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**A Study of Volatile Hydrocarbon Emission Control**

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**by Polyetherimide Hollow Fiber Membranes**

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### Synopsis

Hollow fibers were spun from the polyetherimide solution and used for the separation of volatile organic compounds (VOC) from nitrogen. It was found that a polymer concentration of 27 wt-% in the spin-solution was necessary to obtain any appreciable selectivities. The highest selectivity of n-pentane achieved by a hollow fiber (#14) was 28.7, whereas a selectivity of 65.2 was achieved by a flat sheet membrane (#PEI-8) in the previous work. Although selectivities of #PEI-8 were generally higher than #14 including VOCs other than n-pentane, there was a notable exception of toluene selectivity. Comparing the fluxes for a given selectivity, hollow fiber membranes were lower than flat sheet membranes.

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## Introduction

Many industrial processes handling organic solvents produce solvent containing air exhaust streams. These streams cause not only severe air pollution problems but also a significant economic loss. In the past, when air pollution regulations were lax and the solvents were not expensive, these organic solvent vapors were simply discharged into the atmosphere. Since the 1970's, however, the need for air pollution control was recognized. Industries that produce organic solvent contaminated air streams have come under increasing economic and regulatory pressure.

Conventional technologies to remove volatile organic compounds from air suffer from various shortcomings. For example, incineration is applicable only to high vapor concentration and converts one pollution problem to another. The adsorption method requires a costly regeneration process, and adsorption is sometimes irreversible. A new technology to remove VOC from air emerged recently based on selective membranes. According to the method, one side of the membrane is in contact with feed air stream containing volatile organic vapors (VOCs) while vacuum is applied on the other side of the membrane. VOCs permeate the membrane readily due to the partial pressure gradient, while the permeation of air is negligibly small. Hence, the removal of VOCs from air becomes possible. The volatile-rich stream can be incinerated after compression. This technology is also applicable to

relatively large concentration of volatile organic vapor but does not require any regeneration process.

There are many works in the literature on the vapor permeation experiments (1). They are mostly based on composite silicone rubber membranes, a silicone layer coated on porous membranes of various glassy polymers (2 - 8). It is known, however, that silicone rubber is susceptible to damage by gasoline vapor (9). An attempt was made, therefore, by the present authors to prepare membranes from a single polymeric material of high organic resistance without a coating of silicone. In our previous work, for example, asymmetric aromatic polyimide membranes were investigated for this purpose (10). It was shown that membranes of both high selectivity and reasonably high permeability could be produced by controlling the conditions of membrane preparation properly. Membranes were also prepared from aromatic polyetherimide material and tested for the removal of mixtures of VOCs from nitrogen, and gasoline vapors from nitrogen, both in the presence and in the absence of water (11,12).

In this paper an attempt is made to prepare hollow fiber membranes for the removal of VOCs from air. The advantage of hollow fibers over the flat sheet membranes is the high area to volume ratio of hollow fibers. This will be important particularly when the volume of air to be treated by a membrane module becomes very large. Although the conditions of flat sheet membrane preparation are

essentially applicable to the preparation of hollow fibers, there are considerable differences in the preparation technology of these two membranes. As clearly shown in our previous work, partial evaporation of solvent at 95 °C for more than 1 min is required to prepare flat sheet membranes of sufficiently high selectivities. Obviously, such solvent evaporation is not allowed for the hollow fiber spinning process. It is therefore a technical challenge to prepare hollow fibers of high selectivities with a short evaporation period. The conditions of hollow fiber preparation are shown together with experimental results for the removal of VOCs from nitrogen.

### Theoretical

The molar permeation rate of nitrogen gas through the membrane,  $Q_N$  (mol/m<sup>2</sup> s), is obtained by

$$Q_N = \frac{273V}{(273+t) \times 22,400 \times 60 \times S} \quad (1)$$

where  $V$  is the volumetric permeation rate (mL/min) of nitrogen gas,  $S$  is the effective film area (m<sup>2</sup>) and  $t$  is the temperature (°C). The permeability of nitrogen gas,  $J_N$  (mol/m<sup>2</sup> s Pa), is given by

$$J_N = \frac{Q_N}{\Delta P} \quad (2)$$

where  $\Delta P$  is the pressure difference across the membrane (Pa).

