

CHEMICAL TECHNOLOGY

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PART A: NOTES



CHAPTER 1

PETROLEUM

1.1 INTRODUCTION

Petroleum is a fossil fuel. It is called a fossil fuel because it was formed from the remains of tiny sea plants and animals that died millions of years ago. When the plants and animals died, they sank to the bottom of the oceans. They were buried by thousands of feet of sediment and sand that turned into rock.

Petroleum (or crude oil) is a complex, naturally occurring liquid mixture containing mostly hydrocarbons, but containing also some compounds of oxygen, nitrogen and sulfur. It is often referred to as the “black gold”.

Over time, this organic mixture was subjected to enormous pressure and heat as the layers increased. The mixture changed chemically, breaking down into compounds made of hydrogen and carbon atoms—hydrocarbons. Finally, an oil-saturated rock—much like a wet household sponge—was formed.

All organic material buried underground does not turn into oil. Certain geological conditions must exist within the rock formations for the transformations to occur. First, there must be a trap of non-porous rock that prevents the material from seeping out, and a seal (such as salt or clay) to keep the material from rising to the surface. Even under these conditions, only about two percent of the organic material is transformed into oil.

A typical petroleum reservoir is mostly sandstone or limestone in which oil is trapped. The oil in it may be as thin as gasoline or as thick as tar. It may be almost clear or black. Petroleum is called a nonrenewable energy source because it takes millions of years to form. We cannot make more oil in a short time.

1.2 PETROLEUM FORMATION

Petroleum forms by the breaking down of large molecules of fats, oils and waxes that contributed to the formation of kerogen. This process began millions of years ago, when small marine organisms abounded in the seas. As marine life died, it settled at the sea bottom and became buried in layers of clay, silt and sand. The gradual decay by the effect of heat and pressure resulted in the formation of hundreds of compounds.

Because petroleum is a fluid, it is able to migrate through the earth as it forms. To form large, economically recoverable amounts of oil underground, two things are needed: an oil pool and an oil trap. An oil pool, which is the underground reservoir of oil, may literally be a pool or it could be droplets of oil collected in a highly porous rock such as

sandstone. An oil trap is a non-porous rock formation that holds the oil pool in place. Obviously, in order to stay in the ground, the fluids – oil and associated gas – must be trapped, so that they cannot flow to the surface of the earth. The hydrocarbons accumulate in reservoir rock, the porous sandstone or limestone. The reservoir rock must have a covering of an impervious rock that will not allow the passage of the hydrocarbon fluids to the surface.

The impervious rock covering the reservoir rocks is called a cap rock. As shown in figure given below, oil traps consist of hydrocarbon fluids held in porous rock covered by a cap rock.

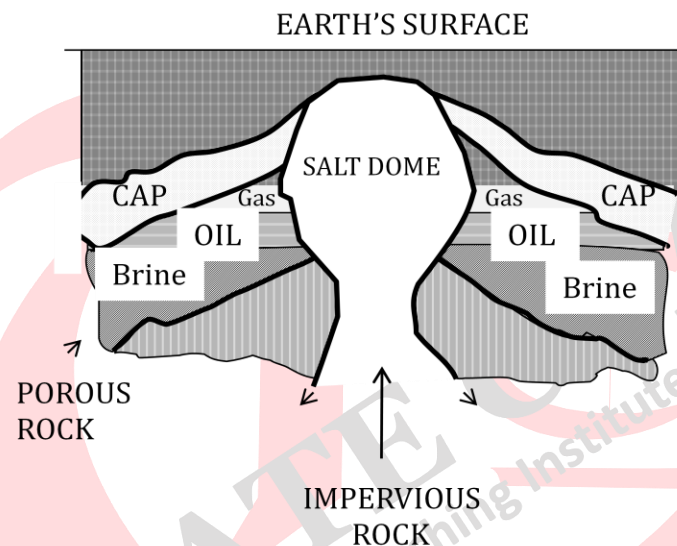


Fig. 1.1 Representative geologic structure of an oil trap: a salt dome.

A hot, wet climate fosters the growth of large amounts of organisms. If this growth takes place in a shallow sea, the eventual drying out of the environment and evaporation of the sea water leaves behind large deposits of salt. Salt makes an excellent cap rock for a reservoir. If these conditions are enhanced by a gentle geological folding of the subsurface rocks, the rock folding can produce very large reservoirs, with the impervious salt deposits acting as a cap. These are precisely the conditions that prevailed in the Middle East, giving rise to the enormous deposits of oil found in that region of the world.

1.2.1 PETROLEUM UTILIZATION

Petroleum utilization is a much more complex process than coal utilization. This is illustrated in figure (a) shown below. 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. Furthermore, a large number of different products is obtained from the petroleum refinery. This is illustrated in figure (b) given below. Most of them are used as fuels. A small but very

important fraction is used as the basis for the (petro) chemical industry which gives us such indispensable products as plastics, pharmaceuticals and textiles.

