ENGINEERING PRACTICE

VOLUME 10 NUMBER 44
MAY 2024

IACPE
INTERNATIONAL ASSOCIATION OF CERTIFIED PRACTICING ENGINEERS

WWW.IACPE.COM

In This Issue

Volume 10 | Number 44

SPECIAL FEATURES

EDITOR
Karl Kolmetz

DIGITAL EDITOR
Shauna Tysor

REFINING CONTRIBUTING AUTHOR
Dr. Marcio Wagner da Silva

PROCESS ENGINEERING CONTRIBUTING AUTHOR
Jayanthi Vijay Sarathy

CONTRIBUTING AUTHOR
Ronald J. Cormier

Compressor Piston Sealing

Mehmet Samancioglu

The reliability of reciprocating gas compressors depends upon the function of certain critical components. Among these, compressor valves, piston and piston rod sealing systems, which has come a long way in last 25 years developments, both in design and material technology.

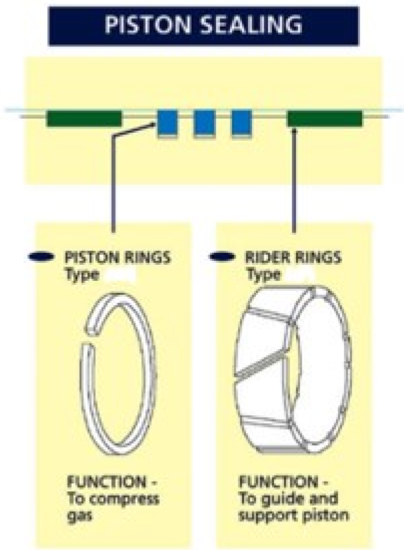


Figure 1. Piston Sealing

Piston Rings

In reciprocating compressors, pistons work against pressure and must have a sliding seal to allow the piston to compress the gas without leakage past the piston. The piston rings provide this sealing for maximum cylinder capacity and efficiency. The piston sealing elements are only subject to the dynamic pressure component varying between the suction and discharge pressure. At piston ring, the gas pressure pushing ring outward against cylinder wall and side of ring results in sealing as shown below.

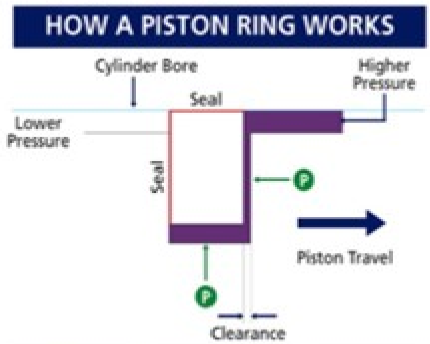


Figure 2. Piston Ring Working

Whereas distribution across the rings has been analyzed and measured and, for a two-ring piston, would look as illustrated in Figure below.

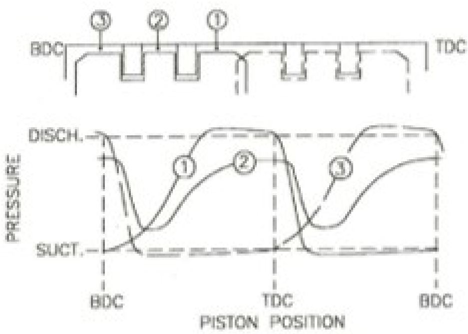


Figure 3. Instantaneous pressure between piston rings

The number of piston rings selected for a particular application is calculated considering the Gas molecular weight, Pressure differential, whether the cylinder is lubricated or non-lubricated, speed of the compressor and Space available on the piston. There is significant variation in the number of piston rings recommended by different manufacturers and compressor builders.

Table 1. Ring Quantities

Pressure deferential	Rings quantities
Up to 300 psi	2
300 to 900 psi	3
900 to 1500 psi	4
Over 1500 psi	6

1. Piston rings made of PTFE will have an end gap clearance of 0.020" to 0.024" per inch of piston diameter when fitted into the cylinder bore. Side clearance in the groove should be 0.010"-0.015" per inch of width. It should be remembered that Teflon expansion rates are approximately seven times those of cast iron.
2. Values for oil-lubricated compressors with cast iron rings are 0.0035" per inch of diameter for the ring. A piston used in a non-lube cylinder is usually made 0.125" to 0.250" smaller in diameter than the cylinder bore, depending on the size.

   Piston Ring back clearance = (0.0025 x cylinder diameter) + 2.5 mm
3. Approximate leak rates from end gap can be in large variations, from 0.03 scfm in a small cylinder all the way up to 40 scfm in a very large one. For new rings in lubricated applications, loss of V.E. with open joint rings will be about 0.5% up to approximately 3%. Power needed to overcome ring friction will usually be only about 0.5% to 2%.

Piston Rings Types

There are two basic ring types: one-piece and segmental. The most common ring joint is an ‘‘open type’’ angle or butt cut. Angle cut has some slight advantage, less gap clearance (0.7 butt cut) . At high speed, 720 RPM and over, there is a tendency for this ring to rotate or spin. This will cause wear of the piston groove especially for an aluminium piston so Butt joint ring should be used. At atmosphere or below 10 psi or vacuum suction an expander may be required to provide additional loading of the ring against the cylinder.

Step cut joint used for performance issue where low leakage is desirable. Segmental two pieces or more type is used when the ring material is not flexible or very hard. There is some reduction in wear if piston rings do leak slightly and thus, distribute the pressure drop over more than one ring. A good rule is that piston rings should be changed when they have worn between 30% - 50% of their original radial thickness.

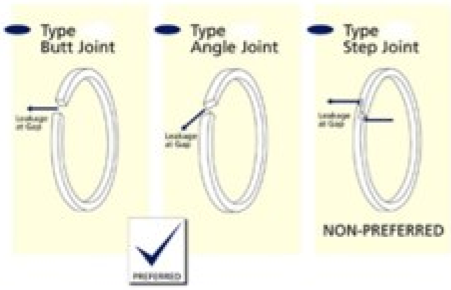


Figure 4. Piston Ring Types

Rider Ring

Rider bands protect the cylinder liner against contact with the piston. (They also allow operation with a lower lubrication feed rate for processes that are damaged by lube oil.).The rider supports piston weight plus one-half rod weight. This load is carried by the projected contact area of a 120 arc (=0.866DW). Loading is usually acceptable if kept below 5 psi for non- lubricated cylinders. For lubricated service American Petroleum Institute Standard API 618 limits rider loading to 10 psi, but this has been extended to more than 70 psi successfully in several applications with improved new materials.

One major problem with riders is preventing them from pressure actuating like the sealing rings. The angle cut rider ring normally used in the centre of the piston between the piston rings with side relief grooves and occasionally face relief grooves to prevent the ring from trying to act as a seal ring. Single acting: rider ring positioned after the piston rings. Double acting: rider ring positioned in between piston rings. A guide when the rider ring standout from the piston O.D. is reduced to 20% of its original then the rider rings should be changed. 0.25 mm minimum.

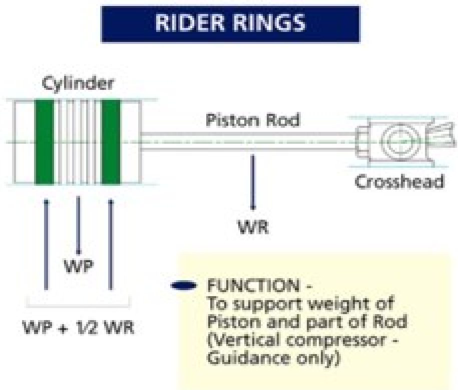


Figure 5. Rider Ring

Rider Ring Diameter Clearance

Steel or Cast-iron Piston = (0.0015 x cylinder diameter) + 0.005

Aluminum piston = (0.0025 x cylinder diameter) + 0.005

Piston Sealing Materials

For lubricated service, time-proven bronze and cast iron are still commonly used materials. For non-lubricated, Low-friction materials can run without lubrication. By careful formulation and selection of filler materials, the self-lubricating properties of filled PTFE materials have been improved to give longer lifetimes, especially in dry gases. But should not be operated under conditions of intermittent oil supply which usually results in high ring wear. Rider bands & piston rings and packing are made from PTFE (Teflon) with various fillers such as Glass fibre 5-15% (hardness), Carbon 10-35% (deformation strength), Graphite 5-15% (excellent wear properties), Bronze 40-60% (high thermal conductivity), MoS2 5%(reduce friction), all the above are compression moulded made.

Or made from HOT Compression moulded, proprietary, filled PEEK compound for higher pressure, PI Polyimide Resin (chemical resistance, temperature), PPS (elevated temperatures and pressures) or high-performance polymer alloys. All these materials are products of powder technology.

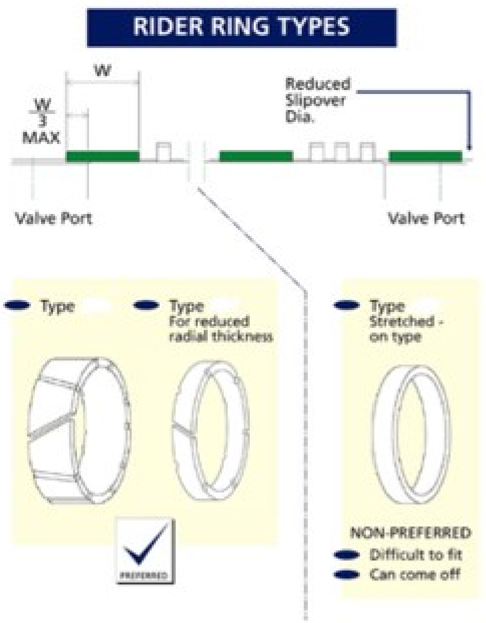


Figure 6. Rider Ring Types

Wear Mechanism

The process by which self-lubricating sealing components provide their own lubrication and wear resistance is described as a transfer mechanism. Self-lubricating materials operate by what is termed an "adhesive wear mechanism". They deposit a thin film onto the sliding counter-surface. This film once stabilized becomes the lubricant against which the component (piston or packing ring) can continue to slide with reduced friction and an acceptably low wear rate.

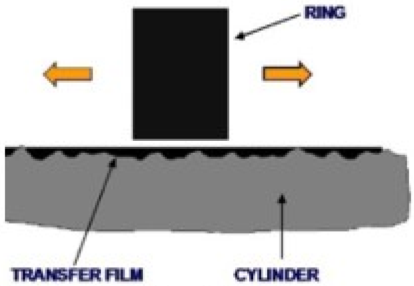


Figure 7. Wear Mechanism

The advances made in self-lubricating materials have put the reciprocating compressor companies back into best position for reliability. A graph shows an ideal wear profile is shown in fig.8. The initial part of the profile corresponds with the deposition of the transfer film, and the time for this transfer depending on the working conditions of the compressor.

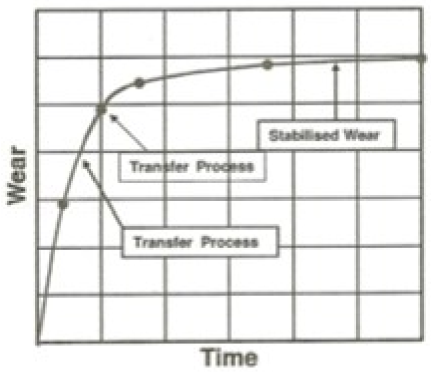


Figure 8. Ideal Wear Profile

Factors influencing the wear mechanism

Apart from the proper selection of self-lubricating material, there are several important operating factors which influence the actual running life which can be obtained in each compressor system. These include,

1. Differential pressure
2. Gas temperature
3. Counter-surface material & surface finish
4. Gas type & dryness
5. Gas cleanliness (e.g. absence of solids or liquids)
6. Cylinder &Packing cooling
7. Speed & stroke

Any selected polymer has gas pressure and temperature application limits. The max differential pressure; filled PTFE (non-lubricated) materials, across the piston up to 580 psi, and packing up to 870 psi. The polymer alloys (non -lubricated) max pressure differential across the piston up to 2100 psi and across packing 3100 psi. Gas mean temperature: filled PTFE (no- lube) materials up to 250 F, Polymer alloys (non-lube) up to mean temperature 350 F.

Liners Material: Most applications grey (flake graphite) cast iron (BSI 1452 grade 250 or 300) has proved to be an ideal choice. The preferred hardness should be at least 200 HB. Optimum liner surface finish is in the range 0.4 to 0.6 microns Ra. There may be several grades of stainless steel which can be centrifugally cast for liner manufacture. Liners which have become polished by abrasive wear should be re-roughened to restore optimum ring life.

Piston rods Material: Alloy (AISI 4140) or stainless steels (AISI 420) have proved successful, but these must be hardened to 50 / 55 Rc to give adequate stability for the transfer film, Optimum Rod surface finish is in the range 0.2 to 0.3 microns.

Gas dryness (bone-Dry): Any gas passes through the process under (-20°C) will contain less than 1000 ppm H2O,then the gas become dry. The influence of gas dryness and, in particular, its water vapour content, significantly affects the transfer process when the components are manufactured from filled PTFE materials.

The abrasive effect of the particles can be highly destructive to a set of self-lubricating rings and to the transfer film which they have so carefully laid down. Cylinder inlet coolant temperature should be less than 10 F from gas inlet temperature, maximum coolant inlet 60 F.

API 618 recommends packing not cooled for standard PTFE material non-lube up to 17 bars , for lube up to 35 bars. Most polymer alloys can stand for non-lube up to 80 bars, for lube up to 100 bar not cooled. The sliding speed limit of Double acting horizontal 700 ft/m for lubricated for non-lubricated 600 ft/m, for vertical compressors with lubricated 800 ft/m for non-lubricated 700 ft/m. The speed of 4 m/s is close to the upper level of average piston speed normally encountered in an oil-free reciprocating compressor. Actual field experience in a closely matching gas type is the best guide to the proper selection of ring (and counter surface) material.

Packing Leakage

Packing Rings are theoretically, very close to zero leak seals. Properly manufactured and applied Packings will leak at an average rate between zero and 0.2 scfm (standard cubic feet per minute). In general, packings that are to be unsatisfactory will be above 0.5 scfm. Gas pressure in the vent needs to be only a few psi above atmospheric pressure. Average rod leak rate is 0.98 to 1.86 scfm based on Pipeline Research Committee.

Conclusions

The development of new polymer alloys has enabled users of oil-free reciprocating compressors to achieve exceptional improvements in consistency and life of the sealing rings.

Are your compressors critical components up to date?

References

Advances in piston and packing ring materials for oil-free compressors, Robin S. Wilson

Compressor Handbook, Paul C. Hanlon

Author

Eng. Mehmet Samancioglu received his degree in Mechanical Engineering (BSc) from the University of Mosul, Iraq in 1978. He began his professional career as a maintenance engineer with NRC refinery, Iraq and went on to become a Rotating Equipment Superintendent. In 1999, he joined CPI compression as Area Sales Manager for a period of about 16 years. In 2018, Mehmet joined Guarniflon SPA- Italy as a Technical Consultant providing Sealing solutions for Reciprocating Gas Compressors. He is also a Technical Advisor developing upgraded sealing materials for dry -running sealing system in the R/D team.

TrayHeart
Tower Internals Design

TrayHeart is a professional software that performs hydraulic calculations for all types of tower trays, random and structured packings and liquid distributors. The development of **TrayHeart** started in 1998 and was continued jointly by universities, companies of the chemical industry and tower internals suppliers. **TrayHeart ...**

- is based on multiple calculation models and large databases of packings, float valves, fixed valves, bubble caps, and liquid distributor templates
- is a supplier-independent tool. There are no preferred product placements or promoted designs
- considers static dimensions, manways and fastenings
- offers an interactive 3D-view for all designs
- can be used for single stage, profile and data validation calculations
- has a unique, logical and multi-lingual user interface, with multiple input and output options
- applies hundreds of online queries to check the feasibility and limits of the calculated designs
- is a well introduced software many companies have relied on for more than 20 years
- has extensive documentation and is licensed on annual basis

For more information:
www.welchem.com
service@welchem.com

Light Olefins Maximization as Potential "Blue Ocean" Strategy for Integrated Downstream Players

Dr. Marcio Wagner da Silva

Introduction and Context

The current scenario presents 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.

According to Figure 1, is expected a growing demand by petrochemicals while the transportation fuels tend to present falling consumption. Still according to Wood Mackenzie data, presented in Figure 2, due to the higher added value, the most integrated refiners tend to achieve higher refining margins than the conventional refiners which keep the operations focused on transportation fuels.

