Origin of Petroleum

Opinions are divided according to the formation of petroleum. Any theory put forward to explain the origin of petroleum must explain the following properties associated with petroleum:-

* The presence of chlorophyll, haemin and resins in it.
* The presence of nitrogen and sulphur compounds in it.
* Its optically active nature
* Its association with sodium chloride (brine).

Theories:-

The origin of petroleum is explain by two major theories

- abiogenic theory
- Biogenic theory.

Abiogenic theory (carbide theory)

According to **Mendeleeff (1876)**, petroleum is of inorganic origin and is formed by hydrogenation and polymerization of lower hydrocarbons. It states that

"Petroleum and other hydrocarbons are formed from inorganic materials deep within the earth mantle through chemical reactions independent of biological processes"

The lower hydrocarbons are produced by action of steam on metal carbides in lower crust in earth under considerable pressure and high temperature.

1. $4Al + 3C \longrightarrow Al_4C_3$

$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_2 + 3CH_4$

2. $C_2H_2 + H_2 \xrightarrow{\text{hydrogenation}} C_2H_4$

3. $Ca + 2C \longrightarrow CaC_2$

$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$

4. $C_2H_4 + H_2 \xrightarrow{\text{hydrogenation}} C_2H_6$

These lower hydrocarbons then undergo polymerization

$3C_2H_2 \xrightarrow{\text{polymerization}} C_6H_6$ (benzene)

$3C_2H_4 \xrightarrow{\text{Polymerization}} C_6H_{12}$ (cyclohexane)

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This theory was later on supported by Moissan, Sabatier and Senderens.

Failures:-

This theory fails to explain:-

* The presence of optically active compounds in petroleum
* Presence of Nitrogen and sulfur compounds
* The presence of prophyrins which are related to natural pigments and chlorophyll and heamin of plants and red blood cells of ~~hum~~ animals respectively.

Biogenic theory:

The biogenic theory of petroleum was first proposed by Mikhail Lomonosov in 1757.

This states that:-

"Rock oil (petroleum) originates from the decomposition of plant and animal remains, buried under layers of sediments and transformed over time under influence of heat and pressure

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within Earth's crust?

The biogenic theory suggests that petroleum is formed from the remains of ancient organic matter primarily microscopic plants (algae) and micro-organism deposited in anoxic (oxygen poor) enviornments such as seas, lakes or swamps. Over millions of years, these organic materials are buried under layers of sediments.

Key processes

* **Deposition:** Organic matter accumulates in sediments in enviornments where oxygen is limited, preventing full decomposition
* **Diagenesis:** The buried organic matter is slowly transformed into kerogen, a solid, waxy substance.
* **Catagenesis:** As pressure and temperature increase with further burial, kerogen breakdown in liquid and gaseous hydrocarbons (oil and gas).
* **Metagenesis** At very high temperature, methane and other gases can form

from the further breakdown of organic material

★ **Migration and accumulation:** The hydrocarbon migrate from source rock through porous rocks and accumulate in reservoir rocks, where they are trapped by impermeable cap rocks

Drawbacks:

1. This theory primarily explains the formation of petroleum in sedimentary rocks, but large reserviors of petroleum are found in non-sedimentary rocks.
2. Some petroleum deposits are believed to be much older than organic material that could have formed them.
3. Some studies have observed that carbon isotopes in certain petroleum deposits do not alway match those associated with biological origins.

Despite these drawback, biogenic theory is still most widely accepted theory regarding the origin of petroleum.

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Other theories:-

Engler's Animal theory:-

This theory states that:-

—— "petroleum is formed primarily from the decomposition of animal fats, particularly those of marine organisms, under conditions of high pressure and temperature over geological time" ——

Plant origin theory:-

This theory was proposed by A.P. Karpinskii. It states that:-

—— "Petroleum is primarily derived from remains of ancient plants especially terrestrial plants, that were burried ~~under~~ and subjected to heat and pressure over millions of years" ——

It is now well established that petroleum is of organic origin and formed by decomposition of animal as well as vegetable matter. But its formation is still a thing of speculation. Following concepts are

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Known regarding the formation of petroleum:-

1. It takes place by means of bacterial decomposition followed by physical and chemical change.
2. It is formed from organic matter by catalytic activity of certain inorganic compounds.
3. According to third view (which is almost accepted) the formation of petroleum is also helped by radioactive rays emitted from radioactive substances present under Earth's crust.

Areeba Alamgir
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Migration

Migration of oil refers to the movement of hydrocarbons (oil and natural gas) from their original source rock, where they are formed, to a reservoir rock where they accumulate in significant quantities. This process occurs over geological time scales and is a crucial part of the formation of oil and gas deposits. Here are the main stages involved in oil migration:

1- Generation of Oil:

Oil is formed primarily from the remains of marine organisms (plankton, algae, etc.) that get buried under sediment. Over millions of years, heat and pressure cause the organic material to break down into hydrocarbons in a process called "maturation."

2- Primary Migration:

Once the hydrocarbons are generated, they begin to move from the source rock, which is typically a sedimentary rock such as shale, towards more porous rocks (such as sandstone or limestone) that can hold oil. This movement is primarily driven by pressure differences and the buoyancy of the oil, which is less dense than water.

3- Secondary Migration:

After hydrocarbons move through smaller fractures or pore spaces within the rock, they can accumulate in larger structures within the subsurface.

Secondary migration refers to the movement of oil through larger pathways, such as faults, fractures, and porous rocks, towards a trap where the oil can accumulate.

4- Accumulation in Reservoirs:

Once the oil reaches a suitable reservoir rock (a rock with good porosity and permeability) it is trapped by a cap rock (impermeable layer) that prevents further upward migration. The oil collects in the reservoir, forming an oil deposit.

5- Tertiary Migration:

This stage involves the final adjustment of the oil position, sometimes caused by later geological events such as tectonic activity, which might cause oil to migrate further or accumulate in new areas.

Factors affecting Migration:

Factors that influence the migration of oil include:

1- **Pressure:** Increasing pressure can push oil out of the source rock and through the surrounding rocks.

2- **Temperature:** Heat can increase the mobility of oil and facilitate its migration.

3- **Permeability:** The ease with which oil can flow through the sounding rocks affects its migration.

4- **Fractures and faults:** These can provide pathways for oil to migrate through the rocks.

5- **Fluid saturation:** The presence of other fluids, such as water or gas, can effect oil migration.

Importance of Migration:

The migration of oil is important for:

1- **Exploration:** Identifying potential oil reservoirs and predicting their location.

2- **Production:** Optimizing oil recovery by understanding the migration patterns and reservoir characteristics.

3. **Reservoir modeling:** Building accurate models of the reservoir to predict oil behaviour and optimize recovery.

The migration of oil is a complex process, and its understanding requires a combination of geology, geophysics and reservoir engineering expertise.

Reservoir of Crude Petroleum

A reservoir of crude petroleum is a natural geological formation where oil is stored, often deep beneath the Earth's surface. These reservoirs play a critical role in the exploration, extraction and production of crude oil.

=> Formation and Composition of Crude Oil Reservoirs:

Crude oil reservoirs form over millions of years through geological processes. The components of an oil reservoir include:

• Source Rock:

The source rock is typically sedimentary rock, such as shale, that contains organic materials (mostly plankton and other microorganisms) that, under heat and pressure, transform into hydrocarbons (oil and gas).

• Migration:

Once the hydrocarbons are generated, they migrate upwards from the source rock due to buoyancy. This migration occurs through porous rocks such as sandstone, or limestone, and these rocks are known as reservoir rocks.

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• Reservoir Rock:

A reservoir rock is a rock formation that has sufficient porosity and permeability to store and transmit oil. Common reservoir rocks include sandstone, limestone.

Porosity: refers to the amount of empty space (pores) in the rock that can hold oil or gas.

Permeability: refers to the ability of the rock to allow fluids (like oil or gas) to flow through it.

• Cap Rock (Seal):

Above the reservoir rock is an impermeable layer, often composed of shale, salt or other tight rock formations. This cap rock traps the oil and prevents it from escaping to the surface. The cap rock is crucial to maintaining the integrity of the reservoir and ensuring that oil remains confined in the reservoir for millions of years.

• Oil:

The oil in a reservoir is primarily composed of hydrocarbons, and may also include water and natural gas. The oil is typically a mixture of various types of hydrocarbons such as alkanes, cycloalkanes and aromatic hydrocarbons.

• **Gas :**

Often, natural gas exists in the combination with crude oil. A gas reservoir is an underground formation where natural gas is stored and can be extracted.

Gas reservoir is of two types.

Non Associated Gas Reservoir: These are gas reservoirs where natural gas is found without oil.

Associated Gas Reservoir: In these reservoirs, natural gas is found in association with crude oil.

