Nitrogen Oxides Decomposition Using A Dielectric Barrier Discharge Reactor

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Abstract

This paper presents experiments performed using a dielectric barrier discharge for mobile engine pollution control purposes. Measurements of NO, NOx decomposition efficiency and the resultant energy cost was achieved for sample gas mixtures (NO/N2, NO2/N2) and for real diesel engine exhaust gas. Experiment results show that a significant NO decomposition rate of 65-76% (in NO (=644ppm and 166ppm)/N2) can be obtained with the reactor used. The related energy cost was <300eV per NO molecule removed. Experiments in NO/N2 also demonstrated that varying the power injection into the reactor lead to a considerable reduction of the energy cost while keeping high decomposition rate. With diesel exhaust gas, 66% of NOx decomposition (initially 115ppm) was achieved for an energy cost of 464eV/NOx.

1. Introduction

The enormous increase in the use of fossil sources, in particular in the industrialized nations, is unfortunately associated with an increase in air pollution. Vehicle exhaust is a significant contributory factor. Among automobiles, diesel vehicles are considered to be the most pollutant, particularly with regard to nitrogen oxides (NOx=NO+NO2), sulphur dioxide (SO2) and particulate emissions (e.g. lubrication oil, soot, unburned fuel) [1]. Because of its detrimental effect on human health and the environment [2], reduction of NOx emission will continue to be a central concern in the future.

Several laboratories have already demonstrated that non-thermal plasma can be an effective post-combustion technique for flue gas treatment [3] and for car exhaust pollution control [4, 5]. From among the different ways to produce non thermal plasma, dielectric barrier discharges (or silent discharges) have been extensively used for various kinds of applications.

Conventional dielectric barrier discharge comprises two electrodes with at least one covered by dielectric (e.g. glass). The discharge is energised by alternating voltages with frequencies ranging from few tens of Hertz to several kHz. Typical gap spacings are of a few mm. Charge accumulation on the dielectric surface generates an electric field that reduces the local field and interrupts the current flow. The dielectric then prevents the transition to a spark discharge. This type of discharge has several advantages. It produces at atmospheric conditions, stable and uniform plasma in the form of a multitude of micro discharges, statistically distributed in space and time. The average electron energy is high enough to generate (through collisions with the background molecules) the reactive species necessary to decompose the NOx. Dielectric barrier discharge is well suited for processing large amounts of gas [6,7].

This paper describes experiments performed using a dielectric barrier discharge reactor, for mobile engine pollution control. Our initial objectives were to decompose small concentrations of NO in nitrogen and NO2 in nitrogen under various operating conditions. The results were then compared with experiments done using exhaust gas from a real diesel engine [8]. The main focus was to measure the NO, NOx decomposition efficiency, the power consumed by the reactor and the resultant specific energy consumption (eV/NO, eV/NOx). From the initial
stage of these experiments we could determine the optimum plasma operating conditions that will lead to further experiments using the real diesel engine.

2. Experimental description

2.1 Power supply and diagnosis apparatus

The electrical circuit used to energize the plasma reactor is shown in fig. 1. It consists of a power amplifier capable of delivering a 500 VA sinusoidal signal with a frequency ranging from 45Hz to 1kHz. This primary wave form was introduced into a transformer to feed the reactor. The applied voltage to the reactor could be continuously varied from 0 to 20kV, at the same frequency range. Charge and secondary voltage were measured with a 0.22μF series capacitor and a capacitive-resistive high voltage probe (Tektronix P6015A). Both charge and voltage were also measured with a digital oscilloscope. The waveform data was transmitted to a computer via a GPIB interface for further analysis.

The power consumed by the plasma reactor was determined by Lissajous' method [9]. The power consumed by the reactor (W) was varied by changing either the peak value of the applied voltage or its frequency.

![Fig. 1. Power supply and electrical diagnosis system](image1)

2.2 Gas flow system

As previously stated by [4], [5] and [10] NO molecules contained in mobile engine exhaust gas should be decomposed via the reduction of NO by N radicals and not via the oxidation of NO to NO₂. The reduction pathway:

\[ N + NO \rightarrow N₂ + O \]  \hspace{1cm} \text{(1)}

leads to acceptable products while the oxidation of NO leads to products that may need further processing or the presence of additives. The objective of optimising the performances of our plasma reactor for diesel engine exhaust gas treatment at first necessitated the decomposition of small concentrations of NO in N₂. This type of gas (i.e. gas without the presence of O₂ and H₂O) will lead to the above more favourable reduction pathway. The N atoms necessary for the reduction of NO are generated through the reaction:

\[ e + N₂ \rightarrow N + N + e \]  \hspace{1cm} \text{.....(2)}

(a) Experiments using sample gas

Fig. 2 shows a schematic diagram of the gas flow system. Sample gas, N₂ base containing 166ppm (or 644ppm) of NO, was used in the first series of experiments. Sample gas, N₂ base containing 208ppm (or 1071ppm) of NO₂, was also used for reference. These concentrations were chosen because they correspond to those found in diesel-powered vehicles' exhaust.

