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INTRODUCTION

Lead phasedown and possibly complete lead phaseout for gasoline use could result in an octane squeeze for North American refiners. Several alternatives to lead addition are being considered including the use of high octane methyl ethers such as tert.-butyl methyl ether (MTBE) and tert.-amyl methyl ether (TAME) for blending into gasoline. These methyl ethers are ideal octane boosting additives for gasoline because of their low vapour pressures which allows the maximum blending with inexpensive butanes and their high octane number values of 110 to 120. The ethers are produced in sulphonic acid resin catalyzed reactions between methanol and the C₄ and C₅ iso-olefins that are currently produced in refinery fluidized catalytic cracking (FCC) units. Olefin-rich streams which contain both iso-olefins and other olefins as well as saturated hydrocarbons are distilled from FCC product.

Since the etherification reaction is reversible and the yield is equilibrium limited (1), there are considerable amounts of unreacted methanol and iso-olefins. The usual refinery practice is to use excess amounts of methanol to improve the yield of ethers from the iso-olefins. While the unreacted methanol can be left in the products and used as an octane boosting agent (octane number of 120), refiners consider methanol to be undesirable in gasoline for the following reasons.

1) Methanol causes corrosion and phase separation in gasoline blends when small amounts of water are present, such as water from humid air.

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2) Methanol forms low boiling azeotropes with hydrocarbons which increases the vapour pressure of the gasoline pool and the subsequent "backing out" of inexpensive butanes of adequate octane number.

3) During utilization of the unetherified non-iso-olefins, such as for alkylation and polymerisation, methanol deactivates the catalysts in alkylation and other processes (2).

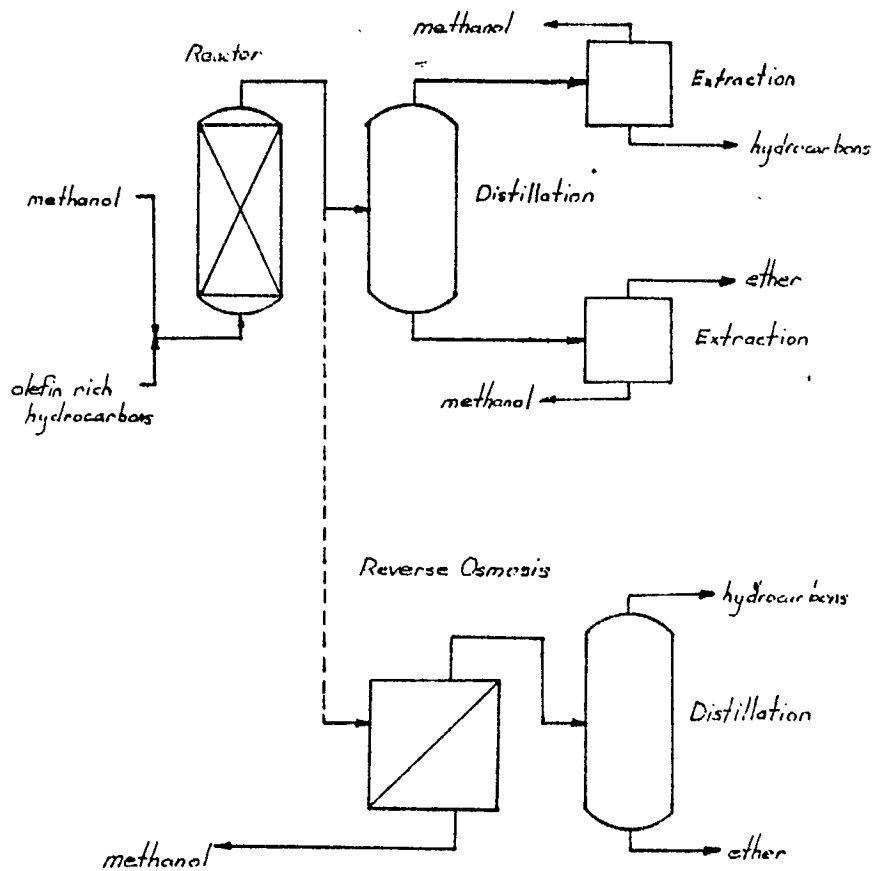
For these reasons, methanol must be removed from etherification reactor effluent and recycled to the reactor feed. Distillation cannot be used to remove the methanol from the etherification reactor product since methanol forms azeotropes with both the unreacted hydrocarbons and the ether product. Conventional treatment includes distillation followed by triethylene glycol extraction of both the distillation tower outlet streams as shown in Figure 1. An alternative process uses polymeric resin adsorption with cycled desorption into the hydrocarbon feed stream.

