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Chapter

A Look at the Industrial Production of Olefins Based on Naphtha Feed: A Process Study of a Petrochemical Unit

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Abstract

Olefins (ethylene, propylene and butadiene) as raw materials play an important role in a lot of chemical and polymer products. In industrial scale, there are several techniques from crude oil, natural gas, coal and methanol for the olefins production. Each of these has some advantages. The petrochemicals with liquid feed can simultaneously produce all of the olefins. Shazand Petrochemical Co. (as the first olefins production unit in Iran) produces all of the olefins using naphtha (light and heavy) feed. In this chapter, the production process of olefins based on naphtha will be studied from the beginning to the end (involving pyrolysis, compression, chilling and fractionation processes).

Keywords: Naphtha, Olefin unit, Petrochemical industry, Separation process

1. Introduction

1.1 Olefins

Olefins are unsaturated compounds with a formula of CnH_2n. The names of these compounds end with –ene, such as ethene (ethylene), propene (propylene), butenes and butadiene. Olefin species are not commonly found in the crude oil. Ethylene and propylene are known as important sources of various industrial chemicals and plastics products. Butadiene is widely used in synthetic rubber production. These as light olefins are industrially produced by pyrolysis and fluid catalytic cracking of the vacuum distillates. Another potential technique for the light olefins production is direct conversion of syngas [1–4].

1.2 Shazand Petrochemical Co.

Shazand Petrochemical Complex produces different range of petrochemical products such as plastics, synthetic rubber and the other chemicals from naphtha (as feedstock). Its total saleable annual production capacity presently is around 620000 tons achieved in eighteen plants to serve domestic and global markets with the standard grades [5]. **Figure 1** shows flow diagram of the Shazand Petrochemical Co. products.
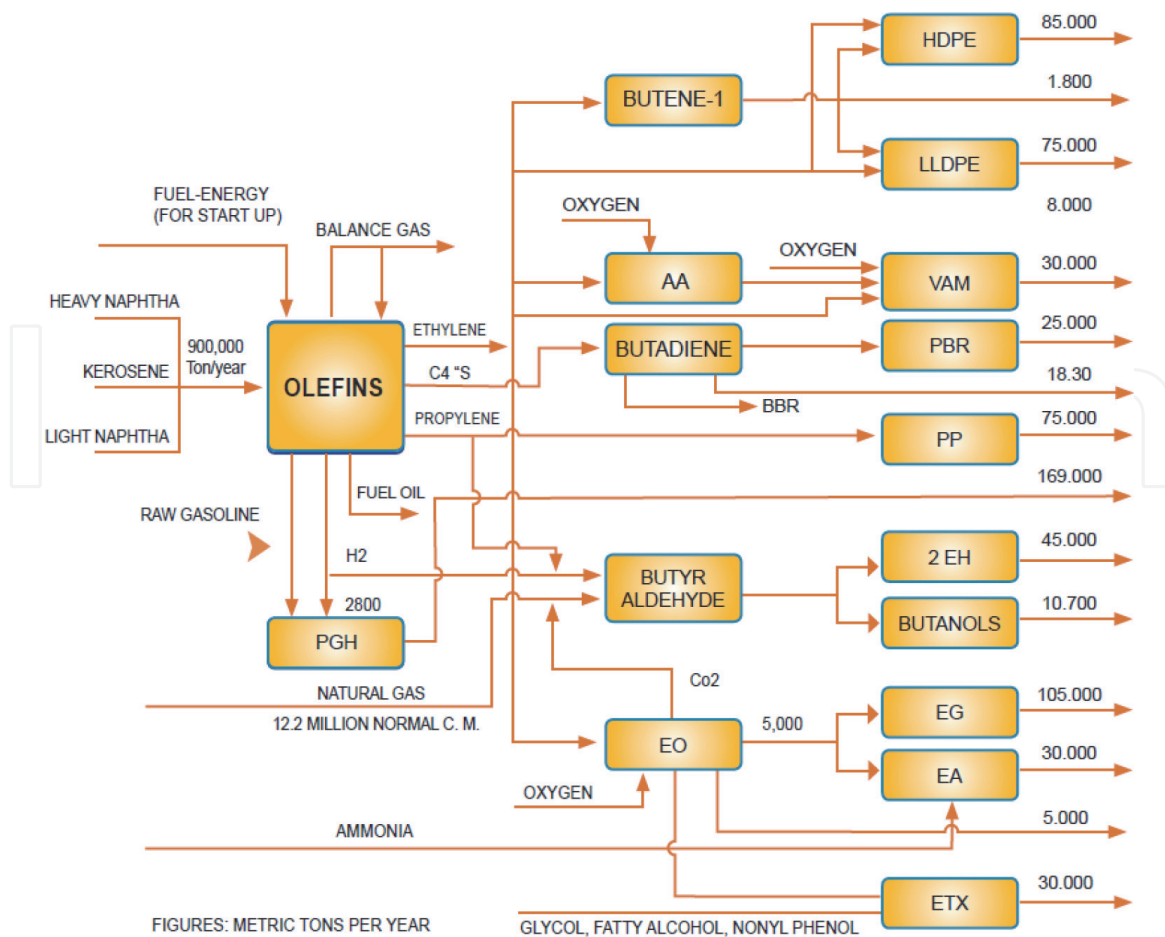
Figure 1.
Flow diagram of the products of Shazand Petrochemical complex [5].

2. Olefin plant

Olefin plants are large, complex units at the heart of petrochemical complexes. Olefin production is a petrochemical process in which saturated hydrocarbons are broken down into smaller, often unsaturated ones. It is the principal industrial method for producing the lighter alkenes commonly known as olefins, including ethene or ethylene, propene or propylene and butadiene. The heavy hydrocarbon compounds are usually cracked at temperatures between 800°C and 860°C. The resulting gas is separated into valuable products suitable for downstream processes. The separation train of a cracker starts with the Hot Section and then the cracked gas is quenched and cooled where heavy fractions are condensed and separated. Later the process steam is condensed and removed from the cracked gas before it enters the compression and chilling sections (Cold Section). The compressed, cracked gas is then separated into specified products. Some fractions (e.g. ethane, propane and butane) are recycled to the furnaces in order to improve overall yields. Today's modern ethylene plants are complex networks of more than 300 individual units, including thermal cracking, cracked gas compression and physical scrubbing, fractionation, adsorptive drying, catalytic hydrogenation and others, operating in the temperature range of 1100°C to −170°C [6–9].