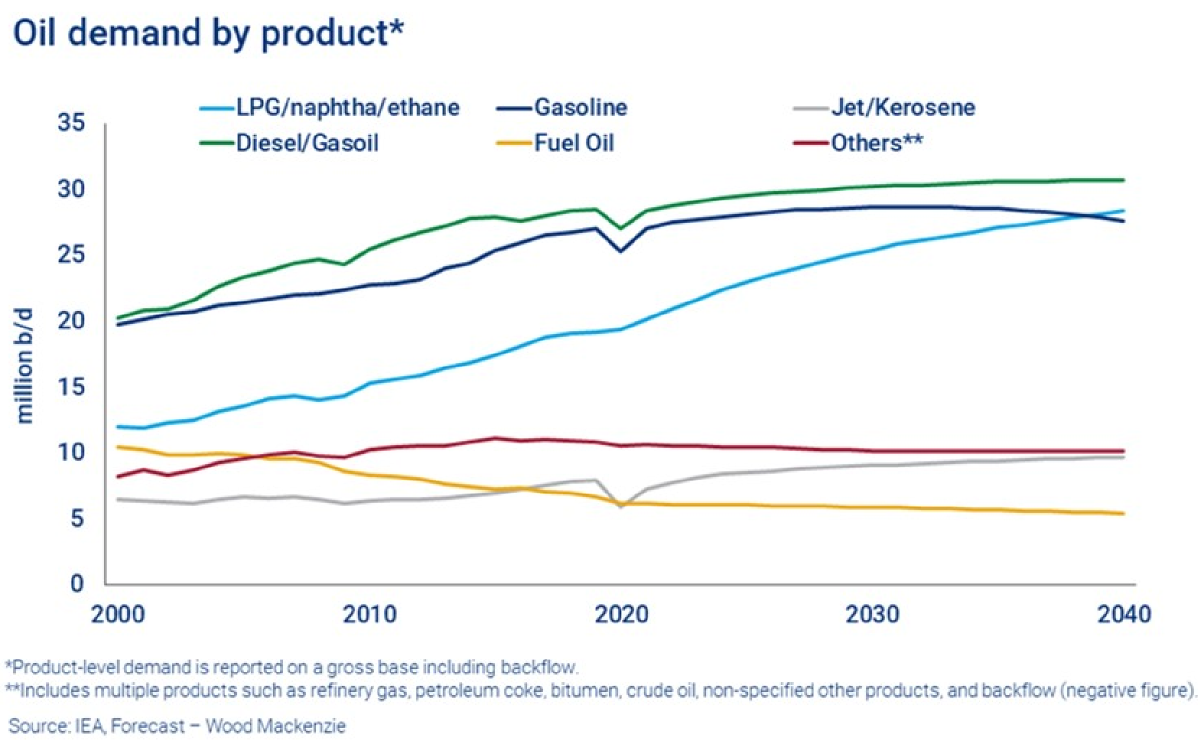


Figure 1 – Global Oil Demand by Derivative (Wood Mackenzie, 2020)

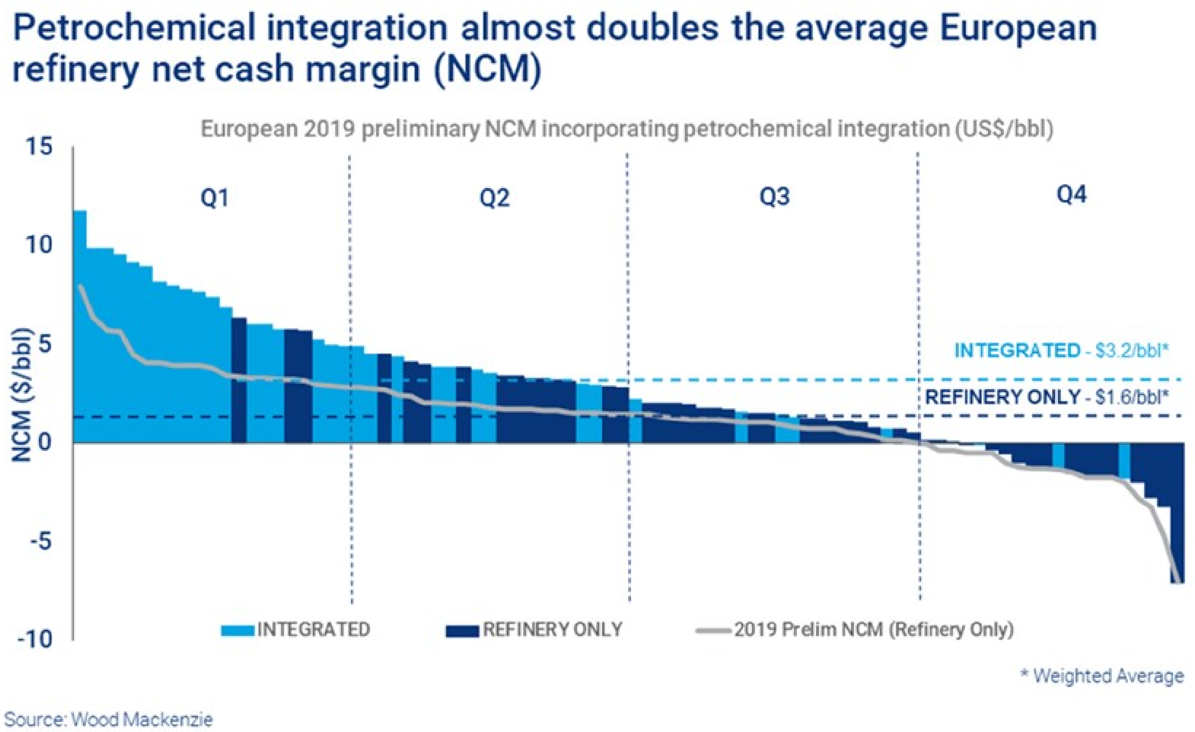


Figure 2 – Refining Margins to Integrated and Non-Integrated Refining Hardware (Wood Mackenzie, 2020)

NCM = Net Cash Margins

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) have 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.

Figure 3 presents an overview of the trend of growing to the petrochemical market in short term.

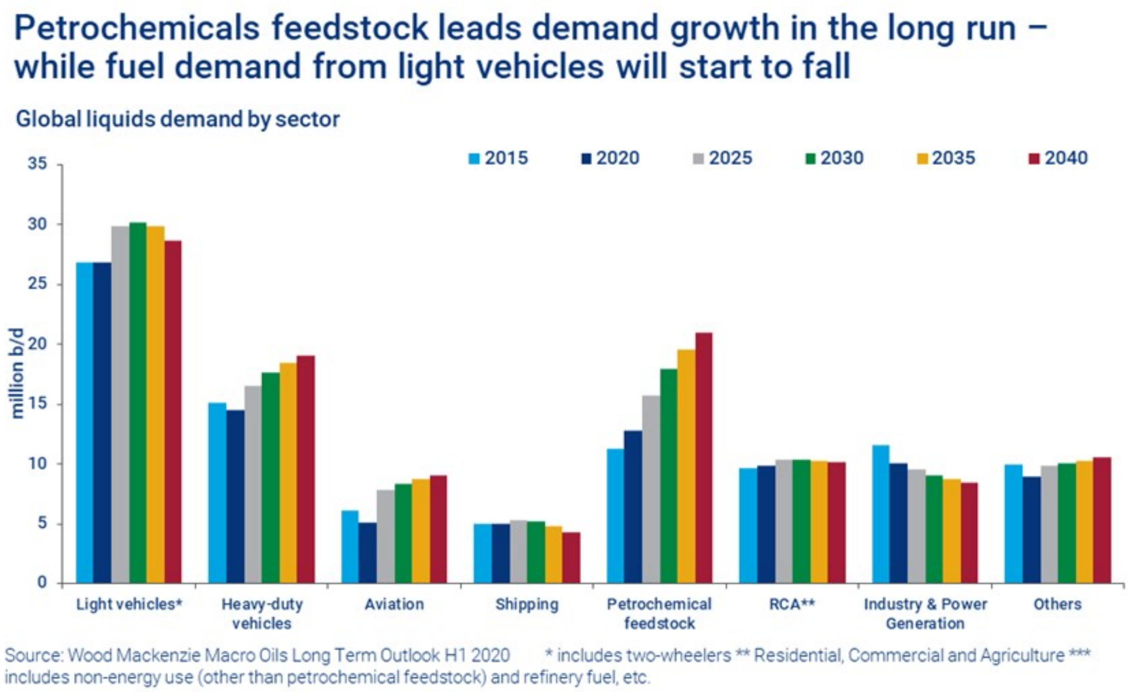


Figure 3 – Growing Trend in the Demand by Petrochemical Intermediates (Wood Mackenzie, 2020)

According to data presented in Figure 3, is expected a significant growth in the market of light olefins like ethylene and propylene, and a refining hardware capable to maximize the yield of these petrochemical intermediates can offer significant competitive advantage through closer integration with petrochemical assets and higher value addition to processed crude oil.

In this scenario, refining technologies like Fluid Catalytic Cracking (FCC) and petrochemical processes like Steam Cracking can appear as a good alternative for new capital investments to improve the refinery capacity to face the new market demand.

It's interesting to highlight that the naphtha alkylation technology as octane boosting route can be attractive to refiners inserted in markets with high demand of gasoline and availability of LPG like the United States. An interesting case study is the Brazilian market which is historically, Brazil relies on external market to supply their needs of LPG. In 2020 the internal production of LPG in Brazil was 9,86 million m3 where 74 % was supplied by refineries (7,34 million m3) while petrochemical plants and natural gas processing units were responsible for the remain internal production, in the same year, the imports of LPG in Brazil reached 3,62 million m3. With the development of pre salt crude oil reserves the natural gas production in Brazil is growing and the production of LPG associated with the natural gas tends to reduce the external dependence of this derivative. According to Brazilian Petroleum Agency (ANP) the imports of natural gas reduced 20 % in 2020 in comparison with 2019, reaching 7,9 billion m3.

This scenario can lead the Brazilian refiners to consider the naphtha alkylation route as octane boosting to produce low sulfur and high-quality gasoline at same time which can deal with an eventual surplus of LPG in the internal market. Considering the growing propylene gap, which is observed at global level, another attractive route to deal with LPG surplus is the propane dehydrogenation (PDH) units that can be applied to add significant value to the LPG.

Based on the description above it's possible to apply the article published by W. Chan Kim and Renée Mauborge called "Blue Ocean Strategy" in Harvard Business Review, to classify the competitive markets in the downstream industry. In this article the authors define the conventional market as a red ocean where the players tend to compete in the existing market focusing on defeat competitors through the exploration of existing demand, leading to low differentiation and low profitability. The blue ocean is characterized by look for space in non-explored (or few explored markets), creating and developing new demands and reaching differentiation, this model can be applied (with some specificities once is a commodity market) to the downstream industry, considering the traditional transportation fuels refineries and the petrochemical sector.

Due to his characteristics, the transportation fuels market can be imagined like the red ocean, where the margins tend to be low and under high competition between the players with low differentiation capacity. On the other side the petrochemicals sector can be faced like the blue ocean where few players are able to meet the market in competitive conditions, higher refining margins, and significant differentiation in relation to refiners dedicated to transportation fuels market.

It's interesting to quote the potential competitive imbalance of the downstream industry in the short term due to the growing demand for petrochemicals. Based on data from 2019 the total capital investments in crude to chemicals refineries is 300 billion US dollars and 64 % of this investment was made by Asian players, to reinforce this trend Figure 4 present a comparison between the relation of crude oil distillation capacity and the integrated refinery capacity for each continent.

Figure 4 shows that the Asian players have a superior integration capacity of their refining assets in comparison with another continents, as mentioned above, this can be translated in a significant competitive advantage to the Asian players and a great potential o competitive imbalance of the downstream market considering the recent forecasts which indicates growing demand for petrochemicals. Furthermore, it's possible to see the power of the China in the Asian and global downstream market.

Considering exclusively the propylene market, the forecasts are even more encouraging for investments in purpose propylene production routes. Figure 5 presents the projection to propylene market size for the next years.

According to Figure 5, the propylene market can reach values higher than 150 billion USA dollars in 2032 with an annual rate of 3,76 % with Asia being the bigger market as expected.

Considering the ethylene market, the scenario is even more attractive once is expected an

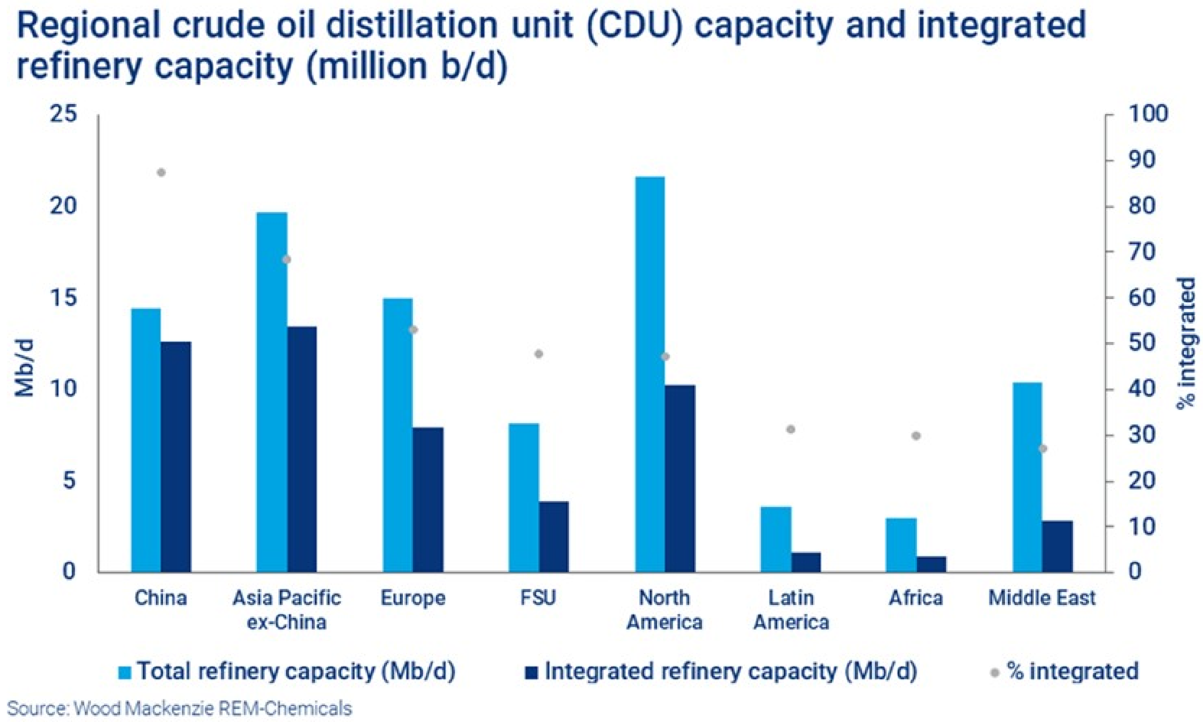


Figure 4 – Crude Oil Distillation Capacity and Integrated Refinery Capacity for Each Continent (Wood Mackenzie, 2023)

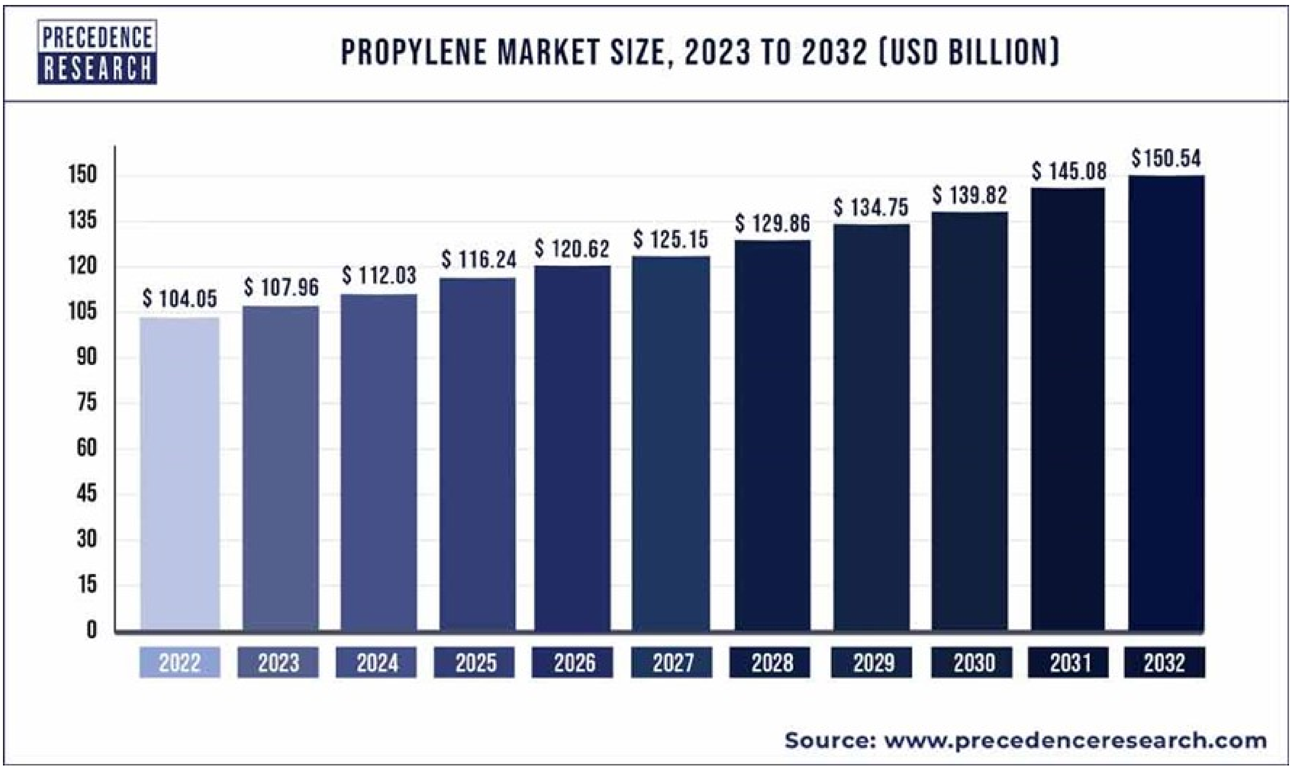


Figure 5 – Evolution of Propylene Market Size for the next years (Precedence Research, 2022)

