

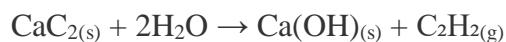
1. Processing of Crude Oil



Q.1: What is abiogenic theory of petroleum origin?

Ans: Abiogenic theory (abiotic or inorganic theory) was proposed by different scientists in the nineteenth century, the famous one of which was the Russian Chemist Dmitri Mendeleev and the French chemist Marcellin Berthelot.

The abiogenic theory of petroleum formation proposes that petroleum (crude oil) is not solely formed from the decay of organic matter but originate from inorganic processes within the Earth's mantle. This theory suggests that hydrocarbons, the primary components of petroleum, can form deep within the earth through abiogenic processes involving chemical reactions between carbon-containing compounds such as carbonates carbides, carbon dioxide etc. which may be converted to hydrocarbons & inorganic materials under high pressure & temperature conditions. Another hypothesis i.e. biogenic theory has lost ground to the dominant view that petroleum is a fossil fuel. One form of this abiogenic theory called carbide theory, proposed by Dmitri Mendeleev, postulated that metallic carbides within the earth reacted with steam (water) at high temperature forming acetylene through catalytic processes involving minerals like iron and nickel which subsequently condensed or polymerized to form heavier hydrocarbons at high pressures and temperatures. These processes occur in deep underground. in a way like in Fischer-Tropsch reaction,



This theory suggests that a full suite of hydrocarbons found in petroleum can be generated in the mantle by abiogenic processes and these hydrocarbons can migrate out of the mantle, into the crust until they escape to the surface or are trapped by impermeable strata, forming petroleum reservoirs.

Abiogenic theories also suppose that certain molecules found within petroleum, known as biomarkers, come from the microbes that the petroleum encounters in its upward migration through the earth crust. Some of them are also found in meteorites, which have presumably never contacted living material, and that some can be generated by plausible reactions in petroleum abiogenically.

Q.2: What is biogenic theory of petroleum origin?

Ans: The biogenic theory of petroleum formation is most widely accepted theory for the origin of petroleum (crude oil) and natural gas. This theory proposes that petroleum is formed from the decomposition and transformation of organic matter derived from once-living organisms, such as plankton, algae, and terrestrial plants, over millions of years.

According to biogenic theory, petroleum originated from living organisms buried deep underground over millions of years ago. The biogenic theory was first proposed in 1757 by Russian scholar Mikhail Lomonosov. The geologists believe that millions of years ago, the dead bodies of the living organisms accumulated in shallow marine water, the organic matter was partially decayed by aerobic and then anaerobic degradation. Over geological time, this partly decayed organic matter mixed with mud was buried under heavy layers of sediment. Further the organic mass was subjected to elevated temperature supplied by earth crust and high pressure, exerted by the overlain masses. This chemically changed the organic matter first into a waxy material known as kerogen during diagenesis, and then with more heat into liquid and gaseous hydrocarbons in a process known as catagenesis. Under these conditions the clay and minerals played the role of catalysts and helped in catalytic cracking of organic matter. Natural radioactivity from underground rocks (shale and sandstone) also contributed in the conversion process. A combined action of bacterial degradation, high pressure and temperature, catalysis and natural radioactivity, the organic matter consist of proteins, fats, carbohydrates etc. was slowly and gradually converted into simpler gaseous and liquid hydrocarbons which is mined as natural gas and crude petroleum today. The hydrocarbons started migration through adjacent rock layers until they become trapped beneath impermeable rocks, within porous rocks called reservoirs. Concentration of hydrocarbons in reservoirs formed oil field, from which it is extracted by drilling and pumping. Geologists often refer to an oil window which is the temperature range at that oil forms, in below the minimum temperature oil remains trapped in the form of kerogen, and above the maximum temperature the oil is converted to natural gas through the process of thermal cracking. Although this happens at different depths in different locations around the world, typical depth for the oil window might be 4-6 km. The biogenic theory is the most acceptable theory as most of the biological markers present in petroleum support this theory.

Q.3: What do you understand about migration?

Ans: Migration of hydrocarbons: "Movement of petroleum from source rock toward a reservoir or seep. Primary migration is expulsion of petroleum from fine-grained source rock, while secondary migration moves petroleum through a coarse-grained carrier bed or fault to a reservoir or seep. Tertiary migration occurs when petroleum moves from one trap to another or to a seep.

Migration is generally described as, "unknown process or group of processes that enable petroleum to move from a source to a reservoir"

Observation of Hydrocarbon migration is difficult because it occurs either too rapidly, too slowly, or elsewhere. Physical conditions responsible for hydrocarbons migration are pressure, temperature, permeability, capillarity, surface tension, molecular size, & density. The main chemical constraint is solubility of migrating hydrocarbons.

