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Improved Decomposition Efficiency of Nitrogen Oxides using Superposing SPCP and Corona Discharges

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Abstract: The superposing effect of an SPCP(Surface discharge-induced Plasma Chemical Process) and corona discharge were studied for the removal of NO_x from industrial flue gases. The NO_x removal rates caused by an SPCP, corona discharge, and superposing discharge were monitored and compared. The parameters included the concentration, flow rate of gas, frequency, and type of discharge. The experimental results showed that the NO_x removal rate with a superposing discharge was 10∼30% higher than that with the other two modes. The maximum obtainable NO_x removal rate with only a SPCP (18 W) on a corona discharge (7 W) was 85% and 12%, respectively. However, the combination of the two modes, produced a 95% NO_x removal rate with a discharge power of 18 W with a lower frequency (450 Hz). A higher NO_x removal rate was observed with a lower frequency in the upper electrode in the combined reactor and a higher frequency in the lower electrode. Accordingly, corona discharge (below 600 Hz) in the current study, a combined with an SPCP electrode (at a lower power) appeared to be the best method to remove NO_x.

Keywords: *superposing, discharge plasma, NO_x, decomposition efficiency*

Introduction

Environmental problems caused by harmful gases emitted from various industrial sources have become a significant issue in recent years, and to cope with these problems, many technologies have been intensively investigated in industrialized nations. Although plenty of useful outcomes and suggestions have been made, few commercial products which effectively decompose pollutant gases have appeared yet.

A recent technology that has received a lot of attention in this context is non-thermal plasma. Non-thermal plasma, sometimes called "cold plasma" or "non- equilibrium plasma" being the opposite to thermal plasma [1], is plasma in which the electron temperature is very high and the ion/molecular temperature is low. In non-thermal plasma, the electron mean energies are considerably higher than those of the components of the ambient gas. The majority of the electric energy goes into producing energetic electrons, rather than into heating gas and ions. Through the electron-impact dissociation and ionization of the background gas molecules, the energetic electrons produce free radicals, ions, and additional electrons, which, in turn, oxidize, reduce, or decompose the pollutant molecules [2].

Penetrante [3] experimentally demonstrated that an electron beam pollution control system is a better process in terms of the decomposition rate and power consumption ratio. However, X-ray hazard associated with an electron beam process has motivated studies into alternative plasma-based technologies, such as those utilizing electrical discharges. Electrical discharges can be produced in many different forms, depending on the geometry of the reaction and the electrical power supply. Masuda [4] studied the removal of organic solvents such as acetone using a surface discharge induced plasma chemical process (SPCP). Mizuno [5] suggested that SO_x and NO_x can be reduced by a ferro-electric packed bed corona discharge. Civitano [6] studied the removal of emissions from a coal firing power plant using pulsed corona discharges. Recently, Shimizu and Oda [7] studied

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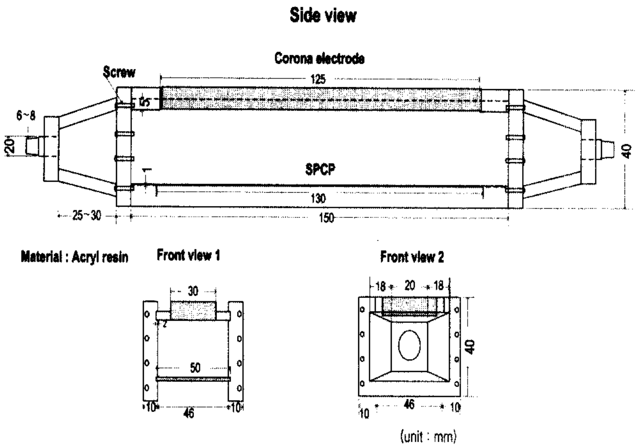

Figure 1. Structure of surface/corona mixed reactor.

