Hydrogen Production from NO and CH_4 Treatment with non Thermal Plasma

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ABSTRACT

In this project a chemical kinetics model and its experimental demonstration to produce hydrogen from nitrogen oxide (NO) and methane (CH_4) treatment is proposed. A reactor with dielectric pellets as discharge barrier is used to perform the experiments to enhance the electric field strength and create a channel across the discharge region.

The research was carried out in 2 phases: The first one was the analysis of the simulation degradation of NO and CH_4. The second step was the experimental methodology to treat the mixture (NO and CH_4).

To produce the non-thermal plasma, an AC power source was also developed. This energy source works with a high frequency series resonant inverter in the range of 20 kHz to 180 kHz, able to generate a voltage of 15 kV. The discharge can be sustained at atmospheric pressure. The experimental conditions of this special case were: 30V, 1-2 A and 27 kHz.

Chemical model elucidates the degradation of NO and CH_4, theoretical results concerning hydrogen production are overestimated when compared to experimental results; therefore a set of additional equations are then proposed.

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 nitrogen dioxide (NO_2) and, soon after, to nitric acid (HNO_3). Concerning the diminution of CH_4, the electron impact reactions are crucial.

Keywords: Hydrogen, non-thermal plasma, toxic gases treatment

1. Introduction

The air quality is elementary to the human welfare and wildlife. Some natural disasters like volcanoes eruptions and fire on forestry areas have impact on it and might alter such balance. Air quality is poorer on the major populated cities with intensive automotive parking lot, especially on the daily rush hour. For this reason the impact coming from the human activities are greater than nature.

The air pollution has no boundaries and has adversely impacts on everybody, altering the ozone concentration on atmosphere producing the greenhouse effect. This production has a direct impact on earth; for this reason many environment agreements to prevent reduce and gradually control the green house effect emissions like the methane gas and nitrogen oxides (NOx) have to be signed.

In Mexico as in other countries, the automobile is the main source of air pollution, especially emissions of carbon monoxide (CO), nitrogen oxides(NOx), hydrocarbons (HC) and particle matter (PM) coming from Otto diesel engines [1].

In Mexico, the daily amount of vehicles moving along roads is around 15 millions. The transportation sector used up to 56% of the total energy in Mexico, which is equivalent to 95 millions of gasoline liters daily used [2]. The main fuel used in Mexico is the Magna gasoline, followed by Diesel fuel (mainly used in heavy trucks) and, finally, the Premium gasoline.

From the uncompleted burning of hydrocarbons, slights portions of CO, CH_4, and volatile organic compounds (VOC's) are formed, besides the formation of nitrous oxide (N_2O) and nitrogen oxides (NOx).

Higher methane concentrations from automobiles are part of an uncompleted combustion process. They are highly depending of temperature operation, especially in an automotive car with no maintenance program (tuned-up) the levels of methane pollution are greater.

In the case of nitrogen oxides (NO_x), they produce photochemical pollution that contributes to the formation of acid rain and leads to rivers acidification, lakes and other water bodies; this contaminant also damages vegetation and buildings. Furthermore NO_x are related to several adverse effects on human health, mainly in eyes, heart and lungs [3, 4].

Emissions of greenhouse gases like methane (CH_4) and nitrogen oxides (NOx) are one of the major problems to solve; additionally methane conversion could offer a promising route to produce higher value-added products (i.e. hydrogen). For this reason, the development of research projects to create sustainable alternative technologies is imperative.

Kinetic model

The kinetic model used to symbolize the treatment of toxic gases with a dielectric barrier discharge reactor is described and developed elsewhere [5, 6].The model defines the micro discharge development in two phases: the first step concerns the formation of the streamer head at 1ns with high values of electric field (600Td) [7]; and the second one is the formation of a streamer channel, connected to the streamer head. When micro discharge is established, the electric field decreases by maintaining itself almost constant until the dielectric wall is reached [7].The energetic electrons transfer their energy toward neutral molecules resulting in quenching, attachment, dissociation or ionization process; other species like free radicals, meta stables, atoms and ions will be also formed.

