Effect of Coexisting Gases on NO Removal Using Corona Discharge

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Effects of H2O, CO2, CH4 and C2H4 contained in automotive exhaust gas on NO removal by using a DC corona discharge were investigated experimentally. In this experiment, N2/O2/NO mixture was used as a base gas of the simulated exhaust gas. To clarify the effect of the individual coexisting gas on NO removal, each coexisting gas was added to the base gas. The results showed that the existence of H2O or CH4 was effective for NO removal with low energy density. Also, when negative corona discharge was applied to the simulated exhaust gas (N2/O2/N2O/CO2/C2H4 mixture), the efficiency of DeNOx was more than 90%. However, the by-products such as CO, O3, HNO3 and N2O increased with increasing the energy density. It was found that the optimum energy density of corona discharge was about 250 J/L for DeNOx of simulated exhaust gas.

Key Words: NO Removal, Corona Discharge, DeNOx, Ozone, Coexisting Gas

1. Introduction

Many researches have been conducted for the removal of nitrogen oxide (NOx), which is one of the serious air pollutants. NOx removal technology using an electrical discharge phenomenon has attracted the attention recently. Non-equilibrium plasma, arc plasma, DC corona discharge, pulsed corona discharge, dielectric barrier discharge and silent discharge etc. are well known as the electrical discharge technologies. These technologies can be applied to deoxidize the NOx exhausted from internal combustion engine by using radicals formed with electrical discharge. In regard to a mechanism of NOx removal, Morimune et al.\(^1\)–(3) studied the effects of moisture and carbon dioxide on NOx reduction using a nitrogen plasma. They concluded that coexisting O2 and H2O had no effect on the NOx reduction, and the NOx reduction ratio of around 10% was obtained by N2 plasma injection. Kato et al.\(^4\) studied on removal of SO2 and NOx by DC and pulsed corona discharge, changing parameters such as gas composition, gas temperature, electrode configuration and polarity of electrode etc. They reported that O2 and H2O were effective to DeSOx and DeNOx, and the pulsed corona discharge with a voltage pulse-width as short as 200 ns of negative polarity showed the possibility to attain 90% DeSOx and DeNOx efficiency.

In the previous paper\(^5\), authors reported that the characteristics of NO removal by DC corona discharge differed remarkably depending on whether or not the oxygen exists in the gas. This report was the second step study of NO removal by using a DC corona discharge. The aim of this study was to clarify the effects of typical coexisting gases such as H2O, CO2, CH4 and C2H4 contained in exhaust gas on NO removal. These effects were experimentally investigated and the mechanism of NOx removal was discussed.

2. Experimental Apparatus and Methods

A schematic diagram of the experimental apparatus is shown in Fig. 1. A corona discharge reactor consists of a quartz glass tube (27 mm inner diameter and 500 mm in length), a straight center electrode (stainless steel wire of 0.28 mm in diameter) and a ground electrode (stainless steel wire of 0.45 mm in diameter). The stainless wire of ground electrode was wound along inside of the reactor wall with 6 mm winding pitch. DC
high potential was applied to the center electrode using a power supply (SPELLMAN, SL-150). The case in which positive or negative potential was applied to the central electrode was called as “positive corona discharge” or “negative corona discharge”, respectively. A mixture of N₂(base)/O₂(10%)/NO(100 ppm) was used as a base gas to be treated in this study. Moisture was added to the base gas by bubbling in a water vessel, which was set just before the entrance of the reactor. Temperature and humidity of the mixture were measured by means of a thermometer and a hygrometer. The moisture of the mixture after bubbling was about 2 vol% in absolute humidity. Carbon dioxide and hydrocarbon (methane and/or ethylene) were added to the base gas with adjusting composition flow rates to attain 10% CO₂ concentration and 100 ppm hydrocarbon concentration. A mixture in which all of H₂O, CO₂ and C₂H₄ were added was used as a simulated exhaust gas. Compositions of the test gases used in the experiment are listed in Table 1. Each gas of N₂, O₂, NO, CO₂, and C₆H₆ was introduced into the reactor through the mixing chamber after controlling their flow rates. All experiments were conducted at a constant gas flow rate of $Q = 1.0 \text{ L/min}$ of the mixture (space velocity, $S. V. = 214.3 \text{ h}^{-1}$).

