

PERVAPORATION AS AN ALTERNATIVE PROCESS FOR THE SEPARATION OF METHANOL FROM C₄
HYDROCARBONS IN THE PRODUCTION OF MTBE AND TAME

Brian Farnand and Soo Hong Noh

MAY 1989

ENERGY RESEARCH LABORATORIES
DIVISION REPORT ERL 89-03 (OP,J)

This work was supported in part by the
federal Panel on Energy R and D (PERD).

ERL 89-03 (OP,J)

PERVAPORATION AS AN ALTERNATIVE PROCESS FOR THE SEPARATION OF METHANOL FROM C₄ HYDROCARBONS IN THE PRODUCTION OF MTBE AND TAME

by

Brian Anthony Farnand, Energy Mines and Resources Canada (CANMET), Ottawa, Ontario, Canada, and Soo Hong Noh, Zenon Environmental Inc., Burlington, Ontario, Canada.

Abstract

Pervaporation was investigated as an alternative process for the separation of methanol from a mixture of C₄ and C₅ hydrocarbons and methyl ethers in the production of MTBE (methyl tertiary-butyl ether) and TAME (tertiary-amyl methyl ether). A preliminary screening of pervaporation membranes was performed by using reactor effluent produced in a pilot scale etherification reactor. Nafion and a cellulose based membrane were chosen for further testing and showed similar performance.

Introduction

In response to the phase out of leaded components in gasoline, alternative sources of octane improvers are required. These include aromatics, methanol and oxygenates, as well as hydrocarbons produced from more typical refinery operations such as isomerization, alkylation, and polymer gasoline. In particular, the light hydrocarbon olefins in the C₄ streams have been useful, since they are produced within a refinery. Further, these olefins are produced to a greater extent in the present octane "squeeze" conditions as refiners operate their fluidized catalytic cracking units at higher severity.

The competition inside the refinery for these olefins is critical to the introduction of new processes for octane improvement. As an example, MTBE uses some of the olefins that would normally be used for alkylation. The competition for these olefins is further complicated by the sensitivity of alkylation catalysts (hydrofluoric acid and sulphuric acid) and by the presence of oxygenates such as alcohol and water. Only isobutylene reacts to make MTBE, while all the other olefins react to a significant extent in alkylation. Present refinery operation with higher severity to increase the octane content produces more reactive olefins than existing alkylation units can process efficiently. This increased supply of olefins influences both the economics and the technical feasibility of introducing new MTBE units into refineries that have existing alkylation units or other C₄ olefins.

The reaction to produce methyl ethers for gasoline octane improvement requires iso-olefins and methanol. Unreacted methanol and the ether product must be removed from the reactor effluent to avoid poisoning alkylation catalysts and to reduce the vapour pressure of gasoline, which is adversely affected by the thermodynamic non-ideal behaviour of methanol in hydrocarbons (Chase and Galvez, 1981; Unzelman, 1984). This nonideal behaviour results in the formation of a vapour-liquid azeotrope that prevents the use of distillation. A significant portion of the cost of ether manufacture is directly attributed to the removal of oxygenates from the reactor product, and the yields of ether are limited by the low methanol concentrations used for the ease of removal. These costs have inhibited the manufacture of MTBE in refineries and the usual source in the North American fuels refinery is from integrated petrochemical operations outside the refinery limits, where pure isobutylene streams can be dedicated to MTBE manufacture, and unreacted methanol in the reactor product can be recycled to

extinction (Bitar et al., 1984). Thus a potential source of inexpensive isobutylene produced inside the refinery is not exploited for high octane blending components.

The purpose of this study is to investigate the removal of unreacted methanol from etherification reactor effluent for a refinery operation. Despite the previous work using reverse osmosis for this separation (Farnand and Sawatzky, 1986), the use of pervaporation has been chosen because of the high selectivity for the removal of methanol from hydrocarbons. Pervaporation does not introduce extraction solvents into the refinery and is not a cyclic operation such as adsorption. Operation at more advantageous concentrations for MTBE production could be possible if the separation of methanol could be performed efficiently (Smith and Huddleston, 1982). Further, the effective removal of methanol from the reactor effluent, followed by distillation to remove the ether product would permit the effective operation of both etherification and alkylation reactors on the same original feed of olefin rich hydrocarbons. Other methods that have been studied for this separation include water washing, glycol extraction, molecular sieve adsorption, and reverse osmosis.

