CONTINUOUS OLEFIN/PARAFFIN SEPARATION WITH PERMYLENE™ FACILITATED TRANSPORT MEMBRANES FROM IMTEX MEMBRANES CORPORATION

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Prepared for Presentation at the 27th Ethylene Producers’ Conference
Austin, Texas, April 26 - 30, 2015
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ABSTRACT

As worldwide demand for light olefins increases, there is an enormous incentive to explore reliable alternatives to distillation for the separation of olefins from paraffins with lower energy consumption, reduced capital cost and less environmental impact. In pursuing increases in production capacity, many facilities are faced with the challenges of expense and complexity of additional distillation equipment. Attempts have been made to develop alternative separation technologies, including significant work on facilitated transport membranes. The main unresolved challenge was membrane performance instability over time. Imtex Membranes Corp. has developed a membrane separation process with its Permylene™ membrane separation technology that has shown performance stability over extended periods of operation during trials using spiral wound membrane elements.

Imtex continued to optimize the hydrogel-based membrane process, and through a significant technology advancement, has demonstrated continuous, uninterrupted operation in olefin/paraffin gas separation. The performance stability of the Imtex membrane stands in contrast to dry solid polymeric and immobilized liquid membrane technologies for which stability, permeation rate and selectivity challenges have been well documented. Results were very encouraging for C2, C3 and C4 splitting applications with the Permylene technology as greater than 99.5% olefin purity was achieved in all cases with steady permeation at commercially viable rates. With these characteristics and its modular nature, Permylene membrane technology is presented as a practical alternative to the costly distillation approach. In addition to ethylene production, this technology can be applied in other commercial applications such as upgrading refinery grade propylene to polymer grade or in propane dehydrogenation and other on-purpose propylene processes that are becoming more prevalent due to the trend towards lighter feeds to ethylene plants.

There is also promising potential for butene/butane separations where traditional distillation separations require large numbers of trays and extremely high reflux ratios. Monomer recovery from polyolefins production or recovering valuable olefins from other types of purge or waste streams are other attractive applications. Extended tests were performed at Imtex to verify the stability and continuity of operations relevant to these applications. The promising findings are presented.
INTRODUCTION AND BACKGROUND

The rising demand for olefins and polyolefins in major end-use industries coupled with favorable operating conditions, primarily in the Middle East and the Asia Pacific region, is expected to drive the global market for olefins and polyolefins through 2030 (1). The availability of abundant ethane feedstock from shale gas is also a major driver for capacity expansion in North America. Ethylene and propylene, along with their derivatives, account for the vast majority of this demand. Global ethylene consumption has grown at an average rate of 4.5% per year since the beginning of the decade while capacity has lagged behind. The demand for propylene is expected to increase by over 40% over the next ten years, and is spurring the growth of on-purpose propylene capacity and production to make up for the imbalance between supply from conventional production methods and demand (2). Olefin / paraffin separation is one of the most important chemical industry processes but also one of the most challenging as it relies on capital and energy intensive technologies. Conventional olefin production in refinery and petrochemical processing has utilized distillation for the recovery of purified olefins from mixtures with their respective paraffins. Such distillation operations account for very large percentage of total separation energy used in the petrochemical industry along with massive capital costs associated with large distillations columns and associated equipment.

In light of this scenario, alternative technologies to further improve extractions of olefins from mixed paraffin streams, as well as to facilitate other separations that are not viable with conventional distillation technology, are of keen interest to the refining and petrochemical industry. Facilitated transport membranes have been the focus of a significant amount of research due to the excellent performance and reasonable cost achievable in comparison to polymeric membranes or inorganic separation materials.

A research paper provides an overview of facilitated transport technology and its application towards olefin-paraffin gas separation (3). It highlights some background and theoretical principles regarding facilitated transport, effective parameters of the process, and some modeling equations, as well as a summary of results achieved from various research groups. The silver cation is commonly referenced, offering a most practical choice, as it provided the required complexation and reversibility and can be obtained at relatively low cost. In spite of many tabulated good performance separation and permeation values, no information is provided on reported or expected continuity or stability of operations.

