

# High Efficiency NO Reduction by Ammonia Radicals Generated from Dielectric Barrier Discharge

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Yuta Kumano<sup>1</sup>, Shinji Kambara<sup>1</sup>, Hiroshi Moritomi<sup>1</sup>, Ken Yukimura<sup>2</sup>, Kensuke Kawamura<sup>2</sup>, Toru Yamashita<sup>3</sup>

<sup>1</sup>Graduate School of Environmental and Renewable Energy Systems, Gifu University, 1-1 Yanagido, Gifu 501-1193, Japan

<sup>2</sup>Department of Electrical Engineering, Doshisha University, 1-3 Tatara Miyakodani, Kyotanabe, Kyoto 610-0321, Japan

<sup>3</sup>Coarl Research Laboratory, Idemitsu Kosan Co.,LTD., Sodegaura, Chiba 299-0267, Japan

## ABSTRACT

Application of pulsed electrical discharge for gas cleaning is gaining prominence. Particularly, various experiments using plasma techniques have been studied to reduce NO<sub>x</sub> generated from fossil fuel combustion. Different kinds of plasma reactors have been developed to remove NO<sub>x</sub> for high efficiency and low cost. However, energy efficiency (g-NO/kWh) is low in their techniques because large amount of exhaust gas are treated in plasma reactors with large power consumption. For improving energy efficiency, we have developed a new De-NO<sub>x</sub> system by ammonia radical injection. NO reduction experiment was performed by injecting ammonia radicals, which were externally generated by flowing the NH<sub>3</sub> gas diluted with Ar gas through a dielectric barrier discharge (DBD) with a one-cycle sinusoidal-wave power source. An intermittent one-cycle-sinusoidal power source was employed as the power source for generating DBD. The discharge was intermittently formed between coaxial cylindrical electrodes with a space of 1.5 mm at an applied peak-to-peak voltage of 3-15kV. The generated radicals were injected to simulation gas (NO/O<sub>2</sub>/N<sub>2</sub>). The simulation gas contained 0-5 % O<sub>2</sub>, and the effect of O<sub>2</sub> on NO<sub>x</sub> removal was investigated. As a result, the maximum energy efficiency in this system was 140 g/kWh.

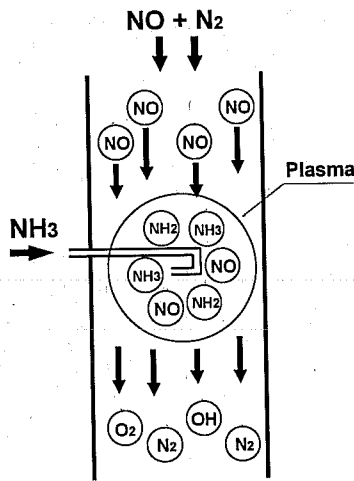
## KEYWORD

radical injection, NO reduction, dielectric barrier discharge

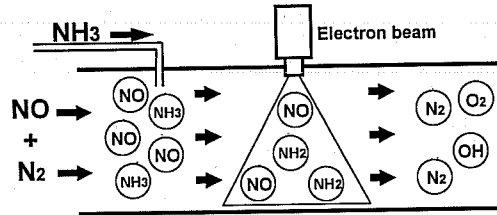
## INTRODUCTION

The conventional technique for NO<sub>x</sub> reduction such as selective catalytic reduction system is needed a large volume and too expensive. For small plants and mobile emission sources, small de-NO<sub>x</sub> system having high cost performance is expected. Plasma techniques utilizing electrical discharges give an innovative approach for economical solution of gas cleaning.

Generally, high temperature and low pressure are required for plasma generating conditions, but low temperature plasma that is available under normal temperature and normal pressure has attracted attention. This low temperature plasma means that a state of only some electrons are accelerated and obtained high energy from an electric field. There are few using low temperature plasma methods that can be used by normal temperature and normal pressure. Various discharge using difference reactors have been studied<sup>1)2)</sup>. Fig.1 shows the outline of the plasma nozzle method and the electronic beam method for flue gas clean up. In these systems, a huge energy is needed because both methods are needed to excite huge flue gas with plasma or electronic beam<sup>3)</sup>.