Types of Crude Petroleum Reservoir:

• **Conventional reservoirs:** These are type of oil reservoir. In conventional reservoirs, oil is relatively easy to extract because it is stored in porous rock formations with good permeability. The oil naturally flows towards production wells due to the pressure difference created during extraction.

• Unconventional Reservoirs :

These reservoirs involve oil that is trapped in more challenging rock formations such as

- **Tight Oil :** Oil trapped in low-permeability rock formations.
- **Shale Oil :** Oil extracted from shale formations, often through hydraulic fracturing (fracking).
- **Heavy Oil and Tar Sands :** These are viscous oils found in ~~st~~ sandstones or other reservoirs, requiring advanced extraction techniques such as stream injection or solvent-based methods.

A reservoir of crude petroleum is a subsurface accumulation of crude oil that is trapped within porous rock formations. Pakistan has several oil reservoirs, with the majority located in the Potwar Plateau region.

Zainab Tahir 16

Exploration and drilling.

At one time drilling for petroleum was a hit a miss affair, and in such cases about 1 out of 300 wildcat (a well whose location is determined without much scientific exploration, especially in a previous untested area) wells struck oil. However, by employing skilled geologists who have studied the origin and occurence of petroleum, as well as geophysicists who are expert in the use of very delicate instruments to determine something about The geological conditions under the earth's surface, the drilling of wells has become so vastly improved that in 1962 1 out of 9 new wells yielded oil or gas. The geologist early recognized that petroleum occurs in oil pools caught in the anticlinal folds of sedimentary rocks. The succes of oil geologist has been due to the correlation of a great deal of experience and data. This include the study of cores from all types of wells and the accurate observation of surface indication, coupled with newer geophysical exploratory procedures, many of which have been developed and perfected by the scientific staff of oil companies. The driller guided by the geologist, now drills holes deeper than 4 mi and reaches gas or oil.

With the use of very sensitive instruments, geophysicists can determine the likelihood of occurence of domes and deposits at considerable distance in the earth. The top of the arch of an anticline or a dome has, by virtue of compression, greater specific gravity than the surrounding rocks; which depicts the various strata surrounding oil-bearing rock or sand. Oil and salts deposits also have a different (lower) specific gravity than accompanying rocks. These variations are measured by delicate gravity instruments, which record changes in the gravity constant g. The plotting of these results gives a gravimetric survey. Other methods of forecasting such anticlines include the exploding of charges at selected intervals, with special instruments located at various points to measure and time the reflected wave initiated by the explosion. This result in a seismic survey. Other methods are also used, such as determination of the electrical conductivity of the earth or the magnetic conditions. These two methods do not seem to be successful as the gravimetric and seismic surveys. All these studies lead to the drilling of a test hole which, if successful, frequently result in the opening up of a new oil feed.

Composition of Petroleum

Crude oil is a mixture of hydrocarbon molecules (1-60 carbon atoms). The simplest hydrocarbon molecule is methane. Hydrocarbons containing up to four carbon atoms are gases, those with five to ninteen carbon atoms are liquid while those with 20 or more are solids. The properties of hydrocarbon depends upon the number and arrangment of carbon and hydrogen atoms in the molecules.

Paraffins (Alkanes) C_nH_{2n+2}

Paraffins can be either straight chains or branched chains. The lighter straight chain paraffins are found in gases. The branched chain paraffins are usually found in heavier fractions of petroleum and have higher octane number. They are stable in storage. They exhibit high calorific value and poor spark knock resistance, unless transformed to branched chain isomers.

Olefins (Alkenes) C_nH_{2n}

Olefins contains only one carbon-carbon double bond in the chain. These hydrocarbons do not occur naturally in petroleum (crude) but they are formed in the result of refining processes. They are unstable due to presence of C=C double bond and readily react with other elements.

Dienes and alkynes C_nH_{2n-2}

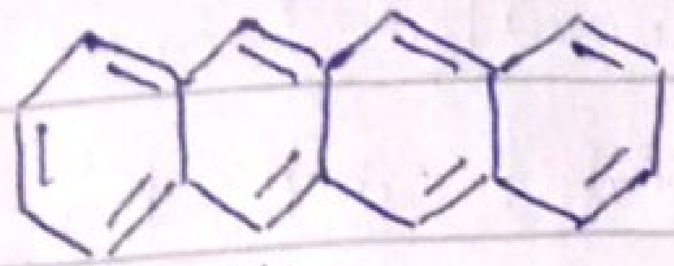
Dienes (diolefins) having two carbon-carbon double bond. The alkynes have carbon-carbon triple bond in molecule. Diolefins such as 1,2-butadiene and 1,3-butadiene and alkynes such as acetylene occur in lighter petroleum fractions in the result of cracking. They are highly unstable and have high combustion temperature and flame speed.

Naphthenes (cyclanes) C_nH_{2n}

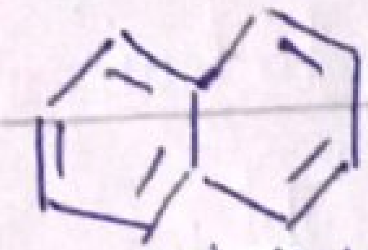
Naphthenes are saturated hydrocarbons in the form of closed ring. They are found in all fractions of crude oil except the very lightest. Single ring naphthenes with 5 and 6 carbon atoms are most pre-dominant, while those with two ring naphthenes found in heavy petroleum fractions. They are more stable except the first few members.

Aromatic C_nH_{2n-6}

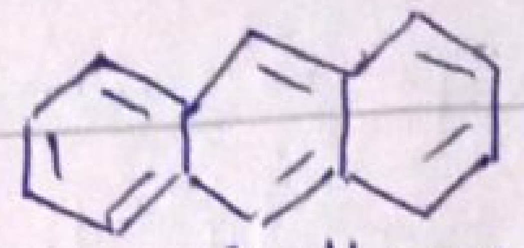
Aromatic are unsaturated ring type hydrocarbons have at least one benzene ring. Aromatics containing more than one benzene rings fused or condensed are termed as polynuclear aromatic hydrocarbons. Lighter aromatic hydrocarbons are found in all fractions but complex are found in heavier fractions only. They are most stable. They have low calorific value due to low carbon content. They have high freezing point and bear good spark knock resistance.



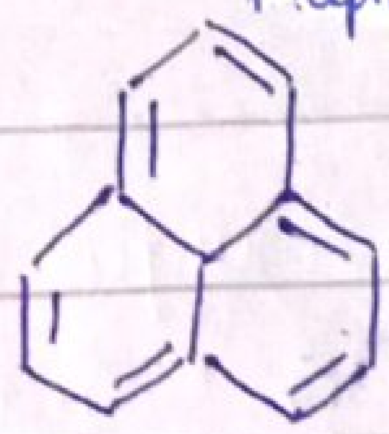
Napthacene



Naphthalene



Anthracene



Phenalene

Non-Hydrocarbons:-

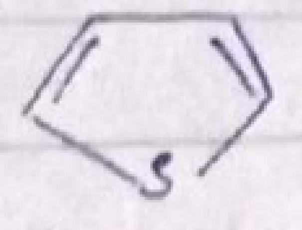
The compounds other than carbon and hydrogen in petroleum are non-hydrocarbon. Compounds containing other atoms are sulfur, nitrogen, oxygen, chlorine and a large number of metals are also found.

1. Sulfur compounds:-

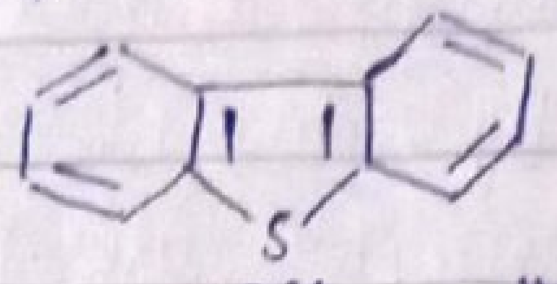
Sulfur may be present as in free form or combined form. Different crude petroleum have different amount and type of sulfur compounds. Higher the density of crude higher will be sulfur contents.

CH_3-SH — Methyl mercaptan

CH_3-S-CH_3 — dimethyl sulfide



Thiophene



Dibenzothiophene

Around 200 compounds have been identified. Sulfur occur in organic (mercaptans) and inorganic (H_2S) forms. The presence of sulphur compounds in petroleum is unwanted because of variety of problems associated with them.

2- Oxygen compounds:-

The amount of oxygen containing compound is relatively low in crude petroleum i.e around 2% per weight. Compounds of oxygen such as phenols, ketenes and carboxylic acids occur in crude oils. The oxygen content increase with increase in boiling points.

