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CO_2 Capture by Aqueous Solution Containing Mixed Alkanolamines and Diethylene Glycol in a Rotating Packed Bed

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Abstract

In this study, an effective absorbent, 23.5% diethylenetriamine (DETA)/19.6% piperazine (PZ)/37.7% diethylene glycol (DEG)/19.2% H_2O, was proposed to capture CO_2 from a nitrogen gas stream containing 10% of CO_2 in a rotating packed bed (RPB). The addition of DEG could improve the solubility of PZ in absorbent, and there was no precipitation observed in CO_2-rich solution after CO_2 absorption for the proposed absorbent. The regeneration energy could be reduced because the heat capacity and vapor pressure of DEG are lower than that of water. The higher gas-liquid contact area and mass transfer rate as well as the smaller size were observed in a RPB as compared with a packed bed to achieve the same CO_2 capture efficiency.

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Keywords: CO_2 Capture, Chemical absorption, Alkanolamine, Diethylenetriamine, Piperazine, Diethylene glycol, Rotating packed bed

1. Introduction

Chemical absorption has been applied to treat acid gases, such as SO_2 and CO_2 in packed bed, and it is regarded as the most applicable technology for CO_2 capture from gas emissions from fossil fuel power plant [1]. However, significant mass transfer limitations exist in the gas-liquid interface and a huge amount of the exhausted gas from power plant is needed to be treated, the volume of packed bed column is quite large. To enhance mass transfer rate between gas and liquid, a RPB device has been suggested. In a RPB, liquid contacts with gas on the surface of packing under high centrifugal force, and hence the gas-liquid contact area as well as the mass transfer efficiency are increased owing to liquid is split into small droplets and thin film when it passes through the packing. As a matter of

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fact, RPB had been proposed to capture CO_2 from fossil fuel power plants [2-7] and hot stove gas in steeling making process [8]. Furthermore, it can also be applied to improve zinc/air battery life and the quality of indoor air [9, 10]. The results indicated that the size of a RPB could be reduced significantly as compared with a packed bed column when the same CO_2 capture efficiency was achieved [2-10]. Furthermore, RPBs can also be applied to regenerate absorbents and achieve the same regeneration efficiency with lower regeneration energy [11].

Alkanolamine-based absorbents are commonly used to capture CO_2. It can be seen from our previous study that diethylenetriamine (DETA) and piperazine (PZ) are most appropriate to be used in a RPB to capture CO_2 because of their high reaction rates [5]. In a recent report by Freeman et al. [12], the concentrated PZ solution was suggested owing to its effective resistant to oxygen degradation and thermal degradation. Because there is the solubility limitation for PZ in water, 14% of PZ in water is suggested to be used in absorption to avoid the precipitation of PZ from water at low temperatures. In our previous study [6], it was also found that concentrated PZ (40.8%) could be dissolved in DEG without precipitation at 20 ^oC, which allows the operation at low temperatures. However, solid precipitation was still observed in CO_2-rich solution after CO_2 absorption, the occurrence of precipitation in a non-aqueous absorbent consisted of amine and alcohol in a CO_2-rich solution was also observed by Lin and Wong [13].

In this study, an effective absorbent consisted of DETA, PZ, DEG and H_2O was proposed to capture CO_2. No precipitation was observed for the proposed absorbent at low temperatures or in CO_2-rich solution after CO_2 absorption. Because the heat capacity of DEG is 2.30 (J/g/K) [14], lower than that of H_2O as 4.18 (J/g/K), lower sensible heat is thus required in the regeneration process. In addition, the vapor pressure of DEG is lower than water, thus lower heat of vaporization is required in regeneration as well. These advantages therefore lead to less regeneration energy as compared with an aqueous solution.

Nomenclature

Q_G	Gas flow rate (L/min)
r_i	Inside radius of the RPB (cm)
r_o	Outside radius of the RPB (cm)
Y_i	CO_2 Concentration in the feed stream (%)
Y_o	CO_2 Concentration in the discharged stream (%)
z	Height of the RPB (cm)

2. Experimental

PZ, DETA, and DEG with a purity of 99% were purchased from Seedchem, Aldrich, and Tedia, respectively. N_2 with a purity of 99.99% and CO_2 with a purity of 99.5% were purchased from Boclh Industrial Gases Co (Taiwan). All the chemicals and gases were used as received. The schematic diagram of the RPB used in this study is shown in Fig. 1. The inner, outer diameters and height of the packing were 2.5, 12.5 and 2.3 cm, respectively. The total volume of the packing in the RPB was of 270.9 cm^3. The stainless wire mesh was used as the packing with a surface area of 887.6 m^2/m^3 and a void fraction of 0.96.