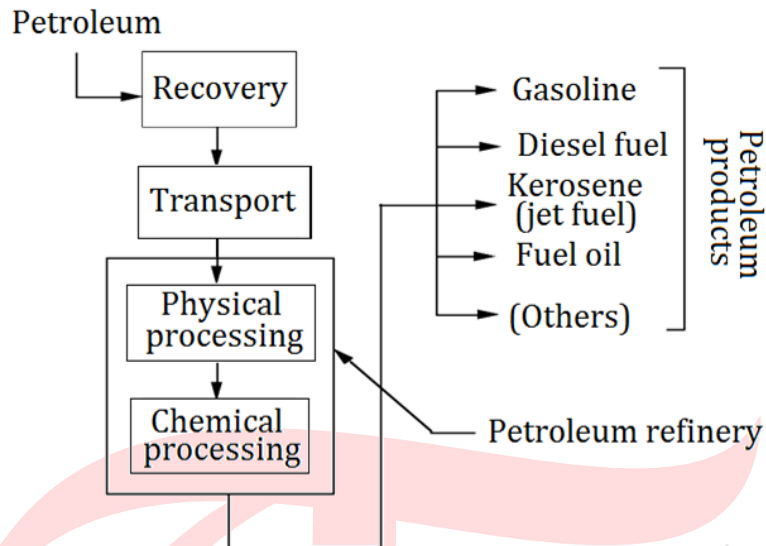


Fig: 1.2 (a) Pathways to petroleum utilization.

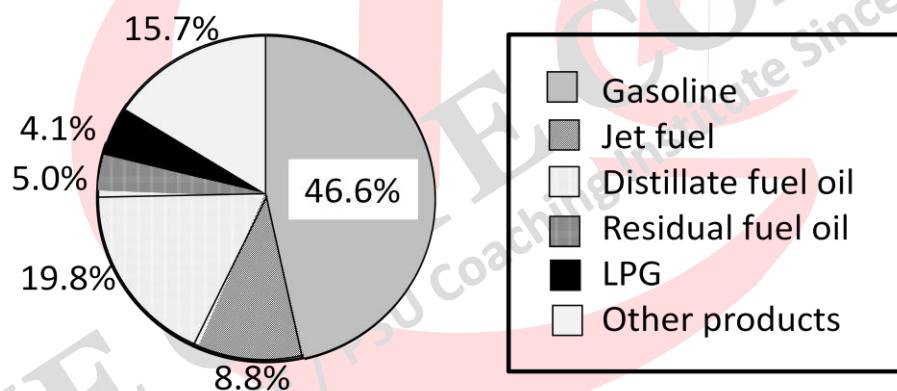


Fig: 1.2 (b) Distribution of products of petroleum refining in the United States

1.2.2 OIL RECOVERY (DRILLING)

After geologists of an oil company have located the general area in which petroleum is thought to occur, a well is drilled. Selecting the site for drilling requires detailed knowledge of the geologic features under the earth's surface. We can see from figure given below that of the three wells shown, all of which are reasonably close to the oil pool, only well B would actually produce oil. Drilling is also done to determine the extent of the reserves. Once the oil has been located, additional drilling might be done over an area around the first producing well to assess the geographic extent of the oil pool and its depth. This information allows geologists to estimate the amount of oil in the pool.

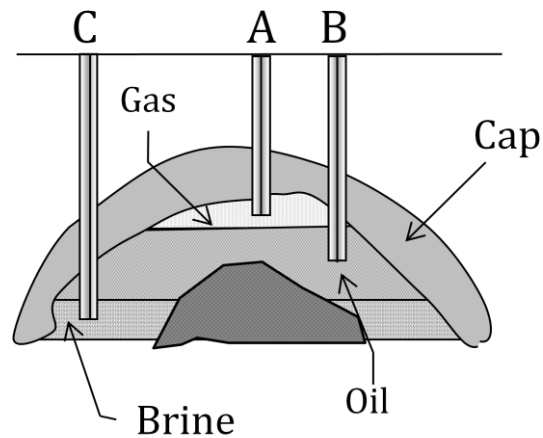


Fig: 1.3 Selection of a site for petroleum drilling.

In this case, the oil in the reservoir is under pressure and will come to the surface by natural flow. The force responsible for the flow of oil may be a water drive, in which water lying under the oil pushes it to the surface, or a gas cap drive, in which a bubble of gas pushing down on the oil forces it to the surface. Settled production occurs when oil has to be pumped from the reservoir.

Enhanced recovery is used when it is no longer possible to pump the oil with conventional techniques. Enhanced oil recovery techniques are sometimes divided into secondary and tertiary recovery. In secondary production, conditions similar to flush production are created. Instead of relying on naturally occurring water or gas to force the oil out, the oil field is flooded with water pumped down into wells to force the oil out, or gas is pumped down a well to create an artificial version of gas cap drive.

