

Removal of NO_x from flue gas with radical oxidation combined with chemical scrubber

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Abstract: In this paper, removal of NO_x (namely DeNO_x) from flue gas by radical injection combined with NaOH solution (26% by weight of NaOH in water) scrubbing was investigated. The experimental results showed that the steady streamer corona occurs through adjusting the flow rate of the oxygen fed into the nozzles electrode. The vapor in the oxygen has influence on the V-I characteristics of corona discharge. Both HNO₂ and HNO₃ come into being in the plasma reactor and the DeNO_x efficiency in the plasma reactor is more than 60%. The overall DeNO_x efficiency of the whole system reaches 81.7% when the NaOH solution scrubbing is collaborated.

Keywords: radical; plasma reactor; DeNO_x process; absorb

Introduction

Non-thermal plasma technology is regarded as one of the most prospective technology for flue gas treatment. Concentration of NO_x as well as other hazardous gases in flue gas can be well reduced by the equipment based on non-equilibrium plasma technology (Chang, 1993). Electron beam irradiation (Kawamura, 1979; Tokunaga, 1980), corona discharge (Masuda, 1990; Dinelli, 1990) and dielectric barrier discharge (Takaki, 1999) are the possible ways to produce non-thermal plasma.

In the DeNO_x process with electron beam irradiation or pulsed corona discharge, the collision between electrons and surrounding molecules will result in an energy loss. To cut down the energy loss, corona discharge radical injection technology has been applied to eliminate the NO_x from the flue gas (Ohkubo, 1994; Park, 1999). In this kind of experiments, NH₃ and C_xH_y are injected into flue gas from nozzle electrodes and directly decomposed into NH and NH₂ in corona zones. Therefore, the energy consumption is reduced because very little N₂ and CO₂ molecules collide with electrons.

The DeNO_x process has been studied (Dros, 1998; Yang, 2000) with gaseous-phase oxidation integrating aqueous-phase scrub technology. In this process, radicals formed in the corona discharge process can convert NO into NO₂ or HNO_x, and then NO₂ and HNO_x are absorbed by water. The DeNO_x efficiency reaches 42%. No other gases but air and oxygen are needed in that process, therefore, secondary pollution is avoided and the cost is low. In addition, the end product of nitric acid is valuable.

Removal of NO_x from simulated flue gas by a corona discharge radical shower system combined with a NaOH solution (26% by weight of NaOH in water) scrubber is investigated in this study. In this work, steady streamer corona can be achieved when the hydrous oxygen is fed into the nozzles of a DC corona radical shower and many active substances, which are important to the DeNO_x process (Li,

1998), are produced. The results suggested that the power consumption in this study is lower than that in point-to-plate reactor used by Dros (Dros, 1998).

1 Experimental device and methods

Fig. 1 shows the experimental system. The power is supplied by a DC high voltage power supply. The rectangular plasma reactor is made of polymethyl methacrylate and has an inner dimension (mm³) of 500 (length) × 100 (width) × 100 (high). There are two stainless steel boards placed at the top and bottom surfaces inside the reactor. These two stainless steel boards with the dimension (mm²) of 450 (length) × 80 (width) serve as the cathode and are linked to the ground. A stainless steel pipe with a length of 100 mm equipped with four pairs of nozzles parallelly acts as the anode. The inner and outer diameters of the stainless steel pipe are 4 mm and 6 mm respectively. The length, the inner and outer diameters of the nozzles is 5 mm, 1.0 mm and 1.6 mm respectively. The anode is placed at the center of the reactor and connected with positive pole of the power supply.

The simulated flue gas is a mixture of N₂ + NO (2000 ppm) and air. The NO concentration of the flue gas changes

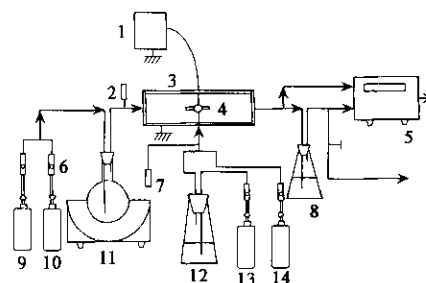


Fig. 1 Schematic diagram of experimental apparatus

1. HV power supply; 2. thermocouple; 3. reactor; 4. nozzle electrode; 5. NO_x analyzer; 6. flowmeter; 7. hygrometer; 8. NaOH solution bottle; 9. dry air; 10. N₂ + NO; 11. heater; 12. humidifier; 13, 14. dry oxygen

with the flow rate of air (Q_1) and the flow rate of N₂ + NO

(2000 ppm)(Q_2). In the experimental process, the flue gas is kept at a constant temperature of 52 °C after being heated up and then conducted to the reactor. The flow rate of the flue gas is 5 liters per minute during the entire experimental process. Dry oxygen and wet oxygen are fed into nozzles after being mixed, and the relative humidity(Rh) of the oxygen is measured by a hygrometer. Flue gas coming out from the reactor is guided to NaOH solution to eliminate the NO₂ and the HNO_x. A NOA-305 analyzer made by Shimadzu Corporation measures the concentration of NO_x.

