Compact Membrane Systems Optiperm™

Efficient, Scalable, Modular
Olefin Paraffin Separation

Updated August 2020

TABLE OF CONTENTS

EXECUTIVE SUMMARY

Today's refineries and petrochemical plants have valuable streams that are going to waste or are capacity-constrained (or both), for lack of a cost-effective modular, scalable separation of olefins from paraffins. Unlocking this constraint can increase throughput and yield, creating value for the topline business, while reducing feedstock, environmental and other costs.

Optiperm™ membranes are a modular solution that allows the debottlenecking and monetizing of olefin streams that are currently not captured and not addressed by incumbent separation technology.

The inherent characteristics of current separation technologies – efficient at scale, but fixed in capacity and centrally located - mean that valuable olefin molecules are lost to purge streams, flares, and bottoms products of everyday plant operations. For decades, this untapped, potential value in refineries and specialty chemical plants has been waiting for a technology that can unlock and monetize this olefin value. Optiperm™, developed as a bolt-on technology to capture and to effectively separate these streams, has shown stability for over 2 years in the lab. Its first field trial at the Delaware City Refinery highlighted its ability to succeed in challenging chemical environments.

UNLOCKING OLEFIN VALUE

Valuable olefins can be left stranded in streams throughout refineries and petrochemical plants and capacity constraints can additionally limit the output of such plants. A cost effective modular, scalable separation of olefins from paraffins has the potential to unlock significant value throughout these plants.

Olefins, the chemical building blocks for all plastics and other valuable consumer products, are usually generated with their sister molecules, paraffins. Separating and purifying olefins for downstream use currently requires energy-intensive separation by large, capital-intensive, fixed capacity equipment in the form of distillation columns. In addition to constraining plants by their fixed capacity, it is estimated that 0.3% of the world's global energy usage is spent separating olefins from paraffins by distillation, a process that is largely unchanged since its introduction to the chemical industry.

Membranes can be placed in conjunction with existing process equipment or as an independent separation process to unlock olefin value wherever it exists. Optiperm™ membranes can be used to recover propylene from polypropylene purge lines, debottleneck distillation columns for C2 or C3 applications, purify C4 olefins for specialty chemical production, and much more. To see an extensive, but not comprehensive, list of all Optiperm™ applications, please visit our website.

Optiperm™ is the first truly commercially applicable membrane technology to enable the widespread separation of light olefins from paraffins. The unique technology combines olefin-selective silver with a rugged fluoropolymer membrane to provide superior, stable olefin separation. The Optiperm™ design, which has been stable for two years in the lab and was refined at the Delaware City Refinery trial, highlights a robust, modular solution that stands up to the toughest olefin separation environments.

