Research on Processing Simulation and Energy Analysis of CO$_2$ Capture by Aqueous Ammonia in Power Plant

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Abstract. The paper proposes a new technology of CO$_2$ capture which is based on a 350MW coal-fired power plant. The traditional and the new CO$_2$ capture model was built by using software Aspen plus. To study the effect of operating parameters on CO$_2$ capture efficiency, ammonia escape and the CO$_2$ capture volume of the two techniques, a further comparative analysis was performed. Getting the following conclusion that the new technology has an obvious advantage on the process of carbon absorption and desorption. The new technology leads to the high rate of reaction as well as the high NH$_3$ utilization in absorption process. On the other hand, the capture volume of CO$_2$ of the new technology is 31% more than the traditional technology in desorption process. Moreover, the regeneration power consumption of the new technology is only 42.6% of the traditional one. So, the new technology is more energy-saving and efficient.

1. Introduction

Because of the extensive use of the fossil fuel, making the CO$_2$ emissions increased in the world. In June 2014, the America government proposed the “clean power plan” [1], which is the first time to limit the CO$_2$ emission in existing power plants. Now, the coal-fired power plants have become the main source of CO$_2$ emission [2].

Nowadays, there are many methods of controlling CO$_2$ emissions in the world, chemical absorption method is relatively efficient and technically feasible [3]. Compare with the MEA, using the ammonia as absorbent has a series of benefits: the CO$_2$ removal efficiency by ammonia can reach as much as 95%-98%, while the MEA is just around 90%. The absorbing ability of ammonia can reach to 1.2kg(CO$_2$)/kg(NH$_3$), which is 3 times as much as MEA [4]. Meanwhile, ammonia does not exist equipment corrosion and oxidative degradation, which makes a large cost reduction. On the other hand, ammonia can also realize the joint removal of pollutants [5].

CO$_2$ capture by ammonia also has some problems: it is hard to control the ammonia escape [6]; the small value of hydrolysis rate of ammonium carbamate makes the low level of the carbonization degree of absorbent, which makes the low ammonia utilization rate [7]; in the post reaction, the CO$_2$ absorption rate of carbonated aqueous ammonia is slow [8]; the further reduction of regeneration power consume is needed [9].

Experiment study of CO$_2$ capture is performed by Zhao, Barzagli, Zhang, Guo [10-13] et al, who researched the effect of reactor module like Sieve plate reactor, wetted wall tower, packed bed, babble fluidization bed and reaction characteristics like the reaction temperature, the flue gas, the ammonia concentration, absorbent flow rate, additive, CO$_2$ concentration in the flue gas and everything of the
sort on the absorption and desorption process. Yu [14] et al designed and operated the large-scale CO₂ capture equipment by using experimental and simulative methods, and proposed different processes to reduce energy consume and increase CO₂ capture efficiency. The power plant at Munmorah State in Australia, Power span company and Alstom company in America have already pushed out a couple of complete process equipment as a demonstration [15-17].

This paper has adopted a new technology in carbon capture by ammonia with reinforced crystallization [18]. Its technological flow sheet is shown in Figure 1. Our group has carried out a series of experimental studies for the technology, obtaining a lot of conclusions about chemical kinetics property and crystal rules. We think that in this process, with the crystallization period stretch, the particle size distribution of product improves gradually. In the first 30 minutes, the average grain diameter of the crystal keep growing, and crystal morphology becomes more complete, the caking problem is also solved in some extent.

**Figure 1.** the technological process of CO₂ capture by ammonia with reinforced crystallization

Compared with the traditional (or the old) technology, the new technology does not let the rich solution flow into the regeneration tower, while being reinforced crystallization in the crystallizer using the ethyl-alcohol as salting-out agent when it is in low carbonization degree, and then flow into solid-liquid separator. Finally, put the crystal into the regeneration tower to be heated. The rest liquid flow into the crystallizer added a certain amount of ethanol to keep the salting-out crystallization behaviour. The gas from the desorption tower flow past a C-N separator, the ammonia and the captured ammonia after escaping is sent into the absorbent reuse unit, then, flow into the absorption tower as the absorbent and be used again.

