

EXPERIMENTAL AND SIMULATION STUDY OF NO_x REMOVAL WITH A DBD WIRE-CYLINDER REACTOR

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ABSTRACT: *Our goal is to develop a wire-cylinder dielectric barrier discharge reactor for NO_x removal from a gas mixture (O₂:10%, CO₂:10%, H₂O:5%, C₃H₆:1000ppmv, NO:250 to 1000ppmv, N₂:balance). The NO conversion has been investigated depending on energy density and the by-products (essentially aldehydes and R-NO_x) have been identified by GC-MS. Isotopic labeling of the O₂ introduced helps to elucidate the reaction mechanisms leading to the formation of those by-products. For each experiment, the electrical characterization of the discharge has been carried with a digital oscilloscope, giving the measurement of the voltage, the current, the power and the electrical charge of the plasma pulses. In the second part, we simulate the NO conversion in a tubular reactor with multiple O* injections in order to qualify the role of the oxygen atoms produced by the electrical pulses.*

Keywords: Dielectric barrier discharge, NO_x removal, wire-cylinder, reaction mechanisms, isotopic labeling, modeling

1. INTRODUCTION

Recently, non-equilibrium plasma processes have been developed for the destruction of atmospheric pollutant gases. In fact, various dielectric barrier discharge (DBD) treatment processes have been developed for pollution removal, using DC or AC corona discharge with point-to-plane^[1,2], multipoint-to-plane^[1,3,4] or wire-cylinder^[5,6] reactors. For this study, we used a wire-cylinder reactor (energy is provided by an AC generator) in order to remove the NO contained in an O₂ (10%), CO₂ (10%), H₂O (5.4%), C₃H₆ (1000ppmv), NO (1000ppmv) and N₂ (balance) gas mixture. The process was electrically monitored, using a 500 MHz digital oscilloscope, to provide an energy balance. The treated gas was analyzed with GC-MS (identification and quantification of carbon containing by-products) and gas analyzer (quantification of NO and NO₂). The treated gas analysis indicates if NO_x treatment actually occurs by oxidation of NO in NO₂, formation of nitric acid (by reaction with water), reduction or trapping by hydrocarbons.

The reactional pathways were determined by isotopic labeling, substituting introduced O₂ by its ¹⁸O₂ isotope. The mass spectra of the different species created by oxidation from O₂ were indeed modified. Checking it with the GC-MS allowed to determine the isotopic composition of the different species in order to understand the reaction mechanisms in the DBD reactor.

Finally, we completed the characterization of the reactor behavior by modeling the impulsional injection of atomic oxygen (reactant created by the discharge) and its role in NO oxidation.

2. EXPERIMENTAL SET-UP

The reactor is a cylindrical dielectric tube (aluminio-silicate tube: $\varnothing_{\text{int}}=15\text{mm}$ / $\varnothing_{\text{ext}}=21\text{mm}$ + glass tube within aluminio-silicate tube: $\varnothing_{\text{int}}=11\text{mm}$ / $\varnothing_{\text{ext}}=15\text{mm}$). The high voltage electrode is a 6 or 8 mm diameter and 35 mm long copper screw (gap=2.5 or 1.5mm), the grounded electrode is a sheet of copper. Energy is supplied by a “Calvatron SG2” high voltage 44kHz AC supply (applied voltage is between 9 and 15 kV peak to peak). The experimental set-up is shown in Fig. 1 and Fig. 2:

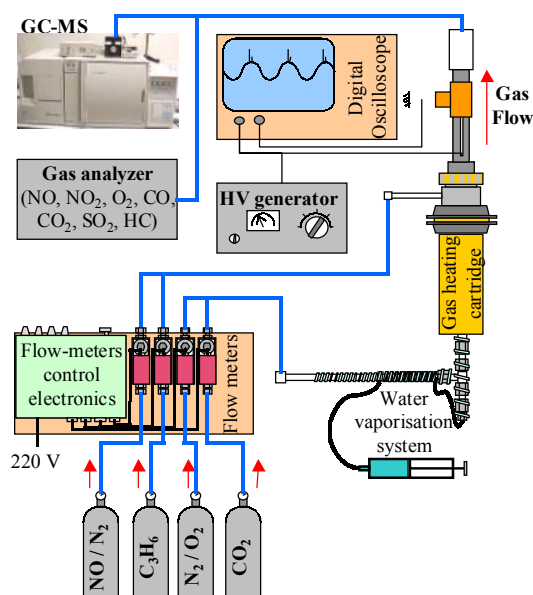


Fig. 1. Experimental set-up of the wire-cylinder reactor, gas feeding system and analysis apparatus