2.1 Hot section

The goal of this section is to take the feed from the sources and pyrolysis it in the furnaces and convert it to organic radicals and hydrocarbons such as hydrogen,

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propane, ethane, ethylene, gasoline, butane, propylene and other heavy compounds which gasoline and fuel oil are the first olefin products. Hot Section consists of six subunits:

- Feed Preheating.

- Cracking Furnaces.

- Primary Fractionation and Fuel Stripping.

- Quench Water/Gasoline System.

- Dilution Steam Generation.

- Low Pressure Steam (LPS) Generation.

2.1.1 Industrial steam cracking

Steam cracking furnaces are process units, devoted to producing ethylene and propylene from a stream of hydrocarbons and steam. Thermal cracking, pyrolysis, with water vapor is a good way to convert inactive paraffinic hydrocarbons to olefin active compounds, which are the main feed for the petrochemical industry. The raw materials used in thermal cracking processes include ethane, propane and butane, liquid naphtha and diesel. The liquid feed of the olefin unit includes light naphtha to heavy diesel. The most important part of an olefin unit is where pyrolysis reactions occur. This part is the reactor inside a heat furnace. Numerous factors such as the amount and type of feed, operating temperature, pressure, the ratio of diluent vapor to the inlet feed, the amount of coke settling, the material and shape of the reactor are effective in the efficiency of products in thermal reactors. In steam cracking, naphtha is diluted with steam and briefly heated in a furnace in the absence of oxygen. Typically, the reaction temperature is very high, around 850°C. The reaction occurs rapidly as the residence time is around some milliseconds and thus the flow rate approaches the speed of sound. When the cracking temperature has been reached, the gas then is quickly quenched in a transfer line heat exchanger or inside a quenching header using quench oil to stop the reaction [10–15].

Pyrolysis as a complex phenomenon has two main parts:

- Dehydrogenation.

- Breaking the C-C bond and converting it to free radicals.

At high temperatures, hydrocarbons become unstable and decompose to hydrogen, methane, C=C and aromatic compounds. The higher the temperature is, the more olefin and aromatic compounds are formed high stability. Therefore, not only light olefin compounds such as ethylene and propylene, but also heavier compounds such as aromatics and tar will be produced.

Research has shown that the cracking reaction is of the first order. The amount of cracking does not depend on pressure. Additionally the activation energy for these reactions is significantly lower than the energy required breaking the C-C bond. Thus, the conversion can be considered as a single molecular reaction and follow the mechanism of first order reactions. According to Rice and Herzfeld, the reaction mechanism is based on the formation of radicals and is a series of chain reactions that result in the production of olefins from hydrocarbons. The

mechanism of chain reactions also explains the low activation energy of these reactions. To be more precise, we consider the following reactions:

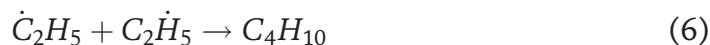a. Break the C-C bond in ethane and turn it into two radicals:

$$C_2H_6 \rightarrow C\dot{H}_3 + C\dot{H}_3 \qquad (1)$$

b. Joining and combining a radical with a feed molecule:

$$C\dot{H}_3 + C_2H_6 \rightarrow CH_4 + C_2\dot{H}_5 \qquad (2)$$
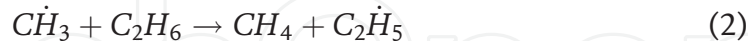
c. Emission stage: Here the new radical is converted to an olefin and hydrogen radical. The hydrogen radical later collides with another feed molecule to form a new radical and a hydrogen molecule:

$$\dot{C}_2H_5 \rightarrow C_2H_6 + \dot{H} \qquad (3)$$

$$\dot{H} + C_2H_6 \rightarrow H_2 + C_2\dot{H}_5 \qquad (4)$$
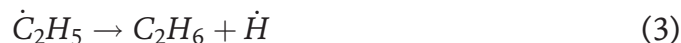
d. Final stage: Chain reactions end in the following four ways:

$$\dot{H} + C\dot{H}_3 \rightarrow H_2 + CH_4 \qquad (5)$$

$$\dot{C}_2H_5 + C_2\dot{H}_5 \rightarrow C_4H_{10} \qquad (6)$$

$$\dot{H} + \dot{H} \rightarrow H_2 \qquad (7)$$

$$\dot{H} + C_2\dot{H} \rightarrow C_2H_2 \qquad (8)$$

The final result of chain reactions is that of steps 3 and 4.

$$C_2H_6 \rightarrow C_2H_4 + H_2 \qquad (9)$$

In the final stage, methane and heavier compounds such as butane are formed.
Speed and rate of reaction transformations:
According to the Arrhenius equation, the reaction rate constant is k = A.exp.$^{-E/RT}$ where A is Arrhenius constant, E is activation energy, R is universal Gas constant and T is temperature.

Since the reaction is a first order, the rate of conversion is obtained from the equation kt = ln 1/1-x.

Where t is the time and x is the amount of conversion of raw materials to crack gas product. This equation is only available at some temperatures because k depends on the temperature. The pressure must be low because at high pressures the reaction follows the second order. Therefore, dilution steam is used to keep the partial pressures low. Conversion of feed to a high quality ethylene product depends on the temperature rising. Temperature should linearly be increased and within a certain range. That is because at high temperatures side effects may occur and these reactions will be of the second-order type, it is likely that ethylene will be converted to methane, which reduces efficiency [16–22].

