Influence of operating temperature on CO_2-NH_3 reaction in an aqueous solution

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Abstract–Although aqueous ammonia solution has been focused on the removal of CO_2 from flue gas, there have been very few reports regarding the underlying analysis of the reaction between CO_2 and NH_3. In this work, we explored the reaction of CO_2-NH_3-H_2O system at various operating temperatures: 40 °C, 20 °C, and 5 °C. The CO_2 removal efficiency and the loss of ammonia were influenced by the operating temperatures. Also, infrared spectroscopy measurement was used in order to understand the formation mechanism of ion species in absorbent, such as NH_2COO^-, HCO_3^-, CO_3^{2-}, and NH_4^+, during CO_2, NH_3, and H_2O reaction. The reactions of CO_2-NH_3-H_2O system at 20 °C and 40 °C have similar reaction routes. However, a different reaction route was observed at 5 °C compared to the other operating temperatures, showing the solid products of ammonium bicarbonates, relatively. The CO_2 removal efficiency and the formation of carbamate and bicarbonate were strongly influenced by the operating temperatures. In particular, the analysis of the formation carbamate and bicarbonate by infrared spectroscopy measurement provides useful information on the reaction mechanism of CO_2 in an aqueous ammonia solution.

Key words: Ammonia Solution, CO_2 Capture, Operating Temperature, Ammonia Loss, FT-IR

INTRODUCTION

Carbon dioxide capture technology has received particular attention for the prevention of global warming and worldwide climate change [1-7]. Of the absorbents for CO_2 capture, an aqueous ammonia solution makes it highly attractive as an affordable substitute for amine solutions in chemical absorption processes, due to its low cost, high capacity for CO_2 per unit of solution, small regeneration energy, and no degradation of absorbents during absorption/regeneration [8,9]. Recently, aqueous ammonia solution has been performed as absorbent for CO_2 capture on pilot scale [10,11]. However, the aqueous ammonia process has major obstacles, such as the loss of ammonia due to its high vapor pressure, resulting in a reduction of CO_2 absorption and the formation of salts such as ammonium carbamate (NH_2COONH_4) or ammonium bicarbonate (NH_4HCO_3) by the reaction between CO_2 and NH_3 in vapor phase, which can block the gas pathway in the CO_2 capture process [12].

To date, the CO_2 capture process using aqueous ammonia has been generally performed by two different processes, which are Alstom and Power Span in terms of the operating temperature [10,11]. Most of the CO_2 capture process was performed at ambient temperature (20-40 °C) to remove the CO_2 from flue gas and is mainly being developed by Power Span [11]. More recently, Alstom has developed the chilled ammonia process, where the CO_2 capture process is operated at low temperature (~10 °C), in order to reduce the energy requirements and costs [10]. This process showed high removal efficiency of CO_2 over 90% at a cost which is estimated to be far less than for other carbon capture technologies. The absorp-

tion reaction between CO_2 and NH_3 at low temperature can prevent the ammonia release due to its vaporizing nature. In particular, the formation reaction of ammonium bicarbonate at low temperature can mainly occur, related to the CO_2 working capacity and regeneration energy [9]. Despite many efforts for CO_2 capture using aqueous ammonia, there have been very few reports regarding a scientific understanding of the processes on aqueous ammonia as a CO_2 absorbent, such as the reaction between CO_2 and NH_3 in the presence of water. Unfortunately, most works have been concentrated on the chemical reaction of CO_2 and NH_3 reaction at ambient operating temperature (20-40 °C) and not low temperature (<10 °C) [1]. In this regard, the influence of temperature on the CO_2 and NH_3 reaction should be studied in terms of CO_2 working capacity, regeneration energy, absorbent loss, precipitate formation, and reaction kinetics.

In this work, we performed the CO_2 capture process in an aqueous ammonia solution as an absorbent with bubble blowing apparatus in order to investigate the influence of the operating temperature on the reaction between the CO_2 and NH_3. In particular, three operating temperatures (5, 20, and 40 °C) were selected in order to compare two different processes, which are Alstom and Power Span, in terms of the removal efficiency of CO_2, the loss of absorbent, and the intermolecular interactions between the CO_2 and NH_3. The studies on the reaction between the CO_2 and NH_3 in terms of the operating temperature could provide academic information and optimized conditions for CO_2 removal efficiency and product content.

