Process Design of Aqueous Ammonia-based Post-combustion CO$_2$ Capture

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Abstract—In the present work, the aqueous ammonia-based post-combustion CO$_2$ capture (PCC) process is simulated using the rate-based model in Aspen Plus, by which the method of sizing column heights is revealed. The heights of the staged CO$_2$ absorbers and the NH$_3$ absorber are determined as 5 m, 6 m, and 6 m; in addition, the heights of the CO$_2$ and NH$_3$ strippers are 12 m and 6 m, respectively. It is well known that the pressurized CO$_2$ stripper can reduce the energy burden for the solvent regeneration, effectively. However, since the staged CO$_2$ absorbers are operated at atmosphere, the pressurized lean solvent needs to be relieved to atmosphere either in the absorber or before entering the absorber. In the present work, the electric power that is used to compress the depressurized vapor back into the CO$_2$ stripper compares with the energy saving from the high pressure CO$_2$ stripper in order to find the optimal operating conditions at which the minimal overall regeneration energy is posed. The minimum requirement can be found at 3.0 GJ/ton-CO$_2$ under the operating conditions of the CO$_2$ lean loading (mol-CO$_2$/mol-NH$_3$) at 0.13 and the CO$_2$ stripper at 2 atm.

I. INTRODUCTION

Post-combustion CO$_2$ capture (PCC) using aqueous ammonia has received great attention as a promising technology because it provides many technical and economic advantages over the conventional amine solvent, such as low cost, low regeneration energy, no sorbent degradation, and the trace of emission being eco-friendly. However, the major drawbacks, e.g., slow absorption rate with CO$_2$ and high volatility of ammonia, lead to that a larger CO$_2$ absorber and a washing column for controlling NH$_3$ slip are needed. Zhang and Guo [1] reported that the diameter and the packed height of the absorber need to reach 40 m and 72 m respectively in order to achieve 90% of CO$_2$ removal. In the following work of Zhang and Guo [2], an ammonia abatement system was suggested where the ammonia stripper for the water wash loop and the carbon dioxide stripper in the carbon dioxide capture loop were designed relatively independently. The overall regeneration energy was reported to be 8.47 GJ/ton-CO$_2$ using the lean solvent with the ammonia concentration at 3 mol/L and the CO$_2$ lean loading at 0.23. In their proposed design, the NH$_3$ absorber is directly added onto the top of the CO$_2$ absorber; therefore, the amount of NH$_3$ washing water needed for controlling the slipped NH$_3$ concentration is inversely proportional to the CO$_2$ loading of the lean solvent. In addition, the flow rate of CO$_2$ lean solvent is proportional to the CO$_2$ lean loading in order to achieve the design criteria of 90% CO$_2$ removal. Therefore, the required energy for regenerating the ammonia washing water and the CO$_2$ lean solvent is highly dependent on the CO$_2$ loading of the lean solvent.

Jilvero et al. [3] proposed a staged absorption with intermediate cooling for capturing 1.3 million tons CO$_2$ per year where the column heights of both CO$_2$ absorbers were reported as 15 m and 5 m, respectively. However, the method of determining the column height was not addressed in their work. The intermediate rich-out solvent from the bottom of the first absorber was cooled down and then fed into the top of the second one. Since the most of ammonia has reacted with the CO$_2$ in the first absorber, the effect of the CO$_2$ lean loading to the amount of NH$_3$ washing water is limited. Therefore, the slipped ammonia concentration from the top of the second absorber only depends on the intermediate cooling temperature [4]. In addition, the flow rate of the ammonia washing water can be significantly reduced because the CO$_2$ loading of the intermediate rich-out solvent is approximated to 0.4, which is much higher than that of the lean solvent fed into the first absorber, i.e., 0.17-0.23 reported in [5].