2 Results and discussion

2.1 Corona discharge characteristic

The discharge mode generates a steady streamer corona through adjusting the flow rate of oxygen (Q_3) and the discharge voltage. Fig. 2 shows a photo of the corona at an applied voltage of 26.5 kV. Bright streamers between the anode and two cathode boards are visible, which benefit the radical generation.

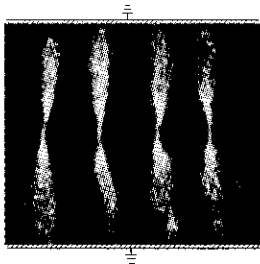


Fig. 2 Photograph of streamer corona
Flue gas: Q_1 (air) = 2.5 L/min, Q_2 (N₂ + NO) = 2.5 L/min;
 t = 52 °C, V = 26.5 kV; nozzle gas: Q_3 (oxygen) = 1000 ml/min, Rh = 68 %

The water vapor is a kind of electronegative gas, H₂O molecules can absorb electrons in the corona zone and then turn to negative ions, which transfer slowly and weaken the corona and discharge current. Fig. 3 shows the curve of discharge current versus applied discharge voltage for two relative humidity of oxygen of 42% and 68%, respectively. It can be concluded that high relative humidity enhance inception voltage and breakdown voltage, but reduce discharge current.

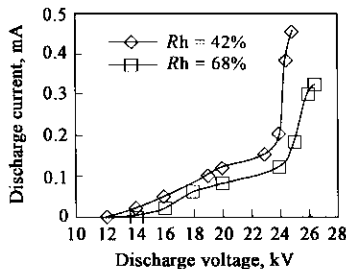


Fig. 3 Effect of humidity on V-I characteristics
Flue gas: Q_1 (air) = 2.5 L/min, Q_2 (N₂ + NO) = 2.5 L/min;
 t = 52 °C; nozzle gas: Q_3 (oxygen) = 1000 ml/min

2.2 NO oxidation in reactor

The relationship between the NO_x concentration at the exit of the reactor and the discharge voltage is shown in Fig.

4 (corresponding to a relative humidity of 42% for the nozzle gas) and Fig. 5 (corresponding to a relative humidity 68% for the nozzle gas).

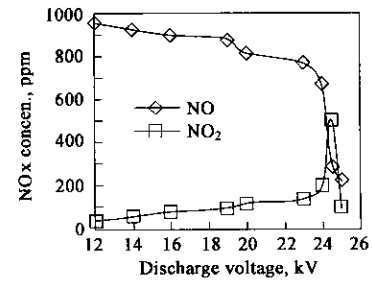


Fig. 4 Concentration of NO_x after the reactor (Rh = 42%)
Flue gas: Q_1 (air) = 2.5 L/min, Q_2 (N₂ + NO) = 2.5 L/min;
[NO]₀ = 1000 ppm, t = 52 °C; nozzle gas: Q_3 (oxygen) = 1000 ml/min

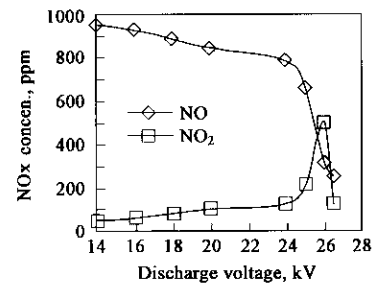


Fig. 5 Concentration of NO_x after the reactor (Rh = 68%)
Flue gas: Q_1 (air) = 2.5 L/min, Q_2 (N₂ + NO) = 2.5 L/min;
[NO]₀ = 1000 ppm, t = 52 °C; nozzle gas: Q_3 (oxygen) = 1000 ml/min

