

Nitrogen oxides and methane treatment by non-thermal plasma

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Abstract. Non thermal plasma was used to treat nitrogen oxides (NO_x) and methane (CH₄), since they are important constituents of hydrocarbon combustion emissions processes and, both gases, play a key role in the formation of tropospheric ozone. These gases are involved in environmental problems like acid rain and some diseases such as bronchitis and pneumonia. In the case of methane is widely known its importance in the global climate change, and currently accounts for 30% of global warming.

There is a growing concern for methane leaks, associated with a rapid expansion of unconventional oil and gas extraction techniques as well as a large-scale methane release from Arctic because of ice melting and the subsequent methane production of decaying organic matter. Therefore, methane mitigation is a key to avoid dangerous levels of global warming.

The research, here reported, deals about the generation of non-thermal plasma with a double dielectric barrier (2DBD) at atmospheric pressure with alternating current (AC) for NO_x and CH₄ treatment. The degradation efficiencies and their respective power consumption for different reactor configurations (cylindrical and planar) are also reported.

Qualitative and quantitative analysis of gases degradation are reported before and after treatment with cold plasma. Experimental and theoretical results are compared obtaining good removal efficiencies, superior to 90% and to 20% respectively for NO_x and CH₄.

1. Introduction

Nitrogen oxide (NO) and methane (CH₄) are important constituents in emissions from hydrocarbon combustion processes having a direct impact on formation of tropospheric ozone. The methane plays a key role in the global climate change; it is currently responsible for 30% of global warming. Concern about methane has increased due to leakage during extraction of unconventional combustibles, as well as the possibility of a large-scale discharge of methane from the Arctic: as the layer ice melts methane, product of decaying organic matter, is released into the atmosphere. Moreover, methane is a growing source of energy, and its mitigation is then necessary to diminish dangerous levels causing global warming.

NO_x refers to a set of emissions mostly composed of nitric oxide (NO), nitric dioxide (NO₂) and nitrous oxide (N₂O), generated in the combustion of any fuel, due to high temperatures and the



availability of oxygen and nitrogen. When gases leave the chimney or exhausts cars, NO is oxidized in the atmosphere to NO₂.

Specifically combustion emissions from vehicles have numerous compounds; a characterization of these emissions mainly reports hydrocarbons (methane, ethane, pentane, octane) nitrogen monoxide, nitrogen monoxide, sulfur dioxide, carbon monoxide and carbon dioxide [1].

Regulations around the world are then continuously implemented in order to reduce these gases, European regulations [2, 3] are strictest and the necessity of green technologies becomes critical.

In our laboratory previous work of gas depollution with non-thermal plasma was realized [4-6]. In this work, in order to simplify and to better understand the effect of non-thermal plasma in this kind of emissions; a mixture of 1100ppm NO_x balanced in air and 5000ppm of CH₄ was used. The influence of the hydrocarbon on NO_x removal is evidenced with higher removal efficiencies when CH₄ concentration augments.

2. Chemical model

The model considers a gas mixture (NO, helium, air, water vapor, CH₄) and two principal phases in the discharge: the first one corresponds to a very energetic microdischarge head responsible of radicals' formation and, the second phase, the interaction of radicals with toxic compounds.

When electric discharge initiates, a seed electron is formed, gain energy from the applied electric field and lose some of it through collisions with neutral molecules (air and water). These molecules produce reactive species such as free radicals N[•], •OH, and O[•]. They interact, after with NO and CH₄ through thousands of reactions.

Time for noxious molecules degradation is very short, typical time to accomplish the first phase is approximately 1x10⁻⁸ s [7, 8], whereas the interaction of radicals with molecules takes place at around few seconds. The chemical process is outlined in Figure 1.

A more detailed description about theoretical model considerations is depicted by Moreno [Moreno 2008]; in this work the influence of helium in the discharge is taken into account. A very energetic metastable of helium is found at He(2³S), with approximately 20eV of intern energy and its interaction during the discharge would be then important by Penning effect. However, when water vapor is present in the discharge, this effect is strongly diminished [9] as well as the generation of O[•] radicals. Subsequently the influence of this metastable in NO_x treatment is not considered in this work.

Furthermore, the influence of He on electrons generation is essential. In several studies the electrons are assumed to be in equilibrium with local field, however this assumption is wrong on the sheath region and, moreover, taking into consideration that gas ionization in atmospheric DBD is significant only over timescale of 1μs [10]; the formation of electrons during the first phase of the microdischarge formation are then calculated in function of electronic temperatures.