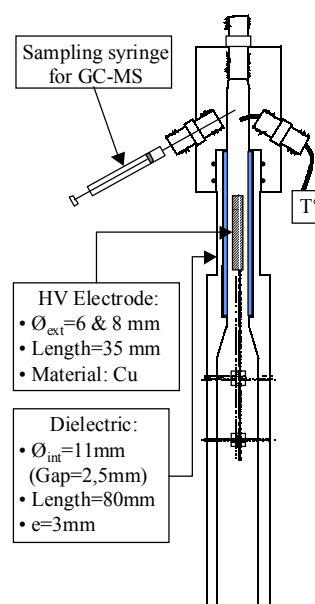


Fig. 2. Detailed scheme of the wire-cylinder reactor

A previous electrical characterization of a reactor^[6,7] is the necessary step preceding the chemical study. It is an important step in energy balance determination and control of energy consumption^[8]. This electrical characterization is made measuring voltage (using a high voltage 1:1000 probe), current, power, electric charge, frequency and pulse time with a LeCroy LT-342 500MHz digital oscilloscope (Fig. 3).

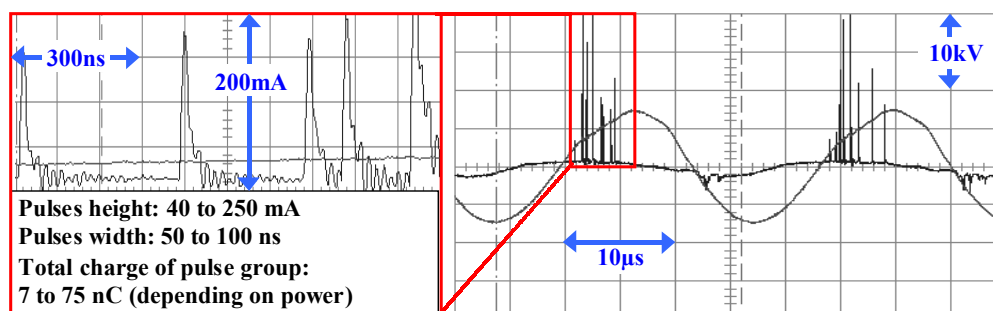


Fig. 3. Oscillogram obtained for the treatment of the O_2 (10%), CO_2 (10%), H_2O (5.4%), C_3H_6 (1000ppmv), NO (1000ppmv) and N_2 (balance) gas mixture

The reactor is fed with a gas mixture at atmospheric pressure. Each gas (except water vapor) is introduced into the reactor by a mass flowmeter. O_2 (10%), CO_2 (10%) and N_2 (balance) are introduced in a heating cartridge while NO (250 to 1000ppmv) and C_3H_6 (1000 or 2000ppmv) are introduced after it. A motorized syringe pusher introduces H_2O (5.4%) in a heated 1/8" diameter and 2 meters long stainless steel tube. Vaporized water is then

introduced into the heated gas. The total gas flow is about 12.9 slpm. The temperature of the gas mixture is measured by a thermocouple at 3 cm after the discharge zone.

Gas is analyzed by:

- GC-MS (Gas Chromatography coupled with a Mass Spectrometer): it allows the identification (sensitivity: ~ppm) and the quantification ($\pm 5\%$ after calibration) of the different hydrocarbon compounds.
- Gas Analyzer (QUINTOX – Kan-May) measuring NO, NO₂ & CO quantities.

