- **T.Y.B.Sc. CBCS COURSE IN CHEMISTRY CH: 504 Industrial Chemistry**
- **Core Course- (Semester I)**
- **Chapter 4: Petroleum Industry (L: 9, M: 12)**

- **A POWERPOINT PRESENTATION FOR T. Y. B. Sc. CBCS COURSE IN INDUSTRIAL CHEMISTRY ON THE TOPIC**

ENTITLED

"Petroleum Industry"

BY

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Dondaicha. Dist- Dhule. **(M. S.)**

----- August 2020 -----

Syllabus of Industrial Chemistry

- Chapter 1 General Aspects of Industrial Chemistry (M-12, L-9)
- Chapter 2 Sugar Industry (M-12, L-9)
- Chapter 3 Fermentation Industry (M-12, L-9)
- Chapter 4 Petroleum Industry (M-12, L-9)
- Chapter 5 Industrial organic Synthesis (M-12, L-9)

Industrial Chemistry

- Environmental Political and Economic Stability to society
- Social Problem solver
- To promote and maintain good health
- For longetivity i.e. for prolonging the life of man, to fight against sickness, pain and disease.
- Synthesize crop enhancing agricultural chemicals to ensure a constant and viable food supply.
- Eradication of deadly diseases by developing pharmaceuticals.
- Studies ozone depletion, acid rain, global warming, water recycling, alternative fuels, endocrine disrupting chemicals, explosives, fertilizers, polymers, etc.
- Innovative plastics, fibres and so many things.
- For wellbeing of mankind and also for animal kingdom.

Industrial chemistry Definition: -

"Industrial Chemistry is the branch of Chemistry, which applies physical and chemical processes towards the transformation of raw materials into products that are of beneficial to humanity."

Or "Industrial chemistry is the development, optimization and monitoring of basic chemical processes applied in industry for changing raw materials and precursors into helpful commercial products for society."

In industrial chemistry emphasis is placed on a holistic understanding of the relationship between natural resources, chemical transformations and waste generation for a sustainable insights derived from green chemistry and environmental chemistry.

“Petroleum Industry”

Introduction: - “The oily mixture of hydrocarbons in its crude form is called petroleum.”

Origin of Petroleum: - Petroleum is of organic origin which is formed by the decomposition of animal and vegetable matter.

India alone only accounts for 0.5% of world production. In India, the chief oil field occurs in Assam (Digboi, Moran, Naharkatia) and in Gujarat (Ankleshwar, Kalol and Cambay). The discovaries of Bombay High and Ratnagiri are the most significant achievements of ONGC (Oil and natural gas commission) in recent years.

Exploration Methods: - “Searching for an oil is called exploration.”

Industrial chemistry Role: -

i) Applied science- Affect society from environmental, economic to political stability.

ii) As a social problem solver.

iii) Synthesize crop enhancing agricultural chemicals to ensure a constant and viable food supply.

iv) Eradication of deadly diseases by developing phrmaceuticals.

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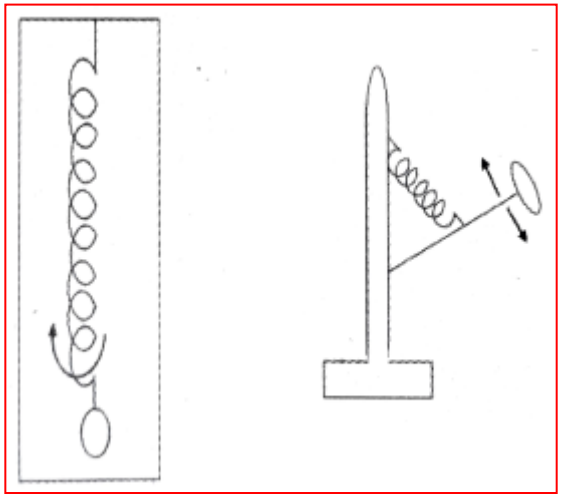
1) Gravimetric method: -

Different rocks have different densities. Igneous rocks (formed from lava) are denser than sedimentary rocks like mudstone, sandstone and shale. Sedimentary rocks bear oil. The area having sedimentary rocks underground shows a lower gravitational attraction than the normal area of oil-less igneous rocks. For measuring gravitational attraction a special instrument called a gravitymeter is used.



2) Seismic method: -

In this method, an artificial earthquake is created by exploding a heavy charge of dynamite, which produce shockwaves. The shockwaves travel faster through hard rocks than loose rocks. The time intervals between firing of the charge of dynamite and the arrival of vibration impulses on shock detectors called geophones kept at a number of places on the surface of the ground are measured and compared. The speed of shock waves is about 330m/s in sedimentary rocks which bears oil, while the speed of shock waves is about 5600 m/s in oil-less igneous rocks. Seismic analysis can determine the presence of domes and deposits at a considerable depth below the surface. Today this is the most widely used method for oil exploration.

3) Electric Method: - This method is based on the fact that oil-saturated rocks show higher electrical resistivity than water saturated rocks. In this method, the resistivity's of various rocks are measured by means of one or more electrodes lowered into bore holes. A current is passed between the electrodes and the ground surface near the well.

4) Magnetic Method: - Oil reserves are generally found in places where salt domes are present within the earth's crust. Salt domes are diamagnetic and they weaken the geomagnetic field of the earth on the surface. The magnetometer measures the magnetic gradient. From the distortion of the gradient, salt deposits are located. The magnetometer can be installed in airplanes or helicopters. The time required for survey in magnetic method is very short.

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Nature of Petroleum: - Crude petroleum is complex mixture made up of 1000 of compounds including gases, liquids and solids, which ranging from methane to asphalt. Since, composition of petroleum varies from place to place; it also varies greatly in colour and consistency. Its colour varies from white to amber to a greenish brown to black. It is foul smelling. It may be of low viscosity or so viscous as to be nearly immobile. Its specific gravity lies between 0.83 to 0.97 gm/cc.