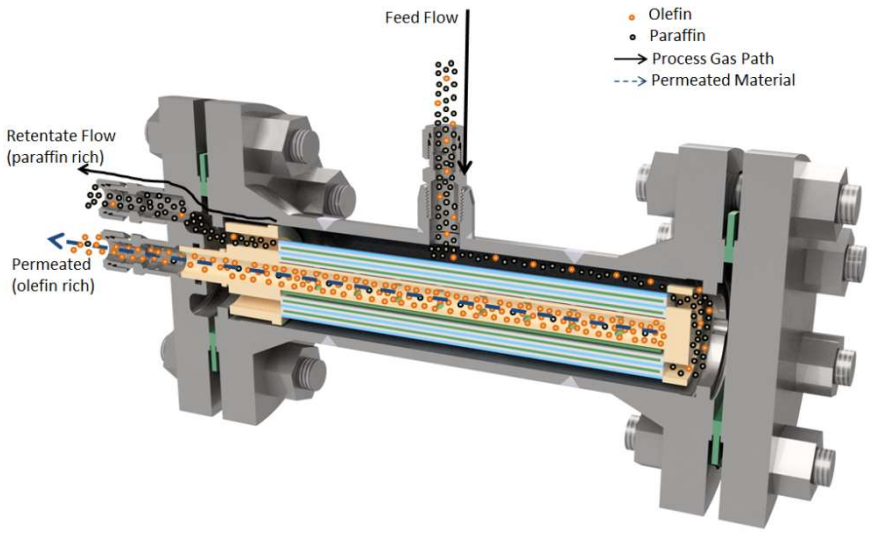
Optiperm™ Silver Management

The proprietary formulation of the Optiperm™ membrane includes silver that is tightly complexed in the polymer structure and is not readily mobile. Extensive testing in the lab and in our first pilot demonstration has shown no measurable silver leaching from the membrane. Leaching could be a contamination risk to downstream processes. Even in the presence of acetylene, where silver acetylide could form, the CMS polymer is designed to keep silver located within the membrane structure and reduce any threat to operators or downstream processes.

The thin nature of Optiperm™ membranes means that they utilize a very small quantity of silver in the membrane. In estimates of a worst case (and highly improbable) scenario in which the full quantity of silver leached out of the membrane, formed silver acetylide, and aggregated downstream and dried, the total energy released would be very low. Please contact us at membranes@compactmembrane.com if you are interested in our white paper on this topic.

OPTIPERM™ MEMBRANE TECHNOLOGY

CMS developed a silver-containing fluoropolymer membrane known as Optiperm™. The technology exploits a mass-transfer mechanism known as facilitated transport. Silver incorporated into the membrane polymer acts as a binding site for the double bond in the olefins, transporting them across the membrane. Saturated paraffins do not have the same interaction. This difference in affinity allows for olefins to pass through the membrane at a significantly higher rate than paraffins. The silver is bound within the fluoropolymer structure. CMS has performed extensive testing in the lab and in the first field trial to establish the performance and stability of this mechanism



How is membrane performance characterized?

Permeance is the rate at which one component travels through a membrane surface area for a given driving force, and is effectively a measure of separation processing volume. Increased permeance enables the processing of large streams with minimal surface area. This performance metric is typically expressed in GPU (gas permeation unit). Optiperm™ membranes have olefin permeances greater than 50. This translates into a propylene flux of 0.16-0.57 ton/ft2/year under normal operating conditions (e.g., 30-200 psi, 30C, and 20-90% olefin).

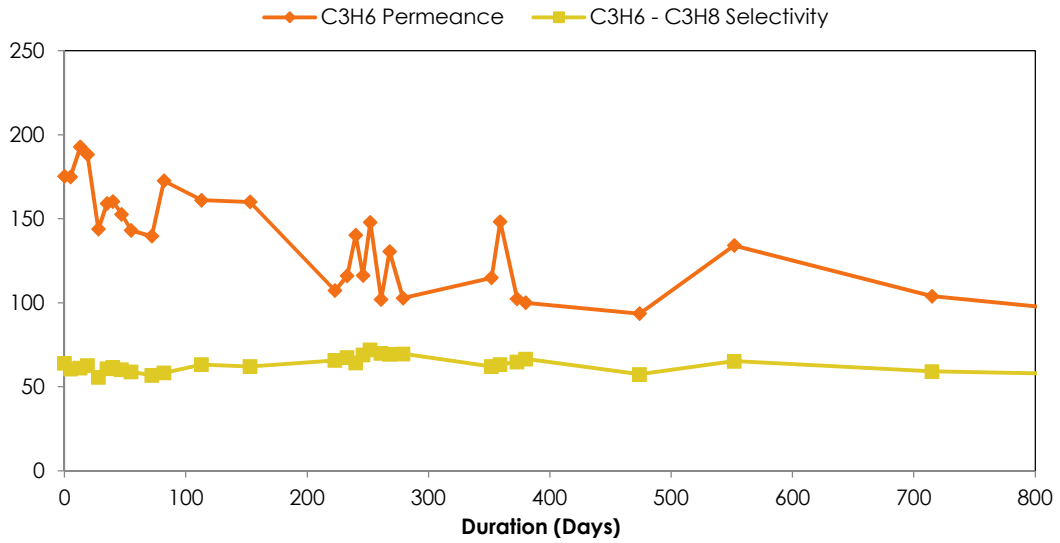
The **selectivity** of one component to another is simply the ratio of the permeance of the two components, and is a measure of separation quality. This tells you how much olefin is passing through the membrane as compared to paraffin. Optiperm™ has selectivity ranging from 20-80 depending on the operating conditions and feed composition, meaning high olefin purity is achieved in the permeate stream. Optiperm™'s unique combination of high permeance and selectivity mean attractive process economics are realized for most use cases.

