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Investigation of the effects of operating parameters on the local mass transfer coefficient and membrane wetting in a membrane gas absorption process

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ABSTRACT

This work presents an investigation of local gas side overall mass transfer coefficient (K_G) of the membrane gas absorption process determined from CO_2 concentration gradients. The experimental K_G was compared with simulation results of non-wetted and partially wetted modes of operation from a plug flow and rated based model to study the effects of various operating parameters on the partial wetting of the membrane and its process performance. The experiments were performed using two types of membranes (polytetrafluoroethylene, PTFE and polyvinylidene fluoride, PVDF), and two absorbents (monoethanolamine, MEA and 2-amino-2-methyl-1-propanol, AMP). A comparison showed that the membrane wetting fraction was lowest at the liquid outlet and varied along the length of the membrane module due to the effect of pressure drop. The effect of liquid velocity on membrane wetting was very obvious at a low membrane wetting fraction whereas it was less noticeable at a higher membrane wetting fraction. The average membrane wetting fractions were lower when PTFE was used with MEA solution than when PVDF and AMP solutions were used in experiments. In addition, the results further showed that the use of CO_2 loaded MEA solution could significantly reduce membrane wetting.

1. Introduction

The continuing increase of energy consumption around the world, especially from fossil fuel sources, has resulted in releasing large amounts of CO_2 to atmosphere. A recent report by the International Energy Agency (IEA) has revealed that 30 billion tons of CO_2 was released in 2010, an increase of 10 billion ton from the 1990 value [1]. Several studies believe that the increase of the concentration of CO_2, a major greenhouse gas, in the atmosphere is responsible for global warming and can cause dramatic effects on the world climate, such as more frequent occurrence of floods and storms, higher temperatures, and higher acidity of the ocean waters [2,3]. Therefore, it is crucial to develop efficient technologies for capturing CO_2 from its sources, especially from industries and power plants.

There are a variety of methods for CO_2 capture, such as absorption into a liquid either water or amine solutions, adsorption on a solid, such as iron oxide, or impregnated activated carbon, cryogenic fractionation, or membrane systems. One of the most widely used and effective methods for CO_2 separation is absorption with amine solutions. The major advantage of this method is that once the amines have been used to absorb CO_2, they can be regenerated simply by heating. They are then ready to be reused in the CO_2 absorption process. In terms of equipment, packed towers, bubble columns, and spray towers are commonly applied. However, these conventional equipments are not easy to operate because of many drawbacks and operational limitations, such as flooding, foaming, entraining, channeling, and high capital cost [4]. An alternative technology which can overcome these disadvantages and which possesses a high potential to replace conventional contactors for the CO_2 capture is membrane contactor or the so-called membrane gas absorption systems. In this process, a hydrophobic membrane is employed as a phase barrier allowing two fluids to contact with each other without the dispersion of one phase into the other. This makes membrane contactors easy to operate because the gas and liquid flow rates are independent, and as such, result in no flooding or foaming issues. The use of membranes,

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especially hollow fiber membrane modules, offers a higher mass transfer area compared to the packed column [5]. Moreover, the membrane contactors are flexible for scale-up. The mass transfer area is well defined and can be directly calculated from the membrane surface area.

However, the membrane contactor also has its own disadvantages. Hydrophobic membranes can be partially wetted by organic solvents, resulting in low flux and short term usage of the membrane. The organic absorbents can penetrate into partial pores of the membrane because of their low surface tensions, and decrease mass transfer flux due to lower gas diffusivity in the wetted membrane phase. Moreover in a long-term operation, the organic absorbents can intrude into membrane matrix and significantly change the membrane morphology, pore size distribution, and membrane porosity [6], and will result in continuous deterioration of the mass transfer performance. To minimize the membrane wetting problem, the operating pressure should be kept below a critical value known as the penetration pressure. However, many researchers [7,8] have found that the partial wetting of the membrane can occur even if the pressure difference between the liquid and gas phases was kept lower than the penetration pressure, possibly due to capillary condensations of water and organic vapors in the membrane pores, and the nonuniform pore sizes of the membranes. The latter factor could lead to the penetration of liquid into the larger pores or membrane wetting could start from the largest to the smaller membrane pores.