The gas after corona discharge treatment was collected in a sampling bag, and concentrations of NO, NO₂, and N₂O in the gas were measured with Fourier Transform Infrared Microspectrometry (HORIBA, MEXA-4000FT). In this study, NOx concentration was defined by the total of NO, NO₂, and N₂O. Furthermore, as for a mixture including CO₂, the concentration of CO formed by corona discharge was also measured. The concentrations of O₃ and HNO₃ were measured using a gas-detecting tube. In the experiment concerning a mixture having H₂O composition, the gas after corona discharge treatment was bubbled in the vessel with 75 cc water for ten minutes, and then the pH value of the solution was measured with pH meter.

3. Results and Discussion

3.1 Voltage-current characteristics

The voltage-current relationships when coexisting gases were added to the base gas are shown in Fig. 2. Figure 2 (a) is the cases of positive potential and Fig. 2 (b) is the negative cases. The symbol “□” in Fig. 2 (b) indicates a limit of stable corona discharge region. A spark discharge occurred over this limit. The electric current increased exponentially after the corona discharge was begun. Even if the coexistence gases such as H₂O, CO₂, CH₄, and C₂H₄ were added to the base gas, voltage-current characteristics were almost similar to those of base gas. However, the polarity influenced the corona discharge region, which is the region from the standing up point of current value to the spark discharge. The corona discharge region was wider.

![Fig. 1 Experimental set-up](image)

![Fig. 2 E-I characteristics of corona discharge](image)

<table>
<thead>
<tr>
<th>Test gas</th>
<th>NO</th>
<th>N₂</th>
<th>O₂</th>
<th>H₂O</th>
<th>CO₂</th>
<th>CH₄</th>
<th>C₂H₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base gas</td>
<td>100 ppm</td>
<td>90 %</td>
<td>10 %</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Base gas + H₂O</td>
<td>100 ppm</td>
<td>88 %</td>
<td>10 %</td>
<td>2 %</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Base gas + CO₂</td>
<td>100 ppm</td>
<td>80 %</td>
<td>10 %</td>
<td></td>
<td></td>
<td>10 %</td>
<td>10 ppm</td>
</tr>
<tr>
<td>Base gas + CH₄</td>
<td>100 ppm</td>
<td>90 %</td>
<td>10 %</td>
<td></td>
<td></td>
<td></td>
<td>100 ppm</td>
</tr>
<tr>
<td>Simulated gas</td>
<td>100 ppm</td>
<td>78 %</td>
<td>10 %</td>
<td>2 %</td>
<td></td>
<td>10 %</td>
<td>10 ppm</td>
</tr>
</tbody>
</table>
in the cases of negative potential than the cases of positive potential\(^6\).

3.2 Observation of corona discharge

As an example of state of corona discharge in the reactor, discharge photographs in the base and simulated exhaust gases are shown in Fig. 3. Figure 3 (a) shows coronas in the base gas. In the case of base gas with positive potential, a blue purple corona (so-called glow corona) appeared continuously on the center electrode. In the negative potential, spots of blue purple corona were appeared on the center electrode, and brightness of the spots was higher than that of positive corona. Thus, it was conjectured that many active species and radicals were existing in the corona discharge field\(^5\) – \(^7\).

Behavior of coronas in the simulated exhaust gas shown in Fig. 3 (b) was very different from that of Fig. 3 (a). Streamer coronas were developed on the whole surface of the center electrode in the case of positive corona discharge. They were remarkably observed when only CO\(_2\) was added to the base gas. There is a report\(^8\) that the state of electrical discharge was changed greatly in the case of positive corona discharge when both H\(_2\)O and CO\(_2\) were contained in a gas, and many active species were formed and contributed to the NO removal. In the negative corona discharge, chain-like radiant spots appeared on the center electrode. The gas temperature in the reactor rises when a corona discharge is maintained for a long time even if the experiment was started at the room temperature condition. However it was presumed that the gas temperature in the reactor was less than 100°C because the reactor could be picked up in the naked fingers just after the long-term experiment with corona discharge.