3- Nitrogen compounds:-

Nitrogen is present in crude petroleum in very small quantity ~0.1 % by weigh %. Nitrogen is found in lighter fraction of crude oil as basic compound, and more often in heavier fractions of crude oil as

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"Refining"

Refining is a process of transforming crudue oil into usable products like gasoline, diesel, kerosene jet fuel, lubricants and petero-chemicals. It involves a series of physical and chemical processes to seperate, purify and convert the components of crude oil.

Steps of refining

Steps like cracking, alkylation, reforming, isomerization ~~etc~~ etc are explained later.

Surface Operation

Surface operation in oil refers to the activities and processes conducted above ground (on the surface) during exploration, production and processing of crude oil and natural gas. These operations include everything from preparing the site for drilling to processing and transporting the extracted oil or gas. Following are the key components of surface operation:

1- Site preparation:

Before drilling begins, the location is prepared to ensure safe and efficient operations.

Land Clearing: Removal of vegetation, leveling the ground, and creating access roads to the site.

Pad Construction: Building a stable foundation for drilling rigs, equipment and storage.

Environmental Protections: Setting up barriers, drainage systems and containment systems to minimize environmental impact.

2- Drilling Operations:

Once the site is ready, surface equipment is used to drill into the subsurface:

Drilling Rigs: Large surface structures that house machinery to drill boreholes into the earth.

Mud Systems: Drilling fluids (or mud) are managed on the surface to lubricate the drill bit, carry cuttings to the surface, and stabilize the wellbore.

Well Lodging and Testing: Surface operations include analyzing the geological formations encountered while drilling.

3- Well Completion:

After drilling reaches the oil-or gas-bearing formation:

Casing and Cementing: Steel pipes (casing) are inserted into the wellbore and cemented in place to stabilize the well and prevent contamination of groundwater.

Wellhead Installation: The wellhead is installed on the surface to control the flow of oil or gas.

Perforation: The casing and cement are perforated to allow hydrocarbons to flow into the well.

4- Production Operations:

Once a well is completed, surface operations handle the extraction of oil and gas:

Separation: Oil, gas and water are separated using surface separators. Three-phase Separators are used to separate the oil, gas and water into distinct streams.

Storage and Transport: Crude oil is stored in tanks or pipelines and natural gas may be compressed or liquefied for transport.

Flowlines: Piping systems on the surface transport fluids from the wellhead to separators or storage tanks.

5- Surface Facilities:

Oil and gas production requires various facilities and equipments on the surface:

Processing units: Includes gas dehydration, crude oil stabilization, and gas sweetening (removal of H_2S and CO_2).

Compressor stations: Used to pressurize gas for transport via pipelines.

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Heaters and Treaters: Heat and treat crude oil to remove water and impurities.

Flare systems: Burn off excess gases for safety in controlled conditions.

6- Environmental and Safety Measures:

Surface operations are heavily regulated to protect the environment and ensure worker safety:

Spill Containment: Measures to handle and contain accidental oil or chemical spills.

Waste Management: Safe disposal or treatment of drilling fluids, cuttings and produced water.

Air Emission Controls: Equipment to minimize the release of greenhouse gases and other pollutants.

7- Decommissioning and Site Restoration:

At the end of well's productive life:

Plugging and Abandonment: The well is sealed with cement plugs to prevent leaks.

Site Cleanup: Removing equipment, remediating soil and restoring the site to its original condition.

Applications of Surface Operations:

- **Upstream Activities:**
  Related to exploration and production; e.g; drilling and well operations.
- **Midstream Activities:**
  Transportation and storage of crude oil or gas.
- **Downstream Activities:**
  Refining crude oil into usable products and processing natural gas.

Fractional Distillation

Fractional distillation of oil is a critical industrial process used to separate crude oil into its various components (fractions), which have different boiling points and are used for diverse applications such as fuels, lubricants, and petrochemicals. This process is performed in an oil refinery using a "fractional distillation column" or "distillation tower."

Overview of Crude oil:

Crude oil is a complex mixture of hydrocarbons with varying molecular sizes, boiling points and properties. The primary goal of fractional distillation is to break down this mixture into smaller, usable fractions based on their boiling points.

The fractions range from light gases like propane to heavy residues like bitumen. Each fraction corresponds to a specific boiling range and has distinct

Principle:

Fractional distillation separates liquids based on boiling points. A

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mixture is heated, vaporizing liquids with lower boiling points. Vapor rises, cools and condenses, separating liquids liquids with higher boiling points, condense and fall back. liquids with lower boiling points remain in vapor phase. Separation occurs in a column with vapor-liquid contact. Resulting in separated liquids collected at different points.

⇒ Process:

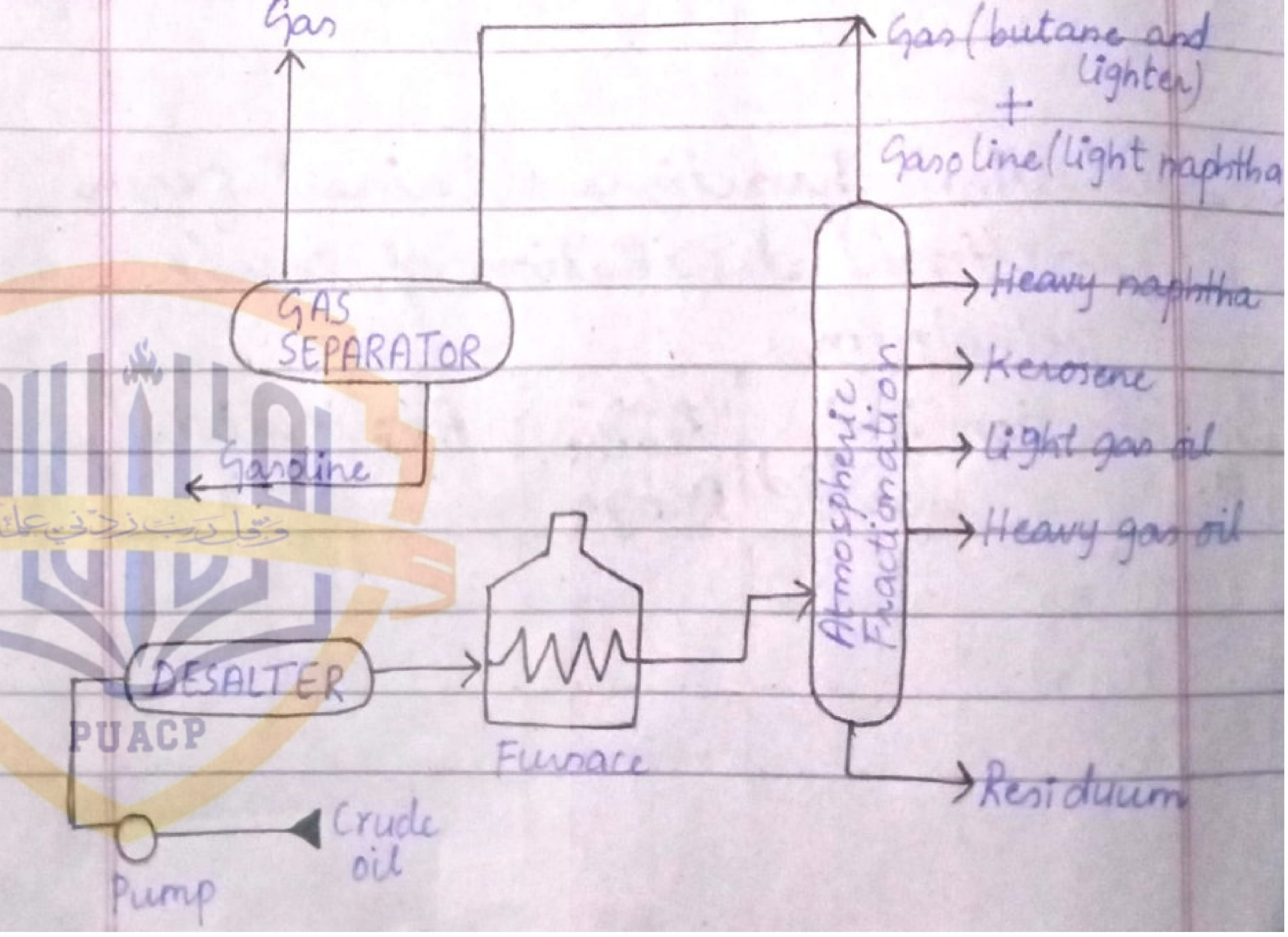
In the atmospheric distillation process, crude oil is heated in tubular furnace or by super-heated steam to about 600 K. Vaporized oil (feed) is separated in the distillation column into streams of diff. boiling points ranges, the lighter and more volatile products separate out higher up the column, whereas the heavier, less volatile, products settle out toward the bottom of distillation column. Distillation column consists of a number of trays or stages, each tray is provided with a number of bubble caps, valves or seives 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 vapor 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 vapourization, 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 ~~drawn off~~ 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 reboiler, and the vapors produced 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 temp. 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 fractional distillation of crude petroleum:

Sr #	Fraction	B.P range (°C)	Hydro-carbon Range	Application
1.	Gases (LPG)	Below 30	$C_1 - C_4$	Domestic fuel

2-	Light naphtha	30-75	$C_5 - C_8$	Petrochemicals, blending motor gasoline
3-	Heavy naphtha	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	$<C_{16}$	Furnace oil, lube oil, vacuum gas oil, asphalt.

