Compact Membrane Systems

Optiperm™ Membrane Demonstrates Stable Performance in Pilot Study of HD5 Propane Production

Abstract: The separation of light olefins from paraffins is one of the most energy intensive in the world. The state of the art separation method is distillation, a technology that has remained unchanged over decades. This large fixed infrastructure gives rise to bottlenecks and waste streams, resulting in value that producers haven't been able to unlock, capture and monetize. Membranes promise a more modular, energy efficient and cost effective method for separation that can deliver new sources of revenue and lower costs. However, membranes have historically been hampered by instability and low performance.

Compact Membrane Systems has developed a novel membrane material using a silver embedded fluoropolymer material to transport olefins across the membrane. This material has demonstrated over 2 years of longevity in laboratory operation and has shown high selectivity and permeance under realistic operating conditions.

CMS has recently completed a pilot study utilizing this membrane material at the Delaware City Refining Company. The Delaware City pilot was operated on a low olefin stream (i.e., ~10-15% propylene concentration in the feed) with the goal of achieving HD5 quality propane and an enriched propylene stream. The pilot study was successful and demonstrated stable membrane performance over the course of the test. Economic analysis using the pilot results demonstrates that the economic case for an industrial scale project is strong with a payback period of 8-16 months.

Background

Ethylene and propylene are major chemical industry raw materials which consume a great deal of energy in their production. The separations of these materials are some of the most costly, energy intensive, and technically challenging separations in the industry due to the close similarity in size and nature of the molecules being separated. Distillation, the technology currently employed for the separation of ethylene and propylene from paraffins, is estimated to consume 250 trillion BTU/year of energy.

The distillation columns to separate these molecules are very capital intensive due to the large number of trays required. To be efficient, columns are primarily used at scale and are relatively fixed in size over time. As a result, legacy plants have streams and opportunities that could generate additional value, if they could be economically separated and purified. These opportunities include de-bottlenecking to expand capacity (creating additional revenue), capturing waste streams (reducing feedstock and product costs), and upgrading product streams.

A membrane based olefin/paraffin separation technology has the potential to provide substantial economic benefits to the petrochemical industry and to reduce the energy required for separation. In addition, membrane systems are scalable, allowing their implementation for smaller, stranded streams where the limited economic value does not justify the investment required by a distillation column. Membrane processes utilizing facilitated transport membranes have been extensively studied for separating olefin/paraffin mixtures. While separations have been demonstrated in the laboratory in the past, problems with membrane stability have prevented development of commercial systems.

Membrane Technology

Compact Membrane Systems (CMS) has developed the Optiperm™ membrane, a silver-containing fluoropolymer that selectively transports olefin molecules from a mixture of olefins and paraffins. The technology exploits a mass-transfer mechanism known as facilitated transport. Silver incorporated into the membrane polymer backbone acts as a binding site for the double bond in the olefins. Saturated paraffins do not have the same interaction with the silver moieties. This difference in affinity enables olefins to pass through the membrane at a significantly higher rate than paraffins. The Optiperm™ membrane has both high olefin permeance and high olefin/paraffin selectivity, meaning high product purities can be achieved with a reasonable membrane area. These characteristics yield very attractive process economics.

Although various membranes for olefin/paraffin separation have been evaluated for many years, the Optiperm™ membrane's difference is stable performance over a significantly longer time period than earlier membranes. The improvement in membrane stability is made possible by incorporating the silver ion into backbone of the fluoropolymer which makes up the bulk of the membrane structure. As with most fluoropolymers, the fluoropolymer used in the Optiperm™ membrane is very resistant to chemical attack. It is this property that has been successfully utilized to create a membrane that provides stable separation performance in olefin/paraffin separations.

The Optiperm™ membrane can perform separations of olefins from paraffins over a wide range of operating temperatures, pressures, and compositions. CMS has demonstrated olefin removal at temperatures up to 70°C (158°F) and pressures up to 250 psig in the lab. For an efficient separation to occur, the olefin-paraffin mixture must be in the gaseous state and the mixture must be highly humidified, as water vapor greatly improves the mobility of the olefin through the membrane. The membrane can remove olefin from both concentrated and dilute streams ranging from 5% to 95% olefin by volume. The membrane can process C_2, C_3, and C_4 olefin/paraffin mixtures.

