CORONA TREATMENT FOR NOX REDUCTION
FROM
STATIONARY DIESEL ENGINE EXHAUST
IMPACT OF NATURE OF ENERGIZATION AND EXHAUST COMPOSITION

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ABSTRACT

A detailed study on the removal of oxides of nitrogen (NO_x) from the exhaust of a stationary diesel engine was carried out using non-thermal plasma (dielectric barrier discharge) process. The objective of the study was to explore the effect of different voltage energizations and exhaust composition on the NO_x removal process. Three types of voltage energizations, namely AC, DC and Pulse were examined. Due to the ease of generation of high voltage AC/DC electrical discharges from automobile/Vehicular battery supply for possible retrofitting in exhaust cleaning circuit, it was found relevant to investigate individual energisation cases in detail for NOx removal. AC and Pulse energisations exhibit a superior NOx removal efficiency compared to DC energisation. However, Pulse energisation is found to be more energy efficient. Experiments were further carried out with filtered/unfiltered (raw) exhaust under pulse energisations. The results were discussed with regard to NOx removal, energy consumption and formation of by-products.

Key words: Non–thermal plasma, Pulse, AC and DC electrical discharge plasma, Filtered/Unfiltered Diesel engine exhaust, NOx removal, by-products.

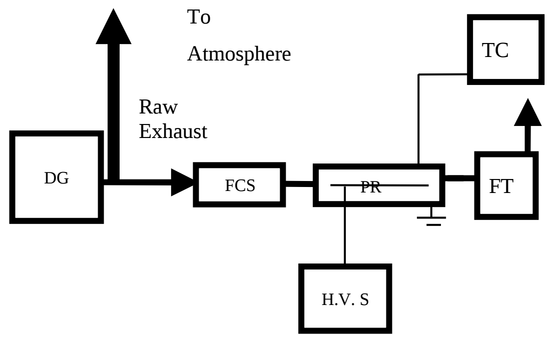
1 INTRODUCTION

REMOVAL of NOx from diesel exhaust has been a challenge to researchers, as many conventional techniques such as catalysis, exhaust gas recirculation and other engine design modifications have failed to bring down the level of NOx to mandatory limits put across various countries. In this context, electrical discharge plasma technique appears to be very promising [1]. However, the success of electric discharge plasma for the pollution control will depend on how well it competes with existing technology based on economic considerations and technical viability. The factors which must be looked in to in this aspect are the input power consumption, bi-product formation, pollutant removal efficiency and suitability of the electric dischargre technique for the actual exhaust conditions.

Many discharge based studies have been done using simulated pure gas mixtures and most of them were carried out at room temperatures. Though it is simpler to understand the detailed mechanisms and reaction pathways with simulated gas mixture treatment, it is very important to study the actual exhaust treatment using plasma reactor as the diesel exhaust consists of various components, which cannot simply be simulated using pure gases. Literature shows that the presence of hydrocarbons and carbonaceous soot in diesel engine raw exhaust enhances the NOx removal efficiency, when the raw exhaust is treated with discharge plasma [2]. However, by-products and acidic compounds formation and power consumption have not been addressed. In this paper, the NOx removal studies were carried out for two cases. In the first case filtered exhaust was treated by different types of voltages like DC [3], AC [4] and repetitive pulses [5-7]. The performance of the discharge reactor was evaluated based on NO oxidation and NO_x removal efficiencies. A higher level of NOx removal performance has been discussed with repetitive pulses. In the second case, filtered/unfiltered diesel engine exhaust was treated with pulsed plasma and the superior performance of plasma treating unfiltered exhaust has been discussed. Further, the experiments were conducted on actual diesel engine exhaust at no load condition at room temperature as well as at higher temperatures

2 EXPERIMENTAL SETUP

The schematic of the diesel engine filtered/unfiltered exhaust treatment setup is shown in Figures 1a and 1b respectively.



