

Characteristics in Separation of CCl_2F_2 /Air Gas Mixture by Polyimide Membrane

Kwang-Rae Lee *

폴리이미드 분리막에 의한 CCl_2F_2 /Air 기체혼합물의 분리특성

이 광 래 *

요 약

폴리이미드 분리막에 의한 CCl_2F_2 /Air 혼합물의 분리특성에 관하여 온도, 압력, stage cut (θ), 주입기체 조성등의 영향을 규명하였다. 본 연구의 실험범위 내에서 이상분리인자(ideal separation factor)는 60-200이었으며, glassy polymer인 폴리이미드 분리막에 대하여 투과도가 높은 air의 투과도는 CCl_2F_2 (dichlorodifluoromethane, CFC-12)에 의하여 상당히 감소함을 알 수 있었다. 그러나, 폴리이미드 분리막에 대한 투과도가 낮은 CCl_2F_2 의 투과도는 air에 의하여 투과도가 증가하였다. 또한, 수학적 모델에 의한 예측치가 실험치와 잘 일치됨을 알 수 있었다.

Introduction

Chlorofluorocarbons(CFCs) are widely used as refrigerants, blowing agents for plastic foams, solvents and degreasing agents in the electronics industry, and propellants for aerosol cans, owing to their characteristic stability, nonflammability, low toxicity, and lack of odor[1]. Because of their stability, however, they

are highly inert in the troposphere and transported upward into the stratosphere, where they are decomposed by UV light to produce chlorine atoms. The chlorine atoms are known to catalyze chain reactions resulting in depletion of the ozone layer in the stratosphere[2]. For this reason, emission of CFCs to the environment has become regulated by the Montreal Protocol.

Although CFC alternatives are beginning to appear in response to

* 강원대학교 공과대학 화학공학과 부교수

environmental regulation, the emission of CFCs to the atmosphere is a world wide concern due to destruction of ozone layer, thereby responsible for warming the atmosphere. Currently reduction processes CFC emissions are classified into two categories; destroying CFCs into unarmful chemicals and recovery/reuse of CFCs.

Several techniques[3] have been studied for the destruction of CFCs, which include O_2 combustion, thermal decomposition, plasma decomposition, catalytic decomposition, chemical conversion and supercritical fluid decomposition. However, the actual destruction methods of CFCs are not well established yet. CFCs themselves are nonflammable and the reaction of CFCs with oxygen cannot proceed by itself because of the endothermicity. However, destruction of CFCs may occur under existence of suitable fuels such as methane[4].

Tokuhaski et al.[4] reported the experimental results of destruction of CFC-12 (dichlorodifluoromethane, CCl_2F_2) with employing CFC-12/methane/air premixed flame and CFC-12/methane diffusion flame. They mentioned formation of trace amount of noxious compounds such as dioxins, as well as, harmful products HCl and/or HF.

Another typical technique for reduction of CFC emissions is recovery/reuse of CFCs. Condensation techniques, which are one of the CFC recovery/reuse processes, are appropriate for the treatment of relatively high concentrations (30%-100mole%) of CFCs [5]. The efficiency of CFCs recovery in

condensation techniques increases with decreasing temperature. At lower temperature (below $0^\circ C$), however, water is condensed with CFCs, and dehydration process is necessary since the CFCs form a hydrant with condensed water.

Adsorption and absorption processes are employed for the recovery of CFC in the range of approximately 0.05 to 10% [5]. Adsorption and absorption processes are not appropriate for treatment of higher concentration of CFCs, as the energy consumption for regeneration depends primarily on the amount of absorbent and adsorbed CFC amount in the absorption and adsorption processes, respectively. Furthermore, the existing techniques of CFC recovery such as condensation, adsorption and absorption do not economically cover the treatment of mixtures in the range of approximately 5 to 30% CFCs. Therefore, it is necessary to develop another CFCs recovery system for treating mixtures in the range of 5 to 30% CFC. In spite of the practical importance of the investigation of separation of air/CFC-12 gas mixture, there have been very few studies on the recovery of CFC by polymer membranes. The only reported membrane recovery system developed by Membrane Technology and Research, Inc. (Menlo Park, Calif.), concentrates organic vapors, chlorinated solvents and chlorofluorocarbons (CFCs), 10 times from their initial 500-1,000ppm levels[6].