The Pilot Study

Background:

The pilot study was carried out at the Delaware City Refining Company facility over 300 days of operation that spanned a period of approximately 15 calendar months. Prior to the initiation of the pilot study, all of the development tests done with CMS Optiperm™ membranes were carried out in the laboratory at small scales. The membranes used in the pilot study had an active area of 1.5 to 3.5 square feet, two orders of magnitude larger than the laboratory test specimens.

In addition to testing much larger membranes, the pilot study had four objectives. These were:

1. Demonstrate the ability of the Optiperm™ membrane to produce an HD5 quality propane (<0.05 propylene) from an 85% to 93% propane feed.
2. Replicate and compare lab performance data developed on 47mm disks with field testing of spiral wound modules
3. Demonstrate capability of operating at field conditions
4. Demonstrate long term durability of facilitated transport membranes at field operating conditions

In addition to overcoming the problems associated with scaling up the membranes for the pilot study, the pilot tests presented many technical challenges that had to be addressed. At least one should be noted as it directly impacts the interpretation of the test results. The process stream that was fed to the membrane was known to contain low concentrations of sulfur compounds. All sulfur compounds are a poison to the facilitating agent in the Optiperm™ membrane. Therefore, sulfur concentrations in the membrane feed had to be reduced to acceptable levels, less than 100 parts per billion. This was accomplished by placing a commercially available nickel bearing adsorbent upstream of the membranes.

Key Pilot Study Results:

Optiperm™ membrane is stable in field operations. The results of one test carried out for the purpose of verifying the stability of the Optiperm™ membrane in the process stream used in the pilot study are plotted in Figure 1. In this test, the membrane was operated at a low stage cut over a 50 day period. The feed propylene concentration was approximately 9% and the feed pressure was 70 psig. The permeate stream produced by the membrane was approximately 25%. Although there is some scatter in the data, the average permeate stream composition is fairly constant over the 50 days of operation.

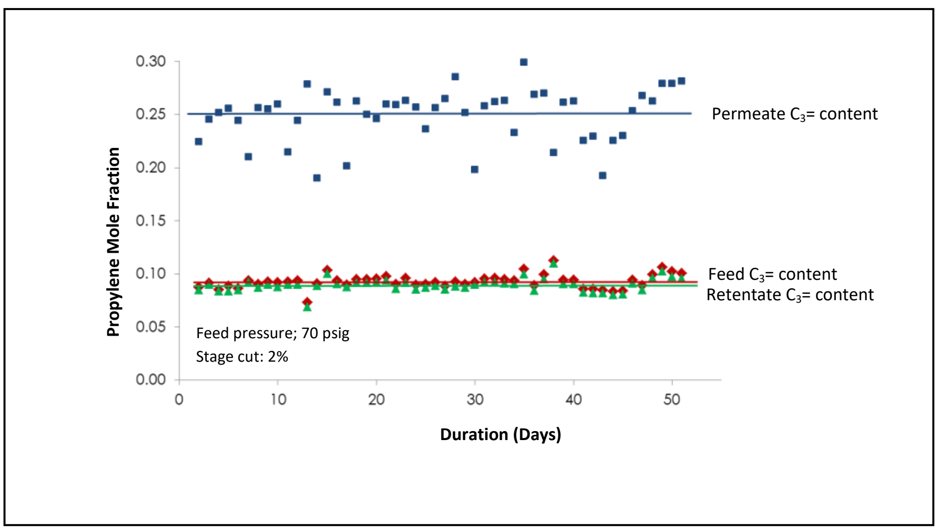

Figure 1. The results of long term aging studies conducted over a 50 day period

As part of our standard procedures for deploying membranes for field testing, we first conduct laboratory tests of the membranes to benchmark the separation performance of the membrane under controlled conditions. The performance data is used to optimize membrane field operating parameters as well as troubleshoot suboptimal field performance. The procedure also calls for returning the membrane to the lab at the midpoint of an extended test in the field and then again at the end of the field test to complete performance testing under controlled conditions.

