Non-thermal plasma for simultaneous NO\textsubscript{x} and SO\textsubscript{2} removal from coal-combustion flue gas

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In the laboratory, NO\textsubscript{x} and SO\textsubscript{2} 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 SO\textsubscript{2} and NO\textsubscript{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 SO\textsubscript{2} and NO\textsubscript{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 SO\textsubscript{2} and NO\textsubscript{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. SO\textsubscript{2} and NO\textsubscript{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 SO\textsubscript{2} and NO\textsubscript{x}. Non-thermal plasma is used to remove SO\textsubscript{2} and NO\textsubscript{x} because NO\textsubscript{x} can be oxidized and SO\textsubscript{2} can be transformed into its acid products, which can then be neutralized by mixing with NH\textsubscript{3}. 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.
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.

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 NOx 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 NOx 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.

![Figure 1. Structure of the generator.](image)

![Figure 2. The system used for direct non-thermal plasma desulfurization and denitrification.](image)

![Figure 3. The system used for indirect non-thermal plasma desulfurization and denitrification.](image)
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the experimental low-temperature plasma reactor at different power levels are shown in Figure.4.

![Graph](image-url)

**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.

![Graph](image-url)

**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.

![Graph](image-url)

**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, NO + O3 → NO2 + O2 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 NOx 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 SO$_2$, O$_3$ can also play an important role. Furthermore, in the indirect technique, only O$_3$ or H$_2$O 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 O$_3$ in the flue gas) - were compared in terms of their SO$_2$- and NO$_x$- removal efficiencies. It can be concluded that the direct removal of NO was more efficient, whereas indirect SO$_2$ removal was more efficient. During the direct oxidation of NO, in addition to NO$_2$ oxidation, the reverse reaction, in which NO is transformed into NO$_2$, occurs. In simultaneous desulfurization and denitrification, indirect oxidation is more efficient for both denitrification and desulfurization, but the reaction of free radicals, O$_3$, and N$_2$ generates substantial quantities of NO$_2$, which is a serious problem. It can be safely concluded that the available NOx-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.

REFERENCES