Augmenting NO\textsubscript{x} reduction in diesel exhaust by combined plasma/ozone injection technique: a laboratory investigation

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Abstract: With the advent of non-thermal plasma technique for diesel exhaust treatment attention is being focused on reducing oxides of nitrogen (NO\textsubscript{x}) both from stationary as well as automobile sources. In this work, an attempt has been made to enhance NO\textsubscript{x} reduction only by utilising a plasma/ozone injection approach without resorting to additional treatments based on catalysts/adsorbents. It was observed that cascading ozone injection with discharge plasma enhances the reduction of NO\textsubscript{x} as high as 95\% for the specific energy of 123 J/l. In the long run, this plasma-only based approach may be beneficial or a possible alternative for catalyst/adsorbent based NO\textsubscript{x} treatments. The results have been discussed and a comparative analysis has been made with respect to individual plasma and ozone injection treatment.

1 Introduction

With the growing concern about controlling the oxides of nitrogen from emission sources, there is a simultaneous spur in the development of new NO\textsubscript{x} controlling techniques, in the past three decades; to overcome the drawbacks associated with the existing catalyst/adsorbent based NO\textsubscript{x} treatments. Amongst the emission sources, much attention is being paid to the diesel exhaust as it contributes almost 50\% of the total NO\textsubscript{x}. The existing NO\textsubscript{x} control techniques incorporated in the stationary/mobile diesel sector mainly revolve around commercially available catalysts/adsorbents and suffer from several issues like short life, reduced DeNO\textsubscript{x} efficiency, high cost, usage of additional energy for regeneration and limited scope of application. This has resulted in looking for alternate techniques for NO\textsubscript{x} abatement which are economical and feasible. The success of electrical discharges for removal of dust in electrostatic precipitators paved the way for initiating the electrical discharge-based approach for controlling the gaseous pollutants.

In the past few years, the electrical discharge approach or the non-thermal plasma approach has been extensively used for controlling various gaseous pollutants including NO\textsubscript{x} and total hydrocarbons in actual/simulated diesel exhaust environments [1–10]. Due to the oxidising nature of the plasma, it has become a necessity now to additionally treat the exhaust (which is pre-treated by plasma) by a catalyst/adsorbent. Ironically, such a kind of plasma-adsorbent/catalyst combination will be more expensive than the existing catalytic/adsorbent standalone system unless the catalyst/adsorbent was made from easily available ingredients such as solid industrial wastes [11–14]. Coupling the industry waste-based adsorbents with plasma, though on one hand reduces the overall cost; on the other hand, it may not be a feasible approach for implementation in the automobile sector due to handling issues associated with adsorbents. It is at this juncture we have thought of exploring the possibility of cascading plasma with indirect plasma system (ozone injection) and this study discusses the research work on this new line of NO\textsubscript{x} reduction technique.

This work has been carried out at the laboratory level to improve the NO\textsubscript{x} abatement in diesel exhaust by using only non-thermal plasma-based cascaded technique. The filtered diesel exhaust was subjected to successive chemical reactions by means of exposure to discharge plasma and ozone injection, not necessarily in this order. We refer hereafter discharge plasma as direct plasma and ozone injection as indirect plasma. To begin with, for the sake of reference, two sets of experiments were carried out. First, the filtered exhaust was treated with only dielectric barrier discharge (DBD) plasma energised with repetitive pulses. The next set of experiments was carried out with indirect plasma treatment involving just ozone injection into the filtered exhaust. Studies were then carried out with a new line of experimental setup wherein ozone was injected into plasma treated exhaust at first, and DBD plasma was exposed to ozone treated exhaust later. This new line of experiments is being carried out for the first time without involving adsorbents or catalysts and with the intention of exploring the feasibility of this new non-thermal, non-adsorbent, non-catalyst plasma for effective NO\textsubscript{x} removal. It was observed that this type of cascading direct and indirect plasma approach has yielded considerable enhancement in DeNO\textsubscript{x} efficiency and the results have been discussed.

