

# NOx removal using ammonia radicals prepared by intermittent dielectric barrier discharge in atmospheric pressure

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**Abstract** The NOx removal was made at a temperature of 950°C by using ammonia radicals. The radicals were efficiently produced by flowing 1-3 % NH<sub>3</sub> in Ar through the dielectric barrier discharge of a one-cycle sinusoidal (OCS)-wave power source. The discharge was intermittently made between coaxial cylindrical electrodes with a space of 1.5 mm at an applied peak-to-peak voltage of 10-35 kV. At the mixing zone in the reaction chamber the spectrum of the NH radical was observed at 336.7 nm. The radicals were introduced to a reaction chamber, and were mixed with 1000 ppm NOx in N<sub>2</sub>. The NOx reduction increased with increasing the concentration of the NH radical. The dependence of NOx reduction on the duty cycle of OCS voltage was also discussed.

**Keywords:** dielectric barrier discharge, NOx removal, ammonia radical

## I. Introduction

The NOx emission from thermoelectric power plant and diesel automobile etc. is an urgent subject to be solved. For large-scale NOx removal using ammonia radicals, plasma processes have been utilized as well as electron beams<sup>1</sup>. In most NOx removal systems using plasma process, the plasma is produced in mixed state of NOx and reaction gas such as ammonia to convert NOx into harmless materials such as N<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O. The NOx removal system of this study has the prominent feature that the radical-producing chamber and reaction chamber for NOx removal are separate. For a large-scale NOx removal, therefore, a high efficiency is expected with this method, where the plasma can be generated in a small volume.

## II. Experimental

Figure 1 shows a schematic diagram of the NOx reduction system using ammonia radicals. It consists of two chambers: one as a radical injector for making ammonia radicals, and the other as a reaction chamber for decomposing the NOx gas by mixing with the ammonia radicals generated in the radical injector.

The electrodes are co-axial in configuration with quartz glass tubes as dielectric materials. The metallic electrodes covered both outer side of the outer glass tube and inner side of the inner glass tube. The gap between the outer and inner glass tube is 1.5 mm. The dielectric

barrier discharge occurred at the gap.

Nitric oxide (NO) was diluted with nitrogen, and ammonia (NH<sub>3</sub>) was diluted with argon gases. The concentrations and flow rates of NO and NH<sub>3</sub> were adjusted in the gas blender by mixing with nitrogen and argon gas. The adjusted NO gas was fed to the reaction chamber, and the adjusted NH<sub>3</sub> gas was fed to the radical injector. The concentration of the de-NO gas after flowing through the reaction chamber was measured with a NO<sub>x</sub> meter set at the exit. During the experiment, the temperature of the reaction chamber was kept to be 950 °C.

The ammonia radicals (NH) were monitored with the spectrometer set above the zone of mixing NO with ammonia radicals. The dielectric barrier discharge was produced with an intermittent power source.

Figure 2 schematically shows the waveform of the applied one-cycle sinusoidal (OCS) voltage. The repetition rate  $R_R$  is defined as the reciprocal of the repetition time  $T_1$  of the discharge.  $T_0$  was approximately 10 μs, and  $R_R$  was 5 to 50 kHz.

The energy input during one cycle of the dielectric barrier discharge was estimated from the accumulated charge and applied voltage by using the Lissajous figure. The time evolutions of the source voltage, current and accumulated charge were simultaneously monitored with an oscilloscope.

### III. Results and Discussion

#### a) Effect of applied voltage $V_{pp}$

Figure 3 shows the plasma-input energy as a function of applied voltage  $V_{pp}$ . The input energy increases with increasing applied voltage at above 20 kV under the constant repetition rate of the OCS source. The discharge power, which is the input energy per unit time, also increases with applied voltage at above 20 kV. Figure 4 shows the NO reduction and the discharge power as a function of applied voltage  $V_{pp}$ . The NO reduction is not proportional to the discharge power. It abruptly increases from 20% at an applied voltage of 25 kV to over 80 % at 30 kV. It is inferred that at an applied voltage below 25 kV the argon ions might

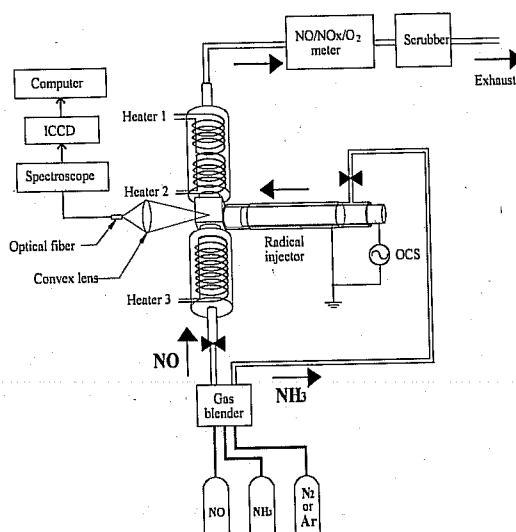


Fig.1 Schematic diagram of experimental apparatus.

