Removal of Nitric Oxide by point to plane and multipoint to plane DBD in exhaust vehicle gases.

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Abstract:

The objective of this study is to characterise point-plane and multipoint-plane DBD corona reactors able to remove NOx in a simulated exhaust vehicle gas. To do so, the plasma chemical reaction pathway has been elucidated from the monitory of the chemical composition of the reactor exhaust gas.

Hydrocarbons and NOx by-products were systematically investigated using a gas chromatography coupled to a mass spectrometry (GC/MS). NOx (NO and NO2) and CO output were also monitored with a gas analyser in order to complete the mass balance.

Temperature, reactant composition and discharge energy densities (controlled by a numerical oscilloscope) were the operating parameters under study in wet and dry air mixture. Different dielectric materials such as Al2O3/SiO2 and TiO2 on Al2O3/SiO2 support have been used.

The (N2/O2/C3H8/NO/H2O) system has been shown to generate a significant amount of aldehyde. CH3NO2 and CH3ONO2 are the main R-NOx compounds produced.

1. Introduction

The purpose of this work is to qualify the control pollution mechanisms in an impulsionnal plasma reactor at atmospheric pressure. Study is carried on NOx removal in the mixture exhaust (O2: 15%, CO2: 10%, H2O: 5%, C3H8: 1000 ppm, NO: 1000 and 350 ppm, N2: Complement).

Corona Discharges are realized in non-uniform gaps. Pointe-plane and multipoint-plane geometries have been used. The first one is adapted to characterize the elementary discharge phenomena. The second reactor is useful to increase the density of elementary discharges and the gas treated flow, which is convenient to the industrial approach. Koichi & al have already investigated the effect of the multipoint electrode configuration on the characteristics of a discharge and NOx removal [1]. A dielectric barrier covers the plane electrode to prevent arcing. Electrical behaviors of those reactors are studied in order to optimize the operating parameters (dielectric, gap, temperature, gas flow, and water vapor...). Stability of the impulsionnlar discharge is qualified by energy cost, impulsion, electrical characterization and efficacy of gas treatment. The output products are analyzed on-line via a Gas Chromatography coupled with a mass spectrometry (for the heavy and semi-volatile compounds) and a gas analyzer as well as Dräger tubes (for NOx and CO).

Oxygen excitement phenomena by direct impact electronic are shown to be important to release reaction mechanisms. Those reactions are responsible, either in gas phase or dielectric surface, of pollutants removal (NO, NO2, C3H8) according to the gas mixture and to the temperature.
2. The experimental set-up and procedure
The experimental apparatus used for measurements and for step by step monitoring of the by-products evolution consist of:
The impulsion Corona Discharge reactors described in figure 1.
A gas inlet system and auxiliary devices (GC/MS, gas analyzer, colorimetric detector tubes “DRÄGER tubes”, water heating system)
The electrical circuit described in figure 2.

![Electrical circuit and energy calculation method](image)

The point-plan and the multipoint-plan reactors are both supplied with Alternative Courant which generate a high voltage varying from 5 to 20 kV peak to peak, at a 45 kHz frequency. In order to characterize the impulsion (frequency, duration, intensity, and energy densities...), a numerical oscilloscope LeCroy 500 MHz has been used.
Indeed, the objective is to convert the reactor energy cost into Joule per liter term in order to qualify the efficiency of NOx treatment.

Point-plan reactor generates impulsive discharges allowing the understanding of the elementary phenomena as soon as electrical, energetic and hydrodynamic [2]. In a first step, the work concerns particularly the balance material settling on the NOx and on the carbon, considering heavy compounds formation. The water role is also studied.
The electrical characteristics as well as the relation between tension, intensity and pulses duration have been investigated. Then, material nature (figure 3) was validated on the dielectric (stumatite, CaTiO$_3$ and TiO$_2$).

![Figure 3: Dielectric analyzes. a) MEB-RX photo b) Analyze by Plasma Spectroscopy Induct by Laser](image)

This study ended as for use a point-to-dielectric barrier distance of 4 mm, a dielectric thickness of 4 mm, an input gas flow included between 0.5 and 2 L/min. An impulsion having a 3 nC charge and 200 ns duration, for a tension of 14 kV peak to peak. The deposed energy varied between 50 and 400 J/L.