Secondary recovery methods extract an additional 10 to 20% of the available oil from a well. Because we cannot rely simply on natural forces, as in flush production, but instead must provide pumps and associated piping to force gas or water underground, secondary recovery is more expensive than primary recovery. Tertiary recovery is even more expensive. In general, it is usually necessary to decrease the viscosity of the oil to achieve further recovery. Since the viscosity of any liquid drops as its temperature increases, tertiary recovery often involves heating the oil underground, such as by injecting steam into the wells. As an alternative, special chemicals (surface-active agents) can be injected into wells to reduce the viscosity.

1.2.3 CLASSIFICATION OF CRUDE

The hydrocarbons found in petroleum are classified into the following types:

- i. **Paraffinic crude oil** containing linear or long chain saturated hydrocarbon.
- ii. **Olefinic crude oil** containing unsaturated compound.
- iii. **Naphthenic crude oil** containing saturated ring compound like cyclohexane.

iv. **Aromatic** hydrocarbons containing one or more aromatic nuclei such as benzene, naphthalene, and phenanthrene ring systems that may be linked up with (substituted) naphthalene rings or paraffin side-chains.

- **Olefinic content in crude oil is least present & Naphthenic content present is maximum i.e. 50%**

1.3 PROPERTIES OF PETROLEUM & ITS PRODUCTS

The elemental composition of petroleum is much less variable than that of coal: 83-87% carbon, 11-16% hydrogen, 0-4% oxygen plus nitrogen, and 0-4% sulfur. Note that most crude oils contain substantially more hydrogen than coals. Only a brief discussion is needed here regarding the distribution of these elements among the thousands of compounds found in petroleum.

Most of the compounds in petroleum contain from five to about twenty carbon atoms. Many of them consist of straight chains of carbon atoms (surrounded by hydrogen atoms), as illustrated below:



Compounds having branched chains and rings of carbon atoms are also present. Here are some examples:

Compounds of the types shown above with chains of carbon atoms either branched or straight, are called paraffins. All paraffins have the molecular formula C_nH_{2n+2} . For example, $n = 8$ for a compound called octane.

The physical state of the paraffins depends on the number of carbon atoms in the molecule. Paraffins with less than five carbon atoms are gases at ordinary temperatures. Paraffins with five to fifteen carbon atoms are free-flowing liquids. Paraffins with more than fifteen carbon atoms range from very thick, viscous liquids to waxy solids. As the number of carbon atoms increases, so, too does the number of possible molecular structures resulting from their combination. For example, the paraffin with five carbon atoms (called pentane) can exist as one linear chain and two branched chains:

As the number of carbon atoms increases beyond five, the number of different molecular structures with the same number of carbon atoms increases drastically (exponentially).

We shall see later, in our discussion of the quality of gasoline, that the branched-chain paraffins are very important in providing good automobile engine performance. The reader will be relieved to know, however, that it will be necessary to learn the structure of

only one or two of the most important branched paraffins, not the million or so possible structures.

Another class of molecules found in petroleum are the aromatic compounds. They have a ring structure and are typically derivatives of a compound called benzene, C_6H_6 . They do indeed have a characteristic aroma, but they typically have a negative environmental impact.

The ones that have a low molecular weight are volatile; for example, they easily evaporate from gasoline at filling stations. Many among them are carcinogenic.

Crude oils can be classified in a number of ways. Consider first a crude oil that is in the very early stages of being produced from kerogen. The long-chain compounds in the kerogen will not have broken apart to a great extent, because the oil or kerogen has not yet been buried very deeply (so it has not been exposed to high temperatures in the earth), nor has it been buried for a very long time. The carbon atom chains in this oil are likely to be very long.

These long chains give the crude oil two properties:

- (a) They make it dense because long, straight chains of molecules can be packed tightly, resulting in a large mass per unit volume.
- (b) They also make it difficult for the molecules to flow past one another, making the crude oil more viscous (slower to flow and harder to pump).

In addition, many sulfur compounds might be present in these oils. They are called young-shallow crudes: young, because they have not had the time to be broken down by the high temperatures inside the earth; and shallow, because they have not been buried deeply. Typically, young-shallow crudes are highly viscous, high-density materials with high sulfur content.

As the oil is buried more deeply inside the earth's crust, it is exposed to higher temperatures. As a result, the molecules can break apart to a greater extent, and some of the molecules containing sulfur will be destroyed. These 'young-deep' crudes will have moderate viscosities, densities and sulfur contents. If the oil has not been buried very deeply, it will not experience the same temperatures as young-deep crude. However, over very long time periods, the same chemical transformations that occur in a short time at high temperatures can also occur at relatively low temperatures. Thus, 'old-shallow' oil might have the same properties as a young-deep one. The analogy with the expression that "time is money" is very appropriate. We know that we can shorten the time required to do something if we are willing to spend more money to do it. In geology "time is temperature:" as temperature increases, the time needed to accomplish a particular change decreases. Crude oils of the young-deep or old-shallow quality occur both in California, around Oxnard, and in Texas, in the vicinity of Scarborough.