(a) plasma nozzle method



(b) electronic beam method

Fig.1 Precious studies for flue gas treatment by plasma techniques

On the other hand, we have developed the high efficiency NO reduction method by ammonia radical injection using the radical chain as shown in Fig.2. The radical injection de-NOx system is a new concept technique. A radical agent, NH<sub>3</sub>, is excited by dielectric barrier discharge (DBD), and they are injected to flue gas as ammonia radicals (NH, NH<sub>2</sub>, N<sub>2</sub>). NO in flue gas is reduced by their ammonia radicals rapidly by radical reaction.

In this system, electric power is consumed to excite only a radical agent, therefore, consumption power is extremely decreased.

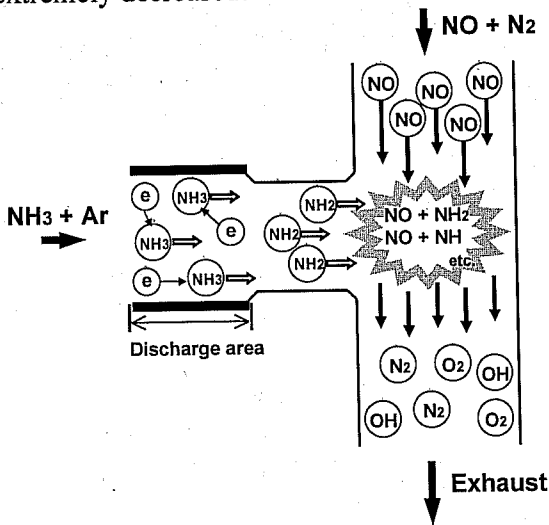


Fig.2 Radical injection system for de-NOx in this study.

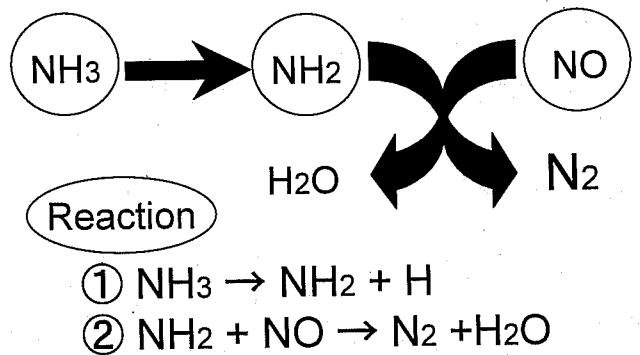


Fig.3 The key radical reaction for de-NOx.

It is clear that the most effective radical for NOx reduction is NH<sub>2</sub> radical from previous work<sup>4)</sup>. Fig.3 shows key radical reactions in this system. NH<sub>2</sub> radical generate from NH<sub>3</sub> by DBD react with NO rapidly, and NO is removed.

In the previous work<sup>5)6)</sup>, effects of discharge voltage and reaction temperature on NO removal were investigated. Effects of O<sub>2</sub> concentration with other experimental conditions are examined in this study because flue gas generated by fuel combustion contains O<sub>2</sub>.

## EXPERIMENTAL METHODS AND CONDITIONS

Fig.4 shows the experimental apparatus of the NO<sub>x</sub> reduction system using ammonia radicals which are produced by intermittent dielectric barrier discharge. The apparatus consists of three sections, radical injector, tube furnace with electric heater, and reaction chamber. The tube furnace was 0.05 m in diameter and 1.3 m long. The radical injector was joined to center of the tube furnace with a reaction chamber.

Simulated gas, nitric oxide (NO) gas by mixing with oxygen, was diluted with nitrogen, and NH<sub>3</sub> gas was diluted with argon. Simulated gas was fed to tube furnace. On the other hand, radical agent (NH<sub>3</sub>) was supplied to radical injector. The concentrations and flow rate of simulated gas and radical agent were adjusted in the gas blender by mixing with nitrogen and argon gas. The NO concentration was 523 to 782 ppm, and the flow rate was 1.34 to 1.88 l/min. O<sub>2</sub> concentration in simulated gas is varied 0 to 5 %. Tube furnace heats simulated gas to an experimental temperature. The reaction temperature is varied 341 to 483 °C.