The formation of active species is maintained during this phase and the removal of NOx and CH_4 is realized when they react with active species. The model takes into account the following chemical species:(e^-, N_2, O_2, H_2O, O_3, NO_2, NO_3, N_2O_5, N_2O, HNO_3, HNO_2, C, $^-CH_3$, CH_3, CH_2, $CH_3O^\bullet$,CH_2O, $O^\bullet$, $N^\bullet$, $OH^\bullet$, $H^\bullet$, $O_2(a^1\Delta g)$, $O(^1D)$, $N_2(A)$, O^-_2 , O^-, O^+_2 and H^-) [5,6,8,9].

Consequently, the chemical model for NOx and CH_4 removal, proposes the simulation of the formation of active species in the streamer head with an initial electron density of 1 cm^{-3} and at 1×10^{-8} s. Rate coefficients were used at an electric field of 600Td for 2DBD [5, 10]. The reaction rate coefficients involving electrons were taken from [11, 15, 16, 17, 18, 19, 20] and the rate coefficients between neutral species from [9, 11, 12 14]. The model, here applied, considers a balance of the chemical species mentioned above. Radicals produced are supposed to be well mixed with the reactants and uniformly distributed within the whole volume. For the development of the kinetic model Matlab® simulation software was used, specifically an equation differential solver called ODE1s based on the Runge-Kutta method for solving differential equations differential equations [19].

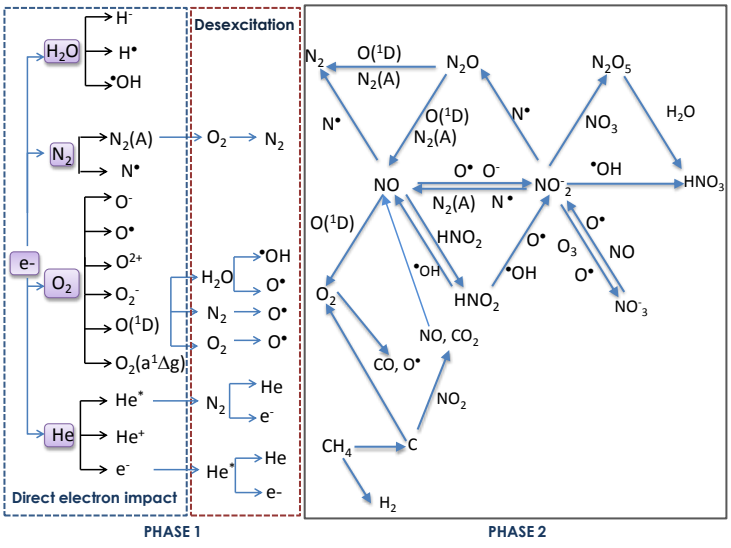

Figure 1. Chemical Model

2. 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 180 kHz, able to generate a voltage of 15 kV [6]. The discharge can be sustained at atmospheric pressure using nitrogen or air, as plasma gas. The experimental conditions of this special case were: 21V, 0.7-1A and 30kHz.

For optical emission diagnosis (OES) a digital spectrometer Jaz Ocean Optics was used, this enables an optical resolution of 0.3 nm (FWHM) covering from 200 nm to 1100 nm.

Inlet and outlet gases were analyzed with a PG-250 Horiba able to identify and quantify CO, CO_2, NO_x, SO_2 and O_2. A mass spectrometer (Cirrus MKS Spectra products) and a gas chromatographer (Thermo Scientific Trace GC Ultra) were also used to identify compounds formed. The experimental system used in the degradation of NO-CH_4 mixture is shown in Figure 2.

