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FEULS AND PETROCHEMICALS ANALYSIS

INTRODUCTION

In this present age of rapid industrial development, the power requirement is increasing day-by-day. Heat energy is the main source of power. Burning of carbon, an exothermic reaction produces heat energy. Hence, the carbon compounds have been used as the main source of heat energy.

Fuel

A fuel is a substance, which on proper burning gives large amount of heat energy on combustion. It is used for domestic and industrial purposes. They contain carbon as a main constituent. Fuels essentially consist of carbon, hydrogen, oxygen and some hydrocarbons and the heat that a particular fuel can

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A fuel may be defined as *energy rich chemical which yields energy by a process of combustion and get converted to energy poor compound*.

Combustion reactions are:

$$C + O_2 \longrightarrow CO_2 + \text{Heat}$$

$$H_2 + \tfrac{1}{2} O_2 \longrightarrow H_2O + \text{Heat}$$

The main sources of fuels are coal and petroleum oils available in earth’s crust and they are called fossil fuels. Fossil fuels is the amount of which are decreasing day by day. The other sources of fuels are radioactive elements and Sunlight.

The combustion is the process of oxidation that provides heat energy. Every combustion is an oxidation but every oxidation is not combustion.

Example: - Combustion of wood and coal, Petrol and kerosene gives heat energy.

Units of Heat:

There are different units for measuring the quantity of heat. They are:

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Units of Heat:

There are different units for measuring the quantity of heat. They are:

(i)Calorie: It is the amount of heat required to increase the temperature of 1 gram of water through one degree centigrade.

1000 calories=1kcal

(ii) Kilocalorie: This is the unit of heat in metric system, and is defined as the quantity of heat required to raise the temperature of one kilogram of water through one degree centigrade.

1 k.cal = 1000 cal

1 k.cal = 3.968 B.T.U

(iii) British thermal unit (B.T.U): This is the unit of heat in English system, it is defined as “the quantity of heat required to increase the temperature of one pound of water through of one degree of Fahrenheit.

1 B.T.U = 252 cal = 0.252 k.cal

(iv) Centigrade heat unit (C.H.U): It is the quantity of heat required to raise the temperature of one pound of water through one degree centigrade.

1 k.cal = 3.968 B.T.U = 2.2 C.H.U

Calorific value of a fuel:

The usefulness of a fuel is measured in terms of its calorific value**.** Higher the calorific value, better the fuel will be.

“*Calorific value of a fuel is the total quantity of heat liberated when a unit mass or volume of the fuel is burnt completely*”.

OR

The calorific value of a fuel can be defined as “the total quantity of heat liberated when a unit mass of the fuel is completely burnt in air or oxygen”.

Example: The calorific value of kerosene oil is 45 kJ/g and charcoal is 33 kJ/g.

(I) ***Gross calorific value*** (***Higher calorific value):*** Gross calorific value of a fuel is defined as the total quantity of heat liberated when a unit mass of the fuel is completely burnt and the combustion products are cooled to room temperature (15^0-60^0C).

$$H_2+1/2O_2 \xrightarrow{\quad\quad} H_2O+Heat$$

Gross calorific value = Heat of reaction + Latent heat of steam produced

+ Sensible heat obtained by cooling the combustion

Products to room temperature

(II) Net calorific value (Lower calorific value): The net calorific value of a fuel is the actual amount of heat available when unit mass of the fuel is completely burnt and combustion products are permitted to escape.

Net Calorific Value = Gross calorific value – Latent heat of water vapors formed.

Table: Calorific Value of some important Fuels

S.N.	***Fuels***	***CalorificValue(KJ/Kg)***
1.	Cow dung cake	6000-8000
2.	Wood	17000-22000
3.	Coal	25000-33000
4.	Petrol	45000
5.	Kerosene	45000
6.	Diesel	45000
7.	Methane	50000
8.	CNG	50000
9.	LPG	55000
10.	Biogas	35000-40000
11.	Hydrogen	150000

Hydrogen gas has the highest calorific value of 150 kilojoules per gram Thus, because of its high calorific value; hydrogen is an extremely good fuel**.** So LPG has a higher calorific value than coal.

Classification of fuels:

Fuels are classified into natural or primary fuels and artificial or secondary fuels. Each type is further subdivided into solid, liquid and gaseous fuels.

(I) On the basis of occurrence, the fuels are further divided into two types.

(i) Natural or primary fuels: - These are found in nature such as Wood, peat, coal, petroleum, natural gas etc.

(ii) Artificial or secondary fuels: - These are prepared artificially from the primary fuels. Example: - charcoal, coke, kerosene, diesel, petrol, coal gas, oil gas, producer gas, blast Furnace gas etc

(*II)The second classification is based upon their state of aggregation like*:

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

A complete classification of fuels with suitable examples is represented in Table.

S.N.	State of fuel	Natural(Primary Fuels)	Artificial (Secondary Fuels)
1.	Solid	Wood, peat, lignite, coal	Wood charcoal, coke
2.	Liquid	Crude petroleum	Kerosene, petrol, diesel, alcohol
3.	Gases	Natural gas	Water gas, producer gas, biogas, coal gas, LPG

Characteristics of a good fuel:

(i) The fuel should be easily available.

(ii) Combustion should be easily control.

(iii) It should be dry and should have less moisture content. Dry fuel increases its calorific value.

(iv) It should be cheap, easily transportable and has high calorific value.

(v) It must have moderate ignition temperature and should leave less ash after combustion.

(vi) The combustion speed of a good fuel should be moderate.

(vii) It should not burn spontaneously to avoid fire hazards.

(viii) Its handling should be easy and should not give harmful gases after combustion such as CO,SO_2,H_2S,CO_2,PH_3 etc.

(ix) The gaseous products of combustion should not pollute the environment.

(x) The combustion of a good fuel should not be explosive.

(xi) Storage cost in bulk should be law.

(xii) A fuel must burn in air with efficiency without much smoke.

Comparison of solid, liquid and gaseous fuels:

S.N.	Solid fuels	Liquid Fuels	Gaseous Fuels
1.	Cheap and easily available	Costly than solid fuels	Except natural gas, other gaseous fuels are costly
2.	Transportation and storage is easy without any risk of spontaneous explosion	It can be transported easily by pipelines. But do not store them in open	Must be stored in leak proof containers and can be transported through pipelines.
3.	Combustion is slow but its control and stop is not easy	Quickly combustible and can be controlled and stopped, when required	Rapidly combustible and controlled stopped easily.
4.	There is least risk of fire accidents	There is greater risk	Very high risk of hazards ,due to their highly inflammable nature
5.	Thermal efficiency is least	Thermal efficiency is higher	Thermal efficiency is highest

6.	Calorific value is least	Calorific value is higher	Calorific value is highest
7.	They cannot be used in internal combustion engines	They can be used	They can also be used as internal combustion engines fuels.

Solid Fuels:

Solid fuels are mainly composed or carban and hydrogen with a little amount of oxygen and nitrogen, sulphur and other volatile matters. The main solid fuels include wood, peat, lignite, coal, charcoal etc.

Type of Solid Fuels:

Solid fuels are two types-

(I)Natural solid fuels:

(a)Wood

(b)Coal- Peat, Lignite, Bituminous, Anthracite

(II)Prepared solid fuels: Coconut charcoal, wood charcoal and coke.

Coal: Coal is regarded as a fossil fuel produced from large accumulation of vegetable debris due to partial decay and alteration by the action of heat and pressure over millions of years.

Classification of Coal:

There are four kinds of coal based on their carbon content and calorific value. The process of conversion of wood into coal occurs in several stages by geographical process known as ”coalification”.

The process may be complete or may be stopped at any state thus giving rise to material of varying carbon content.

wood→ peat→ lignite→ bituminous coal→ anthracite coal

Carbon content and calorific value increases

(A) Peat: It is a brown fibrous mass and is considered as first stage of coal formation. It contains 57% carbon and its calorific value is about 5400 kcal/kg.

(B) Lignite: It is soft brown colored and is a low grade fuel. It contains 60% to 70% carbon and its calorific value is about 6500 to 7500 kcal/kg.

(C) Bituminous coal: The bituminous coals are 3 types.

(a) *Sub bituminous:* Black and smooth in appearance have 75 to 83% carbon content and its calorific value is about 7000kcal/kg.

(b)Bituminous: Carbon content is from 78 to 90% and calorific value is from 8000 to 8500 kcal/kg.

(c) Semi bituminous: Carbon content is 90 to 95% and has calorific value of about 8500 to 8600 kcal/kg.

(D)Anthracite: Highest grade of coal dense and lustrous in appearance. The carbon content is 92-98% and the calorific value ranges between 8650 to 8700 kcal/kg.

Analysis of Coal:

The composition of coal varies widely and hence it is necessary to analyze and interpret the results. The quality of coal is ascertained by the following 2 types of analysis:

(1)Proximate analysis

(2) Ultimate analysis.

(1)Proximate analysis: In proximate analysis, the data collected vary with the procedure adopted. The quality of coal can be assessed by proximate analysis.

The analysis includes the determination of moisture, volatile matter, ash and fixed carbon.

(i) Moisture: About 1 g of finely powdered air-dried coal sample is weighed in a crucible. The crucible is heated in an electric hot-air oven ($105\text{-}110^0$ C) for one hour. The crucible is taken out, cooled in desiccators and weighed. Loss in weight is noted.

$$\%\text{ of moisture} = \frac{(\text{loss of weight}) \times 100}{\text{Total wt. of sample}}$$

(ii)Volatile matter: The dried sample of coal left in the crucible is covered with lid and placed in an electric furnace (muffle furnace) at 9250 C $\pm 20^0$ C for 7 minutes. The crucible is taken out, cooled first in air, then in a desiccators and weighed. Loss in weight is noted.

$$\%\text{ of Volatile matter} = \frac{-(\text{loss of weight}) \times 100}{\text{Weight of coal taken}}$$

(iii) Ash: The residual coal in the crucible is then heated without lid in muffle furnace for half an hour at 700 ± 50^0 C. The crucible is taken out, cooled first in air,then in a desiccators and weighed. Heating, cooled and weighing is repeated until a constant weight is obtained. The residue is reported as ash on percentage basis.

$$\%\text{ of Ash} = \frac{(\text{loss in weight of sample}) \times 100}{\text{Weight of sample}}$$

(iv) Percentage of Fixed carbon: can be calculated mathematically by placing the above three values in the following formula:

$$\%\text{ of fixed carbon} = 100 - \%\text{ of}[\text{ Moisture} + \text{Volatile matter} + \text{Ash matter}]$$

Significance of Proximate analysis:

Proximate analysis plays an important role in assessing the quality of coal.

(i)Lesser is the moisture content, better is the quality of coal as moisture lowers the effectives calorific value of coal.

(ii) Lesser is the volatile matter, better is the quality of coal. If coal contains high volatile matter then a large portion of it escapes unburnt.

(iii) Lesser amount of ash will improve the ranking of coal. Ash is useless, noncombustible matter which reduces the calorific value of coal.

(iv)The presence of fixed carbon increases the rank of coal. Higher is the percentage of fixed carbon, greater is the calorific value of coal and smaller the percentage of volatile matter.

(2) Ultimate analysis:

The ultimate analysis is useful for combustion calculations. It includes the determination of ultimate constituents present in dry coal like carbon, hydrogen, nitrogen, sulfur, ash and oxygen.

(i) **Estimation of Carbon and Hydrogen:** A known amount of coal sample (about 1-2 gm) is burnt in a current of dry oxygen in a combustion apparatus. Carbon and hydrogen of the coal are converted into CO_2 and H_2O respectively. The gaseous products of combustion are absorbed respectively in KOH and $CaCl_2$ tubes of known weights. After the completion of the absorption of the products, the tubes are weighed again, and percentage of the elements are calculated from the results.

$$C + O_2 \rightarrow CO_2$$

$$H_2 + 1/2O_2 \rightarrow H_2O$$
$$2\,KOH + CO_2 \rightarrow K_2CO_3 + H_2O$$
$$CaCl_2 + 7H_2O \rightarrow CaCl_2.7H_2O$$

(ii) **Estimation of Nitrogen:** Nitrogen in coal sample is estimated by kjeldahl method. In this method nitrogen of coal is converted into ammonia and is estimated.

The powdered coal sample is exactly weighed and is heated with concentrated H_2SO_4, K_2SO_4 and mercuric sulfate till the solution becomes clear. Then the solution is treated with excess KOH or NaOH solution and distilled. The ammonia liberated is absorbed in a known volume of standard dilute H_2SO_4 solution. The excess of acid is determined by back titration with standard NaOH solution.

$$\underset{\text{(from coal)}}{\text{Nitrogen} + H_2SO_4} \longrightarrow \underset{\text{(Ammonium Sulphate)}}{(NH_4)_2SO_4}$$

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

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

(iii) **Estimation of Sulphur:** Known amount of powdered coal is taken and it is burnt in oxygen at high pressure in bomb calorimeter. Sulphur in coal gets oxidized to SO_2. It is dissolved in water and treated with $BaCl_2$ solution to precipitate sulphate as $BaSO_4$. The precipitate is filtered and washed, dried and weighed.