(b) Experiments using diesel exhaust gas

The experiment set-up (detailed in [4]), mainly consists of a diesel engine and a cooler to trap water vapour and reduce the gas temperature. In this case oil was injected from the top of the reactor in order to trap particulate emitted from the diesel engine. Without this oil injection, particulate builds up, forming a thick deposit on the electrodes. This layer of dust decreases the gap length which greatly influences the electric characteristics of the discharge.

![Fig. 2. Gas flow system](image2)
necessary gas quantity was transferred to the gas analysers. The NOx meter (Shimazu NOA-305) allowed us to measure both quantities NO and NOx. This meter's measurement technique is based on the chemical luminescence method. The O2 meter (Shimazu POT-101) based on the magnetic measurement method helped us to confirm that NO was reduced to harmless products such as N2 and O2.

<2.3> Experimental conditions

(a) In the case of sample gas, the gas was introduced into the reactor at room temperature and the flow rate was varied from 10 to 30ℓ/min. The reactor was energized by the power supply mentioned in section 2.1 at frequencies between 50Hz and 900Hz.

(b) When using diesel exhaust, the experiments were done under the following conditions. The engine speed and load were set at 1200 rpm and 7kg.m respectively. The gas flow rate into the reactor was 30ℓ/min, the initial concentration of NOx was 115ppm and the gas temperature was maintained between 27 and 30 ºC. The reactor was powered by an alternating HV transformer at a frequency of 50Hz.

3. Results and discussion

Fig. 4 and Fig. 5 show the concentrations of both decomposed NO and generated NO2 during discharge processing, as a function of the power consumed by the plasma reactor. As we also wanted to determine the effect of gas residence time variation on the decomposition process, the results are shown for three different flow rates.

In all cases the percentage of NO decomposed was determined by the following equation:

\[
\%NO_{\text{decomposed}} = \frac{[NO]_{\text{init}} - [NO]_{\text{final}}}{[NO]_{\text{init}}} \times 100
\]

where \([NO]_{\text{init}}\) is the initial concentration of NO in the sample gas (i.e. before plasma treatment) and \([NO]_{\text{final}}\) is the concentration of NO after treatment in the plasma reactor.

In the case of NOx decomposition efficiency \([NO]_{\text{init}}\) and \([NO]_{\text{final}}\) were replaced by the concentrations of NOx (=NO+NO2) before and after treatment.

Fig. 4 shows that when decomposing small concentrations of NO in N2 (166ppm), NO concentration generally decreased to about 55-75% at a power between 40 and 50 Watts. Meanwhile NO2 was generated via the oxidation of NO.

\[
\text{NO} + \text{O} + \text{N}_2 \rightarrow \text{NO}_2 + \text{N}_2
\]

The concentration of NO2 was ≈20ppm at the same power. When increasing the power to 100 Watts and more, NO2 generation could be completely eliminated. This removal mainly occurred via the reduction of NO2 to NO.

\[
\text{NO} + \text{O} \rightarrow \text{NO} + \text{O}_2
\]

\[
\text{NO}_2 + \text{N} \rightarrow \text{NO} + \text{NO}
\]

As these reactions regenerate NO and also consume N atoms, NO decomposition efficiency is reduced.

The plasma reactor shown in Fig.3 was designed to treat a large amount of gas, comprising several pollutants. It is a planar-parallel type reactor with one inner electrode made of a stainless steel mesh (HV) and two grounded electrodes made of PYREX plate glass (\(e_s=4.6\); thickness 2mm) with Nickel coated on their outer surface. The discharge gap between each plate glass and the inner electrode was fixed at 5mm.

The dimensions of this reactor are 400mm long and 300mm wide giving a mean discharge area of 1200 cm² and an active discharge volume of \((1200[cm^2] \times 0.5[cm]) \times 2 = 1200cm^3\). The bottom part of this reactor is an oil separator.
However this decrease of less than 10% did not occur when the gas flow rate was 30ℓ/min.

