



Comparative study of NO removal in surface-plasma and volume-plasma reactors based on pulsed corona discharges

Muhammad Arif Malik*, Juergen F. Kolb, Yaohong Sun¹, Karl H. Schoenbach

Frank Reidy Research Center for Bioelectrics, Old Dominion University, 4211 Monarch Way, Suite 300, Norfolk, VA 23508, USA

ARTICLE INFO

Article history:

Received 16 March 2011

Received in revised form 8 August 2011

Accepted 21 September 2011

Available online 29 September 2011

Keywords:

Nitric oxide

Non-thermal plasma

Surface-plasma

Flue gas treatment

Pulsed power

NO_x removal

ABSTRACT

Nitric oxide (NO) conversion has been studied for two different types of atmospheric-pressure pulsed-corona discharges, one generates a surface-plasma and the other provides a volume-plasma. For both types of discharges the energy cost for NO removal increases with decreasing oxygen concentration and initial concentration of NO. However, the energy cost for volume plasmas for 50% NO removal, EC₅₀, from air was found to be 120 eV/molecule, whereas for the surface plasma, it was only 70 eV/molecule. A smaller difference in energy cost, but a higher efficiency for removal of NO was obtained in a pure nitrogen atmosphere, where NO formation is restricted due to the lack of oxygen. For the volume plasma, EC₅₀ in this case was measured at 50 eV/molecule, and for the surface plasma it was 40 eV/molecule. Besides the higher NO removal efficiency of surface plasmas compared to volume plasmas, the energy efficiency of surface-plasmas was found to be almost independent of the amount of electrical energy deposited in the discharge, whereas the efficiency for volume plasmas decreases considerably with increasing energy. This indicates the possibility of operating surface plasma discharges at high energy densities and in more compact reactors than conventional volume discharges.

Published by Elsevier B.V.

1. Introduction

Atmospheric-pressure nonthermal plasmas with low gas temperatures, such as those generated by pulsed corona discharges and dielectric barrier discharges, are increasingly being used for air pollution control [1–3]. Such discharges are usually filamentary, comprising thin plasma channels (streamers) which propagate in the gas between the electrodes. Such plasmas are referred to as “volume-plasmas” in this report. The streamers can also propagate along solid–gas interfaces, as in surface-flashover, in creeping or sliding discharges [4,5]. They are referred to as “surface-plasmas” in this report. Interest in the application of surface-plasmas for environmental air pollution control is growing, particularly because of their energy efficiency which exceeds that of volume-plasmas [6–10]. This advantage in energy efficiency has been reported for the destruction of toxic volatile organic compounds (VOCs) [6,7], the oxidation of nitrous oxide (NO) to nitrogen dioxide (NO₂) [8,9], and the synthesis of ozone (O₃) [10]. The reason for the higher energy efficiency of surface-plasmas is assumed to be the more efficient mixing of reactive species, and the consequently higher reaction rates, due to the ionic-wind effect and surface mediated reactions.

* Corresponding author.

E-mail address: MArifMalik@gmail.com (M.A. Malik).

¹ On leave from Institute of Electrical Engineering, Chinese Academy of Sciences, Beijing 100190, PR China.

Particularly environmentally harmful species are the nitrogen oxides (NO_x). They are present in diesel engine exhaust and in flue gases. About ninety percent of NO_x exist as NO. In order to remove NO from diesel exhaust or flue gases, it needs to be converted into NO₂ which is easier to remove. Removal of NO₂ can be achieved either by selective catalytic reduction [11–14], by adsorption [15,16], or by dissolution in water followed by reduction [17,18]. Oxygen based active species produced in the plasma, like ozone and atomic oxygen (O), are essential in converting NO into NO₂ [19,20].

Preliminary results under a limited set of experimental conditions show that the surface plasma is more efficient than the volume plasma for the conversion of NO into NO₂ [8,9]. It is desirable to test the surface plasma reactor under a broad range of experimental conditions. This manuscript reports the results of a more comprehensive study on the energy efficiency of surface-plasma and volume-plasma for NO conversion under a broad range of experimental conditions. The NO removal rate was measured as a function of the initial NO concentration and oxygen concentration, and on the specific input energy [21]. The study revealed new information that are of academic interest and important with respect of practical application of the technique.

2. Experimental

The schematic of the experimental setup is shown in Fig. 1. High voltage pulses of positive polarity (up to 30 kV and 500 Hz) were

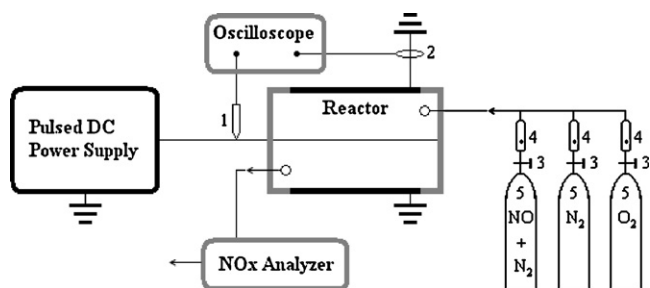


Fig. 1. Schematics of the experimental setup: 1 is the voltage probe, 2 current probe, 3 needle valves, 4 gas flow meters, and 5 pressurized gas bottles. The center line in the reactor depicts the wire anode and the bold lines on top and bottom, the two cathodes.

Table 1

Typical values of electrical parameters in this study.

Reactor	Parameter	Value
Volume plasma	Peak voltage	30 kV
	Voltage pulse width at half maximum	100 ns
	Voltage rise time (10–90%)	45 ns
	Energy per pulse	10 mJ
Surface plasma	Peak voltage	30 kV
	Voltage pulse width at half maximum	90 ns
	Voltage rise time (10–90%)	45 ns
	Energy per pulse	2 mJ

delivered by a “Compact Pulsed Power Modulator MPC3000S-OP1” (Suematsu Electronics Co., Ltd., Japan). The voltage and current diagnostics and energy calculations were the same as in our earlier study [6,9] using Tektronix TDS 3052 oscilloscope, Tektronix P6015A voltage probe and Pearson Electronics Current Monitor, Model 110A. The instant power was calculated from the product (VI) of the measured pulse voltage (V) and current (I). The energy per pulse (Ep) is the time integral ($\int VI dt$) of the power. The displacement current was measured by reducing the applied voltage to values below that required for the discharge breakdown or plasma formation. The typical values of the electrical parameters are listed in Table 1.

Two plasma reactors, i.e., a volume-plasma reactor (Fig. 2) and a surface-plasma reactor (Fig. 3), were employed in this study. The cylindrical electrode in the volume-plasma reactor was kept 2.5 cm away from end-fittings made of acrylic, which minimized the probability that a surface plasma would be generated along the end-fittings. The surface-plasma reactor comprises a wire to two parallel-plate electrodes stretched on the surface of a glass sheet

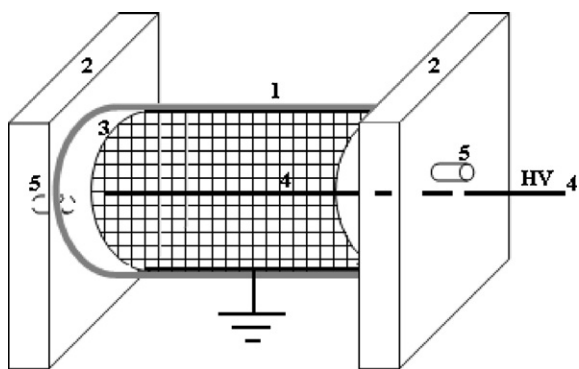


Fig. 2. Coaxial electrodes enclosed in an acrylic container were used for generating a volume-plasma. The components are: 1 is an acrylic cylinder of 4.5 cm ID, 5.1 cm OD, and 15 cm length; 2 are acrylic end-fittings; 3 is a cylindrical cathode of 4.5 cm OD, 10 cm length, made of stainless steel mesh; 4 is a stainless steel wire anode of 150 μ m diameter stretched along the axis of the cylinder; and 5 are gas inlet/outlet.

with a second glass sheet parallel to the first one, with a spacer separating the two dielectric sheets.