3.3 DeNO\textsubscript{x} characteristics in base gas treatment

DeNO\textsubscript{x} characteristics for the base gas, in other words, for the mixture of N\(_2\) (base)/O\(_2\) (10%/NO (100 ppm), are discussed. Figure 4 (a) and (b) was the cases of positive and negative potentials respectively. The horizontal axis indicates the energy density (J/L) that was the input power per unit gas flow rate. The onset condition of corona discharge is indicated as a zero in square brackets [0]. The vertical axis indicates the concentration (ppm) of gas component, and the initial gas concentration before corona discharge treatment is indicated in the left end axis. Moreover, the figures show the pH value of a bubbled water that absorbed the gas after corona discharge treatment. In the case of positive potential, NO concentration decreased with increasing the energy density. On the contrary, NO\(_2\) increased with an increase of the energy density, and N\(_2\)O was formed slightly. Consequently, total NO\textsubscript{x} was not decreased. Further, the pH value decreased gradually with increasing the energy density.

DeNO\textsubscript{x} characteristic in the case of negative potential was similar to that of the positive potential within the energy density less than 250 J/L. However, at an energy density higher than 250 J/L, NO\textsubscript{x} concentration decreased down to around 20 ppm and became to a comparable level of N\(_2\)O concentration at over 600 J/L.

It is considered that the dissolution and the oxidation of NO are caused by various radicals and ozone, and these radicals are formed in the reactions shown as follows.

\begin{align}
N_2 + e &\rightarrow N + N + e \\
O_2 + e &\rightarrow O + O + e \\
O_2 + O &\rightarrow O_3
\end{align}
The pH value had a lowering tendency with the NO₂ increase. It was thought that the pH becomes low with dissolving NO₂ in the water. In the case of negative corona discharge, it was also conjectured that the pH lowering after rapid reduction of NO₂ was caused by the dissolution of NO₂ and other oxides in the water.

From the results mentioned above, it was found that negative corona discharge was more effective for DeNOx reactions than positive corona discharge. Here, we considered the influence of polarity on DeNOx characteristics. Figure 5 shows the illustration of spatial distribution of electron and ions in the reactor for antithetic polarity. In the case of negative corona discharge, an electron moves from a center electrode toward the outer electrode, and the electric field intensity becomes greater gradually from the outer electrode toward the center electrode because electrical charge concentrates on the center electrode. Thus, the radical movement of electron in negative corona discharge is faster than that in positive one. Many electrons might collide with molecules of various chemical species and ions existing in corona discharge field, and they might be activated by the high-speed collisions of electrons. This is the reason why high performance of DeNOx reaction was attained in the negative corona discharge.

In a circular reaction tube with center electrode, the electric field strength in the tube becomes fainter from the center electrode toward the outer electrode because it is inversely proportional to the radius distance from the center axis. Concerning the reaction tube used in this experiment, it is calculated that radical movement of electron in negative corona discharge is around ninety fold faster than that in positive corona discharge.

3.4 Effect of moisture on DeNOx characteristics in base gas treatment

Figure 6 shows the DeNOx characteristics when moisture was added to the base gas. Figure 6 (a) is the case of positive corona discharge and Fig. 6 (b) is the negative case. In the case of positive corona discharge, NO decreased with increasing the energy density. It decreased down to 15 ppm, but NO₂ concentration increased up to about 40 ppm. As for a combination effect of NO decrease and NO₂ increase, 30 ppm reduction gain of the total NOx was obtained. Because of this reduction, the pH value became lower with an increase of the energy density.