Another good review on recent achievements in facilitated transport membranes acknowledges that while membrane separation processes have been extensively used for some important
industrial separations, substituting traditional methods in the process, some applications require the development of new membranes (4). Olefin/paraffin separation was cited as an example where it is advantageous to use a carrier species either in a liquid membrane or fixed in a polymer matrix to enhance both the flux and the selectivity of the transport.

A most thorough research on facilitated transport utilizing solid polymer electrolytes was that of Membrane Technology Research (5). The research focused on solid polymer electrolyte membranes. Extensive testing was based on a polyether-polyamide block copolymer doped with silver tetrafluoroborate, as well as other polymers, and various and mixed salts. Performance stability was the most prominent challenge, as performance deteriorated with time in as brief as a few hours in many cases. The study concluded that silver salt-based facilitated transport membranes, regardless of the polymer matrix used, were not stable even when exposure was limited to only ideal synthetic gas mixtures. The very species targeted for separation by the carrier membranes, olefins, were judged to be the source or cause of membrane instability.

Also significant were attempts with facilitated transport using liquid membranes, more commonly supported liquid membranes (SLMs). The advantages are high permeation rates and separation factors for many potential applications as well as offering the possibility of concentrating ions while making possible the use of expensive extractive materials as the quantities needed are small (6). However, limitations prevented the utilization of SLMs in commercial applications. Common drawbacks were the loss of carrier or solvent to either the feed or permeate phase, limitations in handling high pressure differentials, and degradation by emulsion formation which all caused instability over time (6,7). The recommendation was made that improvement in membrane materials and operating conditions were needed for the success of applying liquid membranes in commercial applications.

Recent approaches have suggested a combined or hybrid approach. Facilitated transport membranes were proposed, to replace distillation, by intensifying the conventional separation process in a modular compact and robust alternative in combination with the use of ionic liquids (8). The study evaluated various membrane contactors and supported ionic liquid membranes (SILM) as well as polymer/ionic liquid composite membranes.

Imtex has been further developing its facilitated transport olefin recovery technology, Permylene™. The Imtex Permylene process uses a flat sheet composite structure based on chitosan material and silver cations as facilitating agents. Chitosan is a linear polysaccharide that is produced commercially by the deacetylation of chitin, which is the structural element in the exoskeleton of crustaceans such as crabs and shrimp. Chitosan is cast into a uniform thin film,
becoming the active layer of the Permylene membrane. Chitosan is very hydrophilic and also has chelating properties with an excellent adsorption capacity for a number of metal ions such as the silver cation. A hydrogel is formed by exposing the chitosan to an aqueous solution containing silver ions. The silver ions present in the hydrogel membrane form reversible π-complexes with the double bonds in the olefin molecules. The olefin molecules are transported across the membrane under the influence of the olefin partial pressure differential between the feed and permeate sides of the membrane and are released on the low pressure permeate side. All gases without carbon-carbon double bonds are rejected. Separation is not dependent on the volatility of the species being separated and the separation factor is very high, allowing product olefin purities of 99.5% or higher to be routinely achieved in most applications.

The synthetic membrane, a unique liquid/solid membrane hybrid as schematically illustrated in Figure 1, presents a viable alternative to distillation in separating olefins from their respective mixtures with paraffins. The membrane structure can be balanced by the degree of deacetylation as well as by the silver loading level utilized. These aspects make chitosan an excellent base membrane for facilitated transport membranes. The patented (9) chitosan based hybrid structure addresses the aforementioned shortcomings of both liquid membranes and solid electrolyte membranes that have been experienced by many researchers.
Imtex Membranes Corp. has continued with the development efforts to evaluate and enhance the performance of the Permylene separation system in various olefin paraffin separation applications (10). Emphasis has been put on improving the continuity of the process, achieving excellent performance without interruption to the operations. Membrane stability is reflected in the repeatability of performance over hundreds of hours of pressurized and uninterrupted testing with spiral wound membrane elements. Some of the important recent studies and results are shared in this paper.
EXPERIMENTAL

