Comparison of NOx Removal Performance from Simulated Diesel Exhaust Gas by Townsend Type Barrier Discharge and Filamentary Type Barrier Discharge

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Abstract: NOx (Nitrogen Oxides) and PM (Particular Matter) emitted from diesel engines are one of the causes of air pollution. In this research, NOx removal performance from simulated diesel exhaust gas by Townsend type DBD (Dielectric Barrier Discharge) and filamentary type DBD was investigated. As the results, it became apparent that (1) NO concentration decreased with the increase of specific input energy of both FD (Filamentary Discharge) and APTD (Atmospheric Pressure Townsend Discharge) modes. However, the decrease of NO concentration by APTD mode was lower than that by the FD mode at the same specific input energy. (2) The maximum energy efficiency were 25 g(NO)/kWh in case of FD mode and 16 g(NO)/kWh in case of APTD mode respectively. As a conclusion, the filamentary type DBD is better than the Townsend type DBD to remove NOx.

Keywords: NOx removal, dielectric barrier discharge, Townsend discharge

1. Introduction

NOx (Nitrogen Oxides) and PM (Particular Matter) emitted from diesel engines are one of the causes of air pollution [1]. As for gasoline engines, three way catalysts are already widely used for removing NOx. However, as for diesel engines, three way catalysts cannot be applicable to the NOx removal, because the large amount of residual oxygen in exhaust gas prevents the function of catalysts. Recently, the urea–SCR (Selective Catalytic Reduction) system is going to be used for NOx removal of heavy–duty diesel autos–trucks [2]. In this method, NH₃ hydrolytically generated from urea solution is used as a reducing agent of NO and NO₂ with a help of catalyst. In order to reduce NOx efficiently, catalyst temperature is necessary to be above 300 °C. Therefore, the NOx removal performance weakens when the catalyst temperature cannot reach a high temperature. For example, the catalyst temperature is low when a driver begins to start the engine or drives a car by a stop–and–go mode in winter season. In order to solve this problem, many engineers have studied the NOx removal method by a combination of urea SCR and non–thermal plasma [1, 3, 4].

We also studied two kinds of NOx removal systems by a combination of urea–SCR and non–thermal plasma. One is a combination of urea–SCR and DBD (Dielectric Barrier Discharge) [5] and the other is a combination of urea–SCR and ozone injection [6]. The combination of ozone injection has an advantage that ozonizers are free from the contamination by soot. These experiments were carried out at a discharge power of about 45 W and at the engine output of 1 kW. As for the combination of urea–SCR and DBD, we found that the NO removal reactions were inactive, but the NO₂ removal and the fast SCR (simultaneous removal of NO+NO₂) reactions were active even at the catalyst temperature of 192 °C. On the other hands, as for the combination of urea–SCR and ozone injection, NOx removal rate at the catalyst temperature of 160 °C was only 10 %, however it increased to 30 % by injecting ozone with the concentration of 1,000 ppm. The maximum NOx removal efficiency was around 40 g(NOx)/kWh, but the efficiency decreased with the increase of NO removal rate. Therefore further improvement was necessary for the practical use of the non–thermal plasma technology.

Besides, in order to find an effective method of increasing the NOx removal efficiency (energy efficiency), we developed a numerical simulation program which calculates the plasma chemical reactions [7]. By using this program, we evaluated the NO removal efficiency by DBD. Since the DBD is composed of many filamentary micro–discharges, the chemical reactions by high energy electrons occur only in the micro discharge channels. These reactions produce various radicals such as O, N, OH etc. However, the radicals have to diffuse to the surrounding area before they react with pollutants. The simulation results showed that this diffusion process is a rate limiting factor of NO removal reactions. Therefore, we considered if a homogeneous DBD is available, the efficiency may increase. In 2008, we found that generation of a novel APTD (Atmospheric Pressure Townsend Discharge) was possible in ambient air, N₂ (99.95 %), O₂ (99.5 %) and He (99.95 %) by using a simple DBD device which uses alumina barriers [8]. This APTD was homogeneous between
barriers and the current waveform had no pulses. As far as we know, it has been a common sense among scientists that the APTD can only be generated in pure N\textsubscript{2} and was very difficult to generate in gases containing O\textsubscript{2}. Therefore, generation of the APTD in air using a simple DBD device was a new finding. In this study, firstly we investigated whether the APTD can be generated or not in the simulated diesel exhaust gas (O\textsubscript{2}: 10 %, NO: 200 ppm, N\textsubscript{2}: as balance). Next, we investigated whether the APTD can improve the NOx removal performance or not.