Composition of Petroleum (Crude oil): -The crude petroleum mostly consists of hydrocarbons & small % of Oxygen, Sulphur and Nitrogen compounds. The average composition shows: C = 83 to 87%, H =11 to 14%, and (O_2, N_2, S) = 0 to 4%.

Several thousand organic compounds have been estimated to be present in crude oil. Compounds containing upto four carbon atoms are generally gases, those containing 5 to 16 carbon atoms are generally liquids and those containing 17 or more carbon atoms are generally solids. The classes of compounds occurring in petroleum are as follows:

1) Paraffin Hydrocarbons: - (C_nH_{2n+2}): These are saturated hydrocarbons including straight chain and branched chain paraffin's and may be gas, liquid or solid (Wax) depending on their molecular weight and structure. e. g. n-hexane, n-heptane, 2,3 dimethyl pentane, methyl hexane.

2) Cycloparaffins (Naphthene hydrocarbons): - Their general formula is C_nH_{2n}. These are saturated hydrocarbons possessing a ring structure generally containing 5 to 7 carbon atoms in the ring. e. g. Cyclohexane, Methyl cyclohexane.

3) Olefins: - General formula C_nH_{2n} for mono-olefins and C_nH_{2n-2} for di-olefins. These are unsaturated hydrocarbons containing one or more double bonds in their structure. These compounds are found only in traces in crude oil as they are highly reactive. These are formed during cracking. e. g. Ethylene, propylene.

4) Aromatic hydrocarbons: - General formula C_nH_{2n-6}. These compounds contain benzene ring. Many aromatics are formed by refining processes. e. g. Benzene, Toluene, Xylene, etc.

5) Polycyclic hydrocarbons: - These compounds contain more than one ring in their structure. e. g. Naphthalene.

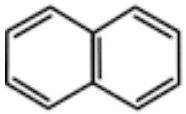
6) Sulphur compounds: - Sulphur is generally found in petroleum in the combined form in amounts upto 6%. e. g. H_2S, Thiophenes, Mercaptans, etc.

7) Nitrogen compounds: - Its nitrogen occurs in the form of pyridines, quinolines, indoles, pyrroles, etc.

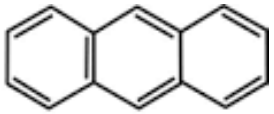
8) Oxygen compounds: - Oxygen occurs in combined form in alcohols, phenols, resins and organic acids.

9) Inorganic compounds: - These include the salt, clay and sand. These are associated with the crude oil during its passage through the oil-bearing strata.

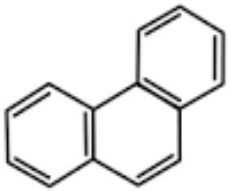
Polycyclic hydrocarbons: -



naphthalene

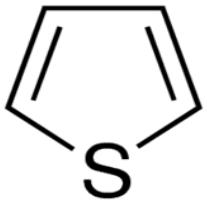


anthracene

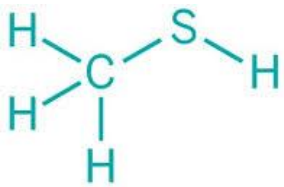


phenantherene

Sulphur compounds: -

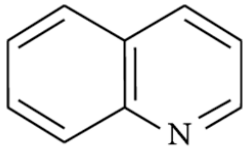


Thiophene

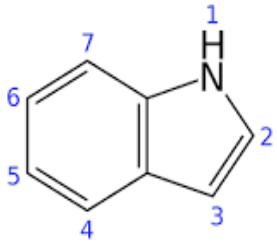


Methyl mercaptan

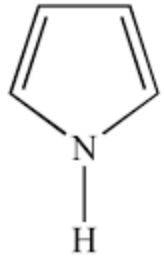
Nitrogen compounds: -



Quinoline



Indole



Pyrole

Refining of crude petroleum: - "The continuous fractional distillation of the crude oil into different useful fractions by removal of undesirable impurities is called refining of petroleum."

The function of oil refinery is to produce economically, the quality and quantity of oil products. Refining involves two major processes, separation and conversion. Refining operations are:-

1) Desalting of crude oil: - Crude oil contains number of inorganic impurities which are harmful to the operation of refinery units. e. g. Chlorides reacts with H_2O to produce corrosive HCl. Sand may cause clogging of the distillation equipment. Hence, it is very essential to remove the salts present in crude oil before subjecting it to distillation. This is carried out either by chemical or electrical desalting.

2) Distillation of crude oil: - Crude oil is separated into different fractions by distillation:

Single stage distillation: - (Topping or Skimming i.e. distillation at near atmospheric pressure): The distillation column is a steel cylinder about 30 meters high and 3 meters in diameter. At a distance of 30 cm, horizontal plates called trays are fitted inside the column. In each tray, there are holes. Each hole is fitted with a short tube, with a bubble caps as shown in fig.2.

