

Non-thermal plasma for simultaneous NO_x and SO₂ removal from coal-combustion flue gas

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In the laboratory, NO_x and SO₂ were removed from simulated flue gas using a plasma generator. Under normal temperature conditions, the efficiencies of desulfurization and denitrification exhibited a linear relationship with plasma input power. Dielectric barrier discharge equipment was used in the mode in which flue gas was directed through the discharge zone (direct oxidation) or that in which ozonized air was produced and injected into the flue gas stream (indirect oxidation). The SO₂ and NO_x removal efficiencies of both methods were measured and compared. Based on the experimental results, the desulfurization and denitrification efficiencies achieved using the indirect plasma were better than those achieved using the direct plasma.

Keywords: non-thermal plasma generator, denitrification, desulfurization, energy consumption

AIMS AND BACKGROUND

In recent years, coal consumption has increased by 2.2% annually, faster than that of any other type of fuel. It is anticipated that coal consumption will continue to increase until 2030. In fact, this increase in consumption will probably exceed 70% compared with the present value, with developing countries contributing 97% of this increase. By 2030, the global rate of coal use for power will increase from 40% to 45% [1]. Burning coal will release large quantities of SO₂ and NO_x, which will negatively impact air quality, produce haze, generate acid rain, severely pollute the environment, and have detrimental effects on health [2]. Controlling the discharge of SO₂ and NO_x in flue gas effectively and economically is an important strategic issue relating to sustainable development. Increasingly stringent global emission standards are inspiring researchers worldwide to exploit new technologies and develop new methods for desulfurization and denitrification. SO₂ and NO_x coexist in flue gas. However, there are no reliable chemical methods to remove these gases via a one-stage process. Therefore, it is necessary to develop new methods for simultaneous desulfurization and denitrification [3-4]. Currently, domestic and foreign research efforts have achieved breakthrough, and many advanced control technologies have been developed, including desulfurization using clean coal, desulfurization

and denitrification using ovens, desulfurization and denitrification in flue gas, desulfurization and denitrification using an electron beam in flue gas, desulfurization and denitrification in flue gas by pulsed plasma, and desulfurization and denitrification by non-thermal plasma [5-6]. Among these, non-thermal plasma technology, a new technology with great promise, is the most popular one studied currently regarding controlling SO₂ and NO_x. Non-thermal plasma is used to remove SO₂ and NO_x because NO_x can be oxidized and SO₂ can be transformed into its acid products, which can then be neutralized by mixing with NH₃. This process generates solid sulfate and ammonium nitrate, which can be subsequently recycled as agricultural fertilizers [7].

In the 1980s, scholars worldwide began to study the use of cheaper non-thermal plasma technology to replace the relatively expensive electron accelerator devices. Pulsed corona discharge plasma flue gas treatment technology is one of the most pursued research directions globally. Japanese scholars have reported that applying pulsed plasma to flue gas can achieve desulfurization and denitrification simultaneously. Based on the electron beam method, they devised a pulsed corona method to produce the plasma, which uses a high-voltage pulsed power supply to replace the electron beam accelerator, and demonstrated the effectiveness of this technique. The pulsed corona method can achieve desulfurization and denitrification simultaneously and collect dust. This technique requires only simple equipment, its operation is easy, and it is substantially cheaper

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than electron beam irradiation. Furthermore, its by-products can be used as fertilizers, and the method does not produce secondary pollution. Therefore, it has attractive prospective applications in research addressing how to mitigate gaseous pollutants. However, this method must overcome one difficulty: how to realize easy control over a high-power, high-voltage pulsed power supply [8]. This article focuses on comparing the use of direct and indirect non-thermal plasma to achieve desulfurization and denitrification in terms of efficiency. Additionally, the efficiency of denitrification alone is compared with that of simultaneous desulfurization and denitrification when non-thermal plasma is used. Finally, the relationship between the energy consumption of the plasma generator and the efficiency of denitrification is determined to facilitate finding a way to reduce energy consumption and thus promote industrialized applications of this technology.

EXPERIMENTAL

Plasma generator

The entire body of the generator was constructed of stainless steel. The discharge area was 150 mm in length and contained a 3-mm space (single-sided). The medium tends to resist the discharge process when the space is smaller and the input and discharge voltages are lower. The thickness of the resistance medium also affects the electrodes' discharge to some extent. The components had the following dimensions: steel pipe: 25mm × 20mm; gear-shaped electrode core: 10 mm; and diameter of the raised stand: 14 mm. The structure and dimensions of the generator are shown in Figure.1.