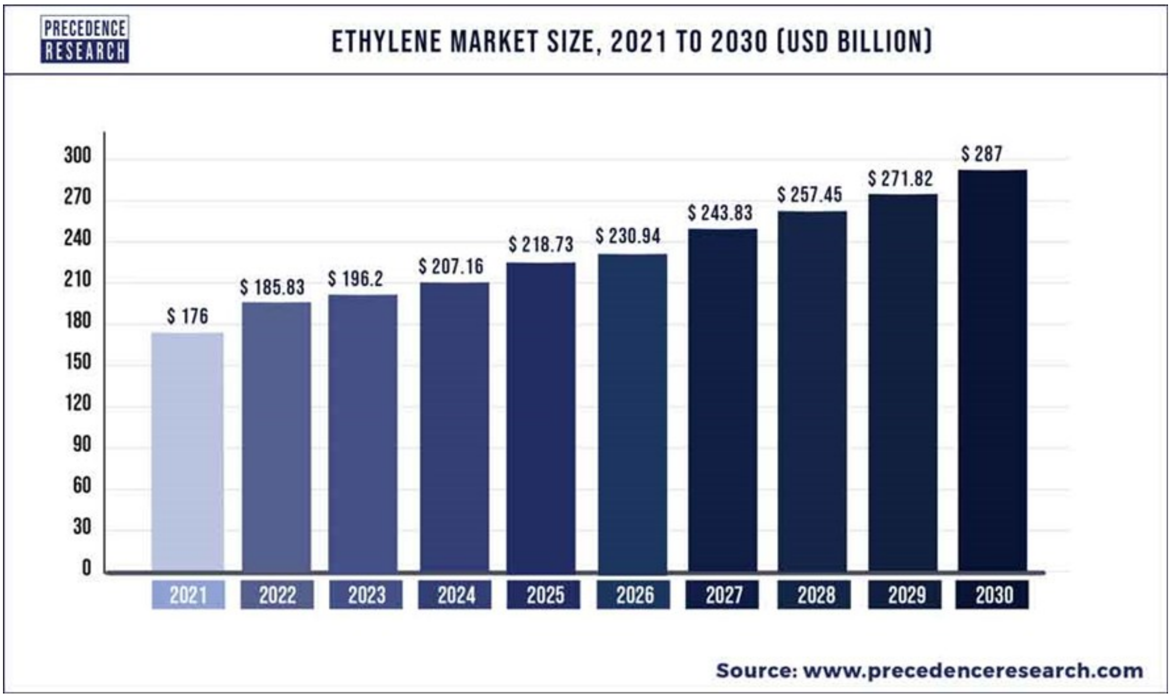


Figure 6 – Evolution of Ethylene Market Size for the next years (Precedence Research, 2022)

annual growth rate of 5,58 % between 2022 and 2030 and the total size of the ethylene market can reach USD 287 billion in 2030 as presented in Figure 6. Again, the Asian continent is responsible of the major part of this growth.

Due to his similarities, better integration between refining and petrochemical production processes appears as an attractive alternative to maximize the yield of petrochemicals. Although the advantages, it's important to consider 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 need to be deeply studied and analyzed case by case.

In this business environment, flexible refining technologies like Fluid Catalytic Cracking (FCC) can ensure high competitiveness to refiners once are capable to produce high quality intermediates both to petrochemicals and transportation fuels, in markets with great demand by petrochemicals, the petrochemical FCC technologies can be an attractive option, despite the high capital spending.

Fluid Catalytic Cracking Technologies

The Fluid Catalytic Cracking (FCC) is one of the main processes which give higher operational flexibility and profitability to refiners. The catalytic cracking process was widely studied over the last decades and became the principal and most employed process dedicated to converting heavy oil fractions in higher economic value streams.

The installation of catalytic cracking units allows the refiners to process heavier crude oils and consequently cheaper, raising the refining margin, mainly in higher crude oil prices scenario or in geopolitics crises that can become difficult the access to light oils. The typical Catalytic Cracking Unit feed stream is gas oils from vacuum distillation process. However, some variations are found in some refineries, like sending heavy coke naphtha, coke gas oils and deasphalted oils from deasphalting units to processing in the FCC unit.

The catalyst normally employed in fluid catalytic cracking units is a solid constituted by small particles of alumina (Al_2O_3) and silica (SiO_2) (zeolite). By the catalyst characteristics and the operational conditions in the catalytic cracking process (temperature higher than 500 oC), the process is inefficient to cracking aromatic compounds, therefore, how much more paraffinic is the feed stream, higher is the unit conversion. Figure 7 presents a process scheme for a typical Fluid Catalytic Cracking Unit (FCCU).

In a conventional scheme, the catalyst regeneration process consists in the carbon partial burning deposited over the catalyst, according to chemical reaction below:

$C + \frac{1}{2} O_2 \rightarrow CO$

The carbon monoxide is burned in a boiler capable of generating higher pressure steam that supplies others process units in the refinery.

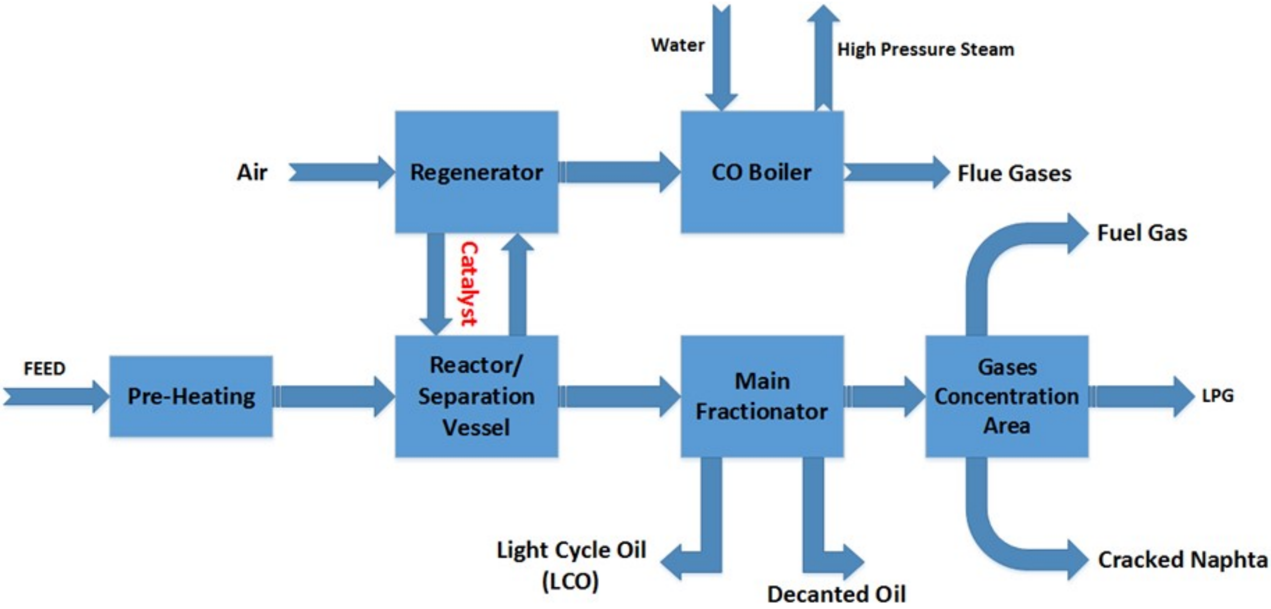


Figure 7 – Schematic Process Flow for a Typical Fluid Catalytic Cracking Process Unit (FCCU)

The principal operational variables in a fluid catalytic cracking unit are reaction temperature, normally considered the temperature in the top of the reactor (called riser), feed stream temperature, feed stream quality (mainly carbon residue), feed stream flow rate and catalyst quality. Feedstock quality is especially relevant, but this variable is a function of the crude oil processed by the refinery, so is difficultly can be changed, but for example, aromatic feedstocks with high metals content are refractory to cracking and conducting to a quick catalyst deactivation.

An important variation of the fluid catalytic cracking technology is the residue fluid catalytic cracking unit (RFCC). In this case, the feedstock to the process is basically residue from atmospheric distillation column, due to the high carbon residue and contaminants (metals, sulphur, nitrogen, etc.) are necessary some adaptations in the unit like catalyst with higher resistance to metals and nitrogen and catalyst coolers furthermore, it's necessary apply materials with most noble metallurgy due the higher temperatures reached in the catalyst regeneration step (due the higher coke quantity deposited on the catalyst), that raises significantly the capital investment to the unit installation. Nitrogen is a strong contaminant to the FCC catalyst because they neutralize the acid sites of the catalyst which are responsible for the cracking reactions.

When the residue has high contaminants content, is common the feed stream treatment in hydrotreating units to reduce the metals and heteroatoms concentration to protect the FCC catalyst.

When the residue has high contaminants content, is common the feed stream treatment in hydrotreating units to reduce the metals and heteroatoms concentration to protect the FCC catalyst.

Typically, the average yield in fluid catalytic cracking units is 55% in volume in cracked naphtha and 30 % in LPG.

The decanted oil stream contains the heavier products and have high aromatic content, is common that this product is contaminated with catalyst fines and normally this stream is directed to use like fuel oil diluent, but in some refineries, this stream can be used to produce black carbon.

Light Cycle Oil (LCO) has a distillation range close to diesel and normally this stream is directed to treatment in severe hydrotreating units (due to the high aromaticity), after this treatment the LCO is sent to the refinery diesel pool.

Heavy cracked naphtha is normally directed to refinery gasoline pool, however, in scenarios where the objective is to raise the production of middle distillates, this stream can be sent to hydrotreating units for further diesel production.

The overhead products from the main fractionator are still in gaseous phase and are sent to the gas separation section. The fuel gas is sent to the refinery fuel gas ring, after treatment to remove H2S, where will be burned in fired heaters while the LPG is directed to treatment (MEROX) and further commercialization. The LPG produced by FCC unit has a high content of light olefins (mainly Propylene) so, in some refineries, the LPG stream is processed in a Propylene separation unit to recover the propylene that has higher added value than LPG.

Cracked naphtha is usually sent to refinery gasoline pool which is formed by naphtha produced by other process units like straight run naphtha, naphtha from the catalytic reforming unit, etc. Due to the production process (deep conversion of residues), the cracked naphtha has high sulfur content and to attend the current environmental legislation this stream needs to be processed to reduce the contaminants content, mainly sulfur.

The cracked naphtha sulfur removal represents a great technological challenge because is necessary to remove the sulfur components without molecules saturation that gives high octane number for gasoline (mainly olefins).

Over the last decades some technology licensers had developed new processes aiming to reduce the sulfur content in the cracked naphtha with minimum octane number loss, some of the main technologies dedicated for this purpose are technology PRIME G+ ™ from Axens, the processes OCTAGAIN ™ and SCANfining ™ from Exxon Mobil, the process S-Zorb™ from ConocoPhillips, and ISAL™ technology from UOP.

Usually, catalytic cracking units are optimized to aim the production of fuels (mainly gasoline), however, some process units are optimized to maximize the light olefins production (propylene and ethylene). Process units dedicated for this purpose have their project and operational conditions significantly changed once the process severity is strongly raised in this case.

The reaction temperature reaches 600 oC and higher catalyst circulation rate raises the gases production, which requires a scaling up of gas separation section.

In several cases, due the higher heat necessity of the unit is advantageous to operate the regenerator with the total combustion of the coke deposited on the catalyst, this arrangement changes the thermal balance of the refinery once it's no longer possible to resort the steam produced by the CO boiler.

Over the last decades, fluid catalytic cracking technology was intensively studied aiming mainly the development of units capable of producing light olefins (Deep Catalytic Cracking) and to process heavier feedstocks. The main licensers for fluid catalytic cracking technology nowadays are the companies KBR, UOP, STONE & WEBSTER, Axens, and Lummus.

Meeting the Market Demand through FCC Optimization – Maximum Olefins Operation Mode

In this operation mode the FCC unit operates under high severity translated to high operation temperature (TRX), high catalyst/oil ratio. The catalyst formulation considering higher catalyst activity through addition of ZSM-5 zeolite. There is the possibility of a reduction in the total processing capacity due to the limitations in blowers and cold area capacity.

It's observed an improvement in the octane number of cracked naphtha despite a lower yield, due to the higher aromatic concentration in the cracked naphtha. In some cases, the refiner can use the cracked naphtha recycle to improve even more the LPG yield.

In the maximum LPG operation mode, the main restrictions are the cold area processing capacity, metallurgic limits in the hot section of the unit, treating section processing capacity as well as the top systems of main fractionating column. In markets with falling demand by transportation fuels, this is the most common FCC operation mode.

Through changing the reaction severity, it is possible to maximize the production of petrochemical intermediates, mainly propylene in conventional FCC units, as shown in Figure 8.

The use of FCC catalyst additives such as ZSM-5 can increase unit propylene production by up to 9,0%. Despite the higher operating costs, the higher revenues from the higher added value of derivatives should lead to a positive financial result for the refiner, according to current market projections. A relatively common strategy also applied to improve the yield of LPG and propylene in FCC units is the recycling of cracked naphtha leading to an over cracking of the gasoline range molecules.

The Propylene Recovery Section

Among the light olefins, propylene is one of the most relevant petrochemical intermediate due to the high demand and added value.

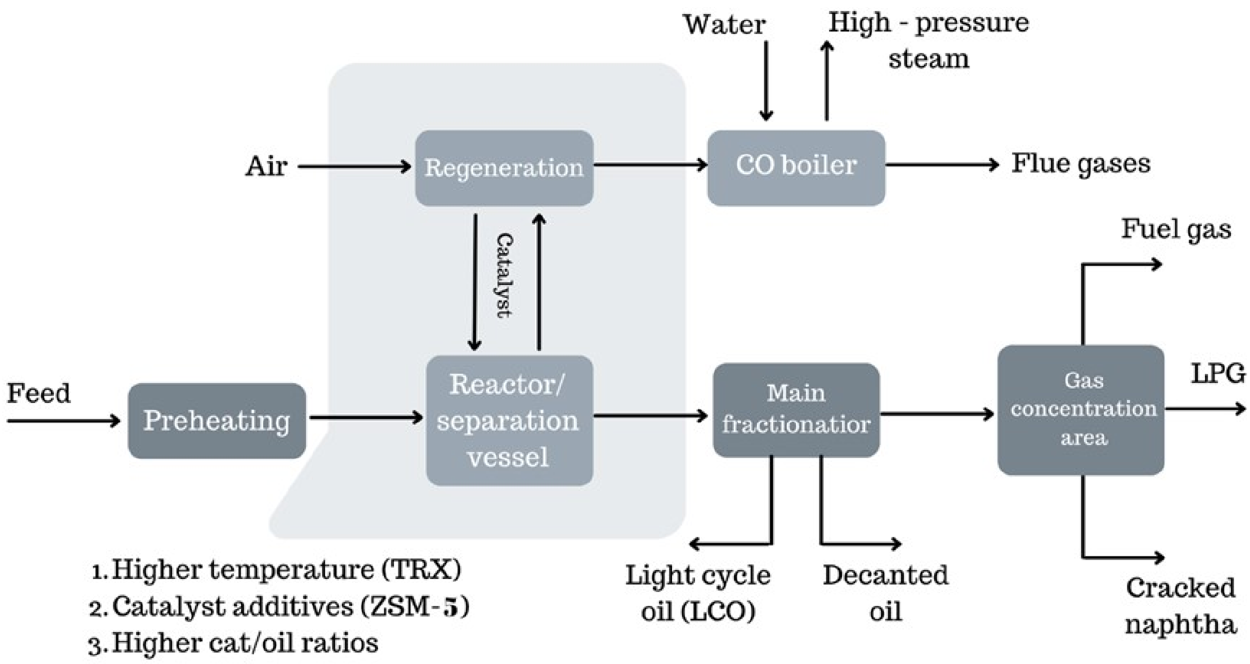


Figure 8 - Optimization of Process Variables in FCC Units to Improve the Yield of Petrochemicals Intermediates.

The propylene can be applied as intermediate to the production some fundamental products, for example:

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

Propylene can be produced through conventional processes like Steam Cracking and Fluid Catalytic Cracking (FCC) or through directed processes like metathesis of ethylene and butane, propane dehydrogenation, olefins cracking, Methanol to Olefins processes (MTO), among others. Currently a major part of the propylene market is supplied by steam cracking units, but close to 28 % of the global propylene demand is from the separation of LPG produced in Fluid Catalytic Cracking Units (FCC).

Normally, the LPG produced in FCC units contains 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 to consider 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 distillation columns with many equilibrium stages and high internal reflux flow rates.

