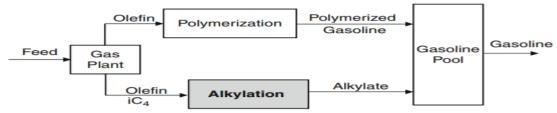
1. Processing of Crude Oil

LONG QUESTIONS:



Q.1: Discuss C₄ alkylation process with the help of flow sheet diagram.

Alkylation: it is the addition of isobutane to butenes to produce high grade gasoline range product (alkylate). Alkylation in the petroleum refinery is the reaction of a low molecular weight olefin with an isoparaffin to produce a higher molecular weight isoparaffin.



Alkylation is the process of producing gasoline range material (alkylates) from olefins such as propylene (C_3) , butylene (C_4) and amylene (C_5) , and isobutane. Butylene is the most widely used olefin because of the high quality of the alkylate produced. Usually isobutylene and propylene are used as olefins while isobutane is used as isoparaffin. Continuous mixed flow reactors are used. Hydrofluoric acid or sulfuric acid catalyst is employed.

Alkylation reactions:

$$(CH_3)_3CH + CH_2 = C(CH_3)_2$$
Isobutane Isobutylene
$$(CH_3)_3CH + CH_2 = CHCH_3$$
Isobutane Propylene
$$(CH_3)_3C - CH_2 - CH(CH_3)_2$$
Isooctane $(2,2,4-\text{trimethylpentane})$

$$(CH_3)_3C - CH_2 - CH_2 - CH_3$$
Isoheptane $(2,2,-\text{dimethylpentane})$

Raw Materials: Olefins: The major sources of olefins are:

i) catalytic cracking ii) coking operations iii) dehydrogenation of paraffins

Note: isobutane may also be cracked commercially to provide olefin (isobutylene) for alkylation unit feed. **Paraffins:** Isobutane is produced in hydrocrackers and catalytic crackers, catalytic reformers, crude distillation, and natural gas processing. In few cases, normal butane is isomerized to produce additional isobutane for the alkylation unit.

C₄-Alkylation: It is the process of producing gasoline range material (alkylates) from olefins such as butylene (C₄) and isobutane. Butylene is the most widely used olefin because of the high quality of the alkylate produced. Alkylation process may be of types: i) H₂SO₄ Catalyzed ii) HF Catalyzed

Reaction Conditions: In the absence of catalysts, alkylation between isobutane and olefin must be run under severe conditions: $T = 500 \, ^{\circ}\text{C} (932 \, ^{\circ}\text{F}) \text{ and } P = 200\text{--}400 \text{ bars } (2940\text{--}7080 \text{ psia}).$

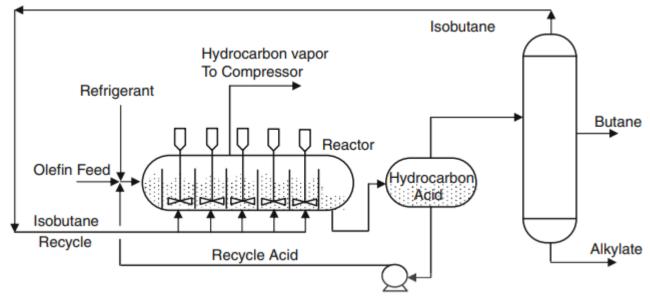
In the presence of an acid catalyst, the reaction temperature will be lower than 50 °C (122 °F), and the pressure will be lower than 30 bars (441 psia).

The major difference in using either acid (H₂SO₄ or HF) is that isobutane is quite insoluble in H₂SO₄ but reasonably soluble in HF. This requires the use of high isobutane/olefin ratios to compensate for low solubility in H₂SO₄.

The alkylation process consists of running the hydrocarbons in liquid form (enough pressure is used to ensure that) and at low temperature and with a high isobutane (iC4) to olefin (isobutylene C₄) ratio. The reaction products are sent to an acid settler where the acid is recycled back to the reactor. Products are then separated into gaseous LPG propane and n-butane and the desired product of alkylate.



