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The Mechanism of Denitrification by Plasma with Different Background Gases in Clearing of the Flue Gas for NO_X

Zhang Lei*†, Chen Jihao*, Sha Xiangling*, Zhang Lei, He Huibin*, Ma Zhenhua* and Yang Dan***
***School of Geology and Environment, Xi'an University of Science and Technology, Xi'an, 710054, China
****China Heavy Machinery Research Institute Co. Ltd., Xi'an, 710032, China
†Corresponding author: Zhang Lei

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ABSTRACT

The denitrification rate of NO by using dielectric barrier discharge plasma method with four different background gases, such as $N_2/NO/O_2$, $N_2/NO/O_2/NH_3$, $N_2/NO/O_2/NH_3/SO_2$ and N_2/NO was studied. The results showed that the denitrification rate of four kinds of background gas increases with the increase of power and the increase of the 20W~40W range was obvious. The NO was dislodged by active species N which was electrolysed from N_2 in the N_2/NO system. The greater the initial concentration of NO, the lower the initial denitrification rate. But the stable NO removal rate reached almost 100%. The greater the concentration of O_2, the lower removal rate of NO and show that the removal of NO was blocked by O_2 in the $N_2/NO/O_2$ system. Compared to the N_2/NO system, the denitrification rate was decreased when added O_2 in the system. The higher the concentration of NH_3, the higher denitrification rate in the $N_2/NO/O_2/NH_3$ system. And the NO was removed by NH and NH_2 that was electrolysed from NH_3. The removal rate was significantly improved compared with the $N_2/NO/O_2$ system. The competitive existence between SO_2 and NO in the electrolysis reaction, resulted the denitrification rate decrease in the $N_2/NO/O_2/NH_3/SO_2$ system. And the greater the concentration of SO_2, the lower the denitrification rate of NO.

INTRODUCTION

The fossil fuel combustion producing toxic and harmful gases such as haze and photochemical smog, etc., has caused the regional compound pollution with the acceleration of the process of industrialization (Zhang et al. 2015a). Nitrogen oxide in flue gas is highly active and highly oxidizing which is the key pollutant in the air pollution. It is highly favoured as the plasma technology has the characteristics of electric conduction and electromagnetic effects and highly active. The study found that it is different from solid, liquid and gaseous in many ways and has high energy electrons and other particles that are close to room temperature (Yu et al. 2009). At present, its application mainly includes the low level of hydrocarbon oxidation, CO oxidation, coal combustion and nitrogen oxide removal, etc. (Yu et al. 2005).

Dielectric barrier discharge is a kind of flexible and reliable, high pressure non equilibrium plasma discharge which has the advantages of high energy utilization, easy control of the discharge process, etc. and has made some progress in research (Yu et al. 2005, Chen et al 2012). However, there are a series of complex chemical reactions that will be produced during the process of dealing with the actual flue gas in the plasma reactor because of the waste gas is a mixture of complex gases. It is very difficult to separate the physical factors affecting power consumption from the chemical factors affecting the chemical conversion of NO (Li et al. 2015). So the impact of a single variable is very important to study the influence of chemical factors on NO removal. At the same time, the discharge power in the process of dielectric barrier discharge is an important electrical parameter, and has important guiding significance for the selection of power supply, the matching of the power supply and the reactor and the optimization of electrical parameters (Zhang et al. 2015b). In addition, the discharge power is an important economic indicator for the evaluation of the dielectric barrier discharge. Therefore, the study on the discharge power should be paid enough attention.

In this experiment, we studied the efficiency of four different gases by the plasma with the chemical composition of mixed gases that was limited, and further to understand the chemical process of gas phase removal of NO. Then, the mechanism of denitrification by plasma with different free radical sources was investigated and the effect of denitrification rates with applied power was studied.

