Korean J. Chem. Eng., **24**(4), 693-697 (2007)

Absorption of SO_2 using PVDF hollow fiber membranes with PEG as an additive

Hyun-Hee Park, Chun-Won Lim, Hang-Dai Jo, Won-Kil Choi and Hyung-Keun Lee†

Energy Conversion Research Department, Korea Institute of Energy Research, Daejeon 305-343, Korea
(*Received 28 August 2006 • accepted 24 November 2006*)

Abstract–In this study, removal of SO_2 from gas stream was carried out by using microporous polyvinylidene fluoride (PVDF) asymmetric hollow fiber membrane modules as gas-liquid contactor. The asymmetric hollow fiber membranes used in this study were prepared polyvinylidene fluoride by a wet phase inversion method. Water was used as an internal coagulant and external coagulation bath for all spinning runs. An aqueous solution containing 0.02 M NaOH was used as the absorbent. This study attempts to assess the influence of PEG additive, absorbent flow rate, SO_2 concentration, gas flow rate and gas flow direction on the SO_2 removal efficiency and overall mass transfer coefficient. The effect of liquid flow rate on SO_2 removal efficiency shows that at very low liquid flow rate, the NaOH available at the membrane surface for reacting with SO_2 is limited due to the liquid phase resistance. As liquid flow rate is above the minimum flow rate which overcomes the liquid phase resistance, the SO_2 absorption rate is controlled by resistance in the gas phase and the membrane. The SO_2 absorption rate with inlet SO_2 concentration was sharply increased by using hollow fiber membranes compared to a conventional wetted wall column because the former has higher gas liquid contacting area than the latter. The mass transfer coefficient is independent of pressure. When the gas mixture was fed in the shell side, the removal efficiency of SO_2 declined because of channeling problems on the shell side. Also, the addition of PEG in polymer dopes increased SO_2 removal efficiency.

Key words: G-L Contactor, Hollow Fiber Membrane, PVDF, Sulfur Dioxide, Absorption

INTRODUCTION

Combustion of fossil fuels in power plants, boilers and incinerators results in the emission of sulfur dioxide. The most common processes for purifying gas streams containing SO_2 are gas absorption systems using conventional absorption columns such as packed or spray towers. The absorption of sulfur dioxide into alkaline media is an important process which is receiving considerable attention as a means of controlling sulfur dioxide emission in stack gas from the combustion of fossil fuels [1]. Advantages of gas-liquid contactor using hollow fiber membrane over the conventional absorption processes such as packed or spray towers include the large interfacial area per unit volume, independent control of gas and liquid flow rates without the flooding, loading, foaming, etc. [2].

The membrane used acts as a fixed interface and keeps the gas and liquid phase separated while the mass transfer of gases takes place through the membrane. Depending on the membrane material, the physicochemical properties of absorbing liquid and the pore of membranes can be filled with either gas or liquid, which will result in large differences in the mass transfer resistance of the membrane employed [3]. The microporous hollow fiber membranes suitable for soluble gas removal should have high surface porosity, suitable pore size, thin separating layer thickness and good mechanical strength. In addition, the hollow fiber should have good resistance for scrubbing and long life. Because aqueous solution is used as the scrubbing medium, a hydrophobic membrane should be used [4].

†To whom correspondence should be addressed.
E-mail: hklee@kier.re.kr
‡This work was presented at the 6th Korea-China Workshop on Clean Energy Technology held at Busan, Korea, July 4-7, 2006.

In this study, SO_2 removal efficiency and absorption rate of SO_2 using asymmetric hollow fiber membranes were investigated experimentally. The asymmetric hollow fiber membranes were made by using PVDF and PEG as an additive. The membranes with different morphological structure were prepared and characterized, and the effects of operating conditions such absorbent flow rate, SO_2 concentration, gas flow rate were tested. Module performance was tested according to the direction of the gas and liquid phase flowing through the lumen and the shell side.