The following expressions are proposed as the reactions in a mixture containing moisture(9).

\[
\begin{align*}
H_2O &\rightarrow H + OH \\
NO + OH &\rightarrow HNO_2 \\
NO_2 + OH &\rightarrow HNO_3 \\
2NO_2 + H_2O &\rightarrow HNO_2 + HNO_3
\end{align*}
\]

NO and NO₂ react with OH, which is produced by the dissociation of H₂O (Eq. (8)) in the corona discharge field, and then nitric acid and nitrous acid are produced. It is considered that NOx reduction is proceeded by these reactions. The pH value became low since the NO₂ is converted into a nitric acid by reacting with water molecule as shown in Eq. (11).

The concentration of nitric acid was measured with a
gas detection tube at the exit of the reactor. Nitric acid was hardly detected in the case of positive corona discharge. The reason was that the misty nitric acid in corona discharge field might be adhered to the inner wall of reactor\(^{(10)}\).

On the contrary, in the case of negative corona discharge, the NO\(_2\) concentration decreased rapidly with a lower energy density as shown in Fig. 6(b). Furthermore, it showed more rapid decrease than the case of base gas (see Fig. 4(b)). It is considered that the reactions of Eqs. (8)–(11) take place in addition to the basic reactions shown in Eqs. (1)–(7). The moisture had not influence on the N\(_2\)O concentration, since the N\(_2\)O concentration was about 10 ppm even if moisture was added to the base gas.

The pH took the minimum value when the NO\(_2\) concentration was at its maximum, and the pH increased gradually with increasing the energy density after rapid decrease of NO\(_2\) concentration. Finally, the pH reached to a value close to the initial value. The recovery of pH value was due to lowering the NO\(_2\) concentration and lowering the dissolved NO\(_2\). Besides the adhesion of nitric acid mist on inner walls of reactor and connection pipe was another reason of pH recovery. Therefore, it might be right that the concentration of real nitric acid formed by corona discharge is higher than that of the measured value.

### 3.5 Effect of carbon dioxide on DeNOx characteristics in base gas treatment

Figure 7 shows the DeNOx characteristics when CO\(_2\) was added to the base gas. In this case, the DeNOx characteristics were strongly affected by the polarity of center electrode. In the case (a) of positive corona discharge, NO decreased with increasing the energy density, but NO\(_2\) and N\(_2\)O were formed significantly at the energy density above 300 J/L. Since NO\(_2\) and N\(_2\)O were produced 130 ppm and 60 ppm in maximum, respectively, the NOx concentration became twice of the initial concentration. On the contrary, in negative corona discharge (b), the DeNOx characteristics were similar to those of the base gas.

Since carbon monoxide might be formed when a mixture containing CO\(_2\) was exposed in the corona discharge field, effect of the electrode polarity on CO formation had to be analysed to make further consideration. The result is shown in Fig. 8. Furthermore, concentration of ozone formed by corona discharge is shown in Fig. 9. It is clear that the negative corona discharge formed a less concentration of CO compared with the positive corona discharge even if the energy density was high. It is suggested that CO\(_2\) addition did not influence so much the DeNOx characteristics in the case of the negative corona discharge. However, the amount of O\(_3\) formation with CO\(_2\) addition was considerably high even if the polarity was negative. It was considered that high concentrations of CO and O\(_3\) were due to the characteristics that CO\(_2\) could be dissociated easilier compared with N\(_2\) and O\(_2\). Thus, it was thought that active molecules dissociated in corona discharge field caused various reactions in a CO\(_2\) addition mixture.

With an increase of the electric current, positive corona could be easily developed compared with negative corona. The electrical discharge patterns varied generally with the electric field intensity around the center electrode. In the case of base gas, however, the pattern of “glow dis-
charge” was only maintained in the experiment. When CO₂ was added to the base gas, the pattern was shifted from “glow discharge” into “streamer discharge”, since a large quantity of dissociated molecules existed in the electrical discharge field.

