Petrochemicals

By
Assist. Prof.
Dr. Kadhum Muttar Shabeeb

Crude Oil Processing and Production of Hydrocarbon Intermediates

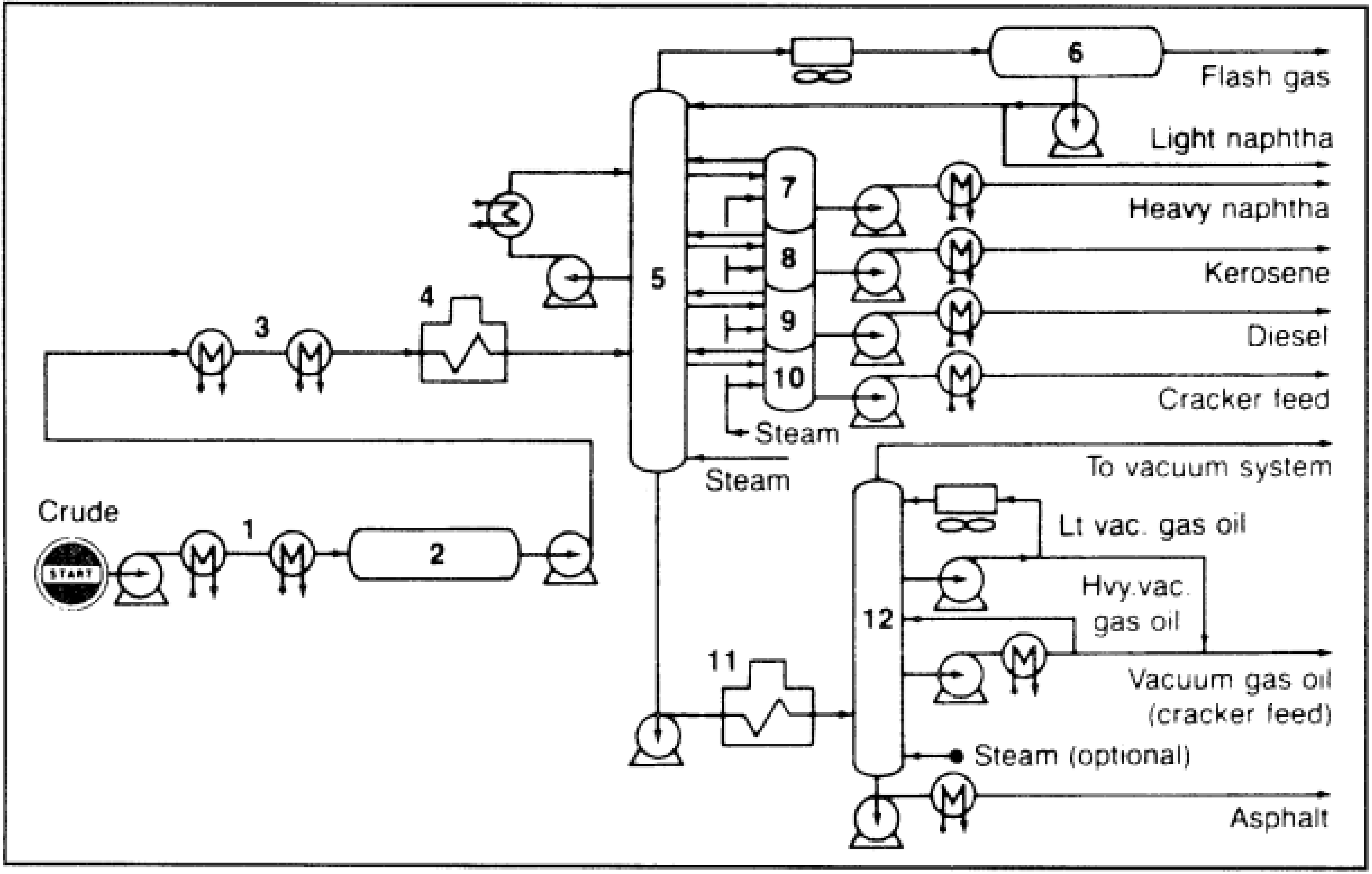
PHYSICAL SEPARATION PROCESSES

1) Atmospheric Distillation

- Atmospheric distillation separates the crude oil complex mixture into different fractions with relatively narrow boiling ranges.
- In general, separation of a mixture into fractions is based primarily on the difference in the boiling points of the components.
- In atmospheric distillation units, one or more fractionating columns are used.
- Distilling a crude oil starts by preheating the feed by exchange with the hot product streams.
- The feed is further heated to about 320°C as it passes through the heater pipe.

- The hot feed enters the fractionator, which normally contains 30–50 fractionation trays.
- Steam is introduced at the bottom of the fractionator to strip off light components.
- The efficiency of separation is a function of the number of theoretical plates of the fractionating tower and the reflux ratio.
- Reflux is provided by condensing part of the tower overhead vapors.
- Reflux ratio is the ratio of vapors condensing back to the still to vapors condensing out of the still (distillate).
- The higher the reflux ratio, the better the separation of the mixture.
- Products are withdrawn from the distillation tower as side streams, while the reflux is provided by returning a portion of the cooled vapors from the tower overhead condenser.
- Additional reflux could be obtained by returning part of the cold side stream products to the tower.

- In practice, the reflux ratio varies over a wide range according to the specific separations desired.
- From the overhead condenser, the uncondensed gases are separated, and the condensed light naphtha liquid is withdrawn to storage.
- Heavy naphtha, kerosine, and gas oil are withdrawn as side stream products.
- The residue is removed from the bottom of the distillation tower and may be used as a fuel oil.
- It may also be charged to a vacuum distillation unit, a catalytic cracking or steam cracking process.
- Figure 3-1 is a flow diagram for atmospheric and vacuum distillation units.