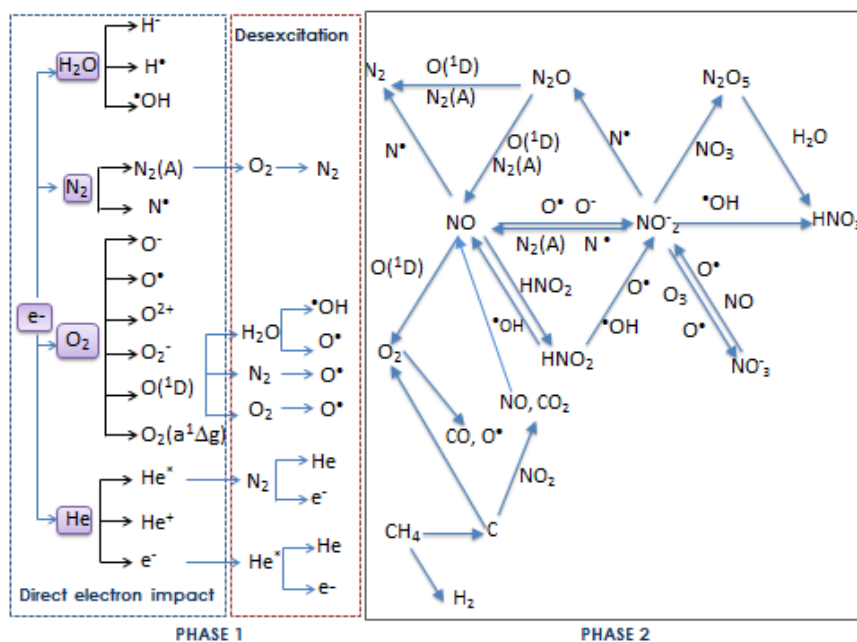


Figure 1. Mechanism of formation of active species in microdischarge head (phase 1) and microdischarge body (phase 2)

3. Experimental setup

To produce the non-thermal plasma, an AC power source was developed. This energy source works with a high frequency series resonant inverter in the range of 20 kHz to 180kHz, able to generate a voltage of 15 kV [11]. The discharge can be sustained at atmospheric pressure using nitrogen or air, as plasma gas. The experimental conditions of this special case were: 36V, 2-5A and 160kHz.

The reactor utilized to treat the gases has a double dielectric barrier configuration. Inlet and outlet gases were analyzed with a PG-250 able to identify and quantify CO , CO_2 , NO_x , SO_2 and O_2 , a mass spectrometer was also used to identify compounds formed. The experimental system used in the degradation of NO - CH_4 mixture is shown in Figure 2.

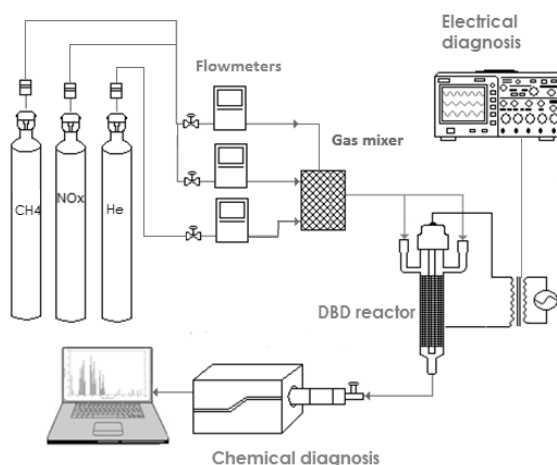


Figure 2. Experimental set up

4. Results

a) Kinetic model

To determinate the electronic temperature (T_e), an optical spectroscopy emission study was realized to the plasma, the Boltzmann plot method was employed with NII lines situated at 340.81nm, 391.90nm and 547.80nm. From this, the electronic temperature was deduced obtaining $T_e = 0.828\text{eV} \cong 9604.8\text{K}$. This temperature was used to subsequently calculate coefficients of reactions with helium [10], as detailed in table 1.