This study continues the previous work [5] to evaluate the energy consumption of a large-scale PCC process for a 500 MW coal-fired power plant using aqueous ammonia solution with 3 mol/L NH$_3$ concentration. It is well known that increasing the operating pressure of the CO$_2$ stripper can effectively reduce the energy consumption of regenerating the CO$_2$ lean solvent. Li et al. [6] and Jilvero et al. [7] set the operating pressure of CO$_2$ stripper at 20 bar and proceeded the techno-economic evaluation for the ammonia-based PCC process. Li et al. [8] based on the CO$_2$ stripper operated at 10 bar and evaluated several configurations of the CO$_2$ stripper, e.g., a rich-split process, cold-rich bypass, inter-heating, and the combinations of these modifications, in order to analyze the related energy savings and the capital costs. The common point of the above-mentioned literature is that they did not address where the destination of the depressurized vapor from the high pressure CO$_2$ stripper is. Since the CO$_2$ absorber is operated at atmosphere, the pressurized lean solvent from the stripper needs to be released into the operating pressure of the absorber. Although the released vapor may take a minor portion of the lean solvent; however, the flow rate of the released vapor could be comparable to that of the flue gas. Therefore, the released vapor from the pressurized lean solvent cannot be ignored during the process design phase.

The remainder of this paper is organized as follows: section 2 gives a brief description about the simulation settings using the rate-based model in Aspen Plus. The details can be

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found in [1], [2], and [5]. In section 3, the benchmark PCC process of using aqueous ammonia is described, and the method of determining the column heights for the staged CO₂ absorbers is proposed. Section 4 presents the integrated stripper design reported in [5], whereas the design is modified for the pressurized CO₂ stripper. In addition, the optimal operating pressure for the CO₂ stripper is determined by minimizing the overall regeneration energy. Finally, conclusions are presented in section 5.

II. SIMULATION MODEL

In this work, the parameters of the rate-based model were set according to the work of Zhang and Guo [1]. The Redlich-Kwong equation of state and the electrolyte-NRTL method were used to compute the properties of the vapor and liquid phases, respectively. Rate-based approach in RADFRAC was used to simulate absorber and stripper behavior. Liu et al. [9] pointed out the simulation results can be influenced substantially by the choice of mass transfer correlations, reaction rate model, liquid holdup and reactor volume, as well as different settings of parameters such as reactor condition and mass transfer correlations. In order to establish a baseline of comparison, the settings used in Zhang and Guo [1] were adopted: (1) Billet and Schultes correlation for mass transfer, (2) Chilton-Colburn correlation for heat transfer, (3) reactor and mass transfer conditions set to default 0.5, and (4) the liquid holdup was set at 4% of the free volume.

III. ABSORPTION PROCESS

A. Benchmark Process

An integrated benchmark process flow diagram based on the separate studies (Zhang and Guo [1, 2] and Jilvero et al. [3]) on CO₂ absorption and ammonia wash was shown in Fig. 1. The flue gas, labeled as stream 1, after SO₂ removal is fed into an absorption column at 50 °C (labeled as CO₂ ABSORBER), where it reacts with the CO₂-lean solvent (stream 2). The liquid rich in CO₂ leaves the column from the bottom (stream 3). After preheating through a series of heat exchangers, the hot CO₂-rich stream (stream 4) is fed into the CO₂ STRIPPER column in which the reboiler duty is applied to release the CO₂ captured for further processing. A lean solution (stream 5) at high temperature is regenerated at the bottom of the CO₂ STRIPPER. The sensible heat of regenerated solvent (stream 5) is recovered by flowing through the above-mentioned heat exchanger so that the CO₂-rich flow (stream 4) is heated to 90 °C.

Since ammonia is highly volatile, an ammonia slip control system is needed before discharging the gas into the atmosphere. The slipped ammonia (stream 6) venting from the top of the CO₂ ABSORBER is fed into the NH₃ wash column (labeled as NH₃ ABSORBER). The NH₃ concentration of the vented gas (stream 7) is reduced to 10 ppm through absorption of the NH₃ washing water (stream 8). The NH₃-rich solvent (stream 9) is preheated by a heat exchanger to recover the sensible heat of lean-out stream (stream 10). The rich solvent (stream 11), heated to about 85 °C is then fed into the NH₃ STRIPPER where the ammonia is stripped. The concentrated NH₃ vapor (stream 12) is condensed as part of the heat source to preheat the CO₂-rich solvent, and is then mixed with stream 5 and fed into the CO₂ ABSORBER as the CO₂ lean-in solvent.