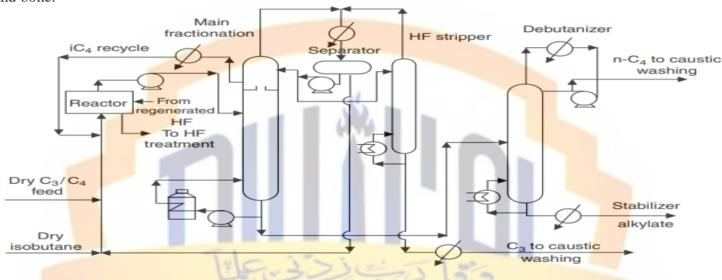
The sulfuric acid alkylation process is the auto-refrigeration process. The olefin is fed to the first reactor in the cascades, together with the recycled acid and refrigerant. Recycled and make-up isobutanes are distributed to each reactor. Evaporated gases are compressed and fed back to the reactor along with the fresh olefin feed which is also cooled by this stream. The reactor operates at a pressure of 90 kPag (10 psig) and at a temperature of 5 °C (40 °F) for up to 40 min.



Flow Sheet for Auto-refrigerated sulfuric acid alkylation process **Hydrofluoric Acid Alkylation:**

The HF processes have no mechanical stirring as in the sulfuric acid processes. The low viscosity of HF and the high solubility of isobutane in the acid allow for a simpler design. The emulsion is obtained by injecting the hydrocarbon feed into the continuous HF phase through nozzles at the bottom of a tubular reactor. Reaction temperature is about 30 $^{\circ}$ C (86 $^{\circ}$ F), allowing for the use of water as a coolant to the reactor. The two processes are quite similar. The residence time in the reactor is 20–40 s. The hydrocarbon phase is sent to the main fractionation column to obtain stabilized alkylate.

Note: H₂SO₄ alkylation processes are favored over the HF processes because of the recent concern about the mitigation of HF vapors. HF is a very hazardous material for humans because it can penetrate and damage tissue and bone.



Q.2: Describe the composition of crude petroleum.

Ans: Crude oil is a complex liquid mixture containing hydrocarbon compounds that consist mainly of carbon and hydrogen in differing proportions. In addition, small amounts of organic compounds containing sulphur, oxygen, nitrogen and metals such as vanadium, nickel, iron and copper are also present. Hydrogen to carbon ratios affect the physical properties of crude oil. As the hydrogen to carbon ratio decreases, the gravity and boiling point of the hydrocarbon compounds increases.

The composition of crude oil, on an elemental basis is given in table:

Element	Composition (wt%)	Element	Composition (wt%)	Element	Composition (wt%)
Carbon	83.0-87.0	Ni	<120 ppm	Sulphur	0.05-6.0
Hydrogen	10.0–14.0	V	<1200 ppm	Nitrogen	0.1-0.2
Oxygen	0.05-2.0	4	ORON		

There are three main classes of hydrocarbons. These are based on the type of carbon–carbon bonds present These classes are:

- Saturated hydrocarbons contain carbon—carbon single bonds known as paraffins (or alkanes) if they are acyclic, or naphthenes (or cycloalkanes) if they are cyclic.
- Unsaturated hydrocarbons contain carbon—carbon multiple bonds (double, triple or both). Unsaturated hydrocarbons are known as olefins (alkenes) that contain a carbon—carbon double bond, while those with carbon—carbon triple bond are alkyenes.

Aromatic hydrocarbons are special class of cyclic compounds related in structure to benzene.

Paraffins: Paraffins (alkanes) are saturated compounds that have the general formula C_nH_{2n+2} , where n is the number of carbon atoms. The simplest alkane is methane (CH₄). Normal paraffins (n-paraffins or n-alkanes) are unbranched straight-chain molecules. Each member of these paraffins differs from the next higher and the next lower member by a –CH₂– group called a methylene group.

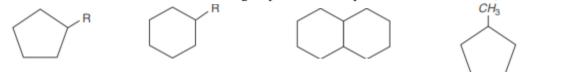
Isoparaffins (or isoalkanes) are branched-type hydrocarbons that exhibit structural isomerization.