The following transport equations are used for the analysis of membrane permeation data when the feed is a mixture of nitrogen gas and an organic vapor.

$$Q_N = A [P_1 (1 - Y_{vap,1}) - P_3 (1 - Y_{vap,3})] \quad (3)$$

$$Q_{vap} = B [(P_1 Y_{vap,1})^2 - (P_3 Y_{vap,3})^2] \quad (4)$$

$$Y_{vap,3} = \frac{Q_{vap}}{Q_{vap} + Q_N} \quad (5)$$

$Q$ 's are permeation fluxes;  $P$ 's are pressures and  $Y$ 's are mole fractions of the organic vapor. Subscripts N and vap represent nitrogen and the organic vapor, respectively. The subscripts 1 and 3 represent the feed and the permeate, respectively. Equation 4 assumes that  $Q_{vap}$  is proportional to the difference in the square of the partial pressure, which was justified in our previous paper (11). It was found by our earlier experiments that the nitrogen permeability changed only about 10 % in the presence of organic

vapors from the value obtained in their absence (11). Therefore, assuming, as an approximation, further that the permeability of nitrogen gas is unaffected by the presence of the organic vapor in the feed,

$$A = J_N \quad (6)$$

The justification for the above assumption was also made in our previous paper (10, 11). Furthermore, permeability of the organic vapor,  $J_{\text{vap}}$  (mol/m<sup>2</sup> s Pa), is defined as

$$J_{\text{vap}} = Q_{\text{vap}} / (P_1 Y_{\text{vap},1} - P_3 Y_{\text{vap},3}) \quad (7)$$

Looking into eqs. 3 and 5,  $Q_{\text{vap}}$ ,  $P_1$ ,  $P_3$ ,  $Y_{\text{vap},1}$  and  $A$  are known quantities from the permeation experiment for pure nitrogen gas and the organic vapor. Consequently, two unknowns,  $Q_N$  and  $Y_{\text{vap},3}$  can be calculated from the above two equations. Then,  $J_{\text{vap}}$  can be calculated by eq. 7 by using  $Y_{\text{vap},3}$  obtained above. Although eq. 4 gives the effect of the partial pressures at feed and permeate sides of the membrane on the permeation flux (11), the equation is not used in the analysis of the data.

## Experimental

**Materials.** Aromatic polyetherimide (PEI) (1000/2000 grade) was

supplied by General Electric Co. in pellet form. The pellets were dried at 150 °C for 4 hours in an oven with forced air circulation as suggested by the supplier. Lithium nitrate ( $\text{LiNO}_3$ ) from Fisher Scientific Co. was dried at 140 °C for 4 hours before being used as an additive in hollow fiber preparation. All organic chemicals were supplied by BDH Inc. and were of reagent grade. Nitrogen gas with a purity of 99.997 % was obtained from Air Products.

**Hollow fiber spinning apparatus.** A schematic diagram of the hollow fiber spinning system is shown in Fig. 1. The apparatus consists of a spin-solution tank (1) with a thermometer (11), an on-line filter (2), a spinneret (3), a high pressure nitrogen cylinder (4), a vacuum pump (5), one or more outer coagulation baths (6,7), a rotameter (8) connected to an internal gelation bath (9) provided with a funnel (10) and necessary control (12 to 17), and safety valves (18). The spin-solution tank (approx. one liter in volume) is jacketed to keep the spin-solution at the required temperature; the tank is also equipped with inlet connections linked to the high pressure nitrogen cylinder and the vacuum pump. The spinneret has a tube-in-orifice form, with a precision orifice containing a centrally positioned inlet tube to deliver the internal coagulant liquid. The internal coagulant is delivered through the inlet tube to create and maintain the bore structure of the fiber.

Under the driving force supplied by the high pressure nitrogen, the spin solution (25 °C) in the tank passes through the filter



into the spinneret, followed by the internal coagulant (25 °C) passing through a flow meter under gravity. The extruded fiber, after passing through an air gap, enters into the outer coagulation bath, which is water in this work. Subsequently, the fiber is forwarded through several roller guides into another water bath. The dimensions of the resulting fiber depends on the details of the spinneret design, length of air gap, fiber extrusion rate, viscosity of the polymer solution and the nature of the internal coagulant. The hollow fibers were further rinsed with distilled water for two hours, followed by immersion in hot water (95 °C) for ten minutes.

