Urea solution of single droplet pyrolysis characteristics research and engineering application

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Abstract. The experimental bench for the pyrolysis characteristics of single droplets of urea solution was established to analyze the variation characteristics of the whole process of single droplet evaporation pyrolysis. The results show that there are a large number of bubbles in the droplets which are very favorable for pyrolysis, the pyrolysis energy and atomization degree are insufficient, leading to the formation of intermediate products, greatly reducing the efficiency of denitrification. Based on the experimental data, the urea pyrolysis system was developed and designed for the SCR denitrification project of a coal-fired boiler in a thermal power plant, and key equipment was optimized, including urea storage and supply system, denitration reactor system, spray gun device, pyrolysis furnace body, etc. The system was put into operation. After that, the NOx concentration was reduced from 250mg/Nm$^3$ to 20 mg/Nm$^3$, and the denitration efficiency reached over 90%. The project has strong engineering application value.

1. Introduction
As one of the main pollutants discharged from power station boilers, NOx has been paid more and more attention by the industry, and its emission standards are also increasing. At present, the most widely used technical means in the field of domestic denitrification is the selective catalytic reduction method using ammonia as a denitrification reducing agent, namely SCR method, which is a kind of denitrification technology with high efficiency, low cost and mature market [1].

The pyrolysis characteristics of urea solution have been described in a large number of literatures and research reports, but there are few researches and reports on the pyrolysis characteristics of single droplet evaporation. Therefore, the pyrolysis characteristics of single droplets are studied. The experimental platform analyzes the variation characteristics of the whole process of single droplet evaporation pyrolysis, and analyzes the influencing factors of its pyrolysis characteristics. Finally, based on the experimental basic data, it guides the development and design of urea pyrolysis system, and the engineering application effect is remarkable.

2. Study on Pyrolysis Characteristics of Single Droplet in Urea Solution
Set up a single droplet analysis test bench (Figure 1), mainly including carbon dioxide laser, high-precision infrared thermometer, ultrasonic suspension, high-speed camera. The experimental platform suspends the droplets in the air stably by the ultrasonic suspension instrument to avoid the interference of the external environment on the droplet shape. Adjusts the power of the carbon dioxide laser (0~200kW) to change the pyrolysis energy of the single droplet. The temperature meter tests and records
the temperature of each stage of the urea single droplet evaporation pyrolysis process. The high-speed camera can record the single droplet evaporation pyrolysis change characteristics in the whole process, and can accurately obtain the droplet decomposition time and its location by statistical image recording information.

![Image of experimental setup](image)

**Figure 1.** Urea solution of single droplet test bed pyrolysis characteristics research

2.1. Analysis of urea single droplet evaporation pyrolysis process

Fig. 2 is a characteristic diagram showing the state change of the single droplet evaporation pyrolysis process of urea solution, which includes four stages of evaporation, precipitation, drying and pyrolysis. Fig. 3 is a recording diagram of the whole process of single droplet evaporation pyrolysis of urea solution under the experimental conditions of solution mass concentration 50%, droplet diameter 1480 μm and laser power 36W.

![Diagram of evaporation, precipitation, drying, and pyrolysis](diagram)

**Figure 2.** Urea solution evaporation pyrolysis schematic diagram

After the droplets obtain heat, the liquid water on the surface is evaporated by heat, and the phase changes into water vapor. As time goes by, the volume of the single droplet gradually becomes smaller, the urea solute gathers toward the center, and the concentration continuously increases until it reaches saturation. The solute precipitation phenomenon can be judged by observing the transparency of the
droplets. In Fig. 3, (a) to (b) are single evaporation processes, no precipitation is precipitated, and the droplets are transparent.

