RESIDENSE TIME EFFECTS ON THE NOX REMOVAL EFFICIENCY IN TWO DIFFERENT DIELECTRIC BARRIER DISCHARGE CELL

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Experimental tests of the removal of NOx compounds were carried out in two dielectric barrier discharge cells (DBD) reactors at Physics plasma laboratory of Mexico Nuclear center Two different geometries of these reactor were studied, one circular 11.94 cm diameter, and another rectangular,16x7 cm, both 2.5 mm gap and 28.0 cm3 reaction volume
A gas mixture composed of 1.0 l/m of molecular nitrogen was injected to each reactor along with an additional flow that provided a concentration of 90 ppm of NO in both cells. The gas mixture was treated with non – thermal plasma generated by dielectric barrier discharge at different working potentials and at a 1.75 kHz frequency. The residual products were identified by means of a Sensonic 2000 gas analyzer..
According to the experimental results, it was identified a greater removal efficiency in the rectangular cell than in the circular one. This might be attributed both to residence time due to geometric effects and to a factor related with the chemical reaction mechanisms, since it has been showed that, at greater powers, the removal efficiency diminishes due to the regeneration of NO by inverse kinetic mechanisms. Our kinetic model proves that the main reaction product was N2O in the presence of a reducing atmosphere
Key words: *dielectric barrier discharge; cold plasma; non-thermal plasma (NTP); high energy electrons chemical kinetics*

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Introduction

Recent applications of non-thermal plasma (NTP) in processes of decontamination of gas flows are a new promising technique. The main characteristic of these degradation processes lies in not increasing the temperature of the gas /1/ while boosting its removal efficiency to values above 99 % without generating polluting by-products.

The cold plasma generated by means of dielectric barrier discharge, is carried out by a collection of short lived filaments or "streamers" distributed at random on the dielectric surface. It`s into the "streamers" that the plasma generation process is.

Fig. 1 Dielectric barrier discharge.

made because each channel of excited gas molecules contains very reactive species such as high energy electrons and free radicals /2/, that interact with the gas molecules resulting as the process of decomposition of the polluting molecules through diverse reaction mechanisms. The generation of the free radicals is very important since the recombination of compounds of the type NO'x to low concentrations /3, 4, 5/.

We used a lacking oxygen gas mixture system except for that removed from the molecule of NO. Such an atmosphere is totally reducing and allows the NO to recombine in its molecular components, N_2 and O_2.

NO removal experiences have been developed in gas flows as a dielectric barrier discharge (DBD) application.

The design will be presented at the experimental part. The main objective to use two cell configurations it was to determine which offers the best removal efficiencies and the way in which it can taken better advantage during processes of decomposition of NO'x compounds .

Experimental setup

The NO chemical reduction was made using N_2 as a carrier gas. The initial concentration of NO was varied between 85 and 95 ppm with a total gas flow of 1,0 l/min. The experimental diagram is presented in figure 2. The gas mixture was directly introduced to the reactor. The initial concentration and that at the end were measured with a Sensonic2000 gas analyzer.

Two types of reactor geometry were tested: one rectangular and a circular. Both geometries follow a flat configuration of parallel electrodes.

In the circular geometry (fig 3) the diameter was 11,94 cm and the gas gap 2,5 mm. The reaction.

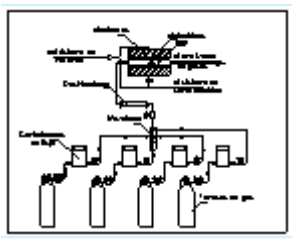

Fig. 2 Gas supply system experimental set up

volume in it was 28 cm^3 The rectangular geometry dimensions were 16 cm x 7cm, 2,5 mm gas gap

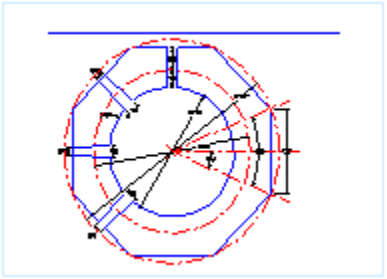

Fig. 3 Metal - water circular DBD cell.

and a reaction volume of 28 cm^3 too. The power was provided by a high voltage transformer which is fed by half-bridge high frequency inverter /6,7/.

