Pore Condensation-Based Separation of VOCs by a Microporous Ceramic Membrane

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Abstract

A pore condensation-based separation technique was studied experimentally using toluene and xylene in a nitrogen stream. The removal rate of toluene and xylene on a microporous ceramic membrane was enhanced by increasing the partial pressure difference across the membrane, but the selectivity was reduced with increasing flux of nitrogen. This was found both in vacuum and pressure modes of operation. The experimental results from this study suggest that the pores near the inlet portion of the module were filled with the organic solvent while the pores near the exit section of the module were slightly opened as the solvent concentration was depleted along the module. The transport mechanism is most likely a combination of surface flow and pore condensation. The removal rate and separation factor of xylene in module 2 were quite high compared to those for toluene. In the case of xylene, the rate of N_2 permeation was reduced considerably relative to toluene, resulting in a much higher separation factor. Condensibility of xylene appeared to be higher than that of toluene, the potential for pore condensation-based separation of xylene was also found to be higher than that for toluene.

Key words : VOCs, pore-condensation, ceramic membrane

1. INTRODUCTION

Transport of gases and vapors through a solid nonporous polymeric membrane occurs by solution-diffusion mechanism in which the species dissolve in the upstream interface of the membrane, diffuse through it, and finally desorb at the downstream interface of the membrane (Stern and Frisch, 1981). When the membrane has micropores or pores, the mechanisms of Knudsen diffusion, surface diffusion, pore condensation, Poiseuille flow, molecular sieving or any combination of them are operative. The transport regime is determined amongst others by the nature of the gas, the pressure, the temperature and the nature of the membrane both in terms of its pore structure and chemical interaction characteristics.

In membranes with small pore diameters, it is possible to induce multilayer adsorption and ultimately pore condensation leading to pore blockage by the condensed film of the vapor. When the partial pressure of the species is below that required by pore condensation, the separation factor is determined by relative diffusion rates between the two species. In the case of pore condensation, the transport of the non-condensible species through the pore is determined by its permeability in the condensed liquid. Since the permeation of non-condensible species through the condensed li-

quid film is much lower than the transport of that liquid by the appropriate driving force, the obtained permeate will be highly enriched in the condensible vapor species. Considering the relative permeabilities of the two species, very high separation factor can usually be obtained as a result of this mechanism.

This study explores the possibility of using pore condensation-cum-surface diffusion phenomenon to remove condensible organic vapors from gas streams, specifically, volatile organic compounds (VOCs) of importance in pollution control.

2. THEORETICAL BACKGROUND

There are a number of theoretical aspects to considerable degrees of complexity in pore condensation separation of a vapor from a gas mixture. These include pore condensibility criterion, flux and selectivity of different species, site-competition among different vapor species, permeation, and permeator models.

If the liquid is confined in a small pore, the vapor pressure over the meniscus is lower than the normal vapor pressure of the liquid. The smaller the radius of the pore, the greater the vapor pressure lowering. The relation between the saturated vapor pressure P_o of species i over a planar interface to that pressure (P_t) in a capillary of radius r_p is given by the Kelvin equation:

$$\frac{\rho RT}{M} \ln \frac{P_t}{P_o} = - \frac{2\gamma \cos\theta}{r_p} \qquad (1)$$

Where, ρ is the density of the condensate, R is the gas constant and T is the absolute temperature, M is the molecular weight of the condensate. γ, θ, and r_p represent the interfacial tension, contact angle and the radius of the pore, respectively.

When all capillaries are filled with the condensate, the saturation vapor pressure of the liquid inside the pores is reduced and a new driving force caused by the action of surface tension at the meniscus arises. This is called capillary suction pressure or capillary force (P_c) and this pressure can be calculated by a force balance at one end of a cylindrical pore filled with a condensate as follows:

$$(2\pi r_p)\gamma \cos\theta = -P_c(\pi r_p^2)$$
$$P_c = - \frac{2\gamma \cos\theta}{r_p} \qquad (2)$$

