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Modeling of carbon dioxide absorption in a gas/liquid membrane contactor

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ABSTRACT

In this study, the behavior of CO_2 absorption in flat sheet membrane contactors is developed. Physical and chemical absorption of CO_2 in co-current and counter-current flow were studied using both distilled water and 2-amino-2 methyl 1-propanol (AMP) as a solvent in the model. The effect of flow pattern, solvent type and gas and liquid velocity on absorption of carbon dioxide through the membrane contactor is obtained. The results indicate that the use of AMP instead of water leads to a better separation for carbon dioxide. Furthermore, unlike the liquid velocity, lower value of gas velocity showed higher performance for absorption.

Keywords: Flat sheet membrane contactor; Carbon dioxide; Absorption

1. Introduction

In many processes, because of incomplete reaction, some of the feed components are present in the final product. For economic reasons, these components must be filtered out. Due to its minimal contribution to global warming and pipe corrosion, the process of CO_2 separation is used in natural gas processing, enhanced oil recovery, biogas purification and flue gas treatment. Physical and chemical techniques such as absorption, adsorption, cryogenic and membrane process can be used for CO_2 separation. Membrane-based gas absorption techniques operate efficiently and can be adapted easily to specific demands of an individual plant. This type of process offers several practical advantages including high surface area per unit contactor volume; independent control of gas and liquid flow rates without any flooding, loading, weeping or foaming; known gas-liquid interfacial area; modularity; low corrosion problems, low operation and capital costs [1–6].

Recently, many researchers have paid attention to use of micro-porous membranes for indirect contacting of two immiscible phases. In the membrane contactors, gas flows in one side of hydrophobic micro-porous membrane while the liquid absorbent flows in the other side [7–9]. Several researchers studied CO_2 absorption through cylindrical membrane contactors. In many cases they modeled behavior of carbon dioxide in membrane phase. Bao and Trachtenberg [10] reported modeling of CO_2-facilitated transport from a CO_2-air mixture using aqueous solution of diethanolamine (DEA) through hollow fiber liquid membrane. The diffusion term was considered in the model, but the effect of fluid velocity was overlooked. They studied the permeability of CO_2

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in solvents such as carbonic anhydrate, alkaline and diethanolamine. Wang and co-workers [11] studied the effects of different sorption systems, operation conditions and membrane characteristics on the removal of carbon dioxide by use of three typical alkanolamines in hollow fiber membrane contactors. A similar system has been recently studied by Al-Marzouqi and co-workers [12] for the transport of CO_2 via hollow fiber membrane contactors. They studied physical absorption of carbon dioxide with distilled water as the solvent, instead. In another research, Paul and co-workers [7] numerically simulated a flat sheet membrane contactor by neglecting convection terms. The study was carried out with the application of aqueous single and mixed amine solutions. Also, Bottino and co-workers [9] investigated separation mechanism due to gas velocity gradient. Heydari Gorji and Kaghazchi [8] modeled CO_2/H_2 separation by facilitated transport membranes immobilized with aqueous single and mixed solutions. In the present work, a general model, in which both convection and diffusion terms considered, was developed to describe CO_2 permeation in flat sheet membrane contactors. A numerical CFD code was generated to solve coupled system equations. CO_2 permeation in gas, membrane and liquid sides of rectangular geometry were implicitly investigated.

2. Theory

2.1. Reaction mechanism of AMP with CO_2

AMP, a primary sterically hindered amine in which the amino group is attached to a tertiary carbon atom, was identified as a promising absorbent to offer capacity and rate advantages over conventional amines [11]. Diffusion coefficient and physical solubility of AMP and water are tabulated in Table 1.

