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Effects of membrane properties on CO_2 recovery performance in a gas absorption membrane contactor

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Abstract

Global warming is a serious global environmental problem. CCS (Carbon dioxide Capture and Storage) is considered to be an emergency measure to mitigate the increase in atmospheric CO_2. Chemical absorption is the major separation technique employed in CCS. Recently, the focus has been on chemical absorption using a membrane contactor with microporous hollow fibres because of the large contact area between the gas and liquid as well as the absence of problems such as flooding and channelling.

In this study, we changed the properties of the polyethylene microporous hollow fibre membranes by two treatments: i) drawing in the axial direction and ii) soaking in concentrated nitric acid solution. The effects of these treatments on CO_2 recovery performance were investigated by a CO_2 recovery experiment using the untreated and treated membranes and a MEA aqueous solution.

The CO_2 recovery rate for the membrane treated by drawing was higher than that for the untreated membrane. Additionally, the CO_2 recovery rate increased with an increase in the drawing ratio. The nitric acid treatment also increased the CO_2 recovery rate compared with the untreated membrane.

Changes in membrane dimensions, porosity and pore size distribution were expected to be major reasons for the increase in CO_2 recovery rate for the membrane treated by drawing. On the other hand, nitric acid treatment did not induce any changes in membrane dimensions or pore size distribution but only reduced the surface roughness. As a result, the decrease in surface roughness was a major reason for the increase in CO_2 recovery rate for the membrane treated with nitric acid.

Keyword: CO_2 separation; hollow fibre; drawing, acid treatment; surface roughness

1. Introduction

Global warming induced by an increase in atmospheric CO_2 is one of the most serious global environmental problems. Various countermeasures against global warming are now being developed. Among them, CCS (Carbon

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dioxide Capture and Storage) is considered an emergency measure and the most practical one to mitigate the increase in atmospheric CO_2. To make CCS feasible it is necessary to develop low-cost separation techniques to recover CO_2 from large-scale emission flue gas sources such as fossil fuel power plants and steel plants.

Chemical absorption with absorbent liquids such as amines is a practical separation technique. Chemical absorption for CO_2 separation is often carried out using a packed tower. However, packed towers have some disadvantages including flooding and channelling. A chemical absorption process using a membrane contactor with microporous hollow fibres has been proposed and is being developed by many researchers [1-6]. With the gas separated from the liquid using a membrane, the flooding problem can be avoided. In addition, the use of thin hollow fibres is expected to significantly increase the contact area between the gases and liquids. As a result, the volume of the equipment and the construction cost can be reduced in comparison to the conventional packed tower. However, the membrane adds additional resistance in mass transfer between the gas and liquid. Therefore, it is necessary to optimize the properties of hollow fibre membranes to enhance the CO_2 separation performance of the membrane contactor.

The membrane material often employed in CO_2 separation by chemical absorption are polymers such as polytetrafluoroethylene (PTFE), polypropylene (PP) and polyethylene (PE). These polymers are hydrophobic and can prevent the chemical absorbent liquid from penetrating the membrane. In our previous study [7], the effects of membrane properties on CO_2 absorption were examined using a membrane contactor with hollow fibres of different sizes and composed of PTFE, PP or PE. The employed absorbent liquid was a 30 wt% MEA aqueous solution. In addition, we analysed the experimental results using a simulation model. The results indicated that the drawn PE membranes showed remarkably high CO_2 recovery rates indicating that the drawing treatment of the hollow fibre membrane was very effective in enhancing mass transfer through it. However, such a remarkable effect could not be predicted by the developed simulation model taking membrane properties such as pore size, porosity and wall thickness into consideration. This indicated that there were other factors involved that were not incorporated into the simulation model such as surface morphology and wettability.

Therefore, the purpose of this study was to determine the effects of drawing treatment in more detail and to determine the effects of other membrane properties such as surface morphology and wettability on mass transfer through the membrane.