This equation is known as Laplace equation. Combining equation (2) with the previous Kelvin equation (1), one gets

$$P_c = \frac{\rho RT}{M} \ln \frac{P_t}{P_o} \qquad (3)$$

Here the new driving force for the capillary condensate flow inside the pore is the capillary pressure drop $(\varDelta P_c)$ or sometimes called capillary potential (Carman, 1952):

$$\varDelta P_c = \frac{\rho RT}{M}(\ln \frac{P_1}{P_o} - \ln \frac{P_2}{P_o}) = \frac{\rho RT}{M} \ln \frac{P_1}{P_2} \qquad (4)$$

Here P_1 and P_2 are gas phase pressures at upstream and downstream side, respectively. If there is a gradient of the gas-phase total pressure, both the gradients of the capillary force and the gas-phase total pressure act as driving forces in the transfer of the capillary condensate and the flow of capillary condensate is like a viscous flow. The capilllary pressure drop $(\varDelta P_c)$ is several hundred times greater than the gas phase pressure drop applied (Lee and Hwang, 1986).

3. EXPERIMENTAL

3. 1 Materials

A tubular microporous ceramic membrane tube known as Membralox^R was obtained from ALCOA separations technology company. This tubular ceramic membrane is comprised of a rigid body of α-alumina support which has a coarse porosity and pore size (10~15 mm) and a γ-alumina membrane skin having 50Å pore diameter in the inner surface layer. Toluene and p-xylene was selected to represent two of the frequently used industrial solvents. Physical properties of gas/vapors used in this study are given in Table 1. The specifications of ALCOA tubular ceramic membrane are shown in Table 2, the specifications of the two modules used in the experiments are shown in Table 3. Fig. 1 shows a photograph of the tubular ceramic membrane and the modules used in these experiments.

3. 2 Experimental Procedure

3. 2. 1 Vacuum mode of operation

The experimental setup for vacuum mode of operation is shown in Fig. 2. Pure nitrogen from a cylinder was introduced into a bubbler which contained VOCs at a controlled rate using an electronic mass flow transducer-controller (MFTC). The VOC-containing nitrogen stream was then passed through the feed side of the tubular ceramic membrane module. A MFTC with digital-readout devices was used to adjust the feed flow rate. All experiments were done at room temperature. A vacuum pump was connected at both ends of the permeate side to provide a driving force for organic vapor permeation.

The feed inlet flow rates were made to change from 20 to 220 cc/min and the permeate side vacuum levels were to vary

Table 1. Physical properties of gases and vapors.

Gas/Vapors	Molecular Weight	Boiling Point (°C)	Vapor Pressure (mmHg)	Liquid Density (g/cm³)	Surface Tension (dyne/cm)	Normalized Vapor Pressure (P_t/P_o)*
Nitrogen	28.0	−195.8	−	−	−	−
Toluene	92.1	110.6	28.4	0.862	27.9	0.382
p−Xylene	106.2	138.4	8.76	0.861	28.0	0.328

*: Calculated based on Kelvin equation at 25°C.

Table 2. Specifications of tubular ceramic membrane.

	Layer	Material	Pore Diameter (μm)	Porosity (%)	Thickness (μm)
Membrane	1	γ-Al$_2$O$_3$	0.005	50	5
	2		0.2	35	30
	3		0.8	40	50
Support		α-Al$_2$O$_3$	10~15	40~45	1500

Table 3. Specifications of the two modules used.

Module Number	Inside Diameter (mm)	Outside Diameter (mm)	Wall Thickness (mm)	Effective Length (mm)	Surface Area (cm²)
1	7.0	10.0	1.5	60.0	15.85
2	7.0	10.0	1.5	225.0	59.45

(a) Microporous Tubular Ceramic Membrane
(ALCOA, Membralox)