In this technology, we just need to heat the solid product, which saves a lot energy consumption to raising the temperature of the water. The gas from the absorption tower flow into the water scrubber, in which the escaped ammonia is removed by washing. The water containing ammonia flow into the water-ammonia separator, in which ammonia is used again as the absorbent and water flow back to the water scrubber to continue washing the flue gas.

To do some modelling research about this new technology, this paper adopts the chemical process software Aspen plus. In this area, Darde et al [19] verified the prospects of the low temperature ammonia by using the UNIQUAC modelling, and assessed this process, and analysed the effect of main technological parameter on demand for heat and electricity. Niu et al [20] proposed a new CO₂ capture technology by ammonia, the process is under ordinary temp and pressure, and the regeneration temp is 85-95℃, so the low-quality energy can be used.

This paper focus on 350MW coal-fired power unit, analyze and calculate the processing flow and energy consumption of the new technology in carbon capture by ammonia with reinforced
crystallization. By contrasting the new and the traditional technology, the paper gets the advantages and disadvantages of the two technologies, tests the feasibility of the new one.

2. Process description

For the sake of contrastive analysis, we build a traditional ammonia CO$_2$ capture model, as show in Figure 2.

The flue gas flow into the absorbent tower from the bottom, then leave from the top after CO$_2$ removal. The ammonia liquid spray from the tower top, and be pressed after absorb the CO$_2$, and then preheated by the lean liquor which come from the bottom of regeneration tower, finally, flow into the regeneration tower to be heated and regenerated. Because the paper focus on the comparison of the energy consume, the lean liquid is not recycled. The flow sheet of the new technology is show in Figure 3.

It is the same with the traditional method in the absorption process. The rich liquid flows out of the absorbing tower from its bottom, and flow into the crystallizer “CRYSTAL”. And then put the ethanol into the crystallizer through the stream “ETHANOL”, which leads to salting-out precipitation. The stream “PRODUCT” contains both the crystal and the residual solution. Next, put this kind of mix components into the “PUMP” to be compressed. Then put them into the solid-liquid separator “SEPARAT0” and “SEPARAT2” for separating. The obtained solid will be put into the “REACTOR” to heat regeneration and generate mixed gas. After that, the mixed gas flow into the component separator “SEP” for component separation. And the separated residual solution can be recycled for absorption process. The pressure of the absorption tower and the reactor are 1.2 Bar.
3. Model setup and regulation

3.1. Process regulation of traditional technology

The simulated flue gas is from the typical 350MW coal-fired power plant. The total flue gas is 45000kmol/h, and the temperature is 60℃. We assume that the composition of flue gas are just N₂ and CO₂, the mass fraction of CO₂ is 14%, and the N₂ accounts for 86%. Because of the small effect on the concerned question, we can do assumptions above.

Henry components are NH₃, N₂, and CO₂, which are the Aspen system default. In the whole simulation system, the existing components are NH₃, N₂, CO₂ and H₂O. Other components make up the NH₃-CO₂-H₂O system. The smart tool “Electrolyte Wizard” in Aspen plus can generate ionic reaction, producing other components, those components include: H₃O⁺, NH₄⁺, OH⁻, HCO₃⁻, CO₃²⁻, NH₂COO⁻. Because the concentration of the reaction liquid is low (mass concentration is less than 20%), it is impossible to generate solids. We set the property method as ELECNRTL. The default reactions that the Aspen plus providing for the NH₃-CO₂-H₂O system is shown in Table 1.

