

COMPARATIVE STUDIES ON SOOT OXIDATION BY NITROGEN DIOXIDE AND OZONE

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ABSTRACT – Non-thermal plasma technology has many applications in various areas. One of the applications is regenerating diesel particulate filter (DPF). DPF is a widely applied device to control the particulate emission of diesel engines. But it needs periodic removal of clogged soot for the smooth running of engine. Conventional high-temperature removal processes easily leads to the breakage of DPF. Herein, low-temperature plasma formed in a dielectric-barrier discharge (DBD) reactor was used to form active oxidants such as ozone and nitrogen dioxide. Experimentally, the effects of discharge power and frequency on the performance of DBD reactor were studied. Two oxidants, O₃ and NO₂, were synthesized and used for incinerating soot in the used DPF. Performances of the two oxidants on the reduction of soot were compared, and it was found that NO₂ is more effective than O₃ for getting rid of soot.

TECHNICAL PAPER –Diesel engines have some advantages such as fuel economy, higher reliability, compactness and longer life, and are popularly used in industry. However, the diesel engine emission poses a serious threat to environment by releasing oxides of nitrogen (NO_x, x = 1 or 2) and particulate matter (PM). The US Environmental Protection Agency (EPA) and European Union have imposed strict standards for these pollutant emissions. Many researchers are studying new technologies to minimize diesel engine emission.

Diesel particulate filters (DPFs) are widely used to control PM emission. It has shown more than 90 % filtration efficiency for PM (1, 2). But the used DPFs need to be regenerated periodically in order to get rid of the soot deposition. Without regeneration, DPFs will be inefficient and the backpressure of engines will increase due to the soot clogging. Ozone and NO₂ have stronger oxidative character and can be utilized in the DPFs regeneration at lower temperature. Dielectric-barrier discharge (DBD) is a kind of non-thermal plasma obtained when one or both of the electrodes are covered with a dielectric layer. DBD has been used in many areas such as pollution control (3), ozone generation (4), and surface treatment (5). Generally, DBD reactors are classified into three types: volume DBD, surface DBD, and coplanar DBD. The cylindrical packed bed reactor used in this study belongs to the volume DBD reactor. Some researches has proved that NO₂ and O₃ are very effective oxidants for the incineration of soot within DPF (6-8). In the present study, O₂ and NO were first discharged in the DBD reactor and changed into oxidants O₃ and NO₂, respectively. Then the DPF was regenerated using the O₃ or NO₂ at low temperature and atmospheric pressure.

EXPERIMENTAL

As shown in Fig.1, the experimental setup consists of the DBD plasma reactor, used DPF with a heater, AC pulse voltage power supply, and gas analyzers.

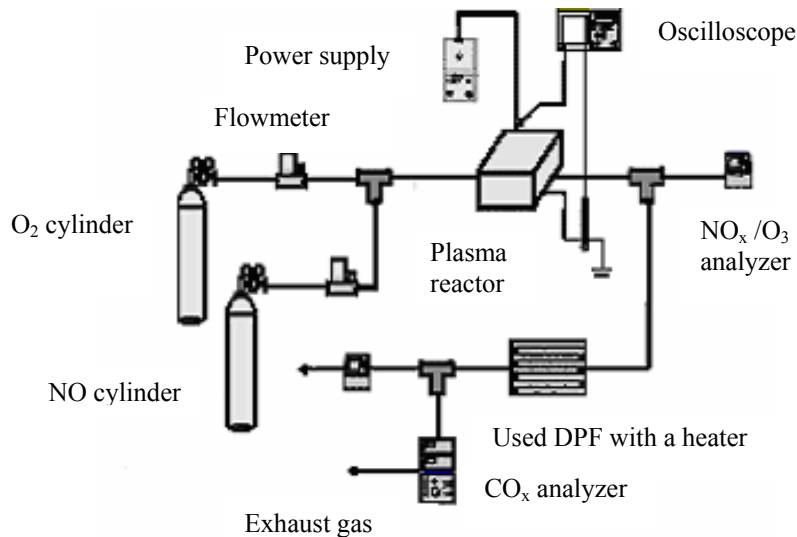


Fig.1 Schematic diagram of the experimental setup

The cylindrical DBD reactor, as shown in Fig.2, is constructed using a glass tube with inner diameter of 17.5 mm, outer diameter of 23 mm, and length of 360 mm. The glass tube has two ports of diameter each of 10 mm. A stainless steel rod of diameter 2 mm and length of 448 mm passing co-axially inside the glass tube acts as the central electrode. Aluminum foil wrapped over the glass tube for the length 250 mm acts as an outer electrode. The inner volume between central and outer electrode is filled by glass beads of diameter 3 mm and of dielectric constant 10 for the length of 223 mm.

