:-

- They can be distributed over a wide area through pipe lines, so that manual labour can be eliminated.
- They are ash less and smokeless and very clean to operate.
- The feed of the gas to the burner can be easily controlled and can be lighted very easily.

- Gases are miscible with air and hence the excess air needed is very less.
- These are quite efficient as the losses due to errors like smoke, convection etc., are minimum

Disadvantages:-Even they are more advantageous,

- Great care should be taken due to their high inflammability.
- More space is required for the storage of gaseous fuels since they occupy large volumes.

Natural gas:-

- Natural gas is obtained from the wells dug in the earth during mining of petroleum. It is mostly composed of methane and small quantities of ethane along with other hydrocarbons.
- If lower hydrocarbons are present in the gas or when the gas is associated with crude oil, it is called dry gas.
- If the hydrocarbons with high molecular weights are present or when the gas occurs along with petroleum, it is called wet gas.
- The average composition of natural gas is

  CH_4 = 70-90%

  C_2H_6 =5-10%

  H_2 =3%

  $CO+CO_2$ = rest
- The calorific value of natural gas is 8000-14000 k.cal/m^3.

  For e.g. : - If natural gas contains H_2S, it can be removed by scrubbing with monoethanolamine.

  $$2\ HO.CH_2.CH_2.NH_2 + H_2S \text{ --------------> } (OH.CH_2.CH_2.NH_2)_2\ H_2S$$

  On heating, H_2S can be liberated.

Uses of natural gas:-

- It is an excellent domestic fuel which can be carried to long distances through pipe lines.
- It is used in the manufacture of chemicals like carbon black, methane, formaldehyde etc.
- Synthetic proteins used as animal feed is obtained by microbiological fermentation of methane.
- It is also used for the generation of electricity in fuel cells.
- Natural gas is also used as a source of H_2. Hence ammonia can be made by reacting N_2 with H_2 obtained from natural gas.

LPG:- liquefied petroleum gas or bottled gas or refinery gas

1. It is obtained as a by-product during the cracking of heavy oils or from natural gas.

2. LPG is dehydrated, desulphurised and traces of odourous organic sulphides are added to give warning of gas leak.
3. LPG is supplied under pressure in containers under the trade name like Indane, Bharat gas etc.
4. Its calorific value is about 27,800 $K.Cal/m^3$.
5. LPG consists of hydrocarbons of volatility that they can exist as gas under atmosphere pressure, but can be readily liquefied under pressure.
6. The main constituents of LPG are n-butane, isobutane, butylene and propane with little or no propylene and ethane.

Uses:-The largest use of LPG is as domestic fuel and industrial fuel.

It is widely used as motor fuel.

Advantages of LPG over gaseous fuel:-

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

Advantages of LPG over gasoline as a motor fuel:-

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

Disadvantages of LPG over gasoline as a motor fuel:-

- Due to its faint odour, leakage cannot be easily detected.
- Handling has to be done under pressure.
- LPG is advantageous only in engines working under high compression ratios.
- Its octane number is quite low and the load sensitivity is very high.

Due to this, the use of LPG is limited only to vehicles like trucks and tractors. LPG leaded with tetra methyl lead can be used as main constituent of diesel fuel for railway diesel locomotives.

CNG: - Compressed natural gas

- It is a natural gas compressed to a high pressure of about 1000 atmospheres.
- A steel cylinder containing 15 kg of CNG contains about $2x10^4$ L or 20 m^3 of natural gas at 1 atmosphere pressure.
- CNG is used as a substitute for petrol and diesel. Because it is less pollution causing fuel.
- During its combustion, no sulphur and nitrogen gases are evolved.No it is better fuel than petrol or diesel for automobiles.
- The initial cost of engine designed to use CNG as a fuel is higher than that of engine designed to use petrol or diesel.In Delhi , it is mandatory for all buses, taxis and auto to use CNG as a fuel.

