ELECTRICAL CHARACTERIZATION OF DBD WIRE-CYLINDER REACTOR : INFLUENCE OF OPERATING PARAMETERS AND BY-PRODUCTS ANALYSIS.

A.VINCENT, F. DAOU, E. FRANCKE, S. CAVADIAS, J. AMOUROUX

Laboratoire de **G**énie des **P**rocédés **P**lasmas et **T**raitements de **S**urfaces
Université Pierre et Marie CURIE (Paris VI)
ENSCP – 11, rue Pierre et Marie CURIE
75231 PARIS cedex 05 - France

ABSTRACT:

The aim of this paper is the development of an impulsional Dielectric Barrier Discharge wire-cylinder reactor for NO_x removal from automotive exhausts. This geometry allows a great gas flux treatment capability and could later be easily introduced in car exhaust lines. In this work, the treated gas is a N_2, O_2, CO_2, C_3H_6, NO, and H_2O mixture.
The reactor behaviour has been characterised with a numerical oscilloscope and the influence of electrical parameters (voltage: 0 to 20kV, energy density, gap: 1 to 7mm), physical parameters (electrode material: Ti-V, copper; dielectric material: alumina, aluminio-silicate; gas temperature: ambient and 150°C; gas flux: 4 to 20L.min^{-1}), or gas composition (water vapour: 0, 5 or 10%) has been investigated. Energy was supplied by a high-voltage AC generator. The electrical signal was especially studied from measuring the voltage, intensity, power, charge and duration of the pulses to calculate the energy balance. The intensity vs voltage curves of each studied configuration was also determined.
The plasma treated gas was on-line analysed by gas-analyser measuring NO, NO_2 and CO. A GC-MS analysis permitted to identify the various reactions by-product like N_2O, hydrocarbon by-products, R-NO_x. Main by-products were detected to be aldehydes, C_xH_y-NO and C_xH_y-NO_2.

I – INTRODUCTION

New European restrictions in NO_x automotive emissions impose new processes developments. Corona discharge treatment applied to polluted gases is an efficient method for NO_x conversion. Many applications of D.C. and A.C. corona discharge applications are well known[1,2].
The treatment of a O_2, CO_2, NO, C_3H_6, H_2O and N_2 gas mixture is presented in this paper. The aim of this study is to qualify the corona discharge wire-cylinder reactor versus different physical parameters (electrode and dielectric material, gap, gas flow, heating, hydration) and the decomposition of different components, particularly C_3H_6. This qualification will be base on electrical measures with a numerical oscilloscope and by-products analysis with a GC-MS (carbon compounds), a gas analyzer and colorimetric detector tubes (NO_x).

II – EXPERIMENTAL SET-UP

As shown in figure 1, the reactor is a cylindrical dielectric pipe (aluminio-silicate / $Ø_{int}$=11mm / $Ø_{ext}$=21mm or alumina / $Ø_{int}$=25mm / $Ø_{ext}$=31mm). The high voltage electrode is a 6mm diameter screw (gap=2.5mm) and the grounded electrode is a copper layer. Energy is supplied by a "Calvatron SG2" high voltage 45kHz AC supply (applied voltage is between 10 and 20kV peak to peak). Electrical characterization is made measuring voltage (using a high voltage 1:1000 probe), intensity, power, electric charge, frequency and pulse time by a 500MHz numerical oscilloscope (LeCroy LT 342). The reactor is fed with a gas mixture at atmospheric pressure. Each gas (except water vapor) is introduced in the mixture by a mass flow meter. H_2O is introduced by a motorized syringe pusher in a heated 1/8" diameter and 2 meters long stainless steel pipe. Vaporized water is then introduced in heated gas. The total gas flow is between 4 and 20L.min^{-1}. Gas mixture temperature is measured by a thermocouple at 3 centimeters after the discharge zone.