The accompanying lab performance data for the 50 day membrane study shown in Figure 1 is presented in Table 1. While there is some variance in the permeance and selectivity measurements over the 50 day trial there is no significant negative trend in the membrane performance.

Table 1. *Membrane lab performance validation during 50 day field trial*

	Pre-field exposure	Mid-point exposure	50day exposure
C_3=permeance (GPU)	128	174	154
C_3= / C_3 Selectivity	37	40	30

Figure 2, compares the observed field performance of membrane to its performance in the lab. Because the feed composition in the field is not constant and sample collection in the field was limited, it is difficult to make a direct comparison to the lab composition data. So, the membrane performance properties that are calculated from the data are compared instead. The permeance and selectivity observed in the field (plotted as individual points) vary but are stable in that they do not trend up or down and on average agree well with the properties observed in the lab (plotted as solid lines). In this set of data, the feed pressure was 115 psig, the feed composition averaged approximately 14% propylene, the retentate contained approximately 7% propylene and the permeate product was enriched to approximately 30% propylene.

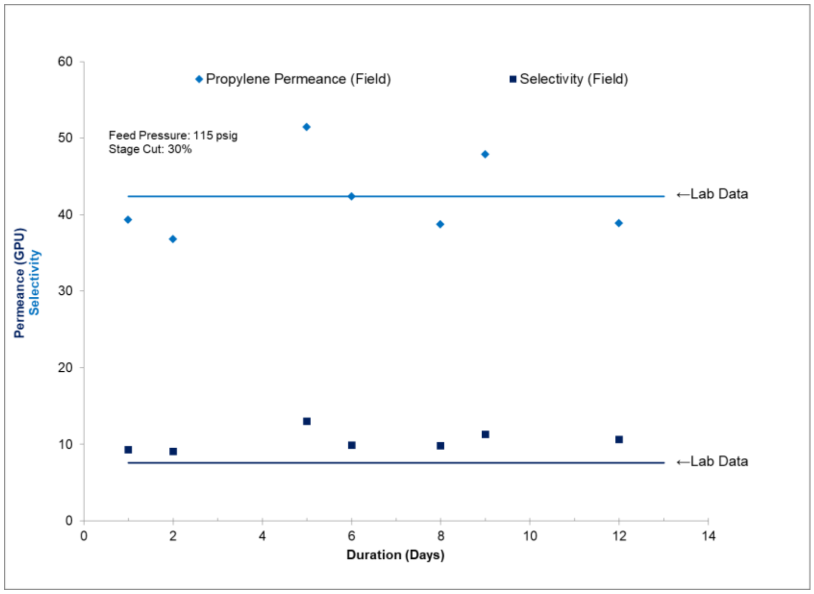

Figure 2. *Optiperm™ membrane is stable and compares well with laboratory data*

Figure 3 presents the results of a test interval during which the objective was to maximize propylene enrichment in the permeate stream. The stage cut was maintained at a low value, 3% to 6%, for this purpose. The feed pressure was 70 psig. The concentration of propylene varied from 16% to 22%. The permeate stream was significantly enriched in propylene. The concentration ranged from 45% to 53%.