CNG is preferred over LPG

i. CNG is much safer fuel, since it ignites at a higher temperature than gasoline and diesel.
ii. The conversion of gasoline operated automobiles into CNG operated vehicle is easy.
iii. The operating cost of CNG fuel is much lower compared to gasoline operation.
iv. Combustion of CNG leads to lesser carbon monoxide emissions than gasoline.
v. CNG mixes better with air than liquid fuals.
vi. Emission from CNG operated vehicle contain no pollutants like smoke, $SO_{2,}$ $SO_{3,}C_6H_{6,}$HCHO etc.

Calorific value of a fuel:-

The total quantity of heat liberated when a unit mass of fuel is burnt completely is called calorific value of a fuel.

Units:-

- **Calorie** is the amount of heat required to raise the temperature of one gram of water through one degree centigrade
- **Kilocalorie** is defined as the quantity of heat required to raise the temperature of one kilogram of water through one degree centigrade.

  1 kilocalorie = 1000 calories
- **British thermal unit** is defined as the quantity of heat required to raise the temperature of one pound of water through one degree Fahrenheit.

  1 B.Th.U = 252 cal =0.252 K.Cal

  1 K.Cal = 3.968 B.Th.U

- **Centigrade heat unit** is defied as the quantity of heat required to raise the temperature of one pound of water through one degree centigrade.

  1 K.Cal = 3.968 B.Th.U = 2.2 C.H.U

- **Higher or gross calorific value(HCV or GCV)** is defined as the total amount of heat produced when unit mass or volume of the fuel is burnt completely and the products of combustion have been cooled to room temperature.

  HCV or GCV = 1/100[8080C+34500(H-O/8)+2240S]

  Where, C, H, O, S are the percentages of carbon, hydrogen, oxygen and sulphur. The calorific values of the components of fuels are outlined below:

Constituent	Calorific value
Hydrogen	34,500
Carbon	8080
Sulphur	2240

- **Lower or net calorific value** is defined as the net heat produced when unit mass or volume of the fuel is burnt completely and the products are permitted to escape.(LCV)

  LCV = HCV – latent heat of water vapour formed

  = HCV – mass of hydrogen X 9 X latent heat of steam

  Because 1 part by mass of hydrogen produces 9 parts by mass of water.

The latent heat of steam is 587 K.Cal/Kg or 1060 B.Th.U/lb of water vapour formed at room temperature.

Problems:

1. Calculate the gross and net calorific value of coal having composition carbon=85%, hydrogen =8%, sulphur =1% ash = 4% nitrogen =2%.

   Solution:

   Given: Carbon=85%, hydrogen=8%, sulphur =1% ash = 4% nitrogen =2%.

   HCV= 1/100[8080C+34500(H-O/8)+2240S]

   = 1/100[8080x85+34500(8-0/8)+2240x1]

   = 1/100[965040]

   = 9650.4Kcal/Kg.

   LCV= HCV-0.09xHx587

   = 9650.4-0.09x8x587

   = 9227.7 Kcal/Kg.

2. Calculate the gross and net calorific value of coal having composition carbon=87%, hydrogen =2%, sulphur =1% ash = 9%, oxygen=1%.

   Given: Carbon=87%, hydrogen=2%, sulphur =1% ash = 9% oxygen =1%.

   HCV= 1/100[8080C+34500(H-O/8)+2240S]

   = 1/100[8080x87+34500(2-1/8)+2240x1]

= 1/100[769887.5]

= 7698.8Kcal/Kg.

LCV= HCV-0.09xHx587

= 7698.8.4-0.09x2x587

= 7593.1 Kcal/Kg.

BIODIESEL:

Introduction:

Biodiesel invented by Sa parente refers to a vegetable oil- or animal fat-based diesel fuel consisting of long-chain alkyl (methyl, propyl or ethyl) esters. Biodiesel is typically made by chemically reacting lipids (e.g., vegetable oil, animal fat (tallow)) with an alcohol.

Biodiesel is meant to be used in standard diesel engines and is thus distinct from the vegetable and waste oils used to fuel *converted* diesel engines. Biodiesel can be used alone, or blended with petrodiesel. Biodiesel can also be used as a low carbon alternative to heating oil.

Blends of biodiesel and conventional hydrocarbon-based diesel are products most commonly distributed for use in the retail diesel fuel marketplace.

