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### PRELIMINARY SELECTION AND USE OF REVERSE OSMOSIS MEMBRANES FOR THE FRACTIONATION OF NAPHTHA

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Preliminary Selection and Use of Reverse Osmosis  
Membranes for the Fractionation of Naphtha

by

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SUMMARY

Preliminary reverse osmosis results for the removal of aromatic components from naphtha are presented. The selection of cellulose acetate and cellulose acetate butyrate membranes was determined from affinity chromatography experiments with candidate membrane materials. The enrichment ratios for benzene, toluene, and xylenes as a group were in the 1.05 to 1.29 range when the permeate was compared with the liquid remaining on the high pressure side of the membrane. Artificially increased aromatic content samples and several operating pressures (4000 to 8000 kPa) were also studied.

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Sélection et Usage Préliminaires des Membranes  
d'Osmose Inverse pour le Fractionnement du Naphtha

par

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SOMMAIRE

Nous présentons ici une étude préliminaire sur une façon de se débarrasser des composés aromatiques que l'on retrouve dans le naphtha. La sélectivité des membranes d'acetate de cellulose et d'acetate/butyrate de cellulose a été étudiée à l'aide de la chromatographie liquide d'adsorption. Le degré d'enrichissement du benzène, du toluène, et des xylènes (pris comme un tout) a varié entre 1.05 et 1.29 lorsque le permeat était comparé avec le liquide restant du côté haute pression de la membrane. Nous avons changé la concentration des composés aromatiques et la pression entre 4000 kPa et 8000 kPa.

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## INTRODUCTION

Membrane processes for the fractionation and upgrading of synthetic crude oil fractions are being studied in our laboratory. These processes are also applicable to conventional crude fractions. The separation of aromatics from non-aromatic components is one of these processes and the initial study involved naphtha fractions. More complex and larger molecular weight synthetic crude fractions will be studied later.

Previous experience with the development of reverse osmosis in aqueous as well as nonaqueous media has demonstrated the utility of affinity chromatography for the qualitative and quantitative prediction of reverse osmosis and ultrafiltration performance [1-4]. This work extends these principles to naphtha, with the simplification of using pure solvents (toluene and heptane) as the carrier liquids in order to represent aromatic and aliphatic naphthas as reported elsewhere [5]. Because of this simplification and other factors, prediction of reverse osmosis performance with naphtha is qualitative. The probe molecules that were used in the affinity chromatography experiments were chosen on the basis that they represent specific compound types, extremes in size, or were found to be present in significant quantities in synthetic naphtha streams [6,7].

The basis for selecting cellulose acetate (E-398,CA) and cellulose acetate butyrate (17% butyrate, CAB) is shown in Table 1 where the relative retention volumes of several aromatic and saturated hydrocarbons on several candidate membrane materials are presented. For this case, the heptane carrier conditions were chosen since the naphtha has a very low aromatic content. From Table 1, it is apparent that CAB

adsorbs the aromatics more strongly than the saturates. In comparison, the CA material appeared to be relatively non-selective with respect to the aromatics.

## EXPERIMENTAL

The synthetic crude naphtha used in this study was a hydrotreated naphtha (C<sub>5</sub> to 195°C) supplied by Suncor and was produced from Athabasca bitumen. As a measure of membrane performance, the combined benzene, toluene, and xylenes (BTX) content of the naphtha was selected on the basis of ease of analysis. Analysis was by capillary gas chromatography with a DB1 30 m column and the 95% confidence interval was found to be  $\pm 0.15$  at 3.0% BTX.

Membranes were fabricated from methods reported in the literature for aqueous reverse osmosis [8]. To transfer the membranes from their water gelation baths to the naphtha stream, the membranes were immersed in successively more concentrated isopropanol in water solutions. After pure isopropanol had been used, the process was repeated with successively concentrated isooctane in isopropanol solutions until pure isooctane was used. This was followed by direct immersion in the naphtha. The membranes were loaded into a static reverse osmosis cell with  $1.33 \times 10^{-3} \text{ m}^2$  of membrane surface presented to the feed solution. For the separation experiments, approximately 20 mL of naphtha was loaded into the cell, and approximately 2 mL of permeate was collected prior to sampling for BTX content. Because of the volatile nature of the naphtha, samples were obtained by inserting the needle of a 10  $\mu\text{L}$  syringe into the permeate's outlet. This syringe was used to inject the sample for GC analysis. The syringe was cleaned prior to use



by inserting the needle into a heated vacuum. The high pressure side was sampled by a similar method, where a small bleed valve was used to remove a small volume of retentate that was collected directly in a 10  $\mu\text{L}$  syringe.