Since membrane wetting could significantly affect the performance of membrane gas absorption using amine solvents, several studies have attempted to estimate and evaluate the effects of operating parameters on the partial wetting of membranes. The Wilson plot method has been applied to determine the membrane mass transfer resistance that included the wetted membrane phase in both gas absorption and desorption using monoethanolamine (MEA) solvent [9,10]. However, a reaction occurring in the wetted membrane phase can cause an error in the estimations, and thus, this method cannot truly reflect the effect of operating parameters on the membrane wetting. An error in the estimations can occur when using this method to determine the membrane resistance in the case of the partially wetted mode with chemical reaction. The Wilson plot method requires a variation of the liquid velocity to obtain a value of the membrane mass transfer resistance. However, in real life situations, the change of liquid velocity also affects the mass transfer resistance of the wetted membrane phase as well as the degree of membrane wetting as reported in several works in the literature [11,12].Therefore this method cannot truly reflect the effect of operating parameters on the membrane wetting. Another method is to develop a model for estimating the mass transfer coefficient or absorption flux, and using membrane wetting (wetting fraction) as a fitting parameter to match the simulation and experimental values. The theoretical value of the non-wetted mode when the gas totally fills the membrane pores is considered as the ideal performance of the process and the deviation between the experimental and simulation values is only due to the occurrence of partial wetting. This method was widely applied by many researchers. Mavroudi et al. [13] developed a mathematical model to predict the CO_2 absorption performance in diethanolamine (DEA) solution using the cross flow membrane module and to estimate the membrane wetting in actual conditions. The study showed that the simulation results that assumed 1.5–7% as the membrane wetting agreed well with the experimental data. Faiz et al. [7] compared the simulated CO_2 fluxes of different percentages of membrane wetting with the experimental results from literature sources. They found that the simulated fluxes that considered 10% and 50% wetting were close to the experimental CO_2 fluxes of 0.005 mol/L MEA using PP membrane and 2 mol/L MEA using PVDF membrane, respectively. Boributh et al. [11] developed a model for a large scale membrane gas absorption for CO_2 capture and proposed a membrane wetting correlation, which developed from the comparisons between experimental and simulation results, as the functions of liquid velocity and amine concentration.

In real operations, membrane wetting can be affected by many factors, including membrane properties itself (such as pore size, pore size distribution and membrane porosity)[14] and several operating parameters, namely inlet liquid pressure [15], liquid velocity, amine concentration [11], and gas and liquid contact time [16]. In addition, one of the parameters that could considerably affect membrane wetting is the change of liquid pressure along the length of the membrane fiber due to pressure drop. Boributh et al. [17] and Goyal et al. [18] showed in their simulation studies that membrane wetting was not constant but varied with the change of liquid pressure along the length of the fiber. These theoretical studies implied that the local overall mass transfer coeffceints were also not constant and could change due to membrane wetting. However, most of the works of membrane gas absorption in the literature reported only average mass trasnfer coefficients calculated from empirical approaches which considered only gas or liquid inlet and outlet conditions. They cannot reflect the effects of membrane wetting, pressure drop, and amine depletion on the change of mass trasnfer coefficent along the length of the membrane. Therefore, the objective of this study is to experimentally investigate the local overall mass transfer coefficent of the membrane gas absorption processes that could be affected by many factors, including the membrane wetting and also to study the effect of various operating parmeters on membrane wetting and mass tranfer performance of the process.

In this work, the local overall gas side mass tranfer coeffceints were determined from the CO_2 concentration gradients in the gas phase. Three membrane modules connected in series with gas sampling points along the length of the module were used in the experiments. The membrane wetting was investigated by comparing the experimental results with the simulation data from a rate based model. The membrane wetting fraction or the extent of liquid filled in the membrane pores was estimated by using it as the fitting parameter in the modelling to match the simulatated with the experimental absorption fluxes. Various operating parameters that could possibly affect the membrane wetting were investigated, including the effect of membrane types (polytetrafluoroethylene, PTFE, and polyvinylidene fluoride, PVDF), amine solution types (MEA and 2-amino-2-methyl-1-propanol, AMP), CO_2 loading and liquid velocity.

2. Theory

2.1. Mass transfer in membrane gas absorption

2.1.1. Resistance-in-series model

There are two operating conditions often found in the membrane gas absorption processes, namely non-wetted and partially wetted modes as shown in Fig. 1. For the non-wetted mode, the mass transfer of gas into the liquid phase encounters three resistances in series, including the gas phase resistance for the diffusion of CO_2 from the bulk gas to the outer surface of the membrane, membrane resistance for the diffusion within membrane pores and the liquid resistance for dissolution of CO_2 into liquid solution. For the partially wetted mode, the resistance from the wetted membrane phase, where the liquid solution partially filled the membrane pores, is taken into consideration. The resistance-in-series models have been widely applied to calculate the overall mass transfer resistance and each individual resistance [19,20]. Their expressions for hollow fiber membrane of the non-wetted (Eq. (1)) and partially wetted modes (Eq. (2)) are as follows:

$$\frac{1}{K_L d_o} = \frac{H}{K_G d_i} = \frac{1}{E k_L^0 d_i} + \frac{H}{k_M d_{\ln}} + \frac{H}{k_G d_o} \tag{1}$$