The reaction of primary amine (R_1R_2NH) with dissolved CO_2 is described by the zwitterions mechanism in a two-step sequence. The first step is the formation of intermediate zwitterions which was formulated as [8]:

$$\mathrm{CO_2} + R_1R_2\mathrm{NH} \underset{k_{z-1}}{\overset{k_z}{\rightleftharpoons}} R_1R_2\mathrm{NH^+CO_2^-} \tag{1}$$

The second step is the removal of proton from the zwitterions by a base, described as:

$$R_1R_2\mathrm{NH^+CO_2^-} + b \overset{k_b}{\rightleftharpoons} R_1R_2\mathrm{NCO_2^-} + b\mathrm{H^+} \tag{2}$$

where b denotes H_2O, OH-and R_1R_2NH in an aqueous amine solution, respectively. Based on steady-state assumption for Zwitterionic mechanism, the rate of CO_2 reaction with primary amine was expressed as:

$$R_{\mathrm{CO_2}} = \frac{\mathrm{K_2}[\mathrm{CO_2}][R_1R_2\mathrm{NH}]}{1+\left(\dfrac{K_{-1}}{K_{\mathrm{H_2O}}}[\mathrm{H_2O}]\right)+\left(\dfrac{K_{-1}}{K_{\mathrm{OH^-}}}\left[\mathrm{OH^-}\right]\right)+\left(\dfrac{K_{-1}}{K_{R_1R_2\mathrm{NH}}}[R_1R_2\mathrm{NH}]\right)} \tag{3}$$

The contributions of H_2O, OH^- are negligible in rate of CO_2 reaction because of their concentrations is much smaller compared to amine concentration. The kinetic constants of reaction between CO_2 and AMP at 298 K are listed in Table 2.

2.2. Model development

A numerical model was developed to describe CO_2 capture in flat sheet membrane contactors by using distilled water as for physical absorption and AMP as for chemical absorption from mixture of gases. Material balance has been carried out on a membrane contactor system to develop the analytical model. A schematic diagram of the membrane contactor is depicted in Fig. 1. The membrane thickness, length and porosity was considered 0.001 m, 0.2 m and 0.4, respectively

The analytical model is a function of gas side, membrane side and liquid side. The effects of these items are described below.

2.2.1. Gas side

The steady state continuity for each species during the mass transfer and chemical reaction rate in membrane contactors is expressed as

$$-\nabla N_t \pm R_t = V_z \frac{\partial C_i}{\partial z} \tag{4}$$

where C_i, N_t, R_t, V_z and z are the concentration, flux, reaction rate of species of i, velocity and distance along the length of the membrane contactor, respectively. Left hand side of the above equation shows the reaction and diffusion term and the right hand side of Eq. (4) shows the convection term. The CO_2 physical absorption in membrane contactor was considered in this study; therefore,

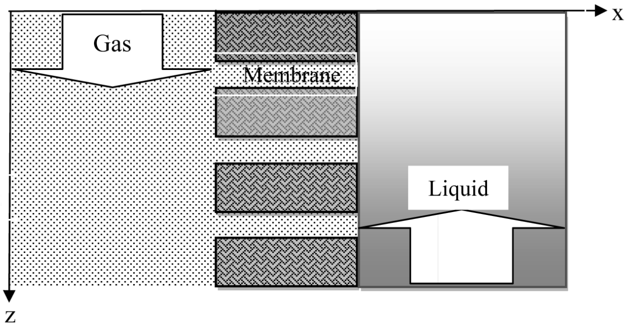

Fig. 1. Schematic diagram of the membrane contactor in counter current flow.

Table 1
Physical properties of AMP and carbon dioxide at 298 K

Aqueous amine solution	m	D_A ($m^2\ s^{-1}$)	D_B ($m^2\ s^{-1}$)	Amine concentration (mol m^{-3})	Reference
Gas phase					
AMP	0.79	1.855E-05	—	—	[12,13]
Membrane phase					
AMP	0.79	3.710E-06	—	—	Present work
Liquid phase					
AMP	0.79	1.330E-09	9.70E-09	1.56E+03	[14,15]
Water	0.79	1.920E-09	—	—	[17]

$D_{CO_2\text{membrane}} = D_{CO_2\text{gas}} \times (\varepsilon/\tau)$
Effective diffusion coefficient is calculated considering the effects of porosity (0.4) and tortuosity (2.0) of the membrane, as provided by the membrane manufacturer.