## RESULTS AND DISCUSSION

The analysis for the BTX content of several membrane permeates and their corresponding high pressure side concentrations are shown in Table 2. The permeation rates for these membranes were difficult to determine because of the volatility of the samples and the low permeation rates. However, for the CAB, the membrane's permeation rates were in the range of  $200 \text{ g.m}^{-2}.\text{h}^{-1}$  at 8000 kPa and for the CA membranes, the permeation rates were in the order of  $100 \text{ g.m}^{-2}.\text{h}^{-1}$  at 8000 kPa. The amount of BTX in the naphtha was artificially increased for two of the CAB experiments, and the operating pressure was varied for both cases.

While the exact pore sizes of these membranes have not been determined, their fabrication was by methods which lead to very high separation of NaCl in aqueous reverse osmosis. However, their solvent exchange with plasticizing solvents may have altered the structure of the membranes. This effect is difficult to estimate, although the permeation rate was smaller than the expected value for the aqueous case and suggests that for the less viscous naphtha, the porosity of the membrane is in the same range or even smaller than the aqueous version of the membranes. This effect may preclude comparison of the two types of membranes since the pore sizes are not equivalent. Relative retention volumes from the affinity chromatography work [5] agree with

the relative amounts that these membranes enrich the permeate with aromatics (BTX). Because of the polar nature of both these membrane materials, their enrichment of the aromatic portion of the naphtha is expected, and this was suggested by the affinity chromatography results.

#### CONCLUSIONS

If comparative pore sizes for the two membranes can be assumed, CAB has better aromatic component selectivity than CA for the reverse osmosis fractionation of naphtha. This effect was predicted by affinity chromatography experiments with probe molecules chosen to represent the components present in naphtha. On this basis, similar methods may be used to select membrane materials amenable to other reverse osmosis fractionations in nonaqueous media.

Table 1 - Ratios of retention volumes with heptane as the carrier solvent [5]

Solute A/Solute B	$V_{R,A}/V_{R,B}$						
	CE	CA	CTA	CAB	CAHP	LDPE	Teflon <sup>R</sup>
toluene/i-octane	1.01	0.91	-	1.46	0.88	1.17	0.99
benzene/hexane	1.01	0.95	-	-	0.92	1.01	0.94
ethylbenzene/i-octane	1.00	1.05		1.57	0.85 <sup>b</sup>	1.14	1.11
toluene/methylcyclohexane	1.01	1.05		1.45	0.88	1.01	1.02
benzene/cyclohexane	1.02	1.05		1.68	1.02	1.01	1.00
bisphenol/hexadecane	1.00	1.07	1.75	3.10	1.14	1.12	1.06
propylbenzene/1-nonene	1.01	0.99	1.17	1.35	1.20	1.02	1.01
pyridine/2,2-dimethylbutane	1.12	1.14	-a	-a	-a	1.02	-
Average Aromatic/Aliphatic	1.01	1.01	-	1.85	0.95	1.08	1.02

<sup>a</sup> No peak for pyridine was eluted, which implies a large value for ( $V_{R,A}/V_{R,B}$ ).

<sup>b</sup> The inverse of 0.85 is 1.18. This can also be used as a comparison with the other values in this table.

Note: CE = Cellulose; CA = Cellulose Acetate; CTA = Cellulose Triacetate; CAB = Cellulose Acetate Butyrate; CAHP = Cellulose Acetate Hydrogen Phthalate; LDPE = Low Density Polyethylene.



Table 2 - BTX content of the high pressure side and the permeate

Membrane	BTX Concentration, %		Ratio BTX Perm/High P.	Pressure kPa
	High Pressure Side	Permeate		
CAB	3.15	3.30	1.07	5000
	3.16	3.53	1.12	5000
	2.97	3.40	1.14	8000
	3.01	3.50	1.16	8000
	6.97 <sup>a</sup>	8.99	1.29	8000
	36.84 <sup>a</sup>	47.13	1.28	8000
CA	3.05	3.20	1.05	8000
	3.24	3.39	1.05	6000
	3.08	3.26	1.06	4000

<sup>a</sup> artificially increased BTX content

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