After the droplet evaporation reaches saturation, the heating solution will continue to precipitate the urea precipitate. It is found that the evaporation rate of the solution in the precipitation stage is slower than that in the evaporation stage, and the precipitation is completed and then enters the drying stage. The concentration of the solution selected in this experiment is relatively high (50%), and it quickly enters the drying stage under laser heating. At the time of 0.952 s (Figure 3 (c)), the droplets have become turbid and solute. Partial precipitation occurs, and (c)–(j) in Fig. 3 are characteristic maps of droplets in the dry stage. At the time of T=4.904s, it enters the pyrolysis stage ((k)-(l) in Fig. 3). At this time, the urea is in a molten state, and it is observed that the droplets undergo pyrolysis reaction accompanied by white smoke and snoring. At the time of T=5.714s, the entire process of evaporative pyrolysis ends.

![Figure 3. Urea solution of single droplet evaporation pyrolysis process](image)
2.2. Analysis of single-drop evaporation pyrolysis process with bubbles

The experiment was also carried out under the conditions of 50% solution concentration, 1480 μm droplet diameter and 36 W laser power. The droplet pyrolysis reaction also experienced the above four stages, T=1.156s (Figure 4(b)), The surface of the droplet is evaporated, the diameter of the droplet is continuously reduced, and heating is continued. At T=2.486s ((c) to (d) in Fig. 4), the air in the droplet is thermally expanded, and the diameter of the droplet continues to increase. When the air pressure in the bubble is large enough, the bubble film will rupture and the droplet diameter will suddenly decrease (Fig. 4(e)), T=3.862s, accompanied by squeaking sound and white smoke, pyrolysis carry out. Comparing the experimental results in 2.1, under the same experimental conditions, the droplet pyrolysis time of the bubble carrying is 1.852 s compared with the droplet without the bubble, and the bubble is a favorable factor affecting the pyrolysis efficiency of the droplet.

Figure 4. Droplet evaporation pyrolysis process diagram containing bubbles
2.3. Intermediate product in the pyrolysis process

The experimental conditions selected were 50% mass concentration, 36 W laser power, and 1480μm droplet diameter. Under the same experimental conditions, according to the experimental results in 2.1, the droplet pyrolysis time is 5.714s, but in this experiment, until the time of T=16.082s, the droplets are still not fully pyrolyzed, and the removal may affect the droplet pyrolysis. The external disturbance condition is inferred to produce an intermediate product that is difficult to pyrolyze during the droplet pyrolysis reaction. At T=3.124s, the droplet diameter is 1026.4μm, which is consistent with the experimental results in 2.1. At T=6.248s, the droplet diameter is 881.2μm. At the same time, white smoke can be observed, and At T=11.214s, the diameter is 427.8μm, and kept until T=16.082s. From T=6.248s to T=16.082s, the droplet pyrolysis reaction has been carried out, but the pyrolysis rate is lower than other experiments under the same conditions. After T=16.082s, the pyrolysis reaction ceased.

The reason for the analysis is that the droplet position is shifted during the pyrolysis process, and the laser heating region is separated, and the urea solute is cooled by the heat to form an intermediate product. The experimental results are consistent with the phenomenon that a large amount of sediment is accumulated in the bottom of the pyrolysis furnace during the operation of the project. The precipitate is an intermediate product generated during the pyrolysis process, which may have many adverse effects, such as blocking the gas circulation passage and reducing the reliability of the SCR denitrification device.

![Figure 5. Sediment of urea solution have single droplet pyrolysis process](image-url)
Based on the experimental results, this paper guides the design of urea pyrolysis unit for a 2 × 58MW coal-fired boiler in a thermal power plant. After the system is put into operation, the denitrification efficiency reaches over 90%, and the engineering application effect is remarkable.

