

Point and multipoint to plane barrier discharge process for removal of NO_x from engine exhaust gases. Understanding of the reactional mechanisms by isotopic labeling

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Abstract:

An experimental study on the removal of NO_x in a simulated vehicle exhaust gas has been carried out using point to plane and multipoint to plane DBD corona reactors.

Hydrocarbon (C₃H₆) and NO_x by-products were systematically investigated with a Gas Chromatography coupled to a Mass Spectrometry (GC/MS). NO_x (NO and NO₂) and CO output were also monitored with a gas analyser in order to complete the mass balance.

¹⁸O tracer technique analyses is applied to investigate the mechanism of propylene decomposition. From the plasma chemical reaction pathway proposed, it is apparent that the oxygen activation is one of the important steps for initiating the oxidation processes and the R-NO_x formation.

We present data for the reaction of the (N₂/O₂/C₃H₆/CO₂/NO/H₂O) system in the corona discharge reactors mentioned above. This system has been shown to generate a significant amount of aldehyde. CH₃NO₂ and CH₃ONO₂ are the main R-NO_x compounds produced.

Reactant composition and discharge energy densities (controlled by a numerical oscilloscope) were the operating parameters under study in wet and dry air mixture. Water vapors played an important role in NO_x removal (especially in NO₂ removal) via the reaction forming HNO₃. Therefore, in wet-gas mixture supplied reactors the highest removal rates of NO_x were as high as 30 %, while in dry-gas only 15 %. Different dielectric materials such as Al₂O₃/SiO₂ and TiO₂ on Al₂O₃/SiO₂ support have been used.

1. Introduction

The purpose of this work is to qualify the NO_x and hydrocarbons control pollution mechanisms in an impulsional plasma reactor at atmospheric pressure. Study is carried on NO_x removal in the gas mixture exhaust (O₂: 10%, CO₂: 10%, H₂O: 5%, C₃H₆: 1000 ppm, NO: 1000, 700 and 350 ppm, N₂: balance).

Corona Discharges are realized in non-uniform gaps. Point-plane and multipoint-plane geometries have been used. The first one is adapted to characterize the elementary discharge phenomena as soon as electrical, energetic and hydrodynamic ones¹. The second reactor is useful to increase the density of elementary discharges and the treated gas 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 NO_x removal^{2,3}. 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 impulsional discharge is qualified by energy cost, impulsions, electrical characterization and efficiency 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 NO_x and CO).

The behavior of the atomic oxygen was examined by mean an isotopic labeling (¹⁸O) and gas chromatography-mass spectrometry identification of the produced stabilized species.

Oxygen excitation phenomena by direct electronic impact 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, hydrocarbon) according to the gas mixture and the temperature.

2. The experimental set-up and depollution procedure by DBD reactor

The experimental apparatus used for measurements and step by step monitoring of the by-products evolution consist of:

- i) The impulsion Corona Discharge reactors described in figure 1,
- ii) A gas inlet system and auxiliary devices (GC/MS, gas analyzer, colorimetric detector tubes "DRÄGER tubes", water heating system). The technics analyze performances are mention in a previous study⁴.
- iii) The electrical circuit described in figure 2,