If a crude oil is buried deeply and for a long time, extensive breaking apart of the carbon chains can occur. At the same time, most of the sulfur compounds in the oil are broken down. Therefore an 'old-deep' crude oil has low viscosity, low density, and very low sulfur content. This combination of properties makes the old-deep crudes the most desirable: they require little refining to remove sulfur and they can be converted to large quantities of high-quality products such as gasoline. Unfortunately, less than 5% of the world's remaining petroleum reserves are of this quality. Some of the best quality crude oils are found in northwestern Pennsylvania, in the vicinity of Bradford, and the term Pennsylvania crude is used as a standard of quality for crude oils. Overseas, old-deep crudes occur in Morocco.

1.4 FLASH POINT

It is minimum temp at which oil gives out sufficient of vapor to form an inflammable mixture with air and catches fire that is flashes when flame is applied is known as Flash Point. Flashes at least sustain for 5 seconds then it is known as fire point and difference between the two is 4-5°C. They tell us upper limit of temperature up to which fuel can be used safely. Flash point and Fire point are measured by Pensky-Martyen apparatus Or Able's Apparatus.

1.5 CLOUD POINT AND POUR POINT

When oil is cooled at specified rate, the temperature at which it becomes cloudy or hazy is known as cloud point of oil. The temperature at which oil just seized to flow is known as pour point. Difference between cloud point and pour point is 4-5°C. Cloud point and pour point are measured by cloud point and pour point Apparatus.

1.6 OCTANE NUMBER

This is the property of gasoline which is used in spark ignition engine to express its knocking characteristic. Knocking characteristics – sudden explosion of fuel air mixture and collisions of flame wave which hit the engine and produce audible knocking. The octane Number is defined as the % by volume of iso-octane with same knocking tendency as that of fuel.

$$\text{Octane No.} = \frac{\% \text{ by volume is octane}}{\text{iso - octane \& n - heptane}}$$

Higher the octane number the minimum is the knocking. In India octane No – 87 is sold & in USA octane No – 94.

OCN can be improved by the addition of tetraethyl lead which acts as anti knocking agent.

OCN increase in the order paraffin < Napthenes < olefins < Iso paraffin < Aromatics

Octane No of 80 indicate that fuel is equivalent to the performances characteristic in a fuel engine fed with 80% by volume of iso-octane and 20% by volume n-heptane.

Branching increases the octane number. Higher is the branching, higher is the octane number.

1.7 CETANE NUMBER

It is the characteristic property of diesel which is used as a fuel in a compression ignition engine. Cetane number is defined as percentage by volume of cetane to the mixture of cetane & α -methyl Naphthalene.

Paraffin > Naphthalene > olefins > iso - paraffin > Aromatics

Ethyl Nitrate or Acetone to increase cetane number. Branching Decreases the cetane number. Higher is the branching, lower is the cetane number. High cetane number facilitates easy starting of engine especially in cold weather.

A good diesel is bad petrol.

1.8 SMOKE POINT

It is the characteristic property of kerosene. It is the maximum height of flame (in mm) without smoke formation obtained when the kerosene is burnt in a standard lamp under a closed controlled condition.

Smoking is mainly due to presence of aromatic content. Therefore aromatic content is undesirable in kerosene. Higher is the smoke point, higher the paraffinic content and lower is the aromatic content. For good quality of kerosene smoke point should be 25 mm.

1.9 ANILINE POINT

The minimum temperature at which oil is completely miscible with equal volume of aniline. It is the measure of aromatic content in the oil. More will be aniline point, lesser will be aromatic content, higher will be paraffinic content. Aniline point give an indication of the possible deterioration of rubber ceiling, packing etc. in contact as aniline have tendency to dissolve rubber.

1.10 ACID VALUE / ACIDITY

It is defined as number of milligram of KOH required to neutralize the free acid present in 1 gm of oil. It indicates the oxidation of oil & its acidic property which will cause corrosion and also results in sludge formation. Ideally it should be less than 0.1 %.

1.11 CARBON RESIDUE

It is the percentage of carbon residue left after the distillation of crude oil or its products in the absence of air. A carbon deposit foul the surface resulting in wear and also affects the regeneration of cracking catalyst. It is measured by Conradson apparatus.

1.12 SULPHUR CONTENT

It is defined as the amount of sulphur present in a given fuel. The presence of sulphur decreases the octane number; produces SO_x in the environment and decreases efficiency of engine. Instrument for measure is Bomb calorimeter

1.13 CALORIFIC VALUE

The calorific value of fuel can be defined as total heat produce when unit mass of fuel is completely burnt with pure oxygen. Two types of calorific values are used named as Gross calorific value & Net calorific value. GCV is always greater than or equal to NCV. Instrument is Bomb Calorimeter.