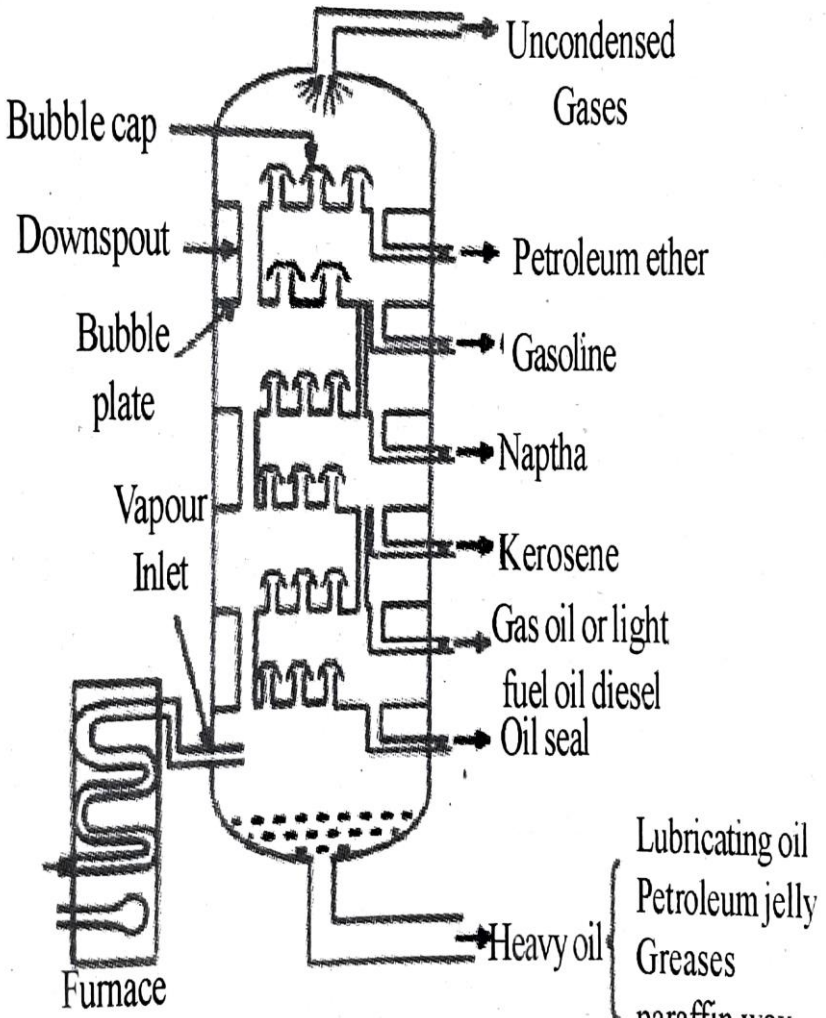
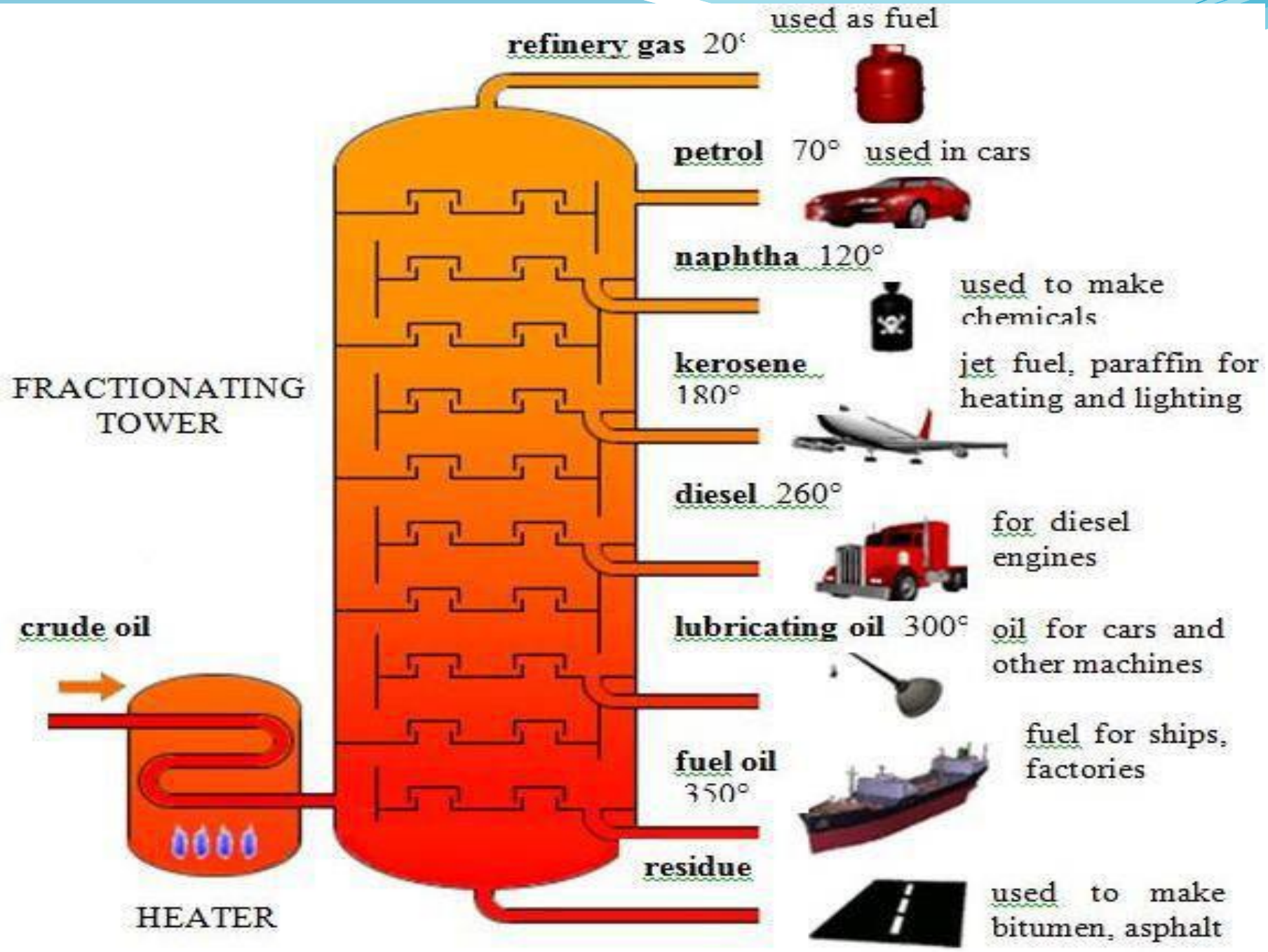
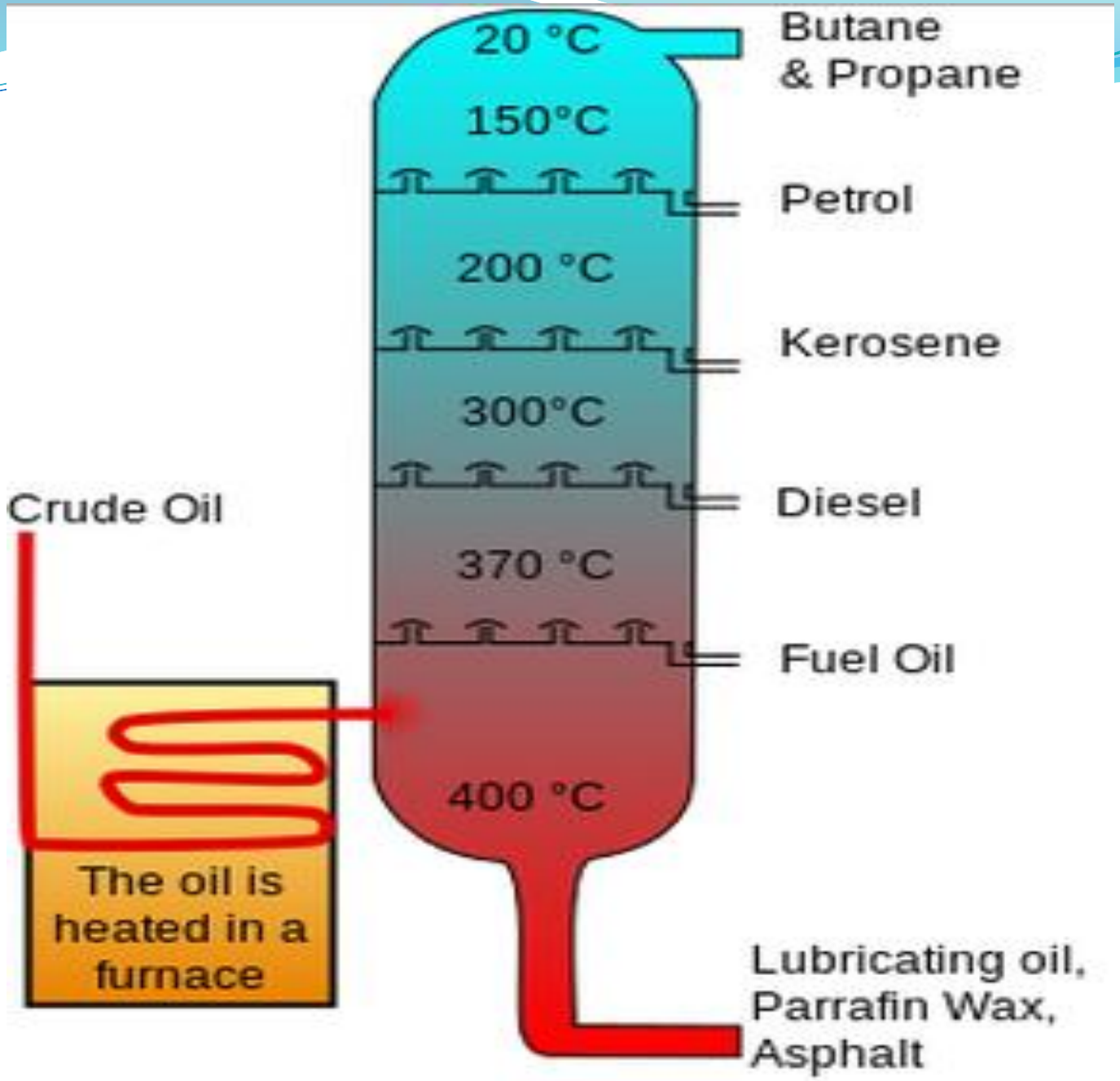


