Carbon Dioxide Capture from Reforming Gases using Acetic Acid-mixed Chemical Absorbents

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The removal of acid gas impurities such as carbon dioxide from industrial gas streams is a significant operation in natural gas processing, hydrogen purifying, refinery off-gas treating, and synthesizing gas for ammonia and methanol manufacturing. Carbon dioxide (CO₂) is a major problem in the production of natural gas as it may contribute to the operational problems such as foaming, corrosion, high solution viscosity, and fouling, thereby decreasing the plant life.1,2 The presence of acid gas in natural gas reforming may also result in the increase of transported gas volume and the decrease of heating value.2

Absorption using aqueous solutions of alkanolamines has been a preferred approach in current industry for CO₂ removal.3–4 Diethanolamine (DEA), a secondary amine, is among the most widely used gas treating solvent because of its less reactivity, low vapor pressure, low solvent cost, and less corrosive property when compared with monoethanolamine (MEA, primary amine) and other alkanolamines.5 However, DEA suffers from nonselective removal in mixed acid gas, higher circulation requirement, and unrecoverable by conventional reclaiming techniques.5 Ammonia solution displays several advantages as CO₂ absorber, such as lower cost, no issues pertaining to the corrosion and degradation, lower operating temperature, and higher CO₂ loading capacity.6,7

Recently, aqueous blend of chemical absorbents to economically improve CO₂ capture has received much attention in the literature.5,8 In this study, DEA and ammonia were mixed with acetic acid which aims to investigate the extent of CO₂ capture from simulated reforming gases. Although acetic acid may pose a potential corrosion problem to the pipelines, its influence is not significant when compared with the CO₂ corrosion rate.9 Absorption of CO₂ is expected to elevate due to the presence of carbonyl groups in acetic acid solution.10,11 Effects of solvent concentration, solvent flow rate, and gas flow rate were studied and discussed.

Experimental

Materials. Gas cylinder was purchased from Linde Gas Singapore Pte. Ltd., Singapore. The composition of CO₂ in a mixture of gases is 30%, with percentages of other gases: 10% CH₄, 10% CO, 5% C₂H₄, 5% C₃H₆ and 40% H₂. Aqueous ammonia (30 wt%), DEA (98 wt %), and acetic acid (99 wt %) were supplied by Sigma-Aldrich (St. Louis, MO, USA). All chemicals were used without further purification. Necessary dilutions were performed using distilled water.

Procedures. Schematic diagram of the experimental setup is shown in Figure 1. The column is made of glass bell with a height of 0.90 m. Column bed height is 0.58 m and was filled with 8 × 8 mm Raschig bead glass sphere. The rig was equipped with a mass flow controller (model Tylan FC-260; Mykrolis Corporation, Billerica, MA, USA) with 0–100 sccm range and accuracy of ±1% of full scale for adjusting the gas flow rate. Rotameter (model FL-1802; Omega Engineering Inc., Stamford, CT, USA) with 0–150 mL/min range and ±1 mL/min accuracy was used to manipulate the liquid flow rate.

A series of tests were carried out to calibrate the system, wherein the flow ranges of gas and liquid were determined. Liquid flow rate was varied at 10, 16, and 22 L/h, while the gas flow rate was adjusted between 40 and 80 mL/min. The ranges were selected due to the equipment limitation and to suit the column dimensions. Different concentrations of absorbents, i.e., 1–6 M NH₃, 0.5–2 M DEA, 1–15 wt % acetic acid, and acetic acid–mixed NH₃ and DEA, were employed to evaluate the removal of CO₂. The pH meter model Hanna HI 8424 (HANNA Instruments, Carrolton, TX, USA) with accuracy of ±0.01 pH was used to measure the absorbent pH. When the header tank reaches a constant level of 1 L, the valve connecting the tank was closed, and the liquid absorbent was allowed to fill and circulate inside the column via peristaltic pump at a desired liquid flow rate. When the packing is wet, the gas flow was initiated and controlled at a desired flow rate. Gas mixture is in contact with the aqueous solvent at ambient temperature and pressure in a countercurrent, packed absorber. The temperature of the absorption column was maintained at 25 °C using a circulating water bath (accuracy ±0.1 °C; LAUDA model E100, LAUDA-Brinkmann, Delran, NJ, USA) connected to a thermostatic chamber. The CO₂
removal was analyzed using an online gas chromatography (model HP 5890 series II; Hewlett-Packard Company, Wilmington, DE, USA) equipped with thermal conductivity. The oven temperature was initially ramped from 40 to 200 °C, and the injection temperature for all solvents was set at 180 °C. Absorption was terminated after the CO₂ level in the outlet reached a steady-state condition.