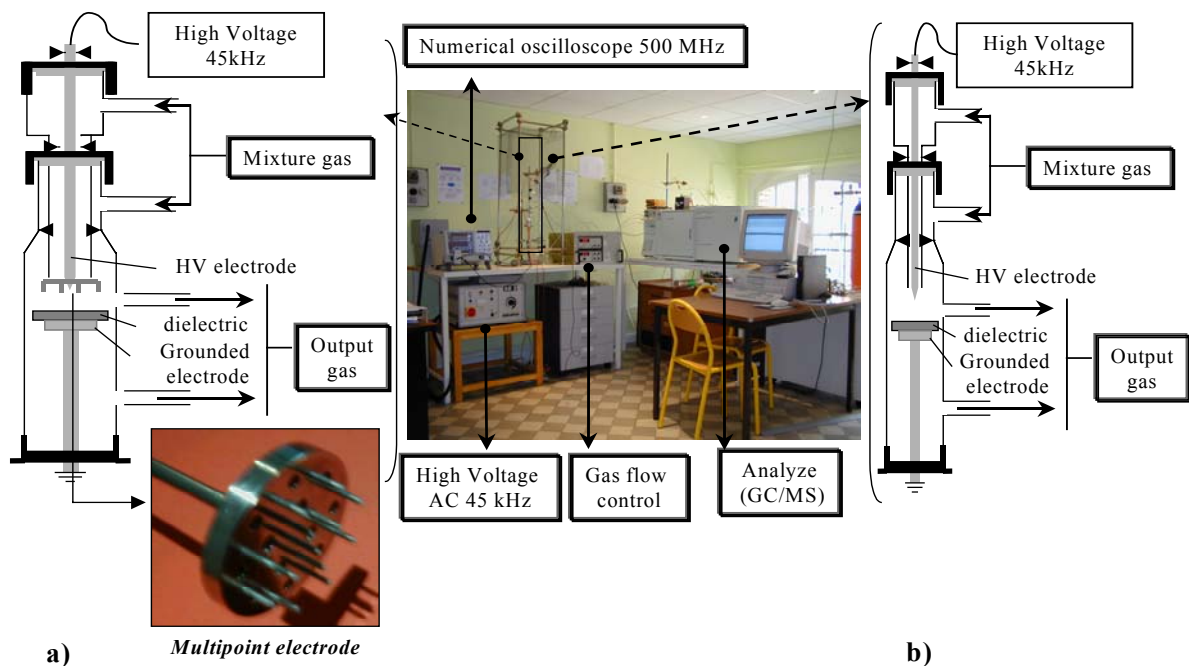


Figure. 1: Experimental set-u; **a)** Multipoint-plane reactor, **b)** Point-plane reactor

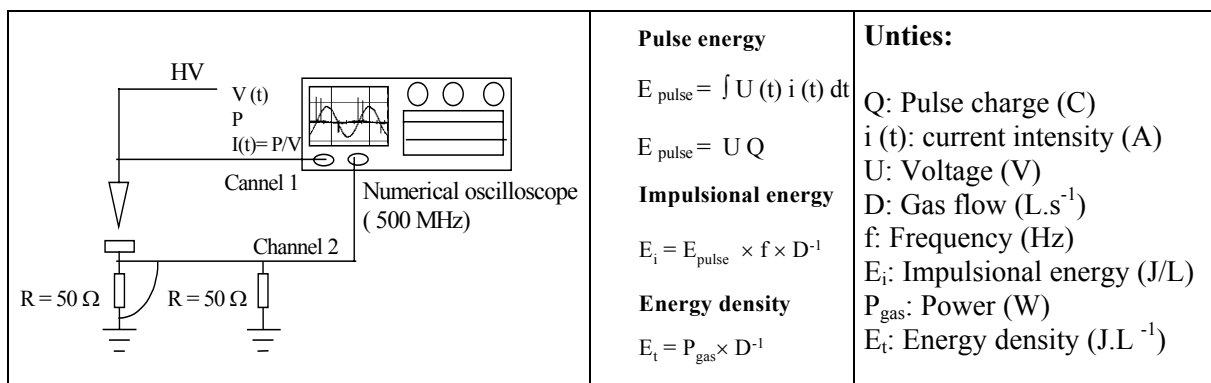


Figure. 2: Electrical circuit and energy calculation method

The point to plane and the multipoint to plane reactors are both supplied with Alternative Voltage 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 NO_x treatment.

In a first step, the work concerns particularly the balance material settling on the NO_x and on the carbon, considering heavy compounds formation. The role of water is also studied.

The electrical characteristics as well as the relation between voltage, intensity and pulses duration have been investigated. Then, material nature was validated on the dielectric (stumatite) and it has already been mention in a previous study⁵.

Electrical characterization (figure.3)