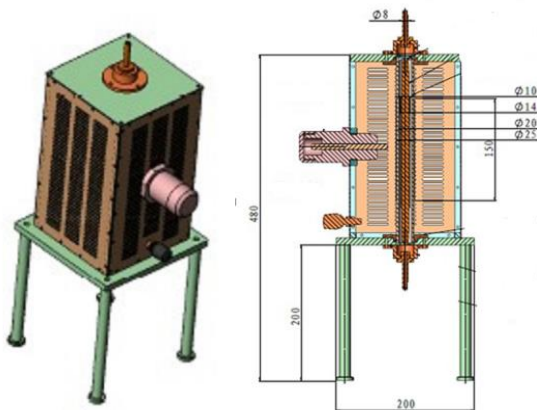


Fig. 1. Structure of the generator.

Experimental platform

(1) Gas supply system. The simulated flue gas used in the experiment consisted of N₂, O₂, NO,

NH₃, and SO₂. NO accounts for more than 95% of NO_x produced by coal-burning power stations, and the NO₂ content is only 5%; thus NO₂ exerts little influence on the behavior of the flue gas. Because NO₂ can be neglected, NO is typically used to model NO_x in experimentally simulated flue gas from power stations [9–10]. The flow of gas in the steel cylinder is controlled with a rotameter. The gas is first mixed in the commingler, and then, the uniform gas enters the tabulation and is preheated. The NH₃ enters the tabulation and subsequently reacts as the tabulation is heated. The basic information about the simulated flue gas is presented in the following table (Table 1):

The NO-removal efficiency was calculated as follows (equation (1)):

$$\text{The efficiency of removing NO(\%)} = \frac{\text{The concentration of NO at entrance} - \text{The concentration of NO at exit}}{\text{The concentration of NO at entrance}} \times 100\% \quad (1)$$

Every gas is fully mixed after entering the commingler. Then, they react with free radicals, and O₂ and steam react when passing through the exit of the plasma generator. This process is known as indirect non-thermal plasma desulfurization and denitrification. The system is shown in Figure.3.

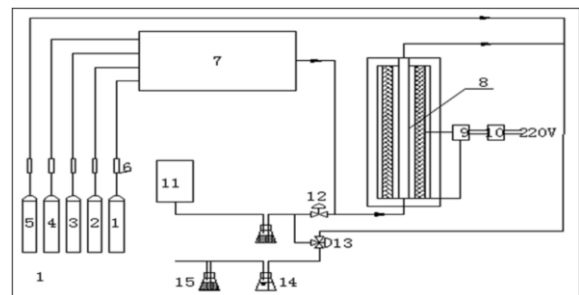


Fig. 2. The system used for direct non-thermal plasma desulfurization and denitrification.

1-O₂ cylinder, 2-SO₂ cylinder, 3-N₂ cylinder, 4-NO cylinder, 5-NH₃ cylinder, 6-flow counter, 7-gas mixer, 8-plasma generator, 9-plasma electric source, 10-voltage transformer, 11-gas analysis equipment, 12-valve, 13-three-way valve, 14-inverted bottle, and 15-dry bottle

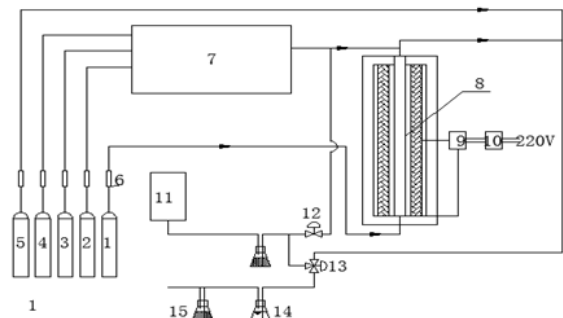


Fig. 3. The system used for indirect non-thermal plasma desulfurization and denitrification. 1-O₂ cylinder, 2-SO₂ cylinder, 3-N₂ cylinder, 4-NO cylinder, 5-NH₃ cylinder, 6-flow counter, 7-gas mixer, 8-plasma generator, 9-plasma electric

source, 10-voltage transformer, 11-gas analysis equipment, 12-valve, 13-three-way valve, 14-inverted bottle, and 15-dry bottle.

Table 1. The basic information of the experimental flue gas.