EXPERIMENTAL SECTION

1. Chemicals

Ammonia solution was obtained from Junsei (28 wt%), which was diluted with the deionized water. Ammonium carbonate, am-
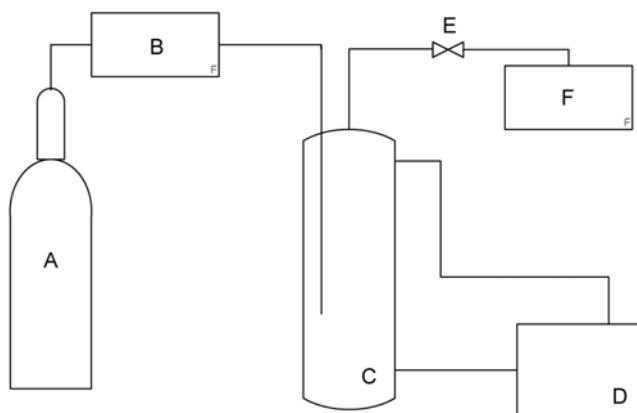
Fig. 1. Schematic diagram of reactor system for CO₂ scrubbing.
A. CO₂ cylinder   E. Sampling port
B. Mass flow controller   F. FT-IR
C. CO₂ scrubber
D. Constant temperature water circulator

monium carbamate, and ammonium bicarbonate were supplied by Sigma-Aldrich.

2. Removal Efficiency of CO₂

A schematic diagram of the experimental system for investigating the reaction between the CO_2 and an ammonia solution is presented in Fig. 1. The CO₂ scrubber was a glass bottle with a 45 mm inner diameter containing 200 mL of 10 wt% ammonia solution. The temperature of the solution was kept within ±1 °C from the setpoint during experiments by circulating water through a water jacket around the reactor. The feed gas served as the mixed gas of 15 vol% CO_2 and 85 vol% N_2. The flow rate of feed gases was controlled by mass flow controllers (MFC, MKS 2259C) at a rate of 1 L/min. The inlet and outlet CO₂ gas concentrations after the removal of the entrapped ammonia and precipitates by sulfuric acid and ice traps were measured by a CO₂ analyzer. Considering that the known optimum concentration of an ammonia aqueous solution for CO₂ absorption is 10 wt%, the concentration of ammonia was fixed with 10 wt% in order to investigate the influence of the operating temperature on the removal of the CO₂ in the aqueous ammonia absorbent. The operating temperatures were 5, 20, and 40 °C maintained by circulating water.

3. Loss of Absorbent

The loss of absorbent was measured by two methods under controlled conditions: 313 K, 1 atm, and 60% relative humidity. First, the changes in the weights of the absorbents by vaporization were measured as a function of time. The weight loss % of absorbent was then calculated by Eq. (1). Weight of absorbent at the initial and measured time was obtained by subtracting the weight of water from that of the aqueous absorbent solution. We assumed that the content of vaporized water (0.073 atm at 313 K) was negligible due to the considerably lower vapor pressure compared to that of ammonia (15.337 atm at 313 K).

Weight Loss %

$$= \frac{\substack{\text{weight of absorbent at the initial time} \\ - \text{weight of absorbent at the measured time}}}{\text{weight of absorbent at the initial time}} \times 100 \quad (1)$$

Second, the gas stream after CO₂ absorption was analyzed as a function of reaction time by gas chromatography (GC), which was performed using an HP 5890 with porapak N (50/80 mesh) as a packed column and a thermal conductivity detector (TCD). The vapor of the sample was collected into a tedlar bag. All samples with a constant volume of 100 μL were injected into the GC port. The loss of ammonia from the absorbent was obtained from Eq. (2).