(iv) Ash determination is carried on as in proximate analysis.

The sum of the percentage of C, H, N, S and ash are subtracted from 100 and recorded as percentage of oxygen.

Percentage of oxygen is obtained by difference-

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

Liquid Fuels- 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.

Petroleum*:* Petroleum (Latin : Petro =rock + leum=oil) Petroleum (Crude oil) is a naturally occurring flammable liquid fuel. It is a dark greenish-brown viscous oil found deep in earth’s crust. Petroleum is the principle source of aliphatic organic compounds. It is composed of various hydrocarbons with small amount of other organic compounds as impurities.

It contains various hydrocarbons together with small amounts of organic compounds having oxygen, nitrogen and sulfur.

The average composition of crude petroleum approximately is -

Carbon - 79.5 - 87.1%:

Hydrogen - 11.5 - 14.8%;

Sulfur - 0.1 - 3.5%;

Nitrogen and Oxygen - 0.1-0.5%

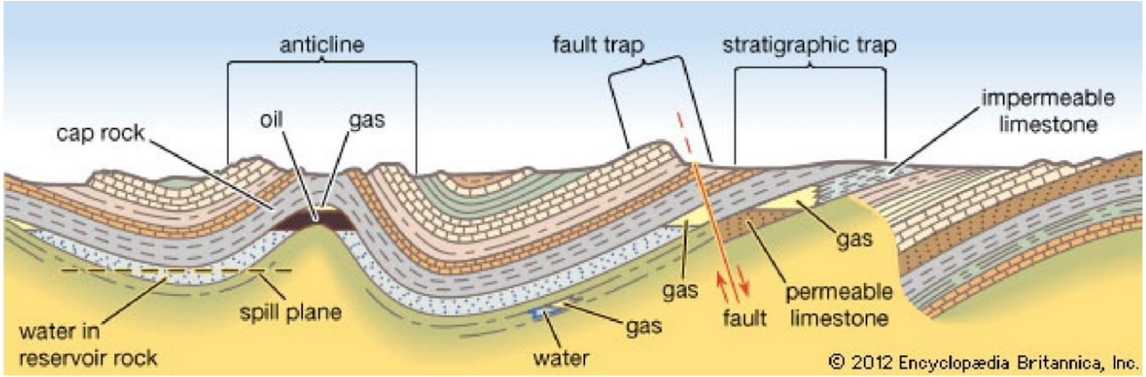


Fig: Principle types of Petroleum Traps

Refining of Petroleum:

Crude oil obtained from the mine is not fit to be marked. It contains a lot of soluble and insoluble impurities which must be removed. Previously the purification of crude oil is done by simple fractional distillation. Further treatment of the products is done by refining. Refining can be 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.

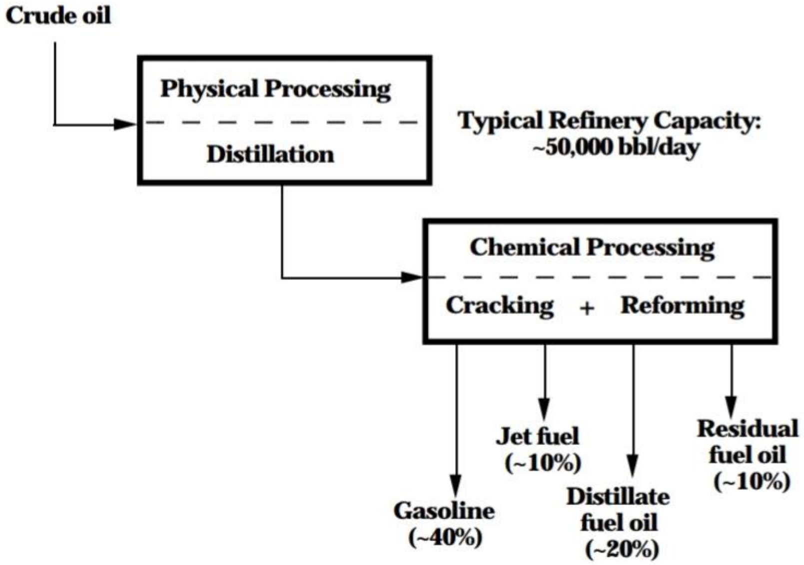


Fig: Schematic representation of a Petroleum Refinery

The process of separation of crude oil or petroleum into different fractions on the basis of their boiling points is known as refining or fractionation of petroleum.

The refining process mainly involves three steps.

(i) Removal of solid impurities

(ii) Separation of water

(iii) Removal of harmful sulfur compounds

(Iv) Fractional distillation.

(i) Removal of solid impurities: The crude oil is a mixture of solid, liquid and gaseous substances. This is allowed to stand undisturbed for some time, when the heavy solid particles settle down and gases evaporate. The supernant liquid is then centrifuged where in the solids get removed.

(ii)Separation of water (Cottrell's process): The crude oil is an extremely stable emulsion of oil and salt water. To separate water from crude oil, the crude oil is allowed to flow between two highly charged electrodes. The colloidal water droplets combine to form large drops and get separated from oil.

(iii) Removal of sulfur compounds: To remove sulfur from the crude oil or petroleum, the crude oil is treated with copper oxide. The sulfur gets precipitated as copper sulfide and is separated by filtration.

(v) **Fractional distillation:** The crude oil is heated to about 400^0 C in an iron retort. All volatile constituents get evaporated. The hot vapors are passed up through a fractionating column. Fractionating column is a tall cylindrical tower having number of horizontal stainless steel trays at short distances. Each tray is provided with small chimney covered with a loose cap. As vapors go up, they become gradually cooler and fractional condensation takes place at different heights of column.

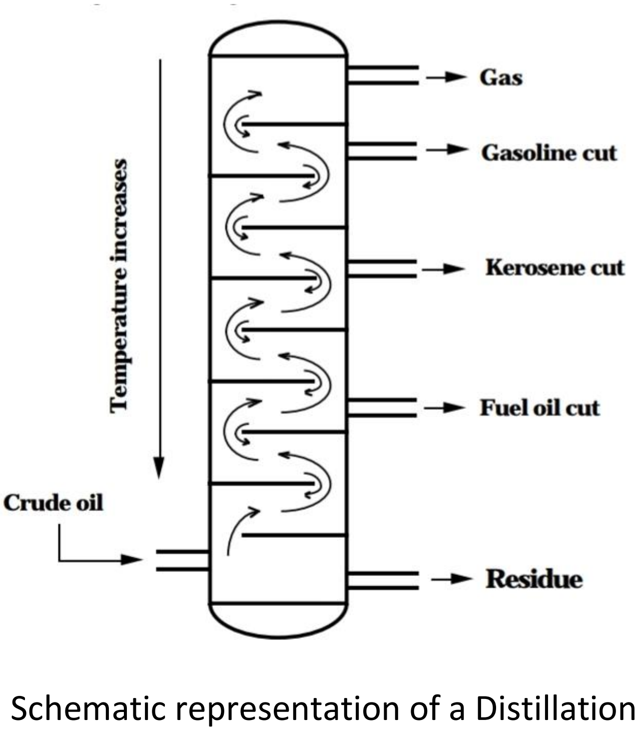


Fig: Schematic representation of a Distillation Tower

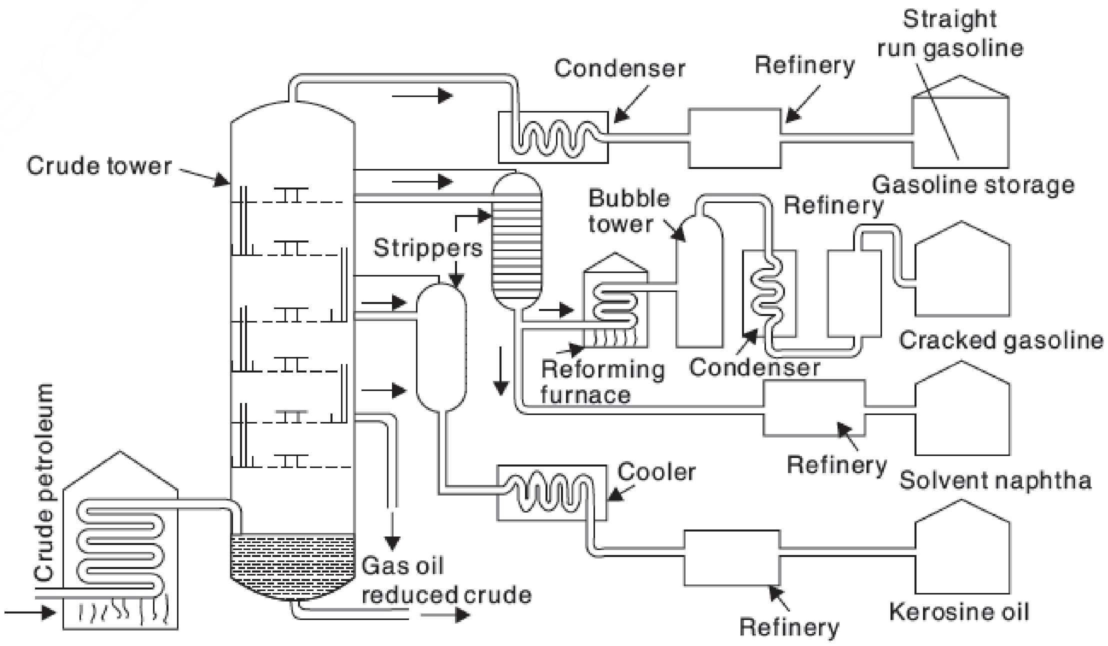


Fig: Petroleum Distillation

Table: Products of fractional distillation of petroleum and their uses:

SL. No.	Fractions	Temperature	Uses
1	Gases	Below 30°C	Used as industrial and domestic fuel(LPG)
2	Petroleum ether	30°C to 80°C	Used as a solvent
3	Gasoline or petrol	90°C to 180°C	Used as a solvent, fuel and in dry cleaning
4	Kerosene oil	180°Cto 250°C	Used as illuminant and fuel
5	Diesel oil or gas oil	250°C to 320°C	Used as fuel for diesel engine
6	Heavy oil or lubricating oil	320°Cto 400°C	Used for lubrication, cosmetics and in medicines

7	Residue or asphalt or pitch	Above 400°C	Used for road making and water proofing of roofs

Petroleum Utilization

Petroleum utilization is a much more complex process than coal utilization. This is illustrated in Figure . In particular, the preparation of petroleum before it is sold to the consumers is very extensive. The reason for this is that, despite their similar elemental composition, the chemical structure of different crude oils may be very different, as discussed above. Furthermore, a large number of different products is obtained from the petroleum refinery. Most of them are used as fuels. A small but very important fraction is used as the basis for the petrochemical industry which gives us such indispensable products as plastics, pharmaceuticals and textiles.

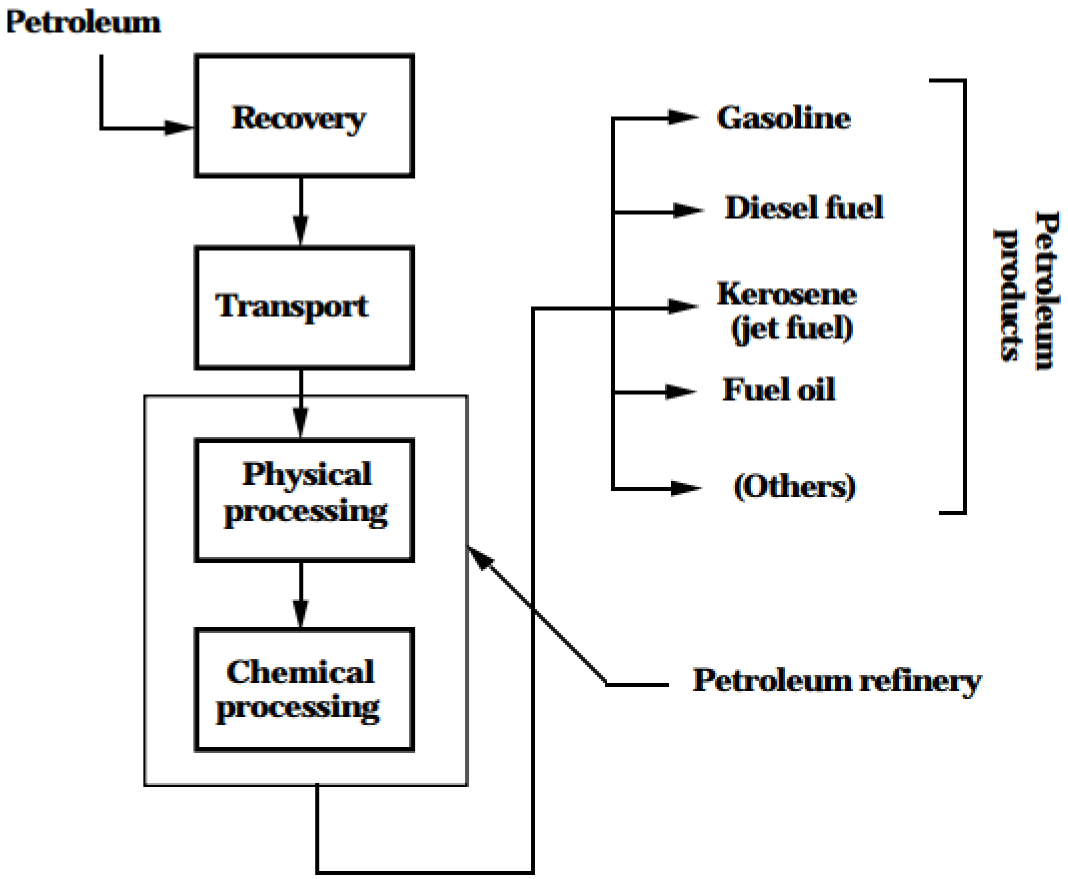


Fig: Pathways to petroleum utilization

Cracking:-

Decomposition of larger hydrocarbon molecules to smaller molecules is cracking. Example:

(i) $C_{10}H_{22} \xrightarrow{\triangle} C_5H_{10} + C_5H_{12}$

(Decane) (Pentene) (Pentane)

(ii) $C_{14}H_{30} \xrightarrow{\triangle} C_7H_{16} + C_7H_{14}$

Methods for Cracking:

Cracking is mainly two types:

A. Thermal Cracking

B. Catalytic Cracking

A. Thermal cracking: This method is also called Burton process. If the cracking takes place at high temperature then it is thermal cracking. In this process, heavier hydrocarbon molecules are converted into light hydrogen rich molecules at higher temperature. It may take place by two ways. They are-

(i) *Liquid-phase Thermal cracking:* The liquid phase cracking takes place at 475^0C to 530^0C at a pressure $100 kg/cm^2$.

