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Experimental study on membrane wetting in gas–liquid membrane contacting process for CO_2 absorption by single and mixed absorbents

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ABSTRACT

The membrane wetting by the liquid absorbents is an important problem in the operation of gas–liquid membrane contacting process. In order to gain a better understanding on the role of absorbents on membrane wetting, monoethanolamine (MEA, primary amine), diethanolamine (DEA, secondary amine), and 2-amino-2-methyl-1-propanol (AMP, sterically hindred amine) were applied as absorbent solutions. The membrane used for the experiments was the hollow fiber polyvinylidenefluoride (PVDF) membrane. The performance of both single and mixed amine solutions on the CO_2 absorption capacity and membrane wetting potential were investigated. In addition, sodium chloride (NaCl, inorganic salt) and sodium glycinate (SG, organic salt) were added into the MEA aqueous solution to observe CO_2 flux and membrane wetting.

The results revealed that the use of MEA solution and SG as absorbents gave highest CO_2 flux. The overall mass transfer coefficients obtained from the experiments also showed the same trend as CO_2 flux, i.e, the values were in the following order: MEA> AMP > DEA. However, the long-term flux was monitored and it was found that MEA also gave lowest flux decline due to the membrane wetting. The use of mixed amine solutions and the addition of NaCl did not help protect the membrane wetting. On the contrary, the addition of SG in to MEA solution can improve flux and resulted in stable CO_2 flux indicating that the membrane wetting was negligible.

1. Introduction

Carbon dioxide (CO_2) is the main gaseous component of the greenhouse gases in the atmosphere, representing about 80%. CO_2 has been known to contribute significantly to global warming. The effective and economical technology for CO_2 capture is, thus, necessary. Conventional gas absorption process for removal of CO_2, including chemical absorption by reactive absorbents, is normally carried out by packed and spray columns. The methods suffer many drawbacks such as flooding, foaming, and high capital and operating costs. These problems can be overcome by using hollow fiber membrane contactors [1].

Membrane contactors are devices that employ porous hydrophobic membrane as a phase barrier allowing two fluids to come to contact with each other for the purpose of mass transfer without dispersion of one phase into the other. This typical process offers several practical advantages including high surface area per unit volume, especially, when the hollow fiber membrane modules are used. Recent reviews of CO_2 absorption using hollow fiber membrane contactors are given in the literature [1,2].

Although the membrane contactors offer many advantages over the conventional contacting equipment, additional mass transfer resistance is introduced due to the membrane. Depending on the membrane material, the liquid absorbent nature and the pressure of the two phases, the membrane pores may be filled with gas or liquid, which corresponds to the non-wetted mode and the wetted mode. In the gas absorption case, the non-wetted mode is preferred because if the membrane pores are wetted by liquid the membrane resistance will increase, resulting in low flux. Wang et al. [3] reported that the reduction of the overall mass transfer coefficient may reach 20% even if the membrane pores were 5% wetted. The study of membrane wetting has been the subject of interest [3–5]. The membrane with high hydrophobicity is more resistant to wetting. The hydrophobicity of membranes is represented in terms of the contact angle between the liquid absorbent and membrane. In general, the hydrophobicity of the membranes is in the order of PTFE (polytetrafluoroethelene) > PP (polypropylene) > PVDF (polyvinylidenefluoride) based on the contact angle data [6]. For a given membrane material and structure,

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Nomenclature

A_T	mass-transfer area based on inside surface area of gas–liquid contact (m^2)
C_l	concentration of carbon dioxide in the liquid phase ($mol\,m^{-3}$)
C_g	concentration of carbon dioxide in the gas phase ($mol\,m^{-3}$)
$\Delta C_{l,av}$	logarithmic mean concentration difference of carbon dioxide in the liquid phase ($mol\,m^{-3}$)
$C_{CO_2,F}$	concentration of carbon dioxide in feed stream ($mol\,mol^{-1}$)
$C_{CO_2,R}$	concentration of carbon dioxide in retentate stream ($mol\,mol^{-1}$)
D	diffusion coefficient of carbon dioxide in the liquid phase ($m^2\,s^{-1}$)
$D_{g,eff}$	effective diffusion coefficient of gas in the pores ($m^2\,s^{-1}$)
d_i	inside diameter of membrane (m)
d_{ln}	logarithmic mean diameter of membrane (m)
d_o	outside diameter of membrane (m)
H	Henry's constant
J_{CO_2}	CO_2 flux ($mol\,m^{-2}\,s^{-1}$)
K_{Ol}	overall mass transfer coefficient ($m\,s^{-1}$)
k_l	individual mass transfer coefficient of liquid phase ($m\,s^{-1}$)
k_m	individual mass transfer coefficient of membrane ($m\,s^{-1}$)
k_g	individual mass transfer coefficient of gas phase ($m\,s^{-1}$)
L	effective length of the membrane module (m)
l_m	thickness of the hollow fiber (m)
ΔP	penetration pressure (Pa)
Q_F	total gas flow rate in feed stream ($m^3\,s^{-1}$)
Q_l	liquid flow rate ($m^3\,s^{-1}$)
Q_R	total gas flow rate in retentate stream ($m^3\,s^{-1}$)
r_p	membrane pore radius (m)
Sh	Sherwood number
T_g	gas temperature (K)
V	velocity ($m\,s^{-1}$)

