# **Removal of NO and SO<sub>2</sub> by Pulsed Corona Discharge Process**

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**Abstract** – Overall examination was made on the removal of NO and  $SO<sub>2</sub>$  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  $N_2$ ; on the other hand, oxidation of NO to NO<sub>2</sub> 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 NO<sub>2</sub>. The removal of NO only slightly increased with the concentration of ammonia while the effect of ammonia on the removal of SO<sub>2</sub> 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  $N<sub>2</sub>O$  increased with the pulse repetition rate, and the presence of  $NH<sub>3</sub>$  and  $SO<sub>2</sub>$  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, SO<sub>2</sub>, Gas Composition, Energy Density, N<sub>2</sub>O, Byproducts

## **INTRODUCTION**

Non-thermal plasma process induced by pulsed corona discharge canbe 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  $SO<sub>2</sub>$  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 dischage 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  $SO<sub>2</sub>$  is known by the oxidation of NO to NO<sub>2</sub> [Civitano, 1993; Oda et al., 1998]. Once NO<sub>2</sub> 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  $NO<sub>2</sub>$ can of course be further oxidized to nitric acid, which can be neutralized by a basic compound. It has been shown that  $SO<sub>2</sub>$  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,  $HO_2$ ,  $O_3$ , 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-

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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  $SO<sub>2</sub>$ , 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  $(N<sub>2</sub>O)$  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-

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**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 m 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  $1,000:1\pm3%$  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 amplitier, 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:

$$
E_P = \int_0^r V I dt'
$$
 (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  $N_2$ ,  $O_2$ ,  $H_2O$ ,  $NO$ ,  $SO_2$  and  $NH_3$ enters the inlet of the corona reactor, as shown in Fig. 3. The total flow rate of the mixed gas was 10  $\ell$ /min. The contents of N<sub>2</sub> and  $O<sub>2</sub>$  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, SO<sub>2</sub> and  $NH<sub>3</sub>$  were controlled by a mass flow controller (Model 1179, MKS Instruments, Inc.). The content of  $H<sub>2</sub>O$  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  $(C_n)$  was 25 kV, and the pulse repetition rate was changed from



Fig. 3. Experimental apparatus for the removal of NO and SO<sub>2</sub> using corona discharge.





"ppm: 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  $NO<sub>2</sub>$  were analyzed at the reactor outlet before and after pulsed corona discharge by a chemiluminescence NO-NO<sub>7</sub>-NO<sub>7</sub> analyzer (Model 42H, Thermo Environmental Instrument Inc.). For the analysis of  $SO<sub>2</sub>$  concentration, a pulsed fluorescent  $SO_2$  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  $(50 \text{ m} \times 0.2 \text{ mm})$  $\times$ 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 staiuless steel colunm (6 ff long and 1/8" in diameter) packed with Porapak N (All Tech) was used for the analyses of byproducts including  $C_2H_6$ ,  $C_3H_6$  and HCHO. Chromosorb 101 (All Tech) was used as the packing material for  $N_2O$ analysis. For the analyses of  $C_2H_6$ ,  $C_3H_6$  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. N<sub>2</sub>O 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,  $HO_2$ , N and  $O_3$ . As presented in Table 2, O, OH,  $HO_2$  and  $O_3$ formed from  $O_2$  and  $H_2O$  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 N<sub>2</sub> (9.8 eV) is larger than that of  $O_2(5.1 \text{ eV})$ or H20 (5.2 eV) [Miztmo 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 file oxidation of NO (a) and re**duction (b).

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

Reactions	
$N+NO \rightarrow N, +O$	(2)
N+OH→NO+H	(3)
$N+O_2 \rightarrow NO+O$	(4)
$NO+OH \rightarrow HNO$	(5)
$HNO2+OH \rightarrow NO2+H2O$	(6)
NO+O→NO,	(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)

Table 2. Reactions for the removal of nitric oxide

ated by reactions (3) and (4) when oxygen is present. Due to such counteraction, most of NO removed was oxidized to  $NO_2$ , as shown in Fig. 5(a). In other words, the reduction of NO to  $N_2$  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 ( $[NO_x]_0$ - $[NO]$ - $[NO_2]$ ) was very snraU when the oxygen content was even decreased to  $2\%$  (v/v).