OPERATING CONDITIONS AND STABILITY

Optiperm™ operates at a wide range of commercially relevant temperatures, pressures, and compositions. CMS has demonstrated olefin removal at temperatures up to 70°C (158°F) and pressures up to 250 psig. Optiperm™ membranes operate in the vapor state, contributing to the lower operating costs compared to pressure swing or cryogenic distillation.

As with all facilitated transport membranes, Optiperm™ requires humidification of the process stream. CMS has developed a proprietary humidification system within the module to ensure optimal performance. The membrane can remove olefin in both concentrated and dilute streams for compositions ranging from 5-95% by volume of olefin. The membrane can process mixtures of C2, C3, or C4 olefin and paraffin. The graph below illustrates Optiperm™'s stable performance profile when separating a 20% propylene/80% propane mixture at 60 psig and room temperature.

The membrane shows stable performance for over 2 years in the laboratory. We assess membrane life at 2 years in most streams and up to 3 years in a high quality feed.



A broad range of tests characterize the membrane resistance to common poisons in refinery gas streams. Optiperm™ membranes are designed to be poison-resistant for short to moderate time periods (hours to days) so process upsets will not be immediately catastrophic to performance. We recommend process streams contain no more than:

<100 ppm acetylene <1% hydrogen <100 ppb total sulfur

Our default approach is to include a sulfur pretreatment unit operation as part of the full membrane system in order to address the concern that sulfur will detrimentally affect membrane lifetime.

ECONOMICS

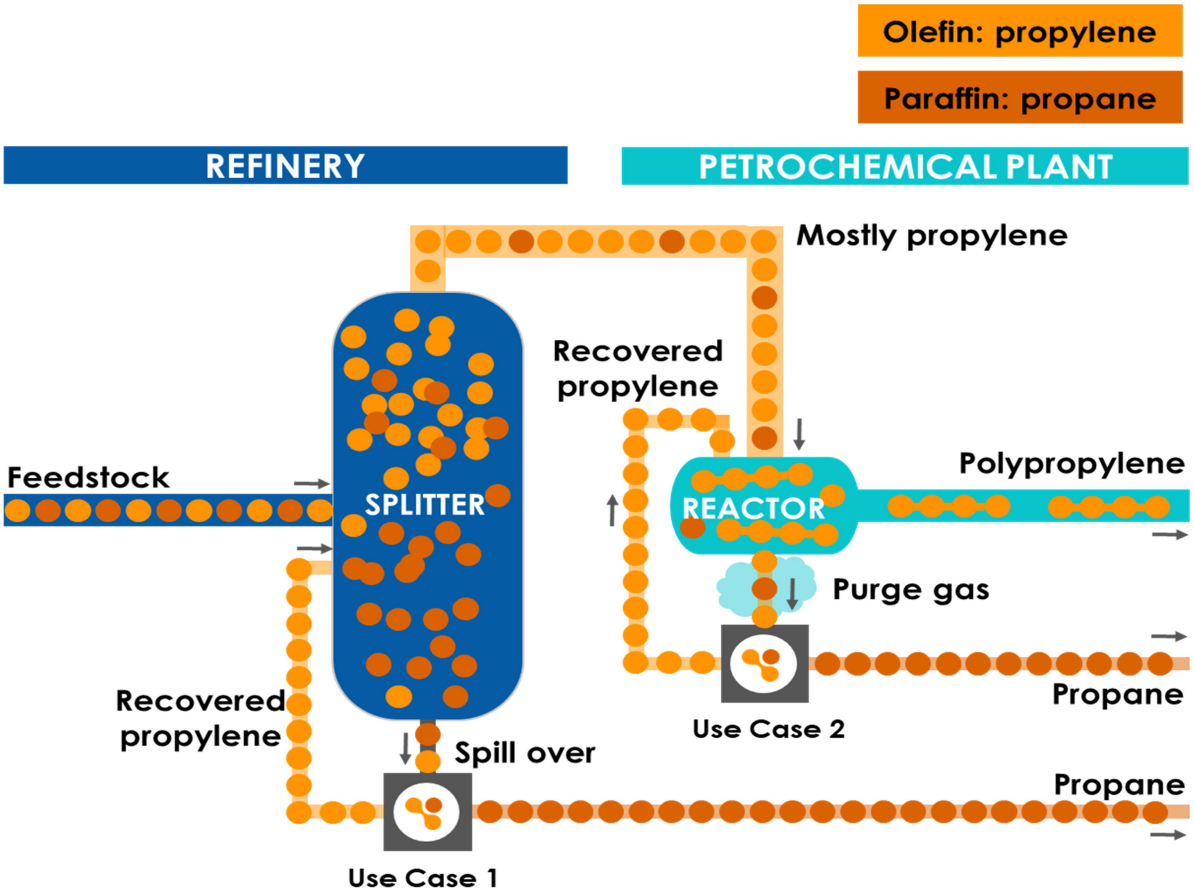
CMS models individual customer process streams to generate an overall system size, economics, and performance based on Optiperm™'s mass transfer capabilities. With lab data, validated in our field test, CMS can size and design membrane systems for a variety of applications. CMS provides custom membrane solution for each customer, based on exact stream compositions and operating parameters. Evaluations include comprehensive CAPEX, OPEX, and utility usage, as well as membrane sizing and sensitivity analysis. CMS has also modeled some typical applications to demonstrate Optiperm™'s strong economic feasibility. On the following pages are two example cases for the recovery of propylene from the bottom of a C3 splitter and polymerization reactor.

