Korean J. Chem. Eng., **25**(2), 279-284 (2008)

Characteristics of absorption and regeneration of carbon dioxide in aqueous 2-amino-2-methyl-1-propanol/ammonia solutions

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(*Received 27 April 2007 • accepted 23 July 2007*)

Abstract−In this study, the removal efficiency, absorption amount, and loading value of CO_2 into aqueous blended 2-amino-2-methyl-1-propanol (AMP)/ammonia (NH_3) solutions were measured by using the absorption and regeneration continual process. The effect of adding NH_3 to enhance absorption characteristics of AMP was investigated. The performance was evaluated under various operating conditions. As a result, the method of blending AMP and NH_3 was not adequate because of a problem with scale formation. Consequently, NH_3 of 1, 3, 5, and 7 wt% was added to 30 wt% AMP. Of these additions, 5 wt% NH_3 was the optimum concentration because the CO_2 removal efficiency and absorption amount were almost 100% and 2.17 kg CO_2/kg absorbent, respectively. Also, the scale problem was almost absent. As the regenerator temperature varied from 80-110 °C, the loading of rich amine was almost constant, but the loading of lean amine was decreased as the regenerator temperature increased. Thus, the optimum regenerator temperature was 110 °C in this experiment.

Key words: Carbon Dioxide, 2-Amino-2-methyl-1-propanol, Ammonia, Absorption, Regeneration

INTRODUCTION

The large increase in greenhouse gases due to the development of technology and the spread of industrialization has greatly contributed to global warming, which accounts for a considerable part of global environmental destruction [1]. In particular, CO_2 is the largest component of greenhouse gases. The importance of carbon dioxide sequestration is gradually being addressed all over the world.

Several technologies are being used to separate CO_2 from the flue gas of conventional fossil fuel-fired power plants. Some representative technologies are chemical absorption, physical absorption, cryogenic methods, and membrane separation [2]. Chemical absorption is generally recognized as the most effective technology at present [3]. Industrially important chemical absorbents are monoethanolamine (MEA), diethanolamine (DEA), and AMP. The sterically hindered amines, such as AMP, are a different class of chemical absorbents and have been used as commercially useful CO_2 absorbent because of their advantages in absorption capacity, degradation resistance, and regeneration energy [4,5]. NH_3 seems to be an alternative solvent for removing CO_2 from flue gas. Although NH_3 solvent has scale formation problems, it has both a high absorption capacity and absorption rate, no absorbent degradation problem, and a low corrosion problem [6-8].

Recently, the use of blends of alkanolamines, a solution of two or more amines in varying concentration, has been shown to produce absorbents with excellent absorption characteristics as well as reductions in energy requirements. A number of research studies related to the absorption of CO_2 into aqueous AMP solutions have been reported in the literature [9-17].

Unlike previous studies of CO_2 solubilities and the kinetics of aqueous amine solutions, this study investigated the CO_2 removal efficiency and the absorption amount and loading value of CO_2 into aqueous blended AMP/NH_3 solutions using the absorption and regeneration continual process. The added effect of NH_3 to enhance absorption characteristics of AMP was studied. The performance was evaluated under several operating conditions.

THEORY

In aqueous solutions of primary (MEA) and secondary (DEA) alkanolamines the following reactions with CO_2 occur [18].

$$CO_2+2RR'NH \rightleftarrows RR'NCOO^- + RR'NH_2^+ \tag{1}$$

Where R is alkyl and R′ is H for primary amines and alkyl for secondary amines.

The zwitterion mechanism originally proposed by Caplow [19] and reintroduced by Danckwerts [18] is generally accepted as the reaction mechanism for Eq. (1).

$$CO_2+RR'NH \rightleftarrows RR'NH^+COO^- \tag{2}$$

If the carbamate is unstable, as in the case of a hindered amine carbamate, it undergoes a carbamate reversion reaction as follows [4]:

$$RR'NCOO^- + H_2O \rightleftarrows RR'NH + HCO_3^- \tag{3}$$

Eq. (3) means that for the hindered amines one mole of CO_2 is absorbed per mole of amine. However, a certain amount of carbamate hydrolysis occurs with all amines so that even with MEA and DEA the CO_2 loading may exceed 0.5, particularly at high pressures.