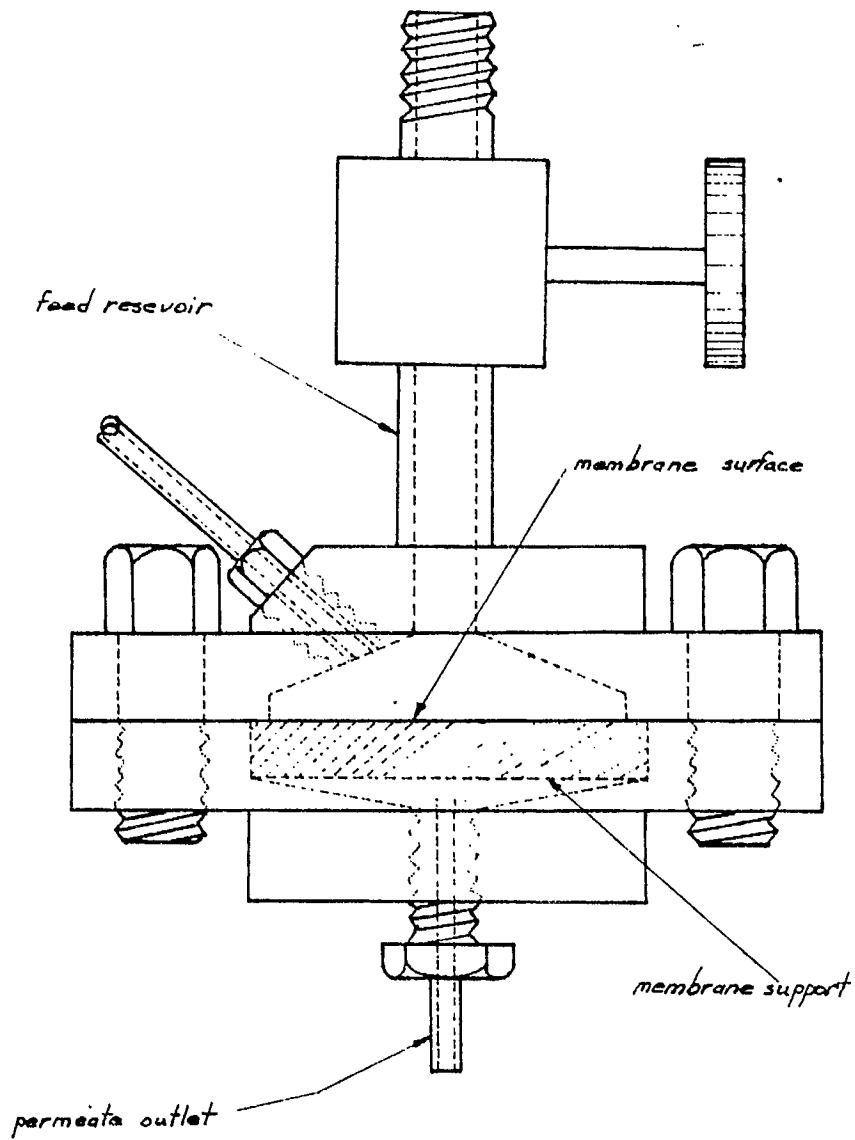
This work reports a preliminary study of reverse osmosis under static conditions to remove methanol from the etherification products. This involves both the selective rejection of methanol from the permeate by non-polar membranes and the selective passage of methanol by polar membranes. Both types of membranes give significant separation factors for methanol. The reverse osmosis separation unit would be situated between the etherification reactor and a distillation column as shown in Figure 1. The absence of liquid extraction units would reduce the operating and capital cost of methyl ether production and enhance the economic feasibility of their use in gasoline. While the final process for methanol removal by reverse osmosis would use flow equipment, the preliminary nature of this study required the use of available static cells.

EXPERIMENTAL

Membranes

Several of the reverse osmosis membranes studied in this work have been developed for use in aqueous reverse osmosis. These membranes were cast in aqueous solutions,





heat-treated, and then solvent exchanged to pentane. The solvent exchange consisted of transferring the membranes from the aqueous solutions into a solution of equal volumes of isopropanol and water. After thirty minutes the membranes were placed in an isopropanol:water (75:25) solution, and after another thirty minute period they were placed in pure isopropanol. This process was then continued with pentane and isopropanol until pure pentane was used. These membranes were then stored in pentane. Other membranes were acquired in dry condition and could be stored without liquid. These were simply fitted into the reverse osmosis cells and used as needed. The details of the membranes used in the work are shown in Table 1.

Reverse Osmosis Test Cells

The reverse osmosis static test cells used for this work were modified Millipore membrane filter holders. The modifications included a hole on the high pressure side to permit a tap into the space above the membrane surface. Another modification was that the reservoir tube on top of the membrane was chilled to -25°C before it was filled with the test solution. This reduced the rate of evaporation which was noticeable because of the small amount (approximately 20 mL) of feed liquid. The effective membrane surface area for these cells was measured to be $1.33 \times 10^{-3} \text{ m}^2$. The operating pressure was supplied by compressed nitrogen gas. A sketch of the apparatus is shown in Figure 2.