2 Experimental setup

In this work, the main emphasis is on cascading direct plasma with indirect plasma or vice-versa with the intention of studying the cascade effect on NO\textsubscript{x} reduction in diesel exhaust. However, for the sake of comparison NO\textsubscript{x} reduction was studied individually with direct plasma as well as with indirect plasma. The whole study was carried out under laboratory conditions with petro-diesel engine as the source of exhaust. Only a small amount of exhaust was used for study and rest was allowed to the atmosphere. Figs. 1a and b show a new line of experiments carried out in this study.

2.1 NO\textsubscript{x} source and particulate filter

A 5 kW petro-diesel generator (PV-4 model, class B1, Prakash marketing India Pvt Ltd, India) was used as the source of NO\textsubscript{x}. Since the work emphasis is on gaseous pollutants the solid particulate from the incoming exhaust was filtered using stainless-steel particulate filters of size 5 microns. A suction pump along with a flow meter was used to control the exhaust flow at 8 lpm. The moisture present in the exhaust was left untouched to enable us to study the effect of OH radicals on NO\textsubscript{x} reduction.

2.2 Sources for direct and indirect plasma

In this work, two sources have been used, pulse power for direct plasma and high voltage alternating current (HVAC) for indirect plasma (ozone injection). Repetitive pulses were generated by
chopping the direct current (DC) at the terminal of filter capacitor (0.5 μF, 50 kV DC), which has been charged by a transformer–rectifier unit (50 Hz, 25 kV). The rotary spark gap arrangement enables the repetitive chopping and rotor speed control facilitates pulse frequency variation. In this study, the repetitive pulse frequency was maintained at 100 Hz. Ozone was generated in a separate air-fed reactor energised by HV AC supply (50 kV, 1.5 kVA, Mayog electrical Pvt Ltd, Bangalore, India).

2.3 Plasma reactors & mixing chamber
The DBD plasma reactors used for direct plasma treatment and for generation of ozone are similar in design. The reactor is a quartz glass tube with a concentric 6 mm metallic pipe acting as a discharge electrode. An aluminium foil wrapped around the glass dielectric formed the ground electrode. The effective discharge length for the plasma reactor was 28 cm with a gas space of 2 mm. Fig. 2a shows the plasma reactor. Fig. 2b shows the mixing chamber made of polyvinylchloride material. The chamber has two inlets and one outlet. One of the inlets always corresponds to ozone injection and the other inlet may correspond either to untreated exhaust or plasma treated exhaust.

2.4 Electrical measurement & gas analysing unit
The repetitive pulse voltage measurement was carried out by a voltage divider (2000:1, 50 kVpp, EP-50K, PEEC, Japan) which was connected to a digital oscilloscope (DL 1540, 200 MS/s, Yokogawa, Japan). Differential power measurement was employed by measuring the powers consumed in the setup with and without the plasma/ozone reactor. The power thus calculated is comparable to the power obtained as a product of voltage and current [15]. The exhaust gas components were measured by a flue gas analyser (Testo-350, Germany). An ozone analyser (AES-LC 3000 Aurozone, India) was used to measure the generated ozone concentration. Care was taken to decompose the excess ozone by an ozone destructor unit to prevent damage to electrochemical sensors of flue gas analyser. The sample input to the analyser was drawn from a gas sampling bottle as shown in Fig. 1.
3 Results and discussion

The work presented is about improving the NO\textsubscript{x} reduction efficiency in diesel engine exhaust in a unique way without utilising catalysts/adsorbents. The idea was to employ only plasma-based technique be it direct plasma or indirect plasma. A new line of setup was devised wherein direct and indirect plasma was cascaded while treating the exhaust. For the sake of comparison on energy considerations the exhaust treatment was carried out with individual direct plasma and indirect plasma techniques, respectively.

The NO\textsubscript{x} reduction study was carried out in four stages on a soot-filtered diesel exhaust at the laboratory level. The exhaust was assumed to have gaseous pollutants in addition to water vapour. In the first stage, the filtered diesel exhaust was exposed to the pulsed plasma shower only. In the second stage, the exhaust was treated with ozone injection in a mixing chamber. In the third stage, plasma-treated exhaust was exposed to ozone injection. In the last stage, ozone-treated exhaust was exposed to plasma shower. In each of these stages, several chemical reactions that include oxidation, reduction, decomposition, and recombination may take place contributing towards overall reduction of NO\textsubscript{x}. The possible reaction pathways corresponding to direct and indirect plasma can be summarised as below along with the reactions that show the formation of radicals such as O, N, hydroxyl (OH), hydroperoxyl (HO\textsubscript{2}) and O\textsubscript{3} molecules [9, 16, 17].