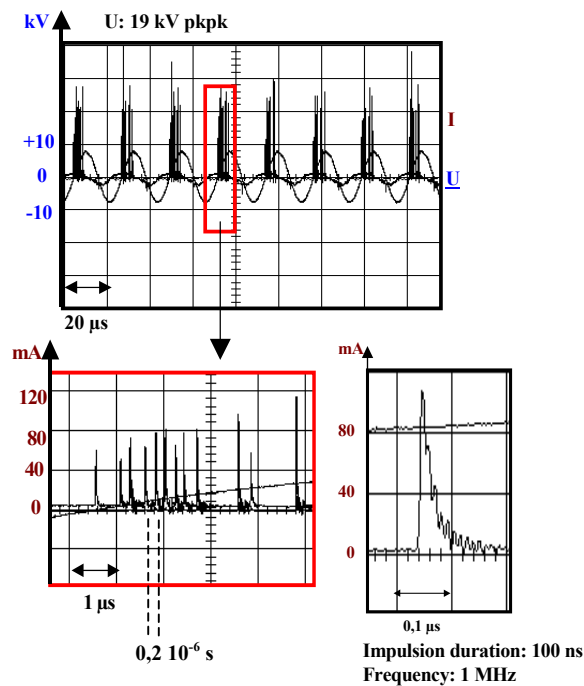


Figure.3: Oscillogram obtained with the multipoint-plan reactor under 19 kV pkpk applied voltage.

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 NL/min. An impulsion having a 3 nC charge and 200 ns duration, for a voltage of 14 kV pkpk. The deposited energy varied between 50 and 400 J/L.

The NO_x removal efficiency 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 (SiO₂ / Al₂O₃) 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 4 to 10 NL/min and from 5 to 200 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, the power of a pulse is estimate roughly at 10⁶ W.

3. Study of the treatment efficiency of the DBD corona reactor in the case of a model gas mixture

The gas mixture (O₂: 10 %, CO₂: 10 %, H₂O: 5 %, C₃H₆: 1000 ppm, NO: 1000 or 350 ppm, N₂: Balance) represents a diesel exhaust in which VOC 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.

The use of the analysis technics showed:

- i) An excess of VOC form carbon with regard to the initial concentration of carbon contained in the introduced propylene, due to the transformation of CO₂ into CO and VOC, during the impulsion 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.

Then the only way to validate the total mass balance is the isotopic labeling (¹⁵NO, ¹⁸O₂, ¹³CO₂...). The results obtained with (¹⁸O₂: 10 %, CO₂: 10 %, C₃H₆: 1000 ppm, NO: 700 ppm, N₂: Balance) system are presented below (section 3.4).

3.1. NO conversion by the depollution device

The evolution of NO and NO₂ contents according to energy density (figure. 4) makes appear an excess of NO₂ production with regard to NO decrease. Further more, the point-plan energy cost is significantly more important than the multipoint to plane one. For example, the NO removal is estimated to 60 % with 80 J/L and 160 J/L input energy density, respectively with multipoint to plane and point to plane reactors. A weak content of NO is probably converted into RNO_x compounds, which are shown in figure. 7.

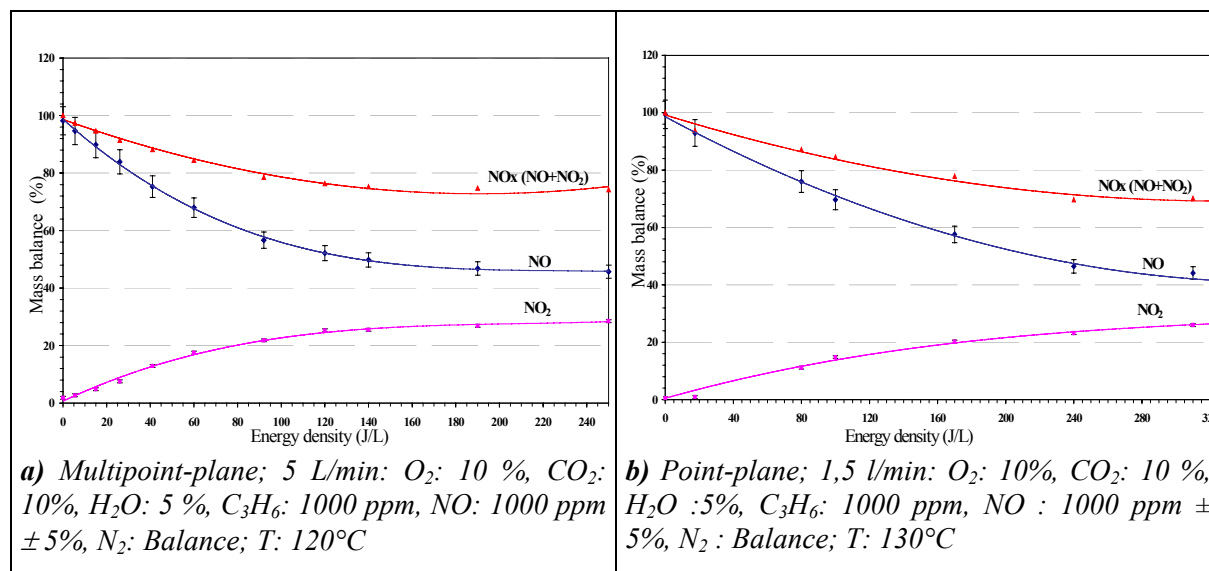


Figure 4: Evolution of the NO_x (NO, NO₂) as a function of the input energy density

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 ppm ± 5%).

