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Propylene Production Routes – Available Ways to Improve the Profitability of the Refining Hardware

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Published Jan 24, 2021

Introduction and Context

The current scenario present great challenges to the crude oil refining industry, prices volatility of raw material, pressure from society to reduce environmental impacts and refining margins increasingly lower. The newest threat to refiners is the reduction of the consumer market, in the last years became common, news about countries that intend to reduce or ban the production of vehicles powered by fossil fuels in the middle term, mainly in the European market. Despite the recent forecasts, the transportation fuels demand is still the main revenues driver to the downstream industry, as presented in Figure 1, based on data from Wood Mackenzie Company.

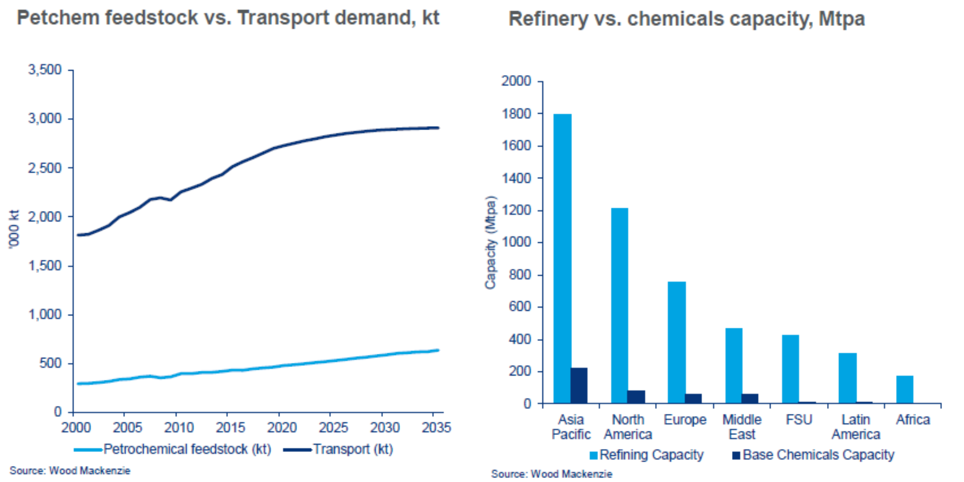

Figure 1 – Relation of Petrochemical Feedstock/Transportation Fuels Feedstock and Installed Capacity (Wood Mackenzie, 2019)

According to Figure 1, the transportation fuels demand represents close to five times the demand by petrochemicals as well as a focus on transportation fuels of the current refining hardware, considering the data from 2019. Despite these data, is observed a trend of stabilization in transportation fuels demand close to 2030 followed by a growing market of petrochemicals. Still according to Wood Mackenzie data, presented in Figure 2, is expected a relevant growth in the petrochemicals participation in the global oil demand.

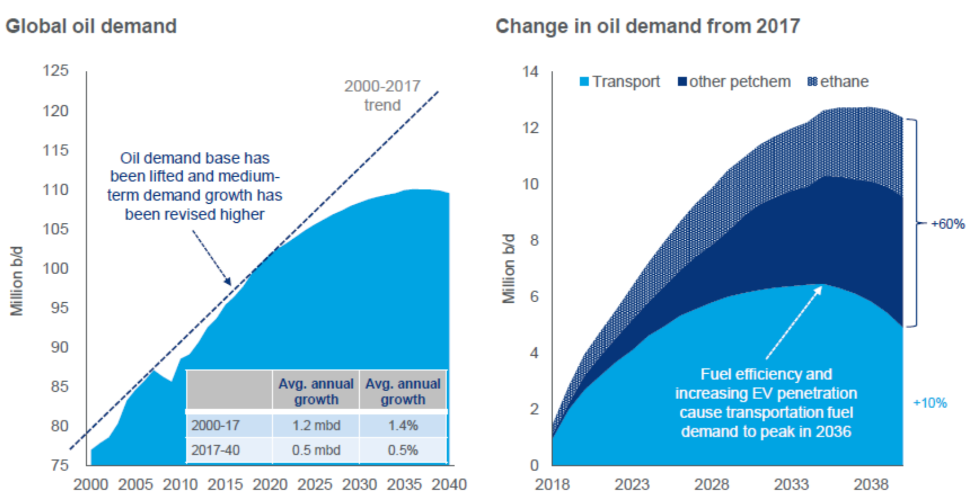

Figure 2 – Change in the Profile of Global Crude Oil Demand (Wood Mackenzie, 2019)

The improvement in fuel efficiency, growing market of electric vehicles tends to decline the participation of transportation fuels in the global crude oil demand. New technologies like additive manufacturing (3D printing) has the potential to produce great impact to the transportation demands, leading to even more impact over the transportation fuels demand. Furthermore, the higher availability of lighter crude oils favors the oversupply of lighter derivatives that facilitate the production of petrochemicals against transportation fuels as well as the higher added value of petrochemicals in comparison with fuels.

Facing these challenges, search for alternatives that ensure survival and sustainability of the refining industry became constant by refiners and technology developers. Due to his similarities, better integration between refining and petrochemical production processes appears as an attractive alternative. Although the advantages, it's important take into account that the integration between refining and petrochemical assets increase the complexity, requires capital spending, and affect the interdependency of refineries and petrochemical plants, these facts needs to be deeply studied and analyzed case by case, and the propylene maximization can be an attractive alternative to refiners in order to ensure participation in a profitable and high demand market.

