Development and Applications of Custom Amorphous Fluoropolymers (CAF)

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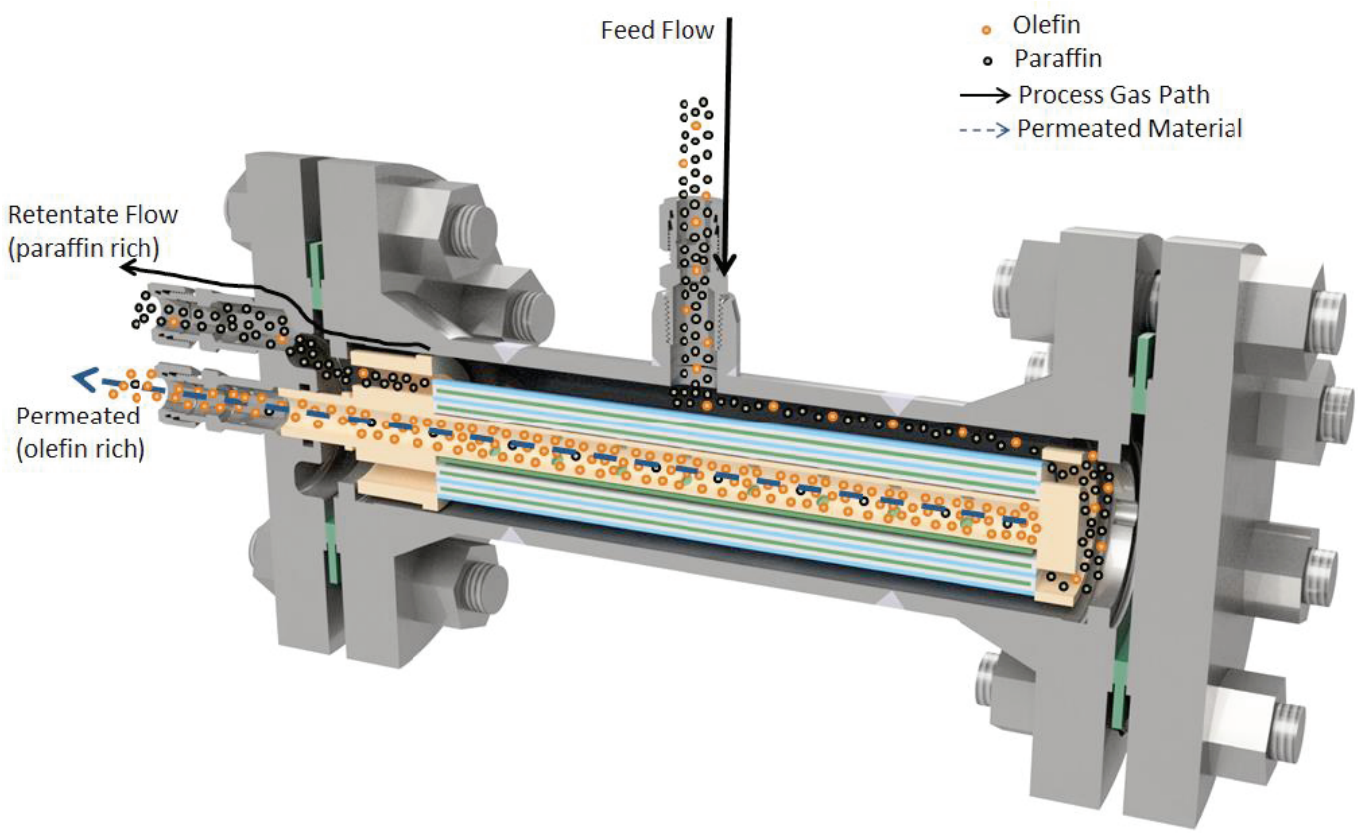
BACKGROUND

Ethylene and propylene are the major chemical industry raw materials and consume a great deal of energy during production. The separations of these materials are some of the costliest, most energy intensive, and most technically difficult separations in the industry. The technology currently employed for the separation of ethylene and propylene from paraffins is distillation and is estimated to consume 250 trillion BTU/year of energy. A membrane based olefin-paraffin separation technology has the potential to provide substantial economic benefit to petrochemical industry and drastically reduce the energy required. Membrane processes utilizing facilitated transport membranes have been extensively studied for separating olefin/paraffin mixtures. While separations have been demonstrated in the laboratory, problems with membrane stability have prevented development of commercial systems..

