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Quarterly Report

ADVANCED COAL LIQUEFACTION

To

PITTSBURGH ENERGY TECHNOLOGY CENTER

October 1, 1993
to
December 31, 1993

DE-AC22-93PC92120

Media and Process Technology Inc.
1155 William Pitt Way
Pittsburgh, PA 15238

March 1, 1994

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1. INTRODUCTION

In this quarter we completed the liquid mixture separation containing model compounds 9, 10 and 11 at room temperature and 80C. The result was analyzed by a mathematical model previously developed for polymeric membranes. This report summarizes the results obtained thus far.

2. MEMBRANE PREPARATION

11 membranes were synthesized via chemical vapor deposition with TEOS as a precursor. Five of them were prepared using a 1" membrane as starting material to minimize the non-uniformity effect along the axial direction. The rest of them were prepared from 10" tubes for future reaction applications. Table 1 lists their gas permeance at room temperature and estimated pore size. The pore size distribution of these membranes was selectively exhibited in Figures 1 to 3.

3. SEPARATIONS OF COAL LIQUIDS

Three groups of liquid separations were conducted. The first group represents compound #9 as a reactant, toluene as a product, and tetralin as solvent. The estimated geometrical dimension of these compounds is listed in Figure 4. The single component flux for these compounds is shown in Figure 5. The permeance for toluene and tetralin correlates well with the gas permeance of each membrane. The single component flux at an elevated temperature, i.e., 80C, is shown in Figure 6. As expected the permeance increases along with the temperature increase due to the reduction in the viscosity. A detailed analysis is summarized in Table 2. The results conclude that significant hindrance diffusion exists for tetralin at 20 and 80C, while no hindrance phenomenon was observed for toluene for the membranes tested. The increase in the toluene flux can be qualitatively correlated with the increase in viscosity.

The mixture separations are exhibited in Figures 7 and 8. As expected the separation of compound #9 from tetralin and toluene was achieved with the use of modified membranes with pore size less than 40A. The 40A membrane shows slight separation based upon molecular diffusion at a lower pressure drop. When the pressure drop increases, the separation of toluene from tetralin increases as shown in Figure 8; no satisfactory explanation can be offered.

The separation for mixtures containing coronene was explored at room temperature. The estimated geometric dimension of the molecules is shown in Figure 9. Some rejection of coronene from toluene was observed for the 40A as well as modified membranes. The pressure drop increase reduced the separation efficiency probably due to the decreased contribution from molecular diffusion. The separation of mixtures containing Compound 11 in toluene was exhibited in Figures 11 and 12. A similar result as the previous group was obtained.

4. MATHEMATICAL MODELING

The separation results were analyzed with a selected mathematical model listed in Appendix 1. The model can quantify the contribution of each transport mechanism in terms of reflection coefficient and diffusivity. These two parameters can then be used to predict the separation performance of a given mixture with a given membrane porous structure. The separation of compound #9 in tetralin using Si284 at 80C was analyzed satisfactorily with the selected model as shown in Figure 13. The reflection coefficient of 0.658 and the diffusivity of $4.72\text{E-}9\text{cm}^2/\text{s}$ was obtained. More analysis will be performed for the liquid mixture separation in the next quarter.

5. CONCLUSION

The membranes synthesized thus far showed satisfactorily separation for the mixtures containing model compounds 9, 10 and 11. Separations at a higher temperature, i.e., 200 to 400C, will be performed in the next quarter to simulate the coal liquefaction environment. The mathematical model selected satisfactorily described some of the mixture systems. More analysis will be performed to complete the analysis in the future.

Table 1
Gas Permeations of Modified Membranes
at Room Temperature

Mem. ID	Pore D. (Å)	He Permeance (m ³ /m ² /atm/hr)	Length (inches)
Unmodified ^b	40	240 ~ 300	1
Si286	36	190.0	1
Si279	30	160.0	1
Si284	28	115.0	1
Si272	< 29	40.0	1
Si276	-	35.0	1
Unmodified ^b	40	240 ~ 300	10
Si417		62.3	10
Si478		20.7	10
Si451		2.11	10
Si472		0.51	10
Si471		0.48	10
Si414		0.04	10

^b The helium permeance is a typical value

Table 2
Temperature Dependence of Single Component Permeances

Membranes	20°C		80°C		80°C/20°C	
	Toluene	Tetralin	Toluene	Tetralin	Toluene	Tetralin
40Å	3.5	.4	-	.8	-	2
Si284	.8	.02	1.4	.17	1.3	8.5
Si279	.25	.01	.9	.10	3.6	10
Si276	.10	-	.2	-	2.0	-

Est'd Viscosity of Toluene = 0.59 CP at 20°C; 0.28 CP at 80°C
 Est'd Viscosity of Tetralin = 2.18 CP at 20°C; 0.78 CP at 80°C

% INCREMENTAL FLOW

● E12462 D=39.9 Å ■ E12269 D=39.6 Å ▲ E12458 D=39.9 Å

Figure 1 Pore Size Distribution of 40A Membranes

Figure 2
Pore Size Distribution of Modified Membrane - Si272
(Initial Flow: 14.3 cc/min; Final Flow: 15.8 cc/min)