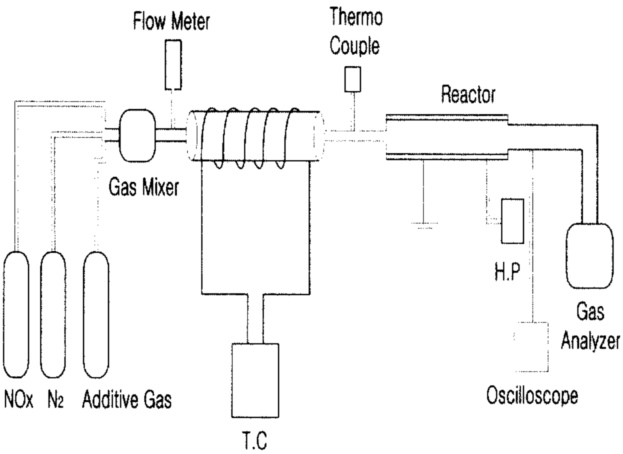

Figure 2. Schematic of experimental system.

the effect of catalysts and additives combined with electrical discharges. Okubo [8] performed that experiments on NO_x removal using a newly designed corona radical shower system. Ito [9] showed that the efficiency of a dielectric barrier discharge reactor could be improved by combining with SPCP.

In this paper, two different discharge systems, a plane ceramic-based surface discharge electrode and a corona electrode with a tungsten needle array, are combined to fabricate a hybrid plasma reactor, then the superposing effect of an SPCP and a corona discharge is investigated to improve the NO_x decomposition efficiency.

Experimental

The principal experimental apparatus utilized in this study was a SPCP and corona mixed reactor. A drawing of the system is shown in Figure 1. An array electrode with embedded needle-shaped electrodes was used for the corona discharges and planar electrodes were used for the SPCP. The experiment was conducted using the gas flow system shown in Figure 2.

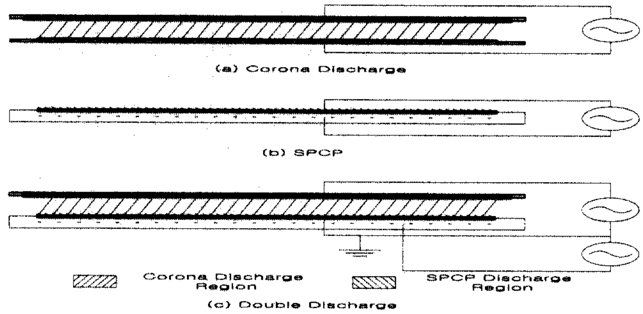

Figure 3. Discharge mode.

NO (1500 ppm in N_2) and NO_2 (500 ppm in N_2) were used as standards. The discharge power was determined from the integrated area of 1 cycle by an oscilloscope connected with a high voltage probe and current probe.

A gas feed of NO gas (300 ~ 500 ppm) and the N_2 balance gas were maintained at 25 ~ 200°C by a temperature controller and flowed into the mixed reactor at a flow rate of 1 L/min ~ 10 L/min. To obtain stable discharges the frequencies for the SPCP and corona discharge were varied within a range of 5 kHz ~ 20 kHz and 450 Hz ~ 2 kHz, respectively. For both modes the appropriate voltage range was 0 ~ 12 kV (0 ~ 80 W). The concentrations of the gas products were monitored using a NO_x meter (Ecom-AC, Germany). The experiment for the superposing discharge was conducted by varing the lower power supply from 2 W to 20 W, while the upper power supply was maintained at 6 W. When the lower power supply was fixed at 6 W, the upper power supply was varied within a range of 1 W ~ 10 W. The experiments were also performed varying the flow rate and the initial concentration of NO and NO_2. The final by-product gas was analysed using a FT-IR (Nicolet, Magna-IR 560) with a 10 cm diameter Pyrex gas cell. Figure 3 depicts the superposing discharge mode composed of needle shaped electrodes (upper electrode) and stripe-planar electrodes (lower electrode)