Migration Stages:

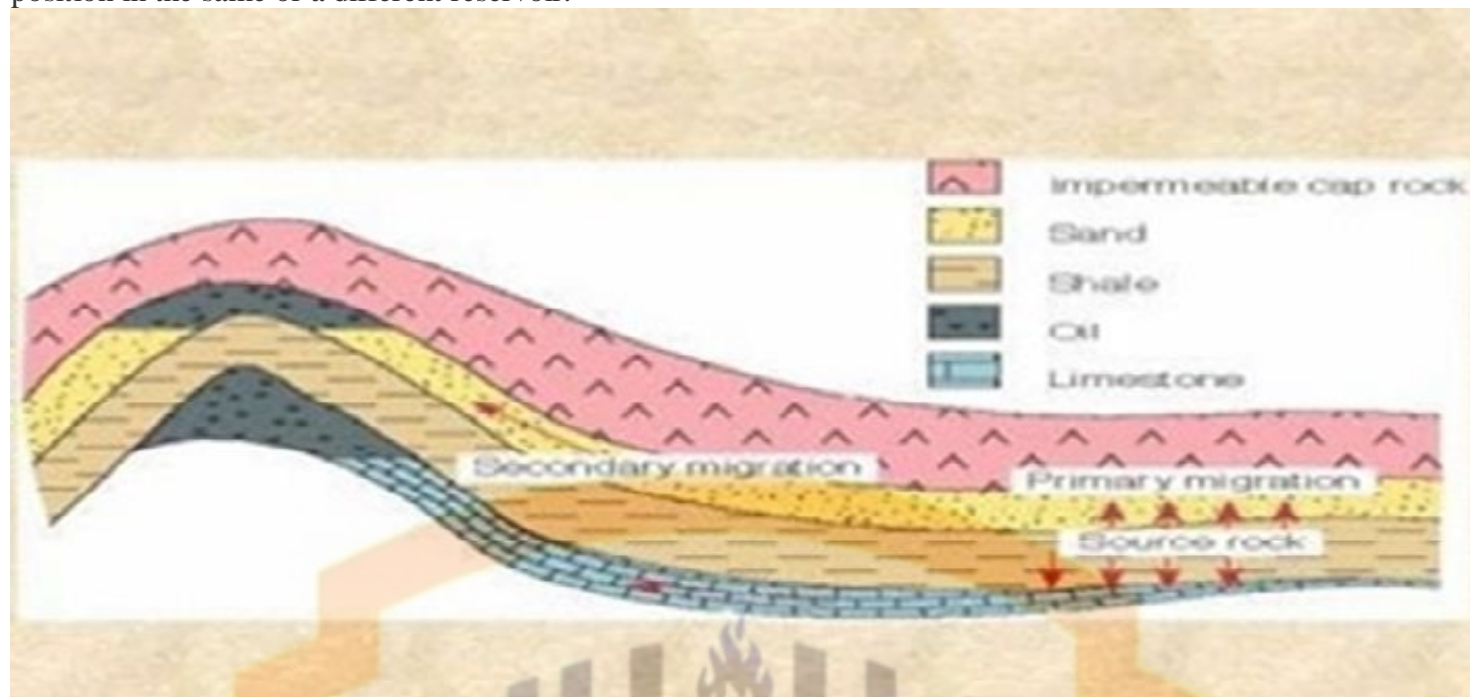
Hydrocarbon migration consists of four stages: primary, secondary, tertiary, and remigration.

Primary Migration: Primary migration is the process by which hydrocarbons are expelled from the source rock into an adjacent permeable carrier bed.

Secondary Migration: Secondary migration is the movement of hydrocarbons along a "carrier bed" from the source area to the trap. Migration mostly takes place as one or more separate hydrocarbons phases (gas or liquid depending on pressure and temperature conditions). There is also minor dissolution in water of methane and short chain hydrocarbons.

Tertiary Migration: It is a migration that occurs when petroleum moves from one trap to another or to a seep.

Remigration: Migration from one reservoir position through an intervening section into another reservoir position in the same or a different reservoir.



Q.4: Name four processes in chemical treatment of petroleum products.

Ans: Chemical treatment processes is necessary in refining petroleum products to improve their quality, performance, and to meet regulatory standards.

- | | | |
|--------------------|------------------------|---------------------|
| i) Desalting | ii) Sweetening | iii) Amine Treating |
| iv) Distillation | v) Catalytic reforming | vi) Isomerization |
| vii) Hydrogenation | viii) Alkylolation | ix) Hydro refining |

Q.5: Mention different unit processes in treatment of crude oil.

