

Removal of NO and SO₂ by Pulsed Corona Discharge Process

Young Sun Mok[†], Ho Won Lee, Young Jin Hyun, Sung Won Ham*, Jae Hak Kim** and In-Sik Nam**

Department of Chemical Engineering, Cheju National University, Ara, Cheju 690-756, Korea

*Department of Chemical Engineering, Kyungil University, Hayang, Kyungbuk 712-701, Korea

**Department of Chemical Engineering, Pohang University of Science & Technology,
Pohang, Kyungbuk 790-784, Korea

(Received 6 September 2000 • accepted 9 March 2001)

Abstract—Overall examination was made on the removal of NO and SO₂ by pulsed corona discharge process. The mechanism for the removal of NO was found to largely depend on the gas composition. In the absence of oxygen, most of the NO removed was reduced to N₂; on the other hand, oxidation of NO to NO₂ was dominant in the presence of oxygen even when the content was low. Water vapor was an important ingredient for the oxidation of NO₂ to nitric acid rather than that of NO to NO₂. The removal of NO only slightly increased with the concentration of ammonia while the effect of ammonia on the removal of SO₂ was very significant. The energy density (power delivered/feed gas flow rate) can be a measure for the degree of removal of NO. Regardless of the applied voltage and the flow rate of the feed gas stream, the amount of NO removed was identical at the same energy density. The production of N₂O increased with the pulse repetition rate, and the presence of NH₃ and SO₂ enhanced it. Byproducts generated from propene used as additive were identified and analyzed. The main byproducts other than carbon oxides were found to be ethane and formaldehyde, but their concentrations were negligibly small.

Key words: Corona Discharge, NO, SO₂, Gas Composition, Energy Density, N₂O, Byproducts

INTRODUCTION

Non-thermal plasma process induced by pulsed corona discharge can be used for the removal of various air pollutants and the conversion of natural gas to higher hydrocarbons [Dinelli et al., 1990; Mizuno et al., 1995; Song et al., 1996; Jeong et al., 2001]. Removal of NO and SO₂ as an application has been one of the major concerns in this field of pulsed corona discharge. Many studies have reported that chemical reactions caused by corona discharge are an effective method for the removal of such pollutants [Dinelli et al., 1990; Mizuno et al., 1995; Song et al., 1996]. The crucial role of corona discharge in the removal of NO and SO₂ is known by the oxidation of NO to NO₂ [Civitano, 1993; Oda et al., 1998]. Once NO₂ is formed by the corona discharge, it can be removed by several methods such as heterogeneous chemical reaction [Song et al., 1996], catalyst [Oda et al., 1998] or wet scrubbing [Shimizu et al., 1997]. A part of NO₂ can of course be further oxidized to nitric acid, which can be neutralized by a basic compound. It has been shown that SO₂ is easily removed when ammonia is added to the flue gas [Civitano, 1993; van Veldhuizen et al., 1998].

The removal of NO results from the reactions with the reactive components such as O, OH, HO₂, O₃, N, etc. [Lowke and Morrow, 1995; Mok et al., 1998a; Tas et al., 1997]. These components originate from water vapor, oxygen and nitrogen, and thus the composition of feed gas stream is a very important factor affecting the removal. As well, the dominant reactions for the removal may depend on the gas composition because it affects the concentration of each radical produced. Meanwhile, the removal of NO can be pro-

moted by using hydrocarbon additive [Ham et al., 1999; Mizuno et al., 1995; Oda et al., 1998; Song et al., 1996]. Although the favorable effect of hydrocarbon on the removal of NO was experimentally proved elsewhere, the mechanism of hydrocarbon-involved reactions and the formation of byproducts have not been fully understood yet. Therefore, analyzing the byproducts and understanding the related mechanism can be a matter of interest.

In this study, the composition of feed gas stream, the operating variables such as peak voltage and flow rate were varied to examine the quantitative effects on the removal of NO and SO₂, to understand which reactions control the process, and to find an integrated electrical parameter related to the removal of NO. The hydrocarbon additive used to promote the removal of NO was propene. The reaction byproducts formed from propene were identified and analyzed. The amount of nitrous oxide (N₂O) generated in this process was measured at several conditions.

EXPERIMENTAL

1. Experimental Apparatus

The schematic diagram of the coaxial type corona reactor is shown in Fig. 1. The central electrode (diameter: 0.5 mm) and the outer cylinder (inner diameter: 70 mm) are anode and cathode, respectively. Positive high voltage pulse was applied to the central wire with the outer cylinder grounded. The effective length of the reactor, i.e., the region that corona discharge covers, is 3 m. Fig. 2 shows the circuit of the homemade high voltage pulse generator. The negative dc high voltage power supply (Glassmann High Voltage Inc.) charges the capacitor C_p (791 pF) until the voltage on the capacitor reaches the spark-over voltage of the spark gap electrode acting as switch. When the spark gap switch is closed as a result of spark-

[†]To whom correspondence should be addressed.

E-mail: smokie@cheju.cheju.ac.kr

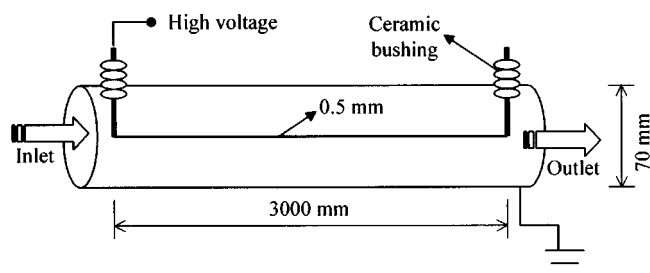


Fig. 1. Schematic of the corona reactor with wire-cylinder electrode combination.