**Formation of O, OH, N & HO\textsubscript{2} radicals & O\textsubscript{3} molecules and associated chemical reactions**

\begin{align*}
O_2 + e &\rightarrow O + O^+ + 2e, \quad (1) \\
N_2 + e &\rightarrow N + N^+ + 2e, \quad (2) \\
H_2O + e &\rightarrow OH^+ + H^+ + 2e, \quad (3) \\
O + H_2O &\rightarrow 2OH, \quad (4) \\
O_3 + H &\rightarrow O + HO_2, \quad (5) \\
O_3 + O &\rightarrow O_5, \quad (6) \\
O + O_3 &\rightarrow 2O_2, \quad (7) \\
N_2 + e &\rightarrow 2N, \quad (8) \\
N + e &\rightarrow N. \quad (9)
\end{align*}

**Group A: pathways pertaining to direct plasma exposure**

\begin{align*}
NO + N &\rightarrow O + N_2, \quad (10) \\
NO_2 + N &\rightarrow O + N_2O, \quad (11) \\
NO_2 + N &\rightarrow NO + NO, \quad (12) \\
O_2 + N &\rightarrow NO + O, \quad (13) \\
NO + O &\rightarrow NO_2, \quad (14) \\
NO_2 + O &\rightarrow NO + O_2, \quad (15) \\
NO + NO_2 &\rightarrow N_2O_3, \quad (16) \\
NO + NO_3 &\rightarrow N_2O_4, \quad (17) \\
NO_2 + NO &\rightarrow 2NO_2, \quad (18) \\
NO + O_3 &\rightarrow NO_2 + O_2, \quad (19) \\
NO_2 + O_3 &\rightarrow NO_3 + O_2, \quad (20) \\
NO_2 + NO_3 &\rightarrow 2NO_2. \quad (21)
\end{align*}

**Group B: pathways pertaining to indirect plasma (ozone injection) exposure.**

In addition to reactions (20) and (21) the following reactions may take place in the presence of ozone:

\begin{align*}
C_2H_4 + O_3 &\rightarrow CH_2O + CH_2OO, \quad (33)
\end{align*}
Before discussing the individual NO removal stages it is worth understanding the reaction pathways pertaining to direct and indirect plasma exposure. Equations (1)–(9) indicate the formation of several radicals O, N, OH, and HO₂ in addition to the production of ozone. The inclusion of OH and HO₂ radical-based reactions are necessary due to the presence of water vapour in the exhaust. Equations (10)–(36) correspond to conversion/reduction of NO/NO₂ depending upon the rate constants. Equations (10)–(13) explain the reduction of NO₂:NO to O/N₂/O²/N/NO. It should be noted here that the possibility of NO reduction is favourable under poor oxygen conditions of the exhaust (O₂ < 5%). Diesel exhaust at no load is generally rich in oxygen (>14%) which makes the plasma-exposed exhaust environment more of oxidising in nature and therefore the possibility of reduction of NO by N radicals is less. Furthermore, in the present case, the average electric field was <115 kV/cm (which corresponds to about 9 eV) the reduction of NO by an N radical is less favourable [18, 19].