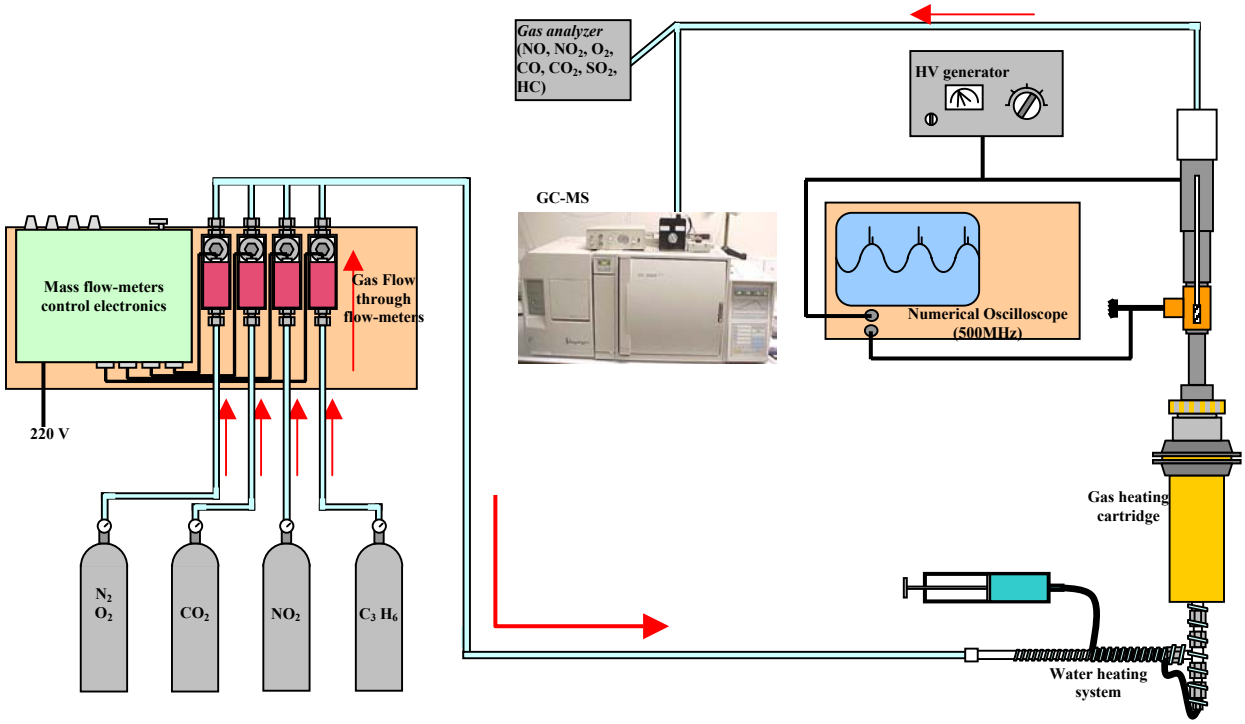

Figure 1: Experimental set-up of the impulsional wire-cylinder reactor, gas feeding system and analysis apparatus

2- Gas analysis apparatus:

The treated gas flows from the reactor to the different analysis apparatus through a heated 1/4" stainless steel pipe. The in-line analyzer are:

- GC-MS (Gas Chromatography coupled with a Mass Spectrometer): it allows the identification (sensitivity: ~ppm) and the quantification (± 5% after calibration) of the different hydrocarbon compounds to provide the carbon mass balance. The chromatographic column is a Chrompack PoraPlotQ (25m-0.32mm-10µm,divinyl-benzen polystyren). Gas introduction is made with a 100µl 6 ways gas sampler, carrier gas is He (pressure: 0.3 kg/cm²).

- Infrared Gas Analyzer (measuring NO, NO_2, O_2, CO_2, CO, SO_2 quantities): performances are indicated on the following table:

Gas measurement	Range	Accuracy	Resolution
O_2	0-25 %	0.1 à 0.2 %	0.1 %
CO	0-10000 ppm	20 ppm : [CO] < 400 ppm 5 % : [CO] < 2000 ppm 10 % : [CO] > 2000 ppm	1 ppm
	0.1-10 %	+/- 5 %	0.01 %
NO	0-5000 ppm	5 ppm : [NO] < 100 ppm 5 % : [NO] > 100 ppm	1 ppm
NO_2	0-1000 ppm	+/- 5 ppm	1 ppm
SO_2	0-5000 ppm	5 %	1 ppm
CO_2	0-fuel value	+/- 0.3 %	0.1 %
Hydrocarbons (HC)	0-5 % Méthane	5 %	0.01 %

Table 1: Utilization range, accuracy and resolution of the gas analyzer

- Colorimetric detector tubes (measuring NO + NO_2 or CO quantity): the utilization range and precision are:
  $NO + NO_2$: 50 – 2500 ppm ± 10%
  CO : 25 – 1000 ppm ± 5%

NO_x analysis with gas analyzer and colorimetric detector were validated after measurements of NO_x at the exit of a NO/N_2 gas bottle (NO: 1800ppmv) and after a 1:1 dilution in N_2 using the mass flow-meters.

