Refining operations

Petroleum refining processes and operations can be separated into five basic areas:

- **Fractionation** (distillation) is the separation of crude oil in atmospheric and vacuum distillation towers into groups of hydrocarbon compounds of differing boiling-point ranges called "fractions" or "cuts."
- **Conversion Processes** change the size and/or structure of hydrocarbon molecules. These processes include: :
  - Decomposition (dividing) by thermal and catalytic cracking;
  - Unification (combining) through alkylation and polymerization; and
  - Alteration (rearranging) with isomerization and catalytic reforming.
- **Treatment Processes** to prepare hydrocarbon streams for additional processing and to prepare finished products. Treatment may include removal or separation of aromatics and naphthenes, impurities and undesirable contaminants. Treatment may involve chemical or physical separation *e.g.* dissolving, absorption, or precipitation using a variety and combination of processes including desalting, drying, hydrodesulfurizing, solvent refining, sweetening, solvent extraction, and solvent dewaxing.

1. Atmospheric distillation

• in the refining process is the separation of crude oil into various fractions or straight-run cuts by distillation in atmospheric and vacuum towers.

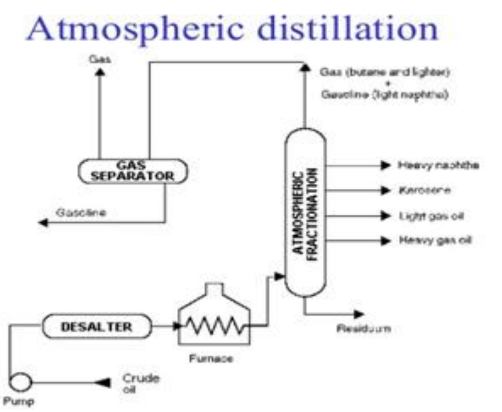
• The main fractions or "cuts" obtained have specific boiling-point ranges and can be classified in order of decreasing volatility into gases, light distillates, middle distillates, gas oils, and residuum.

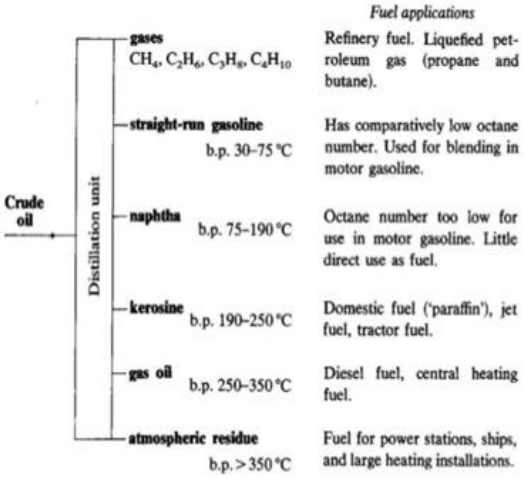
• The desalted crude feedstock is preheated using recovered process heat. The feedstock then flows to a direct-fired crude charge heater then into the vertical distillation column just above the bottom, at pressures slightly 30 the vertical distillation column just above the bottom, at pressures slightly above atmospheric and at temperatures ranging from 340-370°C (above these temperatures undesirable thermal cracking may occur). All but the heaviest fractions flash into vapor.

• As the hot vapor rises in the tower, its temperature is reduced.

• Heavy fuel oil or asphalt residue is taken from the bottom.

• At successively higher points on the tower, the various major products including lubricating oil, heating oil, kerosene, gasoline, and uncondensed gases (which condense at lower temperatures) are drawn off.



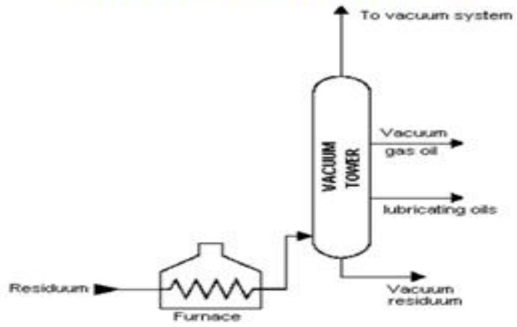


Vacuum distillation unit (VDU)

The temperature required at the furnace outlet for atmospheric distillation unit (ADU) will be excessive if the heavier fractions will be distilled in the ADU. This will be resulted in thermal cracking and loss of the product and fouling of the equipment. This necessitates the use of vacuum distillation column where the distillation occurs under sub-atmospheric conditions.

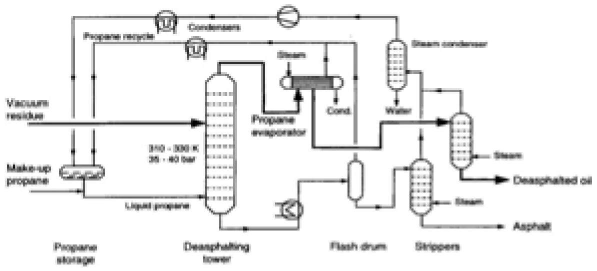
Decreasing pressure of a component decreases the boiling point and vice versa.