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

The high-pressure technology applies 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

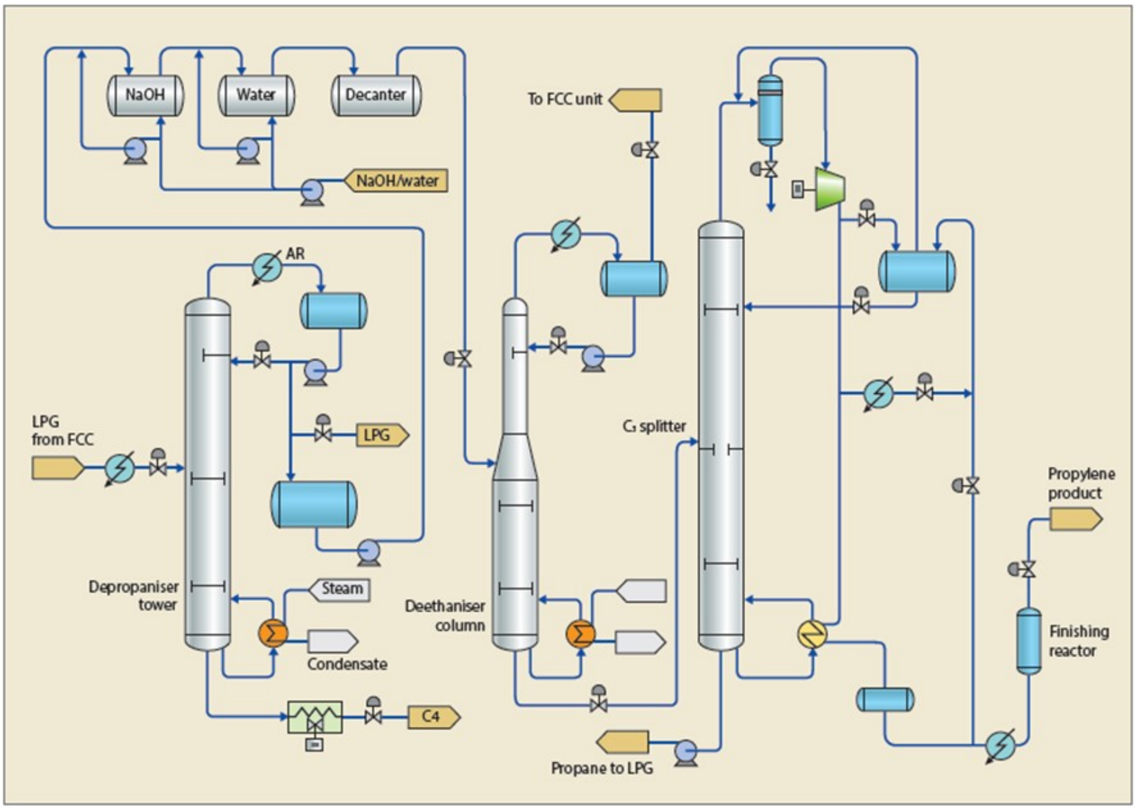


Figure 9 – Typical Process Flow Diagram for an FCC Propylene Separation Unit Applying Heat Pump Configuration

more attractive, despite the higher capital requirements.

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 considered 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, propylene is produced in the refineries with two specifications. The polymer grade that is most common and has 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 9.

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).

Maximizing Olefins – The Petrochemical FCC Technologies

As quoted earlier, in markets with high demand by petrochemicals, the petrochemical

FCC can be an attractive alternative to refiners aiming to ensure higher added value to bottom barrel streams. An example of FCC technology developed to maximize the production of petrochemical intermediates is the PetroFCC™ process by UOP Company, this process combines a petrochemical FCC and separation processes optimized to produce raw materials to the petrochemical process plants, as presented in Figure 10. Other available technologies are the HS-FCC™ process commercialized by Axens Company, and INDMAX™ process licensed by Lummus Company.

It's important to consider that both technologies presented in Figure 10 is based on Petrochemical FCC units that presents especial design due to the most severe operating conditions.

To petrochemical FCC units, the reaction temperature reaches 600 oC and higher catalyst circulation rate raises the gases production, which requires a scaling up of gas separation section. The higher thermal demand makes it advantageous to operate the catalyst regenerator in total combustion mode leading to the necessity of installation a catalyst cooler system.

Figure 11 presents the results of a comparative study, carried out by Technip Company, showing the yields obtained by conventional FCC units, optimized to olefins (FCC to olefins), and the HS-FCC™ designed to maximize the production of petrochemical intermediates.

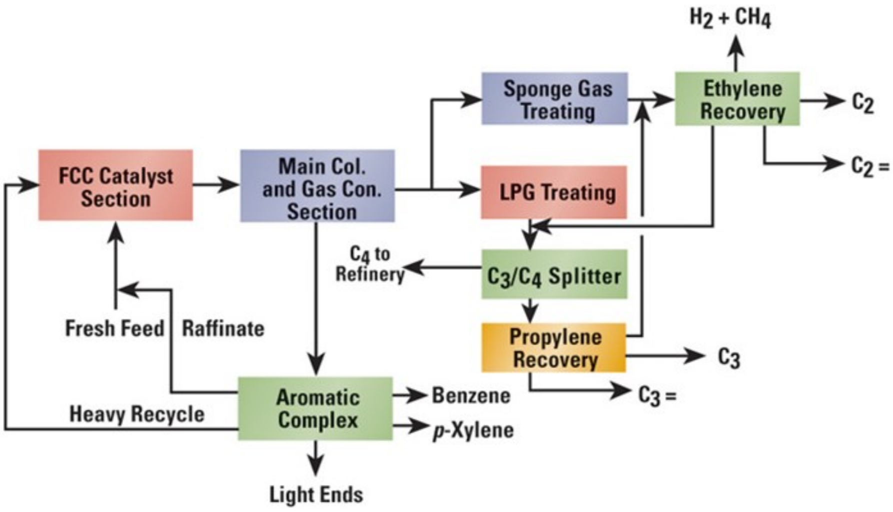


Figure 10 – PetroFCC™ Process Technology by UOP Company.

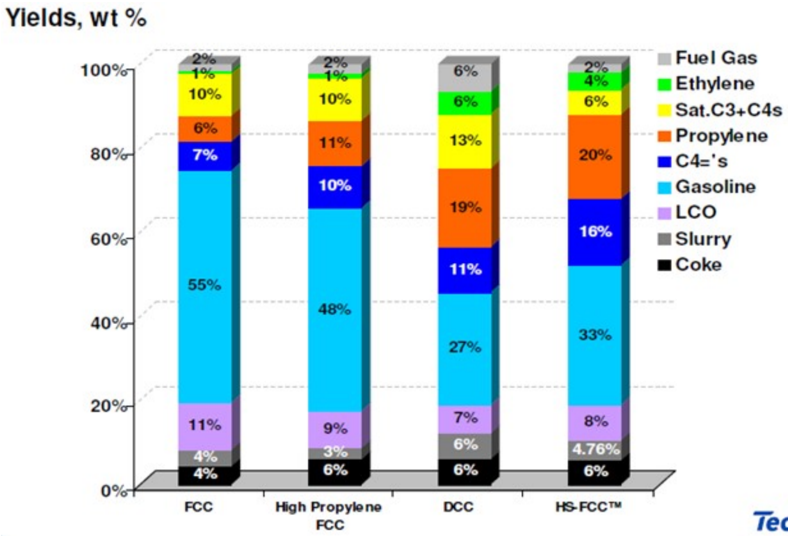


Figure 11 – Comparative Study between Conventional FCCs and Petrochemical FCC (HS-FCC™)

	Conv. FCC	HP FCC	DCC	HS-FCC™
ROT	530°C (986°F)	550°C (1022°F)	580°C (1076°F)	600°C+ (1112°F+)
Contact time	2 - 5 s	2 - 5 s	10 s	0.5 - 1 s
C/O	5	10	15	25
Recycle	None	LCN	LCN	None

It's observed a higher reaction temperature (TRX) and a cat/oil ratio five times higher when are compared the conventional process units and the petrochemical FCC (HS-FCC™), leading to a growth of the light olefins yield (Ethylene + Propylene + C4='s) from 14 % to 40%.

The installation of petrochemical catalytic cracking units requires a deep economic study considering the high capital investment and higher operational costs; however, some forecasts indicate growth of 4,0 % per year to the market of petrochemical intermediates until 2025. In this scenario can be attractive the capital investment aiming to raise the market share in the petrochemical sector, allowing then a favorable competitive positioning to the refiner, through the maximization of petrochemical intermediates.

In refining hardware with conventional FCC units, further than the higher temperature and catalyst circulation rates, it's possible to apply the addition of catalysts additives like the zeolitic material ZSM-5 that can raise the olefins yield close to 9,0% in some cases when compared with the original catalyst. This alternative raises the operational costs, however, as aforementioned can be economically attractive considering the petrochemical market forecasts.

Installation of catalyst cooler system raises the process unit profitability through the total conversion enhancement and selectivity to noblest products as propylene and naphtha against gases and coke production. The catalyst cooler is necessary when the unit is designed to operate under total combustion mode due to the higher heat release rate as presented below.

$C + ½ O_2 \rightarrow CO$ (Partial Combustion) $\Delta H = -27$ kcal/mol

$C + O_2 \rightarrow CO_2$ (Total Combustion) $\Delta H = -94$ kcal/mol

In this case, the temperature of the regeneration vessel can reach values close to 760 oC, leading to higher risks of catalyst damage which is minimized through catalyst cooler installation. The option by the total combustion mode needs to consider the refinery thermal balance, once, in this case, will not the possibility to produce steam in the CO boiler, furthermore, the higher temperature in the regenerator requires materials with noblest metallurgy, this significantly raises the installation costs of these units which can be prohibitive to some refiners with restricted capital access.

Due to the higher production of light olefins, mainly ethylene, another important difference between conventional and petrochemical FCC units is related to the gas recovery section, while in conventional FCC is applied absorber columns, in petrochemical units is applied cryogenic processes though refrigeration cycles in similar conditions which are applied in steam cracking units.

The cryogenic processes applied to olefins recovery raises, even more, the capital requirement to petrochemical FCC units when compared with conventional FCCs, despite this, the growing market for petrochemicals and falling demand for transportation fuels,

Naphtha Steam Cracking Process – Ethylene Focus

The Steam cracking process has a fundamental role in the petrochemical industry, nowadays the most part of the 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 12 presents a typical steam cracking unit applying naphtha as raw material to produce olefins.

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 technologies 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. Another commercial technology dedicated to optimizing the yield of ethylene is the SCORE™ technology developed by KBR and ExxonMobil Companies which combines a selective steam cracking furnace with high performance olefins recovery section.

The cracking reactions occur in the furnace tubes, the main concern and limitation to operating lifecycle of steam cracking units is the

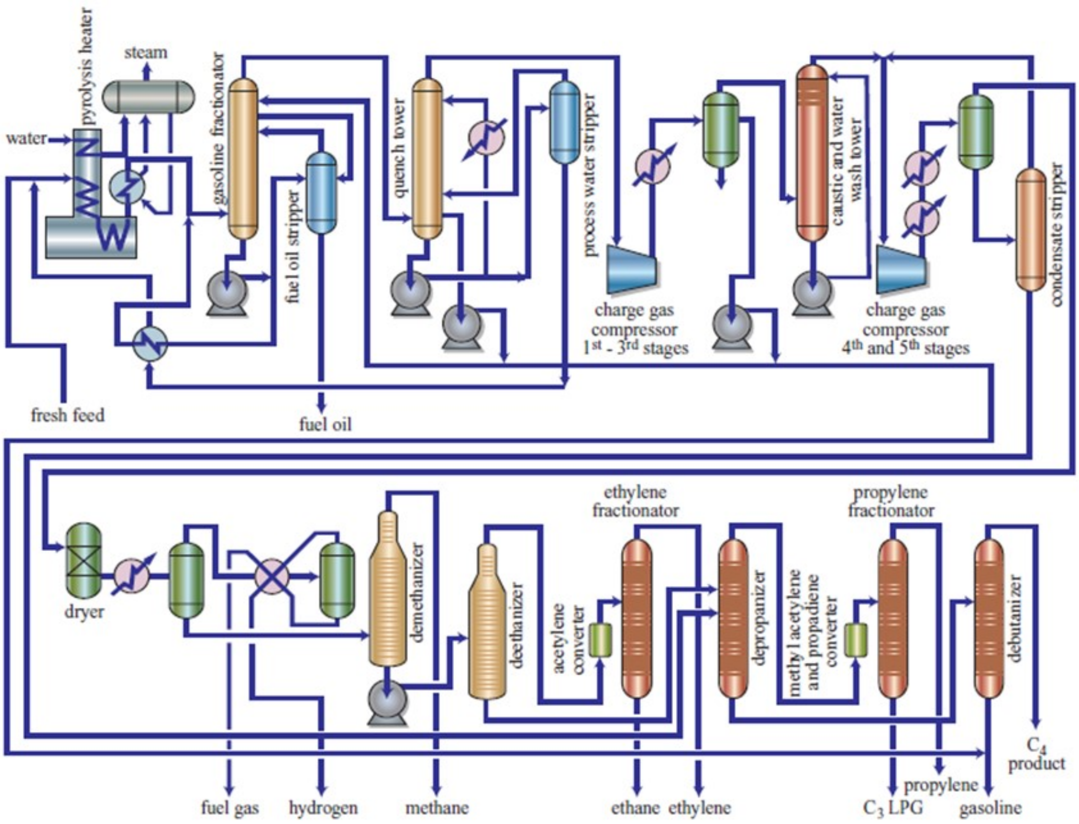


Figure 12 – Typical Naphtha Steam Cracking Unit (Encyclopedia of Hydrocarbons, 2006)

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. Despite be possible to operate with naphtha, nowadays the steam cracking operators have chosen to operate with ethane or LPG against naphtha due to the competitive prices related to the new sources of NGL (Natural Gas Liquid), despite this trend over the last years, in markets where is observed a gasoline surplus, naphtha can still an attractive alternative as feedstock to steam crackers.

According to some forecasts, the demand by propylene will raise from 130 million metric tons in 2020 to around to 190 million metric tons in 2030. Facing the increasingly light feed to refineries and steam cracking units which tends to favor the ethylene production in detriment of propylene, the propylene demand tends to be supplied by on-purpose propylene production routes like propane dehydrogenation, methanol to olefins (MTO), and olefins metathesis.

Light Paraffin Dehydrogenation Technologies

Another alternative to improve the yield of light olefins in the refining hardware is to apply paraffin dehydrogenation technologies. Light paraffin is normally commercialized as LPG or gasoline and presents 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 13 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 such as LPG from atmospheric distillation and units dedicated to separate gases from crude oil.

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 one 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 their 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 14 presents a basic process flow diagram for the OLEFLEX™ technology by UOP Company. Another paraffin dehydrogenation technology from UOP Company is the PACOL™ process.

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 15.

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.

$$R2CH\text{-}CHR2 + O2 \leftrightarrow R2C{=}CR2 + H2O \quad (2)$$

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

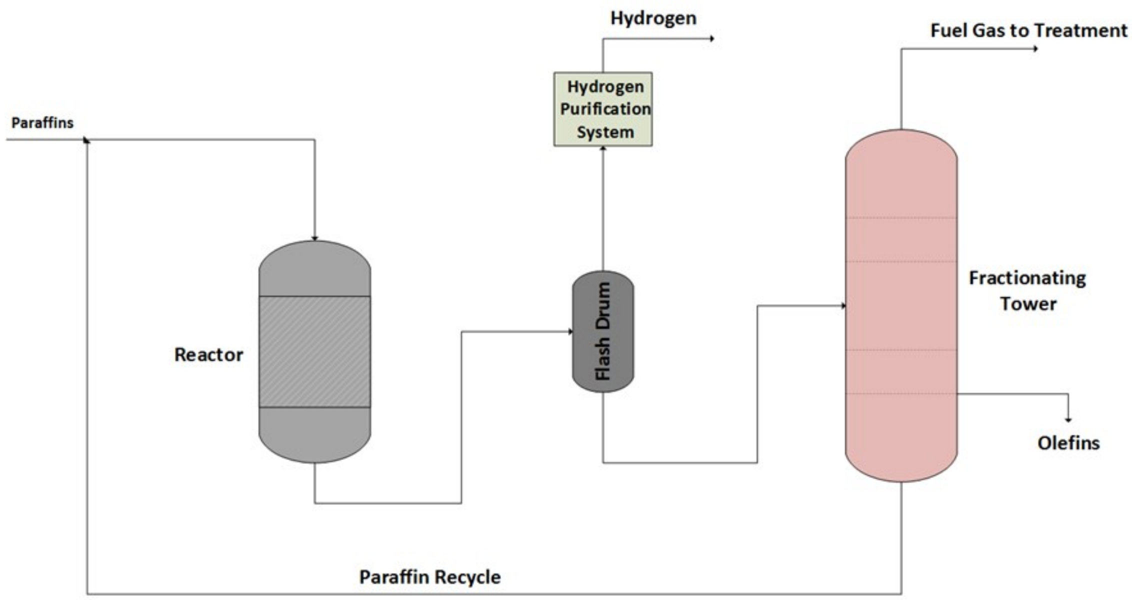


Figure 13 – Process Flow Diagram for a Typical Light Paraffin Dehydrogenation Process Unit.

