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Mass transfer characteristics of CO_2 absorption into a phase-change solvent in a wetted-wall column

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ABSTRACT

CO_2 from coal-fired flue gas is one of the main components of greenhouse gases. Using phase change absorbents as a solvent can effectively decrease the consumption of regeneration energy for CO_2 capture process. This study employed a mixed solution of diethylenetriamine (DETA) and diethylaminoethanol (DEEA) as the new phase change absorbent for CO_2 absorption. The impact of the phase change behavior on the mass transfer characteristics of CO_2 absorption was investigated in a wetted-wall column. Effects of the temperatures, CO_2 loadings, and gas flow rate on the mass transfer coefficient were also conducted. The results indicated that temperature and CO_2 loading had relatively remarkable effects on the total mass transfer coefficient; whereas the gas flow rate had a smaller effect. Kinetic analysis revealed that the mass transfer resistance of CO_2 absorption into the DETA/DEEA phase change absorbent mainly concentrated at the liquid film side. The findings provide a theoretical reference for the development of new CO_2 phase change absorption technology.

1. Introduction

Carbon capture and sequestration (CCS) is a crucial method in mitigating global warming and has received widespread attention among the international community in recent years (Perez-Vega et al., 2016; Chakroun and Ghoniem, 2015; Liu et al., 2016a; Li et al., 2015). Alkanolamine absorption is currently the most widely applied carbon dioxide (CO_2) capture technology (Du et al., 2017; Lv et al., 2015; Zhang and Lu, 2015; Xiao et al., 2016). However, its large energy consumption causes the CO_2 capture costs to account for more than 60% of the total CCS process. Therefore, developing a new low cost and low energy-consuming CO_2 absorption technology has gained increasing attention (Martin et al., 2016; Ciftja et al., 2013; Liang et al., 2015; Zhang and Lu, 2017; Liu et al., 2016b). Phase change absorption process has a great potential to reduce the sensitive heat and stripping heat as only the rich phase is needed for the solvent regeneration. It has been regarded as an ideal alternative to the alkanolamine absorption (Ye et al., 2015; Pinto et al., 2014).

There are two type of phase change absorbent: 1) liquid-solid phase change absorbent, and 2) liquid–liquid phase change absorbent. The liquid–solid phase change absorbent upon the CO_2 absorption produces the precipitates as CO_2 sink (Fernandez et al., 2013; Ma'mun and Kim, 2013; Zhang et al., 2014). For example, if a high concentration of potassium carbonate (K_2CO_3) is used as an absorbent, the product, $KHCO_3$, precipitates due to its relative low solubility. As the precipitates contains low contents of water, the stripping heat can be remarkably reduced. Because of the slow reaction rate of CO_2 absorption by K_2CO_3, a promoter (such as piperazine) is added to increase the CO_2 absorption rate (Oexmann et al., 2008; Sun et al., 2005). However, the liquid-solid phase change process incurs the clogging in the absorber and heat exchange, poor heat efficiency, and difficult absorbent transportation between the absorber and the stripper.

The reaction product of liquid–liquid phase change absorbent remains in liquid phase after the CO_2 absorption and concentrated in the rich phase. For example, the DMX™ (Raynal et al., 2011; Aleixo et al., 2011) phase change absorbent developed by the French Institute of Petroleum is able to achieve auto stratification following CO_2 absorption, which can lower the consumption of regeneration energy to 2.1 GJ/t CO_2 under specific conditions; (Ciftja et al., 2013) discovered through screening that the absorption of CO_2 by a mixture of 5 M diethylaminoethanol (DEEA) and 2 M N-Methyl-1,3-propanediamine (MAPA) produced a clear liquid–liquid stratification. A nuclear magnetic resonance analysis on the upper and lower phases revealed that the lower solution mainly consisted of CO_2 and MAPA, whereas the upper solution largely contained DEEA and a very small amount of CO_2; (Xu et al., 2013a; Xu et al., 2013b) conducted a systematic research on

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Nomenclature

d	Hydraulic diameter of the wetted wall column (cm)
D	Diffusion coefficient (cm^2/s)
E	Enhancement factor
h	Height of the wetted wall column (cm)
F	The interfacial area of wetted wall column(cm^2)
H	Henry's law constant ($Pa\ cm^3/mol$)
k_g	Gas film mass transfer coefficient [$mol/(Pa\ cm^2\ s)$]
K_G	Total Mass transfer coefficient based on gas phase [$mol/(Pa\ cm^2\ s)$]
k_L^0	Physical liquid film mass transfer coefficient (cm/s)
Θ	Driving force of the CO_2 diffusion in the liquid film, dimensionless
P	Partial pressure of CO_2 (Pa)
P^*	Equilibrium pressure (Pa)
Q	Flow rate (mL/s)
Re	Reynolds number
Sc	Schmidt number
Sh	Sherwood number
T	Temperature (K)
μ	Viscosity (cp)
ρ	Density (g/cm^{-3})
W	Perimeter of the column (cm)

an efficient two-phase absorbent composed of 1,4-diaminobutane (BDA) and DEEA, and determined that the optimum ratio, namely 2 M BDA + 4 M DEEA, produced phase separation. The CO_2 absorption amount at the lower layer reached 97% of the total absorption; thus he proposed the use of a mixed solution of 2 M BDA + 4 M DEEA as the mechanism for liquid–liquid phase separation. (Liebenthal et al., 2013; Monteiro et al., 2015a) used a string of discs contactor to study the reaction kinetics of CO_2 absorption by the DEEA/MAPA mixed phase change system under a zero loading condition, and calculated some parameters such as the enhancement factor of the reaction. Compared to conventional chemical absorption, only the rich phase enters the desorption tower and thus significantly reduce the consumption of regeneration energy.