Fig. Distillation of Petroleum


used as fuel
refinery gas 20°
petrol 70° used in cars
naphtha 120°
used to make chemicals
kerosene 180°
jet fuel, paraffin for heating and lighting
FRACTIONATING TOWER
diesel 260°
for diesel engines
crude oil
lubricating oil 300°
oil for cars and other machines
fuel for ships, factories
fuel oil 350°
residue
used to make bitumen, asphalt
HEATER


20 °C
Butane
& Propane
150°C
Petrol
200 °C
Kerosene
300°C
Diesel
370 °C
Fuel Oil
400 °C
Crude Oil
The oil is heated in a furnace
Lubricating oil, Parrafin Wax, Asphalt

The desalted crude oil is heated in a furnace at about 400-430^{0}c and then introduced through the pipe at the bottom of the column. Components like tar and asphalt do not vaporize at this temperature and hence they settle at the bottom of the column. As the hot vapours rise, they begin to cool and condense into fractions, according to their boiling points. The lowest boiling fraction leaves from the top of the column, while, the highest boiling will be taken out from the bottom. Desired products are withdrawn as side streams at appropriate points on the column. When excess liquid is accumulated in any tray, it begins to trickle down to the lower tray. The bubble caps are so prepared that the hot gases while rising up, heat the accumulated liquid in the tray.

The fractions obtained from distillation are not completely pure. Further purification is necessary. The different fractions are further refined to give a variety of useful products as given below;

Fraction	Boiling range	Approximate composition	Uses
1) Uncondensed gas	0-30^{0}c	C_1-C_4	Domestic or industrial fuel (LPG)
2) Petroleum ether	30-70 ^{0}c	C_5-C_7	As a solvent
3) Gasoline (Petrol)	70-90 ^{0}c	C_6-C_8	Motor fuel, dry cleaning, etc.
4) Light petroleum	90-120 ^{0}c	C_6-C_8	As a solvent, dry cleaning, etc.
5) Kerosene oil	150-300 ^{0}c	C_{10}-C_{18}	AS fuel, as an illuminant
6) Diesel oil	250-320 ^{0}c	C_{15}-C_{18}	Diesel engine fuel
7) Heavy oil	320-400 ^{0}c	C_{17}-C_{30}	To obtain petrol by cracking
8) Paraffin wax	On cooling	C_{20} and above	In ointment, candles, shoe polish, Vaseline, etc.
9) Lubricating oil	350-400 ^{0}c	----------	As lubricant
10) Petroleum jelly	--------	---------	Cosmetics, lubricant in medicine
11) Asphalt	Above 400 ^{0}c	C_{30} & above	Road making, waterproofing, paints

Octane number: - The efficiency of petrol (gasoline) is indicated by octane number. The octane number may be defined as "The percentage of iso-otane in a mixture of iso-octane and n-heptane."