In the present work, a polyimide hollow fiber membrane was tested for the permeation of pure air and pur CFC-12 and for the separation of air/CFC-12 gas mixture. Based on these pure permeation

rates, mixture. Based on these pure permeation rates, permeation rates of mixture and separation factor values, process engineering aspects of membrane separation were taken into account to study the performance of a polyimide hollow-fiber membrane module. The

performance of the membrane module was measured and compared with theoretical models developed for CFC-12/air gas mixture separation as functions of process temperature, pressure, stage cut, and feed composition.

Table 1. Permeation Rate of Air

	($10^{-5} \text{cc (STP) / cm}^2 \text{ sec cmHg}$)						
	2 kg/cm ²	3 kg/cm ²	4 kg/cm ²	5 kg/cm ²	6 kg/cm ²	7 kg/cm ²	8 kg/cm ²
30°C	0.421	0.411	0.402	0.391	0.382	0.372	0.359
40°C	0.545	0.542	0.538	0.535	0.531	0.528	0.525
50°C	0.653	0.649	0.646	0.642	0.638	0.634	0.630
60°C	0.832	0.831	0.831	0.831	0.831	0.831	0.830

Experimental

Material

The asymmetric polyimide membrane which was newly developed by UBE Industry, Ltd. Japan, was used in this work. The polyimide hollow-fiber membrane had a thin outer dense layer supported by a microporous structure. The outer and inner diameters were approximately 393 μm and 182 μm , respectively. Effective length and effective surface area of the hollow fibers in the module were 44.6 cm and 165 cm², respectively. Pure gases of Air and CFC-12 with a purity of 99.9% and 99.5% respectively were purchased and the binary gas mixture were prepared from these pure gases in this laboratory by the partial pressure method. To obtain a homogeneous gas mixture (CFC-12/Air) the cylinder was rolled back and forth. The composition was determined with a

gas chromatograph (Hewlett-Packard, 5890 series II).

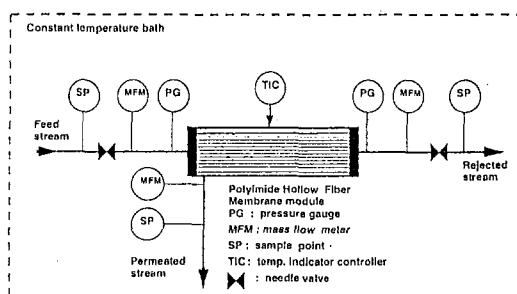


Fig. 1. Schematic diagram of experimental apparatus.

Apparatus

The schematic diagram of the experimental apparatus used for gas separation is shown in Fig. 1. The membrane module and preheating section of the feed gas were placed in a constant temperature air bath to keep the

temperature constant. The air bath was controlled by a temperature indicator (Cole Parmer Co.) and temperature indicator controller (Han Young DX9 temperature controller). The feed gas mixture was introduced into the membrane module keeping the pressure on the permeate side (shell side) lower than that on the feed gas side (tube side). The pressure on the permeate side (shell side) was kept at atmospheric pressure. The permeable components in the feed gas passed through the membrane from the tube side to the outside of the hollow fiber. The pressure of the feed gas side was controlled by a needle valve placed downstream of the tube side. The flow rate of the permeate gas was measured by a soap bubble flow meter at atmospheric pressure and that of the non-permeate flow was measured by a mass flow meter (Teledyne Hasting-Raydist, Model HFM-200L). These flow meters were calibrated with a soap bubble flow meter. The gas compositions of feed, non-permeate, and permeate stream, were analyzed with a gas chromatograph (Hewlett-Packard, 5890 series II). For

calibration of the gas chromatograph, equal volumes (equal mole) of pure gases were injected. The ratio of average peak areas at a fixed attenuation was used as the calibration factor. The average area was based on 4-7 samples. The chromatograph system was equipped with a thermal conductivity detector and analyzed with a Porapak Q 80/100 column (Alltech, Cat. No. 2701). Helium was used as a carrier gas.

Results and Discussion

Permeation rates for pure Air and CFC-12 gases

As discussed by Stern and Frisch[7], the permeability of a gas, which depends upon both solubility and diffusivity, varies from a glassy polymer to rubbery polymer. Glassy polymer has relatively high permeabilities for very small molecules such as helium, due to high diffusivity[8]. Polyimide membrane employed in this work, which is a glassy polymer, has much higher permeation rates for air than CFC-12 as shown in Fig. 4 and 5.