| reaction ID | reaction type | chemical equation |
|-------------|---------------|-------------------|
| 1           | Equilibrium   | NH₃ + H₂O ⇌ OH⁻ + NH₄⁺ |
| 2           | Equilibrium   | H₂O + HCO₃⁻ ⇌ CO₃²⁻ + H₃O⁺ |
| 3           | Equilibrium   | NH₃ + HCO₃⁻ ⇌ H₂O + NH₂COO⁻ |
| 4           | Equilibrium   | 2H₂O + CO₂ ⇌ HCO₃⁻ + H₂O⁺ |
| 5           | Equilibrium   | 2H₂O ⇌ OH⁻ + H₃O⁺ |

The components of absorbent are ammonia water, the initial parameter setting is shown in Table 2.

| initial parameters | value   | initial parameters | value   |
|--------------------|---------|--------------------|---------|
| ammonia concentration/% | 8       | absorber (regeneration) | 1.4     |
| tower pressure/Bar | 1.4     | reflux ratio       | 0.25    |
| Absorber tower temperature/° C | 25      | Outlet steam rate/ kmol/hr | 4500   |

Table 3 provides the module specific setting of the traditional technology simulation system.

| Modules     | user models | function       |
|-------------|-------------|----------------|
| STRIPPER    | RadFrac     | Strict distillation |
| PUMP        | PUMP        | Solution pressure |
| HEATEXC     | Heatx       | Heat exchange   |
| ABSORBER    | RadFrac     | Strict distillation |

3.2. Process regulation of new technology

The new technology has the same process with the old one in absorption process. Because the reaction not only includes ethyl alcohol, but also crystal. The system components of new process is the same with the old process, besides ethyl alcohol and ammonium bicarbonate solid. So it must contains the reaction providing by Aspen plus:
$\text{AMMON-01} \leftrightarrow \text{HCO}_3^- + \text{NH}_4^+$  

(1)

Table 4 provides the specific setting of each main module of the new technology system. The salting out crystallization is carried out in the crystallizer. The crystallizer temperature is $25^\circ\text{C}$, and the pressure is 1200KPa. The direction of the reaction in the crystallizer is against to the reaction above. The initial temperature of the crystallizer is $75^\circ\text{C}$. Regeneration reaction is heating the bicarbonate, and break up into $\text{H}_2\text{O}$, $\text{NH}_3$ and $\text{CO}_2$. The reaction heat of this reaction is 64KJ/mol in $25^\circ\text{C}$ standard condition.

| Modules  | user models | function                      |
|----------|-------------|-------------------------------|
| STRIPPER | RadFrac     | Strict distillation           |
| PUMP     | PUMP        | Solution pressure             |
| CRYSTAL  | Crystallizer| Dissolution crystallization   |
| SEPARAT  | HyCyc       | Solid-liquid separation       |
| REACTOR  | RStoic      | Thermal regeneration          |
| SEP      | Sep         | Component separation          |
| ABSORBER | RadFrac     | Strict distillation           |

4. Comparative analysis of the two technologies

4.1. Accuracy verification of the model

Based on the $\text{CO}_2$ capture process, the model’s veracity is validated. For the two technologies, in absorption process, the relationship between the operating parameter and the target parameter is shown in Figure 4.

As shown in Figure 4, the influence curve which shows the effect of the $\text{NH}_3$ concentration of the absorbent on the $\text{CO}_2$ capture efficiency and outlet $\text{NH}_3$ concentration between the two technologies are coincident. So we can assume that the model of the new technology of $\text{CO}_2$ capture is accurate.

![Figure 4](image-url)  

**Figure 4.** The effect of the $\text{NH}_3$ concentration of the absorbent on the absorption process between two technologies
4.2. The optimization of the new technology in the absorption process

For the carbon capture process, carbonized ratio \( A \) represents the saturation degree of the absorbent, which means the ratio of the carbon content \( N_C \) to ammonia content \( N_N \):

\[
A = \frac{N_C}{N_N}
\]  

(2)

Just because the new technology is proposed, it can greatly increase the carbonized ratio of the product. The relationship between the ammonia concentration of absorbent and the carbonized ratio of the product is shown in Figure 5.