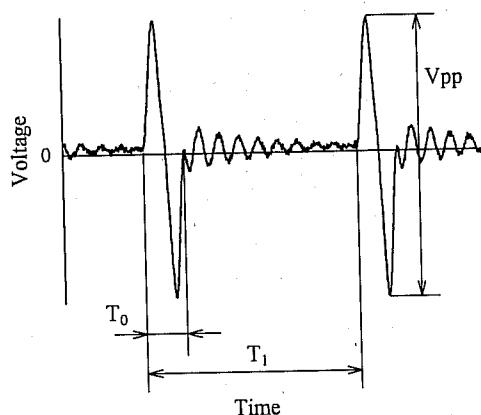
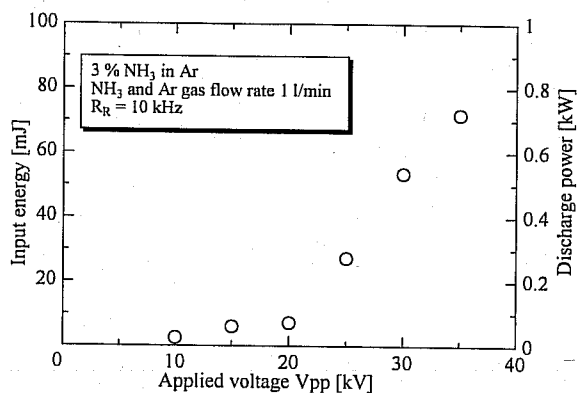
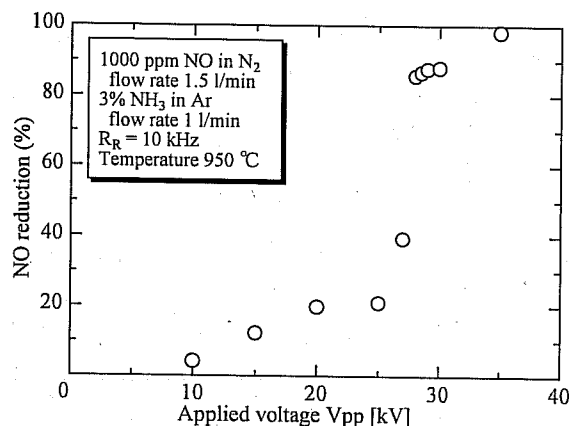


Fig.2 Waveform of voltage supplied from OCS power source.



**Fig.3 Discharge power as a function of applied voltage  $V_{pp}$ .**



**Fig.4 NO reduction as a function of applied voltage  $V_{pp}$ .**

contribute to decompose the NO<sub>x</sub> gas. The ammonia radicals, NH and NH<sub>2</sub> are generated at above 25 kV, where they reduce NO<sub>x</sub> more efficiently.

Figure 5 shows the emission spectra for the radicals produced from 3 % ammonia in argon gas. It is known that one of the ammonia radicals, the NH radical has a strong emission at wavelengths of 336-337 nm<sup>2)</sup>. The abrupt change in the production rate of the NH radicals suggests the existence of the threshold voltage for the production of the ammonia radicals.

A comparison of Figure 5 with Figure 4 shows that the applied-voltage dependence of the NO reduction is similar to that of the intensity of the peak, suggesting a dominant contribution of ammonia radicals in the decomposition of NO<sub>x</sub>.

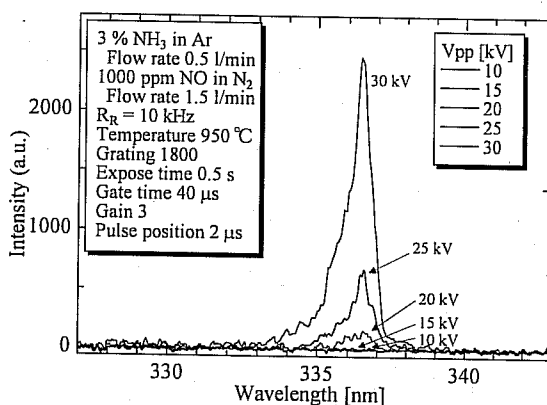
### b) Effect of duty cycle

Figure 6 shows the discharge power as a function of the duty cycle of the OCS power source. The duty cycle was changed by the repetition rate  $R_R$ . The discharge power increases linearly with increasing duty cycle, because of a fixed value of energy input per one pulse. Figure 7 shows the NO reduction as a function of the duty cycle. The NO reduction is largest at a duty cycle of 10 %. This fact suggests that the radicals, which are effective in NO reduction, decrease at a high discharge power.