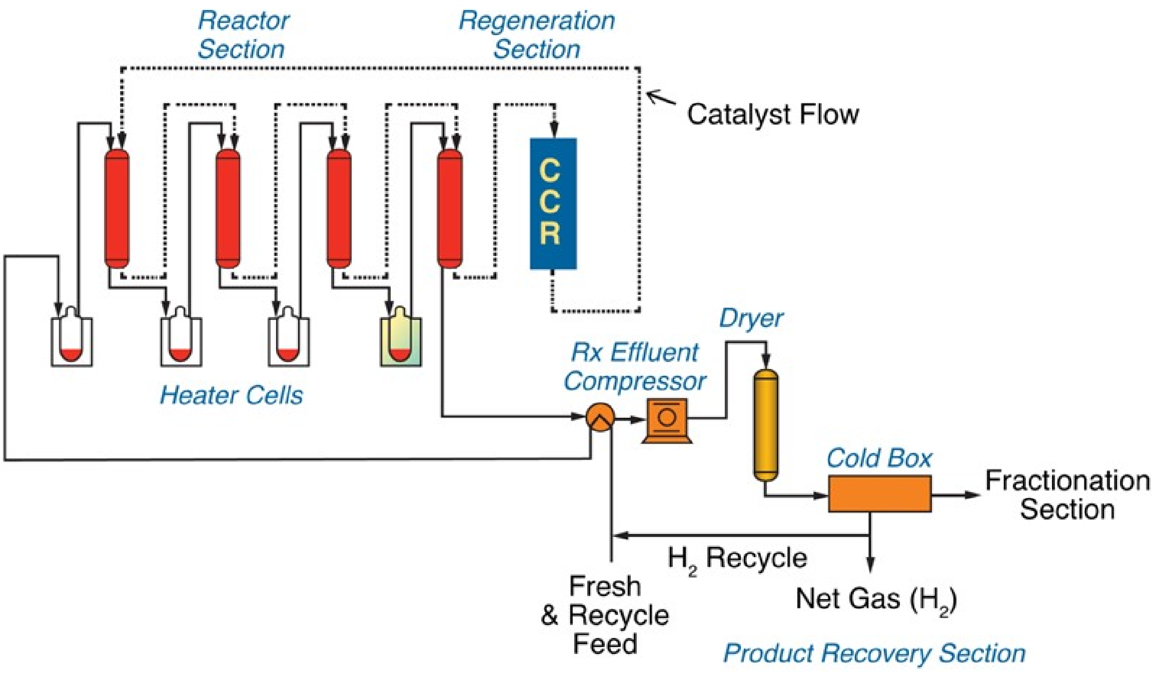


Figure 16 – Basic Process Flow Diagram for the OLEFLEX™ Technology by UOP Company (MARSH & WERY, 2018)

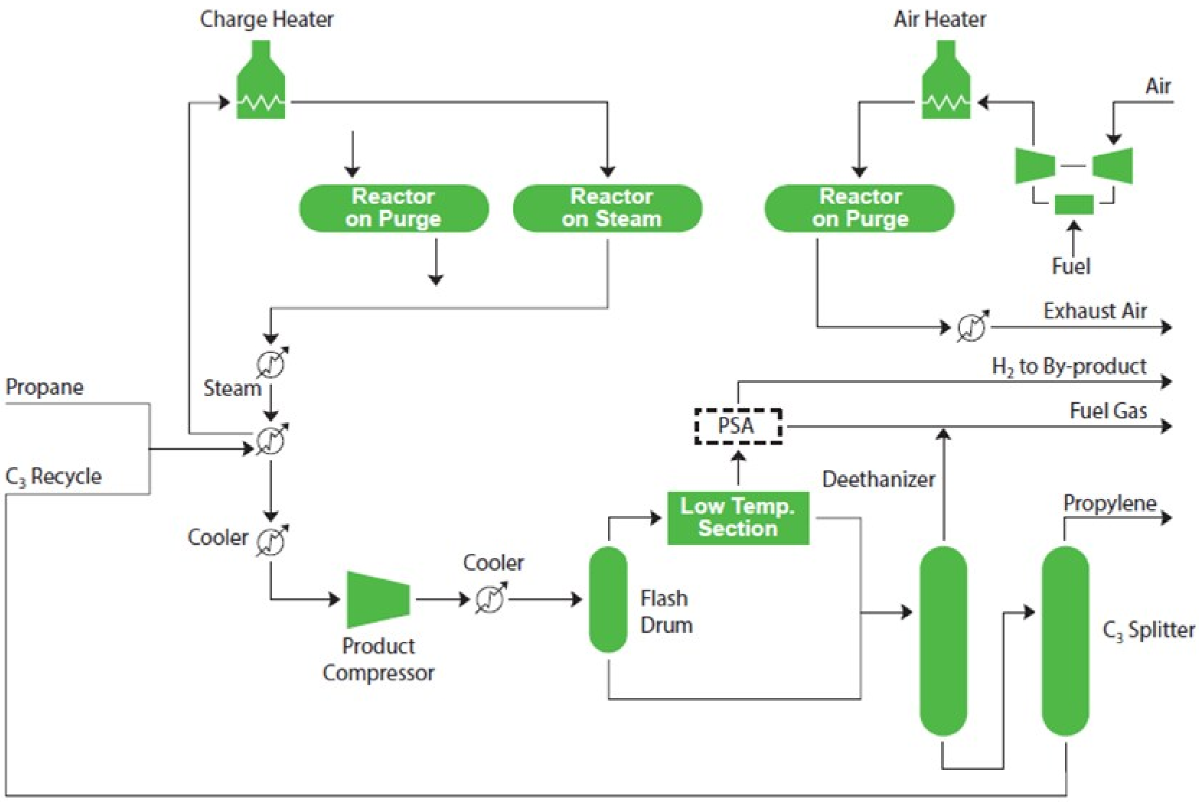


Figure 15 – Simplified Process Scheme to CATOFIN™ Dehydrogenation Technology, by Lummus Company.

Table 1 – FCC and Steam Cracking Comparison

Characteristic	FCC Technologies	Steam Cracking
Mechanism	Catalytic Process	Thermal Process
Residence Time (s)	1 to 5	0,1 to 0,5
Reaction Temperature (oC)	500 to 650 oC	700 to 900
Feedstock	Heavier Molecules (Gasoil)	Lighter Molecules (Naphtha or Ethane)
Main Production Focus	Propylene	Ethylene

The Combination of FCC and Steam Cracking Units – Maximum Olefins Yield

As aforementioned, maximizing the light olefins yield in the refining hardware can be an attractive way to ensure competitiveness in the downstream market according to the recent forecasts. The combination of FCC and steam cracking units in the refining hardware can be an alternative to achieve this goal. Table 1 presents a comparison between steam cracking and FCC technologies.

The characteristics of the FCC and steam cracking units allows high yield of olefins in the refining without competition for feedstocks, once the FCC is a bottom barrel conversion technology based in carbon rejection that applies mainly gasoil as feed stream while the steam cracking process produces mainly ethylene through thermal cracking of ethane and high paraffinic naphtha.

The yield of propylene in the steam cracking units relies on the feedstock quality, being higher in units processing naphtha. In the last years some refiners have been adopting ethane as main feedstock due to his lower prices, this fact reduces the propylene offer from steam crackers, raising the relevance of the propylene from FCC units to ensure the market supply. This fact has been the main driver to the growing of propylene on purpose technologies like propane dehydrogenation, methanol to olefins, and metathesis. Despite this recent trend, the steam cracking units remain the main propylene source to the market with close to 48 % of the market.

An example of refining configuration relying on FCC and steam cracking units is presented in Figure 16. It's interesting to note that a propane dehydrogenation unit (PDH) is applied to improve the olefins yield.

Considering the recent trend of reduction in transportation fuels demand followed by the growth of petrochemicals market makes the synergy between FCC and steam cracking units an attractive way to maximize the petrochemicals production in the refining hardware.

As aforementioned, facing the current trend of reduction in transportation fuels demand at the global level, the capacity of maximum adding value to crude oil can be a competitive differential to refiners. Due to the high capital investment needed for the implementation that allows the conventional refinery to achieve the maximization of chemicals, capital efficiency becomes also an extremely important factor in the current competitive scenario as well as the operational flexibility related to the processed crude oil slate. In the refining scheme presented in Figure 16, it's important to note that the propane dehydrogenation unit is applied to improve the yield of propylene as well as to contribute with the hydrogen balance of the refinery while the residual streams are fed to steam cracking unit, leading to even more light olefins production.

The Synergy of Steam Cracking and FCC Technologies in the Crude Oil to Chemicals Strategy

Due to the increasing market and higher added value as well as the trend of reduction in transportation fuels demand, some refiners and technology developers has dedicated his efforts to develop crude to chemicals refining assets. One of the big players that have been invested in this alternative is the Saudi Aramco Company, the concept is based on the direct conversion of crude oil to petrochemical intermediates as presented in Figure 17.

The process presented in Figure 21 is based on the quality of the crude oil and deep conversion technologies like High Severity or petrochemical FCC units and deep hydrocracking technologies, in this case it's interesting to note the added value to the processed crude through the synergy of FCC and naphtha steam cracking units.

The production focus changes to the maximum adding value to the crude oil through the production of high added value petrochemical intermediates or chemicals to

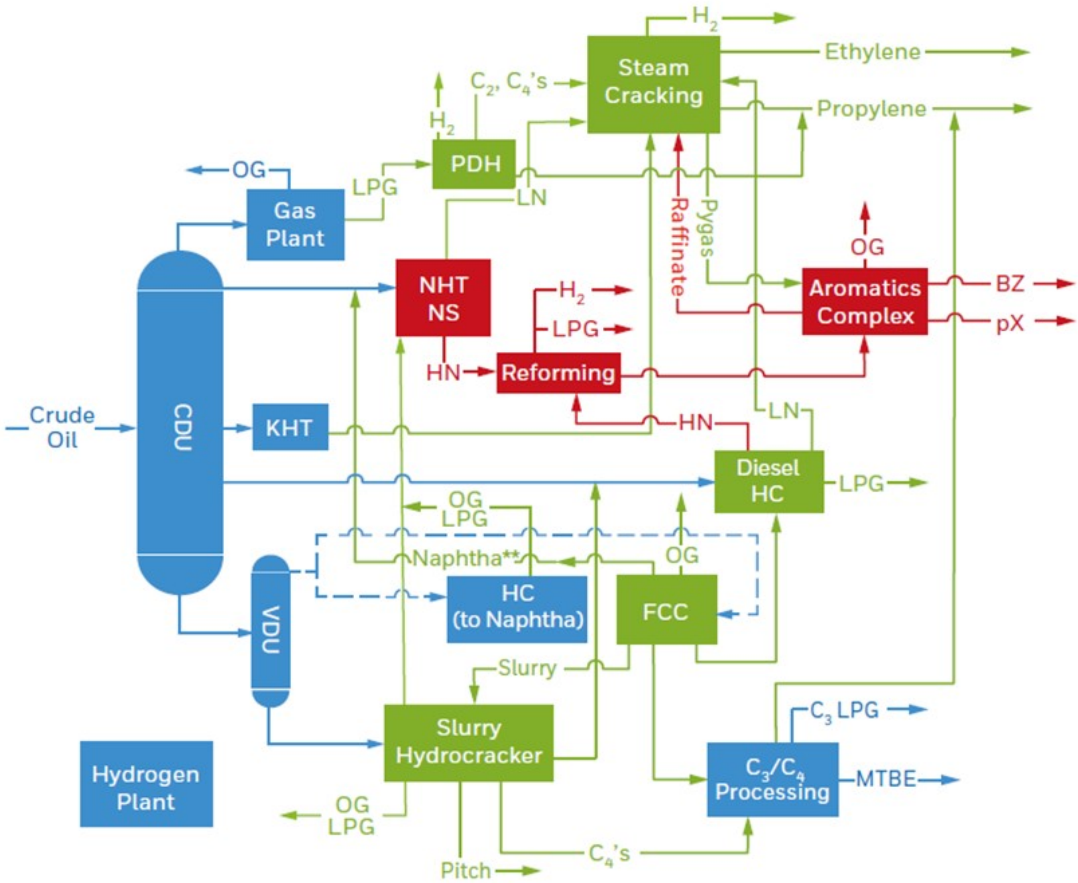


Figure 16 – Integrated Refining Scheme Base on FCC and Steam Cracking Units (UOP, 2019)

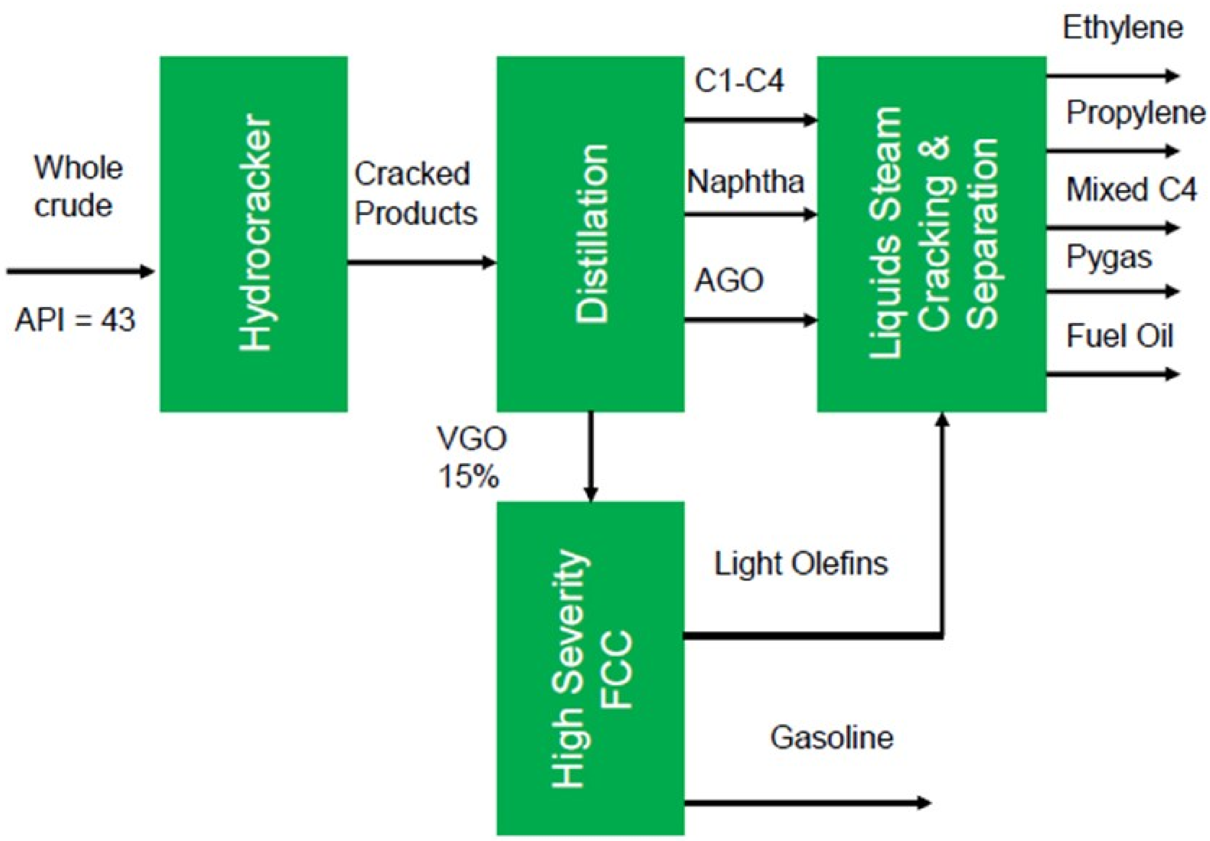


Figure 17 – Saudi Aramco Crude Oil to Chemicals Concept (IHS Markit, 2018)

general purpose leading to a minimum production of fuels. As aforementioned, big players as Saudi Aramco Company have been made great investments in COC technologies aiming to achieve even more integrated refineries and petrochemical plants, raising considerably his competitiveness in the downstream market. The major technology licensors as Axens, UOP, Lummus, Shell, ExxonMobil, etc. has been applied resources to develop technologies capable to allow a closer integration in the downstream sector aiming to allow refiners extract the maximum added value from the processed crude oil, an increasing necessity in a scenario where the refining margins are under pressure.

Although the advantages presented by closer integration between refining and petrochemical assets, it's important to understand that the players of downstream industry are facing with a transitive period where, as presented in Figure 1, the transportation fuels are responsible by great part of the revenues. In this business scenario, it's necessary to define a transition strategy where the economic sustainability achieved by the status (transportation fuels) needs to be invested to build the future (maximize petrochemicals). Keeping the eyes only on the future or only in the present can be a strategic mistake.

Conclusion

The scenario faced by the players of the downstream industry requires even more competitive capacity to ensure higher value addition to the processed crude oils, mainly considering the current trend of reduction in transportation fuels demand followed by the growing market of petrochemicals that requires a higher conversion capacity in the refining hardware aiming to ensure higher yields of added value derivatives. In this scenario, high integrated refining configurations based on residue upgrading and flexible refining technologies can be economically attractive.