Olefins: Olefins (alkenes) are unsaturated hydrocarbons containing carbon–carbon double bonds. Compounds containing carbon-carbon triple bonds are known as acetylenes, and are also known as biolefins or alkynes. The general formulas of olefins and acetylenes are $C_nH_{2n}(R-CH=CH-R)$ and $C_nH_{2n-2}(R-C\equiv C-R)$, respectively. Unsaturated compounds may have more than one double or triple bond.

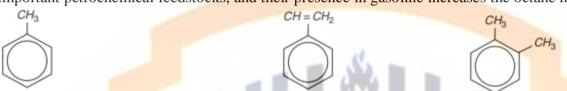
Olefins are not naturally present in crude oils but they are formed during the conversion processes. They are more reactive than paraffins. The lightest alkenes are ethylene (C₂H₄) and propylene (C₃H₆), which are important feedstocks for the petrochemical industry. The lightest alkyne is acetylene.

Naphthenes (cycloalkanes): Naphthenes (cycloalkanes) are saturated hydrocarbons that have at least one ring of carbon atoms. They have the general formula C_nH_{2n} . A common example is cyclohexane (C_6H_{12}). The boiling point and densities of naphthenes are higher than those of alkanes having the same number of carbon atoms. Naphthenes commonly present in crude oil are rings with five or six carbon atoms. These rings usually have alkyl substituents attached to them. Mutli-ring naphthenes are present in the heavier parts of the crude oil.

 CH_3



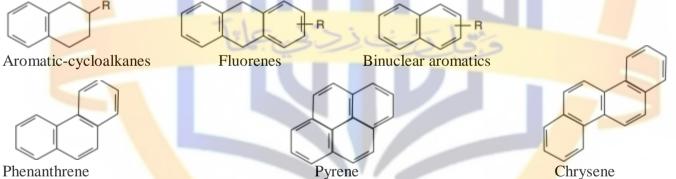
Bicycloalkanes methylcyclopentane Alkylcyclopentanes Alkylcyclohexanes 1,2-dimethylcyclopentane **Aromatics:** Aromatics are unsaturated cyclic compounds composed of one or more benzene rings. The benzene ring has three double bonds with unique electron arrangements that make it quite stable. Crude oils contain different types of aromatic compounds in different concentrations. Light petroleum fractions contain monoaromatics, which have one benzene ring with one or more of the hydrogen atoms substituted by another atom or alkyl groups. Examples of these compounds are toluene and xylene. Together with benzene, such compounds are important petrochemical feedstocks, and their presence in gasoline increases the octane number.



Toluene (methylbenzene)

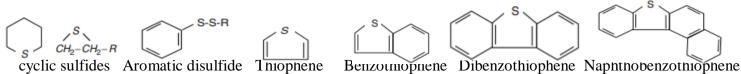
Examples are:

Styrene o-xylene (1,2-Dimethylbenzene) A number of "fused" benzene rings (polynuclear aromatic compounds) are found in the heavy petroleum fractions and their presence is undesirable because they cause catalyst deactivation and coke deposition during processing, besides causing environmental problems when they are present in diesel and fuel oils. The heaviest portion of the crude oil contains asphaltenes, which are condensed polynuclear aromatic compounds of complex structure.

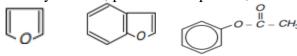


Sulphur Compounds: The Sulphur content of crude oils varies from less than 0.05-10% but generally falls in the range 1–4%. Crude oil with less than 1% sulphur is referred to as low sulphur or sweet, and that with more than 1 wt% sulphur is referred to as high sulphur or sour. Crude oils contain sulphur heteroatoms in the form of elemental sulphur S, dissolved hydrogen sulphide H₂S, carbonyl sulphide COS, inorganic forms and I nvarious organic forms. Sulphur containing compounds of crude oils are mercaptans (thiols), sulphides and polycyclic sulphides.

CH₃SH CH₃CH₂CH₂CH₂SH phenyl mercaptan (thiophenol) methyl mercaptan (methanethiol) n-butyl mercaptan (1-butanethiol) The sulphides and disulphides compounds (cyclic or aromatic) are often present in light fractions. The polynuclear aromatic compounds are normally present in heavier fractions.