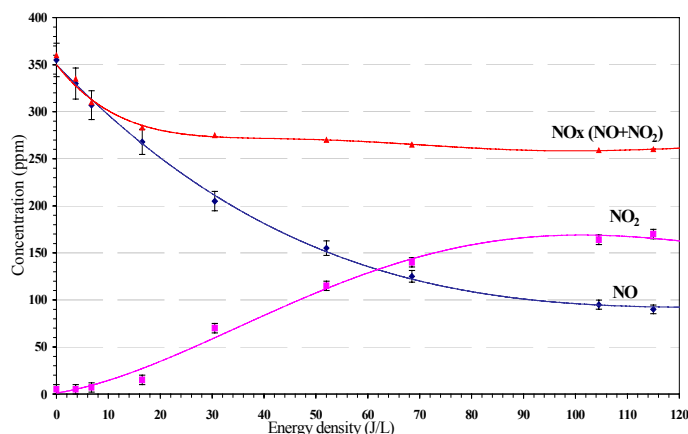


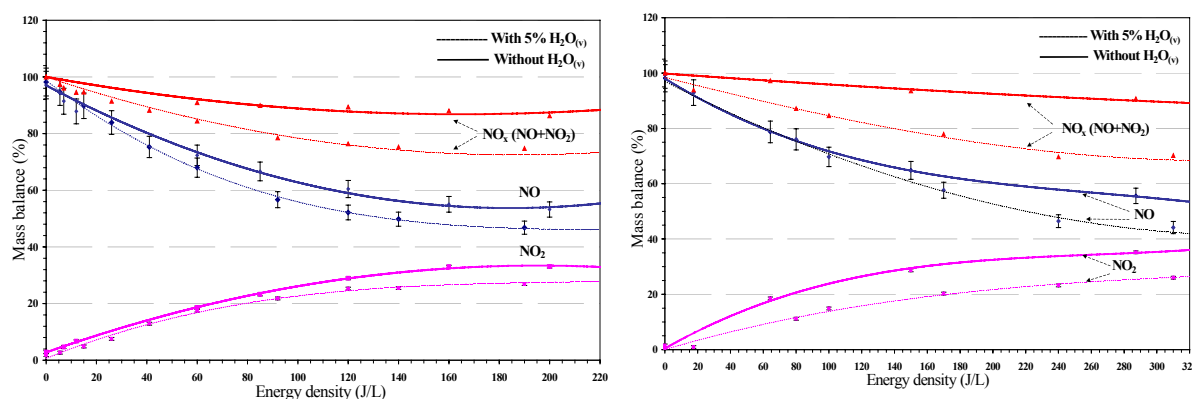
Figure.5: Evolution, as a function of the energy density of the NO_x (NO, NO₂) concentration [Multipoint-plane; 13 L/min; O₂: 10 %, CO₂: 10%, H₂O: 5 %, C₃H₆: 1000 ppm, NO: 350 ppm ± 5%, N₂: Balance; T: 130°C]

For input energy densities varying between 30 and 120 J/L, a significant reduction of NO with increasing of the energy is observed while NO₂ concentration still increases. Thereby NO_x (NO+NO₂) concentration remains almost constant. This suggests that most of NO changes into NO₂ by oxidation. Also it can be noticed that NO_x is easily removed (NO/NO_x as a function of NO) under a lower initial NO concentration and reactor performance in NO and NO_x removal cost energy density is probably affected by the inlet gas flow.

