



## CO<sub>2</sub> absorption by using PVDF hollow fiber membrane contactors with various membrane structures

Saeid Rajabzadeh<sup>a</sup>, Shinya Yoshimoto<sup>a</sup>, Masaaki Teramoto<sup>a,\*</sup>, M. Al-Marzouqi<sup>b</sup>, Hideto Matsuyama<sup>a,\*\*</sup>

<sup>a</sup> Department of Chemical Science and Engineering, Kobe University, 1-1 Rokkodai, Nada-ku, Kobe 657-8501, Japan

<sup>b</sup> Chemical and Petroleum Engineering Department, UAE University, P.O. Box 17555, Al-Ain, United Arab Emirates

### ARTICLE INFO

#### Article history:

Received 21 February 2009

Received in revised form 20 July 2009

Accepted 22 July 2009

#### Keywords:

Poly(vinylidene fluoride) (PVDF)

Hollow fiber membrane contactor

CO<sub>2</sub> absorption

Monoethanolamine (MEA)

Numerical simulation

### ABSTRACT

Seven kinds of asymmetric poly(vinylidene fluoride) (PVDF) hollow fiber membranes with considerable different structures at the outer surfaces were prepared via thermally induced phase separation (TIPS) method and applied for CO<sub>2</sub> absorption as gas–liquid membrane contactors. A commercial microporous poly(tetrafluoroethylene) (PTFE) hollow fiber membrane was also used as a highly hydrophobic membrane. Experiments on the absorption of pure CO<sub>2</sub> into monoethanolamine (MEA) solutions were performed and the effects of membrane structure and inner diameter on the membrane performance were investigated. The module efficiencies were compared for the two patterns of operation, i.e. case 1 operation where liquid flows in the tube side while gas in the shell side and case 2 operation where liquid flows in the shell side while gas in the tube side. CO<sub>2</sub> absorption fluxes observed in case 1 operation were inversely proportional to the inner diameter of the hollow fiber membrane, and CO<sub>2</sub> absorption rate per fiber was almost the same for all membranes. CO<sub>2</sub> absorption rates observed in case 2 operation were much smaller than those in case 1 operations. The performances of the PVDF membranes were comparable with that of the commercial PTFE membrane.

A mathematical model for pure CO<sub>2</sub> absorption in a membrane contactor, which assumes that the membrane resistance is negligibly small and the total membrane area is effective for gas absorption, was proposed to simulate CO<sub>2</sub> absorption rates. Experimental results in case 1 operation were satisfactorily simulated by the model for all membranes with different structures. Experimental results obtained in case 2 operation were also simulated by the model except for a membrane with a very low surface porosity on its outer surface. CO<sub>2</sub> absorption flux increased with increasing the MEA concentration up to the concentration of 2 mol/dm<sup>3</sup>, however, the CO<sub>2</sub> absorption flux hardly increased with further increase in MEA concentration. This behavior is discussed based on the decrease in the effective gas–liquid contacting area with increasing MEA concentration. A method to estimate CO<sub>2</sub> solubility and diffusivity in MEA solutions, which are essential for calculating CO<sub>2</sub> absorption flux by the model, is also described.

© 2009 Elsevier B.V. All rights reserved.

### 1. Introduction

Gas absorption operation has been carried out in many areas such as chemical and petroleum refining processes using various absorption equipments, which include packed columns, plate columns and venturi scrubbers. Although packed columns have been used widely in many industries, there are several disadvantages such as flooding at high flow rates, maldistribution of liquid at low liquid flow rates and foaming. A small gas–liquid interfacial area per unit volume, i.e. specific gas–liquid interfacial area is also a problem [1].

