REVERSE OSMOSIS FRACTIONATION OF ETHERIFICATION REACTOR PRODUCT
STREAMS DURING PRODUCTION OF OCTANE BOOSTING GASOLINE ADDITIVES

by

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ABSTRACT

The fractionation by distillation of etherification
reactor product is complicated by azeotrope formation of both
hydrocarbons and ethers with unreacted methanol. The removal of
methanol is required for several reasons. For reactor products
containing tert-butyl methyl ether(MTBE) and tert-amyl methyl
ether(TAME), reverse osmosis can fractionate methanol from the
product. The methanol can be preferentially permeated through the
membrane as for cellulose esters, or can be selectively rejected
from the membrane surface as for non-polar membranes. The
technical feasibility of a continuous membrane separation process
was assessed based upon bench scale results.

RESUME

La distillation du produit des réacteurs
d'étherification est compliqué par la présence des azéotropes du
méthanol non-réagi avec les éthers et les hydrocarbures. La
séparation du méthanol est nécessaire pour diverses raisons. Dans
le cas des produits de la réaction pour la fabrication du
tertio-butyle méthyle éther(MTBE) et du tertio-amyl méthyle
éther(TAME) l'osmose inverse peut fractionné le méthanol.
L'utilisation des membranes détermine si le méthanol transversera
la membrane, comme c'est le cas pour les membranes d'ester de
cellulose, ou s'il sera préférentiellement retenu comme dans le
cas des membranes non-polaires. Nous avons étudiés cette
séparation afin de déterminer si un processus de séparation
continu est techniquement possible.

INTRODUCTION

Lead phase down in North America has stimulated investigation of other alternatives to boost the octane value of gasoline to meet current and proposed specifications. One of these alternatives is the use of blending agents of high octane index such as tert-butyl methyl ether (MTBE) and tert-amyl methyl ether (TAME). These ethers are produced by the reaction of methanol with C_4 and C_5 iso-olefins that are available in most petroleum refineries. While methanol also has a high octane value as a blending agent, its presence in gasoline has caused phase separation problems, corrosion, as well as a disadvantage related to the thermodynamically non-ideal high vapour pressure of methanol and hydrocarbon blends (Unzelman, 1984). This high vapour pressure imposes a limit on petroleum refiners concerning the use of inexpensive octane boosting butanes in the final gasoline product. Another reason for removing methanol is that the etherification reactor product contains unreacted olefins which are the feedstock for other refining operations such as alkylation and polymerization which use catalysts that are sensitive to methanol poisoning. When the current requirement for methanol co-solvents to prevent phase separation is combined with the penalty of not using butanes in methanol gasoline, the final

cost for octane boosting with methanol can be larger than expected from its pure component properties.

MTBE and TAME do not have high vapour pressures in gasoline blends and are miscible with gasoline. While their purchase cost is greater than that of methanol alone, the overall advantages of their use make them attractive for octane value boosting. However, their cost is sufficiently large that they cannot dislodge the simple aromatics (BTX) as the non-leaded octane blending agents of choice in North America, with localized exceptions (Bitar et al., 1984). One reason for their large cost is the removal of unreacted methanol from the etherification reactor product, since methanol forms a vapour-liquid azeotrope with hydrocarbons as well as the ether product. Several processes for methanol removal have been reported in the literature or are available commercially. These include liquid extraction with water and glycol (Chase and Galvez, 1981), adsorption onto molecular sieves and polymers (Herwig et al., 1984), and operating the reactor with methanol in stoichiometrically lean conditions (Smith and Huddleston, 1982). A schematic of a TAME process is shown in Figure 1A.

This work reports the use of nonaqueous reverse osmosis for the removal of methanol from etherification reactor product. Preliminary results in static reverse osmosis cells have shown that methanol can be selectively passed through the membrane to

separate it from the hydrocarbons and ethers, as well as selectively rejected from the membrane with the hydrocarbons and ethers permeating (Farnand and Sawatzky, 1986). Several improvements have been made to demonstrate this separation in continuous flow reverse osmosis test cells. Since this reverse osmosis test equipment better represents commercial equipment than static cells, a better representation of the reverse osmosis performance for this process can be determined. Schematics of the selective permeation and rejection of methanol in an etherification processing scheme are shown in Figures 1B and 1C.