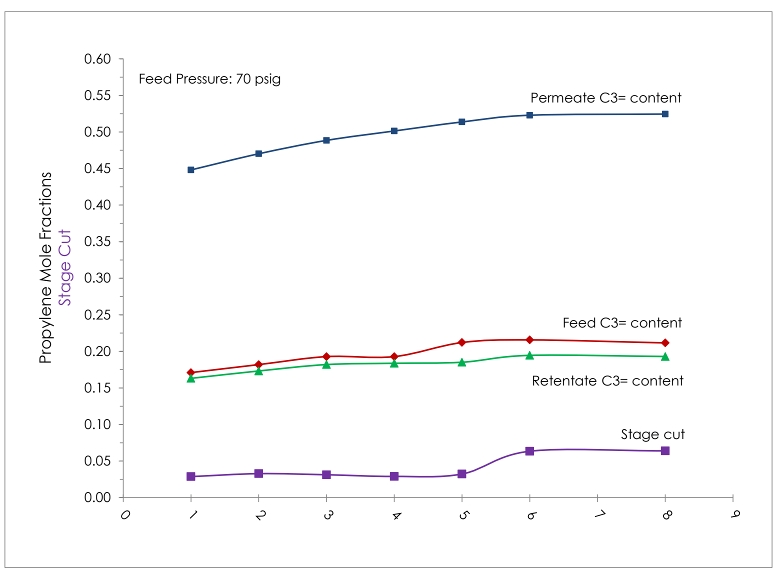

Figure 3. *Optiperm™ demonstrates high propylene enrichment*

During the time interval plotted in Figure 4, the feed flow rate to the test membrane was adjusted to enable production of a retentate stream that meets HD5 propane specifications from a feed stream containing approximately 10% propylene. The membrane consistently produced HD5 over a period of 10 days, until the feed concentration increased above 15% and was out of range for the design of this pilot system. The propane recovery in this test was limited to 55%, which is lower than ideal, and can be attributed to inconsistent feed humidification levels. Membrane performance is very sensitive to feed humidity levels.

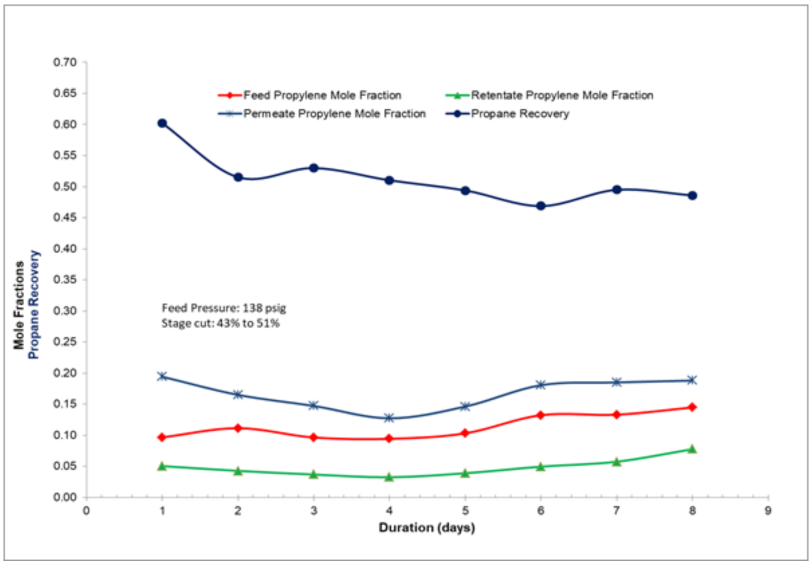

Figure 4. *HD5 propane production w/ Optiperm™ membrane*

As evidenced by the low recovery in the HD5 production test, one of the operational challenges for the pilot unit was maintaining constant feed humidity across a variety of ambient and operating conditions. During the course of the pilot study, CMS developed a method of operating Optiperm^{TM} membranes without humidifying the feed streams, potentially simplifying the operation of these systems. A novel method of humidification was developed that ensured uniform humidification throughout the entire module. CMS tested a simplified version of the new humidification method at DCRC and the membrane was able to produce HD5 propane from a feed containing 13% propylene with a much improved propane recovery; 82% vs. ~55% (see Figure 5). It is planned to incorporate the new humidification method in future pilot installations, simplifying operation and improving performance of the Optiperm^{TM} membranes.