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Another alternative mechanism for the bicarbonate formation was proposed by Chakraborty et al. [20].

$$RR'NH+CO_2+H_2O \rightleftarrows RR'NH_2^++HCO_3^- \qquad (4)$$

The chemical reactions between CO_2 and NH_3 can be expressed by the following reaction [7,21]:

$$2NH_3(l)+CO_2(g)+H_2O(l) \rightleftarrows (NH_4)_2CO_3(s) \qquad (5)$$

$$NH_3(l)+CO_2(g)+H_2O(l) \rightleftarrows NH_4HCO_3(s) \qquad (6)$$

The wet method of ammonia scrubbing into flue gas to capture CO_2 produces ammonium carbonate ($(NH_4)_2CO_3$) and ammonium bicarbonate (NH_4HCO_3) [6,8].

EXPERIMENTAL

1. Apparatus

A schematic diagram of the experimental system for studying CO_2 absorption and regeneration is shown in Fig. 1. The experimental apparatus consisted of a gas injector, absorber, regenerator, and gas analyzer. The absorber and regenerator, which were made of 316 stainless steel with an internal diameter of 50.8 mm, have a height of 900 mm and 800 mm, respectively. Packing material (1/4 inch Raschig rings) was placed inside to enhance the reaction of liquid and gas. The temperature of the absorber and regenerator was measured by a K-type thermocouple with an accuracy of ±0.1 K. Compressed air was sent to the filter to remove particulates and then dehumidified by passing it through a silica gel air dryer. The clean air served as diluting gas and it was mixed with pure CO_2 gas. The flow rates of the gases were controlled by mass flow controllers (5850E, Brooks Instruments, USA). The CO_2 gas analyzer, a ZRF model (Fuji Electric, JPN, 0-20 vol%), was used to measure CO_2 outlet gas concentrations in the absorber. The condenser was connected to the top of the regenerator to prevent loss of absorbent.

2. Procedure

Analytical grade AMP and NH_3 solution with purity of 99% and 28% were supplied by Acros Organics (USA) and Junsei Chemical (JPN), respectively. Aqueous solutions were prepared with distilled water. The CO_2 gas was a commercial grade with a purity of 99.9%. The absorber and regenerator were heated to the desired temperature, and then an absorbent of 250 mL was injected into a storage tank. A pump (AX1-12-PEC-Z, Cheonsei Co. Ltd., KOR) was used to circulate the absorbent which reacted with the CO_2 gas. The outlet CO_2 concentration from the absorber was continually measured by a ZRF model CO_2 gas analyzer. The experimental conditions were as follows: an absorber temperature of 40 °C, regenerator temperature of 80-110 °C, a gas flow rate of 7.5 L/min, a CO_2 inlet concentration of 12 vol%, and a liquid circulation rate of 110 mL/min. The experimental data were taken at steady state.

Rich amine and lean amine were extracted from the absorber and regenerator, respectively, to determine the characteristics of CO_2 absorption and regeneration, and then they were analyzed by titrimetric method. First, 100 mL of distilled water was injected into a 250 mL beaker. The beaker was stirred with magnetic stirrer. The pH of the distilled water was raised to 11.4-11.6 by carefully adding a 0.5 N-NaOH solution. Either a rich or lean amine solution was