Normalized Area

$$= \frac{\substack{\text{Peak area of 10 wt\% ammonia} \\ \text{at the measured reaction time}}}{\text{Peak area of 10 wt\% ammonia at initial time of 10 min}} \quad (2)$$

4. FT-IR Spectra

A spectroscopic instrument was used to analyze the reaction as follows. FT-IR spectra were collected on a JASCO FT-IR 4100. The pressure was set as equal for all samples to avoid differences caused by the pressure and penetrating depth. Each spectrum, which was recorded as the average of 13 scans with a resolution of 4 cm⁻¹,
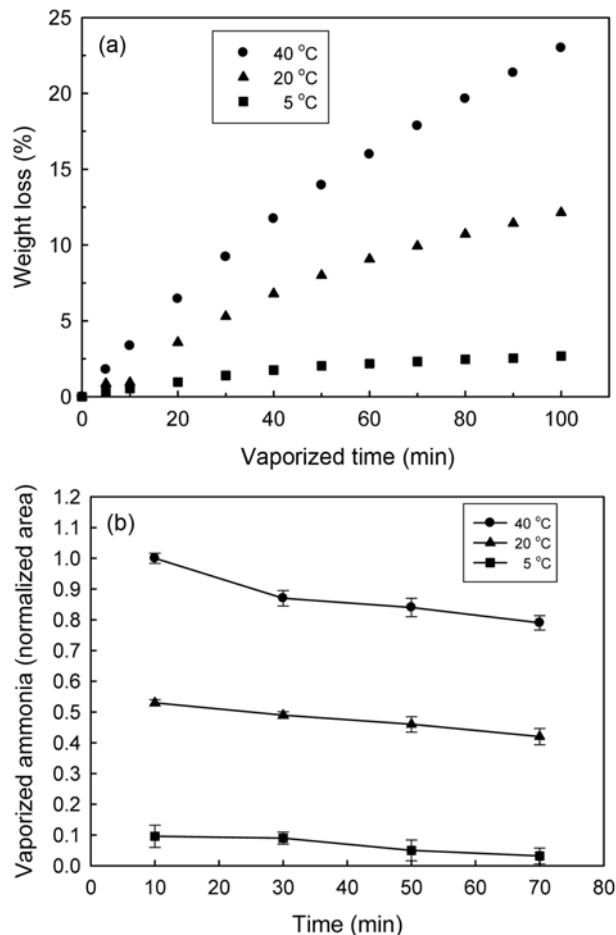

Fig. 2. (a) Weight loss of aqueous ammonia solution by evaporation (operating temperature 5, 20, and 40 °C, 10 wt% aqueous ammonia solution, 1 atm). (b) Weight loss of aqueous ammonia solution during CO₂ absorption reaction by evaporation (operating temperature 5, 20, and 40 °C, 10 wt% aqueous ammonia solution, 1 atm, Normalized area=Measured peak area/peak area of 10 wt% aqueous ammonia solution at 10, 30, 50, and 70 min).

was collected from 4,000 cm^{-1} to 650 cm^{-1}. Then, the spectrum data in the region other than 1,900-900 cm^{-1} were omitted due to the independence of peak from reaction. We collected samples of 2 mL at specific conditions through a sampling port and then directly measured to block further reaction of CO_2 and NH_3.

RESULTS AND DISCUSSION

The ammonia loss by evaporation was considerable problem in the operation of the CO_2 capture process [13]. To investigate the loss of ammonia by evaporation on different operating temperatures, the changes of the absorbent were measured with and without CO_2, as shown in Fig. 2. Considering that the vapor pressures of ammonia at 5 °C, 20 °C, and 40 °C were greatly higher than those of the vapor pressures of water at same conditions, the loss of absorbent was predominantly attributed to the evaporation of ammonia. The contents of the ammonia loss without the CO_2 absorption reaction dramatically decreased as a function of vaporized time at different operating temperature (5, 20, and 40 °C) as shown in Fig. 2(a). When the temperature of the reactor increased, a fast loss rate of the ammonia at initial step and large amount of loss contents were observed due to the nature of the low vapor pressure of the ammonia solution. The difference of the ammonia loss with three operating temperatures also appeared at the vapor phase during the CO_2 absorption reaction as shown in Fig. 2(b). The low vapor pressure of the operating temperature 40 °C greatly decreased the ammonia loss. These findings indicate that the loss of ammonia on the different operating temperatures increased in the following order: 5 °C<20 °C <40 °C.

