Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Facilitated Transport Membrane Hybrid Systems for Olefin Purification

James C. Davis[a]; Ronald J. Valus[a]; Reza Eshraghi[a]; Alex E. Velikoff[a]
[a] BP Research Warrensville Research and Environmental Science Center, Cleveland, Ohio

To cite this Article Davis, James C. , Valus, Ronald J. , Eshraghi, Reza and Velikoff, Alex E.(1993) 'Facilitated Transport Membrane Hybrid Systems for Olefin Purification', Separation Science and Technology, 28: 1, 463 — 476
To link to this Article: DOI: 10.1080/01496399308019500
URL: http://dx.doi.org/10.1080/01496399308019500

SEPARATION SCIENCE AND TECHNOLOGY, 28(1-3), pp. 463-476 (1993)

FACILITATED TRANSPORT MEMBRANE HYBRID SYSTEMS FOR OLEFIN PURIFICATION

James C. Davis, Ronald J. Valus, Reza Eshraghi, and Alex E. Velikoff
BP Research
Warrensville Research and Environmental Science Center
4440 Warrensville Center Road
Cleveland, Ohio 44128-2837

ABSTRACT

A new membrane system has been developed by BP for refinery and chemical plant olefin purification and recovery. This facilitated transport system, coupled with distillation, offers lower capital and operating costs than conventional distillation alone. Initial results on lab scale hollow fiber devices indicate membrane flux ranging from 8.75×10^{-6} to 8×10^{-5} $m^3/m^2/sec$ (2.5 to 23 $scfd/ft^2$) and selectivities from 150 to 300. Pilot plant experiments on propylene/propane and ethylene purge gas recovery over three to six months duration show membrane stability and product purity of 98.5% or greater using refinery grade propylene feed. Hybrid system optimization data for membranes and distillation indicate that using a side draw from the distillation tower provides advantages in terms of membrane area, purity of feed to the membrane, and low per-pass recovery coupled with high overall propylene recovery. Membrane performance data under various conditions will also be presented. In addition to performance data, economic evaluation and energy savings will be discussed.

TABLE 1. OLEFIN SEPARATIONS MEMBRANE RESEARCH

Source	Membrane	Results	Ref.
GE	Ion Exchange	Low Flux	3
Amoco	RO - DOW CA	Better Flux, But Weak	5
Kyoto Inst.	Microporous PP	Low Pressure Capability	6
Monsanto	Hollow Fiber	Used Non-AQ Solvent	7
	Low Selectivity/Flux		

INTRODUCTION

Facilitated Transport membrane processes have been known for many years and widely researched, particularly for oxygen purification from air. An excellent review of the general area is the work of Kimura, et al. in Recent Advances in Separations Science.(1) Olefin FT membranes are also known although far fewer references to working systems are available. (See Table I for example.) Silver ion has been used exclusively in these systems since first disclosed by Hughes, et al. in several patents issued in the 1970's.(2) All of the systems operated at low transmembrane pressure, typically using a sweep gas to reduce partial pressure of the olefin in the permeate stream.

Ion exchange membranes were first proposed by LeBlanc, et al. in 1980.(3) This group at GE used Nafion@ and other cation exchangers loaded with silver ion for olefin separation from non-olefins. Several other research groups have worked on these systems with Yahnke at Amoco reporting in 1977 a system where he trickled a stream of silver ion solution down the outside of hollow fibers to keep the liquid in the membrane pores.(4) He was also limited to low transmembrane pressures and used a sweep gas. Although many of the systems in the literature worked in the laboratory, only one is described as having been tested at pilot scale.

Hughes, Mahoney, and Steigelmann reported the use of cellulose acetate hollow fiber membranes as liquid membrane supports for silver solutions used for the separation of propylene from nitrogen.(5) The membrane used was asymmetric, with a thin, dense skin designed for reverse osmosis and sold by the Dow Chemical Co.

as an RO-4K permeator. Although operated at high feed pressure, the transmembrane pressure was low and a sweep liquid of hexane was use to remove the permeated propylene (and to balance the high feed pressure). Permeation rates were relatively low with flux in the $7x10^{-6}$ to $1.4x10^{-5}$ m^3/m^2-sec (2 to 4 scfd/ft^2) range. Many other references to olefin FT membrane systems are in the literature but all are substantially similar to those mentioned.(6,7)

