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Combined De-NOx Process with NH_3 SCR and Non-thermal Plasma Process for Removing NOx and Soot from Diesel Exhaust Gases

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Abstract

Combined De-NOx process, in which NH3 SCR (Selective Catalytic Reduction) and non-thermal Plasma Process are simultaneously used, has been investigated with a pilot test facility. The pilot test facility treats the combustion flue gases exhausted from a diesel engine that generates 240 kW of electrical power. Test results show that up to 80 % of NOx (NO and NO2) can be removed at 100 - 200 oC. None of conventional De-NOx techniques works under such low temperature range. In addition to NOx, the pilot test results show that soot can be simultaneously treated with the present non-thermal plasma technique. The present pilot test shows that the electrical power consumption to operate the non-thermal plasma reactor is equivalent to 3 - 4 % of the electrical power generated by the diesel engine.

1. Introduction

Legislations of the NOx emission enforced by environmental authorities causes increasing technical concerns on reducing NOx emissions from combustion flue gases. Among several De-Nix techniques, NH_3 SCR technique has been considered as one of the maximum achievable techniques to reduce NOx emissions from lean-burn combustion facilities, which are industry boilers, power plants, diesel engines, and chemical plants. At present, one of the technical issues on applying the NH_3 SCR technique to these various combustion facilities is to lower the operating temperature limit of the process. For example, conventional NH_3 SCR process, which is typically operated at 250 - 400℃ of exhaust temperature range, cannot be applied when diesel engines are operated under cold starting conditions.

The objective of the present study is to develop a De-NOx technique that can be applied to the low operating temperature

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conditions, i.e. lower than 250℃. The technique used in the present study is a combined De-NOx process with SCR and non-thermal plasma techniques. The principles and illustrative test results of the combined De-NOx process are well introduced in recent technical papers, in which the simulated exhaust gases of diesel or lean burn gasoline engines are treated [1, 2, 3]. The combined De-NOx process follows two basic steps: in the first step some certain amounts of chemically inert NO is oxidized to NO_2 through non-thermal process, and in the second step NOx (NO and NO_2) are reduced to N_2 though the SCR process. Despite of the previous demonstrative studies, the technique of the combined De-NOx process is still in an early stage of development. In the previous related studies, the studies have been conducted with small-scale test facilities and with simulated diesel exhaust gases to verify the principles of the chemical reaction pathways. Therefore, numerous practical factors that could affect on the combined De-NOx process have not been tested.

The present study has been performed while treating real diesel exhaust gases emitted from 300 Hp diesel engine (Yanmar Co.). Therefore, all of the practical test conditions, such as effects of soot, water vapor, hydrocarbons and CO contents on the process, durability, economical feasibility, and scale-up techniques of the plasma reactor and the power supply, etc., have been considered. In the early parts of the present paper, comparison test results between DBD and pulsed corona techniques are discussed, which is crucial for estimating the initial cost of non-thermal plasma process. In later parts of the paper, pilot test results are demonstrated and discussed.

2. Preliminary Study

2.1 DBD vs Pulsed Corona

We started the present study with a comparison test of DBD and pulsed corona techniques. This comparison study was conducted with a lab-scale test in which 10 lpm of gas flow was treated. The purpose of this test is to compare the performance of DBD technique with a pulsed corona technique while oxidizing NO in diesel exhaust gases in which O_2 concentration is higher than 5 %. The pulsed corona reactor used in the study consists of simply a metal wire electrode and cylindrical tube (d: 27 mm, L: 30 cm), and operated with a short pulse DC power. The pulse width of the applied voltage is 300 nsec, and the peak voltage is 20 kV. A magnetic pulse compressor is used in the pulse power supply, which is an innovative technique to increase the life-time of the pulse switch prior to maintenance. In the case of DBD, a cylindrical quartz tube (d: 27 mm, L: 30 cm) as a dielectric barrier material and metal electrode are used in DBD reactors. A high voltage AC power supply with 60 Hz of frequency is used to supply the power into the DBD reactors.

Fig. 1 (a) and (b) show the ratio of the inlet to outlet concentrations of NO along with specific energy density. The specific energy is defined as the ratio of the input energy (Joule) to the treated gas volume (liter). In the figures, DBD means the tests conducted with the dielectric barrier discharge reactors that have 2 mm or 4 mm of the electrode gap distance (d). PCD means the tests conducted with the pulsed corona discharge reactors that have 1 mm or 0.5 mm of electrode diameters in the 27mm of outer ground tube.

