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THE SELECTION AND USE OF REVERSE OSMOSIS FOR
AROMATIC/SATURATE FRACTIONATION OF PETROLEUM DISTILLATES

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THE SELECTION OF MEMBRANES AND USE OF REVERSE OSMOSIS FOR
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ABSTRACT

A preliminary study was made of the use of reverse osmosis to upgrade petroleum distillates with respect to their saturate/aromatic content. To select suitable membrane candidates a liquid chromatography method was used to determine the selective adsorption of aromatic and saturate compounds by powdered membrane material. The most promising membranes are defined as those with large retention differences between saturates and aromatics, as expressed by the ratio of retention volumes of pairs of solutes of similar molecular weights. Several of these materials have been fabricated into membranes and results of their aromatic/saturate separations are reported for naphtha and middle distillate petroleum fractioning. The candidate materials considered are commonly used for aqueous reverse osmosis and existing methods were used for membrane fabrication. Consideration of the affinity chromatography and reverse osmosis results can be used to determine the direction of future work in terms of selection of candidate materials.

LA SÉLECTION DE MEMBRANES ET L'UTILISATION DE L'OSMOSE INVERSE POUR LA
SÉPARATION DES AROMATIQUES/SATURÉS CONTENUS DANS LES DISTILLATS DU PÉTROLE

RESUME

Une étude préliminaire porte sur la séparation des composés aromatiques et saturés contenus dans les distillats pétroliers. Pour choisir les membranes les plus prometteuses, nous avons utilisé la chromatographie liquide afin de déterminer les affinités des composés aromatiques et saturés envers les polymères utilisés pour la fabrication des membranes. La comparaison entre les polymères s'est faite sur la base du rapport des volumes de rétention entre les aromatiques et les saturés. Un rapport élevé pour des composés de poids moléculaires similaires indique une bonne séparation. Quelques polymères ont été préparés sous forme de membranes et la séparation par osmose inverse des composés aromatiques et saturés ont été déterminés pour les naphthas et les gas-oils.

Les membranes étudiées furant développées pour l'osmose inverse dans les systèmes aqueux et les méthodes de fabrication sont déjà disponibles. Les résultats de ces expériences peuvent-être utilisés pour orienter les prochaines études.

INTRODUCTION

As part of an ongoing study of distillate fuel upgrading the use of selective fractionation of fuel components by reverse osmosis was investigated. Conventional reverse osmosis membranes are emphasized although a survey of several membrane candidate polymers was made. Because of the large effort required to develop a new reverse osmosis membrane of suitable pore size for novel separation processes liquid chromatography methods were developed for the selection of promising membranes. This follows the methods for aqueous reverse osmosis that were developed previously (Matsuura et al. 1983). The successful implementation of selection criteria for reverse osmosis membrane candidates reduces the efforts required to develop suitable membranes.

Distillate fuels obtained from heavy oil, bitumen, and synthetic crudes tend to be of lower quality than those from conventional light crudes. Methods for their upgrading include hydrogenation, cracking, and the use of additives and blending agents. For membrane upgrading the selective removal of deleterious and inferior quality components followed by severe refining are considered. The membrane fractionation would also produce a higher quality stream that could be added directly to the fuel or subjected to gentle upgrading. The severe refining would be performed on a lower quality stream from which the greater value components have been removed. This reduces the size of the reactor vessels and also reduces the loss of the original higher quality components.

This work concerns the application of reverse osmosis to the aromatic/saturate fractionation of synthetic naphtha and light gas oil. Two membrane types were selected on the basis of liquid chromatography: cellulose acetate and cellulose acetate butyrate.

EXPERIMENTAL

Previously reported liquid chromatography results (Farnand et al. 1984) were compared with the present reverse osmosis results and are shown in Tables 1 and 2. Reverse osmosis membranes were fabricated from Eastman 398-3 cellulose acetate (CA) (Pageau and Sourirajan, 1972) and Eastman cellulose acetate-butyrate (17% butyrated, ASTMViscosity 15, CAB) (Kunst and Sourirajan, 1977). These methods produce membranes capable of greater than 95% separation of NaCl from aqueous solutions. The membranes were solvent exchanged via isopropanol to isooctane to petroleum distillate and then loaded into static (no circulation or stirring) reverse osmosis cells. The high pressure side of the reverse osmosis cell was filled with petroleum distillate and pressurized by nitrogen gas. Samples of the permeate were collected along with samples of the liquid remaining in the high pressure side of the membrane (retentate). These were then analyzed for aromatic and saturate contents. The duration of the experiments was sufficient to collect enough permeate to perform the analysis. The volume of liquid in the high pressure side of the test cell was approximately 20 mL, and approximately 2 mL was removed as permeate.