In Fig. 4, the NO concentration decreases but the NO₂ concentration increases due to NO being oxidized to NO₂ when the applied discharge voltage is increased. The NO concentration falls slowly when the voltage is lower than 24 kV but falls sharply as the voltage is higher than 24 kV because the corona discharge transition to streamer mode as the applied voltage exceeds 24 kV. As a result, the radicals relating to NO oxidation accordingly increase. The NO₂ concentration attains the maximum and the NO concentration is very low when discharge voltage reaches 24.5 kV, then the NO₂ concentration falls following the increasing applied voltage. Dros(Dros, 1998) firstly discovered this sequence of events. The result shown in Fig. 5 is analogous to that shown in Fig. 4. One conclusion can be drawn from Fig. 4 and Fig. 5 that the NO₂ begin to be removed just as the concentration of NO tends to be very low. The reason for this phenomenon may be that when the discharge voltage reaches a threshold value, most of the NO can be converted and more OH radicals are produced, therefore more NO₂ is converted into HNO₃, and the NO₂ concentration begins to decrease rapidly.

It can be concluded based on the above analysis that the NO_x removal efficiency can increase significantly in the corona discharge reactor. The process of the NO_x reduction will be discussed in Section 3.

Fig. 6 shows two curves of DeNO_x efficiency in the reactor as a function of discharge power. The DeNO_x efficiency is very low while the discharge powers is lower than

4 W because the NO oxidation rate is very high but the NOx transition into HNOx is slow at low power condition. The DeNOx efficiencies at two humidity conditions are very close when the discharge power is low because the oxidation of NO dominates the whole process at low power condition and the water vapor slightly affects the oxidation of NO oxidation. When the discharge power exceeds 8 W, the DeNOx efficiency increases promptly because NOx change rapidly into HNOx, and the efficiencies could be more than 60% if enough power is injected into the reactor. In the experiment with point-plane reactor and water-film absorption (Dros, 1998), the DeNOx efficiency achieves a maximum of 42%.

At the high power condition, the more moisture is contained in the oxygen, the higher the DeNOx efficiency is. The reason for this is that the oxygen with a higher relative humidity provides more H₂O molecules and as a result produces more OH radicals at the same power and converts more NO₂ into HNOx.

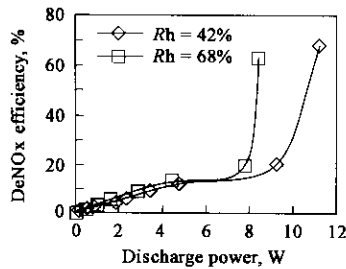


Fig. 6 Effect of discharge power on NOx reduction rate
Flue gas: Q_1 (air) = 2.5 L/min, Q_2 (N₂ + NO) = 2.5 L/min;
[NO]₀ = 1000 ppm, $t = 52^\circ\text{C}$; nozzle gas: Q_3 (oxygen) = 1000 ml/min

2.3 NOx removal after alkali solution scrubber

In the experiment, the flue gas coming from the reactor is conducted to the NaOH solution (26%), where the NO, NO₂ and HNOx contained in the flue gas are absorbed. The gaseous HNOx cannot be measured due to the unavailability of a measuring instrument. Gaseous HNOx can be completely absorbed by the NaOH solution, and therefore, only NOx in the flue gas needs to be measured.

Fig. 7 and Fig. 8 show the change of the NOx concentration behind the reactor and the absorption bottle (the curve signed with AB-NOx) with discharge voltage. The NOx concentration drops after the flue gas passed through the absorption bottle because NO and NO₂ are also partially absorbed by the NaOH solution. The transition curve of NOx concentration is analogous with that of NO concentration, this proves that the NaOH solution absorbs NO₂ completely and dissolves NO in small quantities.

Due to being absorbed by the NaOH solution, the NOx concentration decreases to some extent. The overall NOx reduction rate is calculated and shown in Fig. 9 after measuring the NOx concentration. Apparently, the overall NOx reduction rate increases as the discharge power increases. With a discharge power of 11 W, 81.7% of the NOx is reduced corresponding to a relative humidity of 42%. Only 8 W is needed to reduce the same NOx corresponding to a relative humidity of 68%.