Experimental

A schematic diagram pervaporation equipment used for this experiment is shown in Figure 1. The temperature of the experiment was controlled by immersing the pervaporation test cell in a controlled temperature water bath. Two cold traps were used for collecting the membrane permeate to permit steady state to be achieved. The membrane test cell used did not include a sweep gas for the low pressure side. The high pressure side of the apparatus was slightly pressurized to prevent losses by evaporation. Samples of etherification reactor effluent were supplied by PetroCanada Products, who also performed the chemical analyses.

Results and Discussion

A survey of commercially available thin films was made in an effort to determine quickly which polymeric materials would give selective separation of the methanol or the hydrocarbons. This is similar to the approach used to select reverse osmosis membrane to perform the same separation. First, an attempt was made to measure the contact angle of methanol with the surface of the membrane to give an approximate determination if the membrane could be considered to be methanol attracting or rejecting, as reported in Table 1. These were measured by placing a drop of methanol on the surface of the membrane and measuring the contact angle with a microscope. The thickness of the membrane was measured and is also shown in Table 1. Those films which were not completely wetted by the methanol were eliminated from further study, since they probably would not selectively permeate methanol as well as the methanol wetted films.

Initial membrane screening experiments were performed with the methanol wetted membranes with a solution of 10% methanol in pentane. These results are reported in Table 2. There is no obvious relation observed between methanol contact angle and the pervaporation performance reported in this work. The two membranes chosen for further investigation are Nafion 117, a polymeric perfluorosulfonic acid typically used for electro dialysis, and MT, a cellulose based commercial thin film packaging barrier. These two membranes were then tested in pervaporation experiments to assess their performance as a function of methanol concentration in a methanol-pentane solution. The variation of permeation rate and methanol separation factor are shown in Figures 2 and 3. It is apparent that as methanol concentration decreases, the selectivity for methanol increases and the permeation rate decreases.

Experimental results with pilot plant generated etherification reactor effluent were also investigated. The composition of the two reactor effluents

is shown in Table 3. The results of these experiments are shown in Tables 4 and 5. Poly(vinyl alcohol) membranes were included in these experiments for comparison with commercially popular membrane materials. It should be noted that the poly(vinyl alcohol) membranes used in this work were dense films and not the composite membranes used in commercial operations. The methanol concentration in the TAME experiments was lower than for the MTBE experiments since the processing strategy was to use a very low methanol content in the reactor. The olefins contained in the distillation fraction used for TAME production is usually not processed elsewhere in a refinery, so that there is no competition for the olefins. The TAME reactor effluent can be blended directly into the gasoline pool providing the vapour pressure increase caused by the addition of methanol is not large though the methanol must be matched with a cosolvent to prevent cold weather methanol phase separation. A successful methanol removal process applied to the TAME effluent stream would permit the use of higher concentrations of methanol in the reactor, with a subsequent greater octane increase. Further, the specifications for methanol in the final gasoline product without the use of a co-solvent could also be used to advantage. As was seen with the methanol-pentane solutions, the permeation rates for the TAME solutions with lower methanol content were generally lower and the separation factors were higher than for the MTBE case. It should be noted that the poly(vinyl alcohol) membrane used did not have an observable permeation, but this is probably caused by the thickness of the membrane and its resistance to permeation.

Conclusion

Polar membranes can be used in pervaporation processes to selectively remove methanol from both binary solutions in pentane as well as from MTBE and TAME reactor effluent. This may be attractive for the removal of methanol from reactor effluent as the processing of methyl ethers for use in gasoline inside fuels refineries becomes more financially attractive. Low permeation rates at dilute methanol concentration indicate that complete removal of methanol is difficult to obtain by pervaporation with the membranes studied in this work, and will require a polishing step to protect downstream catalysts. Further work will investigate the use of continuous pervaporation as opposed to the static cells used in this work.

References

Bitar, L.S., Haxbun, E.A., Piel, W.J., Hydrocarbon Processing, p. 93, October 1984.

Chase, J.D., Galvez, B.B., Hydrocarbon Processing, p.89, March, 1981.

Farnand, B.A., Sawatzky, H., in Proceedings of the International Membrane Conference on the 25th Anniversary of Membrane Research in Canada, M. Malaiyandi, O. Kutowy, F. Talbot, editors, September 24-26, 1986, p. 229.

Smith, L.A., Huddleston, M.N., Hydrocarbon Processing, p. 121, March, 1982.

Unzelman, G.H., Oil and Gas Journal, p. 59, July 2, 1984.