Octane rating of a fuel may be defined as the % by volume of iso-octane (2,2,4-trimethyl pentane) in the mixture of iso-octane and n-heptane. Iso-octane has octane number 100, while, n-heptane has octane number zero.

e.g. Petrol having an octane number 60, behaves like a mixture of 60% iso-octane and 40% n-heptane. The value of octane number depends upon the structure of the hydrocarbons.

i) Straight chain hydrocarbons have very low value of octane number. The value decreases further with increases in the length of the carbon chain.

ii) Branching of the hydrocarbon chain increases the value of octane number.

iii) The introduction of multiple bonds (double or triple bond) increases the value of octane number.

iv) Aromatic hydrocarbons have generally very high octane number.

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The octane number of petrol used for automobile is 74 and is known as regular gasoline. Gasoline having octane number 81 or more is called premium gasoline. Petrol of octane number 75-85 and still lower are used in India, whereas, in USA gasoline of octane number 90-110 is very commonly used. Hydrocarbons like 2,2,3 trimethyl pentane has octane number of 116 and it is the best fuel used in an internal combustion engine. An aviation gasoline generally has an octane number higher than 100. For aircraft fuel of octane number as high as 150 is required. The hydrocarbon 2,2,3-trimethyl butane (Triptane) is superior than iso-octane. The octane number of triptane is 124.

An alternating method to increase the octane number of gasoline is by mixing some foreign materials like tetraethyl lead.

Knocking: - “The preignition of fuel in the cylinder, ahead of flame is called knocking.”

Self ignition of a gasoline-air mixture in the cylinder of an internal combustion engine due to heat of compression is termed knocking, which is a reference to the characteristic sound emitted. During knocking, most of the energy that would have changed into power under normal conditions is given out and wasted in the form of heat energy. Knocking also increases the wear and tear of the engine. When the compression ratio of a motor is relatively high, the fuel can detonate in the cylinder causing noise (knock), powerloss and ultimately engine damage.

Antiknock compounds: - Knocking can be decreased by adding certain compounds to the fuel and these compounds are known as anti-knock compounds. They increase the octane number. The anti-knock compound retards the rapid combustion of gasoline vapour in the cylinder. The best known anti-knock compound is tetraethyl lead $[Pb(C_2H_5)_4]$ TEL. It is a volatile liquid and poisonous in nature. In order to prevent the deposition of lead in engines, ethylene dichloride or ethylene dibromide are added to anti-knock composition. They convert the lead oxide formed into volatile lead chloride or bromide which passes out with the exhaust gases. The anti-knock mixture is 63% TEL, 26% ethylene dibromide, 9% ethylene chloride and 2% a dye to give a colour. The maximum limit of TEL legally permitted is 3 ml/gallon.

The tendency of most of the countries is to use unleaded petrol, due to the toxicity of lead. Lead has to disappear from gasoline in future because of its poisoning effect to environment due to air pollution. Other anti-knock compounds in use are TML(Tetramethyl lead $Pb(CH_3)_4$) and AK-33 (Cyclopentadienyl manganese carbonyl), Iodine(I_2), Aniline, Selenium chloride etc.

Cetane number: -The ignition quality of a diesel fuel is indicated by cetane number. It is defined as "The percentage of cetane (n-hexadecane $C_{16}H_{34}$) in a mixture of cetane and α-methyl naphthalene."

In diesel engines, air is compressed and its temperature rises and the diesel fuel injected into the engine is ignited by the hot air. The capability of diesel fuels for self ignition is measured in terms of cetane number (It is the index of ignitability of diesel fuel).

Cetane burns rapidly and has been assigned cetane number equal to 100 and α-methyl naphthalene has been assigned cetane number equal to zero. The cetane number depends on the composition of fuel. It is found that, in diesel engine, the straight chain hydrocarbons are considered to be better fuel than the branched chain hydrocarbons and aromatics. The highest cetane number is shown by paraffin hydrocarbons, a lower cetane number by naphthanes and the lowest cetane number by aromatic or benzene hydrocarbons. Alkyl nitrates improve cetane number. Most of the engines requires fuel with cetane number above 45.

Gasohol (Petrohol): - It is the mixture of petrol and alcohol. The fermented alcohol is used as an octane booster for gasoline. Small amount of alcohol is mixed with gasoline to form gasohol. Corn fermentation is the source of 82% of all ethanol used in gasohol. A 10% alcohol and 90% gasoline blend is used for automobile fuel.

The use of fermented alcohol in motor fuels has been the subject of much controversy. Proponents argue that, alcohol made from renewable biological materials can be used to make India less dependent upon foreign sources of petroleum. The goal of nation is to displace 10% of the nations gasoline with gasohol fuels.

Wood, cellulose and other starchy waste can be fermented into alcohol. But, one of the chief difficulties in using alcohol in gasoline is that the usual 95% alcohol is not miscible with gasoline. Only absolute or 99.5% alcohol is miscible with gasoline for gasohol. This requires costly extra processing, because simple distillation will not produce ethanol above 95% concentration. So far absolute alcohol continues to cost more to produce than gasoline. However, because of Government subsidies the cost of fermentation alcohol is now low enough for it to be competitive with petroleum based synthetic alcohol. Once mixed, alcohol-gasoline mixtures separate if any water enters the system, and this is almost impossible to prevent.

Power alcohol: - Power alcohol is a mixture of 80% Petrol + 20% Ethanol + Small quantity of Benzene. It is used for the generation of power**.** The energy liberated by burning one litre of 100% alcohol is about 23MJ. The various important raw materials used for the manufacture of power alcohol are saccharine materials (such as molasses, sugar beets, sugar canes, etc.), Starchy materials (such as starch potatoes, cereal grains, etc.), cellulosic materials (such as sulphite liquor from paper mills) and hydrocarbon gases.