2.1.2 Cracking furnaces

In the olefin unit, the furnace plays the main role. In general, its job is thermal cracking by which heavy hydrocarbons are broken down and hydrocarbons such as propane, ethane, ethylene, propylene, hydrogen, C4 and C4+ are produced. **Figure 2** shows how feed compound is cracked in the furnace.
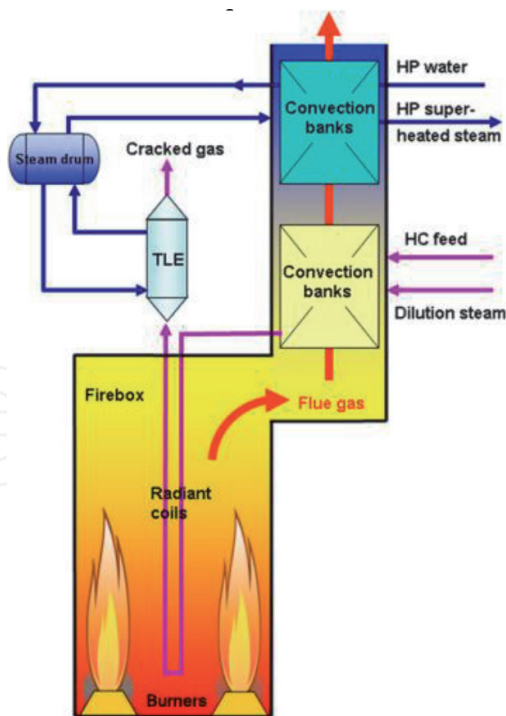
Figure 2.
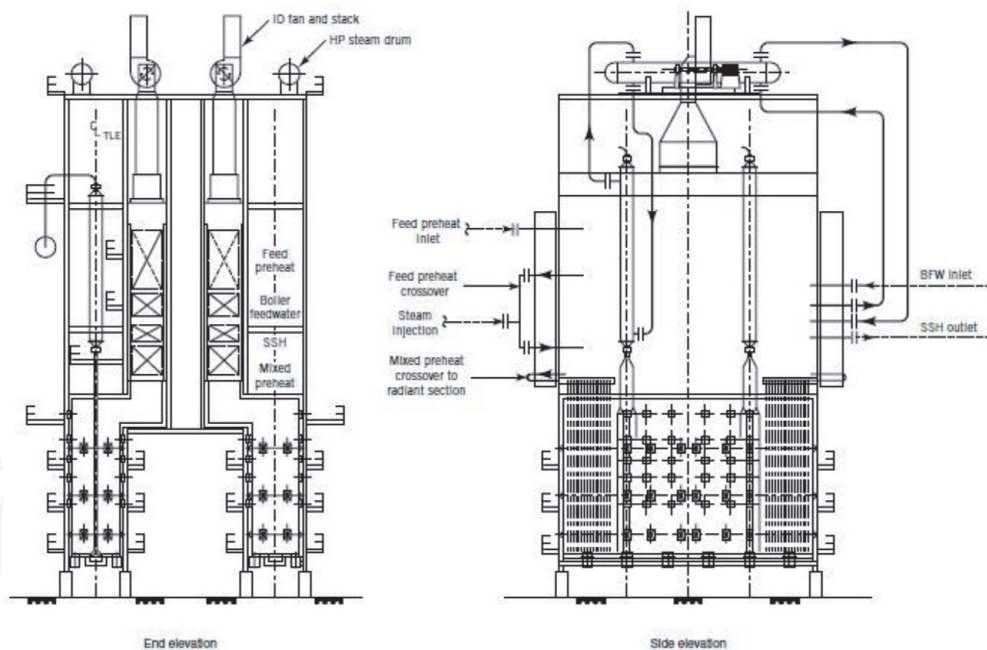*Schematic of the furnace [23].*

Figure 3.
Typical heater configuration (BFW = boiler feed water; SSH = super high pressure steam; HP = high pressure; and ID = induced draft [24]).

2.1.3 Structure of furnaces

In general, furnaces consist of two parts: Radiation and Convection section. There are 10 furnaces in Shazand Petrochemical Olefin Unit, where there are usually 9 furnaces in service and one in de-cocking mode, which will be replaced by another furnace after de-coking. **Figure 3** depicts a typical configuration of an olefin heater.

2.1.3.1 Radiation section (fire box)

This part occupies a larger volume of furnaces and includes 8 coils which are installed in the form of vertical pipes and have 4 coils on both sides. All coils are collected at the end by a collector outlet and the compounds are discharged through a transmission line at the end of the Fire Box. 16 streams are sent to this section through the outlet pipes of the convection section. 108 burners are located on either side of the Radiation Section, which premix fuel and air before reaching the nozzle head. The fuel used for these burners is methane.

2.1.3.2 Convection section

The heat generated in the radiation section is used in the convection section to pre-heat the input feed. The temperature profile in the Radiation Section increases from the bottom to the top, but in the convection section it decreases from the bottom to the top. Therefore, the highest temperature is at the top of the Fire Box. Hence, in general, this type of furnace can be named as reactor which the heated feed enters from above and breaks at the bottom.

2.1.4 Cracking furnace performance

After pre-heating and passing through the emergency valve, the naphtha feed enters the convection section of the furnace. In furnaces, the temperature gradually rises in several stages by coils. The feed temperature rises from 75–105°C and is converted from a liquid to a vapor and mixed with the pre-heated recycled propane and ethane. The diluent steam at 363°C is added to the feed mixture to prevent the hydrocarbon vapor pressure increasing while the mixture's temperature reaches 172°C. Now, the mixture enters the furnace and reaches 603°C in the high temperature coil. The feed flows from this part to the radiation part inside 8 coils which are arranged in vertical tubes and cracking is performed. It finally exits the radiation section with a temperature of 863°C and because side reactions may occur, it quickly enters a heat exchanger called TLE or TLX by which it is cooled with water down to 325°C. The pressure of the mixture is 7.3 bar.

TLE heat exchangers are in the form of shell and tubes which water passes through the shell to cool the cracked gas inside the tubes. Because this temperature is still high, another heat exchanger (called quench fitting) is used to reduce the temperature, which quench oil is mixed with the feed stream and the feed temperature is reduced to 165°C, when the mixture is ready for the next stage (called primary fractionation).