3. EXPERIMENTAL RESULTS

3.1. Analysis of the treated gas

The GC-MS analysis indicate that the great majority of the by-products are oxidized compounds where aldehydes and R-NO_x are quantitatively the most representative ones (higher peaks). This is the demonstration of the prime importance of the oxidation phenomena in this process. NO_x analyses were conducted at different applied power to qualify the pollution removal behavior of the reactor versus energy density (Fig. 4). Before each analysis (simultaneously made by GC-MS and gas analyzer), a measure was made with the discharge off.

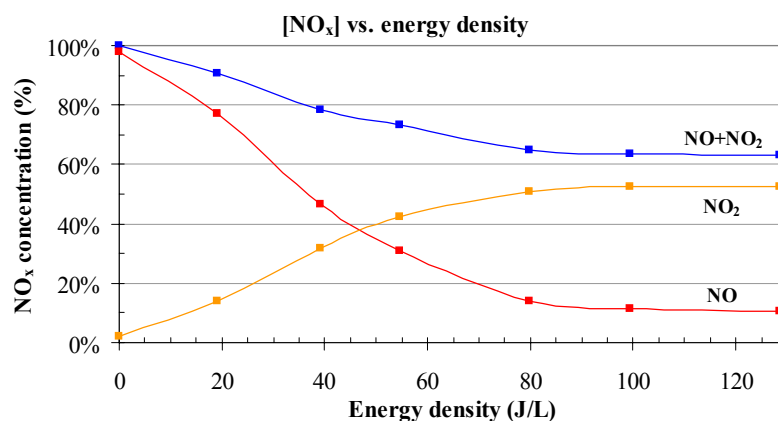


Fig. 4. NO_x concentration vs. energy density for an O₂ (10%), CO₂ (10%), H₂O (5.4%), C₃H₆ (1000ppmv), NO (1000ppmv) and N₂ (balance) gas mixture ($T=150$ to 200°C depending on discharge power, flow=12.9 slpm)

We can notice that NO concentration decreases with energy density increase. This decrease of NO is linked to the NO₂ increase through oxidation processes. The oxidant vector can be O₂ (giving O in the discharge)^[9], CO₂ (giving O and CO)^[10,11] and H₂O (giving OH)^[12,13,14]. Those species are present in excess in the mixture (about 100 to 1 NO molecule). But a significant part of NO_x “disappears”, being trapped by C₃H₆ (giving R-NO_x)^[15] or water (giving HNO₃), adsorbed on the outlet tubes or reduced to N₂+O₂. The influence of the energy density on the formation of the by-products has been presented in a previous article^[16].

3.2. Determination of reaction mechanism by isotopic labeling

After the reactor characterization, we determined the reaction mechanisms by isotopic labeling, using the mass spectrometry of the GC-MS to identify the different by-products isotopes. Then, the substitution of O₂ (¹⁶O-¹⁶O) by labeled O₂ (¹⁸O-¹⁸O) allows us to identify the origin of O atoms in the molecules: O₂ (¹⁸O labeled by-product), CO₂ (unlabeled by-product) or the both (partially ¹⁸O labeled by-product).

The determination of the reaction mechanism requires the knowledge of the by-product mass spectrum and its possible changes in labeling. For example, the gas treatment of ¹⁸O₂ containing gas mixture can modify the CH₃-O-NO₂ isotopic composition, giving a distribution

of isotopes containing 0 to 3 ^{18}O atoms. The ratio between the different areas of chromatographic peaks give the proportion of each isotope produced by the discharge. The chromatograms obtained indicate that the O atom between CH_3 and NO_2 functions is due to the oxidation of CH_3 radicals by $^{18}\text{O}_2$ initially introduced. NO_2 function contains about 10% of $\text{N}^{16}\text{O}^{16}\text{O}$, 50% of $\text{N}^{16}\text{O}^{18}\text{O}$ and 40% of $\text{N}^{18}\text{O}^{18}\text{O}$. We can notice that a great part of NO_2 trapped in this molecule doesn't come from the native NO (which is unlabeled) but was produced from N_2 and $^{18}\text{O}_2$ by the discharge. The other part is essentially due to oxidation of native NO by ^{18}O and caught by $\text{CH}_3\text{-}^{18}\text{O}$ (created from CH_3 and $^{18}\text{O}_2$). $\text{CH}_3\text{-}^{18}\text{O}\text{-N}^{16}\text{O}^{16}\text{O}$ should have been created by oxidation of NO with ^{16}O coming from CO_2 .