Power alcohol can be used as fuel when blended with petrol in internal combustion engines. Blends containing upto 25% of alcohol with petrol has been used as motor spirit. Industrial alcohol containing 95% alcohol and 5% water can also be blended with petrol, using another blending agent such as benzene, ether or tetralin, etc. Industrial alcohol is not soluble in petrol without the blending agent.

Manufacture of petrol from Coal by Bergius method: -

Raw materials: Coal, H_2, Heavy oil, Sn or Ni-oleate catalyst.

Reaction: $nC + (n+1)\ H_2 \rightarrow C_nH_{2n+2}$

Flowsheet:

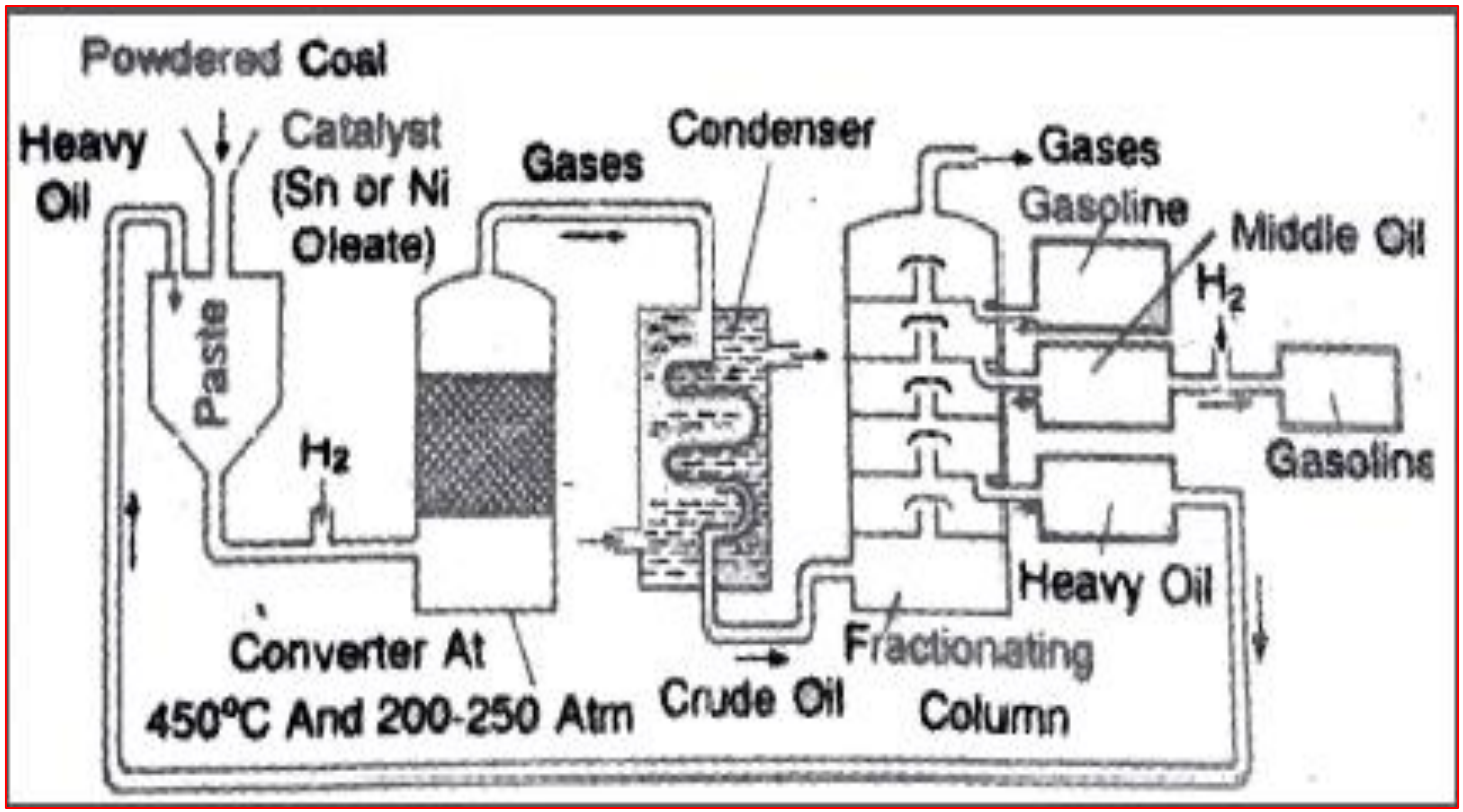

Figure 3: Manufacture of petrol by Bergius Method

Procedure: - The coal is well powdered and is mixed with heavy oil to form a paste. The paste then heated to 450^0c in a current of hydrogen under a pressure of 200-250 atms. as shown in fig.3. Some organic compounds of tin are used as catalyst. Hydrogenation of coal takes place resulting in the formation of hydrocarbons which are similar to petroleum. The liquid thus formed is refined and one of the fractions obtained is the petrol.

A typical gasoline fraction contains 74% paraffins, 22% aromatics and 4% olefins. About one tone of gasoline may be obtained from 1.5-2.0 tones of coal. Friedrich Bergius was awarded Nobel Prize in Chemistry in 1931 for this process.

Cracking processes: - Natural gasoline and straight run gasoline obtained from petroleum are quite insufficient to meet the demand for gasoline as a result of rapid rise in number of automobiles. This deficiency can be fulfilled with the production of gasoline from less volatile fractions of petroleum by means of controlled pyrolysis or cracking. Hence, "The process of breaking of large and relatively non-volatile hydrocarbon fractions of petroleum into mixture of smaller molecules of desired volatility by suitable treatment is called cracking."

or "The cracking is defined as the decomposition or pyrolysis of larger hydrocarbon molecules into smaller fragments under controlled conditions, so as to produce a maximum yield of the desired product gasoline."