EXPERIMENTAL

Membranes. Previous work (Farnand and Sawatzky, 1986) identified two types of membranes that selectively permeate or reject methanol from hydrocarbon and ether solutions. The polar cellulose ester membranes preferentially permeate methanol, and were fabricated from methods that were developed for aqueous separations. The direct use of these membranes in their aqueous form did not give permeate even at large operating pressures. To overcome this difficulty, the cellulose ester membranes were solvent exchanged from water to the hydrocarbon mixture. This was

performed by immersing the membranes in a 50% isopropanol and water solution for 30 min. They were then immersed in a 75% isopropanol solution for 30 min., followed by pure isopropanol. This process was repeated by using pentane and isopropanol solutions until pure pentane was used. The membranes were then removed from the pentane solution and loaded into the reverse osmosis test cells.

The other membranes identified in the previous work selectively permeated the hydrocarbons from the solution. These membranes are polyolefins and are non-polar in nature. These were fabricated by blown film methods and therefore were dry (water free). They were loaded directly into the reverse osmosis test equipment without prior treatment. The details of membrane fabrication procedure and composition are given in Table 1.

Solutions and Analysis. Simulated etherification reactor effluent was made by blending amounts of reagent grade n-pentane, methanol, and TAME in concentrations that represent those reported in the literature. The removal of methanol from these solutions appeared to be a function of the methanol content, so various amounts of methanol were used in these experiments. The availability of reagent grade TAME required that the amount of TAME used in these experiments was slightly less than typical reactor effluent. It should be noted that the n-pentane contained

a small quantity of n-hexane which has been reported as one of the components of the solution.

Analysis of the feed and permeate concentrations was accomplished by capillary gas chromatography. The detection of methanol by the flame ionization detector required a correlation of detector response with the amount of methanol in solution. An automated sampler and injector was used, requiring sample dilution with toluene prior to injection to reduce volatility and flashing of the light hydrocarbons in the injection syringe.

Reverse Osmosis Test Cells. The reverse osmosis test cells were fabricated in-house from detailed blue prints supplied by NRC Canada (Sourirajan and Matsuura, 1985). They were constructed of stainless steel and feature an effective membrane surface area of 1.33×10^{-3} m^2. The flow in these cells is radial in nature, from the inside of the membrane disc to the outer rim of the membrane disc. Alternating cells had a reverse flow scheme due to the nature of the inlet and outlet of the cell. Circulation through the system was provided by a tubular diaphragm reciprocating pump and the pressure was controlled by a back pressure control valve. The temperature was held at 23°C by means of a double pipe heat exchanger. The reservoir tank was at atmospheric pressure with a chilled (-10°C) condenser to contain the light components in the reservoir.

The high volatility of the permeate and feed samples
required special collection methods to reduce the evaporative
losses. The membrane permeate tubes were fitted with sharp
needles, and the samples were collected in septum vials that had
been previously half filled with toluene. When the samples were
collected, the needles were forced through the septum, and into
toluene. The screw cap was then loosened to permit the flow of
the permeate into the vial at approximately atmospheric pressure.
Previous studies with this arrangement showed that evaporative
losses are negligible, and the permeation rate was unaffected.

RESULTS AND DISCUSSION

The experimental results of separation and permeation rates
are shown in Table 2. To determine the separation of the various
components, a mole fraction based separation factor was defined
as

$$\text{separation factor} = \frac{x_{perm}/(1-x_{perm})}{x_{feed}/(1-x_{feed})}$$

(1)

where x is the mole fraction of the component under
consideration. Preferential permeation of methanol by the
cellulose ester membranes and preferential permeation of the

hydrocarbons and ethers by the polyolefin membranes has been confirmed by these results. This suggests that the basis for the separations reported in this work is the selective adsorption of the various components onto the membrane surface, and that this selective adsorption is a function of membrane polarity.