Due to the continuous operation of the furnaces, they must be decontaminated periodically. Therefore, the furnace must be in de-cocking mode approximately every 83 days [23, 25, 26].

2.2 Cold section

The purpose of this section is to separate the following materials from the cracked gas that comes from the Hot Section.

1. Separation of hydrogen and methane

2. Ethylene separation

3. Separation of propylene

4. Separation of C4 compounds

5. Separation of gasoline and heavier compounds

Cold Section consists of compressors and low temperature fractionation sections.

2.2.1 Compressors

In the Cold Section, there are three compressors, two of them are called the Propylene (C-501) and the Ethylene (C-502) compressors, which have a closed cycle and operate according to the Rankin cycle and their task is to cool down the cracked gas to −36°C and − 93°C, respectively. The third compressor (C-201), with a higher capacity than the previous two is utilized to compress the cracked gas from the furnaces where contains the compounds of hydrogen, carbon monoxide, carbon dioxide, acetylene, ethylene, ethane, propadiene, propylene, propane, vinyl acetylene, butadiene, butane, butene, C4+ and water.

First the cracked gas enters a vessel (V-201) where is actually the suction drum of the first stage of a five-stages compressor at 12°C and a pressure of 0.42 bar. Gases escape from the top of the V-201 and liquids (oily water) from the bottom.

Exhaust gases from this tank enter the first stage of the C-201 compressor. The output of this section with a pressure of 3 bar and a temperature of 85°C enters the cooling exchanger (E-201) losing heat to cooling water stream and then exits the exchanger at 35°C and enters to second stage suction drum (V-202). This vessel has a temperature of 29°C and a pressure of 3 bar and at its bottom contains oily water which exits and joins the previous oily water flow from the V-201. In this vessel, pyrolysis gasoline is separated and sent to the tower (T-201). Light gas from the top of the tower is returned to V-201 and semi-light gasoline from the bottom of the tower is sent to a storage tank with pressure and temperature of 0.5 bar and 90°C respectively. There are three more stags in the compressor compressing the cracked gas to 10, 20 and 37 bar, respectively. Other vessels (V-203, 204, 220, 206 and 207) also separate liquids from gas as the compressor's suction drums. The exhausted gas from the third stage must be sweetened and its sulfur compounds and carbon dioxide must be removed by a tower (T-202), where the absorption operation is performed using a caustic solution. In order to prevent the condensation of hydrocarbons and the formation of polymers the output of the V-204, first enters the heat exchanger (E-215) where it reaches a temperature of 45°C and then it enters the tower (T-202).

2.2.1.1 Caustic wash tower (T-202)

The tower consists of three parts: the bottom part of the tower, which performs about 70% of sweetening while the middle part performs about 30% of sweetening operations. At the top of the tower, boiler feed water (B.F.W) is supplied for top-down washing of cracked gas. The feed enters the tower from the first tray of bottom and the water from the top and the caustic solution is continuously circulated inside the tower for more efficiency. The consumed caustic comes out from the bottom of the tower for treatment. Sometimes it is necessary to take the lower part of the tower out of service and wash it to remove the annoying materials and formed polymers. In these cases, feed will enter from the middle part.

Finally, the exhausted gas from the compressor is cooled by a propylene cycle and enters V-207, where the cracked gas is converted into 2 phases of gas and liquid
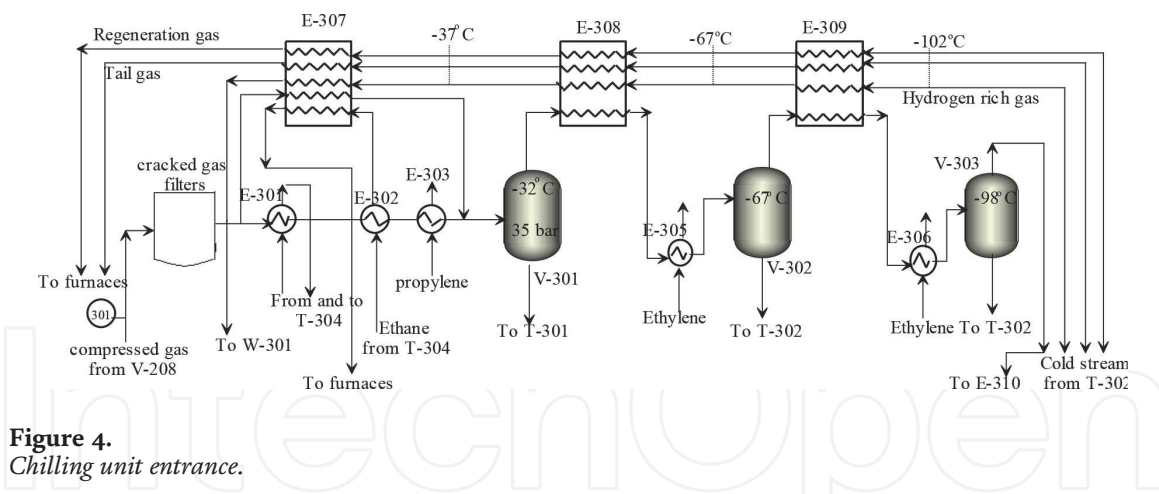
Figure 4.
Chilling unit entrance.

and each phase enters the dryers of the cold section unit separately for drying operations.

2.2.2 Low temperature fractionation

As illustrated in **Figure 4**, this section consists of four plate fin-type heat exchangers (E-307, 308, 309 & 310) which are known as demethanizer feed exchangers cool the cracked gas by separating flows of tail gas, regeneration gas and hydrogen. In fact, the main task of this part is to cool the gas for the feed of demethanizers. The cold section inlet gas first passes through the strainers and reaches $-93°C$ using 5 series kettle-type heat exchangers and also with the help of a cold box. Using flashing in 3 separate vessels (V-301, 302 & 303), feeds for demethanizers (T-301, 302) as well as pressure swing adsorption (PSA) unit are prepared.