Flow rates of nitrogen (N_2), oxygen (O_2) and NO from gas cylinders were controlled by needle valves and monitored with ball-float flow meters. Conditions of one atmospheric pressure, room temperature (25 °C), 1 liter per minute (L/min) flow rate, and 30 kV applied voltage were maintained in the experiments, except when mentioned otherwise. The concentration of oxygen and NO were monitored by an NO_x analyzer (ENERAC Model 500) equipped with oxygen and NO sensors. The resolution of the oxygen and NO sensors was 0.1%, and 1 ppm, respectively, and their accuracy, as specified by the manufacturer, was 0.2%, and 4% of the reading, respectively. Laboratory tests with nitrogen + oxygen mixture, NO + nitrogen, and NO + NO_2 + nitrogen mixtures show the accuracies for oxygen and NO measurements were well within the limits specified by the manufacturer.

In order to get stable inlet concentration of NO the process gases were allowed to flow for 1 h before the discharge was switched ON. The NO concentration at outlet was measured after 15 min of discharge ON. Three readings were averaged and each reading was an average of 3 min online monitoring. Error bars are not shown in figures because they were smaller than the size of symbols representing the experimental values.

Ozone (O_3) was estimated by two methods: (i) indirectly from the amount of NO consumed when the latter was mixed with the exhaust gases and (ii) directly by means of UV-spectroscopy using a UV-Ozone Analyzer model gFFOZ from In USA Incorporated.

The specific input energy (SIE) in units of Joule/liter (J/L) was calculated by using the formula:

$$SIE = \frac{Ep f}{Q} \quad (1)$$

where f is pulse frequency and Q is flow rate of process gas in liters per second (L/s).

The energy cost (EC) in units of electron-volts per NO molecule (eV/molecule) was calculated using the formula [22]:

$$EC = \frac{250SIE}{NO_{in} - NO_{out}} \quad (2)$$

where NO_{in} is the NO concentration at the inlet of the reactor and NO_{out} is the NO concentration at the outlet of the reactor, both in ppm.

The energy yield (EY) in units of the mass (in units of g) of NO removed per kWh input (g/kWh) is being calculated by using the formula:

$$EY = \frac{1120}{EC} \quad (3)$$

where the constant 1120 is calculated on the basis of the fact that $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$, $1 \text{ kWh} = 3.6 \times 10^6 \text{ J}$, $1 \text{ mol} = 6.02 \times 10^{23}$ molecule, and $1 \text{ mol of NO} = 30 \text{ g}$.

3. Results

A review of the scientific literature on volume-plasmas concludes that the NO removal rate is mainly determined by the specific input energy (SIE) [21]. The NO concentration and the corresponding energy cost values have therefore been expressed in terms of the SIE in the following figures. Fig. 4 shows that the NO concentration from air decreases with an increase in SIE. In this case the SIE was controlled by varying the pulse frequency and/or flow rate of the process gas. The energy cost was found to be almost independent of the flow rate, even for different pulse frequencies. In other words, the energy cost is only weakly, if at all, dependent on the pulse frequency under our experimental conditions.

The set of experiments with a flow rate of 1 L/min in a volume-plasma (circles in Fig. 4) was repeated (crosses in Fig. 4) to check

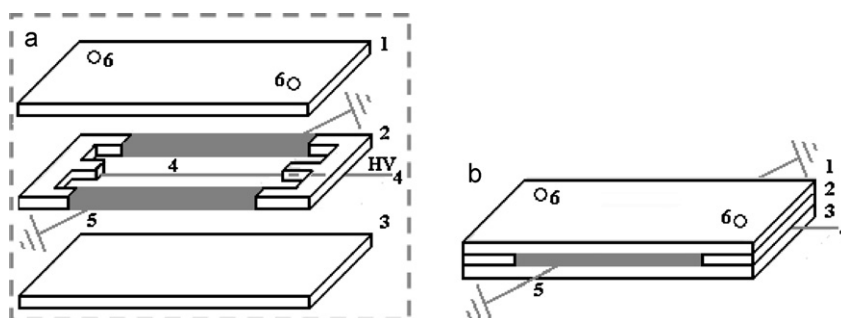


Fig. 3. Wire-to-plate electrodes stretched on a glass sheet surface and enclosed by another glass sheet are used for the generation of a surface-plasma: (a) is a partially exploded view, and (b) is a view of the assembled device. The components are: 1 and 3 are top and bottom glass sheets, 22 cm × 13 cm × 0.6 cm; 2 is a Teflon spacer of 0.2 cm thickness and 2.5 cm stripe on each side; 4 is stainless steel wire anode of 150 μm diameter; 5 are two cathodes made of aluminum foil of 13 cm effective length (wrapped around the sides of the spacer); 6 are gas inlet/outlet. The whole assembly is enclosed in two acrylic sheets and sealed by silicon sealant.

the reproducibility of the results. The results shown in Fig. 4 indicate that the reproducibility of the results is reasonable under our experimental conditions. Similarly the trends shown in this and in the following figures were verified by repeat experiments. It should be mentioned that the inlet NO concentration in the repeat experiment were slightly different. This is because the NO concentration was allowed to stabilize for 1 h before the discharge was switched ON. The stable concentration differed by ~10% from the value initially set as shown in Fig. 4c for the case of 2.0 L/min flow rate. The effect of inlet NO concentration are discussed later in this section.

For the purpose of comparison, the curves in this and in the following figures are drawn to the same scale both for volume-plasma and surface-plasma. Comparison of Fig. 4a with Fig. 4c shows that the surface-plasma is more efficient in removing NO compared to volume-plasma at the same specific input energy.

Fig. 5 shows changes in NO concentration and energy cost dependent on SIE, which in this case was controlled by the applied voltage. Again, the NO concentration decreases and the energy cost increases with an increase in SIE. However, the energy cost increases more strongly with increasing SIE in the case of volume plasma than in the case of surface plasma. The increase in SIE was due to the increased energy per pulse in this case, which had an adverse effect on NO removal in the volume plasma. This adverse effect was mitigated in the case of surface plasma.