In general, existing studies have provided useful references for phase change solvents, analyzing the generated products of the phase change absorbents and the distribution patterns within the two phases of a given absorbent; they have also given detailed descriptions of the phase change processes of the various types of phase change solvents, as well as their phase change performance levels. However, the selection of the phase change solvent lacks of the universal criteria in term of the absorption rate. The mass transfer characteristics is important to figure out the major resistance of the gas absorption, which can help provide the suitable measures to accelerate the overall absorption rate. However, this information is limited in the literature.

In this work, the mass transfer characteristics of a phase change solvent, formulated by a primary amine with multiple amino group as a promoter (diethylenetriamine, DETA) and a tertiary amine as a sink (diethylaminoethanol, DEEA), was investigated in a wetted-wall columns (WWC) to figure out the major resistance of CO_2 absorption into the proposed phase change solvent. Furthermore, the parametric tests were also conducted to optimize the operation conditions for CO_2 absorption. The results from this work can provide a theoretical foundation to develop novel phase change solvent.

2. Experiment

2.1. Experimental materials

The reagents used in this experiment, DETA (≥99%, mass fraction) and DEEA (≥99%, mass fraction), were purchased from Aladdin Biochemical Technology Co., Ltd., in Shanghai. The nitrogen (N_2, ≥99.99%, volume fraction) and CO_2 (≥99.9%, volume fraction) were purchased from Baoding North Special Gases Co., Ltd. All reagents were used without further purification.

2.2. Experimental setup and procedures

This study used a WWC to study the reaction kinetics of CO_2 absorption (Pacheco et al., 2000; Mshewa, 1995); the experimental setup is shown in Figs. 1 and 2. The stainless-steel pipe within the WWC had an outer diameter of 1.26 cm and a height of 9.1 cm, and the contact area of the gas–liquid reaction was 38.52 cm^2. During the gas–liquid contact reaction, the solution was pumped into the stainless-steel tube and formed a layer of liquid film on its outer surface. The simulated flue gas entered the WWC from the bottom and underwent a contact reaction with the counter flowing liquid film.

The flow of the simulated flue gas was controlled through a mass flow controller; the gas entered the WWC at a constant flow rate. Post reaction gas was discharged from the top of the column and passed through a condenser tube and drying tube sequentially, after which a GXH-3011N infrared CO_2 analyzer was used to measure the CO_2 concentration at the exit of the reactor.

A mixed amine phase change absorbent with a specific CO_2 load was prepared and preheated in a constant temperature water bath. The absorbent flow velocity was controlled at 3.25 cm^3/s using a peristaltic pump and sent into the WWC; it was then returned to the preparation liquid after the reaction cycle ended, forming a closed circuit. Throughout the gas–liquid reaction process, because the reaction time was less than one hour, the total amount of the phase change absorbent was much higher than that of the absorbed CO_2. Therefore, the absorbent concentration can be considered to have remained constant, which meant that the effect of the absorbed CO_2 on the loading during the reaction was negligible. The entire tube was insulated with a heating tape. The ambient temperature of the WWC was controlled by the constant temperature water bath.

2.3. Data analysis

2.3.1. Chemistry of the phase change solvent

The DETA within the phase change absorbent DETA/DEEA mixed solution used in this study is a type of secondary amine. Its nitrogen atoms contain active hydrogen atoms that can react with CO_2 to form zwitterions (Xu et al., 2016; Kim et al., 2016), which reacts with amine again to form carbamate (R_1 and R_2 are alkyls):

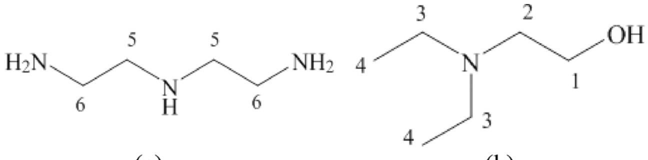
$$R_1R_2NH + CO_2 \rightleftarrows R_1R_2NH^+COO^- \tag{1}$$

$$R_1R_2NH^+COO^- + R_1R_2NH \rightleftarrows R_1R_2NH_2^+ + R_1R_2NCOO^- \tag{2}$$

The overall reaction is as follows:

$$2R_1R_2NH+CO_2 \rightleftarrows R_1R_2NH_2^+ + R_1R_2NCOO^- \tag{3}$$

DEEA, an organic amine, is a tertiary amine; the nitrogen atoms



(a) (b)

Fig. 1. Chemical structure: (a) DETA; and (b) DEEA.