# **Chapter 3: Production of Olefins and Diolefins**

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# 3.1 Introduction

The most important olefins and diolefins used to manufacture petrochemicals are ethylene, propylene, butylenes and butadiene. Butadiene, a conjugated diolefin, is normally coproduced with  $C_2$ - $C_4$  olefins from different cracking processes. Separation of these olefins from catalytic and thermal cracking gas streams could be achieved using physical and chemical separation methods. However, the petrochemical demand of olefins and butadiene are much greater than the amounts these operations produced.

# 3.2 **Production of Ethylene**

Ethylene is a hydrocarbon which has the formula  $C_2H_4$  or  $H_2C=CH_2$ . It is a colorless flammable gas with a faint "sweet and musky" odor when pure. Propene, also known as propylene or methyl ethylene, is an unsaturated organic compound having the chemical formula  $C_3H_6$ .

The main route for producing light olefins, especially ethylene, is the <u>steam cracking</u> of hydrocarbons. The feedstocks for steam cracking units range from <u>light paraffinic</u> <u>hydrocarbon gases to various petroleum fractions and residues</u>. The cracking reactions are principally bond breaking and a substantial amount of energy is needed to drive the reaction toward olefin production. Ethane is the most widely used feedstock for producing <u>ethylene</u>. Ethane is obtained from natural gas liquids. Cracking of ethane can be visualized as a free radical dehydrogenation reaction:

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

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. This process is called **pyrolysis**. Pyrolysis is the thermal cracking of petroleum hydrocarbons with steam, also called steam cracking. Superheated steam also reduces carbon deposits that are formed by the pyrolysis of ethane:

 $CH_3CH_3 \rightarrow 2C + 3H_2$ 

**Application**: To produce polymer grade ethylene (99.95 vol%). Major byproducts are propylene (chemical or polymer-grade), a butadiene-rich  $C_4$  stream,  $C_6$  to  $C_8$  aromatics-rich pyrolysis gasoline and high-purity hydrogen.



Figure 3-1 Lummus Technology process for producing ethylene from ethane.

**Description**: Hydrocarbon feedstock is preheated and cracked in the presence of steam in tubular **SRT** (short residence time) <u>pyrolysis furnaces</u> (1). This approach features extremely high olefin yields, long run length and mechanical integrity. The products exit the furnace at 815-875 °C and are rapidly quenched in the transfer line <u>exchangers</u>

(2) that generate super high-pressure (SHP) steam. The latest generation furnace design is the SRT VI.

Furnace effluent, after quench, flows to the gasoline fractionators (3) where the heavy oil fraction is removed from the gasoline and lighter fraction (liquids cracking only). Further cooling of furnace effluents is accomplished by a direct water quench in the quench tower (4). Raw gas from the quench tower is compressed in a multistage centrifugal compressor (5) to greater than 500 psig. The compressed gas is then dried (6) and chilled. Hydrogen is recovered in the chilling train (7), which feeds the demethanizer (8). The demethanizer operates at about100 psia, providing increased energy efficiency. The bottoms from the demethanizer go to the deethanizer (9). Acetylene in the deethanizer overhead is hydrogenated (10) or recovered. The ethylene-ethane stream is fractionated (11) and polymer grade ethylene is recovered. Ethane leaving the bottom of the ethylene fractionators is recycled and cracked to extinction. The deethanizer bottoms and condensate stripper bottoms from the charge compression system are depropanized (12). Methylacetylene and propadiene are hydrogenated in the depropanizer using CDHydro catalytic distillation hydrogenation <u>technology</u>. The depropanizer bottoms is separated into mixed  $C_4$  and light gasoline streams (14). Polymer-grade propylene is recovered in a propylene fractionator (13).

**Energy consumption**: Energy consumptions are 3,300 kcal/kg of ethylene produced for ethane cracking and 5,000 kcal/kg of ethylene for naphtha feed stocks.

#### **Condition and Mechanism**

The main gas feedstock for ethylene production is ethane. Propane and butane or their mixture, LPG, are also used, but to a lesser extent. They are specially used when co-product propylene, butadiene, and butene are needed. The advantage of using ethane as a feed to cracking units is a high ethylene yield with minimum co-products.