In comparison to the static cell experiments (Farnand and Sawatzky, 1986), it is apparent that the permeation rates are approximately the same even though the operating pressure has been reduced from 5.1 MPa to 2.0 MPa. The separation factors are not as large (different than unity) as those obtained in the static cell experiments with similar membranes at the higher pressures. This suggests that separation factors would be larger in the flow cells at higher operating pressures. In general, the static cell experiments were mass transfer limited, the subsequent osmotic pressure decreased the permeation rate, and the separation factors derived from the static cells are probably smaller than could be obtained in a circulating system.

The large combined methanol and pentane content, in the range of 95%, implies that the effects of the other components can be safely ignored. This assumption is required to compare the effect of methanol content on reverse osmosis separation of methanol as shown in Figure 2. For the cellulose ester membranes, an increase in methanol content caused a decrease in the separation factor for methanol, although the permeate

concentration remained approximately the same for this range of concentration. The separation factors of the CAB membrane for methanol were not as large as those for the CA membranes, but the permeation rate was significantly larger. This could be the effect of the different pore sizes of these membranes and the relationship between the work of separation and the permeation rate, in combination with the reduction in viscosity of the solution permeating the membrane as the methanol content increases. For the polyolefin membranes, the separation factor for methanol was not strongly affected by methanol concentration.

The pore sizes of these membranes are unknown for this solution system, although they are presumed to be as small as those of reverse osmosis membranes in aqueous use. The cellulose ester membranes were fabricated by methods that are typically capable of separating aqueous sodium chloride solutions in the 95% range. The polyolefin membranes did not have permeation even at 10 MPa in pure water. The effect of solvent plasticization of membranes is not well understood and methods to determine the pore sizes of membranes require more data than those presented here. Further, the determination of pore size may be complicated by the changes of methanol content or the other components in solution. The reproducibility of these experiments is difficult to assess because of the lack of data. This information will be necessary to determine the technical feasibility of the

separation, as well as to estimate the expected life span of the membranes that are involved. Further work should include experimental evaluations of these factors.

Basic processing strategies for the removal of methanol from etherification reactor product may be prepared from the present results. The cellulose ester membranes could be used to selectively remove the methanol from the product and recycle it to the reactor. This would be similar to the absorption and extraction processes used for other operations, with the notable exception that it is performed in a single step. With the larger separation factors for methanol by the CA membranes reported in this work, this scheme appears to have the greatest potential. Further, the nature of this scheme involves the selective passage of a minor component through the membrane, which requires less surface area to perform the same service as the case of selective methanol rejection.

The polyolefin membrane results for the selective permeation of the ethers and hydrocarbons would require multiple membrane stages to perform the same level of separation as the cellulose ester membranes, This requires multiple pumps, and also the membrane surface area requirement will increase. The advantage of this scheme is that methanol is retained on the high pressure side of the membrane and, providing the reaction is run at a higher pressure than current practice, it could be recycled

to the reactor before concentration polarization factors increase the osmotic pressure. The economic viability of this effect remains uncertain.

CONCLUSION

Reverse osmosis can be used to selectively remove methanol from etherification reactor effluent, either as permeate or as reject from the membrane surface. Large separation factors for methanol removal favour the use of cellulose acetate membranes, though the development of other membranes to achieve similar or improved performance is possible. Emphasis for future work should be directed towards improvement of methanol separation factors.