The Permylene membrane used in this experimental work was comprised of chitosan material and silver ions from silver nitrate as a facilitation agent. Chitosan is a linear polysaccharide produced commercially by deacetylation of chitin. The membrane units used for these studies are spiral wound elements. Each spiral wound element used in this study had a nominal surface area of 1000 cm². The chitosan layer thickness is estimated to be between 2 to 4 microns. Gas streams analyses were performed using a Gas Chromatograph, Varian/Bruker model 450GC with FID, equipped with FactorFour capillary column VF-1ms 15M x 0.25MM ID DF=0.25. Hydrocarbon gases were obtained from Air Liquide. Both propane and propylene were chemically pure grade, with minimum 99.5% purity. Gas mixers employed Brooks mass flow meters and controls, models SLA5860S and SLA5850S. Silver nitrate, minimum purity 99.8%, was obtained from VWR. The tests were conducted with various olefin/paraffin feed compositions at various operating conditions. A fully automated test apparatus accessible through a human machine interface (HMI) and referred to as Imtex Mark III (Figure 2 and Figure 3) was used to conduct the continuous operation evaluations. Figure 4 is a simplified process flow diagram of the system.

FIGURE 2
Picture of Imtex Mark III
Automated Permylene Separation System
Continuous Olefin/Paraffin Separation with Permylene™ Facilitated Transport Membranes

FIGURE 3
A Screenshot of the Human Machine Interface (HMI) of Imtex Mark III

FIGURE 4
Simplified PFD of the Imtex Mark III Permylene Automated System
RESULTS AND DISCUSSION

In order to gain a more complete understanding of the Permylene membrane process, in particular for configurator process modeling, a series of tests were run comparing the permeate flow rate at different olefin feed compositions. Using a propane/propylene feed gas mixture, the feed propylene composition was varied between 30 -100% at 66 psig, while keeping the retentate flow rate constant at 2000 sccm. An increasing trend was observed for performance versus feed olefin content. Permeate purity values ranging from 99.4 % at a 50% feed composition, to 99.8 % at an 80% olefin feed were obtained. The relationship between membrane performance and feed composition can be seen in Figure 5.

FIGURE 5
Feed 30 to 100% C₃ at 66 psig and Room Temperature using a Spiral Wound Permylene Element
The Imtex Mark III Permylene automated system enabled around the clock testing of a spiral wound membrane element in separating a propylene/propane mixture having 60% propylene content. The test was carried out at 66 psig and room temperature with the hydrogel membrane being continuously hydrated. Permeate purity was typically around 99.5% to 99.6%, with a separation factor well over 100. While the number of hours at these conditions exceeded 1000, as shown in Figure 6, the membrane element was also part of various other tests conducted using the Imtex Mark III. The continuity and robustness of the Imtex Permylene process is reflected in the steady performance as shown. Combining the stable separation performance with the equally steady membrane permeability demonstrated in these tests has built strong confidence in the reliability and commercial viability of the technology.

**FIGURE 6**
Longer Term Testing of a Spiral Wound Membrane Element with Continuous Hydration
In another test, four small spiral wound membrane elements were installed in series in a single pressure vessel. Permeation and separation testing was performed with a propane/propylene gas mixture at 66 psig and room temperature. The feed content was 76% propylene while the retentate was found to be between 41 to 44% propylene. The test was un-interrupted for the duration of close to 100 hours with hydration provided continuously. Steady performance was obtained, as shown in Figure 7, with permeate purity staying in the range of 99.69% to 99.74%.

![Permeate Flow Rate vs Continuous Operating Time](image)

**FIGURE 7**
Feed 76% C₃= and Retentate 41 to 44% C₃=, at 66 psig and Room Temperature, using Four Spiral Wound Elements

In some C₃ applications, some breach of hydrogen can be as high as 10 ppmw for hours. The performance shown in Figure 8 was a test to probe the effect of such breach on Imtex membrane performance. A spiral wound membrane element was used for separating a 60:40 propylene:propane mixture at 66 psig and room temperature.
The feed mixture had a content of 50 ppmw hydrogen for a total period of about 74 hours. There was no visible effect on product permeation rate as shown in the many cycles, with and without hydrogen. Permeate purity remained over 99.7% propylene throughout the test.