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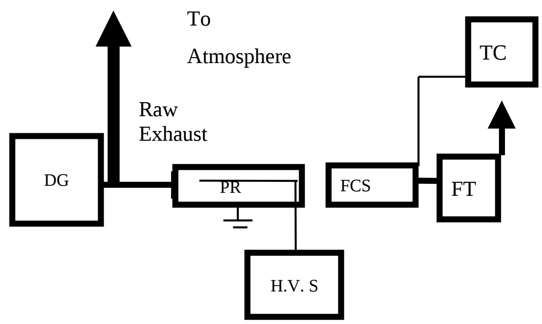

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Figure 1. Experimental setup for diesel engine exhaust treatment using plasma recator system (a) Filtered Exhaust Treatment (b) Unfiltered Exhaust (Raw Exhaust) Tretament. (DG: Diesel generator, FCS: Filtering and Conditioning System; PR: Plasma Reactor; FT: Fourier transform Infrared Spectroscope gas analyzer, TC: Temerature controller, HVS: High voltage source)

High Voltage Source: The high voltage source consist of single phase high voltage transformer rated 230V/ (0-25kV), rectifier, charging capacitor, a Rotary Spark Gap (RSG) and the plasma reactor as a load. The hemispherical rotating electrode of the RSG was connected to a motor through an insulating rod. By changing the speed of the motor the frequency of the pulses applied to the plasma reactor was controlled. While conducting studies with AC and DC, the voltage was taken before and after the rectifier respectively after carefully by-passing RSG. The measurement of voltage was carried out using a 150 MHz digital storage oscilloscope (DL 1540, 200 MS/s YOKOGAWA) connected through a 2000:1 voltage divider (EP-50K, PEEC, JAPAN). The divider has a rating of DC 50 kV, AC 50 kV P-P and pulse 70 kV peak. It has an input resistance of 500 MΩ± 1 % and input capacitance of 10 pF. The input impedance of the divider is 1 MΩ (below 2%). The rise time of the pulse was 24 ns and the frequency of the pulses was 87/130 pps (pulses per second).

Exhaust Source: A 4.4 kW diesel engine was used as the exhaust source. The whole of the exhaust from the engine was not treated in view of infrastructure limitation in the laboratory. Further, as our objective is to examine the underlying principle involved in the exhaust treatment, only a part of the main exhaust from the engine was treated and the exhaust flow rate was controlled and maintained at 2/4 liters per minute.

Plasma Reactor: A dielectric barrier electric discharge reactor (referred to as plasma reactor) was employed in the present studies. The plasma reactor was a cylindrical glass tube (inner diameter: 15 mm and outer diameter: 17 mm) consisting of a stainless steel rod of thickness 1 mm as the inner electrode and aluminium foil wrapped over the glass tube as the outer electrode. The effective length of the reactor where discharge took place was 300 mm. The experiments involving plasma reactor were carried out at temperatures 24 ^{0}C, 100 ^{0}C and 150 ^{0}C.

Filtering system: The by-pass exhaust gas was made to pass through a tube containing steel wool, in order to filter out oil mist and macro-sized particulate matter. The exhaust was then passed through filtering and conditioning system (FCS). The FCS consists of three filters and a moisture separator. The function of the FCS is to filter out the carbonaceous soot, any coarse particles, oil mists and water from the exhaust gas. Proper care has been taken in the development of this conditioning system so as not to affect the sample gas components.

Measuring System: The measurement of NOx, and other gaseous pollutants present in the diesel engine exhaust gas was carried out accurately using a multicomponent FT-IR gas analyzer (DX-4010, Temet Instruments, Finland). The FT-IR uses the CALCMET software to compute the concentrations of the components present in the sample gas from the absorbance spectrum.

3 RESULTS AND DISCUSSIONS

Initially, before taking any measurement with FT-IR, zero calibration of FT-IR was done by passing N_2 gas. Before treating the exhaust gas, the concentrations of CO, total hydrocarbon (THC), NO_x, N_2O and aldehyde were measured. Table. 1 shows the typical concentrations of the pollutants in filtered exhaust under 0% load conditions.

Table 1. Initial concentrations of pollutants in the diesel engine exhaust

Main Pollutants	0 % Load
H_2O	1.0%Vol
CO_2	1.8% Vol
CO	560 ppm
NO	180 ppm
NO_2	40 ppm
THC	70 ppm
Aldehydes	50 ppm

The concentrations of NO and NO_2 were measured individually and then added to get the NO_x concentration. The total hydrocarbons (THC) are the sum of various HC's present in the exhaust, which could be measured using FT-IR analyzer. THC in the present study include methane (CH_4), ethylene (C_2H_4), acetylene (C_2H_2), butane (C_4H_{10}), propene (C_3H_6), benzene (C_6H_6), and toluene (C_7H_8). Aldehydes included formaldehyde and acetaldehyde.

In the present paper, all the results were presented in terms of specific energy density. The specific energy density was calculated as the ratio of average discharge power to the gas flow rate.