(ii) Vapour-phase Thermal cracking: The vapor phase cracking occurs at 600^0C to 650^0C at a low pressure of 10 to 20 kg/cm^2.

B. Catalytic cracking: If the cracking takes place due to the presence of catalyst than it is named as catalytic cracking. The catalysts include alumino silicate with some metal oxides of Ca, Mg, Fe, Cr, Na. The process completes at low temperature and pressure compared to thermal process.

Catalytic cracking may be two types are-

(i) Fixed bed catalyst cracking

(ii) Moving bed catalyst cracking

(i) Fixed bed catalytic cracking: The oil vapors are heated in a pre-heater to cracking temperatures (420 – 450 ^{0}C) and then forced through a catalytic chamber maintained at 425 – 450 ^{0}C and 1.5 kg/cm^{2} pressure. During their passage through the tower, about 40% of the charge is converted into gasoline and about 2 – 4% carbon is formed. The latter adsorbed on the catalyst bed. The vapour produced is then passed through a fractionating column, where heavy oil fractions condense. The vapors are then led through a cooler, where some of the gases are condensed along – with gasoline and uncondensed gases move on. The gasoline containing some dissolved gases is then sent to a 'stabilizer', where the dissolved gases are removed and pure gasoline is obtained. The catalyst, after 8 to 10 hours, stops functioning, due to the deposition of black layer of carbon, formed during cracking. This is re-activated by burning off the deposited carbon. During the re-activated interval, the vapors are diverted through another catalyst chamber.

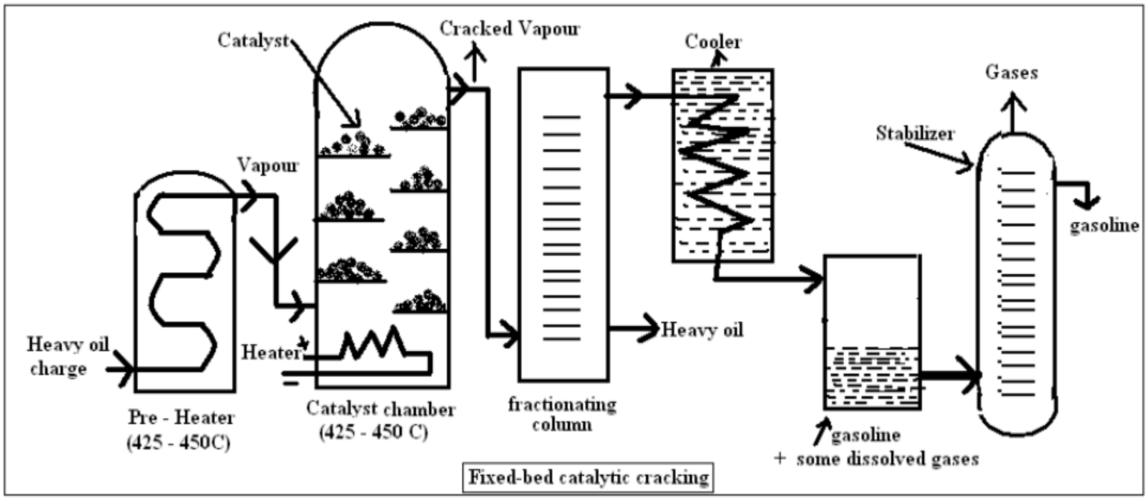


Fig: Fixed-Bed Catalyst Cracking

(ii) Moving bed catalytic cracking:

In moving bed catalytic cracking, the finely divided catalyst is agitated by gas. So that it can be handled like a fluid system and can be pumped as a true liquid. This method provides good contact between the catalyst and reactant.

The optimum conditions for the method include -Catalyst: Al_2O_3 +SiO_2 agitated with gas, Temperature: 550^0 C, Pressure: just above normal pressure.

The finely divided catalyst bed is fluidized by passing heavy oil or gas oil vapors, in a cracking chamber. The cracked vapors are sent into fractionating column to separate into gases, gasoline and un-cracked gases. The un-cracked oils are further subjected to cracking.

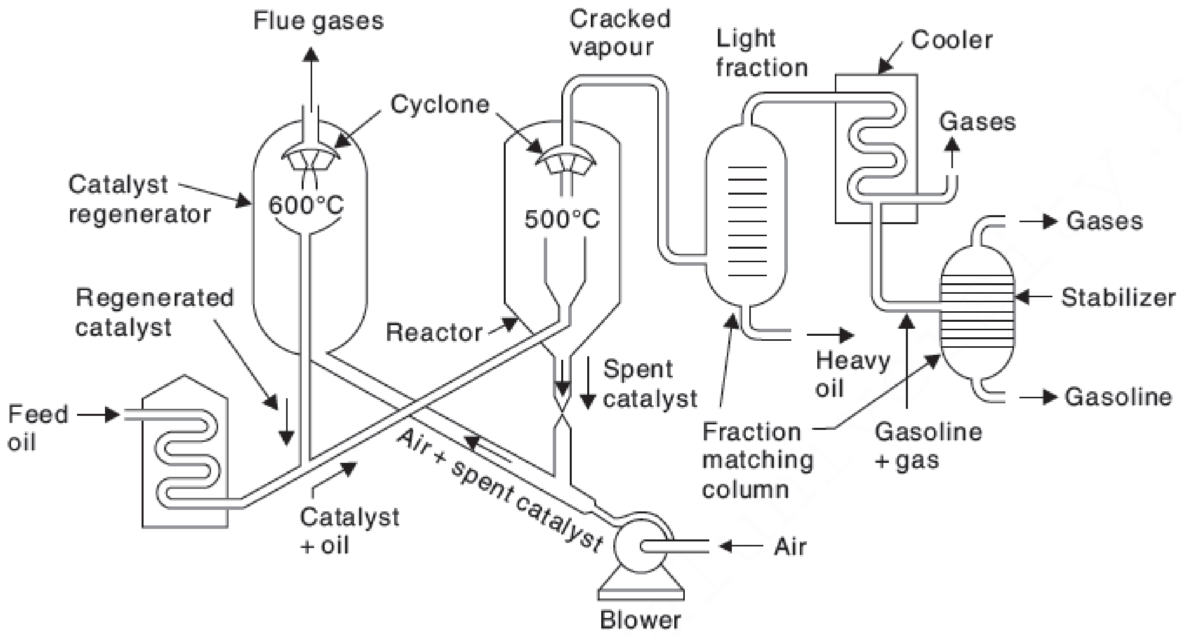


Fig: Moving bed- catalytic cracking

Advantage of catalytic catalytic cracking:

(i) The quality and yield of petrol is better.
(ii) External fuel is not necessary since the coal embedded in the catalyst.
(iii) Operating pressure is lower.
(iv) By product gas evolution being low, yield of petrol is higher.

(v) Due to higher aromatics content, the anti-knocking properties are higher.

(vi) Gum –forming compounds are very low.

Differences between thermal cracking and catalytic cracking .

S.N	Thermal Cracking	Catalyst Cracking
1.	The heavy oil is converted into lower hydrocarbons by means of high temperature.	The cracking is carried out at a temperature of 400^0C-450^0 C in the presence of catalyst.
2.	The yield of gasoline is low.	The yield of gasoline is high.
3.	High pressure is required for thermal cracking.	Low pressure is required for catalytic cracking.
4	The products mainly contain lower hydrocarbons.	The products contain high amount of aromatics.
5.	The gasoline produced has a low octane rating.	The gasoline produced has a high octane rating.

Knocking:

Knocking is premature and instantaneous ignition of petrol-air (fuel-air) mixture in a petrol engine, leading to the production of explosive violence known as knocking. The mixture known as gasoline or petrol, when used in high compression internal combustion engines, has a tendency to knock (also called pinging or pinking).

The cause of knocking is characteristic of the fuel and engine design.

Chemical Structure and Knocking: The chemical structure of the fuel used has a close relation with knocking characteristics.

(i)The knocking tendency decreases with increase in the compactness of the molecule, double bonds and cyclic structure. Thus olefins of the ame carbon chain length posses better anti-knock properties than the corresponding paraffins.

(ii)With normal paraffins, the knocking increases with increase in the length of the hydrocarbon chain.Thus the tendency to knock in straight chain paraffins follow the order.

n-Heptane > n-Hexane > n- Pentane > n- Butane

(iii) Aromatics such as benzene ad toluene have very high anti-knocking properties.

(iv) Branched chain paraffins have better anti-knock properties than straight chain paraffins.

Knocking tendency decreases in the order -

n-alkanes > mono substituted alkanes > cycloalkanes > alkenes> poly substituted alkenes > aromatics.

Causes of Knocking:

The main causes of knocking are:

(i)Poor quality of fuel

(ii)Poor design of engine

(iii) Poor mechanical condition of engine

(IV) Incorrect combustion process

(v) Improper exhaust gas re-circulation

Adverse effects of knocking:

(1) Early ignition

(2) Mechanical damage due to over heating.

(3) Decrease in efficiency and increase in fuel consumption.

(4) Increase in fuel consumption.

(5) Noise and roughness.

Prevention for knocking:

Knocking can be prevented by-

(1) By using anti-knocking agents like tetra ethyl lead (TEL).

(2) By the use of high octane fuel detonation.

(3) By reducing pressure in the inlet by throttling.

(4) By using critical compression ratio.

(5) Improving the combustion chamber design.

(6)Correct ignition timings are necessary for better engine performance and fuel fficiency.

Anti-knock Agent:

knocking can be decreased by adding certain compounds to the fuel and these compounds are known as anti-knocking agents or anti-knocking compounds.

“Thus those compounds which when added to gasoline increase it octane number and decrease knocking are called anti-knocking compounds and they improve the quality of a fuel.”

Small amounts of lead compounds have been used as economical and effective anti-knock additives tetra ethyl lead (TEL).But it damage the environment**.** The higher the anti-knock quality of the fuel, the more power and efficiency of the engine.

The typical anti-knocking agents in use are-

(i) Tetra ethyl lead TEL (1923) (still in use a high octane additive)
(ii) Methyl cyclopentadienyl manganese tricarbonyl (MMT -1959)

(iii) Iron penta carbonyl
(iv) Tetra methyl lead (TML-1960)
(v) Methyl tirtary-Butyl ether (MTBE -1970)
(vi) Ethanol(C_2H_5OH)

Tetra ethyl lead (TEL): $(C_2H_5)_4Pb$ is very important alkylated product and is the principal anti-knock compound for gasolines. It can be prepared as follows:

$$4\,Pb + 4\,Na + 4\,C_2H_5Cl \xrightarrow{70^0C} Pb\,(C_2H_5)_4 + 3\,Pb + 4\,NaCl$$

Tetra ethyl lead (TEL)

The variety of petrol in which tetra ethyl lead is added, it is leaded petrol. When tetra ethyl lead is added, it prevents knocking, there by saves money and energy. Usually 1 to 1.5 ml of TEL is added per 1lit of petrol.

