NOx and Soot Reduction Using Dielectric Barrier Discharge and NH3 Selective Catalytic Reduction in Diesel Exhaust

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Abstract — A combined De-NOx technique of a non-thermal plasma and a selective catalytic reduction (SCR) using NH3 has been investigated to remove NOx from a 300 hp marine diesel engine exhaust under low temperature conditions (100–200 °C). As results, De-NOx efficiencies for the combined process were increased from 20 to 80 % at 100 °C compared to a SCR sole process. Since a non-thermal plasma could convert NO into NO2, a fast SCR reaction by which a equal amount of NO and NO2 reduced to nitrogen could be activated in a relatively low temperature range. Furthermore from the measurement of smoke-meter, over 45 % of PM was reduced and the size distribution of PM was significantly altered after plasma process. This feature will be helpful to continuously regenerative DPF systems.

Keywords — non-thermal plasma, dielectric barrier discharge, NH3 SCR, fast SCR reaction

I. INTRODUCTION

Recently, we are faced with the elevated regulation of NOx from combustion exhaust gases, because it caused smog, an acid rain, and a respiratory disease. Available technologies for aftertreatment of NOx, for instance, are a three-way catalyst and a selective catalytic reduction (SCR) used for gasoline engines and stationary combustion systems, respectively. However, since the three-way catalyst should be operated in stoichiometry, it can not be adopted to lean burn engines such as diesel engines. For a SCR technique especially using NH3 as a reducing agent, though it shows a good performance for oxygen contained flue gases, there is the limitation of operating temperatures (normally its operating temperature is above 300 °C), so that de-NOx efficiencies are quite poor in a low temperature range [1, 2]. In this reason, NH3 SCR can not be used for low temperature flue gases in many stationary combustion systems as well as mobile engines which have a stop-and-go features. In these regards, catalytic processes combined with a non-thermal plasma can be considered as one of the promising candidate for treating NOx from lean burn engines with a low temperature exhaust, and recently many of researchers had interests on this field [2-7].

Another main hazardous product in diesel engines is particulate matter (PM), which is generally formed from soot particles. Since diesel engines are operated with a diffusion flame, soot particles are inevitable. In the present study, we investigated the effects of a non-thermal plasma combined with conventional NH3 SCR process on NOx treatment in a marine diesel engine exhaust with an emphasis on the increasing de-NOx efficiencies in a low temperature range, i.e., 100-200 °C. The principles and illustrative test results of the combined De-NOx process of SCR and oxidation techniques were well introduced in recent researches [2-4, 8-10]. A dielectric barrier discharge (DBD) was considered as the source of a non-thermal plasma (or an oxidation source). We designed and constructed a planar type DBD, which showed a good performance even in humid and highly sooting conditions. Fundamental investigations, such as NO to NO2 conversion characteristics with DBD, the effects of additives were also made with a simulated gas. In addition, the size variation and reduction of PM with the DBD reactor will be discussed.

II. EXPERIMENT

To investigate the basic characteristics of non-thermal plasma and SCR processes, we first considered a lab-scale experiment with a diesel exhaust-like simulated gas. Figure 1 shows the schematic of lab-scale experimental setup. The apparatus consisted of a gas supply system, a mixing and preheating unit, a constant temperature furnace, a DBD reactor and a power supply, a SCR reactor, and measurement systems. To simulate a diesel exhaust, mass flow controllers were used for compressed air, N2, CO2, NO, and C3H6. Here, propylene was used for representing unburned hydrocarbons [11, 12] and the effect of water vapor was not considered for simplicity. The gas compositions are listed in Table 1.

![Fig. 1. Schematic of lab-scale experimental setup.](image-url)
which correspond to 25 and 50% of maximum load condition in a marine diesel engine used in the present study. The flow-rate of ammonia, as a reducing agent in SCR process, was also controlled with MFC, and it was fixed as the same amount of NOx. Total flow-rate of simulated gas was fixed at 20 slpm for lab-scale test.

To identify the effects of operating temperature on each process, the DBD and SCR reactors were located in the constant temperature oven. The simulated gas was mixed and heated up to a target temperature within the mixing and preheating unit, then it was introduced to the DBD reactor. The composition of a mixture was measured by Fourier transform infrared spectroscopy (FTIR, vector33, Bruker) at three different points – the inlet and outlet of the DBD reactor, and the outlet of the SCR reactor. These three points represent an initial condition, the effects of plasma, and the role of a catalyst, respectively.