1.14 MOISTURE CONTENT

It is the amount of moisture content in a given fuel. Water in fuel is undesirable because it cause flame failure. It is measured by Dean & Stark apparatus.

1.15 OVERVIEW OF REFINERY PROCESSES

1.15.1 Crude distillation unit (CDU)

The unit comprising of an atmospheric distillation column, side strippers, heat exchanger network, feed de-salter and furnace as main process technologies enables the separation of the crude into its various products. Usually, five products are generated from the CDU namely refinery gas, naphtha, kerosene, light gas oil, heavy gas oil and atmospheric residue. In some refinery configurations, terminologies such as gasoline, jet fuel and diesel are used to represent the CDU products which are usually fractions emanating as portions of naphtha, kerosene and gas oil. Amongst the crude distillation products, naphtha, kerosene has higher product values than gas oil and residue. On the other hand, modern refineries tend to produce lighter components from the heavy products

1.15.2 Vacuum distillation unit (VDU)

The atmospheric residue when processed at lower pressures does not allow decomposition of the atmospheric residue and therefore yields light vacuum gas oil (LVGO), heavy vacuum gas oil (HVGGO) and vacuum residue. The LVGO and HVGGO are eventually subjected to cracking to yield even lighter products. The VDU consists of a main vacuum distillation column supported with side strippers to produce the desired products. Therefore, VDU is also a physical process to obtain the desired products.

In general products of distillation are:-

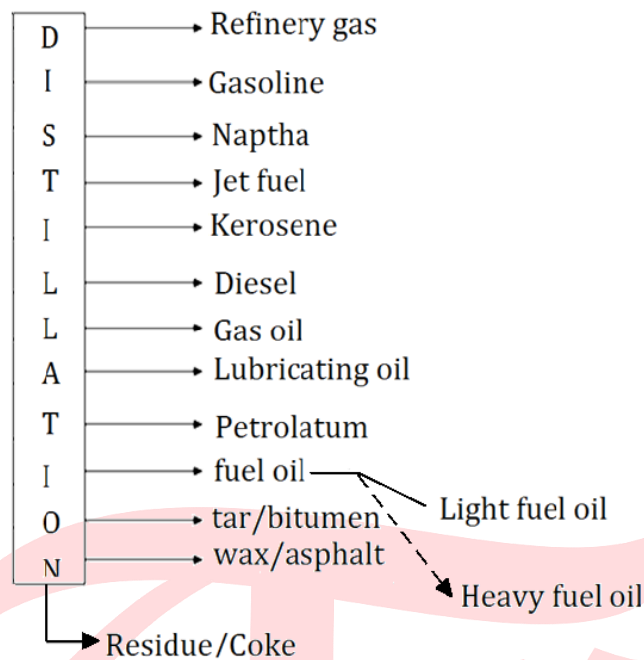


Fig: 1.4

Petrolatum is used in the grease manufacture. Fuel oil is used to ignite the furnace and Gas oil sends to cracking unit to extract fraction of gasoline.

1.16 CRACKING

Cracking is the process by which heavy petroleum fraction (higher boiling petroleum) is converted into lighter petroleum fraction (low boiling petroleum) under high pressure & temperature. It is an endothermic reaction.

1.16.1 Two Types of Cracking

1. Thermal – pressure (1-70 atm), temperature (450-750°C)
2. Catalytic – pressure (1-15 atm), temperature (350-650°C)

Cracking is done to produce gasoline from gas oil and used to produce olefin (pyrolysis). It is also used to produce coke (coking).

1.16.1.1 Thermal Cracking

It is one of the secondary refinery process by which heavy fractions of petroleum are decomposed at high pressure and temperatures between 450°C and 750°C for producing light hydrocarbons. The 'cracked' gasoline is an excellent motor fuel.

Coke is one of the products of cracking process. This is because of the fact that the heavy raw petroleum contains resins and asphaltines and these converted to coke at the cracking temp. The coke is also produced due to the polymerization of olefin hydrocarbon formed in the process of cracking of heavy petroleum fractions.

1.16.1.1.1 Thermal Cracking is 4 Types

1. Vis-breaking
2. Thermal Reforming
3. Pyrolysis
4. Coking

- **Vis-breaking**

It is the low temp; high pressure process 500°C & 20 atm . Feed is generally from ADU (Atmospheric Distillation Unit). The product from vis-breaking comes in the intermediate boiling range from high boiling range and is sent to thermal reforming for the production of gasoline.

- **Thermal Reforming**

It is used to produce light boiling petroleum fraction that is in the range of gasoline from intermediate boiling fraction. Feed is mainly gas oil and intermediate naphtha. It is used to produce gasoline. It is high temperature & high pressure process.

- **PYROLYSIS**

It is high temperature, low pressure process (1 atm, 700°C), it produces olefin, benzene & toluene etc. feed is mainly naphtha.

