
Original Research Article

Analysis of denitrification reduction of liquid ammonia to urea process

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Abstract: With the improvement of environmental protection and safety requirements, the denitrification reduction of liquid ammonia to urea conversion project in power plants is in full swing. This article describes the necessity of converting liquid ammonia to urea, explains the process principle of urea to ammonia, analyzes the advantages and disadvantages of urea pyrolysis to ammonia and hydrolysis to ammonia, and draws relevant conclusions, providing theoretical support for the denitrification reduction of liquid ammonia to urea conversion process in coal-fired thermal power plants.

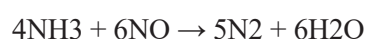
Keywords: Denitrification process; Urea to ammonia technology; Process analysis

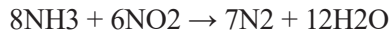
1. Introduction

The energy structure of “rich coal, poor oil, and little gas” has led to an increasing expansion of the capacity of coal-fired power generation units, and the emissions of sulfur oxides and nitrogen oxides from coal-fired power plants are the main sources of air pollution. Liquid ammonia, as a commonly used reducing agent in coal-fired flue gas denitrification, poses serious safety hazards due to its low boiling point, flammability, and transportation restrictions. With the increasingly strict national requirements for the emission standards of nitrogen oxide pollutants and the introduction of relevant policies by the National Energy Administration, the requirements for the safe disposal of hazardous chemicals in the power industry are becoming more and more severe. It is required to use urea as a reducing agent to replace the primary and secondary major hazards of liquid ammonia in coal-fired power plants, improve denitrification safety, and reduce management risks.

2. The necessity of renovating the flue gas denitrification ammonia area in coal-fired power plants

Selective catalytic reduction (SCR) is widely used in industry due to its high denitrification efficiency. The basic principle is to use NH₃ to reduce NO_x in flue gas, ultimately converting it into nitrogen and water that are non-toxic and harmless to the atmosphere and human body. To promote conversion efficiency and reduce reaction temperature, a specialized solid catalyst is installed in the flue gas to allow the reduction reaction to occur on the surface of the catalyst. The commonly used reducing agents in the denitrification system of power plants include ammonia water, liquid ammonia, and urea. Ammonia is the main reducing agent directly involved in the reaction in SCR technology. In the preparation of ammonia, the technology of using liquid ammonia to produce ammonia has a simple process and low investment and operating costs. It is the mainstream technology route for reducing agent preparation in SCR systems in China. The mechanism of NH₃-SCR denitrification is as follows:





With the increasingly strict national requirements for safe operation, the drawbacks of ammonia as a reducing agent are becoming more and more prominent. The high toxicity, pungent odor, low boiling point (about $-33.4\text{ }^\circ\text{C}$), flammability and other physical properties make liquid ammonia a significant hazard source as an SCR flue gas denitrification reducing agent. According to the Identification of Major Hazardous Sources (GB18218-2009), when the storage capacity of liquid ammonia production sites exceeds 10 tons, it is considered a major hazardous source. Meanwhile, gaseous ammonia can severely irritate the skin and respiratory tract, and inhalation can easily cause headaches, dizziness, and even suffocation. In addition, ammonia can cause corrosion of equipment, pipelines, etc., leading to the occurrence of liquid ammonia accidents and posing significant safety hazards. Therefore, in order to ensure the personal safety of staff and the safe operation of power production, and to achieve sustainable and stable development of coal-fired power plants, it is necessary to eliminate the above safety hazards.

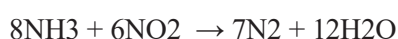
With the increasingly tight policies related to environmental protection and hazardous material safety management, the emission control of coal-fired power plant flue gas is becoming stricter. On the other hand, due to the control of major hazard sources, the use of denitrification reducing agent liquid ammonia is subject to more restrictions. Therefore, the renovation of the denitrification ammonia area project in coal-fired power plants is urgently needed. Among them, urea pyrolysis and hydrolysis to produce ammonia technology are gradually gaining favor. At the same time, relevant policies of the National Energy Administration encourage power plants to transform liquid ammonia plants into safer urea to ammonia plants. The conversion of liquid ammonia to urea has become a widely recognized flue gas denitrification engineering technology route.