2.2.2.1 Hydrogen purification

The purpose of this unit is to provide pure hydrogen for hydrogenation of acetylene, methyl acetylene and propadine in reactors of olefin unit and hydrogenation of pyrolysis gasoline in PGH unit as well as for heavy density polyethylene (HDPE), linear low density polyethylene (LLDPE) and polypropylene (PP) units. 99.99% purity is essential for hydrogen, which is done by PSA. In this unit, the pressure swing adsorption is used to purify hydrogen.

2.2.2.2 Demethanizer and methane separation (T-301 and T302)

Figure 5 shows demethanizer package of olefin plant in Arak petrochemical complex. In demethanizer, methane is removed by fractionation as an over head product. The bottom product, consisting of ethane and heavier compounds, is the feed to the deethanizer. The first demethanizer (T-301) has 20 trays at which input feed enters from tray 16, is supplied from the bottom of the V-301. The bottom temperature of the tower is 17°C, which is supplied by kettle-type re-boiler and quenched water. The top flow cooled by a propylene cycle to $-35°C$, enters the second demethanizer.

The vapor at the top of T-301 is the main feed for T-302, injected at tray 28, which has 50 trays. The feed of this tower also includes the second, third and fourth chilling stages coming from the bottom of V-302, V-303, V-304 and injected at tray 46. For each of these feeds, it is possible to change the entry point up to two trays higher. The boiling heat is supplied by the condensed propylene (3°C) in the re-
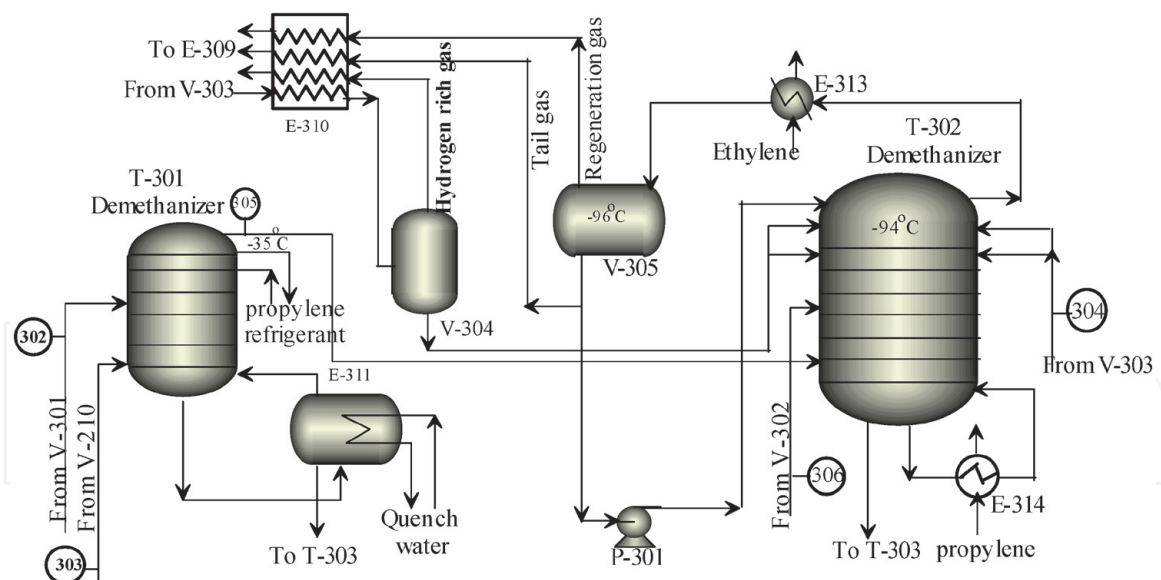
Figure 5.
Demthanizer towers number 1 and 2 (T-301 and T-302).

boiler (E-314), where the flow rate of the propylene is set by the temperature of tray 17 and the bottom product of the tower is sent to the deethanizer (T-303). The impure vapor at the top is cooled by a partial ethylene condenser (−101°C). The pure gas product is sent from V-305 to plate-type exchangers to reach a temperature of 10°C and then it goes to the regeneration system. Part of V-305 liquid is sent to the top of the tower by the pump (P-301) as a reflux.

2.2.2.3 Deethanizer (T-303)

As shown in **Figure 6**, in the deethanizer system of olefin plant, ethane is removed as an overhead product. Propane and heavier components leave the deethanizer as bottom products and are fed to the depropanizer. The bottom products of the first demethanizer (T-301) and the second demethanizer (T-302) enter T-303 separately. Re-boiler heat is generated by low pressure steam (LPS) and the temperature is controlled by the twentieth tray. Exhaust gases are transferred from the top of the tower to the acetylene hydrogenation section. The stream of hydrogenated acetylene returns to the partial condenser (E-315) which is cooled by
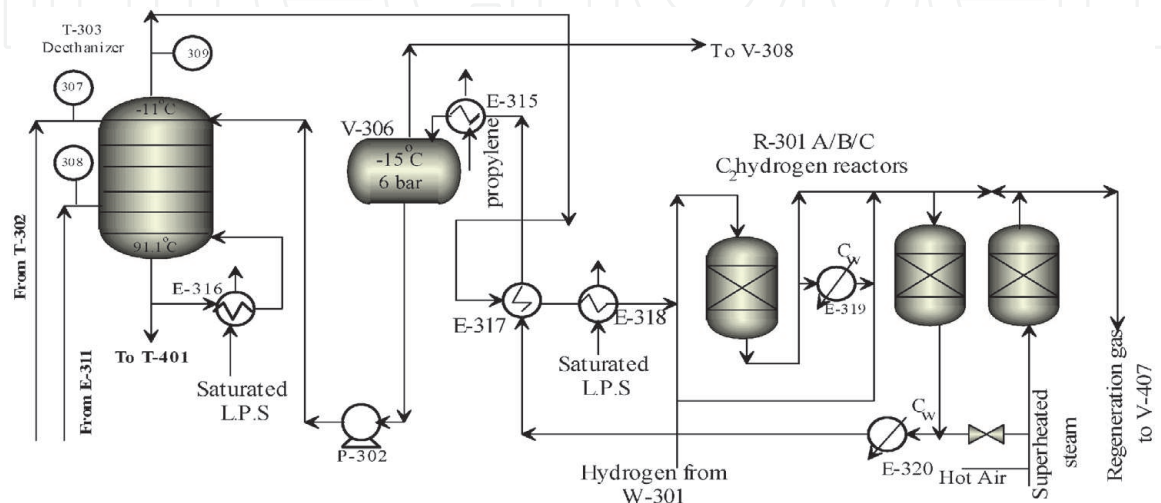