- Role of H₂O:

With an energy density estimated at 100 J/L and using the multipoint to plane configuration, the NO removal in the gas mixture (O₂: 10%, CO₂: 10%, C₃H₆: 1000 ppm, NO: 1000 ppm ± 5%, N₂: Balance) is 50 % with water vapor (5% in volume) against 40 % without it. Also when 5% of water vapor was included, the NO₂ production was remarkably decreased. It was caused by the reaction of water with NO and NO₂, which led to formation of HNO₂ and HNO₃. This affects the conversion rate of the total NO_x (NO+NO₂), which 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:

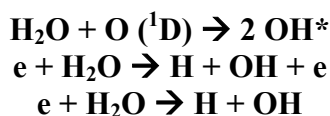


a) Multipoint-plane reactor; 5 L/min at 120 °C b) Point-plane reactor; 1,5 l/min at 130°C

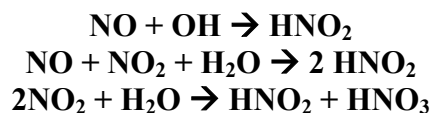
Figure. 6: Effect of the hydration of the gas mixture (O₂: 10 %, CO₂: 10%, C₃H₆: 1000 ppm, NO: 1000 ppm ± 5%, N₂: Balance)

The conversion way of NO in a humid atmosphere has been already studied⁶⁻⁸:

OH is formed first by the reaction of H₂O with O (¹D) and by the electron impact dissociation of H₂O according to:



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



The role of water is, therefore, obviously affirmative. On the other hand, the discharge character was not significantly affected by the water vapor.

3.2. The surface catalyze phenomena (hetero-exchange) (stumatite or stumatite + TiO₂):

The interaction between TiO₂ surfaces and different molecules is widely studied in surface-related applications such as catalysis and photocatalysis^{9,10}.

According to several studies, titanium oxide catalyst is one of the most investigated photocatalytic systems and has been found to be able to decomposing a wide variety of organic and inorganic pollutants and toxic materials, in both liquid and gas-phase systems^{11,12}.

On the other hand, the selective catalytic reduction (SCR) of nitric oxide with oxygenated hydrocarbons using Titania based oxides and included within zeolites cavities^{12,13} have been reported. The formation of surfaces inorganic species such as nitrate $-\text{NO}_3^-$, nitro $-\text{NO}_2$, and nitrite $-\text{NO}_2^-$ were observed.

In the following work, we use a powdered TiO_2 substrate which is placed over the dielectric support (stumatite); The concentration of NO , NO_2 and NO_x ($\text{NO}+\text{NO}_2$) at the inlet and the outlet were measured by the gas analyzer and hence the NO and NO_2 removal percentage was calculated. We have noticed that the presence of the Titania powder contributes to decrease the NO_2 production. Nevertheless the NO removal rate is practically the same (Figure 6). This result is also obtained with the point to plane reactor and it have been already study⁵.

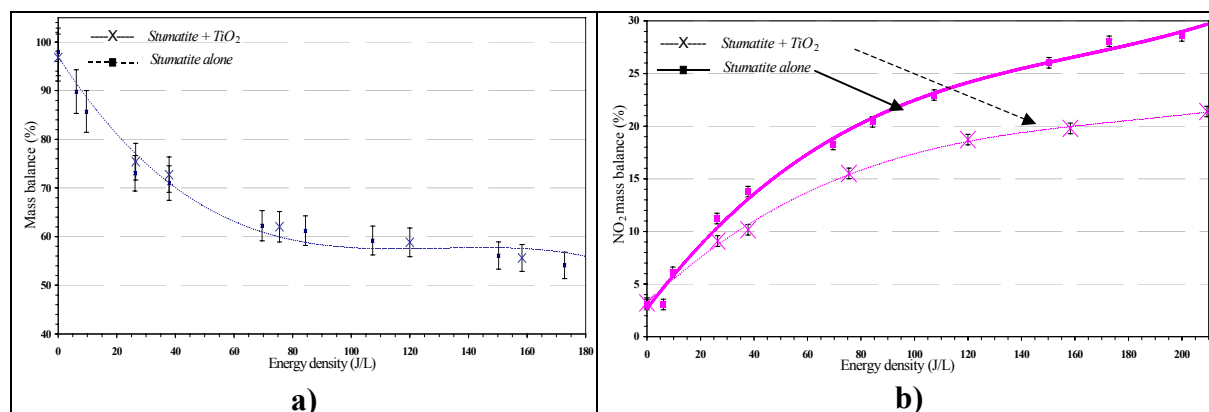


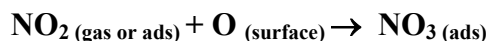
Figure 6: Effect of the addition of TiO_2 powders upon the NO (a) and the NO_2 (b) emission. [Multipoint-plane; 5 L/min: O_2 : 10%, CO_2 : 10 %, C_3H_6 : 1000 ppm, NO : 1000 ppm \pm 5%, N_2 : Balance; T: 120°C].