3. Development and design of urea pyrolysis system

3.1. Project Overview
This project is a thermal power plant 2×58MW coal-fired boiler, boiler inlet denitration device inlet parameter design: the unit full load flue gas flow is 126000 Nm\(^3\)/h, flue gas temperature 360°C, gray fly concentration is 3g/Nm\(^3\), NOx concentration is 450mg/Nm\(^3\), wherein the O\(^2\) content is 6% and the SO\(^2\) concentration is 990 mg/Nm\(^3\). The SCR inlet flue gas component content was calculated from the above data (Table 1).

| Tab.1 SCR Inlet flue gas composition
|---------------|----------|-------------|
| project unit | numerical value |
| Boiler outlet flue gas flow | Nm\(^3\)/h | 145040 |
| O\(_2\) content in flue gas | vol\% | 3.92 |
| SO\(_2\) content in flue gas | vol\% | 0.04 |
| CO\(_2\) content in flue gas | vol\% | 13.28 |
| H\(_2\)O content in flue gas | vol\% | 8.75 |
| Inlet flue gas NOx | mg/Nm\(^3\) | 508 |
| Outlet flue gas NOx | mg/Nm\(^3\) | 152 |
| NH\(_3\) escape amount | ppm | 3.05 |

3.2. Pyrolysis process
The project adopts the arrangement scheme of high temperature and high dust, that is, the SCR reactor is arranged between the high temperature air preheater of the boiler and the low temperature economizer, and above the flue of the furnace. The ammonia flow is adjusted by monitoring the inlet and outlet nitrogen oxide concentrations in real time to meet engineering operational requirements.

When urea is used as a reducing agent, its quality should meet the requirements of the technical specifications of the urea standard [3] (national standard GB 2440-2001). According to the experimental conclusion, the ratio of urea to water is 1:1, and the concentration of urea solution is 50%.

3.3. Spray gun design
The urea spray gun is a key component of the urea pyrolysis system, and its atomization performance directly affects the rate and efficiency of urea pyrolysis. The pyrolysis rate of urea solution mainly depends on the following factors: solution concentration, pyrolysis energy, droplet diameter. According to the conclusion of the literature [2], the droplet diameter has the greatest influence on the pyrolysis rate, followed by the pyrolysis energy, and the solution concentration has the weakest influence. The diameter of the droplet depends entirely on the structure and type of the gun.

After the urea solution is atomized by the spray gun, it is broken into a large number of tiny diameter droplets, which greatly increases the evaporation surface area of the solution, increases the contact area with the surrounding hot air, and greatly improves the solution evaporation and urea solute pyrolysis rate and efficiency. In order to systematically evaluate nozzle atomization droplet characteristics, Lefebvre[6]-[7] proposed a number of metrics, including: average droplet diameter, atomization uniformity, atomization range, spray cone angle, atomization efficiency. Etc. where the average diameter of the droplets and the diameter distribution are the most important parameters [6]-[7].

Incorporating the atomization ability and economy of various nozzles, the bubble type two-fluid atomizing nozzle was selected as the urea solution spray gun of this project. After repeated
commissioning on site, the pressure of compressed air was selected from 0.75 MPa ~ 1 MPa to obtain better atomization effect.

(a) Spray gun not compressed air          (b) Spray gun into the compressed air

Figure 6. Spray gun spray effect

3.4. Pyrolysis furnace body design

3.4.1. Mixed gas flow rate and ammonia concentration calculation. The urea solution droplets in the pyrolysis furnace are evaporated by heat and pyrolyzed. The main reaction is:

Urea aqueous solution evaporates and precipitates urea particles:

\[(\text{NH}_2\text{C})_2\text{CO} \cdot 7\text{H}_2\text{O(aq)} \rightarrow (\text{NH}_2)_2\text{CO(s)} + 7\text{H}_2\text{O(g)}\]  (1)

Pyrolysis of urea produces equimolar ammonia and isocyanic acid:

\[(\text{NH}_2)_2\text{CO} \rightarrow \text{NH}_3 + \text{HNCO}\]  (2)

Further hydrolysis of isocyanic acid to form equimolar ammonia and carbon dioxide:

\[\text{HNCO} + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{CO}_2\]  (3)

At high temperatures, when water is present, the following reaction will occur:

\[(\text{NH}_2)_2\text{CO} + \text{H}_2\text{O} \rightarrow 2\text{NH}_3 + \text{CO}_2\]  (4)

The above formula shows that urea reacts mainly in the pyrolysis furnace to produce NH$_3$ and carbon dioxide [8]. Theoretically, 28.3 kg of ammonia gas can be produced per 100 kg of 50% urea solution.