Table 2. Permeation Rate of CFC-12

[10^{-5} cc(STP)/cm² sec cmHg]

	3 kg/cm ²	4 kg/cm ²	5 kg/cm ²	6 kg/cm ²	7 kg/cm ²	8 kg/cm ²
30°C	0.0045	0.0048	0.0055	0.0074	—	—
40°C	0.0035	0.0049	0.0063	0.0061	0.0066	0.0073
50°C	—	0.0039	0.0050	0.0058	0.0065	0.0074
60°C	—	0.0038	0.0046	0.0052	—	—

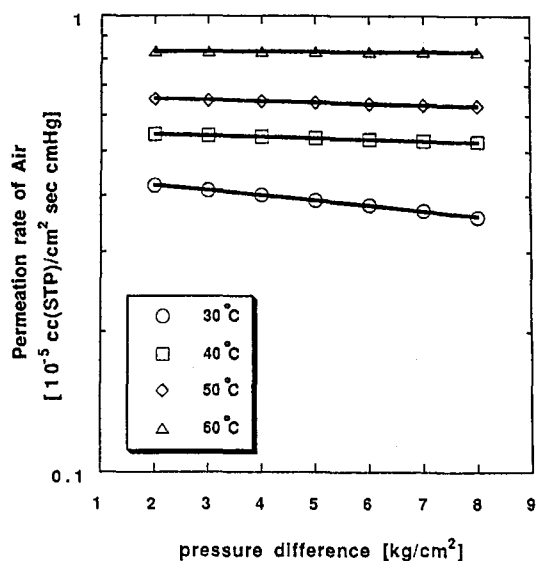


Fig. 2. Pressure dependence of permeation rate of air

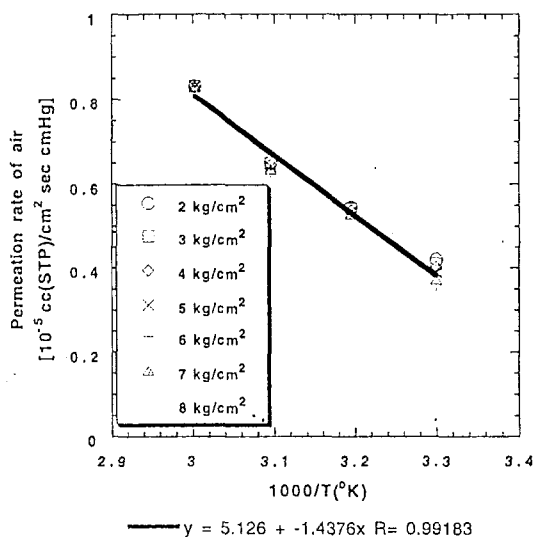


Fig. 3. Temperature dependence of permeate rate of air

Temperature dependence

The permeation rates of pure air and pure CFC-12 gases were measured in the temperature range of 30-60°C and in the range of a pressure difference from 2 to

8 kg/cm². Since the asymmetric membrane has a thin dense layer, which acts as the permselective layer, the thickness of this dense layer has to be used if one wants to calculate the true gas permeability coefficients. In the absence of an exact measurement of the dense layer, the permeation rate given in [cc(STP)/cm-sec-cmHg] can be used instead of actual permeability [cc(STP)/cm-sec-cmHg]. Throughout this paper, such permeation rate has been used exclusively.

The permeate stream pressure (shell side) was kept at 1 atm. Permeation rate of air increased with increasing temperature. The temperature seems to have much effect on the permeation of air, but not on CFC-12 as shown on Figs 3 and 4. Figures 3 and 4, which show Arrhenius-type plots, give the permeation rates of pure air and CFC-12 as function of temperature at various pressure ratios. The temperature dependence of permeation rate can be represented by:

$$Q = Q_0 \exp(-E_p / RT) \quad (1)$$

where E_p is the apparent activation energy for permeation. The experimental permeation rate and the reciprocal temperature produced a linear relationship as shown in Figs. 3 and 4. The apparent activation energies for permeation, which were determined by regression, show that temperature dependence of air is greater than that of CFC-12. Therefore the ideal separation factor is increased with increasing temperature as shown in Fig. 4.

Ideal separation factor

The ideal separation factor, which is the permeation ratio of pure air and pure CFC-12, is shown in Fig.6. The ideal separation factor (air/CFC-12) indicates the polymer's ability to separate air and CFC-12. As shown in Fig.6 and Table 1 and 2, the ideal separation factor (air/CFC-12) is around 60 to 200 in the temperature and pressure ranges studied. It implies that the polyimide membrane employed in this work has a promising potential for separation of air/CFC-12 mixture.

The increase of separation factor with increasing temperature in Fig.6 is due to the fact that the activation energy for air is larger than that for CFC-12 as shown in Fig.4.