- **COKING**

The main aim of coking is the production of gasoline not the production of coke. It is low temperature and high pressure process (more severe condition than Vis-breaking). Feed is the residue left from thermal reforming or pyrolysis. Coke is mainly used as electrodes in aluminum industry.

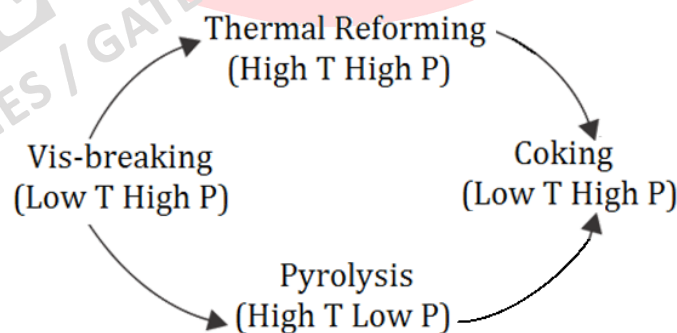


Fig: 1.5

1.16.1.2 Catalytic Cracking

Catalytic cracking compare to thermal cracking produce less coke, less gas with high performance and octane no of gasoline. Catalyst used in the catalytic cracking is in the form of bed, powder or pellets that includes silica, alumina, natural clay, zeolite etc. Pellets & beds are used in fixed bed catalytic cracking but powder catalyst used in fluidized catalytic

cracking gives higher yield of gasoline where higher pressure reduces octane number of gasoline. Now after this the light gaseous hydrocarbons produced by catalytic cracking are highly unsaturated and are usually converted into high-octane gasoline components in polymerization or alkylation processes.

1.17 FLUIDIZED CATALYTIC CRACKING

It is the most important catalytic cracking that uses a reactor in series with a regenerator. In the reactor catalyst of zeolite ZSM-5 is used which helps in the cracking of hydrocarbon oil vapors into products that lies in the gasoline boiling range. As the process continues, catalyst active sites get coked and hence, regeneration is required. For regeneration purpose, catalysts are fed to the regenerator in which there is supply of air or oxygen. Carbon deposits on the catalyst active sites undergo combustion reaction to form carbon dioxide and release enormous amount of heat which also increases the temperature of the regenerated catalyst which then enter into the reactor. Hence, no need to supply heat because in regenerator catalyst has desired temperature.

Catalyst is Zeolite in powder form. The cost of makeup catalyst is also very low. Residence time is too low only 3-5 sec.

1.18 HYDRO CRACKING

This is combination of catalytic cracking & hydrogenation. Cracking is done in the presence of hydrogen and is known as hydro cracking, the catalyst used as tungsten sulphide for vapour phase & Iron (Fe) for liquid phase.

It completely removes sulphur, nitrogen, oxygen & also helps in saturating the olefinic character.

1.18.1 Hydro Treating

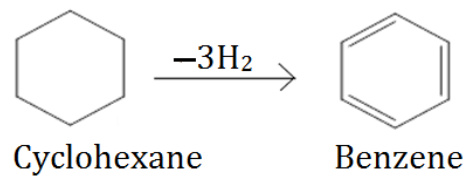
Mild operation compare to hydro cracking, it removes the sulphur, nitrogen and halides and trace metals and also used to stabilize the olefin. The catalyst used is cobalt molybdenum.

1.19 REFORMING

This is a process by which octane rating of gasoline blend is increased by rearranging the molecular structure of a petroleum fraction. The predominant reaction during reforming is the dehydrogenation of naphthalene to form high octane aromatic. Feed is naphtha, Preference of feed is coking naphtha > virgin naphtha > catalytic naphtha.

Dehydrogenation of naphthenic to aromatic.

Cyclohexane – benzene

**Fig: 1.6**

Like cracking, reforming is also of two types:

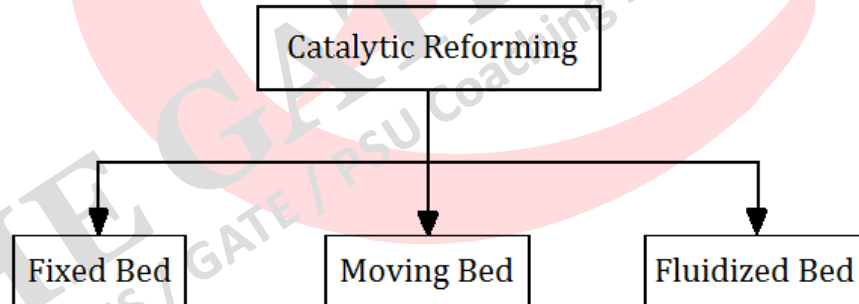
- i. Thermal
- ii. Catalytic reforming

1.19.1 CATALYTIC REFORMING

Catalytic reforming is used to convert hydrocarbons to aromatic which have high octane rating, e.g., toluene gives a 104 motor octane number.