(b) Module 1 (Teflon Housing)
Effective Length : 6.0 cm
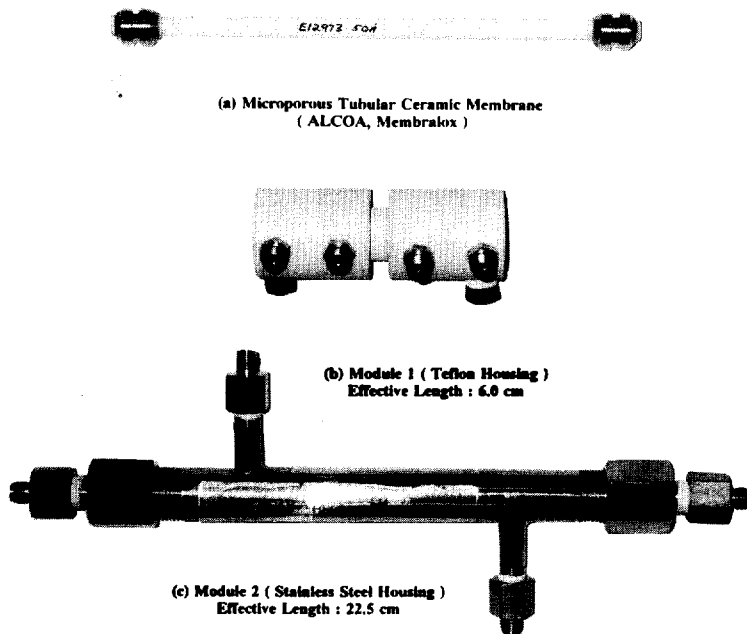
(c) Module 2 (Stainless Steel Housing)
Effective Length : 22.5 cm

Fig. 1. Photograph of the tubular ceramic membrane and modules.
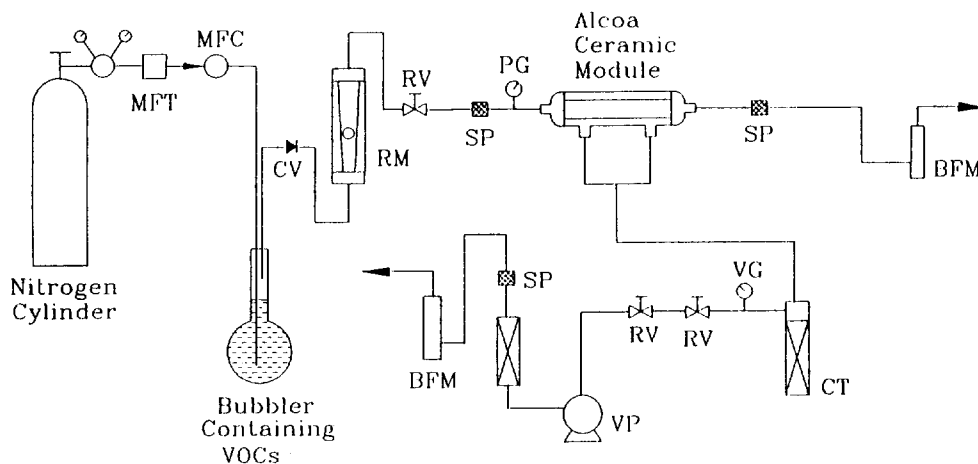
Fig. 2. Experimental setup for vacuum mode of operation.

BFM	:Bubble Flow Meter	PG	:Pressure Gauge	CT	:Cold Trap	RM:Rotameter
CV	:Check Valve	RV	:Regulating Valve	MFC	:Mass Flow Controller	
SP	:Sampling Port	MFT	:Mass Flow Transducer	VG	:Vacuum Gauge	
OF	:Oil Filter	VP	:Vacuum Pump			

from -127 mmHg up to -635 mmHg. Feed side pressure was kept constant at atmospheric pressure. Once the feed side flow and the desired vacuum level on the permeate side were achieved, 1.0 c.c. of feed inlet and outlet samples were taken periodically with GASTIGHT syringe and injected into the GC until steady values were obtained. A flame ionization detector and a Chromosorb W-HP column were used for the analysis of solvent vapor concentration.

3. 2. 2 Pressure mode of operation

In the pressure mode of operation, a back pressure regulator controlling the upstream pressure was placed after the membrane module to create the proper pressure level, therefore serving as the driving force. The nitrogen stream containing VOCs passed through the feed side of the membrane module. The feed side pressure was varied from 10 to 30 psig and the permeate side was maintained at atmospheric pressure. One end of the permeate side was closed so that the permeate flow is countercurrent to that of feed flow; 1.0 cc of the feed inlet and outlet as well as the permeate samples were taken and analyzed using a GC.

The experimental feed concentration ranges were slightly higher than theoretical pore condensation concentration in both solvents. Table 4 provides the experimental feed concentration ranges for two solvents

Table 4. The concentration range of experimental feed vapors.