The naphtha was analyzed by determining the amount of benzene, toluene and xylenes (BTX) using capillary gas chromatography. The naphtha was very low in aromatics. The light gas oils were rich in aromatics as determined by gas chromatography-mass spectrometry analysis.

RESULTS AND DISCUSSION

Results for the CA and CAB membranes with naphtha are shown in Table 3. Both of these membranes selectively permeated BTX although the CAB membrane had larger ratios of BTX change. These results are reflected in the results of the liquid chromatography for heptane carrier. The heptane carrier is more relevant to the naphtha case because of the small amount of aromatics and the liquid chromatography results have larger ratios of retention volumes of aromatic components compared with the saturate components. Providing the effects of diffusion and steric hindrance are negligible, the liquid chromatography results indicate that CA and CAB have greater affinity for the aromatic components, and that CAB should perform better than CA. This latter trend is confirmed by the reverse osmosis performance of these two membranes.

Results for the light gas oils are shown in Table 4 for both membranes. The ratios of aromatic contents of the permeate compared with the retentate are 1.25 and 1.34 for the CAB membranes and 1.10 for the CA membrane. These are in the same range as the results for the change of BTX content in the naphtha for the same membranes. The results of the liquid chromatography with an aromatic carrier (toluene) as shown in Table 2 suggest that CAB will have a larger fractionation of the aromatics than the CA membranes. This prediction requires the assumption of equivalent pore sizes of the two membranes, which cannot be guaranteed since the membranes were solvent exchanged.

The permeation rates of these experiments were not measured accurately but were determined about 200 $g.m^{-2}.h^{-1}$ for CAB and naphtha at 8000 kPa and 100 $g.m^{-2}.h^{-1}$ for CA and naphtha at 8000 kPa. The light gas oil permeation rate was in the same range.

CONCLUSIONS

Preliminary results show that membranes can be used for aromatic/saturated fractionation of petroleum distillate. Also, liquid chromatography can be used to select the membrane materials that will give better results. Future work will focus on testing polymers different from those studied here.

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TABLE 1

RATIOS OF RETENTION VOLUMES WITH HEPTANE AS THE CARRIER SOLVENT

Solute A/Solute B	$V_R, A/V_R, B$						
	CE	CA	CTA	CAB	CAHP	PE	Teflon[R]
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[b]	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
Bisphenyl/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	–[a]
Average Aromatic/aliphatic	1.01	1.01	–	1.85	0.95	1.08	1.02

[a] No peak for pyridine was eluted, which implies a large value for $(V_R, A/V_R, B)$.

[b] The inverse of 0.85 is 1.18. This can also be used for comparison with the other values in this table.

TABLE 2

RATIOS OF RETENTION VOLUMES WITH TOLUENE AS THE CARRIER SOLVENT

Solute A/Solute B	V_R, A/V_R,B						
	CE	CA	CTA	CAB	CAHP	PE	Teflon[R]
Benzene/hexane	1.01	1.15	–	–	1.04	0.98	0.99
Ethylbenzene/i-octane	1.03	1.17	–	–	1.07	–	–
Benzene/cyclohexane	1.06	1.20	–	–	–	1.01	0.92
Bisphenyl/hexadecane	1.00	1.00	0.91	0.99	1.29	0.99	0.98
P-xylene/heptane	1.00	1.16	1.18	1.55	0.97	1.01	–
Propylbenzene/1-nonene	1.02	1.14	1.10	1.18	1.03	0.99	–
Pyridine/2,2-dimethylbutane	1.00	1.14	0.98	–[a]	0.98	1.04	1.08
Average Aromatic/aliphatic	1.02	1.14	1.05	1.27	1.09	1.00	0.96

[a] No peak for pyridine was eluted, which implies a large value for (V_R, A/V_R,B).

TABLE 3

BTX CONTENT OF THE RETENTATE AND THE PERMEATE FOR NAPHTHA

Membrane	BTX Concentration, %		Ratio BTX Perm/Retentate	Pressure kPa
	Retentate	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[a]	8.99	1.29	8000
	36.84[a]	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

[a] artifically increased BTX content experiment

TABLE 4

FRACTIONATION OF LIGHT GAS OILS WITH CAB AND CA MEMBRANES

Composition	CAB 5000 kPa		CAB 5000 kPa		CA 8000 kPa	
	Retentate	Permeate	Retentate	Permeate	Retentate	Permeate
Paraffins, %	38.9	33.1	38.4	34.1	28.0	17.9
Olefins, %	1.0	3.1	2.1	2.1	0.4	0
Naphthenes, %	36.3	34.1	34.3	30.9	17.2	23.3
Aromatics, %	23.8	29.7	25.1	33.6	54.3	59.7