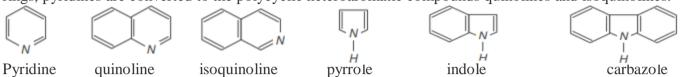


Oxygen Compounds: The oxygen compounds of crude oil is usually less than 2%. These include alcohols, ethers, carboxylic acids, phenolic compounds, ketones, esters and anhydrides. Examples are:



Benzofuran phenylacetate Furan

Nitrogen Compounds: Crude oils contain very low amounts of nitrogen compounds. In general, the more asphaltic the oil, the higher its nitrogen content. Nitrogen compounds are more stable than sulphur compounds and therefore are harder to remove and poison cracking catalyst. The nitrogen compounds in crude oils may be classified as basic or non-basic. Basic nitrogen compounds consist of pyridines. The greater part of the nitrogen in crude oils is the non-basic nitrogen compounds, which are generally of pyrrole types. When fused with benzene rings, pyridines are converted to the polycyclic heteroaromatic compounds quinolines and isoquinolines.



Metallic Compounds: Metallic compounds exist in all crude oil types in very small amounts. They cause poisoning to the catalysts used for hydroprocessing and cracking. Even minute amounts of metals (iron, nickel and vanadium) in the feedstock to the catalytic cracker affect the activity of the catalyst and result in increased gas and coke formation and reduced gasoline yields. For high-temperature power generators, the presence of vanadium in the fuel may lead to ash deposits on turbine blades and cause severe corrosion, and the deterioration of refractory furnace linings. Part of the metallic constituents of crude oils exist as inorganic water-soluble salts, mainly as chlorides and sulphates of sodium, potassium, magnesium and calcium. These are removed in desalting operations. More important are metals which are present in form of oil-soluble organometallic compounds. Zinc, titanium, calcium and magnesium appear in the form of organometallic soaps. However, vanadium, nickel, copper and iron are present as oil-soluble compounds, capable of complexing with pyrrole compounds.

Asphaltenes and Resins: The specific gravity (or API), are considerably influenced by high-boiling constituents, in which the heteroatoms (sulphur, nitrogen and metals) concentrate.

Asphaltenes are dark brown friable solids that have no definite melting point and usually leave carbonaceous residue on heating. They are made up of condensed polynuclear aromatic layers linked by saturated links. These layers are folded, creating a solid structure known as a micelle. Their molecular weights span a wide range, from a few hundred to several million. Asphaltenes are separated from petroleum in the laboratory using non-polar solvents such as pentane and n-heptane. They lead to coke formation and metal deposition on the catalyst surface causing catalyst deactivation.

Resins are polar molecules in the molecular weight range of 500–1000, which are insoluble in liquid propane but soluble in n-heptane. The resins are responsible for dissolving and stabilizing the solid asphaltene molecules in petroleum. The resin molecules surround the asphaltene clusters (micelles) and suspend them in liquid oil.

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Q.3: What is octane number & how it can be improved? Ans: **OCTANE NUMBER:**

Knocking: For petrol engines, a high compression is essential for efficiency, but air-gasoline mixture ignites prematurely under high compression and produces a sharp metallic sound called knocking. Knocking reduces efficiency because a part of energy is converted into metallic rattle and damages the engine.

Edger in 1927 devised an arbitrary sale for rating fuels on the basis of knocking. He observed that normal straight chain alkanes knock badly but branched chain ones very much less. The term octane number is introduced after observing that n-heptane (octane number zero) knocks badly and has maximum knocking property and the isooctane (2,2,4-trimethylpentane) is adopted as a standard antiknock fuel and is assigned the octane number of

100 to it. CH₃-CH₂-CH₂-CH₂-CH₂-CH₃ (CH₃)₂CH-CH₂-C(CH₃)₃

2,2,4 trimethyl pentane (Isooctane) (Octane number 100) n-Heptane (Straight chain) (Octane number (0)

Definition: The octane number of a given fuel may be defined as the percentage of isooctane in a mixture of isooctane and n-heptane that has the same knocking characteristics of the fuel under examination in a standard onecylinder engine operated under standard conditions.