EXPERIMENTAL SETUP

The formation and content of gas was studied by changing the gas concentration in the plasma reactor and the mecha-

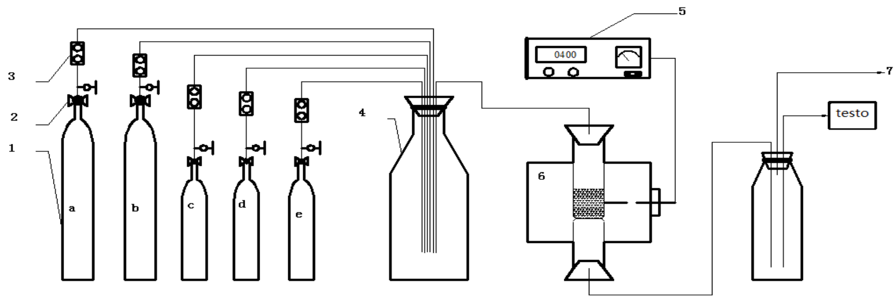

Fig. 1: The experimental technology of catalyst activity evaluation.
1- cylinder; 2- pressure relief valve; 3- gas flow meter; 4- mixed gas cylinder; 5- tube type furnace temperature controller; 6- high temperature combustion tube type furnace; 7- gas analyzer

nism of denitrification with different background gases was researched. Table 1 summarizes the specifications of test gas. The catalyst evaluation device is shown in Fig. 1.

The gas detection unit for Germany Testo 340 flue gas analyser with a standard pressure/velocity measurement function is used. The content of NO, NO_2 and O_2 are displayed on the display screen by the built-in sensor. The product parameters are as follows: O_2 sensor measuring range: 0~21%, NO sensor measuring range: 0~3000 ppm, and SO_2 sensor measuring range: 0~5000 ppm.

RESULTS AND DISCUSSION

Effect of denitrification rates with different concentration of NO in N_2/NO system: The effect of denitrification rates with different concentrations of NO in N_2/NO system is studied. The power is 50 W, the current is 1.6 A, and the total air intake is 1000 mL/min as shown in Fig. 2.

The denitrification rate by plasma is very high in the N_2/NO system as shown in Fig. 2. The denitrification rate's turning point was 1 min at the initial concentrations of NO. The denitrification rate experienced a sharp decline before 1 min in the process, and then increased to 100% in 6 min. This is due to the active free radical N produced by N_2 at the accumulation stage in the beginning of a few minutes (Xie et al. 2014). The removal rate of NO increased with the accumulation of free radicals. The denitrification reaction began with the accumulation of free radicals and the removal was increased. After a period of time, the system reached the dynamic equilibrium state and the denitrification rate stability. In addition, the greater the initial concentration of NO in the beginning of a few minutes, the lower the denitrification rate. The denitrification rate increase with the increase of applied power as shown in Fig. 3. This is because the energy is used to change the kinetic energy of the particles before the effective chemical reaction happened. This phenomenon is called 'starting power'. The removal rate of NO changed slowly with the further increase of the power. But there is a trend to continue to improve. The electric field intensity in the discharge gap remains unchanged because of the shielding effect of space charge. That is, the change of power has little effect on the density of high energy electrons. However, there is no discharge in the change of the entire cycle of alternating power and only when the applied power reached to the initial breakdown power. The effective discharge time will be prolonged when the applied power was raised, and the removal rate of NO can be improved (Sun et al. 2010).

Effect of denitrification rates with different concentrations of O_2 in N_2/NO/O_2 system: The effect of denitrification rates with different concentrations of O_2 in N_2/NO/O_2 system is studied. The power is 50 W, the current is 1.6 A, the total air intake is 1000 mL/min and the NO intake is 18 mL/min as shown in Fig. 4.

The higher the concentration of O_2, the lower is the stable denitrification rate of NO, as shown in Fig. 4. The stable denitrification rate was about 80% when the intake of O_2 was 40 mL/min. The denitrification rate decreases when O_2 is added in the system, compared with Fig. 2. The oxygen which is a negative gas, adsorbed the electrons in the discharge area and formed negative ions that move slowly in the plasma discharge reactor. The discharge becomes difficult and the current was reduced. Thereby the speed and density of the high energy electrons generated by the discharge was reduced (Hu et al. 2014, Du et al. 2011). So the denitrification rate was decreased.

The denitrification rate increased with the increase of the power that ranged from 20 W to 80 W in N_2/NO/O_2 system, as shown in Fig. 5. The stable denitrification rate reached 60% when the power was 80 W. Compared with Fig. 3, it can be derived that the denitrification rate significantly decreased with the O_2 added under the same power conditions.