=> Schematic Diagram:



⇒ Fractionation Efficiency: Design of column.

- Trays and plates:
  The column contains horizontal trays or plates that hold condensed liquids. Vapors pass through these trays or plates, creating vapor-liquid interaction that improves separation.
- Temperature Gradient:
  The column is hotter at the bottom and cooler at the top, allowing for a gradient of boiling points.
- Reflux:
  Part of the condensed liquid is sent back into the column to improve purity of the fractions.

⇒ Advantages of Fractional Distillation in Oil:

- Efficient Separation: Separates crude oil into fractions with distinct uses.
- Customizable output: Can adjust column settings to produce more of the desired fractions based on market demand.

- Feedstock for Cracking: Provides raw material for catalytic or thermal cracking to produce additional lighter fractions.

=> Challenges in Fractional Distillation:

1- Energy Intensive: The process requires significant energy to heat crude oil to high temperatures.

2- Environmental Impacts: Produces emissions and requires handling of by-products like sulfur compounds.

3- Complex Mixtures: Crude oil contains impurities and compounds that may complicate the separation process.

4- Cost: Fractionation requires expensiv equipment and maintenance.

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"Cracking"

Petroleum cracking is fundamental chemical process in petroleum refining industry wherein large hydrocarbons (~~gas~~ crude oil) are broken down into smaller (LPG, gasoline) more useful compounds typically through chemical thermal or catalytic methods. The primary goal of cracking is to convert heavier, less valuable fraction of crude oil into lighter, more valuable products like gasoline, diesel, kerosene and other petero chemical feedstoks.

Types:-

There are two major types of cracking

Thermal cracking.

Catalytic cracking.

Thermal cracking:-

Thermal craking is the decomposition of large ~~hy~~ hydrocarbon molecules under elevated temperature and pressure

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to form small molecule.

Conditions:-

Temperature 450–750°C.

Pressure 700–1000 KPa

Residence time few seconds to several minutes

Advantages:-

* The main advantage of thermal cracking is its simplicity and effectiveness in breaking down heavy hydrocarbons into valuable lighter products such as gasoline.
* It doesn't require any catalyst
* It allows for efficient conversion of low value residues in to higher value products.

Today, in modern refinery thermal cracking is replaced by steam cracking, visbreaking and coking process.

Steam cracking:-

Steam cracking is a chemical process primarily used in petrochemical industry to break

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down large hydrocarbon molecules into smaller, useful products such as ethylene, propylene and other olefins.

In steam cracking, gaseous or liquid hydrocarbon fuel LPG, naphtha and ethane is diluted with steam and briefly heated in a furnace without air.

Principle of steam cracking thermal cracking:-

Steam cracking relies on high temperatures (800-900°C) to break chemical bonds in hydrocarbon feedstocks (e.g, naphtha, ethane, propane or gas oil)

Role of steam

- Steam is added to dilute the hydrocarbon feedstock and reduce partial pressures of hydrocarbons, which minimizes unwanted side reactions.
- It also helps to enhance the cracking efficiency by increasing

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heat transfer and preventing secondary reactions.

Radical mechanism

The cracking process involves free radical chain reactions.

Selective products

The process conditions (temperature, feedstock type, residence time and steam ratio) determine the yield of products like ethylene, propylene, butadiene.

- Rapid cooling (quenching) of cracked gases is essential to freeze the reaction and prevent further decomposition of desired products.

Applications

Plastic manufacturing.
Synthetic rubber production
Feedstock for other petrochemical processes.

Advantages

The advantages of using steam in cracking are

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steam reduces the hydrocarbon partial pressure, facilitate cracking at lower temperature

Without steam, vaccum may be required, which may lead to explosion in case of linkage due to entry of air. The presence of steam avoids explosion in such cases

Steam avoids coke formation by reacting with carbon to produce CO (water gas).

Visbreaking:-

Visbreaking is a mild form of thermal cracking that lowers the viscosity of heavy crude oil residues without affecting the boiling point range.

In this process, the residue from the atmospheric distillation tower is heated (425-510°C) at atmospheric pressure and mildly cracked in a heater. It is then quenched with cool gas oil to control over-cracking

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and flashed in a distillation tower

Uses/ Advantages :

The major uses of visbreaking are

It lowers the viscosity of heavy crude oil residue without affecting its boiling point.

Minimize the quantity of residual oil produced in distillation of crude oil.

Reduce pour point of waxy residue.

Coking:-

Coking is a severe form of thermal cracking which is used to produce carbonaceous material called coke and some lighter products or distillates It involves heating heavy crude oil residues to high temperatures (450 – 550°C) in absence of oxygen.

This process generates valuable by-products such as lighter hydrocarbons (used as fuels or feedstocks) and petroleum coke, which is used in industries like aluminum production, steel manufacturing and power

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generation. Coking improves the economic value of heavy residues and enhances refinery efficiency.

Catalytic Cracking

Catalytic cracking is commonly used process in modern oil refinery which is carried out in presence of catalyst.

In this process, the feed which is heavy naptha or heavy gas oil is mixed with steam, and passed to reactor containing catalyst at 450-550°C and atmospheric to 100 psi pressure to produce lighter distillate. The product is rich in branched, cyclic and aromatic hydrocarbon

Types of catalytic cracking

There are two types of catalytic cracking

Fluid catalytic cracking.

hydro cracking.

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"Fluid Catalytic Cracking"

Fluid catalytic cracking is a core process in petroleum refining primarily used to convert heavy hydrocarbons from crude oil into lighter, more valuable products such as gasoline, diesel and olefins.

FCC is carried out to break down long chain hydrocarbon molecules in heavy oils in shorter, more useful molecules. The typpical feed stock of FCC is vaccum gas oil (VOG) and atmospheric residue from crude distillation unit

Catalyst:-

Fine powdered catalysts, typically zeolites which remain fluidized under specific conditions.

Process:-

The feedstock is preheated and introduced into a reactor. The

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feedstock is then mixed with a hot powdered catalyst (zeolite based) in rise reactor. High temperature and low pressure facilitate cracking process. The hydrocarbon chain break into smaller molecules like LPG, olefins, gasoline etc. The mixed cracked hydrocarbons and catalyst enters a cyclone seperator where catalyst is removed. The spent catalyst coated with carbon deposit (coke) is sent to regenerator. Air is injected to burn off the coke, regenerating the catalyst, which is reheated and recycled back to reactor. Cracked hydrocarbons are sent to fractionators for seperation into products like gasoline, diesel and gases.

Advantages of FCC:-

Produces high octane gasoline.