EXPERIMENTAL

1. Preparation of PVDF Hollow Fiber Membranes

The asymmetric hollow fiber membrane was prepared by the wet phase inversion method. Commercially available polyvinylidene fluoride (Kynar® k-761) was used as membrane material and N-methyl-2-pyrrolidone (NMP) was used to prepare polymer solution. Polyethylene glycol (PEG, Mw=600) was used as an additive to 10% on weight basis of the PVDF.

The required quantity of NMP was taken in a three-liter wide-neck reaction flask and PVDF powders were added. The spinning solution components were mixed thoroughly, heated to 60 °C for about 24 hr, and PEG as an additive was then added to the dope. The stirring was continued at 60 °C until the PEG was completely dissolved and it was filtered by using a glass filter. It was maintained at room temperature for 24 hr to remove air bubbles. Viscosity was measured at 20 °C with a Brookfield viscometer (model; LVDV II-pro).

The degassed dope was transferred to a stainless steel reservoir and pressurized to 3-5 kg/cm^2 by using nitrogen. The two spinnerets with an orifice diameter/inner diameter of the tube of 0.35/0.6 mm, 0.8/1.3 mm, respectively, were used to obtain the hollow

Table 1. Hollow fiber membrane spinning conditions

Dope composition	
PVDF, Kynar® k-761, Mw=440,000	20 wt%
NMP	70, 80 wt%
PEG, Mw=600	10 wt%
Dope temperature	20 °C
Coagulation bath composition	
Air gap	0 cm
Internal coagulant	water
Internal coagulant temperature	15 °C
Injection rate of dope solution	2.4-4.0 ml/min
Injection rate of internal coagulant	2.0-3.5 ml/min
Coagulation bath temperature	15 °C
Winding-up speed	3.6-8.2 m/min

fiber membranes.

Water was used as an internal coagulant and external coagulation bath for all spinning runs. The fibers were spun by the wet process (air gap=0) at the room temperature. The prepared hollow fiber membranes were immersed in a water bath to complete the solidification process and thoroughly washed in water. Table 1 shows the spinning conditions. The cross-sectional structure was examined by a scanning electron microscope (Hitachi, model; S-4700). The average pore size and the effective surface porosity of the hollow fiber membranes were obtained by gas permeation method [5-7]. N_2 gas was selected as the standard gas for permeation experiments, and the permeation flux through the prepared asymmetric hollow fiber membranes was measured at different pressures.

2. SO_2 Absorption Test

The hollow fiber modules designed for the experimental studies consisted of a 10 mm diameter and 150 mm length. The membrane module consisted of acryl tube and hollow fibers, which were fixed with epoxy resin at both ends of the tube. The number of hollow fiber membranes was 40. We called the hollow fiber membrane made