2. Experimental

2.1 Materials

In this study, experiments to examine the effects of membrane properties on CO_2 absorption performance were performed using a countercurrent-type hollow fibre membrane contactor. The membrane material employed was PE and its inner and outer diameters were 0.7 mm and 1.2 mm, respectively. The mean pore size was 0.1 μm. The properties of the original hollow fibre membrane were changed by the following treatments: i) the fibre was drawn in the axial direction by a factor of 1.25 and 1.50 compared with its original length: ii) the inner surface of the membrane was soaked in concentrated nitric acid solution (Nitric acid (1.38), Wako Pure Chemical Industries, Ltd.) for one week. Treatment ii) was employed to change the surface morphology without inducing any changes in the other properties like the membrane dimensions, pore size and porosity. A piece of the untreated and treated hollow fibre membranes was installed at the centre of a cylindrical acrylic tube with an inner diameter of 6 mm and an effective length of about 200 mm, which we hereinafter refer to as a membrane module.

2.2 Experimental method

The membrane module was installed in a thermostatic oven and tubes for the gas and liquid flows were connected to the module, as shown in Fig. 1. A simulated mixture gas of 10%-CO_2/90%-N_2 was used and a 30 wt%-monoethanolamine (MEA) aqueous solution was the absorbent. The liquid flowed on the lumen side of the hollow fibre. On the other hand, the flow rate of each component was adjusted by a mass flow controller (MFC) and both gases were mixed and fed to the shell side of the hollow fibre in the module after the mixture passed through a humidification bottle. The gas and liquid flowed in a countercurrent pattern.

The experiment was carried out at 25 °C. The composition of the gas coming out of the membrane module was analyzed using a gas chromatograph (GC-8A, Shimadzu Corp.) and the CO_2 recovery rate was determined.

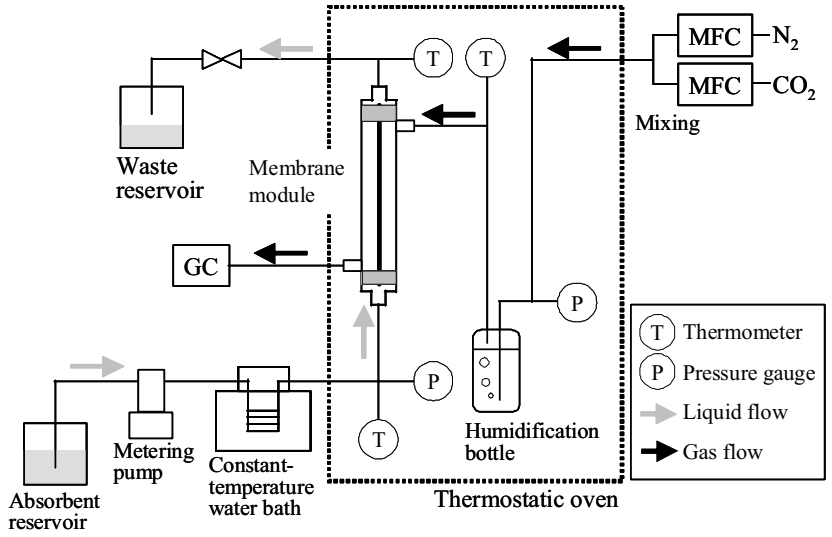


Figure 1 Experimental setup

The inner surfaces of each membrane were observed using a scanning electron microscope (SEM, S-3000N, Hitachi High-Technologies Corp.) and the surface roughness was measured using a laser microscope (LEXT-OLS3000, OLYMPUS Corp.). Furthermore, the pore size distribution of each membrane was measured by a mercury porosimeter (AutoPore IV MIC-9500, Micromeritics Instrument Corp.).

3. Results

3.1 Membrane size

Table 1 shows the inner and outer diameters of each hollow fibre membrane as measured by laser microscopy. The diameters were not changed by nitric acid treatment while they decreased after the drawing treatment. With an increase in the drawing ratio, the diameters became narrower and the wall thickness of the membranes was also expected to decrease with an increase in the drawing ratio.