Ans: The various unit processes are employed to separate, purify, and convert the crude oil into valuable products. These unit processes include:

- | | | |
|--------------------|------------------------|---------------------|
| i) Desalting | ii) Sweetening | iii) Amine Treating |
| iv) Distillation | v) Catalytic reforming | vi) Isomerization |
| vii) Hydrogenation | viii) Alkylolation | ix) Hydro refining |
| x) Fractionation | | |

Q.6: What is octane number and how it is improved?

Ans: Graham Edger in 1927 proposed an arbitrary scale, Octane Number, to express the anti-knock properties of gasolines.

Among alkanes, n-heptane [$\text{CH}_3(\text{CH}_2)_5\text{CH}_3$] knocks severely, while 2,2,4-trimethylpentane (isooctane) $(\text{CH}_3)_3\text{CCH}_2\text{CH}(\text{CH}_3)_2$ has low knocking under identical conditions. So, n-heptane was arbitrarily assigned an octane number of zero and isooctane was arbitrarily assigned a value of 100.

By blending these two hydrocarbons in various proportions, primary reference fuels were prepared.

Thus, octane number is defined as the 'percentage by volume of isooctane in a mixture of isooctane and n-heptane blend, which has the same knocking characteristics as the gasoline sample under examination, in the same set of conditions and the same critical compression ratio in the same engine'.

e.g. a gasoline with an octane number of 90 has the same knocking characteristics as a mixture of isooctane and n-heptane containing 90% by volume of isooctane.

Automobile gasoline's have octane number ranging from 75 to 95.

Aviation gasolines have a greater knock resistance, and their octane numbers are greater than 100.

The octane number of spirit blend gasoline are computed using the relationship:

$$\text{Octane number} = \frac{[\text{power number} - 100]}{3} + 100$$

Where, power number is an arbitrary number proportional to the power being extracted by the engine.

Improvement of octane number:

Isomerization, alkylation, aromatization, reformation etc, also increase the octane number of fuel.

In the case of alkanes, the octane number increases with the number of branches in the chain and decreases with increase in chain length.

2,2,4-trimethylbutane (triptane) has octane number 124.

Alkenes have higher octane number than alkanes containing the same number of carbon atoms.

Cycloalkanes have a higher-octane rating than alkanes with same number of carbon atoms. Cyclopentane & Cyclohexane has octane number 85 & 77 respectively.

The highest-octane numbers are associated with the aromatic hydrocarbons. Benzene has octane number of 106. Ethyl alcohol has octane number of 95.

To increase the octane number of ordinary gasoline, ethyl fluid is added, and it is a mixture of TEL (tetraethyl lead) 60%, ethylene dibromide (26%), ethylene chloride (9%), and a red dye (2%). 1-3 mL of ethyl fluid is sufficient for one gallon of petrol.

Engine efficiency & octane number:

An ordinary engine requires per horsepower 230 c.c. gasoline having octane number 100. But same engine will consume 325 c.c. gasoline having octane number 73.

Q.7: What are products of refining?

Ans: Petroleum refining (oil refining or petroleum processing) is the transforming of crude oil into various useful products such as gasoline, diesel, jet fuel, lubricants, and petrochemicals. Crude oil is a complex mixture of hydrocarbons, along with small amounts of impurities of compounds containing sulfur, nitrogen, and metals.

The products obtained from petroleum refining can be broadly categorized into three main categories:

- i) **Fuel products:**
 - a) **Gasoline:** Gasoline is one of the primary products of petroleum refining and is used as fuel for automobiles.
 - b) **Diesel:** Diesel fuel is another important product used primarily in diesel engines for transportation and in various industrial applications.
 - c) **Jet Fuel:** Jet fuel is specifically designed for use in aircraft engines.
 - d) **Kerosine Oil:** Kerosene is used as a fuel in lamps, stoves, and heaters.
 - e) **Liquified Petroleum gas (LPG):** LPG consists of propane and butane and is used for heating, cooking, and as fuel for vehicles.
- ii) **Non-Fuel Products:**
 - a) **Lubricating Oils:** These oils are used to reduce friction and wear between moving parts in machinery and engines.
 - b) **Bitumen:** Bitumen, also known as asphalt, is used in road construction and roofing materials.
 - c) **Paraffin Wax:** Paraffin wax is used in candles, cosmetics, and as a sealing agent in food packaging.
 - d) **Solvents:** Petroleum refining produces various solvents used in cleaning, paints, and other industrial applications.
 - e) **Petrochemical Feed Stock:** Some fractions obtained from petroleum refining serve as feedstocks to produce various chemicals and plastics.
- iii) **Petrochemicals:**
 - a) **Ethylene:** It is used to produce plastics, including polyethylene.
 - b) **Propylene:** It is used in the manufacture of plastics, synthetic fibers, and various chemical products.
 - c) **Benzene, Toluene, Xylene (BTX):** These are used in the production of various chemicals, including plastics, synthetic fibers, and pharmaceuticals.