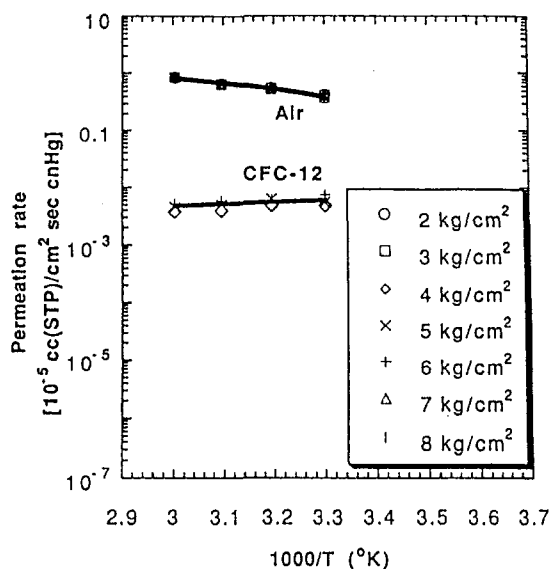


Fig.4. Temperature dependence of pure air and CFC-12 gas permeation rate

Pressure dependence

Pressure dependence of the permeation rates of air and CFC-12 were examined in the range of pressure differences from 2 to 8 kg/cm^2 . Figs 2, 5 and 6 show that the permeation rates and ideal separation factor (air/CFC-12) are not much affected by the pressure difference, whereas permeation rates of CFC-12 increased slightly with increasing pressure difference in the range of lower pressure (below 6 kg/cm^2) as represented in Fig.5. While the pressure difference seems to have very little effect on the permeation of air and CFC-12, the temperature has a much greater effect on the permeation rate of air (Figs.2 and 5). No effect of pressure on permeation rates of air implies that the membrane has no pin holes.

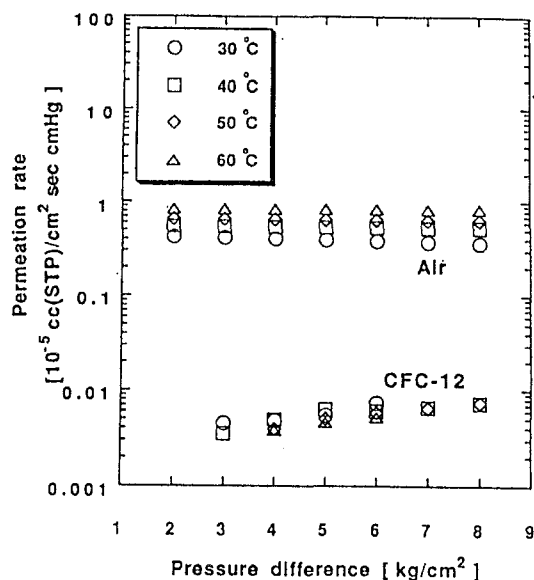


Fig.5. Pressure dependence of pure gas permeation rate

Permeation rates for CFC-12/air gas mixture

CFC-12/Air gas mixture

Since the permeation rate of one gas species can be influenced by another species in the mixture[9], the separation factors of a gas mixture might be substantially different from the ideal separation factor. As mentioned above, the ideal separation factor, which is the permeation ratio of pure air and CFC-12 gas, is not much affected by the pressure difference (Fig. 6). However, the separation factor of air and CFC-12 gas mixture is appreciably affected by the pressure ratio and feed compositions. The fact can be seen from Figs. 7 and 8.