NO_2 is a radical molecule with a large electron affinity (2.3 eV^{14}), that can bond to the n-type semiconductor TiO_2 via O, N, or a combination of both.

Rodriguez & al.¹³ studied the behavior of NO_2 / Titania system (TiO_2 (110) single crystal and powders). They considered that the main product of the adsorption of NO_2 on TiO_2 is surface nitrate with a small amount of chemisorbed NO_2 . Photoemission data and density functional calculation indicate that the surface nitrate forms throughout the disproportionation of NO_2 on substantial amount of Ti that exposed powders of TiO_2 on their surfaces^{15,16} according to:



rather than direct adsorption of NO_2 on O centers of the oxide surface:



The system need a certain amount of input energy to decompose the produced nitrate:



The behavior of the NO_2 /titania system illustrates the importance of surface exchange when dealing with DeNO_x reactions on oxides.

3.3. Analysis of the impulsional discharge by-products VOC

The analyze of the by-products treatment of a gas mixture containing (CO_2 , NO , O_2 , H_2O , N_2 and C_3H_6) is realized by GC / MS [chromatographique column ChromPack PoraPlot-

Q (25 m-0.32 mm-10 μ m, phase polymer: polystyrene - divinyl-benzene); introduction of gas through a 100 μ L sampler; vector gas: helium (pressure: 0.3 kg / cm)].

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 VOC, 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 CO production. A minority of RNO_x generated by the reaction radical / NO_x is as well-formed (Figure 7). The destruction propylene rate varies between 40 and 70 % according to the geometry of electrodes, the dielectric, the energy density and the gas mixture.

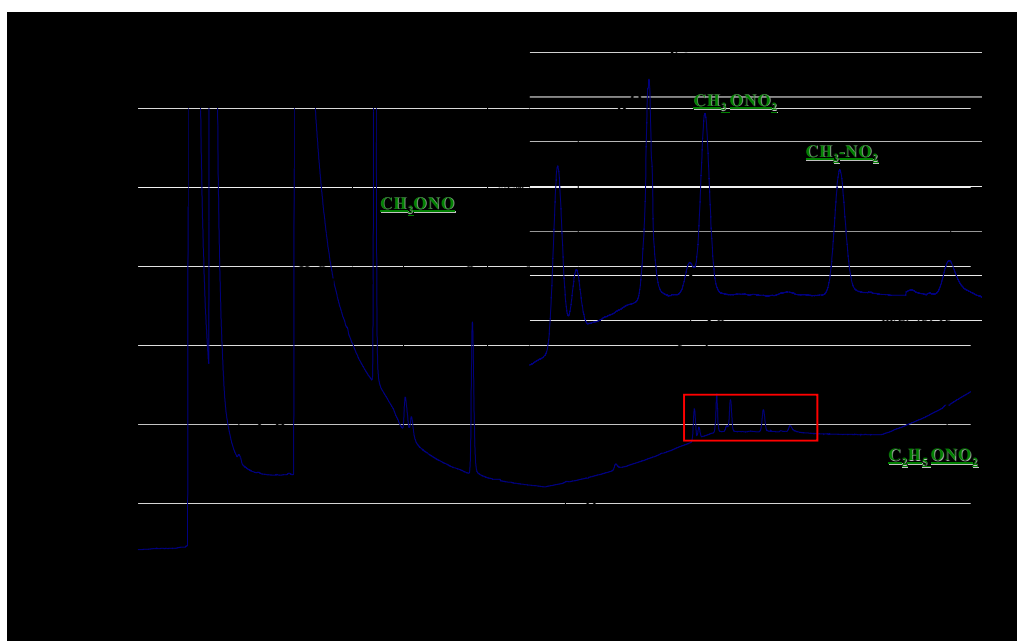


Figure 7: Chromatogram of gas mixture treated by corona discharge [Multipoint-plane; 5 L/min: O₂: 10 %, CO₂: 10%, H₂O: 5 %, C₃H₆: 1000 ppm, NO: 1000 ppm \pm 5%, N₂: Balance; T: 130°C]

4. Understanding of the discharge chemical reaction using O₂ labeled: study of oxygen exchange

- Experimental section

Experiments were carried out in a conventional apparatus already described in this paper (section.2). The electrode configuration used is the multipoint to plane one and the (¹⁸O₂: 10 %, CO₂: 10 %, C₃H₆: 0.3%, NO: 700 ppm \pm 5%, N₂: Balance) is the gas mixture treated, with a 2,5 L min⁻¹ flow at 150°C.