Table 2
Kinetic parameters of reaction between carbon dioxide and AMP at 298 K

Aqueous amine solution	AMP
k_2 ($m^3\ mol^{-1}\ s^{-1}$)	8.100E-01
$k_2 k_{R_1R_2NH}/k_{-1}$ ($m^6\ mol^{-2}\ s^{-1}$)	2.335E-03
Reference	[18]

the reaction terms in all three regions (gas side, membrane side and liquid side) are negligible.

In a rectangular geometry, the differential equations for CO_2 capture in membrane contactors, using Fick's law of diffusion for the estimation of the diffusion term, is written as:

$$V_{z\,\text{gas side}} \frac{\partial C_{CO_2\ \text{gas side}}}{\partial z} = D_{CO_2\ \text{gas side}} \frac{\partial^z C_{CO_3\ \text{gas side}}}{\partial x^2} \tag{5}$$

The boundary conditions were considered as

At $z = 0$ $\quad C_{CO_2\ \text{gas side}} = C_{\text{initial}} = C_0$

At $x = 0$ $\quad \dfrac{\partial C_{CO_2}}{\partial x} = 0$

At $x = X_{\text{gas}}$ $\quad C_{CO_2\text{gas side}} = C_{CO_2\text{membrane side}}$

2.2.2. Membrane side

The steady state material balance for the transport of CO_2 inside the membrane was considered by diffusion term alone in physical absorption. In this study, it is considered that gas flow filled the membrane side, while it is possible that liquid diffuse through membrane side by soaking in solvent. This assumption is given in Eq. (6):

$$D_{CO_2\text{membrane side}} \frac{\partial^2 C_{CO_2\text{membrane side}}}{\partial x^2} = 0 \tag{6}$$

where boundary conditions for membrane are given as:

At $x = X_{\text{gas}}$ $\quad C_{CO_2\ \text{membrane side}} = C_{CO_2\ \text{gas side}}$

At $x = X_{\text{membrane}}$ $\quad C_{CO_2\ \text{membrane side}} = C_{CO_2\ \text{liquid side}}/m$

where m is physical solubility.

2.2.3. Liquid side

The steady state material balance for transport of CO_2 in liquid side is given as

$$V_{z\,\text{liquid side}} \frac{\partial C_{CO_2\text{liquid side}}}{\partial z} = D_{CO_2\text{liquid side}} \frac{\partial^2 C_{CO_2\text{liquid side}}}{\partial x^2} - R_{CO_2} \tag{7}$$

where R_{CO_2} is the reaction between amine and carbon dioxide described by Zwitterionic mechanism.

In counter current flow, boundary conditions are given as

At $z = L$ $\quad C_{CO_2\text{liquid side}} = 0$

At $x = X_{\text{membrane}}$ $\quad C_{CO_2\text{liquid side}} = m \times C_{CO_2\text{membrane side}}$

At $x = X_{\text{liquid}}$ $\quad \dfrac{\partial C_{CO_2}}{\partial x} = 0$

In co-current flow, boundary conditions are given as

At $z = 0$ $\quad C_{CO_2\text{liquid side}} = 0$

At $x = X_{\text{membrane}}$ $\quad C_{CO_2\text{liquid side}} = m \times C_{CO_2\text{membrane side}}$

At $x = X_{\text{liquid}}$ $\quad \dfrac{\partial C_{CO_2}}{\partial x} = 0$

2.3. Physical properties

For CO_2–water and CO_2–amine systems at 298 K and 1 atm, physical properties are presented in Table 1.

3. Results and discussion

The behavior of CO_2 absorption in a flat sheet membrane contactor is described by Eqs. (5), (6) and (7). It is obtained that the results changes based on the type of solvent, flow pattern, gas velocity and liquid velocity.

3.1. Solvent

Effect of solvent type on absorption performance was investigated. Contour of carbon dioxide concentration through membrane contactor for AMP and distilled water are shown in Figs. 2–3.