Vacuum distillation



Propane deasphalting

- Coke-forming tendencies of heavier distillation products are reduced by removal of asphaltenic materials by solvent extraction.
- Liquid propane is a good solvent (butane and pentane are also commonly used).
- Deasphalting is based on solubility of hydrocarbons in propane.
- Vacuum residue is fed to a countercurrent deasphalting tower.
- Alkanes dissolve in propane whereas asphaltenic materials (aromatic compounds), 'coke-precursors' do not.
- Asphalt is sent for thermal processing.



Solvent extraction

- The purpose of solvent extraction is to prevent corrosion, protect catalyst in subsequent processes, and improve finished products by removing unsaturated, aromatic hydrocarbons from lubricant and grease stocks.
- The solvent extraction process separates aromatics, naphthenes, and impurities from the product stream by dissolving or precipitation. The feedstock is first dried and then treated using a continuous countercurrent solvent treatment operation.
- In one type of process, the feedstock is washed with a liquid in which the substances to be removed are more soluble than in the desired resultant product. In another process, selected solvents are added to cause impurities to precipitate out of the product. In the adsorption process, highly porous solid materials collect liquid molecules on their surfaces.
- The solvent is separated from the product stream by heating, evaporation, or fractionation, and residual trace amounts are subsequently removed from the raffinate by steam stripping or vacuum flashing.
  - Electric precipitation may be used for separation of inorganic compounds.
  - The solvent is regenerated for reused in the process.
  - The most widely used extraction solvents are phenol, furfural, and cresylic acid.
  - Other solvents less frequently used are liquid sulfur dioxide, nitrobenzene, and 2,2' dichloroethyl ether.
  - The selection of specific processes and chemical agents depends on the nature of the feedstock being treated, the contaminants present, and the finished product requirements.

Solvent dewaxing

- Solvent dewaxing is used to remove wax from either distillate or residual basestock at any stage in the refining process.
- There are several processes in use for solvent dewaxing, but all have the same general steps, which are::
  - mixing the feedstock with a solvent;
  - precipitating the wax from the mixture by chilling; and
  - recovering the solvent from the wax and dewaxed oil for recycling by distillation and steam stripping.
- Usually two solvents are used: toluene, which dissolves the oil and maintains fluidity at low temperatures, and methyl ethyl ketone (MEK), which dissolves little wax at low temperatures and acts as a wax precipitating agent.
- Other solvents sometimes used include benzene, methyl isobutyl ketone, propane, petroleum naphtha, ethylene dichloride, methylene chloride, and sulfur dioxide.
- In addition, there is a catalytic process used as an alternate to solvent dewaxing.

Thermal Cracking

Description

- Because the simple distillation of crude oil produces amounts and types of products that are not consistent with those required by the marketplace, subsequent refinery processes change the product mix by altering the molecular structure of the hydrocarbons.
- One of the ways of accomplishing this change is through "cracking," a process that breaks or cracks the heavier, higher boiling-point petroleum fractions into more valuable products such as gasoline, fuel oil, and gas oils.
- The two basic types of cracking are thermal cracking, using heat and pressure, and catalytic cracking.
- Tow general types of reaction occur during thermal cracking

1. (primary reactions): The decomposition of large molecules into small molecules

$$\underset{\text{butane}}{CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3} \longrightarrow \underset{\text{methane}}{CH_4} + \underset{\text{propene}}{CH_3\text{-}CH{=}CH_2}$$

$$\underset{\text{butane}}{CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3} \longrightarrow \underset{\text{ethane}}{CH_3\text{-}CH_3} + \underset{\text{ethylene}}{CH_2{=}CH_2}$$

2. (secondary reactions): Reactions by which some of the primary product interact to form higher molecular weight materials (secondary reactions):

$$CH_2{=}CH_2 + CH_2{=}CH_2 \longrightarrow CH_3\text{-}CH_2\text{-}CH{=}CH_2$$

ethylene ethylene butene

or

$$R\text{-}CH{=}CH_2 + R'\text{-}CH{=}CH_2 \longrightarrow \text{tar, heavy oil, coke}$$

(The mechanism of this thermal reactions is free radical mechanism

So prpose oe suggest the mechanism of the above two reaction

Catalytic Cracking

- **Introduction**
- Catalytic cracking breaks complex hydrocarbons into simpler molecules in order to increase the quality and quantity of lighter, more desirable products and decrease the amount of residuals.
- This process rearranges the molecular structure of hydrocarbon compounds to convert heavy hydrocarbon feedstock into lighter fractions such as kerosene, gasoline, LPG, heating oil, and petrochemical feedstock.
- The catalysts used in refinery cracking units are typically solid materials (zeolite, aluminum hydrosilicate, treated bentonite clay, fuller's earth, bauxite, and silica-alumina) that come in the form of powders, beads, pellets or shaped materials called extrudites.