The oxygen labeled is produced from AIR LIQUID Industrial services, it's a (N₂: 80%, ¹⁸O₂: 20 \pm 0,4%) mixture.

- ¹⁸O₂ isotopic exchange

The GC/MS analysis is realized after plasma treatment under 20W power and 18 kV applied voltage. 90% (650 ppm) of NO is removed, respectively 300 and 6000 ppm of NO₂ and CO are produced. The GC/MS qualitative analyze strongly supports the results already obtained with the ¹⁶O₂ (figure.7) owing to the fact that the hydrocarbon oxide molecules formed by the corona discharge are chiefly identified in aldehyde and alcoholic functions. Nevertheless, one can distinguish the oxygen atoms belonging to the CO₂ or the NO from

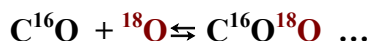
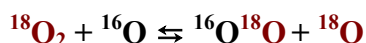
those provided by the $N_2/^{18}O_2$ mixture. Here is a summary of the overall result about distribution of atomic oxygen in different molecules (table. A and B):

^{16}O	^{18}O	$^{16}O/^{18}O$	
$CH_3-CH_2-C \begin{matrix} \nearrow O \\ \searrow H \end{matrix}$ (~ 95%)	$CH_3-C \begin{matrix} \nearrow O \\ \searrow CH_3 \end{matrix}$ (~ 90%)	$H_2C^{16}O / H_2C^{18}O$	$H_2^{16}O / H_2^{18}O$ $C^{16}O_2 / C^{18}O_2 / C^{18}O^{16}O$
$CH_3-C \begin{matrix} \nearrow O \\ \searrow H \end{matrix}$ (~ 90%)		$CH_3-^{16}OH / CH_3-^{18}OH$	
$CH_3-C \begin{matrix} \nearrow ^{16}O \\ \searrow OH \end{matrix}$		$CH_3-CH_2-^{16}OH / CH_3-CH_2-^{18}OH$ (~ 1/2)	
		$CH_2=CH-C \begin{matrix} \nearrow O \\ \searrow H \end{matrix}$ ($^{16}O/^{18}O \sim 2$)	

Table. A. Distribution of ^{18}O in VOC by-products

It can be noted that the majority of the carbonyl function remains exactly the same (no oxygen exchange) in the aldehyde and acid molecules except for the formaldehyde (H_2CO) and CO/CO_2 equilibrium. CO function probably results from a reduction of carbon dioxide.

CO oxidation and exchange: From the identification of carbon dioxide labeled ($C^{18}O_2$, $C^{16}O^{18}O$), information on the type of exchange mechanism in gas phase may be proposed. They are described by the possible following reactions:



CO_2 labeled can be produced too by total oxidation of hydrocarbon molecule by $^{18}O_2$. Distribution of ^{18}O in RNO_x species is presented below.

specie	CH_3ONO_2	ratio
radical portion	$N^{18}O_2/N^{16}O_2$	9
	$N^{18}O^{16}O/N^{16}O_2$	~ 5
	$N^{18}O_2/N^{18}O^{16}O$	2
specie	CH_3NO_2	ratio
radical portion	$CH_3N^{18}O_2/CH_3N^{16}O_2$	50
	$CH_3N^{18}O^{16}O/CH_3N^{16}O_2$	20
specie	$CH_3CH_2ONO_2$	ratio
radical portion	$N^{18}O_2/N^{16}O_2$	7
	$N^{18}O^{16}O/N^{16}O_2$	~ 2,5
	$N^{18}O_2/N^{18}O^{16}O$	3
$C_2H_5-^{18}O$ is the majority produced		
specie	CH_3ONO	
Specially $CH_3-^{18}O-N^{16}O$		

Table. B. Distribution of ^{18}O in RNO_x produced.

Chemical mechanisms presented in figure.8 summarize part of the reactional pathway occurring during the plasma treatment.