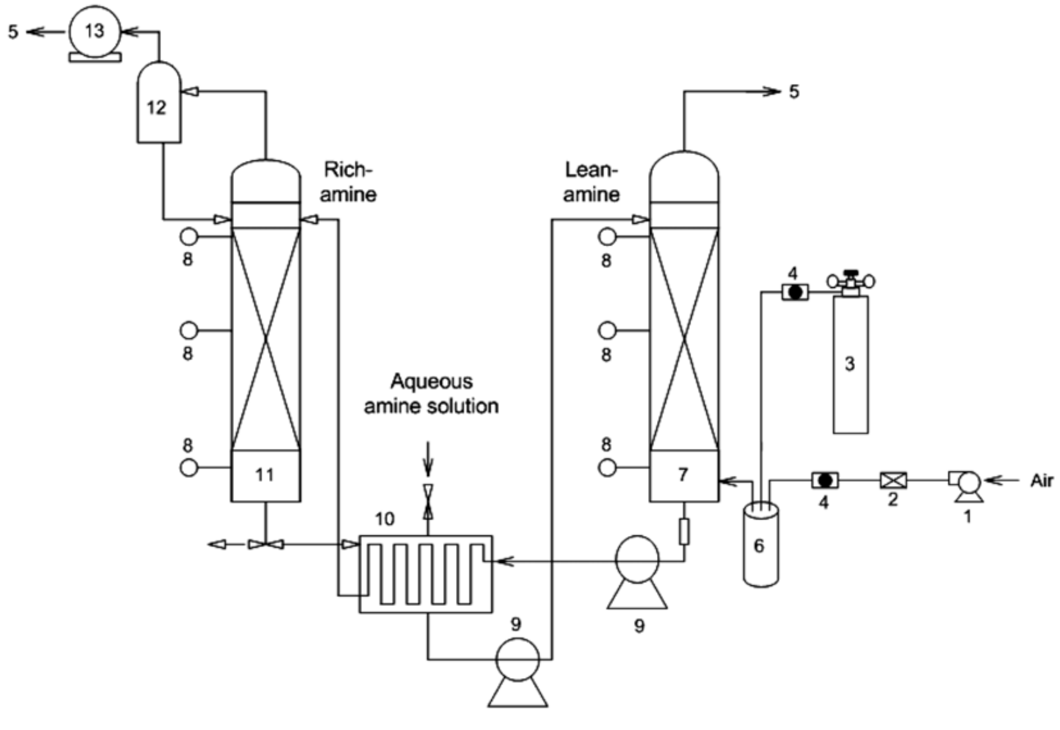

Fig. 1. Schematic of experimental apparatus.

1. Air compressor
2. Filter
3. CO_2 cylinder
4. Mass flow controller
5. CO_2 analyzer
6. Mixing chamber
7. Absorber
8. Thermocouple
9. Liquid pump
10. Heat exchanger and storage tank
11. Regenerator
12. Condenser
13. Gas meter

added to the beaker by a 10 mL pipette for the rich amine solution or a 25 mL pipette for the lean. And then 0.5 N-NaOH was added to the amine solution by the titrimetric method until its pH reached 11.5.

RESULTS AND DISCUSSION

1. Effect of AMP/NH_3 Blends

The CO_2 outlet concentrations were investigated by using the absorption and regeneration continual process for blended AMP/NH_3 absorbents. The conditions of the experiment consisted of the regenerator temperatures of 80-110 °C and a gas flow rate of 7.5 L/min.