Parameter	Temperature	Initial concentration of NO	Initial concentration of SO ₂	Flow of the simulated flue gas
Numerical value	20°C	380ppm	500ppm	500ml/min

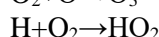
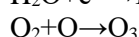
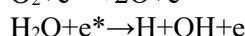
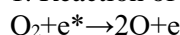
(2) Gas analysis system. Using online gas analysis equipment (MGA-5, MRU, Germany) allowed online measurement of the densities of NO, NO₂, SO₂, NH₃, CO, and O₂ with an accuracy of ±1 ppm. Once inserted, a gas-sampling pump extracted sample gas from the flue through the sampling pipe and tube. After the sampled gas was dehydrated and desooted using a gas-water filter, the inserted electrochemical sensor determined the density of each component gas. The oxygen content of the sample was measured using a two-electrode electrochemical sensor. Toxic gases, such as CO, NO, NO₂, SO₂, and H₂S, were analyzed using a three-electrode sensor. The electrochemical sensors utilized gas-diffusion technology. The advantage of this technique is that the output signal is proportional to the volume concentration (or ppm) of the analyzed gas. The three electrodes included the sensing electrode (S), counter electrode (C), and reference electrode (R). When the gas of interest reaches the sensing electrode, an oxidation or a reduction reaction occurs on the surface of the electrode, and the concentration of the gas can be obtained by measuring the resulting current (μA) and subjecting the signal to microprocessor processing.

Reaction mechanism [11-13]

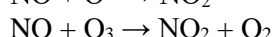
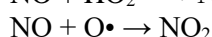
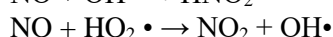
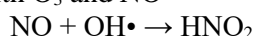
Plasma was first studied in 1808 by Davy, and in the 1930s, Langmuir proposed the concept of "plasma". Gas that is ionized at high voltage is called plasma. More specifically, plasma consists of gas that is ionized, for example, by electric discharge and heat release. When the number of particles is sufficient, plasma is formed by the particles containing electrons, ions, and atoms. The number of positive charges is equal to the number of negative charges in plasma, and it is an electrically conductive fluid. Plasma has conductive and electromagnetic characteristics, and its activity is very strong. In many ways, it is different from solids, liquids, and gases. Therefore, it is known as the fourth state of matter [14]. Dielectric barrier discharge (DBD) non-thermal plasma is a high-pressure, low-temperature, and

non-equilibrium plasma. Because it can be generated at atmospheric pressure or higher, it can obtain the active particles required to induce chemical reactions without the need for vacuum equipment. It exhibits unique light-, heat-, sound-, and electricity-related physical and chemical processes, the distance between the DBD electrodes is several millimeters, and it generates high concentrations of free radicals (O•, OH•, and HO₂•). These free radicals react with NO_x and SO₂ and result in desulfurization and denitrification. The relevant chemical reactions are as follows:

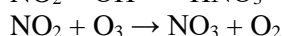
1. Reaction of wet air in a plasma reactor



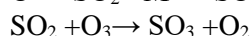
2. Reaction of free radicals (O, OH, and HO₂) with O₃ and NO



3. Further reaction of free radicals, O₃, and NO₂ generated by the reaction between the free radicals and O₃



4. Reaction of free radicals (O, OH, and HO₂), O₃, and SO₂



RESULTS AND DISCUSSION

Analysis of NO_x removal from flue gas by non-thermal plasma

When the simulated flue gas contained only N₂, O₂, and NO and the flow rate was 500 ml/min, the NO concentration in the inlet was generally controlled at 400 ppm, the plasma generator input voltage was 15 V, the generator initiates the discharge, the maximum voltage is 40 V, and the current is 1.3 A. The NO_x-removal efficiencies of

the experimental low-temperature plasma reactor at different power levels are shown in Figure.4.

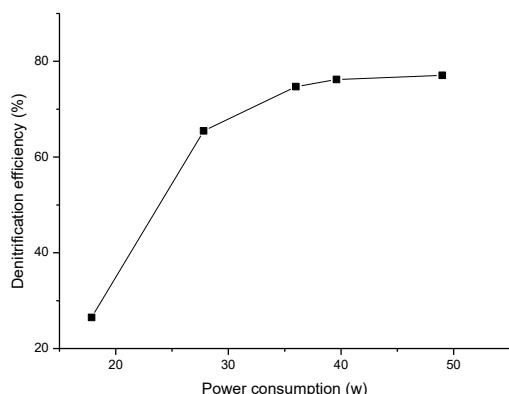


Fig. 4. Analysis of NOX removal from flue gas by non-thermal plasma.

The removal efficiency of the catalyst improved continually as the plasma input power increased. The removal efficiency exceeded 80% when the input power exceeded 35 W and reached 91.7% when the input power was 52.8 W. The removal efficiency was positively proportional to the input voltage and current; however, the increase in the removal efficiency was not large. When the voltage reached a certain level and the dielectric barrier discharge was disrupted, the removal efficiency decreased sharply.

