



CAPTURING VALUE

Evan Sohodski, Compact Membrane Systems, USA, introduces a membrane technology that can help to minimise olefin losses and capture additional value.

Refineries and chemical plants are designed to maximise the value of the raw material inputs that they turn into saleable products. Whether it is refining crude oil into fuels or reacting olefins into plastics, a key production goal is to capture the maximum value from feed streams and minimise losses and waste in the process. Waste minimisation can be accomplished through recycle loops, catalyst regeneration, solvent recovery, and yield improvements. In spite of these common practices, many olefin-based processes still lose

valuable material through offgas streams, reactor purge streams and downstream process bottlenecks.

Compact Membrane Systems (CMS) has developed a membrane technology, Optiper™, which efficiently separates light olefins and paraffins in order to address these olefin losses and capture additional value that is not currently tapped. An example of this uncaptured value can be found in the production of polypropylene (PP), one of the most commonly produced plastics in the US. During the manufacturing process, propylene reacts to form PP (PP)

Membrane mechanics

Permeance is a measure of how fast a molecule can go through an area of membrane based on a given driving force. For gas separations, the driving force for a species is simply its partial pressure difference across a membrane.

The unit for permeance is gas permeation unit (GPU). The selectivity of one species to another, i.e. an olefin to paraffin, is simply the ratio of the two species' permeance values. As a result, this measure is unitless.

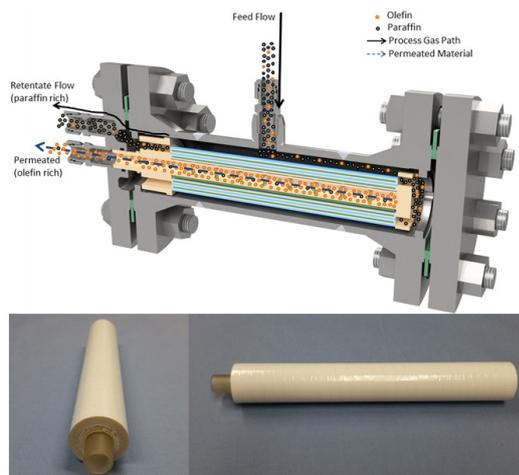


Figure 1. Cross-view depiction of a spiral wound olefin-paraffin module with actual cartridges.

plastic precursor. However, propane in the feed stream accumulates in the reaction vessel and must be purged. Although the release of propane is necessary for efficient reactor performance, valuable propylene is lost as a result. This article presents a theoretical case study where the membrane systems are used to recover propylene from such a purge stream. For a typical PP production facility, the membrane systems provide an attractive return on investment and competitive payback period for a reasonable capital investment.

Olefins separation technology

The search for membranes that are capable of economically separating and purifying olefins has been ongoing for decades. This membrane systems perform on critical dimensions that have traditionally stymied solutions. For economically attractive use, successful solutions need to demonstrate the following:

- Durability: standing up to process streams for months to years.
- High permeance: flow rates of olefin molecules fast enough to handle large volumes with a sufficiently small footprint and volume of membranes.
- Sufficient selectivity: a meaningful separation of olefins from paraffins.

Laboratory tests evaluating the membrane systems have shown high and stable permeance to C_2 , C_3 and C_4 olefins. Recent work has focused on the separation of

propane and propylene. CMS has conducted extensive characterisation of olefin permeance across a range of propylene loadings, temperatures, pressures, and contaminant loadings. Furthermore, long-term operation has been demonstrated in the presence of olefin for 3 – 12 months for laboratory-scale flat-sheet membranes, and moved to scale-up of commercial-scale cartridges for field use. Figure 1 shows how the module operates when processing a feed of olefin and paraffin.

Spiral elements exhibit performance on par with their laboratory-scale equivalents. Over the past six months, a pilot-scale, fully automated test unit is operating at a local refinery. This system aims to demonstrate the performance of the membrane systems in the separation of propylene from an actual refinery mixed olefin and paraffin process stream.

Successful membrane scale-up has allowed the performance of detailed simulations of the process economics of the membrane systems. Ongoing collaborations with a number of refining and petrochemical companies determine where the systems add the most value to their olefin-rich processes. A common industry application is the recovery of propylene in the production of PP. A full system has not yet been installed; as a result, this article centres on a hypothetical case study conducted by engineering staff for a PP reactor purge stream application.

Case study

The primary objective is to reduce propylene losses and feedstock expenditures and recover propylene from a PP reactor purge stream. Thus, the recovered propylene will be used as feedstock back to the reactor, reducing the overall consumption of propylene for a given volume of PP production.

The secondary objectives are to identify the optimal levels of propylene recovery to maximise economics, characterise solution sensitivities to changes in system performance and market conditions, and optimise system design.