The following are typical operating conditions for an ethane cracking unit and the products obtained:

Conditions:	
Temperature, °C	750-850
Pressure, Kg/cm <sup>2</sup>	1-1.2
Steam/HC	0.5
Yield wt %	
Hydrogen + methane	12.9
Ethylene	80.9
Propylene	1.8
Butadiene	1.9
Other*	2.5
* Other: Propane 0.3, butanes 0.4, buter	nes 0.4, C <sub>5</sub> <sup>+</sup> 1.4

The feed into an ethylene furnace can be ethane, propane, butane, gas oil, or naphtha.

# Mechanism:

1- Dehydrogenation of ethane:

 $\begin{array}{c} CH_3\text{-}CH_3 {\rightarrow} CH_2 {=} CH_2 + H_2 \\ Ethane & Ethylene \\ CH_3CH_2CH_3 {\rightarrow} CH_2 {=} CH_2 {+} CH_4 \\ Propane & Ethylene \end{array}$ 

2-Dehydrogenation of propane:

 $CH_3CH_2CH_3 \rightarrow CH_2 = CHCH_3 + H_2$ 

**Furnace design**: The furnace is tubular type arranged either vertical or horizontal, and made of stainless steel and contain burners mounted in the bottom or on a side of these burners with NG, reduced crude or fuel oil burns to give heat.

Process Variableshow we can increase the rate of olofine or ethylene productionThe important process variables are reactor temperature, residence time, andsteam/hydrocarbon ratio. Feed characteristics are also considered, since they influencethe process severity.

#### 1. Temperature

Steam cracking reactions are highly endothermic. Increasing temperature favors the formation of olefins, high molecular weight olefins, and aromatics. Optimum

temperatures are usually selected to maximize olefin production and minimize formation of carbon deposits. Reactor temperature is also a function of the feedstock used. Higher molecular weight hydrocarbons generally crack at lower temperatures than lower molecular weight compounds.

2. Residence Time

In steam cracking processes, olefins are formed as primary products. Aromatics and higher hydrocarbon compounds result from secondary reactions of the formed olefins. Accordingly, 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; residence times of 0.5-1.2 sec are typical.

#### 3. 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. Heavier hydrocarbon feeds require more steam than gaseous feeds to additionally reduce coke deposition in the furnace tubes.

#### 4. Feedstocks

Feeds to steam cracking units vary appreciably, from light hydrocarbon gases to petroleum residues. Due to the difference in the cracking rates of the various hydrocarbons, the reactor temperature and residence time vary. As mentioned before, long chain hydrocarbons crack more easily than shorter chain compounds and require lower cracking temperatures.

The rates of cracking hydrocarbons differ according to structure. Paraffinic hydrocarbons are easier to crack than cycloparaffins. Isoparaffins such as isobutane and isopentane give high yields of propylene.

# 3.3 Production of Ethylene Using Liquid Feedstocks

Liquid feedstocks for olefin production are <u>light naphtha</u>, <u>full range naphtha</u>, <u>reformer</u> <u>raffinate</u>, <u>atmospheric gas oil</u>, <u>vacuum gas oil</u>, <u>residues</u>, and <u>crude oils</u>. The ratio of olefins produced from steam cracking of these feeds depends mainly on the feed type and, to a lesser extent, on the operation variables. For example, steam cracking light naphtha produces about twice the amount of ethylene obtained from steam cracking vacuum gas oil under nearly similar conditions. Liquid feeds are usually cracked with lower residence times approximately and higher steam dilution ratios than those used for gas feedstocks. An additional pyrolysis furnace for cracking co-product ethane and propane and an effluent quench exchanger are required for liquid feeds.

Figure 3-2 is a flow sheet for cracking gas oil or naphtha for ethylene production. One advantage of using liquid feeds over gas feedstocks for olefin production is the wider spectrum of co-products. For example, steam cracking naphtha produces, in addition to olefins and diolefins, pyrolysis gasoline rich in BTX. The following conditions are typical for naphtha cracking: *Temperature: 800 °C Pressure: Atmospheric Steam/HC: 0.6–0.8 Kg/Kg Residence time: 0.35 sec* 



Figure 3-2 TICHNIP flow sheet of an ethylene plant using Gasoil/Naphtha liquid feedstock.

**<u>Application</u>**: to produce polymer-grade ethylene and propylene, a butadiene-rich  $C_4$  cut, an aromatic  $C_6$ - $C_8$  raw pyrolysis of hydrocarbons ranging from ethane to vacuum gasoil (VGO).