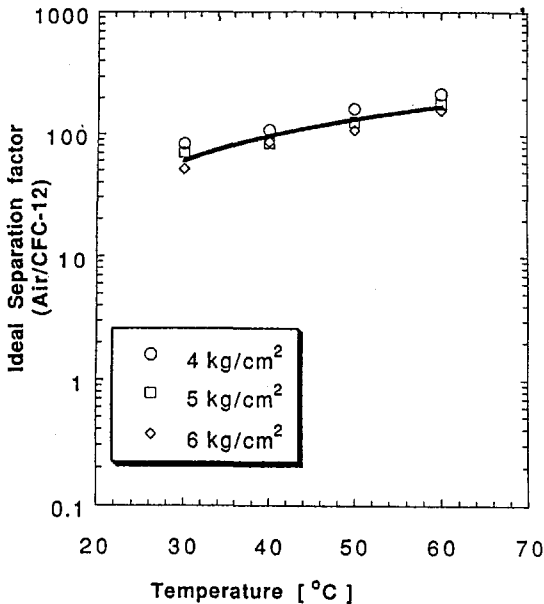


Fig. 6. Temperature dependence of ideal separation factor

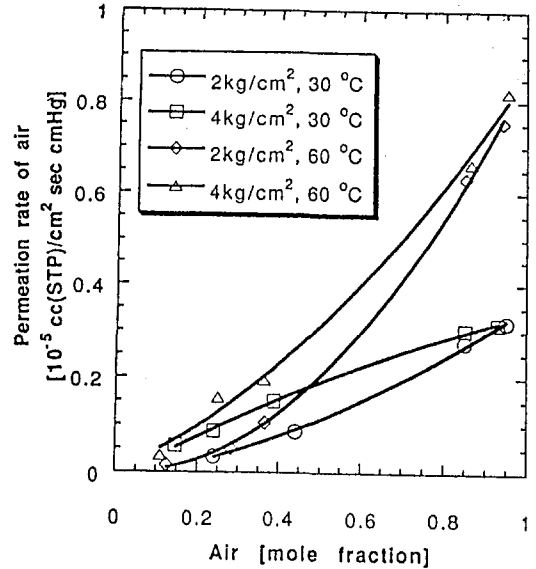


Fig. 7. The effect of temperature, pressure and feed composition on permeation rate of air

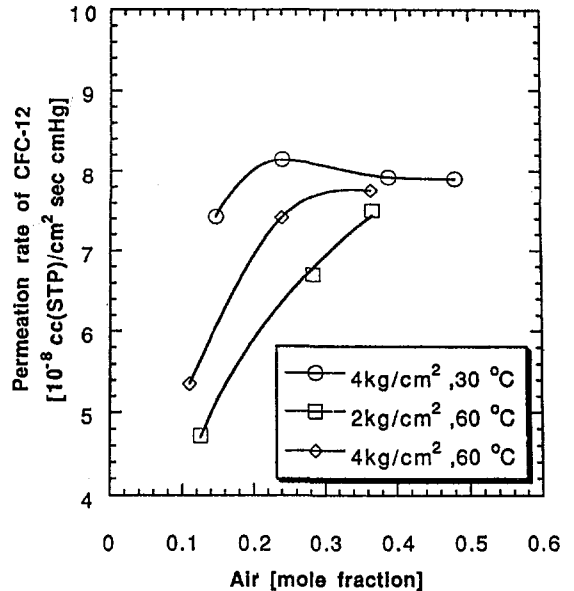


Fig. 8. The effect of temperature, pressure and feed composition on permeation rate of CFC-12

As Koros et al. [10] discussed, for a rubbery polymer (silicone rubber) the constituents of a multicomponent gas mixture permeate essentially independently of one another. For the glassy polymer (cellulose acetate), the presence of hydrocarbon in the mixed gas can affect both fast and slow gas permeabilities by as much as 20~60% [8]. Seok et al. [8] showed that the permeability of cellulose acetate (glassy polymer) to the mixed gas (He/CH₄, He/C₂H₄, He/C₂H₆) increased 18-51% for helium (more permeable gas) and decreased 1-27% for hydrocarbons (less permeable gas). They reported that those effects might be caused by the swelling of the membrane and the changing of the membrane structure by the hydrocarbon. In this study, however, the permeation rate of polyimide membrane (glassy polymer) to the mixed gas (air/CFC-12) decreased 10-90% for air (more permeable gas) and increased for the CFC-12 (less permeable gas) with variation of mixture gas composition as represented in Fig. 7 and 8, respectively. With this experimental result, we might infer that there were no swelling and no changing of the membrane structure by the presence CFC-12. In addition, the performance of a membrane module for separation of air/CFC-12 mixture depends on several operating variables such as temperature, pressure ratio, stage cut, and feed gas composition.

Effect of temperature and pressure

The permeation rates of air and CFC-12 for various compositions of air/CFC-12 gas mixture were determined as shown in Figs. 7 and 8 at 30°C and 60°C for a trans-membrane pressure difference of 2 and 4 *kg/cm²* at a very low stage cut (permeate rate/feed flow rate, θ) of 0.001. Very low stage cut (permeate flow rate/feed flow rate) holds the concentration of tube side constant and same with feed composition along the membrane column. Figure 7 shows that the effect of temperature on permeation rate of air is greater than pressure in the range of high concentration of air. Figures 7 and 8 show the permeation rate of air and CFC-12 for air/CFC-12 gas mixture increase with increasing both temperature and pressure, in contrast to the case of pure gas. As described earlier, the permeation rate of pure air is affected by temperature only, not by pressure difference. The effect of pressure for air/CFC-12 gas mixture might be caused by the presence of CFC-12.