6
Flash gas
Light naphtha
7
Heavy naphtha
8
Kerosene
9
Diesel
10
Cracker feed
5
4
3
Steam
Steam
To vacuum system
Crude
START
1
2
Lt vac. gas oil
Hvy.vac. gas oil
12
11
Vacuum gas oil (cracker feed)
Steam (optional)
Asphalt

2) Vacuum Distillation

- Vacuum distillation increases the amount of the middle distillates and produces lubricating oil base stocks and asphalt.
- The feed to the unit is the residue from atmospheric distillation.
- In vacuum distillation, reduced pressures are applied to avoid cracking long-chain hydrocarbons present in the feed.
- The feed is first preheated by exchange with the products, charged to the vacuum unit heater, and then passed to the vacuum tower.
- Distillation normally occurs at a temperature range of 400–440°C and an absolute pressure of 25–40 mmHg.
- Products obtained as side streams are vacuum gas oil (VGO), lube oil base stocks, and asphalt.

3) Absorption Process

- This process selectively removes a certain gas from a gas mixture using a liquid absorbent.
- In the refining industry, this process is used extensively to free the product gas streams from acid gases (mainly H_2S) either by using a physical or a chemical absorbent.

4) Adsorption Process

- Adsorption processes use a solid material (adsorbent) possessing a large surface area and the ability to selectively adsorb a gas or a liquid on its surface.
- Examples of adsorbents are silica (SiO_2), anhydrous alumina (Al_2O_3), and molecular sieves (crystalline silica/alumina).
- Adsorption processes may be used to remove acid gases from natural gas and gas streams.

- Adsorption processes are also used to separate liquid mixtures. For example, molecular sieve 5A selectively adsorbs n-paraffins from a low octane naphtha fraction.

- Branched paraffins and aromatics in the mixture are not adsorbed on the solid surface. The collected fraction containing mainly aromatics and branched paraffins have a higher octane number than the feed.

- Desorbing n-paraffins is effected by displacement with another solvent or by using heat.

- The recovered n-paraffins in this range are good steam cracking feedstocks for olefin production.