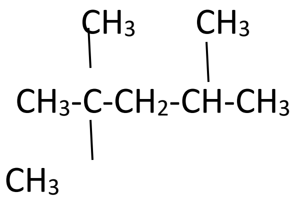
Octane number:-

The knocking characteristic of a fuel can be easily expressed by octane number. The antiknocking value of n-heptane is taken as 0 (zero) because n-heptane knocks very badly. Whereas the anti-knock value of iso-octane is approximately taken as 100 because iso-octane knocks very little. Actually the octane number is the percentage of iso-octane in a mixture of n-heptane in order to matches the knocking characteristics of the fuel. In this way, an "80-octane" fuel is one which has the same combustion characteristics as an 80:20 mixture in iso-octane and n-heptanes.

"Octane number of a fuel is defined as the percentage of isooctane present in a mixture of isooctane and n-heptane, which as the same knocking characteristic as that of fuel under examination, under same set of condition.

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

n-Heptane



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_3$$

(2,2,4-Trimethy pentane)

Anti-knocking value =0(zero) Anti-knocking value =100

The octane number of poor fuels can be raised by the addition of extremely poisonous materials as tetra ethylene lead $(C_2H_5)_4Pb$ and diethyl-telluride $(C_2H_5)_2Te$.

Octane rating: It has been found that n-heptane, Knocks very badly and hence, its anti-knock value has arbitrarily been given zero. On the other hand, isooctane (2: 2: 4 – trimethyl pentane). It gives very little knocking, so its anti-knock value has been given as ‘100’. Thus, octane number (or rating) of a gasoline (or any other internal combustion engine fuel) is the percentage of isooctane in a mixture of

isooctane and n-heptane, which matches the fuel under test in 103 knocking characteristics. In this way, an “80-octane” fuel is one which has the same combustion characteristics as an 80:20 mixture of isooctane and n-heptane.

The octane number of fuel may be improved by—

(i)Low octane petrol is blended with high octae compounds like alcohol.

(ii) The addition of anti-knock compounds like TEL , MTBE etc.

(iii) Reforming.

Fuel	Research Octane number(RON)	Moor Octane number(MON)
Gasoline(petrol	92-98	80-90
Diesel	-25	-
Methanol	106	92
Ethanol	107	89
Propane(LPG)	112	97
Methane (CNG)	120	120

Fuel	Octane number	
o-xylene	107	
Ethanol	108	

t-butyl alcohol	113
p-xylene	116
Methyl t-butyl ether	116
Toluene	118

Fig: The Octane rating of some hydrocarbon and common additives

Fuel	Octane number
n-heptane	0
n-hexane	25
n-pentane	62
Isooctane	100
Benzene	106
Methanol	107

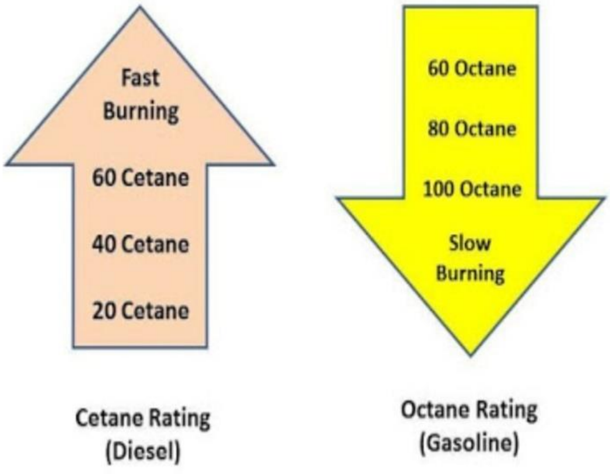


Fig: Comparison of Octane and Cetane rating

Differences between Octane number and Cetane number:

	Octane number	Cetane number
1.	It is the percentage of isooctane in a mixture of isooctane and n-heptane that matches the fuel under test in knocking characteristics.	It is the percentage of hexadecane in a mixture of hexadecane and α-methyl naphthalene which have the same knocking characteristics as the diesel fuel.
2.	It is used to find the suitability of gasoline or any other internal combustion engine fuel.	It is used to find the suitability of a diesel fuel.
3.	The octane number of internal combustion fuels can be increased by the addition of tetraethyl lead (TEL),$(C_2H_5)_4Pb$ and diethyl telluride, $(C_2H_5)2Te$.	The cetane number of diesel fuel can be increased by the addition of 'pre ignition dopes' such as ethyl nitrite, isoamyl nitrite, acetone peroxide etc.
4.	Hydrocarbons which are poor diesel fuels are quite good gasoline fuels.	The order of ignition quality among hydrocarbon constituent of a diesel fuel is n-alkanes > naphthalenes > alkenes > branched alkanes > aromatics. Thus, the hydrocarbons which are poor gasoline fuels are quite good diesel fuels.
5.	Straight chain hydrocarbons are worst fuels as they have low octane number	Straight chain hydrocarbons are best fuels as they have high cetane number.
6.	Important for predicting the knocking of an engine.	Important for predicting the ignition of an engine.

Cetane number:

Cetane number is a measure of the ease with which a fuel will ignite under compression. Cetane number of fuel mainly depends on the nature and composition of its hydrocarbons.

Definition: The percentage of hexadecane in a mixture of hexadecane and αmethyl naphthalene is known as cetane number.

Two hydrocarbons α-methyl naphthalene (aromatic) and n-cetane (hexadecane) are specified as standards. n-cetane has low ignition lag. Hence its cetane number is fixed as 100 while α-methyl naphthalene has long ignition lag and its cetane number is fixed as zero.

Diesel fuel	Cetane number	Remarks
Cetane (n-hexadecane)	100	Very short ignition delay
α-methyl naphthalene	0	Longer ignition delay

Example: consider the following series-

n-alkanes > naphthalenes > alkenes > branched alkanes > aromatics.

(1) Ignition delay increases from left to right.

(2) Ignition quality increases from right to left.

(3) Cetane number increases from right to left.

The cetane number of fuel may be increased by the addition of pre-ignition dopes such as ethyl nitrite, iso amyl nitrite, acetone peroxide. 2,2,4,4,6,8,8-heptamethyl nonane (HMN) with a cetane number of 15 is now considered as the low quality diesel in view of its availability and purity. On the revised scale (HMN reference) the cetane number represents the percentage cetane in the blend with HMN plus 15/100 of the % HMN.

Example: A blend of 50% cetane and 50% HMN has a cetane number of 50+15/100X50 = 57.5%.

Higher cetane number related with improved combustion, cold starting and reduced noise, white smoke, hydrocarbon, carbon monoxide, an particulate emissions.

Fuel	Ocetane number
Gasoline(petrol	0-5
Diesel	45-55
Methanol	5

Ethanol	5
Propane(LPG)	-2
Methane (CNG)	0

Thus fuel with high cetane number(but lower octane number) is ideal or diesel engines.(figure)

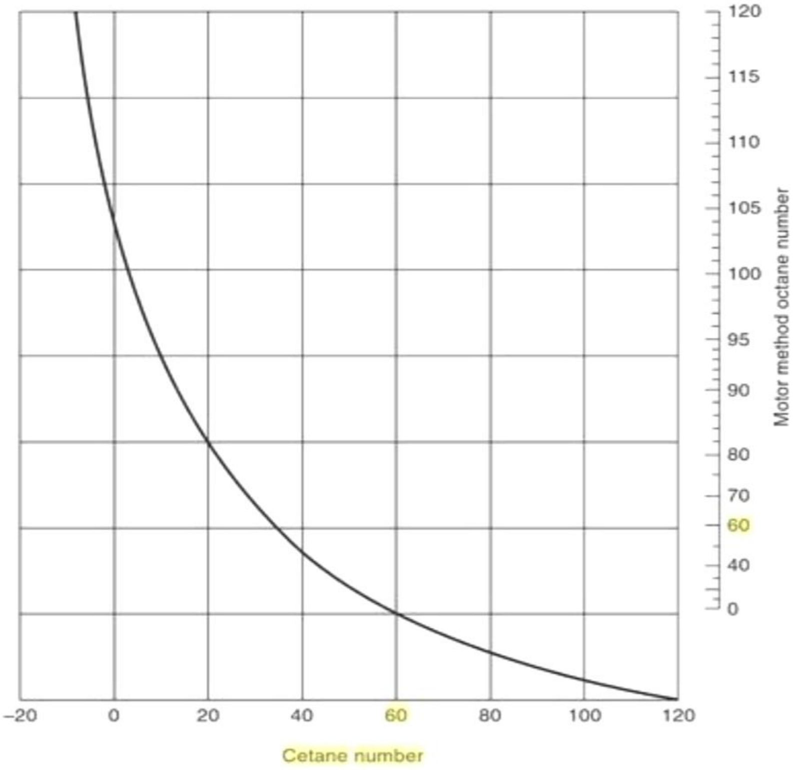


Fig: Cetane and Octane number correlation for hydrcarbon

Determination of Aniline Point of Petroleum Samples:

Determination of aniline point is a test to evaluate base oils that are used in oil mud. The test indicates if oil is likely to damage elastomers (rubber compounds) that come in contact with the oil. The aniline point is called the "aniline point temperature," which is the lowest temperature (°F or °C) at which equal volumes of aniline ($C_6H_5NH_2$) and the oil form a single phase. Aniline point of oil gives an indication of the possible tendency of deterioration of oil when it comes into contact with packing ,rubber sealing etc. in general oils with a high aromatic content are more detrimental to rubber products than those with a low aromatic content. The relative aromatic content of an oil is indicated by its aniline point and oils with a high aromatic content have a low aniline point and vice versa. The higher the aniline point of the oil , the more desirable it is for drilling fluid usage. In our experiment, 5 ml aniline and 5ml diesel were taken in a test tube provided with thermometer and heat was given until both aniline and diesel become completely miscible. The aniline point of diesel was found at the temperature of 94°C.

The aniline point is the lowest temperature at which equal volume of aniline and oil are completely miscible. This method is suitable for transparent liquid samples having an initial boiling point above room temperature and where the aniline point is below the bubble point and above the solidification point of the aniline sample mixture. The procedure is useful in characterizing pure hydrocarbons. The lower the aniline point, the greater the solvency or reactivity of the oil, which in turn gives an indication of the oils aromaticity. Paraffinic hydrocarbons have higher aniline points than aromatic types.

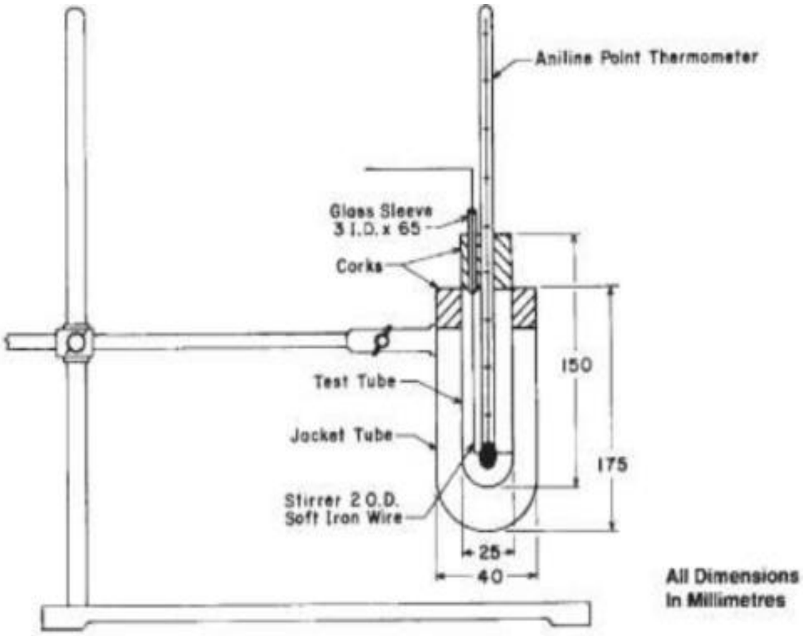


Fig: Aniline Point Apparatus

Procedure:

(i)Clean and dry the apparatus.

(ii)Deliver 10 ml of aniline and 10 ml of the dried sample into the test tube fitted with stirrer and thermometer.

(iii) If the material is too viscous for volumetric transfer, weigh to the nearest 0.01 gm a quantity of the sample corresponding to 10 ml at room temperature.

(iv) Center the thermometer in the test tube so That, the immersion mark is at the liquid level, making sure that the thermometer bulb does not touch the side of the tube.

(v)Center the test tube in the jacket tube. Stir the mixture rapidly using a 50-mm stroke, avoiding the introduction of air bubbles. If the aniline-sample mixture is not miscible at room temperature, apply heat directly to the jacket tube so that the temperature rises at a rate of 1 to 3°C (2 to 5°F)/min by removing or reducing the heat source until complete miscibility is obtained.

(vi) Continue stirring and allow the mixture to cool at a rate of 0.5 to 1.0°C (1.0 to 1.8°F)/min.

(vii) Continue cooling to a temperature of 1 to 2°C (2.0 to 3.5°F) below the first appearance of turbidity, and record as the aniline point the temperature at which the mixture suddenly becomes cloudy throughout this temperature, and not the temperature of separation of small amounts of material, is the minimum equilibrium solution temperature.