Fig. 6 shows the effect of oxygen concentration in the ambient gas on NO removal. Again, the NO concentration decreases and the energy cost increases with an increase in SIE. However, the decrease in NO concentration was found to be strongly dependent on the oxygen concentration. A gradual reduction of oxygen concentration from 20 to 5% resulted in a gradual reduction of NO removal rate

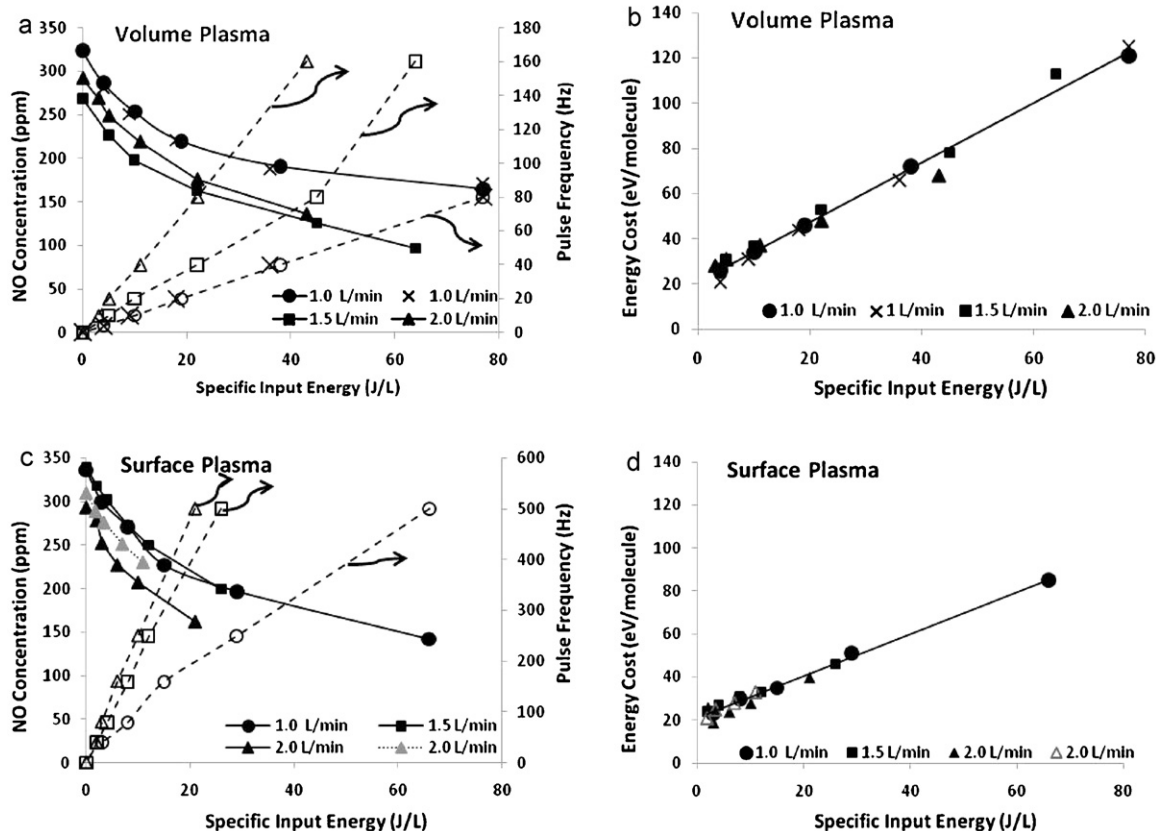


Fig. 4. NO concentration in the treated gas (filled symbols) and pulse frequency (open symbols) ('a' and 'c') and the energy cost ('b' and 'd') versus SIE for different flow rates of the process gas. The SIE was varied by varying the pulse frequency. The peak applied voltage was 30 kV and the process gas was NO + air mixture (20% oxygen).

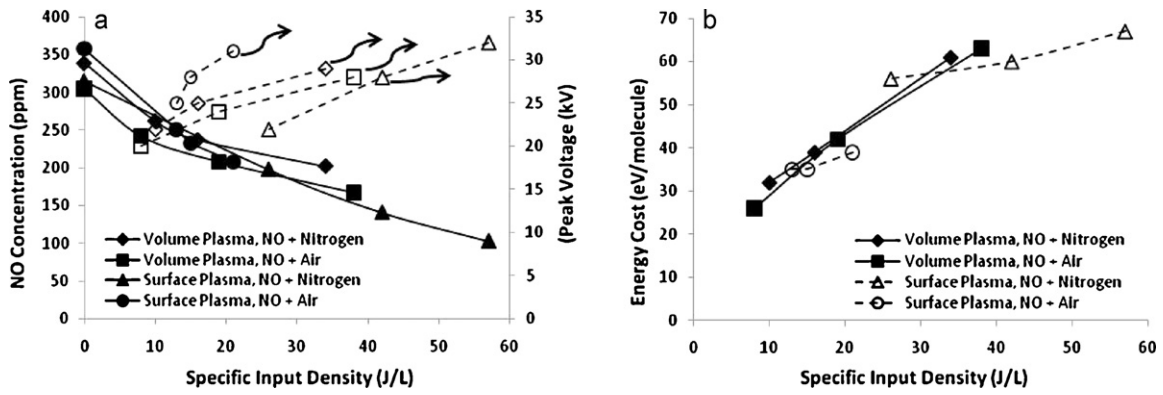


Fig. 5. NO concentration in the treated gas (filled symbols) and applied voltage (open symbols) 'a' and the energy cost 'b' versus SIE. The SIE was varied by varying the applied voltage. The pulse frequency was 40 Hz in the case of volume-plasma, 250 Hz in the case of surface-plasma with NO + air (20% oxygen), and 500 Hz in the case of surface-plasma with NO + nitrogen.

for the same SIE. However, the trend was found to be reversed at 0% oxygen, i.e., the NO removal rate from NO + nitrogen jumped to a maximum value. The reasons for the behavior of NO removal rate with respect to oxygen concentration are explained in the following discussion section.

The results of measurements on the effect of the initial NO concentration from NO + nitrogen system is shown in Fig. 7. The energy cost for NO removal decreases as the initial NO concentration increases at the same SIE. The effect of flow rate of the process gas is shown in Fig. 8. The energy cost for NO removal remains the same at the same SIE in the range of flow rate of the process gas from 1 L/min to 2 L/min.

Another way of comparing the performance of nonthermal plasma reactors is to use energy constant (k_E in units of L/J) from the following equation [3,21,23]:

$$\ln \left(\frac{NO_{in}}{NO_{out}} \right) = -k_E(SIE) \quad (4)$$

Higher value of k_E means higher NO removal efficiency. Eq. (4) was a good fit to the data of Fig. 7a and b as shown in Fig. 7d and e, respectively under the conditions of "NO conversion > 85%". When oxygen was present in the process gas the equation was a good fit to the data under the condition of "SIE < 50 J/L", which was in accordance with the conclusions from earlier studies on NO removal by