Given the fact that the NO reduction is less favourable in direct plasma exposure the other possibilities are NO conversion/excitation. Equations (14)–(23) correspond to the formation of NO₂ and other higher oxides of nitrogen through the oxidation of nitric oxide which is present in major proportion in diesel exhaust. Simultaneously, owing to the presence of water vapour, we can expect the formation of nitrous and nitric acids through the reactions with hydroxyl and hydroperoxyl radicals as is evident from (24)–(32). At this juncture, it is appropriate to discuss the definition of NOX and its interpretation from the perspective of NOX analysers. The commercially available analysers generally interpret NOX as the sum of NO and NO₂. During the exhaust treatment by direct plasma the majority of NO gets converted to NO₂ and the rest may get oxidised to either acidic components of nitrogen (HNO₂/HNO₃) or higher oxides of nitrogen (NOₓ/O₂/N₂Oₓ). If it is the latter case then NOX reading in the analyser should be equal to NO + NO₂ + NO₃ + N₂O₄ + N₂O₅. This is impractical as the commercial analysers usually, do not come equipped with NO₂/N₂O₅/N₂O₄ sensors. Having said this one should exercise caution in the interpretation of analyser readings. Looking into (14)–(32) it can be inferred that the rate constants of formation of HNO₂/HNO₃ (25) and (28), far exceed that of NOₓ/N₂O₄/N₂O₅ (21)–(23). Therefore we can approximate NOX as equal to the sum of NO & NO₂. This is also justified by the proportional increase in NOₓ with respect to applied voltages. However, at higher voltages, the formation of OH/HO₂ radicals increases causing more production of HNO₂/HNO₃ when compared with the formation of NOX. This is reflected in the form of a significant decrease in NOX at higher energies. In summary, direct plasma treatment of diesel exhaust laced with water vapour results in the formation of NOX/HNO₂/HNO₃ with individual concentrations varying as a function of applied energy.

The reactions pertaining to the ozone injection (indirect plasma) correspond to (20), (21) and (33)–(38) in this case the filtered exhaust enters a mixing chamber where ozone gets injected separately. Being an active oxidising agent O₃ mainly reacts with NO forming NO₂. It has been observed that this NO₂ formation keeps increasing as a function of ozone concentration until the ratio O₃:NO is within a critical range (1.0–2.4) and beyond that NOX keeps decreasing indicating the formation of higher oxides of nitrogen such as NO₃ and N₂O₅ (21) and (23) [10]. Therefore, our earlier definition of NOX = NO + NO₂ should now include NOX + N₂O₅. However, the NOX values shown by a commercial analyser correspond to NO + NO₂ only and hence care must be taken in the interpretation of NOX for O₃:NO ratio greater than the critical range. In this indirect plasma, there will not be any production of radicals such as O/N/OH/HO₂ due to the absence of direct plasma exposure to the exhaust. However, it has been observed that the hydrocarbons in the exhaust react with ozone forming carbonyl biradicals which may be responsible for the overall reduction of NOX independent of the ratio O₃:NO (33)–(36). The presence of water vapour in the exhaust also aids in the formation of HNO₂/HNO₃ particularly at room temperature [20, 21] as shown in (39) and (40). In summary the indirect plasma or ozone injection treatment of diesel exhaust results in the substantial amount of NO conversion to NO₂ in addition to the overall reduction of NOX through conversion of NO/NO₂ to HNO₂/HNO₃. While the former conversion is dependent on the O₃:NO ratio the latter is independent of it.

Table 1 shows diesel exhaust composition at no load and at room temperature. The exhaust was filtered for solid particulate and flow was maintained at 8 bpm throughout the current study. A pipe type reactor was used for the direct plasma study energised with repetitive pulses. A similar reactor was used for the generation of ozone from dry air using AC energisation. Though NOX removal studies were separately carried out for direct plasma and indirect plasma, of significance are the studies involving cascading direct plasma with indirect plasma as schematically represented in Figs. 1a and b.

Fig. 3 shows the variation of oxides of nitrogen in the direct plasma treatment of diesel exhaust. The filtered exhaust was exposed only to the pulse energisation. The NOX concentration was steadily increasing owing to the oxidation/reduction reactions corresponding to (15), (19) and (20). Around 70 J/l NOX reaches a peak and then starts decreasing due to the increased production of HO/HO₂ at higher energies leading to more formation of HNO₂/HNO₃ (25) and (28). While this acidic component starts to form with the initiation of plasma it is the concentration that gets enhanced at higher energies. For this reason, we see a steady decrease of NOX under direct plasma energisation up to about 51%.