As shown in Fig. 2, the dielectric barrier discharge (DBD) reactor (100(W)×70(D)×100(H) mm), which was constructed by stacking up a planar electrode together with spacers for gas flow, was used as a non-thermal plasma source. The planar electrode consisted of two α-Al₂O₃ ceramic plates bonded each other. At one of the attached surface, a silver paste was coated. AC power supplies with 60Hz and 10kHz frequencies were used separately for the lab-scale test and a pilot-scale test, respectively to supply adequate electrical power in each experiment. The delivered electrical power was measured by automated power measurement system using a charge-voltage diagram (Lissajous diagram) [13] with an additional capacitor of 2 μF. For the SCR process, commercialized NH₃ SCR catalyst (SK Corp.) was used.

<table>
<thead>
<tr>
<th>% of Max. Load of Engine</th>
<th>Exhaust Composition</th>
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<tr>
<td></td>
<td>O₂ [%]</td>
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<tr>
<td>25%</td>
<td>17.6</td>
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<tr>
<td>50%</td>
<td>15.4</td>
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[NOx] = [NO] + [NO₂]

To investigate the practical applicability of the plasma/SCR combined process to real diesel exhaust, 300 hp rating marine diesel engine (Yanmar) was used (see Fig. 3). 100 Nm³/h was bypassed from a main exhaust stream, while the total flow-rate is about 1,000 Nm³/h at full load condition. Note that at this flow-rate Q = 100 Nm³/h, space velocities are S.V = 4,500/h and 450,000/h for the catalyst and the plasma reactor, respectively. NOx removal efficiencies were also measured with the FTIR spectrometer.

![Fig. 2. Planar type DBD reactor.](image)

![Fig. 3. Pilot-scale plasma/SCR combined system with marine diesel engine.](image)

### III. RESULTS AND DISCUSSION

#### A. Effects of Non-thermal Plasma on NOx

In general, important chemical reactions relating to NO and NO₂ are as follows.

1. \( \text{NO} + \text{N} \rightarrow \text{N}_2 + \text{O} \)  
2. \( \text{NO} + \text{O} + \text{M} \rightarrow \text{NO}_2 + \text{M} \)  
3. \( \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \)  
4. \( \text{NO} + \text{OH} + \text{M} \rightarrow \text{HNO}_2 + \text{M} \)  
5. \( \text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH} \)  
6. \( \text{NO}_2 + \text{N} \rightarrow \text{N}_2\text{O} + \text{O} \)  
7. \( \text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M} \)  
8. \( \text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2 \)

As can be seen in (1)-(8), radicals or molecules such as O, O₃, OH, N, and HO₂ are needed in the reactions. Since a non-thermal plasma was known to make lots of chemically active species, we used the DBD as the source of radicals.
In N2/O2 mixtures, much of a input energy could be used for O2 dissociation rather than N2 dissociation [11]. Furthermore since (1) is a relatively slow reaction, the reactions relating to N radical can not be considered for simplicity. In the present lab-scale experiment, we did not consider the effects of H2O. In this regard, (2), (3), and (8) can be important reactions. These O and O3 involved reactions are composed with the oxidation of NO to NO2 and the backward conversion of NO2 to NO. In this point of view, one can conceive that at certain thermodynamic state including a concentration and temperature the reactions can be equilibrated, i.e., NO to NO2 conversion can be saturated with the input power of plasma.

Figure 4 shows NO to NO2 conversion efficiencies along with a SED (specific energy density) defined as a input energy per the unit volume of a gas to be treated, i.e., SED = input power for plasma generation/gas flow-rate. Here, the rectangle and circle symbols indicate simulated mixtures with and without HC (C3H6), respectively, and a conversion efficiency was defined by the volume fraction of NO2 for the total amount of NOx. As shown in the figure, for the case without HC, NO2 conversion rate is relatively insensitive to SED demonstrating saturated feature at about 13 %. However, owing to the addition of HC, the production of NO2 is significantly increased, for instance 45 % of NO is oxidized to NO2 at SED = 200 kJ/m3. It is to be noted that the change of total amount of NOx (NO + NO2) was negligible for both conditions, meaning that NOx can not be reduced to nitrogen by the sole process of a non-thermal plasma.

The increase of NO to NO2 conversion efficiency with the addition of propylene can be explained as follows. Propylene can be partially oxidized with the aid of O radical, and through this partial oxidation can produce lots of reactive species with a chain reaction [14]. Chemical reactions relating these species are

\[
\text{NO} + \text{CH}_3\text{O}_2 \rightarrow \text{NO}_2 + \text{CH}_3\text{O} \quad (9) \\
\text{NO} + \text{O}_2\text{C}_2\text{H}_4\text{OH} \rightarrow \text{NO}_2 + \text{OC}_2\text{H}_4\text{OH}. \quad (10)
\]

Above reactions are known as faster than (2) and (3). Furthermore in defect of O radical, the backward reaction of NO2 to NO in (8) can be decreased. In this reason, high conversion efficiency can be obtained with the addition of HC. In Fig. 5, we plotted NO to NO2 conversion efficiencies for various operating temperatures with the simulated gas of 25 % load condition. As can be seen, at 150 and 200 °C NO2 conversion exhibits its optimum, while the conversion became deteriorated as the temperature increases. It partly because the temperature sensitive characteristic of (8) compared to (2), (3), (9), and (10), i.e., NO2 to NO backward conversion reaction prevail over the NO oxidation at high temperatures.