Fig. 3 displays the CO_2 removal efficiency of aqueous ammonia absorbent at various operating temperature (5, 20, and 40 °C) as a function of the reaction time. The temperature of the inlet CO_2 gas was kept at the operating temperature by circulating water. The CO_2 removal efficiency was sharply increased and then slightly decreased during CO_2 capture reaction in an aqueous ammonia solution for operating temperatures of 5-40 °C. The operating temperatures affected CO_2 capture with using aqueous ammonia solution in this experimental condition. The CO_2 removal efficiency at low operat-
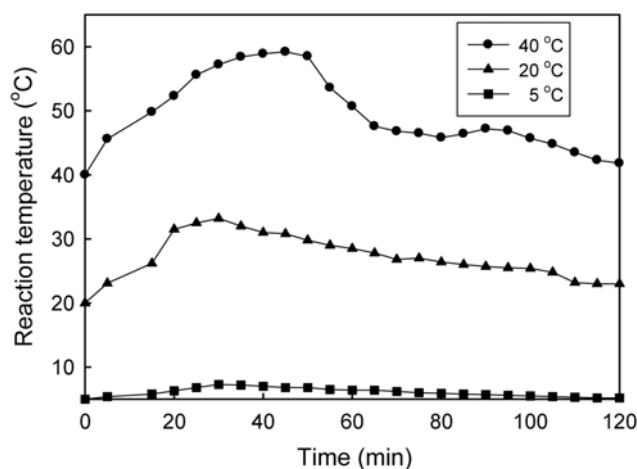
Fig. 4. Temperature variations of 10 wt% aqueous ammonia solution (1 atm) under different operating temperature 5, 20, and 40 °C.

ing temperature of 5 °C was slightly enhanced, compared to the high operating temperatures of 20 °C and 40 °C. Although the CO_2 absorption capacity depended on various factors such as the concentration of the ammonia solution, the flow rate of feed gas, and so on [14], the total CO_2 removal capacities of aqueous ammonia absorbent in this experimental condition in order to investigate the effect of the operating temperature were calculated from respective areas of curves. The comparative results of the influence of operating temperature on the CO_2 absorption capacities are the following: 40 °C<20 °C <5 °C. These results on different operating temperatures were attributed to the influence of the temperature on the loss of absorbent and the chemical reaction between the CO_2 and NH_3. In addition, Fig. 4 shows the plots of temperature variations in the absorber with respect to operating time under different operating temperatures. The exothermal reaction occurred predominantly at the CO_2 and NH_3 reaction. The maximum temperature increased with increase of operating temperature.

The absorption of CO_2 in an aqueous ammonia solution involves various chemical reactions between the CO_2, NH_3, and H_2O [15-17]. The fundamental understanding of the mechanism for the formation of crystals such as ammonium bicarbonate, ammonium carbamate, and ammonium carbonate, is of prime importance due to the relations of the CO_2 working capacity, regeneration energy, and blocking the gas pathway, which is the critical problem [12]. The possible reactions for the formation of ammonium bicarbonate between CO_2 and NH_3 in aqueous media are derived from the two alternative mechanisms [15]. The first mechanism is the conversion reaction of the ammonium carbonate into ammonium bicarbonate by the reaction with CO_2 and H_2O. The reactions are as follows:

$$NH_3(g)+H_2O(l) \leftrightarrow NH_4OH(l) \tag{3}$$

$$2NH_4OH(l)+CO_2(g) \leftrightarrow (NH_4)_2CO_3(s)+H_2O(l) \tag{4}$$

$$(NH_4)_2CO_3(s)+CO_2(g)+H_2O \leftrightarrow 2NH_4HCO_3(s) \tag{5}$$

In the second mechanism, ammonium carbamates can be converted into ammonium bicarbonates by the reaction of NH_3 with CO_2 in the gas phase. The reactions are as follows:
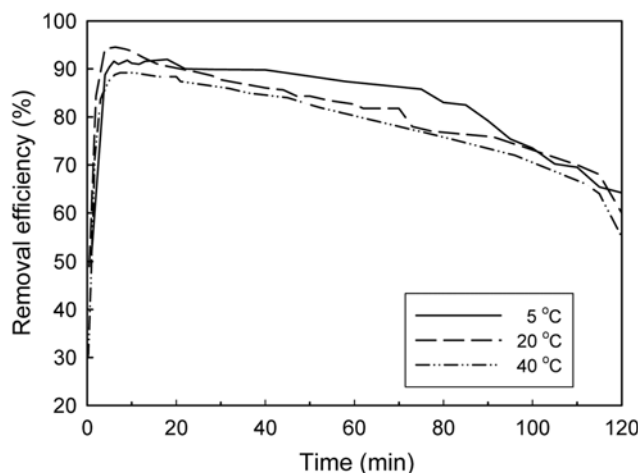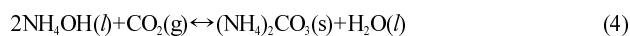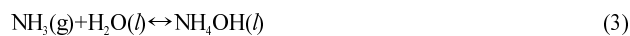

Fig. 3. Removal efficiency of 10 wt% aqueous ammonia solution (1 atm) at different operating temperature 5, 20, and 40 °C.
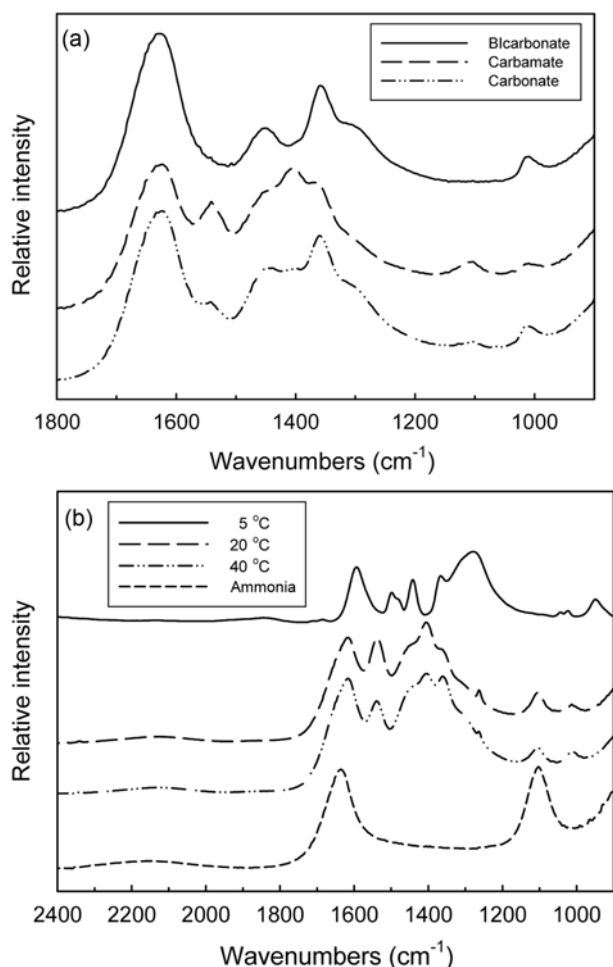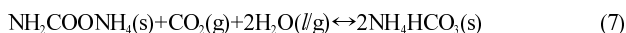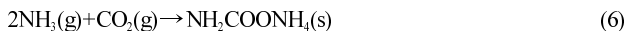
Fig. 5. (a) IR spectra of standard ammonium bicarbonate, ammonium carbamate, and ammonium carbonate solid. (b) IR spectra of the standard ammonia solution and ammonia absorbents after the CO$_2$ and NH$_3$ reaction in 10 wt% aqueous solution at different operating temperature 5, 25, and 40 °C.