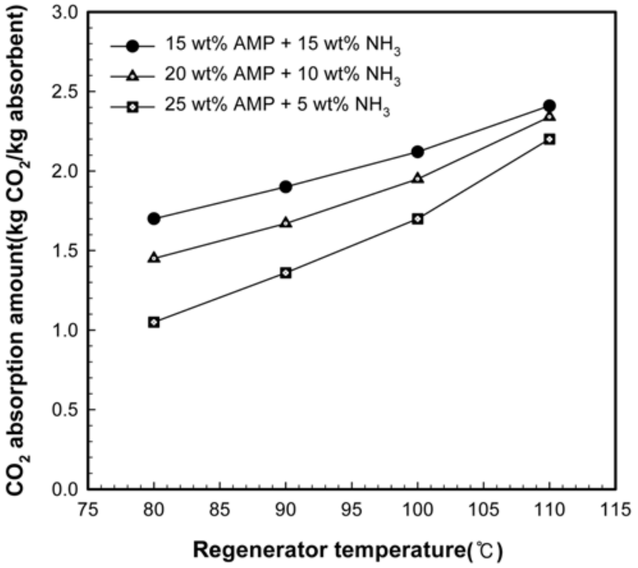

Fig. 2. Effect of CO_2 absorption amount as a function of regenerator temperatures in blended absorbents (wt% AMP/wt% NH_3).

Fig. 2 shows the effect of the mixture ratio and regenerator temperatures on the CO_2 absorption amount in the blended absorbents (wt% AMP/wt% NH_3). At each regenerator temperature, the amount of CO_2 absorption with AMP/NH_3 ratio (25/5, 20/10, and 15/15) was 1.05-2.20, 1.45-2.34, 1.70-2.41 kg CO_2/kg absorbent. As the concentration of NH_3 increased, the absorption amount increased.

This trend could be caused by the higher CO_2 absorption rate of NH_3 than that of AMP. Also, reactivity and CO_2 absorption capacity improved based on reaction (2) and additional reaction (5), (6). As the regenerator temperature varies so does the CO_2 absorption amount because the removal efficiency of AMP is greatly dependent on regenerator temperature.

As can be seen from Fig. 3, although CO_2 absorption amount (kg CO_2/kg absorbent) increased as the mixing ratio of NH_3 increased, CO_2 removal efficiency decreased faster by time. This result is due to the increase of ammonium carbamate and ammonium bicarbonate. The generation of these products is demonstrated by the reaction of CO_2 and NH_3 in the existing studies [6,8]. Therefore, this method of blending AMP and NH_3 used in this experiment seems inadequate, but the gradual addition of NH_3 can be expected to be a better method.

2. Effect of the Additive Ratio of NH_3 to AMP

To determine the effect of concentrating NH_3 by 1, 3, 5, 7 wt%, the absorption and regeneration continual process was studied blending NH_3 with 30 wt% AMP. The experimental conditions were as follows: absorber temperature of 40 °C, regenerator temperature of 110 °C, and gas flow rate of 7.5 L/min.

As seen from Fig. 4, the CO_2 outlet concentration with NH_3 concentrations in 30 wt% AMP is presented by time. The initial CO_2 removal efficiency increased by the addition of NH_3. With an increase of 2 wt% NH_3, the time which CO_2 concentration maintained 0% was increased approximately 5 minutes.

Fig. 5 shows the CO_2 absorption amount (kg CO_2/kg absorbent) by the additive ratio of NH_3 to 30 wt% AMP. These experimental

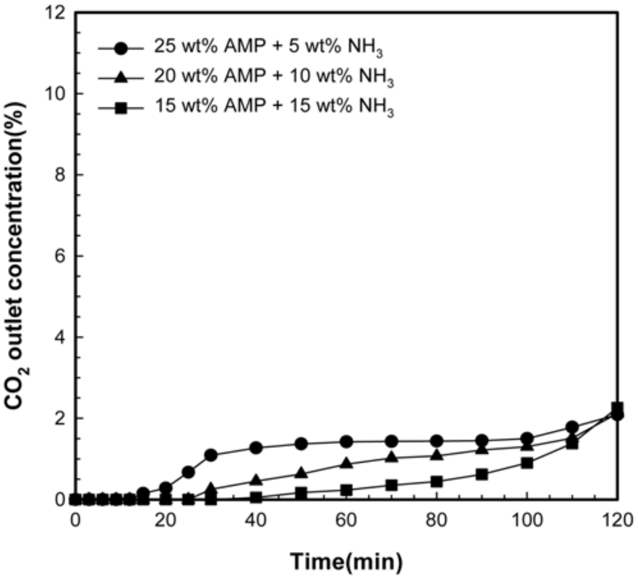

Fig. 3. Effect of operating time on CO_2 removal efficiencies of blended absorbents (wt% AMP/wt% NH_3).