Membrane contactors for gas absorption using microporous hollow fiber membrane modules have been attracting attention as an alternative technology, which overcomes the disadvantages of conventional gas absorption apparatuses [1–3]. In a membrane contactor for gas absorption, a gas mixture flows on one side of a hydrophobic microporous membrane while a liquid absorbent flows on the other side. The gas–liquid interface is formed at the pore openings adjacent to the liquid. In the membrane module, gas diffuses from the gas side across the membrane and reaches the gas–liquid interface, where gas is absorbed in the liquid. Here, it should be noted that the membrane pores should not be filled with liquid but with gas. As liquid phase diffusivity is four orders of magnitude lower than gas phase diffusivity, the mass transfer resistance through liquid-filled pores is much larger than that through gas-filled pores.

The advantages of gas absorption using hollow fiber membranes are as follows [1–3]:

\* Corresponding author. Tel.: +81 78 803 6279; fax: +81 78 803 6279.

\*\* Corresponding author. Tel.: +81 78 803 6180; fax: +81 78 803 6180.

E-mail addresses: [teramoto@kobe-u.ac.jp](mailto:teramoto@kobe-u.ac.jp) (M. Teramoto), [matuyama@kobe-u.ac.jp](mailto:matuyama@kobe-u.ac.jp) (H. Matsuyama).

### Nomenclature

$C_{\text{CO}_2\text{-int}}$	concentration of $\text{CO}_2$ at gas–liquid interface [mol/m <sup>3</sup> ]
$C_i$	concentration of species $i$ [mol/m <sup>3</sup> ]
$C_{i,\text{initial}}$	concentration of species $i$ at the inlet [mol/m <sup>3</sup> ]
$C_{i\text{-shell}}$	concentration of species $i$ in the shell [mol/m <sup>3</sup> ]
$C_{i\text{-tube}}$	concentration of species $i$ in the tube [mol/m <sup>3</sup> ]
$d$	inner diameter of hollow fiber membrane [m]
$D_i$	diffusivity of species $i$ [m <sup>2</sup> /s]
$D_{i\text{-shell}}$	diffusivity of species $i$ in the shell [m <sup>2</sup> /s]
$D_{i\text{-tube}}$	diffusivity of species $i$ in the tube [m <sup>2</sup> /s]
$Ha$	Hatta number defined by Eq. (20)
$H_{\text{CO}_2}$	Henry's constant of $\text{CO}_2$ [mol/(m <sup>3</sup> Pa)]
$J_{\text{CO}_2}$	$\text{CO}_2$ absorption flux [mol/m <sup>2</sup> s]
$k$	reaction rate constant [m <sup>3</sup> /(mol s)]
$K$	mass transfer coefficient [m/s]
$L_p$	distance between pores [m]
$\Delta p$	liquid entry pressure [Pa]
$p_{\text{CO}_2}$	partial pressure of $\text{CO}_2$ [Pa]
$q$	$(D_{\text{MEA}}/D_{\text{CO}_2})(C_{\text{MEA, initial}}/2C_{\text{CO}_2\text{-int}})$
$Q_L$	absorbent flow rate [m <sup>3</sup> /s]
$Q_{\text{CO}_2}$	$\text{CO}_2$ absorption rate per fiber [mol/s]
$r$	radial distance [m]
$r_1$	inner radius of hollow fiber membrane [m]
$r_2$	outer radius of hollow fiber membrane [m]
$r_3$	inner radius of shell [m]
$Sh$	Sherwood number
$v_{\text{AV}}$	average liquid velocity [m/s]
$z$	axial distance [m]
$Z$	length of fiber [m]
<i>Greek letters</i>	
$\delta_L$	liquid boundary layer thickness [m]
$\theta$	contact angle [°]
$\sigma$	surface tension of liquid [N/m]

- The two fluid flow rates can be changed independently without flooding, loading and weeping or foaming.
- Use of hollow fiber membranes can make the specific gas–liquid contacting area much larger compared to conventional gas absorbers.
- Gas–liquid interfacial area remains undisturbed by the change of gas and liquid flow rates.
- Phase separation after absorption operation is not necessary because one phase is not dispersed into other phase in the module.
- Scale-up is easy.

On the other hand, the disadvantages of membrane contactor are:

- Membrane can introduce another resistance to mass transfer.
- Membrane is subject to fouling.
- Membrane contactors are subject to shell side bypassing, which results in a loss in efficiency.