Proceeding with the same methodology allows us to determine the isotopic composition of the different by-products. These compositions are summed up in the Table I and reactional pathways are proposed in Fig. 5.

Table I. Composition of the by-products obtained for the treatment of an $^{18}\text{O}_2$ (10%), CO_2 (10%), H_2O (5.4%), C_3H_6 (2000ppmv), NO (1000ppmv) and N_2 (balance) gas mixture ($T=140^\circ\text{C}$, flow=12.9 slpm)

| Specie | Fragment or molecule isotope | Proportion | Source of O |
|-----------------------------------|--|------------|--|
| $\text{CH}_3\text{-CHO}$ | $\text{CH}_3\text{-CH}^{16}\text{O}$ | 95% | CO (from CO_2) |
| | $\text{CH}_3\text{-CH}^{18}\text{O}$ * | 5% | |
| $\text{CH}_3\text{-HCOCH}_2$ | $\text{CH}_3\text{-CH}^{16}\text{OCH}_2$ | 15% | O (from O_2) |
| | $\text{CH}_3\text{-CH}^{18}\text{OCH}_2$ * | 85% | |
| $\text{C}_2\text{H}_3\text{-CHO}$ | $\text{C}_2\text{H}_3\text{-CH}^{16}\text{O}$ | 25% | O (from O_2) |
| | $\text{C}_2\text{H}_3\text{-CH}^{18}\text{O}$ * | 75% | |
| $\text{C}_2\text{H}_5\text{-CHO}$ | $\text{C}_2\text{H}_5\text{-CH}^{16}\text{O}$ | 80% | CO (from CO_2) |
| | $\text{C}_2\text{H}_5\text{-CH}^{18}\text{O}$ * | 20% | |
| $\text{CH}_3\text{-CO-CH}_3$ | $\text{CH}_3\text{-}^{16}\text{O-CH}_3$ | 40% | O (from O_2 & CO_2) |
| | $\text{CH}_3\text{-}^{18}\text{O-CH}_3$ * | 60% | |
| $\text{CH}_3\text{-O-NO}$ | $\text{CH}_3\text{-}^{16}\text{O-N}^{16}\text{O}$ | 13% | O (from O_2) & NO |
| | $\text{CH}_3\text{-}^{18}\text{O-N}^{16}\text{O}$ * | 60% | |
| | $\text{CH}_3\text{-}^{18}\text{O-N}^{18}\text{O}$ * | 27% | |
| $\text{CH}_3\text{-O-NO}_2$ | $\text{CH}_3\text{-}^{18}\text{O-N}^{16}\text{O}^{16}\text{O}$ * | 10% | O (from O_2) & NO |
| | $\text{CH}_3\text{-}^{18}\text{O-N}^{16}\text{O}^{18}\text{O}$ * | 50% | |
| | $\text{CH}_3\text{-}^{18}\text{O-N}^{18}\text{O}^{18}\text{O}$ * | 40% | |
| $\text{CH}_3\text{-NO}_2$ | $\text{CH}_3\text{-N}^{16}\text{O}^{16}\text{O}$ | 20% | O (from O_2) & NO |
| | $\text{CH}_3\text{-N}^{16}\text{O}^{18}\text{O}$ * | 55% | |
| | $\text{CH}_3\text{-N}^{18}\text{O}^{18}\text{O}$ * | 25% | |