**Hollow fiber spinning and hollow fiber bundle preparation.** The compositions of the spin-solutions, the conditions of hollow fiber spinning and hollow fiber drying are summarized in Table I. Table II summarizes the hollow fiber dimensions. Twenty pieces of pin-hole free fibers of ca. 30 cm length were collected into a bundle, each end being covered with epoxy glue and potted into a polypropylene tube of length 6 cm. After 2 h of epoxy curing, the bundle was assembled into a hollow fiber test cell, which was further connected to the vapor permeation system shown in Fig. 2. The effective surface area of the hollow fiber bundle was 120 cm<sup>2</sup>.

Nitrogen gas was then introduced to the bore side of the hollow fiber bundle under the pressure of 145 kPa gauge (21 psig) and at the flow rate of 60 - 100 mL/min while vacuum was maintained on the

shell side. Nitrogen permeation through the membrane was allowed to continue for 4 h during which period all organic vapors and water adsorbed to the membrane were removed. Subsequently, the permeation experiments of nitrogen and organic vapors were started.

**Permeation experiments.** The details of permeation experiments were given in our earlier report (10). A mixture of organic vapor and nitrogen gas was produced by bubbling nitrogen gas from a porous sintered ball immersed in a chosen organic liquid at room temperature. The hollow fiber test cell was then housed in an isothermal chamber whose temperature was controlled within  $\pm 0.5$  °C. If necessary, the feed gas mixture was preheated to the experimental temperature in a heating coil before it was introduced to the permeation cell. The permeate side of the test cell was connected to two cold traps, followed by a DuoSeal vacuum pump (Model 1400). The permeation of the organic vapor was induced by maintaining its partial pressure on the permeate side lower than the feed side. The membrane permeated organic vapor was condensed and collected initially in one of the cold traps, and then this cold trap was switched to the other after the steady state was reached. The permeation rate was determined gravimetrically by weighing the condensed vapor sample collected for a predetermined period. The durability of hollow fibers was tested by repeating the nitrogen permeation experiment before and after the organic permeation experiments that lasted for about three months. The

reproducibility of the data assured stability of hollow fibers when they are exposed to organic vapors.

The feed gas stream was connected to a Varian gas chromatograph (Model 3400) both at the inlet and at the outlet of the feed chamber of the permeation cell through bypass valves to determine the composition of the feed mixture. The feed flow rate was so high that the concentration change from the inlet to the outlet of the feed chamber was negligible. The permeation rate of pure nitrogen was determined in the following way. A bubble flow meter was connected to the feed chamber outlet of the permeation cell and the feed inlet valve was closed. When the permeate side of the permeation cell was evacuated by a vacuum pump, nitrogen was sucked from the bottom of the bubble flow meter into the feed chamber pushing a soap film in the buret downwards. The nitrogen flow rate was determined from the speed of the movement of the soap film. The permeation experiments were conducted normally at 23 °C while the pressure on the permeate side was maintained at 493 to 667 Pa (3.7 to 5.0 mmHg). The compositions of the feed gas mixture and the permeate sample collected in the cold-trap were determined by gas chromatograph (Varian 3400) using a chromosorb (CHROM 102) column with a length of 2 m and a diameter of 0.318 cm.

## Results and Discussion

Table III summarizes the results of permeation experiments with respect to nitrogen gas and n-pentane vapor. The permeabilities of nitrogen,  $J_N$ , and n-pentane,  $J_{C5}$ , and their ratios,  $J_{C5}/J_N$  considered as the hollow fiber selectivity, are given for each hollow fiber. The data were summarized in Table III in the order of increasing polymer concentration. In Fig. 3 the highest selectivity achieved for a polymer concentration is plotted versus the polymer concentration. The selectivity increases as the concentration increases, and it is obvious that a polymer concentration higher than 27 % is necessary to obtain a notable selectivity. The highest selectivity achieved was 28.7 with hollow fiber 14 that was prepared from a polymer solution containing 30 wt-% polymer. It should be noted that the n-pentane selectivity with the PEI-8 membrane, which was used as a standard flat sheet membrane for vapor separation from air in our previous study, was 65.2. In other words, we were able to produce hollow fiber membranes whose selectivity is lower than that of flat sheet membranes but high enough for the practical purpose. The nitrogen permeability,  $J_N$ , was  $1.33 \times 10^{-11}$  and  $1.73 \times 10^{-11}$  mol/m<sup>2</sup> s Pa, respectively, for hollow fiber 14 and PEI-8 membrane.