5) Solvent Extraction

- Liquid solvents are used to extract either desirable or undesirable compounds from a liquid mixture.
- Solvent extraction processes use a liquid solvent that has a high solvolytic power for certain compounds in the feed mixture. For example, ethylene glycol has a greater affinity for aromatic hydrocarbons and extracts them preferentially from a reformate mixture (a liquid paraffinic and aromatic product from catalytic reforming).
- The raffinate, which is mainly paraffins, is freed from traces of ethylene glycol by distillation.
- Other solvents that could be used for this purpose are liquid sulfur dioxide and sulfolane (tetramethylene sulfone).
- The sulfolane process is a versatile extractant for producing high purity BTX aromatics (benzene, toluene, and xylenes). It also extracts aromatics from kerosines to produce low-aromatic jet fuels.

CONVERSION PROCESSES

Conversion processes in the petroleum industry are generally used to:

1. Upgrade lower-value materials such as heavy residues to more valuable products such as naphtha and LPG.
2. Improve the characteristics of a fuel. For example, a lower octane naphtha fraction is reformed to a higher octane reformate product.
3. Reduce harmful impurities in petroleum fractions and residues to control pollution and to avoid poisoning certain processing catalysts.

- Conversion processes are either thermal, where only heat is used to effect the required change, or catalytic, where a catalyst lowers the reaction activation energy.
- The catalyst also directs the reaction toward a desired product or products (selective catalyst).

THERMAL CONVERSION PROCESSES

- The three important thermal cracking techniques are coking, viscosity breaking, and steam cracking.

1) Coking Processes

- Coking is a severe thermal cracking process designed to handle heavy residues with high asphaltene and metal contents.

- These residues cannot be fed to catalytic cracking units because their impurities deactivate and poison the catalysts.

- Products from coking processes vary considerably with feed type and process conditions. These products are hydrocarbon gases, cracked naphtha, middle distillates, and coke.

2) Viscosity Breaking (Vis-breaking)

- Viscosity breaking aims to thermally crack long-chain feed molecules to shorter ones, thus reducing the viscosity and the pour point of the product.

- In this process, the feed is usually a high viscosity, high pour point fuel oil that cannot be used or transported, especially in cold climates, due to the presence of waxy materials.

- Wax is a complex mixture of long-chain paraffins mixed with aromatic compounds having long paraffinic side chains.

- Vis-breaking is a mild cracking process that operates at approximately 450°C using short residence times. Long paraffinic chains break to shorter ones, and dealkylation of the aromatic side chains occurs.

CATALYTIC CONVERSION PROCESSES

- Catalytic conversion processes include naphtha catalytic reforming, catalytic cracking, hydrocracking, hydrodealkylation, isomerization, alkylation, and polymerization. In these processes, one or more catalyst is used.

1) Catalytic Reforming

- The aim of this process is to improve the octane number of a naphtha feedstock by changing its chemical composition.
- Hydrocarbon compounds differ greatly in their octane ratings due to differences in structure.
- In general, aromatics have higher octane ratings than paraffins and cycloparaffins. Similar to aromatics, branched paraffins have high octane ratings.
- The octane number of a hydrocarbon mixture is a function of the octane numbers of the different components and their ratio in the mixture.

- Increasing the octane number of a low-octane naphtha fraction is achieved by changing the molecular structure of the low octane number components.
- Catalytic reforming is considered the key process for obtaining benzene, toluene, and xylenes (BTX).
- These aromatics are important intermediates for the production of many chemicals.
- The feed to a catalytic reformer is normally a heavy naphtha fraction produced from atmospheric distillation units.
- Naphtha from other sources such as those produced from cracking and delayed coking may also be used.
- The catalysts generally used in catalytic reforming are dual functional to provide two types of catalytic sites, hydrogenation-dehydrogenation sites and acid sites.
- Bimetallic catalysts such as Pt/Re were found to have better stability, increased catalyst activity, and selectivity.

- Many reactions occur in the reactor under reforming conditions. These are aromatization reactions, which produce aromatics; isomerization reactions, which produce branched paraffins; and other reactions, which are not directly involved in aromatics formation (hydrocracking and hydrodealkylation).