The gas stream flowed from the outer side into the RPB. The absorbent was pumped from the central axis tube into the RPB. Both gas and liquid were heated by the heaters equipped with a temperature controller before entering the RPB. The CO_2 gas contacted with the absorbent counter-currently in the RPB. After absorption, the gas stream left from the axis of the RPB and CO_2-rich absorbent was discharged from the outer side of the RPB. The CO_2 concentrations of both the feed and discharged gas stream were measured by a NDIR CO_2 analyzer (Drager, Polytron IR CO_2). The CO_2 capture efficiency in terms of overall mass transfer coefficient (K_Ga) and height of transfer unit (HTU) were used for the comparison of absorbents, and were calculated by the Eqs (1) and (2):

$$K_G a = \frac{Q_G}{\pi z (r_o^2 - r_i^2)} \ln\left(\frac{Y_i}{Y_o}\right) \quad (1)$$

$$HTU = \frac{r_o - r_i}{\ln\left(\frac{Y_i}{Y_o}\right)} \quad (2)$$

where Q_G is gas flow rate, z, r_o and r_i are the height, outside and inside radiuses of the RPB, respectively. Y_i and Y_o are CO_2 concentration in the feed and discharged stream, respectively. A smaller HTU value represents a smaller reactor volume needed for capturing CO_2.

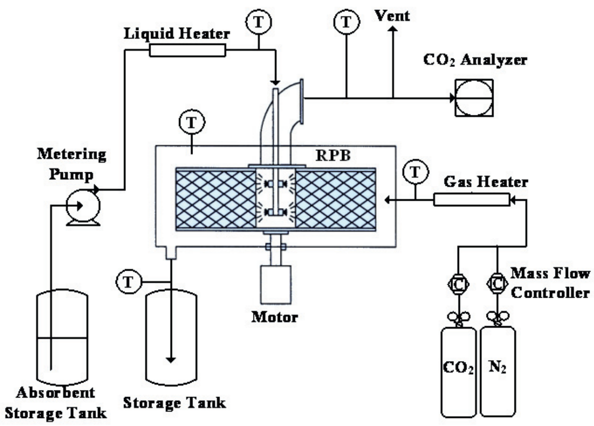

Fig. 1. Experimental apparatus for CO_2 capture in a rotating packed bed.

The precipitation temperature of the absorbent was observed visually. The absorbent was placed in a flask with a stirring speed of 150 rpm, and 50 °C water bath was used to ensure PZ could fully be dissolved in absorbent. The water bath was then cooled slowly, and the temperature was recorded when the precipitation was observed.

3. Results and Discussion

In our previous study, it was observed that 40.8% PZ could be dissolved in DEG without precipitation at 20 °C [6]. However, solid precipitation was still observed in CO_2-rich solution after CO_2 absorption for 40.8% PZ/59.2% DEG. To solve this problem, a mixed solvent consisting DEG and water was proposed in this study. To insure a high CO_2 capture efficiency in RPB, DETA was therefore chosen to mix with PZ because of its high reaction rate with CO_2. Table 1 reveals that the precipitation temperature of 23.5% DETA/19.6% PZ/56.9% H_2O is lower than that of 40.8% PZ/59.2% H_2O. It is noted that the precipitation temperature of the proposed absorbent, 23.5% DETA/19.6% PZ/37.7% DEG/19.2% H_2O, was not observed even at a temperature of 0 °C, significant lower than those of 23.5% DETA/19.6% PZ/56.9% H_2O and 40.8% PZ/59.2% H_2O. Furthermore, no sold precipitation was observed in CO_2-rich solution after CO_2 absorption. The proposed absorbent thus shows its potential for CO_2 capture and was used in the subsequent study.

Table 1. Precipitation temperature of the absorbents

Absorbent	Content (%)	Precipitation Temperature
PZ/H_2O[a]	40.8/59.2	41.4[c]
$DETA/PZ/H_2O$	23.5/19.6/56.9	31.2
$DETA/PZ/ DEG/H_2O$[b]	23.5/19.6/37.7/19.2	ND[d]

[a]The molality PZ is 8 m.
[b]The molality of DETA and PZ are 4 m and 4 m, respectively; the molar ratio of DEG and H_2O is 25/75.
[c]42 °C for the reported value [12].
[d]Below 0 °C.