For a consumed power below 100 to 120 Watts, the smaller the gas flow rate, the higher (smaller) the NO decomposition efficiency (concentration) was. This was due to a longer gas processing time. For a power higher than 120 Watts, the effect of gas flow rate variation is not clearly shown on Fig. 4. It is interesting to note that when the power was greater than 120 Watts, NO concentration decreased only for a gas flow rate of 30ℓ/min. This is an effect that will be validated or invalidated with further experiments at higher gas flow rate.

With 644ppm of NO, the concentration of generated NO\(_2\) is higher than with 166ppm of NO. NO\(_2\) is also nearly eliminated for a power higher than 100Watts. In Fig. 5, NO concentration increased with an increase in gas flow rate, for a power lower than \(\approx 100\)Watts, whereas it was in Fig.4 for a power below 100 to 120Watts.

Experiments were done for a gas flow rate of 25ℓ/min. In all cases, for a power between 0 and 80Watts, NO\(_x\) decomposition efficiency increased with the power. When decomposing small and large amounts of NO\(_2\) in N\(_2\), each at the same power consumption, the difference in NO\(_x\) decomposition efficiency is similar to that of NO/N\(_2\) sample gas. The maximum NO\(_x\) decomposition was 63% for a power of 50Watts (NO\(_2\) 208ppm) while at the same power, it was 18% for 1071ppm of NO\(_2\).
Fig. 6. Comparison between NO$_2$/N$_2$ and NO/N$_2$ sample gases at varying concentrations.

In Fig. 7 the results of experiments in NO/N$_2$ sample gas are compared with experiments done using the exhaust gas from a real diesel engine. NO$_x$ decomposition efficiency is shown as a function of the power consumption at the same gas flow rate (30liter/min).

Fig. 7. Comparison between NO/N$_2$ sample gas and diesel exhaust gas.

For a power below 60watts, NO$_x$ decomposition efficiency for both cases is nearly equal. The diesel exhaust had a maximum of 66% of NO$_x$ decomposition efficiency for a power of 70Watts. The same efficiency was obtained in sample gas for a power of 134Watts. This discrepancy is due to the difference in gas composition. In diesel exhaust, NO$_x$ decomposition is also due to plasma chemistry reactions involving O$_2$, H$_2$O [11], unburned hydrocarbons [12] and lubricant oil. Despite the difference between the gas compositions and taking into consideration the fact that we used oil injection only in the case of diesel exhaust (see section 2.2.b) both experimental results are under certain conditions comparable. Experiments in sample gas can therefore lead to useful information concerning plasma operating conditions and help to improve the performance of the reactor when processing diesel exhaust. We will also take into consideration the effect of each component in diesel exhaust gas, to improve future investigations.

The specific energy consumption (or energy cost) defined as the dissipated energy in a process per removed pollutant (eV/molec.), is a parameter that has been established to evaluate the efficiency of NO$_x$ (or NO only) decomposition with respect to energy consumption. The specific energy consumption is given by:

$$W_{spc}(eV/molec.) = 897 \times \frac{W(Wh/m^3)}{\Delta n(ppm)} \quad \ldots(7)$$

Where: $W(Wh/m^3)$ is the energy density expressed in Watt-hour per cubic meter. $\Delta n$ is the difference between initial NO$_x$ (or NO only) concentration (before plasma treatment) and final NO$_x$ (or NO only) concentration (after plasma treatment) in ppm. The factor 897 is a conversion factor that permits the specific energy consumption to be expressed in units of electron volts per molecule.

Fig. 8 shows NO decomposition efficiency as a function of the injected energy density into the reactor. The results are presented for NO/N$_2$ sample gas used with two different concentrations (166 and 644ppm of NO).

For both cases NO decomposition is not always increasing with the energy density. With 166ppm of NO in N$_2$ the decomposition efficiency shows two maxima. The first one has a value of 76% at an injected energy density of 38 Wh/m$^3$. This is a significant decomposition of NO. The corresponding specific energy consumption is 275 eV per molecule of NO decomposed.

Further increase of the injected energy density leads to the second maximum which is 82.5% at a energy density of 207 Wh/m$^3$. Despite this high decomposition rate, the related specific energy consumption is rather high. It is 1359eV per molecule of NO decomposed. With 644ppm of NO in N$_2$ the decomposition efficiency increases with the injected energy density (up to 65% at 98 Wh/m$^3$) and then it decreases. An efficiency of 65% is also significant, especially when decomposing high
concentrations of NO. The specific energy consumption is rather low. It is 212eV per molecule of NO decomposed.