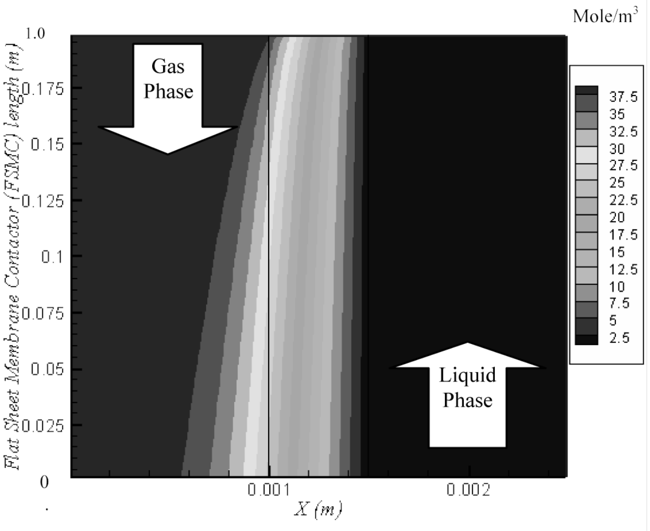

Fig. 2. CO_2 concentration in counter-current flow with AMP as solvent.

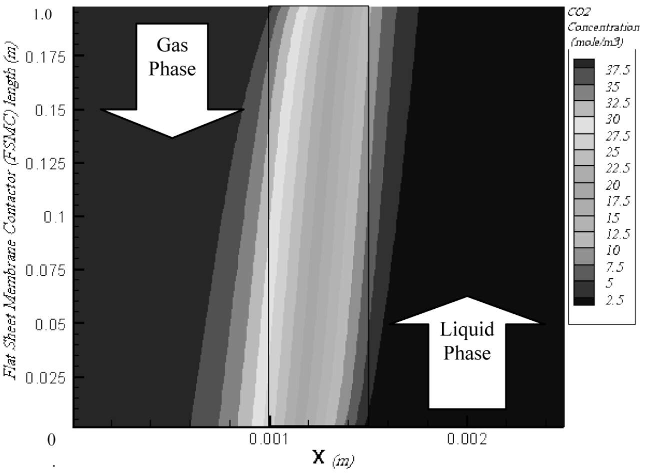

Fig. 3. CO_2 concentration in counter-current flow with water as solvent.

The results indicated that using AMP improved the performance of CO_2 absorption in comparison with distilled water as a solvent. This is due to chemical reaction of amine and CO_2 which introduced by Zwitterionic mechanism. In counter-current flow, the results dictate that amine absorb carbon dioxide 16% more than water. CO_2 concentration in three regions consisting of gas, membrane and liquid for both amine and water is shown in Fig. 4. The gas region is shown in Fig. 6 conclusively.

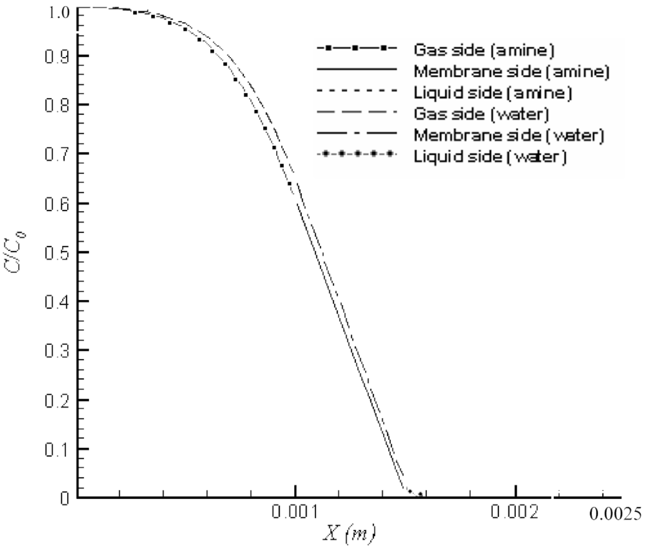

Fig. 4. CO_2 concentration in membrane contactor for both amine and water in counter-current flow.