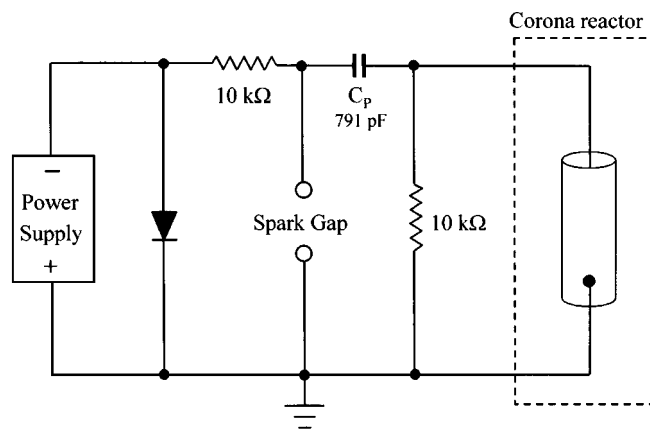


Fig. 2. Circuit of the high voltage pulse generator.

over, the energy stored in the capacitor is delivered to the corona reactor, producing narrow high voltage pulse.

For voltage measurement, a high voltage probe (Tektronix P6015) having DC attenuation of 1,000 : $\pm 3\%$ was used with a digital oscilloscope (Tektronix TDS 620B) of which bandwidth and sample

rate are 500 MHz and 2.5 GS/s. For current measurement, a current transformer (Tektronix CT-4), a current probe (Tektronix A6302) and a current amplifier (Tektronix AM503B) were used. The A6302 current probe covers frequencies up to 50 MHz. The CT-4 is a high current transformer that extends the measurement capability of the current probe. The current probe was connected to the current amplifier, which amplifies the current sensed by the current probe and converts it to a proportional voltage that is displayed on the oscilloscope.

The pulse energy delivered to the corona reactor was calculated with the voltage and current waveforms measured:

$$E_p = \int_0^t V I dt' \quad (1)$$

where E_p is the energy delivered per pulse, V is the pulse voltage, I is the pulse current and t is the pulse width. Due to the characteristics of the spark gap pulse generator used here, each pulsing produces slightly different waveforms. Therefore, at least one thousand waveforms acquired were averaged for the calculation of the energy.

2. Methods

Feed gas stream composed of N₂, O₂, H₂O, NO, SO₂ and NH₃ enters the inlet of the corona reactor, as shown in Fig. 3. The total flow rate of the mixed gas was 10 l/min. The contents of N₂ and O₂ that were major constituents of the gas stream were adjusted by flow meters with keeping the total flow rate unchanged, and the concentrations of NO, SO₂ and NH₃ were controlled by a mass flow controller (Model 1179, MKS Instruments, Inc.). The content of H₂O was varied by using its vapor pressure, i.e., by changing the temperature of the water bath in which a bottle containing water was immersed. The concentration of propene utilized as an additive was adjusted by a mass flow controller (Model 1179, MKS Instruments, Inc.). Typical charging voltage of pulse-forming capacitor (C_p) was 25 kV, and the pulse repetition rate was changed from

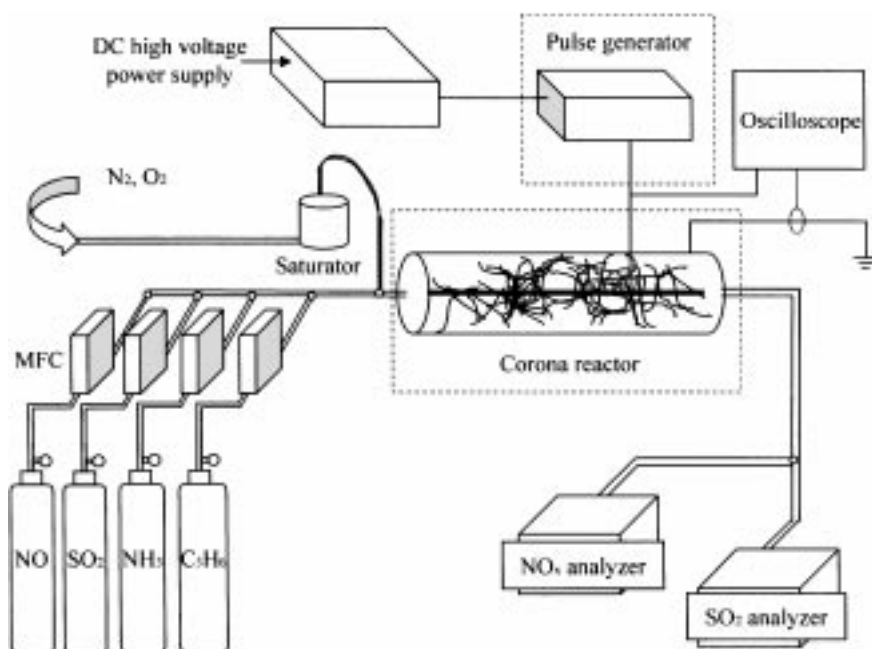


Fig. 3. Experimental apparatus for the removal of NO and SO₂ using corona discharge.

Table 1. Experimental conditions

Variable, unit	Typical value	Range
Flow rate, l/min	10	5-10
[NO _x] ₀ ([NO] ₀ + [NO ₂] ₀), ppm ^a	211 (165+46)	211 (165+46)
H ₂ O content, % (v/v)	2	0-5
O ₂ content, % (v/v)	20	0-20
[SO ₂] ₀ , ppm ^a	254	254
[NH ₃] ₀ , ppm ^a	0	0-575
Pulse repetition rate, Hz (pulses/s)	10-38	10-38
[C ₃ H ₆] ₀ /[NO _x] ₀	0	0-0.85
Capacitor-charging voltage, kV	25	15-25
Temperature, °C	25	25-40

^appm: parts per million, volumetric.

10 to 38 Hz (pulses/s). Table 1 summarizes the detailed experimental conditions of this study.