Q.8: Why is isomerization of light naphtha carried out?

Ans: "Isomerization is the process in which light straight chain paraffins (C6, C5 and C4) of low octane number are transformed with proper catalyst into branched chains with the same carbon number and high-octane numbers".

The hydrotreated naphtha is fractionated into heavy naphtha between 90–190 °C which is used as a feed to the reforming unit.

Light naphtha containing upto C5 is used as a feed to the isomerization unit at 80 °C.

There are two reasons for this fractionation:

- i) the first is that light hydrocarbons tend to hydrocrack in the reformer.
- ii) The second is that C6 hydrocarbons tend to form benzene in the reformer. Gasoline specifications require a very low value of benzene due to its carcinogenic effect.

Q.9: Name any four fractions with carbon range obtain from fractional distillation of petroleum.

Ans: Following are the main fractions obtained by fractional distillation of petroleum.

Sr. #	Fraction	B.P. Range °C	Composition	Uses
1	Natural gas	Up to room temperature	CH ₄ -C ₄ H ₁₀	Fuel, Petrochemicals
2	Straight run Gasoline Refractionated to yield	40-200		
a)	Petroleum ether	40-80	C ₄ H ₁₂ -C ₆ H ₁₄	Solvent
b)	Gasoline or Petrol	80-200	C ₄ H ₁₀ mostly C ₁₃ H ₂₈ C ₆ H ₁₄ -C ₈ H ₁₈	Motor fuel; solvent; dry cleaning
3	Kerosene	200-300	C ₁₁ H ₂₄ -C ₁₆ H ₃₄	Illuminant; fuel for stoves, for making oil gas
4	Gas oil or Diesel oil	300-400	C ₁₆ H ₃₄ -C ₁₈ H ₃₈	Fuel for diesel engines, for conversion to gasoline by cracking
5	Residual Oil-Refractionated under vacuum to give:	Above 400		
a)	Lubricant oil	Viscous liquids	C ₁₈ H ₃₈ -C ₂₀ H ₄₂	Lubrication
b)	Paraffin wax (on cooling)	M.P. 50-60	C ₂₀ H ₄₂ -C ₃₀ H ₆₂	Ointments; candles, vaseline, wax paper.
c)	Non-volatile Residue; Asphalt or Petroleum coke	Solids		Paints; road surfacing;

Q.10: Explain the term isomerization.

Ans: Isomerization Process: “Isomerization is the process in which light straight chain paraffins of low octane number (C6, C5 and C4) are transformed with proper catalyst into branched chains with the same carbon number and high-octane numbers”.

The hydrotreated naphtha is fractionated into heavy naphtha between 90–190 °C which is used as a feed to the reforming unit.

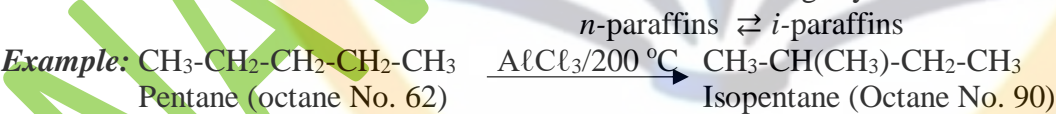
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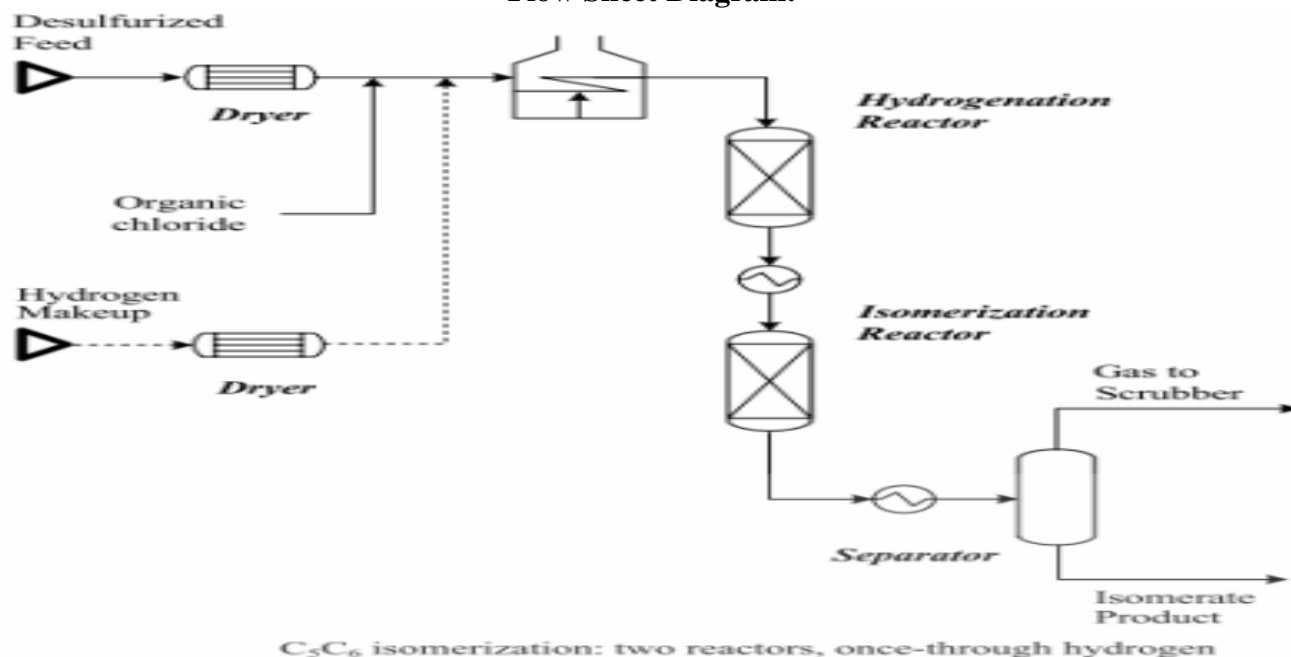
- iii) the first is that light hydrocarbons tend to hydrocrack in the reformer.
- iv)The second is that C6 hydrocarbons tend to form benzene in the reformer. Gasoline specifications require a very low value of benzene due to its carcinogenic effect.