The higher the octane number of the fuel, less the knocking property. The higher the octane number, better is the quality of a fuel.

Example: The fuel with octane number 60 would give the same knocking as a mixture by volume of 60%, isooctane and 40% n-heptane.

- As the number of carbon atoms in straight chain alkane increases octane number decreases but octane number increases with branching of chains.
- Alkenes have higher octane number than the corresponding alkanes, and the octane number increases as the double bond is shifted to the center of the molecule.
- ➤ Olefins, cyclo-paraffins and aromatic hydrocarbons have high octane numbers than n- paraffins.
- The gasoline obtained by cracking has higher octane number because it contains higher percentage of alkenes and aromatic hydrocarbons.
- In general the quality of gasoline is improved by the presence of highly branched paraffins, olefins, cyclic olefins and aromatic hydrocarbons.
- An ordinary engine requires 230 c.c. gasoline per horsepower of octane number 100, but it consumes 325 c.c. gasoline per horsepower if the octane number is 73.

Octane Number of different Hydrocarbons:

Name	Octane #	Name	Octane #	Name	Octane #	Name	Octane #
Benzene	106	n-nonane	-45	2,3- dimethyl butane	95	aviation gasoline	> 100
ethyl alcohol	95	n-heptane	0	2,3,3-trimethylpentane	99	regular gasoline	74
n-pentane	61	cyclopentane	85	2-methyl hexane	45	premium gasoline	81
propane	100	cyclohexane	77	2,3-dimethylpentane	93	2,2- dimethylpentane	83
n- butane	92	n-octane	-27	2,2,3-trimethylbutane	116	2,2,3-trimethyl butane	124
n-hexane	25	isooctane	100			(Triptane)	124

Improvement of Octane Number:

Blending of additives:

- > TML (Tetramethyl lead), TEL (Tetraethyl lead) is an antiknocking compound and their function is to convert gasoline into branched chain hydrocarbons by alkylation and polymerization.
- ➤ The clopentadienyl manganese carbonyl (AK-33X) is now used as antiknock agent, because it also avoids lead pollution.
- > The tricryl phosphate (TCP) also improve the quality of the gasoline.
- An antiknock liquid, called ethyl fluid is added. This fluid is a mixture of TEL (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. [The ethylene dibromide scavenges combustion chamber from metallic lead formed from TEL by converting it to the bromide. The TEL has been found to be more effective on saturated hydrocarbons than on unsaturated ones.]
- The selected grades of spirits mixed with TEL [tetra ethyl lead] having octane numbers greater than 100. The octane number is indicated by the color of the mixture, e.g. spirit blends having octane numbers of 92, 91-96, 100-130 and 118-135 have red (orange), blue, green and brown color respectively. For spirit blends, having octane numbers greater than 100, the octane rating is expressed as:

Octane number =
$$\frac{\text{Power number} - 100}{3} + 100$$

In the above expression, power number is the quantity proportional to the power supplied by the engine.

Other Methods:

The straight run gasolines provided by distillation of petroleum consist mainly of alkanes and hence the octane rating varies from 73 to even 20. Isomerization, alkylation, aromatization, reformation etc., also increase the octane number of fuels.

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

 $H_3C(CH_2)_4CH_3 H_3C \rightarrow (CH_3)_2CHCH_2CH_2CH_3$ n-hexane 2-methylpentane

Aromatization: Dehydrogenation of Cycloalkanes to produce aromatic compounds.



Q.4: Briefly explain fractional distillation of petroleum.

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Ans: Crude distillation unit (CDU) is the main unit of refinery, also known as atmospheric distillation unit. Its size and operating cost are the largest in the refinery. The capacity of the CDU ranges from 10,000 barrels per stream day (BPSD) or 1400 metric tons per day (tpd) to 400,000 BPSD (56,000 metric tpd). The economics of refining favours larger units. The unit produces raw products which have to be processed in downstream unit to produce products of certain specifications.