NH<sub>3</sub> concentration as the radical agent was 965 ppm, and the concentration was decided to keep NH<sub>3</sub>/NO mol fraction between 1.0 and 1.5. The residence time of radical agent in the radical injector is varied 4.06 to 5.71 s.

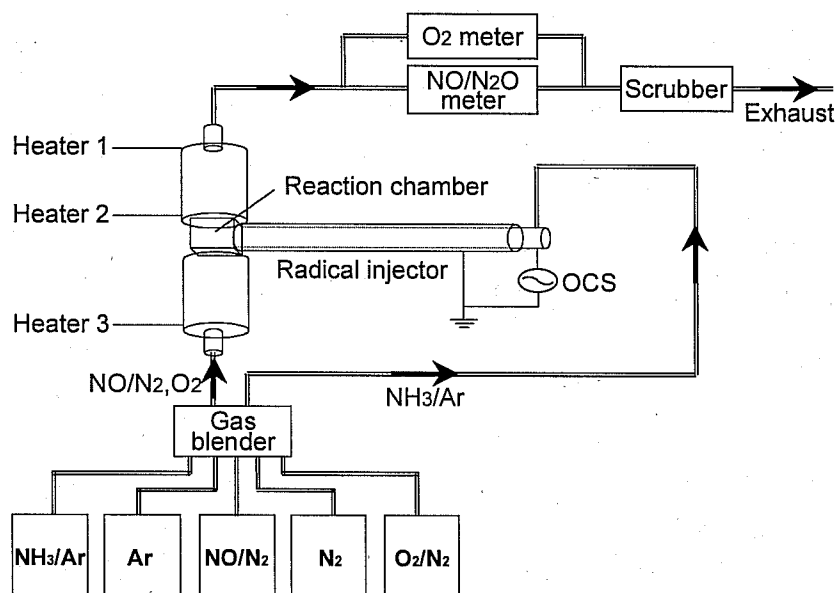


Fig.4 Schematic diagrams of experimental apparatus.

In the radical injector, applied voltage is varied 3 to 15 kV with repetition rate of 10 kHz. NH<sub>i</sub> radicals having rapid chemical reaction rate are externally generated by NH<sub>3</sub> gas diluted with Ar gas through a DBD with a one-cycle sinusoidal-wave power source. NO concentration before and after plasma resolution is measured with the NO<sub>x</sub> meter installs in the exhaust gas side, and NO reduction is calculated. NO reduction is defined by the equation (1).

$$\text{NO reduction} = \frac{[\text{NO}]_i - [\text{NO}]_f}{[\text{NO}]_i} \times 100\% \quad (1)$$

Energy efficiency of NO reduction is defined as the mass flow-rate of reduced NO per discharge power.

## RESULTS AND DISCUSSION

Fig.5 shows relation between NO reduction and applied voltage at  $O_2$  concentration of 1% and  $NH_3/NO$  mole fraction of 1.5. The residence time of radical agent in the radical injector is 5.71 s. De-NOx reaction occurs at applied voltage about 5 kV and NO reduction reaches 99.5% at 483 °C. However, NO reduction decreases when applied voltage is too high because  $NH_3$  is decomposed to  $NH$  and/or  $N$  radicals, and  $NH_2$  fraction is decreased.  $NH_2$  radicals are more effective radical for NO reduction than  $NH$  or  $N$  radicals. Therefore, a lot of  $NH$  or  $N$  radicals are generated and NO reduction when the applied voltage is too high.

Fig.6 shows NO reduction at reaction temperature of 483°C and  $NH_3/NO$  mole fraction of 1.5 and residence time of 5.71 s as a function of  $O_2$  concentration. De-NOx occurs in the case of  $O_2$  is included. In the case of applied voltage of 3 kV, it tends to increase the NO reduction with increasing  $O_2$  concentration. On the other hand, in the case of more than 5 kV, NO reduction is decreased with increasing  $O_2$  concentration.

Molecular oxygen generates OH, which has an important role for the reduction reaction of NO. However, when  $O_2$  concentration is high,  $NH_i$  radicals react with O and OH radicals, in the result, NO reduction decreases under high  $O_2$  concentration.