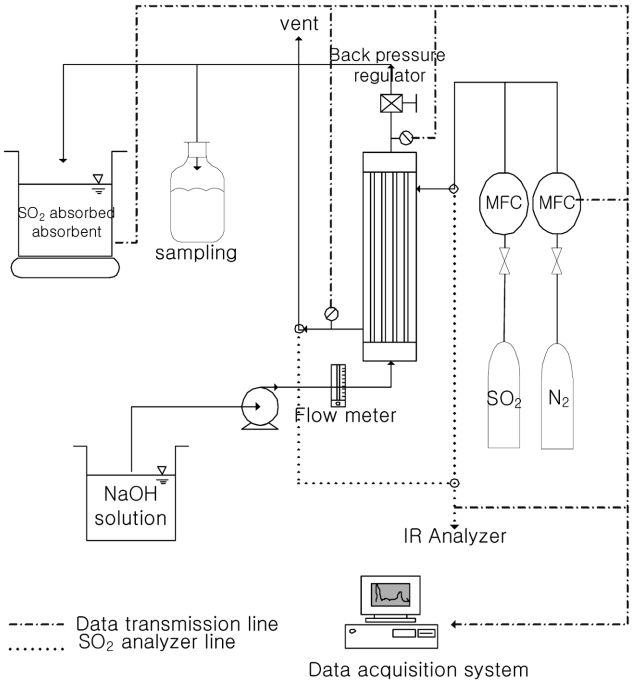
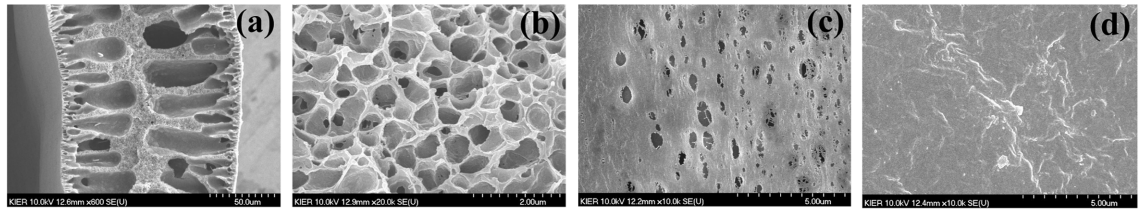
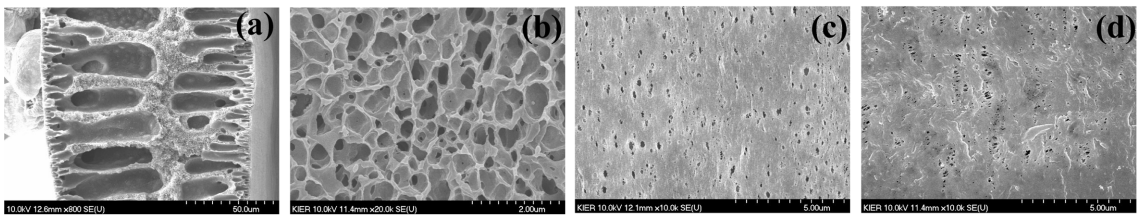


Fig. 1. Schematic diagram of experimental apparatus used in this study.

of PVDF 20 wt% and NMP 80 wt% as KM-1, while that of PVDF 20 wt%, NMP 70 wt% and PEG 10 wt% as KM-2. Without specific mention in this study, most experimentation was performed by using KM-1. The experimental setup for absorption of SO_2 is shown in Fig. 2. Feed gas mixture of varying concentrations was prepared by mixing a gas stream containing 5% of SO_2 and N_2 gas adjusted with mass flow controllers (Brooks, model; 5850E series). The feed gas mixture was passed through the shell side of the hollow fiber, while 0.02 M NaOH aqueous solution controlled by piston pump was fed into the lumen side of the membrane module.



(A) KM-1



(B) KM-2

Fig. 2. Effect of PEG additive on the morphology of hollow fiber membranes; (a) cross section, (b) middle structure, (c) membrane inside, (d) surface.

The liquid solution flowed at the bottom of the module and gas mixture flowed at the top of the module in the counter-current direction. The pressure at the gas phase side was varied between 0.5 and 1.2 kg_f/cm^2, while that of the liquid side was usually higher than that at the gas phase side. The inlet and outlet SO_2 concentrations were analyzed with SO_2 gas analyzer (SIEMENS, model; ultramat-23). The experimental conditions are shown in Table 1.

RESULTS AND DISCUSSIONS

1. Morphology Study of Prepared Hollow Fiber Membranes

The effect of PEG as an additive on the morphology is shown Fig. 2. The outer diameter and inner diameter of KM-1/KM-2 hollow fiber were measured to be 985/1210 and 765/932 μm, respectively. It can be seen that the long finger-like structure from the internal wall to the outer wall and the two layers is clearly shown. Sponge-like structure is shown at the center of the hollow fiber membranes. The appearance of the hollow fiber structures is attributed to the rapid precipitation occurring at both the inner and outer fiber walls resulting in long fingers and to the slow precipitation giving the sponge-like structure at the center of fiber.