3. Urea to ammonia process

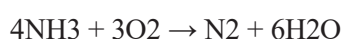
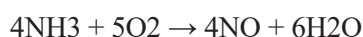
Urea is a white or pale yellow crystal that is easily soluble in water, with the chemical formula $\text{CO}(\text{NH}_2)_2$, a nitrogen content of about 46.7%, and a melting point of $132.7\text{ }^\circ\text{C}$. Urea has poor thermal stability and can generate biuret when heated. Rapid heating can decompose it into NH_3 and CO_2 . When urea is used as a reducing agent, it can be divided into urea direct injection and decomposition to produce ammonia based on its different usage methods. According to the different decomposition mechanisms and processes, urea decomposition to produce ammonia can be further divided into urea hydrolysis to produce ammonia and urea pyrolysis to produce ammonia.

3.1. Direct injection of urea to produce ammonia

Direct injection of urea to produce ammonia belongs to selective non catalytic reduction (SNCR) denitrification technology, which does not require the use of catalysts. The urea solution is directly injected into the furnace, and after pyrolysis, the urea will quickly decompose to obtain NH_3 . NH_3 reacts directly with NO_x to generate N_2 and water, which are non-toxic and harmless to the atmosphere and human health. In this process, the denitrification reaction temperature is relatively high, around $800\text{-}1200\text{ }^\circ\text{C}$. During the SNCR reaction, the NH_3 obtained from the decomposition of urea not only participates in the reduction process of NO_x , but also excess NH_3 is re oxidized to NO_x . The reaction process is as follows:



At the same time as the above denitrification process occurs, excess NH_3 will also undergo the following reactions:



Based on the above reaction process, the denitrification efficiency of urea direct injection ammonia production is limited by multiple factors, including temperature, retention time of urea solution in the furnace reaction zone, proportion of ammonia nitrogen, and so on. Research has found that the optimal molar ratio of NH_3 to NO_x is 1-2, and when the residence time of urea solution is 1 second, the denitrification rate can reach 82%.

3.2. Urea decomposition to produce ammonia

The production of ammonia by urea decomposition is divided into hydrolysis and pyrolysis.

Urea hydrolysis to produce ammonia is the process of dissolving urea in water to form a solution with a concentration of approximately 40-50%. The hydrolysis reaction occurs under high temperature, high pressure, or catalytic conditions, producing NH_3 , CO_2 , and water vapor.

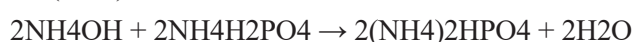
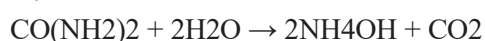


There are two commonly used methods for urea hydrolysis to produce ammonia: conventional hydrolysis and catalytic hydrolysis. Conventional hydrolysis to produce ammonia can be seen as a reverse reaction for preparing urea, and urea solution is usually recovered and utilized in the field of fertilizers. The hydrolysis reaction is a strongly endothermic reaction, mainly divided into two steps:



This process generally uses steam indirect heating, with a temperature and pressure of 150 °C and 0.6MPa respectively during operation. However, the reaction rate of this process is slow, resulting in a corresponding slow change in the unit. Due to the low temperature saturated steam pressure obtained by the urea hydrolyzer being recyclable, the energy consumption level of this process is relatively low. The hydrolysis reactor is the core of this process, used for urea hydrolysis to produce ammonia gas^[5]. A urea solution with a concentration of about 50wt% and a temperature of about 50 °C is transported from the urea solution storage tank to the urea hydrolysis reactor through a urea solution circulation device. The hydrolysis reaction is carried out at a temperature of 130 °C to 160 °C and a pressure of 0.4MPa to 0.6MPa to generate a mixture of NH_3 and CO_2 . The urea hydrolysis reactor includes all valves, pipelines, instruments, and steam tracing control systems connected to the hydrolysis module and the hydrolysis reactor body (each pipeline has steam blowing and steam/electric tracing). Currently, representative urea hydrolysis reactor production design units in China are Sichuan Chengguang, Chengdu Ruisi, Xi'an Thermal Power Institute, etc.

Another type of catalytic hydrolysis for ammonia production is to add a catalyst during the process of urea hydrolysis, mainly consisting of $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ components. Due to the action of the catalyst, the hydrolysis reaction route is changed, greatly improving the urea hydrolysis rate. The reaction rate is more than 9 times that of conventional hydrolysis rate, and the catalyst can be recycled and reused^[6]. The reaction pathway is as follows:

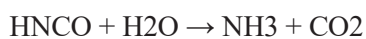
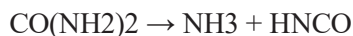




Catalytic hydrolysis for ammonia production has a faster reaction rate and higher responsiveness to the demand for urea and ammonia, which can alleviate the problem of equipment pipeline blockage to a certain extent. However, the proportion of catalyst components in this process technology is a commercial secret in China, which has a significant impact on the large-scale use of catalysts. Urea catalytic hydrolysis is widely used in power plants under Datang Group. Representative companies in the domestic catalytic hydrolysis process include Datang Environment and Beijing Xinye.