Production

- Biodiesel is commonly produced by the transesterification of the vegetable oil or animal fat feedstock.
- Chemically, transesterified biodiesel comprises a mix of mono-alkyl esters of long chain fatty acids.
- The most common form uses methanol (converted to sodium methoxide) to produce methyl esters (commonly referred to as Fatty Acid Methyl Ester - FAME) as it is the cheapest alcohol available, though ethanol can be used to produce an ethyl ester (commonly referred to as Fatty Acid Ethyl Ester - FAEE) biodiesel and higher alcohols such as isopropanol and butanol have also been used.
- Using alcohols of higher molecular weights improves the cold flow properties of the resulting ester, at the cost of a less efficient transesterification reaction.
- A lipid transesterification production process is used to convert the base oil to the desired esters. Any free fatty acids (FFAs) in the base oil are either converted to soap and removed from the process, or they are esterified (yielding more biodiesel) using an acidic catalyst.
- A by-product of the transesterification process is the production of glycerol. For every 1 tonne of biodiesel that is manufactured, 100 kg of glycerol are produced.

B factor: Much of the world uses a system known as the "B" factor to state the amount of biodiesel in any fuel mix: 100% biodiesel is referred to as **B100**, while

20% biodiesel, 80% petrodiesel is labelled **B20**

5% biodiesel, 95% petrodiesel is labelled **B5**

2% biodiesel, 98% petrodiesel is labelled **B2**

Properties

- Biodiesel has better lubricating properties and much higher cetane ratings than today's lower sulfur diesel fuels.
- Biodiesel addition reduces fuel system wear, and in low levels in high pressure systems increases the life of the fuel injection equipment that relies on the fuel for its lubrication.

Older diesel Mercedes are popular for running on biodiesel.

- The calorific value of biodiesel is about 37.27 MJ/kg.
- Biodiesel is a liquid which varies in color —between golden and dark brown — depending on the production feedstock.
- It is immiscible with water, has a high boiling point and low vapor pressure.
- The flash point of biodiesel (>130 °C, >266 °F) is significantly higher than that of petroleum diesel (64 °C, 147 °F) or gasoline (45 °C, 52 °F).
- Biodiesel has a density of ~ 0.88 g/cm³, higher than petrodiesel (~ 0.85 g/cm³).
- Biodiesel has virtually no sulfur content, and it is often used as an additive to Ultra-Low Sulphur Diesel (ULSD) fuel to aid with lubrication, as the sulfur compounds in petrodiesel provide much of the lubricity.

Applications

- Biodiesel can be used in pure form (B100) or may be blended with petroleum diesel at any concentration in most injection pump diesel engines.
- New extreme high-pressure (29,000 psi) common rail engines have strict factory limits of B5 or B20
- Biodiesel has different solvent properties than petrodiesel, and will degrade natural rubber gaskets and hoses in vehicles (mostly vehicles manufactured before 1992), although these tend to wear out

Railway usage

- British train operating company Virgin Trains claimed to have run the world's first "biodiesel train", which was converted to run on 80% petrodiesel and only 20% biodiesel, and it is claimed it will save 14% on direct emissions.

- The Royal Train on 15 September 2007 completed its first ever journey run on 100% biodiesel fuel supplied by Green Fuels Ltd.
- In eastern Washington ran a test of a 25% biodiesel / 75% petrodiesel blend during the summer of 2008,.
- Also in 2007, Disneyland began running the park trains on B98 (98% biodiesel). The program was discontinued in 2008 due to storage issues, but in January 2009, it was announced that the park would then be running all trains on biodiesel manufactured from its own used cooking oils. This is a change from running the trains on soy-based biodiesel.

Aircraft use

- A test flight has been performed by a Czech jet aircraft completely powered on biodiesel. Other recent jet flights using biofuel, however, have been using other types of renewable fuels.

As a heating oil

Biodiesel can also be used as a heating fuel in domestic and commercial boilers, a mix of heating oil and biofuel which is standardized and taxed slightly differently than diesel fuel used for transportation.