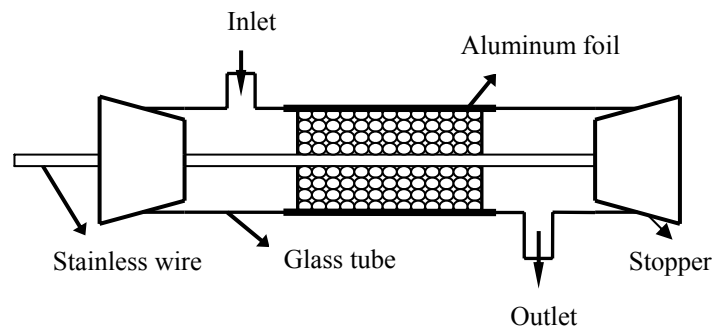


Fig.2 Cylindrical packed bed DBD reactor

When the glass beads are exposed to external electric field, a spontaneous polarization occurs in the direction of the electric field, resulting in a high electric field at the contact points of the beads. These beads also lead to uniform distribution of gas flow and discharges in the reactor (9).

One of the characteristics of this DBD reactor is that a lower applied voltage can be used for the formation of plasma over a large separating distance of electrodes.

A high-voltage AC pulse power supply (NW-HSPS3002, Pulse Generator) was used in forming plasma and producing O₃ or NO₂. The applied voltage and current were measured by using an oscilloscope (Tektronix TDS 744A) connected with a 1000:1 voltage probe (Tektronix, P6015A) and a current probe (Tektronix, A6303) with an amplifier (Tektronix, AM503).

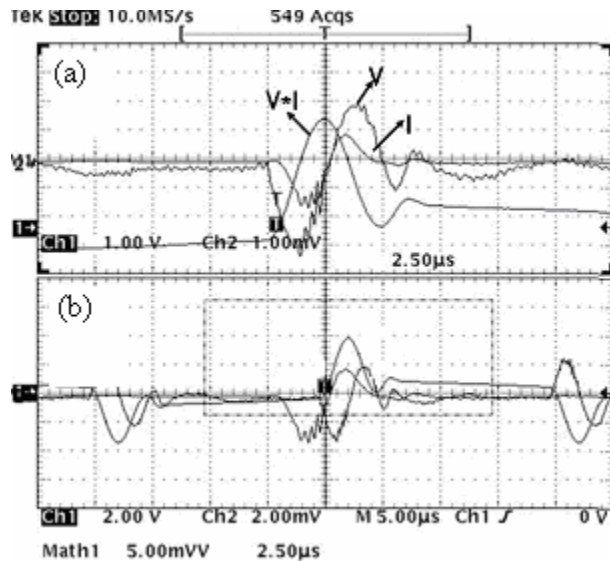


Fig.3 (a) Magnification of a single pulse and (b) Voltage, current and power waveforms of the DBD.

The discharge power per pulse was obtained by integrating the discharge voltage and current waveforms, i.e.,

$$E_p = \int_0^t V \times I \times dt$$

where E_p is the energy delivered per pulse, V is the pulse voltage, I is the current, and t is the time for one cycle.

The average discharge power was calculated by multiplying the discharge energy per pulse by the pulse repetition rate. Fig.3 shows the voltage, current, and power waveforms of the DBD.

An ozone gas analyzer (Eco-sensor, UV-100) was used to measure the concentration of O₃, and the concentration of NO_x was measured by using a nitrogen oxides analyzer (Teledyne, Model 9110AH). An emission gas monitor (Teledyne, PEM 9002) was used for measuring the concentration of CO and CO₂ at the exit of DPF.

RESULTS AND DISCUSSION

Performance of the plasma reactor To optimize the generation conditions of O_3 and NO_2 by using DBD, effects of the discharge power and frequency were studied. As shown in Fig. 4, the breakdown discharge power was different at different frequencies and it was lower for lower frequency. Thus, higher conversion efficiency may be obtained at lower frequencies. In Fig. 4a, at 25 kHz, the concentration of O_3 was almost near to zero until the discharge power increased to a critical value of about 11.5 W, and after this, O_3 concentration increased in proportional to the discharge power.

