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Optimum Conditions for De-NOx by Dielectric Barrier Discharge

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Abstract NO in N_2 gas was removed by injecting ammonia radicals, which were externally generated by flowing the NH_3 gas diluted with Ar gas through dielectric barrier discharge with a one-cycle sinusoidal-wave power source. The discharge was intermittently formed between coaxial cylindrical electrodes with a space of 1.5 mm at an applied peak-to-peak voltage of 2-15 kV. The generated radicals were introduced in a reaction chamber and mixed with NO gas, which was diluted with N_2. The dependence on the discharge power was measured by varying the repetition rate and applied voltage. The energy efficiency increased with decreasing the discharge power. The maximum energy efficiency was obtained at small values of the NH_3 concentration and the discharge power.

Keywords: Dielectric barrier discharge, NOx removal, Ammonia radical

1. Introduction

The nitrogen oxide (NOx) emission from thermoelectric power plants, diesel automobiles and so forth is an urgent problem that must be solved. For large-scale NOx removal using ammonia radicals, plasma processes have been utilized in addition to the electron-beam process [1-3]. The plasma processes have attracted attention because of their low equipment costs and simple system. The reported plasma processes used the dielectric barrier discharge (DBD, silent discharge) [4,5] and the corona discharge [4,6,8]. In most NOx removal systems using the plasma process, the plasma is produced in a mixed state of NOx and reaction gas such as ammonia to convert NOx into harmless gases such as N_2, O_2 and H_2O. The mixed state production of the plasma is disadvantageous for scaling up the equipment.

The authors have developed the radical injection NOx removal system, in which the ammonia radicals are generated by a DBD in a separate chamber and injected into a mixing zone of the reaction chamber. The radical injector is compact in scale and easy to sale up by its multiple setting. As a power source for generating plasma in the radical injector, an intermittent one-cycle sinusoidal (OCS) output has been used to find an appropriate discharge conditions for efficient use of the power source.

This paper discusses the optimum conditions for NOx reduction and for its energy efficiency about the flow rate of ammonia (NH_3) gas, the concentration of NH_3, the applied voltage to DBD electrodes, and repetition rate of OCS output.

2. Experimental

2.1 Experimental facilities

Figure 1 shows a schematic diagram of the NOx reduction system using ammonia radicals, which are produced by intermittent dielectric barrier discharge. Nitric oxide (NO) gas was diluted with nitrogen, and NH_3 was diluted with argon gas. The concentrations and flow rate of NO and NH_3 were adjusted in the gas blender by mixing with nitrogen and argon gas. The NO concentration was 908-978 ppm by volume, and the gas flow rate was 1.58 l/min. It was fed to the reaction chamber, which was externally heated by three electric heaters.

The concentration ($NO+NO_2$) of the processed gas after flowing through the reaction chamber was measured with a NOx meter set at the exit of the reaction chamber. The gas exhausted from the NOx meter flows into the water-shower gas-process system. The NO reduction is defined as the ratio of NO reduced to the initial concentration of NO, and the energy efficiency of NO reduction is defined as the mass flow rate of reduced NO per discharge power. The reaction temperature was varied from 230 to 600 ℃. It was measured at the mixing zone in the reaction chamber by a thermocouple.

The optimum conditions for NOx reduction and for its energy efficiency were obtained concerning the applied voltage to DBD electrodes, the repetition rate of OCS output, the mean residence time of NH_3 gas, and concentration of NH_3. The mean residence time of NH3 gas is defined as a duration that the discharge length in the radical injector is divided by a flow rate of the NH_3 gas

2.2 Radical injector

A schematic diagram of the radical injector is shown in **Fig.2**. The electrodes are coaxial in configuration with quartz glass tubes as dielectric materials. The outer glass tube is 61 mm in diameter and 2 mm thick, while the inner glass tube is 50 mm in diameter and 2 mm thick. Thus, the gap between the outer and inner glass tube is 1.5 mm. The dielectric barrier discharge occurred at the gap. The grounded outer electrode is made of a mesh steel sheet, and the inner electrode made of a stainless steel. **Figure 3** schematically shows a waveform of the applied OCS voltage. The repetition rate RR is defined as the reciprocal of the repetition time T1 of the discharge. T0 was approximately 10 μ s, and R_R was varied from 3 to 30 kHz. That is, the OCS voltage was intermittently applied to the gap for a duration of 10 μ s at a duty cycle of 3 to 30%. The discharge time is defined as total times of the duration of the dis-