$$2NH_3(g)+CO_2(g) \rightarrow NH_2COONH_4(s) \qquad (6)$$

$$NH_2COONH_4(s)+CO_2(g)+2H_2O(l/g) \leftrightarrow 2NH_4HCO_3(s) \qquad (7)$$

To investigate the formation of the byproducts at the different operating temperatures, the FT-IR results are discussed in this work (10 wt% ammonia solution and 1 atm). Fig. 5(a) shows the representative bands of standard ammonium bicarbonate, ammonium carbamate, ammonium carbonate, and 10 wt% of ammonia solution. According to the previous work, ammonium bicarbonate displayed two prominent infrared absorption bands at around 1,450 and 1,350 cm^{-1} assigned to the COO$^-$ asymmetric and symmetric bands of bicarbonate [18,19]. Three distinct bands of carbamate appeared at around 1,550, 1,400, and 1,100 cm^{-1}. These features correspond, respectively, to the CO$_2$ asymmetric (1,550 cm^{-1}), the CO$_2$ stretching (1,400 cm^{-1}), and the C-N stretching (1,100 cm^{-1}) bands of NH$_2$CO$_2^-$ groups [20,21]. The ammonium carbonate displayed generally strong infrared absorption bands attributed to the ammonium ions (1,450 cm^{-1}) and carbonate groups (1,540, 1,350, and 1,020 cm^{-1}).

The chemical reactions between the CO$_2$ and NH$_3$ in the presence of the water were elucidated by the FT-IR spectra as shown in Fig. 5(b). The two broadening peaks corresponding to ammonia solution without the CO$_2$ absorption at around 1,630 and 1,100 cm^{-1} were attributed to the hydrogen bonding between ammonia and amine groups. After CO$_2$ absorption reaction of 120 min, the new peaks were confirmed according to the different operating temperatures, which were attributed to the chemical reactions between the CO$_2$, NH$_3$, and H$_2$O. When the absorption reaction of CO$_2$ occurred by the aqueous ammonia solution at the operating temperature ranging from 20 to 40 °C, prominent peaks at approximately 1,550, 1,400, and 1,100 cm^{-1} appeared through a very similar chemical reaction route, where these new bands were ascribed to the formation of carbamate. However, the intensities of these three bands increased with the low operating temperature of 5 °C. Taking into the consideration that the intensities of these peaks were strong with the increase of the amount of carbamate ions, the low operating temperature of 5 °C had a faster reaction for the formation of carbamate through the reaction 6 proceeds predominantly. The absorption reaction of CO$_2$ in aqueous ammonia solution at 5 °C of low operating temperature showed representative peaks of bicarbonate at approximately 1,450 and 1,350 cm^{-1}. In particular, white solid salts were obtained by the filtration and drying of the absorbent after CO$_2$ absorption reaction at 5 °C of the operating temperature. This product was confirmed by the strong features of FT-IR results at 1,597, 1,501, 1,441, and 1,371 cm^{-1}, which were attributed to the ammonium bicarbonate NH$_4^+$HCO$_3^-$. These results indicated that the operating temperature influenced the chemical reactions of CO$_2$ with NH$_3$ in the presence of the water.

CONCLUSIONS

We demonstrated the influence of operating temperature condition on the reaction of CO$_2$ and NH$_3$ in an aqueous solution. The removal of CO$_2$ with ammonia solution was performed with a bubble blowing apparatus and was dependent on the operating temperature, where the removal efficiency was increased with reduction of operating temperature: 40 °C<20 °C<5 °C. In addition, the ammonia loss was influenced by the operating temperatures, showing that the loss of absorbent increased with rising temperature. The chemical characteristics of CO$_2$-NH$_3$-H$_2$O reaction under different operating temperature conditions were investigated by FT-IR measurements. The reactions of CO$_2$-NH$_3$ at 20 °C and 40 °C showed similar reaction routes, while a different reaction route was observed at 5 °C, displaying reaction product of ammonium bicarbonate solid after reaction time of 120 min.

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