The Challenge

To be successful in operation in a refinery in conjunction with a propylene splitter, a membrane system capable of operating at splitter pressure and temperature is highly desirable. Typically, pressures and temperatures on the order of 15 bar and 45°C. are encountered. Other characteristics required are chemical resistance to trace contaminants in the feed propylene, long membrane life, and reliable operation. It would also be preferable to avoid a sweep gas since that requires an additional separation step. Sustainable flux of $1.75x10^{-5}$ m^3/m^2-sec (5 scfd/ft^2) is as reasonable target for economical application.

The High Transmembrane Pressure Conundrum

Much of the data available to date on this separation using FT membranes reports the use of either ion exchange membranes or microporous membranes (Table II). In the case of the ion exchange membranes, even though they will withstand substantial transmembrane pressure, studies in our laboratory showed that at substantially higher transmembrane pressures the membrane flux was not much higher than that at lower pressures. The microporous membranes suffer from a low bubble point due to the pore diameter and only moderate transmembrane pressures can be tolerated without forcing the liquid out of the pore. As demonstrated in the work of Hughes, et al.(5), cellulosic membranes are severely weakened by the silver nitrate solution. As a result the transmembrane pressure Hugh's membrane could withstand was substantially reduced. This is a common problem, many polymers either swell or dissolve in strong transition metal ion solutions. Hence, all of the olefin FT membrane systems either can't operate at the required transmembrane pressure or exhibit no advantage in doing so.

TABLE 2. MEMBRANE FLUX AND SELECTIVITY

Source	Conditions	DP	Flux	Selectivity	
		bar	m^3/m^2-sec		
Teramoto	N_2 sweep, polypro MF membrane FT solution flow between films	0	2.8×10^{-7}	20	(6)
Amoco	CA RO membrane, hexane sweep high feed pressure - balanced	low	1.7×10^{-5}	100	(5)
BP	Nafion 117, 1 barg feed He sweep on permeate side	1	7.7×10^{-6}	300	*
BP	Nafion 117, feed = 12.1 bar no sweep	11.1	1.4×10^{-5}	80	*

* This study

An additional problem associated with operation at high pressure is the tendency for the membrane to dry out extremely rapidly when the transmembrane pressure is high. It is impossible to provide enough water in the feed to make up the losses on the permeate side if a water saturated sweep is not used. For example, if the feed pressure is ten times that of the permeate, the permeate will be only 10% saturated unless water is withdrawn from the membrane to bring the permeate to near saturation. Clearly, the higher the membrane flux, the shorter the lifespan of the liquid layer becomes under these conditions.

How then, can research and development provide the necessary membrane system high flux, high selectivity, long membrane life, and a robust separation system capable of meeting the petrochemical industry's needs? From the work that has already been discussed, it is clear that a somewhat different approach will be necessary. The work using a reverse osmosis membrane was intriguing but the flux was too low and the membrane was too weak to meet our requirements. A study of several different ion exchange membranes strongly indicated that, for the system and conditions targeted, flux was essentially flat for pressure differentials above 3 bar. All other membrane materials were found to either swell or dissolve completely in silver ion solutions as low as 1 M.

A poly(sulfone) based membrane with reasonable flux (> 2×10^{-5} m^3/m^2- sec) was found and suitable hollow fibers obtained to allow further study. At that point, long term runs at high transmembrane pressures (10 bar and higher) indicated that water loss from the membrane caused failure within a week of continuous running. Two methods were developed to improve membrane life - recirculation of permeate through a water saturator and back through the permeate side of the module, and recirculation of the silver nitrate stream through the permeate side of the module on an intermittent basis or continuously (Figures 1 and 2). The latter method is similar to the work of Cussler and Qi on gas/liquid membrane contactors.(8) A principal difference between this work and Cussler's is the use of a membrane capable of withstanding high transmembrane pressure without the loss of facilitator fluid.

