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 the 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 HAS DEVELOPED** a membrane separation process 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 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, Imtex membrane technology is presented as a practical alternative to the costly distillation approach.

This technology can be applied in commercial applications such as ethylene production, 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. The technology is also particularly effective 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 beneficial applications. Extended tests have been performed at Imtex to verify the stability and continuity of operations relevant to these applications. Performance results are presented.
BACKGROUND

Olefin and Polyolefin production is a hundred billion dollar business globally. For many decades, distillation has been the separation process for recovery of purified olefins from mixtures with their respective paraffins. A recent U.S. Department of Energy study indicated distillation operations account for 95% of the total separation energy used in the refinery and chemical processing industries with 40,000 distillation columns operating in over 200 different processes. Another study stated that olefin production is the single most energy consuming process in the chemical industry. The breakdown of the specific energy consumption shows that 30% of the total yearly energy consumption is associated with separation processes and 80% of that energy is utilized for olefin/paraffin separation. This large energy requirement provides an incentive to improve the energy efficiency in olefin/paraffin separation. Furthermore, due to the difficulty of achieving these separations, the distillation columns are often very tall, involving many trays, leading to high capital costs for the equipment.

In light of this, alternative technologies continue to be the focus of industrial research and development. For example, reactive absorption where silver or copper salts are used to extract the olefin from mixed gas in an absorber/stripper process was attempted by Union Carbide and BP/Stone and Webster. Other processes that have been evaluated include extractive distillation and molecular sieves.

One of the most thorough research studies was carried out in a DOE sponsored program led by Membrane Technology and Research, Inc. (MTR), in partnership with SRI International and ABB Lummus Global. The research focused on solid polymer electrolyte membranes. Performance stability was the most prominent challenge. There was clear deterioration of performance with time, seen in periods as short as a few hours. 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 olefin/paraffin mixtures. They attributed the issue to a previously unrecognized phenomenon labeled as “olefin conditioning” implying that the very species targeted for separation by the carrier membranes (olefins) were a source of membrane instability.

Despite these and other endeavors, a viable and reliable alternative to conventional distillation had yet to be developed.
IMTEX MEMBRANE TECHNOLOGY

Imtex has successfully developed a chitosan-based synthetic membrane technology that separates olefins from paraffins and other gases. This patented technology addresses the shortcomings of the aforementioned approaches, including the avoidance of the damaging “olefin conditioning” phenomenon, even when operated over much longer periods.

Olefins are characterized by their carbon-carbon double bond. In the presence of an olefin containing feed stream, an olefin-Ag+ π-complex forms on the feed side of the membrane, migrates through the gel structure of the membrane towards the lower concentration side then de-complexes on the permeate side. Paraffin and other molecules that contain no double carbon-carbon bond are rejected.

Imtex has developed spiral wound membrane elements for use in test and commercial applications. Figure 1 is a photo showing various sizes of rolled test elements and a full size commercial scale element.

MEMBRANE PERFORMANCE AND STABILITY

Excellent separation is achieved over a wide range of olefin content in feed gas mixtures. Figure 2 shows the performance of Imtex membranes as a function of ethylene content in an ethylene/ethane feed mixture.

The membrane was also successfully tested over an operating pressure range applicable to typical C2 splitter conditions. The membrane demonstrated higher permeation rates at higher pressures with very small decrease in the selectivity. Figure 3 shows the membrane performance over an operating feed pressure range between 60 and 360 psig.
All of the results from testing under typical C$_2$ and C$_3$ splitter conditions were encouraging, achieving 99.5% purity of ethylene and propylene at very high olefin recovery levels.

**Figure 2:** Separating Ethylene/Ethane Mixtures at 66 psig and Room Temperature Using a Imtex Spiral Wound Membrane Element.

**Figure 3:** Feed 85/15 Ethylene/Ethane Mixtures at room temperature and various pressures.
Figure 4 shows the performance of the Imtex membrane for both C₂ and C₃ applications. The greater molecular weight of propylene drives a higher mass flow rate.