Effects of Pressure

There are three pressure considerations for a membrane system. First, like temperature, the operating pressure must be designed to prevent condensation in the feed stream or at the membrane. Second, flux does increase slightly at increased pressure until you hit the maximum saturation of olefin molecules at facilitated transport sites. CMS has a large body of data to understand when this point is reached and can help optimize the design of the system for the ideal pressures. Lastly, pressure affects the compression that is required to bring the stream back to the system pressure, after the membrane process or in a recycle loop. The permeate (olefin rich stream) exits the membrane at approximately atmospheric pressure so if the process is running at high pressure, compression costs can offset some of the economic value created by the membrane system. CMS runs proprietary membrane models to examine these effects and optimize membrane system pressure in order to deliver the most economically attractive package and system design to the customer.

Achievable Purity

Optiperm™ technology can produce high quality olefin up to 99.5%. CMS has not evaluated a case in which producing greater than 99.5% olefin was economically attractive for customers, due to the large number of membrane modules required (akin to a distillation column with many trays). The ability of Optiperm™ to economically produce high quality olefin heavily depends on feed and operating conditions and is modeled on a case by case basis. As noted earlier in this document there is a tradeoff between purity and recovery which must also be taken into consideration.



Case 1: C3 Splitter Bottom

C3 splitters are used to separate C3 olefin (propylene) from C3 paraffin (propane). Depending on the conditions at which the column is running, olefins are often spilled out the bottom in concentrations ranging from 1-20% of the stream.

The Optiperm™ membrane can be used to recover that propylene while also upgrading the propane to a higher purity. In this example, we've assumed a moderate amount of olefin in the C3 splitter bottoms (10%) and are using the membrane to generate HD10 propane and permeate a propylene rich stream which can be recovered as RGP, CGP, or PGP. Alternatively, it can simply be returned to the column to expand capacity. The evaluation here evaluates the latter, where the concentrated propylene is recycled to the splitter. A simple diagram is shown above.

The proposed system augments a 40,000 ton propylene per year C3 splitter running at 215 psig column pressure. The system assumes standard membranes replaced every 2 years and generates:

- 14 month payback period
- IRR of >70%

These economics are robust over a wide range of conditions. As expected, more frequent membrane replacement, lower olefin permeance, and inexpensive market prices for propane and propylene increase the payback period of the membrane system. Nevertheless, in cases evaluated across a range of likely scenarios, the investment is still strongly positive with the IRR remaining greater than 50%.