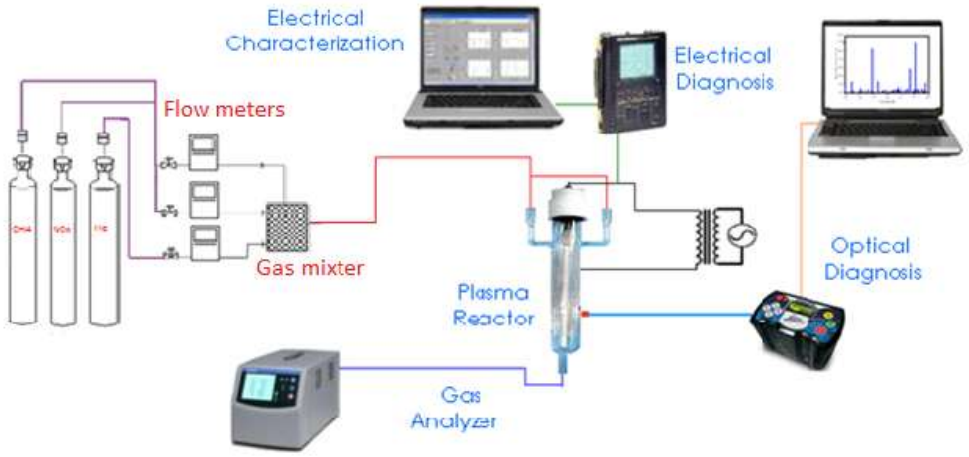

Figure 2. Experimental set up

The schematic of the reactor is shown in Fig. 3, it consists of a tube of quartz with an internal radius of 12.3 mm, a length of 212 mm and a thickness of 1.2 mm. Two copper concentric central electrode of radius of 2 mm is set inside the quartz tube. A metallic mesh covering the quartz tube plays the role of the external electrode.

Into the quartz tube, several glass pellets uniformly distribute the plasma. Spherical pellets were chosen because the electric field is concentrated and numerous filamentary discharge channels are formed along the pellet surface, enabling better interaction between plasma and the gas to be treated [20].

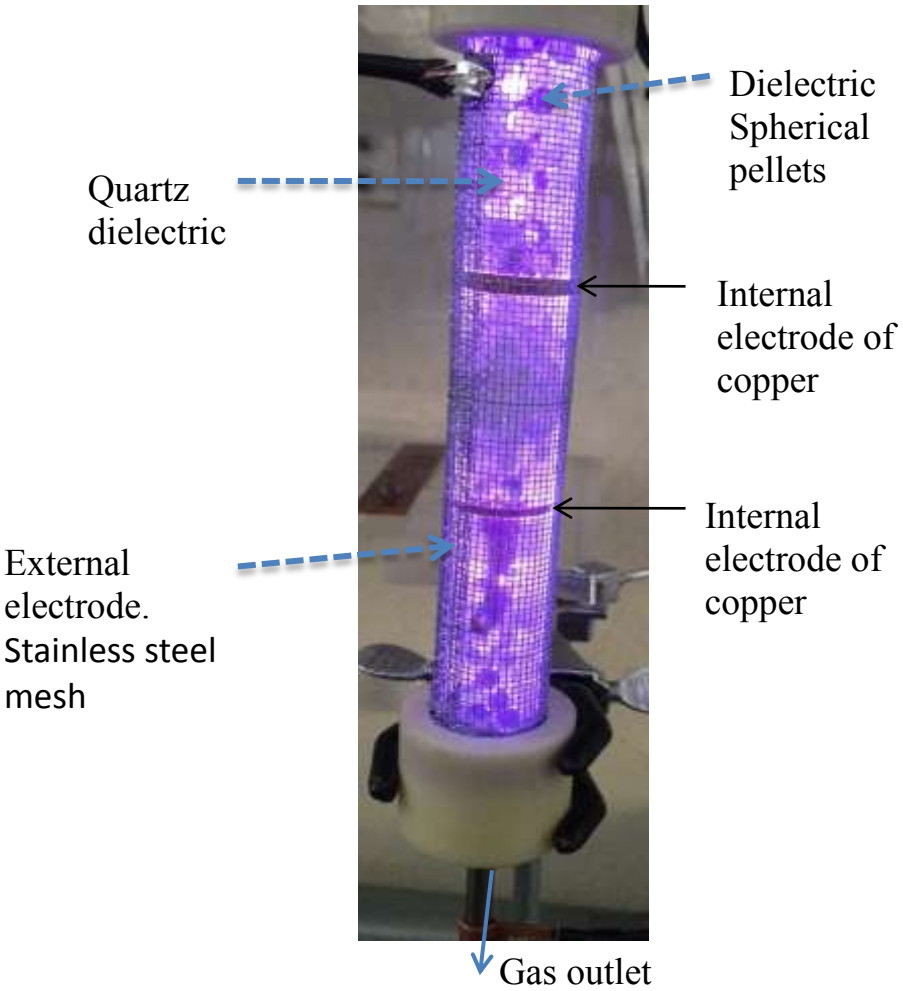

Figure 3.Plasma reactor

To obtain electronic temperature (T), Boltzmann plot method is applied to data obtained from OES study. The spectroscopic data were obtained from [27].