3.1 Diesel Engine Exhaust Treatment by Discharge Plasma reactor (PR)

In this section, two types of investigations were made. The first investigation was on the effect of type of energisation and the second investigation was on the effect of exhaust composition. In the first case filtered diesel engine exhaust was treated by plasma reactor (filled with dielectric pellets) energized by different types of voltages like DC, AC and repetitive pulses and in the second case filtered/unfiltered diesel engine exhaust was treated by pulsed plasma reactor.

3.1.1 Effect of type of energisation:

The electric field in the plasma reactor results in energetic electrons. These electrons collide with other background gas molecules, resulting in production of more excited species and ions. However, most of them get quickly converted to radicals as given by following reactions:

$$O_2^* + M \rightarrow O_2 + M \quad (1)$$
$$O_2^+ + e \rightarrow O + O(^1D) \quad (2)$$
$$O^+ + e^- \rightarrow O \quad (3)$$
$$N_2^* \rightarrow 2N \quad (4)$$
$$N_2^+ + e^- \rightarrow 2N \quad (5)$$
$$N^+ + e^- \rightarrow N \quad (6)$$

The following reaction mechanisms are expected to occur under the influence of discharge plasma leading to NO/NO_x removal.

NO-NO_2 conversion reactions involving O/ O_3/NO_3 radicals

$$O_2 + e \rightarrow O + O + e \quad (7)$$
$$NO + O \rightarrow NO_2 \quad (8)$$
$$O_2 + O \rightarrow O_3 \quad (9)$$
$$NO + O_3 \rightarrow NO_2 + O_2 \quad (10)$$
$$NO + NO_3 \rightarrow NO_2 + NO_2 \quad (11)$$

NO reduction reactions

$$N_2 + e \rightarrow N + N + e \quad (12)$$
$$NO + N \rightarrow N_2 + O \quad (13)$$

NO_2 conversion reaction

$$NO_2 + O \rightarrow NO + O_2 \quad (14)$$
$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad (15)$$
$$NO_2 + NO_3 \rightarrow N_2O_5 \quad (16)$$
$$NO_2 + N \rightarrow N_2O + O \quad (17)$$

Fig. 2 compares NO_x removal efficiency for different energisation. Only the maximum value of removal efficiency is considered. It is clear from the bar graph that the pulse energization exhibits maximum efficiency when compared to AC and DC energizations.

When oxygen rich filtered exhaust is treated by the pulse powered plasma reactor, a large number of O radicals are formed due to the production of high energetic electrons. These O radicals enable efficient oxidation of NO to NO_2. Further, owing to very high electric field, production of N radicals is more probable, which results in NO reduction. This contributes to a high NOx removal efficiency in case of pulse energisation.

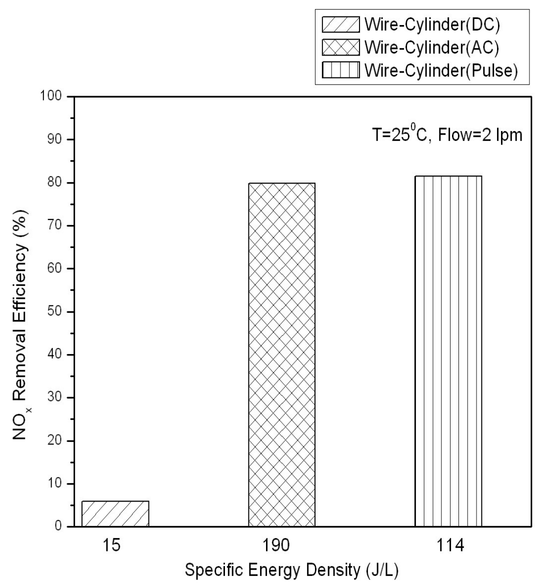

Fig. 2 Relative representation of NO_x removal efficiency under different energisation at no load

When filtered exhaust is treated by the AC powered plasma reactor, as the average electric field is not as high as that observed in the pulse energized reactor, the production of N radicals is less probable. This contributes to a lower NOx removal in case of AC energisation.

When filtered exhaust is treated by the DC powered plasma reactor the average energy gained by the electrons under DC is insufficient to generate any radicals, be it O or N, and hence, the probability of oxidation or reduction reactions taking place is minimal.This results in poor NOx removal in case of DC energisation.

3.1.2 Effect of Exhaust composition:

In this part of experiment, filtered and unfiltered (raw) diesel engine exhausts are treated separately by pulse powered discharge plasma reactor at different temperatures.

The fig. 3 compares the NO_x removal in case of filtered and unfiltered (raw) exhaust treatment at a plasma temperature of 150℃.