* signals an ^{18}O containing molecule

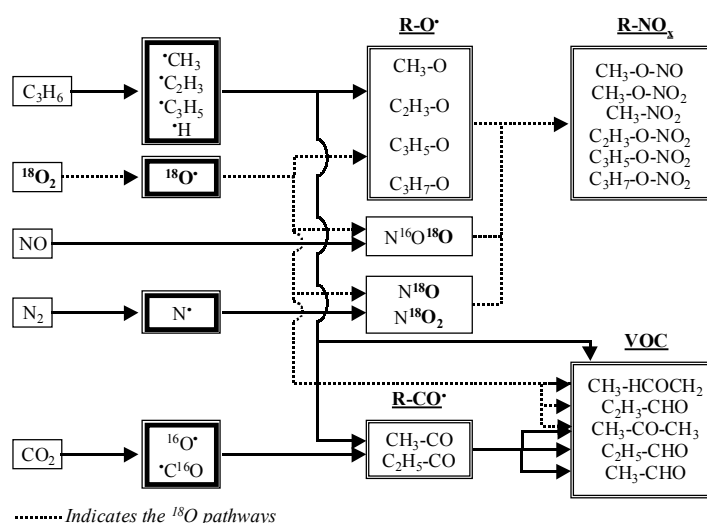


Fig. 5. Determination by isotopic labeling ($\text{O}_2 \rightarrow ^{18}\text{O}_2$) of reactional pathways leading to the formation of the VOC's and R-NO_x

The main R-NO_x emitted (CH₃-O-NO, CH₃-O-NO₂ and CH₃-NO₂) are essentially produced by oxidation of NO by O (itself essentially due to O₂) but it contains a significant part of NO₂ created from N₂ & O₂ in the discharge. For the main VOC emitted (acetaldehyde, propanal and propylene oxide) the two first are essentially produced by oxidation of HC fragments with CO while CH₃-HCOCH₂ is directly formed by oxidation of C₃H₆ with O (from O₂ and CO₂).

4. MODELING AND SIMULATION OF THE REACTOR

The reactor characteristics for the modeling are:

- HV electrode: copper screw with 35 thread of screw, gap: 1,5 mm
- Each thread of the screw is a streamer zone
- The electrical wind and ions velocity (about 10 m.s⁻¹ and 60-180 m.s⁻¹ respectively^[17]) creates a plasma diffusion cone: the gap is crossed over in less than 300 μs
- The impulsional charge linearly increases with power (electrical period: 22 μs)
- The gas flow is 20 L.min⁻¹ (gas velocity: 5.4 m.s⁻¹, average residence time: 7 ms)
- The gas mixture is, O₂ (10 %), NO (250 to 1000 ppmv) and N₂ (balance)

The cylindrical geometry of the reactor and flow pattern suggests the use of a plug flow reactor (PFR) model. A preliminary study revealed that to approach the PFR model to experimental data, it is required to consider an important axial dispersion. This phenomenon is explained by the presence of electrical wind caused by discharge, which is responsible for the great mobility of reaction species. But the PFR modeling didn't succeed to take into account the NO conversion profile. When the axial dispersion increases in a PFR, its behavior tends to a continuous stirred reactor (CSTR). Then, we decided to model the wire-cylinder reactor as a cascade of CSTR.

In order to argue on this amazing choice, we should consider that the electrical wind in each plasma cone (the threads of the screw are the initiating point of the streamers propagation) produces an important retro-mixing. The reactor will then be split into 35 elementary reactor, each one corresponding to a tread of screw. Because ions and electrical wind are fast enough to reach the elementary reactor boundaries within the elementary residence time (7 ms / 35 elementary reactor → 200 μs elementary residence time), we consider that each reactor behaves like a continuous stirred tank reactor (CSTR). The reactor will be modeled as a cascade of 35 elementary reactor with a continuous feeding of N₂, O₂ and NO, and with an impulsional feeding of oxygen atoms created by electronic impact on O₂ molecules. Fig. 6 illustrates the equivalence of our wire-cylinder reactor with the cascade of CSTR considered in the simulation.