The concentrations of NO and NO₂ were analyzed at the reactor outlet before and after pulsed corona discharge by a chemiluminescence NO-NO₂-NO_x analyzer (Model 42H, Thermo Environmental Instrument Inc.). For the analysis of SO₂ concentration, a pulsed fluorescent SO₂ analyzer (Model 43C, Thermo Environmental Instrument, Inc.) was employed. Byproducts generated from propene were identified by a gas chromatograph-mass spectroscope (Platform II, Micromass UK, Ltd.) and a DB-5 capillary column (50 m×0.2 mm×0.33 μm) of J&W Scientific. The concentrations of the identified components were analyzed by a gas chromatograph (Hewlett Packard 5890) equipped with flame ionization detector (FID) and thermal conductivity detector (TCD). A stainless steel column (6 ft long and 1/8" in diameter) packed with Porapak N (All Tech) was used for the analyses of byproducts including C₂H₆, C₃H₆ and HCHO. Chromosorb 101 (All Tech) was used as the packing material for N₂O analysis. For the analyses of C₂H₆, C₃H₆ and HCHO, FID was employed and the oven temperature of the gas chromatography was maintained at 313 K for 5 minutes and increased to 454 K with a linear ramping rate of 20 K/min. N₂O was analyzed by using TCD at isothermal condition of 318 K during the course of the experiments.

RESULTS AND DISCUSSION

1. Feed Gas Composition

1-1. Effect of Oxygen Content

NO was removed under various oxygen content with the other variables kept constant as in Table 1. Fig. 4 and Fig. 5 show the effect of oxygen content on the removal of NO. The removal of NO can be explained as competition between oxidation and reduction. The main radicals responsible for the removal of NO may be O, OH, HO₂, N and O₃. As presented in Table 2, O, OH, HO₂ and O₃ formed from O₂ and H₂O are related to the oxidation of NO, and N radical is concerned with the reduction. Note that the production of N radical is more difficult than that of O or OH because the bond dissociation energy of N₂ (9.8 eV) is larger than that of O₂ (5.1 eV) or H₂O (5.2 eV) [Mizuno et al., 1986].

As the oxygen content was decreased up to 2% (v/v), the removal of the NO decreased because the production of the oxidation rad-

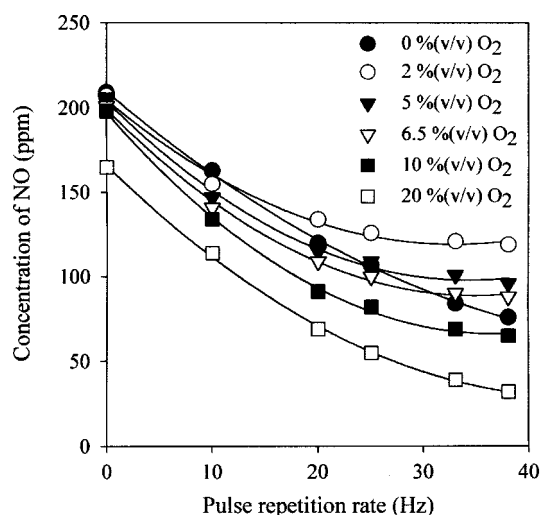


Fig. 4. Effect of oxygen content on the removal of NO.

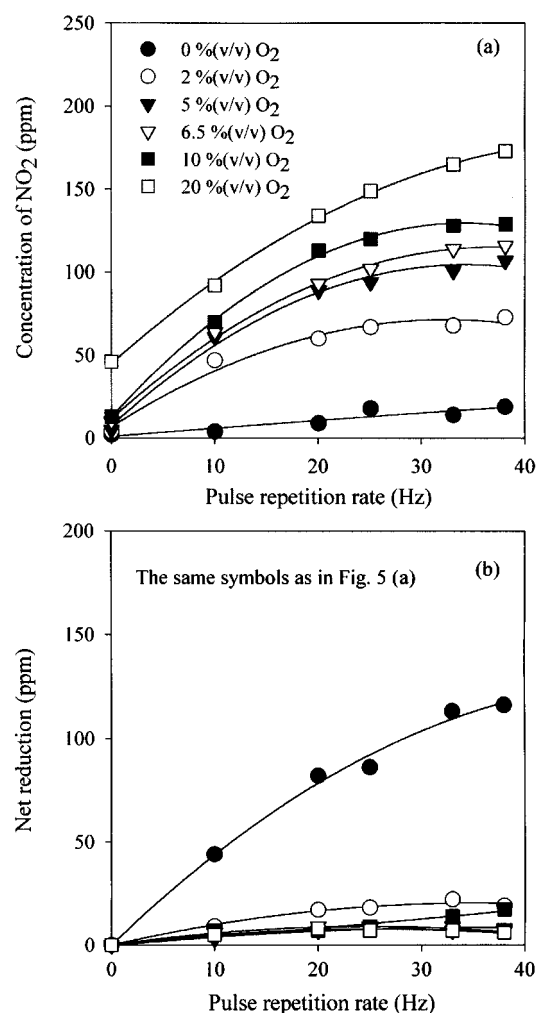


Fig. 5. Effect of oxygen content on the oxidation of NO (a) and reduction (b).

icals gradually decreased with it. Considerable amount of N radical can also be produced in this system, and NO can be reduced to N₂ according to reaction (2) in Table 2. However, NO can be gener-

Table 2. Reactions for the removal of nitric oxide

Reactions	
$N+NO \rightarrow N_2+O$	(2)
$N+OH \rightarrow NO+H$	(3)
$N+O_2 \rightarrow NO+O$	(4)
$NO+OH \rightarrow HNO_2$	(5)
$HNO_2+OH \rightarrow NO_2+H_2O$	(6)
$NO+O \rightarrow NO_2$	(7)
$NO+HO_2 \rightarrow NO_2+OH$	(8)
$NO+O_3 \rightarrow NO_2+O_2$	(9)
$NO_2+OH \rightarrow HNO_3$	(10)

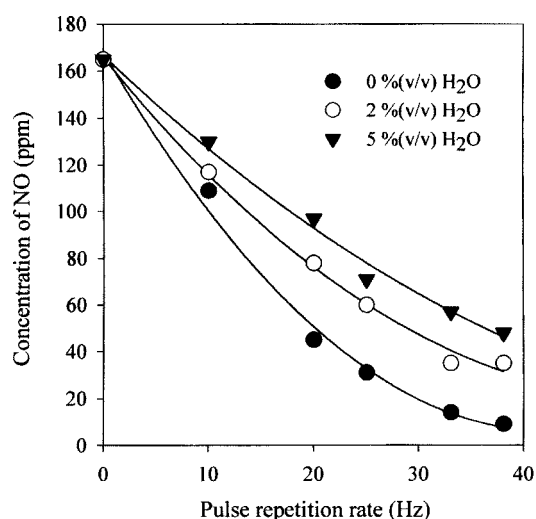
ated by reactions (3) and (4) when oxygen is present. Due to such counteraction, most of NO removed was oxidized to NO₂, as shown in Fig. 5(a). In other words, the reduction of NO to N₂ by N radical almost offset the generation of NO, and thus the net effect of N radical on the reduction of NO is minor. As can be seen in Fig. 5(b), the removal of NO by reduction path ($[NO]_0 - [NO] - [NO_2]$) was very small when the oxygen content was even decreased to 2% (v/v).