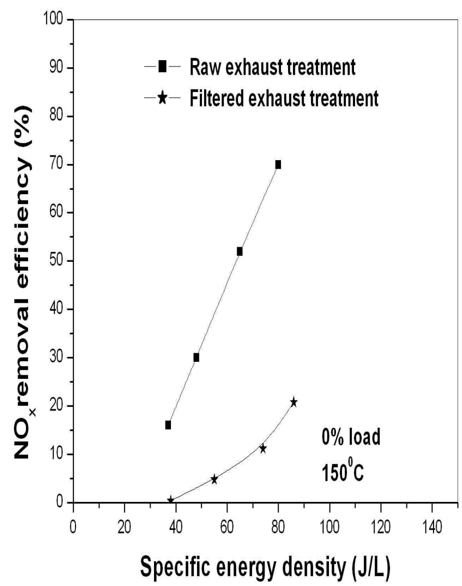

Fig 3 NOx removal by pulse powered plasma reactor treating filtered and raw diesel exhaust

At a given temperature and energy density, the NO_x removal with unfiltered (raw) exhaust treatment is higher than that with filtered exhaust treatment. This is explained as below:

The other possible reaction pathways responsible for NOx removal in addition to the reactions # 1-17 are [8, 9]:

CH3O + NO →CH3ONO --- (18)
CH3O + NO2→CH3ONO2---- (19)
CH2CHO + NO →CH2CHONO (20)
NO_2 + OH →HNO_3 ------- (21)

In the unfiltered (raw) exhaust treatment, as NO is mainly converted to N_2 and the NO_2 remains almost constant, the NO_x removal will be more effective [8]. However, in the filtered exhaust treatment, as oxidation reactions are more predominant in the plasma, the NO is mainly converted to NO_2 and further, NO_x removal is favoured mainly by methoxy radical induced reactions # 19 – 20 and acid forming reaction # 21 [8]. However, as actual diesel exhaust contains lower concentrations of hydrocarbons and water, the above reactions contribute less to the NO_x removal.

Further, the difference in the NO_x removal efficiency becomes large at higher temperature due to pronounced temperature effect on NO_x removal in filtered exhaust plasma treatment. This is because the effectiveness of the reactions # 3 – 6 depends on concentrations of NO, NO_2 and CH_3O. The formation of NO_2 gets affected at elevated exhaust temperature which results in decreased NO_x removal at elevated exhaust temperature [9]

However, in case of unfiltered (raw) exhaust plasma treatment, the NO_x removal takes place mainly through reduction of NO to N_2 because of depleted O, OH environment [10]. As this reaction is not much affected by exhaust temperature, the NO_x removal is not affected largely at an elevated temperature

The fig.4 compares aldehydes concentration in filtered and unfiltered (raw) exhaust plasma treatments at room temperature and at 0% load.

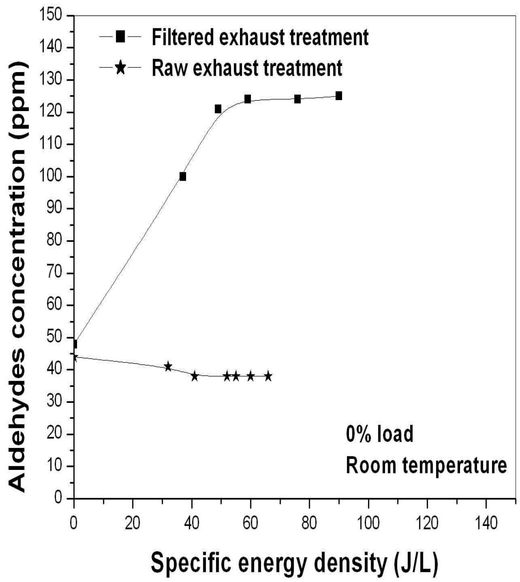

Fig 4. Aldehydes concentration in filtered and raw diesel exhaust plasma treatment

The concentration of aldehydes increases with increase in specific energy density in case of filtered exhaust treatment, while there is hardly any increase in the aldehydes concentration in case of raw exhaust treatment, This is explained as below,

The radicals (O, OH and O_3) produced in plasma discharges react with hydrocarbons to liberate alkyl(R), alkoxy (RO), and acyl (RCO) radicals. The alkoxy radical such as CH_3O reacts with oxygen to liberate aldehydes such as HCHO. In the filtered exhaust plasma treatment, the O/OH radicals are effectively used in the liberation of aldehydes, thus increasing the concentration of aldehydes with increase in specific energy density. However, in raw exhaust treatment, as these radicals are effectively used for soot oxidation, liberation of aldehydes gets affected, thus the aldehydes concentration remains almost constant.