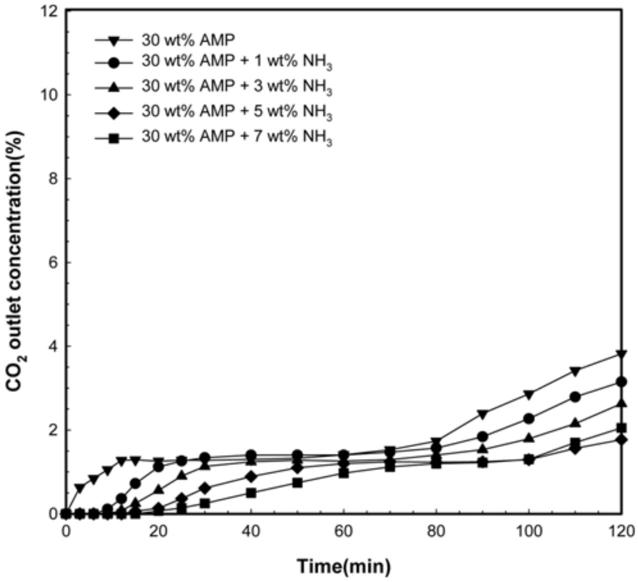

Fig. 4. Effect of operating time on CO_2 removal efficiencies of NH_3 additives in 30 wt% AMP.

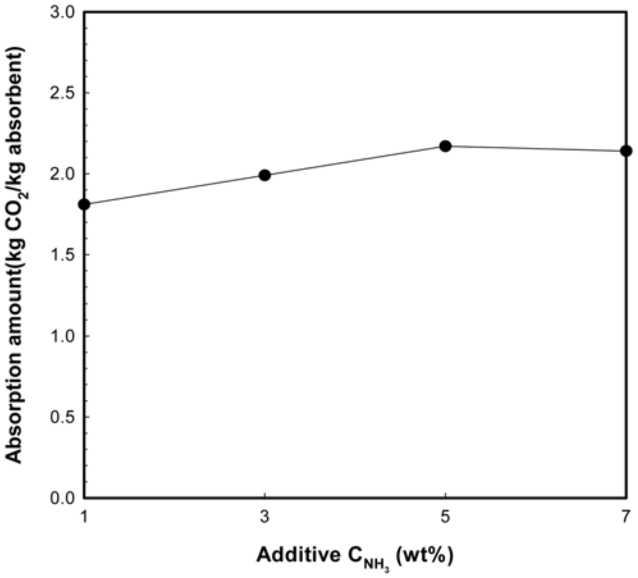

Fig. 5. Effect of CO_2 absorption amounts as a function of NH_3 additive concentrations in 30 wt% AMP.

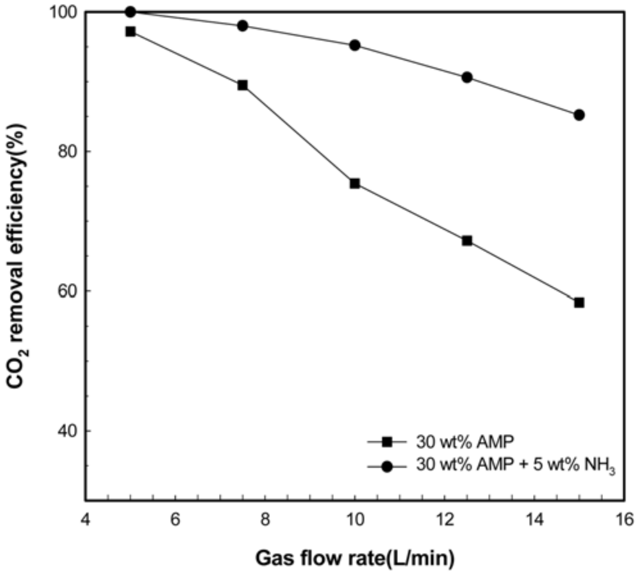

Fig. 7. Effect of gas flow rate on CO_2 removal efficiencies of 30 wt% AMP and 30 wt% AMP+5 wt% NH_3.