![Figure 5](image1.jpg)

**Figure 5.** The effect of ammonia concentration of the absorbent on the carbonized ratio

With the increasing of the ammonia concentration, the carbonized ratio become lower. That is because the higher the ammonia concentration, the higher the ammonia-carbonized ratio of the reactant, the main product is \( \text{NH}_2\text{COONH}_4 \), and the carbonized ratio of \( \text{NH}_2\text{COONH}_4 \) is lower than \( \text{NH}_3\text{HCO}_3 \) (because 1 N atom corresponding to 1 C atom for \( \text{NH}_3\text{HCO}_3 \), while 2 N atoms corresponding to 1 C atom for \( \text{NH}_2\text{COONH}_4 \)). So the carbonized ratio and the ammonia concentration is anti related.

Figure 6. shows the relationship between the \( \text{NH}_3 \) concentration and fraction of \( \text{NH}_3\text{HCO}_3 \) in rich liquid product as well as the ammonia conversion rate. With the ammonia concentration increasing, the fraction of \( \text{NH}_3\text{HCO}_3 \) becomes less, and the ammonia conversion rate is decreased.

![Figure 6](image2.jpg)

**Figure 6.** Relationship between the \( \text{NH}_3 \) concentration of absorbent on the fraction of \( \text{NH}_3\text{HCO}_3 \) and the ammonia conversion ratio
By above knowable, the lower the ammonia concentration of absorbent is, the higher the carbonized ratio of the product, and the higher the fraction of NH$_4$HCO$_3$, as well as the ammonia conversion rate. So as to the concentration, the lower concentration of ammonia is more economic.

But low concentration absorbent has a problem: the reaction gets to the late period very fast and the absorption rate becomes slow in the late period. The relationship between reaction rate and the reaction time is shown in Figure 7.

On one hand, improving the carbonized ratio help to increase the ammonia use ratio; on the other hand, reducing the carbonized ratio can guarantee the absorption rate, so the carbonized ratio can’t be too high. That is the contradiction.

To overcome the contradiction above, this paper adopt the method of strengthening the crystallization of low carbonation degree ammonia. The relationship between the carbonized and the ammonia concentration for the two technologies is shown in Figure 8.

It shows that, with the variations of ammonia concentration, the carbonized ratio keeps at a high level around 99%. If the crystallizing process of the low degree carbonated rich liquid are strengthened, the main product is NH$_4$HCO$_3$, which makes the high carbonized ratio. While the rich liquid of low carbonized ratio is produced in the early stage of the reaction, so the reaction rate will keep fast.

In this way, at high concentration of ammonia, we can not only guarantee the reaction rate but also guarantee the high carbonized ratio, which makes the reaction rate and ammonia use rate keeping at a high level.

![Figure 7](image7.png)

**Figure 7.** The relationship between the reaction time and reaction rate

![Figure 8](image8.png)

**Figure 8.** Relationship between the ammonia concentration and the carbonized ratio for the two technologies
To validate the validity of the analysis above, the paper conducts comparative analysis of the experimental study by Yu Mengmeng et al. We choose the ammonia with mass fraction of 2% and 10% to capture CO₂, divide into three types: 2% ammonia; 10% ammonia; 10% ammonia and then reinforced crystallization. The carbonized ratio of the overall product and the carbonating solution is shown in Figure 9. It can be seen that, although there are some errors between the experiment and simulation study, it has the same trend that, with the increasing of ammonia concentration, the carbonized ratio of carbonized liquid is decreased. Also, the carbonized ratio of the overall product and the carbonized liquid is increased after the reinforced crystallization when the rich liquid is at low carbonized ratio. Thus verify the accuracy of the model analysis.