Figure 6.
Deethanizer tower (T-303) and acetylene reactors.

propylene to −20°C and goes to V-306 for separation. The liquid of vessel *i* pumped to T-303 by the P-302 as reflux and the pure gas goes to the C2 splitter tower (T-304).

2.2.2.4 Acetylene hydrogenation

Top products of T-303 first enter E-317 and temperature reaches 45°C and for hydrogenation they enter the first stage of the reactors (R-301 A/B /C) and mix with hydrogen coming from PSA Unit (w-301), the amount of hydrogen is automatically controlled by the feed flow rate. The hydrogenation process temperature on the catalyst bed must be increased (45°C -70°C). To ensure the conversion of all available acetylene, the second reactor is used in series where the output flow of the first reactor is mixed with hydrogen again and enters the second one. To ensure the continuity of operations, three reactors have been designed and two of them are in service and one is in standby mode.

2.2.2.5 Separation of ethylene from ethane (T-304, C2 splitter)

Figure 7 illustrates the loop by which ethylene is separated from ethane as the stream passes through the splitter. Top flow of T-303 enters gas dryer (V-308) and produced water in the reactors is removed. The feed enters T-304, with total 130 trays, at tray 34 or 38. The top 10 trays of this tower are called pasteurization section to separate lighter compounds from ethylene product. Two re-boilers have been provided for this system. Pressure inside the tower varies from about 21.2 to 22.4 bar and the temperature from −27 to −3.4°C. The main re-boiler of the tower is located at the bottom of the tower and uses condensed propylene (at 3°C) for heating. The second re-boiler (E-301) is an internal re-boiler located at tray 39. The condenser of this tower (E-321) works with propylene vapor at −35°C. Top products enter V-309, which is known as Splitter Reflux Accumulator. Off gas is returned to V-206 as a splitter recycle. The liquid of V-309 is also returned to the tower by the pump (P-303) as Reflux. The ethylene product obtains from tray 120 flows to ethylene product surge drum (V-310). The ethylene collected in V-310 has 21.3 bar pressure and a − 27°C temperature. Ethylene product is normally sent to battery limits and after heating. It turns into a gaseous state with a pressure of 21 bar. The excess ethylene is sent to the ethylene tank in liquid form for storage.
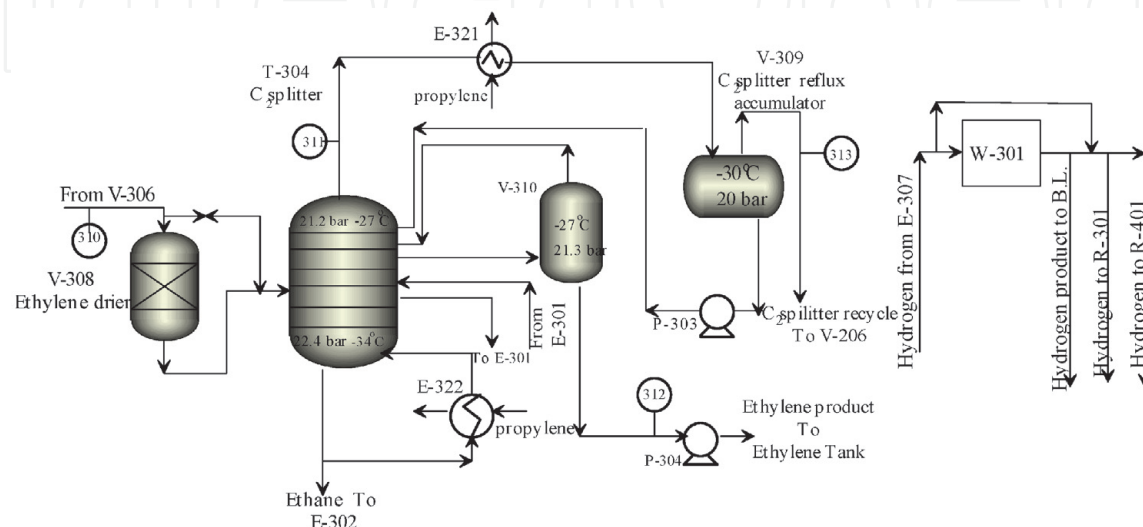

Figure 7.
The configuration of splitter for separation of ethylene from ethane.

The temperature of liquid ethylene in tank is about −128°C and has an atmospheric pressure.

2.2.2.6 Depropanizer (T-401)

As represented in **Figure 8** a depropanizer is a distillation column that is used to separate propane from a mixture containing butane and other heavy components. In the depropanizer, propane is removed as an overhead product and butane and heavier compounds are fed to a debutanizer. This section is known as medium temperature fractionation. The bottom product of T-303 (deethanizer) is mixed with some recycled flow and feed to T-401 at tray 26. The condenser (E-401) works with propylene cycle at 12°C. There are two re-boilers (E-402) that work with low pressure steam (LPS) and change temperature from 42–90°C. The top product of T-401 is collected inside V-401 after condensation (E-401). Part of the liquid is pumped by P-401 to the tower as reflux and another part is directed to the hydro-genation section in R-401 reactors.