Three types of catalyst are used

- i. Precious metal oxide like platinum on alumina or silica-alumina base.
- ii. Non-precious like molybdenum chromium or chromia.
Generally reforming is done at 450-550°C and 15-45 kg/cm²
- iii. In the precious metal oxides, halides promote the activity of platinum on alumina based, but if silica alumina base is used then no halide are required.

**Fig: 1.7**

1. Fixed
 - i. Non regenerative process → platforming
 - ii. Regenerative process → hydro forming.
2. Moving Bed
 - i. TCR (thermo catalytic reforming)
 - ii. Hyper forming
3. Fluidized
Fluidized Hydro forming process

1.20 POLYMERIZATION

Gases produced in cracking are rich in C_2 and C_4 compounds (olefin). Therefore, it undergoes polymerization in the presence of phosphoric acid to give a product in the gasoline product range. Gasoline products are named as polymer gasoline.

e.g., 2 Isobutane \rightarrow Di-isobutane

Polymerisation is an important process in gasoline manufacturing as most gasoline formulations require inclusion of some light naphtha to meet the front-end distillation and octane specifications. However, C_5/C_6 normal paraffins in this boiling range have low octane, which makes them very difficult to include in the gasoline formulation. Branched chain C_5 and C_6 hydrocarbons have higher octane, making them more suitable for inclusion in gasoline.

1.21 ALKYLATION

In petroleum refining alkylation means reaction of an olefin with iso-paraffin to produce a larger iso-paraffin having higher octane number.

e.g., Iso-butane reacts with propane to give iso-heptane catalyst H_2SO_4 , HF.

Alkylation is an important refining process for the production of alkylates, a high octane gasoline blending component. Alkylate product is a mixture of branched hydrocarbons of gasoline boiling range. Alkylate has a motor octane (MON) of 90-95 and a research octane (RON) of 93-98. Because of its high octane and low vapor pressure, alkylate is considered an excellent blending component for gasoline.

1.22 ISOMERIZATION

In petroleum refining isomerization is done to convert straight chain paraffin to iso-paraffin in the presence of aluminum chloride as catalyst.

N-butane \rightarrow Isobutane

1.23 PURIFICATION OF PETROLEUM PRODUCTS

Removal of sulphur & its component like H_2S , mercaptan from petroleum product is known as sweetening.

Sour crude: sweet crude

Sweetening Process

- i. Doctor's process
- ii. Solutizer process
- iii. Catalytic desulfurization process
- iv. Catalytic desulfurization Hydrogen process.
- v. Copper chloride process

Solutizer process: It is same as extraction process, solvent used are methanol or naphthenic acid.

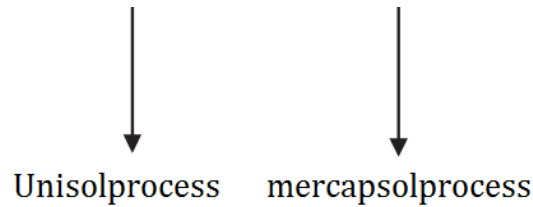


Fig: 1.8

De-Waxing

The removal of wax from petroleum products specially from lubricating oil

Process for de-waxing are

- a. Chilling & pressing (Old process)
- b. Solvent De-waxing (same as extraction, solvent used is methyl ethyl ketone or propane).

De - Aromatization

Removal of aromatic compound from kerosene is called as de-aromatization.

Solvent use- liquid SO_2 . Condition for using this solvent moisture should not present in the feed. If moisture presents solvent become highly corrosive.

1.24 LIQUID FUEL FROM SOLID FUEL

(I) Bergius process

(II) Fischer-Tropsch process

1.24.1 Bergius process:

Coal is converted into finally powder form and made into a paste with heavy oil and then heated upto 400°C to 500°C under 200-250 atm in presence of organic compound of tin in a converter (Reactor followed by cracking & hydrogenation to yield).

- i. Gasoline
- ii. Middle oil
- iii. Heavy oil

Middle oil + hydrogenation give gasoline. It is efficiency lower than Fischer-Tropsch process.

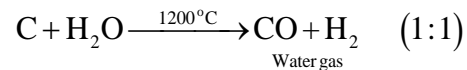
1.24.2 Fischer-Tropsch Process:

The Fischer-Tropsch process is a gas to liquid process that involves reacting CO with H_2 on a metal catalyst to form various hydrocarbon chains. Franz Fischer and Hans Tropsch produced the Fischer-Tropsch process to create hydrocarbons from coal derived gas.

This is done in 3 steps

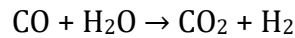
1) Formation of water gas

This involves conversion of coal into water gas by heating it at 1200°C.



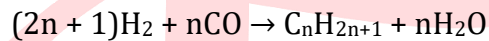
2) Formation of synthesis gas

A part of CO is removed and combined with steam again to form CO₂ and CO₂ is removed by absorption.