Isomerization Catalysts: The most common catalyst for isomerization of n-butane is platinum (Pt) on alumina promoted by chloride. The high activity of this catalyst allows operation at relatively low temperature. This is beneficial because the reaction is controlled by equilibrium, at low temperature, equilibrium favors isobutane. Pt/alumina catalysts can’t be regenerated, and they are highly sensitive to water and other contaminants. In units that isomerize n-pentane and n-hexane, the reactions are catalyzed either by Pt/alumina or Pt on zeolite. The zeolite catalysts require higher temperatures, but they are less sensitive to water. As with butane isomerization, the reactions are controlled by equilibrium, so lower reaction temperatures favor branched isomers.

Isomerization Reactions: Isomerization is a reversible and slightly exothermic reaction:



Flow Sheet Diagram:



Q.11: What is the role of sweetening process in crude oil refining?

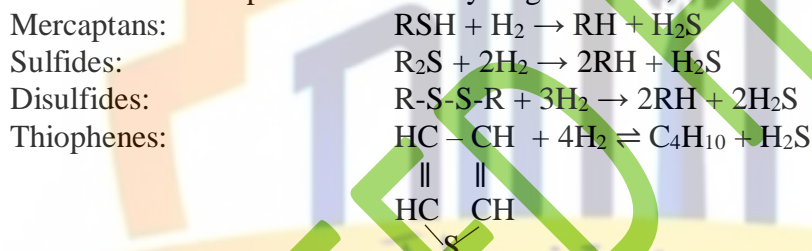
Ans: The sweetening process in crude oil refining is the removal of sulfur compounds, particularly hydrogen sulfide (H₂S), from petroleum products. The role of sweetening is due to:

1. Sulfur compounds and their derivatives in crude oil causes air pollution on burning forming sulfur dioxide (SO₂), which can lead to acid rain.
2. Sulfur compounds, especially hydrogen sulfide, are highly corrosive to refining equipment and pipelines. The sweetening process protects the infrastructure of refinery from damage, extending the life of the equipment and reducing maintenance costs.
3. Hydrogen sulfide is highly toxic and poses significant health and safety risks to workers in the refinery.

Common Sweetening Processes are:

a) Hydrotreating b) Amine Treating c) Claus Process d) Oxidative Sweetening

a) Hydrotreating: It involves treating the crude oil with hydrogen in the presence of a catalyst. The hydrogen reacts with sulfur compounds to form hydrogen sulfide, which is then removed.



b) Amine Treating: It involves use of amine solutions to absorb hydrogen sulfide from the gas or liquid streams in the refinery. e.g. $\text{RNH}_2 + \text{H}_2\text{S} \rightarrow \text{RNH}_3^+ + \text{HS}^-$ $\text{RNH}_2 + \text{HS}^- \rightarrow \text{RNH}_3^+ + \text{S}^{2-}$
 RNH₂ represents a primary or secondary amine. e.g. $\text{HN}(\text{CH}_2\text{-CH}_2\text{-OH})_2$

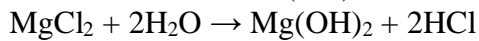
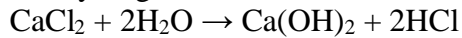
Q.12: Why desalting of crude oil is important?