After the experiment is carried out for a period of time,

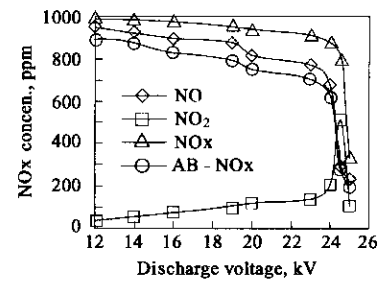


Fig. 7 NOx reduction in the system (Rh = 42%)
Flue gas: Q_1 (air) = 2.5 L/min, Q_2 (N₂ + NO) = 2.5 L/min;
[NO]₀ = 1000 ppm, $t = 52^\circ\text{C}$; nozzle gas: Q_3 (oxygen) = 1000 ml/min

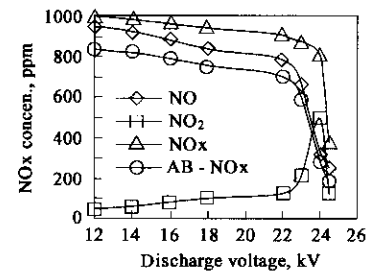


Fig. 8 NOx reduction in the system (Rh = 68%)
Flue gas: Q_1 (air) = 2.5 L/min, Q_2 (N₂ + NO) = 2.5 L/min;
[NO]₀ = 1000 ppm, $t = 52^\circ\text{C}$; nozzle gas: Q_3 (oxygen) = 1000 ml/min

part of the solution in the absorption bottle is analyzed with a capillary electrophoresis apparatus (Waters Quanta 4000). The ultraviolet absorbency characteristics of NO₂⁻ and NO₃⁻ ion are shown in Fig. 10. The peak area corresponding to NO₂⁻ is larger a little than that corresponding to NO₃⁻, this indicates that the solution contains more NO₂⁻ ions.

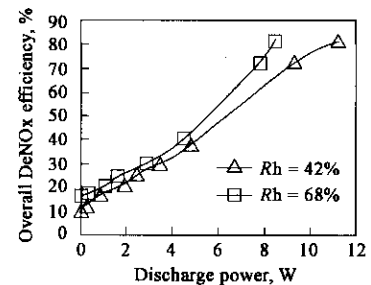


Fig. 9 Effect of discharge power on overall NOx reduction rate
Flue gas: Q_1 (air) = 2.5 L/min, Q_2 (N₂ + NO) = 2.5 L/min;
[NO]₀ = 1000 ppm, $t = 52^\circ\text{C}$; nozzle gas: Q_3 (oxygen) = 1000 ml/min

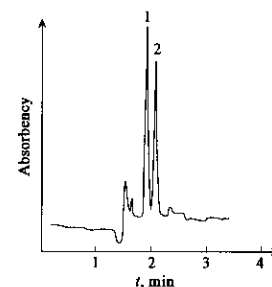
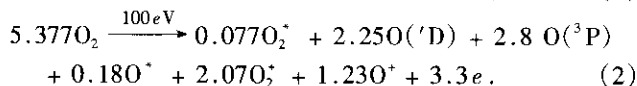
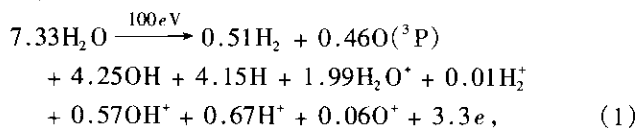


Fig. 10 Concentration of NO₃⁻ and NO₂⁻ in NaOH solution
1. NO₂⁻; 2. NO₃⁻

3 Mechanism of the DeNOx process

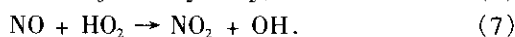
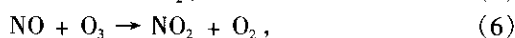
In the experiment, the gas fed into the electrodes is a mixed gas of O₂ and H₂O which is decomposed in the corona zone to generate radicals such as O, OH and so on (Li, 1998).



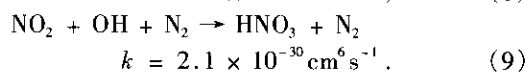
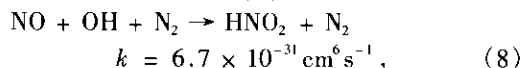
The primary O radical either reacts with oxygen molecule to produce ozone molecule (O₃), which oxidability is strong, or combines with primary OH radical to form HO₂ radical, which is a good oxidant.



Then, radicals O, HO₂ and O₃ oxidize the NO contained in the flue gas to NO₂ through following reactions.



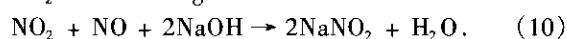
The combinations of OH radicals with NO and NO₂ molecule give birth to HNO_x (x = 1, 2) in the reactor.