Thus, further two expressions are proposed in consideration of the formation of a large amount of CO and O₃ when carbon dioxide is added to the base gas.

\[
\begin{align*}
\text{CO}_2 & \rightarrow \text{CO} + \text{O} \quad (12) \\
\text{O}_2 & \rightarrow \text{O} + \text{O} \quad (13)
\end{align*}
\]

Dissociated oxygen atom reacts with nitrogen oxide etc. Reaction process is as follows.

\[
\begin{align*}
\text{O}_2 + \text{O} & \rightarrow \text{O}_3 \quad (14) \\
\text{N}_2 + \text{O} & \rightarrow \text{N}_2\text{O} \quad (15) \\
\text{N}_2\text{O} + \text{O} & \rightarrow 2\text{N}_2\text{O} \quad (16) \\
\text{NO} + \text{O} & \rightarrow \text{NO}_2 \quad (17)
\end{align*}
\]

CO and O₃ react with nitrogen oxide as follows,

\[
\begin{align*}
\text{CO} + \text{NO}_2 & \rightarrow \text{CO}_2 + \text{NO} \quad (18) \\
\text{O}_3 + \text{NO} & \rightarrow \text{O}_2 + \text{NO}_2 \quad (19)
\end{align*}
\]

In positive corona discharge, it is considered that the O atom reactions shown in Eqs. (15) – (17) are predominant and might result in the increases of NO₂ and N₂O. Besides it is conjectured that the NOx increases considerably because the reduction of NO₂ with CO and the oxidation of NO with O₃ might be promoted by the high concentrations of CO and O₃. On the other hand, in negative corona discharge, the DeNOx characteristic was similar to that in the case of base gas. This is because the reaction with ozone was predominant from the fact that the amount of generation of O₃ was larger than that of CO.

3.6 Effect of hydrocarbon on DeNOx characteristics in base gas treatment

CH₄ and C₂H₄ were selected as the main hydrocarbons contained in the exhaust gas of diesel engine, and the influence of these hydrocarbons on DeNOx was investigated. Figure 10 shows the result when 100 ppm ethylene was added to the base gas. In the case of positive corona discharge, the concentration of C₂H₄ decreased with an increase of the energy density, and it finally became around 45 ppm. In this case, NO was converted to NO₂ with lower energy density compared with in the case of base gas, but total NOx was not decreased. On the other hand, in the case of negative corona discharge, NOx began to decrease at about 150 J/L and then decreased rapidly up to 10 ppm at 280 J/L. The NOx reduction occurred at lower energy density compared with in the case of base gas. Moreover, the decrease of C₂H₄ concentration had the similar tendency to the NOx concentration, and both concentrations decreased down to 10 ppm at the energy density of 280 J/L. It was found that the dissociation of C₂H₄ by corona discharge affected the conversion of NO to NO₂ and the NOx removal. There was a possibility that nitro-compound was formed by the hydrocarbon addition. However, the nitro-compound was not discussed here because the analysis of nitro-compound was impossible with the gas analyzer used in this experiment.
The following expression is proposed as the reactions of \( \text{C}_2\text{H}_4 \) in corona discharge field\(^{(11),(12)} \). Possible reaction scheme is explained as follows. At first, \( \text{C}_2\text{H}_4 \) is decomposed by O atom that is formed by the dissociated with the electrical discharge.

\[
\text{C}_2\text{H}_4 + \text{O} \rightarrow \text{CH}_3 + \text{CHO} \quad (20)
\]

Next, methyl radical reacts with oxygen as follows.

\[
\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{O}_2 \quad (21)
\]

\[
\text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{O} + \text{NO}_2 \quad (22)
\]

NO is oxidized by \( \text{CH}_3\text{O}_2 \), and \( \text{CH}_3\text{O} \) reacts as follows.

\[
\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{HO}_2 \quad (23)
\]

\[
\text{CH}_2\text{O} + \text{O} \rightarrow \text{CHO} + \text{OH} \quad (24)
\]

CHO reacts with oxygen, and carbon dioxide is produced as follows.