After urea pyrolysis, the pressure in the pyrolysis furnace is measured by atmospheric pressure, the temperature is taken from the outlet temperature of the pyrolysis furnace at 385°C, the flow rate of the urea solution injected into the pyrolysis furnace is $Q_l=69$ kg/h, and the dilution air is taken at the inlet temperature of the electric heater at 50 °C. The pyrolysis furnace inlet temperature is 430°C, the flow rate $Q_g=860$ m$^3$/h, the solution concentration is 50%, then the urea mass in the solution is $m_{\text{urea}}=34.5$ kg, and the urea molecular weight is 60.06. It is calculated that the gas volume increases by 8.01% after injection into the urea solution, and the volume fraction of ammonia gas is 2.78%. Therefore, the gas flow rate in the urea pyrolysis section furnace is 2086.09 m$^3$/h, that is, the flow rate is $Q=0.579$ m$^3$/s.

3.4.2. Pyrolysis furnace empty tower flow rate and pyrolysis furnace inner diameter calculation. The interaction between the urea solution droplets and the hot air in the pyrolysis furnace is divided into three stages of mixing, evaporation and pyrolysis. The flow rate of the pyrolysis furnace empty tower is $v=0.5$ m/s, and the pyrolysis furnace is calculated in 3.4.1. The mixed gas flow rate $Q = 0.779$ m$^3$/s.
Pyrolysis furnace cross-sectional area is:

\[ S = \frac{Q}{V} = 1.158 \text{m}^2 \]

The inner radius of the pyrolysis furnace is:

\[ r = 0.607 \text{m} \]

3.5. Engineering Applications

After the system is commissioned, run stably for a period of time, and take the system 24h operation record. The SCR inlet temperature is about 350 °C, the inlet NO\textsubscript{x} concentration is 200mg/Nm\textsuperscript{3}, and the outlet NO\textsubscript{x} concentration is 20mg/Nm\textsuperscript{3}. The SCR denitration efficiency is 90%. The engineering application shows that the urea pyrolysis system is stable in operation, the parameters of each operation index are stable, and the SCR outlet NO\textsubscript{x} concentration is lower than the ultra-low emission requirement \((\leq 50 \text{mg/Nm}^3)\), and the engineering application effect is remarkable.

![Figure 7. SCR inlet NO\textsubscript{x} concentration](image)

![Figure 8. SCR outlet NO\textsubscript{x} concentration](image)

4. Conclusion

Experiments show that the diameter of urea droplets has a significant effect on the pyrolysis rate. The spray gun device in the injection system is a key component, and the degree of atomization directly affects the pyrolysis efficiency. At the same time, the droplets of urea containing bubbles are compared to the heat of droplets without bubbles, The solution process is much more rapid and intense because the bubble expands and ruptures during heating, increasing the heated area of the urea droplets, and the large amount of bubbles in the droplets is very favorable for the pyrolysis reaction. Insufficient pyrolysis energy and atomization of the urea solution will result in incomplete pyrolysis reaction, intermediate products, experimental results and engineering operations confirm the existence of the intermediate product, greatly reducing the reliability and denitration efficiency of the SCR denitration device, This should be avoided. Based on the experimental data, guide the design of urea pyrolysis system, including
urea storage and supply system, denitration reactor system, spray gun device, pyrolysis furnace body, etc. The system operation is stable and reliable, and the export NOx concentration is lower than the ultra-low emission requirement ($\leq 50\text{mg/Nm}^3$), the SCR denitration efficiency is up to 90%, and the engineering application effect is remarkable.

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