Domestic PP production reached nearly 4.4 million t in 2014. Production methods vary in terms of the catalysts employed, reaction phase, and operating temperatures and pressures. In general, polymer grade propylene (PGP) (99.5+% C_3H_6 , 0.5% C_3H_8 , balance impurities) is fed to a reactor at a moderate temperature (150 – 190°F) and high pressure (440 – 590 psi). After reacting, the PP product is sent to a separator and transferred to a degassing bin. The unreacted propylene-rich gas mixture is recompressed and recycled back to the reactor. Reprocessing of the propylene monomer causes inert propane to build-up in the reactor. Left untouched, the propane takes up space in the reactor and reduces catalyst efficiency. As a result, a certain amount of material must be continually purged from the recycle loop and returned to a C_3 splitter for recovery or burned as fuel. In the worst case it may even be flared. In the process of removing undesired propane from the process, valuable propylene is lost.

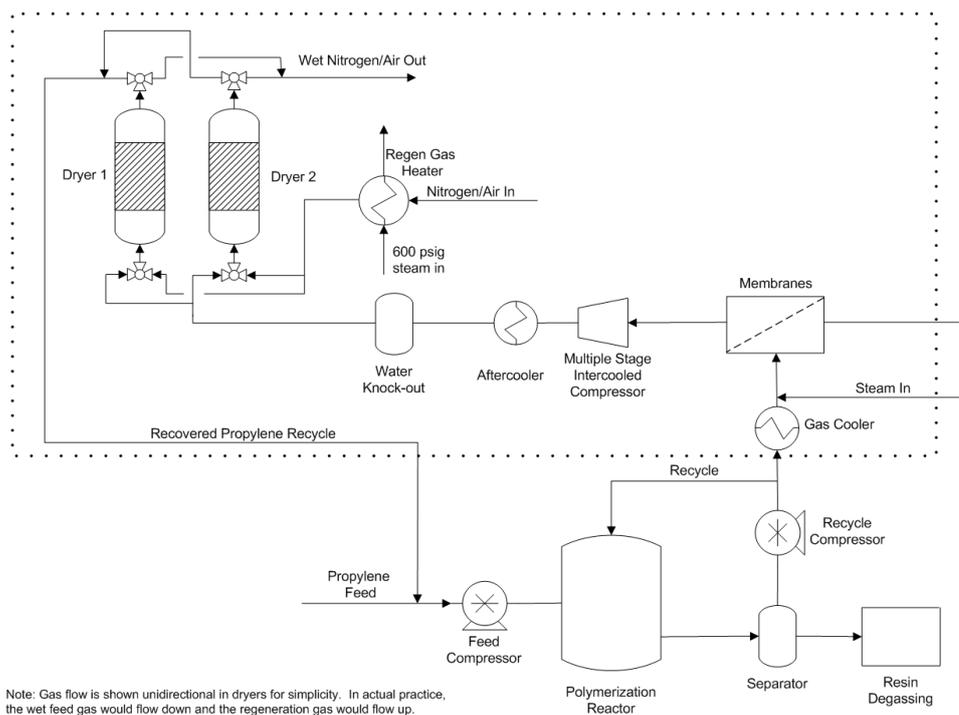
Membrane technology gives PP producers an economical method for recovering propylene that is

conventionally lost as purged material, while still preventing accumulation of inert propane. A simple process flow diagram (Figure 2) illustrates the integration of the membrane system (enclosed in the dotted line) into a PP manufacturing process.

The optimum propylene recovery unit includes a membrane bank, along with several standard chemical processing unit operations. The unreacted propylene and inert propane (90% C₃H₆/10% C₃H₈) are sent to a compressor and split into a recycle stream and feed stream to the membrane system. A gas cooler after the compressor is employed to remove excess heat of

compression. A steam injector is placed before the membrane to humidify the olefin/paraffin mixture before processing by the membrane as humidity significantly increases membrane performance. A majority (~88% C₃H₆) of the material fed to the membrane permeates through the membrane, enriched in propylene to 96%. The retentate, or material that does not permeate the membrane, is enriched in propane (50% C₃H₈) and sent to combustion. The olefin-rich permeate is recompressed, cooled, and fed to a water knock-out vessel to remove any entrained water. The knock-out operation is followed by a thermal-swing drying system to remove water from the saturated process stream. Hot nitrogen is used for regeneration of the dryer beds. The dried propylene gas is then recombined with the PGP feed to the reactor. The recovered propylene can be in place of fresh PGP feed or to increase the capacity of the polymerisation reactor.

A list of base case assumptions is shown in Table 1. The fresh reactor feed, PGP, is priced at current market value. The membrane system is sized to recover 90% of the propylene normally lost in the purge stream. The membrane service life of three years allows synchronisation of replacement with periodic plant shutdowns. Under these base case assumptions, the membrane system delivers attractive returns with a 135% internal rate of return (IRR) and payback time of under 12 months. The US\$1 million capital investment is quickly offset by the decreased raw material cost for the PGP. A central advantage to the membrane system is its modularity and linear scalability with process flow. For low to moderate flows, like the purge stream in this case study, large unit operations such as distillation columns are impractical for incremental propylene recovery due to



Note: Gas flow is shown unidirectional in dryers for simplicity. In actual practice, the wet feed gas would flow down and the regeneration gas would flow up.