Figure 3
Pore Size Distribution of Modified Membrane - Si284
(Initial Flow: 46.9 cc/min; Final Flow: 20.0 cc/min)

Figure 4
UPGRADING OF COAL LIQUID - COMPOUND 9

Figure 5
Permeances vs. Trans Membrane Pressure at 20°C

✱ 40Å-toluene

✱ 40Å-tetralin

⊙ Si284-toluene

⊙ Si284-tetralin

⊞ Si279-toluene

⊞ Si279-tetralin

▲ Si272-toluene

Si272-tetralin

▼ Si276-toluene

Si276-tetralin

Figure 6
Permeances vs. Trans Membrane Pressure at 80°C

40Å-toluene

× 40Å-tetralin

● Si284-toluene

○ Si284-tetralin

■ Si279-toluene

□ Si279-tetralin

▼ Si276-toluene

Si276-tetralin

Figure 7
Compound #9 Rejection vs. Trans Membrane Pressure at 20°C

Figure 8
Compound #9 Rejection vs. Trans Membrane Pressure at 80°C

✕ 40Å-#9

✕ 40Å-toluene

● Si284-#9

○ Si284-toluene

■ Si279-#9

□ Si279-toluene

Figure 9
CORONENE/TETRALIN

Structure

Molecular Dimension (Å)

(18Å x 18Å)

(12Å x 6Å)

figure 10
Coronene Rejection vs. Transmembrane Pressure at 20°C

Rejection = $(C_f - C_p) / C_f \times 100\%$

Figure 11
COMPOUND 11/TOLUENE

Structure

Molecular Dimension ($\text{\AA}$)

($13\text{\AA} \times 11\text{\AA}$)

($6\text{\AA} \times 7\text{\AA}$)

Figure 12

Compound #11, Rejection vs. Transmembrane pressure at 20°C

Figure 13
Separation of Compound # 9 in Tetralin
Using Si284 at 80°C

Reflection coefficient = $1/1.5202 = 0.658$

Solute diffusive permeability = $1.4337\text{E-}7 * 0.658 = 9.43\text{E-}8\text{m/s}$

If $L_{eff} = 5\mu = 5.0\text{E-}4 \text{ cm}$

$D_{eff} = 9.43\text{E-}6 \text{ cm/s} * 5.0\text{E-}4 \text{ cm} = 4.72\text{E-}9 \text{ cm}^2/\text{s}$

APPENDIX 1

Ultrafiltration: Statistical-Mechanical Model

The theory of liquid-phase transport using microporous membranes is reviewed. The experimental procedures to measure membrane separation are finalized based on our study. The case of coal liquid separation using microporous ceramic membranes is in the category of ultrafiltration. Basically, two mechanisms play in this field, molecular diffusion and convective flow. Molecular diffusion is determined by the characteristics of solute and solvent as well as their interaction forces, such as electrical potential. Convective flow is simply the function of fluid mechanics, such as viscosity and pressure. When these two mechanisms apply to porous media, each transport mechanism is further modified by the pore size, pore shape and pore density (or porosity) of the membrane as well as any interaction forces between solute and membrane surface. Usually, they are expressed by the hindrance factors of diffusion and convection. Theoretically, these factors can be calculated based on the ratio of molecular size to pore diameter and further modified by the related interaction forces, if any. However, since the pore diameter of the modified membrane cannot be measured by pore size analyzer ($< 20\text{\AA}$), and the molecular size of compound #9 is not available, it is not possible to calculate hindrance factors. Furthermore, since our modified membranes have an inherit pore size distribution and irregular pore shape (tortuosity ~ 3.9), the estimation of hindrance factors is difficult.

Mason and Lonsdale proposed a statistical-mechanical model, which gave a general description of the fluid transport in porous media (1). Ultrafiltration was one of its special cases. Niemi and Palosaari simplified this model and presented an experimental method to calculate these parameters, which could properly describe a given membrane separation (2). They derived equations to correlate the experimental data and theory, then directly determined two important parameters, effective diffusivity (D_{eff}) and effective convective flow through membrane. Once the bulk diffusivity (D_{∞}) of solute is known (from literature or experiment), the hindrance factor of diffusivity (H_d) can be calculated for a given membrane system by Equation 1. Based on this semi-empirical approach, all parameters can be determined without knowing pore diameter and molecular size.

$$D_{\text{eff}} = H_d \cdot D_{\infty} \quad [1]$$

Experimentally, the rejection ($R, \%$) is obtained from the compositions of feed and permeate by GC analysis. The permeate flux ($J_v, \text{m}^3/\text{m}^2/\text{hr}$) is varied with pressure drop across the membrane. According to equation 2, the reflection coefficient (σ) and solute diffusive permeability (P) can be calculated from the intercept and slope, respectively. Equation 3 and 4 are used to calculate the D_{eff} and hindrance factor of convective flow, respectively.

$$\frac{1}{R} = \frac{P}{\sigma} + \frac{1}{J_v} + \frac{1}{\sigma} \quad [2]$$

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