Fig. 8. NO decomposition efficiency (%) as a function of the injected energy density (Wh/m³)

With the objectives of determining the optimum plasma operating conditions, it was then necessary to look in detail, how the energy was injected into the reactor. To decompose 166ppm of NO it was injected, for the two particular cases mentioned before, as follows:

At 76% of efficiency, the frequency of the secondary voltage was 100Hz and the peak value of the voltage was 17kV.

At 82.5% the frequency was also 100Hz and the peak value was 20kV.

With 644ppm of NO at 65% the frequency of the secondary voltage was 300Hz and its peak value was 14.5kV.

The optimum plasma operating conditions with respect to energy consumption are then determined for decomposition of small concentrations of NO by applying low frequency voltage and intermediate peak value voltage. For decomposition of large concentrations of NO these optimum conditions are obtained by increasing the frequency while decreasing the peak value of the voltage. These plasma operating conditions will certainly help to improve the performance of the reactor for diesel exhaust gas treatment.

A list of the results for NO and/or NOₓ decomposition obtained during these experiments, for each type of gas, is shown in table 1. In this table, the gas type, initial concentration (NO or NO₂ or NOₓ), the maximum decomposition efficiency achieved, the efficiency for decomposition of 50% of NO or NOₓ (when possible), and the related energy cost are given. It should be mentioned that for NO/N₂, the NOₓ columns refer strictly to the same experimental conditions as NO columns.

Table 1. List of NO, NOₓ decomposition efficiency and corresponding energy cost.

<table>
<thead>
<tr>
<th>Gas type</th>
<th>NO decomposition (%)</th>
<th>Related energy cost (eV/NO)</th>
<th>NOₓ decomposition (%)</th>
<th>Related energy cost (eV/NOₓ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO/N₂</td>
<td>Max 82.5</td>
<td>1398</td>
<td>80</td>
<td>1398</td>
</tr>
<tr>
<td>166 ppm</td>
<td>76</td>
<td>275</td>
<td>75</td>
<td>1394</td>
</tr>
<tr>
<td>NO/N₂</td>
<td>Max 65</td>
<td>171</td>
<td>44.4</td>
<td>194</td>
</tr>
<tr>
<td>644 ppm</td>
<td>50</td>
<td>152</td>
<td>12</td>
<td>218</td>
</tr>
<tr>
<td>NO/N₂</td>
<td>Max 63</td>
<td>148</td>
<td>15</td>
<td>155</td>
</tr>
<tr>
<td>200 ppm</td>
<td>-</td>
<td>-</td>
<td>Max 25</td>
<td>154</td>
</tr>
<tr>
<td>NO/N₂</td>
<td>Max 66</td>
<td>146</td>
<td>43</td>
<td>464</td>
</tr>
<tr>
<td>1071 ppm</td>
<td>-</td>
<td>-</td>
<td>Max 50</td>
<td>410</td>
</tr>
</tbody>
</table>

From table 1 we see that for NO/N₂ and diesel exhaust, significant NO, NOₓ decomposition was achieved using a dielectric barrier discharge. The results in NO/N₂ sample gas show that varying the way to inject energy into the reactor can lead to a considerable reduction of the energy cost while keeping a high decomposition rate. The specific energy consumption was in diesel exhaust 464eV/NOₓ for a reduction of 66% of 115ppm. We intend to reduce the energy cost for diesel engine exhaust treatment by applying the optimum plasma operating conditions determined from experiments in NO/N₂ sample gas.

4. Conclusion

We have successfully developed a dielectric barrier discharge for pollution control purposes. The evaluation of NO, NOₓ decomposition efficiency and energy cost was made using NO/N₂ sample gas and diesel exhaust gas.

This reactor when used with NO/N₂ had a significant NO decomposition rate and a rather low specific energy consumption. The energy cost for decomposing 76% of an initial concentration of 166ppm of NO was 275eV/NO. It was 212eV/NO when decomposing 65% of the same gas but with a higher initial concentration of NO (644ppm).

From experiments in sample gas we found that varying the way of injecting power into the reactor lead to a considerable reduction of the energy cost while keeping a high NO decomposition rate.
Significantly, this reactor also decomposed 66% of 115ppm of NOx, contained in real diesel engine exhaust with an energy cost of 464eV/NOx. These results demonstrate that this type of dielectric barrier discharge (1 HV electrode and 2 grounded electrodes) can be very effective for pollution control. This reactor which has a capacity to treat 1.2e of gas, will in the near future be tested under practical conditions (higher gas flow rate).

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References


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