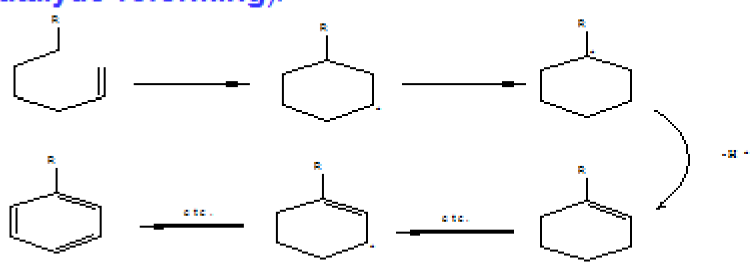
A)There are three basic functions in the catalytic cracking process:

- Reaction: Feedstock reacts with catalyst and cracks into different hydrocarbons;

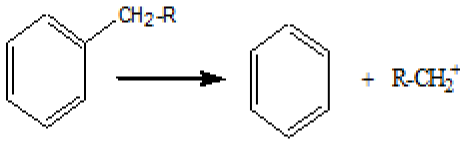
$$R\text{-}CH_2\text{-}CH_2\text{-}R' + \text{catalyst} \longrightarrow R\text{-}CH_2\text{-}CH^+\text{-}R'$$

$$R\text{-}CH_2\text{-}CH^+\text{-}R' \xrightarrow{-H^+} R\text{-}CH{=}CH\text{-}R'$$

- The intermediate alkene may cyclized by internal addition of a carbonium ion to a double bond may occur (**Catalytic reforming**):



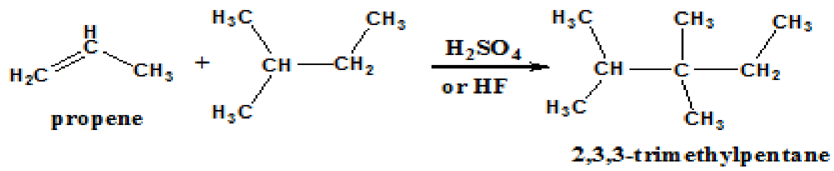
- Dealkylation of alkyl benzenes may occur without ring degradation below 500° C

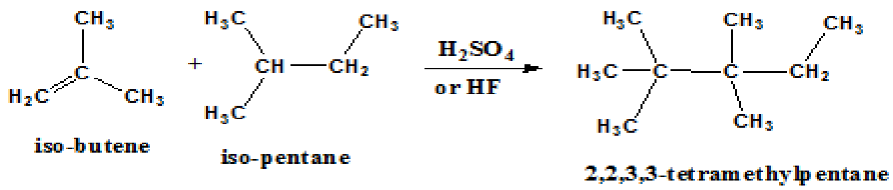


Alkylation

- **Introduction**
  - Alkylation combines low-molecular-weight olefins (primarily a mixture of propylene and butylene) with isobutene in the presence of a catalyst, either sulfuric acid or hydrofluoric acid.
  - The product is called alkylate and is composed of a mixture of high-octane, branched-chain paraffinic hydrocarbons.
  - Alkylate is a premium blending stock because it has exceptional antiknock properties and is clean burning.
  - The octane number of the alkylate depends mainly upon the kind of olefins used and upon operating conditions.

Alkylation





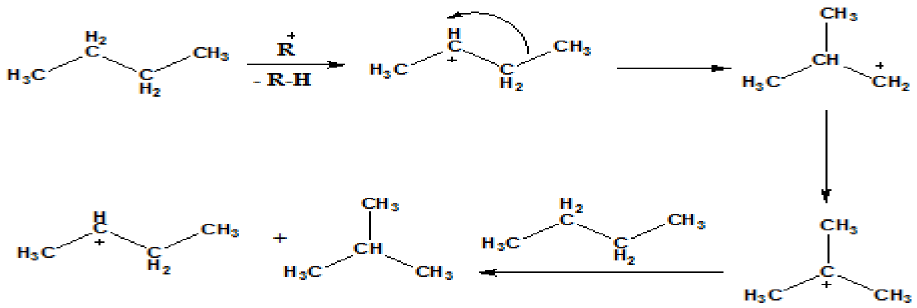
Isomerization

- Isomerization converts n-butane, n-pentane and n-hexane into their respective isoparaffins of substantially higher octane number.
- The straight-chain paraffins are converted to their branched-chain counterparts whose component atoms are the same but are arranged in a different geometric structure.
- The catalyst used may be aluminum chloride promoted with HCl

$$AlCl_3 + HCl \rightleftharpoons [AlCl_4]^- H^+$$

or a platinum containing catalyst.

- Paraffins are isomerized by means of the formation and rearrangement of a carbocation.



Polymerization

- Polymerization in the petroleum industry is the process of converting light olefin gases including ethylene, propylene, and butylene into hydrocarbons of higher molecular weight and higher octane number that can be used as gasoline blending stocks.
- Polymerization combines two or more identical olefin molecules to form a single molecule with the same elements in the same proportions as the original molecules.
- Polymerization may be accomplished thermally or in the presence of a catalyst at lower temperatures.