The combination of FCC and steam cracking units in the refining hardware can ensure a high yield of light olefins, mainly ethylene and propylene, which presents growing demand ensuring closer integration with petrochemical assets as well as economic results. In the current scenario of the downstream industry, a refining hardware capable to maximize light olefins is a significant competitive advantage and the combination of FCC, Steam cracking, and Paraffin dehydrogenation technologies can help the refiners to reach this goal.

Despite these advantages is important to consider the high capital investment in petrochemical and integrated refining technologies and the time of these investments is a strategic decision to refiners aiming to be prepared to the future of the downstream market, although these risks, the petrochemical integration seems a significant driver to the future of the crude oil refining market and the FCC and steam cracking technologies can develop a highlighted role in this scenario. Although the benefits of petrochemical integration, it's fundamental to take in mind the necessity to reach a circular economy in the downstream industry, to achieve this goal, the chemical recycling of plastics is essential. As presented above, there are promising technologies which can ensure the closing of the sustainability cycle of the petrochemical industry.

References

Advances in Catalysis for Plastic Conversion to Hydrocarbons – The Catalyst Group (TCGR), 2021.

CHANG, R.J. – Crude Oil to Chemicals – Industry Developments and Strategic Implications – Presented at Global Refining & Petrochemicals Congress (Houston, USA), 2018.

COUCH, K. The Refinery of the Future – A Flexible Approach to Petrochemicals Integration. Honeywell UOP Company, Presented in 12th Asian Downstream Summit, 2019.

Deloitte Company. The Future of Petrochemicals: Growth Surrounded by Uncertainties, 2019.

Encyclopedia of Hydrocarbons (ENI), Volume II – Refining and Petrochemicals (2006).

GARY, J. H.; HANDWERK, G. E. Petroleum Refining – Technology and Economics. 4th ed. Marcel Dekker., 2001.

GELDER, A. Refinery-Petrochemical Integration Disrupts Gas-Based Cracker Feedstock Advantage, Wood Mackenzie, 2023.

\GELDER, A.; BAILEY, G. The Future of Petrochemicals: A Tale of Two Transitions, Wood Mackenzie, 2020.

LAMBERT, N.; OGASAWARA, I.; ABBA, I.; REDHWI, H.; SANTNER, C. HS-FCC for Propylene: Concept to Commercial Operation. PTQ Magazine, 2014.

MALLER, A.; GBORDZOE, E. High Severity Fluidized Catalytic Cracking (HS-FCC™): From concept to commercialization – Technip Stone & Webster Technical Presentation to REFCOMM™, 2016.

MUKHERJEE, M.; VADHRI, V.; REVELLON, L. Step-Out Propane Dehydrogenation Technology for the 21st Century. The Catalyst Review, 2021.

Refinery-Petrochemical Integration (Downstream SME Knowledge Share). Wood Mackenzie Presentation, 2019.

ROBINSON, P.R.; HSU, C.S. Handbook of Petroleum Technology. 1st ed. Springer, 2017.

SARIN, A.K. – Integrating Refinery with Petrochemicals: Advanced Technological Solutions for Synergy and Improved Profitability – Presented at Global Refining & Petrochemicals Congress (Mumbai, India), 2017.

SILVA, M. W. – More Petrochemicals with Less Capital Spending. PTQ Magazine, 2020.

YOUSSEF, F.; ADRIAN, M. H.; WENZEL, S. – Advanced Propane Dehydrogenation, PTQ Magazine, 2008.

Author

Dr. Marcio Wagner da Silva is Process Engineer and Stockpiling Manager on Crude Oil Refining Industry based in São José dos Campos, Brazil. Bachelor's in chemical engineering from University of Maringa (UEM), Brazil and PhD. in Chemical Engineering from University of Campinas (UNICAMP), Brazil. Has extensive experience in research, design and construction to oil and gas industry including developing and coordinating projects to operational improvements and debottlenecking to bottom barrel units, moreover Dr. Marcio Wagner have MBA in Project Management from Federal University of Rio de Janeiro (UFRJ), in Digital Transformation at PUC/RS, and is certified in Business from Getulio Vargas Foundation (FGV).

When Industrial Flare Stacks Malfunction

Jayanthi Vijay Sarathy

Industrial flares are designed to burn off gases / vapours and not liquids. Although there'd always be some liquid droplets getting entrained with the gas, but it is not normal to see bucket loads of hydrocarbon liquids getting ejected out along with the gas. Such a phenomenon is known as rain flare or burning rain.

A flare system consists of the following key equipment, process lines which collect vapour release from pressure safety valves (PSV) and blowdown lines during an unplanned event, a liquid knockout (KO) drum to separate the vapours from the hydrocarbon liquids stream, a flash back seal drum to prevent any air ingress from back flowing into the liquid KO drum and a flare stack with spark ignition device and associated instrumentation to ignite the flare gas.

Flare stacks can function during various operational situations, such as during startup and shutdown of the process facility, during equipment depressurization and venting any excess process gas during operations due to a process upset. Since one cannot be sure when there would be a process upset releasing vapours, the flare is constantly kept lit to avoid undesirable discharge of flare gas.

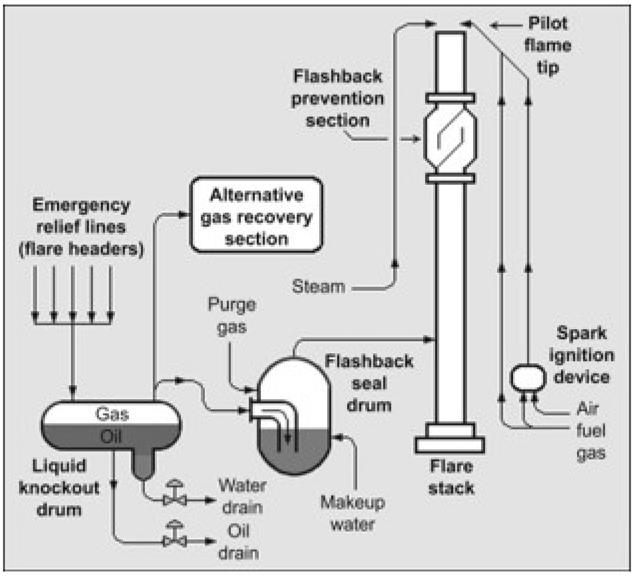


Figure 1. Typical Schematic of Flare System [1]

The following article covers some of the process related issues that can cause industrial flare stacks to malfunction and spew out liquids.

Improper Design of Liquid Knockout Drum

The primary purpose of a liquid knockout (KO) drum is to collect the vapour discharge from various PSVs and blowdown lines. However, when the KO drum results in overfilling, liquids can enter through the vapour side of the vessel and eventually reach the flare stack, waiting to be entrained. Some ways, a KO drum can fail are,

1. The drain lines at the bottom of the KO drum needs to be sufficiently sloped to ensure, the liquids drain out by gravity. For this a slope of 1:500 is required. If the drain lines are not properly sloped, the drain rate would be lower than expected.

2. In case, a pump is used to draw out liquids, the pump draws out rate must ensure, the liquid level stays at the normal liquid level (NLL) mark. To improve reliability, the drain pumps can be installed with a 2 x 100% [1W + 1S] configuration. If liquid accumulation in the KO drums is expected to be slower requiring draining between intervals, then the working pumps can be operated at LAH with the standby pump operating at LAHH.

3. KO drums require liquid droplets to settle down to the vessel bottom. Depending on the design standard, liquid droplet size can be maintained in the order of < 300 for Low Pressure KO drums to < 600 microns for High pressure (HP) KO drums, as per API 521, or 400 to 500 microns as per API RP 14J. For this, it is necessary to ensure the inlet mixture velocity is low, with gas load factors between 0.15 m/s to 0.25 m/s depending on the type of inlet device.

4. Another source of liquid build up is the failure of the liquid level control valve at the base of the KO drum. In case, liquids are drawn out with a pump, any power failure can cause liquid levels to rise and eventually enter the flare stack via, the vapour outlet.

5. KO drums are expected to hold the maximum possible discharge liquids. Therefore, a higher hold-up time (20 to 30 min as per API 521) gives the operator sufficient time to respond before the KO drum's HHLL trip is initiated.

6. KO drums also have a high-level switch which initiates a shut-off to the flow into the KO drum. In case the switch (LZH) fails to respond, the liquid level would continue to rise until it gets entrained into the flare stack, causing a fire ball.

7. Flare KO drums need to be provided with a 2oo3 voting philosophy to initiate a emergency shutdown (ESD) when High-High Liquid level (HHLL) conditions are reached in the KO drum. One might argue if a total plant level shutdown is necessary. However, this need not always be the case, because utilities like instrument air is required to reset and re-open the ESDV when the liquid level in the KO drum drops below HHLL (due to the bottom liquids transfer pumps).

   Performing a total shutdown of the facility can actually exacerbate the situation with more liquids entering the KO drum beyond the HHLL, since the facility's piping and equipment volumes are depressurized into the flare header after a total facility shutdown.

Excessive Makeup Water in Seal Pot

As the name suggests, the seal pot acts a barrier to any carried over oil droplets from the KO drum to the flare stack. In case of air ingress through the flare stack, the seal pot again acts as a barrier between the liquid KO drum & flare stack.

Due to the ensuing vapour velocities, it is expected that some of the water in the seal pot is entrained along with the KO drum vapours. To prevent low water levels, make-up water is added to maintain the level in the seal pot. However, if the shutdown valve on the make-up water line fails to close at high water levels, then it can again result in water entraining from the seal pot and eventually entering into the flare stack.

Underestimating PSV Relieving Rates

The size of the KO drum and the flare stack diameter depends on the venting rates from the PSVs and blowdown lines. If all the various relieving scenarios are not accounted for, it can result in underestimating the total flare capacity as well as the size of the KO drum. This can result in liquids accumulating much faster, breaching the liquid levels settings in the KO drum and liquid entrainment through the flare stack.

Another scenario which can cause liquid entrainment is during brownfield expansion projects when the flare capacity and KO drum size is not revisited. This can again result in excessive gas flow rates due to smaller piping sizes, nozzle sizes, liquid entrainment due to smaller vessel volume and lower holdup times. Therefore, if the existing flare capacity is insufficient, then provisions must be made to install an additional flare.

Lack of Heat Tracing

In cold weather conditions, any water at the bottom of the KO drum can freeze and liquid phase turning into waxes. This can effectively prevent the operator from knowing when the High Liquid level (HLL) has been breached. Therefore, for cold winter conditions, heat tracing needs to be provided to prevent any water freezing. To prevent any wax formation, the heat tracing needs to ensure, the temperature of the liquid phase is at least 5 to 100C above the pour point.

In cold conditions, there is also the possibility of moisture in the air condensing and settling in the flare stack. In the event of high gas velocities, there can be liquid entrainment.

Improper Piping Arrangement

Flare piping needs to be sloped to ensure proper draining, with 1:500 for the main flare header and 1:200 for the sub headers. However, the piping from the main header to the flare stack must avoid any pockets or low points.

In the event of low vapour velocities, any carried over liquids can accumulate at the low points, thereby creating a liquid column that result in slug flow due to the accumulated gas pressure, upstream of the slug. This can spew out the liquid mass into the flare stack and result in burning rain. If low points are unavoidable, then drip legs need to be installed to drain out any liquids.

Piping Dead Legs

Piping dead legs are a typical spot for liquid to accumulate. With the piping arranged like a maze, high gas velocities can result in liquid mass shooting through the piping to the flare stack and eject itself out as a rain flare.

Excess Steam in Steam assisted flares

In flares which use steam as a medium to lower flame temperatures and smokeless flames, any excess steam can create a back pressure in front of the flare tip. This back pressure can cause the flame to back propagate and cause structural damage to the flare. The quality of steam injected should be as dry as possible. But with steam quality < 100%, it affects the flare performance (poor combustion efficiency). In case of excess steam or vapor flow, the flame can get extinguished causing vapors and liquids to exit the flare stack unburnt.

Bypassing the KO drum

In case of brownfield developments, when additional PSVs and blowdown lines are added, if the KO drum is bypassed directly to the flare stack, with the view that the venting rates are negligible, then this can again cause liquids to rain through the flare stack. Centrifugal compressors can be another source of liquids via the lube oil and seal oil leaking into the flare line, as the seals suffer from wear and tear over time, and leakages during compressor loop depressurization. Therefore, these streams also must be diverted to the KO drum to separate the oil phase from the contaminated vapors.

Orientation of the KO Drum

KO drums can be horizontal or vertical. However, the choice between them is based on gas-liquid loading. If the vented gas is expected to contain less liquid content and insufficient plot plan area, then vertical vessels can be installed.

However flare gas with higher liquid content would require a horizontally oriented vessel with sufficient holdup time. The pressure drop across a horizontal drum is lower compared to a vertical installation, which also makes it economical.

References

Blowdown and Flare Systems, Alireza B., 2014

https://www.chemengonline.com/optimizing-pressure-relief-systems/

Author

Vijay Sarathy holds a Master's Degree in Chemical Engineering from Birla Institute of Technology & Science (BITS), Pilani, India and is a Chartered Engineer from the Institution of Chemical Engineers, UK. His expertise over 10 years of professional experience covers Front End Engineering, Process Dynamic Simulation and Subsea/Onshore pipeline flow assurance in the Oil and Gas industry. Vijay has worked as an Upstream Process Engineer with major conglomerates of General Electric, ENI Saipem and Shell.

KLM Technology Group is a technical consultancy group, providing specialized services and training to improve process plant operational efficiency, profitability and safety. We provide engineering solutions by offering training, technical services, best practices, and engineering designs to meet the specific needs of our partner clients. Since 1997, KLM Technology Group has been providing engineering, operations, and maintenance support for the hydrocarbon processing industry.

WWW.KLMTECHGROUP.COM

Engineering Solutions, Standards, and Software

KLM Technology Group

When Guidelines for Propylene Splitters

Timothy M. Zygula, Karl Kolmetz

Introduction

The Chemical Processing Industry has been continually pushing the capacity envelope of new and existing distillation columns. While increasing the capacity of existing columns is not unusual, great care needs to be taken when a revamp is being considered. There is a fine line between success and failure when a column is designed at or near the upper end of the capacity envelope.

The authors will detail the methodology used when designing a new or considering a capacity increase for an existing propylene splitter. This paper will discuss design aspects that need to be considered when designing a propylene splitter. The authors will also present a generic case study of a propylene splitter revamp. Some of the topics that will be covered by the authors are:

1. Process simulation of a propylene splitter – proper simulation techniques

2. From the simulation to the field – tray efficiencies

3. Utilizing a process simulation to develop column hydraulics

4. The types of internals that have been used in propylene splitter columns

5. Design considerations that need to be addressed when considering a revamp.

General Design of Distillation Column

Separations are a major part of the chemical processing industry. It has been estimated that the capital investment in separation equipment is 40-50% of the total for a conventional fluid processing unit. In a plant one of the main unit operations is material separation. This includes distillation, storage tanks, flash drums and other equipment of this nature. Of the total energy consumption of an average plant, the separation process accounts for about 50% to 70% of the energy consumption of the plant. Within that area of the material separation, the distillation unit operation method accounts for normally greater than 80% of the energy consumed for this process.

In general, the initial design of a distillation tower involves specifying the separation of a feed of known composition and temperature. Constraints require a minimum acceptable purity of the overhead and the bottoms products. The desired separation can be achieved with relatively low energy requirements by using many trays, thus incurring larger capital costs with the reflux ratio at its minimum value. On the other hand, by increasing the reflux ratio, the overhead composition specification can be met by a fewer number of trays but with higher energy costs.

Design of a Propylene Splitter

Determining the design of a Propylene Splitter requires an understanding of the simulation model used to generate the internal loads and physical properties, vapor and liquid equilibrium data utilized, tray hydraulics, and how the selection of the internals will affect the actual efficiency of the installed equipment in the field.

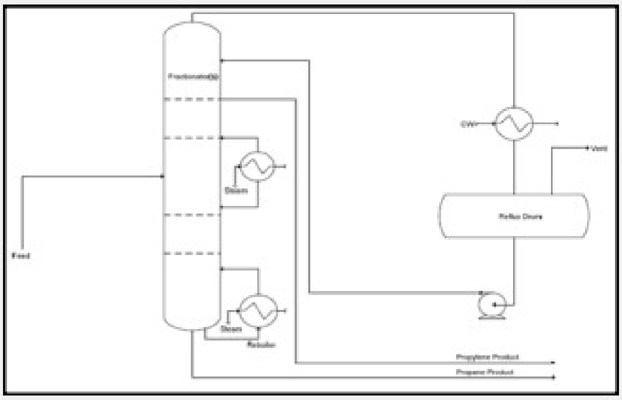
The typical design of a propylene splitter is not complex and there are two general variations in design. The first is a high-pressure system, and the second is called a heat pumped system. A high-pressure system is designed to utilize cooling water as the source to cool the overhead vapor, and a high pressure is needed to condense the propylene vapor at ambient temperatures of about 40 degrees C.