In the next stage of the experiment, the filtered exhaust was allowed into a mixing chamber where provision was made to inject separately generated ozone. The concentration of NO and O₃ was monitored at the inlet of the mixing chamber so as to monitor the ratio of O₃:NO. Fig. 4 shows the variation of ozone concentration as a function of applied AC energy. With the injection of the ozone into the mixing chamber, one can expect more of oxidation reactions with the gaseous pollutants. Equation (20) shows the conversion of NO to NO₂ and this is predominant until the O₃:NO is about close to one. Beyond this ratio, there will be the simultaneous production of NO₂ along with N₂O₅ through a linking/intermediate reaction involving NO₃ formation (21) and (23). For very high ozone concentrations, though not studied in this work, wherein the ratio O₃:NO > 2.4 there will be excess N₂O₅ formation without any production of NO₂ leading to drooping NO₂ characteristics.

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**Table 1. Diesel exhaust gas composition at no load**

| Gas   | Concentration |
|-------|---------------|
| NO    | 329 ppm       |
| NO₂   | 95 ppm        |
| NOₓ   | 424 ppm       |
| O₂    | 16.48%        |
In the current study, the O\textsubscript{3}/NO ratio was between 0.68 and 1.8. It can be inferred from Fig. 5 that the NO\textsubscript{x} reduction efficiency is more or less saturated around 22% for a given value of ozone. This small decrease of NO\textsubscript{x} may be due to the chain reactions wherein ozone reacts with hydrocarbons in the exhaust giving rise to carbonyl biradicals (CH\textsubscript{2}OO) which in turn reacts with NO forming formyl radicals and HNO\textsubscript{2} (33)–(36) [17]. Another pathway for the decrease in NO\textsubscript{x} may be due to the formation of hydrogen peroxide when ozone reacts with the water vapour in the exhaust (38). H\textsubscript{2}O\textsubscript{2}, in turn, reacts with NO/NO\textsubscript{2} forming HNO\textsubscript{2}/HNO\textsubscript{3} thus affecting the reduction of NO\textsubscript{x} (39) and (40), though the reduction is not very significant.

Having studied the NO\textsubscript{x} reduction with direct and indirect plasma we then cascaded the two treatment techniques i.e. direct plasma and indirect plasma as shown in Fig. 1a. In the direct plasma, the exhaust was treated by pulse energisation and in the indirect plasma, ozone was produced with AC energisation before getting injected into the chamber where plasma-treated exhaust gets mixed. Here we need to take into account the reactions that are taking place in the plasma zone as well as that in the mixing chamber when ozone is injected. The ozone concentration was kept constant at 355 ppm. Fig. 6 shows the effect of cascading the plasma techniques on overall NO\textsubscript{x} reduction. The specific energy shown corresponds to the summation of the energies employed in the direct plasma and indirect plasma. Since ozone injection was kept constant the energy utilised for the same remains constant in the indirect plasma at about 50 J/L. On the other hand, it should be noted here that in these cascaded cases, the only variable energy is in the direct plasma treatment.

When the exhaust enters the pulse energised plasma chamber oxidation of NO to NO\textsubscript{2} dominates along with the formation of HNO\textsubscript{2}/HNO\textsubscript{3} as explained earlier (with respect to Fig. 3). Substantial NO\textsubscript{2} reduction (about 51%) might have taken place in the plasma treatment. This treated exhaust, which is now rich in NO\textsubscript{2}/HNO\textsubscript{2}/HNO\textsubscript{3}, enters the mixing chamber where ozone is getting injected. It should be noted here that the ratio of O\textsubscript{3}/NO at the upstream of the mixing reactor starts exceeding beyond 2.4 as the NO level starts decreasing at the downstream of the plasma reactor (due to NO oxidation). In the mixing chamber now, we have a situation where there is the presence of water vapour and a higher O\textsubscript{3}/NO ratio indicating that there will be a possibility of formation of HNO\textsubscript{2}/HNO\textsubscript{3} and/or formation of higher oxides of nitrogen (NO\textsubscript{3}/N\textsubscript{2}O\textsubscript{5}/N\textsubscript{2}O\textsubscript{6}). The possible pathways for NO\textsubscript{2} conversion to HNO\textsubscript{2}/HNO\textsubscript{3} can be explained by (33)–(40) involving NO/NO\textsubscript{2} reactions with hydrocarbons/water vapour/hydrogen peroxide. The unreacted NO present in the plasma-treated exhaust may react with carbonyl biradicals (35) and hydrogen peroxide (39) producing mainly formaldehyde (CH\textsubscript{2}O)/HNO\textsubscript{2}. Similarly, the pathways for NO\textsubscript{2} conversion to higher oxides of nitrogen can be explained by (20)–(23) involving NO/NO\textsubscript{2} reactions with O\textsubscript{3}/NO\textsubscript{3} in which case the interpretation of NO\textsubscript{x} will not be just summation of NO + NO\textsubscript{2} instead it will be NO + NO\textsubscript{2} + NO\textsubscript{3} + N\textsubscript{2}O\textsubscript{4} + N\textsubscript{2}O\textsubscript{5}. However, the commercial analysers
which is exiting the ozone mixing chamber, when it enters the plasma chamber will be exposed to radical-induced chemical reactions (10)–(32). These carbonyl biradicals and H\textsubscript{2}O\textsubscript{2} in turn, react with NO and NO\textsubscript{2} forming HNO\textsubscript{3}/HNO\textsubscript{2}, respectively, (35), (36), (39), and (40), thus reducing the overall NO\textsubscript{x}. The unreacted NO/NO\textsubscript{2}, which is exiting the ozone mixing chamber, when it enters the plasma chamber will be exposed to radical-induced chemical reactions (10)–(32).