Figure 1 Pervaporation Schematic

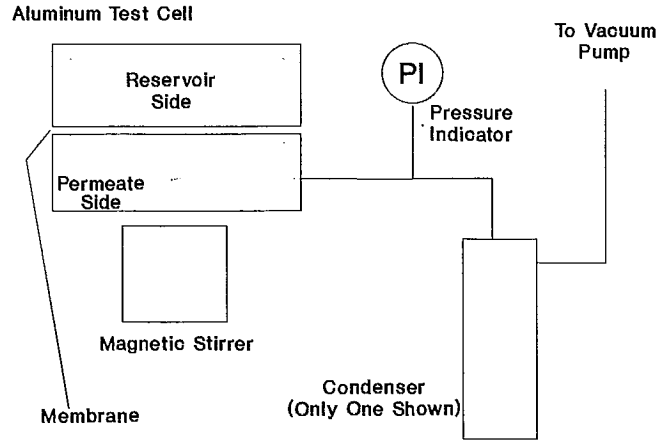


Figure 2 Permeation Rate with Concn

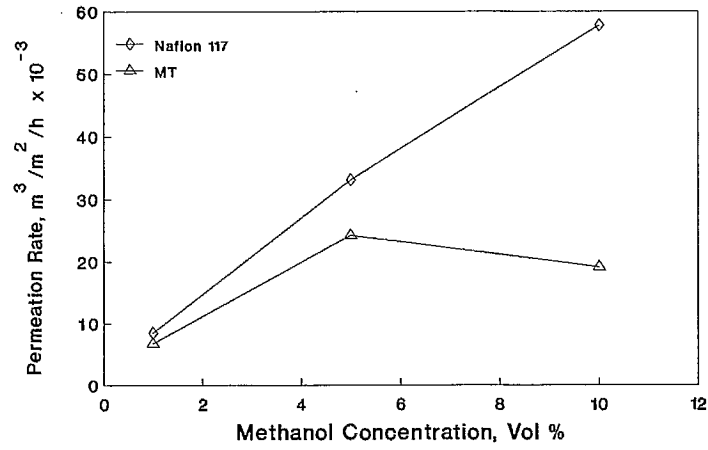


Figure 3 Separation Factor with Concn

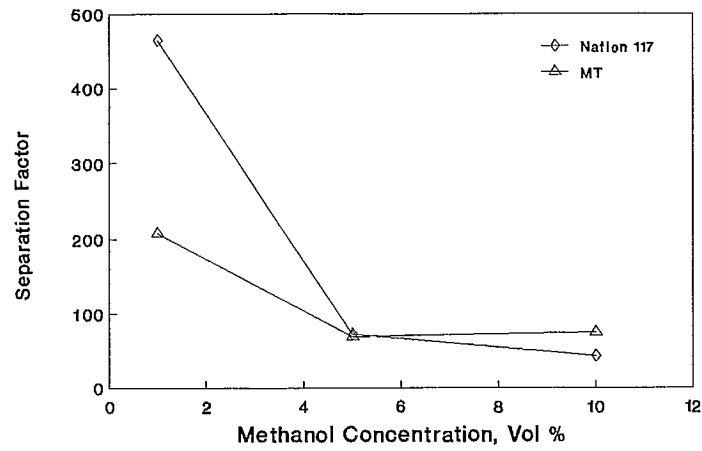


Table 1 Properties of Selected Membrane Materials

Membrane	Membrane Material	Thickness μm	Contact Angle
Kodacel TA	Cellulose Esters	76	62°
PVA	Polyvinyl Alcohol	76	-
MT	Cellulose Base	76	69°
Ultem	Polyetherimide	127	80°
Stabar K200	Polyether Ketone	25	86°
Stabar S100	Polyether Sulphone	25	85°
Nafion 117	Perfluorinated Copolymer	178	-
Nafion 417	Perfluorinated Copolymer	254	-
Lexan	Polycarbonate	51	85°
Saran F-120	Vinylidene chloride-acrylonitrile	25	-
Kynar	Polyvinylidene fluoride	51	89°
UWB	Polyacrylic Acid-Nylon 6	-	-

Table 2 Membrane Screening Experiment Results^a

Membrane	Permeation Rate ($\text{mL m}^{-2} \text{h}^{-1}$)	Permeate MeOH Conc Vol %	Separation Factor
Nafion 117	323.1	83	44
PVA	104.9	87	60
Saran F120	b	-	-
Stabar K200	c	-	-
Stabar S100	15.6	83	44
MT	260.5	89	73
Ultem	b	-	-
UWB	66.3	85	51

^a Feed methanol concentration of 10% in pentane, room temperature, 40 mm of Hg.