A heat pump system utilizes a compressor to reduce the tower pressure to allow the distillation column to be smaller. In most distillation applications, relative volatilities can be improved by lowering the pressure. This results in a lower number of stages required and reflux ratios, but at the cost of higher energy requirements of the compressor.

A good rule of thumb is that if the propylene system is associated with an ethylene plant, in which there is typically an abundance of quench water that can be used to heat the C3 Splitter reboiler a non-heat pump system may be the best choice. If no source of sufficient low-grade heat is available for example in a refinery FCC unit or propane dehydrogenation unit, then the use of a Heat Pump is typically the economical choice.

HIGH PRESSURE SYSTEM

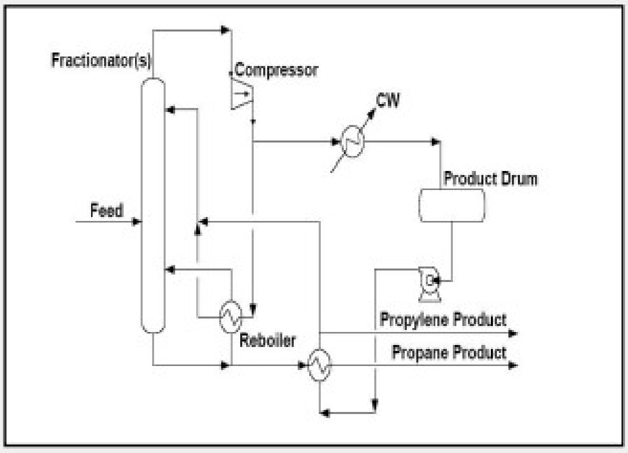
FIGURE 1



The first is a called a high-pressure system, and the second is called a heat pumped system. A high-pressure system is designed to utilize cooling water as the source to cool the overhead vapor, and a high-pressure system is needed to condense the propylene vapor at ambient temperatures of about 40 degrees C.

HEAT PUMPED SYSTEM

FIGURE 2



A heat pump system utilizes a compressor to reduce the tower pressure to allow the distillation applications relative volatilities can be improved by lowering the column pressure. This results in a lower number of required theoretical stages and reflux flow. These savings are offset by the required energy cost of the compressor.

Process Simulation of a Propylene Splitter – Proper Simulation Techniques

Simulation of a propylene splitter seems very simple and can be done quickly by 3rd year engineering students. There are a small number of components, and the equipment layout is not complex. The challenge of a propylene splitter is that, unless you use the correct vapor and liquid equilibrium data, the simulation can have greater than 15% inaccuracies as compared to actual field data.

Physical properties are critical to the success of a simulation model and are also very important to the accuracy of the model. Poor physical property data may prevent your simulation model from converging. The most typical problem is missing parameters in the thermodynamic package utilized. This is not unusual in most commercial simulation packages. Physical property parameters for most compounds are not known for every thermodynamic model at every pressure and temperature range. Many times, this fact is overlooked when a design model is constructed. Simulation models are constructed and executed with thermodynamic parameters missing. Although the model may appear to be correct but may be incorrect because of the missing thermodynamic data. Then there is the problem that all the thermodynamic data are present, but the data are not accurate. This problem is even worse than the problem of missing data since the results from the simulation model will appear to be correct but are totally wrong. Most simulation packages won't alert the users that there is a problem. It is the job of the user to determine if the results from a simulation model are accurate (1).

The best way to confirm if your thermodynamic data is correct is to see if you can find any laboratory data or data from literature on your system. This may not always be practical because good thermodynamic test data are hard to find. Sometimes that data may have to be generated in a pilot plant before any design work begins. Research the system being modeled. Published thermodynamic data on the system being modeled may exist. If data is obtained, the data must cover the same temperature and pressure range that you are designing. Next, run a simulation with the same system and see if you can match the data. Most data on propylene splitters have been compiled from years of operating experience. Many companies that license technology have done extensive testing and have developed propylene splitter data for design purposes.

The most accurate Vapor Liquid Equilibrium (VLE) data for Propylene Splitters might be Ping Robinson, but there is a huge data base of distillation columns designed and built utilizing Soave Redlich Kwong (SRK), and many de - signers utilize SRK to be able to utilize the existing data- base for actual tray efficiency in the field. The standard

SRK equation of state model handles the propane / propylene binary K values adequately over the typical operating pressure range of these towers, which is 5 bar (100 psia) to 20 bar (320 psia). The other miscellaneous lights, heavies, and intermediate boilers, such as Propadiene (PD), methyl-acetylene (MA or propylene), ethane and iso-butane, are also adequately modeled using the SRK equation of state. (3)

Methyl-acetylene (MA) is an intermediate boiler that is lighter than propane and heavier than propylene. Even at small ppm concentrations in the feed will, over time, result in a buildup of MA in the tower. Concentrations inside C3 Splitter towers 10 to 20 trays from the bottom can be as high as 15% to 20% depending on the severity of propylene recovery required. Many propylene splitter systems have a sample point in these 10 to 20 trays range from the bottom to be able to sample the MA concentration in the column. MA, being a triple bonded hydrocarbon at elevated concentrations, above 40%, can auto decompose with potential adverse consequences. Propadiene (PD) is heavier than both propane and propylene and will never have a significant concentration in the overhead product.

Many choices are available for enthalpy models in simulation packages. SRK will do an adequate job but there may be better choices. This is important because there are always light components (i.e. methane, ethylene) that will be present in the feed, and they will be close to their critical temperature. The choice of enthalpy model will help in the tower consistently achieving convergence. (3)

One other area of concern is the specific heat of liquid propylene. Some Propylene Splitters will have subcooled reflux return or a subcooled feed. The performance of a C3 Splitter so that your model will reflect the real world.

High Pressure: High-pressure distillation in a column can have challenges. There are many factors to be considered when designing at high operating pressures (1). At higher operating pressures the relative volatility of the system is lower which increases the separation difficulty. As a direct result of increased separation difficulty, the reflux requirements for the column would increase. The column would also require more stages and increased duties for the reboiler and condenser to perform the separation. Propylene Fractionators are high liquid traffic columns that require internals that can handle high liquid traffic.

At higher operating pressures the reboiler temperature rises, thereby requiring a more expensive heating medium. If the same heating medium is used a reboiler with a larger heat transfer area would be required. At high operating pressures the vapor density would increase and therefore lower the required vapor handling capacity. This would lead to a reduction in the diameter of the column, which would reduce the capital equipment costs.

High Pressure Distillation Tray/Column Design

As the distillation pressure is increased, the vapor density increases. When the critical pressure is approached, the compressibility factor of a saturated vapor usually has a value less than 0.75. Thus, the vapor density of the gas phase is quite high at pressures greater than 40% of critical. As the operating pressure is increased for the same Cs (Capacity Factor) value, the vapor mass flow rate will be much greater than atmospheric operating pressure because of the high vapor density. While at the same time the liquid mass flow rate will be greater at high operating pressure than atmospheric operating pressure. Therefore, liquid flow rates per unit of column cross-sectional area will be higher as operating pressure increases. The capacity of the fractionating device at high pressure may be dependent on its ability to handle these high liquid flow rates.

In a propylene fractionator column, the tower cross sectional area is the sum of the trays active area plus the total downcomer area. The amount of required active area (Vapor-Liquid Bubbling Area) is determined by vapor flow rate. The downcomers handle a mixture of clear liquid, froth, and aerated liquid. The downcomer area required to handle the high liquid flow not only increases with the liquid flow rate, but also with the difficulty in achieving separation between the liquid and vapor phases. The volume required for the downcomer increases at a lower surface and a smaller density difference between the liquid and vapor. Because of the large downcomer area required to handle the high liquid flow rates the area may be 40% to 80% greater than the calculated tray active area for the vapor flow rates for propylene fractionator distillation. The downcomer area becomes a significant factor in the determination of the tower diameter.

Simulation Accuracy

To determine the accuracy of a simulation it is always desirable to construct a McCable-Thiele diagram from the data generated from the simulation. The data from the simulation can be easily transferred to a software package where the graph can be constructed. This graph is used more as a tool to identify possible problems that won't be discovered until the column fails. The following is a list of the areas where a McCable-Thiele diagram can be used as a powerful analysis tool (1).

pinched regions - Pinching is readily seen on an x-y diagram.

Mislocated feed points - the feed point should be where the q-line intersects the equilibrium curve.

This is generally the rule in binary distillation. However, it is not always true in multicomponent distillation. A key ratio plot is often developed in the design phase. This type of plot is far superior to an x-y diagram for identifying misocated feeds, especially with large multicomponent systems. Determining if the column is being over refluxed or reboiled - this can be recognized by too wide of a gap between the component balance line and the equilibrium curve throughout the column. Identify cases where feed or intermediate heat exchangers are needed. Most commercial simulation programs will provide the information required to generate these plots.

Column Sizing

Once the internal liquid and vapor traffic is obtained from the simulation model, the diameter of the column must be obtained. Most simulation packages have tower- sizing routine. These routines are easy to use and yield quick results. However, these results should be verified by calculation.

Column sizing is done on a trial-and-error basis. The first step is to set the design limits. The design limits are as follows:

1. Maximum Design rates – Vapor/Liquid Traffic is needed at Maximum Operating rates.

2. Design rates - Vapor/Liquid Traffic is needed at Design Operating Conditions.

3. Minimum Design rates - Vapor/Liquid Traffic is needed at Minimum Operating rates.

Sizing calculations need to be performed in areas of the column where the vapor/liquid traffic is expected to be highest and lowest for each section. For example,

The top tray and bottom tray in the column

The fee tray

Any product draw-off tray or heat addition/ removal tray.

Tray where the vapor liquid loading peaks.

There are also shortcut methods to sizing a column, which involve using a flooding correlation. These methods minimize the number of trial-and-error calculations. Using the method as outlined by Kister (2) the first step is to determine the C-Factor at the most heavily loaded point in the column. Using an entrainment flooding correlation like the Kister and Haas correlation the C-Factor at flood can be calculated.

CSB = 0.144 [d2H s/rL]0.125 [rG rL]0.1 [S/ hct]0.5 – Kister and Haas (2)

Next the vapor velocity at flood based on net column area minus the tray downcomer area needs to be calculated. This calculation is done for the top and bottom section of the column (2).

uN = CSB [(rL - rV)/ rV](1/2) – Flooding Vapor Velocity, ft/s

Next, the bubbling area required for the top and bottom sections of the column needs to be calculated using equation 3. In new designs columns should be designed for 80% flood (2).

3. AN = CFS/[(SF)(0.8)uN] – Bubbling Area Required (Column Cross Sectional Area less downcomer top area, ft2)

Next, the downcomer top area needs to be calculated using equation 4. This calculation is done for the top and bottom section of the column (2).

AD = GPM/VDdsg – Downcomer Area.

Once this has been completed the tower cross sectional area can be calculated using equation 5. The tower diameter can be calculated from the tower area. (2).

5. AT = AN + AD – Tower Cross Sectional Area, ft2

The following are the definitions of the parameters used in the above equations.

CSB – C-Factor at flood, ft/s

dH – Hole Diameter, in

S – Tray Spacing, in

hct - Clear liquid height at the transition from the froth to spray regime, in of Liq

rG, rL - Vapor and Liquid Density, lb/ft3

s - Surface Tension, Dyne/cm

SF – Derating Factor or Foaming Factor

GPM – Tray Liquid Loading, GPM

VDdsg – Downcomer, GPM/ft2

AN – Tray Bubbling Area, ft2

AD – Downcomer Top Area, ft2

AT – Total Tower Cross Sectional Area, ft2

Column Internal Design

Once the preliminary tower diameter has been set the internals can be chosen. The task of choosing the type of tower internal to use is very important. The type of column internals used dictates a column's efficiency and capacity. All the modeling and careful design work will mean nothing if the wrong type of column internals is chosen. For propylene fractionation trays are the only type of internal that should be considered. The types of internals that have been used in propylene splitter columns are:

· Conventional Cross Flowing Trays

· Counter Contacting Trays

· Structured Packing

· High-Capacity Trays

· Multiple Downcomer Trays

Conventional Multipass Trays

Conventional Multipass trays are typically used when a column is initially designed. Four pass or six pass trays are usually used because of their ability to handle high liquid loads like seen in propylene fractionation. The downside to using multipass trays is the reduction in separation efficiency that is experienced due to the reduction in active area. Great care must be taken when sizing downcomers in high-pressure distillation applications. The difference between vapor and liquid densities becomes smaller and separation of vapor from liquid in a downcomer becomes more difficult. This can result in increased aeration back- up and possible premature downcomer flooding. (2)

Multi-Downcomer Trays

Multi-Downer trays are used for large liquid loads, particularly when the volumetric ratio between vapor and liquid rates is low. These situations occur in medium to high-pressure distillation, in absorption and stripping, and in direct contact heat transfer applications. Multi -Downcomer trays can be used at close tray spacing. This will allow a reduction in both height and diameter of a new column compared to a column fitted with conventional multi-pass trays. Vessel shell costs can be significantly reduced with the use of Multi-Downcomer trays. When retrofitting an existing column with Multi-Downcomer trays, a significantly greater number can be installed, providing increased product purities and recoveries, as well as reduced reflux ratio for reduced energy consumption and/or increased column capacity. The use of Multi-Downcomer trays has often reduced the number of columns needed in difficult separations, such as the fractionation of propylene-propane.

Tray Efficiencies

From the simulation to the field – tray efficiencies

The tray efficiencies in Propylene Splitters have been a widely discussed issue. In actual operation they have ranged from 40 percent to 100%, so it is easy to see why this is a widely discussed issue. In general, if the boiling points of the overhead product (light key component) and bottoms product (heavy key component) are close, less than 5 degrees C, the actual tray efficiency in the field will be high. If the boiling points of the overhead and bottoms product are far apart, the actual tray efficiency will be low. The ratio of the boiling points is classified as the relative volatility. For example, a Propylene Splitter has close boiling points between the overhead and bottoms product, about 7 degrees C. This requires many ideal stages for separation in a process simulation, but each stage will have high efficiency in the field. For a normal cross -flowing tray 90% tray efficiency can be obtained. For chemical grade propylene, 95% purity, about 100 ideal trays might be required in a simulation, and 110 actual stages may be required in the field. Tray efficiencies are generally classified as either overall efficiency (Fenske), point efficiency, or average tray efficiency (Murphree). The overall efficiency term is quite straightforward. It is the number of actual stages achieved versus the number of trays in the tower or section of the tower. Point efficiency and Murphree tray efficiency are similar. They represent the ratio of the actual compositional change and the theoretical compositional change at equilibrium. (2)

The compositional change is usually measured in the vapor phase but can be measured in the liquid phase. The difference between the point efficiency and Murphree tray efficiency calculation is the reference point. Point efficiency is measured at a specific point and the Murphree tray efficiency is measured across a complete tray. Therefore, the compositional gradients normally found on a tray will affect the Murphree tray efficiency but will not affect the point efficiency. When the liquid and vapor both have homogeneous compositions, point efficiency and Murphree tray efficiency will be equal.

In practical terms, trays with little or no liquid flow path length will essentially achieve point efficiency while trays with conventional flow path will achieve a higher Murphree tray efficiency due to the compositional gradient of the liquid flowing across the tray deck.

There are various aspects of equipment design that can affect efficiency. Any time a device can maximize the vapor/liquid contact while maximizing the compositional approach between the vapor and liquid, that device will maximize the efficiency of the tower. Conversely, any device characteristics that limit contact or compositional approach will lessen the efficiency of the tower. Characteristics that may affect efficiency are discussed below.

Weir Height: With trays operating in the froth regime, an increase in weir height will directionally increase efficiency. Kister has noted that the removal of even a small outlet weir can noticeably decrease the effective tray efficiency. Weir height is especially important in liquid limited systems or systems where a slow chemical reaction is taking place. (2)

Flow Path Length: Directionally, an increase in flow path length will increase efficiency. This was discussed earlier in the difference between point efficiency and Murphree tray efficiency. This holds true unless the length of the flow path creates anomalies in the tray operation such as liquid back mixing or vapor cross flow channeling. (2)

Liquid and Vapor Maldistribution: As would be expected, vapor and liquid maldistribution will cause decreases in efficiency. Generally, maldistribution problems are generated by the distribution of feeds to the columns rather than by the contacting devices themselves. When reviewing internal designs, it is very important to pay attention to feed pipe designs. Good liquid distribution across the tray is essential for high efficiency. Feed pipe designs that distribute liquid at high velocities should be avoided. Vapor distribution is also an important factor to consider. Most columns use chimne trays vapor distribution devices.

Design Case: Below is a typical design case for a propylene splitter. Typically, a propylene splitter would be designed with 200 theoretical stages or between 290 to 310 actual trays. The column design being presented in this paper was designed with 200 theoretical stages. Simulation models showed that 200 theoretical stages produced 99.6-mole% propylene in the overhead product stream of this column. This is based on a column feed rate of 2700 lbmol/hr and an overhead heat duty of -282 mmBTU/HR. The reboiler duty of the column design being detailed is 180 mmBTU/HR. This column has only one feed location. The composition range of the feed stream feeding the propylene splitter column is detailed in TABLE 1. Typical design parameters for a propylene splitter column have been compiled in TABLE 2.