Recognizing the importance of butenes/butanes separations, some probing testing was conducted with Permylene hydrogel membranes. As shown in Figure 9, a spiral wound element was used in testing the separation of 1-butene from a mixture with n-butane. Test temperatures were up to 65 °C while test pressures were up to 70 psig. Promising results were obtained with permeate purity ranging from 99.34% to 99.85% 1-butene. This opens the opportunity to pursue numerous very valuable applications with Permylene technology in areas where distillation may be very difficult or entirely unavailable.

FIGURE 8
Performance of a Spiral Wound Permylene Membrane with over 74 hours of Exposure to 50 ppm (w) Hydrogen in C₃ Gas Mixture. Permeation Rate is as Shown. Permeate Purity Remained Above 99.7%.

FIGURE 9
Feed Composition: 90% 1-Butene, 10% Butane | Permeate Purities: 99.34% – 99.85% 1-Butene
Figure 10 exhibits the effect on permeate flow rate (PFR) when the hydration solution flow rate (SFR) is set to 0 g/min with a pure propylene feed at 66 psig. A single spiral wound membrane element was used for this trial. Initially, the permeate flow rate increases as the hydrogel is wet and equilibrium is being established. Two hours into the trial, the permeate flow rate plateaus for about one hour. After this point, the permeate flow rate begins to linearly decrease. This is due to membrane dehydration occurring. The minimum flow rate observed in Figure 10 was approximately 760 sccm while the peak was at over 1000 sccm.

![Figure 10](image-url)

**FIGURE 10**
Pure Propylene Permeation trial Without Hydration
**Figure 11** shows the effect on permeate flow rate when running at 10 g/min solution flow rate with pure propylene feed at 66 psig. As the test started with solution flow rate at 10 g/min, it can be observed that the permeate flow rate increases to a maximum value of about 1070 sccm. Comparing Figures 10 and 11, it is evident that the permeate flow rate is more stable when the membrane is continuously hydrated. The permeate flow rate in Figure 11 remained relatively steady for the 6 hours at 10 g/min solution rate. In Figure 10, the permeate flow rate remains constant for only 1 hour before a significant decrease in the flow begins. When the solution rate was increased to approximately 30 g/min, the permeate flow rate further increased to approximately 1160 sccm. This confirms the capability of maintaining and increasing permeation rates by means of maintaining or altering hydration solution flow rate.

**FIGURE 11**
Pure Propylene trial with 10 to 30 g/min Hydration Rates
Likewise, the maintenance of performance with continuous hydration was confirmed with four Permylene membrane elements installed in series in a pressure vessel. As shown in Figure 12, pure propylene permeation is maintained at the same level for about 100 uninterrupted hours by employing continuous hydration concurrently with pressurized gas feed. The step changes shown reflect changing concentration or molarity of hydration solution according to the infrequent, once a day, water top up.

FIGURE 12
Pure Propylene trial Using Four Permylene Spiral Wound Elements with Continuous Hydration
Using a single small spiral wound Permylene element, a propylene recovery test was conducted at 66 psig and room temperature. In Figure 13, the trial began with the 80/20 propylene/propane feed. The initial recovery was only approximately 25%. Half an hour into the run, the retentate flow rate was decreased to 600 sccm. As a direct result, the recovery doubled to a value of 50%. After 100 minutes of run time, the solution flow rate was decreased from 39 g/min to 0 g/min. The recovery then increased by approximately 15% to an approximate value of 65%. Decreasing the retentate further from 450 sccm resulted in the recovery increasing to a value of nearly 80%. This is a reasonably good recovery considering the experimental limitation of using a single small spiral wound membrane element with a short, about 10 cm length, along the feed side.