^b No visible permeate.

^c Insufficient permeate for analysis.

Table 3 MTBE and TAME Reactor Effluent Concentration^a

Component	MTBE	TAME
Methanol	3-5%	0.3-2%
MTBE	70-80%	0%
TAME	1-2%	10-20%
Isopentane	4-6%	30-40%

^a Major components only.

Table 4 MTBE Reactor Effluent Pervaporation Experimental Results

Membrane	Permeation Rate mL m ⁻² h ⁻¹	Permeate MeOH Conc Vol %	Separation Factor
Nafion 117	41	58.5%	35
Nafion 417	145	50.2%	25
Nafion 417	490	58.0%	35 ^c
PVA	b	-	-
MT	89	55.6%	32
MT	102	71.4%	63 ^c

^a 40 mm Hg, Room Temperature unless noted, feed concentration as in Table 3.

^b No permeate.

^c 50°C.

Table 5 TAME Reactor Effluent Pervaporation Experimental Results^a

Membrane	Permeation Rate mL m ⁻² h ⁻¹	Permeate MeOH Conc Vol %	Separation Factor
Nafion 117	54	98.5%	3283
Nafion 117	314	89.7%	445 ^c
PVA	b	-	-
MT	30	90.6%	3002 ^d

^a 40 mm Hg, Room Temperature unless noted, feed concentration as in Table 3.

^b No permeate.

^c 50°C.

^d 45°C.

INTRODUCTION

In response to the phase out of leaded components in gasoline, alternative sources of octane improvers are required. These include aromatics, methanol and oxygenates, as well as hydrocarbons produced from more typical refinery operations such as isomerization, alkylation, and polymer gasoline. In particular, the light hydrocarbon olefins in the C₄ streams have been useful, since they are produced within a refinery. Further, these olefins are produced to a greater extent in the present octane "squeeze" conditions as refiners operate their fluidized catalytic cracking units at higher severity.

The competition inside the refinery for these olefins is critical to the introduction of new processes for octane improvement. As an example, MTBE uses some of the olefins that would normally be used for alkylation. The competition for these olefins is further complicated by the sensitivity of alkylation catalysts (hydrofluoric acid and sulphuric acid) and by the presence of oxygenates such as alcohol and water. Only isobutylene reacts to make MTBE, while all the other olefins react to a significant extent in alkylation. Present refinery operation with higher severity to increase the octane content produces more reactive olefins than existing alkylation units can process efficiently. This increased supply of olefins influences both the economics and the technical feasibility of

introducing new MTBE units into refineries that have existing alkylation units or other C₄ olefins.

The reaction to produce methyl ethers for gasoline octane improvement requires iso-olefins and methanol. Unreacted methanol and the ether product must be removed from the reactor effluent to avoid poisoning alkylation catalysts and to reduce the vapour pressure of gasoline, which is adversely affected by the thermodynamic non-ideal behaviour of methanol in hydrocarbons (Chase and Galvez, 1981; Unzelman, 1984). This nonideal behaviour results in the formation of a vapour-liquid azeotrope that prevents the use of distillation. A significant portion of the cost of ether manufacture is directly attributed to the removal of oxygenates from the reactor product, and the yields of ether are limited by the low methanol concentrations used for the ease of removal. These costs have inhibited the manufacture of MTBE in refineries and the usual source in the North American fuels refinery is from integrated petrochemical operations outside the refinery limits, where pure isobutylene streams can be dedicated to MTBE manufacture, and unreacted methanol in the reactor product can be recycled to extinction (Bitar et al., 1984). Thus a potential source of inexpensive isobutylene produced inside the refinery is not exploited for high octane blending components.

The purpose of this study is to investigate the removal of unreacted methanol from etherification reactor effluent for a refinery operation. Despite the previous work using reverse osmosis for this separation (Farnand and Sawatzky, 1986), the use of pervaporation has been chosen because of the high selectivity for the removal of methanol from hydrocarbons. Pervaporation does not introduce extraction solvents into the refinery and is not a cyclic operation such as adsorption. Operation at more advantageous concentrations for MTBE production could be possible if the separation of methanol could be performed efficiently (Smith and Huddleston, 1982). Further, the effective removal of methanol from the reactor effluent, followed by distillation to remove the ether product would permit the effective operation of both etherification and alkylation reactors on the same original feed of olefin rich hydrocarbons. Other methods that have been studied for this separation include water washing, glycol extraction, molecular sieve adsorption, and reverse osmosis.