![Figure 1. A combined CO₂ absorption and ammonia wash process.](image1)

B. Sizing CO₂ and NH₃ Absorbers

Zhang and Guo [1] reported that the column height of the CO₂ absorber needs 72 m in order to achieve 90% CO₂ removal, when the CO₂-lean solvent temperature is set at 38 °C. Fig. 2 shows that the CO₂ reaction rate in the liquid phase along with the column height from the top (0 m) to the bottom (72 m) in which the positive value indicates the net production of CO₂. The details of the simulation settings can be found in [1]. As the figure shown, the CO₂ was absorbed efficiently only on the top of the column where the section height is around 0-5 m. Then, the absorption reaction was struggling from the column height 5 m to 70 m. Finally, the CO₂ was released from the liquid at the bottom of the absorber, since the inlet temperature of the flue gas was set as 50 °C which led to the CO₂ reverse reaction occurring. Therefore, reducing the inlet temperatures of the CO₂-lean solvent and the flue gas may improve the CO₂ absorption reaction, effectively.

![Figure 2. CO₂ reaction rate profile along with the column height.](image2)
In this study, the temperature of cooling water and the minimal approach of heat exchangers were set as 25 °C and 5 °C, respectively; therefore, the inlet temperatures of the CO₂-lean solvent and the flue gas were set as 30 °C. Fig. 3 compares the CO₂ removal efficiency under the suggested settings of Zhang and Guo [1] and this work. The CO₂ removal efficiency has been improved significantly, as shown in Fig. 3. The column height can be reduced from 72 m to 18 m under the design criteria of 90% CO₂ removal, as long as decreasing inlet temperatures of the absorber to 30 °C. Fig. 4 shows that the CO₂ reaction rate profiles in the liquid phase along with the column heights where the reversed reaction of releasing CO₂ in the bottom is suppressed, effectively; however, the inefficient absorption reaction can be observed when the column height was set as 9 m. Therefore, the height of CO₂ absorber was determined as 5 m at which the CO₂ removal efficiency is 86.7%, as shown in Fig. 3.

Figure 3. Comparison of CO₂ removal efficiency under different inlet temperatures.

Figure 4. CO₂ reaction rate profile under the new operating condition.

Jilvero et al. [3] proposed to use a two-stage absorption with intermediate cooling to significantly reduce the slipped NH₃ concentration. In their work of [3], the height of the second absorber was set as 5 m and the method of determining the height was absent. In this work, the temperature of chilled water was set as 10 °C; therefore, the bottom flow of the first CO₂ absorber could be cooled down to 15 °C, and then fed into the top of the second CO₂ absorber. Jilvero et al. [3] described that the objective of the second absorber is to reduce the gas-phase ammonia concentration. Since the most of ammonia has reacted with the CO₂ in the first absorber, the vapor pressure of NH₃ on the top of the second absorber is only dependent on the temperature of solvent fed into the absorber [4], which is 15 °C in this study. The venting gas from the top of the first absorber was fed into the bottom of the second absorber that was reacted with the cooling rich-out solvent. It should be noted that the height of the second CO₂ absorber would not affect the slipped NH₃ concentration from the top of the absorber. Fig. 5 shows the additional CO₂ removal efficiency by the second absorber. The additional 9% removal efficiency could be achieved, if the column height was set as 6 m. Therefore, the total height of both CO₂ absorbers was 11 m that can achieve 95.7% removal efficiency that is higher than that of using single absorber with 18 m column height, which is 90.2%, as shown in Fig. 3.

Figure 5. Determination of the column height for the 2nd CO₂ absorber.

Figure 6. Determination of the column height for the 2nd CO₂ absorber.

For a rate-based model, the absorption efficiency is determined by the solvent flow rate and the retention time in the absorber. In the present work, since the slipped NH₃ concentration was controlled less than 10 ppm [4], the retention time of the lean solvent was inversely proportional to the flow rate of the washing water in a constant of the slipped ammonia concentration. In addition, the column diameter was determined by 80% of the maximum flood capacity in most cases; therefore, the height of the NH₃ absorber was inversely proportional to the flow rate of the ammonia washing water, as
shown in Fig. 6. The figure shows that the NH$_3$ absorber with 6 m of column height is relatively efficient for considering the balance of the washing water flow rate and the equipment size.

