Theoretical and experimental studies of membrane wetting in the membrane gas–liquid contacting process for CO_2 absorption

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Abstract

A systematic simulation has been carried out in membrane contactors to study CO_2 capture by water and diethanolamine (DEA) aqueous solutions from a CO_2/N_2 mixture under the wetted and the non-wetted operation modes. Two types of microporous hollow fiber membrane modules made of polypropylene (PP) and polyvinylidene fluoride (PVDF) hollow fibers were used to conduct CO_2 absorption experiments. The corresponding experimental data were used to verify simulated results.

Experimental study showed that the membrane wetting could not be completely avoided especially in the case of chemical absorption. Both experimental and theoretical study disclosed that the membrane wetting would result in a significant drop of CO_2 flux. The simulation results further revealed that for the physical absorption of CO_2 by water, the proportion of membrane phase resistance in the overall mass transfer resistance increased from less than 5 to about 90% when the operation mode was shifted from non-wetted to wetted. As for the chemical absorption, analysis on the mass transfer resistance revealed that the ratio of the membrane resistance increased sharply from 10 to 70% when only 10% membrane length was wetted. With the introduction of an extra resistance caused by the membrane wetting, the mass transfer in the wetted membrane phase finally became the rate-controlling step. It was not as effective to enhance the CO_2 flux by increasing the inlet gas velocity or the liquid velocity as in the non-wetted mode of operation.
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1. Introduction

Since 1980s, membrane contactors have been extensively studied as a promising alternative of traditional gas–liquid contacting equipment such as packing towers or bubble columns. In a membrane contactor where the membrane acts as a physical barrier between the gas and liquid phases, the problems often encountered in the conventional equipment like flooding, foaming, entraining and channeling can be completely avoided. In addition, the compact modular design provides a large gas–liquid interface and the flexibility to scale up or down.

Membrane contactors were firstly studied as a blood oxygenator in the mid-1970s [1]. Since then, their applications have been extended to many fields, including the capture of acid gases

(CO_2, SO_2, H_2S), removal of organic vapor, production of ultra pure water by deoxygenating, air humidity control and so on [2]. Zhang and Cussler were the pioneers to introduce membrane contactors in the application of CO_2 removal, followed by many investigations in this area [3,4]. The increasing interest can be partly attributed to the serious concern on the global warming caused by the greenhouse effect.

Although membrane contactors offer many advantages over the traditional contacting equipment, additional mass transfer resistance will be introduced by membrane itself in a gas–liquid contacting process. Depending on the membrane material, the liquid nature and the pressures of two phases, the membrane pores may be filled with gas or liquid, which corresponds to the two operation modes: non-wetted mode and wetted mode. In most cases, the non-wetted mode is preferred as the membrane resistance will increase significantly if the membrane pores are wetted by liquid. Kreulen et al. measured the mass transfer resistances of non-wetted and wetted membranes and found that for

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physical absorption where the mass transfer rate is limited in the liquid phase, the additional resistance of the non-wetted membrane did not influence the overall mass transfer while the wetted membrane caused the substantial increase of the overall mass transfer resistance [5]. Experimental study of CO_2 absorption in water revealed that the membrane wetting could reduce the gas absorption rate considerably [6]. Rangwala reported that the difference between the experimental and theoretical results for CO_2 absorption was caused by the partial wetting of the membrane [7]. Many other researchers attributed the long-term performance deterioration of the membrane contactors as a result of the membrane wetting [8–10].

Mathematic simulations were also conducted to understand the influence of membrane wetting on mass transfer and explain the experiments results in the gas–liquid membrane contactor. However, most of these studies were based on physical absorption. For instance, Karoor and Sirkar developed theoretical models for CO_2 absorption by water in the wetted mode [6]; Malek et al. systematically investigated the mass transfer change under partially wetted mode for dissolved oxygen removal from water [11]; Wang et al. set up a theoretical model for pure CO_2–water system in partially wetted mode [8]; Mavroudi et al. established a first-order kinetic expression to describe the membrane resistance change with time for pure CO_2 absorption in water [12]. Considering that chemical absorption is a more practical way for CO_2 removal and the membrane is more vulnerable to be wetted by chemical absorbents, it is necessary to systematically study the wetting mechanism especially in the case of the chemical absorption.