# **Description**

Hydrocarbon feedstocks are preheated (also to recover heat) and then cracked by combining with steam in a tubular pyrolysis furnace at an outlet temperature ranging from 1,500°F to 1,600°F. The furnace technology can be either an SMK type (for gas cracking) or GK6 type (for liquid cracking). The GK6 type design can be oriented to a high olefins yield with very flexible propylene/ethylene ratios, or to a high BTX production. This specific approach allows long run length, excellent mechanical integrity and attractive economics.

The hydrocarbon mixture at the furnace outlet is quenched rapidly in the transfer line exchangers (TLEs) or selective line exchangers (SLEs), generating high-pressure steam. In liquid crackers, cracked gas flows to a primary fractionator, after direct quench with oil, where fuel oil is separated from gasoline and lighter components, and then sent to a

quench water tower for water recovery and gasoline production.

For a liquid cracker, a double demethanizing stripping system operating at medium pressure and reboiled by cracked gas, minimizes the refrigeration required (heat integration) as well as the investment for

separating methane

# 3.4 Production of Propylene

Steam cracking of propane is similar to ethane except for the furnace temperature, which is relatively lower (longer chain hydrocarbons crack easier). However, more byproducts are formed than with ethane. Propane gives higher propylene and butadiene yields, and significantly more aromatic pyrolysis gasoline. Residual gas (mainly  $H_2$  and methane) is about two and half times that compared with ethane.

Application: The Oleflex process is used to produce polymer-grade propylene from propane.



*Figure 3-3 Olyflex process of propylene plant using propane feedstock.* 

**Description:** The complex consists of a <u>reactor section</u>, <u>continuous catalyst regeneration (CCR) section</u>, <u>product separation section</u> and <u>fractionation section</u>. Four radial-flow reactors (1) are used to achieve optimum conversion and selectivity for the endothermic reaction. Catalyst activity is maintained by continuously regenerating catalyst (2). Reactor effluent is compressed (3), dried (4) and sent to a cryogenic separation system (5). A net hydrogen stream is recovered at approximately 90 mol% hydrogen purity. The olefin product is sent to a selective hydrogenation process (6) where dienes and acetylenes are removed. The propylene stream goes to a <u>deethanizer</u> (7) where light-ends are removed prior to the <u>propane-propylene splitter</u> (8). Unconverted feedstock is recycled back to the <u>depropanizer</u> (9) where it combines with fresh feed before being sent back to the reactor section.

# 3.5 Production of Diolefins

Diolefins are hydrocarbon compounds that have two double bonds. Conjugated diolefins have two double bonds separated by one single bond. Due to conjugation, these compounds are more stable than mono olefins and diolefins with isolated double bonds. Conjugated diolefins also have different reactivities than mono olefins. The most important industrial diolefinic hydrocarbons are butadiene and isoprene.

# 3.5.1 **Butadiene** $(CH_2 = CH-CH = CH_2)$

It is a colorless gas that is easily condensed to a liquid. BP: -4.4°C

1,3- Butadiene is a simple conjugated diene with the formula  $C_4H_6$  and it is a monomer for the most widely used synthetic rubber, a copolymer of styrene butadiene rubber (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.

# Principle

Butadiene is obtained as a by-product from ethylene production. It is then separated from the  $C_4$  fraction by extractive distillation using furfural.

Butadiene could also be produced by the <u>catalytic dehydrogenation of butanes</u> or a butane/butene mixture.

$$CH_3CH_2CH_2CH_3 \rightarrow CH_2=CH-CH=CH_2 + 2H_2$$

Figure 3-4 is the Catadiene fixed-bed dehydrogenation of C<sub>4</sub> mixture to butadiene.

The first step involves dehydrogenation of the butanes to a mixture of butenes which are then separated, recycled, and converted to butadiene. The process may also be used for the dehydrogenation of mixed amylenes to isoprene. In the process, the hot reactor effluent is quenched, compressed, and cooled. The product mixture is extracted: unreacted butanes are separated and recycled, and butadiene is recovered.



Figure 3-4. Catadiene process for producing butadiene from butane.

**Description:** The CATADIENE reaction system consists of parallel fixedbed reactors and a regeneration air system. The reactors are cycled through a sequence consisting of reaction, regeneration and evacuation/purge steps. Multiple reactors are used so that the reactor feed/ product system and the regeneration air system operate in a continuous manner.