\[
\text{CHO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2 \quad (25)
\]

It was found that the oxidation of NO was promoted by the \( \text{C}_2\text{H}_4 \) addition. Moreover, the amount of \( \text{O}_3 \) generation in the case of negative corona discharge is shown in Fig. 11. The ozone formation related with \( \text{C}_2\text{H}_4 \) addition was higher than that without \( \text{C}_2\text{H}_4 \) addition. Thus, it was considered that the \( \text{O}_3 \) took a part in the rapid NOx reduction as shown in Fig. 10(b). On the other hand, \( \text{CH}_3\text{O} \) addition did not contribute to the DeNOx reaction because \( \text{CH}_4 \) concentration was not changed even if the energy density increased up to 1 500 J/L.

### 3.7 DeNOx characteristics in simulated exhaust gas treatment

In the previous sections, the effects of component gases on DeNOx characteristics have been individually described. This section described the DeNOx characteristic of the simulated exhaust gas, which was containing \( \text{H}_2\text{O}, \text{CO}_2 \) and \( \text{C}_2\text{H}_4 \) with the base gas. Figure 12 shows the result of the case of negative corona discharge that was more effective for DeNOx reaction. The DeNOx characteristics were almost similar to the base gas. Namely, NO was decreased with increasing the energy density, while \( \text{NO}_2 \) increased once and then decreased down to almost 0 ppm at 250 J/L. \( \text{N}_2\text{O} \) concentration was about 2 ppm in the vicinity of the minimum NOx concentration at 250 J/L and was 10 ppm at 600 J/L. A large amount of \( \text{O}_3 \) was formed after the NOx reduction. About 40 ppm HNO\(_3\) was formed after the NOx reduction. CO concentration began to increase rapidly with a little energy increase at the low energy condition.

Figure 13 shows the energy densities that were necessary for 90% NOx reduction for all conditions of coexisting gas addition in the cases of negative corona discharge. It was found that the NOx was removed at relatively low energy density in two conditions of \( \text{H}_2\text{O} \) added base gas.
and simulated exhaust gas, but high energy density was needed for CO₂ addition case. Thus, it was considered that the existence of moisture became a key for DeNOx treatment in a corona discharge field.

4. Conclusions

Effects of coexisting gases on NOx removal using a corona discharge were investigated experimentally. The main conclusions of the research are as follows.

1. When moisture was added to the base gas (NO/O₂/N₂), NOx concentration decreased about 30% at the energy density of 500 J/L in the case of positive corona discharge. On the other hand, in the case of negative corona discharge, NOx began to decrease at lower energy density, and 90% of NOx was removed at about 250 J/L. It was also confirmed that a part of NOx was converted into nitric acid.

2. When CO₂ was added to the base gas, the NOx concentration increased up to about twice at 920 J/L in the case of positive corona discharge. In the case of negative corona discharge, the energy density necessary for 90% NOx reduction was about 200 J/L higher than that for the case of base gas. CO and O₃ of high concentration were formed in both cases of positive and negative corona discharge. Thus, the existence of CO₂ in exhaust gas was not desirable for NOx removal using corona discharge.

3. In the case of C₂H₄ addition to the base gas, NOx was hardly removed by positive corona discharge though NO was oxidized into NO₂. However, in the negative corona discharge, NOx was decreased by the dissociation of C₂H₄ as well as NOx with a lower energy density compared with the base gas.

4. In the DeNOx of simulated exhaust gas by negative corona discharge, NOx was decreased with lower energy density compared with the case of base gas. CO was formed even if the energy density was low, while N₂O, O₃, and HNO₃ were formed remarkably at high energy density condition where NOx was almost removed.

In this paper, the effects of various coexisting gases on DeNOx characteristics were investigated under the condition of constant gas flow rate of 1.0 L/min. In order to apply these results to actual engine exhaust gas, it is required to investigate the effects of temperature, residence time and flow pattern of the gas on DeNOx treatment.

References