Denitrification efficiency under simulated increased flow of flue gas

As shown in Figure.5, the denitrification efficiency increased in the context of a simulated increase in flue gas flow.

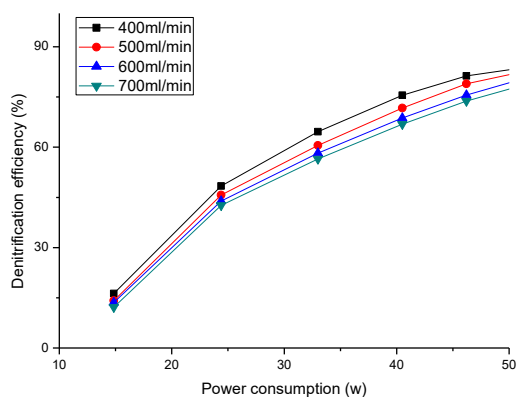


Fig. 5. Analysis of the denitrification performance as the flow is varied.

As the flue gas flow increased, the denitrification efficiency decreased. Relative to the power consumption under the same plasma reactor

conditions, the denitrification efficiency decreased by 10%, and the reaction mechanism of the plasma remained constant. Breaking more molecular bonds requires the consumption of more energy; hence, energy is conserved. Figure 5 shows the flue gas denitrification efficiencies of four different simulated flows under the same input voltage and current conditions. As the flow increased, the denitrification efficiency decreased; the top curve shows the minimum tested flow and its denitrification efficiency.

Analysis of simultaneous desulfurization and denitrification via direct oxidation

The experimentally determined removal efficiencies of simultaneous desulfurization and denitrification are shown in Figure6.

Relative to denitrification alone, the addition of SO₂ substantially influenced the removal efficiency, although the effect varied. When the input power of the reactor increased to 66 W, the denitrification efficiency was only 24.1%, as shown by the top curve of the figure above. However, increasing the input voltage to 40 V greatly affected the discharge reaction. Initially, in the discharge plasma reactor, the denitrification efficiency is very low, while before and after the test reactor, the SO₂ density is almost constant, as shown in the bottom curve in the figure above. Thus, little to no effect was observed in terms of SO₂ removal, whereas a huge effect was observed on the NO-removal performance. Several underlying reasons are possible: 1. SO₂ could inhibit the generation of O₃. 2. Previous research has shown that SO₂ consumes OH [15], which could limit the supply of OH available to react with NO [3]. The mixed gas could inhibit plasma discharge.

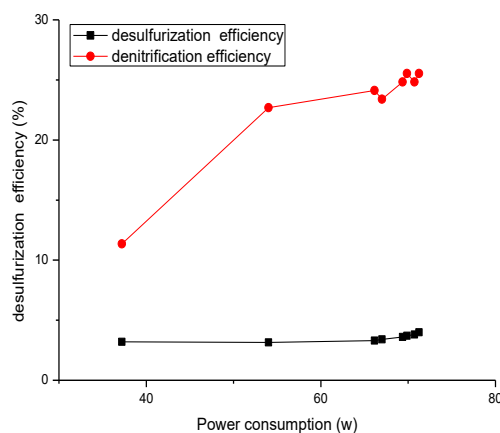


Fig. 6. Analysis of the removal efficiencies of simultaneous direct desulfurization and denitrification.

Analysis of simultaneous desulfurization and denitrification via indirect oxidation

The experimentally determined efficiencies of indirect simultaneous desulfurization and denitrification are shown in Figure 7. When the input voltage was 15 V, the reaction began in the discharge plasma reactor, and the reactor input power was 18.9 W. Then, the input voltage was increased to 23 V, the input power became 33.81 W, the flow of gas into the reactor was 500 mL/min, the initial NO concentration was 380 ppm, and the initial SO₂ concentration was 500 ppm to ensure high denitrification efficiency.

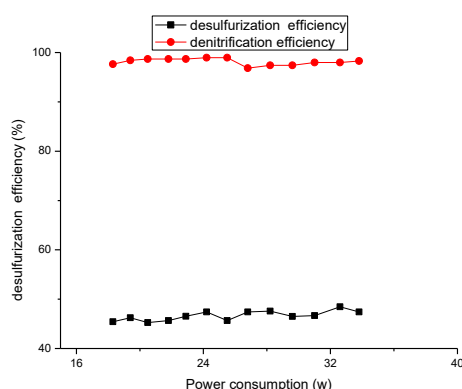


Fig. 7. Analysis of the removal efficiencies of simultaneous indirect desulfurization and denitrification.