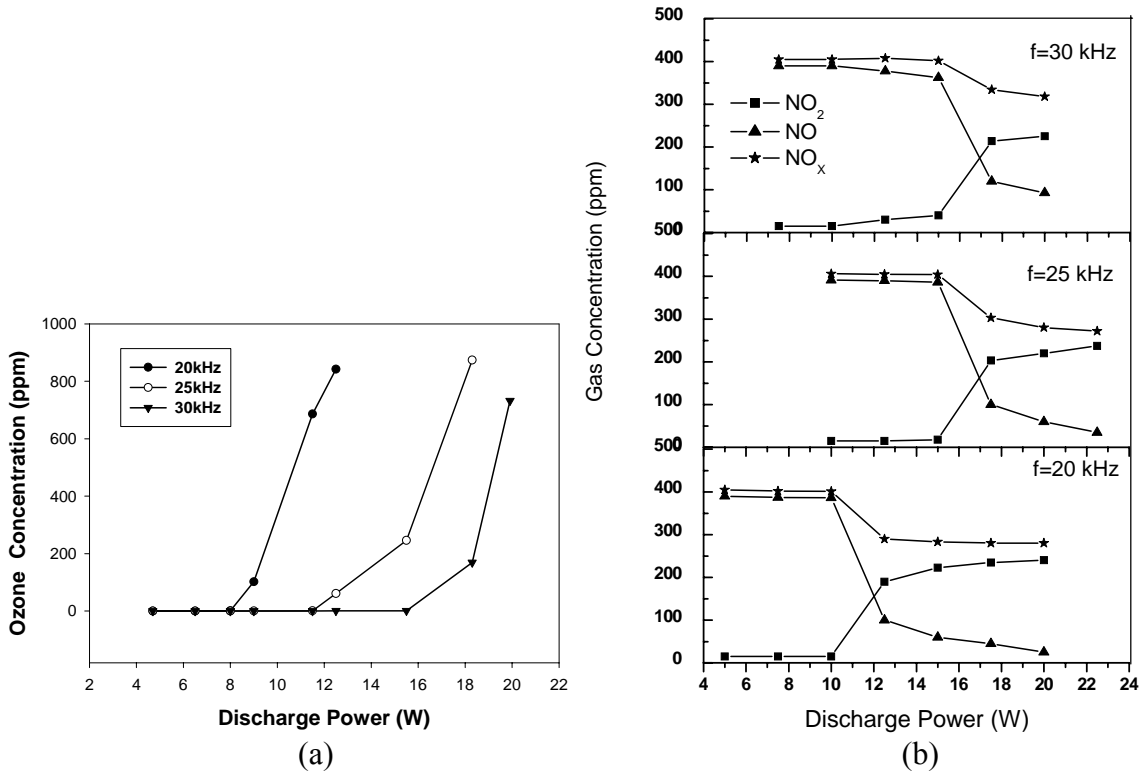


Fig. 4 Gas concentration varying with different discharge power and frequency. Flow rate of the reactants: a) $O_2 = 3.5$ L/min and b) $NO = 3.5$ L/min and $O_2 = 1$ L/min.

Similarly, at frequency 25 kHz, the concentration of NO_2 is around 10 ppm until a critical value of 14.5 W was reached and then it suddenly increased to 200 ppm with following a stable value of 225 ppm Fig. 4b. Suddenly, the concentration of NO dropped at 14.5W and reached to a value of 25 ppm. The concentration of NO_x was varied with respect to the concentration of NO_2 and NO that seems to be equal to sum of these two gases.

Regeneration of DPF Soot was deposited in several rectangular DPFs (34×50, IBIDEN CO., LTD) using an automobile diesel engine at normal load, and these DPFs were regenerated by O_3 and NO_2 , respectively.

To avoid the weight loss of DPF resulting from the volatile matter contained in the diesel soot, before every regeneration process, DPF was treated by hot pure oxygen at temperature 140 °C for 15 min without plasma reactor turning on. It was found that the weight loss of DPF was

neglectable. Regeneration was carried out for 2.5 h, and at every 15 min interval the concentration of gases was measured at the exit of DPF.