In the absence of oxygen, as an extreme case, the degree of NO removal was higher than in the presence of oxygen of 2.0 to 6.5% (v/v) (see Fig. 4). This result is because the generation of N radical was restricted, and thus net reduction of NO by N radical increased, as shown in Fig. 5(b). Because there is no source for O and O₃, the production of a small amount of NO₂ in the absence of oxygen must have resulted from OH radical produced by the dissociation of water vapor as the reactions (5) and (6) in Table 2. Consequently, we can say that the main reactions for the removal of NO are the oxidation at oxygen-rich condition while reduction prevails in the opposite condition.

Table 3 reports the energy delivered to the corona reactor calculated by Eq. (1) at different oxygen contents. According to the variations of oxygen content, pulse properties such as peak current, pulse width and voltage rising time change. These changes eventually affect the discharge energy delivered to the corona reactor. Nitrogen has relatively large ionization potential (15.5 eV), compared with O₂ (12.1 eV) and H₂O (12.6 eV) [Mizuno et al., 1986]. Due to the large ionization potential of nitrogen, the energy delivered to the reactor in the absence of oxygen was less than that in the presence of 2% (v/v) oxygen. However, further increases in the oxygen content rather decreased the energy delivered. The decrease in the energy with the increase in the oxygen content can be explained by large electron attachment coefficient of oxygen [Gallimberti, 1988]. Since the electron attachment process reduces the number of electrons, the pulse current decreases with the oxygen content.

Table 3. Energy delivered to the reactor at different O₂ contents

O ₂ content, % (v/v)	Energy/pulse, mJ
0	110.5
2	130.2
6.5	122.9
10	114.8
20	90.4

**Fig. 6. Effect of water vapor content on the removal of NO.**

The decrease in the current surely decreases the energy delivered to the reactor. Nevertheless, the increase in the oxygen content increased the removal of NO, as shown in Fig. 4. This result indicates that the oxidation radicals mentioned above mainly cause the removal of NO when oxygen is contained in the gas stream.

1-2. Effect of Water Vapor Content

The dependency of the removal of NO on the H₂O content is presented in Fig. 6. The water vapor provides OH and HO₂ radicals capable of oxidizing NO to NO₂, and thus it was expected that the increase in H₂O content would increase the oxidation rate unless the other conditions were changed. When the H₂O content was increased, however, the rate of the oxidation acted contrary to the expectation. It can be explained from two aspects that the rate of the oxidation decreased despite the increase in the H₂O content. First, OH radical produced from H₂O can deplete ozone as follows [Atkinson et al., 1992]:



According to our previous study, ozone produced during corona discharge is the most important species for the oxidation of NO [Ham et al., 1999; Mok et al., 1998a]. The increase in the H₂O content gives rise to the increase in the production of OH radical. This increase in the concentration of OH radical hampers the formation of ozone, which results in the decrease in the oxidation of NO. As shown in Fig. 7, nitric oxide can be converted to NO₂ even in the absence of water vapor, which may serve as evidence that ozone plays an important role in the oxidation chemistry. Second, the energy delivered to the corona reactor per pulse little by little decreases with the increase in the H₂O content. The energy delivered per pulse was 102, 90.4 and 84 mJ at 0% (v/v), 2% (v/v) and 5% (v/v) of the H₂O content, respectively. Dissociative attachment ($e+H_2O \rightarrow OH+H^-$) can explain the decrease in the pulse current, i.e., the energy delivered [Gallimberti, 1988; Lowke and Morrow, 1995]. Therefore, although the pulse repetition rate is identical, the power delivery (P) expressed as Eq. (12) below decreases.

$$P=fE_p \quad (12)$$

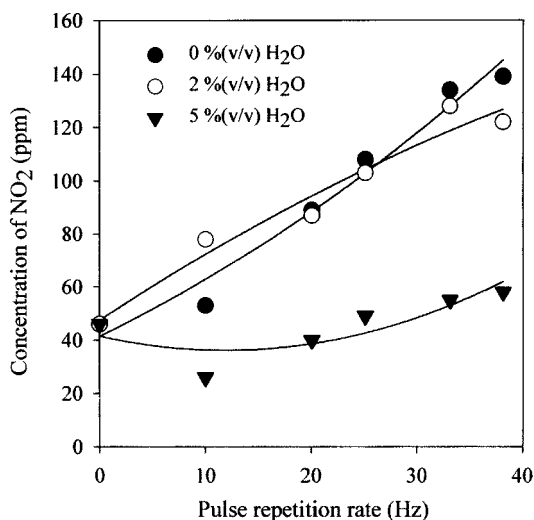


Fig. 7. Concentration of NO₂ at the reactor outlet as a function of water vapor content.

Here, f is the pulse repetition rate. The concentrations of the radicals produced are proportional to the power delivery, and as a result the decrease in the power delivery decreases the rate of the oxidation. In the mean time, the concentration of NO₂ was lower when the H₂O content was higher, as depicted in Fig. 7. The OH radical causes the further oxidation of NO₂ to nitric acid as in reaction (10), which may explain why the increase in H₂O content gives rise to the increase in the conversion of NO₂.