Due to the hydrophilic nature of PEG, addition of the PEG in the polymer dopes increased the precipitation rate, which may have resulted in the formation of larger finger structure near the outer and inner skin surface. Also, the inside and surface pore size of the hollow fiber increased [8].

Using a gas permeation method, the KM-1 and KM-2 membranes were found to have an average pore size (r) 0.136, 0.172 μm, respectively, and surface porosity over the pore length (ε/L_p) of 1.41×10^2, $1.64\times10^2\ m^{-1}$, respectively. As mentioned above, PEG is an organic pore-former, so an increase in the effective porosity and pore size of the membrane KM-2 was obtained.

2. Effect of Liquid Flow Rate and Inlet SO_2 Concentration

The effect of liquid flow rate on the SO_2 removal efficiency and overall mass transfer coefficient was examined. The gas phase flowed through the fiber lumen side and the liquid phase flowed through the shell side. The effect of liquid flow rate was tested by maintaining the gas flow rate at 2 L/min, feed SO_2 concentration at 400 ppm and gas pressure at 0.5 kg_f/cm^2. Fig. 3 shows that the SO_2 removal efficiency and overall mass transfer coefficient were increased with the liquid flow rate. The overall mass transfer coefficient was calculated by using the logarithmic mean concentration driving force as follows.

$$K_G = \frac{Q_g}{A}\ln\left(\frac{C_{in}}{C_{out}}\right) \quad (1)$$

Where Q_g is flow rate of feed gas (m^3/sec), A is outer surface area of the hollow fibers (m^2), C_{in} is concentration of SO_2 in the inlet stream (ppm), and C_{out} is concentration of SO_2 in the outlet stream (ppm).

The effect of liquid flow rate on SO_2 removal efficiency and overall mass transfer coefficient was almost neglected when liquid flow rate was above 4 ml/min. This result means that at very low liquid flow rate, the NaOH available at the membrane surface for reacting with SO_2 is limited due to the liquid phase resistance. As liquid flow rate is above the minimum flow rate which overcomes the liquid phase resistance, the SO_2 absorption rate is controlled by resistance in the gas phase and the membrane [9].

Also Fig. 4 shows that the SO_2 absorption rate with inlet SO_2 concentration was sharply increased using hollow fiber membranes compared to a conventional wetted wall column because the former has higher gas liquid contacting area than the latter [10]. This means that SO_2 species at the gas-liquid interface is rapidly depleted by using hollow fiber membranes. The absorption rate was calculated by using Eq. (2).

$$r_{SO_2} = \frac{Q_g}{V}\frac{P_{SO_2,in} - P_{SO_2,out}}{RT} \quad (2)$$

Where Q_g is flow rate of feed gas (m^3/sec), V is volume of module (m^3), $P_{SO_2,in}$ is concentration of SO_2 in the inlet stream (ppm), $P_{SO_2,out}$ is concentration of SO_2 in the outlet stream (ppm) and T is reaction temperature.

3. Effect of Gas Pressure

The effect of feed gas pressure on the overall mass transfer coefficient is shown in Fig. 5. The overall mass transfer coefficient was

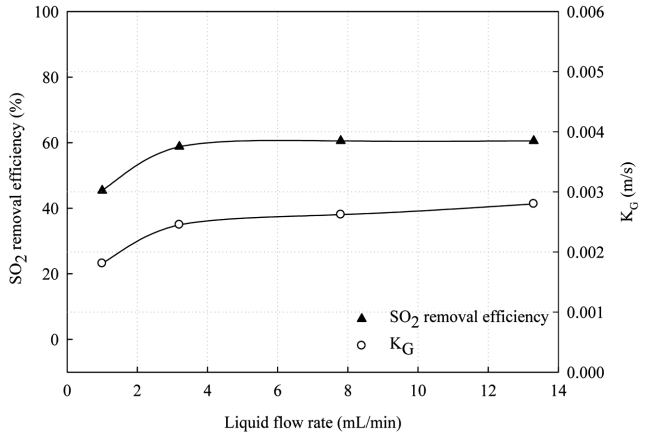


Fig. 3. Effect of liquid flow rate on SO_2 removal efficiency and overall mass transfer coefficient (SO_2=400 ppm, Q_g=2 L/min, P_g=0.5 kg_f/cm^2, gas flow; shell side).