2.2.2.7 Debutanizer (T-402)

As shown in **Figure 9**, the debotanizer tower contains 40 trays. The feed enters on tray 21 or 25 directly from the bottom of the depropanizer tower. The vapors of the top of the tower are condensed by the condenser (E-403) and then collected in the accumulator (V-402). By the P-403 one flow is returned to the tower as a reflux and another flow is sent to the battery limits as C4 product. The bottom product of T-402 is light gasoline which is mixed with heavy gasoline, cooled together in E-405 and finally sent for storage.
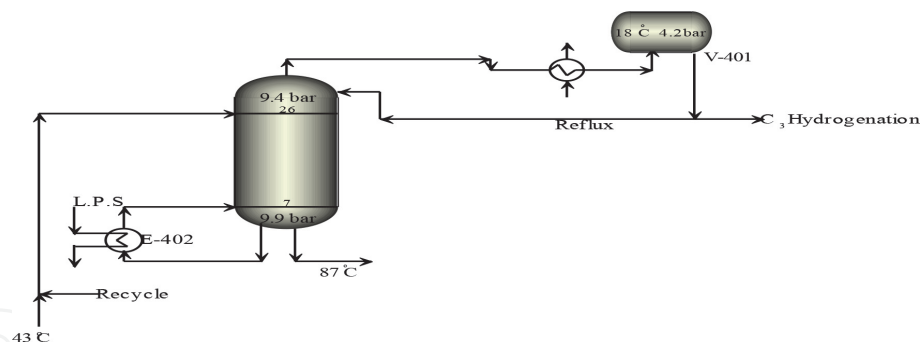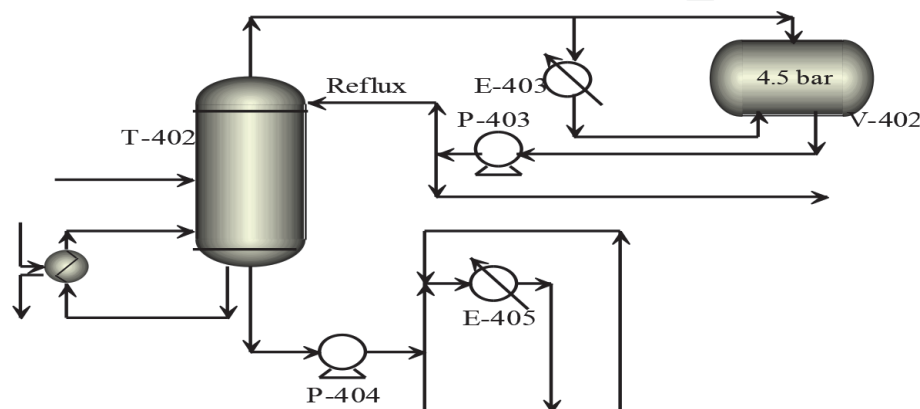

Figure 8.
Depropanizer tower (T-401).

Figure 9.
Debutanizer tower (T-402).

2.2.2.8 Hydrogenation of C₃ cut

The top product of the depropanizer is mixed with recycles and fed to the hydrogenation section in order to convert methyl acetylene and propadiene. The feed is mixed with hydrogen and enters the first reactor. **Figure 10** shows the reactor in which hydrogen is compounded with the feed stream as well as C_3 stripper. For hydrogenation, three reactors have been installed, two in service and one in standby mode. The output of the reactors enters T-403 (**Figure 11**) to separate the light components where the bottom product of this tower enters the C_3 splitter (T-404), with 200 trays, at tray 55 or 68. The tower condenser (E-410) is cooled by cooling water. The produced propane is directed to E-412 for cooling and then to battery limits. A by-product (propane) is taken from tray 4 or 8 and
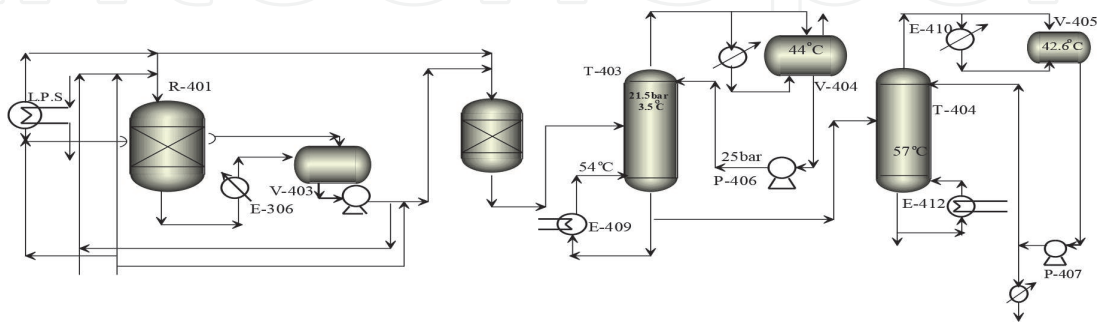

Figure 10.
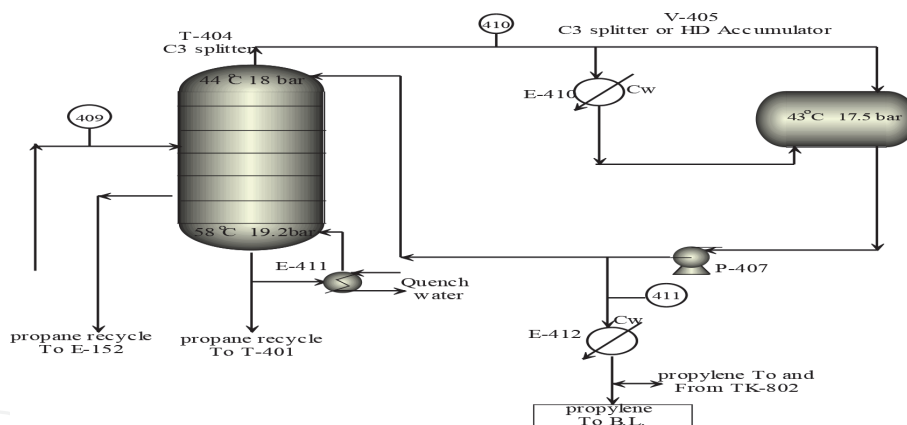*C₃ reactor and stripper to add hydrogen to the feed stream.*