IV. REGENERATION PROCESS

A. Integrated Stripper Design

In Fig. 1, the influence of the concentrated NH$_3$ flow (stream 12), which was drawn from the top of the NH$_3$ stripper, on the CO$_2$ lean-in flow (stream 2) was not addressed by Zhang and Guo [1], since stream 12 was not in the process flow diagram of their work [1]. In their subsequent work, Zhang and Guo [2] reported that the energy of the concentrated NH$_3$ flow was used to preheat the CO$_2$ rich-in flow (stream 4), and then mixed with the CO$_2$ lean-out (stream 5), as shown in Fig. 1. However, the effect of combining stream 12 and stream 5 was not discussed by Zhang and Guo [2]. In the previous work [5], the vapor of the concentrated NH$_3$ was directly introduced into the bottom of the CO$_2$ stripper; therefore, the latent heat of the stream could be used to regenerate the CO$_2$ lean solvent. The overall energy for regenerating the CO$_2$ lean solvent and the NH$_3$ washing water can be dramatically reduced from 8.47 GJ/ton-CO$_2$ [2] to 4.0 GJ/ton-CO$_2$ at the atmospheric CO$_2$ stripper.

B. Sizing CO$_2$ and NH$_3$ Strippers

In this subsection, the ammonia concentration and CO$_2$ lean loading of the CO$_2$ lean solvent were set as 3 mol/L and 0.23, respectively, and the stripper drove the CO$_2$ loading back to 0.23 according to the settings of [1]. In addition, the simulation conditions of the NH$_3$ washing water were set as 0.025 mol/L of NH$_3$ concentration and 1.2 of CO$_2$ loading according to the work of [2], and the stripper revived the NH$_3$ concentration back to 0.04 mol/L. In the works of [1] and [2], the column heights of the CO$_2$ and NH$_3$ strippers were reported as 12 m and 8 m; however, the method of determining the column height was absent. As mentioned earlier, the solvent flow rate is inversely proportional to the retention time in an absorber for the specified removal efficiency. The similar concept can be applied for sizing the strippers. For a specified regeneration rate, the retention time in the stripper is inversely proportional to the energy consumption of the reboiler, as shown in Fig. 8. By considering the balance of the equipment size and the energy consumption, it is reasonable to set the column height of CO$_2$ stripper around 10-14 m according to Fig. 8(a), and the height of NH$_3$ stripper can be set around 4-8 m by Fig. 8(b). In the following simulation cases, the heights of the CO$_2$ and NH$_3$ strippers are set as 12 m and 6 m, respectively.

Figure 7. Flow diagram of the proposed integrated process.

It is well known that the pressurized CO$_2$ stripper can effectively relieve the energy burden of solvent regeneration. Li et al. [6] suggested that the reboiler duty of the CO$_2$ stripper can be reduced to 2.87 GJ/ton-CO$_2$ whereas the stripper was operated at 20 bar. In addition, Li et al. [8] evaluated several stripper processes for analyzing the related energy savings and capital costs. These evaluations were based on the benchmark configuration where the CO$_2$ stripper was operated at 10 bar. However, the CO$_2$ absorbers were operated at atmosphere, in general. The high pressure lean solvent needs to be depressurized to atmosphere either in the absorbers or before entering the absorbers. The released vapor of the pressurized lean solvent was not addressed in the literature [6-8]. In the present work, the pressurized lean solvent was introduced into a flash drum at atmosphere; then, the released vapor combining with the concentrated NH$_3$ was fed into a compressor and pressurized to the operating pressure of the CO$_2$ stripper, as shown in Fig. 7. In addition, the CO$_2$ rich flow needs to be pumped into the pressurized stripper. In this study, 35.6% of conversion efficiency [6] is used to calculate the thermal energy that is converted from the electric power of the compressor and the pump in order to find the minimum of the overall energy.
In the present work, the design criterions of the PCC process are: (1) removing 90% CO₂ of the flue gas, and (2) controlling the slipped NH₃ concentration below 10 ppm. Fig. 9 shows that the flow rate of CO₂ lean solvent is decreasing along with decreasing the CO₂ loading, and the simulation results of the lean flow rate are close to the previous work [5]. In addition, the washing water flow rate is independent on the variation of the CO₂ lean loading, since the amount of slipped ammonia is decided by the temperature of intermediate rich-out solvent, which is 15 °C of stream 3a in Fig. 7. However, the result of the washing water flow rate is only one-tenth amount comparing to the previous results [5]. That demonstrates that the staged absorption with intermediate cooling design can effectively reduce the amount of the washing water flow. Fig. 10 shows the energy consumption for both strippers and the overall energy. As expected, the less lean solvent is needed, the less regeneration energy is consumed, as the less flow rate of the CO₂ lean solvent needs to be regenerated. The minimum of the regeneration energy can be found on the regenerated limit of CO₂ lean loading (~0.17) where the overall energy is 3.8 GJ/ton-CO₂, which is close to the previous result (4.0 GJ/ton-CO₂) [5].