Typical products from the unit are:

- a) Gases
- b) Light straight run naphtha (light gasoline or light naphtha)

- c) Heavy gasoline (military jet fuel)
- **d**) Kerosene (light distillate or jet fuel)
- e) Middle distillates called diesel or light gas oil (LGO)
- f) Heavy distillates called atmospheric gas oil (AGO) or heavy gas oil (HGO)
- g) Crude column bottoms called atmospheric residue or topped crude.

Process Description: Fractional distillation is a primary refining process in which the mixture is separated into its components of different molecular weights by virtue of difference in their boiling points. In this process, crude oil is separated into its various fractions like kerosene, diesel and heavy residue etc.

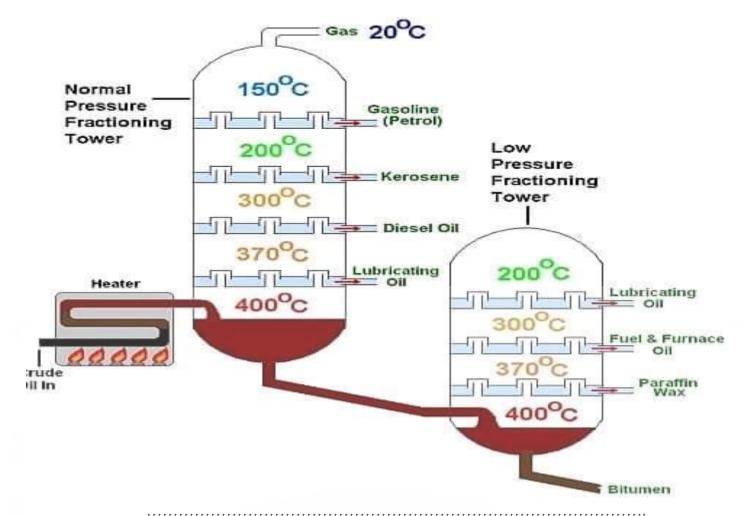
Crude oil is pumped from storage tanks where it is freed from sediments and free water by gravity. It goes through a series of heat exchangers where it is heated with hot products coming out from the distillation column etc. The temperature of the crude feed can reach 120–150 °C (248–302 °F). The crude oil contains salt in the form of dissolved salt in the tiny droplet of water which forms a water-in oil emulsion. This water cannot be separated by gravity or through mechanical means. It is separated through electrostatic water separation. This process is called desalting. In the electrostatic desalter, the salty water droplets are caused to coalesce and migrate to the aqueous phase by gravity. It involves mixing the crude with dilution water (5–6 vol%) through a mixing valve. The crude is further heated in product heat exchangers. The preheating of the crude using the hot products cools down the products to the desired temperature for pumping to the storage tanks. The furnace is required to boost the temperature to between 330 and 385 °C (626 and 725 °F) depending on the crude composition.

The crude petroleum is fractionally distilled in large size stills and various fractions are separated after condensing them in towers, known as fractionating columns or distillation tower or fractionating tower or atmospheric pipe still. In the atmospheric distillation process, crude oil is heated in tubular furnace or by super-heated steam to about 600 K. Vaporized feed (oil) is separated in the distillation column into streams of different boiling point ranges, the lighter and more volatile products separate out higher up the column, whereas the heavier, less volatile, products settle out toward the bottom of the distillation column. Distillation column consists of a number of trays or stages, each tray is provided with a number of bubble caps, valves or sieves for the passage of the vapors to the upper tray, and a down comer channel by which the liquid flows down the tray. The feed vapors passing through the trays, the heavy components condense to liquid and the lighter fraction rises to the next. The heat of condensation released by fraction of vapors during condensation, works for heat of vaporization vaporizes the lighter components again. Thus, the bubble cap acts as a condensation and evaporation unit, or unit distillation column. Each tray has a liquid corresponding to the boiling range, which may be drawn off as a side stream, passed through condenser and is removed for further treatment, and some liquid is returned to the upper portion of the column as reflux. Upper half part of the column is therefore known as rectifying section. The liquid flows down to lower trays, which is collected at the bottom tray, heated by steam or re-boiler, and the vapors produces are introduced in the lower part of the column, to strip any lighter components, which move to the rectifying section. The lower portion of the column (below feed plate) is therefore called stripping section. The products obtained are then purified, transformed, adapted, and treated in a number of subsequent refining processes to obtain marketable products. The residue collected at the base of the column is distilled at 390-400 °C and under vacuum (120 mm of Hg) to carry out operation at low temperature without decomposition, the fraction obtained include light gas oil, heavy gas oil, lubricating base oil, waxes and pitch. Various products obtained during fractional distillation of crude petroleum are given in table below.