So, H₂ obtained mixed with rest of the water gas in a ratio of Syn gas 1:2 CO: H₂

3) Gas to liquid fuel



Synthesis gas is passed at atmospheric pressure over a cobalt thorium oxide catalyst at 180-200°C.

To increase the yield of cobalt catalysts are now replaced with iron oxide catalyst.

Fischer-Tropsch plant located in South Africa, produces 20% of fuel for South Africa as a result of the availability of cheap coal.

1.25 GASEOUS FUEL

1.25.1 Natural Gas

It is the mixture of paraffinic hydrocarbon in which methane is the main constituent.

It occurs in gas fields and oil fields.

Dry natural gas → when the concentration of removal condensate is less than 15 g/m³

Wet natural gas → when the concentration of removal condensate is more than 15 g/m³.

Gross calorific value is more for wet than for dry.

1.25.2 LNG → Liquid Natural Gas

To use natural gas in its pure form is tough hence, to use it as an alternative fuel for an engine. It is compressed to high pressure of 200 atm to transport natural gas; it is cooled to -160°C to convert it into LNG which is transported in a cylinder.

1.25.3 Advantage of CNG or LNG

1. Octane number of CNG is very high (130).
It has an octane number > 100 then it is called performance number.
2. Long life of engine, better cold starting property.
3. Less emission of unburned HC.

Disadvantage

Large tanker for storage, heavy cylinder is requiring (highly press).

LPG

1. It is mainly mixture of propane and butane is use only as cooking gas.
2. C_3 & C_4 are easily liquefied at low pressure, supplied in light cylinder generally mixture of 80% butane and 20% propane is known s LPG.

It is prepare by pure butane & propene distillation of crude oil and wet natural gas.
LPG is volatile liquid which expand 247 times its volume as vapour.
1L of LPG in liquid = 247 L of LPG in vapour.

Advantages

1. Non-toxic
2. Doesn't support life.
3. Odour less
4. Heavier than oil.

Methyl merchptane are added to detect the leakage of LPG from cylinder.

1.26 PRODUCER GAS

It comprises mainly of CO: N_2 in 1:2, it is made from solid fuel mainly bituminous coal.
Calorific value – 1250-550 Kcal/ m^3
It is used in gas furnaces.

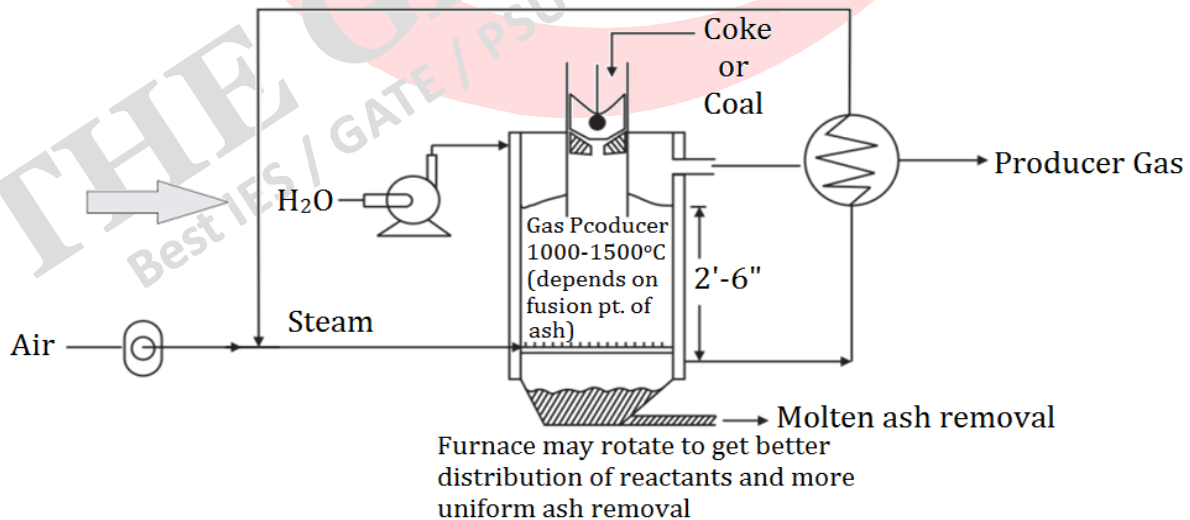


Fig: 1.9 Manufacture of producer gas.

CO ₂	Co	N ₂	H ₂	CH ₄
4-6%	20-30%	46-55%	11-20%	0-3%

1.26.1 Water gas

It comprises mainly of CO: H₂ in 1:1, it is made from solid fuel mainly anthracite coal.

Calorific value – 2800 Kcal/Nm³

CO ₂	Co	N ₂	H ₂	CH ₄
3-5%	40-42%	3-6%	48-51%	0.1 to 0.5%

Application

- i. Fuel in furnaces.
- ii. Use in fertilizer industry to produce ammonia & urea.
- iii. It is also known as blue gas because it burns with blue flame.