Keywords: custom amorphous fluoropolymers, olefin/paraffin separation, chemical/thermal stability, high olefin selectivity & flux

1 MEMBRANE TECHNOLOGY

Compact Membrane Systems (CMS) has developed OptipermTM membrane, a customized amorphous fluoropolymer (CAF) containing silver ions that selectively transport olefin molecules from a mixture of olefin and paraffin. CMS Optiperm membranes are based on a silver-containing fluoropolymer material. 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 as depicted in the cartoon below. 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 do paraffins.



The two key membrane properties that characterize the effects of facilitated transport are **permeance** and **selectivity**.

- **Permeance** is defined as the rate at which one component travels through a given surface area of membrane for a given driving force. This performance metric is typically expressed in GPU (gas permeation unit). Optiperm membranes have olefin permeances greater than 150. This translates into a propylene flux of 0.25-0.85 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. 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

The Optiperm membrane has both high permeance and high selectivity, meaning high purities can be reached with a reasonable membrane area. These characteristics yield very attractive process economics.

The membrane can perform separations of olefins from paraffins at a wide range of temperatures, pressures, and compositions. CMS has demonstrated olefin removal at temperatures up to 70°C (158°F) and pressures up to 250 psig. For an efficient separation to occur, the olefin-paraffin mixture must be in the gaseous state. Separation performance requires humidification as water vapor improves the mobility of the olefin through the membrane. The membrane can remove olefin in both concentrated and dilute streams for compositions ranging 5-95% by volume of olefin. The membrane can process mixtures of C2, C3, and C4 olefin and paraffin. Typical lab evaluations involve exposing the membrane to a stream of fixed pressure, temperature, and composition. The chart displayed on the next page shows a performance profile for a membrane separating a 20% propylene/80% propane mixture at 60 psig and room temperature. The membrane has shown stable performance over >9 months, a vast improvement over current state of the art materials.

A broad range of tests have been conducted to characterize the membrane resistance to common poisons in refinery gas streams. These include testing under conditions such as 5% hydrogen or 500 ppm acetylene. We have seen good resistance to both hydrogen and acetylene from the Optiperm membranes. Based on our testing, we recommend process streams contain:

1. <100 ppm acetylene
2. <2% hydrogen
3. <100 ppb total sulfur

We generally include a sulfur pretreatment unit operation as part of the full membrane upgrading system to eliminate the concern that sulfur will detrimentally affect membrane lifetime.

2 MEMBRANE PRODUCTION AND SCALE UP

CMS is currently scaling up manufacturing to meet expected demand for the Optiperm membrane. These scale up activities include membrane module scale-up, supply-chain diversification, QC development, procurement of large scale coating equipment and expansion of manufacturing space. An example of a prototype Optiperm spiral wound membrane is shown below

This work will allow CMS to be producing its Optiperm membrane at significant quantities by 4Q 2017.

3 PILOT TESTS

We are working with numerous players in oil and gas and petrochemical spaces. Several interested parties have requested on-site evaluation of the Optiperm membrane. Our relationship with Delaware City Refining Company (DCRC) has led to a scheduled pilot system launch in May of 2017. The unit will provide real-world evidence of membrane stability in realistic conditions validating our laboratory testing. Overall the project will confirm the technical and economic viability of a full scale system. Tests will be conducted over 6 months during which time the skid will operate autonomously save for regular sampling and maintenance.

The main features of the system:

- Data acquisition system constantly monitors pressure, temperature, flow, humidity, and alarm status
- Coriolis mass flow control and measurement equipment ensures accurate evaluation membrane performance
- Glycol heating system maintains uniform temperature in unit plumbing and equipment
- Humidification vessel keeps process gas saturated with water vapor to optimize membrane performance
- Alarms for high and low temperature, flow, oxygen content, and flammable gas content
- Quick disconnect sample ports allow operators to quickly take gas samples