III – EXPERIMENTAL RESULTS – DISCUSSION

1- Electrical characterization of the reactor:
Electrical characterization of a reactor[3] is an important step in energy balance determination and in reduction of energy consumption[4]. The electrical behavior of the reactor has been provided by measuring voltage, intensity, frequency, charge (figure 2).

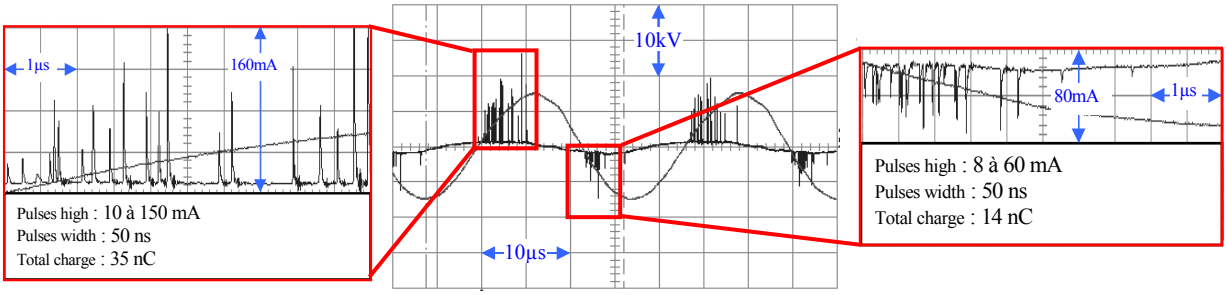

Figure 2: Oscilloscope screen showing voltage and intensity measures obtained during the treatment of the gas mixture (T=100°C, gas flow=4.5L.min^{-1}, gap=2.5mm, dielectric: aluminio-silicate)

The voltage range applied to obtain an appropriate corona discharge mode depended on the gap. Nevertheless, this wire-cylinder reactor allows a stable multi-impulsional discharge

mode. The most utilized gap was 2.5mm (dielectric: aluminio-silicate, figures 3, 4 & 5) but some experiences (especially the study of the influence of warming and hydration on the intensity vs voltage characterization) were conducted with a 7mm gap (dielectric : alumina, figure 6). The usable voltage range depends essentially on gap and dielectric material. Discharge breakdown was between 11kV pkpk (figures 3 & 4) and 17kV pkpk (figures 5 & 6) and study range was about 5kV pkpk over breakdown.

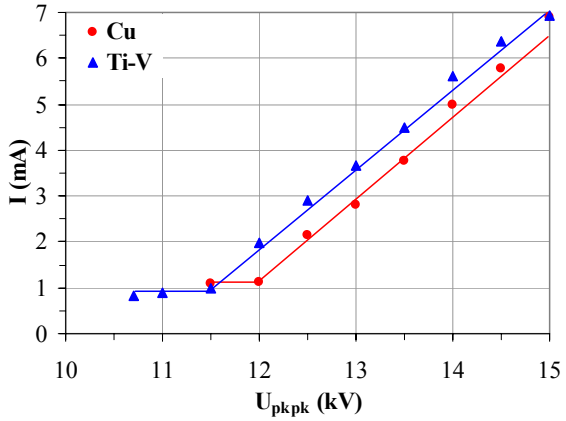

Figure 3: Influence of the HV electrode material on the intensity vs voltage curves (dielectric=aluminio-silicate, gap=2.5mm, gas flow=20L.min^{-1}, T=120-205°C)