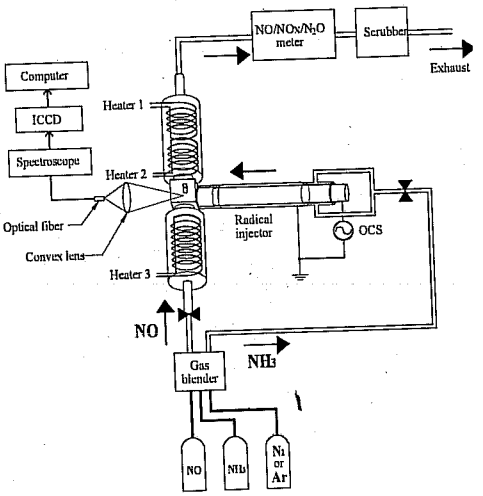


Fig. 1. Schematic diagrams of experimental apparatus.

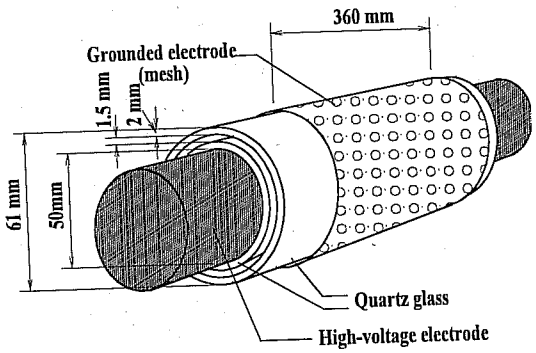


Fig. 2. Radical injector with its dimensions.

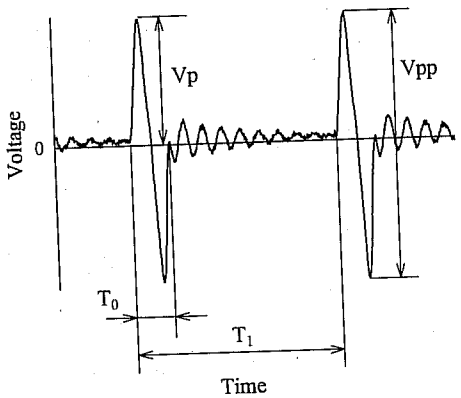


Fig. 3. Waveform of voltage supplied from a one-cycle sinusoidal power source.

charge in one cycle.

Figure 4 shows a schematic diagram of the electrical circuit for producing a DBD and for measuring electrical characteristics. The output peak-to-peak voltage of the power supply was 2 to 15 kV. The voltage was raised by a pulse transformer (winding ratio of 1:15). The time evolutions of source voltage, current and accumulated charge were simultaneously monitored with an oscilloscope.

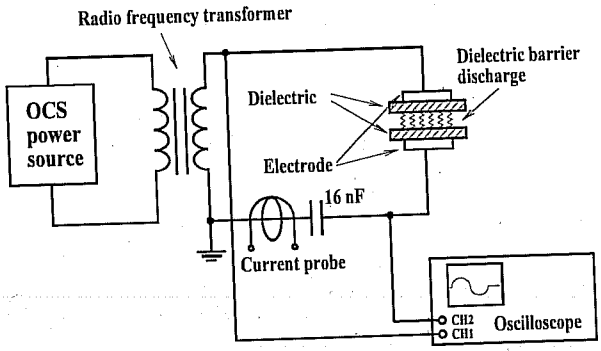


Fig. 4. Circuit for measurements of electric characteristics.