Table 1. Reaction coefficients of He reactions

| Reaction | Reaction coefficient (cm^3/s) |
|--|---|
| $\text{e} + \text{He} \longrightarrow \text{He}^* + \text{e}$ | 1.6277×10^{-19} |
| $\text{e} + \text{He} \longrightarrow \text{He}^+ + 2\text{e}$ | 1.6429×10^{-22} |
| $\text{e} + \text{He}^* \longrightarrow \text{He}^+ + 2\text{e}$ | 3.5503×10^{-10} |
| $\text{He}^* + \text{He}^* \longrightarrow \text{He}^+ + \text{He} + \text{e}$ | 2.7×10^{-10} |
| $\text{He}^* + \text{N}_2 \longrightarrow \text{N}_2^+ + \text{He} + \text{e}$ | 7×10^{-11} |

The evolution of species formed in the plasma reactor can be appreciated in Figure 3a. A quasi instantaneous conversion of NO to HNO_3 can be observed. The diminution of methane concentration is not so important; it is around 20% as can be observed in figure 3b. An interesting product of methane decomposition is the hydrogen; in figure 3c a concentration of approximately 290ppm is obtained.

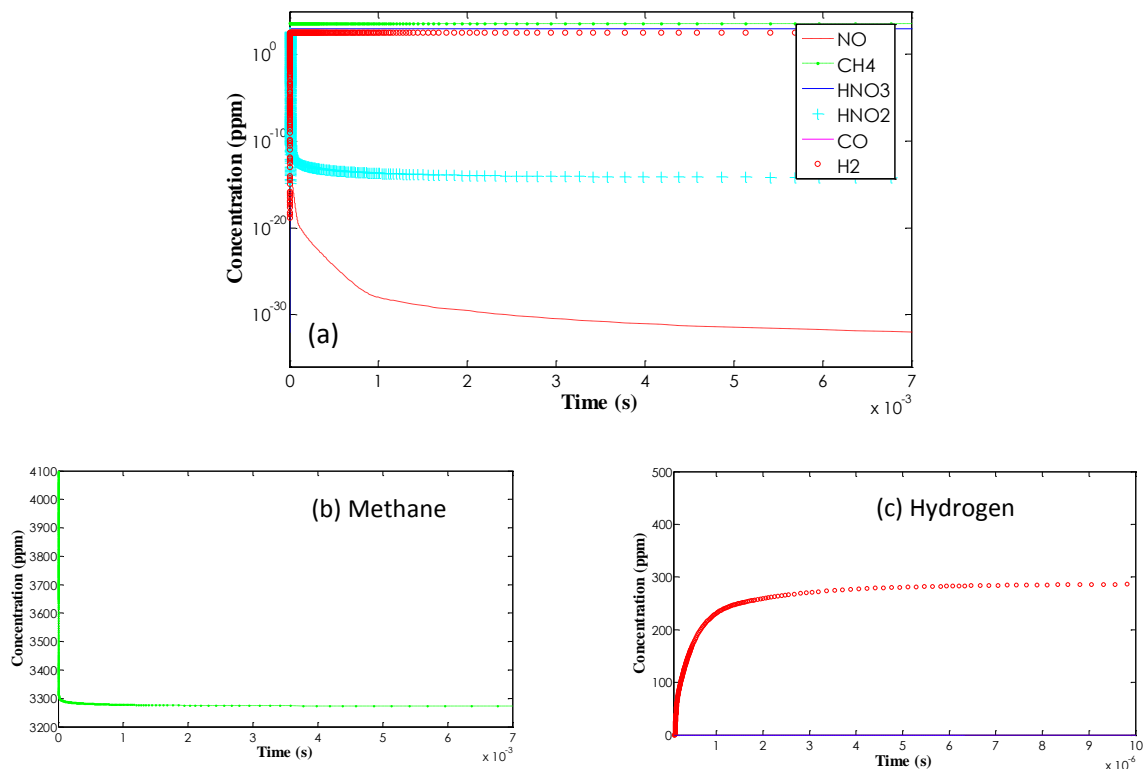


Figure 3 (a) Species concentration in plasma, (b) methane diminution, (c) H_2 production

b) Experimental results

Results from a qualitative analysis are showed in figure 4. A reduction of NO and CH₄ is visible and any acids (i.e HNO₃) cannot be observed.