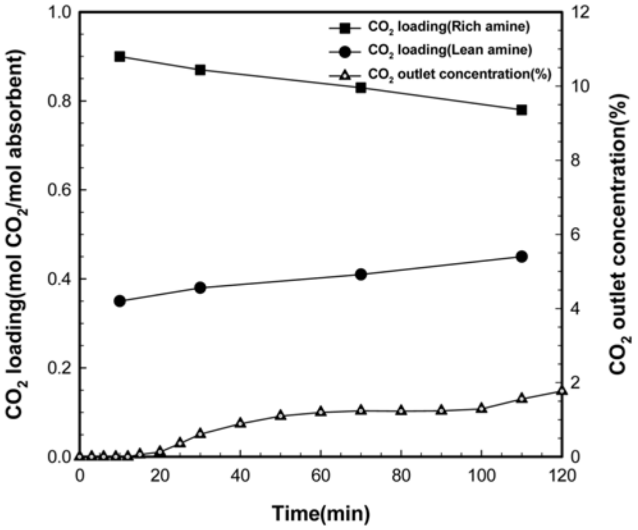

Fig. 6. Effect of operating time on CO_2 loading and CO_2 removal efficiencies of 30 wt% AMP+5 wt% NH_3.

results were calculated by using the data of the breakthrough curves shown in Fig. 4. As can be seen, the CO_2 absorption amount by additive ratio of NH_3 was 1.81, 1.99, 2.17, and 2.14 kg CO_2/kg absorbent. This result was caused by the improved CO_2 reactivity and CO_2 absorption capacity. The reasons for this improvement are explained in paragraph 1.

However, the amount of CO_2 absorption when 5 wt% NH_3 was added was higher than when 7 wt% was added. The reason for this result is the 7 wt% NH_3 caused the efficiency of removing CO_2 to decrease faster than 5 wt% did due to the scale formation problem. At 100 minutes, the removal efficiency of 7 wt% was lower than that of 5 wt%; consequently, it is reasonable to conclude that 7 wt% is inadequate in a continual process. Therefore, 30 wt% AMP+5 wt% NH_3 is the best concentration because CO_2 absorption capacity is improved and scale formation is almost absent.

Fig. 6 shows the changes of CO_2 outlet concentrations and CO_2 loading values by aqueous 30 wt% AMP+5 wt% NH_3 solution as a function of operating time. The experimental conditions were as follows: the absorbent concentration was 30 wt% AMP+5 wt% NH_3, the absorber temperature was 40 °C, the regenerator temperature was 110 °C, and the gas flow rate was 7.5 L/min. The CO_2 loading values were calculated after they were extracted and analyzed after 10, 30, 70, and 110 minutes of operation. CO_2 outlet concentration increased with operating time. The CO_2 loading values of rich amine were analyzed by operating time decreased 0.90, 0.87, 0.83, 0.78 mol CO_2/mol absorbent, because the capacity to absorb CO_2 decreased over time. However, the CO_2 loading values of lean amine increased 0.35, 0.38, 0.41, 0.45 mol CO_2/mol absorbent, which could be due to the CO_2 regeneration efficiency decreasing, so that the CO_2 loading in the regenerator increased.

3. Effect of Gas Flow Rate

CO_2 efficiency was tested with gas flow rates of 5-15 L/min. As can be seen from Fig. 7, as gas flow rate increased, the efficiency of CO_2 removal went from 97.2% to 58.4% with an aqueous solution of 30 wt% AMP and 100% to 85.2% with the 30 wt% AMP+ 5 wt% NH_3 solution. The difference of efficiency was from 2.8 to 26.8% in two absorbents. This result was caused by addition of the higher reaction rate of NH_3.