EXPERIMENTAL METHOD

A membrane module made from isomorphous cellulosic hollow fibers was prepared by using epoxy to pot 90 fibers into an eight inch long, 1/4 inch diameter stainless steel tube as described previously(9). The fibers were obtained from a CD Medical hemodialyzer with a nominal molecular weight cutoff of 5000. The active length of the fibers was 14 cm and the fiber i.d. was 212 microns. The calculated surface area was 87 cm^2 based on the i.d. since the fiber was fed from the inside of the bore. 2$\underline{M}$ Silver nitrate solution was fed into the fiber and allowed to stand for 30 minutes and then drained. A mixture of 13.8% ethylene, 14.0% ethane, and 72.2% helium was saturated with water at 8.4 bar and 25^o C. and fed to the bore side of the membrane. A mass flow controller was used to determine the amount of reject gas exiting the bore of the fibers. The amount of permeate gas was measured using a mass flow meter and the gas analyzed on a Carle GC designed for separation of refinery gases. In experiments with vapor recycle, a peristaltic pump set at approximately 20 times the permeate rate was used to pump permeate through a water saturator and back into the module, insuring a near saturated vapor on the permeate side of the membrane.

Subsequent experiments were performed with ion-exchange membranes and polysulfone membranes using similar modules and feeds. In the thermal cycle experiment, 3$\underline{M}$ silver nitrate solution was recirculated at 7 cc/min and 6.7 barg

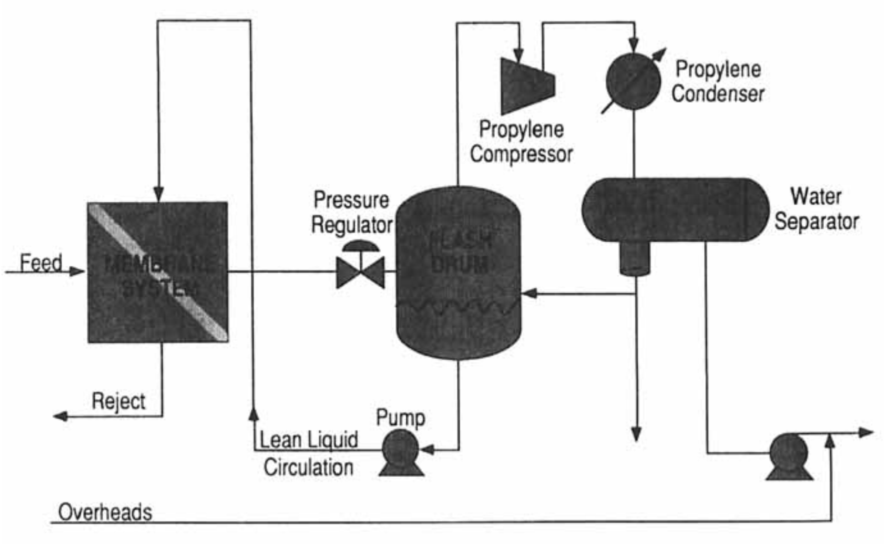


FIGURE 1. Liquid Facilitator Recycle FT Membrane System

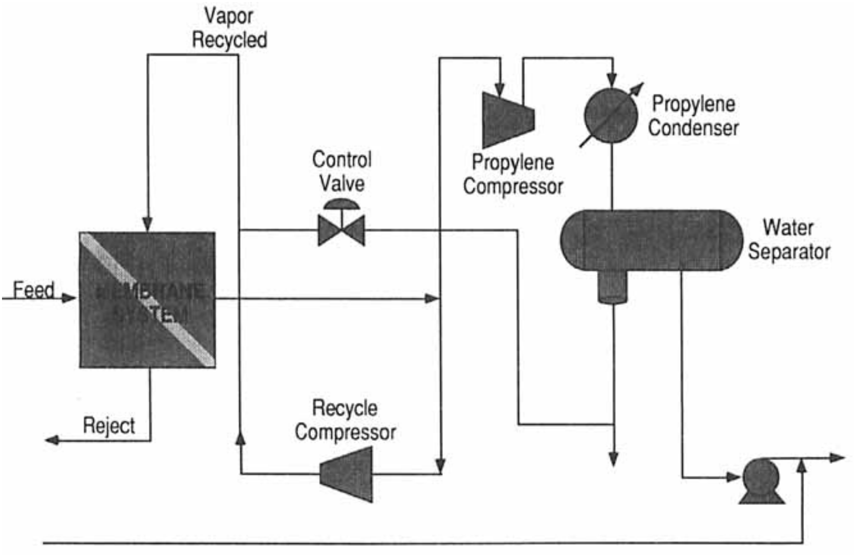


FIGURE 2. Liquid Recycle FT Membrane System

through the bore of the fibers. The feed in that case was 70% ethylene and 30% nitrogen - the olefin permeate was recovered at 3.4 barg and varying flash drum temperatures from 30 to 90° C.