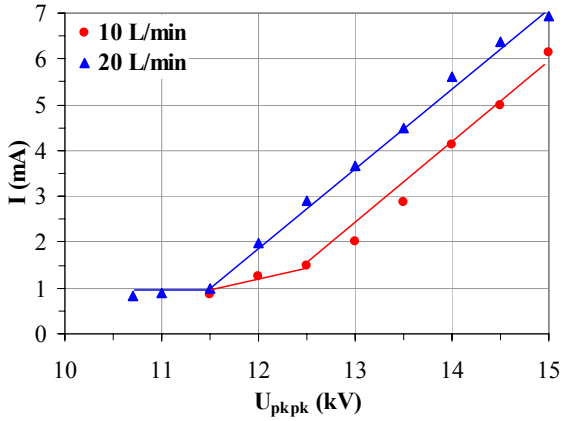

Figure 4: Influence of the gas flow on the intensity vs voltage curves (Ti-V electrode, dielectric= aluminio-silicate, gap=2.5 mm, T=100-210°C)

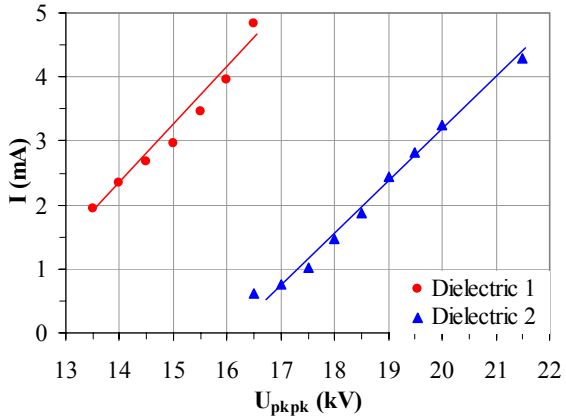

Figure 5: Influence of the dielectric material on the intensity vs voltage curves (Ti-V HV electrode, dielectric=aluminio-silicate, gap=2,5mm, gas flow=10L.min^{-1}, T=150°C)

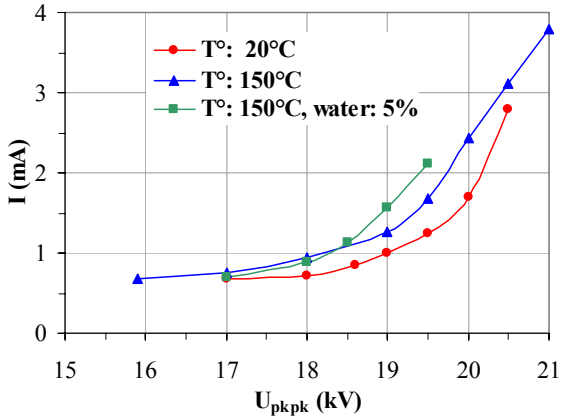

Figure 6: Influence of heating and hydration on the intensity vs voltage curves (HV electrode: Ti-V, dielectric=aluminia, gap=7mm, gas flow=4L.min^{-1})

We can notice that heating, hydration, gas flow or material of the HV electrode (here: copper or titanium-vanadium alloy) have a weak influence on the intensity vs voltage characterization, contrary to dielectric material. Note that measured temperature in figures 3 and 4 is not constant because the gas is heated by the discharge proportionally to its power. In the case of the figures 5 & 6, the indicated temperature are the temperature obtained without plasma.

To perform the energy balance, we determined the contribution of the impulsional power on the total power measurement and the impulsional charge at different voltages (figure 7). We can see that impulsional power is about half the total power.

U_{pkpk} (kV)	9,7	10,3	10,7	11,1	11,4	12,0
Total power (W)	4,2	7,6	13,1	18,4	24,0	28,6
Impulsional power (W)	1,2	3,1	8,4	9,3	10,5	13,5
Ratio P_i/P_t (%)	29	40	64	51	44	47
Pulses number / periode	2	3	5	7	8	8
Intensity (mA)	1,2	2,1	3,4	4,7	6,0	6,8
Impulsional charge (nC)	7	16	44	56	58	75
Impulsional energy (mJ/periode)	0,03	0,07	0,19	0,21	0,23	0,30

Figure 7: Measures of power, intensity and charge at various voltages

Importance of electrical charge should be noticed because it is proportional to active species (radicals and ions) produced by the discharge. Those active species will react together or with neutral molecules to create a great variety of hydrocarbon compounds and R-NO_x.