Convert heavy, less valuable feed

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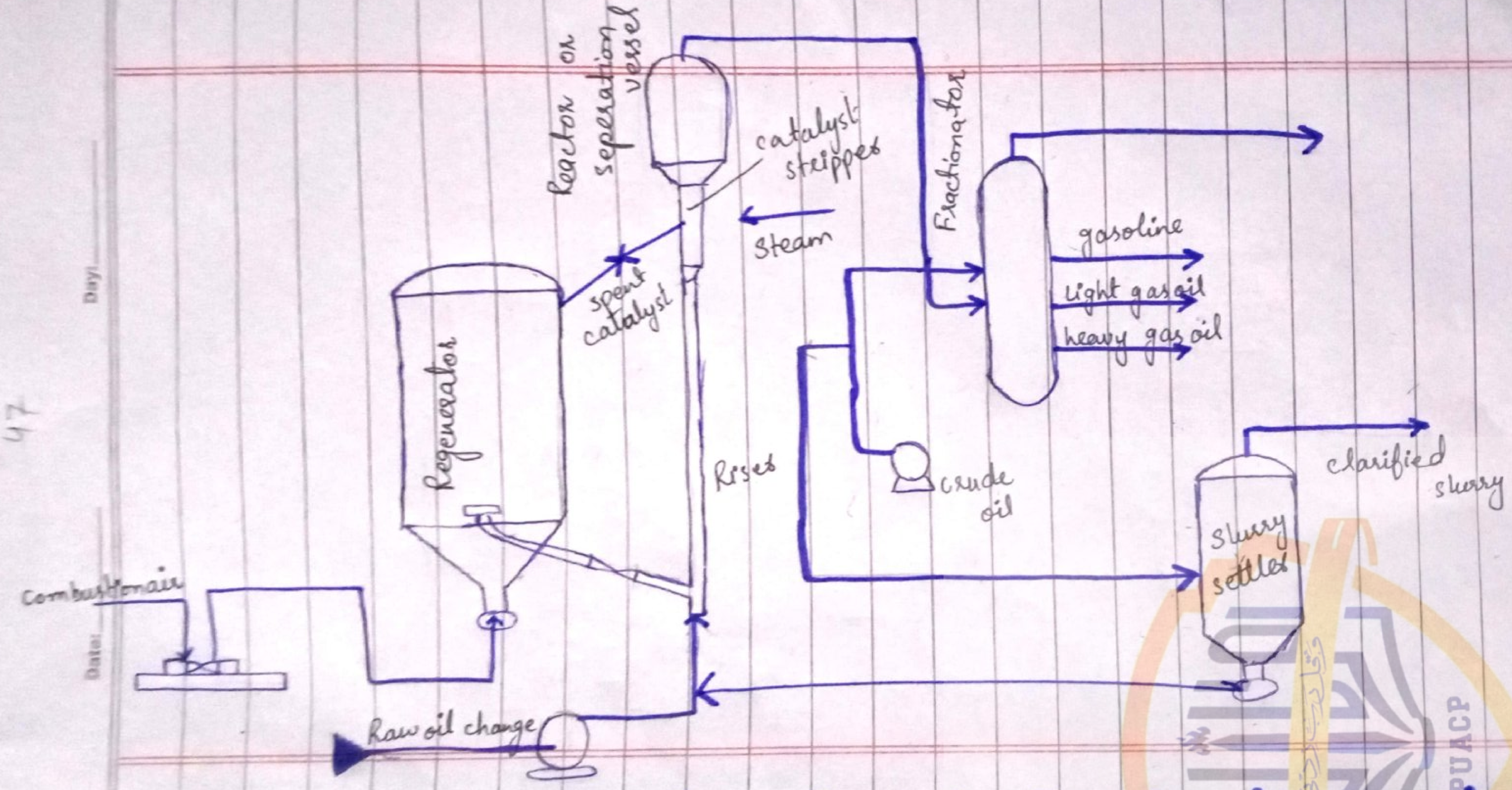
stock into lighter valuable products.
Operates continuously making it highly efficient.

Hydrocracking:-

Hydrocracking is a process in which a hydrocracker takes gas oil, which is heavier, and has a higher boiling range than distillate fuel oil, and cracks the heavy molecule into distillate and gasoline in the presence of hydrogen and catalyst.

Why hydrocracking is more preferred

* Hydrocracking produce high-quality jet fuel, diesel, naphtha.
* It has lower operating cost.
* It is more flexible.
* It improves yield and quality of gasoline.



Fluid Bed Cataytic Cracking reactor.

Date: Day:

"Octane Number"

For high speed petrol engine a high compression is essential for efficiency but a straight chain air gasoline mixture ignites prematurely under high compression and burns in an explosive disorderly fashion producing a sharp metallic sound called **Knocking**.

effects of knocking

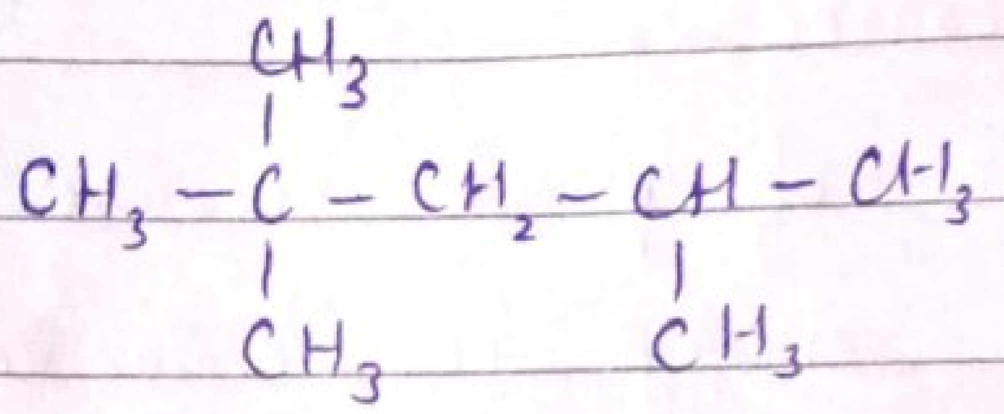
Knocking causes:-

* Great loss of power because a part of energy is converted into metallic rattle
* It cause damage to engine.

Discovery of octane number

In order to classify fuel as according to knocking property, an arbitary scale for rating fuels has been established by Egler (1927). He observed that normal straight chain alkane knocks badly but branched ones very much less

The efficiency of a fuel is rated by giving certain octane number. . The term octane number is introduced after observing that n-heptane (octane no. 0) knocks badly and has maximum knocking property and iso-octane is adopted as a standard antiknock fuel and has assigned octane no. 100.



(2,4-trimethyl pentane) (octane no. 100)

Definition

"The octane number of a fuel may be define as the percentage of iso-octane in a mixture of iso-octane and n-heptane that has same knocking characteristics of a fuel under examination in one cylinder engine operating under standard conditions"

Factors affecting octane number

* In alkane series, the octane number decreases as the carbon chain is lengthened and increase with branching of chain.
* Alkenes have higher corresponding octane number than corresponding alkanes and octane number increases as double bond is shifted near the centre of molecule.

Methods to increase octane number of fuel:

Increasing the octane number improves engine performance and efficiency. Here are some methods to increase octane number

* Blending with high octane components.

Methyl tert-butyl ether (MTBE) and ethyl tert-butyl ether and ethanols are added to increase octane number

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* **Refining process**

Catalytic cracking, isomerization and alkylation are also carried out to increase octane number.

* **Used of aromatics**

Adding aromatic hydrocarbon like toluene increase the octane number, although these two have environmental concerns.

* Hydrocarbon modification.

Convert alkanes into aromatic compounds, which have higher octane number (dehydrocyclization)

* Biofuels

Fuels derive from renewable sources such as biobutanol and bioethanol, can improve octane ratings.

* Increasing compression ratio in engines.

Designing engines to operate with high compression ratio can encourage the use of high octane fuels.

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High quality octane fuel in Pakistan

95 RON fuel , 97 RON fuel.

Cetane Number

The cetane number is a measure of fuel's ignition delay , the time period between start of injection and first identifiable pressure increase during combustion of fuel.

Diesel engines typically perform well with a cetane no. ~~of~~ between 40 and 55.

Cetane no. is usually used for the measurement of quality or ~~pre~~ performance of diesel fuel.

Reforming

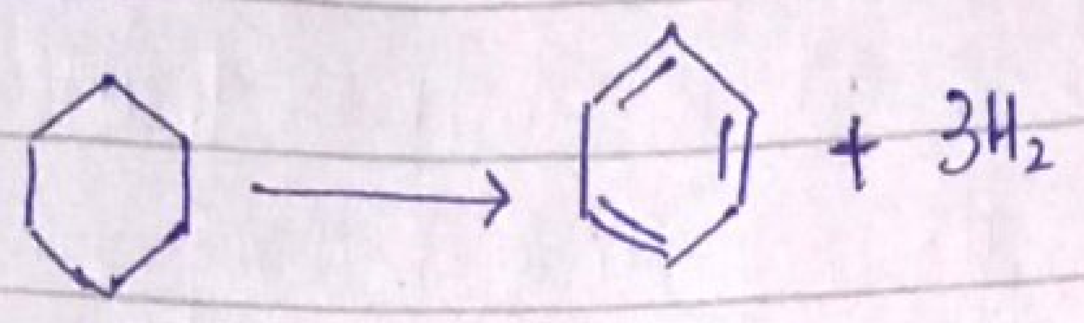
The conversion of naphthas to obtain products of higher octane number. Reforming is an important refining process by which the octane number of the distillates in the gasoline boiling range is improved. Generally, the straight chain hydrocarbons are converted into branched or even cyclic hydrocarbons for increasing their octane number. Reforming involves both cracking and isomerization.