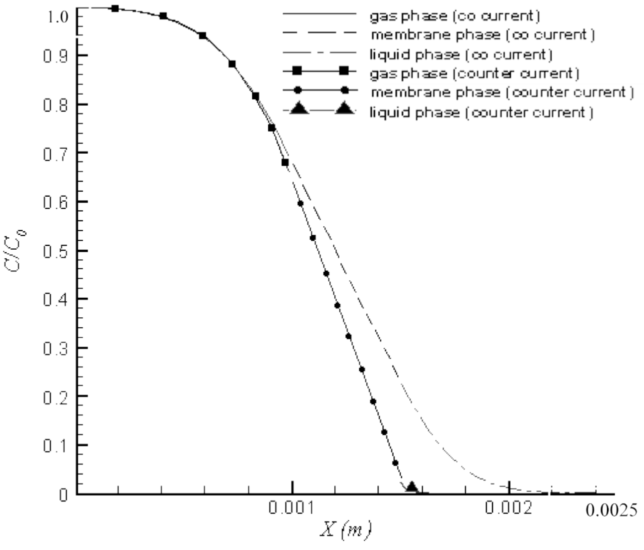

Fig. 5. Comparison between co-current and counter-current flow pattern in membrane contactor.

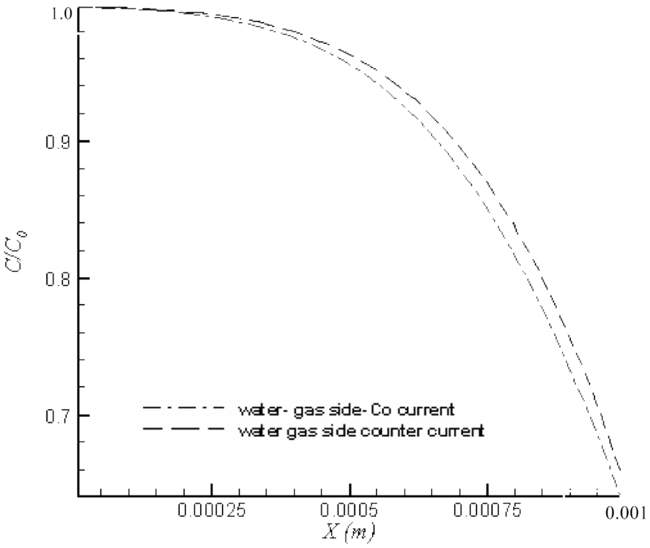

Fig. 6. Comparison between co-current and counter-current flow pattern in gas phase.

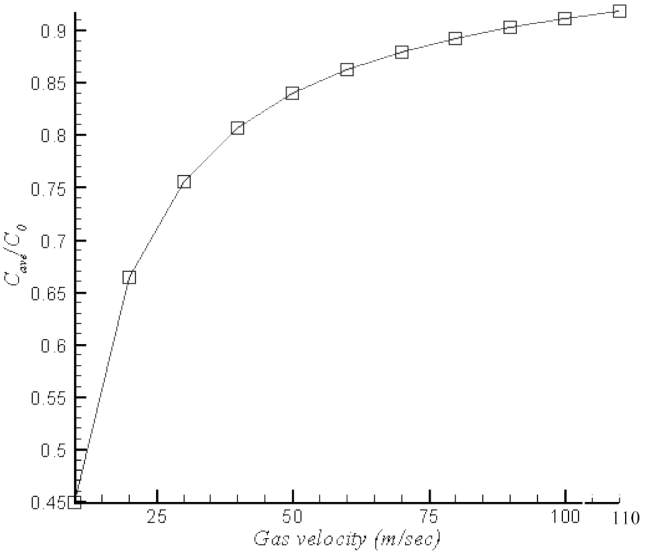

Fig. 7. The effect of gas velocity on CO_2 concentration.