It is interesting to note that PEI-8 membrane started from 25 wt-% polymer solution whereas hollow fiber 14 started from 30 wt-% polymer solution. Whereas partial evaporation of solvent at 110 °C for 1.8 min was required in PEI-8 membrane, no such evaporation

period was necessary for hollow fiber 14. This is very important since an evaporation period of 1.8 min is not practical in the spinning hollow fibers.

The selectivity,  $J_{C5}/J_N$ , and the nitrogen permeability,  $J_N$ , are plotted in Fig. 4. There is a correlation between the selectivity and nitrogen permeability. When the former increases, the latter decreases, as expected. Figure 4 also includes the experimental  $J_{C5}/J_N$  versus  $J_N$  data for flat sheet membranes obtained in our previous work (12). For a given value of  $J_{C5}/J_N$  an order of magnitude higher  $J_N$  value was obtained for the flat sheet membrane. Lower polymer concentrations in the casting solution together with the partial evaporation of the solvent are believed to be the reason for the formation of thinner active surface layers of the flat sheet membranes.

Table IV summarizes the permeability and selectivity of hollow fibers 7 and 14 with respect to some aliphatic and aromatic hydrocarbons as well as water. The table also includes the data of flat sheet membrane PEI-8. The general pattern of the selectivity looks similar both for the hollow fiber and the flat sheet membrane. A notable difference was the extremely high selectivity of toluene when the hollow fiber membrane was used.

## **Conclusions**

The following conclusions can be drawn from the above experimental results.

- 1) It is possible to prepare hollow fibers from polyetherimide polymer for the separation of volatile organic vapors from nitrogen.
- 2) The polymer concentration of the spin-solution should be more than 27 wt-% in order to obtain hollow fibers of sufficiently high selectivities.
- 3) Because of the high polymer concentration in the spin-solution and because of the lack of the partial evaporation step of solvent, the flux of the hollow fiber is much less than that of the flat sheet membrane when the selectivity of both membranes are the same.
- 4) Hollow fiber membranes show extremely high selectivities for aromatic hydrocarbons.

## **Acknowledgement**

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## Nomenclature

- A : Permeability of nitrogen gas in eq. 3,  $\text{mol/m}^2 \text{ s Pa}$   
B : Constant defined by eq. 4 for vapor component,  $\text{mol/m}^2 \text{ s Pa}^2$   
 $J_N$  : Permeability of nitrogen gas,  $\text{mol/m}^2 \text{ s Pa}$   
 $J_{\text{vap}}$  : Permeability of vapor,  $\text{mol/m}^2 \text{ s Pa}$   
P : Pressure, Pa  
Q : Permeation flux,  $\text{mol/m}^2 \text{ s}$   
S : Effective membrane area in eq. 1,  $\text{m}^2$   
V : Volumetric permeation rate, mL/min  
Y : Mole fraction

## Subscripts

- N : nitrogen  
vap : organic vapor  
1 : feed  
3 : permeate

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Table I. Conditions of hollow fiber spinning

Hollow fibers	1	4	5	6	7	8	9
Polymer solution composition							
PEI	25	27	28	28	29	29	29
LiNO <sub>3</sub>	0.6	0.6	0.6	0.6	1.0	1.0	1.0
DMAc	74.4	72.4	71.4	71.4	70.0	70.0	70.0
Spinning conditions							
air gap length, cm	186	100	80	80	30	60	100
spin solution pressure, psig	30	40	40	40	40	40	40
external coagulant <sup>a</sup> temperature, °C	13	13	14	14	16	16	16
Solvent exchange	b	b	b	c	b	b	b
Fiber drying	e	d	d	d	d	d	d