Fig.7 shows NO reduction at reaction temperature of 483°C and  $O_2$  concentration of 1 % and  $NH_3/NO$  mole fraction of 1.5 as a function of residence time. Volume of radical injector is  $94.2 \text{ cm}^3$ . Residence time is varied 4.06 to 5.71 s. In all condition of the applied voltage, NO reduction is decreased with increasing the residence time. It is seemed that the generating  $NH_i$  radicals depend on the input energy which the radical agent receives in the radical injector. Therefore, we studied relation between an input energy density and NO reduction.

Table 1 lists applied voltage [kV], an energy per one pulse [mJ] and energy per second [W]. The energy per second can calculate from the product of energy per one pulse and pulse repetition rates (10kHz). Energy density is defined by the equation (2).

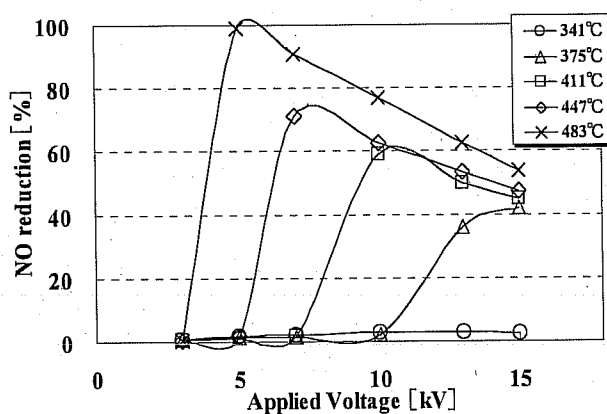


Fig.5 NO reduction as a function of applied voltage. ( $O_2 = 1\%$ ,  $NH_3/NO = 1.5$ , residence time = 5.71 s, parameter = reaction temperature)

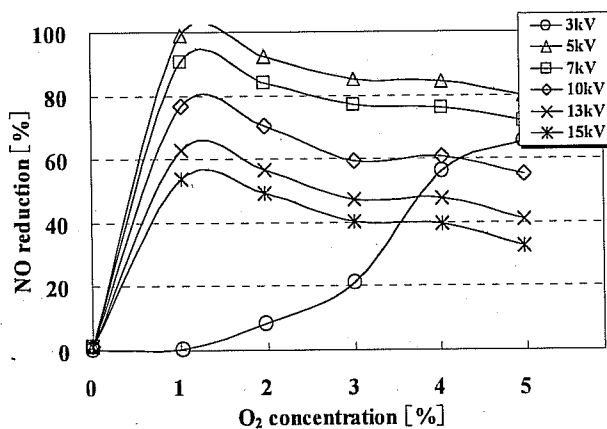


Fig.6 NO reduction as a function of  $O_2$  concentration. (483C,  $NH_3/NO = 1.5$ , residence time = 5.71 s, parameter = applied voltage)

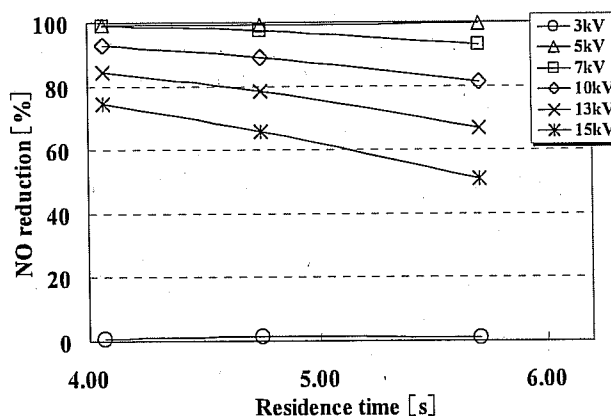


Fig.7 NO reduction as a function of residence time. (483C,  $NH_3/NO = 1.5$ ,  $O_2 = 1\%$ , parameter = applied voltage)

Energy density [J/cm<sup>3</sup>]

$$= \frac{\text{Energy per second [W]} \times \text{Residence time [s]}}{\text{Volume of radical injector [cm}^3\text{]}} \quad (2)$$

Fig.8 shows NO reduction at reaction temperature of 483°C and NH<sub>3</sub>/NO mole fraction of 1.5 as a function of energy density. De-NO<sub>x</sub> occurs suddenly at energy density about 0.2 J/cm<sup>3</sup> and NO reduction reaches 99.9%. After that, it tends to decrease linearly NO reduction with increasing energy density. It is found that NO reduction is able to organize by input energy density under a constant reaction temperature and O<sub>2</sub> concentration. Therefore, it is thought that the generating NH<sub>i</sub> radicals depend on the input energy density.