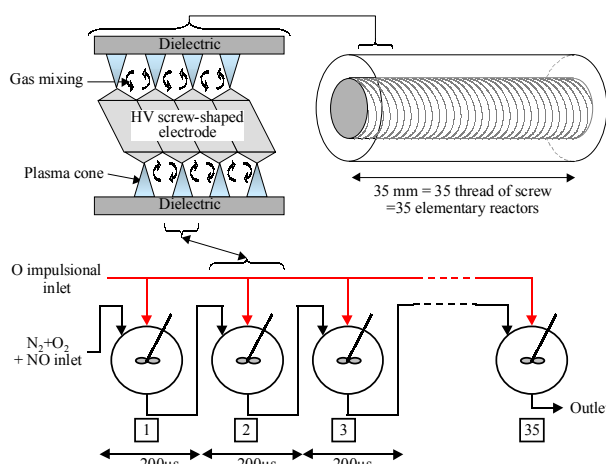


Fig. 6. Equivalence between DBD reactor and the serial CSTR system

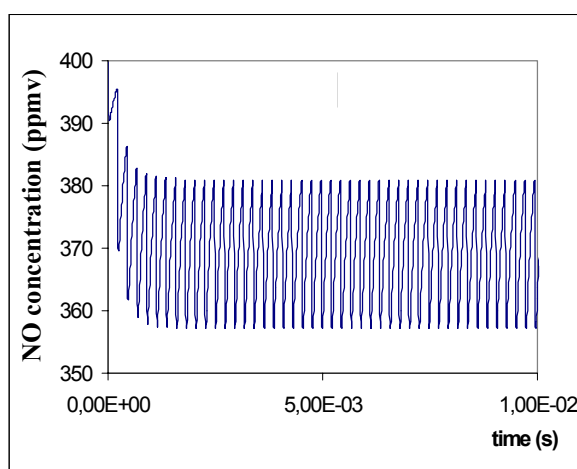
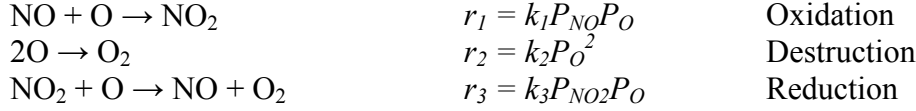


Fig. 7. NO concentration evolution in the first CSTR

In order to model effects of electrical discharge on the reactor operation, some hypotheses were used based on experimental observations. First, it was considered that the atomic oxygen created by discharge is the main species responsible for the mixture reactivity. Second, the electron impulsion flow creates an impulsion flow of atomic oxygen. Finally, a simplified reaction pathway, consisting of three reactions and shown below, was used to provide a global comprehension of the reactor behavior.



From these hypotheses, the electrical discharge represents a direct variation of the concentration of atomic oxygen in each elementary reactor. To characterize the electrical discharge, the electric impulse duration is determined analyzing the electrical signal in a numeric oscilloscope and the impulse period is calculated directly from the frequency. Due to the short duration of the electric impulse (10 ns) with regard to the period (22 μs), we can consider the impulse as instantaneous. In consequence, the impulse can be translated like an instantaneous injection of atomic oxygen to each elementary reactor. Subsequently, the oxygen injection extent is calculated directly from the energy density.

Once the reactor model is proposed, the reactions that govern the system behavior must be described. For a multi-component feed to a perfectly mixed tank, the mass balance for component j would be as shown in equation 1.

$$\frac{d(C_{jo}^k V^k)}{dt} = F_i^k C_{ji}^k - F_o^k C_{jo}^k + r_j^k V^k \quad (1)$$

where F^k is volume flow (inlet or outlet) of j component, C_{ji}^k is the concentration of j species in the inlet stream of k^{th} reactor, C_{jo}^k is the concentration of j species in the outlet stream of k^{th} reactor, V^k is the elementary reactor volume and r_j^k is the reaction of rate of the generation of component j .

Inlet conditions in the k^{th} reactor are obtained directly from outlet conditions from the previous reactor. Nevertheless, in the case of atomic oxygen, the inlet term is a time function expressed as:

$$C_{O_i}^k = C_{O_o}^{k-1} + C_{O_{imp}}^k(t) \quad (2)$$

where the $C_{O_{imp}}^k(t)$ term means atomic oxygen injection. So, this term is a discrete function expressed by equation 3 and $C_{O_o}^{k-1}$ is atomic oxygen flow from $(k-1)^{\text{th}}$ reactor

$$C_{O_o}^k(t) \begin{cases} = \Delta C_{O_{inj}}^k & t = mT_{inj} \\ = 0 & t \neq mT_{inj} \end{cases} \quad (3)$$

where $\Delta C_{O_{inj}}^k$ represents the instantaneous injection of atomic oxygen, T_{inj} is the injection period and m is an integer.