Efficiency decreased as the liquid-gas ratio decreased because a large amount of gas was inserted within a limited time frame. As flow rate of the mixed gas increased, the amount of CO_2 also increased. Therefore, by reaching relatively high CO_2 loading ratio, reaction and absorption capacity decreased.

When 5 wt% NH_3 was added to 30 wt% AMP, CO_2 removal efficiencies were 100% and 99% when gas flow rates were 5 and 7.5 L/min, respectively. The two conditions are highly efficient. Therefore, a gas flow rate of 7.5 L/min was determined, after the effects of corrosiveness were taken into consideration.

4. Characteristics of Absorption and Regeneration by NH_3

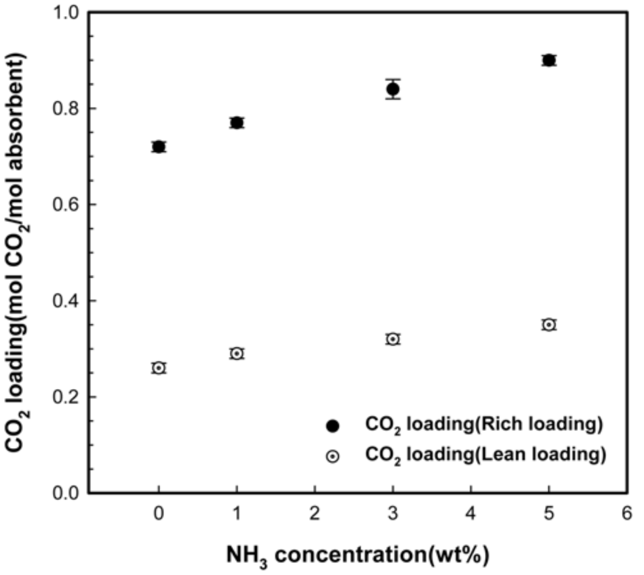

Fig. 8. Effect of CO_2 loading values of lean- and rich-amine as a function of NH_3 additives into 30 wt% AMP.

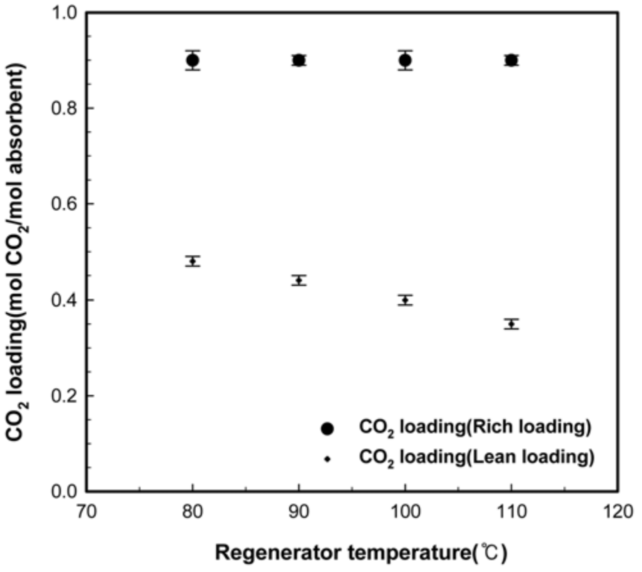

Fig. 9. Effect of CO_2 loading values of lean- and rich-amine as a function of regenerator temperature of 30 wt% AMP+5 wt% NH_3.

Concentration

This experiment was conducted to determine the characteristics of CO_2 absorption and regeneration when 1, 3, and 5 wt% NH_3 was added to 30 wt% AMP by analyzing rich and lean amine from the absorber and regenerator.