Effect of denitrification rates with different concentra-

Table 1: Specifications of test gas.

Gas composition	Concentration (%)	Specifications (L/MPa)
N_2	99.8	40/12
NH_3	99.2	40/12
NO	4.1	8/12
O_2	99.8	40/12
SO_2	4.1	8/12

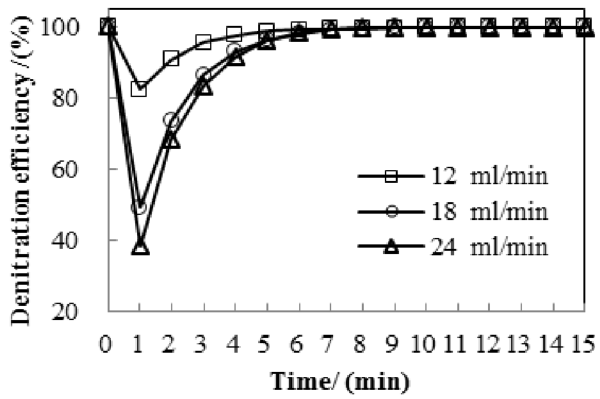

Fig. 2: The effect of denitrification rates with different concentrations of NO in N_2/NO system.

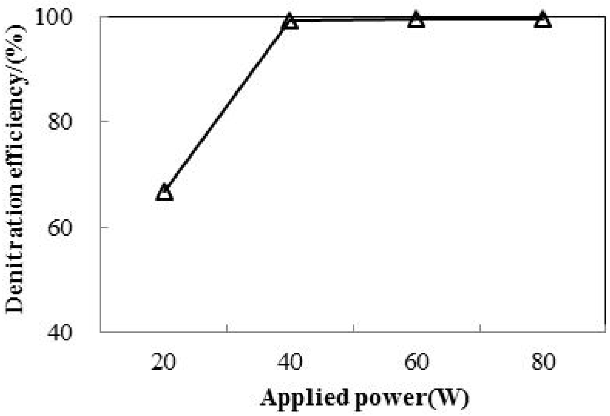

Fig. 3: The effect of denitrification rates with applied power in N_2/NO system (18 mL/min NO).

tions of NH_3 in $N_2/NO/O_2/NH_3$ system: The effect of denitrification rates with different concentrations of NH_3 in $N_2/NO/O_2/NH_3$ system is studied. The power is 50 W, the current is 1.6 A, the total air intake is 1000 mL/min, the NO intake is 18 mL/min and the O_2 intake is 60 mL/min as shown in Fig. 6.

The stable denitrification rate is about 60%, 70% and 75% when the intake of NH_3 is 1 mL/min, 3 mL/min and 5 mL/min, as shown in Fig. 6. The pH value of the system gradually increased with the increase of the concentration of ammonia that led to promote the absorption of NO to be carried out in the direction of the generation, and then increased the removal efficiency (Zhang et al. 2014, Kusano et al. 2005). The effect of increasing the concentration to improve the absorption of NO is obvious when the ammonia is at lower concentrations. But the effect is almost negligible when the ammonia concentration exceeds a certain range. In addition, the increase of ammonia concentration will increase the ammonia vapour pressure and reduce the utilization efficiency of ammonia, and also bring the ammonia escape, aerosol and secondary pollution.

The denitrification rate increased with the increase of the power that ranged from 20 W to 80 W in $N_2/NO/O_2/NH_3$ system as shown in Fig. 7. And the denitrification rate increased rapidly between 40 W and 20 W and slowly between 60 W and 80 W. And the denitrification rate was about 65% when the power was 80 W. In contrast to Fig. 5, in the condition of the same power, the increase of the NH_3 was increased. Comparing with Fig. 4, it can be derived that the denitrification rate was significantly increased with the NH_3 added under the same power conditions.

Effect of denitrification rates with different concentrations of SO_2 in $N_2/NO/O_2/NH_3/SO_2$ system: The effect of denitrification rates with different concentrations of SO_2 in $N_2/NO/O_2/NH_3/SO_2$ system is studied. The power is 50 W, the current is 1.6 A, the total air intake is 1000 mL/min, the NO intake is 18 mL/min, the O_2 intake is 60 mL/min and the NH_3 intake is 3 mL/min as shown in Fig. 8.