The advantages of urea hydrolysis for ammonia production mainly include: (1) it can solve safety hazards such as storage, transportation, and leakage in processes such as liquid ammonia and gas ammonia. (2) The hydrolysis ammonia production system occupies a small area, about 1/4-1/2 of the liquid ammonia evaporation system, reducing investment costs. (3) The operating temperature of the hydrolysis ammonia production system is relatively mild, the reaction is safer, and the energy consumption cost is reduced. However, there are also some drawbacks in the process of hydrolysis to produce ammonia. For example, during the operation of this process, the operating temperature cannot exceed 165 °C, otherwise the equipment will be severely corroded; At the same time, temperature control and detection of the pipeline should be carried out to avoid crystallization of the superheater and blockage of the pipeline, which may cause safety accidents.

The process of urea pyrolysis for ammonia production is to directly spray urea solution into a high-temperature pyrolysis chamber. Urea is decomposed into gaseous NH₃, CO₂, and water vapor by heating, and then gaseous NH₃ is injected into the SCR denitrification system. The heat source of the high-temperature pyrolysis chamber can be injected through high-temperature hot air or directly heated and introduced using a burner^[7]. Urea is unstable at high temperatures, and its thermal decomposition reaction is as follows:



In the process of urea pyrolysis for ammonia production, the decomposition temperature of the high-temperature pyrolyzer can reach up to 330-650 °C, resulting in high energy consumption and low utilization rate of urea. Urea decomposition can be achieved by preheating and reheating the boiler air, thereby reducing energy consumption. However, during the operation of the pyrolysis system, due to the need for a stable heat source, dust may adhere to the surface of the electric heater, affecting the heat transfer efficiency; The outlet of the pyrolyzer is prone to crystallization, and the urea spray gun is prone to blockage, requiring regular cleaning and testing.

In addition, the pyrolysis reaction is greatly affected by the ambient temperature inside the pyrolysis furnace. At low temperatures, intermediate products such as cyanuric acid, melamine, diisocyanate, glyoxime, biuret, and triamide are generated, which can easily combine with dust in the hot air to form porous crystalline substances that are difficult to decompose, causing equipment blockage and reducing the efficiency of urea pyrolysis conversion. In addition, the HNCO formed during the pyrolysis process is difficult to decompose into NH₃ under the atmospheric conditions of the pyrolysis furnace, so the urea conversion rate of the pyrolysis process is limited to a certain extent, generally ranging from 80% to 90%^[8].

4. Safety and economic analysis of liquid ammonia to urea conversion

Liquid ammonia is a highly corrosive volatile substance with a colorless, toxic, and pungent odor. When its vapor is mixed with air and exposed to open flames or high temperatures, it can easily cause combustion and explosion, with an explosion limit of 15% -28%. When liquid ammonia is used as a denitrification reducing

agent, it is prone to ammonia leakage and poses a serious safety hazard. Ammonia vapor has strong corrosiveness to eyes, skin, respiratory tract, etc. When the concentration of ammonia in the air reaches 0.5%, it can be fatal if inhaled in a short period of time. At the same time, the storage, loading and unloading, transportation and other requirements for liquid ammonia are strict, with strict fire separation distance requirements between equipment, workshops and roads, and workshops and external workshops, resulting in a large footprint and increased investment costs for the entire process. Urea is not a hazardous chemical, and its storage and use process is safer, without producing toxicity or strong corrosiveness. The cost of urea is relatively low compared to liquid ammonia, which can reduce cost investment. However, the investment cost of renovation projects is high, and the energy consumption of pyrolysis to produce ammonia is high. Whether using liquid ammonia or urea as reducing agents, the maintenance costs are comparable, and the consumption of steam, water, etc. is also similar. The procurement cost and operating electricity cost of reducing agents are the main expenses. Therefore, controlling the cost of reducing agents and the electricity cost consumed is the key to controlling the production cost of denitrification.

5. Conclusion

With the increasing tightening of environmental policies, it is an inevitable trend for coal-fired power plants to convert flue gas from denitrification to ammonia to urea. More and more power plant denitrification to ammonia to urea projects have been carried out vigorously. The use of urea as a reducing agent has high safety, relatively simple production and operation processes, relatively small pollution and corrosion, and reduced management costs. Although the initial construction investment is high and the operating cost increases significantly, it can eliminate major hazards from the source of raw materials and reduce the risk of liquid ammonia leakage causing casualties to surrounding personnel, achieving the intrinsic safety of denitrification equipment operation in coal-fired power plants.

About the author

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