In addition to the oxidation of NO to NO\textsubscript{2}, there will be the simultaneous conversion of NO/NO\textsubscript{2} to HNO\textsubscript{3}/HNO\textsubscript{2} due to the formation of OH/HO\textsubscript{2} radicals. The reaction of NO with OH and HO\textsubscript{2} are more probable, (25) and (28), than the reaction of NO\textsubscript{2} with OH (29). It should be noted here that the exhaust which is entering into the plasma zone is laden with unreacted ozone from the previous mixing chamber (indirect plasma) and there will be the production of ozone inside the plasma chamber too (direct plasma). Together there will be a copious amount of ozone available in the plasma chamber which reacts with NO to form NO\textsubscript{3} (21) and NO\textsubscript{2}, in turn, may react with HNO\textsubscript{3} forming HNO\textsubscript{2} (30). As seen from Fig. 7 it can be inferred that the reduction of NO + NO\textsubscript{2} (\textequiv NO\textsubscript{3}) is quite high and a maximum DeNO\textsubscript{X} efficiency of about 95% was obtained with this plasma-based approach for a specific energy of about 123 J/l.

The reduction efficiency of NO\textsubscript{x} was compared for the direct plasma and indirect plasma cases. It is evident from Fig. 8 that the cascaded connection is far better than the individual cases be it direct plasma or indirect plasma for a given specific energy. Within the two cascaded treatments, ozone + plasma treatment gave better NO\textsubscript{x} reduction than plasma + ozone treatment at any given specific energy. A possible explanation for this increased NO\textsubscript{x} reduction may be due to the formation of HNO\textsubscript{3}/HNO\textsubscript{2} in the plasma zone as the rate constants associated with the reactions of OH/HO\textsubscript{2} radicals with NO in the plasma zone are higher than that associated with NO to NO\textsubscript{2} oxidation.

It can be observed from Fig. 8 that with single plasma treatment DeNO\textsubscript{X} efficiency of 51% was achieved for about 90 J/l and with cascaded plasma treatment (ozone + plasma) the DeNO\textsubscript{X} efficiency was about 95% at 123 J/l, i.e. about 1.3 times the energy spent on single plasma treatment. On the similar lines with cascaded plasma + ozone treatment even at 140 J/l, the efficiency was not more than 70%.

Finally, the current work has been compared with that available in the literature as shown in Table 2. It is practically difficult to get a common platform for comparison but to the extent possible we can only display NO\textsubscript{x} as NO + NO\textsubscript{2}. The decrease of NO\textsubscript{x} was about 65% (corresponding to a specific energy of 140 J/l) as can be seen in Fig. 6.