Catalytic reforming:-

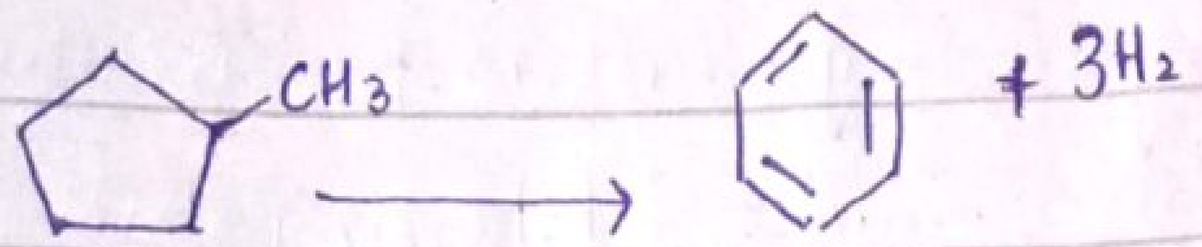
Catalytic reforming involves the conversion of hydrocarbons into aromatic hydrocarbons in the presence of catalyst. Catalyst usually contain rhenium, platinum or chromium.

In the catalytic reformer, the feed is paraffins and naphthenes, which can undergo number of reactions, the extent to which each reaction has occur depending upon the catalyst and operating conditions. The main reactions involved in the reforming are dehydrogenation, isomerization, dehydrocyclization and hydrocracking. The main types of overall reactions occuring during catalytic reforming are as following.

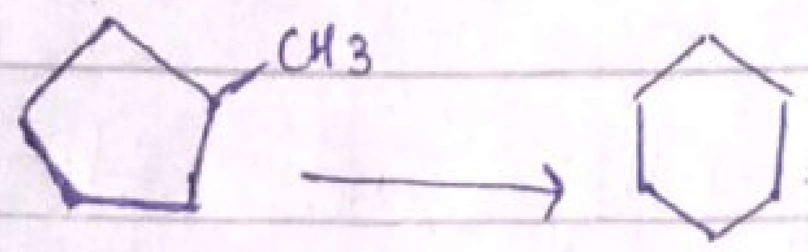
1: Dehydrogenation of cyclohexane to aromatics.



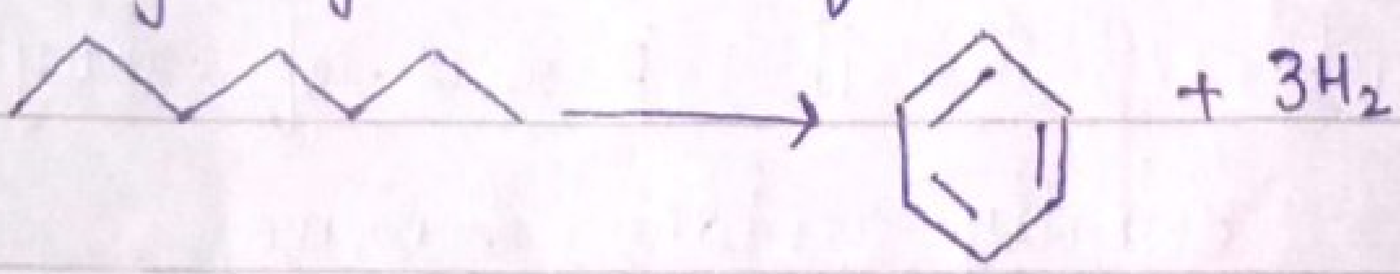
2: Dehydroisomerization of cyclopentane to aromatics.



3: Isomerization of alkanes



4: Dehydrocyclization of alkanes



5: Hydrocracking of alkanes

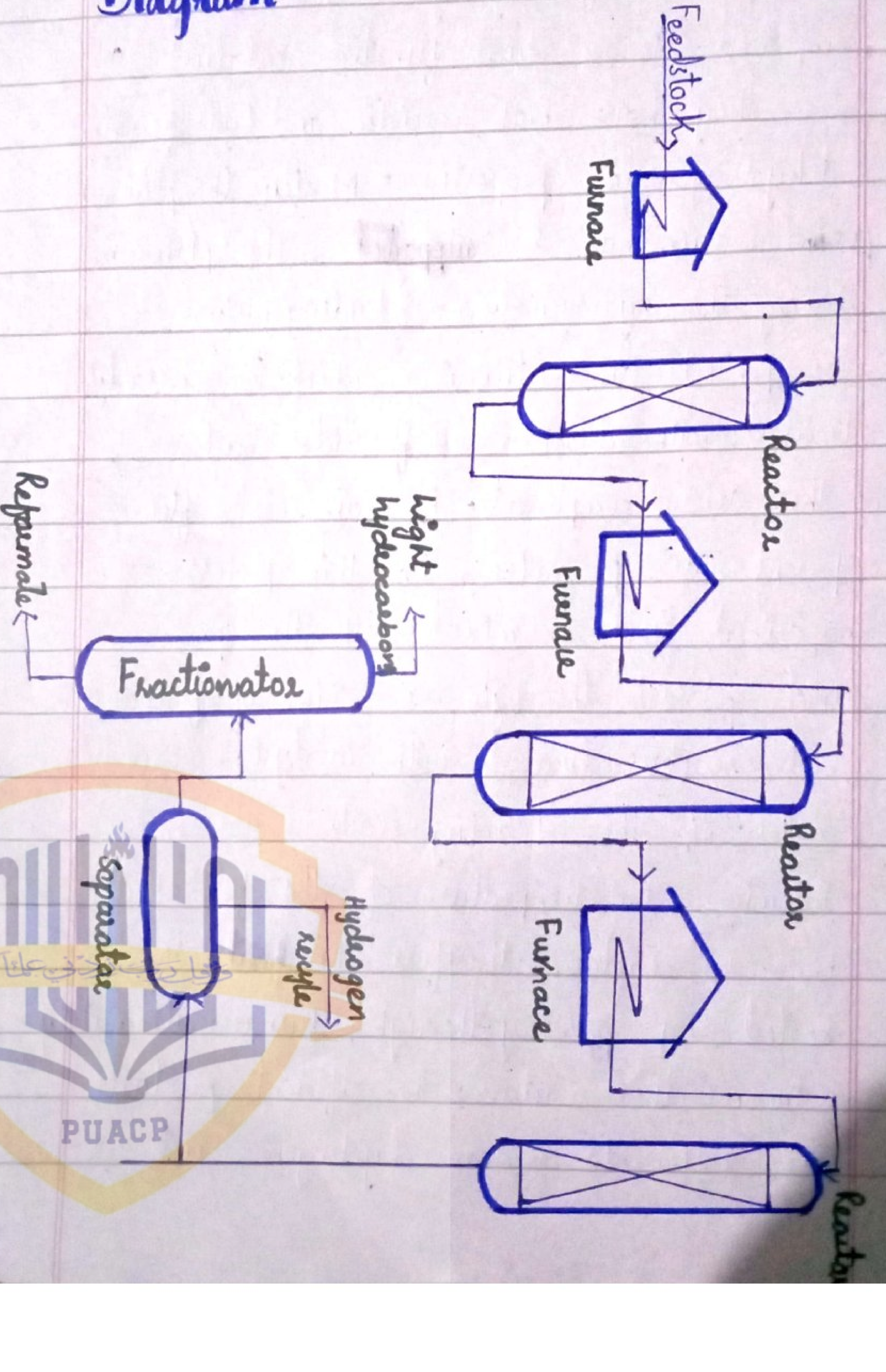
$$C_{10}H_{22} + H_2 \longrightarrow C_6H_{14} + C_4H_{10}$$

The improvement of the octane number produced by catalytic reforming is largely due to formation of the branched chain and aromatic hydrocarbons. Typically it increases the octane number of the feed

with a boiling range of 70 to 190°C
from about 40 to 95°C. Catalytic
reforming involves reacting of feed
vapours over a catalyst at a temprature
in the range 450 to 550°C and pressure
in the range of 10 to 50 atm, in
the presence of hydrogen. The catalyst
employed is a dual function catalyst
i.e, they have both acidic and hydrogenation
dehydrogenation properties. Mostly the platinum
supported on alumina is employed, the platinum
being the hydrogenation - dehydrogenation
component and alumina, which is generally
treated with chlorides or fluorides, act as
the acidic component. Rhenium is often
present as promoter. In this process
vaporized feed is mixed with H_2 gas
and passed through a series of fixed
bed reactors loaded with catalysts. Since
most of the reforming reactions are endo-
thermic, the temprature of the feed falls
in a reactor, therefore the feed is
heated by passing through furnaces alternately
between the reactors. The effluent products
are cooled to remove hydrogen rich

gas for recycling and the liquid product called reformate is separated into various fractions in fractionator. The reformator is rich in alkylated, isomerized, cyclic and aromatic compounds, and used for blending of straight run gasaline.

Diagram



Thermal reforming:-

Thermal reforming employed temperatures of 510-565°C at moderate pressure about 4MPa or 600psi to obtain gasolines (petrols) with octane number of 70 to 80 from heavy naphthas with octane numbers of less than 40. Thermal reforming is often applied to low quality gasoline stocks to improve their combustion characteristics.