3.2. Flow pattern

Co-current and counter-current flow patterns were investigated in this study. Inlet gas and liquid velocities were considered 109.6 m/s and 0.02 m/s, respectively and initial CO_2 concentration was considered 40 mol/m^3. It was observed that counter-current flow pattern improved performance of CO_2 separation because of increase in driving force and mass transfer. The comparison between co-current and counter current flow pattern when water was used as solvent is shown in Figs. 5–6. The results indicate that when counter-current flow pattern was used, separation performance was increased about 7% compared to co-current flow pattern using water as solvent. When carbon dioxide considered in gas phase in counter-current and co-current flow pattern, 3.28 mol/m^3 and 3.05 mol/m^3 CO_2 was observed respectively. The effect of flow pattern is more distinguishable when amine was used as solvent. The results of flow pattern by considering amine as a solvent indicate that separation performance was increased about 16% in comparison with co-current.

3.3. Gas velocity

In order to investigate the influence of gas velocity on performance of carbon dioxide separation, in counter-current flow pattern, five values of gas velocity (20, 40, 60, 80 and 100 m/s) were considered. Accordingly, the results disputed in Fig. 7 by considering distilled water as a solvent. By increasing the gas flow rate, the amount of absorbed gas decreased drastically. The residence time of CO_2 was increased when gas flow rate decreased. Hence better separation was achieved. Further investigation indicates that when gas velocity reached 20 m/s, about 55% of CO_2 were absorbed.

3.4. Liquid velocity

In order to investigate the influence of liquid velocity on performance of CO_2 separation, in counter-current flow pattern, five values of liquid velocity (0.02, 0.04, 0.06, 0.08 and 0.1 m/s) were considered. In addition, distilled water is considered as solvent and the result is shown in Fig. 8. The results indicate that by considering gas velocity equal to 109.6 m/s, increasing the liquid velocity from 0.01 m/s to 0.1 m/s increases the CO_2 absorption about 2%. Furthermore, results showed that liquid velocities have no significant influence on separation performance at velocities higher than 0.1 m/s. Besides, the results in Fig. 2 indicate that when AMP is used as solvent for CO_2 separation, the concentration of carbon dioxide is decreased instantly and distribution becomes steady in liquid phase. Accordingly, variety of liquid velocity do not have affect of carbon dioxide separation by using of AMP as solvent.

To compare our results with experimental data, we considered our membrane contactor the same as Wang and co-workers [19]. In this case, physical carbon dioxide adsorption in water was considered. A co-current flow parallel-plate gas-liquid membrane contactor (gas and liquid phase thickness = 0.02 m, membrane phase thickness = 0.00004 m, membrane contactor length = 0.18 m, membrane porosity = 0.4) was used by Wang. Fig. 9 shows the dimensionless CO_2 concentration in the liquid outlet stream both theoretically and experimentally with $V_{z\ \text{gas side}}$ = 0.167 cm/s. The increase of the liquid flow rate produces the positive effect not only raising the absorp-

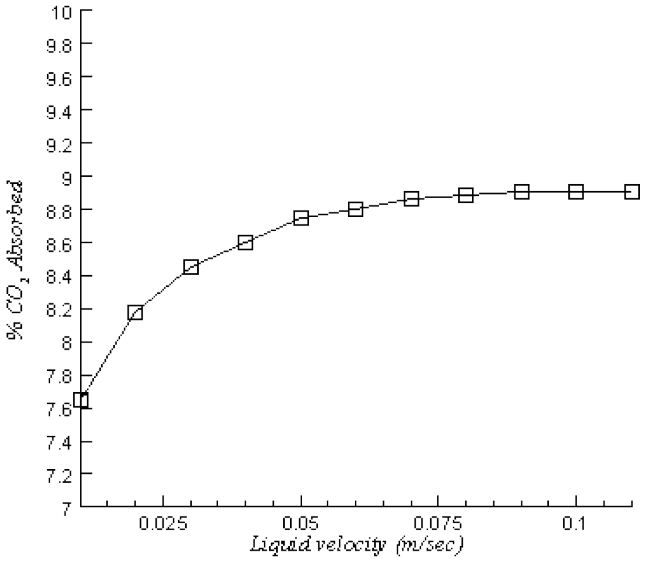

Fig. 8. The effect of liquid velocity on CO_2 absorption.