Ans: The brine in the form of very fine water droplets emulsified in the crude oil. Salts in the crude oil are mostly in the form of dissolved salts in fine water droplets emulsified in the crude oil. This is called a water-in-oil emulsion, where the continuous phase is the oil, and the dispersed phase is the water. The water droplets are so small that they cannot settle by gravity. The salts can also be present in the form of salts crystals suspended in the crude oil. The salt content expressed as NaCl, of the crude oil measured in pounds per thousand barrels (PTB) can be as high as 2000. Desalting of crude oil is an essential part of the refinery operation. The salt content should be lowered to between 5.7 and 14.3 kg/1000 m³ (2 and 5 PTB).

Poor desalting has the following effects:

- a) Salt in crude oils is a major cause of the plugging of exchangers and coking of pipe still tubes.
- b) Salts deposit inside the tubes of furnaces and on the tube bundles of heat exchangers creating fouling, thus reducing the heat transfer efficiency.
- c) Corrosion of overhead equipment.
- d) The salts carried with the products act as catalyst poisons in catalytic cracking units.

Types of Salts in Crude Oil: Salt are mostly magnesium, calcium and sodium chlorides. These chlorides, except for NaCl, hydrolyze at high temperatures to hydrogen chloride:

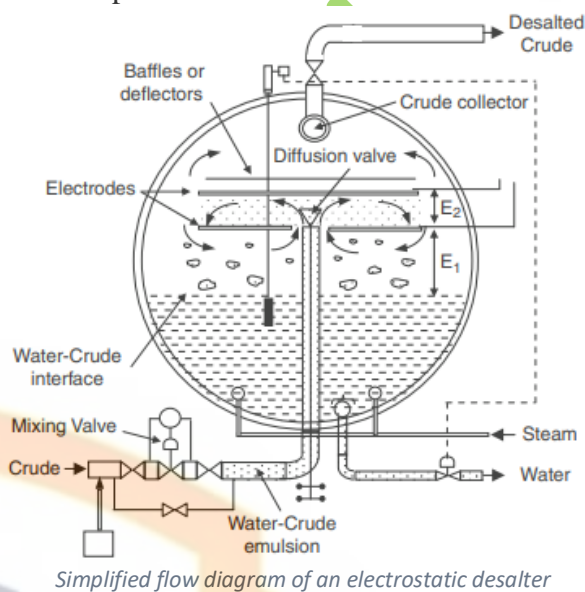


NaCl does not hydrolyze. Hydrogen chloride dissolves in the overhead system water, producing hydrochloric acid, an extremely corrosive acid.

Desalting Process: To remove the salts from the crude oil, the water-in-oil emulsion has to be broken, thus producing a continuous water phase that can be readily separated as a simple decanting process. **Water washing:** Water is mixed with the incoming crude oil through a mixing valve. The water dissolves salt crystals and the mixing distribute the salts into the water, uniformly producing very tiny droplets. Demulsifying agents are added at this stage to aid in breaking the emulsion by removing the asphaltenes from the surface of the droplets. **Heating:** The crude oil temperature should be in the range of 48.9–54.4 °C (120–130 °F) **Coalescence:** The water droplets are so fine in diameter in the range of 1–10 mm that they do not settle by gravity. Coalescence produces larger drops that can be settled by gravity. This is accomplished through an electrostatic electric field between two electrodes. The electric field ionizes the water droplets and orients them so that they are attracted to each other. Agitation is also produced and aides in coalescence. **Settling:** The water droplets settle after coalescence.

Description of Desalter: A typical desalter contains two metal electrodes as shown in figure. A high voltage is applied between these two electrodes. For effective desalting the electric fields are applied as follows: A high voltage field called the ‘secondary field’ of about 1000 V/cm between the two electrodes is applied. The ionization of the water droplets and coalescence takes place here. A primary field of about 600 V/cm between the water–crude interface and the lower electrode is applied. This field helps the water droplets settle faster. The desalter of this design achieves 90% salt removal.