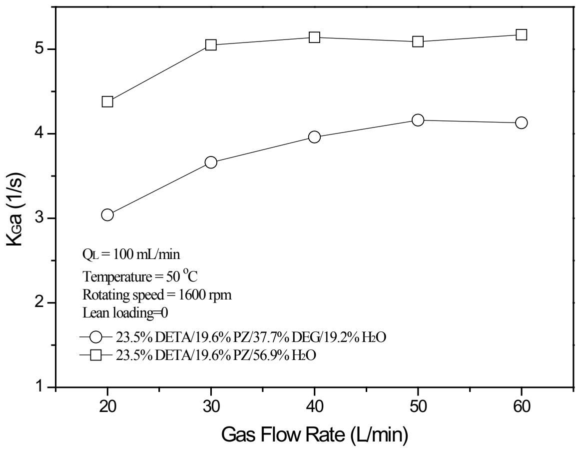

Fig. 2. Dependence of K_Ga on gas flow rate for different absorbents.

Fig. 2 shows the dependency of gas flow rate on K_Ga for the absorbents with and without DEG. At the rotating speed of 1600 rpm, K_Ga of the absorbent 23.5% DETA/19.6% PZ/56.9% H_2O were higher than those of 23.5% DETA/19.6% PZ/37.7% DEG/19.2% H_2O at all gas flow rate. This was due to that the reaction rate with CO_2 of the absorbent containing DEG is lower than that without DEG, resulting from the lower solubility parameter possessed by DEG. Though the absorbent, $DETA/PZ/H_2O$, possessed higher K_Ga than $DETA/PZ/DEG/H_2O$, the addition of DEG could improve the solubility of PZ in water, improving the feasibility for the CO_2 absorption operation. Fig. 3 shows the dependency of gas flow rate on K_Ga for the proposed absorbent, 23.5% DETA/19.6% PZ/37.7% DEG/19.2% H_2O, at different lean loadings. The K_Ga of the absorbent was found to decrease with increasing lean loading of the absorbent. When lean loading of the absorbent is increased, the concentration of free amine in the absorbent is decreased accordingly. In addition, the diffusivity of CO_2 in the absorbent is decreased when CO_2 is present in solution. These facts lead to less absorption of CO_2 at high lean loadings. Though the K_Ga was decreased with lean loading, the K_Ga for the proposed absorbent, 23.5% DETA/19.6% PZ/37.7% DEG/19.2% H_2O, were in a range from 1.78 to 4.16 (1/s), still higher than 0.068 (1/s) for the use of an aqueous alkanolamine solution in a packed bed column [15], indicating a better mass transfer performance of a RPB compared with a conventional packed bed column.

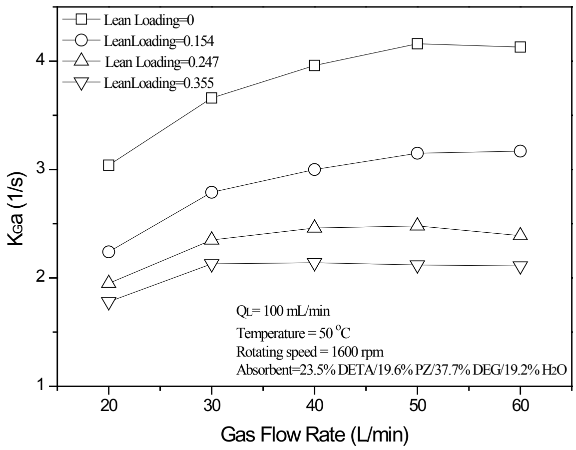

Fig. 3. Dependence of K_Ga on gas flow rate of the absorbent at various lean loadings.

Fig. 4 shows the dependency of gas flow rate on HTU for the absorbent, 23.5% DETA/19.6% PZ/37.7% DEG/19.2% H_2O, at various lean loadings. It is seen that HTU was increased with increasing gas flow rate for different lean loadings. The gas-side mass transfer resistance is believed to reduce when gas flow rate is increased, leading to a positive effect on CO_2 capture efficiency. However, the contact time between gas and liquid is reduced and the amount of CO_2 passes through the system is increased, these two facts led to negative effects on CO_2 capture efficiency. From the results obtained in this study, it then concludes that the negative effects overweighed the positive effects on CO_2 capture efficiency, leading to an increase of HTU with increasing gas flow rate. It can also be seen from Fig. 4 that HTU of the absorbents used in this study were all lower than 11 cm, significantly lower than that of the conventional packed bed column where HTU was found to be about 340 cm [15]. The significant decrease of HTU using RPB was believed due to the increased gas-liquid contact area and mass transfer rate in a RPB as compared with a packed bed column, and hence, the smaller size of a RPB is therefore required to achieve the same CO_2 capture efficiency.