As shown in the figures, the removal efficiencies (1 - (Ci - Co)/Ci) are varied depending on the specific energy, reactor geometry, species of the carrier gases (air or nitrogen), and the types of the reactor (DBD and PCD). Here, Ci is the initial concentration of NO, and Co is the outlet concentration of NO, respectively. The present figures show that the removal efficiencies are dominantly affected by two factors: one is the specific energy and the other one is the type of the carrier gases, i.e. N_2 or air. The variations of the electrode configurations also affect on the removal efficiencies, but this factor is not significant compared to other two parameters.

From the practical points of view, the most important conclusion obtained from the above comparison test is that the performance of the DBD is better than that of PCD as long as the NO removal process is operated in air (79 % N_2 + 21 % O_2). Based on the present results and supplementary tests, we obtained several features of NO removal process; 1) the removal process of NO in N_2 carrier gas is a direct reduction process, which means that NO is reduced to N_2. 2) the removal process of NO in air is an oxidation process in which NO is converted to NO_2. 3) NO oxidation process is dominant when the O_2 concentration in the carrier gases is higher than 3 %. Therefore, it can be expected that NO oxidation process is the governing reaction pathway in diesel flue gases in which O_2 concentrations are normally higher than 5 %. In conclusion, we decided to use DBD technique to treat diesel emissions in the present study. In the present decision, technical accessibility of DBD is also considered.

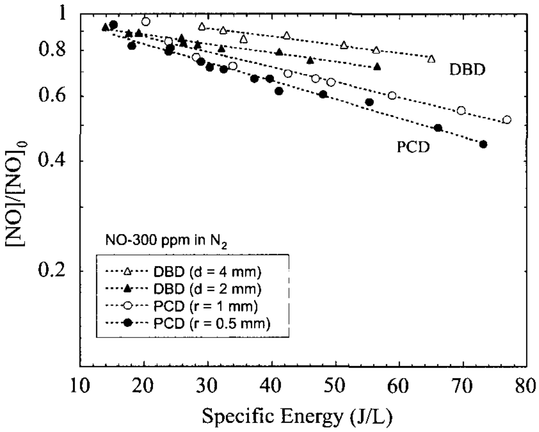


Fig. 1 (a) NO reduction efficiency along with SED while NO is reduced to N2 in nitrogen gas

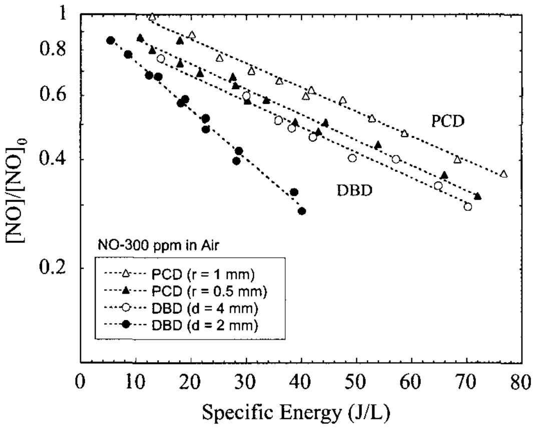
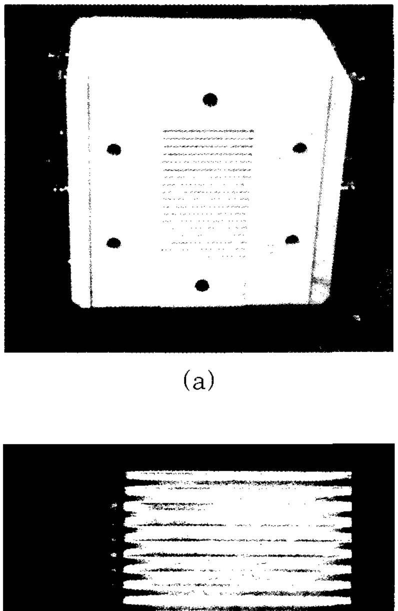


Fig. 1 (b) NO oxidation efficiency along with SED while NO is oxidized to NO2 in air.