Hollow fibers	10	11	12	13	14
Polymer solution composition					
PEI	29	29	29	30	30
LiNO <sub>3</sub>	1.0	1.0	1.0	1.0	1.0
DMAc	70.0	70.0	70.0	69.0	69.0
Spinning conditions					
air gap length, cm	30	60	100	75	90
spin solution pressure, psig	40	40	40	40	40
external coagulant <sup>a</sup> temperature, °C	16	16	16	18	18
Solvent exchange	b	b	b	b	b
Fiber drying	e	e	e	d	d

Table I. continued

Hollow fibers	5111	5071	5072
Polymer solution composition			
PEI	28	28.5	28.5
LiNO <sub>3</sub>	0.6	0.6	0.6
DMAC	71.4	70.9	70.9
Spinning conditions			
air gap length, cm	80	100	100
spin solution pressure, psig	40	40	40
external coagulant <sup>a</sup> temperature, °C	14	14	14
Solvent exchange	-	b	c
Fiber drying	d	d	d

<sup>a</sup> Both internal and external coagulants are water except internal coagulants of hollow fibers 7-12, 5071 and 5072 which are 15 wt-% aqueous glycerol solution.

<sup>b</sup> Successive immersion in aqueous ethanol solutions with 30, 50 and 100 wt-% ethanol, in each solution for one hour.

<sup>c</sup> Immersion in 50 wt-% aqueous glycerol solution for 20 h.

<sup>d</sup> In air at ambient temperature.

<sup>e</sup> In air at 50 °C for 15 min.

Table II. Hollow fiber geometries

Hollow fibers	4	5	6	7	8	9	10
Outer diameter, mm	1.13	1.16	1.14	1.66	1.53	1.44	1.57
Inner diameter, mm	0.58	0.66	0.61	0.73	0.74	0.76	0.71
Hollow fibers	11	12	13	14	5111	5071	5072
Outer diameter, mm	1.46	1.40	1.38	1.21	1.16	1.01	1.01
Inner diameter, mm	0.77	0.86	0.67	0.65	0.66	0.66	0.66

Table III. Permeability and selectivity data of hollow fibers

Hollow fiber	Polymer con. wt-%	Permeability x 10 <sup>10</sup>		Selectivity J <sub>C5</sub> /J <sub>N</sub>
		J <sub>N</sub>	J <sub>C5</sub>	
4	27	9.30	17.50	1.88
5111	28	14.8	14.5	0.98
5	28	1.42	7.94	5.59
6	28	0.96	6.06	6.32
5071	28.5	0.69	4.11	5.95
5072	28.5	a		
7	29	0.39	6.52	16.67
10	29	a		
8	29	0.52	6.02	11.62
9	29	11.5	12.0	1.04
11	29	14.6	17.4	1.20
12	29	560	562	1.01
13	30	a		
14	30	0.13	3.83	28.67

<sup>a</sup> No permeation of nitrogen observed

Table IV. Permeability and selectivity of different vapors

Gas or vapor	Hollow fiber 7		Hollow fiber 14		PEI-8
	$J_{N(vap)}$ $\times 10^{10}$ mol/m <sup>2</sup> s Pa	$J_{vap}/J_N$	$J_{N(vap)}$ $\times 10^{10}$ mol/m <sup>2</sup> s Pa	$J_{vap}/J_N$	$J_{vap}/J_N$
Nitrogen	0.39		0.13		
n-Pentane	6.52	16.67	3.83	28.7	65.2
Cyclohexane	21.6	55.33	10.4	77.8	435
n-Heptane	39.3	100.6	18.5	139	622
Toluene	512.7	1311	275.3	2069	1147
Water	3166	8099	1411	10585	

## Figure captions

1. A schematic diagram of hollow fiber spinning system.
2. A schematic diagram of vapor permeation system  
1,7-nitrogen cylinder; 2,8-valve; 3,9-flowmeter; 4,10-pressure gauge; 5,11-water bath; 6-saturator for organic vapor; 12-saturator for water vapor; 13-mixer for two gas lines; 15-hollow fiber module; 16-GC; 17-cold trap; 18-vacuum gauge; 19-vacuum pump
3. Selectivity versus PEI concentration in the spin-solution
4. Nitrogen permeability versus n-pentane selectivity  
solid line, hollow fibers  
broken line, flat sheet membranes