For every spectral line, this method plots $\ln\left(\frac{\varepsilon_{hb}\lambda}{g_h A_{hb}}\right)$ versus E_h. The negative slope obtained from the line represents $1/kT$.

Where:
ε_{hb}: Line emissivity
λ: Wavelength (nm)
g_h: statistical weight (upper level)

A_{hb}: Spontaneous emission probability
E_h: Excitation energy (upper level) in eV
k: Boltzmann constant (8.6173324×10^{-5} eV K^{-1}).

3. Results and discussion

3.1 Chemical model

During first nanoseconds, the energetic electrons collide with neutral molecules appearing primary radicals ($^{\bullet}OH$, $O^{\bullet}$ and $N^{\bullet}$). Ions and excited molecules, like excited oxygen, $O^1(D)$, forms radicals by rapid quenching. Soon after, the electron–ion and ion–ion reactions create secondary radicals. NO and CH_4removal is mainly controlled by oxidation reactions. The role of $O^{\bullet}$ radical is the oxidation of NO to $NO_2$and N_2.

NO and NO_2 could be removed by the $^{\bullet}OH$ radical to form HNO_2 and HNO_3, respectively, but also NO can be reduced by $N^{\bullet}$ radical [8, 22]. The evolution of species formed in the plasma reactor can be appreciated in Figure 4a.

The diminution of methane concentration is around 30% as can be saw more detailed in figure 4b. An interesting product of methane decomposition is the hydrogen; in figure 4c a concentration of approximately 400ppm is observed. The formation of CO is also formed from the decomposition of methane.

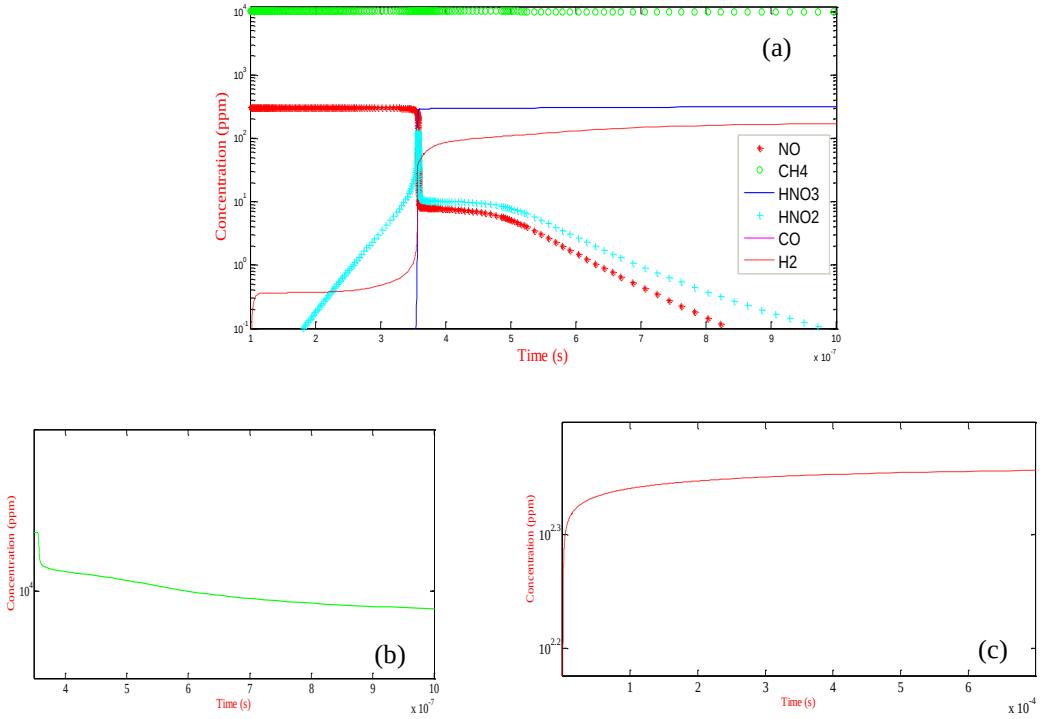

Figure 4.NO-CH_4 plasma treatment. **(a)** Degradation NO-CH_4. **(b)** Degradation CH_4. **(c)** Hydrogen production