Propylene – A Fundamental Petrochemical Intermediate

The propylene is one of the most important petrochemical intermediates nowadays being the second largest consumed in the world, behind the ethylene. The propylene can be applied as intermediate to the production some fundamental products, for example:

- Acrylonitrile;
- Propylene Oxide;
- Cumene;
- Acrylic Acid;
- Polypropylene;

The polypropylene is responsible for the major part of the propylene demand followed by acrylonitrile and propylene oxide.

Propylene is normally produced in three commercial grades: Refinery grade, with a purity varying from 50 % to 70 %, the refinery grade is applied in the production of cumene for example. The chemical grade (92 % to 96 %), applied to produce acrylonitrile, propylene oxide, and acrylic acid and finally the polymer grade (up to 99,5 %) applied to produce polypropylene.

The main sources of propylene are the steam cracking process, the FCC units in crude oil refineries, olefins metathesis, propane dehydrogenation, and methanol to olefins processes. Figure 3 presents an overview of the propylene sources, based on data from 2014.

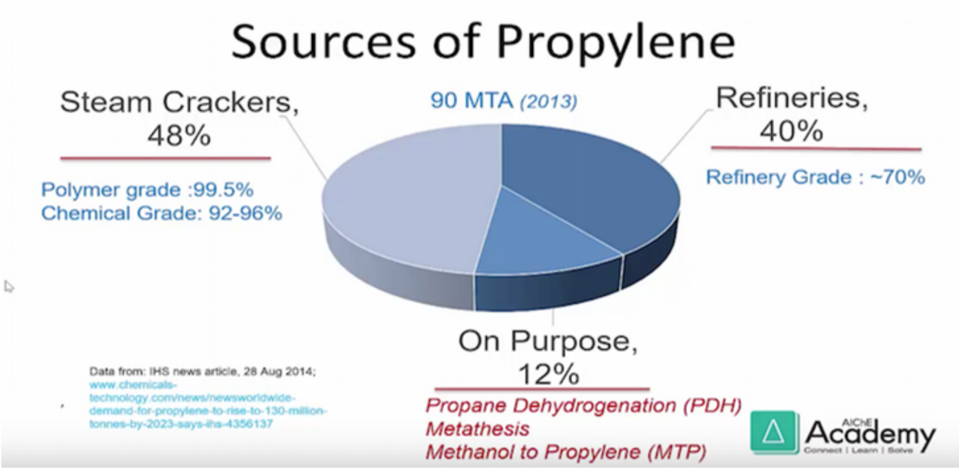

Figure 3 – Propylene Sources (SAWYER, G. 2014)

The steam cracking units are the main propylene supplier followed by the Fluid Catalytic Cracking (FCC) units in crude oil refineries.

According to some recent forecasts, the petrochemical market tends to rise in the next years and, in middle term, will be responsible by the major part of the crude oil consumption over passing the transportation fuels this fact have been made the refiners to looking for closer integration with petrochemical assets through the maximization of petrochemical intermediates in their refining hardware as an strategy to ensure better refining margins and higher value addition to the crude oil. Figure 4 present an overview of the trend of growing to the petrochemical market in short term.

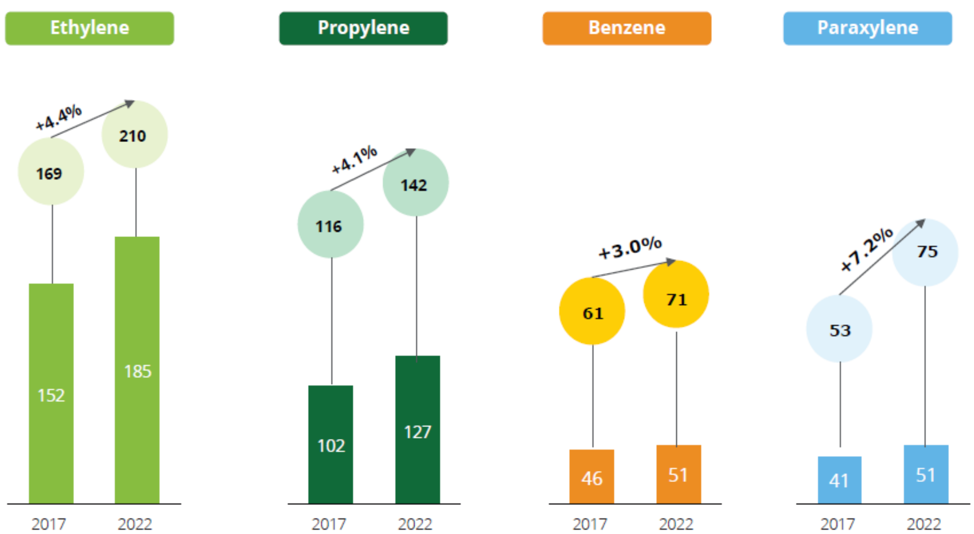

Figure 4 – Growing Trend in the Demand by Petrochemical Intermediates (Deloitte, 2019) - ***Note: Bars represent total demand (million metric tons or MMT), circles represent total capacity (MMT).***

According to Figure 4, is expected a growth of 4,4 % in the ethylene demand and 4,1 % of propylene demand until 2022. Due to its higher added value and growing consumer market, the production of petrochemical intermediates has become the focus of many refiners and process technologies developers.

Propylene Production Routes

As quoted above, currently a major part of the propylene market is supplied by steam cracking units, but a great part of the global propylene demand is from the separation of LPG produced in Fluid Catalytic Cracking Units (FCC). Figure 5 present a feedstocks and derivatives profile in a typical FCC unit.