The final stage of the experiment was carried out by allowing the filtered exhaust to flow through the indirect plasma and then through the direct plasma, i.e. a reversal of the aforementioned case. The exhaust flow was maintained at 8 lpm before passing through the mixing chamber where it was mixed with a pre-fixed ozone concentration of 355 ppm which corresponds to an O\textsubscript{3}/NO ratio of 1.07. The experimental setup is shown in Fig. 1b. The exhaust which is rich in nitric oxide gets oxidised to NO\textsubscript{2} in the presence of ozone in the mixing chamber (20). The formation of higher oxides of nitrogen such as N\textsubscript{2}O\textsubscript{5}/N\textsubscript{2}O\textsubscript{5} may not be expected as the O\textsubscript{3}/NO ratio is much below 2.4 [9]. As explained earlier there will be the production of carbonyl biradicals (CH\textsubscript{2}OO) and hydrogen peroxy (H\textsubscript{2}O\textsubscript{2}), respectively, when ozone reacts with the hydrocarbons (ethene/propene) and water vapour (33), (34), and (38). These carbonyl biradicals and H\textsubscript{2}O\textsubscript{2} in turn, react with NO and NO\textsubscript{2} forming HNO\textsubscript{3}/HNO\textsubscript{2}, respectively, (35), (36), (39), and (40), thus reducing the overall NO\textsubscript{x}. The unreacted NO/NO\textsubscript{2}, which is exiting the ozone mixing chamber, when it enters the plasma chamber will be exposed to radical-induced chemical reactions (10)–(32).

**Table 2** Comparison of present work with published literature on diesel engine exhaust cleaning

| Authors          | Flow rate, lpm | AC/DC pulse | DeNO\textsubscript{X} % | Voltage/energy/power |
|------------------|----------------|-------------|-------------------------|----------------------|
| Locke et al. [22]| 1 pulse (70 Hz)| 53          | 146 J/l                 |
| Sankarsan et al. [23] | 4 pulse (80 Hz) | 86          | 100 J/l                 |
| Sankarsan et al. [24] | 10 pulse (60 Hz) | 65          | 97 J/l                  |
| Vinogradov et al. [25] | 8 DC           | 55          | 60 J/l                  |
| Yankelevich et al. [26] | pulse (400 Hz) | 25          | 39 kV                   |
| Yamamoto et al. [27] | 3 AC (60 Hz)   | 20          | 5 W                     |
| Song et al. [28]  | 5 AC (15.5 kHz)| 67          | 120 J/l                 |
| Srinivasan et al. [29] | Pulse         | 73          | 60 J/l                  |
| Du et al. [30]    | 220.7 AC (5 kHz) | 55          | 9 kV                    |
| Zhou et al. [18]  | HFAC (16 kHz)  | 72.5        | 20 kV                   |
| Sarah [8]         | 5 AC (1.2 kHz) pulse (80 Hz) | 47          | 216 J/l                 |
| present work     | 8–10 pulse (100 Hz) | 95          | 123 J/l                 |

**Fig. 7** Variation of oxides of nitrogen in cascaded ozone injection + direct plasma treatment

**Fig. 8** Relative performance of plasma/ozone injection methods in NO\textsubscript{x} removal

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have surveyed several works related to the study of real diesel exhaust with plasma/ozone injection approach only.

4 Conclusion

The present work involves a non-catalytic/non-adsorbent non-thermal plasma based approach to enhance the reduction of NO\textsubscript{x} in a controlled diesel engine exhaust. The cascaded connection of indirect plasma (ozone injection) with direct plasma has shown good NO\textsubscript{x} reduction efficiency of 95\% (for about 123 J/L) which is much higher than that obtained with individual treatments alone be it ozone injection or direct plasma. On the other hand, it takes about 90 J/L in the direct plasma case to achieve DeNO\textsubscript{x} efficiency of 51\% and it was verified experimentally that even with two plasma reactors connected in cascade (direct plasma + direct plasma) the maximum NO\textsubscript{x} reduction was 66\% at 125 J/L which is well below that achieved in the cascaded connection of ozone + plasma at about the same specific energy. This type of non-thermal cascaded plasma based approach, where the cascaded plasma refers to combination or serial connection of two plasma systems namely direct plasma and indirect plasma (ozone injection), has shown a higher DeNO\textsubscript{x} efficiency without the use of any additional adsorbents or catalysts. Therefore, this cascaded plasma approach may be a better option for addressing NO\textsubscript{x} either in stationary diesel exhaust or mobile diesel exhaust since the cleaning system was solely based on the plasma.

5 References

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