Fresh n-butane feed is combined with recycle feed from a butadiene extraction unit. The total feed is then vaporized and raised to reaction temperature in a charge heater (1) and fed to the <u>reactors</u> (2). Reaction takes place at vacuum conditions to maximize n-butane conversion and butadiene selectivity. The reactor effluent gas is quenched with circulating oil, <u>compressed</u> (3) and sent to the <u>recovery section</u> (4), where inert gases, hydrogen and light hydrocarbons are separated from the compressed reactor effluent. Condensed liquid from the recovery section is sent to a depropanizer (5), where propane and lighter components are separated from the  $C_4s$ . The bottoms stream, containing butadiene, n-butenes and n-butane, is sent to  $\frac{1}{2}NSEL$  butadiene extraction unit, which recovers butadiene product and recycles n-butenes and n-butane back to the CATADIENE reactors.

After a suitable period of onstream operation, feed to an individual reactor is discontinued and the reactor is reheated/regenerated. Reheat/regeneration air heated in the regeneration air heater (6) is passed through the reactors. The regeneration air serves to restore the temperature profile of the bed to its initial onstream condition in addition to burning coke off the catalyst. When reheat/regeneration is completed, the reactor is re-evacuated for the next onstream period.

## Another Route

Butadiene could also be obtained by the reaction of acetylene and formaldehyde in the vapor phase over a copper acetylide catalyst. The produced 1,4-butynediol is hydrogenated to 1,4-butanediol. Dehydration of 1,4-butanediol yields butadiene.

$$HC = CH + 2H - C - H \longrightarrow HOCH_2C = CCH_2OH$$

1,4 butynediol

HOH<sub>2</sub>CC=CCH<sub>2</sub>OH+2H<sub>2</sub>→ HOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH

$$HOCH_2CH_2CH_2CH_2OH \rightarrow CH_2 = CH--CH = CH_2 + 2H_2O$$

# 3.5.1 **Isoprene** (H<sub>2</sub>C=C—CH=CH<sub>2</sub>)

Isoprene (2-methyl 1,3-butadiene) is the second most important conjugated diolefin after butadiene. In its pure form it is a colorless volatile liquid and its polymers are the main component of natural rubber. 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.

# Principle

Isoprene is prepared using propylene and is an important commodity for polymerization reactions and products. Isoprene is manufacture start with propylene using three consecutive reactions. These are:

**1**. Dimerization of propylene to obtain 2-methyl-1-pentene



The reaction occurs at 200°C and about 200 atm in the presence of a tripropyl aluminum catalyst

2. Isomerization of 2-methyl-1-pentene to obtain 2-methyl-2-pentene



 Pyrolysis of 2-methyl-2-pentene to obtain isoprene along with methane as a side – product.
Pyrolysis required



Application: The process technology consists of three major blocks namely:

- Dimerization-separator-recycle network (DSR)
- Isomerization-separator-recycle network (ISR)
- Pyrolysis-separator-recycle network (PSR)



Figure 3-5 Flow sheet of isoprene production

# **Description**:

Propylene feed is mixed along with unreacted propylene (recovered in a distillation column in the DSR) to enter a mixer. The mixer is fed with tripropyl aluminium

catalyst (this catalyst is in liquid phase) and the mixture is compressed to about 200 atms. At these conditions, the mixture is in the liquid phase.

The liquid phase dimerization feed enters the dimerization reactor. The dimerization reactor is a CSTR with dowtherm fluid circulated in the cooling jacket to remove the heat generated from the exothermic reaction. After the reaction, the liquid stream is subjected to flash operation. From the flash tower a vapor and liquid stream are produced. The liquid stream consists of the catalyst + solvent whereas the vapor stream consists of the unreacted propylene, light ends and the product formed.

The liquid stream from the flash tower is recycled back to the dimerization CSTR and the vapor stream enters a fractionation tower that produces light ends such as  $C_1$ - $C_2$  as the top product. The bottom product consists of propylene and dimerized product i.e., 2-methyl-1-pentene.

This product is subjected to again fractionator in a separate tower to obtain 2-methyl-1pentene as the bottom product and propylene as the top product. The top propylene product is then recycled back to mix with the fresh propylene feed stock and enter the mixer unit with the fresh propylene feed stock and enter the mixer unit.

## **Operating conditions:**

**Dimerization reaction** 

- Catalyst is tripropyl aluminium
- A solvent carrier is used that enables the recovery of the catalyst from the product.
- Operating conditions are 150- 200°C and 200 atms

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Isomerization reaction
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- •The reaction requires an acid catalyst on porous carrier
- Operating conditions are 150-300°C and normal pressure conditions

Pyrolysis reaction

- HBr catalyst is used
- Operating conditions are  $650-800^{\circ}$ C and normal pressure.