Fig. 2 shows the DBD reactor developed for applying in diesel exhaust gases. As shown in the figure, planar type electrodes made of Al_2O_3 are used. Physical dimension of the DBD is about 50 mm × 50 mm × 100 mm. Fig. 2 also shows the UV light emission generated from the DBD reactor, which are taken by an intensified CCD camera. In order to design an optimal planar type DBD reactor, we carried out various parametric studies in which gap distances, electrode thickness, and barrier materials had been varied. One of the most important parameters to decide the performance of the DBD reactor is the gap distance. The optimal gap distances range from 1 mm to 3 mm under the present test conditions.



(a)

(b)

Fig. 2 (a) Planar type DBD reactor and (b) Light emission from the reactor

2.2 Reaction Pathways of De-NOx

The reaction pathway of the combined process for treating diesel flue gases can be schematically expressed as the following two steps:

1st step(occurred in the non-thermal plasma reactor)

$$NO + O_2 + \text{Plasma} \rightarrow NO_2$$

2nd step (occurred in the SCR reactor)

$$NO_2, NO + NH_3 + \text{Catalyst} \rightarrow N_2$$

As indicated in the above reaction pathways, the main role of the non-thermal plasma process is the conversion of chemically inert NO to NO_2. According to previous studies [1], NO_2 showed better reactivity compared to NO, which results in extended temperature windows and varieties of the catalysts that are durable against to hydro-thermal and sulfur poisoning.

In order to confirm the above advantages of the combined De-NOx process, a lab scale test has been conducted. The treated gas flow rate of the lab-scale test is 30 lpm. The plasma reactor used in the test is the DBD reactor shown in fig. 2. The test was carried out with the following gas compositions: nitrogen (77.7 %), oxygen (18 %), CO_2 (4.3 %), CO (150 ppm), NOx (520 ppm), HC (116 ppm), NH_3 (500 ppm). This gas composition is made to simulate the diesel exhaust gases. The treated gases were electrically heated and the reactor was located in an electrical oven to control the operating temperatures.

Figure 3 shows the NOx removal efficiency along with the operating temperature conditions. In the figure, we also compared the combined process with the conventional SCR process. As shown in the figure, the combined process removes NOx under the low temperature conditions (100, 125, and 150℃). In contrast, the conventional SCR process does not work well under such low temperature conditions. The supplementary tests showed that higher operating temperature (〈 250℃) conditions are needed to achieve 80 % of NOx removal efficiency when the conventional SCR technique was exclusively used. Another test results showed that the electrical power needed for operating the non-thermal plasma reactor used in the combined De-NOx process would be equivalent to less than 3 % of the power generated by the diesel engine. Such power consumption to operate the plasma reactor is apparently lower than the case of direct heating of the catalysts by electrical heaters or burners.

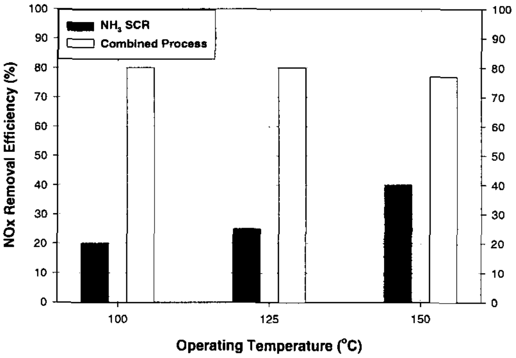


Fig. 3 NOx removal efficiencies with conventional SCR and the combined process at different temperatures

3. Pilot Test

Figure 4 shows the pilot test facilities, which consist of 1) diesel engine, 2) a conventional NH_3 SCR reactor, 3) non-thermal plasma reactor, and 4) other supplementary test facilities. The diesel engine used in the present study generates about 240 kW of electrical power and 1,000 Nm^3/hr of combustion flue gases at the maximum load. The flow rates and temperature conditions are controlled before the flue gases are treated by the combined De-NOx process. As shown in the figure, the flue gases are pretreated through the DBD reactor, and then treated by the SCR reactor.