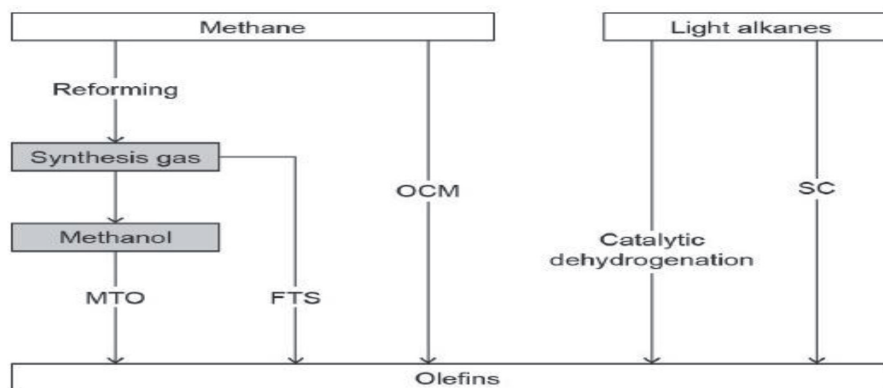**Figure 11.**
C3 splitter (T-404).

Figure 12.
Different technologies of interest for the production of light olefins from methane and light alkanes [27].

recycled to the furnaces. The tower re-boiler (E-412) works with quench water. The bottom product which contains C_4 and heavier compounds is recycled to the depropanizer (T-401). **Figure 12** illustrates C_3 splitter configuration in olefin plant.

3. New trends in olefin production

In this section, some of the most promising alternatives are compared with the conventional steam cracking process. **Figure 12** depicts novel technologies for the production of light olefins from methane and light alkanes. These technologies emerge especially from the abundance of cheap propane, ethane, and methane from shale gas and stranded gas. Continuing search for alternative and preferably also more sustainable processes and feeds will eventually be required in order to fulfill the future demand for commodity chemicals. The following technologies are of interest: the catalytic dehydrogenation of light alkanes, the oxidative coupling of methane (OCM), and syngas-based routes such as the Fischer-Tropsch synthesis (FTS) and methanol synthesis followed by methanol to olefins (MTO) [27–31].

Biomass is also considered a promising alternative feed that can be converted into the valuable olefins, among other chemicals and fuels (**Figure 13**). Through processes such as fermentation, gasification, cracking and deoxygenation, biomass derivatives can be effectively converted into C_2–C_4 olefins. In this respect, biomass and waste streams are believed to be important for the production of chemicals in the future. In recent years, bio-ethanol has been extensively studied as an alternative feed for C_2H_4 production (**Figure 14**). Other bio-derived compounds such as
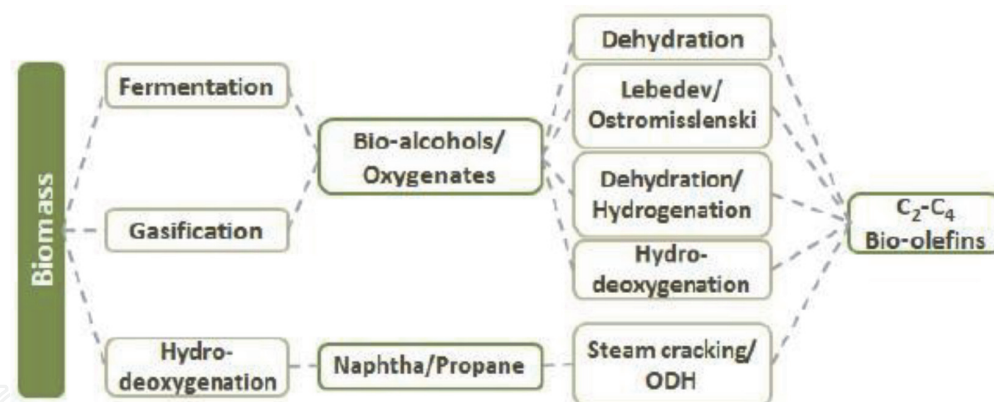

Figure 13.
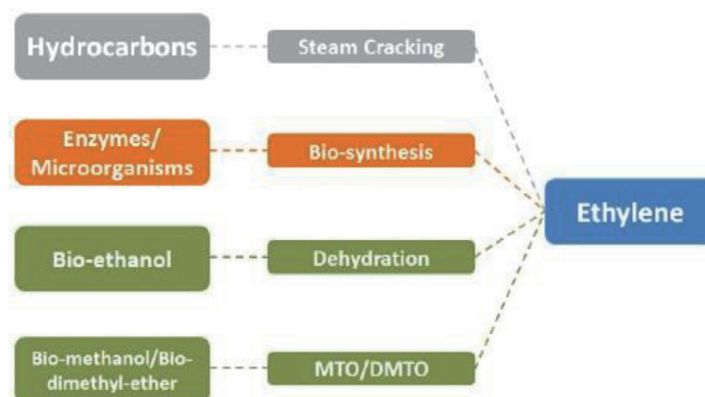*Biomass to olefins primary routes [32].*

Figure 14.
Schematic chart of C_2H_4 production methods [32].

methanol and dimethyl-ether, can be also be used as a feed for C_2H_4, via methanol to olefins (MTO) and dimethyl-ether to olefins (DMTO) processes. Bio-ethylene can also be produced via bio-synthesis from various enzymes or micro-organisms [32–36] (**Figure 14**). Similarly for production of C_3H_6 and C_4H_6 bio materials have been proven promising using different processes rather than steam cracking.

4. Conclusions

Liquid feed petrochemicals have a high product variety and can produce basic olefins simultaneously. Nevertheless, production costs are higher in liquid feed petrochemicals than in gas based petrochemicals. Because oil is a non-renewable resource, it must be replaced with new technologies in the near future. Methane and ethanol as renewable resources are an appropriate alternative that can be converted into functional olefins using new environmentally friendly technologies.

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