The table. 2 gives the measured pH values in case of filtered and unfiltered (raw) exhaust plasma treatment at room temperature under 0% load. The untreated/treated diesel exhaust was passed through a beaker containing doubly distilled water for a known duration of time, whose pH was measured. This pH value represents acidity of various acidic compounds including HNO_3. It is observed that pH value decreases (acidic nature of the exhaust increases) with the increase in pulse voltage for filtered exhaust plasma treatment, while it remains almost constant for unfiltered exhaust plasma treatment. This is explained as below:

Table 2 pH values in filtered /raw exhaust plasma treatment

Pulse voltage (kV)	pH value in filtered exhaust	pH value in Unfiltered exhaust
0	4.6	4.6
20.5	4.17	4.4
21.2	3.88	4.4
23.2	3.6	4.3
24.0	3.42	4.3

The formation of HNO_3 depends on concentration of NO_2 and OH radicals (reaction #21). In filtered exhaust plasma treatment, with increase in pulse voltage, as the concentrations of both NO_2 and OH increase, resulting in increased formation of HNO_3 and thus, decreased pH value. However, in unfiltered exhaust plasma treatment, with increase in pulse voltage, the NO_2 concentration hardly increases. As a result very little acid formation takes place and thus the pH value remains almost constant.

Further, it is noted that for a given pulse voltage, the energy consumption was less with unfiltered (raw) exhaust plasma treatment. The improved energy consumption and NO_x removal efficiency in raw exhaust plasma treatment, results in decreased energy per NO_x molecule removal.

4 CONCLUSIONS

In this study, two types of investigations were made. The first investigation was on the effect of type of energisation and the second investigation was on the effect of exhaust composition on the performance of plasma reactor. The major inferences drawn from this work are summarized as below:

The pulse energisation is more effective in terms of higher NOx removal and energy utility compared to DC/AC energisation.

Presence of carbonaceous soot in the diesel engine unfiltered (raw) exhaust enhances NOx removal capability of a plasma process, particularly at higher temperature. It directly reacts with NO_2 and decreases the NOx concentration. In addition, as the O/OH radicals are effectively used for soot oxidation, liberation of aldehydes gets affected, thus the aldehydes concentration remains almost constant. Further, the improved NO_x removal efficiency and energy consumption in unfiltered exhaust plasma treatment, results in decreased energy per NO_x molecule removal.

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REFERENCES

[1] R. Hackam and H. Akiyama, "Air pollution control by electrical discharges," IEEE Trans. Dielectrics and Elec. Insul, vol 7, no 5, pp. 654-683, Oct 2000.

[2] J. O. Chae, "Non thermal plasma for diesel exhaust treatment," J electrostat,, vol. 57, no 3, pp.251-262, Mar 2003.

[3] Yamamoto T, Rajanikanth B. S., Okubo M., Kuroki T and Nishino M, 2003, IEEE Trans. IA, 39(6): pp1608-1613.

[4]. Masuda S, 1998, Pure and Applied Chemistry, 60: pp727-731.

[5].Chang J S, Lawless P A and Yamamoto T, 1999, IEEE Trans. on Plasma Science, 19: pp1152-1166.

[6]. Elliason B and Kogelschatz U, 1991, IEEE Trans. on Plasma Science, 19: pp1063-1077.

[7]. Vogtlin G E and Penetrante B M, 1993, Non-Thermal Technologies for Pollution Control, part A&B, NATO series, Springer-Verlag.

[8] B.S.Rajanikanth, Das S, Srinivasan AD, Unfiltered diesel engine exhaust treatment by discharge plasma: Effect of soot oxidation, plasma science & technology vol 6, no 5, pp 2475-2480, Oct 2004

[9] B.S.Rajanikanth, A. D. Srinivasan and V. Ravi, "Discharge Plasma treatment for NO_x reduction from diesel engine exhaust: A laboratory investigation," IEEE Trans. Dielectrics and Elec. Insul., vol.12, no.1, pp. 72-80, Feb 2005.

[10] Kanichi Fujii, M.Higashi and N.Suzuki, Simultaneous removal of NO_x, CO_x, SO_x and Soot in diesel engine exhaust, Non-Thermal Plasma Techniques for Pollution Control, NATO Series, Part-A, Ed: Penetrante and Schultheis, pp.257-279, 1992.