Based on simulation results (Fig. 4a, 4b and 4c), a rapid diminution of NO is obtained, being notice able the increase of N_2, HNO_2 and HNO_3. The degradation of methane is lower, but significant, leading to the formation of atomic carbon and an added value: the hydrogen production at low power consumption (24 to 27W).

3.2 Experimental Model

3.2.1 Chromatography and mass spectroscopy results

Several experimental tests were done; gaseous products were analyzed with different methods. For the methane analysis a first approach was obtained with gas chromatography. In figure 5, two chromatograms, with and without plasma treatment, were plotted. The methane peak at time retention of 4.10min considerably diminishes when plasma is applied and intensities of oxygen and nitrogen lines increase, it could probably explain the dissociation of NO into N_2 and O_2.

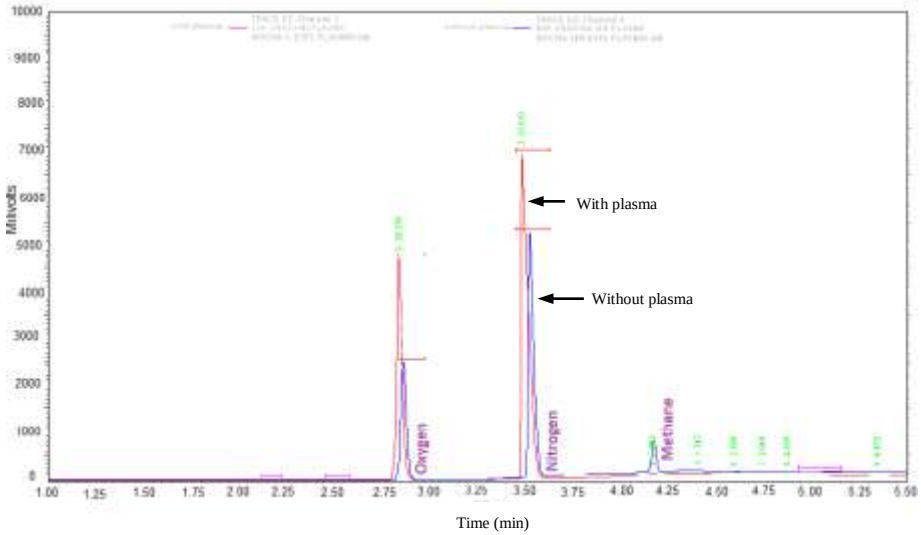

Figure 5: Gas chromatography with and without plasma treatment

Additional results from a qualitative analysis are showed in figure 6 (a and b). A reduction of NO and CH_4 is visible and any acids (i.e. HCO,) cannot be observed. After the plasma treatment a formation of HCO^+, CO, C can be observed (figure 6b).The formation of H_2 is also reported in Figure 6b.