Table 1 Inner and outer diameters of each membrane

Treatment	Inner diameter [mm]	Outer diameter [mm]
No	0.70	1.20
Nitric acid	0.70	1.20
Drawing-1.25	0.62	1.11
Drawing-1.5	0.60	1.06

3.2 Surface roughness

Table 2 shows the roughness parameters for the inner surface of each membrane as obtained by laser microscopy. R_a is the mean deviation of the assessed profile and R_c is the mean height of the profile elements. Both R_a and R_c decreased after the treatment indicating that the surface became smoother. In the case of nitric acid treatment, both parameters decreased by about 30 %. The membrane surface was corroded by immersion in the nitric acid solution over a long time although polyethylene is relatively resistant to acid and alkali sorbents. Both parameters were smaller for higher drawing ratios in the case of the drawing treatment but the effect on surface roughness was less than that of nitric acid treatment.

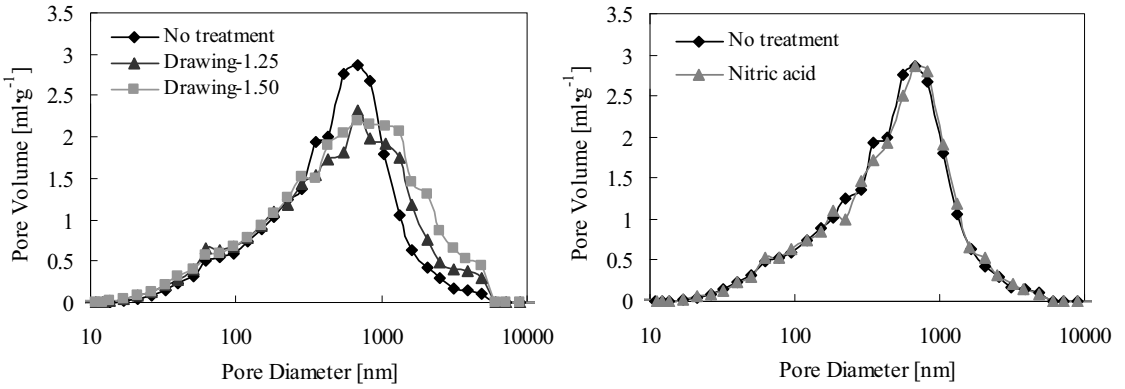
Table 2 Surface roughness of each membrane

Treatment	R_a [μm]	R_c [μm]
No	0.55	1.46
Nitric acid	0.38	1.08
Drawing-1.25	0.52	1.39
Drawing-1.5	0.45	1.25

3.3 Pore size distribution

The measured pore size distributions of the membranes are shown in Fig. 2. Figure 2(a) shows a comparison of the pore size distribution for the membranes that were not treated and those that underwent drawing treatment. The distribution of the untreated membrane has a relatively sharp peak around 1000 nm in pore diameter while the average pore diameter was estimated to be 263 nm. In the case of drawing treatment, the pore size distribution agreed well with that of the untreated membrane for pore diameters less than 200 nm. However, the peak became smaller and the number of pores larger than 1000 nm in diameter increased. Furthermore, the distribution shifted to a larger pore diameter as the drawing ratio increased for pores larger than 1000 nm.

On the other hand, the pore size distribution of the membrane after nitric acid treatment agreed well with that of the untreated membrane over the measured range of pore diameters. This indicated that nitric acid treatment did not influence the pore structure in the membrane wall at all.



(a) No treatment and drawing treatment (b) No treatment and nitric acid treatment

Figure 2 Pore size distribution of each membrane

3.4 CO_2 recovery

The results obtained from the CO_2 absorption experiments are shown in Fig. 3. This figure shows CO_2 recovery rates at different liquid velocities for each membrane.

The mean gas velocity was 0.1 m/s. For all the membranes investigated, the CO_2 recovery rate increased with an increase in the liquid velocity. Additionally, all the treated membranes had higher CO_2 recovery rates than the untreated membrane. For the membranes that underwent drawing treatment, the CO_2 recovery rate increased by 2-3 % and 5-6 % compared with those that did not undergo treatment for drawing ratios of 1.25 and 1.50, respectively. On the other hand, the CO_2 recovery rate for the membrane treated with nitric acid increased by 1-3 % compared with those that did not undergo treatment. The difference in CO_2 recovery rate between the membrane treated with nitric acid and the membrane that was not treated decreased with an increase in the liquid velocity while it did not change much with a