Cracking is the process used to convert heavy petroleum fractions into lighter more valuable fractions. A variety of products obtained from cracking are Carbon, gasoline, gas oil, etc. The main objective of cracking is the production of gasoline. Gasoline obtained by cracking of gas oil is called cracked gasoline.

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Thermal cracking: - "Breaking of larger molecules into smaller molecules by application of heat alone without catalyst is known as thermal cracking."

Thermal cracking is a complex process consisting of various chemical reactions induced by heat. A large molecule is sensitive to heat, which breaks down into smaller fragments. In thermal cracking, the charge is heated to 500-550^{0}c in a pipe heater under a pressure of about 100 psi.

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

Paraffin Olefin

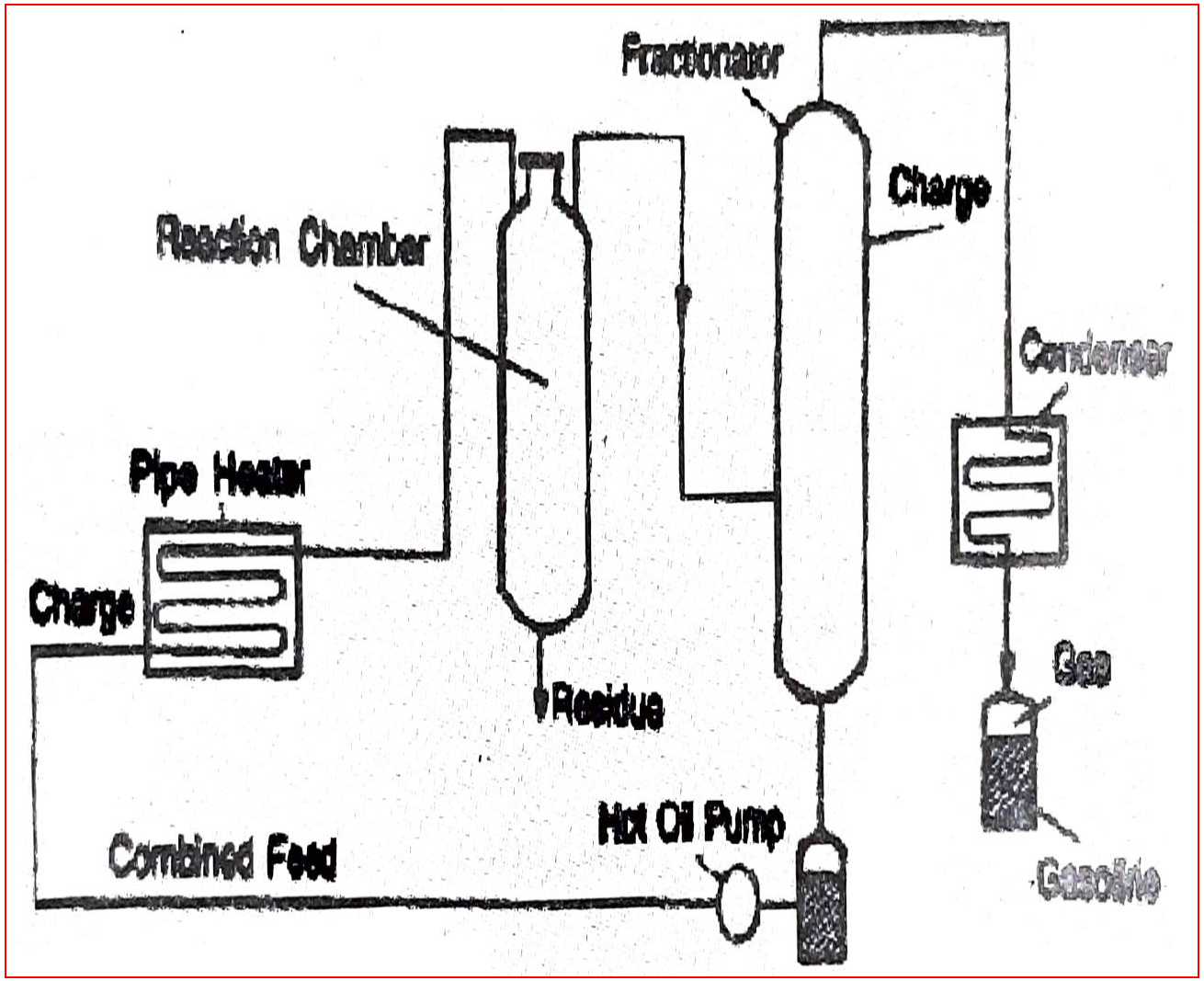
(Saturated) (Unsaturated)

The lower molecules of paraffin and olefin thus formed may be further decomposed. They can even be fully cracked to carbon and H_2 at a certain high temperature.

$$CH_4 \rightarrow C + 2H_2$$

The charge is introduced in the fractionator in which it is fractionated along with the cracked products from the reaction chamber. The vapours of gas and gasoline go out from the fractionators at the top. These vapours are condensed in a condenser to obtain gas and gasoline. The liquid products from the fractionators pass on to the hot oil pump which transfer these products to cracking tubes from where the heated products go to the reaction chamber. Here cracking reactions are allowed to complete. The vapour products go to the fractionators, where they are fractionated into mixture of gas and gasoline. The coke left or deposited in the reaction chamber is periodically withdrawn.

Figure 4: Thermal Cracking



Catalytic Cracking: - "Decomposition of larger hydrocarbon molecules into smaller molecules in presence of a catalyst is known as catalytic cracking."

Two types of catalysts used in catalytic cracking are natural and synthetic.

The natural catalyst is composed of silica and alumina, while, synthetic catalyst contains crystalline zeolites.

Catalytic cracking is more popular than thermal cracking, because:

1) The gasoline obtained by this method has more octane number (= 80) than obtained by thermal cracking (Octane number =72).

2) Yields in catalytic cracking consist of less gas, less gum, coke and gum forming compounds than thermal cracking.

3) Catalyst lowers the activation energy of reaction and as a result rate of catalytic cracking increases.