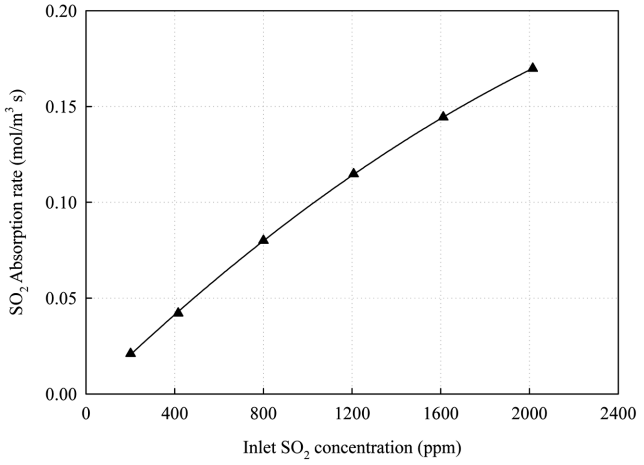


Fig. 4. Effect of inlet SO_2 concentration on SO_2 absorption rate (Q_g =2 L/min, Q_L=13.3 ml/min, P_g=0.5 kg_f/cm^2, gas flow; shell side).

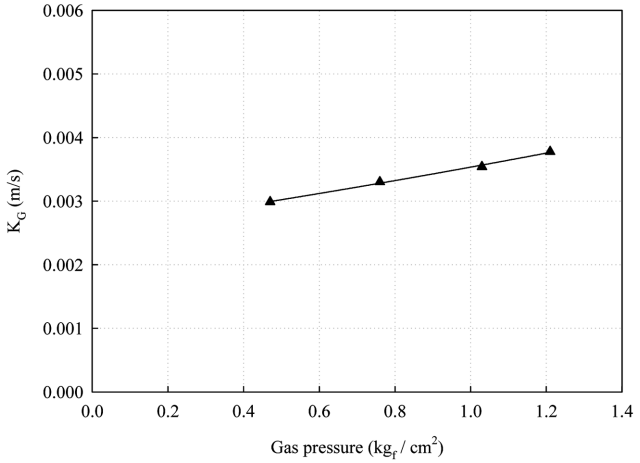


Fig. 5. Effect of gas pressure on overall mass transfer coefficient (SO_2=400 ppm, Q_g=2 L/min, Q_L=13.3 ml/min, gas flow; shell side).

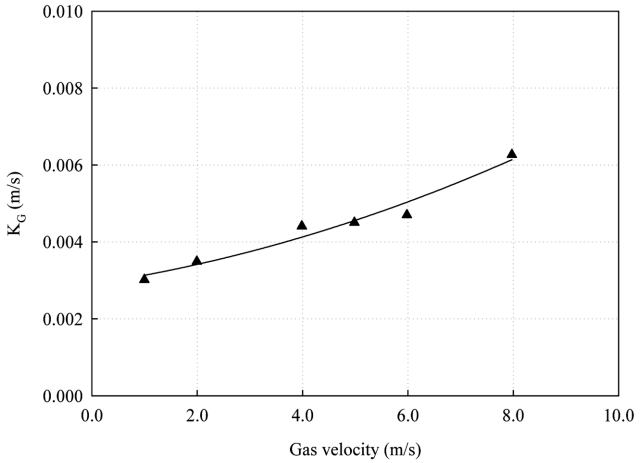


Fig. 7. Effect of gas velocity on overall mass transfer coefficient in 0.02 M NaOH (SO_2=400 ppm, Q_L=13.3 ml/min, P_g=0.5 kg_f/cm^2).