Results and Discussion

Superposing effect on NO and NO_2 decomposition

The superposing discharge effect on the NO removal rate is represented in Figures 4 and 5. The initial concentration and flow rate of NO was 300 ~ 500 ppm (in N_2) and 2 L/min, respectively. For the corona discharge (upper electrode), the frequency was 450 Hz and the discharge power varied within a range of 0 ~ 9 W. For the superposing discharge, the discharge power was fixed at either 3.5 W or 6W. The frequency and discharge power of the SPCP (lower electrode) was 10 kHz and 0 ~ 20 W, respectively. Figure 4 represents the NO

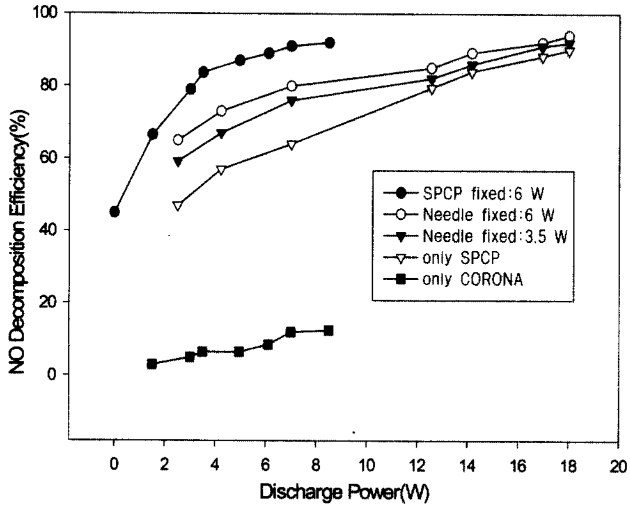

Figure 4. Superposing discharge effect on NO decomposition(NO 300 ppm).

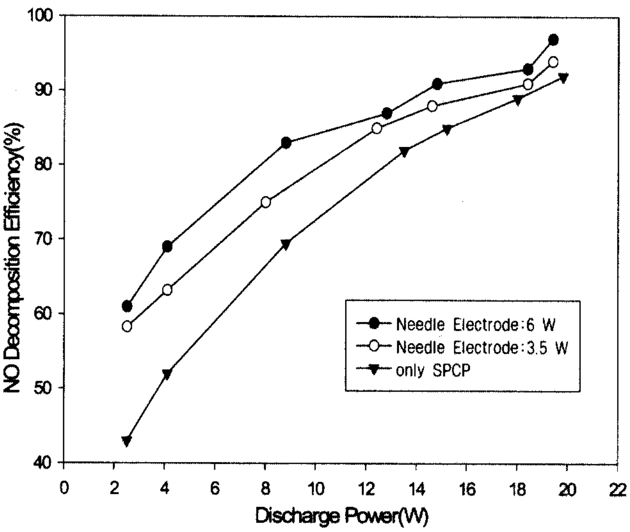

Figure 5. Superposing discharge effect on NO decomposition(NO 500 ppm).

removal rate, which was about 12% and 85% with the corona discharge (7 W) alone and SPCP (18 W) alone, respectively. With the superposing discharge, the NO removal rate increased by 10% (3.5 W) and 20% (6 W) compared to that with only the SPCP. With a fixed discharge power for the SPCP (6 W) and a variable power for the upper electrode (0 ~ 8 W), the corresponding NO removal rate was 45% (at 0 W) and 92% (at 8.5 W). These results show that the NO removal rate increased by 30% compared to that with the SPCP alone, and that by the superposing discharge effect on the NO removal rate reached 92% with a low power of 8.5 W, although it was about 90% with a high power of 18 W with only the SPCP. Accordingly, it would appear that, in the corona discharge region, only the specific localized area near to the needle array was influenced in relation with the energy transfer and discharge distribution, whereas under the superposing discharge much more energy was transferred throughout the reactor, including other regions, due to the addition of the SPCP discharge [9].