1-3. Effect of Ammonia Concentration

Pulsed corona discharge process generally uses ammonia to form ammonium salts as the final products of SO₂ and NO_x removal. The effect of ammonia on the removal of NO and SO₂ was examined and the results are presented in Figs. 8 and 9. In this experiment, the concentration of ammonia was varied up to 575 ppm, corresponding to 0.8 of stoichiometric equivalence. Here, the stoichiometric equivalence of NH₃ refers to two moles of NH₃ per one mole of SO₂ plus one mole of NH₃ per one mole of NO_x.

As shown in Fig. 8, the removal of NO was observed to increase

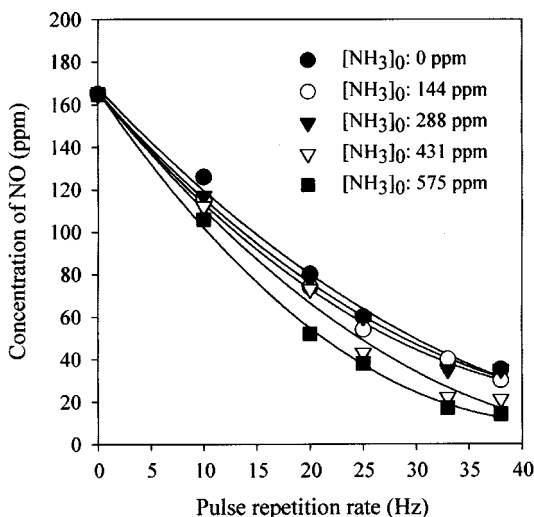


Fig. 8. Effect of ammonia concentration on the removal of NO.

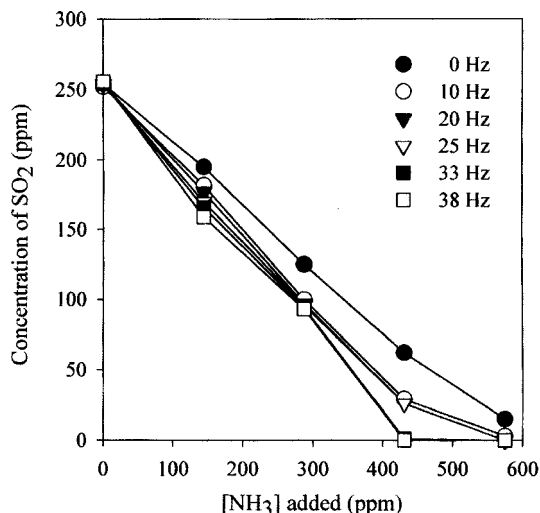
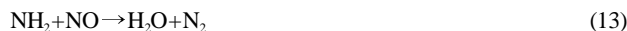


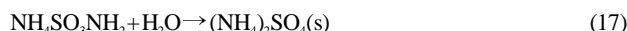
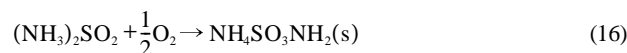
Fig. 9. Effect of ammonia concentration on the removal of SO₂.

with the concentration of ammonia although it was not significant. The use of ammonia was mainly aimed to form ammonium salts such as ammonium sulfate and ammonium nitrate, but it can dissociate to generate NH₂ radical capable of reducing NO to N₂. The reduction of NO by NH₂ radical can be expressed as follows [Chang, 1989; Urashima et al., 1998]:



Due to this reaction, the removal of NO slightly increased with the ammonia concentration.

While the removal of NO was not largely affected by the amount of ammonia added, the removal of SO₂ was strongly dependent on it, as shown in Fig. 9. Although the corona discharge promoted the removal a little, considerable amount of SO₂ was removed even without corona discharge when sufficient amount of ammonia was added. The chemical reactions between SO₂ and NH₃ in the presence of oxygen and water vapor can be expressed as [Hartley, Jr. and Matteson, 1975]



As a result of these reactions, SO₂ can be removed even without corona discharge. As shown in a previous study, however, a variety of products can be formed when corona discharge does not occur [Mok et al., 1998b]. On the contrary, most of SO₂ removed under corona discharge condition is converted into ammonium sulfate that can be used as a fertilizer. Therefore, the corona discharge is still important to obtain ammonium sulfate as a product of SO₂ removal.

1-4. Effect of Additive Concentration

The effect of propene used as additive on the removal of NO is presented in Fig. 10. The injection ratio of propene to initial NO_x was varied from 0 to 0.85 with the increment of 0.17. The higher the injection ratio of propene was, the higher the removal of NO

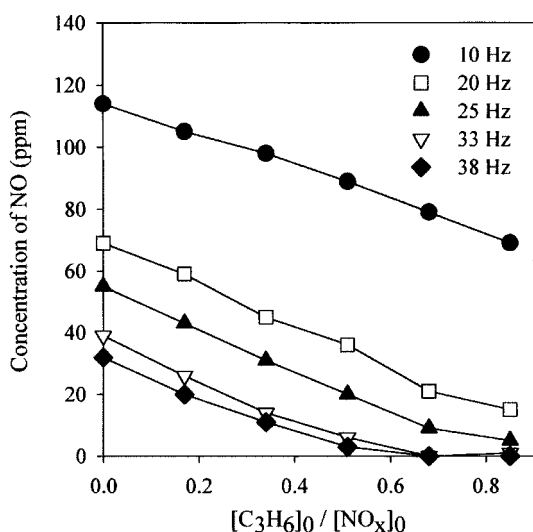


Fig. 10. Effect of propene concentration on the removal of NO.