Results and Discussion

Effect of Aqueous Absorbents Concentration. Figure 2 shows the effect of aqueous absorbents concentration on the absorption of CO₂. In general, the removal of CO₂ increased with increasing concentration of DEA and ammonia. Results show that the absorption notably increased from 19.7 to 97.3% when the aqueous ammonia concentration rose from 1 to 6 M at fixed liquid and gas flow rates of 22 L/h and 40 mL/min, respectively.

This could be attributed to the fact that the increase of ammonia concentration yields a higher amount of active NH₃ available to diffuse at the gas–liquid interface and reacts with CO₂. The reactions at the liquid phase of the gas–liquid interface of the CO₂-ammonia system are given as follows:

\[ \text{CO}_2(g) + 2\text{NH}_3(aq) \rightarrow \text{NH}_2\text{COONH}_4(aq) \] (1)

Reaction (1) is actually composed of the following two steps:

\[ \text{CO}_2(g) + \text{NH}_3(aq) \rightarrow \text{NH}_2\text{COO}^-(aq) \] (2)
\[ \text{NH}_4^+(aq) + \text{NH}_2\text{COO}^-(aq) \rightarrow \text{NH}_4^+(aq) + \text{NH}_2\text{COO}^-\text{(aq)} \] (3)

NH₂COONH₄ then hydrolyzes in solution and generates free ammonia as follows:

\[ \text{NH}_2\text{COO}^-(aq) + \text{H}_2\text{O(l)} \rightarrow \text{HCO}_3^-\text{(aq)} + \text{NH}_3(aq) \] (4)
\[ \text{NH}_3(aq) + \text{H}_2\text{O(l)} \rightarrow \text{NH}_4^+(aq) + \text{OH}^-(aq) \] (5)

Reaction (2) is very fast and irreversible, while reaction (3) is instantaneous. The reaction between aqueous ammonia and carbon dioxide is a second-order reaction with first-order for CO₂ and NH₃, respectively, and is mainly controlled by reaction (2) with the rate constant of about 300 L/(mol·s) at 298.15 K.\(^{12,13}\)

Similarly, the removal of CO₂ increased from 49.2 to 84.3% by increasing the aqueous DEA concentration from 0.5 to 2 M. On molar basis, however, DEA displayed a greater CO₂ absorption compared with ammonia. The proposed reaction mechanisms between CO₂ and secondary amine suggest that the removal is due to the formation of carbamate in the liquid amine system. In aqueous media, there is a requirement of 2 mol-amine/mol-CO₂ to form stable carbamate or bicarbonate compounds for CO₂ absorption.

\[ \text{RR'NH} + \text{CO}_2 \leftrightarrow \text{RR'NH'COO}^-\text{(zwitterion)} \] (6)
\[ \text{RR'NH} + \text{COO}^- + \text{RR'NH} \leftrightarrow \text{RR'NCOO}^-\text{(carbamate)} \]
\[ + \text{RR'NH}^{2+} \] (7)

The overall reaction is:

\[ 2\text{RR'NH} + \text{CO}_2 \leftrightarrow \text{RR'NCOO}^- + \text{RR'NH}^{2+} \] (8)
\[ \text{RR'NCOO}^- + \text{H}_2\text{O} \leftrightarrow \text{RR'NH} + \text{HCO}_3^- \] (9)

The first reaction of DEA with CO₂ is to form zwitterion, followed by carbamate which probably offers greater CO₂ loading compared with ammonia.\(^{14}\) However, from the operational point of view, suitable blend of DEA and ammonia would be beneficial so as to overcome the problems related to corrosion and regeneration.

Effect of Gas Flow Rate. Figure 3 displays the effect of gas flow rate on CO₂ absorption at fixed liquid flow rate of 22 L/h. For all different concentrations of absorbents and acetic acid-
mixed absorbents studied, the removal of CO\textsubscript{2} was found to decrease with increasing gas flow rate from 40 to 80 mL/min. Absorption of CO\textsubscript{2} by 6 M NH\textsubscript{3} and 2 M DEA, both decreased from 97.3 to 91.2\% and 84.3 to 68.5\%, respectively. Results indicate that, at fixed liquid flow rate, low gas flow rate allows sufficient time for CO\textsubscript{2} to be in intimate contact with the liquid absorbents, which leads to a higher mass transfer coefficient and greater probability for CO\textsubscript{2} to be removed. Furthermore, decreasing the gas flow rate can quickly replenish CO\textsubscript{2} in the gas–liquid interface, which helps to maintain higher partial pressure of CO\textsubscript{2}.