The electric diagnostics in the plasma generator was performed by a Tektronics oscilloscope TDS 2014. The voltage in the dielectric barrier discharge was measured with a high voltage P601A probe from tektronics while the current in the discharge was gauged using a 0.1–1.0 W, 1.0V/A, transformer from Pearson Electronics.

The experimental power in the cell during a dielectric barrier discharge cycle was calculated from the accumulated charge and the voltage output according to Q-V Lissajous figure [8] [9] to determinate dielectric charge, Qdie=Cdie*Vdie, specific energy E'=P/Q [joules/l] and the CDBD power supply $P=2*Q_{die}*V_{enc}*f.$, where Qdie is the dielectric charge[coulombs], Vdie is the dielectric voltage [Volt], Venc is the ignition voltage[V], P is the consumed DBD cell power and Q is the gas flow /l/.

Chemical kinetics

In the absence of O_2 NO was most likely chemically reduced to N_2 by N atoms as described by reaction 5 and 6 of table 1. The main reactions pathways for NO removal were generated by electron impact dissociation of N_2 (reaction 1 y 2 table 1) Although the process consider more than 15 species and 50 reactions we only include in table 1 some reactions for NO removal in order to describe the evolution of the excitation and ionization species produced in the N_2-NO mixture.

Some of these reactions are presented in table 1. (e, O, N, N_2(X, O_2, N_2(A), O_2(a), NO, NO_2, N_2O, O_3, N($_2$D), N_2(C), Where N_2(X), N_2(A), and N_2(C), refers to the ground level molecules $A^3\sum_g^+$ and the electronically excited molecules $A^3\sum_g^+$ and $C^3\prod_u$, respectively.

o_2 (a) represents the electronically excited state $a^1\,\Delta$.

The reaction rates collected from literature and the respective references are given in table 1.

We assumed an initial 10^{13} cm^{-3} electron density which is a most typical value in DBD processes.

Some first order ordinary differentials equation set had been developed using the Rosenbrock's algorithm which is a trustworthy integrator for stiff differential equations and it has been possible to trace the temporary evolution of the species. Due

The value of the concentrations is initially set to zero for all the species except for NO, where an equal 0,01N concentration is assumed along with a 0,99N one for N_2. Here, N is the total density at the atmospheric pressure.

Results and discusion

Eficiency, Power, Electrical field and Specific Energy

The results of the experimental power are shown in table 2. The discharge was carried out

Table 1
Main chemical reactions process
NO removal in DBD cell

	Reaccion	Ref
1	$e+N_2 \rightarrow e + N_2(A)$	10
2	$e + N_2 \rightarrow e + N + N$	10
3	$e + O_2 \rightarrow e + O_2(a)$	10
4	$e + O_2 \rightarrow e + O + O$	10
5	$N + NO \rightarrow N_2 + O$	11
6	$N + NO_2 \rightarrow N_2 + O_2$	11
7	$NO + NO_2 \rightarrow N+O+NO$	110
8	$N + NO_2 \rightarrow N_2 + O + O$	11
9	$N + NO_2 \rightarrow N2O + O$	11
10	$N + NO_2 \rightarrow NO + NO$	11
11	$O + NO_2 \rightarrow NO + O_2$	11
12	$O + O_3 \rightarrow O_2 + O_2$	11
13	$NO + O_3 \rightarrow O_2 + NO_2$	11
14	$N + O + N_2 \rightarrow NO + N_2$	11
15	$N+O+O_2 \rightarrow NO+O_2$	11
16	$O + O_2 + N_2 \rightarrow O_3 + N_2$	11
17	$O + NO + N_2 \rightarrow NO_2 + N_2$	11
18	$O + NO + O_2 \rightarrow NO_2 + O_2$	11
19	$O + NO + NO \rightarrow NO_2 + NO$	12
20	$O + NO + NO_2 \rightarrow NO_2 + NO_2$	12
21	$O + NO + N_2O \rightarrow NO_2 + N_2O$	12
22	$N_2(A) + O_2 \rightarrow N_2 + O + O$	13
23	$N_2(A) + O_2 \rightarrow N_2O + O$	13
24	$N_2(A) + O_2 \rightarrow N_2 + O_2(a)$	14
25	$N_2(A) + N_2O \rightarrow N_2 + N + NO$	13
26	$N_2(A) + N_2 \rightarrow N_2 + N_2$	13
27	$N_2(A) + NO \rightarrow N_2 + NO$	14
28	$O_2(a) + O \rightarrow O_2 + O$	15
29	$O_2(a) + O_2 \rightarrow O_2 + O_2$	15
30	$O_2(a) + O_3 \rightarrow O_2 + O_2 + O$	15
31	$O_2(a) + N \rightarrow NO + O$	15
32	$O_2(a) + N_2 \rightarrow O_2 + N_2$	15
33	$O_2(a) + NO \rightarrow O_2 + NO$	12
34	$N_2(A) + O \rightarrow N(_2D) + NO$	12
35	$N(_2D) + NO \rightarrow N_2O$	12
36	$N(_2D) + N_2O \rightarrow NO + N_2$	12
37	$N_2(A) + N_2(A) \rightarrow N_2(C)+N_2(X)$	12