An additional method of operation was developed to eliminate or reduce the need for a compressor on the permeate side of the membrane. This technique, thermal cycle, consists of heating the loaded silver nitrate solution exiting the membrane prior to the flash drum and operating the silver nitrate stream at higher pressure. The result is an equlibrium shift releasing olefin from the silver nitrate which is then cooled and returned to the module for reloading with olefin.

RESULTS

Use of the recycle system has allowed high transmembrane pressures with concomitant increases in flux under standard operating conditions such as 14.1 barg feed and 0.7 barg permeate at 45°C. Selectivities of 150 to 300 for propylene over propane have been achieved using refinery grade propylene (~70% pure) as the feed. Permeate purities have typically been 99.5%. Membrane flux varies from 4.2×10^{-5} to 8.75×10^{-5} (12 to 25 scfd/ft^2) depending upon the operating conditions. These values for flux and selectivity are suitable for commercial installations upgrading refinery grade propylene to either polymer or chemical grade. Table III illustrates values for propylene and ethylene separations with membranes as noted.(11)
3M Silver nitrate flow through the fibers was 11 cc per minute, module temperature was 20° C., and the membrane module was 67 cm^2 for the thermal cycle experiments.

Process Engineering Aspects

Obviously, having a membrane with the appropriate selectivity, life, and flux is an essential but insufficient answer to the problem posed earlier. It does not answer the question of where to apply the membrane for the maximum benefit. SRI has produced a report for DOE in which a propane dehydrogenation crude product purification was studied using a hypothetical membrane in combination with a C3 splitter(10). Our problem is somewhat different in terms of the feed concentration

TABLE 3. RESULTS OF HIGH PRESSURE OLEFIN SEPARATIONS

Source	Conditions	DP bar	Flux m^3/m^2-sec	Selectivity
BP	PSO Membrane - 14.1 barg Feed = 70% Propylene 30% Propane	6.2	$4.2\mathrm{x}10^{-5}$	200
CD	Cellulosic - 7.05 barg Feed = 13.8% Ethylene 14% N_2 balance helium	7.4	$9\mathrm{x}10^{-5}$	150

THERMAL CYCLE EXPERIMENTS

Temp (Flash)	Conditions	DP	Flux	Selectivity
30° C.	PSO Membrane - 10.1 barg	6.7	8.9	150
50	same	6.7	14.9	180
70	same	6.7	22.0	180
90	same	6.7	23.0	300

and the membrane performance but the approach is similar. Obviously there are three places one can easily envision operating a membrane system in conjunction with a splitter: on the feed to enrich the tower feed, on the overhead to increase product purity, or (as SRI proposed) on the bottoms to recover propylene normally lost with the propane (Figure 3).

In examining the alternatives, a less obvious option was discovered. By positioning the membrane such that it is fed by a side draw or from the overhead reflux loop of the tower (Figure 4), several new options and advantages were discovered. For example, the reject stream from the membrane can be returned to the tower at the point where the vapor composition is the same as the vapor in the tower, thus reducing the overall impact on tower operation. In addition, the reflux ratio on C3 splitters is usually quite high so the membrane can be operated at relative low per pass recovery