SL.NO:	SAMPLE	VOLUM OF SAMPLE TAKEN(ml)	VOLUME OF ANILINE TAKEN (ml)	ANILINE POINT (^{0} C)
1.	Diesel	5	5	71
2.	Petrol	5	5	65
3.	Kerosene	5	5	74
4.	Jet fuel	5	5	80
5.	Bio diesel	5	5	59.5

Specified volumes of aniline and sample, or aniline and sample plus n-heptane, are placed in a tube and mixed mechanically. The mixture is heated at a controlled rate until the two phases become miscible. The mixture is then cooled at a controlled rate and the temperature at which two phases separate is recorded as the aniline point or mixed aniline point.

Determination of Flash- Point of Petroleum Samples:

Flash points are determined experimentally by heating the liquid in a container and then introducing a small flame just above the liquid surface. The temperature at which there is a flash/ignition is recorded as the flash point.

Fuel	Flash point	Auto-ignition temperature
Gasoline (petrol)	−43 °C (−45 °F)	280 °C (536 °F)
Diesel (2-D)	>52 °C (126 °F)	210 °C (410 °F)
Jet fuel (A/A-1)	>38 °C (100 °F)	210 °C (410 °F)
Kerosene	>38–72 °C(100–162 °F)	220 °C (428 °F)

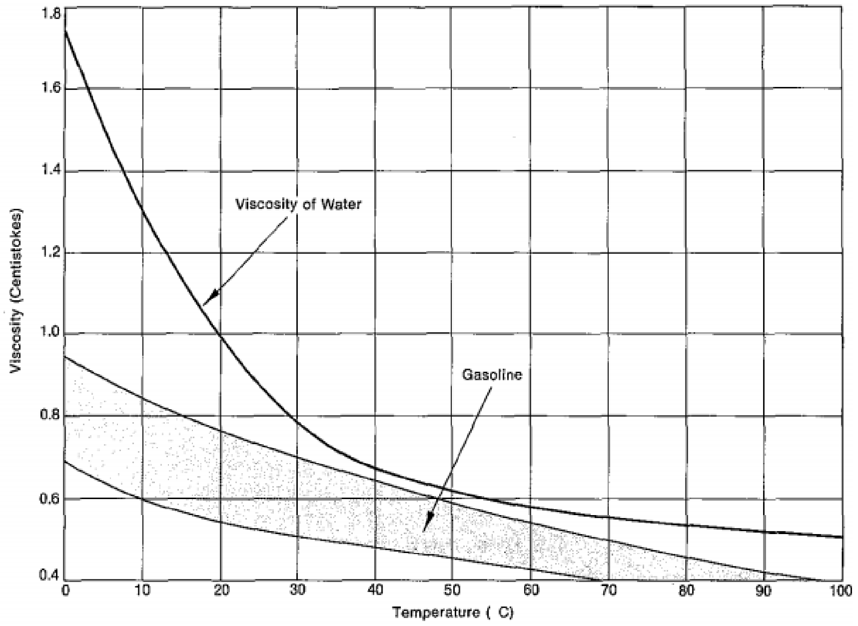


Fig: Flash Point curve of Gasoline(Petrol)

Procedure: Method for liquids flashing between -18 to 18.5^{o} C is prescribed in the standard. The generalized procedures are accordingly narrated below.

(i) Fill the water bath completely and the air chamber which surrounds the oil cup to a depth of at least 38mm with 50:50 mixture of corrosion inhibiting ethylene glycol and water mixture.

(ii) Cool the bath to -27^{o} C or at least 9^{o} C below the expected flash point of the material being tested whichever is higher. Do continuous stirring while cooling the samples.

(iii) Use an alcohol thermometer to avoid mercury freezing at low temperatures. Liquid which crystallizes on cooling should not be cooled below crystallization points.

(iv) Place the cup in bath and replace the thermometer by the oil cup thermometer.

(v) Pour the sample till the level reaches the point of the index gauge without agitation avoiding air bubble formation to the extent feasible.

(vi) Do not move the apparatus after filling and heating rate should be less than 1^{o} C per minute.

(vii) Provide the test flame time to time after 9^{o} C less from the expected flash point temperature is met. Apply test flames with every 0.5^{o} C after that till flash is realized.

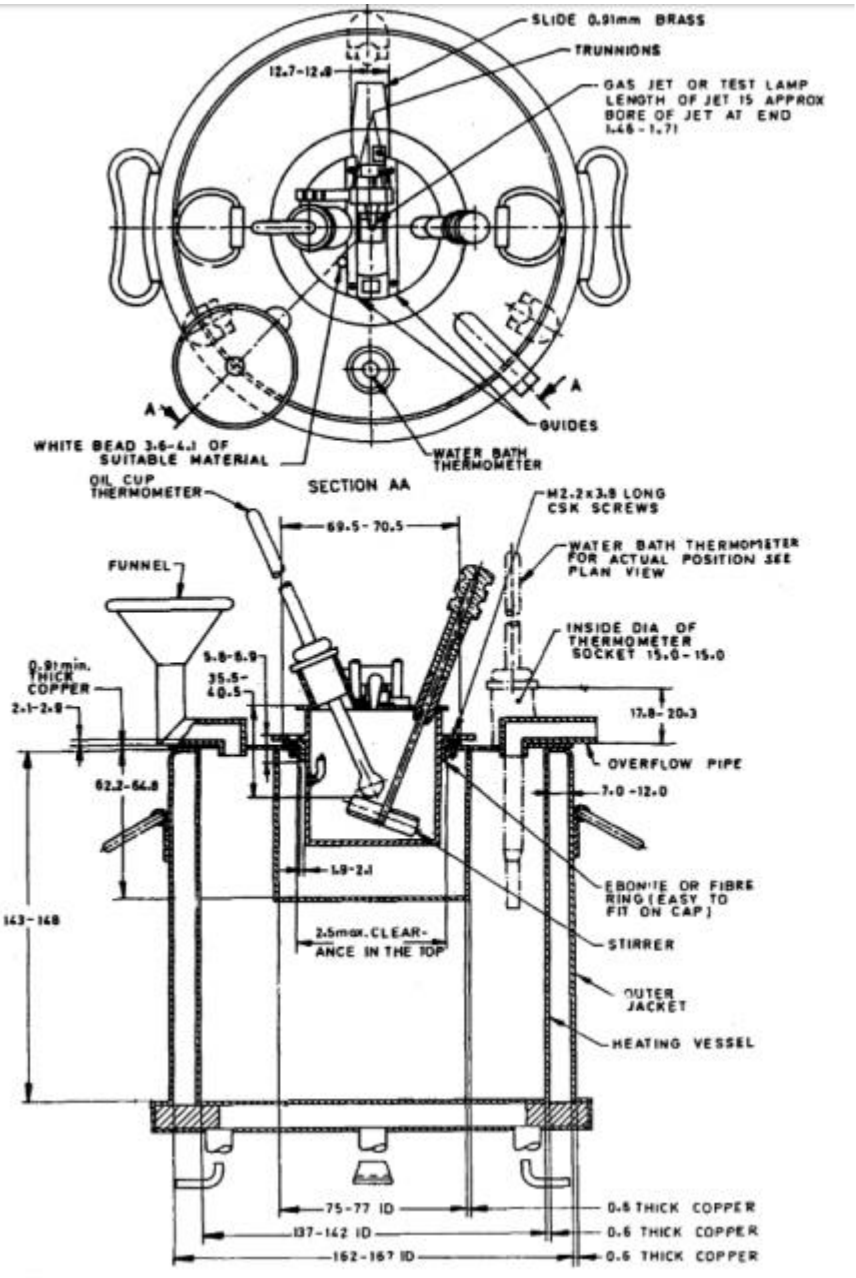


Figure: Standard sketch for Abel flash point apparatus (All dimensions in mm)

The flash point is an important concept in fire investigation and fire protection because it is the lowest temperature at which a risk of fire exists with a given liquid. It is crucial in many circumstances to establish the presence of some liquids and to know their flash point during the investigation process.

Gaseous fuels

The gaseous fuels are most preferred because of their ease of storage, transport, handling and ignition. These are classified into two types.

a) Primary fuels Example: Natural gas,CNG,

b) Secondary fuels example : LPG,Coal gas, producer gas, water gas, Carbureted gas etc.

The important gaseous fuels are-

(i) Natural gas

(ii) LPG (Liquefied Petroleum Gas)

(iii) CNG (Compressed Natural Gas)

(iv) Producer gas

(v)Water gas

(vi) Gober gas (bio-gas)

(vii) Coal gas

(i)Natural gas:

Natural gas is primarily methane gas. It is a fossil fuel. If lower hydrocarbons like methane and ethane are present, the natural gas is known as dry or lean gas. If higher hydrocarbons are present along with methane, the natural gas is known as wet or rich gas. The calorific value of natural gas varies from 8000-14000 K.cal/m^3.

Composition:

Constituents	Methane	Ethane	Propane	Butane	H,CO,CO_2
Percentage	85.5	5.5	3.7	1.8	0.5

Sometimes natural gas contains H_2S which is removed by scrubbing with 2-amino ethanol.

$$H_2S + 2\ NH_2\text{-}CH_2\text{-}CH_2OH \rightarrow \quad (H_2N\text{-}CH_2\text{-}CH_2OH)_2\ .H_2S$$

$$\downarrow\Delta$$

$$H_2N\text{-}CH_2\text{-}CH_2O \quad + H_2S$$

Applications:

(1)It is very good domestic fuel.

(2)Used in synthesis of synthetic proteins which are used as animal food.

(3)Used as raw material for the manufacture of carbon black, methanol, formaldehyde and other chemicals.

(4) Methane on microbiological fermentation gives synthetic proteins which are used as animal feed.

(ii) LPG (Liquefied Petroleum Gas)

The gas is obtained from natural gas or as a byproduct in refineries during cracking of heavy petroleum products. Nowadays LPG has been a common fuel for domestic work and also in 105 most of the industries.

The main components of LPG are n-butane, isobutane, butylenes and propane (traces of propene and ethane).

Composition:

Constituents	n- butane	Isobutane	Propane
Percentage	38.5	37	24.5

The hydrocarbons are in gaseous state at room temperature and 1 atmospheric pressure but can be liquefied under higher pressure.

LPG is kept in metallic cylinder attached with burner through pipe. It has two stoppers, one at the cylinder and other at burner. LPG has special odour due to the presence of organic sulphides (methyl mercaptan) which are added specially for safety measure.

Characteristics of LPG:-

1. It has high calorific value (27,800 kcal/m3) .

2. It gives less CO and least un-burnt hydrocarbons. So it causes least pollution.

3. It gives moderate heat which is very good for cooking.

4. Its storage is simple. It is colourless.

5. It has tendency to mix with air easily.

6. Its burning gives no toxic gases though it is highly toxic.

7. It neither gives smoke nor ash content.

8. It is cheaper than gasoline and used as fuel in auto vehicles also .

9. It is dangerous when leakage is there.

Applications

(i) ***In Food industry:*** LPG is widely used in the food industry like hotels, restaurants, bakeries, Canteens etc. Low sulphur content and controllable temperature makes LPG the most Preferred fuel in the food industry.

(ii***)In Automotive Industry:*** The main advantage of using automotive LPG is, it is free of lead, Very low in sulphur, other metals, aromatics and other contaminants.

(iii)***In Glass & Ceramic***: The use of a clean fuel like LPG enhances the product quality thereby reducing technical problems related to the manufacturing activity of glass and ceramic products.

(iv)***In Farming industry***: LPG in the farming industry can be used for the following are Drying of crops, Cereal drying, Curing of tobacco and rubber, Soil conditioning and Horticulture etc.

(v)***In Building Industry:*** LPG being a premium gaseous fuel makes it ideal for usage in the Cement manufacturing process.

(vi)LPG is used in metal industry, aerosol industry, textile industry and it can also be used in Steam rising.

(iii) CNG (Compressed Natural Gas):

CNG is a good alternative fossil fuel. It mainly contains methane (CH_4). When natural gas is compressed at high pressure (1000atm) or cooled to -160^oC, it is converted to CNG. It is stored in cylinder made of steel. It is now replacing gasoline as it releases less pollutant during its combustion. In some of the metro cities, CNG vehicles are used to reduce pollution.

Composition:

Constituents	Methane	Ethane	Propane	Butane	pentane
Percentage	88.5	5.5	3.7	1.8	0.5

Characteristics of CNG

1. Natural Gas being lead/sulphur free, its use substantially reduces harmful engine emissions.

2. Natural gas being lighter than air, will rise above ground level and disperse in the atmosphere, in the case of a leakage.

3. Natural Gas in the gaseous state, and is colourless.

4. Predominantly Methane is available in the lean gas, hence CNG contains mostly methane.

Applications

1. It was used to generate electricity, heat buildings, fuel vehicles, power industrial furnaces and Air conditioners.

2. Natural gas is also consumed in homes for space heating and for water heating
3. It is used in stoves, ovens, clothes dryers and other appliances.