in the N_2-NO mixture at a 1,0 l/min flow rate and several voltages peak to peak from 4,25 to 5,25 kV, with a fixed frequency of 1,73 kHZ practically constant. eficiency,

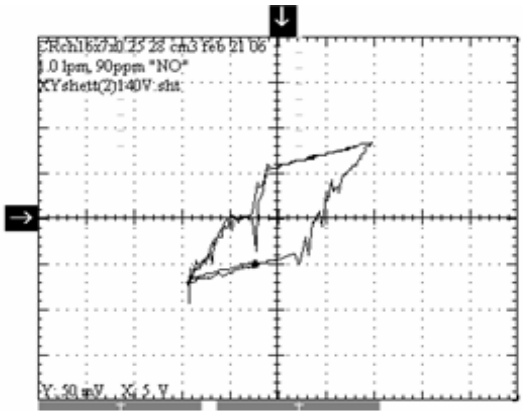

Fig. 4 Q-V Diagram 1 l/min, 90 ppm , 140V.

Table 2
Electric characteristics

DBD cell	Circular		Rectangular	
Applied Voltage(V)	120	140	120	140
Vi (Ignition voltage volts)	4,25	4,13	5,25	5,0
E (Electrical Field kV/cm)	17	16,5	21	20
P (Power supply J/s)	18,6	16,7	14,7	36,8
E' Specific energy J/l)	0,30	0,28	0,21	0,62
Er (Reduced E td)	170	165	210	200

In figure 5, the metal-water electrodes discharge is observed during a removal of NO'x. in the circular cell A white area can be appreciated on the gas inlet.

No reduction

Calculations of the composition evolution as a function of time were made at 170, 165, 210 y 200 Td (table 2), since "NO" removal in function of the reduced electric field. In figure 6 the NO deflection is observed at the point where the atomic nitrogen

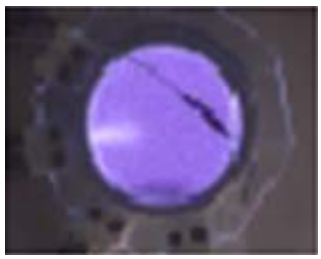

Fig. 5 Metal – water DBD plasma formed by filaments.

concentration grows. The NO removal is dominated by the reaction 8 to10 of table 1. The increment of atomic oxygen is also observed. The radical N is formed by the dissociation of molecular nitrogen. $N+NO \rightarrow N_2+O$ ki = $1,7x10^{-11}$ cm^3/s to 300 °K

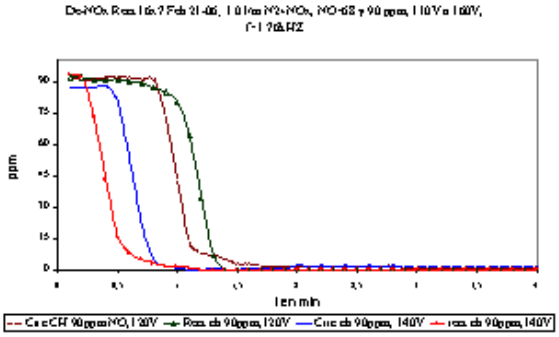

Fig. 6 Temporary variations of species.