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Table 1
Membrane Fabrication Details

Membrane No.	Name	Material	Solution	Cast time	Heat treat
1	Glad[a]	Polyethylene	molten	–	–
2	CA	Cellulose acetate(E-398)	b	1 min	$90^{\circ}C$
3	CA	Cellulose acetate(E-398)	b	1 min	$90^{\circ}C$
4	CAB	Cellulose acetate butyrate[c]	d	5 min	$90^{\circ}C$
5	CA	Cellulose acetate	b	1 min	$90^{\circ}C$
6	Handi[e]	Polyethylene	molten	–	–

[a] manufactured by Union Carbide.
[b] refer to Pageau and Sourirajan (1972).
[c] 17 % butyrated.
[d] refer to Sourirajan and Kunst (1977).
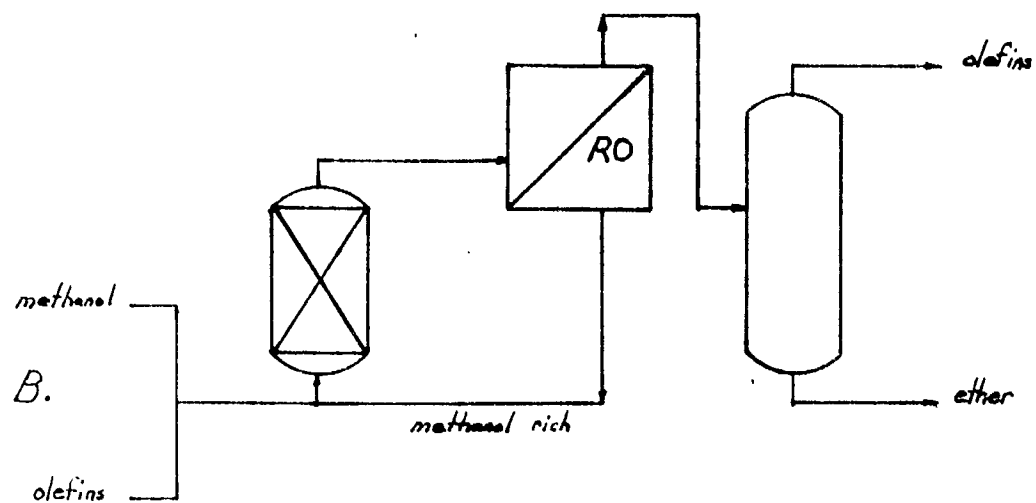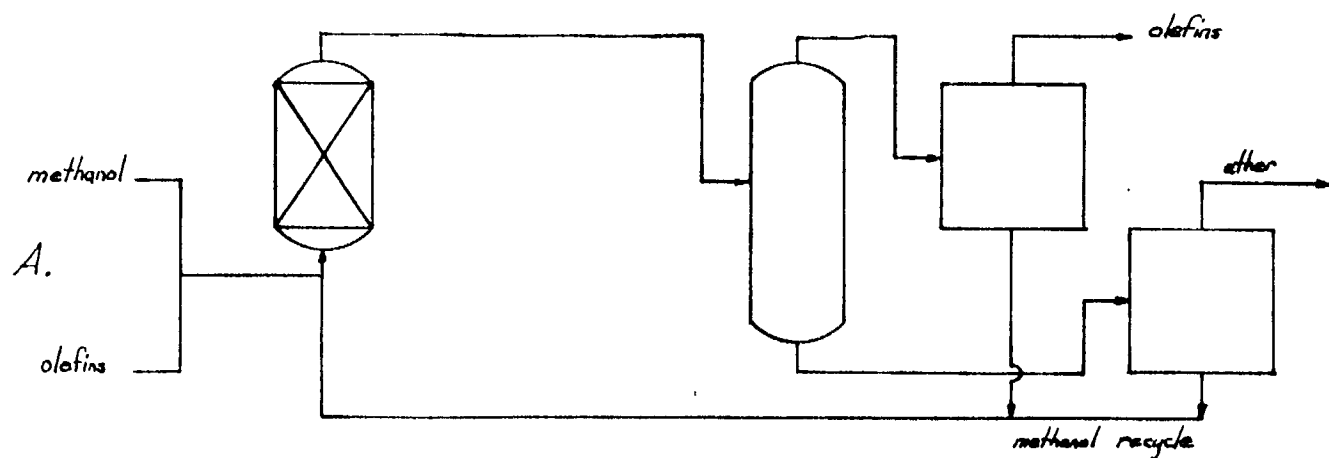[e] manufactured by Dow Chemical.