Solvents	Saturated Conc. (ppmv)	Pore Condensation Conc. (ppmv)	Exp. Feed Conc. Range (ppmv)
Toluene	37,421[a]	14,300[b]	15,000 ~ 29,000
p-Xylene	11,526	3,779	4,000 ~ 6,000

[a] : Calculated using saturated vapor pressure data (Perry & Green, 1984).
[b] : Calculated based on Kelvin equation at room temperature (25°C).

used in the experiments.

4. RESULTS AND DISCUSSION

4. 1 Vacuum Mode of Operation

In the vacuum mode of operation, feed side pressure was kept constant at atmospheric pressure while the permeate side pressure was reduced in subsequent experimental runs by increasing the level of vacuum. In most cases, the percent removal of toluene as well as its separation factor decreased as the total feed flow rate increased at a particular permeate side pressure. Inlet toluene concentration levels used here (around 27,000 ppmv) were higher than that predicted by Kelvin equation for pore condensation (14,300 ppmv).

In module 2, the difference between the feed inlet and outlet flow rates increased as the feed inlet flow rate increased. As the total flow rate increased, more nitrogen passed through the pores, which will lead to the reduction of the separation factor. The percent removal of toluene increased as the permeate side pressure was
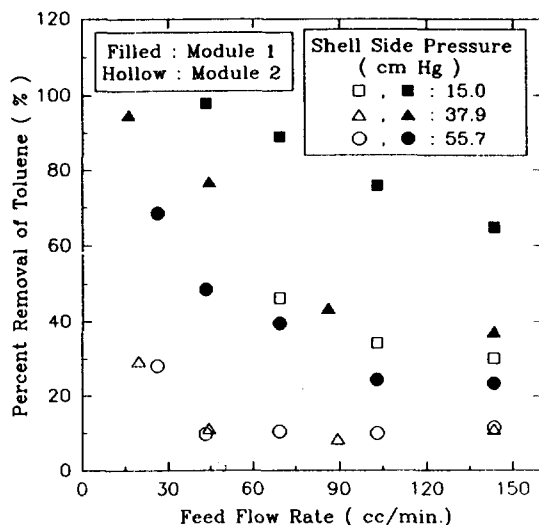

Fig. 3. Percent removal of toluene vs. feed flow rate at varying permeate-side pressure.

lowered. The percent removal of toluene in module 1 was always 2~3 times higher than that of a module 2 at a given operating condition (see Fig. 3). However, the separation factor was significantly less in module 1 compared to module 2. This was mainly due to the much higher flux of both toluene and nitrogen through the pores in module 1 under same operating conditions.

As the permeate side pressure decreased (increasing vacuum), percent removal of toluene increased. However, the separation factors were far lower in both modules. At 150 mmHg permeate side pressure, percent removal of toluene was over 90% at a small feed flow rate but the separation factor was limited to ca. 2.0 only due to a high nitrogen permeation rate.

In module 2, permeator outlet toluene concentration was in most cases higher than the theoretical pore condensation concentration. This implies that the vapor transport mechanism can be considered as pore condensation. However, the nitrogen permeation rate through the pores are still considerably high, especially when the permeate side pressure is very low. In other words, there are some pores in the membrane partially or totally open which allows nitrogen permeation through them. It is likely that the membrane pores near the inlet portion of the permeator are rather easily filled with the solvent, and the pores near the exit section of the permeator will be opened as the solvent concentration is depleted along the permeator.

In module 1, the percent VOCs removal was very high compared to module 2. The separation factor, however, was usually lower than that of module 2. Fig. 4 shows the separation factor in both modules as a function of the feed flow rate. In addition, the permeator outlet toluene concentration

in most cases was much lower than the theoretical pore condensation concentration. For this reason, the nitrogen permeation was always higher than that in module 2, which also reduces the separation factor. It is difficult to assume the existence of pore
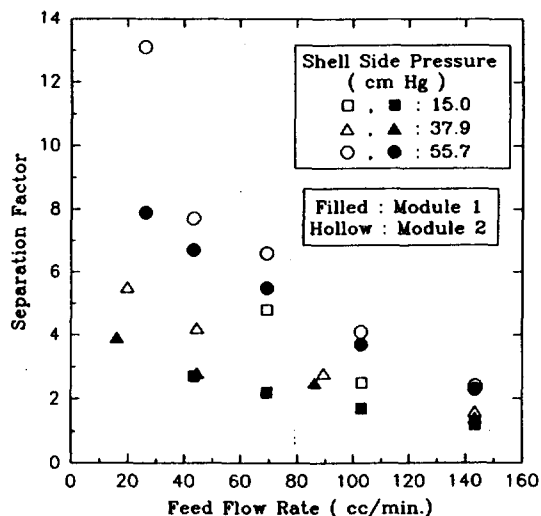