C. Pressurized CO₂ Stripper

As mentioned previously, the released vapor from the pressurized CO₂ stripper was not addressed in the literature [6-8]. Fig 11 shows that the ratio of the mass flow rates of released vapor to the lean solvent is around 4-7% that might be the reason why the released vapor was ignored in the literature. However, Zhang and Guo [1] reported that the ratio of the mass flow rates of liquid to gas is 6.975 for the CO₂ absorber, and the ratio is 6.263 in the present work. As shown in Fig. 11, the mass flow rate of released vapor takes around 25-45% of the flue gas that is a significant value cannot be ignored. In addition, the released vapor contains 11 vol% of CO₂ and 36 vol% of NH₃. If the high pressure lean solvent was depressurized in the CO₂ absorber, the more CO₂ lean solvent and NH₃ washing water would be needed to capture the extra CO₂ and NH₃ from the depressurized vapor. The snowball effect could be triggered unless the lean solvent was depressurized before entering the CO₂ absorber.

The regeneration energy for the CO₂ stripper varies from 3.5 GJ/ton-CO₂ (1 atm) to 1.5 GJ/ton-CO₂ (3 atm), as shown in Fig 12(a). The simulation results are consistent with that the energy consumption of the CO₂ stripper is decreasing along with the higher operating pressure of the stripper. However, the electric power of the compressor and pump, the
compressor taking up to 98% of the total electric power, is also increasing along with the increasing of the stripper pressure, as shown in Fig 12(a), in which 35.6 % of conversion efficiency is used to convert the electric power to the thermal energy. The overall energy consumption is summarized in Fig. 12(b); the figure shows that the higher operating pressure of the CO₂ stripper may not always lead to the lower overall regeneration energy when taking the electric power of the compressor into account. The minimum of overall energy consumption can be found at 3.0 GJ/ton-CO₂ where the CO₂ stripper is operated at 2 atm and the CO₂ lean loading is around the regenerated limit (~0.13).

The systematic method for sizing the column heights of the PCC process that captures the CO₂ of the flue gas from a 500 MW coal-fired power plant was proposed. In this study, the temperatures of the cooling water and the chilled water were set as 25 °C and 10 °C, respectively; meanwhile, the minimal approach of heat exchangers was set at 5 °C. The column heights of the staged CO₂ absorbers and the NH₃ absorber were decided as 5 m, 6 m, and 6 m that can achieve the design criteria of 90% CO₂ removal and controlling the slipped NH₃ concentration at 10 ppm. The higher operating pressure of the CO₂ stripper can lead to the less energy consumption for solvent regeneration. However, the destination of the depressurized vapor was not addressed in the literature. As the present work demonstrated, more than 40% of the flue gas mass flow rate could be released, if the CO₂ lean solvent was depressurized from 3 atm to atmosphere. The released vapor cannot be ignored during the process design phase, and that should be recompressed and fed it back to the CO₂ stripper. The electric power of compression was used to compare with the energy saving from the higher operating pressure of the CO₂ stripper. The optimal operating pressure for the CO₂ stripper could be found at 2 atm and the CO₂ lean loading was around 0.13 where the minimum of the overall thermal energy was 3.0 GJ/ton-CO₂. The energy reduction is around 25% comparing with the previous work [5], which was 4.0 GJ/ton-CO₂.

REFERENCES