Effect of stage cut (θ)

The stage cut (permeate rate/feed flow rate, θ) can be changed by varying the feed flow rate at a constant pressure ratio, temperature, and feed composition. The effect of stage cut on the air mole fraction in the permeate stream is presented in Fig. 9 with a 69%

air feed stream and a pressure difference of 2 kg/cm^2 at constant temperature of 30°C .

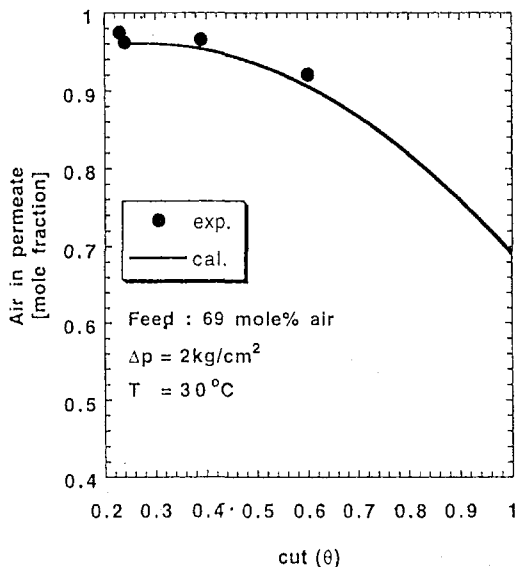


Fig. 9. Theoretical curve of air concentration in permeate stream as a function of stage cut

Fig.9 shows that the permeate composition is a function of stage cut. This function represents the effect of the flow regime in the non-permeate side stream and the driving force distribution caused by concentration polarization along the membrane column, since the stage cut is subject to the feed flow rate at a constant pressure ratio. The solid curve shown in Fig.9 is obtained by theoretical calculation using counter-current flow case in model 1 described below[11-13].

As shown in Fig.9, the experimental points fall quite well on the theoretical curves.

Effect of feed gas composition on permeation rate

The experimental results of the actual permeation rates of gas mixtures are shown in Figs. 7 and 8 as a function of air concentration in the feed gas mixture at a constant temperature of 30 and 60°C , and at a pressure difference of 2 and 4 kg/cm^2 with a constant stage cut of 0.001. It can be seen that the permeation rates are greatly affected by feed gas composition. The permeation rates of air through polyimide membrane were substantially decreased by the presence of CFC-12 (less permeable gas), whereas the permeation rates of CFC-12 was increased by the presence of air (more permeable gas). At given temperatures and pressure differences, the permeation rates of air approach to the pure gas permeation rates with increasing composition.

Mathematical models

Two kinds of mathematical model are necessary to analyze the performance of a gas separation module as a function of operative conditions and process design variables; Model 1 describes the concentration profile and flow rate profile at given process conditions, but it doesn't tell the changes of composition, flow rate, and pressure drop along the membrane column. To predict these operating variables along the membrane column, Model 2 is needed.

Model 1 : There are several mathematical models available to predict the performance of a gas separation membrane module[11-13]. These models are classified as counter-current flow, co-current flow, crossflow, perfect mixing,

and one-side mixing. The model considered in this work is counter-current, which is complied with this experimental experimental study, and is based on the same assumptions defined by previous investigators[11-13].

$$\frac{dq}{dx} = \frac{q}{x + \frac{\alpha^*}{(1 - \alpha^*) + (P_r - 1)/(x - P_r y)}}$$

$$y = \frac{xq - x_0}{q - 1}, \quad x \neq x_0 \quad (2)$$

initial conditions

$$\begin{aligned} x &= x_0, \quad q = 1 \\ y &= y_0 \end{aligned} \quad (3)$$

where

$$\frac{y_0}{1 - y_0} = \frac{\alpha^*(x_0 - P_r y_0)}{1 - x_0 - P_r(1 - y_0)}, \quad (4)$$

to find

$$q = \frac{1}{1 - \theta} \quad \text{at } x = x_i \quad (5)$$

and

$$y_p = \frac{x_i - (1 - \theta)x_0}{\theta} \quad (6)$$

For the solution of this model, the fourth-order Runge-Kutta integration method is employed. The solution to equation(2)is an initial value problem with initial conditions of eqns. (3) and (4). In order to solve these initial value problem, the integration is carried out from the outlet point for counter-current mode, since the concentration of the more permeable gas (air) in the permeate gas stream can be obtained by using Weller-Steiner Case I [11, 12]at the initial point.