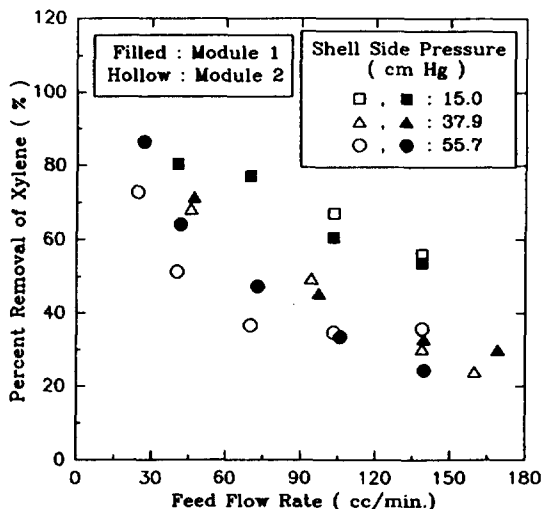Fig. 4. Separation factor (tol/N$_2$) vs. feed flow rate at varying permeate-side pressure.

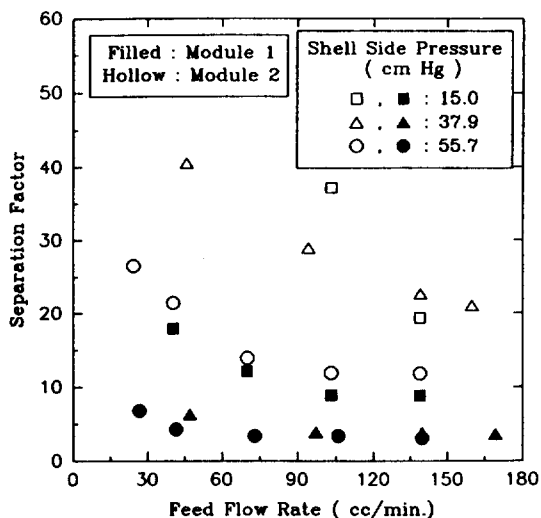Fig. 5. Percent removal of xylene vs. feed flow rate at varying permeate-side pressure.

Fig. 6. Separation factor (xyl/N₂) vs. feed flow rate at varying permeate-side pressure.

condensation in module 1 since the theoretical separation factor in the Knudsen flow regime is about 1.8 which is similar to some of the results presented here.

Similar experiments were made with xylene using two modules. Feed solvent concentrations were above the concentration required for the pore condensation. Three different levels of permeate side vacuum were applied, the feed side was maintained at atmospheric pressure. Percent removal of xylene was generally higher in module 1 compared to module 2, and separation factor was smaller in module 1 as was found for toluene. Nitrogen permeatin rate in module 1 was quite high as was the case for toluene, however, the nitrogen flux in module 2 was considerably lower compared to the case of toluene. Fig. 5 and 6 show the percent removal of xylene and separation factor as a function of feed flow rate. The blocked fraction of the membrane tube length can be considered much higher in this case than that for toluene.

In module 1, percent removal was rela-

tively high, but separation factor was still small due to the nitrogen leakage through the pores. This is similar to that observed for toluene. It can be assumed that some pores of the module 1 were partially open through which the nitrogen was leaking. In the case of module 2, percent removal of xylene was of similar level as toluene, but the separation factor was enhanced by less permeation of nitrogen through the membrane. From the values of separation factor obtained at this stage, it is still difficult to assume that all pores in the membrane are filled with condensate. It is most likely that the pore size distribution is very narrow in ceramic membranes, there is still a possibility that some pores with bigger size may not be completely filled with the condensate at particular partial vapor pressure. Therefore, the vapor species may be transferred partially as a pore condensate and also partially as a surface flow.