Distillate fractions obtained from crude petroleum by fractional distillation

	- In the state of						
Sr. #	Fraction	Boiling point range °C	Hydrocarbon range	Application			
1	Gases (LPG)	below 30	C_1 - C_4	Domestic fuel.			
2	Light naph <mark>tha,</mark>	30-75	C_5 - C_8	Petrochemicals, Blending motor gasoline			
3	Heavy Naph <mark>tha</mark>	75-190	C_9 - C_{12}	Motor gasoline (motor car fuel)			
4	Kerosene	190-250	C_{12} - C_{14}	Domestic fuel, aviation fuel, Tractor fuel			
5	Diesel	250-350	C_{14} - C_{16}	Diesel fuel, heavy machinery fuel, central heating fuel			
6	Atmospheric residue	> 350	> C16	Furnace oil, Lube oil, Vacuum gas oil, asphalt.			

PUACP



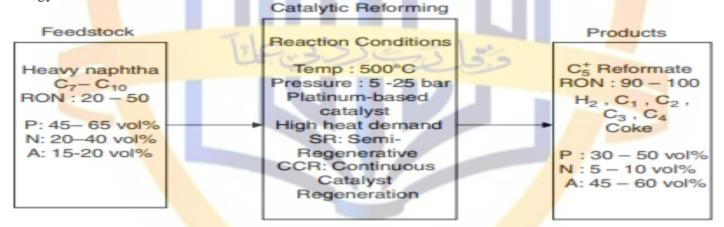
Q.5: What is catalytic reforming and why it is used?

Explain the catalytic reforming of crude oil highlighting the main steps involved.

What is catalytic reforming, explain its significance.

Ans: Catalytic reforming of heavy naphtha constitute a very important source of products having high octane numbers which are key components in the production of gasoline. If benzene is present in the final gasoline it produces carcinogenic material on combustion. Elimination of benzene forming hydrocarbons (hexane) will prevent the formation of benzene. These light paraffinic hydrocarbons can be used in an isomerization unit to produce high octane number isomers.

Catalytic reforming is the process of transforming C₇–C₁₀ hydrocarbons with low octane numbers to aromatics and iso-paraffins which have high octane numbers. It is a highly endothermic process requiring large amounts of energy.



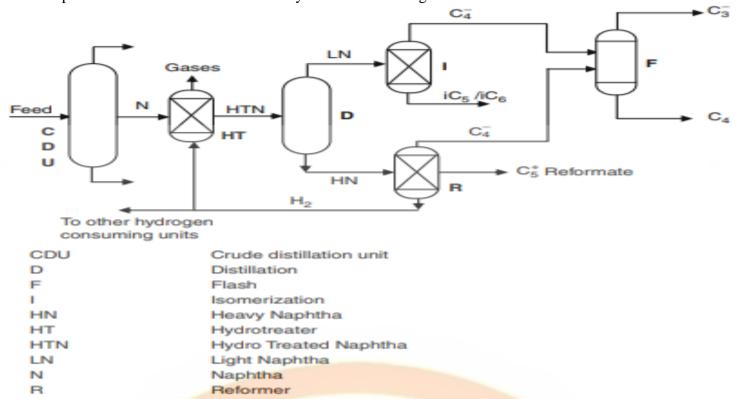
Catalytic reforming process [p = paraffins, N = Naphthenes, A = aromatics]

The catalytic reformer is one of the major units for gasoline production in refineries. It can produce 37% by mass of the total gasoline pool. Other units such as the fluid catalytic cracker (FCC), the methyl ter-butyl ether (MTBE) production unit, alkylation unit and isomerization unit, also contribute to gasoline pool.