The predictions of the counter-current case are compared with the experimental data in Fig. 9 as functions of stage cut (θ) at constant temperature of 30°C, a constant feed concentration (69 mole% air),

and a constant pressure difference of 2kg/cm². As mentioned above, for the glassy polymer (polyimide), the presence of CFC-12 in the mixed gas affects the permeabilities of both air and CFC-12 gas. In this theoretical calculation, the actual separation factor (α) was used instead of the ideal separation factor (α^*). It appears that the experimental data correlate well with the calculated values based on the counter-current theoretical model. Also, the predicted performance of the counter-current case is compared in Fig. 10 as functions of the feed composition at constant stage-cut (θ) of 0.39, constant temperatures of 30°C and 60°C, and constant pressure difference of 2kg/cm².

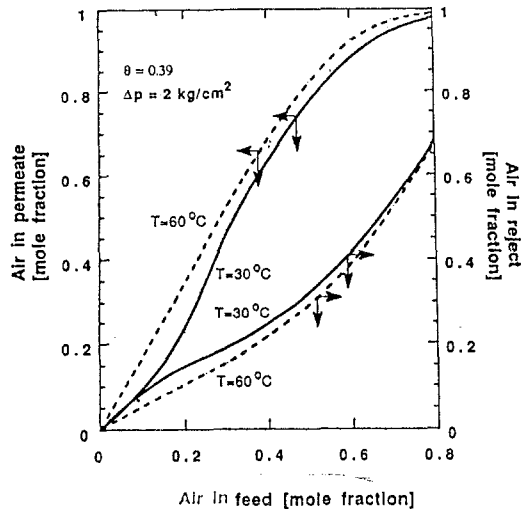


Fig. 10. Theoretical curve of air concentration in permeate and reject stream

Model 2 : The mathematical model discussed above doesn't tell the change of composition, flow rate, and pressure drop along the flow path in the tube side and shell

side. To predict these operating variables, another mathematical model developed by Thorman et al. [14] for gas separation in capillary membranes was employed.

The governing equations are given as follows.

$$\frac{dp}{dz} = \frac{8\mu KRTq}{\pi NP_h r_i^4} \quad (7)$$

$$\frac{dq}{dz} = \frac{2\pi N}{\ln(r_o/r_i)} \left[(Q_1 - Q_2)(xP_h - yP_l) + Q_2(P_h - P_l) \right] \quad (8)$$

$$\frac{dx}{dz} = \left(\frac{2\pi N Q_1 (xP_h - yP_l)}{\ln(r_o/r_i)} - x \frac{dq}{dz} \right) / q \quad (9)$$

The shell-side performance is calculated by the material balance :

$$G = q - q_o \quad (10)$$

$$y = (xq - x_o q_o) / G \quad (11)$$

The eqns. (7), (8), and (9) are solved simultaneously by the fourth-order Runge-Kutta method with the boundary conditions at the end of the column :

$$x = x_o \quad (12)$$

$$q = q_o \quad (13)$$

$$G = 0 \quad (14)$$

The shell-side composition at the very end of the column is obtained by solving a quadratic equation :

$$\frac{y_o}{1 - y_o} = \frac{Q_1}{Q_2} \left[\frac{(x_o P_h - y_o P_l)}{(1 - x_o) P_h - (1 - y_o) P_l} \right] \quad (15)$$

The numerical calculation may be started from either end and the same procedure can be repeated to the other end. If the material balance does not agree at the feed point, another set of initial conditions are made within the

limits of experimental errors, until the composition and flow rates match at the feed position. Wilke's equation [15] can be employed for predicting binary mixture viscosities.

The calculated composition profiles along the flow path in the tube side and shell side are shown in Fig. 11 at pressure differences of 2 and 4 kg/cm², stage cuts (θ) of 0.35 and 0.61 with a constant temperature of 60°C. Fig. 11 shows that the agreement between the experimental data and calculated results are excellent for this study.

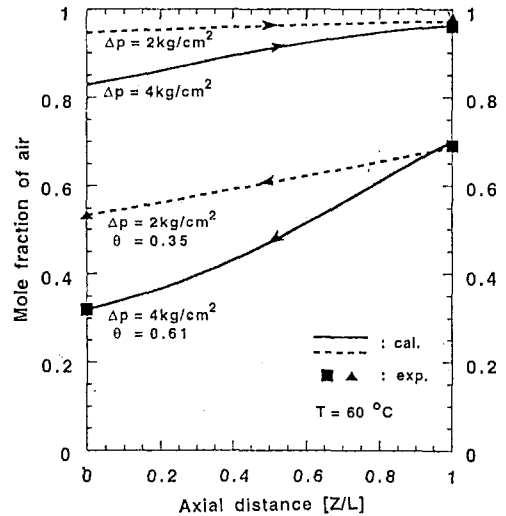


Fig. 11. The theoretical curves of concentration of air as Z/L

Conclusions

A polyimide hollow-fiber membrane was tested by measuring the permeation rates of pure air and CFC-12. The ideal separation factor (pure air/pure CFC-12) was of 60 to 200 in the ranges of temperature and pressure studied. It was

shown that the polyimide membrane had a promising potential for separation of CFC-12 from CFC-12/air mixture.