EXPERIMENTAL

A schematic diagram pervaporation equipment used for this experiment is shown in Figure 1. The temperature of the experiment was controlled by immersing the pervaporation test cell in a controlled temperature water bath. Two cold traps were used for collecting the membrane permeate to permit steady state to be achieved. The membrane test cell used did not include a sweep gas for the low pressure side. The high pressure side of the apparatus was slightly pressurized to prevent losses by evaporation. Samples of etherification reactor effluent were supplied by PetroCanada Products, who also performed the chemical analyses.

RESULTS AND DISCUSSION

A survey of commercially available thin films was made in an effort to determine quickly which polymeric materials would give selective separation of the methanol or the hydrocarbons. This is similar to the approach used to select reverse osmosis membrane to perform the same separation. First, an attempt was made to measure the contact angle of methanol with the surface of the membrane to give an approximate determination if the membrane could be considered to be methanol attracting or rejecting, as reported in Table 1. These were measured by placing a drop of methanol on the surface of the membrane and measuring the contact angle with a microscope.

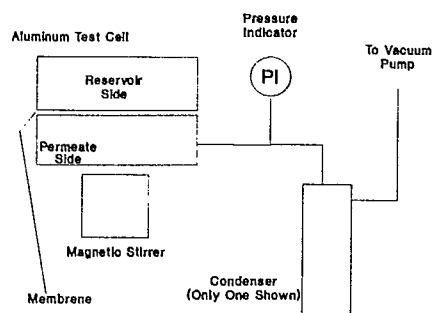


Figure 1 Pervaporation Test Cell Schematic

Table 1 Properties of Selected Membrane Materials

Membrane	Membrane Material	Thickness µm	Contact Angle
Kodacel TA	Cellulose Esters	76	62°
FA	Polypropyl Alcohol	76	-
MT	Cellulose Base	76	69°
Ultras	Polyethersulfide	127	68°
Stabar K200	Polyether Ketone	25	86°
Stabar 2100	Polyether Sulphone	25	85°
Nafion 117	Perfluorinated Copolymer	178	-
Nafion 417	Perfluorinated Copolymer	254	-
Laxan	Polycarbonate	51	85°
Saran F-120	Vinylidene chloride-acrylonitrile	52	-
Kynar	Polyethylene fluoride	51	89°
WB	Polycrylic Acid-Nylon 6	-	-

The thickness of the membrane was measured and is also shown in Table 1. Those films which were not completely wetted by the methanol were eliminated from further study, since they probably would not selectively permeate methanol as well as the methanol wetted films.

Initial membrane screening experiments were performed with the methanol wetted membranes with a solution of 10% methanol in pentane. These results are reported in Table 2. There is no obvious relation observed between methanol contact angle and the pervaporation performance reported in this work. The two membranes chosen for further investigation are Nafion 117, a polymeric perfluorosulfonic acid typically used for electrodialysis, and MT, a cellulose based commercial thin film packaging barrier. These two membranes were then tested in pervaporation experiments to assess their performance as a function of methanol concentration in a methanol-pentane solution. The variation of permeation rate and methanol separation factor are shown in Figures 2 and 3. It is apparent that as methanol concentration decreases, the selectivity for methanol increases and the permeation rate decreases.

Table 2 Membrane Screening Experiment Results*

Membrane	Permeation Rate ($\text{ml m}^{-2} \text{h}^{-1}$)	Permeate MeOH Conc Vol %	Separation Factor
Nafion 117	313.1	85	44
FVA	104.3	87	60
Savan F120	b	-	-
Stabar K200	c	-	-
Stabar 3100	13.4	83	44
MT	240.3	89	73
Ulisse	b	-	-
UVA	44.3	85	51

* Feed methanol concentration of 10l in pentane, room temperature, 40 mm Hg.
 b No visible permeate.
 c Insufficient permeate for analysis.