The energy input during one cycle of the DBD was estimated from the accumulated charge and the voltage across the output windings of the transformer using the V-Q curve of the Lissajous figure. In general, the plasma discharge power P(t) is obtained from the product of the instantaneous current I(t) and the applied voltage V(t),

$$P(t) = I(t)V(t) \qquad (1)$$

The accumulated charge was obtained from the voltage Vc(t) across a series capacitor C_0 = 16 nF ($C_0 >> C_d$ and C_{gap}, where C_d and C_{gap} are the capacitances of the dielectric material and the gap, respectively) that was connected in series at the ground side in the circuit.

$$I = C_O(dV_C / dt) \qquad (2)$$

Therefore,

$$P(t) = C_0(dV_c / dt)V(t) \qquad (3)$$

When V(t) is independent of time and is constant V*, an integration of Eq. (3) from t = 0 to the half period t of the applied voltage yields,

$$\int_0^\tau P(t)dt = V^* \int_0^\tau dQ = V^* Q \qquad (4)$$

Thus, the energy E consumed by the discharge, which is expressed by the first term of Eq.(4), is equal to the product of the average discharge voltage V* and the charge Q accumulated in a series capacitor C0. Therefore, E multiplied by 2, which is equal to the area enclosed by the charge-voltage curves in the Lissajous figure, indicates the input energy during one cycle of DBD. The input energy multiplied by the repetition rate yields the discharge power, i.e. the power consumed by the discharge,.

3. Results and discussion

3.1 Electrical characteristics

A glow-like discharge was observed visually, and the current waveform on oscillogram showed no series of spikes, which is

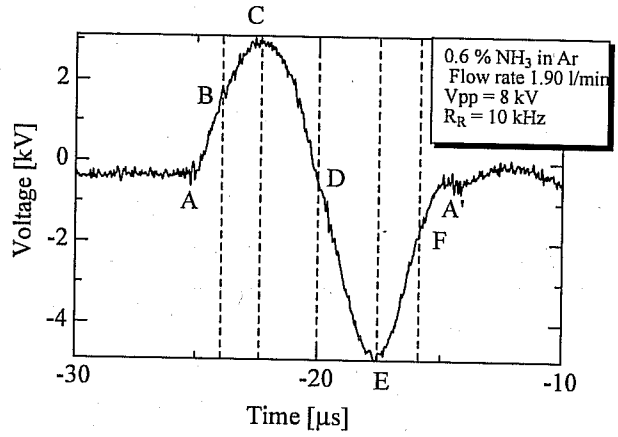


Fig. 5. Waveform of voltage at Vpp of 8 kV.

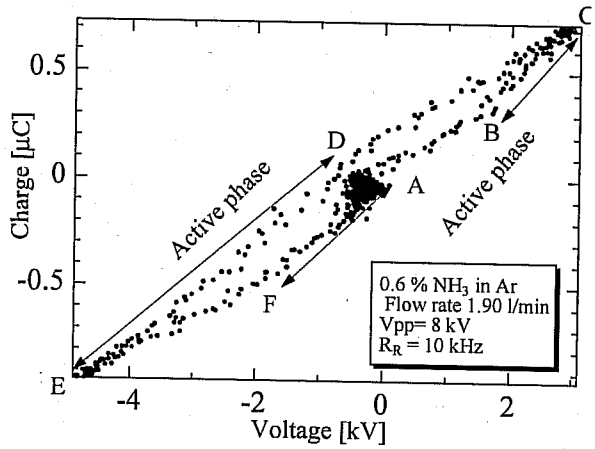


Fig. 6. V-Q Lissajous figure.

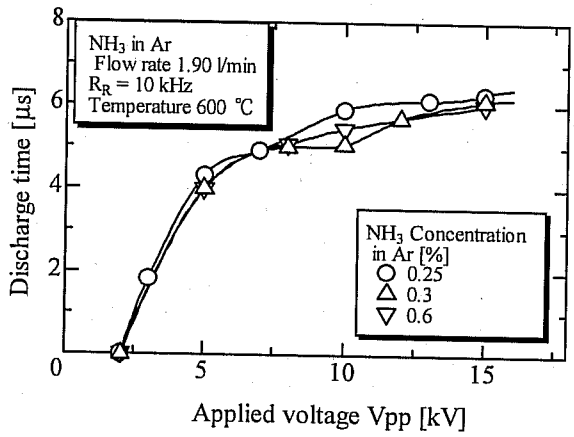


Fig. 7. Discharge time as a function of applied voltage and NH_3.concentration.

characteristic of the filamentary discharge. Examples of the voltage waveform and the voltage-charge Lissajous figure for glow-like DBD are shown in **Figs.5** and **6**, respectively. Corresponding phases are marked by *A-F* in both figures.