Also, various concentrations of air/CFC-12 gas mixtures were prepared and separation experiments were carried out as a function of operating variables for polyimide membrane module. The permeation rate of polyimide membrane (glassy polymer) to the mixed gas (CFC-12/air) decreased 10-90% for air (more permeable gas) and increased for the CFC-12 (less permeable gas) with variation of mixed gas composition.

The experimental results of substantial decrease in permeation rates of air (more permeable gas) through polyimide (glassy polymer) membrane by the presence of other gases are consistent with results of others' studies [8, 10].

The performance of the membrane module was well correlated and predicted by mathematical models.

Acknowledgement

This work was supported by NON DIRECTED RESEARCH FUND (1993), Korea Research Foundation. The authors wish to thank UBE Industries, Ltd. in Japan for providing membrane module.

List of symbols

E_p	apparent activation energy for permeation
G	shell side flow rate, permeate (cm^3/min)
K	unit conversion factor
N	number of capillaries
P, P_h, P_i	absolute pressure, tube side, shell side (kg/cm^2)

P_r	pressure ratio of permeate side to feed side
Q_0	preexponential constant of permeation rate
Q_1, Q_2	permeation rate, more permeable gas, less permeable gas ($cm^3(STP)/sec-cm-cmHg$)
R	gas constant
T	temperature
q'	dimensionless flow rate
q, q_0	tube side flow rate, reject stream
r_o, r_i	radius of capillary, out side, inside (cm)
x, x_i, x_o	mole fraction of more permeable gas in tube side, feed stream, reject stream
y, y_p, y_o	mole fraction of more permeable gas in shell side, at outlet point of permeate, at outlet point of reject stream
z	axial distance (cm)
α, α^*	separation factor, ideal separation factor
θ	stage cut (permeate rate/feed flow rate)

Reference

1. Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd ed., Vol.10, John Wiley & Sons, NY, p.860 (1982).
2. M.J. Molina and F.S. Rowland, Stratospheric sink for chlorofluoromethanes: chlorine atomic catalyzed destruction of ozone, Nature, 249(1974), 810.
3. Ministry of international trade and

- industry of Japanese government, Destruction technologies of CFC's (Interim Report), (1989).
4. K. Tokuhashi, Y. Urano, S. Horiguchi and S. Kondo, Incineration of CFC-12 by burner methods, *Combust. Sci. and Tech.*, 72(1990), 117.
 5. S. Asakura and K. Kawata, The present situation and the practical use trend of CFC recovery and reuse technology, 26(8), (1990)31.
 6. J. Stone, The recycling loop closes for solvents, *Chem. Eng.*, June, (1991)43.
 7. S. A. Stern and H.L. Frisch, The selective permeation of gases through polymers, *Ann. Rev. Mater. Sci.*, 11(1981)523.
 8. D.R. Seok, S.G. Kang and S.T. Hwang, Separation of helium and hydrocarbon mixtures by a two membrane column, *J. Membrane Sci.*, 27(1986)1.
 9. D.J. Maclean and T.R. Metzger, Fundamentals of gas permeation, *Hydrocarbon Processing*, August, (1983)47.
 10. W.J. Koros, R.T. Chern, V. Stannett and N.B. Hopfenberg, A model for permeation of mixed gases and vapors in glassy polymers, *J. polym. Sci.*, 19(1981)1513.
 11. S.T. Hwang and K. Kammermeyer, *Membrane in Separations*, John Wiley & Sons, NY(1975).
 12. C.T. Blaisdell and K. Kammermeyer, Counter-current and co-current gas separation, *Chem. Eng. Sci.*, 28(1973)1249.
 13. Y. Shindo, N. Itoh and K. Haraya, On gas separation by permeation with one side mixing, *Sep. Sci. Technol.*, 23(1988)1183.
 14. S.T. Hwang and J.M. Thorman, The continuous membrane column, *AIChE J.*, 26(1980)558.
 15. C.R. Wilke, A viscosity equation for gas mixtures, *J. Chem. Phys.*, 18(1950)517.