For a system with n components, there are n component balances. The total mass balance and the component balances are not independent. Generally, the mass balance and $n-1$ component balances are used. However, in our case, the total mass balance equation is not used in reason of low concentration of reaction species (max. 1000 ppm). So, it was applied a mass balance for each component only for the minority species. The result is a system of n ordinary differential equations.

The well-known 4th order Runge-Kutta method was used to determine the evolution of concentrations as a function of time along the reactor. With the aim of adjusting experimental data and modeling results, optimization of parameters was carried out using kinetic constants.

Simulation results are shown in Fig. 7, Fig. 8 and Fig. 9. In Fig. 7, we can observe the evolution of NO concentration in the first CSTR reactor. As is shown, after a transient period, a cyclic quasi-steady state is established.

Fig. 8 illustrates the evolution of the main reaction species of the 35th outlet flow. Percentage conversion is shown as a function of time. As can be seen, the cyclic quasi-steady state is found again and NO_x conversion is quite stable after 3 ms approximately.

Finally, Fig. 9 shows NO_x destruction rate as a function of energy density. Simulation and experimental data are compared in the case of four concentrations. A good agreement between simulation and experiment is verified, so the CSTR cascade model describes in a pertinent way the plasma DBD reactor.

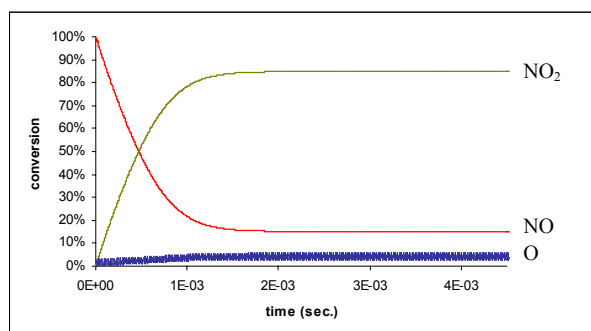


Fig. 8. Species concentration vs. time in outlet stream of 35th CSTR

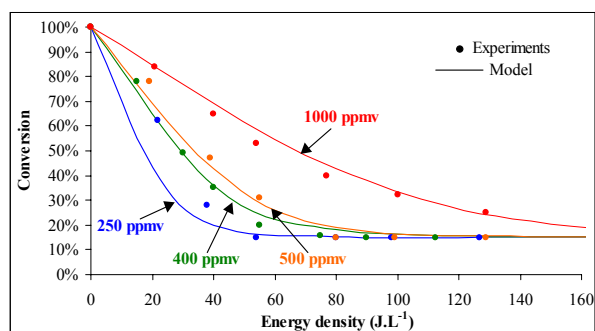


Fig. 9. NO destruction rate vs. energy density for different initial concentrations

5. CONCLUSION

In this study, we could validate the realization of a wire-cylinder DBD reactor adapted to the NO_x removal. The chemical behavior of this reactor has been interpreted by the determination of the different species created by the discharge (NO_x, VOC and R-NO_x have been checked with gas analyzer and GC-MS), the understanding of the reaction mechanisms by isotopic labeling and the modeling of the reactor. The main discharge by-products are aldehydes, acetone and R-NO_x but there are also traces of hydrocarbons, alcohols or acetonitrile. Most of them are oxidized compounds. The isotopic labeling of introduced O₂ (substituted by ¹⁸O₂) indicates that R-NO_x (formed by trapping of NO_x in hydrocarbons) are essentially due to oxidation of NO by O₂ native oxygen or to the reaction of N₂ with atomic oxygen coming from introduced O₂. The origin of O atoms contained in VOC is partially due to introduced O₂ and partially due to CO₂, depending on the species.

Finally, the oxidation of NO by the discharge in the wire-cylinder has been simulated. For this, we used a dynamic Continuous Stirred Tank Reactor model with a simplified set of reactions. The impulsional behavior of the reactor has been considered as pulsed introduction of atomic oxygen. This model efficiently describes the influence of the gas flow or of the NO introduced concentration in the reactor.

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