Figure 2. Process flow diagram of an olefin-paraffin separation system within a polypropylene reactor circuit.

Table 1. Case study base case assumptions

Olefin value	US\$0.45/lb
Polyolefin capacity of plant	31 500 tpy
Paraffin content in reactor feed	0.5% C ₃ H ₈
Paraffin mole fraction in reactor	0.1
Membrane propylene permeance	70 GPU
Propylene/propane selectivity	10
Membrane lifetime	3 years
Membrane feed pressure	240 psia
Propylene recovery	90%

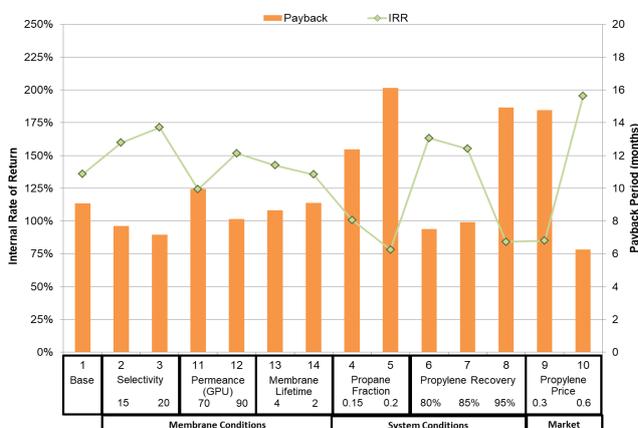


Figure 3. Sensitivity analysis for varying key technical, process, and economic variables that affect the separation. This shows attractive results for a range of cases.

economies of scale. It is in these low flow cases (offgas, vents, reactor purges, etc.) that investment in membranes outclasses traditional hydrocarbon unit operations like distillation.

As is the case for most refinery and petrochemical processes, the economic viability of an operation can depend on market factors for raw materials and utilities, as well as the overall operating performance of its component technologies. A sensitivity analysis of a membrane-based propylene recovery system was completed to gauge the influence of both economic and performance parameters on overall project economics. The results of the analysis are shown in Figure 3.

On the membrane performance side, the effect of varying the membrane service life, permeance, and selectivity are considered. High permeance, selectivity, and service life give the most attractive investment. However, lower permeance and shortened membrane lifetime still present an economically viable system.

On the system side, the effect of purge stream composition and target propylene recovery was examined. Although propylene recovery above 90% and higher propane content (15 and 20%) in the purge gas increased payback times and lowered the investment return, the resulting economics were still attractive. Finally, the system viability was examined under varied PGP market conditions. Even at the low end of US\$0.30/lb, the membrane system is still viable. The economic robustness of the membrane system results from the alternative use of the purged propylene when the purge stream is not recovered. As a fuel, the value of the

propylene (and propane) hovers between US\$0.06 – 0.09/lb. Incorporating the membrane system allows the PP producer to realise the entire differential between the fuel value of the olefin and its purchase price.

Conclusion

A pilot installation of the company's membrane system is currently operational at the Delaware City Refining Co. and a second pilot project has been announced in collaboration with DowDupont (and funded in part by the RAPID Manufacturing Institute). A number of industry players are working to design and size the membrane systems to work in conjunction with C₂ and C₃ splitters. These applications involve placing a membrane system in-line with the distillate or bottoms streams to expand column capacity. For the C₃ case, the system can be designed to produce HD5 or HD2 quality propane using the C₃ splitter bottoms stream. Recently the target applications have been expanded to include C₄ separations and other olefin rich processes streams. This development stems from customer interest in using the membrane systems to separate butenes from C₄ mixtures to debottleneck alkylation units and the recovery of light olefins from fuel gas streams.

Process enhancements to improve the bottom line require creativity as 'low-hanging fruit improvements' are addressed and disappear. Enhancements that allow producers to fully capture the value of the raw materials are crucial to enhance product margin, unlock new sources of value, reduce waste and improve overall top and bottom line performance. 



Compact Membrane Systems

Membranes for difficult separations

Providing membrane solutions to industry

- *Custom gas separations (i.e., CO₂/CH₄, olefins/paraffins, oxygen-enriched air, nitrogen-enriched air)*
- *Dehydration of lubricating fluids*
- *Purification of solvents*
- *Liquid degassing*
- *Sensing applications*

CMS is an advanced materials company, developing state of the art membrane technology and products for use in a variety of industrial applications. Compact Membrane Systems enables its customers to operate more efficiently and safely with increased uptime, lower costs, and a reduced environmental footprint