Simulated Etherification Products and Analysis

Simulated etherification reactor effluents were made by mixing methanol, methyl tertiary-butyl ether (MTBE), tertiary-amyl methyl ether (TAME), pentane, and 2-methyl-2-butene in appropriate proportions. Collection of the membrane permeate required unusual methods to prevent the evaporative loss of methanol because of its high vapour pressure in the presence of hydrocarbons. Further, the high vapour pressure of the pentane/methanol mixtures created difficulties for injection into the gas chromatograph (GC) used for concentration analysis. The automated sampling that was used for GC analysis caused the pentane rich samples to evaporate in the injector syringe with a slight

TABLE 1.

REVERSE OSMOSIS MEMBRANE DETAILS

Membrane	Material	Solution	Fabrication	Gelation	Heat Treatment
CA	Cellulose Acetate, 39.8% Acetylated	a	cast	water	10mins. x 95°C
CAB	Cellulose Acetate Butyrate, 17% Butyrate	b	cast	water	3mins. x 90°C
PVC	Polyvinyl Chloride (high molecular weight)	8.16%PVCinTHF	cast	water	10mins. x 55°C
Saran ^c	Polyvinylidene Chloride (PVDC) (Major) + PVC (trace)	molten	blown film	-	-
Stretch ^d	PVC (Major) + chlorinated polyethylene (trace)	molten	blown film	-	-
Handi ^e	Polyethylene	molten	blown film	-	-
Glad ^f	Polyethylene (Major) + Polyvinyl Acetate (trace)	molten	blown film	-	-

a Pageau et al. (5)

b Sourirajan and Kunst (6)

c fabricated by Dow Chemical

d fabricated by Esso Chemical (Canada)

e fabricated by Dow Chemical

f fabricated by Union Carbide

enrichment of methanol. These two difficulties were overcome by collecting the permeate samples into previously chilled autosampler vials that were half filled with toluene. As well, the samples were collected through the septum of the autosampler vial by a needle attached to the permeate collection tubing. This sealed collection apparatus reduced the evaporative losses to acceptable levels as measured by successive analyses for concentration. The presence of the toluene prevented evaporation of the sample in the GC autosampler injection syringe and increased the reproducibility of analysis.

The GC column used for this work was a non-polar capillary column (DB-1, J & W Scientific) of 30m in length. A Varian 6000 GC was used with a split injection, Helium carrier gas, Nitrogen make-up gas and a flame ionization detector (FID) with a Varian 402 Data Station for GC peak area computation. Since the FID response with respect to the amount by weight of methanol in the sample was not linear, the technique required calibration by samples of known concentration. The response of other components was assumed to be linear with respect to their weight concentration after being normalized for the methanol contribution.

RESULTS AND DISCUSSION

Separation in multicomponent systems can be described by a separation factor defined as follows:

$$\alpha_1 = \frac{X_1/(1-X_1)}{Y_1/(1-Y_1)} \quad \text{-----}(1)$$

where α_1 is the separation factor for component 1, X_1 is the mole fraction of component 1 in the permeate and Y_1 is the mole fraction of component 1 in the liquid remaining on the high pressure side of the membrane at the end of the experiment (retentate). The experimental separation factors and permeation rates are shown in Tables 2,3 and 4 with the operating pressure. The temperature of the system was ambient laboratory temperature.

It is apparent from these results that there are two different types of membrane performance. These are the selective permeation of methanol as seen in the cellulose ester membranes, and the selective rejection of methanol as seen in the polyolefinic membranes. While only a small number of membranes has been assessed, it is assumed that this effect is a function of the polarity/non-polarity of the membrane materials involved. Further, the CA membrane had the largest separation factor for methanol and in the case of methanol and pentane solutions, no permeate was collected over a 3 hour period even at 10 MPa, the upper operating pressure limit of the apparatus. If membrane compaction can be ignored, it is possible that the pores of the CA membrane were filled with methanol and the pressure energy is inadequate to displace it with pentane. This effect was observed with ethanol in heptane solutions at low ethanol concentration (3) and typically CA and CAB membranes do not permeate if they have not been solvent exchanged from water.

The pore sizes of membranes are difficult to assess in nonaqueous solutions because of plasticization and the apparently low separation of dilute components in hydrocarbon solutions. The physicochemical methods of Sourirajan and Matsuura (4) that combine reverse osmosis experimental results with pore flow and surface interactions for the determination of pore size are difficult to apply and interpret because of these factors. The polyolefin membranes appear to be impermeable in aqueous solutions with the exception of the PVC membrane. The cellulose ester membranes were fabricated by methods that have large salt separations in aqueous solutions. From this, all of the membranes reported in this work were assumed to have pore sizes similar to those of reverse osmosis membranes capable of 90% and greater separation of salt in aqueous solution.