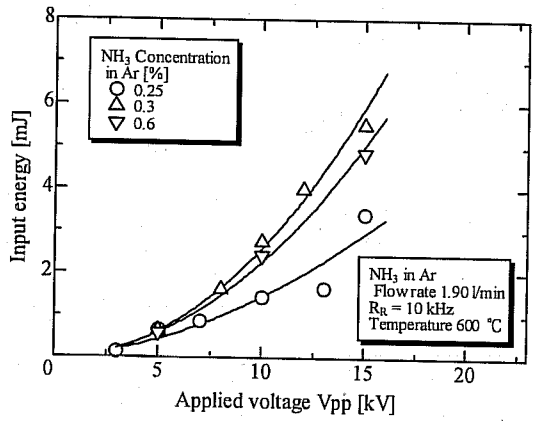


Fig. 8. Input energy as a function of applied voltage and NH_3.concentration.

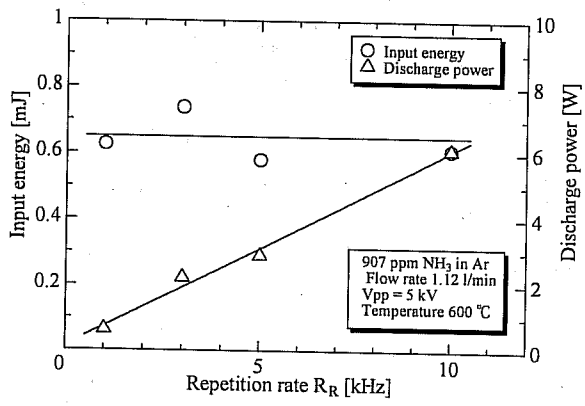


Fig. 9. Input energy and discharge power as functions of repetition rate.

The figure is not like a parallelogram, which is a typical form for DBD. The parallelogram is distorted at the rising period *A-B*, due to the application of OCS pulse voltage. The voltage starts to increase at *A* followed by *B* which corresponds the firing of discharge. Therefore, *A* agrees with *B*, if a continuous sinusoidal power source is used. The slope of the parallelogram, which represents the total capacitance of both the dielectric material and the discharge gap, becomes large during the discharge. Thus, the discharge occurs during *B-C*, *D-E*, and *F-A* in one cycle.

Figures 7 and **8** respectively show the discharge time and the input energy in the DBD for three kinds of NH_3 concentrations as a function of the applied voltage. Apparently, the NH_3-concentration dependences of discharge time and input energy are weak At each NH_3 concentration, the discharge time linearly increases with increasing applied voltage at <5 kV and hits the ceiling of about 6 μ s at above -10 kV. The saturated discharge time is about 60% of the total duration of the one cycle. On the other hand, the increase in input energy continuously accelerates with increasing applied voltage, and consequently the input energy per unit discharge time increases with increasing applied voltage. Thus, the increase in input energy is not solely due to the increases in discharge time at