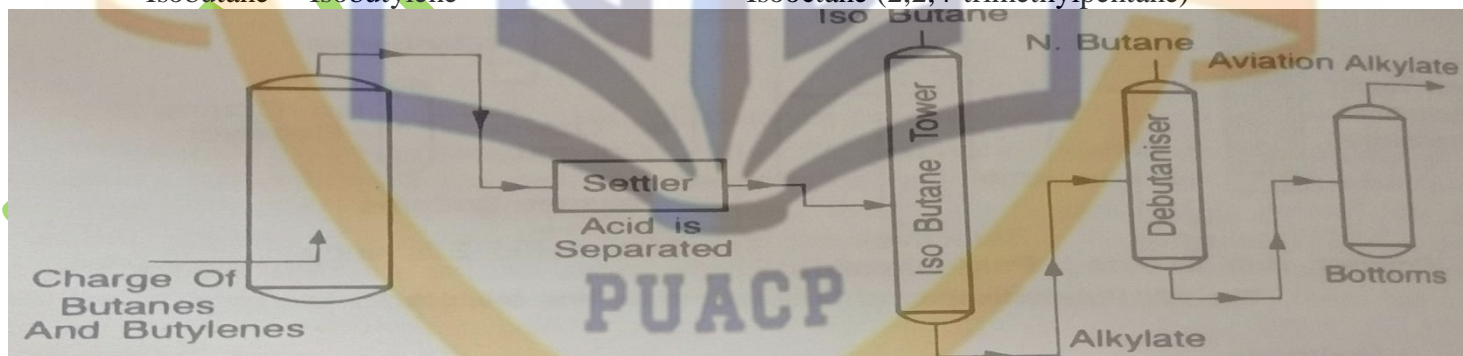
However, 99% salt removal is possible with two-stage desalters as shown in the figure. A second stage is also essential since desalter maintenance requires a lengthy amount of time to remove the dirt and sediment which settle at the bottom. Therefore, the crude unit can be operated with a one stage desalter while the other is cleaned.



Q.13: Explain the term “alkylation” in petroleum processing.

Ans: Alkylation is the process of producing gasoline range material (alkylates) from olefins such as propylene (C₃), butylene (C₄) and amylene (C₅), and isobutane. Butylene is the most widely used olefin because of the high quality of the alkylate produced.

Alkylation is catalyzed by a strong acid, either sulfuric (H_2SO_4) or hydrofluoric (HF). In the absence of catalysts, alkylation between isobutane and olefin must be run under severe conditions such as $T = 500^\circ\text{C}$ (932°F) and $P = 200\text{--}400$ bars ($2940\text{--}7080$ psia). In the presence of an acid catalyst, the reaction temperature will be lower than 50°C (122°F), and the pressure will be lower than 30 bars (441 psia).



Q.14: Write name with structures of three sulfur containing compounds found in crude petroleum.

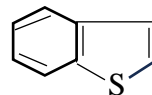
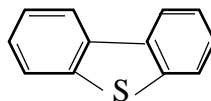
Ans: Sulfur-containing compounds are commonly found in petroleum. Some of the sulfur-containing compounds found in petroleum includes:

i) Thiols (Mercaptans): R-SH (where R represents an alkyl or aryl group) e.g. methanethiol CH_3SH

ii) **Thiophenes:** C_4H_4S



iii) **Dibenzothiophenes** $C_{12}H_8S$ and **Benzothiophene:**



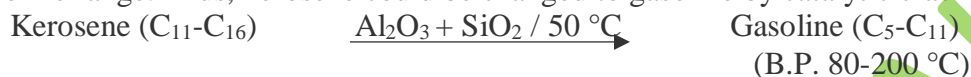
iv) **Organosulfides:** $R-S-R'$ (where R and R' represent alkyl or aryl groups) e.g. dimethyl sulfide CH_3-S-CH_3 , diethyldisulfide $C_2H_5-S-S-C_2H_5$

v) **Sulfones:** $R-SO_2-R'$ (where R and R' represent alkyl or aryl groups) e.g. dimethyl sulfones $CH_3-SO_2-CH_3$

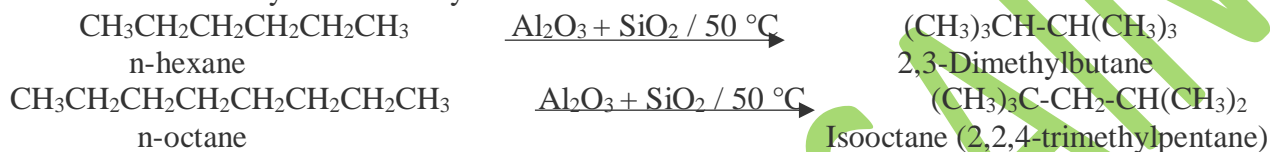
Q.15: Describe catalytic cracking with example.

Ans: Cracking: When long-chain alkanes are heated well above their boiling points ($500-800\text{ }^\circ\text{C}$) with or without a catalyst, they are broken (or cracked) to yield smaller alkanes, alkenes and hydrogen. Such thermal decomposition with reference to petroleum hydrocarbons is called Cracking.