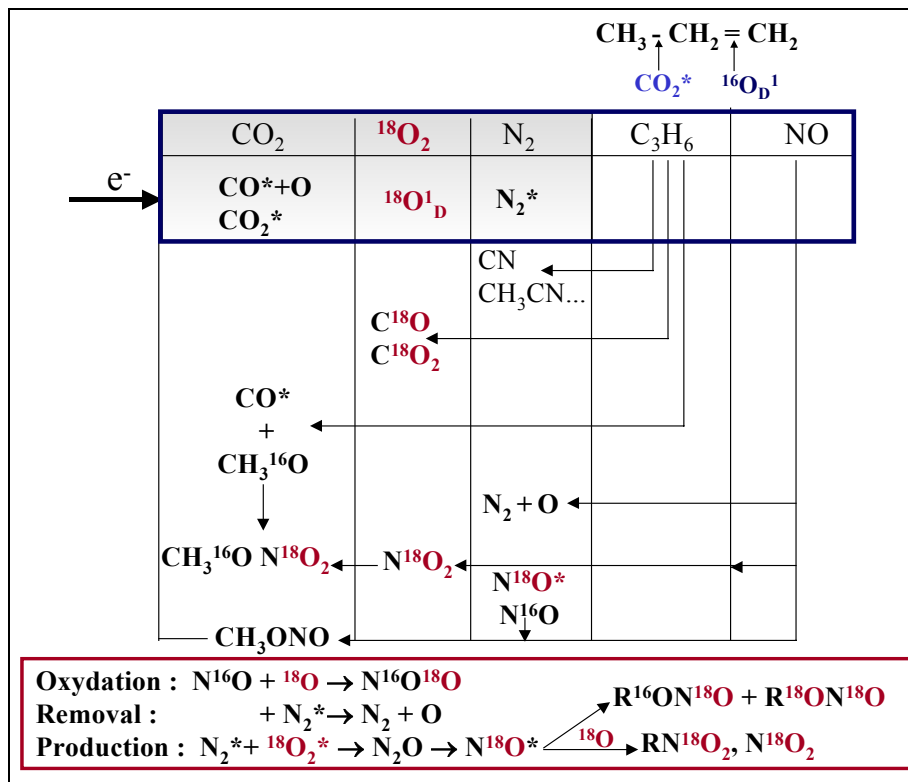


Figure.8. Chemical mechanism study.

¹⁸O coming from (C₃H₆/NO/CO₂/N₂/¹⁸O₂) discharge system is preferentially bonded to a methyl (-CH₃) or ethyl radical (-C₂H₅). A large part of NO_x reacting with radical carbon in order forming RNO_x species is produced by N₂/¹⁸O₂ system.

5. Conclusion

The removal of NO_x (NO and NO₂) using barrier discharge has been experimentally investigated. Point to plane and multipoint to plane configurations were used. Plasma can be produced at atmospheric pressure in a 2 mm gap with 8 kV peak to peak concerning the multipoint to plane reactor, and in a 4 mm gap with 14 kV pkpk for the point to plane one. Impulsion generated by multipoint to plane configuration is characterized by a 2 nC charge, a 100-mA intensity and 100 ns duration. To note, that the point to plane energy cost is significantly more important than the multipoint to plane one.

With the multipoint to plane configuration, at 350 ppm of NO concentration, NO can be removed to 70% from the gas treated. Production of NO₂ increases with the NO conversion. The energy density that input into the discharge to reduce 50% of NO from the gas mixture (containing 350 ppm of NO) is approximately 40 J/L.

We are observed that OH radicals improve the efficiency of depollution reactors. However (NO, NO₂ and OH) system induce to form HNO₂ and HNO₃.

The GC/MS analyze used in order to investigate the (N₂/O₂/C₃H₆/CO₂/NO/H₂O) by-products system showed that this gas mixture generates a significant amount of aldehyde, alcoholic and some RNO_x compounds.

The chemical behavior observed in (C₃H₆/NO/CO₂/N₂/¹⁸O₂) plasma gas proves that production of VOC compounds by C₃H₆ oxidation process depends on the reactivity of

atomic oxygen coming from $N_2/^{18}O_2$ mixture and CO_2/O_2 exchange too. $CH_3-^{18}O$, $C_2H_5-^{18}O$ radical and CO_2 labeled have been identified.

It is observed that main of NO_x trapped at nitro compound in gas phase are produced by the discharge.

Lastly, the behavior of the NO_2 /Titania system illustrates the importance of surface reaction phenomena in NO_x removal application.

Acknowledgments

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