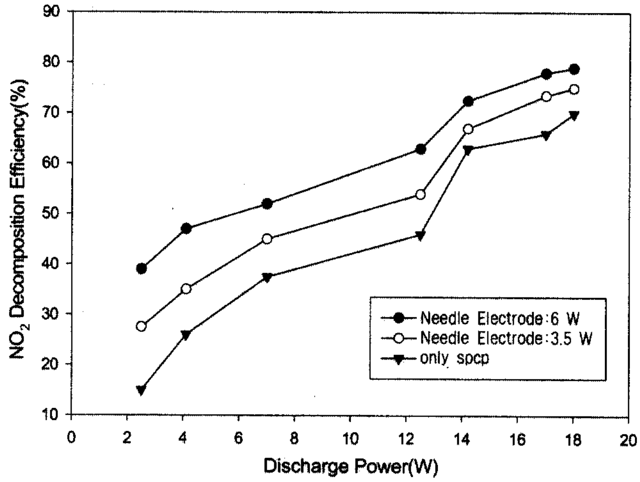

Figure 6. Superposing discharge effect on NO_2 decomposition.

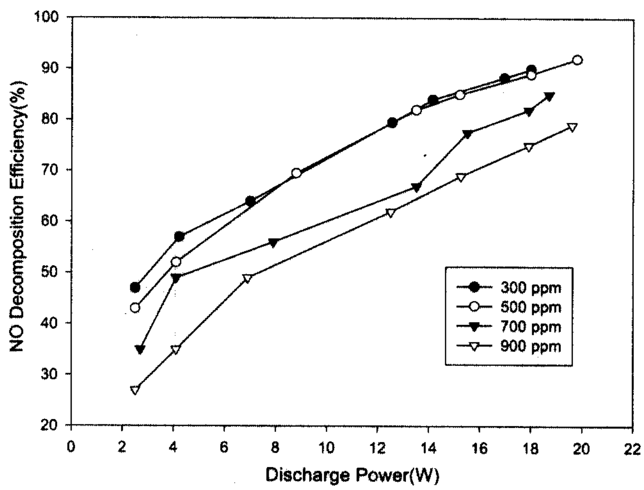

Figure 7. Effect of concentration on NO decomposition (only SPCP).

As shown in Figure 5, the NO removal rate increased due to the superposing effect along with a higher initial concentration of NO (500 ppm). With the superposing discharge (corona : 6 W), the NO removal rate increased by 20%. The NO removal rate due to the superposing discharge in the current study was higher than with the combined effect of the SPCP and barrier discharge performed by Ito *et al.* [10]. Figure 6 demonstrates the superposing effect on NO_2 removal under the same experimental conditions as those in Figure 5. The NO_2 removal rate also increased about 25% due to the superposing discharge effect. The maximum obtainable removal

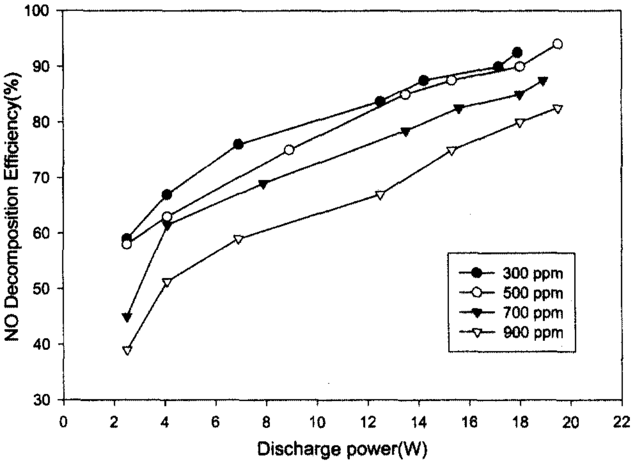

Figure 8. Effect of concentration on NO decomposition(Needle electrode : 3.5W).