At once, the atomic oxygen will contribute to the formation of NO_2, following mechanisms 17 and 18 of table 1. Yet, this reaction will be limited by the quantity of atomic oxygen

$O+NO+N_2 \rightarrow NO_2+N_2$ ki = $6,34x10^{-32}$ cm^6/s to 300 °K

$O+NO+O_2 \rightarrow NO_2+O_2$ ki = $6,34x10^{-32}$ cm^6/s to 300 °K

At higher energies, the nitrogen excited states of atoms and molecules begin to be important: the N_2O is diminished by the reaction 36.

$N(_2D) + N_2O \rightarrow NO + N2 \rightarrow$ + ki = $3,0x10^{-12}$ cm^3/s to 300 °K

the NO removal is increased with the reduced electric field We can see in table 2 the efficiency reduction on NO removal al high reduced field

No experimental reduction

A 1.0 l/min NO + N2 gas mixture flow was fed in a DBD cell of parallel plates of circular and rectangular geometry and the voltage repetition rate was 1.75 kHZ.

The evolution of the NO removal by cold plasma application is shown in figures 6 Since the gas analyzer registered the data every 6s, it was possible to follow the temporary evolution as closely as in figure 4 approximately for 6.0 min sampling in detecting the concentration change. A delay time is taken before begin the NO removal and after only few seconds an abrupt degradation

is carried out For 90 ppm 120V the NO degradation began 30s after the voltage is started and after 75s (1.7 min) the removal efficiency reach the maxim efficiency. For 140 V a higher efficiency was reached faster (1 min).

Table 3
Eficiencies Denox,s
90ppm,120V, celda circular

Lect	min	Lec in	Lec out	η en %
10	1	92	42	54,35
20	2	92	2	97,83
30	3	92	1	98,91
40	4	92	1	98,91
90ppm,120V, celda Rectangular				
Lect	min	Lec in	Lec out	η en %
10	1	92	80	13,04
20	2	92	0	100,00
30	3	92	0	100,00
40	4	92	0	100,00
90ppm,140V, celda circular				
Lect	min	Lec in	Lec out	η en %
10	1	87	1	98,85
20	2	87	2	97,70
30	3	87	2	97,70
40	4	87	2	97,70
90ppm,140V, celda rectangular				
Lect	min	Lec in	Lec out	η en %
10	1	93	0	100,00
20	2	93	0	100,00
30	3	93	0	100,00
40	4	93	0	100,00

Table 3 presents the removal efficiency in power function for 1, 2, 3 and 4 min after the voltage was applied and after the equipment detects the first "NO" concentration change. These results were obtained from registered dates and evolution graphic of figures 4

Conclusions

We have carried out these experiments using a circular and a rectangular DBD cell For dilute amounts of NO in N_2 the overall removal is determined by only a few reaction and the electrical energy is consumed in electrical impacts reaction with N_2 mainly via reduction by the radicals N

The N_2 dissociation is function of E/N so the input electrical energy is consumed in electron impact reaction with N_2. Higher removal efficiencies were obtained in the rectangular geometry than in the circular geometry. This might be attributed to the residence time due to geometry of the cells and a factor related with the chemical reaction mechanisms since it has been showed that at greather residence time the removal efficiency diminishes due the regeneration of NO o the production of NO by NO_2 dissociation. The reduction rate increase when the voltage is applied and it is in a very sharp form but NO_2 production increase too so NOx,s removal efficiency decrease for longer treatment time. The efficiency in the circular cell never increase upper 99% otherwise decrease with the time This might be explained due the resident time that into de circular cell al least it is 2.0 time than into the rectangular because the inlet flow gases is very near the outlet flow gas so part of the treated gas remain more time and is subjected to the DBD discharge again.

The chemical reduction allowed to determine the presence of N_2O among the final compounds produced by the decomposition of NO_2. Mass spectrometry has confirmed the presence of these species.

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