4. 2 Pressure Mode of Operation

In the pressure mode, the feed toluene concentration was generally lower than that in the vacuum mode at a similar total feed flow rate, the feed toluene concentration was even lower at higher feed-side pressure. In this case, permeate side was maintained at atmospheric pressure while the feed side was pressurized using a back-pressure regulator up to 30 psig.

The effect of feed-side pressure on the separation performances is shown in Fig. 7 and 8. Module 2 was used in this case. As shown in Fig. 7, increasing feed pressure improved the percent removal of the solvent through an increase in the driving force. The effects of regulating the feed side pressure on separation factor are illustrated in Fig. 8. A higher feed pressure generally yielded lower values of separation factor. For the same permeate side pres-
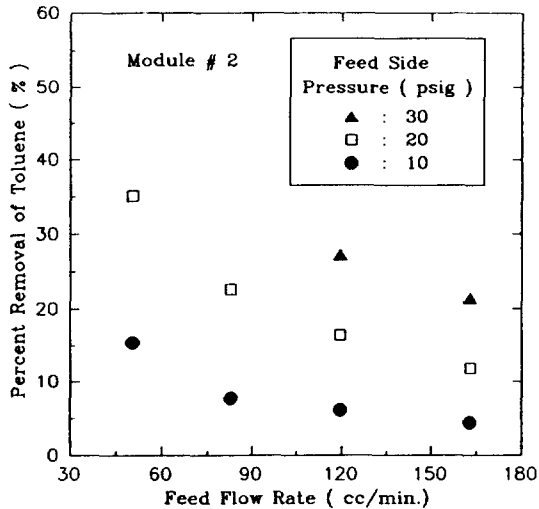
Fig. 7. Percent removal of toluene vs. feed flow rate at varying feed-side pressure.
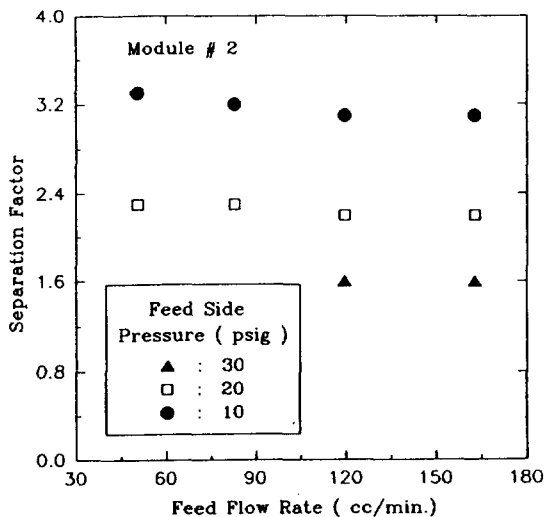

Fig. 8. Separation factor (tol/N₂) vs. feed flow rate at varying feed-side pressure.

sure, a higher feed pressure in the feed side allowed enhanced permeation of solvent and nitrogen through the non-blocked portion of the membrane module. Since the feed solvent concentration was even lower than pore condensation concentration in some cases (especially at higher feed side pressure, 20~30 psig), it is reasonable to assume that there were both blocked and non-blocked portion of the membrane module with solvent.

In general, an increase in membrane effective length (or effective surface area) reduces the ratio of the blocked to the non-blocked portion of the membrane module, thus reducing the separation performance. These results also imply that pore condensation is not the only transport mechanism. Possible explanations for this behavior are such that: (1) low feed solvent concentration for pore condensation to occur; (2) long a module to block all pores of the membrane. Such a behavior is due to a combined effect of surface flow and pore condensate flow. Higher separation factor can be obtained with a high feed solvent concentration and a relatively shorter membrane module. For the pressure mode of operation, the toluene permeance was found to be in the order of 10^{-9} gmol/sec · cm² · cm Hg.

Judging from the experimental data, it can be concluded that the pore condensation phenomenon is more favored by xylene than by toluene. Many factors can be pointed out: first of all, pore condensation concentration predicted by Kelvin equation is much lower for xylene compared to that for toluene. Furthermore slightly bigger size of the xylene molecule compared to toluene may result in pore filling with fewer adsorption layers. The site-competition between the two different vapor species with the γ-alumina pore surface will definitely affect the separation performances. In addition, the condensibility of xylene is greater than that of toluene.