Hydrotreater Unit: The straight run naphtha from the crude distillation unit is hydrotreated to remove sulphur, nitrogen and oxygen which can all deactivate the reforming catalyst.

Fractionation: The hydrotreated naphtha (HTN) is fractionated into light naphtha (LN), which is mainly C_5 – C_6 , and heavy naphtha (HN) which is mainly C_7 – C_{10} hydrocarbons. It is important to remove C_6 from the reformer feed because it will form benzene which is considered carcinogenic upon combustion. Light naphtha (LN) is isomerized in the isomerization unit. Light naphtha can be cracked if introduced to the reformer. Hydrogen, produced in the reformer can be recycled to the naphtha hydrotreater, and the rest is sent to other units demanding hydrogen.

The research octane number (RON) is defined as the percentage by volume of iso-octane in a mixture of iso-octane and n-heptane that knocks with some intensity as the fuel is being tested.

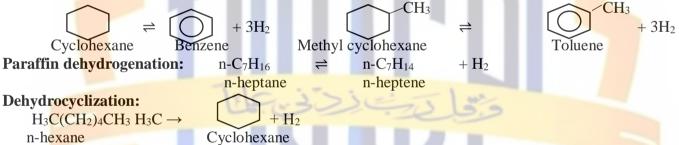


Reforming Reactions in Reformer:

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

 $H_3C(CH_2)_4CH_3$ $H_3C \rightarrow (CH_3)_2CHCH_2CH_2CH_3$ $n-C_7H_{16} \Rightarrow i-C_7H_{16}$ n-hexane 2-methylpentane n-heptane n-hept

Dehydrogenation: Dehydrogenation of Cycloalkanes to produce aromatic compounds.



Dehydrogenation and dehydrocyclization reactions are highly endothermic.

Hydrocracking: Hydrocracking reactions are the main sources of <C₄ hydrocarbons (C₁, C₂, C₃ and C₄). The reactions are highly exothermic and consume high amounts of hydrogen. Cracking results in the loss of the reformate yield. Hydrocracking of n-Paraffins to produce light gases that are removed from gasoline fraction. CH₃(CH₂)₈CH₃ + H₂ Catalyst 2CH₃(CH₂)₃CH₃ $C_{10}H_{22} + H_2 \rightarrow C_2H_5 - CH(CH_3) - C_2H_5 + C_4H_{10}$ n-Pentane Decane Isohexane

Coke can also deposit during hydrocracking resulting in the deactivation of the catalyst. The catalyst has to be reactivated by burning off the deposited coke. Coke formation is favoured at low partial pressures of hydrogen. Hydrocracking is controlled by operating the reaction at low pressure between 5–25 atm (74–368 psia), not too low for coke deposition and not too high in order to avoid cracking and loss of reformate yield.

Catalysts for Reforming: The catalyst used for reforming is composed of platinum metal on chlorinated alumina. Platinum acts as the centre for the dehydrogenation reaction, and chlorinated alumina acts as an acidic site to promote structure changes, such as cyclization of paraffins and isomerization of the naphthenes. Iridium (Ir) is added to boost activity, Rhenium (Re) is added to operate at lower pressures and Tin (Sn) is added to improve yield at low pressures. The use of Pt/Re is now most common in semi-regenerative (SR) processes with Pt/Sn is used in moving bed reactors. The quantity of chlorine used is approximately 1 wt% of the catalyst and the quantity of platinum is from 0.2 to 0.6 wt%. Impurities that might cause deactivation or poisoning of the catalyst include: coke, sulphur, nitrogen, metals and water. Because of these problems, the reformer feed has to be severely hydrotreated to remove most of these impurities, and the reformer should be operated at high temperature and low pressure to minimize coke deposition. Paraffin and naphthene dehydrogenation reactions are very rapid and usually occur in the first reactor. The isomerization of paraffin and naphthenes is fast, whereas hydrocracking is slow and takes place in the last reactor.