Moreover, we studied the experimental apparatus improvement because the range of the optimum energy density is narrow to obtain high NO reduction. To expand the optimum condition, secondary injection nozzle is added on reaction chamber. The part of raw NH<sub>3</sub> gas for radical injector is injected at radical injector exit through the secondary injection nozzle. We expected that NH<sub>2</sub> radical is regenerated by reaction of NH/N radical and NH<sub>3</sub>. Fig.9 shows relation between energy density and NO reduction with/without secondary injection at reaction temperature of 483°C and NH<sub>3</sub>/NO mole fraction of 1.5 and O<sub>2</sub> concentration of 1%. Secondary injection method is more efficient than normal injection method under the variety of applied voltage.

Table 1 Relation between applied voltage and energy per one pulse and energy per second.

Applied voltage [kV]	Energy per one pulse [mJ]	Energy per second [W]
3	0.085	0.85
5	0.273	2.73
7	0.727	7.27
10	1.212	12.12
13	1.939	19.39
15	2.545	25.45

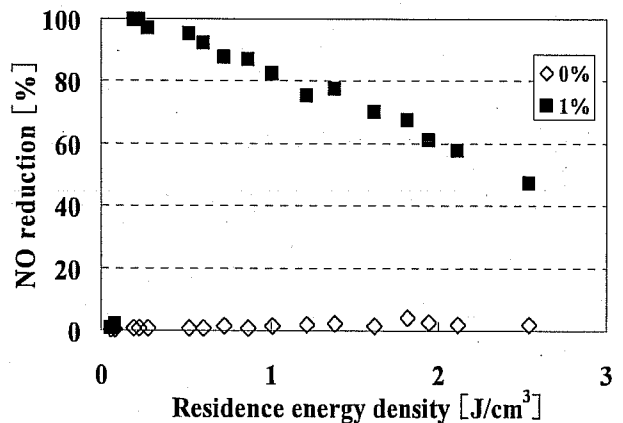


Fig.8 NO reduction as a function of energy density. (483C, NH<sub>3</sub>/NO = 1.5, parameter = O<sub>2</sub> concentration)

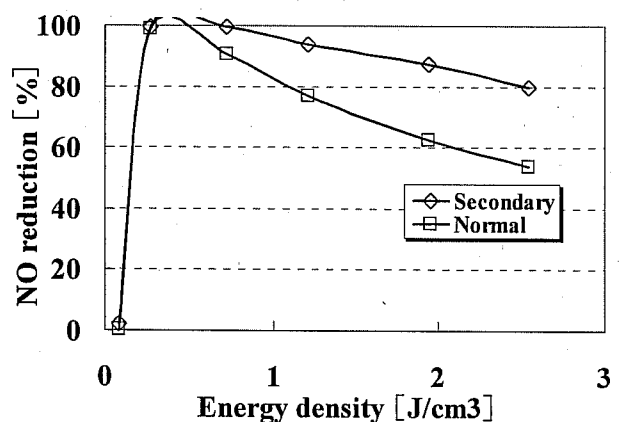


Fig.9 NO reduction as a function of energy density. (483C, NH<sub>3</sub>/NO = 1.5, O<sub>2</sub> = 1%, parameter = method)

## CONCLUSION

It is found that NO reduction of 99.9% is obtained by radical injection de-NO<sub>x</sub> system. NO reduction increases with increasing applied voltage and O<sub>2</sub> concentration, however, NO reduction decreases with increasing their parameter over optimum condition. The behavior of NO reduction in this system is explained by energy. To expand optimum condition, secondary injection of radical agent is performed. It is found that improved method are increased NO reduction under wide range of energy density.

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