It is suggested that the reaction constant of Reaction (9) is two times higher compared with the reaction constant of Reaction (8). The reason for more NO₂⁻ ion in the solution may be that little NO is oxidized into NO₂ in the discharge reactor at the low power condition, so the HNO₂ produced by Reaction (8) is more than the HNO₃ produced by Reaction (9).

Some conclusions can be drawn from Reaction (5) to Reaction (7) that O, O₃, HO₂ radicals are important to oxidize NO to NO₂, so the water vapor affected little on the DeNOx efficiency in the reactor at the low power condition, this is justified by experimental results too. The OH radical dominates the transition from NOx to HNOx and the relative reactions are completed in the plasma reactor. The experimental results indicated that more than 60% NOx is converted into HNOx in the reactor when the discharge power excess 8 W and HNOx is completely absorbed in the absorption bottle.

Part of unreacted NOx is conducted to the absorption bottle and removed through the Reaction (10). Reaction (10) yields additional NO₂⁻ ions. This is another explanation for more NO₂⁻ ions existing in the NaOH solution.



The chemical process in the reactor is too complex to be analyzed clearly, only the main chemical reactions are discussed above. To reveal the mechanisms, more research works need to be done.

4 Conclusions

An experimental investigation was conducted to remove NOx from flue gas by DC corona radical shower system combined with an alkaline solution scrubber and the following conclusions are obtained:

(1) The experimental results suggested that the gas flow affects the corona discharge characteristic. The water vapor in the oxygen restrains the discharge, increases the inception voltage and the breakdown voltage. In addition, it lowers the discharge current.

(2) In this experiment, NO is converted in two ways. One is being oxidized to form NO₂; the other is reacting with OH radical to produce HNO₂. As high as 60% of NOx can be converted to HNOx in the reactor.

(3) With a fixed discharge power, increasing the humidity of the oxygen fed into the nozzle electrodes result in an increase of DeNOx efficiency in this experiment because more OH radicals are generated.

(4) To reduce NOx with the method used by this research, the key-point to increase DeNOx efficiency is to convert NO into the form that can be absorbed easily by the NaOH solution. The total DeNOx efficiency in this experiment reached a maximum of 81.7% after the products being absorbed by the NaOH solution.

Acknowledgement: The authors thank to Institute for Thermal Power Energy of Zhejiang University for its helpful support.

References:

- Chang J S, 1993. Energetic electron induced plasma process for reduction of acid and greenhouse gases in combustion flue gas [M]. No-thermal plasma technologies for pollution control; Part A. Berlin: Springer.
- Dinelli G, Civitano L, Ren M, 1990. Industrial experiments on pulsed corona simultaneous removal of NOx and SO₂ from flue gas[J]. IEEE Trans on Indus App, 26(3): 535—541.
- Dros M, Mizeraczyk J, Czech T *et al.*, 1998. Removal of NOx by DC and pulsed corona discharges in a wet electrostatic precipitator model[J]. Journal of Electrostatics, 45: 25—36.
- Kawamura K, Hirasawa A, 1979. Pilot plant experiment of NOx and SO₂ removal from exhaust gases by electron beam irradiation[J]. Radiate Phys Chem, 13(1): 5—12.
- Li Q, Li J, 1998. The chemical kinetics analysis of removal of oxides of sulphur and nitrogen from flue gas with pulsed corona[J]. Journal of Environmental Science, China, 18(3): 1—7.
- Masuda S, 1990. Control of NOx by positive and negative pulsed corona discharges[J]. IEEE trans. on Indus App, 26(2): 374—383.
- Ohkubo T, Kanazawa S, Nomoto Y *et al.*, 1994. NOx removal by a pipe with nozzle-plate electrode corona discharge system[J]. IEEE Trans on Indus App, 30(4): 856—860.
- Park J Y, Chang J S. 1999. Simultaneous removal of NOx and SO₂ from NO-SO₂-CO₂-N₂-O₂ gas mixtures by corona radical shower systems[J]. J Phys D: April Phys, 32:1007—1011.
- Takaki K, Jani M A, Fujiwara T, 1999. Removal of nitric oxide in flue gases by multipoint to plane dielectric barrier discharge[J]. IEEE Trans on Plasma Sc, 27(4): 1137—1145.
- Tokunaga O, Suzuki N, 1980. Radiation chemical reactions in NOx and SO₂ removals from flue gas[J]. Radiate Phys Chem, 24(1): 145—165.
- Yang C L, Chen L, 2000. Oxidation of nitric oxide in a two-stage chemical scrubber using DC corona discharge[J]. Journal of Hazardous Materials, B80: 135—146.