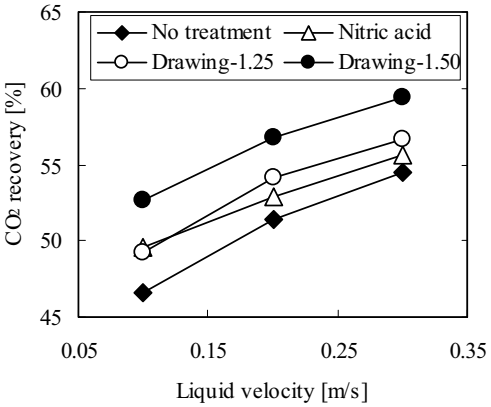


Figure 3 CO_2 recovery from CO_2 absorption experiments using various membranes

change in liquid velocity for the membranes that underwent drawing treatment.

4. Discussion

As mentioned above, for the membranes that underwent drawing treatment the inner and outer diameters and the resultant wall thicknesses were less than those of the untreated membrane. This decrease in wall thickness is expected to enhance mass transfer through the membrane because of the increase in the CO_2 partial pressure gradient between its two sides. The decrease in inner diameter is also expected to enhance the mass transfer in the liquid phase since the boundary layer formed above the inner surface of the tube becomes thinner as the tube diameter decreases resulting in an increase in the CO_2 concentration gradient in the liquid phase near the surface. On the other hand, the decrease in the inner diameter also leads to a decrease in the packing factor, which is defined as the ratio of the cross-sectional area of the hollow fibre to that of the acrylic tube. This decreases the contact area between the gas and liquid phases in the membrane module, which results in a decrease in the CO_2 recovery rate. In addition, drawing treatment resulted in a shift of the pore size distribution to larger values compared with the untreated membranes, as shown in Fig. 2. This result indicates that the porosity of the membranes increased and the paths of the gas increased. These changes surely enhance mass transfer in the membrane. Therefore, drawing treatment induces some positive and negative changes in terms of the membrane's dimensions and structure. On balance, the positive changes outweighed the negative changes and as a result the CO_2 recovery rate increased because of the drawing treatment used in this study.

On the other hand, nitric acid treatment did not induce any changes in membrane dimension or pore size distribution. Among the properties investigated in this study, the only effect of nitric acid treatment was a decrease in the roughness of the membrane's inner surface. Kandlikar et al. [8] reported that the acid treatment of the inner surface of 0.62 and 1.067 mm diameter stainless steel tubes caused a reduction in surface roughness because of corrosion. They also reported that a roughness of several micrometers had a significant effect on heat transfer over the surface, especially for the 0.62 mm diameter tube. The reason why a decrease in surface roughness of the membrane enhances mass transfer may be explained as follows: when the surface has high peaks or deep valleys in the profile, that is, the surface is "rough", the flow stagnates in the valley and the stagnating liquid cannot be easily replaced with fresh liquid, which results in a reduction in the mass transfer rate. If the surface is really smooth, the flow does not stagnate and the mass transfer rate is higher than that of a rough surface.

Other properties that require further investigation are the wettability and the size of the pore entrance on the inner surface of the membrane. A close relationship exists between them. As the size of the pore entrance to the liquid phase increases, the liquid meniscus intrudes into the membrane. This intrusion of the liquid is influenced by the wettability of the membrane by the absorbent liquid. The intrusion of the liquid meniscus leads to the stagnation of liquid flow resulting in a significant reduction of the mass transfer rate [9-12]. Wang et al. [11] reported that the surface roughness of polypropylene microporous hollow fibre membranes increase and the wettability also increases after a long period of immersion in a diethanolamine (DEA) solution. In this study, the surface roughness decreased after nitric acid treatment, which may result in a reduction in wettability.

From the above discussion, the major reason for the increase in CO_2 recovery rate by nitric acid treatment is the decrease in surface roughness. The surface roughness after drawing treatment was less than that for an untreated membrane. Changes in membrane dimensions, porosity and pore size distribution were expected to be the main contributors to the increase in CO_2 recovery rate. However, the decrease in surface roughness after drawing treatment also enhanced the mass transfer to some extent.

The dependency of the CO_2 recovery rate on the liquid velocity after nitric acid treatment is different from that in the other cases, as shown in Fig. 3. The relationship between surface morphology and flow field over the surface needs to be investigated further.