Design considerations that need to be addressed when considering a grass root or revamped column

Operating Flexibility: The column should be designed with some operating flexibility. When reviewing the required efficiency, it is usually a good idea to review the sensitivity of the product purity to losses of efficiency in the tower. One way to do this is to construct a plot of required stages versus reflux ratio. (4) Knowing the sensitivity that reflux has on product purity will allow the designer to decide if the available reflux is sufficient to achieve the purity goal under different operating scenarios.

Minimum Reflux or Minimum Amount of Required Internals: One design consideration is to determine the minimum reflux needed to achieve the required separation. To determine the amount of minimum reflux is required, one develops a reflux-stage plot and extrapolates from it. To develop this plot, simulation runs are performed at a various number of stages while keeping the material balance, product compositions, and the ratio of the feed stage to the number of stages constant. The reflux ratio is allowed to vary. Then a plot of the number of stages versus reflux or reflux ratio is plotted. The curve is extrapolated asymptotically to an infinite number of stages to obtain the minimum reflux ratio. Once the minimum reflux has been determined then it must be decided if the design will be done at minimum reflux or with less installed internals. This is usually an economic choice. If the column is designed at minimum reflux the savings is lower required energy for the column operation. Usually, the reboilers and condensers are smaller. The diameter of the column is also smaller. This choice may hinder future capacity revamps due to the size of the equipment.

TABLE 1

Feed Stream Component	Composition Range (Mole%)
Propadiene	0.0 to 0.03
Propylene	92.0 to 96.0
Propane	4.0 to 7.0
Butanes	0.02 to 0.05
C5 non Aromatics	0.04
C6 non Aromatics	0.11
C7 non Aromatics	0.0
C8 non Aromatics	0.03
Benzene	0.0
Toluene	0.0

TABLE 2

Design Specifications	Overhead Of Column	Bottom Of Column
Tower Diameter(in)	200 to 300	200 to 300
Typical Number of Theo. Stages	133	70
Column Temperature(F)	20(Top)	44(Bottom)
Column Pressure (PSIA)	71(Top)	86(Bottom)
Propylene Mole% Column	99.6(Top)	14(Bottom)
Propane Mole% Column	0.04(Top)	81(Bottom)
PD Mole % Column	0.002(Top)	0.01(Bottom)

If the column is designed for the minimum required internals required energy would be higher. The condenser and reboiler will be larger. This option does give flexibility for future capacity upgrades. (1)

Optimization of Feed Stage: Another design consideration is to design the column at the optimum feed stage location. Once all of the simulation runs are completed two main plots can be created. One plot will be a McCabe-Thiele diagram and the other will be a concentration versus feed stage diagram. The McCabe-Thiele diagram is plotted using the mole fraction data calculated for each stage by the simulation. The equilibrium data and the operating lines are also determined from the simulation results. Determining the optimal feed stage will help to maximize efficiency of the column. (2) In the second type plot, the key component concentration in the product streams is plotted against the feed stage numbers. The minimum in the curve will represent the optimum feed stage. One can generally assume the ratio of optimum feed stage to total number of stages is independent of the number of stages. (2) In this type of plot, it is important to note that the total number of stages is kept constant. Also, if the distillate rate is increased, it is normal to move the feed stage up the column as required. (1)

Conclusions

In conclusion, it is important to note that when designing or revamping a propylene splitter great care must be taken during the design phase of the project. To get the maximum efficiency and capacity out of a propylene splitter one must consider the accuracy of the simulation and the thermodynamic model being used to model the column. Once the simulation has been completed great care must be taken when evaluating the sizing of new and existing equipment. Verification of the design, which includes the amount of reflux required and feed location is essential to obtain maximum efficiency. All these factors talked about in this paper are essential to obtain a good efficient design of a propylene splitter.

Acknowledgements

The authors acknowledge the contributions that friends and colleagues around the world have made through papers, presentations and discussions to understand distillation phenomena. The authors also want to thank the efforts made by friends to increase personal development - sometime with, and sometimes without success.

References

Zygula, T. M., Dautenhahn, P. C. Ph.D., P.E. "Use of Process Simulation for Distillation Design" AIChE Spring National Conference, March 2000, Atlanta, Georgia.

Kister, H. Z. "Distillation Design", McGraw-Hill Book Company Inc., New York, 1992.

Zygula, T. M., Dautenhahn, P. C. Ph.D., P.E. "The Importance Of Thermodynamics On Process Simulation Modeling" AIChE Spring National Conference, March 2001, Houston, Texas.

Pilling, Mark, Column Efficiency – What to Expect and Why, Prepared for Presentation at 4th Topical Conference on Separations Science and Technology, November 1999 Session T1006 – Distillation Hardware and Application I.

The View from Rock Bottom: Greening Up Energy Sources, While Still Meeting Future Demand

Ron Cormier

Fossil fuels—coal, oil and gas—supply most of the world's energy and also form the basis of many products essential for everyday life. Their use is the largest generator of CO2 emissions, which drives global climate change. This phenomenon is also prompting joint determination of renewable alternatives, hopefully crafting a carbon-neutral society by as early as 2050. There are clear paths for renewable electricity to replace fossil-fuel-based energy, though transport fuels and chemicals produced in oil refineries will still be needed.

We can attempt to close the carbon cycle associated with their use by electrifying refinery processes and by changing the raw materials that go into a refinery from fossils fuels to carbon dioxide for making hydrocarbon fuels and to agricultural and municipal waste for making chemicals and polymers.

With enough long-term commitment and support, the science and technology for such a completely fossil-free refinery, delivering the products required after 2050 (less fuels, more chemicals), could be developed. This future refinery will require substantially larger areas and greater mineral resources than is the case at present and critically depends on the capacity to generate large amounts of renewable energy for hydrogen production and carbon dioxide capture. Can the world make the chemicals it needs without oil? With solar and wind booming, the chemical industry now dabbles with forgoing petroleum as its source.

Black, gooey, greasy oil is the starting material for more than just transportation fuel. Including natural gas/liquids, oil is also the source of dozens of petrochemicals that companies transform into versatile and valued materials for modern life: gleaming paints, tough and moldable plastics, pesticides, lubricants, and detergents.

By breaking the hydrocarbons in oil and natural gas into simpler compounds and then assembling those building blocks, scientists long ago learned to construct molecules of exquisite complexity. Fossil fuels aren't just the feedstock for those reactions; they also provide the heat and pressure that drive them. As a result, industrial chemistry's use of petroleum accounts for 14% of all greenhouse gas emissions.

Now, growing numbers of scientists and, more importantly, companies think the same final compounds could be made by harnessing renewable energy instead of digging up and rearranging hydrocarbons and spewing waste carbon dioxide (CO2) into the air. First, renewable electricity would split abundant molecules such as CO2, water, oxygen (O2), and nitrogen into reactive fragments. Then, more renewable electricity would help stitch those chemical pieces together to create the products that modern society relies on and is unlikely to give up.

Asphalt for example: IF there is no oil refining, there is no residual "bottom of the barrel" with which to build roads for transport and commerce. The road to greener asphalt covers more than 90 percent of the 2.7 million miles of paved roads in the United States. It's a durable yet flexible material, creating smooth pavement for our traveling convenience. But the steady pounding of autos and semi-trucks, the yearly squeeze and release of the freezing and thawing cycles, the heat of the sun's rays, and the effects of constant oxidation eventually win out. Asphalt will break down—and when it does, we rip up our roads and start over.

When such worn surfaces are rehabbed, the asphalt rubble we see piled alongside the highway during road construction season isn't simply junk to be land-filled. With a little repurposing, it can regain its flexibility and usefulness—and thanks to environmental, logistical and financial motivations, there's growing interest in putting more recycled asphalt back on the road.

Reusable, in theory, humans have used asphalt since ancient times. “The asphalt industry remains the country’s most diligent recycler, with more than 99 percent of reclaimed asphalt pavement being put back to use,” the National Asphalt Pavement Association states in the 2017 report on its annual recycled materials and warm-mix asphalt usage industry survey. Yet the results of that same survey put the average percentage of reclaimed asphalt pavement in new asphalt mixtures nationwide at 20.1—meaning most of the material that’s laid down on roads is still newly refined liquid asphalt and mined aggregate.

Meanwhile, there were more than 102 million tons of reclaimed asphalt pavement stockpiled across the country at the end of 2017, according to the report. It’s not only the asphalt. Continued mining of these aggregates from natural deposits is not sustainable. Asphalt is very expensive, relatively speaking, so we can reuse it, and more importantly, aggregate rocks are recycled too—i.e., don’t throw them away. Recycling is becoming almost a necessity to remain cost-effective. With that in mind, the Modified Asphalt Research Center recently began an 18-month project with the Recycled Materials Resource Center to performance-test asphalt mixes using 30-50% recycled content. By defining the properties that affect performance and establishing more effective testing methods, this collaboration hopes to pave the way for wider adoption of asphalt containing higher levels of recycled content. It should be noted that concrete repurposing studies are underway, as well as those in asphalt, further extending the original material and reducing methane emissions.

Better living through renewables….

Industrial chemists make most molecules by breaking down and refining hydrocarbons in oil and natural gas into smaller compounds. Researchers now want to use renewable electricity to energize simple starting materials such as water and carbon dioxide (CO_2) and stitch the pieces together into the same compounds.

Steam Cracking….Today, monomer ethylene, which forms the basis of many plastics, is made mostly by steam cracking. Typically, a feedstock of ethane, gas liquids, and steam go into a furnace at up to 850°C. The heat tears a pair of hydrogen atoms from ethane to make ethylene, which is then separated out in compression and distillation phases.

Electro-synthesis…This newer, low-temperature approach uses electricity—ideally from solar and wind power—and a metal catalyst to split apart water and CO_2 molecules, generating hydrogen and CO_2. Electricity and catalysts then recombine those pieces to make ethylene gas and liquid ethanol.

New Wave Processes….

The simplest processes, those that make H_2 and CO, are already reaching that second benchmark. Commercial electrolyzers can already perform at better than 60% efficiency in splitting water to produce H_2. Siemens for example, uses an established technology called proton-exchange membrane (PEM) electrolyzers, which apply voltage between two electrodes, one on each side of a polymer membrane.

The voltage splits water molecules at a catalyst-coated anode into O_2, hydrogen ions, and electrons. The membrane only allows hydrogen ions to pass to the other catalyst-coated electrode, the cathode, where they meet up with electrons to generate H_2 gas. The cost of the H_2 produced has fallen dramatically in recent years as the size of electrolyzers has increased to an industrial scale. Still, the cost of the electrolyzers, as well as their component electrode materials and catalysts, needs to drop further to generate H_2 at a price competitive with massive thermal plants that break apart methane.

Other companies also rely on PEM electrolyzers but add a second catalyst to the cathode to split piped-in CO_2 into CO and O_2. The CO can be captured and sold for use in chemical manufacturing. Or it can be combined with hydrogen ions and electrons generated at the anode to construct a range of other building blocks for industrial chemistry, including gases such as ethylene—the raw material for certain plastics—and liquids such as ethanol and methanol. One company has already produced 16 commodity chemicals and is working to scale up its reactors over the next few years to process tons of CO_2 per day, most likely captured from flue gas from power plants and other industrial sources.

The growing supply of renewable energy has some chemists thinking about ways to generate carbon-neutral fuels. During 2023, in Dresden, Germany, a company called Sunfire completed a test run of a high-temperature electrolysis reactor, known as a solid-oxide fuel cell, that promises even higher efficiency than PEM electrolyzers. The reactor is at the heart of a four-stage test plant that generates fuel from water, CO_2, and electricity. The first stage of the boxcar-size plant separates CO_2 from air and then feeds the CO_2 to Sunfire's fuel cell. It works a bit differently from its PEM counterparts: It uses electricity to split both water and CO_2 at the cathode, generating a mix of CO, H_2, and negatively charged oxygen atoms, or oxide ions.

Those ions travel through an oxygen-permeable solid membrane to the anode, where they give up electrons and combine to produce O_2. The mix of CO and H_2, known as synthesis gas, then moves to a third reactor, which assembles them into more complex hydrocarbons. At the fourth stage, those hydrocarbons are combined with more H_2 and refashioned into the mix of hydrocarbons in gasoline, diesel, and jet fuel. Because the plant works at high temperatures, the water- and CO_2-splitting reactions convert electrical energy to chemical bonds at nearly 80% efficiency, the company says.

Sunfire's test plant now makes about 10 liters of fuel per day. The company is already scaling up the technology and plans to open its first commercial plant, in Norway, next year. The setup will be part of a larger plant that will use 20 megawatts of hydropower to produce 8000 tons of transportation fuel per year, enough to supply 13,000 cars. Its method will avoid producing 28,600 tons of CO_2 annually from fossil fuels.

Better Catalysts…..

Though simple industrial chemicals may be poised for greening, directly synthesizing most complex hydrocarbons with electricity remains too inefficient and costly. Even making compounds with just two carbons, such as ethylene and ethanol, typically captures only about 35% of the input of electrical energy in the final compound. With three-carbon compounds and beyond, the efficiency can drop below 10%. The problems are twofold: First, every time new bonds are forged, some energy is lost. And generating more-complex hydrocarbons inevitably means making more side products. That outcome forces producers to separate their desired compound, at extra cost.

But innovations are starting to help there, too, including better catalysts. In the 21 August, 2023 online issue of Joule, for example, Sargent and his colleagues report creating a device that uses a membrane coated with a copper catalyst to convert CO_2 and steam to a mix of two-carbon compounds, including ethylene and ethanol, with 80% efficiency. They achieved that efficiency by pressing one electrode directly onto the membrane, thereby eliminating a fluid-filled gap that was sapping energy and was causing the device to break down quickly.

How Quickly????….

…will the vast chemical complexes sprawling over the world's industrial zones shift from fossil fuels to green power, is a matter of debate. One major hurdle is that renewables are intermittent, meaning chemical plants relying on them will be inefficient. Economists capture the idea with a measure called the capacity factor, a ratio of a plant's output over time compared with what's theoretically possible. Fossil fuel–powered chemical plants can run around the clock, although downtime for maintenance and for other issues typically reduces their capacity factor to about 60%.

But the inputs to a plant powered by renewables themselves have low-capacity factors: Wind and hydropower typically come in just under 50%, and solar drops to below 25% because of nighttime and cloudy days. Full capacity is only being used for a few hours a day. The upshot, is that any plant powered by renewables would take longer to make a profit, making investors reluctant to back such projects.

Plants driven by renewables could stay online longer if they drew on multiple power sources or had a steadier power supply thanks to batteries or another form of energy storage, but those solutions can add cost. Current improvements are still a long way away from generating most commodity chemicals profitably from renewables.

Producing enough renewable electricity to remake the chemical industry is also a challenge. Researchers concluded that running the global chemical industry on renewables would require more than 18 petawatt hours of electricity, or 18,000 terawatt hours, every year. That's 55% of the total global electricity production expected from all sources in 2030 (Reminds me of Dr. Howard Brown in the movie, “Back to the Future”!)

In Conclusion….

Perhaps the most likely outlook for future industrial chemistry is a “gradual greening”. Until chemists can find catalysts able to make complex hydrocarbons with high efficiency, companies may use renewable electricity to produce simple molecules such as H2 and CO and then fall back on fossil fuels to drive the reactions to stitch those together into more complex hydrocarbons. But as chemists develop new reactors and find ever-more improved combinations of catalysts—and as renewable energy continues to surge—the plants that churn out chemical building blocks will inevitably become more like the green variety, fully sustained by sun, air, and water.

Replacing a world of fuels, lubricants, and chemical products from current oil and gas sources will result in many obstacles, yet will provide robust career-supporting challenges, to be solved by up-and-coming STEM talent. We at Engineering Practice Magazine laud this future and expect that such transition to cleaner energy is a wonderful environment awaiting solutions. Please encourage a STEM student to also further these needed skillsets though IACPE certification as well.

Until July's next installment of *The View from Rock Bottom, we at EPM* wish our readership the start of an enjoyable and relaxing summer.

RESOURCES

- Bill Tumas, associate lab director, National Renewable Energy Laboratory, Golden, Colorado, at American Chemical Society meeting.
- Daniel Kammen, physicist, University of California, Berkeley.
- Eelco T., C Vogt & Bert M. Weckhuysen Nature, Volume 629, pp. 295 –306 2024
- Etosha Cave, Scientific Director, Opus 12.
- Gunfire Corporation, Dresden, GermanyHarry Atwater, Chemist, Caltech. Head of the Joint Center for Artificial Photosynthesis, a solar fuel collaboration among Caltech, and Lawrence Berkeley National Laboratory.
- Hussain Bahia, Vilas Distinguished Professor of Civil and Environmental Engineering, University of Wisconsin-Madison
- Joule Magazine, 21 August 2023 online issue, Sergeant, et.al.
- Nate Lewis, Chemical Engineer, Caltech.
- National Asphalt Pavement Association, 2017 Report, “annual recycled materials and warm-mix asphalt usage industry survey”.
- Proceedings of the National Academy of Sciences, June 4, 2023, issue.

IACPE
INTERNATIONAL ASSOCIATION OF
CERTIFIED PRACTICING ENGINEERS

IACPE.COM