4. In some of the metro cities, CNG vehicles are used to reduce pollution.

(iv) Producer gas

Producer gas is a mixture of carbon monoxide and nitrogen. It also contains traces of hydrogen and carbon dioxide .Its calorific value is about 1300 kcal/m^3. It is cheapest gaseous fuel.

Composition: The average composition of producer gas is below-

Constituents	Carbon monoxide	Hydrogen	Nitrogen	Carbon dioxide	Methane
Percentage(%)	22-30	8-12	52-55	3	small

Preparation:

Producer gas is prepared by passing air over a red hot coke at about 1100°C in a reactor called gas producer.

The reactor consists of a steel vessel lined inside with refractory bricks. At the top, it is provided with cup and cone arrangement and an exit for producer gas. At the bottom, it has an inlet for passing air. There is an exit for the ash at the base.

(a)Ash zone: It mainly consists of ash. It is about0.8m thick and is the lowest zone. As air and steam is passed through this zone, their temperature is increased.

(b)Combustion zone :

$$C + O_2 \longrightarrow CO_2 + 97 \text{ kcal}$$

$$C + 1/2O_2 \longrightarrow CO + 53 \text{ kcal}$$

(c)Reduction zone :

$$C+CO_2 \longrightarrow 2CO \quad -36Kcal$$

$$C+H_2O \longrightarrow CO + H_2 \quad -29kcal$$

$$C+2H_2O \longrightarrow CO2+2H_2 \quad -19kcal$$

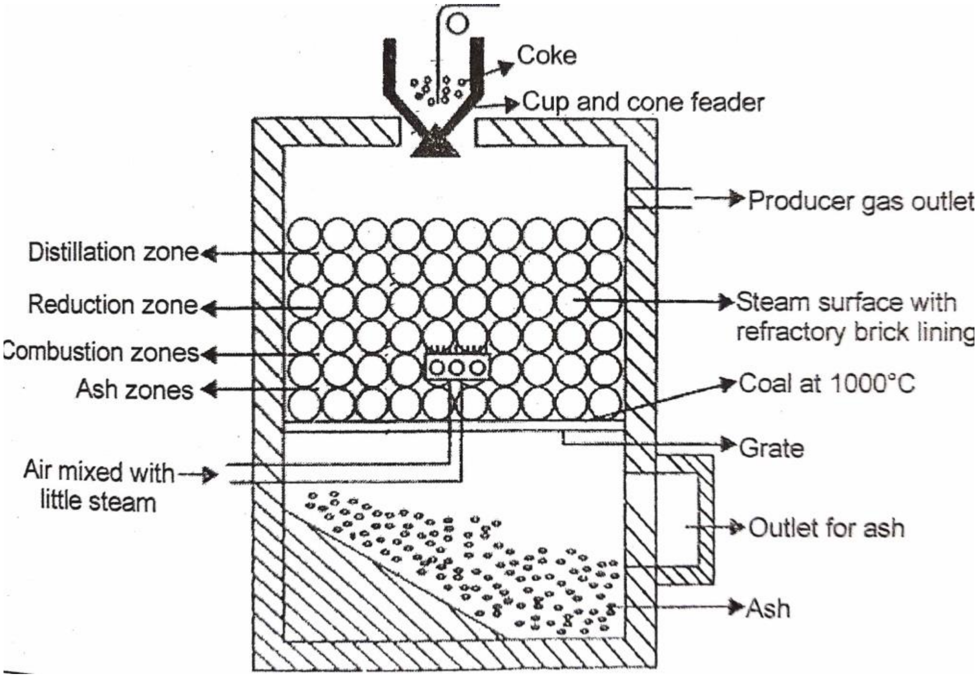


Fig: Gas Producer for the manufacture of producer gas

Uses

1. It is used as a fuel in the extraction of metal.

2. It is used in the manufacture of glass.

3. It is used as a reducing agent in metallurgy.

(v) Water gas (Blue gas)

Water gas is a essentially mixture of carbon monoxide and hydrogen (combustible gases). It also contains traces of carbon dioxide and nitrogen. It is not luminous and burns with a blue flame. Its calorific value is 2800 kcal/m^3.

Composition: The average composition of water gas is below: -

Constituents	Carbon monoxide	Hydrogen	Nitrogen	Carbon dioxide	Methane
Percentage(%)	44	48	4	4	0.80

Preparation

Water gas is prepared by passing steam and little air alternatively over a red hot coke at about 900^{0}C- 1000°C in a reactor. It is an endothermic reaction. So the temperature of the system decreases.

$$\underset{\text{(Coke)}}{C} + \underset{\text{(Steam)}}{H_2O} \longrightarrow CO + H_2 \ -29 \text{ kcal} \quad \text{(Endothermic reaction)}$$

But, the reaction between carbon and air is exothermic and raises the temperature to about 1000°C

$$C + O_2 \longrightarrow CO_2 + 97 \text{ kcal} \quad \text{(Exothermic reaction)}$$

$$2\,C + O_2 \longrightarrow 2CO + 59 \text{ kcal}$$

Thus, the steam and air are sent in alternatively to maintain the temperature at about 1000°C.

The reactor consists of a steel vessel lined inside with refractory bricks. At the top, it has cup and cone feeder and an exit for water gas. At the base, inlet pipes for steam and air are provided. At the bottom, out let for ash is also available.

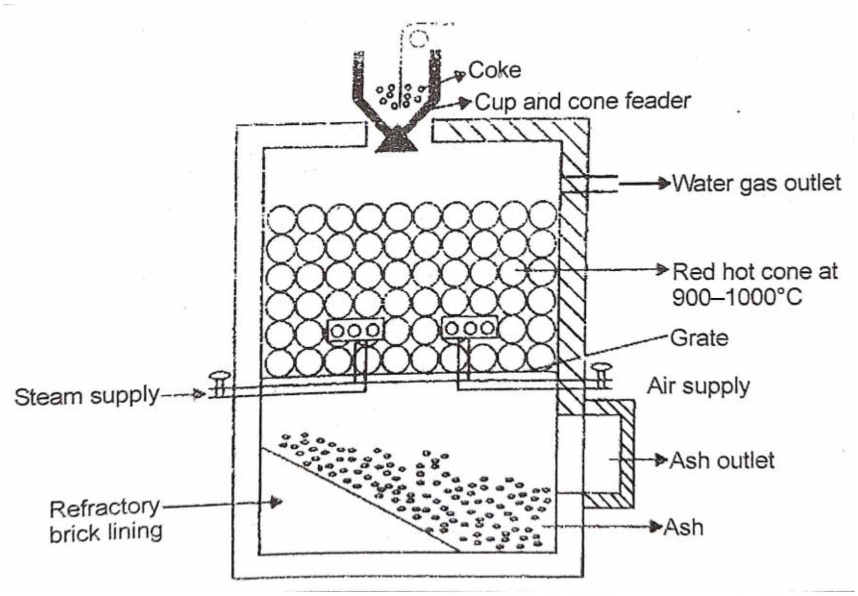


Fig: Water gas production

Uses

1. It is used as a good source of hydrogen gas on commercial scale.

$$2C + O_2 \longrightarrow 2CO_2 + \text{Heat}$$

$$H_2 + \frac{1}{2} O_2 \longrightarrow H_2O + \text{Heat}$$

2. It is used as an illuminating gas.

3. It is used as a fuel in ceramic industries

4. Because of its high calorific value, water gas is used as a good fuel.

5. It is used in the manufacture of methyl alcohol.

$$CO + 2H2 \xrightarrow{ZnO} CH_3OH$$

6. It is also used welding purpose.

(vi) Bio-gas (Gober gas)

The cheapest and most available biogas is gober gas.It consists mainly of methane. It bums with a blue flame and it average calorific value is about 5300 kcal/m^3.

Composition: The average composition of bio- gas is below: -

Constituents	Methane	Carbon dioxide	Hydrogen	Nitrogen
Percentage(%)	55	35	7.4	2.6

Production:

Gober gas is manufactured in gober gas plant, which consist of

(i) A well constructed of masonary work (also works as digester). The digest is usually built below the ground level.
(ii) A gas holder which covers digester and made of weld steel sheets.
(iii) A pipeline 10 cm in diameter.

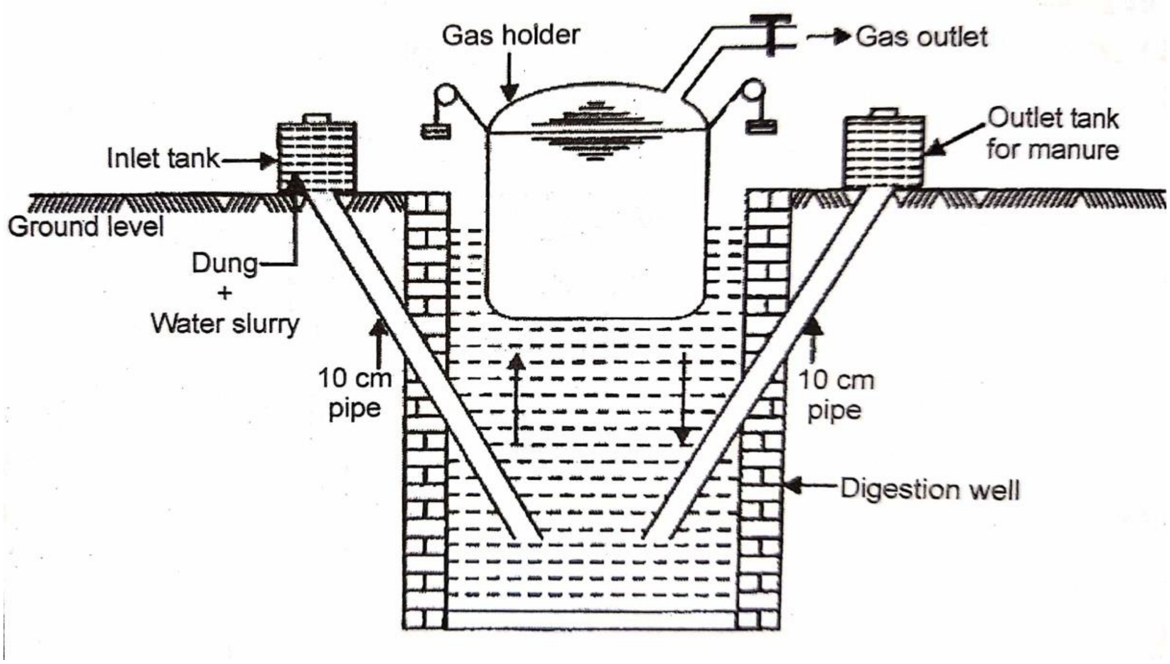


Fig: Preparation of Gober gas (Biogas) by Gober gas plant

Cattle during in the form as slurry (made by mixing equal parts of water) is poured to digester. A carbonic bacteria present in the dung digest this slurry in a process called anerobic fermentation. The optimum temperature for this fermentation is 34-48^{0}C .The gas generated, due to continuous decay, is mostly methane and collected in gas holder. It is interesting to note that in addition to cattle dung gober gas plant can also digest human refuge, poultry sweeps etc.

Advantages :

(i) Gober gas is free from smoke, dust dirt etc., hence by it use, environment and utensil remain comparatively clean.
(ii) Gober gas does not contain poisonence gas, CO as ingredient.
(iii) By producing gober gas, we in fact are optimally utilizing waste.
(iv) It can provide the flame temperature of 540^0C, with proper burners.
(v) Heat generated by direct burning 1 kg of dry cattle dung in 23.4 kcal but if the same amount of cattle dung is converted first into gober gas (160 litre gas per kg dung) , It can supply 188 kcal of heat.

Applications

(i) The spent slurry is a richer manure than the original gober.
(ii) Gober gas can also be used for lighting and power purposes like running water pumps, chaff cutting machines etc.
(iii) It is used as a domestic fuel specially in village here dung in available in plenty. About 45 kg of dung per day is required to produce 2.8 $m^3$of the gas which is sufficient for an average family.

(vi) Coal gas

Coal gas was the primary source of gaseous fuel .Coal gas is a flammable gaseous fuel made by the destructive distillation of coal containing a variety of calorific gases including hydrogen, carbon monoxide, methane and volatile hydrocarbons together with small quantities of non-calorific gases such as carbon dioxide and nitrogen.

Composition:

The composition of coal gas varied according to the type of coal and the temperature of carbonisation. Typical composition of the Coal gas is as follows:

Constituents	Hydrogen	Methane	Carbon monoxide	Ethylene
Percentage(%)	50	35	10	5

Production:

During gasification, the coal is mixed with oxygen and steam while also being heated and pressurized. During the reaction, oxygen and water molecules oxidize the coal into carbon monoxide (CO), while also releasing hydrogen gas (H_2). This process has been conducted in both underground coal mines.

$$\underset{\text{(Coal)}}{C} + O_2 + H_2O \rightarrow H_2 + CO$$

If the refiner wants to produce gasoline, the SynGas is collected at this state and routed into a Fischer-Tropsch reaction. If hydrogen is the desired end-product, however, the SynGas is fed into the water gas shift reaction, where more hydrogen is liberated.

$$CO + H_2O \rightarrow CO_2 + H_2$$

Uses: It was used for lighting, cooking, and heating and was often supplied to households via a municipally owned piped distribution system.