![Figure 4: Separation of C₂s and of C₃s with Imtex Membrane.](image)

Imtex membranes were also tested in separating C₄s. Initial testing was conducted with gas mixtures of 1-Butene/n-Butane at 40 psig and a temperature of 40 °C. As shown in Figure 5, n-butane content in the permeate stream was between 0.1 to 0.3%. C₄ olefins permeability is even higher than ethylene and propylene. Further C₄ testing at temperatures up to 65 °C was recently performed and the findings were very encouraging. This has opened the door to applicability in several practical commercial applications.

Imtex membrane elements have been subjected to testing for extended periods, covering hundreds of hours to verify stability and show performance after long term use. Figure 6 shows repeatable excellent performance of a spiral wound module tested for over 1500 hours. The membrane has consistently achieved over 99.5% olefin purity. Combining this excellent stable separation performance with the equally important high olefin permeability has built strong confidence in the commercial viability of the technology.
CONTINUOUS OLEFIN SEPARATION AND PERMEATION

The most significant recent advancement of the Imtex technology has been the successful development of the continuous mode of operation with pressurized gas. To maintain peak membrane performance, it is no longer required that a membrane module be taken...
off-line periodically for rehydration. This continuous mode of operation has been extensively tested and is now an integral component of the standard operating process. Membrane rehydration is now achieved concurrently with optimal gas separation and permeation. Hundreds of test hours have been logged on various spiral wound membrane elements validating the stability of this continuous mode of operation. An example of the tests can be seen in Figure 7 below.

Figure 7: Feed 76% C3= and Retentate 41 to 44% C3= 66 psig and room temperature, using four spiral wound membrane elements.
FIELD DEMONSTRATION READINESS

Imtex is currently operating a fully automated Bench Scale System (BSS) in our R&D facility which incorporates Imtex’s continuous mode of operation. The BSS design is also intended for field demonstration purposes and is easily replicated for operating site deployment. The BSS is a self-contained, fully documented unit encompassing all aspects of the Imtex process, including controls and safety systems, ready for installation at any site. Below are photos of the BSS which can be equipped with a membrane element of a size suitable for feed flow of 0.1 to 3 kg per hour. Fully controlled through a PLC, the system is operating on round-the-clock basis and is equipped with a data logging historian.

Figure 8 (left): The Automated Bench Scale System (BSS). Figure 9 (right): Human Machine Interface (HMI) of BSS.
A higher capacity system is also available to demonstrate the technology at higher flow rates through the use of standard commercial-scale membrane elements. This Pilot Demonstration System (PDS) is shown in Figure 10.

**COMMERICAL SYSTEM DESIGN**

The Imtex membrane system commercial design takes a modular approach to accommodating various production capacities. The fundamental building block is the membrane element. Membrane elements are combined in series within pressure housings called Modules in quantities of 5-10 per vessel. Modules are combined in groups of 3-8 in a structural frame in units called Cassettes. Commercial systems consist of one or more cassettes sharing all required ancillary equipment. An example is shown in Figure 11.
APPLICATIONS AND BENEFITS

The breadth of olefins applications in the refining and petrochemicals industries is extensive. Prominent applications include:

» Olefins production from cracking
» Olefins recovery from purge streams
» On purpose propylene and butenes production
» Oil refining and upgrading
» Speciality chemicals

The benefits that can be derived from deploying the Imtex membrane technology in these application areas vary based on the specific characteristics of the existing processes and target markets. Some of these benefits are:

» Lower Capital Cost (CAPEX) - relative to distillation
» Lower Energy Cost – relative to distillation
» Reduced Environmental Impact from Emissions
» Recovery of Valuable Olefins from Waste Streams
» Olefin Stream Value Upgrading
» New Product Opportunities

CONCLUSION

In addition to excellent selectivity and permeability, Imtex membranes demonstrate performance stability over time. The key shortcomings in prior attempts to use alternative separation technologies, including other facilitated transport membranes, in olefin/paraffin separation have been overcome.

Imtex is in a position to demonstrate the membrane technology in industrial olefins applications. Imtex can readily provide Bench Scale Systems (BSS) and Pilot Demonstration Systems (PDS) for field deployment.

Imtex continues to be active with a number of operating companies evaluating their specific requirements and devising appropriate process integration strategies. Imtex welcomes the opportunity to evaluate other applications with the potential to realize significant benefits.
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