**FIGURE 13**
Propylene Recovery Tests with Varying Retentate and Solution Flow Rates
IMTEX PERMYLENE CONFIGURATOR

The driving force for olefin permeation can be reasonably expressed by the olefin partial pressure differential between the feed and permeate sides of the membrane. Based on this differential partial pressure, and verified through some probing experiments, more recovery is achievable up to the extent at which these partial pressures become equal. At that point the achievable actual recovery would equal the theoretical maximum recovery. Higher feed pressure, higher olefin content in the fresh feed, and lower permeate olefin partial pressure are all helpful factors towards achieving better recoveries. A handy tool that makes use of variables like these and others including total feed flow rates, and sizes a membrane system to achieve a certain performance, is referred to as the Permylene Configurator. The Configurator makes use of the inputs and estimates and summarizes the performance of a Permylene system including providing the calculations around individual modules that are operated in series. It is a useful practical tool for assessing the suitability and performance of Imtex Permylene technology for any application under consideration.
1-BUTENE / I-BUTANE SEPARATION

Below is a comparison between distillation and a hybrid distillation / Imtex Permylene membrane system. The Permylene system is used for recovering 1-Butene (replacing a 60 kta B1 column). Configurator calculations and summary output is shown in Figure 14. A schematic of the process is shown in Figure 15. In consultation with industry experts, actual return costs of the a 60 kta 1-Butene column are included in Table 1 where the Permylene membrane system is compared in terms of CAPEX, energy and equipment weights. Due to the compactness and modularity of the efficient gas-phase Permylene process, significant benefits are realized as shown.
Continuous Olefin/Paraffin Separation with Permylene™ Facilitated Transport Membranes

FIGURE 15
Schematic of B1 and B2 Distillation and Hybrid Separation Process

<table>
<thead>
<tr>
<th>Process Scheme</th>
<th>CAPEX (MM$)</th>
<th>Heating Duty (MMKcal/hr)</th>
<th>Cooling Duty (MMKcal/hr)</th>
<th>Equipment Weight, Dry (t)</th>
</tr>
</thead>
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<tr>
<td>Distillation</td>
<td>16.4</td>
<td>8.08</td>
<td>9.20</td>
<td>228</td>
</tr>
<tr>
<td>Membrane</td>
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<td>0.67</td>
<td>1.27</td>
<td>45</td>
</tr>
<tr>
<td>Benefit</td>
<td>&gt; 75%</td>
<td>&gt; 90%</td>
<td>&gt; 85%</td>
<td>80%</td>
</tr>
</tbody>
</table>

TABLE 1
CAPEX, Energy and Equipment Weights Comparison
CONCLUSION

Significant advancements have been made to Imtex's Permylene membrane technology since it was first introduced to the EPC in a paper presented in 2013. Further validation of its excellent selectivity and permeability with strong stability over extended periods of operation was achieved across a broader range of applications. This further strengthens the contrast between the performance of Permylene technology and the stability shortcomings seen in prior attempts to use facilitated transport membranes for olefin/paraffin separation. Permylene technology has undergone an important transformation from being a semi-batch process where hydration maintenance of the membrane periodically needed to be done offline. The technology now operates in a fully continuous manner with membrane hydration maintenance taking place concurrently with hydrocarbon separation. This breakthrough has improved the applications simplicity, operational efficiency, performance consistency and general market acceptability of the Permylene membrane technology.

Permylene technology is applicable to several petrochemical production scenarios such as: olefins production from cracking, olefins recovery from purge streams, on-purpose propylene or butenes production, recovery of byproduct olefins from oil refining and upgrading and specialty chemicals production. Benefits that can be realized include: lower capital and operating costs than conventional distillation, reduced environmental emissions, recovery of valuable olefins from waste streams, olefin stream value upgrading and new product opportunities.

Imtex is working with several petrochemical companies on specific applications where Permylene technology could be beneficially deployed. Pilot demonstration systems with either small scale or full commercial size membrane elements will be installed to assess the technology prior to commercial deployment in those applications. Some early stage commercial system deployments are also being discussed. Imtex is also actively seeking collaboration opportunities with other industry technology providers where complimentary technology may exist, or where commercial marketing and deployment partnership opportunities are present.
ACKNOWLEDGEMENT

Imtex Membranes Corp. gratefully acknowledges the financial support that has been provided by the Industrial Research Assistance Program (IRAP) of the National Research Council of Canada, Sustainable Technology Development Canada (SDTC) and the Innovation Demonstration Fund (IDF) of the Ministry of Economic Development and Innovation of Ontario to enable the development and advancement of Imtex membrane technology. Imtex also acknowledges the financial support of Monteco Ltd.

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