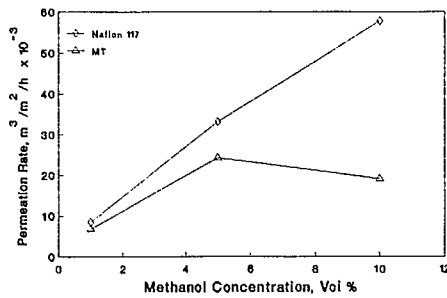


Figure 2 Permeation Rate With Concentration

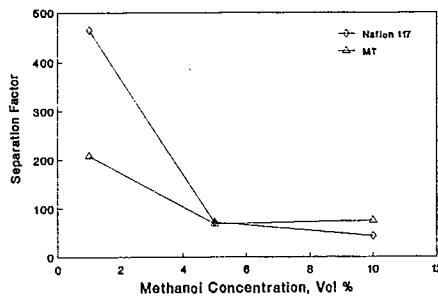


Figure 3 Separation Factor With Concentration

Experimental results with pilot plant generated etherification reactor effluent were also investigated. The composition of the two reactor effluents is shown in Table 3. The results of these experiments are shown in Tables 4 and 5. Poly(vinyl alcohol) membranes were included in these experiments for comparison with commercially popular membrane materials. It should be noted that the poly(vinyl alcohol) membranes used in this work were dense films and not the composite membranes used in commercial operations. The methanol concentration in the TAME experiments was lower than for the MTBE experiments since the processing strategy was to use a very low

Table 3 MTBE and TAME Reactor Effluent Concentration*

Component	MTBE	TAME
Methanol	3-5%	0.3-2%
MTBE	70-80%	0%
TAME	1-2%	10-20%
Isopentane	4-6%	30-40%

* Major components only.

Table 4 MTBE Reactor Effluent Pervaporation Experimental Results

Membrane	Permeation Rate $\text{ml m}^{-2} \text{h}^{-1}$	Permeate MeOH Conc Vol %	Separation Factor
Nafion 117	41	58.51	35
Nafion 117	145	58.21	25
Nafion 117	490	58.01	35*
FVA	b	-	-
MT	89	55.61	52
MT	102	71.48	63*

* 40 mm Hg, Room Temperature unless noted, feed concentration as in Table 3.
 b No permeate.
 c 50°C.

Table 5 TAME Reactor Effluent Pervaporation Experimental Results*

Membrane	Permeation Rate $\text{ml m}^{-2} \text{h}^{-1}$	Permeate MeOH Conc Vol %	Separation Factor
Nafion 117	54	98.51	5283
Nafion 117	314	69.71	445*
FVA	b	-	-
MT	30	90.61	1002*

* 40 mm Hg, Room Temperature unless noted, feed concentration as in Table 3.
 b No permeate.
 c 50°C.
 d 45°C.

methanol content in the reactor. The olefins contained in the distillation fraction used for TAME production is usually not processed elsewhere in a refinery, so that there is no competition for the olefins. The TAME reactor effluent can be blended directly into the gasoline pool providing the vapour pressure increase caused by the addition of methanol is not large though the methanol must be matched with a cosolvent to prevent cold weather methanol phase separation. A successful methanol removal process applied to the TAME effluent stream would permit the use of higher concentrations of methanol in the reactor, with a subsequent greater octane increase. Further, the specifications for methanol in the final gasoline product without the use of a co-solvent could also be used to advantage. As was seen with the methanol-pentane solutions, the permeation rates for the TAME solutions with lower methanol content were generally lower and the separation factors were higher than for the MTBE case. It should be noted that the poly(vinyl alcohol) membrane used did not have an observable permeation, but this is probably caused by the thickness of the membrane and its resistance to permeation.

CONCLUSION

Polar membranes can be used in pervaporation processes to selectively remove

methanol from both binary solutions in pentane as well as from MTBE and TAME reactor effluent. This may be attractive for the removal of methanol from reactor effluent as the processing of methyl ethers for use in gasoline inside fuels refineries becomes more financially attractive. Low permeation rates at dilute methanol concentration indicate that complete removal of methanol is difficult to obtain by pervaporation with the membranes studied in this work, and will require a polishing step to protect downstream catalysts. Further work will investigate the use of continuous pervaporation as opposed to the static cells used in this work.

REFERENCES

- Bitar, L.S., Haxbun, E.A., Piel, W.J., Hydrocarbon Processing, p. 93, October 1984.
- Chase, J.D., Galvez, B.B., Hydrocarbon Processing, p.89, March, 1981.
- Farnand, B.A., Sawatzky, H., in Proceedings of the International Membrane Conference on the 25th Anniversary of Membrane Research in Canada, M. Malaiyandi, O. Kutowy, F. Talbot, editors, September 24-26, 1986, p. 229.
- Smith, L.A., Huddleston, M.N., Hydrocarbon Processing, p. 121, March, 1982.
- Unzelman, G.H., Oil and Gas Journal, p. 59, July 2, 1984.