As a continuation of our previous effort of modeling CO_2 absorption in a hollow fiber membrane contactor with a non-wetted mode of operation or wetted mode in the physical absorption of pure CO_2 [8,13], the present work focused on CO_2 capture by water (physical absorption) and diethanolamine (DEA) aqueous solutions (chemical absorption) from a CO_2/N_2 mixture in a wetted mode of operation. Two situations of the liquid flow either in the fiber lumen or in the shell side were considered. The effect of membrane wetting on the mass transfer was numerically studied under different operating conditions. Meanwhile, two types of microporous hollow fiber membrane modules made of polypropylene (PP) and polyvinylidene fluoride (PVDF) hollow fibers were used to conduct CO_2 absorption experiments. The corresponding experimental data were used to verify the simulated results.

2. Theoretical

2.1. Reaction between CO_2 and DEA

The reaction mechanism between CO_2 and primary or secondary amines was described in the previous paper [13] and reaction rate can be expressed as follows [14,15]:

$$r_A = \frac{[DEA][CO_2]}{1/k_2 + 1/((k_2 k_{H_2O}/k_{-1})[H_2O] + (k_2 k_{OH^{-1}}/k_{-1})[OH^{-1}] + (k_2 k_{DEA}/k_{-1})[DEA])} \tag{1}$$

Table 1
Parameters used in modeling

C_{AG} at the inlet	$8.42 \, \text{mol m}^{-3}$
C_{B0}	$2000 \, \text{mol m}^{-3}$
D_A (in water)	$1.92\text{E}{-}9 \, \text{m}^2 \, \text{s}^{-1}$ [18]
D_A (in 2 M DEA solution)	$1.05\text{E}{-}9 \, \text{m}^2 \, \text{s}^{-1}$ [18]
D_B	$4.97\text{E}{-}10 \, \text{m}^2 \, \text{s}^{-1}$ [18]
D_G	$1.65\text{E}{-}5 \, \text{m}^2 \, \text{s}^{-1}$ [19]
$D_{K,A}$	$5.05\text{E}{-}6$ (PP), $2.5\text{E}{-}5$ (PVDF) $\text{m}^2 \, \text{s}^{-1}$
$D_{M,G}$	$3.87\text{E}{-}6 \, \text{m}^2 \, \text{s}^{-1}$
H (in water)	$0.833 \, \text{mol mol}^{-1}$ [18]
H (in 2 M DEA solution)	$0.765 \, \text{mol mol}^{-1}$ [18]
k_2	$2.375 \, \text{m}^3 \, \text{mol}^{-1} \, \text{s}^{-1}$ [16]
$\frac{k_2 k_{H_2O}}{k_{-1}}$	$2.20\text{E}{-}06 \, \text{m}^6 \, \text{mol}^{-2} \, \text{s}^{-1}$ [16]
$\frac{k_2 k_{DEA}}{k_{-1}}$	$4.37\text{E}{-}04 \, \text{m}^6 \, \text{mol}^{-2} \, \text{s}^{-1}$ [16]
$R_i/R_o/R_e$	$110/150/237$ (PP) μm $300/500/633$ (PVDF MT 1) μm $300/500/731$ (PVDF MT 2) μm

where the effect of hydroxyl ion (OH^-) can be neglected without causing a substantial loss of accuracy [14]. The values of kinetic parameters are listed in Table 1.

2.2. Numerical model

As shown in Fig. 1, there are three mass transfer regions in a membrane contactor, i.e. the liquid phase, the gas phase and the membrane phase. The model equations were set up accordingly. The liquid absorbent was assumed to flow in either the lumen side or the shell side while the gas mixture of CO_2/N_2 with a volume ratio of 20/80 flows in the other side co-currently. Since the fiber length is not very long, the co-current flow arrangement can tremendously simplify the calculation.

The following assumptions have been adopted: (1) a steady state and isothermal condition have been achieved; (2) the axial diffusion is negligible; (3) for the liquid flow in the lumen, a fully developed parabolic liquid velocity profile is presented within the lumen of the hollow fiber; (4) the liquid flow in the shell side can be characterized by Happel's free surface model [17]; (5) Henry's law is applicable at the gas–liquid interface; (6) the liquid in the membrane pores is stagnant when the membrane is wetted.

2.2.1. Mass transfer in the liquid phase

The conservation equations for the mass transfer in the liquid phase are as follows:

$$v_z \frac{\partial C_A}{\partial z} = D_A \frac{\partial^2 C_A}{\partial r^2} + \frac{D_A}{r} \frac{\partial C_A}{\partial r} - r_A \tag{2}$$

$$v_z \frac{\partial C_B}{\partial z} = D_B \frac{\partial^2 C_B}{\partial r^2} + \frac{D_B}{r} \frac{\partial C_B}{\partial r} - r_B \tag{3}$$

where the subscripts of A and B denote CO_2 and DEA, respectively.