2) Catalytic Cracking

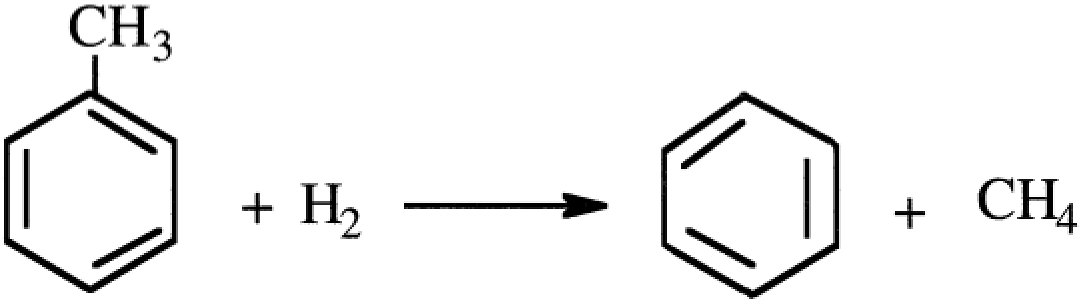
- Its principal aim is to crack lower-value stocks and produce higher-value light and middle distillates.
- The process also produces light hydrocarbon gases, which are important feedstocks for petrochemicals.
- Catalytic cracking produces more gasoline of higher octane than thermal cracking.
- The catalysts generally used in catalytic reforming is synthetic amorphous silica-alumina, which is more active and stable. Incorporating zeolites (crystalline alumina-silica) with the silica/alumina catalyst improves selectivity towards aromatics.

3) Hydrocracking Process

- Hydrocracking is essentially catalytic cracking in the presence of hydrogen.
- It is one of the most versatile petroleum refining schemes adapted to process low value stocks.
- Generally, the feedstocks are not suitable for catalytic cracking because of their high metal, sulfur, nitrogen, and asphaltene contents.The process can also use feeds with high aromatic content.
- Products from hydrocracking processes lack olefinic hydrocarbons.
- The product slate ranges from light hydrocarbon gases to gasolines to residues.
- Depending on the operation variables, the process could be adapted for maximizing gasoline, jet fuel, or diesel production.

4) Hydrodealkylation Process

- This process is designed to hydrodealkylate methylbenzenes, ethylbenzene and C9$^+$ aromatics to benzene.
- The petrochemical demand for benzene is greater than for toluene and xylenes.
- After separating benzene from the reformate, the higher aromatics are charged to a hydrodealkylation unit.
- The reaction is a hydrocracking one, where the alkyl side chain breaks and is simultaneously hydrogenated.
- For example, toluene dealkylates to methane and benzene, while ethylbenzene produces ethane and benzene.



5) Hydrotreatment Processes

- Hydrotreating is a hydrogen-consuming process primarily used to reduce or remove impurities such as sulfur, nitrogen, and some trace metals from the feeds. It also stabilizes the feed by saturating olefinic compounds.

6) Alkylation Process

- Alkylation in petroleum processing produces larger hydrocarbon molecules in the gasoline range from smaller molecules.
- The products are branched hydrocarbons having high octane ratings.
- The term alkylation generally is applied to the acid catalyzed reaction between isobutane and various light olefins, and the product is known as the alkylate.

7) Isomerization Process

- Isomerization is a small-volume but important refinery process. Like alkylation, it is acid catalyzed and intended to produce highly-branched hydrocarbon mixtures.
- The low octane C5/C6 fraction obtained from natural gasoline or from a light naphtha fraction may be isomerized to a high octane product.

8) Oligomerization of Olefins (Dimerization)

- This process produces polymer gasoline with a high octane.
- Both phosphoric and sulfuric acid were used as catalysts.
- At present, the feedstock is either a propylene-propane mixture or propylene-butane mixture where propane and butane are diluents.
- The product is an olefin having a high octane number. When propylene is used, a trimer or a tetramer is formed.