Table 4. Oxidation of nitric oxide by alkyl, acyl and alkoxy radicals

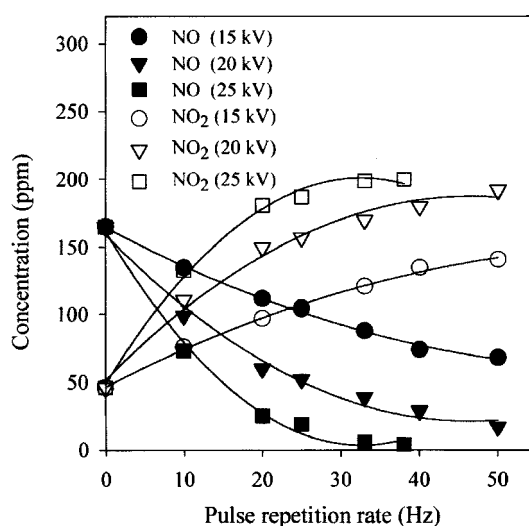
Reactions	Rate constants ^a at 298 K	
$\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{O}_2$	$8.0 \times 10^{-31} [\text{M}]$	(18)
$\text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{O} + \text{NO}_2$	7.6×10^{-12}	(19)
$\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2$	1.9×10^{-15}	(20)
$\text{HCHO} + \text{OH} \rightarrow \text{HCO} + \text{H}_2\text{O}$	1.1×10^{-11}	(21)
$\text{HCO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2$	5.6×10^{-12}	(22)
$\text{CH}_3\text{CHO} + \text{OH} \rightarrow \text{CH}_3\text{CO} + \text{H}_2\text{O}$	1.6×10^{-11}	(23)
$\text{CH}_3\text{CO} + \text{O}_2 \rightarrow \text{CH}_3\text{CO}_3$	5.0×10^{-12}	(24)
$\text{CH}_3\text{CO}_3 + \text{NO} \rightarrow \text{CH}_3 + \text{CO}_2 + \text{NO}_2$	1.4×10^{-11}	(25)

^acited from Atkinson et al. [1992]; unit: cm³/molecules/s; M: three-body reaction partner.

was observed at the same pulse repetition rate. The important radicals formed from propene may be alkyl, alkoxy and acyl radicals such as CH₃, CH₃O and CH₃CO [Ham et al., 1999; Mok and Nam, 1999; Seinfeld, 1975]. The formations of such radicals are initiated by the reactions with OH, O and O₃ [Seinfeld, 1975]. It is natural that the amounts of CH₃, CH₃O and CH₃CO should increase with the concentration of propene. The promotion of the removal with the concentration of propene can be explained by the increased amounts of these components. Table 4 shows the probable oxidation scheme of nitric oxide facilitated by CH₃, CH₃O and CH₃CO. For example, CH₃ and CH₃O react with oxygen as the reactions (18) and (20) in Table 4. The CH₃O₂ produced by reaction (18) oxidizes nitric oxide by changing its oxidation state as reaction (19). The HO₂ radical formed from reaction (20) is an oxidative radical capable of oxidizing NO according to reaction (8). HCO produced by reaction (21) can also generate HO₂ radical as reaction (22). CH₃CHO that is a decomposition product of propene oxidizes NO to NO₂ by way of reactions (23) to (25), producing CO₂ and CH₃. Methyl radical may be recycled as in reactions (18)–(22).

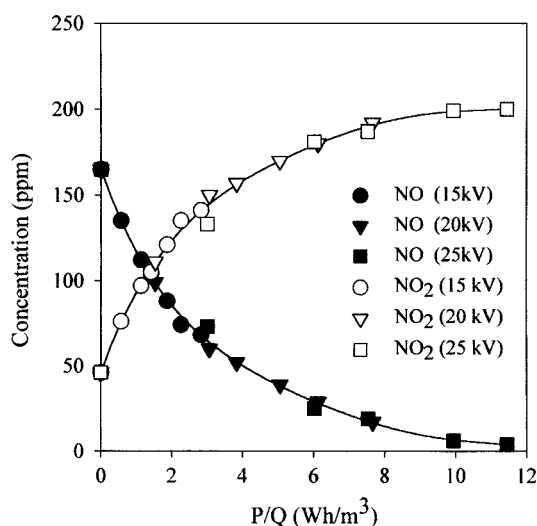
2. Operating Parameters

Fig. 11 represents the concentrations of NO and NO₂ measured at the reactor outlet according to the variations of charging voltage

Fig. 11. Effect of charging voltage of C_p on the removal of NO.

of the capacitor C_p. As can be seen, the degree of oxidation was higher at higher charging voltage. Increase in the charging voltage causes an increase in the energy delivered to the reactor. When the charging voltage was 15, 20 and 25 kV, the energy delivered to the reactor was 17, 48 and 90.4 mJ per pulse. This increase in the energy delivery with the charging voltage results in an increase in the oxidation of NO. We can redraw Fig. 11 in terms of energy density defined as the ratio of the delivered power (P) to the flow rate of the gas stream (Q). When the horizontal axis was converted to the energy density as Fig. 12, the experimental data fell into the same curve regardless of the voltage level. This result means that the energy utilization efficiency for the removal of NO is independent of the voltage. Therefore, it can be concluded that the important thing in the removal of NO is not the voltage itself, but the amount of energy delivered.

Similar results can be obtained when the flow rate of the feed gas stream is changed. The flow rate was varied from 5 l/min to 10 l/min. It is a correct result that the removal rate of NO decreases

Fig. 12. Concentrations of NO and NO₂ at the reactor outlet versus energy density (P/Q).

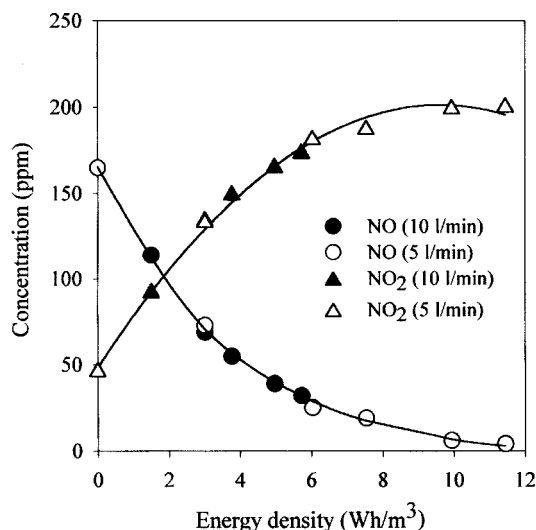


Fig. 13. Effect of flow rate of the feed gas stream on the removal of NO.