B. Characteristics of Plasma/SCR Combined Process

As discussed in the previous section, NOx can not be reduced to nitrogen with a non-thermal plasma process in the presence of oxygen. Some portion of NO was oxidized to NO2 demonstrating negligible change of the total amount of NOx. In this regard, NH3 SCR process was adopted after the plasma process to achieve the full reduction of NOx. In Fig. 6, the concept of plasma/SCR combined process was depicted. As shown in the figure, plasma and SCR reactors are connected in series. In
Combustion flue gases, over 90 % of NOx consisted of NO. A plasma reactor converts a certain amount of NO to NO2. Some portion of NO can be reduced by NH2 radical within the plasma reactor. Then NO+NO2 reduced to N2 in NH3 SCR reactor, since NO2 or NO+NO2 mixture could be more easily reduced at low temperature. Chemical reactions concerning NOx reduction in NH3 SCR process are

\[
\begin{align*}
4\text{NO} + 4\text{NH}_3 + \text{O}_2 &\rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} & (11) \\
\text{NO} + \text{NO}_2 + 2\text{NH}_3 &\rightarrow 2\text{N}_2 + 3\text{H}_2\text{O} & (12)
\end{align*}
\]

Here, (11) represents the standard SCR reaction and (12) is correspond to so-called fast SCR reaction. The reaction rate of (12) is significantly faster than that of (11), especially when a gas temperature is lower than 200 °C [3, 8-10]. In addition, when NH3 was injected before a plasma reactor, NH2 radical produced from NH3 by a plasma process also affects to NOx [3].

\[
\begin{align*}
\text{NH}_2 + \text{NO} &\rightarrow \text{N}_2 + \text{H}_2\text{O} & (13) \\
\text{NH}_2 + \text{NO}_2 &\rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} & (14)
\end{align*}
\]

From (14), undesirable N2O formation occurred through a plasma process, however, in the present experiment, N2O leakage can not be detected after SCR reactor.

Since over 90 % of NOx can be reduced to N2 above 250 °C using a NH3 SCR process, to identify synergetic effects with plasma process operating temperatures were varied from 100 to 200. We considered 25 % load condition in Table I and the amount of NH3 was matched with that of NOx. In Fig. 7, we plotted NOx reduction rates for the non-thermal plasma, the NH3 SCR, and the plasma/SCR combined processes. As shown in the figure, for the plasma sole process with SED = 84 kJ/m3, about 30 % of NOx is removed irrespective of temperature through (13) and (14). On the contrary, for the SCR sole process, it shows significant dependence on temperatures. At 100 °C, NOx reduction rate is about 20 %, while it reaches about 85 % at 200 °C. However, the NOx reduction rate is dramatically changed for plasma/SCR combined process in relatively low temperature. About 80 % of NOx can be reduced through the plasma/SCR combined process in the temperature range of 100-150 °C. As depicted in Fig. 7 for 100 °C, the arithmetic sum of NOx reduction rate for plasma/SCR combined process is about 36 %, i.e., 20 % (plasma) + 80% (remained portion of NOx relative to the initial amount after the plasma reactor) × 20% (SCR performance) = 36%. While it reaches at 80% for combined process demonstrating synergetic effect of combining two processes.

This can be explained based on the fast SCR reaction, (12). A generated NO2 within the plasma reactor can activate reaction in (12) in the SCR reactor. To clarify the synergetic results, we investigated de-NOx efficiencies for the SCR sole process with flowmeter controled NO/NO2 mixtures. As results, a NOx reduction rate for a mixture of NO+NO2 showed its optimum at around [NO2]/[NOx] = 0.4 to 0.6, which is the supportive result of fast SCR reaction. However, de-NOx performance of combined process was deteriorated compared to SCR process over 170 °C as shown in Fig. 7. Through a parametric test with additives, we concluded that this result was originated from the HC addition. It was found that aldehyde, which is generated in the plasma reactor from HC, can serve as a reducing agent in catalytic process, while it reduced NO2 to not N2 but NO in the SCR reactor.