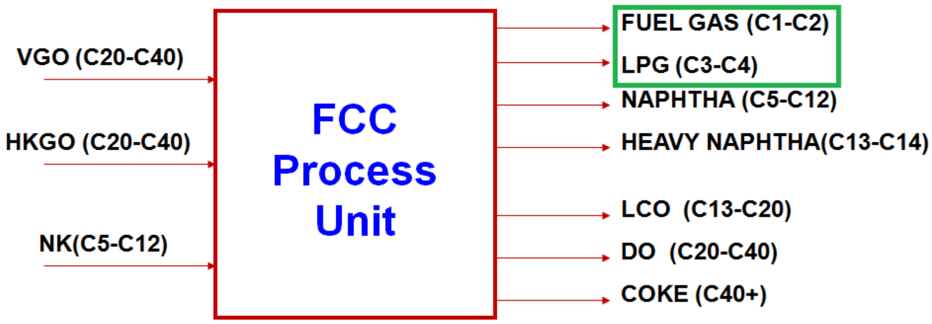

Figure 5 – Production and Feedstocks Profile in a Typical FCC Unit

Normally, the LPG produced in FCC units contain close to 30 % of propylene and the added value of the propylene is close to 2,5 times of the LPG. According to the local market, the installation of propylene separation units presents an attractive return over investment. Despite the advantage, a side effect of the propylene separation from LPG is that the fuel stays heavier leading to specifications issues, mainly in colder regions, in these cases alternatives are to segregate the butanes and send this stream to gasoline pool, add propane to the LPG or add LPG from natural gas. It's important take into account that some of these alternatives reduce the LPG offer, which can be a severe restriction according to the market demand.

A great challenge in the propylene production process is the propane and propylene separation step. The separation is generally hard by simple distillation because the relative volatility between propylene and propane is close of 1.1. This fact generally conducts to distillation columns with a large number of equilibrium stages and high internal reflux flow rates.

There are two technologies normally employed in propylene-propane separation towers that are know like Heat-Pump and High Pressure configurations.

The high pressure technology apply a traditional separation process that uses a condenser with cooling water to promotes the condensation of top products, in this case, it's necessary to apply sufficient pressure to promote the condensation of products in the ambient temperature. Furthermore, the reboiler uses steam or another available hot source. The adoption of high pressure separation route requires a great availability of low pressure steam in the refining hardware, in some cases this can be a restrictive characteristic and the heat pump configuration is more attractive, despite the higher capital requirements.

The separation process applying heat pump technology uses the heat supplied by the condensation of top products in the reboiler, in this case reboiler and condenser is the same equipment. To compensate the non-idealities it's necessary to install an auxiliary condenser with cooling water.

The application of heat pump technology allows decrease the operating pressure by close of 20 bar to 10 bar, this fact increase the relative volatility propylene-propane, making the separation process easier and, consequently, reducing the number of equilibrium stages and internal reflux flow rate required for the separation.

Normally, when the separation process by distillation is hard (with relative volatilities lower than 1.5) the uses of heat pump technology show more attractive.

Furthermore, some variables need to be considerate during the choice of the best technology for the propylene separation process like availability of utilities, temperature gap in the column and installation cost.

Normally, the propylene is produced in the refineries with to specifications. The polymer grade that is most common and have higher added value with a purity of 99,5 % (minimum) this grade is directed to polypropylene market. The chemical grade where the purity varies between 90 to 95% is normally directed to other uses. A complete process flow diagram for a typical propylene separation unit applying heat pump configuration is presented in Figure 6.

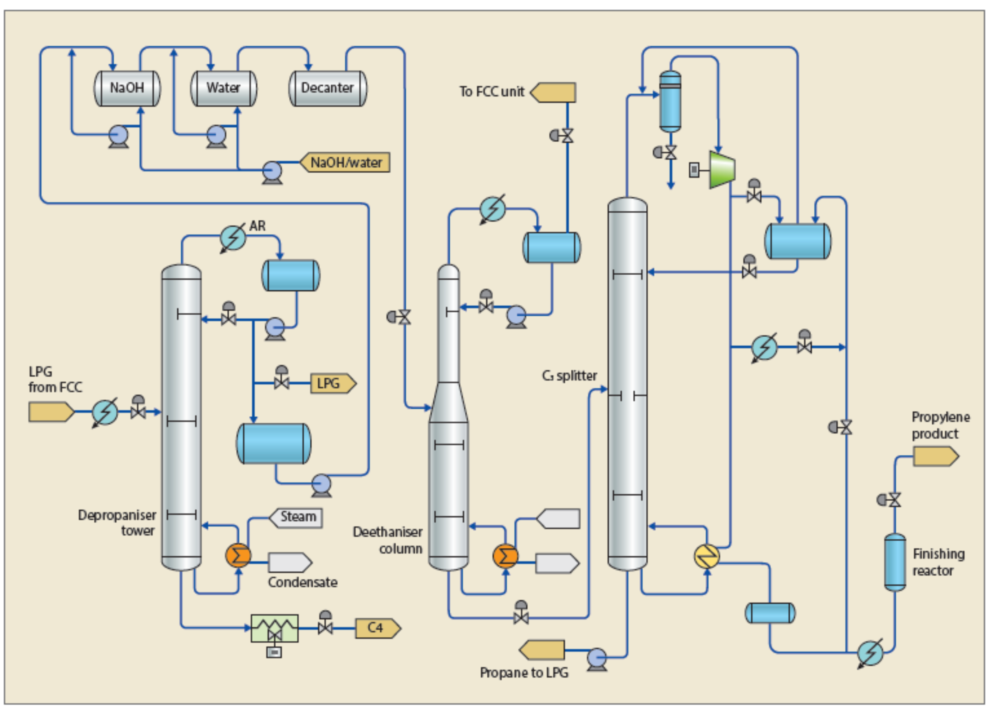

Figure 6 – Typical Process Flow Diagram for a FCC Propylene Separation Unit Applying Heat Pump Configuration