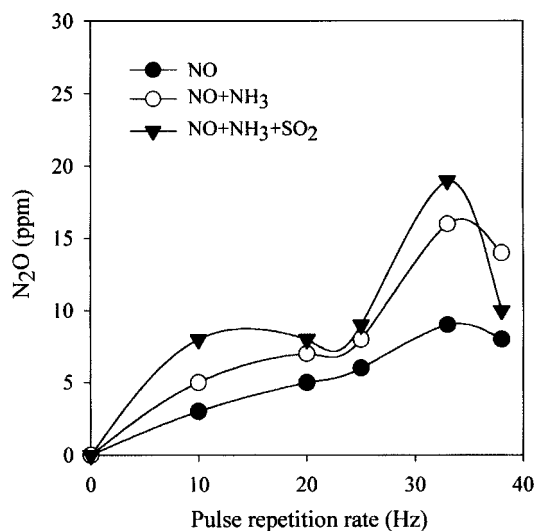


Fig. 14. Evolution of nitrous oxide as a function of pulse repetition rate.

as the flow rate is increased. However, in terms of the energy density, the amount of NO removed was identical regardless of the flow rate, as shown in Fig. 13. This figure emphasizes once again that the energy density is an important measure in the removal of NO.

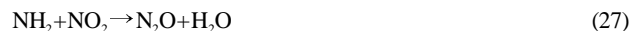
3. Byproduct Characterization

Fig. 14 represents the evolution of N₂O as a function of pulse repetition rate. The byproduct N₂O not only acts as a greenhouse effect gas, but also contributes to deplete ozone when it is transported vertically to the stratosphere. Therefore, its formation should be considered in this process. The main reaction related to the formation of N₂O is that of N with NO₂ [Lowke and Morrow, 1995; Mätzing, 1991]:

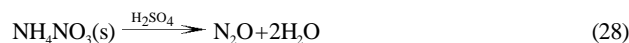


Since the concentrations of N and NO₂ are a function of pulse repetition rate, the formation of N₂O gradually increased with it, but

the concentration was very low. When small amount of NH₃ (170 ppm) was added, slightly more N₂O was produced. During corona discharge, some NH₃ can produce NH₂ radical as mentioned above. The most prominent characteristic of this NH₂ radical is its reducing property. Thus, it readily reduces NO₂ to N₂O as follows [Mätzing, 1991]:



Reaction (27) may account for the increased N₂O production in the presence of NH₃. Since SO₂ often coexists in most flue gases, the effect of SO₂ on N₂O generation was also examined. As shown in Fig. 14, N₂O formation was more significant when both NH₃ (170 ppm) and SO₂ (254 ppm) were added. The conversion of SO₂ into H₂SO₄ in the corona discharge process is well known. According to the literature [Mätzing, 1991], a part of ammonium nitrate formed may decompose at the surface of H₂SO₄ as follows:



Accordingly, the presence of SO₂ enhances the generation of N₂O.

Although propene enhances the oxidation rate of NO as shown in Fig. 10, it may generate some undesirable byproducts. Fig. 15 presents the formation of byproducts as a function of pulse repetition rate when 143 ppm of propene was initially added to the feed gas stream. Complete oxidation to CO and CO₂ is a desirable mode of propene addition. In this experimental condition, however, it was not completely decomposed, and small amounts of C₂H₆ and HCHO were detected at the reactor outlet. The sum of CO and CO₂ concentrations was determined by a material balance, i.e., the initial concentration of propene minus the remaining concentration of propene and the concentrations of HCHO and C₂H₆ produced. Among them, C₂H₆ was speculated to result from the recombination of CH₃ radicals, and the generation of HCHO can be interpreted by using Table 4. As in reaction (20), HCHO can be produced by the reaction between CH₃O and O₂. Provided that sufficient energy is delivered to the corona reactor, HCHO may eventually be converted to CO according to reactions (21) and (22). CO₂ can be generated from the further oxidation of CO or by reaction (25). Although it

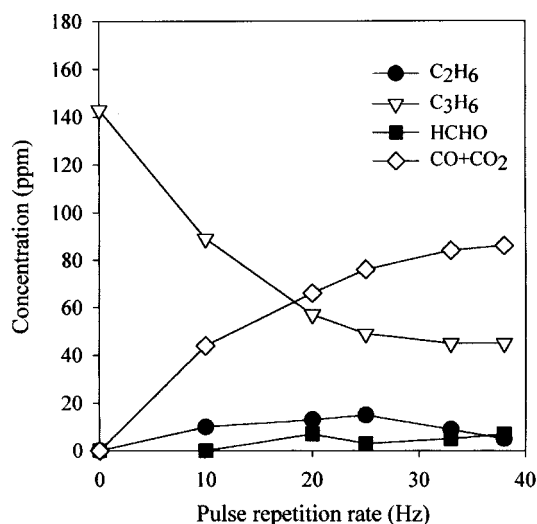


Fig. 15. Decomposition products of propene as a function of pulse repetition rate.

was not fully discussed here, a variety of minor reactions can also be possible because many intermediates can be produced from the propene in this system. However, judging from the byproducts identified, the leading reactions related may be the ones in Table 4.

CONCLUSIONS

This study was aimed at examining the effects of several important variables quantitatively on the removal of nitric oxide and the formation of byproducts. The removal of nitric oxide is competition between oxidation and reduction, and the mechanism is dominated by gas composition. In the absence of oxygen, most of NO removed was reduced to N₂ while it was oxidized to NO₂ even at low oxygen content, 2% (v/v). When there was no water vapor, corona discharge was able to oxidize NO to NO₂. But, further oxidation of NO₂ to nitric acid was attained only in the presence of water vapor. The concentration of ammonia did not largely affect the removal of nitric oxide; however, it had a great influence on the removal of SO₂. The increase in the charging voltage increased the removal of nitric oxide, but the amount of nitric oxide that can be removed at a given energy density was independent of the voltage level. Likewise, the removal of NO in terms of the energy density was identical regardless of the flow rate of the feed gas stream. The production of nitrous oxide was a strong function of the pulse repetition rate, and the presence of NH₃ and SO₂ also affected the production of N₂O. The addition of propene largely increased the oxidation of nitric oxide. Propene was found to generate ethane and formaldehyde as byproducts, but their concentrations were very low.