The above figure shows that initially, the denitrification efficiency is very high (above 97%), while the desulfurization efficiency is 46%. This is different from the results observed for simultaneous direct desulfurization and denitrification, for which the desulfurization efficiency is very low. In the direct technique, the concentration of NO was controlled, and the input power was increased until the low-temperature plasma reactor achieved a high voltage, resulting in disruption of the desulfurization and denitrification efficiency. In contrast, indirect desulfurization and denitrification requires only input voltage supplied to the DBD, and even when the input power is low, this technique can achieve very efficient denitrification and desulfurization. According to its reaction mechanism, indirect desulfurization and denitrification in a plasma generator generates O₃, which reacts with and removes SO₂ and NO. However, $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ generates a large quantity of NO₂, which has a high activity. Therefore, this technique requires additional measures (the addition of a reducing agent or adsorbent) to remove NO₂ and thereby truly achieve denitrification.

Effect of NH₃ on denitrification performance

The addition of NH₃ somewhat improved the denitrification efficiency when the conditions were otherwise the same. The denitrification efficiency with and without NH₃ is plotted in Figure 8.

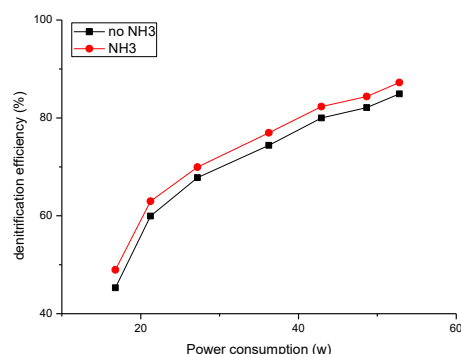


Fig. 8. Comparison of the denitrification performance with and without NH₃.

During direct non-thermal plasma desulfurization and denitrification, the efficiency can increase, although it will decline after 5 s, as shown above. The reason the plasma reactor discharge is affected at the same time remains unknown. The generator begins to discharge when the voltage is 15 V in the absence of SO₂ and at 40 V in the presence of SO₂.

During indirect simultaneous denitrification and desulfurization, the NO-removal rate is very high, but a substantial amount of NO is converted to NO₂. However, an experimental phenomenon was observed: when the O₂ input flow is reduced, NO₂ conversion is also substantially reduced. Additionally, it was found that the N₂ and free radicals produced by the plasma generator could react to produce a large quantity of NO₂. During indirect simultaneous desulfurization and denitrification, the required input voltage is the minimum voltage able to trigger the plasma reactor discharge, and increasing the input voltage and input power increases the production of free radicals and O₃. Additionally, the efficiencies of desulfurization and denitrification are not increased but the amount of NO₂ is, as demonstrated in the analysis presented above.

CONCLUSIONS

Based on our analysis of these experimental results, the following conclusions regarding the removal of NO_x from flue gas by non-thermal plasma can be reached:

The removal efficiency exceeds 80% when the input power exceeds 35 W. The removal efficiency of the catalyst improves continually as the plasma

input power increases. When the same power consumption is maintained in the plasma reactor, the efficiency decreases. This finding is in accord with the reaction mechanism of plasma: as more molecular bonds are broken, the power consumption increases, in accordance with the conservation of energy principle. During simultaneous desulfurization and denitrification, the denitrification and desulfurization efficiencies can be very high, in addition to the reaction of free radicals with NO and SO₂, O₃ can also play an important role. Furthermore, in the indirect technique, only O₃ or H₂O need to be ionized in the reactor; thus, providing a very small voltage can generate free radicals, resulting in very low power consumption and obvious energy savings. The two methods—the direct oxidation process (where gas flows through the reactor) and the indirect oxidation process (where the reactor generates free radicals and O₃ in the flue gas) - were compared in terms of their SO₂- and NO_x- removal efficiencies. It can be concluded that the direct removal of NO was more efficient, whereas indirect SO₂ removal was more efficient. During the direct oxidation of NO, in addition to NO₂ oxidation, the reverse reaction, in which NO is transformed into NO₂, occurs. In simultaneous desulfurization and denitrification, indirect oxidation is more efficient for both denitrification and desulfurization, but the reaction of free radicals, O₃, and N₂ generates substantial quantities of NO₂, which is a serious problem. It can be safely concluded that the available NO_x-removal technologies involving

non-thermal plasma remain in the experimental stage. The industrialization of this process will require additional research effort to reduce the energy consumption and enhance the removal efficiency.

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