The LPG from FCC unit is pumped to a depropanizer column where the light fraction (essentially a mixture of propane and propylene) is recovered in the top of the column and sent to a deethanizer column while the bottom (butanes) is pumped to LPG or gasoline pool, according to the refining configuration. The top stream of the deethanizer column (lighter fraction) is sent back to FCC where is incorporated to refinery fuel gas pool, or in some cases can be directed to petrochemical plants to recover the light olefins (mainly ethylene) present in the stream while the bottom of the deethanizer column is pumped to the C3 splitter column, where the separation of propane x propylene is carried out. The propane recovered in the bottom of the C3 splitter is sent to LPG pool where the propylene is sent to propylene storage park. The feed stream passes through a caustic wash treating aiming to remove some contaminants that can lead to deleterious effect to petrochemical processes, an example is the carbonyl sulfide (COS) that can be produced in the FCC (through the reaction between CO and S in the Riser).

Nowadays, the falling demand by transportation fuels has been made the refiners to optimize the FCC units aiming to maximize the propylene yield following the trend of a closer integration with petrochemical sector. Among the alternatives to maximize the propylene yield in FCC units is the use of ZSM-5 as additive to the FCC catalyst as well as the adjustment of the process variables to most severe conditions including higher temperatures and catalyst circulation rates. Another interesting alternative is to recycle the cracked naphtha to the process unit aiming to improve the LPG and consequently the propylene yield.

The installation of propylene separation units can present a significant capital investment to refiners but considering the last forecasts that reinforces the trend of reduction in the demand by transportation fuels, this investment can be a strategic decision the all players of the downstream industry in the middle term both to ensure higher added value to the processed crude oil and market share.

Steam Cracking Units

The Steam cracking process has a fundamental role in the petrochemical industry, nowadays the most part of light olefins light ethylene and propylene is produced through steam cracking route. The steam cracking consists of a thermal cracking process that can use gas or naphtha to produce olefins, in this review we will describe the naphtha steam cracking process.

The naphtha to steam cracking is composed basically of straight run naphtha from crude oil distillation units, normally to meet the requirements as petrochemical naphtha the stream needs to present high paraffin content (higher than 66 %). Figure 7 presents a typical steam cracking unit applying naphtha as raw material to produce olefins.

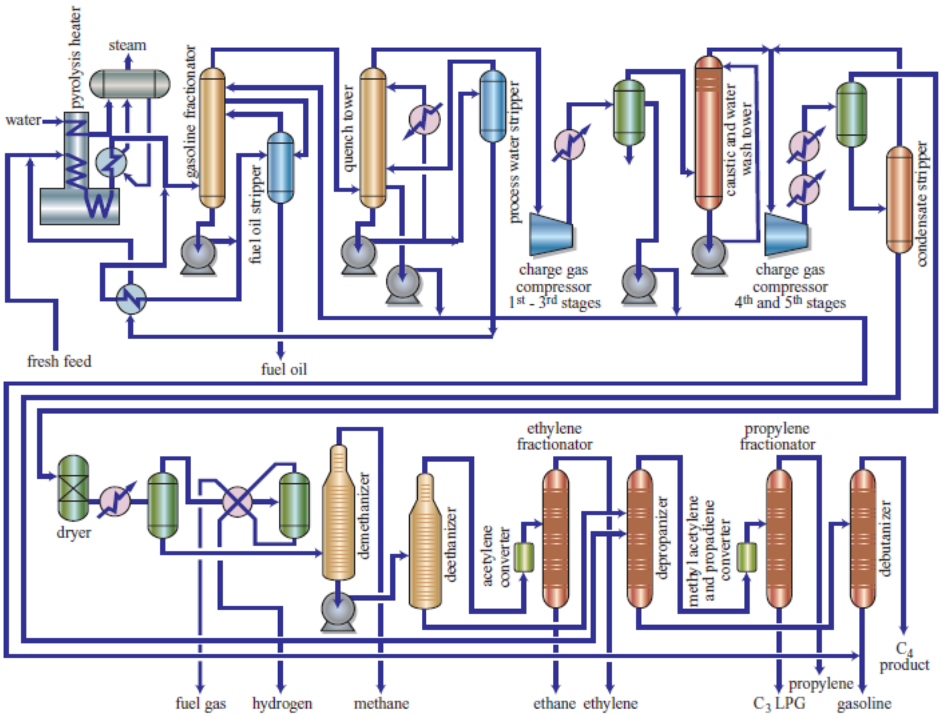

Figure 7 – Typical Naphtha Steam Cracking Unit (Encyclopedia of Hydrocarbons, 2006)

Due to his relevance, great technology developers have dedicated his efforts to improve the steam cracking technologies over the years, especially related to the steam cracking furnaces. Companies like Stone & Webster, Lummus, KBR, Linde, and Technip develop technologies to steam cracking process. One of the most known steam cracking technology is the SRT™ process (Short Residence Time), developed by Lummus Company, that applies a reduce residence time to minimize the coking process and ensure higher operational lifecycle.