Inthe 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 NO was restricted, and thus net reduction of NO by N radical increased, as shown in Fig. 5(b). Because there is no source for  $\circ$  and  $\circ$ <sub>3</sub>, the production of a small amount of  $NO<sub>2</sub>$  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 conditicn 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 eventuaUy affect the discharge energy delivered to the corona reactor. Nitrogen has relatively large ionization potential (15.5 eV), compared with  $O_2$  (12.1 eV) and  $H_2O$  (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 O<sub>2</sub> 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  $H_2O$  content is presented in Fig. 6. The water vapor provides OH and  $HO<sub>2</sub>$  radicals capable of oxidizing NO to NO> and thus it was expected that the increase in  $H<sub>2</sub>O$  content would increase the oxidation rate unless the other conditions were changed. When the  $H<sub>2</sub>O$  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  $H<sub>2</sub>O$  content. First, OH radical produced from  $H_2O$  can deplete ozone as follows [Atkinson et al., 1992]:

$$
OH + O3 \rightarrow HO2 + O2
$$
\n
$$
(11)
$$

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  $H_2O$  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  $NO<sub>2</sub>$  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  $H<sub>2</sub>O$  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  $H_2O$  content, respectively. Dissociative attachment (e+ $H_2O \rightarrow OHH$ 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.





Fig. 7. Concentration of NO<sub>2</sub> at the reactor outlet as a function of **water vapor eontenL** 

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  $NO<sub>2</sub>$  was lower when the H20 content was higher, as depicted in Fig. 7. The OH radical causes the further oxidation of  $NO<sub>2</sub>$  to nitric acid as in reaction (10), which may explain why the increase in  $H<sub>2</sub>O$  content gives rise to the increase in the conversion of NQ.

1-3. Effect of Ammonia Concentration

Pulsed corona discharge process generally uses ammonia to form ammonium salts as the final products of  $SO<sub>2</sub>$  and  $NO<sub>r</sub>$  removal. The effect of ammonia on the removal of NO and  $SO<sub>2</sub>$  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  $NH<sub>3</sub>$  refers to two moles of  $NH<sub>3</sub>$  per one mole of  $SO<sub>2</sub>$  plus one mole of NH<sub>3</sub> per one mole of NO<sub>x</sub>.

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 SO:.** 

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  $NH_2$  radical capable of reducing NO to  $N_2$ . The reduction of NO by NH, radical can be expressed as follows [Chang, 1989; Urashima et al., 1998]:

$$
NH2 + NO \rightarrow H2OH N2
$$
 (13)

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 SO<sub>2</sub> was strongly dependent on it, as shown in Fig. 9. Although the corona discharge promoted the removal a little, considerable amount of  $SO<sub>2</sub>$  was removed even without corona discharge when sufficient amount of ammonia was added. The chemical reactions between  $SO_2$  and  $NH_3$  in the presence of oxygen and water vapor can be expressed as [Hartley, Jr. and Matteson, 1975]

$$
NH3 + SO2 \rightarrow NH3 SO2
$$
 (14)

$$
\text{NH}_3\text{SO}_2 + \text{NH}_3 \rightarrow (\text{NH}_3)_2\text{SO}_2 \tag{15}
$$

$$
(NH3)2SO2 + \frac{1}{2}O2 \rightarrow NH4SO3NH2(s)
$$
 (16)

$$
NH4SO3NH2+H2O \rightarrow (NH4)2SO4(s)
$$
\n(17)

As a result of these reactions,  $SO<sub>2</sub>$  can be removed even without corona discharge. As shown in a previous study, however; a variety of products canbe formed when corona discharge does not occur [Mok et al., 1998b]. On the contrary, most of  $SO<sub>2</sub>$  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  $SO<sub>2</sub>$  removal. 1-4. Effect of Additive Concentration

The effect of propene used as additive onthe 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 <sup>a</sup> at 298 K	
$CH_3 + O_2 \rightarrow CH_3O_2$	$8.0 \times 10^{-31}$ [M]	(18)
$CH_3O_2 + NO \rightarrow CH_3O + NO_2$	$7.6 \times 10^{-12}$	(19)
$CH_3O+O_2 \rightarrow HCHO+HO_2$	$1.9\times10^{-15}$	(20)
$HCHO + OH \rightarrow HCO + H2O$	$1.1 \times 10^{-11}$	(21)
$HCO+O2\rightarrow CO+HO2$	$5.6 \times 10^{-12}$	(22)
$CH_3CHO+OH \rightarrow CH_3CO+H_2O$	$1.6\times10^{-11}$	(23)
$CH_3CO + O_2 \rightarrow CH_3CO_3$	$5.0 \times 10^{-12}$	(24)
$CH_3CO_3+NO \rightarrow CH_3+CO_2+NO_2$	$1.4 \times 10^{-11}$	(25)

