Petrochemicals

By

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- Production Of Olefins & Diolefins
- Chemicals Based on Methane

Production of Olefins

Steam Cracking of Hydrocarbons

- The main route for producing light olefins, especially ethylene, is the steam cracking of hydrocarbons.
- The feedstocks for steam cracking units range from light paraffinic hydrocarbon gases to various petroleum fractions and residues.
- The cracking reactions are principally bond breaking, and a substantial amount of energy is needed to drive the reaction toward olefin production.
- The simplest paraffin (alkane) and the most widely used feedstock for producing ethylene is ethane.
- Cracking ethane can be visualized as a free radical dehydrogenation reaction, where hydrogen is a coproduct:

$$CH_3CH_3 \rightarrow CH_2{=}CH_2 + H_2 \qquad \Delta H_{590^\circ C} = +143\ KJ$$

- The reaction is highly endothermic, so it is favored at higher temperatures and lower pressures.
- Superheated steam is used to reduce the partial pressure of the reacting hydrocarbons’ (in this reaction, ethane).
- Superheated steam also reduces carbon deposits that are formed by the pyrolysis of hydrocarbons at high temperatures. For example, pyrolysis of ethane produces carbon and hydrogen: $CH_3CH_3 \rightarrow 2C + 3H_2$

- Ethylene can also pyrolyse in the same way.
- Additionally, the presence of steam as a diluent reduces the hydrocarbons’ chances of being in contact with the reactor tube-wall.
- Deposits reduce heat transfer through the reactor tubes, but steam reduces this effect by reacting with the carbon deposits (steam reforming reaction).
- Many side reactions occur when ethane is cracked.

Process Variables

• The important process variables are reactor temperature, residence time, and steam/hydrocarbon ratio.

Temperature

•Increasing temperature favors the formation of olefins, high molecular weight olefins, and aromatics.

Residence Time

Short residence times are required for high olefin yield. When ethane and light hydrocarbon gases are used as feeds, shorter residence times are used to maximize olefin production and minimize BTX and liquid yields.

Steam/Hydrocarbon Ratio

• A higher steam/hydrocarbon ratio favors olefin formation. Steam reduces the partial pressure of the hydrocarbon mixture and increases the yield of olefins.

PRODUCTION OF DIOLEFINS

The most important industrial diolefinic hydrocarbons are butadiene and isoprene.

Butadiene

- Butadiene is the raw material for the most widely used synthetic rubber, a copolymer of butadiene and styrene (SBR).
- In addition to its utility in the synthetic rubber and plastic industries (over 90% of butadiene produced), many chemicals could also be synthesized from butadiene.
- Butadiene is obtained as a by-product from ethylene production.
- It is then separated from the C4 fraction by extractive distillation using furfural.
- Butadiene could also be produced by the catalytic dehydrogenation of butanes or a butane/butene mixture.

- Butadiene could also be obtained by the reaction of acetylene and formaldehyde in the vapor phase over a copper acetylide catalyst.

Isoprene

- Isoprene (2-methyl 1,3-butadiene) is the second most important conjugated diolefin after butadiene.
- Most isoprene production is used for the manufacture of cis-polyisoprene, which has a similar structure to natural rubber. It is also used as a copolymer in butyl rubber formulations.
- The following reviews the important approaches for isoprene production.

1) Dehydrogenation of Tertiary Amylenes
2) From Acetylene and Acetone
3) From Isobutylene and Formaldehyde
4) From Isobutylene and Methylal (dimethoxymethane)

Chemicals Based on Methane