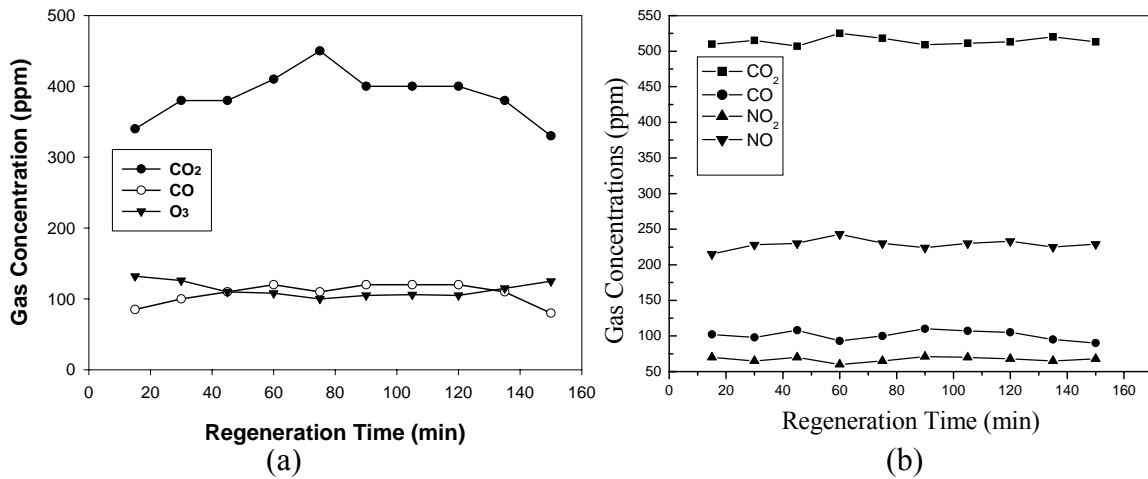
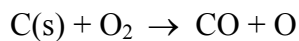
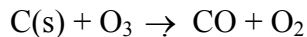
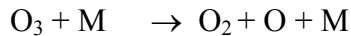
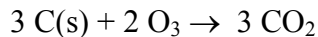
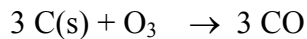


Fig.5 Relation between the gas concentrations and regeneration time using a) O₃ (O₂ = 3.5 L/min, f = 25 kHz and P = 18.3 W) and b) NO₂ (NO = 3.5 L/min, O₂ = 1 L /min, f = 25 kHz and P = 17.5 W).

In the regeneration process using O₃, it was suggested that soot was mainly oxidized by oxygen atom come from the unstable O₃ (10). There were different possible reactions occurring in the DPF:

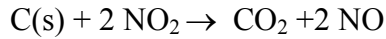


The overall reactions are

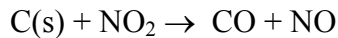


As shown in the Fig.5a, as the O₂ gas containing 835 ppm ozone produced at discharge power of 18.3 W was induced into the DPF, the concentration of CO and CO₂ quickly increased due to the oxidation of soot. Concentration of CO₂ increased to the maximum of 450 ppm and then gradually decreased to 320 ppm. Concentrations of CO and O₃ varied in the ranges of 85 – 110 ppm and 80 – 120 ppm, respectively. After regenerating for 2.5 h, the weight of DPF was measured and its weight loss was 2.1 g.

In regeneration process using NO₂, the gas mixture containing 203 ppm NO₂ was used to oxidate soot in the DPF. As shown in Fig.5b, about 70 % NO₂ was reduced to NO. We suggested that the soot mainly was oxidized by NO₂ according to the following reactions,



There is CO produced, and we suggested that there existed the reaction as follows:



It is found that 2.6 g of soot was removed from the DPF after 2.5 h of regeneration.

Performance comparison of O₃ and NO₂ Specific energy density in the plasma is an important parameter (11). Experimentally, NO₂ oxidized more soot than O₃. The specific energy density (SED) was defined as

$$SED = 60 P/Q \text{ (J/L)} \quad (8)$$

where P is the discharge power (W) and Q is the gas flow rate (L/min).

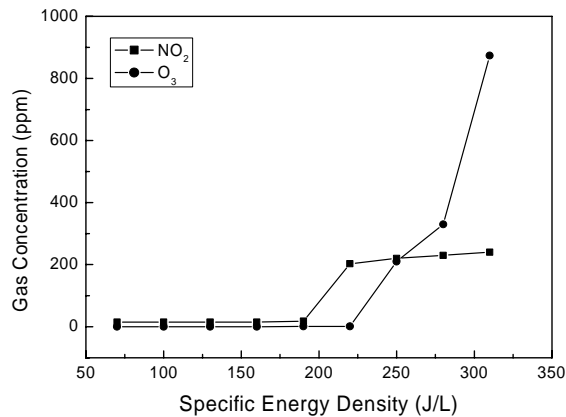


Fig.6 the gas concentration varied with the specific energy density (f=25 kHz).

As shown in Fig. 6 the specific energy density used for producing 203 ppm NO₂ was less than that used for producing 835 ppm of O₃. Therefore, NO₂ was a better candidate for effective removing the soot from DPF than O₃.

CONCLUSION

Non-thermal plasma was used to produce oxidative gases O₃ and NO₂, which were used to get rid of soot deposited in DPF.

Some conclusions can be got from this investigation:

1. O₃ and NO₂ were used in regenerating DPF, respectively. It was found that nitrogen dioxide is more effective than ozone for oxidizing soot.

2. The conversion of the gases in the DBD reactor increased with increasing discharge power and decreasing frequency.

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