ACKNOWLEDGEMENT

This study was supported in part by the 2000 Research and Development Fund of Cheju National University.

NOMENCLATURE

C_p	: pulse-forming capacitor [pF]
E_p	: energy delivered to the corona reactor per pulse [J]
f	: pulse repetition rate [Hz]
I	: pulse current [A]
P	: power delivered to the corona reactor [W]
Q	: flow rate of feed gas stream [l/min]
t	: time [s]
V	: pulse voltage [kV]

REFERENCES

- Atkinson, R., Baulch, D. L., Cox, R. A., Hampson, Jr. R. F., Kerr, J. A. and Troe, J., "Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement IV," *J. Phys. Chem. Ref. Data*, **21**, 1125 (1992).
- Chang, J. S., "The role of H₂O and NH₃ on the Formation of NH₄NO₃ Aerosol Particles and De-NO_x Under the Corona Discharge Treatment of Combustion Flue Gases," *J. Aerosol Sci.*, **20**, 1087 (1989).
- Civitano, L., "Industrial Application of Pulsed Corona Processing to Flue Gas," Non-Thermal Plasma Techniques for Pollution Control: Part B, Penetrante, B. M. and Schultheis, S. E., eds., Springer-Verlag, Berlin, 103 (1993).
- Dinelli, G., Civitano, L. and Rea, M., "Industrial Experiments on Pulse Corona Simultaneous Removal of NO_x and SO₂ from Flue Gas," *IEEE Trans. Ind. Appl.*, **26**, 535 (1990).
- Gallimberti, I., "Impulse Corona Simulation for Flue Gas Treatment," *Pure Appl. Chem.*, **60**, 663 (1988).
- Ham, S. W., Park, H. H. and Mok, Y. S., "Removal of Nitric Oxide Using Non-Thermal Plasma Technology," *HWAHAK KONGHAK*, **37**, 759 (1999).
- Hartley, Jr. E. M. and Matteson, M. J., "Sulfur Dioxide Reactions with Ammonia in Humid Air," *Ind. Eng. Chem., Fundam.*, **14**, 67 (1975).
- Jeong, H. K., Kim, S. C., Han, C., Lee, H., Song, H. K. and Na, B. K., "Conversion of Methane to Higher Hydrocarbons in Pulsed DC Barrier Discharge at Atmospheric Pressure," *Korean J. Chem. Eng.*, **18**, 196 (2001).
- Lowke, J. J. and Morrow, R., "Theoretical Analysis of Removal of Oxides of Sulphur and Nitrogen in Pulsed Operation of Electrostatic Precipitators," *IEEE Trans. Plasma Sci.*, **23**, 661 (1995).
- Mätzing, H., "Chemical Kinetics of Flue Gas Cleaning by Irradiation with Electrons," *Advances in Chemical Physics: Vol. LXXX*, Prigogine, I. and Rice, S. A., eds., John Wiley & Sons, New York, 315 (1991).
- Mizuno, A., Clements, J. S. and Davis, R. H., "A Method for the Removal of Sulfur Dioxide from Exhaust Gas Utilizing Pulsed Streamer Corona for Electron Energization," *IEEE Trans. Ind. Appl.*, **22**, 516 (1986).
- Mizuno, A., Shimizu, K., Chakrabarti, A., Dascalescu, L. and Furuta, S., "NO_x Removal Process using Pulsed Discharge Plasma," *IEEE Trans. Ind. Appl.*, **31**, 957 (1995).
- Mok, Y. S., Ham, S. W. and Nam, I., "Mathematical Analysis of Positive Pulsed Corona Discharge Process Employed for Removal of Nitrogen Oxides," *IEEE Trans. Plasma Sci.*, **26**, 1566 (1998a).
- Mok, Y. S., Nam, I., Chang, R. W., Ham, S. W., Kim, C. H. and Jo, Y. M., "Application of Positive Pulsed Corona Discharge to Removal of SO₂ and NO_x," *Proc. Int. Conf. Electrostatic Precipitation*, Kyongju, Korea, 270 (1998b).
- Mok, Y. S. and Nam, I., "Removal of Nitric Oxide in a Pulsed Corona Discharge Reactor," *Chem. Eng. Technol.*, **22**, 527 (1999).
- Oda, T., Kato, T., Takahashi, T. and Shimizu, K., "Nitric Oxide Decomposition in Air by using Nonthermal Plasma Processing with Additives and Catalyst," *IEEE Trans. Ind. Appl.*, **34**, 268 (1998).
- Seinfeld, J. H., "Air Pollution," McGraw Hill, New York (1975).
- Shimizu, K., Kinoshita, K., Yanagihara, K., Rajanikanth, B. S., Katsura, S. and Mizuno, A., "Pulsed-Plasma Treatment of Polluted Gas using Wet-low-temperature Corona Reactors," *IEEE Trans. Ind. Appl.*, **33**, 1373 (1997).
- Song, Y., Choi, Y., Kim, H., Shin, W., Keel, S., Chung, S., Choi, K., Choi, H., Kim, S. and Chang, K., "An Experimental Study of Power Saving Technique in Non-thermal Plasma DeSO₂/DeNO_x Process," *J. Korea Air Poll. Res. Assoc.*, **12**, 487 (1996).
- Tas, M. A., van Hardeveld, R. and van Veldhuizen, E. M., "Reactions of NO in a Positive Streamer Corona Plasma," *Plasma Chem. Plasma Proc.*, **17**, 371 (1997).
- Urashima, K., Chang, J. S., Park, J. Y., Lee, D. C., Chakrabarti, A. and Ito, T., "Reduction of NO_x from Natural Gas Combustion Flue Gases by Corona Discharge Radical Injection Techniques," *IEEE Trans. Ind. Appl.*, **34**, 934 (1998).

- van Veldhuizen, E. M., Zhou, L. M. and Rutgers, W. R., "Combined Effects of Pulsed Discharge Removal of NO, SO₂, and NH₃ from Flue Gas," *Plasma Chem. Plasma Proc.*, **18**, 91 (1998).