Increasing the concentration of acetic acid from 1 to 15 wt \% in 6 M aqueous ammonia decreased the removal of CO\textsubscript{2}. At 40 mL/min gas flow rate, the CO\textsubscript{2} absorption was found to decrease from 97.3 (6 M NH\textsubscript{3}) to 84.4\% (1 wt \% acetic acid–6 M NH\textsubscript{3}), before it drops to 44.2\% (15 wt \% acetic acid–6 M NH\textsubscript{3}). It has been reported that the presence of carbonyl groups in solution could improve the solubility of CO\textsubscript{2}.\textsuperscript{10,11} Ahmadi\textsuperscript{11} reported a high CO\textsubscript{2} solubility of 0.123 mol CO\textsubscript{2}/mol carbonyl (94.6 g/L) in a concentrated acetic acid solution at 25 °C. In this work, however, lower CO\textsubscript{2} removal by acetic acid-mixed absorbents indicates that CO\textsubscript{2} solubility is less influenced by the carbonyl groups, but strongly dependent on the solution pH. It is commonly understood that CO\textsubscript{2} is a weak acid that favors to react with basic solutions. For aqueous ammonia, increasing the concentration from 1 to 6 M increases the solution pH from 10.9 to 11.8. Higher pH value that corresponds to a higher molarity was observed. Similarly, the solution pH rises from 9.3 to 10.9 for 0.5 to 2 M DEA solution. Clearly, the CO\textsubscript{2} removal was increased at higher concentration of these two absorbents. However, the solution pH decreased from 10.8 to 9.6 by adding different concentrations of acetic acid in 6 M NH\textsubscript{3}. Thus, the decrease in basicity of aqueous absorbent may result in a lower removal of CO\textsubscript{2}. The trend is also true for 1 wt \% acetic acid–6 M ammonia–2 M DEA absorbent blend. For this acetic acid-mixed absorbent, the removal of CO\textsubscript{2} lies between 2 M DEA and 6 M NH\textsubscript{3}, and is slightly greater than that of 1 wt \% acetic acid–6 M ammonia.

**Effect of Liquid Flow Rate.** Figure 4 shows the removal of CO\textsubscript{2} against different absorbent flow rate. In general, the increase in liquid flow rate has resulted in the increase of CO\textsubscript{2} absorption. A slight increase of CO\textsubscript{2} removal from 93.9 to 97.3\% was recorded for 6 M NH\textsubscript{3} at flow rates between 10 and 22 L/h. The trend is valid for all absorbents and mixed absorbents studied.

According to the two-film theory, the rise in liquid flow rate increases the resistance in liquid phase that provides appreciable liquid-side mass transfer coefficient.\textsuperscript{15} However, the interfacial area for contact between gas and liquid in packed column (random or structures) generally increases with the increase of liquid flow rate.\textsuperscript{8,15} Previous studies on CO\textsubscript{2} absorption in membrane contactor\textsuperscript{16} and rotating packed bed\textsuperscript{17} also revealed the same trend; decreasing liquid phase resistance with increasing liquid flow rate, thus increasing the probability for CO\textsubscript{2} to be captured in liquid absorbent.

From Figure 4, a higher uptake of CO\textsubscript{2} by absorbents at a lower gas flow rate (40 mL/min) is also in line with the fact that the resistance is dominant in liquid phase, and therefore the mass transfer in column is highly dependent on liquid flow rate.

It should be mentioned that the solubility of CO\textsubscript{2} in liquid phase for effective removal also depends on the nature of absorbents. Because the overall CO\textsubscript{2} removal performance that is important, a slightly lower amount of CO\textsubscript{2} absorbed by ammonia and DEA absorbent blend could be useful from the operational point of view.

**Figure 3.** Effect of gas flow rate on CO\textsubscript{2} absorption at fixed liquid flow rate of 22 L/h.

**Figure 4.** Effect of absorbent flow rate on CO\textsubscript{2} absorption at 40 mL/min (nonconnected symbols) and 80 mL/min (connected symbols).
Conclusion

Concentration of ammonia and DEA affects the CO2 removal; increasing the absorbents concentration increases the CO2 removal. On molar basis, DEA shows a greater CO2 absorption than ammonia. Acetic acid-mixed absorbents display a lower CO2 removal than the nonmixed ones. Decrease in solubility due to the decrease in solution pH has resulted in a lower CO2 absorption by acetic acid-mixed absorbents. Liquid flow rate offers only small influence on the absorption of CO2, while decreasing the gas flow rate increases the CO2 removal. On the operational point of view, blend of ammonia and DEA absorbent would be beneficial for CO2 removal from reforming gases as it could partly solve the problems associated with regeneration and corrosion.

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