2- Analysis of carbon by-products

The GC-MS analysis of treated gas mixture allows the identification and the quantification of the different by-products. The following figure (figure 10) presents the obtained chromatogram.

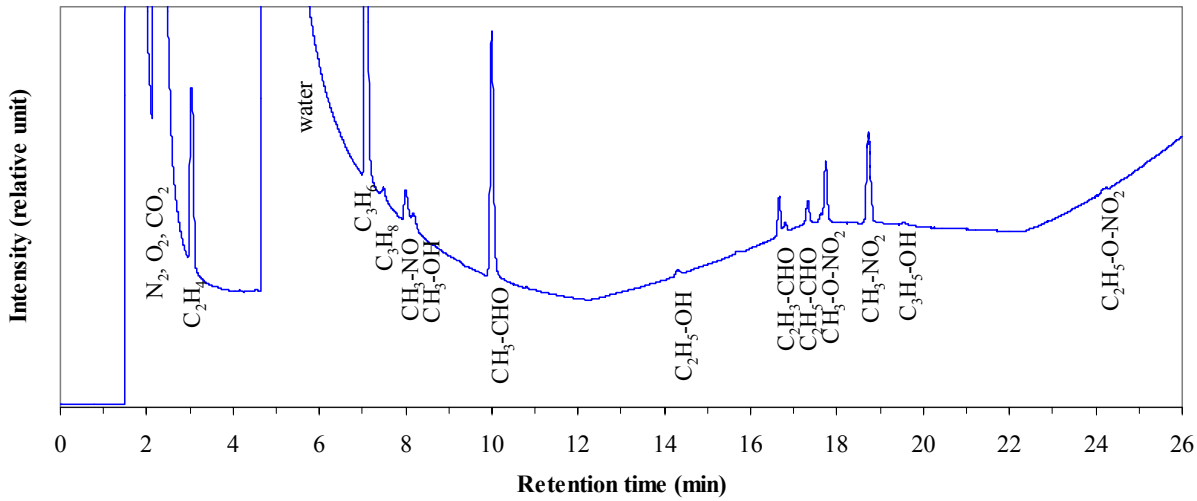

Figure 10: Chromatogram of O_2 (10%), CO_2 (10%), NO (1000ppmv), C_3H_6 (1000ppmv), H_2O (5%) and N_2 (balance) gas mixture treated by plasma in the wire-cylinder reactor (Ti-V electrode, dielectric=aluminio-silicate, gap=2.5mm, gas flow=4.5L.min^{-1}, T=150°C, power=18W)

Aldehydes (formaldehyde, acetaldehyde and C_3-aldehydes) and R-NO_x (nitromethane, nitrosomethane) are the main by-products obtained, but some alcohol, ketons (methanol, ethanol, acetone) and other carbon compounds are identified as well. The presence of this great number of oxidized carbon compounds indicates the prior role of atomic oxygen in reactional phenomena.

3- Analysis of NO_x reaction:

After electrical characterization of the different physical parameters (temperature, hydration, gas flow, electrode and dielectric material), we investigated the influence of hydration and electrode material (in presence of water) on NO_x removal (figures 8 & 9). First, we can note that some NO introduced is oxidized in NO_2 without plasma (due to contact with O_2).

Secondly, when the energy density increases, the ($NO+NO_2$) quantity decreases (possibly due to reduction of NO to N_2+O_2 and/or reaction of NO with carbon radicals creating R-NOx) and NO_2 increases (due to oxidation of NO). The presence of water (5%) strongly increases the maximum rate of NO_x removal (48% vs 32%) contrary to electrode material. It also can be noted that, for a given removal rate, the presence of water or the use of a copper electrode decreases the necessary energy density. For example, the removal of 30% NO_x removal drops from 65 to 50 J/L (-25%) using a copper electrode.