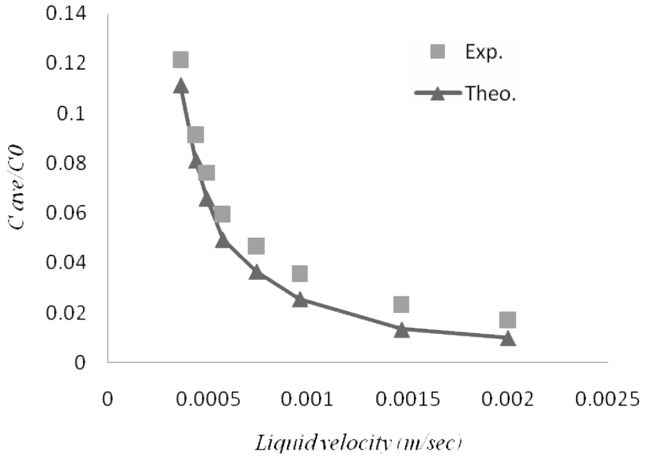

Fig. 9. The average concentration of liquid outlet vs. liquid flow rate with $V_{z\ \text{gas side}}$ = 0.167 cm/s.

tion efficiency but also reducing the carbon dioxide concentration in the liquid outlet stream. The agreement between experimental data and the result in present work is fairly good.

4. Conclusion

An analytical study of CO_2 absorption in liquid/gas membrane contactor was discovered. Two different solvents were considered to illustrate the effect of chemical and physical absorption in membrane contactor. The results indicate that using AMP improve the separation performance about 16% compared to distilled water in counter-current flow pattern. In addition, the effect of flow pattern, gas velocity and liquid velocity on absorption was studied. It was obtained that counter-current flow yields a better absorption performance. Gas velocity had a significant affects on absorption process when a lower value of gas velocity was considered. This is because of increasing the residence time of CO_2. Finally, liquid velocity had negligible influence on absorption process.

Symbols

C_{CO_2} — CO_2 concentration, mol m^{-3}
$C_{CO_2\text{gas side}}$ — CO_2 concentration in gas side, mol m^{-3}
$C_{CO_2\text{membrane side}}$ — CO_2 concentration in membrane side, mol m^{-3}
$C_{CO_2\text{liquid side}}$ — CO_2 concentration in liquid side, mol m^{-3}
C_{initial} — Inlet CO_2 concentration, mol m^{-3}
$C_{R_1R_2NH}$ — Amine concentration, mol m^{-3}
D_{CO_2} — Diffusion coefficient of CO_2, $m^2\ s^{-1}$
$D_{CO_2\text{gas side}}$ — Diffusion coefficient of CO_2 in gas, $m^2\ s^{-1}$
$D_{CO_2\text{membrane side}}$ — Diffusion coefficient of CO_2 in membrane, $m^2\ s^{-1}$
$D_{CO_2\text{liquid side}}$ — Diffusion coefficient of CO_2 in liquid, $m^2\ s^{-1}$
k_b — Second-order reaction rate constant for base b, $m^3\ mol^{-1}\ s^{-1}$
k_2 — Second-order reaction rate constant, $m^3 mol^{-1}\ s^{-1}$
k_{-1} — Reverse first-order reaction rate constant, s^{-1}
L — Length of membrane contactor, m
m — Physical solubility
R_{CO_2} — Overall reaction rate of CO_2, mol s^{-1}
$V_{z,\text{ gas side}}$ — Gas velocity in gas side, m s^{-1}
$V_{z,\text{ liquid side}}$ — Liquid velocity, m s^{-1}
x — Distance parameter, m
X_{gas} — Gas phase thickness, m
X_{membrane} — Gas and membrane sides thickness, m
X_{liquid} — Gas, membrane and liquid sides thickness, m
z — Distance parameter, m

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