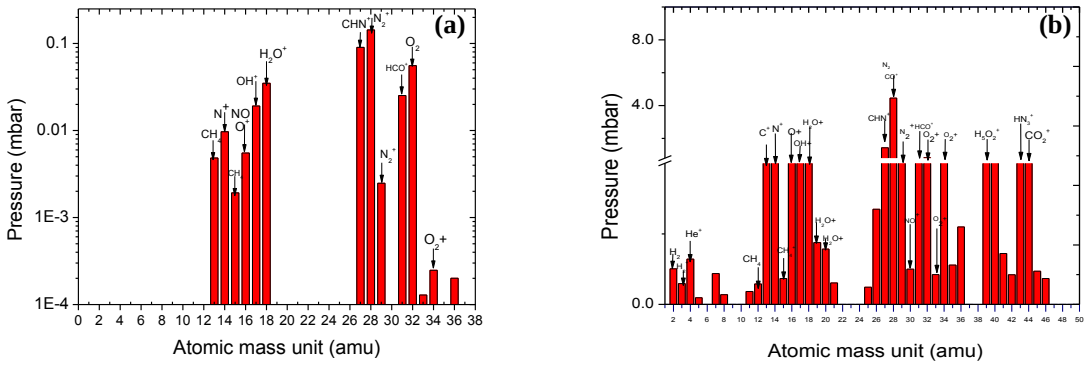

Figure 6. Mass spectra of CH_4 and NO (a) without plasma treatment (b) with plasma treatment.

From chromatographic and mass spectra results the dissociation of NO by non thermal plasma could be explained with the following reactions:

$$N_2 + e^- \rightarrow N^\bullet + N^\bullet + e^- \quad \text{.....(1)}$$

$$N^\bullet + NO \rightarrow N_2 + 1/2\,O_2 \quad \text{.....(2)}$$

OES analysis was achieved under three specific experimental conditions, plasmas with mixtures of CH_4+He (figure 7a), NO + He (figure 7b) and CH_4+NO + He (figure 7c).

In figure 7a is possible to appreciate few lines of C, H and He atoms. Any C_2 band can be appreciated between 513nm and 517nm. This band, normally knew as Swan band, is precursor of carbon nanostructures in electric arc [23]. The absence of the C_2 band is consistent with the no formation of carbon soot in the plasma reactor.

In figure 7b the spectral lines are characteristic of He plasma with NO. Atomic He and O are founded. N_2 positive band is observed between 350and 370nm.

From Boltzmann plot method the electronic temperatures calculated at 14W and 17 respectively were 2.71eV and 2.78eV. The calculation was obtaining from data of OII lines situated at 274.73nm and 340.72nm. When a mixture of NO_x and CH_4 is introduced into the He plasma, atomic lines of C almost disappear, He and N become more intense and ionized nitrogen appears. In order to maintain the stability in the plasma discharge the input power has to be increased, this could explain a better ionization of nitrogen.

In this case the electronic temperature diminishes until approximately 2eV, and it could be explained by an energy loss of electron kinetic energy by collisions to form ions. Results obtained from OES analysis illustrate the influence of power input; even if the variation in power is not significant (from 14W to 18W) the line emission considerably increases with power input, in this case the species population in excited and ionized levels growth (see figures 7a to7c).