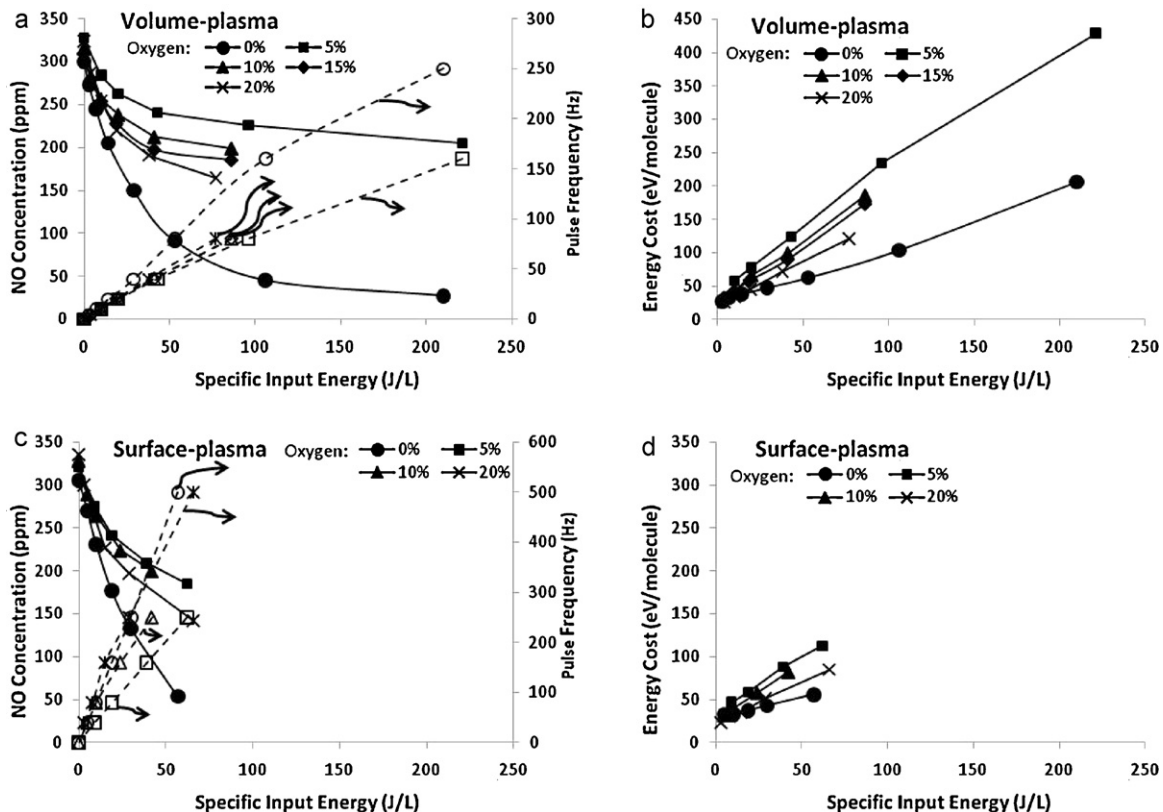


Fig. 6. NO concentration (solid symbols, pulse frequency (open symbols) ('a' and 'c') and energy cost ('b' and 'd') in the treated gas versus SIE for different initial concentrations of oxygen in the ambient gas. The SIE was varied by varying the pulse frequency.

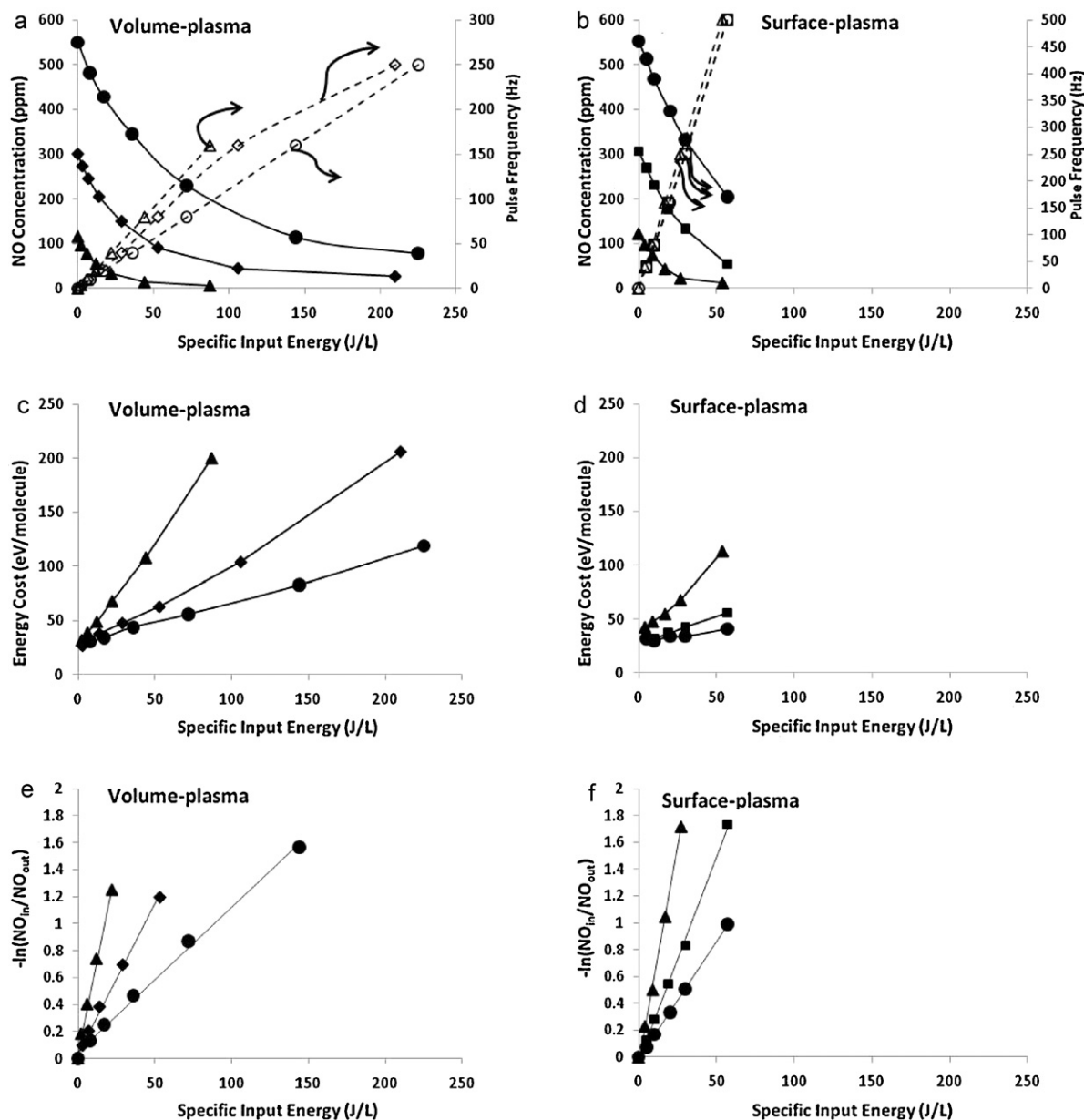


Fig. 7. NO concentration (solid symbols), pulse frequency (open symbols) ('a' and 'b'), energy cost ('c' and 'd'), and semi-log plot of data based on Eq. (4) ('e' and 'f') in the treated gas versus SIE for different initial concentrations of NO in nitrogen. The SPI was varied by varying the pulse frequency.

nonthermal plasma [21]. The k_E values along with coefficient of determination (R^2) values obtained by fitting Eq. (4) to the data under the conditions mentioned above are summarized in Table 2. The R^2 values are reported because they are a statistical measure of how well the regression line approximates the real data points. The R^2 varies from 0.0 to 1.0, where 0.0 indicates that the regression line does not fit and 1.0 indicates that it perfectly fits the data.

A summary of the results of the studies depicted in Figs. 4–8 is given below.

- The NO removal rate increases with increase in specific input energy. Pulse frequency, flow rate of the process gas, and applied voltage determine the specific input energy.
- The energy cost for removal of NO increases with increase in specific input energy.