2. Oxidation of NO by O radical and O\textsubscript{3}

NO oxidation reactions are as follows.

\[
e + O_2 \rightarrow 2O + e^- \quad \text{(R1)}
\]
\[
O + O_2 + M \rightarrow O_3 + M \quad \text{(R2)}
\]
\[
NO + O + M \rightarrow NO_2 + M \quad \text{(R3)}
\]
\[
NO + O_3 \rightarrow NO_2 + O_2 \quad \text{(R4)}
\]
\[
NO_2 + O \rightarrow NO + O_2 \quad \text{(R5)}
\]

In the DBD reactor, O radicals which are generated by electrical discharge (R1) react with O\textsubscript{2} molecules and generate O\textsubscript{3} (R2). Since O and O\textsubscript{3} are a strong oxidizing agent, NO in simulated diesel exhaust gases is oxidized to NO\textsubscript{2} by reactions (R3) and (R4). Here, a reaction (R5) is a back reaction from NO\textsubscript{2} to NO, which becomes dominant at a higher discharge power level. This reaction worsens the NOx removal performance at high discharge power level.

3. Experimental system

3.1 Experimental setup

Fig. 1 shows an experimental setup of NOx removal experiments. In this system, a simulated diesel exhaust gas was used instead of a real diesel exhaust gas. The simulated diesel exhaust gas was prepared by mixing NO gas of 400 ppm diluted by N\textsubscript{2} and dry air. The flow rate of the NO diluted by N\textsubscript{2} gas and that of dry air were both 2.0 L/min. Concentrations of NO and O\textsubscript{2} were 200 ppm and 10 % respectively. The simulated diesel exhaust gas was supplied to a plane type DBD reactor with the flow rate of 4.0 L/min. This system consists of a H.V. power source, a measurement system of electrical characteristics, gas supply equipment, a DBD type reactor and a NOx analyzer. AC high voltage was applied to the reactor by a step-up transformer. Frequency of the applied voltage was changed from 50 Hz to 600 Hz, and the maximum applied voltage was 15 kVp. The applied voltage and the current were measured by an oscilloscope (Tektronix 2024B, 200MHz, 2.0GS/s) using a H.V. probe (Pulse Electronic Engineering, EP–50K, 1/2000) and a differential probe (Yokogawa Electric Corporation, 700924, 100MHz) respectively. An integral of the current (charge \(q\)) was measured from the voltage drop across an integral capacitor. Besides, the discharge power was calculated by multiplying the area of \(V–q\) lissajous figure by power frequency. NOx (= NO + NO\textsubscript{2}) concentration was measured by the NOx analyzer (Testo Testo350XL).

3.2 DBD reactors

Fig. 2 (a) and (b) show pictures of plane type DBD reactors. They can generate the FD and the APTD respectively. In case of soda–glass barrier, the aluminum foil electrodes were pasted on barrier plates. The electrode size was 80 mm × 80 mm × 0.1 mm and the barrier size was 100 mm × 100 mm × 2.8 mm. On the other hand, in case of alumina barrier (Kyocera A473), thin tungsten film electrodes were implanted into alumina barriers as shown in Fig. 2 (c). The effective electrode size was 80 mm × 80 mm × 0.1 mm and the barrier size was 100 mm × 100 mm × 1 mm. The gap spacing was fixed to 2 mm.
4. Results

4.1 Discharge mode

In this experiment, we investigated whether our APTD could be generated in the simulated diesel exhaust gas. Fig. 3 (a)–(e) show discharge appearances in a gap between barrier plates. The exposure time of digital camera was 2 seconds when photographs were taken without image intensifier (case (b)) and 5ms with image intensifier (case (c), (d) and (e)). The photograph (c) and (d) show the instance of positive and negative polarity respectively. In Fig. 3 (c) and (d), filamentary discharges were not recognized. The luminescence gradually increased from cathode to anode and a strong luminescence appeared on the barrier surface of anode side. Fig 4 shows the applied voltage, the gap voltage, the barrier voltage and the current of the discharge. In Fig. 4 (a), it is seen that the current flows continuously and has only one peak in a half cycle. These features completely coincide with the features of the APTD we reported [9]. Therefore we concluded that our APTD can be generated even in the simulated diesel exhaust gas. Finally, in case of the DBD using soda–glass, the discharge was the FD mode as seen in Fig. 3 (e). The current has many pulses as shown in Fig. 4 (b) and is different from that of APTD mode.