Greek letters

ε_m	membrane porosity
θ	contact angle (°)
σ	surface tension ($mN\,m^{-1}$)
τ_m	membrane tortuosity

its hydrophobic character may be altered due to morphological change by the interaction of liquid. Khaisai et al. [6] compared the CO_2 absorption performance of PTFE, PP, and PVDF membranes. They concluded that based on the cost of PVDF membranes, and its comparable performance to PTFE membrane, PVDF remains a membrane of interest.

Important measures to prevent the wetting problem include the selection of liquids with suitable surface tension. It was reported that when the liquid surface tension decreased (which may be due to the presence of organic compounds) from about 33 mN/m to 30 mN/m, the transmembrane pressure difference of the PP membrane was decreased from about 0.9 bar to 0.1 bar leading to the rapid increase of membrane wetting [7]. The study of Yan et al. [4] on CO_2 removal using PP membrane by aqueous solutions of potassium glycinate (PG), monoethanolamine (MEA), and methyldiethanolamine (MDEA) revealed that aqueous PG solution has a lower potential of membrane wetting due to its suitable physical properties (e.g. surface tension). PG also has good reactivity towards CO_2 compared with MEA and MDEA.

To achieve high CO_2 absorption rate, reactive absorbents are widely employed in practice. The commonly used absorbents for CO_2 capture are aqueous solutions of amines which are weak bases that react with CO_2 to form complexes with weak chemical bonds. These chemical bonds are easily broken upon mild heating, leading to absorbent regeneration. The preferred amines are MEA, diethanolamine (DEA), and MDEA in terms of high CO_2 loading capacity, rapid absorption rate and low cost for regeneration. MEA, a primary amine, has been used extensively because of its high reactivity and low cost. However, its maximum loading is limited by stoichiometry to 0.5 mol CO_2 per mole of amine. DEA is less corrosive with reasonable CO_2 absorption rate. The advantages of MDEA, a tertiary amine, over MEA include its higher loading capacity and its low heat of reaction leading to low energy requirement for regeneration.

The use of mixed absorbents for CO_2 removal is of increasing interest. Glasscock et al. [8] investigated CO_2 absorption by mixed amines in a batch liquid continuous gas-stirred cell reactor. The simulation of CO_2 absorption was carried out. A differential equation based model was developed and used to study the reaction kinetics for CO_2 with MEA, DEA, MDEA and the mixtures of MEA/MDEA and DEA/MDEA. It was demonstrated that MDEA participated in the DEA kinetics, but not the MEA kinetics. Finally, it was concluded that the performance of the MEA/MDEA system was much more sensitive to loading than the DEA/MDEA system. The absorption of CO_2 into aqueous solution of amine mixtures was also reported by Mandol et al. [9]. It was found that the addition of small amount of MEA to aqueous solutions of MDEA or AMP significantly enhanced the enhancement factor and rate of absorption for both solvents. Apart from the mixtures of MEA, DEA, AMP and MDEA, the use of piperazine (PZ) as the activator for those amines is also the subject of interest [10–12].

The use of mixed amines is an interesting and promising approach since it may bring about improvement in gas absorption and in reducing energy requirement for regeneration. However, previous works [9–12] on using mixed absorbents did not include the long-term flux, wetting characteristics, and there was a lack of important data (contact angle, surface tension, and viscosity) influencing the membrane wetting. Mixed amines may also result in different membrane wetting characteristics of the system. Accordingly, it is the interest of the present work to systematically investigate the removal of CO_2 by a hollow fiber membrane contactor using both single and mixed amine solutions. PVDF membrane was selected for the study. Mixed amines of MEA, DEA, and AMP including SG (sodium glycinate) as well as inorganic salt, sodium chloride (NaCl), at different compositions were used for CO_2 removal. The wetting study was carried out by monitoring the long-term CO_2 flux of the mixed amine solutions. In addition, the effect of salts, i.e. SG and NaCl on CO_2 flux and on membrane wetting was also presented.

2. Theory

2.1. Basic principle of mass transfer in gas–liquid membrane contactor

The resistance-in-series model has been widely applied to describe the mass transfer mechanism in the gas–liquid membrane contacting process. Fig. 1 illustrates the mass transport of the interested gas for non-wetted operating mode of membrane contactors, i.e., diffusion from the bulk gas through the membrane pores and dissolution in the liquid absorbent. The resistance-in-series model