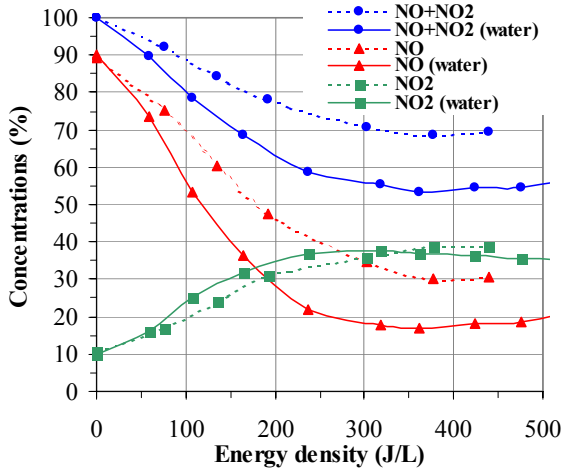

Figure 8: Influence of water on the NO & NO_2 removal (dielectric=aluminio-silicate, gap=2.5mm, $[NO]_i$=720ppmv, gas flow=4.5L.min^{-1}, T=100-180°C)

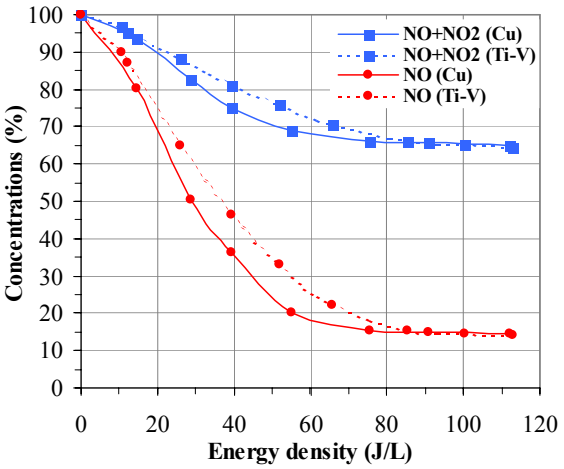

Figure 9: Influence of the HV elctrode material on the NO & NO_2 removal (dielectric=aluminio-silicate, gap=2.5mm, $[NO]_i$=450ppmv, gas flow=20 L.min^{-1}, T=120-205°C)

4- Carbon mass balance

The quantification of the main carbon compounds obtained after gas mixture treatment is: 20% of C_3H_6, 38% of CO, and 42% of other compounds ($C_xH_yO_z$, R-NO_x, CO_2 and deposits on the walls). Those results are presented in the following figure:

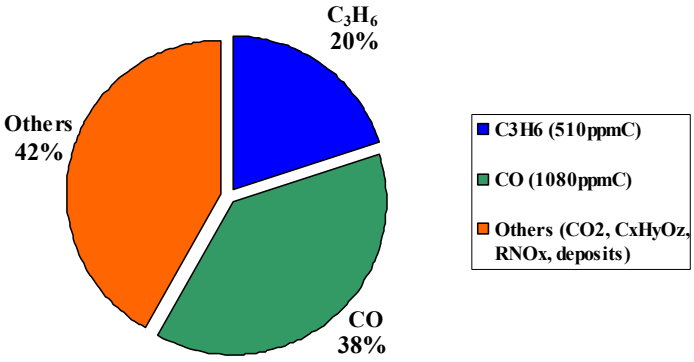

Figure 11: Carbon mass balance of of O_2 (10%), CO_2 (10%), NO (1000ppmv), C_3H_6 (1000ppmv), H_2O (5%) and N_2 (balance) gas mixture treated by plasma in the wire-cylinder reactor (Ti-V electrode, dielectric=aluminio-silicate, gap=2.5mm, gas flow=4.5L.min^{-1}, T=150°C, power= 18W)

IV – CONCLUSION

Previous studies have well established electrical behavior and NO_x treatment capabilities of the corona discharge wire-cylinder reactor. Each impulsion generated by plasma has a 1 to 15nC electrical charge (intensity from 10 to 150mA for an average 50ns duration). Different gap distances have been tested, indicating an optimum gap to 2.5mm. Discharge breakdown voltage is 11 to 16kV pkpk. The NO_x removal performances (80% of NO conversion for a 60J/L energy density input) emphasizes the validity of the process for chemical treatment of polluted gases. The major role of oxygen in treatment reactions has been proven by the GC-MS analysis of the carbon by-products (presence of various hydrocarbons, aldehydes, alcohols and R-NO_x).

Acknowledgments
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