![Figure 9. Relationship between the ammonia concentration and carbonized ratio of the overall product and the carbonating solution](image)

4.3. The optimizing of the new technology in the regeneration process

To analyse the effect of the NH₃ concentration, the paper initially set 100000 kmol/h as the ammonia flow. The effect of ammonia mass fraction on the CO₂ regeneration process is shown in Figure 10.

It can be seen that, when in high concentration level of the ammonia, the CO₂ outlet flow is 4300 kmol/h in the new technology, which is 30% more than the old one for 2640 kmol/h. Therefore, the new technology capture more CO₂ than the old technology.

![Figure 10. Comparison of effects of the NH₃ mass fraction on CO₂ regeneration process for the two technologies](image)
With the concentration of ammonia increased in old technology, although the regeneration energy consumption is decreased slightly, it is more than 138MW. If adopting the new technology, the regeneration energy consumption decreased with the ammonia concentration reduced. And the minimum value can reach to 20MW, as the ammonia concentration is 2%. When the ammonia concentration is 6%, the regeneration energy consumption is 59MW, which is 40% of the old technology.

When the ammonia concentration is 6%, the effect of absorbent flow on desorption process is shown in Figure 11. It can be known from Figure 11. that, with the flow rate of absorbent increasing, the outlet flow rate of CO$_2$ is increased for both technologies. That is because the captured CO$_2$ is increased with the flow rate of absorbent grown, which makes the carbon content of the rich liquid or the crystal increased, as well as the regenerated CO$_2$. For the old technology, the increasing of absorbent will lead to more rich liquid, which makes the regeneration energy consume increased. For the new process, because of the saving energy for heating the liquid, the growth of regeneration energy consume is not big. And we can also figure out that not only the regeneration energy consume of the new technology is far below the old one, but the outlet flow rate of CO$_2$ is more than old one.

![Figure 11. Effect of absorbent flow on the desorption process between two technologies](image)

Figure 12. shows the effect of the temperature of the lean solution on the CO$_2$ regeneration process. It can be seen that with the rising temperature of the absorbent, the outlet flow rate of CO$_2$ is decreased, as well as the regeneration energy consumption. That is because the high temperature will lead to the severe volatility of ammonia, inhibiting the absorption of CO$_2$, so the amount of CO$_2$ regeneration is cut down. For old technology, the high temperature of absorbent will lead to the high temperature of rich liquid, which makes an unsubstantial rise in temperature for the liquid as well as the lower regeneration energy consumption. For new technology, the regeneration energy consumption is slightly decreased with the absorbent temperature going up, the reason is that the new technology saves a quantity of energy needed for the temperature-raising of solution.
5. Conclusion
The paper takes the 350MW coal-fired power plant as a reference, and analysis the CO₂ capture process by ammonia on a large-scale. The advantages and disadvantages of the new and the old technologies were contrastively analyzed.

Through simulating absorption process, the new technology reinforce the ammonia liquid of low carbonized ratio into crystallization, which makes the end of reaction before it comes to the late stage, thus guarantee the reaction rate. And after crystallization, the carbonized ratio of the product is high, leading to the high carbon nitrogen ratio of the product, which keeps the high utilization rate of ammonia.

In desorption process, the amount of CO₂ capture is 4300 kmol/hr in the new technology, which is 30% higher than the traditional one for 2640 kmol/hr. More important, the regeneration heat duty of the new technology is 59 MW, which is only 40% of the old one for 147MW. So, the new technology is more economic. The works of this paper can provide a new reference for CO₂ capture technology.

Given the above, the new technology which reinforce the ammonia liquid of low carbonized ratio into crystallization, quickening the absorption reaction rate, rising up the utilization rate of absorbent. Meanwhile, by heating the crystal to regenerate the CO₂, the new technology reduces the regeneration energy consumption. Because of a lot of advantages of the new technology, it can provide a reference direction for the carbon capture technology in the future.

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