4) It has greater ability to tolerate high sulphur feed stocks.

5) Gasoline obtained by catalytic cracking contains low % of olefins and higher % of isoparaffins and aromatic hydrocarbons.

Hydrocracking: -This process is a combination of catalytic cracking and catalytic hydrogenation at high pressures using dual function catalysts. e.g. Nickel on silica-alumina. Lower operating temperatures can be used. Since, hydrogen is available; the alkenes produced by catalytic cracking are simultaneously converted into alkanes.

C_7H_{15}-$C_{15}H_{30}$-C_7H_{15} + H_2 → C_7H_{16} + C_7H_{16} + $C_{15}H_{32}$

Heavy gas oil — St. chain gasoline — Branched chain gasoline — Recycle stock

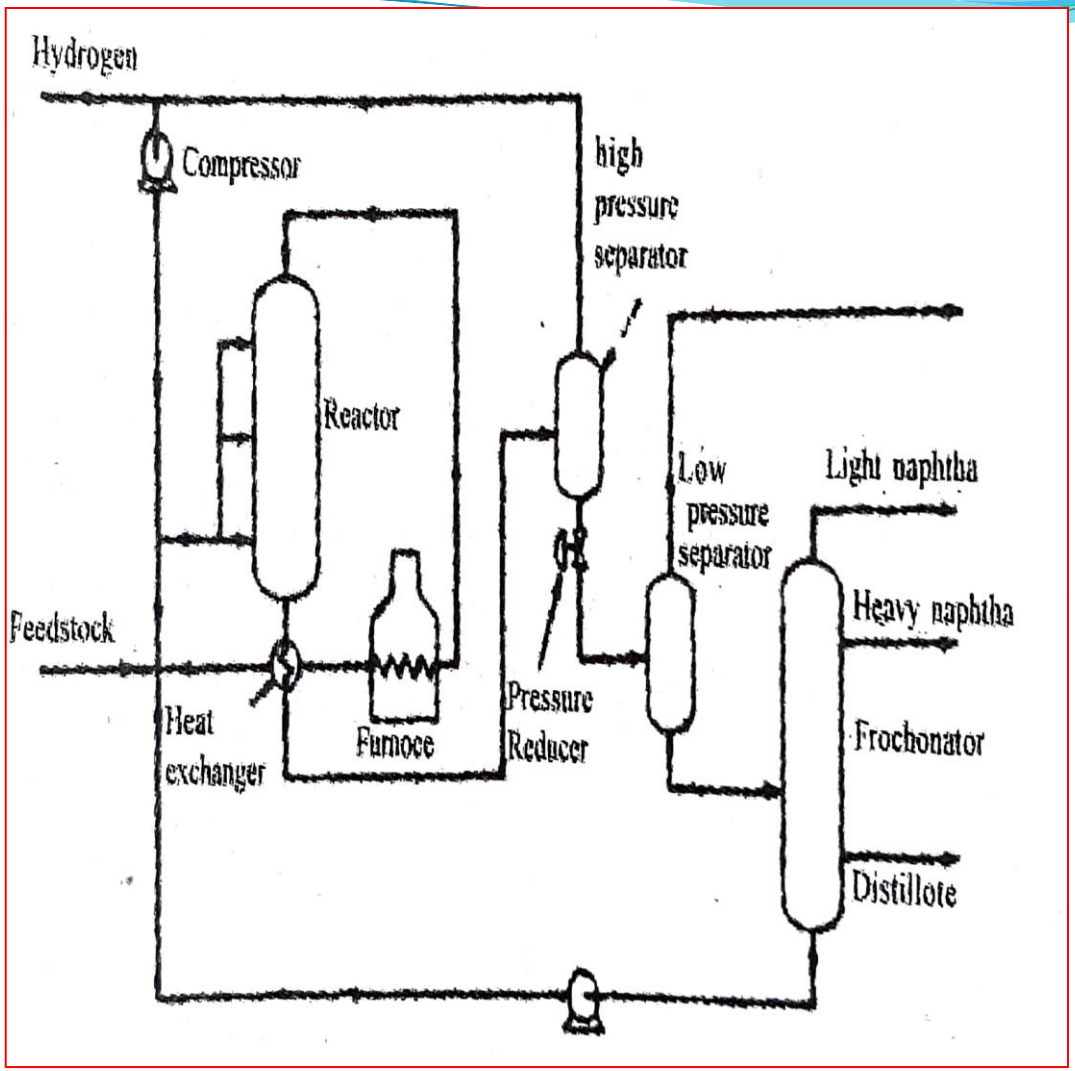


Figure 5: Hydrocracking

Petroleum Producing Countries in the World: -

Petroleum oil is now obtained from wells situated in many parts of the world. Petroleum resources are not distributed evenly around the world. Despite the rapid increase of alternative energy sources, oil production continues to play an important role in the global economy. According to recent data collected by the Energy Information Administration (EIA), total world oil production in 2019 averaged 80,622,000 barrels per day.

Approximately 68% came from the top ten countries. In 2019, from the 10 larger oil producer countries, the largest oil producing country of the world is U.S.A., which produces more than 19% of the total world production. The other major oil producing countries are Saudi Arabia (12%), Russia (11%), Canada, China and Iraq (5% each), United Arab Emirates and Brazil (4% each), Iran and Kuwait (3% each).

India alone only accounts for 0.5% of world production. In India, the chief oil field occurs in Assam (Digboi, Moran, Naharkatia) and in Gujarat (Ankleshwar, Kalol and Cambay). The discoveries of Bombay High and Ratnagiri are the most significant achievements of ONGC (Oil and natural gas commission) in recent years. Oil production in India comes primarily from three onshore states, Assam, Gujarat and Rajasthan, which together account for more than 96 per cent of oil from onshore fields, and from the old offshore Mumbai High Field. India imports 82% of its oil needs and aims to bring that down to 67% by 2022 by replacing it with local exploration, renewable energy and indigenous ethanol fuel.