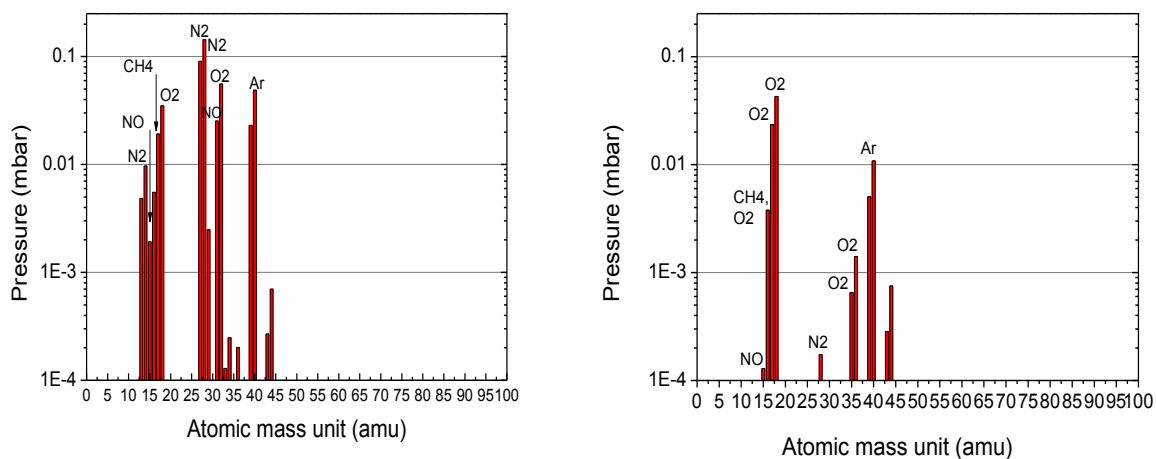


Figure 4. Mass spectra of methane and nitrogen monoxide (a) without plasma treatment (b) with plasma treatment.

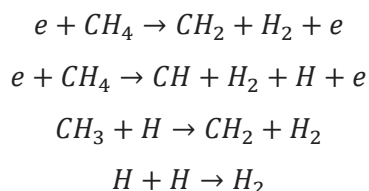
The experiences were achieved at 30-35volts and 2-5A; in table 2 the removal efficiencies and the formation of new species are also reported in function of input power. The specific input energy (SIE) is calculated as the relation of the discharge power and the flow rate of feed gas. The NO removal is reported as NO_x, an imperceptible, or any, concentration of NO₂ is obtained.

Table 2. Experimental conditions and removal efficiencies and production of CO, CO₂ and H₂

| Voltage [V] | I [A] | Pa [W] | SIE [kJ/L] | NO _x removal (%) | CH ₄ removal (%) | H ₂ [ppm] | CO [ppm] | CO ₂ [ppm] |
|----------------|----------|-----------|---------------|--------------------------------|--------------------------------|-------------------------|-------------|--------------------------|
| 33.99 | 2.04 | 69.33 | 4.55 | 92.91 | 21.05 | 70 | 650 | 1000 |
| 29.52 | 2.57 | 75.86 | 4.55 | 95.23 | 22.30 | 76 | 610 | 1000 |
| 34.21 | 3.32 | 113.57 | 6.81 | 98.31 | 20.01 | 72 | 630 | 1150 |
| 35.00 | 3.33 | 116.55 | 6.99 | 99.33 | 24.07 | 75 | 600 | 1200 |
| 35.99 | 5.50 | 198.00 | 11.88 | 100 | 32.51 | 90 | 600 | 200 |

From Table 2, the best removal efficiencies at lower SIE of CH₄ and NO_x respectively are 22.3% and 95.23%. At these conditions the production of H₂ and CO are relatively higher, this gas mixture is characteristic for its high energetic capacity [12]. Okumoto et al [13] have obtained CH₄ conversions from 5% to around 30% at SIE under 5kJ/L.

From the comparison between the chemical model and experiences, the prediction about the NO diminution is explained correctly with the mechanism proposed. The generation of H_2 is overestimated in the model; at our experimental conditions the following equations [14] must be studied with more precision:



5. Conclusions

Results depict the feasibility to non-thermal plasma technology, specifically a 2DBD reactor, for the treatment of automotive toxic gas pollutants. It is important to remark that results obtained from theoretical model suggest the formation of acids (HNO_3 , HNO_2), some studies are under development in our laboratory to resolve this problem with a nanostructured carbon filter. O^* and *OH radicals mostly generated by O_2 and H_2 molecules play an important role in NO removal. Results obtained from the model, illustrate that in a mixture of NO in humid air, the main path for the NO removal is the oxidation to NO_2 and, soon after, to HNO_3 . Concerning the diminution of CH_4 the electron impact is crucial.

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