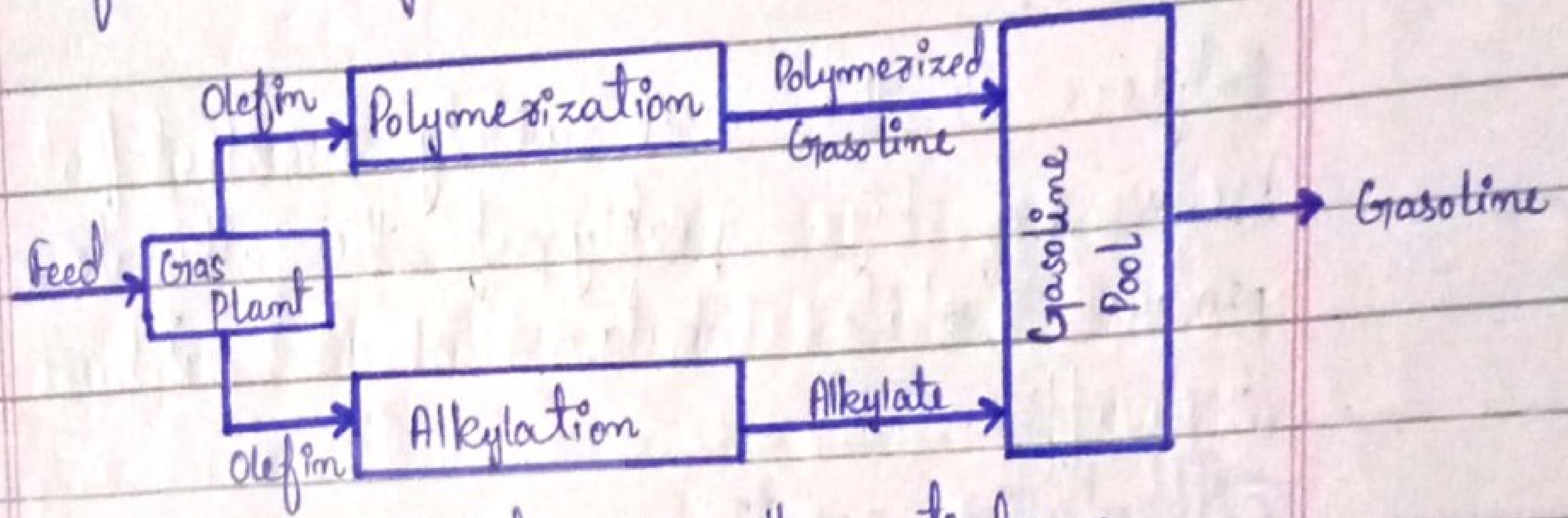
Drawbacks of thermal reforming:-

- The product yield is unstable in storage and tends to form heavy polymers and gums.
- These polymers and gums can cause combustion problems.

Due to these drawbacks thermal reforming is replaced by catalytic reforming.

Alkylation

In catalytic polymerisation, butene and isobutene are polymerised to iso-octene which has lower octane number. Its octane number is increased by hydrogenating it into iso-octane which has an octane number of 100. Alkylation is the process in which iso-octane can be directly obtained in a single step. This is another important method of converting olefins into gasoline.



Alkylation: Alkylation in the petroleum refinery is the reaction of a low molecular weight olefin with an isoparaffin to produce a higher molecular weight isoparaffin. In this process, unsaturated hydrocarbons primarily a mixture of propylene and butylene are reacted with ~~un~~ saturated hydrocarbons such as isobutane in the presence of sulfuric acid or hydrofluoric acid as catalyst to form a mixture of branched-chain paraffinic hydrocarbons called alkylate. Alkylate has high octane number and is therefore used for blending straight run gasoline. The octane number of the alkylate depends mainly upon the kind of olefins used and upon operating conditions. The catalysts used are sulphuric acid, boron fluoride, anhydrous hydrogen fluoride and aluminium chloride etc. Common catalysts for gasoline alkylation are HF or H_2SO_4.

Butylene is the most widely used olefin because of high quality of the alkylate produced while isobutane is used as isoparaffin.

Alkylation reactions:

Unsaturated + isosaturated $\xrightarrow{\text{catalyst}}$ saturated branched chain

$$(CH_3)_3CH + CH_2=C(CH_3)_2 \xrightarrow{H_2SO_4} (CH_3)_3C-CH_2-CH(CH_3)_2$$

Isobutane Isobutylene Isooctane (2,2,4-trimethylpentane)

$$(CH_3)_3CH + CH_2=CH(CH_3) \xrightarrow{H_2SO_4} (CH_3)_3C-CH_2CH_2CH_3$$

Isobutane Propylene Isoheptane (2,2-dimethylpentane)

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Raw materials:

Olefins: The major sources of olefins are (i) catalytic cracking (ii) coking operations (iii) dehydrogenation of paraffins

Paraffins: Isobutane is produced in hydrocrackers and catalytic crackers, catalytic reformers, crude distillation and natural gas processing.

Alkylation types:

It may be of two types.

(i) H_2SO_4 Catalyzed

(ii) HF Catalyzed

Reaction Conditions: In the absence of catalysts, alkylation must be run under severe conditions: $T = 500°C$, $P = 200-400$ bars

The reactions is favored by higher temperatures, but competing reactions among the olefins to give polymers prevent high-quality yields. Thus alkylation usually is carried out at low temperature in order to make the alkylation reactions predominate over the polymerization reactions.

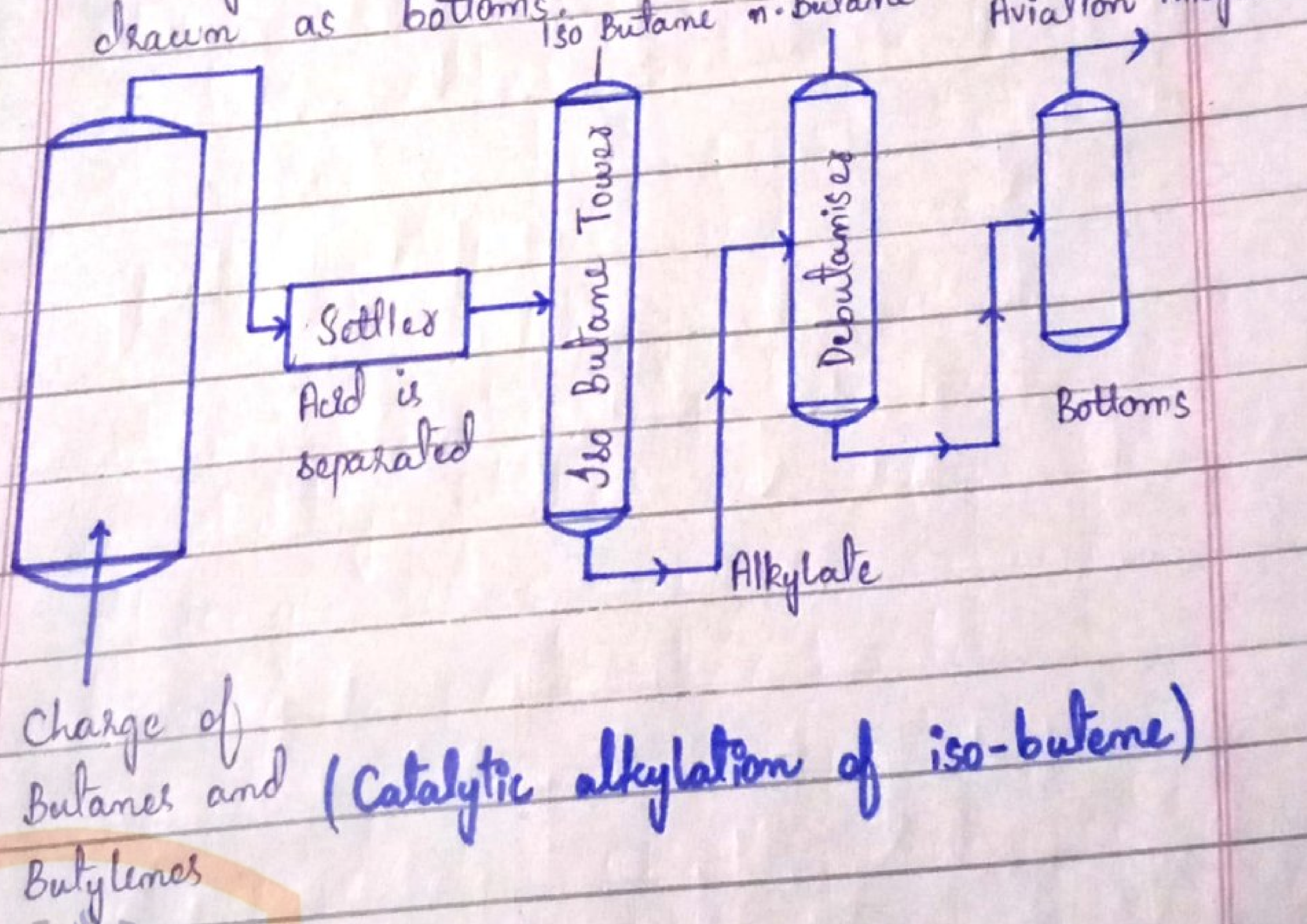
Temperature for HF-catalyzed reaction is approximately 100°F and for H_2SO_4 they are approximately 50°F.