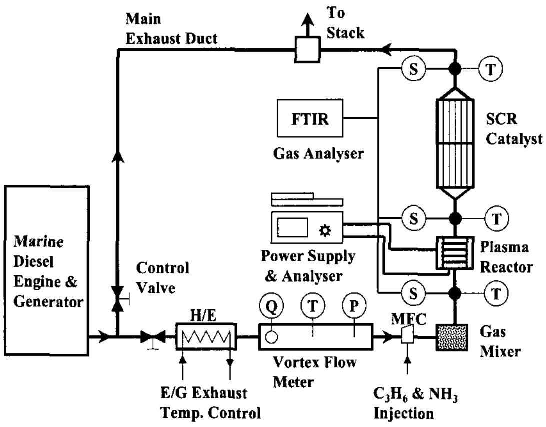


Fig. 4 Schematics of the pilot test facility

As shown in the photo picture of the pilot test facility (figure 5), the volume of the non-thermal plasma reactor that located at the inlet section of the SCR reactor is significantly smaller than the SCR reactor. The space velocity of the plasma reactor is estimated as 1,000,000 hr^{-1}, and the space velocity of the SCR reactor is 4,000 hr^{-1}. In the test, a high voltage (6 - 8 kV) and medium frequency (10 kHz) AC power supply is used, which can be fabricated with commercialized techniques and components. So far, the AC power supply has been operated for more than one year without maintenance problems. A FTIR gas analyzer is used to detect NO, NO_2, N_2O, SO_2, hydrocarbons, NH_3, CO, O_3, HNO_3, etc. In addition, a chemilluminescent NOx analyzer is used in the test.

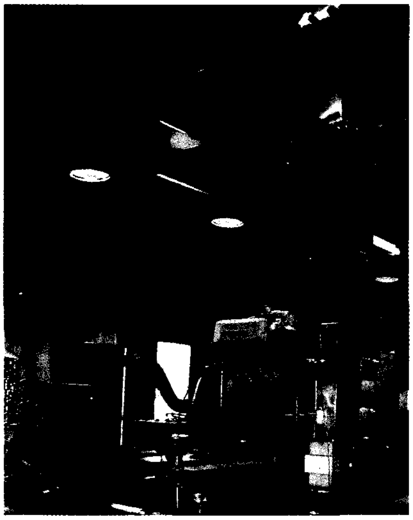
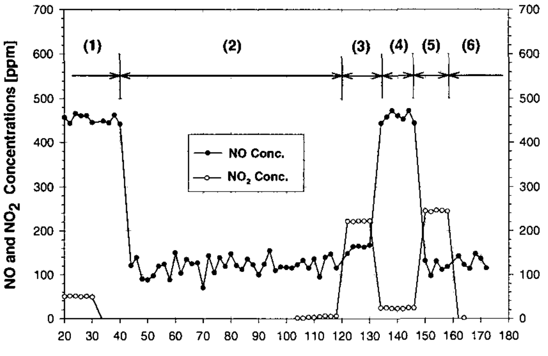


Fig. 5 Photo picture of the pilot test facility



(1) initial condition, (2) SCR outlet, 1.0 kW, (3) plasma outlet, 1.0 kW, (4) plasma outlet, 0 kW, (5) plasma outlet, 1.4 kW, (6) SCR outlet, 1.4 kW

Fig. 6 NO and NO2 concentrations at various operating conditions

Fig. 6 shows the NOx removal test results obtained from the pilot test, which shows the variations of NO and NO_2 concentrations along with time and various test conditions. The temperature was maintained at 100℃, and the flow rate treated was set to 100 Nm^3/hr.

During the test period (1) shown in the figure, 450 ppm of NO and 50 ppm of NO_2 in the diesel exhaust gas were measured. During the period (2), the NOx concentrations were measured at the outlet of the SCR reactor, and the power was supplied to the plasma reactor. The removal efficiency, which is defined as the ratio of the NOx (NO + NO_2) concentration at the SCR outlet to the plasma reactor inlet, reaches 75 %. During the period (3), 160 ppm of NO and 220 ppm of NO_2 were measured at the outlet of the plasma reactor. The NOx concentration measured in the period (3), which is 380 ppm, is lower than the initial NOx concentration, i.e. 500 ppm. This unbalanced NOx concentration can be attributed to the reaction pathway described as $NH_2 + NO \rightarrow N_2 + H_2O$. This direct reduction of NO has been theoretically predicted radical reaction in non-thermal plasma reactor [5]. During the period (4), the power was not supplied, and the NOx concentrations were measured at the outlet of the plasma reactor. In this period, the measured NOx concentrations were immediately recovered to the initial NOx concentrations. During the periods (5) and (6), the input power increased from 1.0 kW to 1.4 kW. Here, the electrical power measured at the plasma reactor using with Q-V plot technique. As shown in the figure, increasing the supplied power did not notably enhance the NOx removal efficiency. This observation implies that NOx reduction process is not exclusively governed by the supplied power, and is affected by other test parameters, such as temperature, flow rates, gas compositions treated, etc. The electrical power used in the present test is 1.0 kW for treating 100 Nm^3/hr of flue gas, which is equivalent to 4 % of the electrical power generated by the diesel engine.