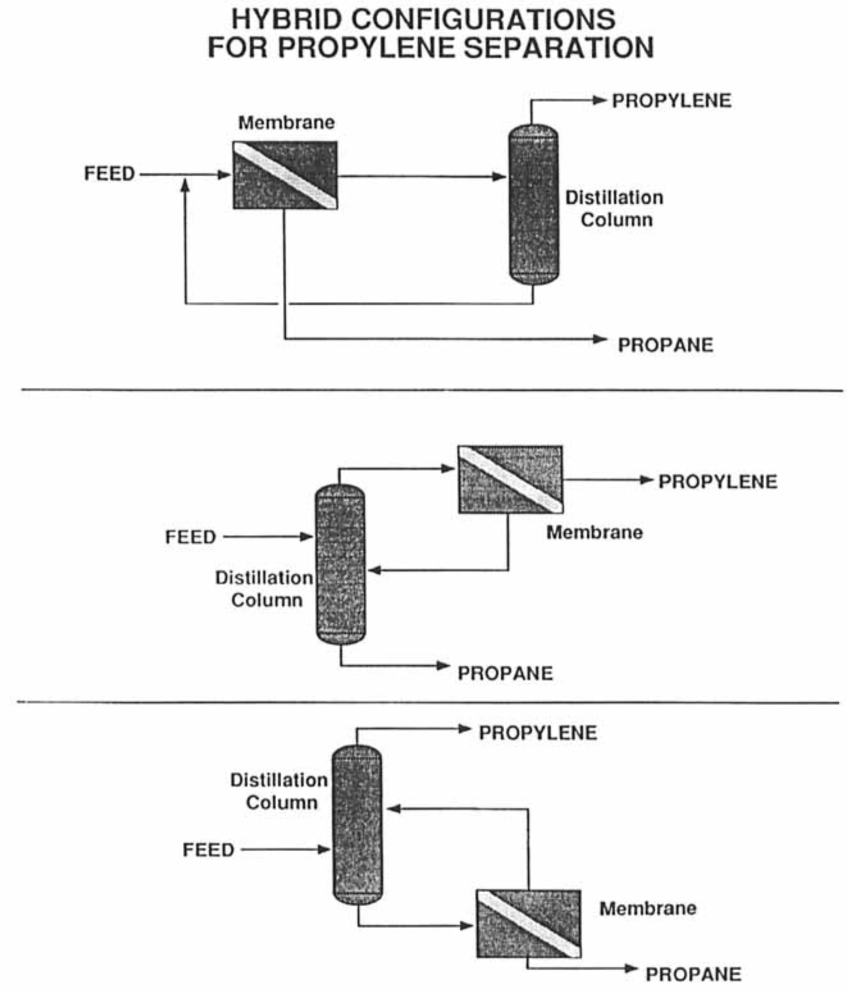

HYBRID CONFIGURATIONS
FOR PROPYLENE SEPARATION
PROPYLENE
Membrane
FEED
Distillation Column
PROPANE
PROPYLENE
FEED
Membrane
Distillation Column
PROPANE
PROPYLENE
Distillation Column
FEED
Membrane
PROPANE