Case 2: Recovery from Polypropylene Reactor Purge

This second application recovers propylene that is typically lost to a purge stream meant to prevent buildup of inert propane in a polypropylene reactor. As in the first case, the recovered propylene can be recycled to the process to increase capacity without purchasing additional feedstock. The membrane system in the scheme on the preceding page is added onto a 125,000 ton per year polypropylene reactor operating at 240 psia with a 10% propane/ 90% propylene feed. The membrane system is designed with a 90% recovery of propylene. A system supplied with standard Optiperm™ membranes replaced every two years yields:

- 5 month payback period
- IRR of > 250%

These economics are very favorable and a similar sensitivity analysis to the previous case shows that the membrane lifetime and prices of the corresponding value streams are the biggest driver to the economics. Again, the IRR remains greater than 150% in a range of reasonable scenarios.

Have an application that you are considering for separation or upgrade? Or a question?

Remember that CMS can…

- Run feasibility testing in house
- Provide lab scale samples
- Model system economics
- Construct and deploy pilot rigs
- Determine optimal system design

DEMONSTRATION UNITS

Optiperm™ successfully completed its first field demonstration at the Delaware City Refinery Company in 2018. The pilot showed stable membrane performance for 50+ days in the presence of poisons while producing an HD5 propane stream. The main objective of the pilot was achieved when the field results validated data collected in the lab. During the trial, membrane module design was improved, robust pre-treatments were demonstrated, and a proprietary humidification system was developed to operate the membranes with ease in the field. For more details, read the full case study here.

CMS has in house engineering design and fabrication facilities. To ensure that we can meet customer needs, we have relationships with a number of third party engineering firms that can meet our customers' high standards.

A number of demonstration units are scheduled for deployment in the next 18 months. The first is a project with Dow, partially funded by AIChE's RAPID program. A large membrane demonstration unit will be deployed at Dow's Freeport Texas site on a C3 stream. This pilot has been designed to produce chemical grade propylene product.

The second unit will be deployed at a Braskem site. This pilot is targeted to use commercial-sized membrane modules in a multi-stage unit for olefin recovery from a polypropylene reactor purge. The goal of this pilot is to simultaneously produce >90% purity of olefin and paraffin rich streams. Both pilots will validate CMS's new proprietary humidification system, pretreatment design, and large membrane modules.

Additional 2021 pilots, including a specialty C4 application, will be announced soon. Please visit www.compactmembrane.com/news for updates or contact CMS to be added to the mailing list.

Facilitated transport membranes need water, how do you handle this?

CMS has developed a proprietary humidification system that is included in the membrane housing. This ensures that an additional process step is avoided and that humidification can be monitored and controlled during operation.

Figure 1 Photos of a pilot unit on site at the Delaware City Refinery

MEMBRANE PRODUCTION CAPABILITIES

CMS has in house capabilities for coating and assembling spiral wound flat sheet and wound hollow fiber elements. CMS is currently scaling up manufacturing to meet expected demand, with commercial sized module production by the end of 2020. Scale up activities include membrane module scale-up, supply-chain diversification, QC development, procurement of large scale coating equipment and expansion of manufacturing space.

CMS gratefully acknowledges support from the U.S. Department of Energy, AIChE's RAPID program, and the State of Delaware Bridge Grant for the development of the fundamental research and scale up of Optiperm™ technology.

CMS BACKGROUND

Compact Membrane Systems (CMS) was founded in 1993. CMS develops fluoropolymer membranes for tough chemical separations in industrial gas and liquid applications and has developed and produced membranes for use in transformers, wind turbines, marine systems, pharmaceutical manufacturing, and bulk gasoline storage, among other applications. Manufacturing and development are performed at our site in Newport, Delaware.

Contact

To discuss a specific separation project, understand more about our membranes, or inquire about pilot availability, please contact:

Bill Charlton

VP of Operations
bcharlton@compactmembrane.com
302-314-1823

Hannah Murnen

Chief Technology Officer
hmurnen@compactmembrane.com
312-498-4522

Christine Parrish

Business Development Lead
cparrish@compactmembrane.com
302-314-1838