Since the sulfuric acid-catalyzed reactions are carried out below normal atmospheric temperatures, refrigeration facilities are included.
The major difference in using either acid (H_2SO_4 or HF) is that isobutane is quite insoluble in H_2SO_4 but reasonably soluble in HF. This requires the use of high isobutane / olefin ratios to compensate for low solubility in H_2SO_4.

Alkylation process :

Isobutane is alkylated with butylenes in the presence of 90-100% concentrated sulphuric acid at temperatures 0-10°C in order to reduce the oxidizing property of sulphuric acid. The mixture of isobutane and butylene is charged in the reactor. Sulphuric acid and hydrocarbons are thoroughly mixed in the reactor to form an emulsion. The mixture is passed on to a settler, from where spend acid is removed. The acid can be used repeatedly and there is no acid-disposal problem.

The hydrocarbon layer from the settler is transferred to a fractionator, where isobutane is separated. Then the alkylate is goes to de-butaniser, where butane is separated and collected. The alkylate is then passed to a re-run tower for the recovery of aviation alkylate fraction from the top. High boiling alkylated products are with-drawn as bottoms.



(Catalytic alkylation of iso-butene)

Polymerization:

Polymerization is a process for converting by-product hydrocarbon gasses produced in cracking into liquid hydrocarbons suitable for use as high-octane motor and for petrochemicals. To combine oleferic gases by polymerization to form heavior fraitions, the combining fraitions must be unsaturated. Hydrocarbon gases from cracking stills, particularly olefins, have been the foundation of polymerization.

Propylene, normal butylene and iso butylene are the olefins usually polymerized in vapor phase. The following reaction is typical of polymerization reactions.

$$2CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2 \longrightarrow CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2 \xrightarrow{H_3PO_4} C_{12}H_{24}$$

Isobutylene — Diisobutylene — Tetramer (tetrapropylene)

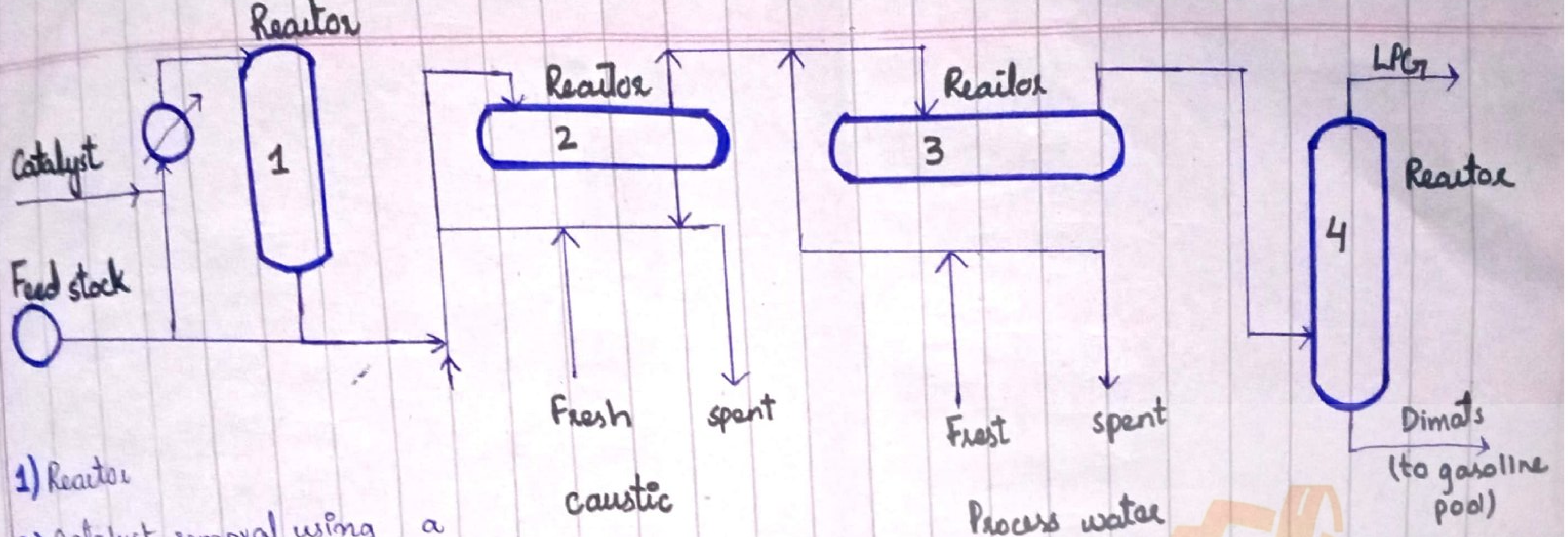
Vapor phase cracking produces considerable quantities of unsaturated gases, hence polymerization units are often operated in conjunction with this type of cracking.

Thermal polymerization is practical only for large-scale operations because of the difficulty in obtaining good heat control in small sized units.

Catalytic polymerization:- is practical on both large and small scale and is further more adaptable to combination with reforming to increase quality of gasoline. The catalysts used include sulphuric acid, copper pyrophosphate or phosphoric acid.

A newer version of polymerization was introduced. It is a dimersol process.

The **Dimersol process** uses a soluble catalytic complex injected into the feed before it enters the reactor. The heat of reaction is taken away by circulating a portion of the bottoms back to the reactor after passing it through a cooling water exchanger. The product goes through a neutralizing system that uses caustic to destroy the catalyst so that the resulting polymer is clean and stable.



1) Reactor
2) Catalyst removal using a caustic wash.
3) Water wash
4) Distillation

Finishing Processes

The finishing process is a critical step in petroleum refining, as it enables the production of high-quality products that meet specific standards and regulations.

Finishing process in petroleum refining.

⇒ Treatment Processes:

- **Blending:** Combining different streams to achieve a desired product composition. This involves mixing various petroleum fractions, additives, and other chemicals to produce a final product that meets specific quality and performance standards.
- **Additivation:** Adding chemicals or additives to enhance product performance or stability. Additives can improve fuel efficiency, reduce emissions, enhance lubricity or provide other benefits.
- **Filtration:** Removing impurities or contaminants to improve product quality. Filtration can involve physical or chemical methods to remove particles, water, or other impurities.

CamScanner

⇒ **Product Finishing:**

- **Gasoline finishing:** Processes to produce market-ready gasoline, including blending, additivation, and filtration. Gasoline finishing may also involve processes like vapour recovery and splash blending.
- **Diesel finishing:** Processes to produce market-ready diesel fuel, including blending, additivation and filtration. Diesel finishing may also involve processes like cold flow improvement and stability enhancement.
- **Jet-fuel finishing:** Jet fuel finishing may also involve processes like thermal stability testing and freeze point control.

⇒ **Quality Control and Testing:**

- **Product Testing:** Methods and procedures for testing finished products to ensure they meet quality and performance standards. Product testing may involve physical, chemical and performance tests.
- **Quality Control Measures:** Procedures Quality control measures may involve statistical process control, sampling and testing.

⇒ Packaging and Distribution :

- **Packaging Options:** Types of packaging used for finished petroleum products, such as drums, tanks and pipelines.
- **Distribution Channels:** Methods for transporting finished products from the refinery to the end-user, including trucking, railing and piping.

⇒ Environmental and Safety Considerations:

- **Environmental Impact:** Measures to minimize the environmental impact of the finishing process are waste management, emission control and spill prevention.
- **Safety Precautions:** Procedures for ensuring the safety of personnel and equipment during the finishing process are personal protective equipment, training and emergency response planning.

⇒ Hydrogenation Processes :

- **Hydrotreating:** A process that uses hydrogen to remove impurities from petroleum products such as diesel fuel and jet fuel.

• **Hydrocracking:** A process that uses hydrogen to crack heavy petroleum fractions into lighter, more valuable products.

• **Hydrogenation of Aromatics:** A process that uses hydrogen to remove impurities and improve quality of aromatic petroleum products such as gasoline and jet fuel.