The cracking reactions occurs in the furnace tubes, the main concern and limitation to operating lifecycle o steam cracking units is the coke formation in the furnace tubes. The reactions carry out under high temperatures, between 500 oC to 700 oC according to the characteristics of the feed. For heavier feeds like gas oil, is applied lower temperature aiming to minimize the coke formation, the combination of high temperatures and low residence time are the main characteristic of the steam cracking process. The main focus of a naphtha steam cracking unit is normally producing ethylene, but the yield of propylene in a typical naphtha steam cracking unit can reach 15 %.

Propane Dehydrogenation

Among the main technological routes dedicated to the production of these compounds, we can highlight the production of light olefins through the dehydrogenation route of light paraffin (C2 - C5), according to the local market supplied by the refiner, the capital investment in process units capable to produce light olefins through paraffin dehydrogenation can be an attractive strategy.

Light paraffin is normally commercialized as LPG or gasoline and present reduced added value when compared with light olefins.

Dehydrogenation process involves the hydrogen remove from paraffinic molecule and consequently hydrogen production, according to the reaction (1):

R2CH-CHR2 ⇔ R2C=CR2 + H2 (1)

The dehydrogenation reactions have strongly endothermic characteristics, and the reactions conditions include high temperatures (close to 600 oC) and mild operating pressures (close to 5 bar). The catalyst normally applied in the dehydrogenation reactions are based on platinum carried on alumina (others active metals can be applied).

Figure 8 shows a schematic process flow diagram for a typical dehydrogenation process unit.

The main processes that can produce streams rich in light paraffin are physical separation processes as LPG from atmospheric distillation and units dedicated to separate gases from crude oil.

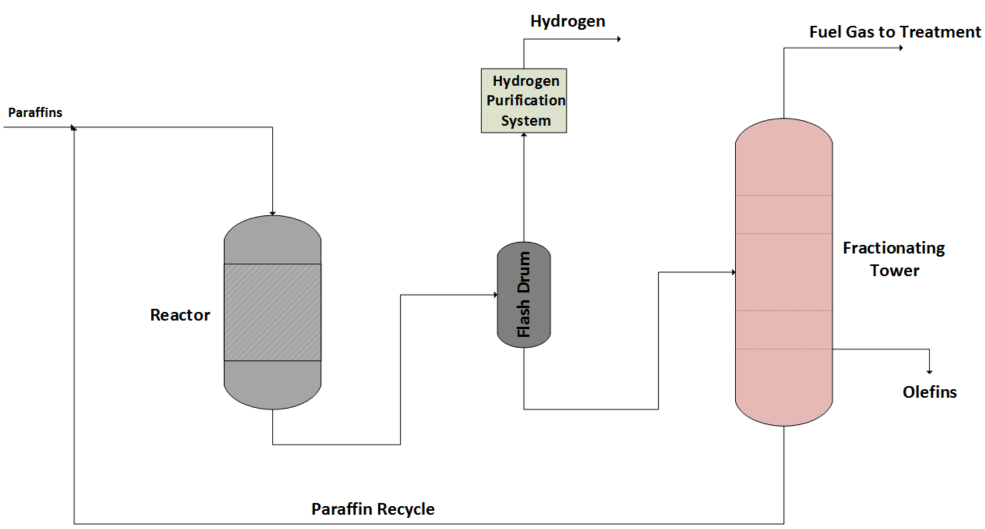

Figure 8 – Process Flow Diagram for a Typical Light Paraffin Dehydrogenation Process Unit.

The feed stream is mixed with the recycle stream before to entre to the reactor, the products are separated in fractionating columns and the produced hydrogen is sent to purification units (normally PSA units) and, posteriorly sent to consumers units as hydrotreating and hydrocracking, according to refining scheme adopted by the refiner. Light compounds are directed to the refinery or petrochemical complex fuel gas pool, after adequate treatment while the olefinic stream is directed to petrochemical intermediates consumer market.

During the dehydrogenation process there is a strong tendency to coke deposition on the catalyst surface and, periodically is carried out the regeneration of the catalytic bed through controlled combustion of the produced coke. Some process arrangements present two reactors in parallel aim to optimize the processing unit operational availability, in these cases while a reactor is in production the other is in the regeneration step.

Due to the growing market and high added value of light olefins, great technology developers have been dedicated his efforts to develop paraffin dehydrogenation technologies. The UOP company developed and commercialize the OLEFLEX™ that is capable to produce olefins from paraffin dehydrogenation with a continuous catalyst regeneration process, despite the higher initial investment, this technology can minimize the unavailability period to regenerate the catalyst. Figure 9 presents a basic process flow diagram for the OLEFLEX™ technology by UOP Company.