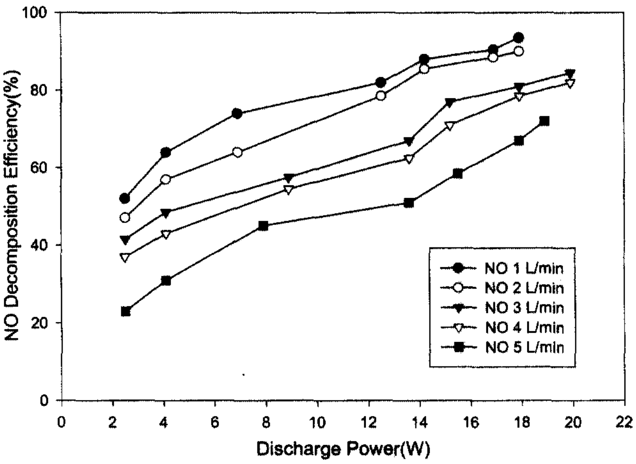

Figure 9. Effect of flow rate on NO decomposition.

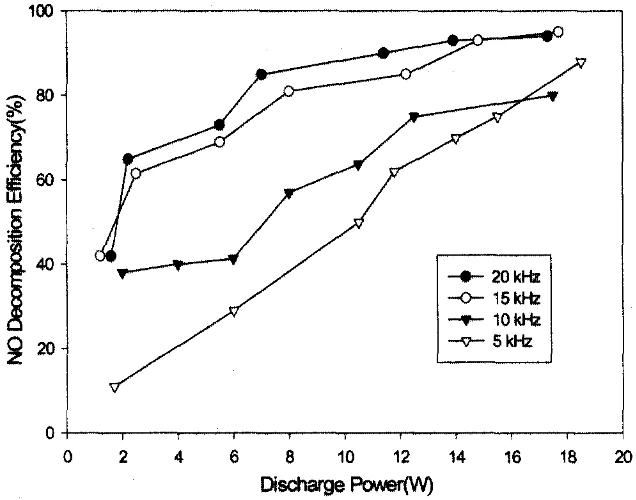

Figure 10. Effect of frequency on NO decomposition.

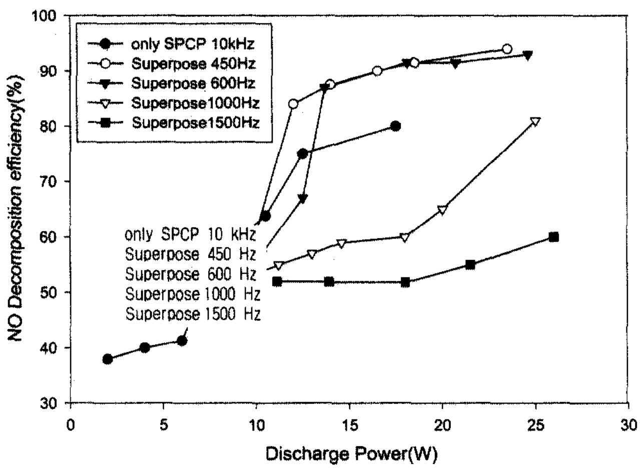

Figure 11. Effect of superposing discharge frequency on NO decomposition.

rate of NO and NO_2 was 95% and 80%, respectively.

Effect of concentration and flow rate

The NO removal rate due to the SPCP and superposing discharge is shown in Figures 7 and 8 with an initial concentration of NO within a range of 300 ~ 900 ppm. Figure 7 represents the effect of the SPCP (10 kHz) alone and Figure 8 the effect of needle electrodec(3.5 W) Decreasing the concentration of NO enhanced the NO decomposition efficiency. This was because the higher energy necessary to decompose NO was obtained at a lower concentration with a specific power. Accordingly, it would seem that the decomposition efficiency increased with a small concentration because of the high probability of N · and O · radicals, produced as a result of collision with the base gases, reacting with NO or free electrons reacting with NO directly. Figure 9 shows the effect of the NO gas flow rate on NO removal when using an SPCP with an initial concentration of NO (300 ppm). The NO gas flow rate varied within a range of 1 ~ 5 L/min. With a higher flow rate, a lower NO removal rate was obtained. With a discharge power of 18 W the NO removal rate was 95% and 70% for a NO flow rate of 1 L/min and 5 L/min, respectively. As the residence time for passing through the reactor increased, the collision frequency of NO with free electrons increased and the energy necessary to react became high; hence it would appear that the decomposition efficiency rose due to an increase in the radicals reacting with NO gas .