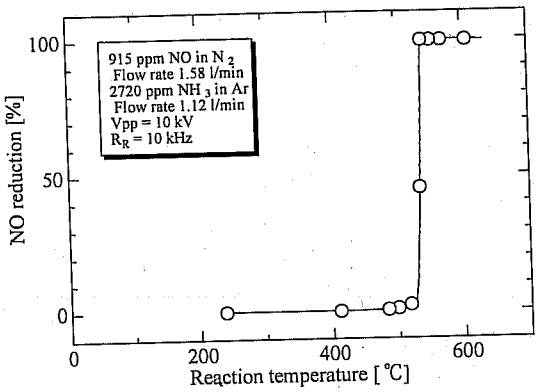
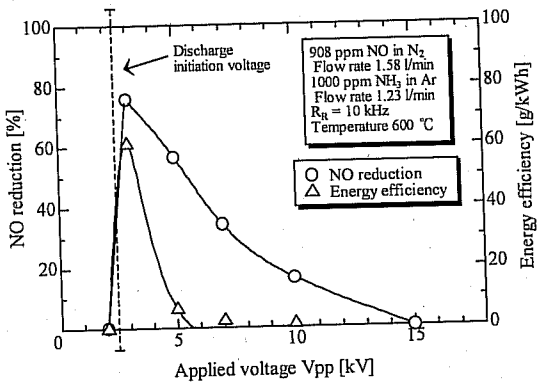
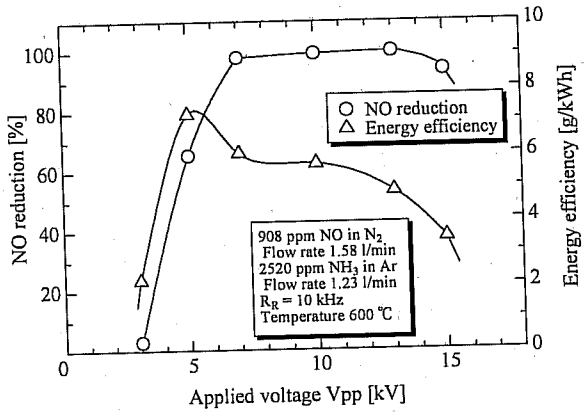


Fig. 10. NO reduction as a function of reaction temperature.



(a) NH_3 1000ppm



(b) NH_3 2520ppm

Fig. 11. NO reduction and its energy efficiency as functions of applied voltage for ammonia concentrations of (a) 1000 ppm and (b) 2520 ppm.

applied voltage above about 5kV.

Figure 9 shows the input energy in the DBD plasma and discharge power as a function of the repetition rate of OCS power source. At a constant applied voltage, the input energy is independent of the repetition rate, and therefore the discharge power is proportional to the repetition rate.

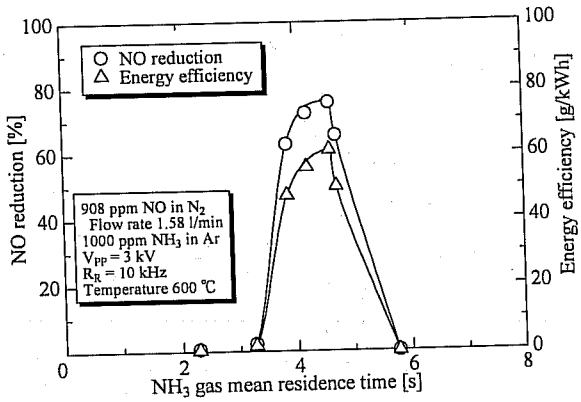


Fig. 12. NO reduction and its energy efficiency as functions of mean residence time for NH_3 gas.

3.2 Reaction temperature

Figure 10 shows the NO reduction as a function of reaction temperature. De-NOx occurs at a temperature above 500 ℃ and 100% de-NOx can be attained at 550 ℃. When DBD was switched off, no de-NOx could be obtained even at a temperature 1000 ℃. Low-temperature de-NOx using the DBD plasmas indicates that the radical formation plays an important role for de-NOx. The following results were obtained at a reaction temperature of 600 ℃.

3.3 Optimum conditions

(a) Applied voltage

Figure 11 shows the NO reduction and its energy efficiency at NH3 concentrations of 1000 and 2520 ppm as a function of applied voltage. The discharge-firing voltages of the DBD were about 2.5 kV for both NH3 concentrations. The energy efficiencies show the maximum values. Thus the optimum applied voltages are 3 and 5 kV for NH_3 concentrations of 1000 and 2500 ppm, respectively. For NH_3 concentration of 2520 ppm, the NO reduction show the maximum values at the same applied voltage as that for the energy efficiency, but for NH_3 concentration of 2520 ppm, the 100 % NO reduction occurs at higher applied voltages of 7 -13 kV. It is noted that the difference in optimum energy efficiency are very large between the two NH3 concentrations. The latter is about one-tenth of that for the former. The low energy efficiency suggests that larger energy is necessary for de-NOx at a higher NH3 concentration, although the NH_3-concentration dependences of discharge time and input energy are weak as shown in **Figs. 6** and **7**. Thus, the optimum condition for NOx reduction strongly depends on NH_3 concentration..