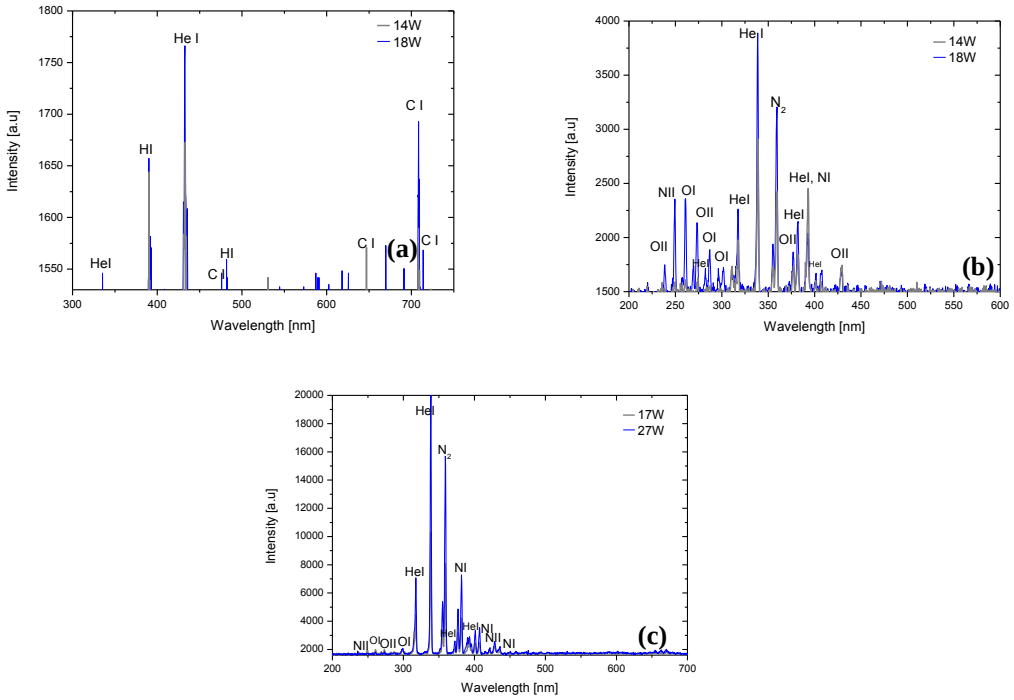

Figure 7.OES analysis. (a) He+CH_4 plasma, (b) He + NO plasma (c) He+CH_4+NO plasma

3.2.2. Removal efficiencies.

From Table 1 it can be observed that best removal efficiencies of CH_4 and NO respectively are 29% and 99% at approximately 5-6KJ/l.

At these conditions the production of H_2 and CO are relatively higher; this gas mixture has an energetic capacity of 2265kcal/m^3.Okumoto et al [22] have obtained CH_4 conversions from 5% to around 30% at SIE under 5kJ/Lin pulsed discharge plasma.

Table 1. Experimental conditions and removal efficiencies and production of CO, and H_2 (Treatment of NO-CH_4 mixture)

Voltage [V]	**I [A]**	**Pa [W]**	**NO removal (%)**	**CH_4removal (%)**	**H_2 [ppm]**	**CO [ppm]**
30	0.8	24	99.99	20	400	200
33	0.78	25.9	99.99	25	364	280
31	0.87	27	99.99	21	492	149
32	0.85	27.2	99.99	29	500	285

Additional experiments were done with an "individually" treatment of NO and CH_4. The NO removal slightly diminishes certainly due to a catalytic effect of the CH_4. The catalytic effect of hydrocarbons can be seen in [24].

The analysis was done with NO gas analyzer Horiba PG-250, using the chemiluminescence method. Methane was evaluated with the gas analyzer Gasboard 3200L method using non-dispersive infrared (NDIR). Hydrogen was quantified through the analyzer iBrid MX6, which uses the electrochemical analysis method.

Table 2: Treatment of NO and CH_4

Contaminants	Voltage [V]	I [A]	Pa [W]	Removal (%)
NO	**25**	**0.75**	**18.75**	**98**
CH_4	**21**	**0.84**	**17.64**	**23**

From the comparison between the chemical model and experiences, the prediction of NO diminution is properly explained with the mechanism proposed (figure 1). However the generation of H_2 is overestimated in the model, so at our experimental conditions the following equations [25, 26, 27] must be studied with more precision:

$$e + CH_4 \rightarrow CH_2 + H_2 + e \quad (3)$$
$$e + CH_4 \rightarrow CH + H_2 + H + e \quad (4)$$
$$CH_3 + H \rightarrow CH_2 + H_2 \quad (5)$$
$$H + H \rightarrow H_2 \quad (6)$$
$$O(´D) + CH_4 \rightarrow HO + CH_3 \quad (7)$$
$$CH_3 + O \rightarrow CO + H_2 + H \quad (8)$$
$$CH_3 + CH_3 \rightarrow C_2H_5 + H \quad (9)$$
$$C_2H_5 + H \rightarrow C_2H_4 + H_2 \quad (3)$$

4. Conclusions.

$O^{\bullet}$ and $^{\bullet}OH$ radicals mostly generated by O_2 and H_2O molecules play an important role in NOx removal. Results obtained from the model, illustrate that the main path for the NO removal is the oxidation to NO_2 and, soon after, to N_2 and HNO_3.

Results of the numerical simulation showed good agreement with experimental data of the removal process, achieving more than 99% removal of NO and 29-30% CH_4. The efficiency of removal of contaminants with non-thermal plasma is demonstrated. Concerning the diminution of CH_4 the electron impact and $^{\bullet}CH_3$ are crucial.
The removal efficiency results for the NO-CH_4 mixture depicts the feasibility to use this technology for the treatment of automotive toxic gas pollutants; whit the added value of obtaining products with a high energetic value (formation of CO and H_2)

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