The present pilot test shows that the plasma process can be also effective to control the emission of hydrocarbons and soot. During the tests, about 30 % of hydrocarbons was removed. The validity of the present removal data of hydrocarbons can be supported by previous study for treating hydrocarbons with non-thermal plasma process [6].

In the meantime, the size distributions of the soot emitted from the plasma reactor has been measured, and is varied with non-thermal plasma. Figure 7 shows the variation of the soot size distributions measured at the outlet of the plasma reactor. Figure 7 (a) is the soot size distribution when the power is off, and figure 7 (b) is the soot size distribution when the power is on.

As shown in the figures, the average size of the soot decreases when the plasma reactor is activated. Since the present data shows the diameter-volume distributions, the present data strongly suggests that the total mass of the soot are also decreased by non-thermal plasma process. At present, detailed mechanism of the mass reduction of the soot is not clear. Further investigations, which are investigations of carbon balance, electrostatic precipitation, elemental analysis of the treated soot, etc., are needed to verify the detailed soot removal mechanism.

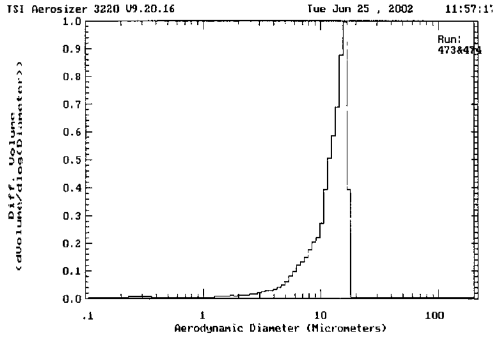


Fig. 7 (a) size-volume distribution when the power is off

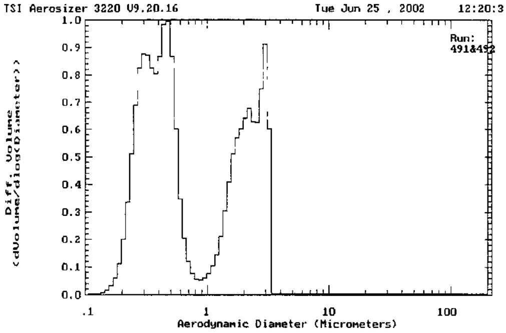


Fig. 7 (b) size-volume distribution when the power is on

4. Conclusion

Based on the lab-scale and the pilot-scale tests, the present study shows that the application of the non-thermal plasma technique is feasible to extend the temperature windows of the conventional NH$_3$ SCR process. Detailed test results of the present study can be summarized as following.

1) The dielectric barrier discharge technique used in the present study shows the better performance on the NO oxidation process compared with the pulsed corona technique. This conclusion is of practical important to utilize the non-thermal plasma technique, since the installment cost of the dielectric barrier discharge technique is significantly cheaper than that of the pulsed corona technique.

2) The combined De-NOx process tested with the real diesel combustion flue gases reduces NOx emission under low temperature conditions, i.e. 100 °C. At present, none of the commercialized De-NOx techniques works under such low temperature conditions.

3) The test shows that the electrical power needed to generate non-thermal plasma is equivalent to 4 % of the electrical power generated by the diesel engine. This power consumption for De-NOx process under the low temperature condition is economically acceptable, considering the energy cost to increase the flue gas temperature using with additional burners and heat exchangers.

4) The DBD reactor used in the present study is operated without any arcing problems while treating the real diesel combustion flue gases in which electrically conductive soot particles are included. Previously, operation of DBD technique under such harsh condition was not reported, to the author's best knowledge. In addition, the measurement results of the soot particle size and mass confirm that the mass and size of the soot treated by the non-thermal plasma can be reduced. This conclusion is of important for further diesel emission studies, since the present emission standards require the reduction of NOx and soot particles simultaneously.

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