- The energy cost for removal of NO shows a parabolic curve with respect to oxygen concentration with a maximum at small concentration of oxygen (5% in the present case).
- Surface plasma is more effective in NO removal and more energy efficient than volume plasma, particularly at low oxygen concentration in the ambient gas.
- The increase in energy per pulse for surface plasma has a less adverse effect on the energy cost than for volume plasma.

4. Discussion

The high voltage pulses of short rise time and short duration, as used in the present study, cause a shift in the electron energy distribution in the nonthermal (streamer) plasma to higher energies. This shift results in increased dissociation, excitation, and ionization rates [19,20]. The dissociation of ambient gas molecules produces

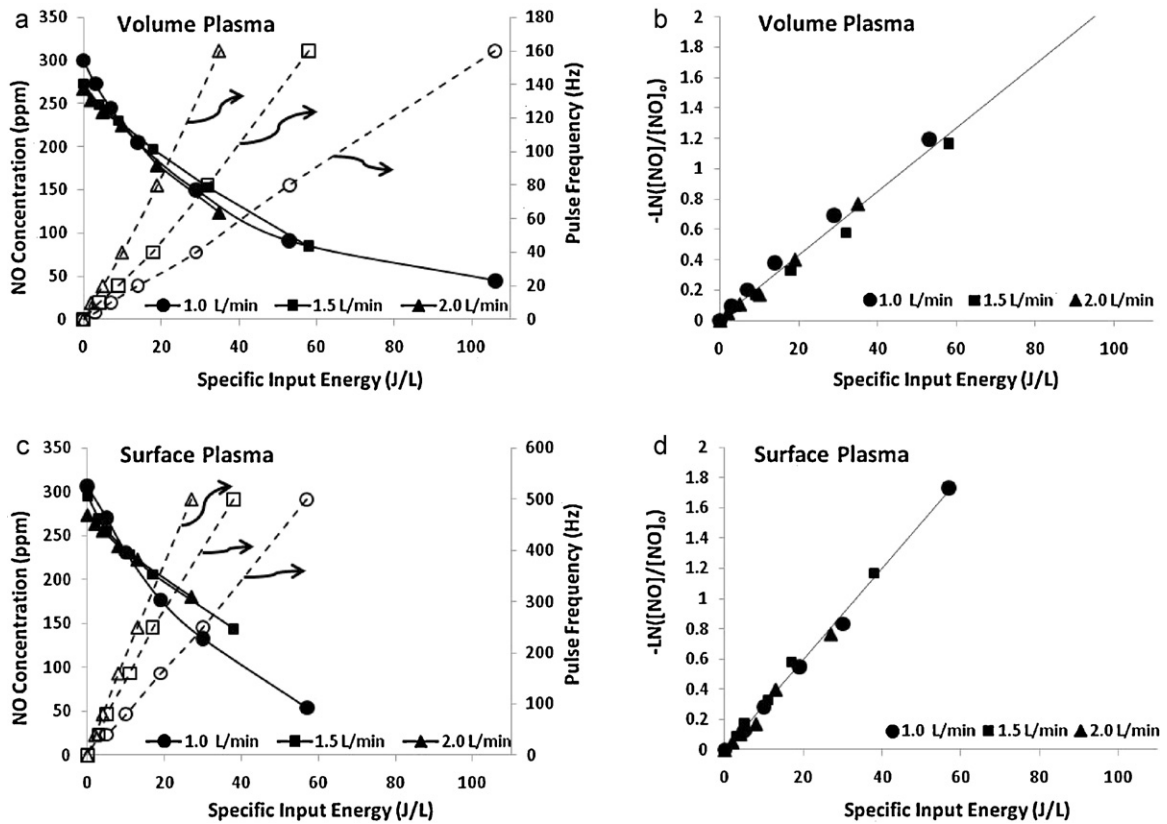


Fig. 8. NO concentration (solid symbols), pulse frequency (open symbols) ('a' and 'c') versus SIE and semi-log plot of data based on Eq. (4) ('b' and 'd') for different flow rates of process gas. The SIE was varied by varying the pulse frequency. The process gas was NO + nitrogen.

Table 2

Values of energy constant (k_E) and coefficient of determination (R^2) obtained by fitting Eq. (4) to the data from the present study under different oxygen (O_2), nitric oxide (NO), flow rates (Q), applied voltage (V) and plasma type.

O_2 (%)	NO (ppm)	Plasma	Q (L/min)	V (kV)	k_E (L/J)	R^2
Effect of flow rate (Q) of the process gas						
20	~300	Volume	Variable: 1–2	30	0.016	0.93
20	~300	Surface	Variable: 1–2	30	0.020	0.90
0	~300	Volume	Variable: 1–2	30	0.021	0.98
0	~300	Surface	Variable: 1–2	30	0.030	1.0
Effect of applied voltage (V)						
20	305	Volume	1.0	Variable: 20–30	0.015	0.96
20	358	Surface	1.0	Variable: 20–30	0.026	0.99
0	339	Volume	1.0	Variable: 20–30	0.015	0.96
0	315	Surface	1.0	Variable: 20–30	0.020	1.0
Effect of oxygen concentration in the process gas						
20	324	Volume	1.0	30	0.013	0.93
20	336	Surface	1.0	30	0.018	0.95
10	315	Volume	1.0	30	0.009	0.88
10	328	Surface	1.0	30	0.015	0.97
5	328	Volume	1.0	30	0.007	0.89
5	321	Surface	1.0	30	0.015	0.99
0	300	Volume	1.0	30	0.022	1.0
0	306	Surface	1.0	30	0.031	1.0
Effect of initial NO concentration						
0	550	Volume	1.0	30	0.011	1.0
0	553	Surface	1.0	30	0.018	1.0
0	300	Volume	1.0	30	0.022	1.0
0	306	Surface	1.0	30	0.031	1.0
0	115	Volume	1.0	30	0.056	1.0
0	122	Surface	1.0	30	0.064	1.0

free radicals and other chemically active species by reactions such as the following:



The chemically active species react with NO:





At high SIE, more reactive species are produced. That, in turn, allows the removal of more NO molecules from the gas. It explains the observation that NO removal increases with an increase in SIE.

Some of the chemically active species react with each other:



The chemically active species are inhomogeneously distributed, initially localized in and around the thin plasma channels [24]. They have a very short life time. Therefore, at high SIE, the local concentration of the chemically active species increases which favors their mutual reactions. This explains why the energy cost increases with an increase in SIE.

Metastable excited-state nitrogen atoms (N^*) lead to an undesired reaction with oxygen forming NO:



The NO removal by ground state atomic nitrogen (reaction (9)) is mainly countered by NO formation by the metastable excited-state nitrogen atoms (reaction (14)) [20].

Atomic oxygen is also involved in an undesired reaction with NO_2 , forming NO:



The NO removal by oxygen based active species (reactions (7) and (8)) is partially countered by the NO formation reaction (reaction (13)) and the reverse reaction (reaction (15)) [20].

The concentration of N^* and NO_2 is increased under high SIE. Consequently, the rates of reactions (14) and (15) are increased, an effect which contributes to the higher energy cost under higher SIE.