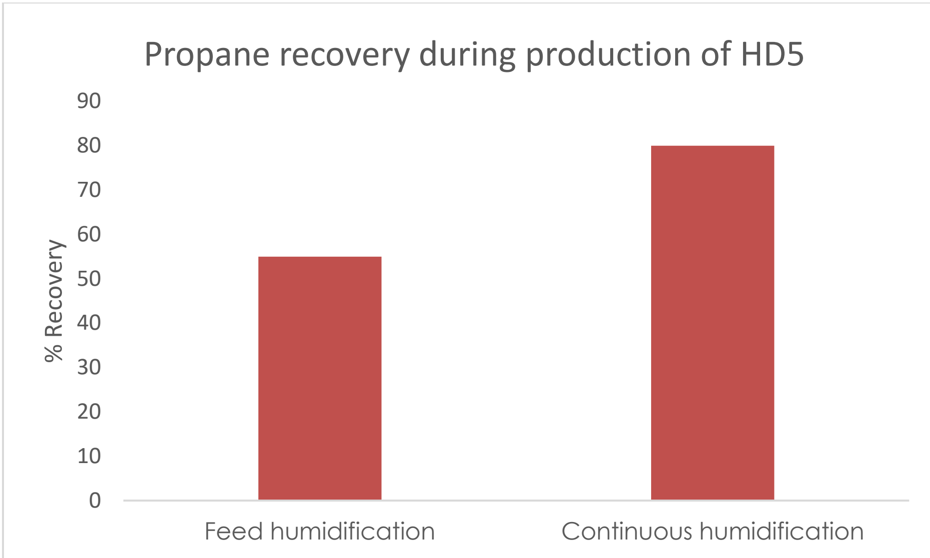

Figure 5. *Propane recovery during HD5 production*

Economic Analysis of a Commercial Scale Process

A commercial scale process for the simultaneous production of HD5 grade propane and refinery grade propylene was evaluated for economic feasibility. A plant capacity of 175,000 tons per year of feed was assumed. A process flow diagram of the membrane process is presented in Figure 6. A two-stage membrane process was chosen for this separation to enable independent selection of the two product stream compositions. A single-stage membrane process can be used to produce HD5 propane, but the composition of the propylene enriched product stream would be a dependent variable.

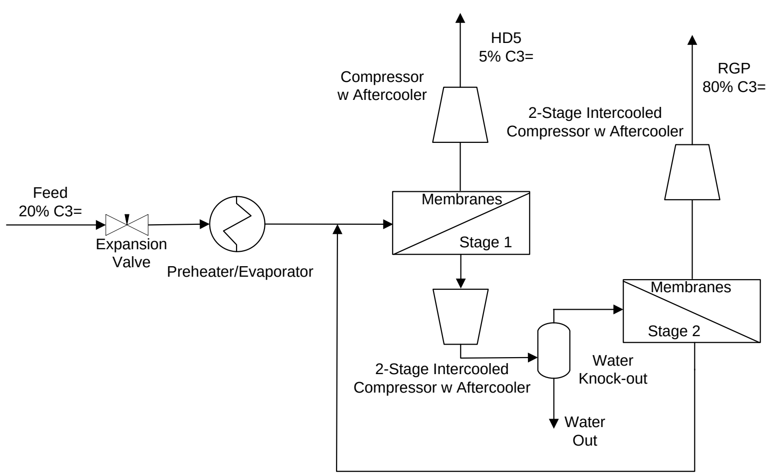

Figure 6. *Process flow diagram of a two-stage membrane process*

The results of the economic analysis are presented in Table 2. The installed capital cost of the system is $13.1 million. The annual operating cost is $4.9 million, including membrane replacement costs and all other maintenance costs. The annual net benefit, calculated as the value of the two product streams less the value of the feed stream and the operating costs, is between $10 million to $20 million. The wide variation in these values results from allowances for variations in values of the feed and product streams. The corresponding simple payback periods are both excellent at 16 and 8 months.

Table 2. *Economics of Commercial Scale Membrane Process*

Capex including all auxiliary equipment ($MM)	13.1
Opex including all maintenance costs ($MM)	4.9
Estimated net annual benefit ($MM)	10 - 20
Payback time (months)	16 - 8

Key Conclusions

- **Field membrane performance is stable**. Membrane pre-qualification and post-field performance tests confirm stable membrane performance parameters with permeance and selectivity matching the pre field testing values.
- **Field membrane performance matches laboratory data** at similar conditions, supporting both analytical results and economic analyses.
- **The membrane can produce an HD5 quality propane product.** This was the primary goal of the pilot study.
- **The new humidification method developed by CMS significantly improves membrane performance and avoids operational complexity of maintaining a humid vapor feed**. A commercial scale system design will incorporate all of the design and control elements required to implement the new humidification method in order to consistently produce on spec products including HD5 propane and propylene-rich streams.
- **The spiral module membrane design and materials of construction are durable in this application, performing as expected** with no mechanical failures noted in 300 days of field testing using multiple spiral wound membrane modules.
- **The payback time for a commercial scale separation process to produce HD5 and RGP is excellent.**