The regeneration energy estimated in this study was based on the following assumptions: (1) ideal mixing, (2) CO_2-rich loading as 0.82 mol of CO_2/mol of amine for DETA+PZ; 0.48 mol of CO_2/mol of amine for MEA, (3) regeneration efficiency of 50%, (4) the stream with a temperature of 10 K lower than the temperature in the stripper, (5) regeneration temperature at 100.7 ^oC, and (6) regeneration pressure at 1.8 atm. The thermal properties of DETA and PZ can be seen from Yu and Tan [7]. The regeneration energy of 30% MEA/70% H_2O was first calculated to assure the accuracy of the calculation, as shown in Table 2. It can be seen that the regeneration energy was 3.81 (GJ/ton CO_2), sufficiently close to the reported value of 3.89 (GJ/ton CO_2) in the literature [16]. Furthermore, the proportions of reaction heat, vaporization heat and sensible heat were found to be 48.6%, 30% and 21.4%, respectively, close to 51%, 26% and 23% reported in the literature [17]. It can also be seen from Table 2 that the regeneration energy of 23.5% DETA/19.6% PZ/37.7% DEG/19.2% H_2O was 2.63 GJ/ton CO_2, about 21.5% lower than that of 23.5% DETA/19.6% PZ/56.9% H_2O (3.35 GJ/ton CO_2). Obviously, the lower regeneration energy required was resulted from the lower heat capacity and vapour pressure possessed by DEG as compared with water.

Though the CO_2 capture efficiency of the absorbent, 23.5% DETA/19.6% PZ/37.7% DEG/19.2% H_2O, was lower than that of 23.5% DETA/19.6% PZ/56.9% H_2O, the precipitation temperature of the former absorbent is significant lower than the latter absorbent. There was also no sold precipitation observed in CO_2-rich solution after CO_2 absorption, and this thus improve the applicability in the CO_2 absorption operation. Furthermore, the regeneration energy could be reduced when DEG was mixed with water because the heat capacity of DEG is lower than that of water, and the heat of vaporization of water is reduced with the addition of DEG in the solution. Under the considerations of solid precipitation and the regeneration energy, the addition of DEG is a possible means for CO_2 capture.

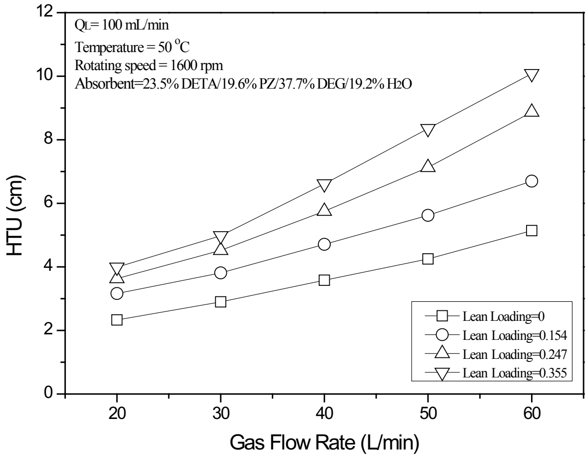

Fig. 4. Dependence of HTU on gas flow rate of the absorbent at various lean loadings.

Table 2. Regeneration energy of the absorbents.[a]

Absorbents	Reaction heat (kJ)	Vaporization heat (kJ)	Sensible heat (kJ)	Regeneration energy (GJ/ton CO_2)
23.5% DETA/19.6% PZ/37.7% DEG/19.2% H_2O	133.71	49.98	32.95	2.63
23.5% DETA/19.6% PZ/56.9% H_2O	133.71	100.62	41.22	3.35
30% MEA/70% H_2O	96.87	59.85	42.64	3.81

[a]the value of regeneration energy is calculated on the basis of 1 kg absorbent.

4. Conclusions

The absorbent, 23.5% DETA/19.6% PZ/37.7% DEG/19.2% H_2O, was proposed to use in a RPB for CO_2 capture in this study. After the addition of DEG, the solid precipitation of the absorbent is avoided even at low temperatures and no sold precipitation was observed in CO_2-rich solution after CO_2 absorption. In addition, the regeneration energy can be reduced because the heat capacity and vapor pressure of DEG are lower than those of water. The K_Ga obtained using the proposed absorbent in a RPB were found to be significantly higher than those in the conventional packed bed column, indicating a better mass transfer performance by RPB. In a consequence, a smaller size of a RPB is required to achieve the same CO_2 capture efficiency.

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