In the absence of oxygen, the NO is removed by reaction (9) and NO formation (reactions (13)–(15)), does not take place that explains lower energy cost compared to the presence of any amount of oxygen. Due to the lower energy requirement, the adsorption of NO followed by its thermal desorption into nitrogen and removal by plasma techniques, is being developed [15,25].

In the presence of oxygen, the nitrogen-based active species do not play a role in NO removal as reaction (9) of N is mainly countered by the effect of N^* in reaction (14). The NO removal by oxygen-based active species (reactions (7) and (8)) is only partially countered by the reverse reaction (reaction (15)) or other NO formation reactions. Therefore, oxygen-based active species are the main contributors to NO removal when oxygen is present in the ambient gas [20,25]. The concentration of oxygen-based active species increases as the oxygen concentration increases. It explains the decrease in energy cost with an increase in oxygen concentration. The NO_2 builds up as SIE is increased resulting in a dominant role of reverse reaction (15). Increased rate of loss of radicals by reaction (15) and other radical loss reactions under high SIE makes the first order kinetics (Eq. (4)) a poor fit as observed in the present study as well as in the earlier reports [21,26].

Dry air in absence of NO was fed to the reactor to estimate NO formation by reactions such as reactions (13) and (14). The NO was not detected in the exhaust gas. This is because the plasma reactors are good sources of O and O_3 , which oxidize NO into NO_2 by reactions (7) and (8). If NO is mixed with the exhaust gas, one mole of NO is converted to NO_2 by one mole of O_3 by reaction (8) [27]. The O_3 formed with dry air feed was estimated based on this principle and it was verified by direct O_3 estimation by UV-spectroscopy.

The energy yield for ozone production was ~ 90 g/kWh in the case of surface-plasma and ~ 128 g/kWh in the case of volume-plasma, which is comparable to ~ 110 g/kWh reported in literature for case of volume-plasma reactor based on pulsed corona discharges [28]. The volume plasma reactors are expected to remove NO with a lower energy cost compared to surface plasma based on energy yield for ozone production. Results of this study do not agree with this prediction, indicating that some species other than O_3 also have a significant contribution in NO removal.

Recent literature shows that atomic oxygen and atomic nitrogen in plasma are adsorbed and stabilized on dielectric surfaces. They become available for reactions with NO through the following surface mediated reactions [29,30]:



The lifetime of the adsorbed atomic oxygen (O_{ads}) and adsorbed atomic nitrogen (N_{ads}) extends to hours [29,30]. The adsorption and stabilization of the chemically active species is favored in a surface plasma reactor due to close proximity of the plasma to the surface compared to volume plasma. It explains lower energy cost for NO removal in surface plasma compared to volume plasma. This holds particularly for low oxygen concentrations where the supply of O becomes the bottle neck in the NO conversion reactions.

Any increase in energy per pulse, e.g., by an increase in applied voltage in our experiments, results in an increased concentration of the chemically active species in and around the plasma channels. It favors mutual reactions of reactive species, like reactions (10)–(13). That is why the increase in energy per pulse is commonly associated with a significant increase in energy cost for NO conversion in volume plasmas [31,32]. For example, Khacef et al. reported 25% NO_x removal at 35 mJ/pulse. At 195 mJ/pulse the NO_x removal was reduced to zero, under the same experimental conditions and at the same SIE of 30 J/L [31]. This adverse effect on the NO removal rate, caused by an increase in energy per pulse is, for surface plasmas, mitigated by the adsorption and stabilization of the chemically active species at the dielectric surface. It explains the observation that an increase in energy per pulse has a less adverse effect on the energy cost for NO conversion in the case of surface plasma compared to volume plasma.

It should be mentioned here that only selected chemical reactions are listed in the above discussion. These are the ones which help to explain the main observations in this study. A comprehensive list of reactions and their rate constants are given in earlier literature [20,33]. The NO conversion in plasmas is usually explained on the basis of free radical reactions as in the above discussion. However, the possibility of NO removal through ionic reactions, particularly those that may be initiated by the oxidation of NO to NO^+ cannot be ruled out [34]. It is well known that cations are adsorbed on the dielectric surfaces [35], which may favor surface mediated reactions of the ions. The surface mediated reactions of ions may also be a factor in the energy efficient NO removal in the case of surface plasma compared to volume plasma.

The energy costs for NO conversion, estimated from the scientific literature, vary over a wide range, from 3 to 500 eV/molecule [22]. This is due to the fact that the energy cost depends on multiple factors, such as the presence of catalysts [11–13], hydrocarbons [36–39], and ammonia [40,41], the pressure [42], temperature [38], material of construction of electrodes [43], and electrical gas discharge parameters [44]. To narrow the range, we have compared the energy cost for 50% NO removal (EC_{50}) found in this study, with that reported in literature, where the EC_{50} values were listed for NO + nitrogen in the absence of additives at atmospheric pressure and room temperature. Even under those conditions, the energy

costs still vary from 40 eV/molecule [36] to 200 eV/molecule [45], most likely the variations are due to different electrical parameters. For example, the energy cost decreases with a decrease in pulse duration [46,47], decrease in current [46], decrease in applied voltage [47], decrease in energy per pulse [31], and an increase in voltage rise time [48].

The EC_{50} we measured was ~ 50 eV/molecule in volume-plasma and ~ 40 eV/molecule in surface-plasma. This is significantly less than the 175 eV/molecule in the case of volume-plasma, and slightly less than the 50 eV/molecule in the case of surface-plasma obtained in our earlier study [9]. In this earlier study, the pulse generator was a Marx bank. In the present study it was replaced by a “Compact Pulsed Power Modulator MPC3000S-OP1”. The major change with the change of the pulse generator was the energy per pulse which was reduced from 80 mJ/pulse in the case of the Marx bank [9] to 10 mJ/pulse for the pulsed power generator presently used. The change in the EC_{50} from 175 to 50 eV/molecule can therefore be explained by the decrease in energy per pulse, in accordance with the literature [32,47,49]. Based on EC_{50} being at the lower end of the range of reported values (40–200 eV/molecule), it can be said that the volume plasma reactor in this study is comparable to the optimized plasma reactors reported in literature.

For the case of surface-plasma, the energy per pulse was reduced from ~ 20 mJ/pulse for the experiments with Marx bank [9], to ~ 2 mJ/pulse with the presently used pulsed power generator. It resulted in a decrease in EC_{50} from ~ 50 eV/molecule to ~ 40 eV/molecule. This observation supports our conclusion that the adverse effect of an increase in energy per pulse is mitigated in the case of surface plasma. This is desirable because a higher energy per pulse allows for the treatment of larger volumes of process gases, required for practical applications. It should be mentioned here that the surface plasma reactor was optimized earlier with respect to the factors that have significant effect on energy cost for VOCs removal [6].

It is well known that different plasma regimes have different energy efficiency for destruction of toxic VOCs [6,7,50–52]. The NO removal from air has been compared in volume plasma and surface plasma reactors based on dielectric barrier discharges [8]. The EC_{50} calculated from the reported data [8] is 288 eV/molecule in the case of volume plasma and it reduced to 135 eV/molecule in surface plasma. The corresponding EC_{50} values for the case of pulsed corona discharges in this study are significantly lower: 120 eV/molecule is volume plasma and 70 eV/molecule in surface plasma for NO removal from air. In some of the comparative studies [51,52] the electrode geometries were exactly the same in the compared reactors. These parameters were different in this study due to differing requirements to produce predominantly volume plasma in one case and predominantly surface plasma in the other. It should be mentioned that the effect of electrode geometries may also have contributed to the results compared in this study [53].