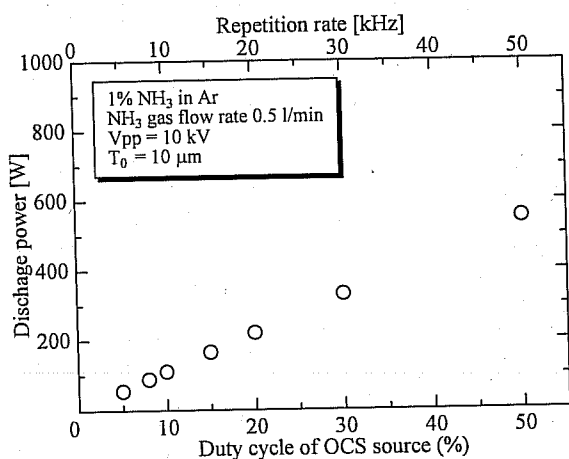
### c) Effect of mean residence time of NH<sub>3</sub> gas

Figure 8 shows the NO reduction and the discharge power as a function of the mean residence time of NH<sub>3</sub> gas. The NO reduction increases with increasing the mean residence time at below 1.8 s, and decrease at above 5.4 s, indicating 100 % reduction at 5.4 s.

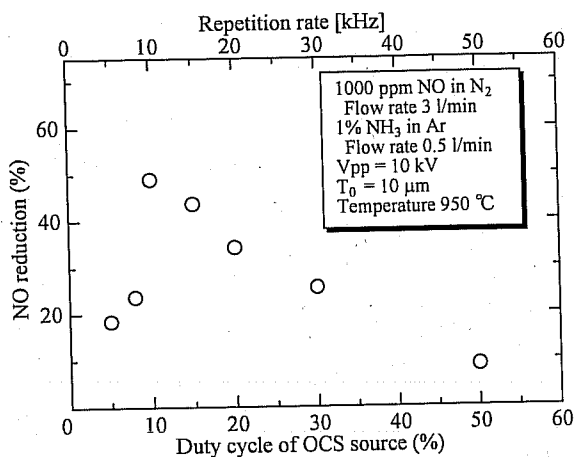
It is expected that the reduction of NO is influenced by the residence time in discharge area, where the discharge power is



**Fig.5 Emission spectra of NH radical for various applied voltages  $V_{pp}$ .**

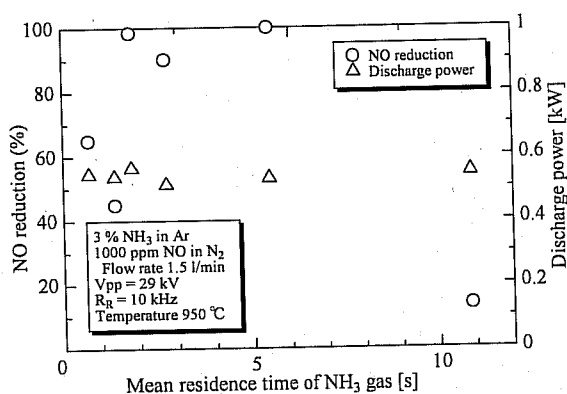


**Fig.6 Discharge power as a function of duty cycle (repetition rate).**



**Fig.7 NO reduction as a function of duty cycle (repetition rate).**

independent of the mean residence time of  $\text{NH}_3$  gas, as shown in Figure 8. The low NO reduction at a mean residence time below 1.8 s is explained by an insufficient quantity of the generated radicals, which are effective to the NO removal. In the meantime, the decreased NO reduction at a mean residence time above 5.4 s is attributable to the fact that the effective radicals are changed to less effective ones, when they are overexposed to the plasma.



**Fig.8 NO reduction and discharge power as a function of mean residence time of  $\text{NH}_3$  gas.**

#### IV. Conclusions

$\text{NO}_x$  was reduced by the plasma-treated gas. The plasma was generated by dielectric barrier discharge. The plasma-treated ammonia in argon was injected into the reaction chamber from the radical injector.

The NO reduction and the discharge power abruptly increased at applied voltages of 20-25 kV. The change of the emission spectrum observed at the exit of the radical injector was consistent with that of the NO reduction, i.e., the concentration of the  $\text{NH}$  radicals increased with increasing applied voltage. The discharge power increased with increasing duty cycle, and the NO reduction had an optimal value at duty cycle 10%. The optimal mean residence time of  $\text{NH}_3$  for 100 % NO reduction was 5.4 s.

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