PETROCHEMICALS ANALYSIS

Introduction: Petrochemicals refers to all those compounds that can be derived from the petroleum refinery products. Petrochemicals are chemical products made from the hydrocarbons present in raw natural gas and petroleum crude oil. It can be seen that petrochemicals are produced from simple compounds such as methane, ethylene and acetylene but not multi component products such as naphtha, gas oil etc. A relatively small number of hydrocarbon feedstocks form the basis of the petrochemical industries, namely methane, ethylene, propylene, butanes, butadiene, benzene, toluene and xylenes.

Petrochemicals, produced from petroleum, can be classified as olefins and aromatics. Olefins include ethylene, propylene, and butadiene which are raw materials for making plastics. Aromatics include benzene, toluene, and xylene which are raw materials for making dyes and synthetic detergents. These products are used by consumers as engine coolant, polyester fiber, rubbing alcohol, synthetic rubber, and epoxy.

The Future of Petrochemicals takes a close look at the consequences of growing demand for these products, and what we can do to accelerate a clean energy transition for the petrochemical industry. Already a major component of the global energy system, the importance of petrochemicals is continuing to grow. Demand for plastics – the most familiar group of petrochemical products

Definition :

Petrochemicals are chemicals derived from petroleum products. Examples of petrochemicals are plastics, rubbers, fibres, paints, solvents, and detergents. In fact, petroleum products are mixtures of hydrocarbons, whereas the raw materials for petrochemicals are pure hydrocarbons separated and converted to desirable products, such as polymers, solvents, and surfactants.

Products similar to petrochemicals derived from non-petroleum sources are not strictly petrochemicals. For example, cellulose, natural rubber, natural resins, nylon 11, and ethanol of plant origin are strictly non-petrochemicals. Coal distillation is also a source of varieties of coal chemicals, e.g., benzene, toluene, xylene, and naphthalene. In fact, before petroleum sources were known, coal chemicals were used to produce a variety of products. Many of the chemicals from non-petroleum sources are co-processed with petrochemicals to the finished product. Non-hydrocarbons obtained from petroleum, e.g., hydrogen, carbon monoxide, carbon dioxide, sulfur, and carbon, are also loosely called petrochemicals. Hydrogen, nitrogen and oxides of carbon manufactured from steam reforming and partial oxidation of naphtha are also petrochemicals. These are used for production of ammonia, urea, melamine, fertilizer, etc.

These are the chemicals that are made from petroleum and natural gas. Petroleum and natural gas are made up of hydrocarbon molecules, which comprises of one or more carbon atoms, to which hydrogen atoms are attached.

About 5 % of the oil and gas consumed each year is needed to make all the petrochemical products. Petrochemicals play an important role on our food, clothing, shelter and leisure. Because of low cost and easy availability, oil and natural gas are considered to be the main sources of raw materials for most petrochemicals.

They are usually in several stages and may be grouped as

(1) Feedstocks (first-generation petrochemicals)

(2) Intermediates (second-generation petrochemicals)

(3) Finished products (third-generation petrochemicals)

1.FEEDSTOCKS:

Feedstocks are the raw hydrocarbons obtained from crude oil refining by distillation and thermal and catalytic processes. For instance, hydrocarbon gases and naphtha are available from atmospheric distillation of crude oil; similarly, benzene, toluene, and xylene, obtained by catalytic reforming and catalytic cracking processes, are the major raw materials for the manufacture of second-generation petrochemicals. Benzene, toluene, xylene, and heavier aromatics are also generated as by-products from petrochemical plants. Thus, the feedstocks for petrochemical plants are either directly obtained from refineries or are further processed to generate them in the petrochemical plant itself. Natural gas and refinery products are the major source of feedstocks for petrochemicals.

2.INTERMEDIATES :

Thermal cracking of ethane, propane, butane, and naphtha produces cracked gases or olefins (ethylene, propylene, butylenes, acetylene, etc.) and liquids (benzene, toluene, xylene, etc.). Olefins are the starting material (monomers) for polyolefin plants. Olefins are also reacted with other hydrocarbons or non-hydrocarbon chemicals to generate vinyl chloride, ethylene glycol, neoprene, ethylene oxide, etc., and these are used as the starting materials (monomers) for the manufacture of a variety of polymers.

3.FINISHED PRODUCTS:

Using the above intermediates, a variety of plastics, rubber, fibre, solvent, paint, etc., are manufactured. Polymerisation reactions are carried out for these monomers or intermediates to various polymers, resinous and liquid products. Plastics are available in the form of extrudates, granules, powders, beads, etc., from the manufacturing units as the finished products. These are converted into plastic commodities, such as bags, films, furniture, and products of various shapes and sizes by casting, moulding, or blowing machines, as the marketable products.

Classification:

Petrochemicals can be broadly classified into three categories-

a. ***Light Petrochemicals:*** These are mainly used as bottled fuel and raw

materials for other organic chemicals. The lightest of these -- methane, ethane and ethylene -- are gaseous at room temperature. The next lightest fractions comprise petroleum ether and light naphtha with boiling points between 80 and 190 degrees Fahrenheit.

b. Medium Petrochemicals: Hydrocarbons with 6 – 12 carbon atoms are called "gasoline", which are mainly used as automobile fuels. Octane, with eight carbons, is a particularly good automobile fuel, and is considered to be of high quality. Kerosene contains 12 to 15 carbons and is used in aviation fuels, and also as solvents for heating and lighting.

c. Heavy Petrochemicals: These can be generally categorized as diesel oil, heating oil and lubricating oil for engines and machinery. They contain around 15 and 18 carbon atoms with boiling points between 570 and 750 degrees Fahrenheit. The heaviest fractions of all are called "bitumens" and are used to surface roads or for waterproofing. Bitumens can also be broken down into lighter hydrocarbons using a process called "cracking."

Petrochemical processes:

(i) Reactors: Reactors are the most important units in petrochemical processes. Petrochemicals are manufactured by following simple reactions using relatively purer feedstocks. Therefore, reaction chemistry for petrochemicals manufacture is very well established from significant amount of research in this field. Essentially all petrochemical processes need to heavily depend upon chemical transformation to first product the purification. The reactors used are tubular, stirred tank or kettle type. These may be packed bed or fluidized bed types, Both single and multiple numbers of reactors are used. The selection of a suitable reactor is a challenging decision in a petrochemical manufacturing unit.

(ii) Separation: With distillation being the most important unit operation to separate the unreacted feed and generated petrochemical product, the separation processes also play a major role in the process flow sheet. Where multiple series parallel reactions are involved, the separation process assumes a distillation sequence to separate all products from the feed. A characteristic feed recycle will be also existent in the process topology. Apart from this, other separation technologies used in petrochemical processing units include phase separators, gravity settling units and absorption columns. Therefore, the underlying physical principle behind all these separation technologies is well exploited to achieve the desired separation.

(iii)Dependence on Reaction pathway: A petrochemical can be produced in several ways from the same feedstock. This is based on the research conducted in the process chemistry. For instance, phenol can be produced using the following pathways:

- Peroxidation of Cumene followed by hydrolysis of the peroxide
- Two stage oxidation of Toluene
- Chlorination of Benzene and hydrolysis of chloro-benzene
- Direct oxidation of Benzene

We can observe that in the above reaction schemes, there are two reaction

pathways for phenol from benzene i.e., either chlorination of benzene or oxidation of benzene. Therefore, choosing the most appropriate technology for

production is a trivial task.

(iv) Complexity in pathway: In the above Cumene example case, it is interesting to note that toluene hydrodealkylation produces benzene which can be used to produce phenol. Therefore, fundamentally toluene is required for the generation of various petrochemicals such as benzene and phenol. In other words, there is no hard and fast rule to say that a petrochemical is manufactured using a suggested route or a suggested intermediate petrochemical. Intermediate petrochemicals play a greater role in consolidating the manufacture of other downstream petrochemicals.

NAPHTHA CRACKING:

Major plastics are manufactured from olefins, which are available either by cracking of gases (gas-based petrochemicals), such as methane, ethane, propane and butane, or from naphtha (naphtha-based petrochemicals). Due to the larger availability of naphtha and the low energy requirement for cracking as compared to gases, naphtha cracking is widely accepted for the manufacture of olefins. Naphtha is a mixture of hydrocarbons boiling in the range of the lowest boiling component (C5) to 150°C, which contains paraffins, naphthenes, and aromatics in various proportions. It is found that paraffins, i.e., straight chain hydrocarbons, yield olefins when heated at a high temperature. The branched chain and aromatic hydrocarbons, on the other hand, become heavier or decomposed to carbon. It is also a fact that the yield of olefins decreases with the increasing molecular weight (hence with boiling point) of the hydrocarbons. For example, if ethane is thermally cracked, it will yield 80% ethylene, while from propane, butane, naphtha, and gas oil as feed stocks, if cracked separately the yields will be 45%, 37%, 30%, and 25%, respectively. Hence, the desirable feedstock naphtha should have a very high content of paraffins and be in the lower boiling range. A suitable boiling range for feedstock naphtha for olefin production is below 100°C and should have a paraffin content of more than 75%. Usually, naphtha in the boiling range of 90°C−150°C is catalytically reformed (as discussed in Chapter 3) in a refinery either to produce gasoline or aromatics. Hence, in the refinery, C5−90°C cut is separated in the naphtha re-distillation unit and is sold to the petrochemical industry. Naphtha cracking is carried out in a tube-still furnace at a temperature above 800°C. Due to thermal cracking, the following cracking endothermic reaction takes place.

$$C_nH_{2n+2} = CH_4 + C_2H_4 + C_3H_6 + C_4H_8 + C_5H_{10} + C_2H_6 +$$

$$C_3H_8 + C_4H_{10} + C_5H_{12} + \ldots\ldots. + H_2$$

Table: Typical Operating Conditions in a Naphtha Cracking Furnace

Process Variable	Values
Temperature	800°C
Pressure	Atmospheric
Steam to naphtha ratio	0.6 kg/kg
Reaction time	< 1 sec
Cycle time for cracker	20 days
Yield of ethylene	30% of the feed

By-products of cracking are propylene, butylene, butadiene, and aromatics, such as benzene, toluene, xylene, isomeric paraffins, naphthenic components, and polynuclear aromatics. Products from the cracking furnace are quenched by hot oil and cooled before they are sent to the separation units. The product mixture then flows through a series of separators, e.g., demethaniser, de-ethaniser, depropaniser, and debutaniser units, which are multiplated distillation columns.

(i) PRIMARY FRACTIONATOR OR STABILISER :

Cracked liquids and gases are separated in a fractionating column the bottom product of which is the heavy cracked oil rich in high boiling aromatics. This heavy oil is also partly used as the quenching medium for the products from the furnace and partly sold as the carbon black feedstock (CBFS) due to its heavy aromatic contents. Cracked gases containing hydrocarbons, both saturated and unsaturated, from methane to C7 hydrocarbons emerge from the top of the column, which is then compressed and amine (or caustic) washed to remove hydrogen sulfide and carbon dioxide gases. This is illustrated in Figure.

(ii)HYDROGEN SEPARATOR:

Amine or caustic washed gases are then passed through a flash separator vessel, where liquid hydrocarbon gases are separated from hydrogen at high pressure and low temperature. Hydrogen from this vessel is used in the hydrogenating units, such as pyrolysis gasoline and butadiene hydrogenation, or as a fuel. ***Demethaniser:*** Liquified gases from a hydrogen separator are then separated from methane in a distillation column where methane (C1) emerges from the top and is used as a fuel for the cracking furnace. The bottom of the column is then passed to a de-ethaniser.

De-ethaniser: It is also a distillation column that separates ethane and ethylene mixture (C-2 mixture) as the top product from the rest of the liquified gases containing propane, propylene, butane, butylenes, etc.

Ethane-ethylene separator: A C-2 mixture from the top of the de-ethaniser column is then passed through another distillation column that separates ethylene as the top product and ethane as the bottom product. Ethylene is sent to storage and is used up in the polyethylene (PE) synthesis plant. Ethane from this column is recycled to a small cracking furnace to yield additional ethylene. ***Depropaniser:*** The liquified gas mixture from the bottom of the de-ethaniser is separated from propane and propylene (C-3 mixture), which leaves from the top of the column and enters the propane–propylene fractionator. The bottom product contains the butanes, butenes, butadiene, and heavier components, which are then separated from the butane–butene mixture (C-4 mixture). ***Propane–propylene separator:*** In this column, propylene is recovered as the top product and propane as the bottom product. Propylene is stored and used for manufacturing polypropylene, and propane is sold as a domestic fuel—liquified petroleum gas (LPG).