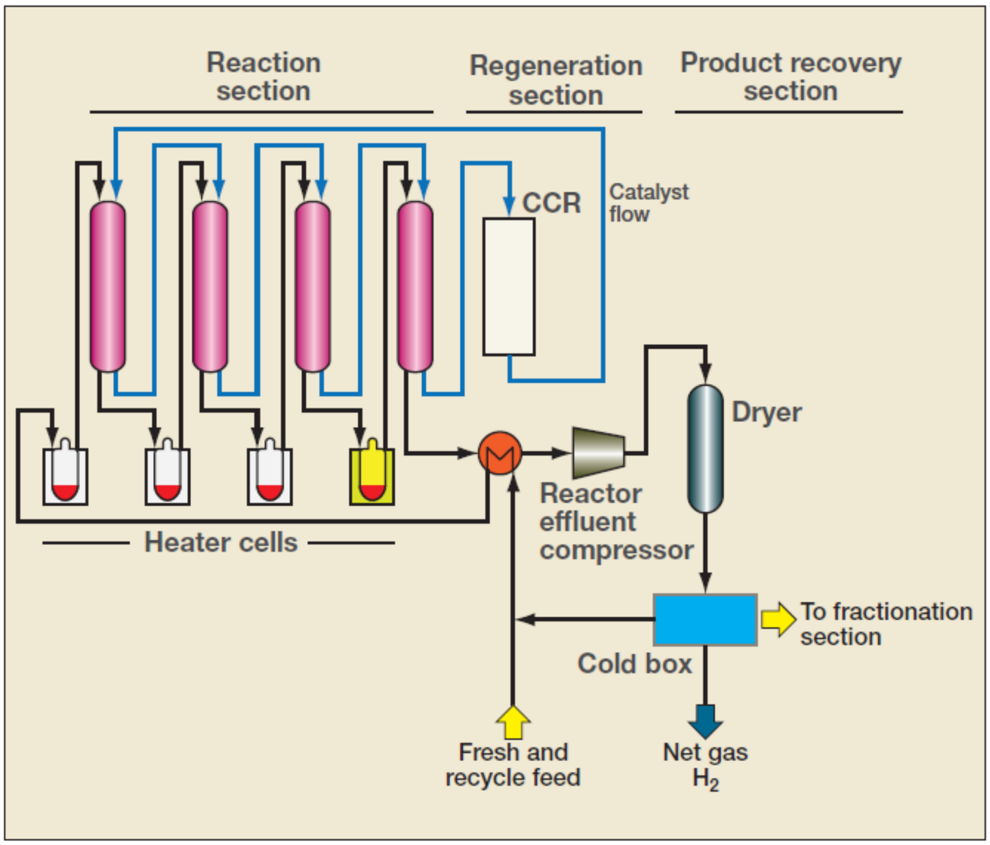

Figure 9 – Basic Process Flow Diagram for the OLEFLEX™ Technology by UOP Company (MARSH & WERY, 2018)

Another available technology is the CATOFIN™ process, licensed by Lummus Company, as aforementioned, in this case, is applied two reactors in parallel, as presented in Figure 10.

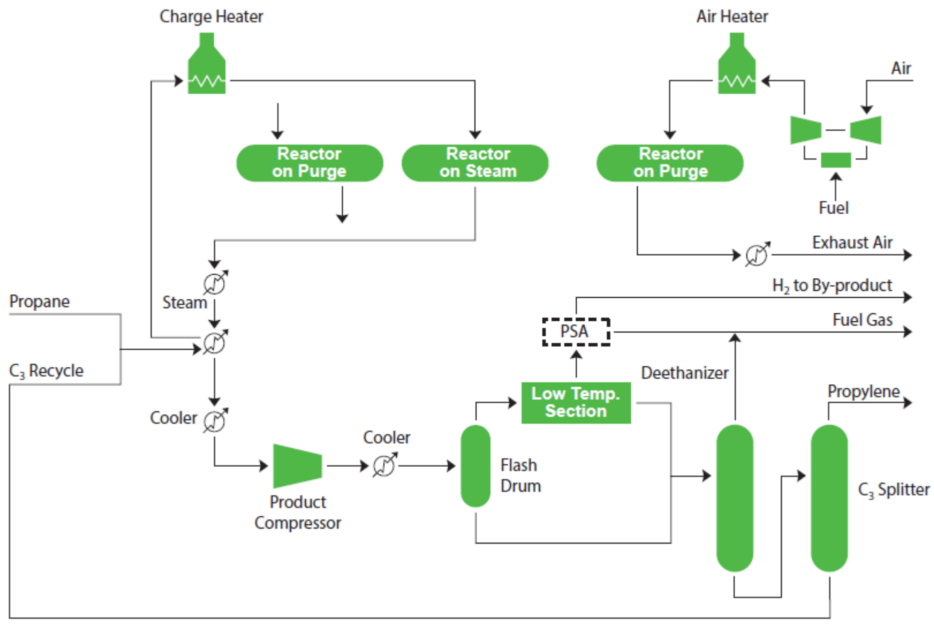

Figure 10 – Simplified Process Scheme to CATOFIN™ Dehydrogenation Technology, by Lummus Company.

Others dehydrogenation technologies available are the processes STAR™ commercialized by ThyssenKrupp-Uhde Company and the process FBD™ by SnamProgetti Company.

Due to his chemical characteristics, olefinic compounds can be employed in the production of a large quantity of interest products as polymers (polyethylene and polypropylene) propylene oxide and oxygenated compounds production intermediates (MTBE, ETBE, etc.).

As a process of high energy consumption, there is a great variety of research in the sense of developing more active and selective catalysts that reduce the need for energetic contribution to the dehydrogenation process. One of the main variations of the dehydrogenation process is the process called oxidative dehydrogenation that occurs according to reaction 2.

R2CH-CHR2 + O2 ⇔ R2C=CR2 + H2O (2)

This reaction is strongly exothermic, and this is the main advantage in relation of the traditional dehydrogenation process, due to the high risk of paraffin combustion against the dehydrogenation reaction.

Olefins Metathesis

The olefins metathesis process involves the combination of ethylene and butene to produce propylene as presented in reaction 3.

H2C=CH2 + H3C-HC=CH-CH3 → 2 H2C=HC-CH3 (3)

The main technology licensors for olefins metathesis processes are the

Lummus Company, and IFP (Institut Français du Pétrole). Figure 11 presents a basic process flow arrangement for the OCT™ technology, developed by Lummus Company.