4.2 NOx removal experiments

Fig. 5 shows NO concentration measured at the outlet of DBD reactors. In case of FD mode, it is seen that the NO concentration decreased with the increase of specific input energy and it attained to 14 ppm at 153 J/L. The NO 2 concentration increased with the increase of specific input energy and it attained to 221 ppm at 153 J/L. On the other hand in case of APTD mode, the NO concentration decreased with the increase of specific input energy as well, and it attained to 40 ppm at 140 J/L. The NO 2 concentration increased with the increase of specific input energy and it attained to 170 ppm at 140 J/L. The above data showed that the NO removal performance is higher by the FD mode than by the APTD mode at the same specific input energy.

Fig. 6 shows a NO removal rate. The NO removal rate means the ratio of removed NO to initial NO. As for FD mode, the NO removal rate increases with the increase of specific input energy. However, the saturation appeared above the specific input energy of around 90 J/L. Therefore the maximum NO removal rate of 94 % was obtained at 90 J/L. As for APTD mode, the NO removal rate increases with the increase of the specific input energy and it attained to the

Figure 3. Discharge photographs of APTD and FD.

Figure 4. Electrical characteristics of APTD and FD in simulated diesel exhaust gas.

Figure 5. NO and NO 2 concentration.

Figure 6. NO removal rate.
The maximum value of 81% at the specific input energy of 140 J/L. Therefore, the NO removal rate by APTD mode was lower than that by FD mode.

Fig. 7 shows the relation between energy efficiency and NO removal rate. Here the energy efficiency (g(NO)/kWh) was calculated by dividing the mass flow rate of removed NO (g/h) by the discharge power (kW). As for FD mode, the maximum energy efficiency was 25 g(NO)/kWh at the NO removal rate of 40%, however it decreased with the increase of NO removal rate and it attained to the value of 10 g(NO)/kWh at 94%. As for APTD mode, the energy efficiency increased with the increase of NO removal rate and it attained to the maximum value of 16 g(NO)/kWh at 15%. However it decreased with the further increase of NO removal rate. In summary, it is apparent that the energy efficiency by APTD mode was lower than that by the FD mode.

5. Discussions

Here, we discuss why the NO removal performance by APTD mode was lower than that of FD mode. The reason seems to be as follows. Reactions of (R3) and (R4) show the oxidation of NO to NO2 and NOx removal performance is governed by the generation process of O radicals and O3. The FD mode consists of many filamentary micro-discharges (streamer discharges). It is reported that the reduced electrical field $E/n$ at the streamer head is 500–800 Td (1 Td = 10⁻¹⁷ Vcm²) and electron energy of FD is 1–10 eV [10, 11]. Here average electron energy of about 6–9 eV would be ideal for the dissociation of O₂ molecule by electron impact (R1) [11]. Therefore, the FD mode can dissociate O₂ molecule into O radicals effectively and showed higher NO removal performance. However, because the APTD is not a streamer discharge, the reduced electrical field during discharge is around 157 Td. This value was calculated by dividing the sustaining electrical field of 37.9 kV/cm (= 7570 V / 0.2 cm) with the number density of simulated diesel exhaust gas of $2.42 \times 10^{19}$ cm⁻³ at 0.1 MPa and 300 K. It is lower than that in FD mode. Therefore, in case of APTD mode, the electrons cannot get sufficient energy to dissociate O₂ efficiently which leads to lower NO removal performance.

6. Conclusions

We set up two DBD reactors which can generate different discharge modes and investigated the NOx removal performance from a simulated diesel exhaust gases. The experimental results obtained are as follows;

1. Our APTD can be generated in the simulated diesel exhaust gas, the composition of which is O₂ of 10%, NO of 200 ppm and N₂ as a balance.
2. NO concentration decreased with the increase of specific input energy by both FD and APTD modes. However, the NO removal performance was better by FD mode than by APTD mode at the same specific input energy.
3. Efficiencies were 25 g(NO)/kWh by FD mode and 16 g(NO)/kWh by APTD mode respectively. The maximum efficiencies appeared at NO removal rate of 40% in case of FD mode and at 15% in case of APTD mode respectively. As a conclusion, the filamentary type DBD is better than the Townsend type DBD to remove NOx.

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References