Debutaniser: Butane, butenes, and butadiene (C-4 mixture) are recovered as the top product and components heavier than the C-4 mixture, i.e., C-5 and heavier, are recovered as the pyrolysis gasoline (bottom product). Pyrolysis gasoline is catalytically hydrodesulfurised before it is sold or blended as a gasoline component. A gasoline hydrodesulfurisation unit is similar to a naphtha pre-treatment unit described in Above. A simplified flow sheet of a naphtha cracking unit (NCU) is shown in Figure ….. Typical yields of products from a naphtha cracking unit is presented in Table …

Reaction

$$C_xH_y + H_2O + O_2 \longrightarrow C_2H_4 + C_2H_6 + C_2H_2 + H_2 + CO + CO_2 + CH_4 + C_3H_6 + C_3H_8 + C_4H_{10} + C_4H_8 + C_6H_6 + C + \text{Heavy oils}$$

Table : Major Petrochemicals from Petroleum Products

S.N	***Products from Refinery/Oil Fields***	***Value-added Petrochemicals***
1	Natural gas (from oil/ gas fields) or methane	Carbon black, methanol, acetic acid, formaldehyde, synthesis gas, chlorinated methanes, ethylene glycol, MTBE, acetylene, chloroprene, vinyl chloride, vinyl acetate, etc
2	Ethane	Ethylene, polyethylene, ethyl alcohol, ethylene oxide, ethylene glycol, styrene, vinyl chloride, acrylonitrile, etc.
3	Propane	Propylene, polypropylene, propylene oxide, isopropanol, acrylonitrile, acetone, etc.
4	Butanes	Isobutanol, butadiene, acrylonitrile, polybutadiene, etc.

5	Benzene	Phenol, styrene and polystyrene, dodecyl benzene, cyclohexane, caprolactum fibres, nylons, etc
6	Toluene	Nitrotoluene, phenol
7	o-Xylene	Phthalic anhydride
8	Naphtha	Olefins for PE, PP, LPG, CBFS, pyrolysis gasoline, butadiene, linear alkyl benzene, etc.

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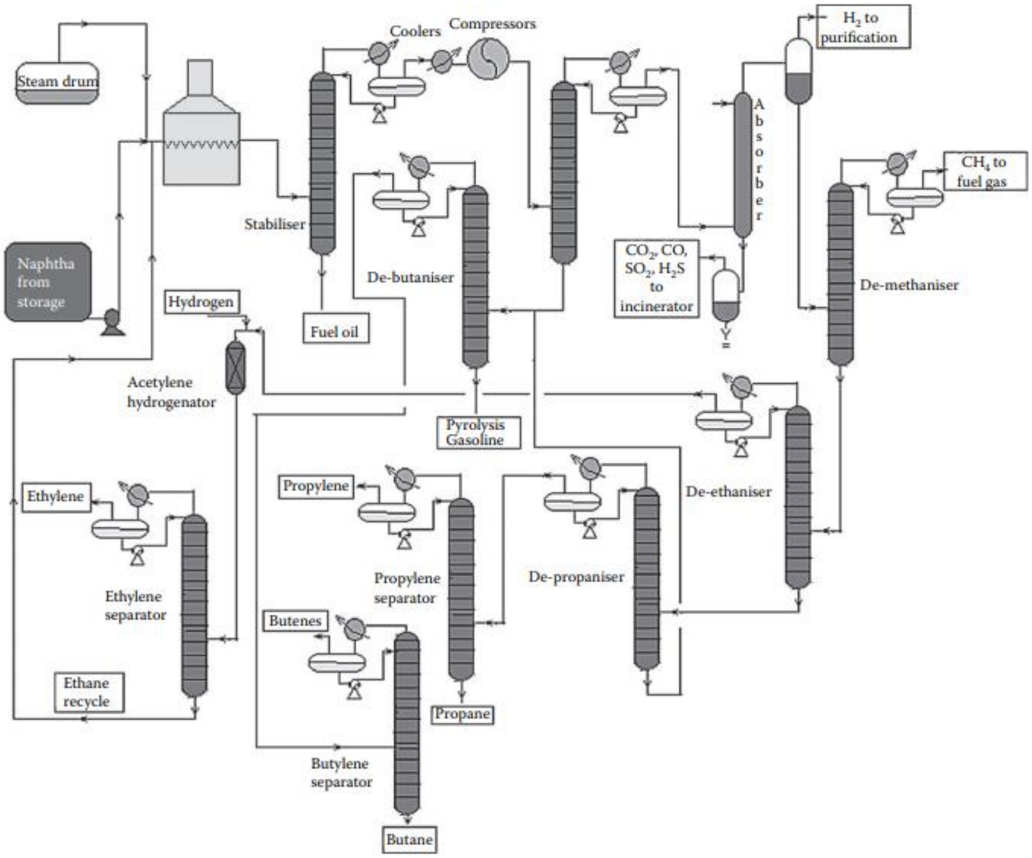

Fig: A simplified naphtha cracking unit.

CONVERSION PROCESSES FOR SELECTED PETROCHEMICALS

1.POLYETHYLENE

Polyethylene (PE) has evolved as a major plastic and is obtained by polymerising ethylene. Three main types of PE plastics are obtained—low density polyethylene (LDPE), linear low density polyethylene (LLDPE), and high density polyethylene (HDPE)—depending on the type of polymerising process.

Ethylene is a highly reactive monomer that starts combining with other molecules of ethylene in the presence of a catalyst (Ziegler–Nutta catalyst) under a certain pressure and temperature. The reaction steps are in three stages, namely, initiation, propagation, and termination. A radical molecule is formed in the presence of the catalyst in the initiation step. The radical then starts combining with the monomers repeatedly in the propagation stage, which continues indefinitely as long as the monomer molecules are available during reaction until quenched at the termination stage.

2.POLYPROPYLENE

Polypropylene is a valuable polymer and is used as plastic for making pipes, ropes, fibres, etc. It is manufactured by catalytic reaction in a stirred tank reactor, where Ti and aluminium halides are used as catalysts at a temperature of 60°C−70°C and a pressure of 1−2 MPa. An unreacted monomer is recycled after it is separated from the catalyst and polymer mixture in a flash chamber under vigorous stirring conditions. The mixture of polymer and catalyst is then passed to a centrifugal separator where a catalyst and polypropylene polymer is recovered. Further processing of the spent catalyst in the presence of alcohol is carried out to recover the active components of the catalyst for its reuse.

3 .Ethylene Glycol

Ethylene glycol is manufactured by catalytic oxidation of ethylene followed by hydration to glycol. High purity ethylene is converted to ethylene oxide in the presence of silver oxide as the catalyst in a tubular reactor at 250°C−300°C and 1 atm pressure. Air or pure oxygen may be used for the reaction. Ethylene dichloride is dosed in the reactor in very small amounts to avoid ethylene combustion. About 1 mol ethylene to 10 mol air ratio is maintained in the reactor. About 60%−70% of conversion occurs in a reaction time of only 1 sec. Ethylene oxide and unconverted ethylene are scrubbed with water and unconverted ethylene is recycled. The reactions are-

$$C_2H_4 + 1/2\ O_2 \longrightarrow C_2H_4O$$

$$C_2H_4O + H_2O \longrightarrow C_2H_4(OH)_2$$

4.POLYVINYL CHLORIDE

Polyvinyl chloride (PVC) is a polymer of vinyl chloride,

$$nCH_2 = CHCl \longrightarrow (-CH_2 - CHCl - CH_2 -)n.$$

It is a thermoplastic, widely used for many applications, and is commonly produced by the emulsion polymerisation method. An aqueous emulsion is produced in a mixer with ammonium salts of fatty acids and a vinyl chloride monomer and the reaction is allowed to continue in a stirred tank reactor. A very low pH is maintained during the reaction. The product containing the polymer latex and unreacted monomer are separated in a gas–liquid separator. The separated vapour of the monomer is recycled after scrubbing with caustic solution to neutralise the acidic vapours. The polymer from the separator is then dried for making powder of polymer.

5.POLYBUTADIENE

Butadiene (molecular formula $CH_2 = CH - CH = CH_2$) is obtained as the by-product from an NCU. By catalytic (Ziegler–Nutta) polymerisation of butadiene, a product that resembles natural rubber is obtained. A solvent is used to keep the catalyst and the monomer in the solution during the reaction. The product is separated from its unconverted monomer, which is recycled. The solvent is evaporated, stripped, and recycled. The polymer from the evaporator is then dried to get the final product.

6.PHENOL FORMALDEHYDE

Phenol (C_6H_5OH) and formaldehyde (HCHO) in the presence of an aqueous ammoniacal medium condense to a phenol-formaldehyde resin. The reaction is carried out in a kettle-type reactor at a temperature of 160°C and at atmospheric pressure. The reaction time is less than 1 h. The product from the reactor is usually blended with hexamethylene triamine and other fillers to make finished resins ready for moulding processes. Depending on the ratio of phenol to formaldehyde, a variety of grades of this resin may be made. This is a thermosetting type resin.

7.UREA FORMALDEHYDE

Urea $(CONH_2)2$ and formaldehyde (HCHO) also readily react to polymerise into urea-formaldehyde resin. Polymerisation is carried out in a glass-lined (or stainless steel) stirred tank reactor in an ammoniacal or weak alkaline medium.

The polymerisation reaction takes place at room temperature and atmospheric pressure. This resin is also a thermosetting resin.

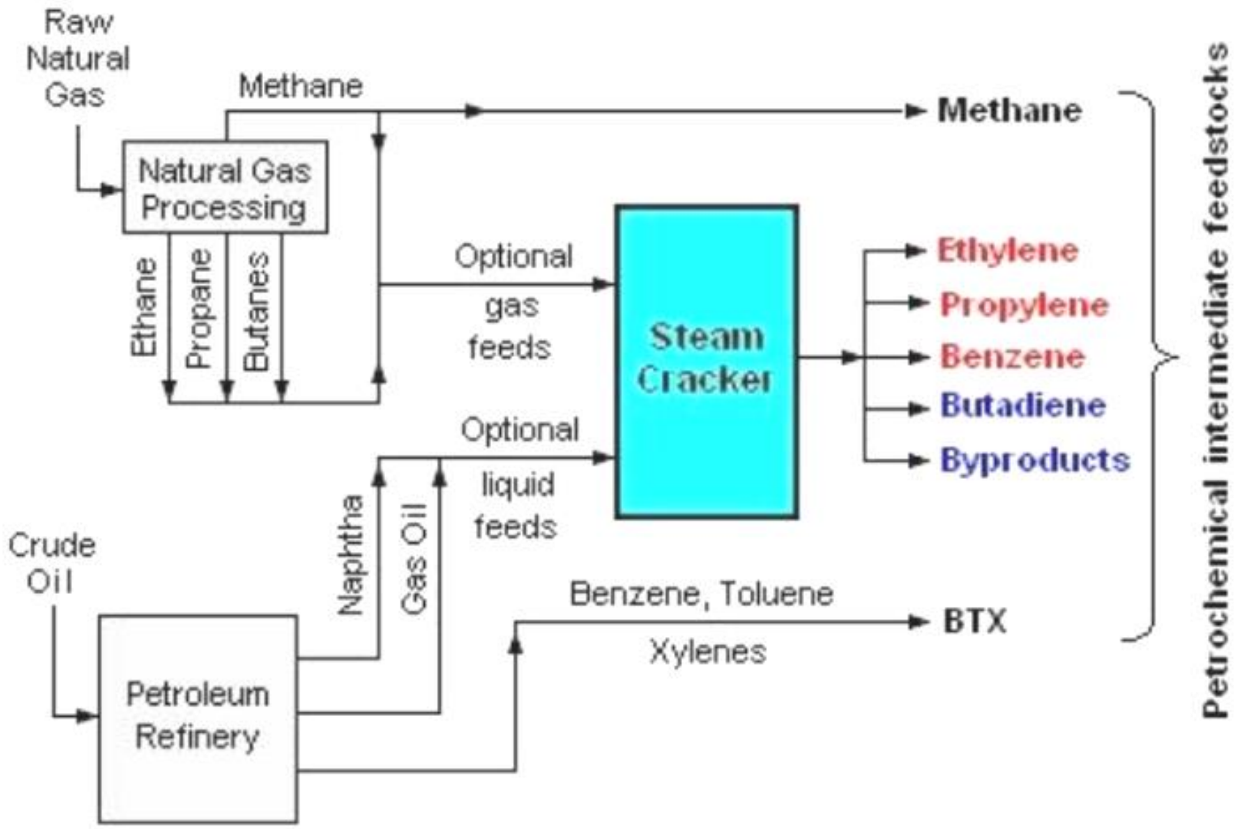

Fig : Block flow diagram schematically depicts the major hydrocarbon sources used in producing petrochemicals

The use of adjustable speed drives in a petrochemical plant offers many advantages:

(1) Elimination of the control valve providing reduction of fugitive emission of 430 kg per year.

(2) Elimination of control valve piping with reduced space

(3) Increased pumping capacity by the pumps

(4) Continuous control of flow

(5) Improved reliability

(6) Reduction of power consumption leading to cost savings. An energy saving of 30% has been reported by using adjustable speed drives consistent with data from industrial applications