Fig. 8 shows CO_2 loading by the amount of NH_3 added to 30 wt% AMP. As can be seen, CO_2 loading increased as the amount of NH_3 in both rich and lean amine increased. CO_2 loading was 0.72, 0.77, 0.84, and 0.90 mol CO_2/mol absorbent for 0, 1, 3, and 5 wt% NH_3 was added to 30 wt% AMP, respectively, and for lean amine, it was 0.26, 0.29, 0.32, 0.35 mol CO_2/mol absorbent, respectively. As can be seen, CO_2 loading increased as the amount of NH_3 in both rich and lean amine increased. These results need to be compared with commercially useful amine, MEA. In case of MEA, rich loading is 0.4 mol CO_2/mol absorbent and lean loading is 0.15 mol CO_2/mol absorbent [8]. Therefore, CO_2 loading of blended AMP/NH_3 absorbents is better than that of MEA.

This increase could have been caused by the addition of NH_3 as mentioned in paragraph 1. Consequently, absorbents increase their CO_2 capacities in the rich amine. As this rich amine entered the regenerator in the absorption and regeneration continual process, lean amine increased. The changes to the values of rich and lean amine caused by the increased concentration of NH_3 have clarified the characteristics of absorption and regeneration.

5. Characteristics of Absorption and Regeneration by Regenerator Temperature

According to previous research, CO_2 removal efficiency by the AMP is when using AMP is highest at the regenerator temperature is 110 °C [22]. The best regenerator temperature for NH_3 is about 80 °C [8]. Hence, the regenerator temperatures used in this experiment to determine the characteristics of absorption and regeneration were 80-110 °C. The concentration of absorbent was 30 wt% AMP+5 wt% NH_3.

Fig. 9 shows the effect of CO_2 loading in the absorber and regenerator. For rich amine, CO_2 loading remained almost constant of 0.90 mol CO_2/mol absorbent in spite of the regenerator temperature of 80, 90, 100, 110 °C. For lean amine, it decreased 0.48, 0.44, 0.40, and 0.35 mol CO_2/mol absorbent for each respective temperature.

As discussed in paragraph 1 and demonstrated in the existing study [22], regeneration efficiency of AMP differs from regenerator temperature. Lean amine loading decreased because the amount of CO_2, which was discharged from the regenerator, increased as the efficiency of regeneration increased. Rich amine loading was almost constant, which was due to the constant absorber temperature.

The analysis of the rich and lean amine in this experiment revealed the amount of CO_2 loading in the absorber and regenerator, respectively, which clarified the characteristics of absorption/regeneration based on the effect of regenerator temperature.

CONCLUSIONS

This experiment was designed to determine the effects of blending AMP with an increasing amount of NH_3. CO_2 absorption amount increased as the mixing ratio of NH_3 increased. However, it is inadequate in CO_2 regeneration because of the scale formation problem. Consequently, the amount of NH_3 added to 30 wt% AMP was 1, 3, 5, and 7 wt%. When 5 wt% NH_3 was used, the amount of CO_2 absorption (kg CO_2/kg absorbent) was the highest and the scale formation problem was almost absent. Hence, 30 wt% AMP+5 wt% NH_3 was the best concentration. The CO_2 loading of rich and lean amine was analyzed by using 1, 3, and 5 wt% of NH_3 by regenerator temperature. As the additive concentration of NH_3 increased, both rich and lean loading increased, respectively. As regenerator temperatures increased, rich loading was almost constant, but lean loading decreased. The characteristics of absorption/regeneration reaction were clarified by analyzing CO_2 rich and lean loading numerical values. Therefore, the optimum experimental conditions when NH_3 is added to AMP could be presented. It is expected to improve the efficiency of the process due to the improvement of the capacity of absorbent. Also, the results of this experiment could be useful for simultaneously removing and recovering CO_2.

ACKNOWLEDGMENTS

This research was supported by a grant (2006-C-CD11-P-03-3-010-2007) from Energy Technology R&D of Korea Energy Management Corporation and the Brain Korea 21 Project in 2007.

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