Effect of frequency on NO decomposition

Figures 10 and 11 represent the effect of frequency variation on the NO removal rate. NO (500 ppm in N_2) flowed at a flow rate of 2 L/min onto the SPCP electrode. The frequency applied to the SPCP electrode was within a range of 5 kHz~20 kHz. As shown in Figure 10, with a lower power (2 W) the NO removal rates were 11% and 42% for frequencies of 5 kHz and 20

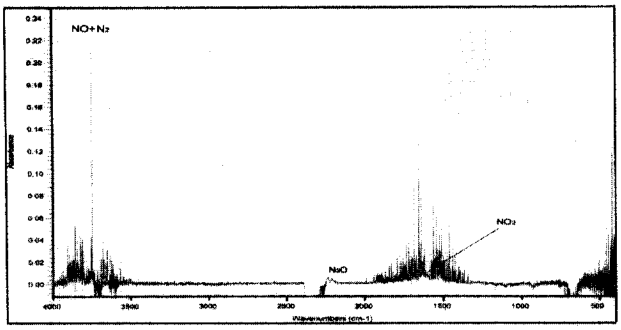

Figure 12. Infrared absorbance spectrum of the gas residue.

kHz, respectively. A higher NO removal rate was obtained with a higher applied frequency. This was due to the increased receiving electrical energy per unit of time with a higher frequency. Oda [11] suggested the same tendency in a study of CFC dissociaton. The effect of the superposing discharge is shown in Figure 11. The NO removal rate was maintained at a flow rate of 2 L/min when the frequency on the SPCP electrode (6 W) was fixed at 10 kHz and that on the corona electrode varied between 450 Hz and 1500 Hz. With the SPCP discharge alone the NO removal rate was 41% (at 6 W) and 80% (at 18 W). However, with the superposing discharge (SPCP:6W, corona:12 W), the NO removal rate was 95%. This result shows that the superposing discharge was more efficient than the SPCP alone. With a higher frequency (1 kHz or 1.5 kHz), the superposing discharge was less efficient than the SPCP discharge. Therefore, the corona discharge (below 600 Hz) combined with the SPCP electrode(low power) would appear to be the best method to remove NO_x.

By-product analysis

Figure 12 shows the typical FT-IR spectra of the sampled gases after discharge within a range of 4000 ~ 500 cm^{-1} in the case of the N_2-NO mixture gas system. The initial concentration of NO was 500 ppm, base gas N_2, flow rate 2 L/min, and discharge power 15 W. It was confirmed by the spectra that NO was converted to NO_2 and only a small amount of N_2O was generated. N_2O is considered as one of the by-products due to a radical reaction ($2NO \rightarrow N_2O + 1/2\ O_2$), as suggested by Breault and Mclarnon [12].

Conclusions

An experimental study was carried out to identify a method for enhancing the decomposition efficiency of nitrogen oxides (NO_x) using a superposing SPCP and corona discharge. The experimental results showed that the NO_x removal rate with the superposing discharge was 10~30% higher than that with the other two modes. With the combination of the two modes, 95% NO_x removal rate was observed with a discharge power of 18 W for a lower frequency (450 Hz). The NO_x removal rate caused by the superposing discharge increased with a longer retention time and lower initial concentration of NO_x. With a higher frequency, a higher NO_x removal rate was obtained. This was due to the increased number of electrons generated by the higher frequency. For instance, the NO removal rate with a discharge power of 18 W was 85% and 95% with frequencies of 5 kHz and 20 kHz, respectively. Accordingly, a corona discharge (below 600 Hz) combined with an SPCP electrode (at lower power) would appear to be the best method to remove NO_x.

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