Some experiments were also performed at constant values of feed flow rate, feed and permeate side pressures for approxima-
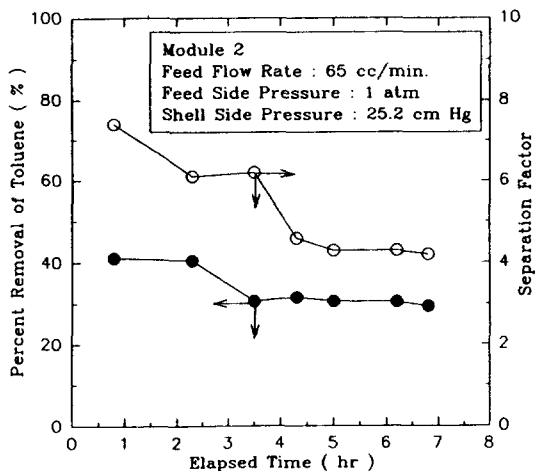
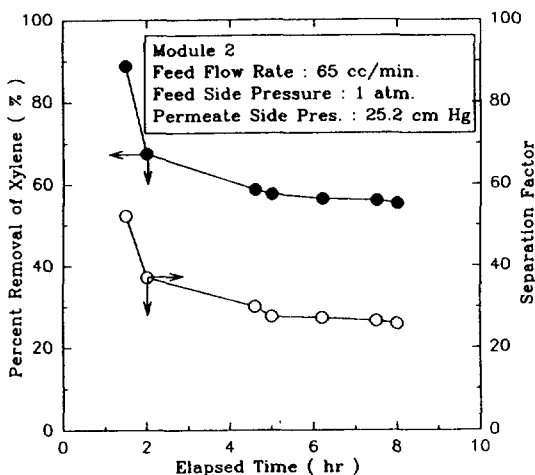Fig. 9. Percent removal and separation factor for toluene vs. elapsed time.

Fig. 10. Percent removal and separation factor for xylene vs. elapsed time.

tely 8 hours. Percent removal and separation factor were plotted in Fig. 9 and 10, respectively as a function of elapsed time. Experimental data showed that a constant value of solvent removal and separation factor could be obtained after 4~5 hours.

5. CONCLUSIONS

Experimental aspects of a pore condensation-based separation technique were studied for the removal of VOCs from N_2 using a microporous ceramic membrane. The increasing partial-pressure difference across the membrane yields a higher removal rate of VOCs but lower separation factor in vacuum as well as pressure modes of operation. There seemed to be some pores in the membrane permeator partially open which allows nitrogen permeation. It is likely that the membrane pores near the inlet portion of the permeator can easily be filled with the solvent and that the pores near the exit section of the permeator will be opened as the solvent concentration is depleted along the permeator. Accordingly, the transport mechanism of gas/vapor through this microporous ceramic membrane can be considered as an interplay of surface flow and pore condensate flow. The condensibility of xylene appeared to be higher than that of toluene leading to better performance. Pore condensation study by modifying/reducing the pore size of ALCOA ceramic membrane or using other membranes having a smaller pore size can be suggested for future studies of pore condensation-based separation of VOCs from N_2.

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미세다공성 세라믹 막에서의 기공응축기구에 의한 휘발성 유기화합물의 분리

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요 약 문

미세다공성 세라믹 막을 이용하여 기공응축기구에 의한 휘발성유기화합물(toluene, xylene)의 분리에 관한 연구를 수행하였다. 막을 통한 휘발성 유기화합물의 제거율은 막 양단의 분압차가 증가할 수록 증가하였으나, 선택도는 질소 투과율의 증가로 인하여 감소되었으며, 이 현상은 진공 및 압력모드에서 모두 나타났다. 실험결과로 판단하면, 막의 입구부분의 기공들은 거의 응축이 된 반면, 출구부분의 기공들은 유기증기의 농도가 감소함에 따라, 응축이 일어나지 않은 부분이 있음을 알 수 있어서, 막을 통한 유기증기의 투과기구는 기공응축과 표면확산의 조합으로 설명할 수 있었다. 모듈 2에서의 xylene의 투과율 및 선택도는 toluene의 경우보다 더 높았고, xylene의 응축도도 toluene보다 높게 나타나서 기공응축기구에 의한 xylene의 분리는 toluene의 경우보다 더 높음을 알 수 있었다.