5. Conclusions

The energy efficiency for NO removal is dependent on the concentration of oxygen in ambient gas. The lowest energy cost for removal of NO was observed in mixtures of NO with nitrogen at high initial NO concentration.

Surface-plasma reactor has lower energy cost and higher energy constant k_E than volume-plasma reactor employed in this study, particularly for low oxygen concentrations, and under high specific input energy conditions.

The adverse effect of the observed increase in applied voltage/energy per pulse on the energy cost for NO removal is mitigated by replacing volume plasma reactor with surface plasma reactor.

Acknowledgements

This work is supported by the “Frank Reidy Fellowship in Environmental Plasma Research” and with internal funds of the Frank Reidy Research Center for Bioelectrics.

References

- [1] M.A. Malik, S.A. Malik, Pulsed corona discharges and their applications in toxic VOCs abatement, *Chin. J. Chem. Eng.* 7 (4) (1999) 351–362.
- [2] A. Mizuno, Industrial applications of atmospheric non-thermal plasma in environmental remediation, *Plasma Phys. Control. Fus.* 49 (2007) A1–A15.
- [3] H.H. Kim, Nonthermal plasma processing for air-pollution control: a historical review, current issues, and future prospects, *Plasma Process Polym* 1 (2004) 91–110.
- [4] N.L. Allen, P.N. Mikropoulos, Streamer propagation along insulating surfaces, *IEEE Trans. Dielectr. Electr. Insul.* 6 (1999) 357–362.
- [5] V. Bloschitsyn, Review of Surface Discharge Experiments, 2010, <http://arxiv.org/abs/1005.5044v1>.
- [6] M.A. Malik, Y. Minamitani, K.H. Schoenbach, Comparison of catalytic activity of aluminum oxide and silica gel for decomposition of volatile organic compounds (VOCs) in a plasma-catalytic reactor, *IEEE Trans. Plasma Sci.* 33 (2005) 50–56.
- [7] L. Oukacine, J.M. Tatibouet, J. Jolibois, E. Moreau, Ionic wind effect on the chemical reactivity, in: *Int. Symp. Non-Thermal/Thermal Plasma Pollut. Control Technol. & Sustainable Energy*, St. John's Newfoundland, Canada, June 21–25, 2010.
- [8] E. Odic, M. Dhainaut, M. Petit, C. Karimi, A. Goldman, M. Goldman, Towards a better understanding of the electrical parameters monitoring the chemical reactivity of dielectric barrier discharges at atmospheric pressure, in: *Proc. 3rd Int. Symp. Non-Thermal Plasma Technol. Pollut. Control*, Seogwipo, Cheju Island, Republic of Korea, 2001, pp. 62–67.
- [9] M.A. Malik, K.H. Schoenbach, A novel pulsed corona discharge reactor based on surface streamers for NO conversion from N_2 – O_2 mixture gases, *Int. J. Plasma Environ. Sci. Technol.* 5 (1) (2011) 50–57.
- [10] E. Odic, M. Dhainaut, M. Petit, A. Goldman, M. Goldman, C. Karimi, Approach of the physical and chemical specific properties of pulsed surface dielectric barrier discharges in air at atmospheric pressure, *J. Adv. Oxid. Technol.* 6 (2005) 41–47.
- [11] J.O. Chae, Non-thermal plasma for diesel exhaust treatment, *J. Electrostat.* 57 (2003) 251–262.
- [12] Y. Itoh, M. Ueda, H. Shinjoh, K. Nakakita, M. Arakawa, NO_x reduction under oxidizing conditions by plasma-assisted catalysis, *R&D Rev. Toyota CRDL* 41 (2) (2006) 49–62.
- [13] S.Y. Park, B.R. Deshwal, S.H. Moon, NO_x removal from the flue gas of oil-fired boiler using a multistage plasma-catalyst hybrid system, *Fuel Process. Technol.* 89 (2008) 540–548.
- [14] X.Q. Wang, Y. Li, W. Chen, G.H. Lv, J. Huang, G.X. Zhu, X.Q. Wang, X.H. Zhang, D.C. Wang, K.C. Feng, S.Z. Yang, Characteristics of NO_x removal combining dielectric barrier discharge plasma with selective catalytic reduction by C_3H_6 , *Jpn. J. Appl. Phys.* 49 (2010) 086201.
- [15] A. Mihalciou, K. Yoshida, M. Okubo, T. Kuroki, T. Yamamoto, Design factors for NO_x reduction in nitrogen plasma, *IEEE Trans. Ind. Appl.* 46 (6) (2010) 2151–2156.
- [16] S. Mohapatra, S.B. Rajanikanth, Cascaded cross flow DBD-adsorbent technique for NO_x abatement in diesel engine exhaust, *IEEE Trans. Dielectr. Electr. Insul.* 17 (5) (2010) 1543–1550.
- [17] T. Yamamoto, H. Fujishima, M. Okubo, T. Kuroki, Pilot-scale NO_x and SO_x removal from boiler emission using indirect-plasma and chemical hybrid process, *IEEE Trans. Ind. Appl.* 46 (1) (2010) 29–37.
- [18] S.M. Thagard, Y. Kinoshita, H. Ikeda, K. Takashima, S. Katsura, A. Mizuno, NO_3^- reduction for NO_x removal using wet-type plasma reactor, *IEEE Trans. Ind. Appl.* 46 (6) (2010) 2165–2171.
- [19] S. Masuda, Pulse corona induced plasma chemical process: a horizon of new plasma chemical technologies, *Pure Appl. Chem.* 60 (1988) 727–731.
- [20] B.M. Penetrante, R.M. Brusasco, B.T. Merritt, G.E. Vogtlin, Environmental applications of low-temperature plasmas, *Pure Appl. Chem.* 71 (1999) 1829–1835.
- [21] H.H. Kim, G. Prieto, K. Takashima, S. Katsura, A. Mizuno, Performance evaluation of discharge plasma process for gaseous pollutant removal, *J. Electrostat.* 55 (2002) 25–41.
- [22] M. Gundersen, V. Puchkarev, A. Kharlov, G. Roth, J. Yampolsky, D. Erwin, Transient plasma-assisted diesel exhaust remediation, in: R. Hippler, H. Kersten, M. Schmidt, K.H. Schoenbach (Eds.), *Low Temperature Plasmas: Fundamentals, Technologies, and Techniques*, second ed., Wiley-VCH Verlag GmbH, Weinheim, 2008, pp. 543–550.
- [23] B.M. Penetrante, M.C. Hsiao, J.N. Bardsley, B.T. Merritt, G.E. Vogtlin, A. Kuthi, C.P. Burkhardt, J.R. Bayless, Identification of mechanisms for decomposition of air pollutants by non-thermal plasma processing, *Plasma Sources Sci. Technol.* 6 (1997) 251–259.
- [24] G.V. Naidis, Modelling of plasma chemical processes in pulsed corona discharges, *J. Phys. D: Appl. Phys.* 30 (1997) 1214–1218.
- [25] M. Okubo, M. Inoue, T. Kuroki, T. Yamamoto, NO_x reduction after treatment system using nitrogen nonthermal plasma desorption, *IEEE Trans. Ind. Appl.* 41 (4) (2005) 891–899.