There are several important factors to be considered in the selection of the membrane. For gas–liquid contacting, the liquid entry pressure  $\Delta p$ , above which the liquid penetrates into the membrane pores, is given by the Laplace–Young equation [4]

$$\Delta p = \frac{2\sigma \cos \theta}{r} \quad (1)$$

Here,  $\sigma$  is the surface tension of liquid,  $\theta$  is the contact angle, which increases with increasing the hydrophobicity of the membrane, and  $r$  is the pore radius. This equation is useful in selecting suitable membranes for gas–liquid membrane contactors. The criteria for the membrane selection are as follows:

- Membrane must be highly hydrophobic to prevent the membrane pores from being filled with aqueous absorbent solutions.
- Membrane pores must be small to prevent the penetration of absorbents into the pores since the smaller the pore radius, the larger the liquid entry pressure.
- Membrane porosity must be large so that a large gas–liquid interface is available for gas absorption.
- The membrane must have enough mechanical strength.
- Membrane must not be expensive.

From these points of view, several hydrophobic microporous membranes have been used for membrane gas absorption, which include PE (polyethylene), (PP) polypropylene, PVDF (poly(vinylidene fluoride)) and PTFE (poly(tetrafluoroethylene)). Microporous PE and PP membranes have been often used in the membrane contactors since they are cheap and their modules are available commercially. However, since their hydrophobicity is not as high as fluorine-containing polymeric membranes such as PTFE and PVDF membranes [5], microporous PE and PP membranes are wetted by some absorbents with low interfacial tensions, which drastically decreases the module efficiency [6]. Microporous PTFE membrane is the most hydrophobic membrane and shows good gas absorption performance as well as good stability without membrane wetting [7]. However, PTFE membrane is considerably expensive.

A microporous PVDF membrane is one of the promising candidates for use in membrane contactors due to relatively high hydrophobicity, high chemical resistance and reasonable material cost. Several papers have been published on membrane gas absorption using microporous PVDF hollow fiber membrane modules [8–17]. Yeon et al. [10] performed a series of experiments on the absorption of  $\text{CO}_2$  from a  $\text{CO}_2/\text{N}_2$  mixture into aqueous amine solutions using a pilot-scale hollow fiber membrane contactor prepared by using commercially available PVDF membranes with the pore size of 30 nm. They reported that when an aqueous monoethanolamine (MEA) solution was used as absorbent, the membrane was wetted after 8 h of operation. However, when a mixed aqueous solution of MEA and triethanolamine (TEA) was used, a high  $\text{CO}_2$  removal was maintained during the experiment for 80 h. Atchariyawut et al. [13] investigated absorption of  $\text{CO}_2$  into water, NaOH and MEA solutions using a commercial microporous PVDF membrane and found in a long-term experiment for 15 days that when a 2 mol/dm<sup>3</sup> MEA solution was used the  $\text{CO}_2$  flux continuously decreased, which suggested the membrane wetting. They also reported in other paper [14] that when a 2 mol/dm<sup>3</sup> NaOH solution was used, the membrane mass transfer resistance occupied about 99% of the total resistance. Khaisri et al. [17] compared the membrane resistances and absorption performances of three different commercial hydrophobic microporous membranes, including PVDF, PP and PTFE membranes, for the  $\text{CO}_2$  absorption into aqueous MEA solutions. They found that the  $\text{CO}_2$  absorption performance was in the order of PTFE > PVDF > PP, and also that the PTFE membrane had excellent stability compared to other membranes.

It is very important to investigate the effect of membrane structure on the membrane performance in membrane contactors. In-house made PVDF membranes were used in several studies [8,9,11,12,15,16]. However, few studies were performed to investigate the effect of membrane structure on the gas absorption performance by using membranes of different structures. Kong and

Download English Version:

<https://daneshyari.com/en/article/643234>

Download Persian Version:

<https://daneshyari.com/article/643234>

[Daneshyari.com](https://daneshyari.com)