The performance of these membranes for methanol removal as part of a reverse osmosis separation process for etherification reactors can be assessed based upon the results of Tables 3 and 4. The large separation factors for CA membranes indicate that they would be the preferred choice for a separation process, providing the methanol enriched permeate can be recycled to the reactor. A major advantage is that methanol, as a minor component, is permeated through the membrane. This will reduce the membrane surface area requirement and with large separation

TABLE 2.

REVERSE OSMOSIS SEPARATION OF METHANOL IN PENTANE SOLUTIONS^a

Membrane	Casting time, min	Operating pressure, MPa	Permeation rate, kg/m ² /h	Separation factor, Methanol
CA	1	10.0	nil	-
CAB	1	8.0	1.31	1.68
Saran	-	6.0	1.23	0.59
Saran	-	4.0	1.25	0.56b
Saran	-	4.0	1.07	0.61b
Saran	-	8.0	44.26	0.32
Stretch	-	8.0	6.56	1.02
PVC	3	1.0	19.95	0.56
PVC	6	5.0	1.98	0.36

^a nominal feed concentration of 0.34 weight % methanol.

^b feed concentration of 6.67 weight % methanol.

factors it will require only a single stage of membrane separation. The alternative scheme would selectively permeate methanol free reactor product. This would require more membrane surface area per stage and more stages because of the low separation factors to obtain a methanol concentration of less than 0.1 % by weight. In order to prevent the methanol concentration on the high pressure side from becoming too large (osmotic pressure considerations), a large volume fraction of the retentate stream could be recycled to the reactor where methanol would be consumed by etherification. The necessary increase in reactor size may preclude this strategy.

The use of static cells is not ideal for the assessment of performance of the membranes in this work. For example, the large separation factors for the CA membranes obtained in this work are probably mass transfer limited. If increases can be obtained in nonaqueous membrane performance as seen in aqueous cases when system turbulence and mass transfer are improved, the technical viability of the process would improve as well. The study of the same experiment in circulating reverse osmosis equipment would

TABLE 3.

REVERSE OSMOSIS SEPARATION OF SIMULATED MTBE REACTOR EFFLUENT^a

Membrane	Cast time, min	Press, MPa	Permeation rate, kg/m ² /h	Separation Factor			
				MeOH	Pent	2m2butene	MTBE
CA	1	6.0	4.67	1.55	0.77	0.90	0.92
CA	1	6.5	-	7.67	0.24	0.47	0.56
CA	1	10.0	0.31	19.4	0.12	0.33	0.42
CAB	5	3.0	2.49	1.64	0.73	0.90	1.01
CAB	5	4.5	3.72	1.59	0.76	0.89	0.96
Saran	-	5.0	0.93	0.94	1.06	0.97	0.99
Handi	-	5.0	0.18	0.49	1.44	1.16	0.89
Handi	-	7.0	0.92	0.33	1.68	1.21	0.79
PVC	6	5.0	0.07	0.91	1.18	1.01	1.03

^a nominal feed concentration of 10.5 % methanol, 67 % pentane, 15.6 % 2-methyl-2-butene, and 6.6 % MTBE.

permit preliminary design and economic feasibility determinations for process evaluation. This work is continuing, and preliminary experiments have shown performance improvements for both the polar and non-polar membranes, as well as a large influence of methanol concentration and operating pressure.

CONCLUSION

The selective permeation and rejection of methanol has been demonstrated in static cells. The separation of methanol from etherification reactor product appears to be technically viable but information is inadequate for economic viability estimation.

TABLE 4.

REVERSE OSMOSIS SEPARATION OF SIMULATED TAME REACTOR
EFFLUENT^a

Membrane	Cast time, min	Press, MPa	Permeation rate, kg/m ² /h	Separation Factor			
				MeOH	Pent	2m2butene	TAME
CA	1	10.0	0.68	19.8	0.12	0.28	0.27
CA	1	5.0	0.63	1.91	0.68	0.82	0.82
CAB	5	5.0	0.55	5.19	0.70	0.33	0.62
Saran	-	5.5	0.09	0.76	1.16	1.05	1.01
Saran	-	7.0	1.22	0.97	1.01	1.01	1.04
Handi	-	5.5	1.77	0.72	1.22	1.06	0.84
Handi	-	6.5	15.88	0.90	1.06	1.02	0.98
Glad	-	4.5	1.02	0.42	1.49	1.15	0.87
Glad	-	7.0	19.15	0.92	1.05	1.02	0.97

^a nominal feed concentration of 10.5 % methanol, 66.5 % pentane, 15.6 % 2-methyl-2-butene, and 7.4 % MTBE.

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