- [26] K. Yan, E.J.M. van Heesch, A.J.M. Pemen, P.A.H.J. Huijbrechts, From chemical kinetics to streamer corona reactor and voltage pulse generator, *Plasma Chem. Plasma Process.* 21 (1) (2001) 107–137.
- [27] S.Y. Mok, Oxidation of NO to NO₂ using the ozonization method for the improvement of selective catalytic reduction, *J. Chem. Eng. Jpn.* 37 (2004) 1337–1344.
- [28] W.J.M. Samaranayake, Y. Miyahara, T. Namihira, S. Katsuki, T. Sakugawa, R. Hackam, H. Akiyama, Pulsed streamer discharge characteristics of ozone production in dry air, *IEEE Trans. Dielectr. Electr. Insul.* 7 (2000) 254–260.
- [29] D. Marinov, O. Guaitella, A. Rousseau, Y. Ionikh, Production of molecules on a surface under plasma exposure: example of NO on pyrex, *J. Phys. D: Appl. Phys.* 43 (2010) 115203.
- [30] O. Guaitella, M. Hubner, S. Welzel, D. Marinov, J. Ropcke, A. Rousseau, Evidence for surface oxidation on Pyrex of NO into NO₂ by adsorbed O atoms, *Plasma Sources Sci. Technol.* 19 (2010) 045026.
- [31] A. Khacef, J.M. Cormier, J.M. Pouvesle, Energy deposition effect on the NO_x remediation in oxidative media using atmospheric non thermal plasmas, *Eur. Phys. J. Appl. Phys.* 33 (2006) 195–198.
- [32] A. Khacef, A.J.M. Cormier, J.M. Pouvesle, Non thermal plasma NO_x remediation: from binary gas mixture to lean-burn gasoline and diesel engine exhaust, *J. Adv. Oxid. Technol.* 8 (2) (2005) 150–157.
- [33] G. Sathiamoorthy, S. Kalyana, W.C. Finney, R.J. Clark, B.R. Locke, Chemical reaction kinetics and reactor modeling of NO_x removal in a pulsed streamer corona discharge reactor, *Ind. Eng. Chem. Res.* 38 (1999) 1844–1855.
- [34] E. Marotta, C. Paradisi, A mass spectrometry study of alkanes in air plasma at atmospheric pressure, *J. Am. Soc. Mass Spectrom.* 20 (2009) 697–707.
- [35] A. Kumada, S. Okabe, K. Hidaka, Residual charge distribution of positive surface streamer, *J. Phys. D: Appl. Phys.* 42 (2009) 095209.
- [36] Y.S. Mok, J.H. Kim, I. Nam, S.W. Ham, Removal of NO and formation of byproducts in a positive-pulsed corona discharge reactor, *Ind. Eng. Chem. Res.* 39 (2000) 3938–3944.
- [37] A. Mizuno, K. Shimizu, A. Chakrabarti, L. Dascalescu, S. Furuta, NO_x removal process using pulsed discharge plasma, *IEEE Trans. Ind. Appl.* 31 (1995) 957–963.
- [38] P.M. Penetrante, W.J. Pitz, M.C. Hsiao, B.T. Merritt, G.E. Vogtlin, Effect of hydrocarbons on plasma treatment of NO_x, in: *Proc. 1997 Diesel Engine Reduction (DEER) Workshop*, 1997, pp. 123–127.
- [39] C.H. Tsai, Y.F. Wang, H.H. Yang, C.N. Liao, Effects of ethylene on NO conversion and product distributions in an rf discharge reactor, *J. Hazard. Mater.* 150 (2008) 401–407.
- [40] J.-S. Chang, K. Urashima, Y.X. Tong, W.P. Liu, H.Y. Wei, F.M. Yang, X.J. Liu, Simultaneous removal of NO_x and SO₂ from coal boiler flue gases by DC corona discharge ammonia radical shower systems: pilot plant tests, *J. Electrostat.* 57 (2003) 313–323.
- [41] B.M. Obradovic, G.B. Sretenovic, M.M. Kuraica, A dual-use of DBD plasma for simultaneous NO_x and SO₂ removal from coal-combustion flue gas, *J. Hazard. Mater.* 185 (2011) 1280–1286.
- [42] G.B. Zhao, S.V.B.J. Garikipati, X. Hu, M.D. Argyle, M. Radosz, The effect of gas pressure on NO conversion energy efficiency in nonthermal nitrogen plasma, *Chem. Eng. Sci.* 60 (2005) 1927–1937.
- [43] H. Barankova, L. Bardos, Effect of the electrode material on the atmospheric plasma conversion of NO in air mixtures, *Vacuum* 84 (2010) 1385–1388.
- [44] M. Fujiwara, Short-pulse discharge for simultaneous pursuit of energy and volume-efficient NO_x removal, *Jpn. J. Appl. Phys.* 45 (2A) (2006) 948–950.
- [45] B.M. Penetrante, M.C. Hsiao, B.T. Merritt, G.E. Vogtlin, P.H. Wallman, M. Neiger, O. Wolf, T. Hammer, S. Broer, Pulsed corona and dielectric-barrier discharge processing of NO in N₂, *Appl. Phys. Lett.* 68 (26) (1996) 3719–3722.
- [46] T. Namihira, S. Tsukamoto, D. Wang, S. Katsuki, R. Hackam, H. Akiyama, Y. Uchida, M. Koike, Improvement of NO_x removal efficiency using short-width pulsed power, *IEEE Trans. Plasma Sci.* 28 (2) (2000) 434–442.
- [47] M. Kosuge, M. Fujiwara, M. Ishida, Analyses of pulse duration influence on the NO_x removal by a pulsed corona discharge with luminescence measurement, *Trans. IEE Jpn. A* 120 (A 2) (2000) 167–173 (in Japanese).
- [48] K. Shinmoto, K. Kadowaki, S. Nishimoto, I. Kitani, Influence of voltage rise time for oxidation treatment of NO in simulated exhausted gas by polarity-reversed pulse discharge, *IEEJ Trans. F&M* 129 (4) (2009) 211–216 (in Japanese).
- [49] C.L. Song, F. Bin, Z.M. Tao, F.C. Li, Q.F. Huang, Simultaneous removals of NO_x, HC and PM from diesel exhaust emissions by dielectric barrier discharges, *J. Hazard. Mater.* 166 (2009) 523–530.
- [50] H.H. Kim, H. Kobara, A. Ogata, S. Futamura, Comparative assessment of different nonthermal plasma reactors on energy efficiency and aerosol formation from the decomposition of gas-phase benzene, *IEEE Trans. Ind. Appl.* 41 (1) (2005) 206–214.
- [51] M. Schiorlin, E. Marotta, M. Rea, C. Paradisi, Comparison of toluene removal in air at atmospheric conditions by different corona discharges, *Environ. Sci. Technol.* 43 (2009) 9386–9392.
- [52] E. Marotta, M. Schiorlin, M. Rea, C. Paradisi, Products and mechanisms of the oxidation of organic compounds in atmospheric air plasmas, *J. Phys. D: Appl. Phys.* 43 (2010) 124011.
- [53] N. Georgescu, Gas treatment with repetitive pulsed corona plasmas: experiments with various geometries, *IEEJ Trans. FM* 124 (10) (2004) 921–926.