C. NOx Removal in Diesel Engine Exhaust

To investigate the applicability of the combined process in a diesel engine exhaust, we construct the 100 Nm3/h rating pilot-scale plasma/SCR combined system as shown in Fig. 3. The engine was set to 25 % load condition throughout the whole experiments, and we put a heat exchanger into the exhaust line to control the exhaust temperature. The plasma reactor operated excellently with highly humid and sooting condition, and it worked properly even after 1,000 hr operating time. Since the NO to NO2 conversion in plasma reactor was mainly related to the amount of C3H6 addition as well as input power as shown in Fig. 4, we investigated NOx reduction rates of combined system for various input powers and C3H6 addition. It is to be noted that the additional C3H6 was supplied through a mass flow controller.

Figure 8 shows the NOx reduction efficiencies along with the normalized C3H6 concentration for various input power conditions at 100 °C. As results, since de-NOx efficiency is saturated at about 80%, we chose the combination of SED = 40 kJ/m3, which corresponds to 1.1 kW input power with flow-rate of 100 Nm3/h, and [C3H6] = 1.5[NOx] = 800 ppm as an operating condition. Note that to determine an operating condition in commercial applications the comparison of fuel cost between making electricity with engine and supplying HC should be made.
Figure 8 shows the NOx reduction efficiency for various operating conditions. The NOx reduction efficiency is plotted against the ratio of \([\text{C}_3\text{H}_6]/[\text{NOx}]\) for different operating conditions. The figure shows that the NOx reduction increases with the increase in the ratio of \([\text{C}_3\text{H}_6]/[\text{NOx}]\).

![Fig. 8. NOx reduction efficiencies for various operating conditions.](image)

Figure 9 shows the NOx reduction for SCR and combined system together with the percentage of \([\text{NO}_2]/[\text{NOx}]\) along with temperature. The NOx reduction efficiency for SCR and combined system is plotted against the temperature. The figure shows that the NOx reduction increases with the temperature for both SCR and combined system, and the percentage of \([\text{NO}_2]/[\text{NOx}]\) decreases with the increase in temperature.

![Fig. 9. NOx reduction efficiencies for SCR and combined system together with the percentage of \([\text{NO}_2]/[\text{NOx}]\) along with temperature.](image)

IV. CONCLUSION

The non-thermal plasma process combined with consumption of the plasma reactor to be 5-6 kW approximately. This power can cover about 500 Nm³/h, which can be enough for a warming up period considering that the exhaust flow-rate is about 1,000 Nm³/h at full load. Since the estimated power corresponds to 2% of the engine power, and moreover the plasma reactor should be turned off after exhaust temperature increases, probably the operating cost of the plasma reactor does not matter in practical applications. In addition, the degradation of catalyst from unwanted byproduct such as ammonium nitrate can be fixed by occasional high temperature (>-250°C) operations.

D. Effects of Non-thermal Plasma on PM

Through the present pilot-scale test, it was also found that the present planar type DBD can be effective to change the emission characteristics of PM. The size distribution and blackness of PM were measured at the outlet of the plasma reactor using a particle size analyzer and a smokemeter, respectively. Figure 10 shows the size variation of PM. As shown in the figure, the initial distribution pattern (solid line) is significantly altered by the plasma process (dotted line). With the aid of the plasma process, the average size of PM is quite reduced to the order of 1 μm demonstrating the double peak of its distribution. The average size is in the order of 10 μm for the untreated PM. Since the reduction of average size means the increase of total surface area of PM, this result can be helpful to a continuously regenerative DPF system, which used NO2 as an oxidizing agent for PM. Furthermore, 45% reduction in the blackness can be observed with the plasma process. From the above results, we can conceive that through the plasma reactor mass reduction can be possible as well as its average size reduction. However, at present, the detailed mechanism of PM reduction is not clear, and further investigation will be a future study.
conventional NH₃ SCR process was successfully applied to the marine diesel engine exhaust. To treat 550 ppm of NOₓ from the diesel engine, we chose the flow-rate of 100 Nm³/hr, electric power of 1.1 kW (SED=40 kJ/m³), and 800 ppm C₃H₆ addition among the various optimal operating conditions. Here, we need to supply as much amount of NH₃ as NOₓ, i.e., [NH₃] = 550 ppm for the SCR. As results, de-NOₓ efficiencies for combined process were increased from 20 to 80 % and from 55 to 90% at 100 and 200 °C, respectively compared to the SCR sole process. We estimated that the power consumption is about 2 % of engine power.

In addition to the NOₓ reduction, we found that PM in the diesel exhaust, mainly consists of soot, was affected by the plasma process. From the measurement of smoke-meter, over 45 % of PM were reduced after the plasma process. Furthermore, the size of PM is significantly decreased. It suggested that the non-thermal plasma process can be a viable method for PM reduction or assisted one for other DPF systems.

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