Figure 3

PROPANE/PROPYLENE SEPARATION MEMBRANE PROCESS

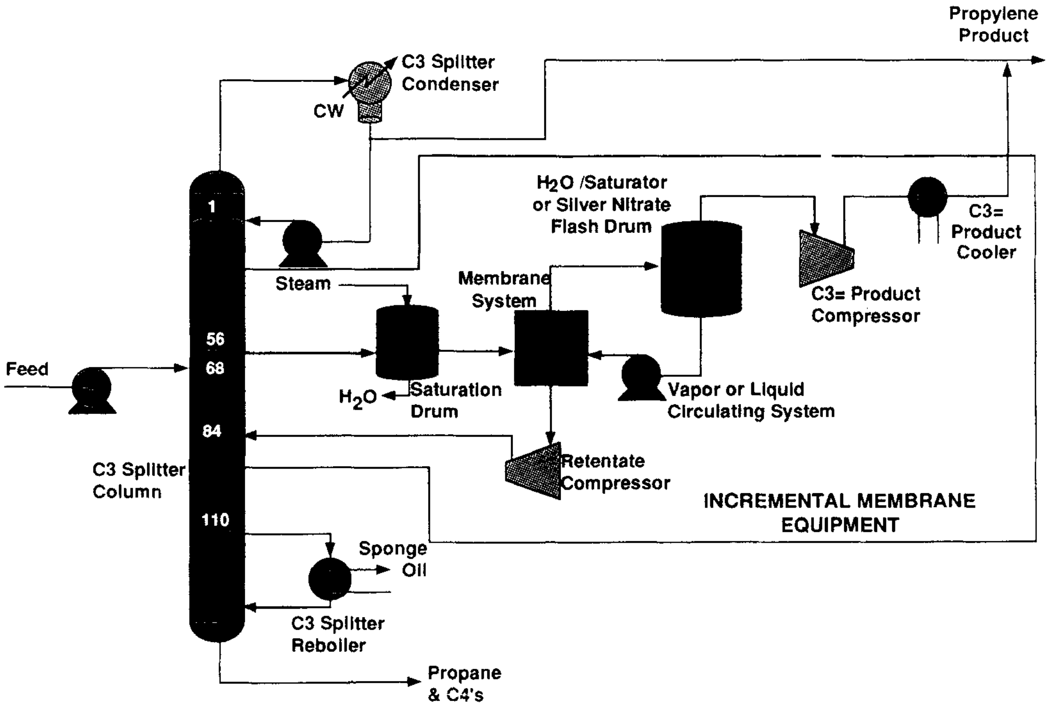
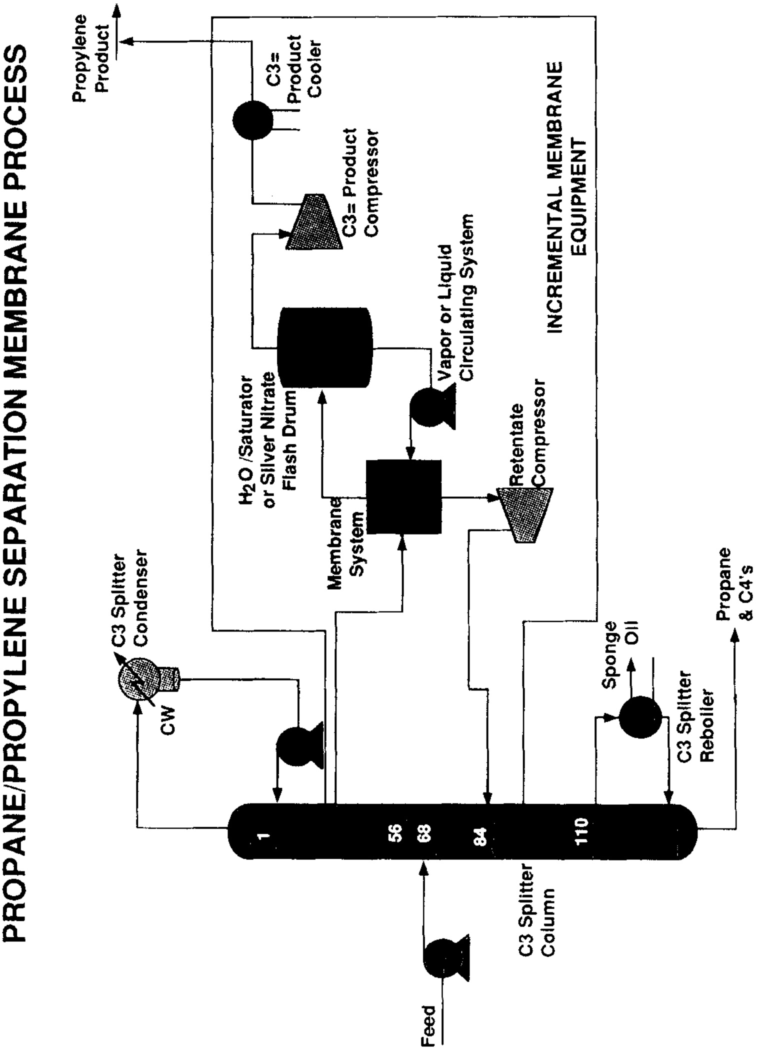


Figure 4



PROPANE/PROPYLENE SEPARATION MEMBRANE PROCESS

Figure 5

TABLE 4.
EXPECTED SAVINGS USING MEMBRANE/SPLITTER HYBRIDS

Purity	Scale	Energy	Capital	Operating
Chemical[1]-95%	1850 bbl/d	150×10^9 BTU/yr	50%	50%
Polymer[2]-99+%	10,000 bbl/d	500×10^9 BTU/yr	17-23%	8%

[1] Debottlenecking existing splitter from 3000 bbl/d feed to 4800 bbl/d.
[2] Grassroots facility including offsites equivalent to 43% of capital.

without the usual penalty. Hence, the system is operating under the most favorable conditions for membranes - low recovery and relatively high feed purity. An additional advantage is the placement of the draw above the feed tray, resulting in a "purified feed" with far fewer of the undesirable components which may react with the silver ion.