From the Fig. 8, it can be obtained that the denitrification rates first experienced decline, and then rise, and finally fall after addition of SO_2. The initial denitrification rate is maintained at a relatively high level when the intake of SO_2 is lower. The denitrification rate experienced a slow rise between 6 and 10 min in the process and then a rapid decline. Comparing the three curves, the greater the SO_2 concentration the lower the denitrification rate.

The reaction is more complex because there are many kinds of background gases in $N_2/NO/O_2/NH_3/SO_2$ system. SO_2 was mainly removed by reaction with OH radicals and NO was mainly removed by O, NH, NH_2 and OH radicals when the SO_2 existed. The amount of OH free radical is certain because of the input energy density. So the decreased removal rate of NO due to the SO_2 competition for OH free radicals. At the same time, SO_2 can directly react with NH_3 that can also affect the absorption of HNO_3 generated by NO. So the denitrification rate was decreased after the SO_2 is added.

The denitrification rate increased with the increase of the power that ranged from 20 W to 80 W in $N_2/NO/O_2/NH_3$

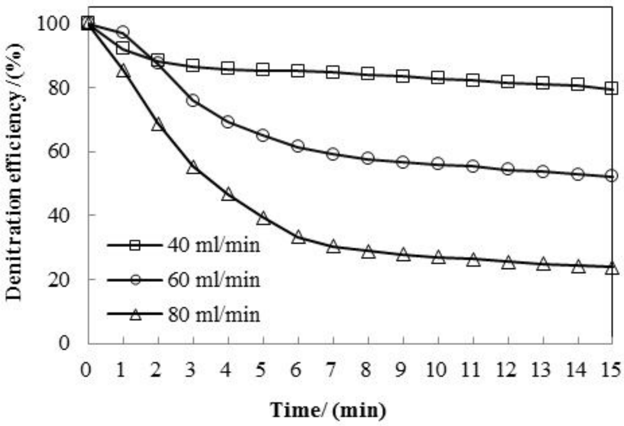

Fig. 4: The effect of denitrification rates with different concentrations of O_2 in $N_2/NO/O_2$ system.

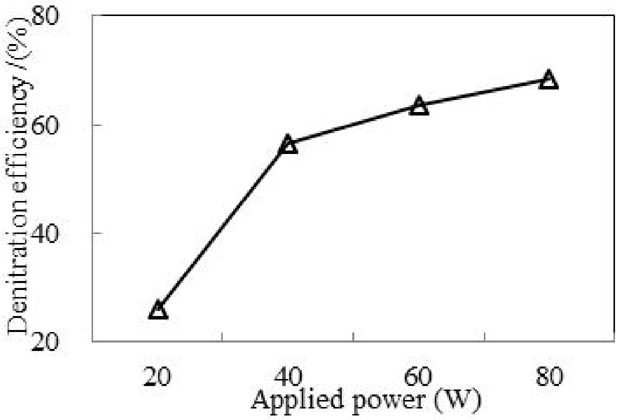

Fig. 7: The effect of denitrification rates with applied power in $N_2/NO/O_2/NH_3$ system (3 mL/min NH_3, 60 mL/min O_2, 18 mL/min NO).

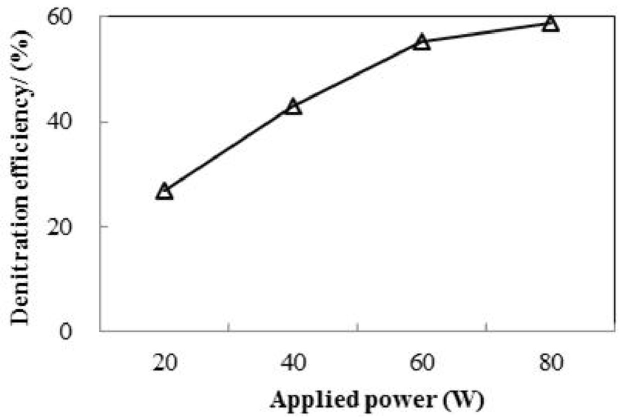

Fig. 5: The effect of denitrification rates with applied power in $N_2/NO/O_2$ system (60 mL/min O_2, 18 mL/min NO).