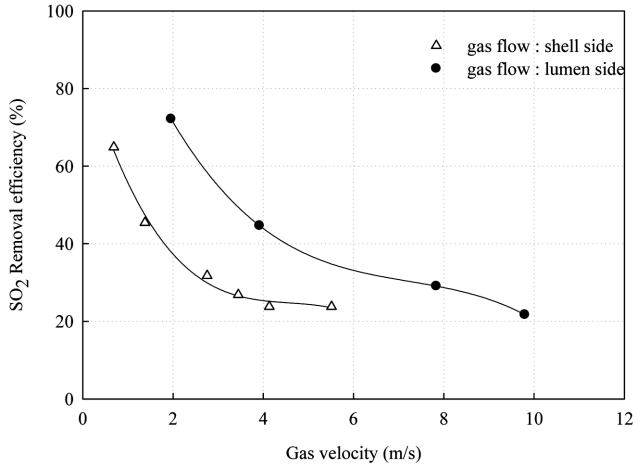


Fig. 6. Effect of gas flow direction on SO_2 removal efficiency and overall mass transfer coefficient in 0.02 M NaOH (SO_2=400 ppm, Q_L=13.3 ml/min, P_g=0.5 kg_f/cm^2).

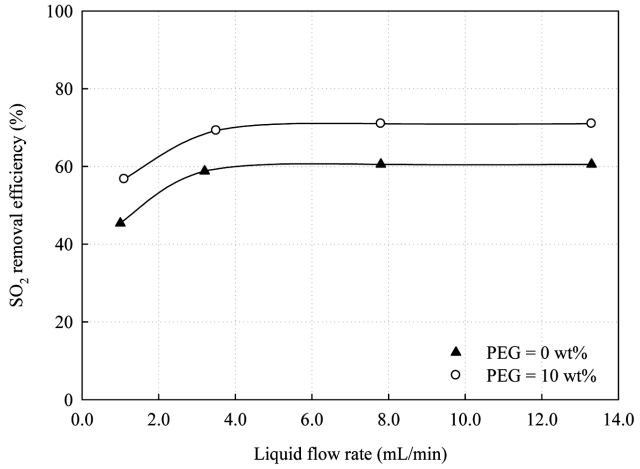


Fig. 8. Effect of PEG additive on overall mass transfer coefficient (SO_2=400 ppm, Q_g=2 L/min, P_g=0.5 kg_f/cm^2, gas flow; shell side).

Table 2. Experimental conditions for SO_2 absorption test using hollow fiber

Item	Test condition
Absorbent	0.02 M NaOH
Inlet SO_2 concentration	200-2000 ppm
Gas flow rate	2-16 L/min
Liquid flow rate	1-15 ml/min
Gas pressure	0.45-1.2 kg_f/cm^2
Liquid pressure	0.5-1.25 kg_f/cm^2

little changed as the gas pressure increased. In the analysis of soluble gas removal such as SO_2, H_2S using porous membrane, the overall diffusion coefficient of a soluble gas was considered as a combination of Knudsen diffusion coefficient and gas phase diffusion coefficient. Thus the mass transfer coefficient is independent of pressure.

4. Effect of Gas Flow Direction and Gas Velocity

The effect of gas flow direction was studied by using KM-1 hollow fiber membranes. A feed gas stream containing 400 ppm SO_2 was fed at a flow rate of 2-16 L/min while liquid flow rate was maintained at 13.3 ml/min. Fig. 6 shows that higher performance is achieved when gas flows in the fiber lumen side. In this case gas flows in the fiber shell may have channeling problems on the shell side due to the module bundle [11].

The effect of gas velocity on the overall mass transfer coefficient is presented in Fig. 7. As can be seen, gas velocity was increased with the overall mass transfer coefficient [12].

5. Effect of PEG as an Additive

Fig. 8 shows the effect of PEG as an additive on SO_2 removal efficiency. Addition of PEG in polymer dopes increased SO_2 removal efficiency because the inside and surface porosity of hollow fiber membranes was increased. With the much higher effective porosity of the membranes leading to a higher gas liquid contacting area, the membrane coefficient and better SO_2 removal efficiency is expected under the same operation conditions [13].