While generating substantial advantages in operation of the system and overall performance, the side draw system also allows debottlenecking of existing splitters and is particularly advantageous for splitters producing chemical grade propylene. By using membranes, the splitter can be debottlenecked by producing a permeate with high purity which can be blended with a lower purity overhead to produce the desired 95% product. One BP Research study showed an 80% increase in splitter capacity with no substantial increase in utilities.

For higher product purities the side draw is increased in volume and the membrane area increased to account for a higher fraction of the total product permeating through the membrane. Ultimately, for the maximum purity the membrane is placed on the overhead, using the existing reflux loop to provide the advantage of low per-pass recovery, while sizing the membrane to permeate 100% of the tower overhead product (Figure 5).

Pilot Plant Results

A pilot plant using refinery grade propylene has operated continuously for three months and a total of over six months at the Warrensville Labs. Flux varied from

3.2×10^{-5} to 7×10^{-5} (9 to 20 scfd per ft^2) and product purity varied from 98.5% to 99.7%. The system operated reliably and produced purified propylene at a rate of 40 kg (1/2 barrel) per day.

Process engineering and economic evaluation based on the pilot plant results indicate substantial capital and operating savings for splitter debottlenecking and for grassroots systems. (Table IV) Typical propylene/propane splitter savings were estimated at 20 to 50% on capital and up to 50% on operating expense. Energy savings for a 10,000 bbl/day grassroots facility producing polymer grade propylene were estimated at 500 billion BTU per year and for a chemical grade debottleneck of 1250 bbl/day energy savings are expected to be 150 billion BTU per year.

This new membrane system for propylene upgrading and recovery has potential for significant impact on refinery operations. With the expected increase in refinery light-end olefins due to the Clean Air Act Amendment of 1990, substantial increases in propylene production are probable. New capital may be required to meet the need for recovering the additional propylene and the lower capital potential of this membrane system will require consideration along with conventional equipment.

CONCLUSIONS

This study has shown that the use of appropriately designed membranes, coupled with process engineering input, allows operation of facilitated Transport membranes at both high transmembrane pressure and high flux. These results are particularly interesting in the propylene/propane separation when coupled as a hybrid with a conventional distillation tower. Performance and economics are consistent with reasonable goals for refinery and chemical plant operation of these membranes. Both the ability to withstand severe conditions of pressure and temperature and the lifespan of the facilitated transport membrane system have been extended to commercially feasible levels.

REFERENCES

1. S.G. Kimura, S.L. Matson, and W.J. Ward, III, in Recent Developments in Separation Science, Vol. 5, N.N. Li, Ed., CRC Press, Cleveland, 1979, p. 11.

2. R.D. Hughes and E.F. Steigelmann, Method of Separation of Ehylene and Ethane, USP 3,758,605 (1973); Hughes, et al., Process of Separating Complexable Materials, USP 3864418 (1975).

3. O.H. LeBlanc, Jr., et al., J. Membr. Sci. 6, 339 (1980).

4. R.L. Yahnke, Membrane Process for Separating Materials,USP 4,060,566 (1977).

5. R.D. Hughes, J.A. Mahoney, and E.F. Steigelmann, E. F., in Recent Developments in Separation Science, Vol. 9, N.N. Li, and J.M. Calo, Eds., CRC Press, Cleveland, 1986, p. 173.

6. M. Teramoto, et al., J. Membr. Sci 45, 115 (1989).

7. M. Kraus, Membrane Method for Olefin Separation, USP 4,614,524 (2986).

8. E.L. Cussler and Z. Qi, J. Membr. Sci. 23, 321 (1985).

9. J.C. Davis, R.J. Valus and E.G. Lawrence, Sep. Sci. and Techn. 3, 1039 (1988).

10. Gottschlich, D. E. and Roberts, D. L.; U.S. Department of Energy Report - EG&G Subcontract No. C88-101848, Contract No. DE-AC07-76ID01570, June, 1990.

11. R.J. Valus, et al., High Pressure Facilitated Membranes for Selective Separation, USP 5,057,641 (1991).