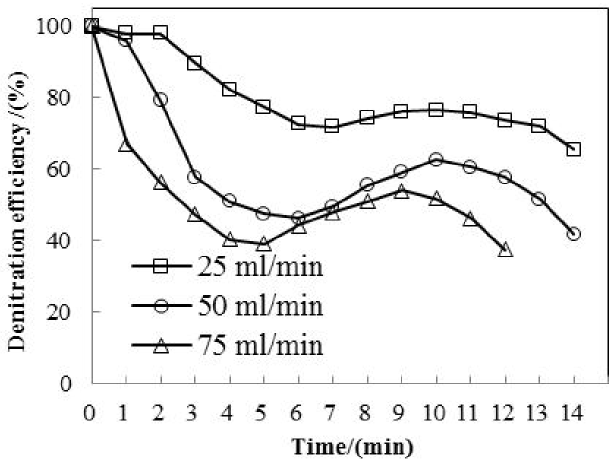

Fig. 8: The effect of denitrification rates with different concentrations of SO_2 in $N_2/NO/O_2/NH_3/SO_2$ system.

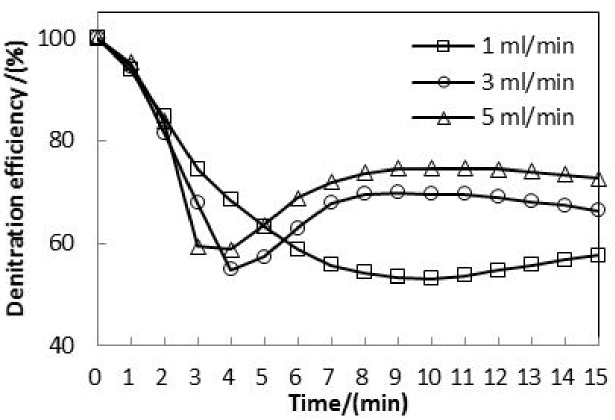

Fig. 6: The effect of denitrification rates with different concentrations of NH_3 in $N_2/NO/O_2/NH_3$ system.

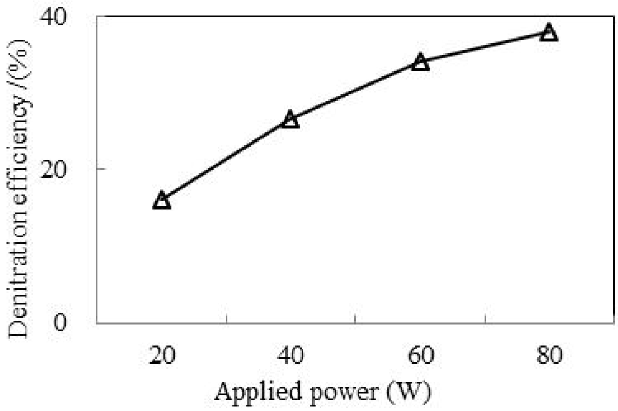

Fig. 9: The effect of denitrification rates with applied power in $N_2/NO/O_2/NH_3/SO_2$ system (50 mL/min SO_2, 3 mL/min NH_3, 60 mL/min O_2, 18 mL/min NO).

/SO_2 system as shown in Fig. 9. But the increase is small. The denitrification rate was about 15% when the power is 20 W and the denitrification rate was about 38% when the power is 80 W. Compared with Fig. 7, it can be derived that the denitrification rate was significantly decreased with the SO_2 added under the same power conditions.

CONCLUSIONS

1 The denitrification rate of NO was increased with the increase of the power, with the four kinds of background gases, when the discharge power was in the range of 20 W~80 W. And the effect of power on the performance of plasma denitrification was remarkable when the power was in the range of 20 W~40 W.

2 The flue gas denitrification was inhibited by the initial concentration of O_2, the content of SO_2 and the concentration of NO. And the greater concentration of these gases, the more serious the effect of inhibition. In addition, the increase of ammonia concentration will increase the denitrification rate. But it also bring the ammonia escape, aerosol and secondary pollution when the NH_3 is too much.

3 The denitrification rate can be stabilized at around 38% when the plasma discharge power is 80 W and the SO_2, NH_3, O_2 and NO intake are respectively 50 mL/min, 3 mL/min, 60 mL/min and 18 mL/min.

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