5. Conclusion

Polyethylene microporous hollow fibre membranes were treated by drawing in the axial direction and by soaking in a concentrated nitric acid solution. A CO_2 recovery experiment was also carried out using untreated and treated membranes and a MEA aqueous solution.

The CO_2 recovery rate for the membrane treated by drawing was larger than that for untreated membrane. The CO_2 recovery rate increased with an increase in the drawing ratio. We confirmed that the drawing treatment of the hollow fibre membrane was very effective in enhancing mass transfer. The nitric acid treatment also had a higher CO_2 recovery rate compared with the untreated membrane.

Upon drawing, the inner and outer diameters and the resultant membrane thicknesses decreased because of the treatment. In addition, the pore size distribution shifted to larger values. Furthermore, the surface roughness reduced slightly. From these membrane property measurements, changes in the membrane dimensions, porosity and pore size distribution were expected to be major reasons for an increase in the CO_2 recovery rate for the membrane treated by drawing.

On the other hand, nitric acid treatment did not lead to any changes in membrane dimensions or pore size distribution. This treatment only induced a reduction in surface roughness, which is expected to prevent the liquid flow from stagnating and from intruding into the membrane. As a result, the major reason for the increase in CO_2 recovery rate by nitric acid treatment is considered to be the decrease in surface roughness.

As shown in this study, the properties of membranes significantly affect the CO_2 recovery performance of a membrane contactor. Therefore, it is important to enhance mass transfer through the membrane by optimizing the properties of the membrane to reduce the amount of absorbent liquid used and thereby the heat energy required for the stripping process.

References

[1] Zhang Qi, Cussler EL. Microporous hollow fibres for gas absorption. I. Mass transfer in the liquid. J Membrane Sci 1985;23:321-332.

[2] Zhang Qi, Cussler EL. Microporous hollow fibres for gas absorption. II. Mass transfer across the membrane. J Membrane Sci 1985;23:333-345.

[3] Matsumoto H, Kitamura H, Kamata T, Nishikawa N, Ishibashi M. Fundamental study of CO_2 removal from thermal power plant flue gas by hollow-fiber gas-liquid contactor. Kagaku Kogaku Ronbunshu 1992;18:804-812.

[4] Feron PHM, Jansen AE. Capture of carbon dioxide using membrane gas absorption and reuse in the horticultural industry. Energy Convers Mgmt 1995;36:411-4.

[5] Nishikawa N, Ishibashi M, Ohta H, Akutsu N. CO_2 removal by hollow-fiber gas-liquid contactor. Energy Convers Mgmt 1995;36:415-8.

[6] deMontigny D, Tontiwachwuthikul P, Chakma A. Comparing the absorption performance of packed columns and membrane contactors. Ind Eng Chem Res 2005;44:5726-5732.

[7] Takahashi N, Mano H, Okabe K, Nakamura M, Fujioka Y, Mimura T, et al. Experimental and Theoretical Analyses of Effects of Membrane Properties on CO_2 Absorption Performance of a Hollow Fiber Membrane Contactor. Kagaku Kogaku Ronbunshu 2008;34:76-84.

[8] Kandlikar SG, Joshi S, Tian S. Effect of surface roughness on heat transfer and fluid flow characteristics at low Reynolds number in small diameter tubes. Heat Transfer Engineering 2003;24(3):4-16.

[9] Kreulen H, Smolders CA, Versteeg GF, van Swaaij WPM. Determination of mass transfer rates in wetted and non-wetted microporous membranes. Chem Eng Sci 1993;48:2093-2102.

[10] Mavroudi M, Kaldis SP, Sakellaropoulos GP. Reduction of CO_2 emissions by a membrane contacting process. Fuel 2003;82:2153-9.

[11] Wang R, Li DF, Zhou C, Liu M, and Liang DT. Impact of DEA solutions with and without CO_2 loading on porous polypropylene membranes intended for use as contactors. J Membrane Sci 2004;229:147-157.

[12] Wang R, Zhang HY, Feron PHM, Liang DT. Influence of membrane wetting on CO_2 capture in microporous hollow fiber membrane contactors. Separation and Purification Technology 2005;46:33-40.