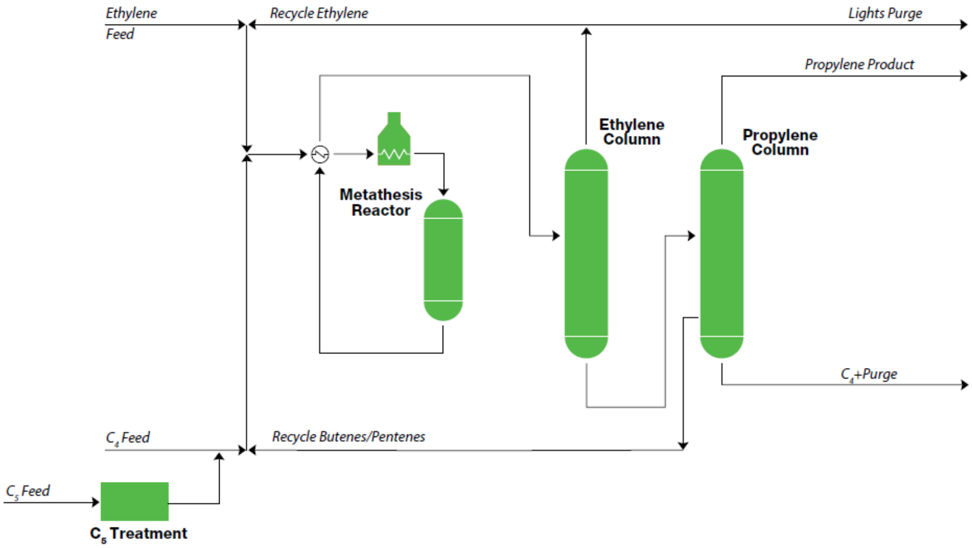

Figure 11 – Process Flow Diagram for OCT™ Olefins Metathesis Technology by Lummus Company.

The economic viability of olefins metathesis units relies on the price gap between propylene and ethylene as well as the ethane availability in the market.

Methanol to Olefins Technologies (MTO)

Another alternative route to produce liquid hydrocarbons from syngas is the non-catalytic conversion of the natural gas to methanol followed by the polymerization to produce alkenes. Methanol is produced from natural gas according to the following chemical reactions:

CH4 + H2O = CO + 3H2 (Steam Reforming)

CO + H2O = CO2 + H2 (Shift reaction)

2H2 + CO = CH3OH (Methanol Synthesis)

In the sequence, the methanol is dehydrated to produce Dimethyl-Ether, which is posteriorly dehydrated to produce hydrocarbons, as shown in the sequence:

2 CH3OH = CH3OCH3 + H2O (Methanol Dehydration)

CH3OCH3 = C2H4 + H2O (Dimethyl-Ether Dehydration)

The methanol conversion to olefins into hydrocarbons is called Methanol to Olefins (MTO) or Methanol to Gasoline (MTG) technologies. Figure 12 presents a typical unit dedicated to produce methanol from natural gas through the two-step reforming process.

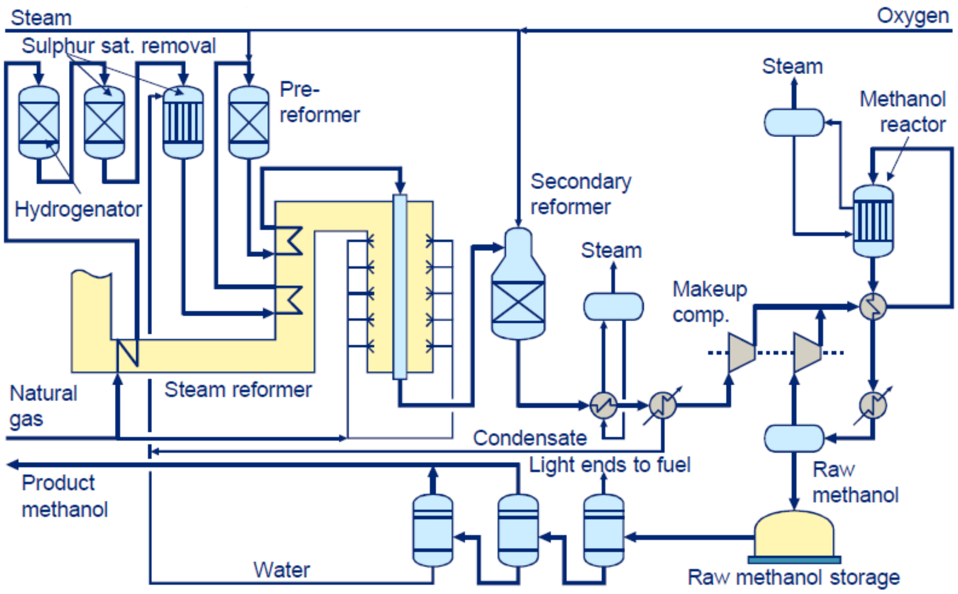

Figure 12 – Methanol Production Process from Natural Gas through two-reforming Process (PEIRETTI, 2013)

An alternative technology developed by the Haldor Topsoe Company to produce methanol from natural gas is the Altothermal reforming process, called ATR™ that offers improvements related to the reforming furnace. A significant advantage of the ATR™ process is the lower required ration Steam/Carbon in the reforming step that offer great scale economy when compared with traditional production processes (One step and two-step reforming processes). Figure 13 presents a basic process flow diagram for the ATR™ process, developed by Haldor Topsoe Company.