"cited from Atkinson et al. [1992]; unit:  $cm^3/molecules/s$ ; M: threebody 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  $CH_3$ , CH<sub>3</sub>O and CH<sub>3</sub>CO [Ham et al., 1999; Mok and Nam, 1999; Seinfeld, 1975]. The formations of such radicals are initiated by the reactions with OH, O and  $O_3$  [Seinfeld, 1975]. It is natural that the amounts of  $CH_3$ ,  $CH_3O$  and  $CH_3CO$  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  $CH<sub>3</sub>, CH<sub>3</sub>O$  and  $CH<sub>3</sub>CO$ . For example,  $CH<sub>3</sub>$  and  $CH<sub>3</sub>O$  react with oxygen as the reactions (18) and (20) in Table 4. The CH<sub>3</sub>O<sub>2</sub> produced by reaction (18) oxidizes nitric oxide by changing its oxidation state as reaction  $(19)$ . The  $HO<sub>2</sub>$  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  $HO<sub>2</sub>$  radical as reaction (22). CH<sub>3</sub>CHO that is a decomposition product of propene oxidizes  $NO$  to  $NO<sub>2</sub>$  by way of reactions (23) to (25), producing  $CO<sub>2</sub>$  and CH<sub>3</sub>. Methyl radical may be recycled as in reactions (18)-(22).

#### **2. Operating Parameters**

Fig. 11 represents the concentrations of  $NO$  and  $NO<sub>2</sub>$  measured at the reactor outlet according to the variations of charging voltage



Fig. 11. Effect of **charging voltage** of C~ **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 90.4mJ 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  $5/\text{min}$  to 10 *l*/min. It is a correct result that the removal rate of NO decreases



Fig. 12. Concentrations of NO and NO<sub>2</sub> at the reactor outlet ver**sus 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  $N<sub>2</sub>O$  as a function of pulse repetition rate. The byproduct  $N_2O$  not only acts as a greenhouse effect gas, but also corffibutes 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  $N_2O$  is that of N with NO<sub>2</sub> [Lowke and Morrow, 1995; Mätzing, 1991]:

$$
N + NO_2 \rightarrow N_2O + O \tag{26}
$$

Since the concentrations of N and  $NO<sub>2</sub>$  are a function of pulse repetition rate, the formation of  $N<sub>2</sub>O$  gradually increased with it, but

the concentration was very low. When small amount of  $NH<sub>3</sub>$  (170) ppm) was added, slightly more  $N<sub>2</sub>O$  was produced. During corona discharge, some  $NH<sub>3</sub>$  can produce  $NH<sub>2</sub>$  radical as mentioned above. The most prominent characteristic of this NH<sub>2</sub> radical is its reducing property. Thus, it readily reduces  $NO<sub>2</sub>$  to  $N<sub>2</sub>O$  as follows [Mätzing, 1991]:

$$
NH2+NO2 \rightarrow N2O+H2O
$$
 (27)

Reaction  $(27)$  may account for the increased N<sub>2</sub>O production in the presence of  $NH_3$ . Since  $SO_2$  often coexists in most flue gases, the effect of  $SO_2$  on  $N_2O$  generation was also examined. As shown in Fig. 14,  $N<sub>2</sub>O$  formation was more significant when both  $NH<sub>3</sub>$  (170) ppm) and  $SO<sub>2</sub>$  (254 ppm) were added. The conversion of  $SO<sub>2</sub>$  into  $H<sub>2</sub>SO<sub>4</sub>$  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  $H_2SO_4$  as follows:

$$
NH_4NO_3(s) \xrightarrow{H_2SO_4} N_2O + 2H_2O \tag{28}
$$

Accordingly, the presence of  $SO_2$  enhances the generation of  $N_2O$ .

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  $CO<sub>2</sub>$  is a desirable mode of propene addition. In this experimental condition, however, it was not completely decomposed, and small amounts of  $C_2H_6$  and  $HCHO$ were detected at the reactor outlet. The sum of  $CO$  and  $CO<sub>2</sub>$  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  $C_2H_5$  produced. Among them,  $\text{C}_2\text{H}_4$  was speculated to result from the recombination of  $\text{CH}_3$ radicals, and the generation of HCHO can be interpreted by using Table 4. As m reaction (20), HCHO can be produced by the reaction between  $CH<sub>3</sub>O$  and  $O<sub>2</sub>$ . Provided that sufficient energy is delivered to the corona reactor, HCHO may eventually be converted to CO according to reactions  $(21)$  and  $(22)$ . CO<sub>2</sub> can be generated fiom 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 idenlifted, the leadmg 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  $N_2$ , while it was oxidized to  $NO_2$ , even at low oxygen content,  $2\%$  (v/v). When there was no water vapor, corona discharge was able to oxidize  $NO$  to  $NO<sub>2</sub>$ . But, further oxidation of NO<sub>2</sub> 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 SO> The increase in the charging voltage increased the removal of nitric oxide, but the amount of nitric oxide that can he 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  $NH_3$  and  $SO_2$  also affected the production of  $N<sub>2</sub>O$ . The addition of propene largely increased the oxidation of nitric oxide. Propene was found to generate ethane and formaldehyde as bypreducts, but their concentrations were very low.

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## **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  $[1/mm]$
- t : time [s]
- V : pulse voltage [kV]

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