In this study, the NOx removal has been performed using multipoint-plan geometry including 13 points, each one with 5 mm height and 1 mm diameter. The thickness of the dielectric barrier (SiO$_2$ / Al$_2$O$_3$) is 4 mm. The points-to-dielectric barrier distance is 2 mm. The input gas flow rate and the energy in the plasma reactor varied respectively from 5 to 13 L/min and from 5 to 350 J/L. Impulsions have by mean a 2 nC charge, a 100 mA intensity and 100 ns duration. Plasma can be generated with 8 kV pkpk voltage.

3. Study of mass balances in the case of a model gas mixture

The gas mixture (O$_2$: 10 %, CO$_2$: 10 %, H$_2$O: 5 %, C$_3$H$_6$: 1000 ppm, NO: 1000 and 350 ppm, N$_2$: Complement) represents a diesel exhaust in which COV is represented by the propylene. The main difficulty of this study consists on validating the mass balances on contents included between 100 and 3000 ppm. Actually, experimental measurements induced a deficiency of the mass balance, due to the process of hydrocarbon conversion into solid aerosol particles and to the formation of many acid compounds as consequence of condensation mechanisms.

However, the use of the analysis techniques showed:

i) An excess of COV form carbon with regard to the initial concentration of carbon contained in the introduced propylene, due to the transformation of CO$_2$ into CO and COV, during the impulse discharge at high temperature (130°C).

ii) Hydrocarbon conversion into solid aerosol. Their analysis have been investigated by GC / MS to consider the polycyclic forming.

iii) The NO$_x$, H$_2$O, HNO$_3$ condensations.

Then the only way to validate the total mass balance is the isotopic labeling.

3025
4. NO conversion

The evolution of NO and NO₂ contents according to energy density (figure 4) makes an excess of NO₂ production with regard to NO decrease. Further more, the point-plane energy density cost is significantly more important than the multipoint-plane one. For example, the NO removal is estimated to 50% with 100 J/L and 250 J/L input energy density, respectively in multipoint-plane and point-plane reactors. A weak content of NO is probably converted into RNOₓ compounds which shown in figure 7.

![Figure 4: Evolution, as a function of the energy density of the NO, (NO, NO₂) concentration](image)

The role of the following parameters has been investigated:
- NO concentration and gas flow: The evolution of NO and NO₂ concentrations as a function of the input energy density is shown in figure. 5. The experimental conditions are the same as in Figure 4 (a) except flow rate and initial NO concentration (13 L/min and 350 ± 5% ppm).

![Figure 5: Evolution, as a function of the energy density of the NO, (NO, NO₂) concentration (Multipoint-plane: 13 L/min; O₂: 10%, CO₂: 10%, H₂O: 5%, C₄H₁₀: 1000 ppm, NO: 350 ± 5% ppm, N₂: Complement, T: 130°C)](image)

For input energy densities varying between 40 and 120 J/L, a significant reduction of NO with increasing of the energy is observed while NO₂ concentration still increases. Thereby NOₓ (NO+NO₂) concentration remains almost constant. This suggests that most of NO change into NO₂ by oxidation. Also it can be noticed that NOₓ is easily removed (NO/NOₓ as a function of NO) under the lower initial NO concentration and reactor performance in NO and NOₓ removal cost energy density is probably affected by the inlet gas flow.

- Role of H₂O: With an energy estimated at 100 J/L and using the multipoint-plane configuration, the NO removal in the gas mixture (O₂ (10%), CO₂ (10%), C₄H₁₀ (1000 ppm),
NO (1000 ± 5% ppm), N\textsubscript{2} is equal to 40 % without water against 50 % with water (5% in volume). The conversion rate of the total NO\textsubscript{x} (NO+NO\textsubscript{2}) increases from 15% to 30%.

Here is a summary of the overall results (point-plane and multipoint-plane reactors) with a similar gas system composition at 100 J/L and 300 J/L energy density:

<table>
<thead>
<tr>
<th>Energy: 100 J/L</th>
<th>With 5% H\textsubscript{2}O</th>
<th>Without H\textsubscript{2}O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point-plane</td>
<td>NO  (5% ppm)</td>
<td>NO\textsubscript{2}  (5 ppm)</td>
</tr>
<tr>
<td>(1 L/min)</td>
<td>790 ppm</td>
<td>160 ppm</td>
</tr>
<tr>
<td>Multipoint-plane</td>
<td>500 ppm</td>
<td>200 ppm</td>
</tr>
<tr>
<td>(5 L/min)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Energy: 300 J/L</th>
<th>With 5% H\textsubscript{2}O</th>
<th>Without H\textsubscript{2}O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point-plane</td>
<td>NO  (5% ppm)</td>
<td>NO\textsubscript{2}  (5 ppm)</td>
</tr>
<tr>
<td>(1 L/min)</td>
<td>450 ppm</td>
<td>280 ppm</td>
</tr>
<tr>
<td>Multipoint-plane</td>
<td>420 ppm</td>
<td>280 ppm</td>
</tr>
<tr>
<td>(5 L/min)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The conversion way of NO in a humid atmosphere has been already studied [3]:

OH is formed first by the reaction of H\textsubscript{2}O with O (\textsuperscript{1}D) and by the electron impact dissociation of H\textsubscript{2}O according to:

\[
\text{H}_2\text{O} + \text{O} (\textsuperscript{1}D) \rightarrow 2 \text{OH} \\
\text{e} + \text{H}_2\text{O} \rightarrow \text{H} + \text{OH} + \text{e} \\
\text{e} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{OH}
\]

Oxidation of NO takes place by a number of reactions, the main ones being,

\[
\text{NO} + \text{OH} \rightarrow \text{HNO}_2 \\
\text{NO} + \text{NO}_2 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_2 \\
2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_2 + \text{HNO}_3
\]

- The dielectric material (stumatite or stumatite + TiO\textsubscript{2}) modifies the NO\textsubscript{x} behavior (Figure 6). The presence of TiO\textsubscript{2} on the dielectric support (stumatite) makes the oxidation of NO via NO\textsubscript{2} less efficient.

![Figure 6: Evolution according to the energy density of the NO\textsubscript{x} (Point-plane: 1 L/min, O\textsubscript{2}: 10%, CO\textsubscript{2}: 10%, C\textsubscript{6}H\textsubscript{6}: 1000 ppm, NO: 1000 ±5% ppm, N\textsubscript{2}: Complement; T: 130°C)](image-url)
5. Analysis of the impulsive discharge by-products COV

The analyze of the by-products treatment of a gas mixture containing CO₂, CO, and C₃H₆ is realized by GC / MS [chromatography column ChromPack PoraPlot Q (25 m-0.32 mm-10μm, phase polymer: polystyrene - divinly-benzene); introduction of gas throw a 100 μL sampler, vector gas: helium (pressure: 0.3 kg / cm²)].

The CO measurement was obtained by the gas analyzer. According to input energy, we observe an increase of the CO content and an excess of the balance carbon with regard to the initial concentration of carbon contained in the introduced propylene. That is certainly due to the transformation of CO₂ into CO and COV, during the impulsion discharge at high temperature.

Finally, study shows in both cases (point-plane or multipoint-plane reactors) the oxidation phenomena of the propylene via aldehyde and alcoholic compounds, along with the CO₂ and CO production. A minority of RNOₓ, generated by the reaction radical / NOx is as well formed (Figure 7). The destruction propylene rate varies between 40 and 70 % according to the geometry of electrodes, the dielectric and the gas mixture.

![Figure 7: Chromatogram of gas mixture treated by corona discharge (Multipoint-plane: 5 L/min: O₂: 10 %, CO₂: 10%, H₂O: 5 %, C₃H₆: 1000 ppm, NO: 950 ±50 ppm, N₂: Complement, T: 130°C)](image)

6. Conclusion

The removal of NOₓ (NO and NO₂) using barrier discharge has been investigated experimentally. Point-plane and multipoint-plane geometries were used. Plasma can be produced at atmospheric pressure in a 2 mm gap with 8 kV peak to peak concerning the multipoint-plane reactor, and in a 4 mm gap with 14 kV pkpk for the point-plane reactor. Impulsion generated by multipoint-plane configuration is characterized by a 2 nC charge, a 100 mA intensity and 100 ns duration. With this reactor, at 350 ppm of NO concentration, NO can be removed to 70% from the gas used. The production of NO₂ increases with the NO removal. The energy density that input into the discharge to reduce the NO is approximately 40 J/L at 50% reduction from a gas mixture containing 350 ppm of NO.

Removal of NO, NO₂ and production of COV compounds by oxidation process depend on oxygen atomic reactivity.
. The dielectric nature controls the electrical parameters of the impulsional discharge like the pulse characteristics, electron energy distribution and the oxidation reactions of the COV in various phases.

Acknowledgments
Authors acknowledge GIE, Peugeot Citroen, Renault and the CNRS-ECODEV for the financial support and Mrs. M.F Gonnord for the development of GCMS analysis.

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