In Catalytic Cracking, silica (SiO_2) or alumina (Al_2O_3) is used as a catalyst. The process of cracking is of tremendous importance in petroleum industry. Crude Oil contains about 18 per cent of the gasoline fraction. Due to high demand of gasoline (motor fuel), the higher-boiling fractions of crude oil are converted to lower-boiling hydrocarbons of gasoline range. Thus, kerosene could be changed to gasoline by catalytic cracking.



Catalytic cracking of higher-boiling fractions of petroleum increases the proportion of gasoline and also produces alkenes and branched-chain hydrocarbons by isomerization.



Thus the product is high quality motor fuel, its octane number being greatly improved.

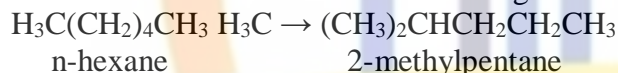
Q.16: What is reforming?

Ans: "It is the process of upgrading gasoline (increasing its octane number) in the presence of a catalyst. The increase in octane number of straight chain gasoline occurs through structural modifications such as conversions of straight hydrocarbons into branched, cyclic, and aromatic hydrocarbons."

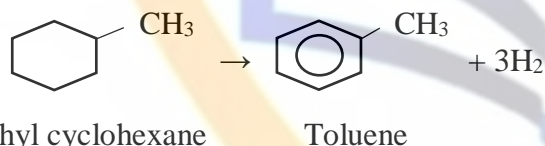
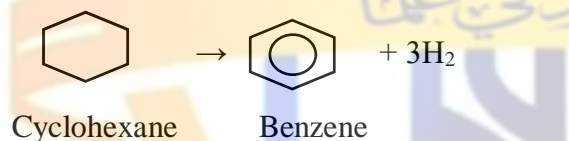
Reforming Process: The feed stock (straight run gasoline) is preheated to remove sulfur and nitrogen content to acceptable limits to avoid platinum catalyst being poisoned. The vapours of the feed stock is mixed with hydrogen and preheated to 500°C . The mixture is compressed (15–50 atmosphere) and then fed into a series of three cylindrical reactors containing the platinum catalyst supported on alumina-silica base. The reformed products are fractionated to get stabilized gasoline

Reforming Reactions:

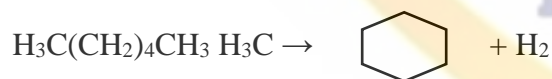
Isomerization: The conversion of straight chain hydrocarbons into branched chain hydrocarbons.



Dehydrogenation: Dehydrogenation of Cycloalkanes to produce aromatic compounds.

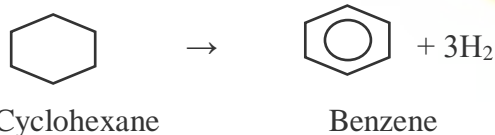


Cyclization and dehydrogenation: Cyclization of straight chain hydrocarbons followed by dehydrogenation to produce aromatic hydrocarbons.

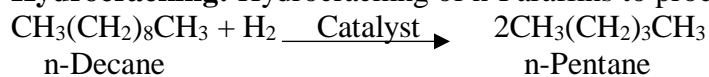


n-hexane

Cyclohexane



Hydrocracking: Hydrocracking of n-Paraffins to produce light gases that are removed from gasoline fraction.



Q.17: Write two examples of fractional distillation.

Ans: Fractional distillation is a separation technique used to separate a mixture of liquids into various boiling fractions (components) based on differences in their boiling points (also chemical composition).

According to ASTM, fractional distillation (also known as differential distillation) is a process used to separate components of a liquid mixture based on differences in their boiling points, utilizing a fractionating column to achieve this separation.

Petroleum Refining: Crude oil is a complex mixture of hydrocarbons having different boiling points. Fractional distillation of crude petroleum gives various components.

Crude oil is heated (350-400 °C) in a furnace to get vapors which are passed through fractionating column (tall, vertical tower filled with trays or packing). These vapors are condensed as the temperature decreases into various boiling fractions. Components with higher boiling points condense at lower levels of the column, while those with lower boiling points condense at higher levels. Different fractions, such as gasoline, kerosene, diesel, and lubricating oil, are collected at various heights of the column.

Separation of Ethanol from Water: Ethanol is prepared from starch or molasses by fermentation containing upto 12-14% ethanol. Ethanol can be separated from water till it forms an azeotropic mixture. The vapors of ethanol and water are passed through fractionating column, (packed with materials like glass beads to increase surface area and improve separation). Ethanol, (B.P. = 78.37 °C) vaporizes before water (B.P. = 100 °C). The ethanol vapors condense into liquid form obtained as distillate while water and impurities remain in the distillation flask as residue.