Table 2
Reverse Osmosis Experimental Results[a]

Run No.	Memb No.	Feed Concn, wt%				Perm rate[b]	Separation Factor			
		MeOH	n-C5	TAME	n-C6		MeOH	n-C5	TAME	n-C6
1	2	4.38	94.72	0.08	0.80	0.824	8.166	0.130	1.244	0.570
	3					0.718	10.37	0.103	1.127	0.440
	4					5.226	2.201	0.471	1.612	0.865
	5					0.612	15.27	0.070	0.931	0.426
	6					1.170	0.752	1.296	1.873	0.990
2	1	10.54	83.41	5.46	0.59	0.957	0.478	1.782	1.122	1.312
	2					1.117	3.892	0.298	0.883	0.712
	3					1.170	3.713	0.298	0.760	0.607
	4					6.072	1.506	0.723	0.680	1.024
	5					0.878	4.953	0.220	0.850	0.626
	6					0.798	0.582	1.667	0.760	1.235
3	1	9.57	84.56	5.21	0.65	1.117	0.520	1.712	0.997	1.182
	2					0.971	5.697	0.193	0.857	0.573
	3					1.144	4.180	0.262	0.941	0.509
	4					6.782	1.222	0.808	1.217	0.998
	5					0.997	5.868	0.183	1.038	0.537
	6					–	0.704	1.233	1.437	1.021

[a] pressure of 2 MPa, temperature of $25^{\circ}C$.
[b] permeation rate in $kg/h/m^2$

Figure 1   A. Etherification schematic
           B. Etherification with polar reverse osmosis separation
           C. Etherification with non-polar reverse osmosis separation

A.

methanol

olefins

olefins

ether

methanol recycle

B.

methanol

olefins

RO

olefins

methanol rich

ether

←———— REACTOR ——+——REVERSE OSMOSIS+DISTILLATION——+——EXTRACTION————→

C.

methanol

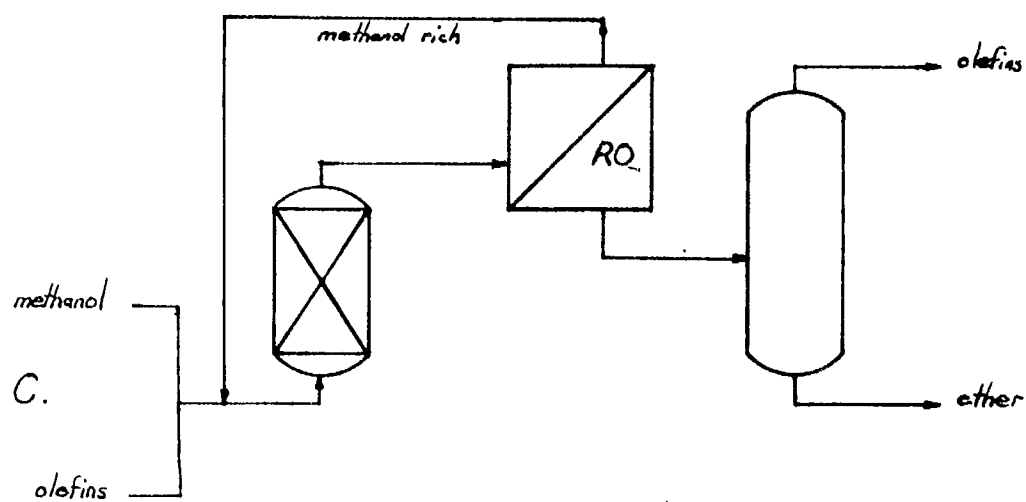olefins

methanol rich

RO

olefins

ether

FIGURE 2   REVERSE OSMOSIS   PERFORMANCE
WITH METHANOL   CONCENTRATION