CONCLUSION

In this study, SO_2 removal efficiency and absorption rate of SO_2 using asymmetric hollow fiber membranes were investigated experimentally. The asymmetric hollow fiber membranes were made by using PVDF and PEG as an additive.

Addition of the PEG in the polymer dopes increased the precipitation rate, which resulted in the formation of larger finger structure near the outer and inner skin surface. Also, the inside and surface pore size of the hollow fiber increased.

The effect of liquid flow rate on SO_2 removal efficiency and overall mass transfer coefficient was almost neglected when liquid flow rate was from above 4 ml/min. This result means that at very low liquid flow rate, the NaOH available at the membrane surface for reacting with SO_2 is limited due to the liquid phase resistance. As liquid flow rate is above the minimum flow rate which overcomes the liquid phase resistance, the SO_2 absorption rate is controlled by resistance in the gas phase and the membrane.

The SO_2 absorption rate with inlet SO_2 concentration was sharply increased by using hollow fiber membranes compared to a conventional wetted wall column because the former has higher gas liquid contacting area than the latter. When the gas mixture was fed in the shell side, the removal efficiency of SO_2 decreased because of channeling problems on the shell side. Addition of PEG in polymer dopes increased SO_2 removal efficiency because inside and surface porosity of hollow fiber membranes was increased.

NOMENCLATURE

K_G : overall mass transfer coefficient [m/s]
Q_g : flow rate of feed gas [m^3/sec]
A : outer surface area of the hollow fibers [m^2]
C_{in} : concentration of SO_2 in the inlet stream [ppm]
C_{out} : concentration of SO_2 in the outlet stream [ppm]
r_{SO_2} : SO_2 absorption rate [mol·m^3/s]
V : volume of module [m^3]
$P_{SO_2,in}$: concentration of SO_2 in the inlet stream [ppm]
$P_{SO_2,out}$: concentration of SO_2 in the outlet stream [ppm]
T : reaction temperature [°C]
r : average pore size of hollow fiber membrane
L_p : pore length of hollow fiber membrane

Greek Letter

ε : surface porosity of hollow fiber membrane

REFERENCES

1. A. Lancia, D. Musmarra and F. Pepe, *Ind. Eng. Chem. Res*., **36**, 197 (1997).
2. Z. Qi and E. L. Cussler, *J. Membr. Sci*., **23**, 321 (1985).
3. S. Karoor and K. Sirkar, *Ind. Eng. Chem. Res*., **32**, 674 (1993).
4. R. Wang, H. Y. Zhang, P. H. M. Feron and D. T. Liang, *Sep. Purif Technol*., **46**, 33 (2005).
5. K. Li, J. F. Kong, D. Wang and W. K. Teo, *AIChEJ*., **45**, 1211 (1999).
6. I. Cabasso, K. O. Robert, E. Klein and J. K. Smith, *J. Appl. Polym. Sci*., **21**, 1883 (1977).
7. H. Yasuda and J. T. Tsai, *J. Appl. Polym. Sci*., **18**, 805 (1974).
8. D. Wang, K. Li and W. K. Teo, *J. Membr. Sci*., **163**, 211 (1999).
9. H. K. Lee, H. D. Jo, W. K. Choi, H. H. Park, C. W. Lim and Y. T. Lee, *Desalination*, **200**, 604 (2006).
10. H. K. Lee, B. R. Deshwal and K. S. Yoo, *Korean J. Chem. Eng*., **22**, 208 (2005).
11. D. Wang, W. K. Teo and K. Li, *Sep. Purif. Technol*., **27**, 33 (2002).
12. H. Kreulen, C. A. Smolders, G. F. Versteeg and W. P. M. van Swaaij, *J. Membr. Sci*., **78**, 217 (1993).
13. D. Wang, K. Li and W. K. Teo, *J. Membr. Sci*., **178**, 13 (2000).