(b) Flow rate of NH_3 gas

Figure 12 shows the NO reduction and its energy efficiency at a NH3 concentration of 1000 ppm as a function of mean residence time of NH3 gas. They show the maximum values at the same value of the mean residence time. i.e., 4.6 s. The corresponding flow rate of NH3 gas is 1.23 l/min. Thus, there is an optimum mean residence time (flow rate) for NOx reduction and for its energy efficiency.

(c) NH_3 concentration

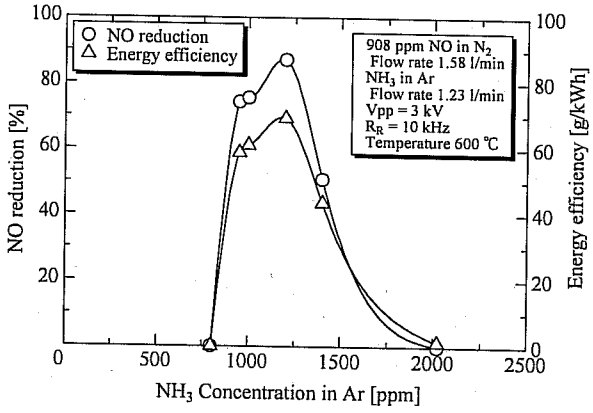


Fig. 13. NO reduction and its energy efficiency as a function of ammonia concentration.

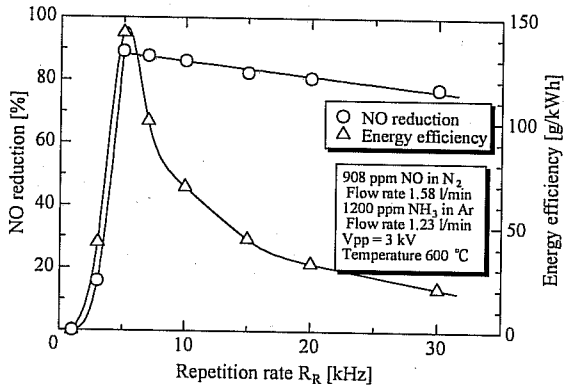


Fig. 14. NO reduction and its energy efficiency as functions of repetition rate.

Figure 13 shows the NO reduction and its energy efficiency at a flow rate of NH_3 gas of 1.23 l/min (the optimum flow rate) as a function of NH_3 concentration in a concentration range from 750 to 2500 ppm. Both NO reduction and energy efficiency show the maximum values (90% and 70 g/kWh) at an NH_3 concentration of 1200 ppm. Thus, there is an optimum NH_3 concentration for NOx reduction and for its energy efficiency.

(d) Repetition rate

On the basis of the above-mentioned results, a NH_3 concentration of 1200 ppm, a NH_3 flow rate of 1.23 l/min and an applied voltage of 3 kV were adopted as the optimum values for de-NOx. **Figure14** shows the NO reduction and its energy efficiency as a function of repetition rate. Both NO reduction and energy efficiency show the maximum values at a repetition rate of 5 kHz. Thus, there is an optimum repetition rate for NOx reduction and for its energy efficiency. The value of the maximum energy efficiency, 140 g/kWh, is very high for de-NOx at a NO concentration of 908 ppm, indicating highly energy-efficient de-NOx can be obtained at these optimum conditions. A value of the energy efficiency, 380 g/kWh, has also been reported for NOx reduction at a NO concentration of 200 ppm by using corona shower [7]. This means that the ammonia radical injection methods are energy efficient for de-NOx.

4. Summary

Ammonia radicals produced in an intermittent dielectric barrier discharge plasma were injected into NO flowing reaction chamber. There are optimum conditions for NOx reduction and for its energy efficiency in the NH_3 concentration, the NH_3 flow rate, the repetition rate, and the applied voltage. Under a set of the optimum values of these conditions, the maximum value of the energy efficiency, 140 g/kWh, was obtained at a NO concentration of 908 ppm. The ammonia radical injection methods are energy efficient for de-NOx.

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