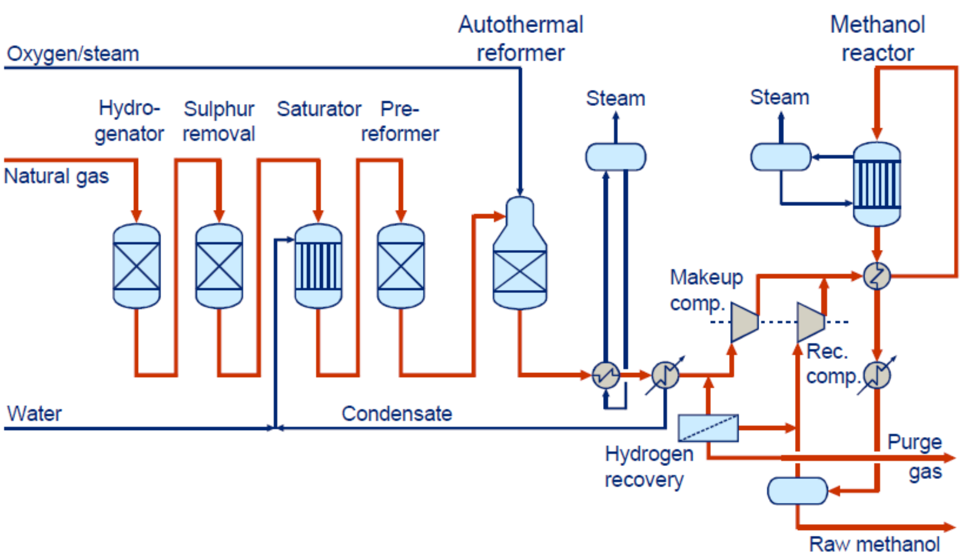

Figure 13 – Altothermal (ATR™) Process for Methanol Production from Natural Gas by Haldor Topsoe Company (PEIRETTI, 2013)

The most known processes dedicated to converting methanol in hydrocarbons are the processes MTG™ developed by ExxonMobil Company and the MTO-Hydro™

process, developed by UOP Company. Figure 14 presents the process flow diagram for the MTG™ process by ExxonMobil Company.

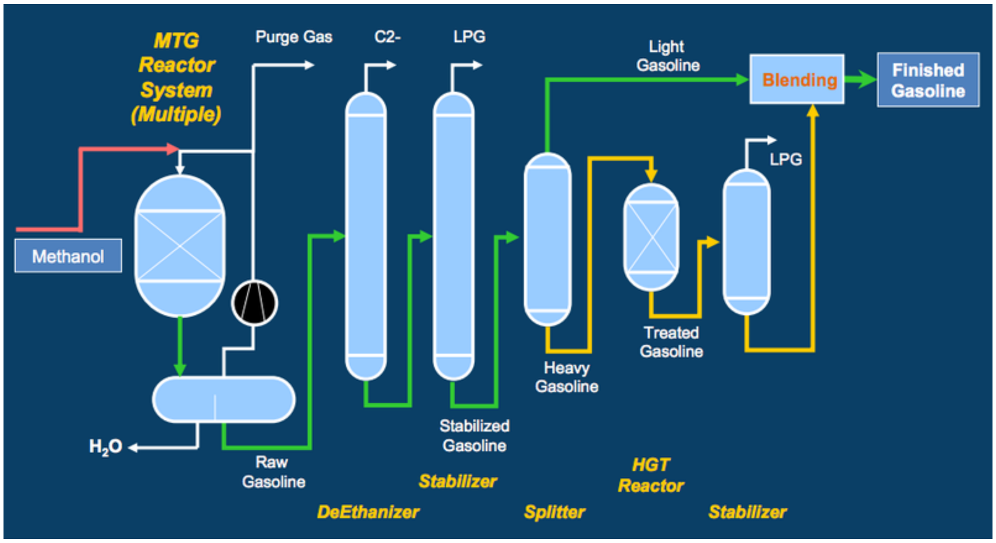

Figure 14 – Process Flow Diagram for MTG™ Technology by ExxonMobil

The MTO technologies presents some advantages in relation to Fischer-Tropsch processes, once show higher selectivity in the hydrocarbon production, furthermore, the obtained products require lower additional processing steps to achieve commercial specifications, another important point in that the installation cost is normally lower to MTO process plants when compared with FT units, once Fischer-Tropsch units are economically viable only in large scale. Regarding the olefins production, the maximization of these derivatives can be especially attractive in the current scenario where there is a trend of reduction in transportation fuels demand followed by the growing market of petrochemicals, creating the necessity of closer integration between refining and petrochemical assets aiming to maximize the added value, share risks and costs, as well as ensure market share in a highly competitive scenario of the downstream sector. Other great technology developers for methanol production process are Johnson Matthey Company, Linde Company, Chiyoda Corporation, Jacobs Company, and Lurgi Company.

Conclusion

The propylene maximization in the refining hardware can offer attractive opportunities to refiners, especially those inserted in markets with saturated demand by transportation fuels like gasoline. The synergy between refining and petrochemical processes raises the availability of raw material to petrochemical plants and makes the supply of energy to these processes more reliable at the same time ensures better refining margin to refiners due to the high added value of petrochemical intermediates when compared with transportation fuels. It's important to consider that integrated processes lead to higher operational complexity, however, given current and middle term scenarios to the refining industry, better integration between refining and petrochemical processes is fundamental to the economic sustainability of the downstream industry.

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I am interested. I am having 17+years of experienced in Oil and Gas onshore and offshore deep water FPSO and platform projects. 13 years worked in FPSO offshore SBM offshore Brazil (udhayanadar@yahoo.com)

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