Negative corona discharge in mixtures of CO_2 and N_2: modeling and experiments

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Abstract: The decomposition of CO_2 by the effect of negative corona discharge has been experimentally and numerically investigated for different admixtures of N_2. The chemical kinetics model used in the simulation includes a wide variety of reactions between electrons, ions, atoms and molecules, such as ionization and recombination, electron-impact dissociation, dissociative recombination, dissociative attachment, thermal reactions between neutral chemical species, etc. Using the current-voltage characteristic as input data, the radial distributions of charged and neutral species has been predicted for different applied voltages and gas compositions. The generation of ozone, carbon monoxide and nitrogen oxides during the application of the corona discharge has been measured using ultraviolet and FTIR spectrophotometry.

Keywords: corona discharge, carbon dioxide, carbon monoxide, ozone

1. Introduction

Many plasma studies have been directed towards the possibility of decomposing CO_2 from industrial and energy exhausts, thus contributing to the pollution abatement [1]. These studies have clearly shown that CO_2 can be efficiently decomposed in CO and O_3 under the application of non-thermal plasmas [2]. Additionally, the efficiency of the decomposition process can be altered using mixtures of CO_2 with other gases, which also opens the possibility of generating additional species of industrial interest [3,4].

In this work, the decomposition of CO_2 with admixtures of N_2 by negative wire-to-cylinder corona discharge is numerically and experimentally investigated. The numerical simulation provides a useful insight into the spatial distribution of charged and neutral species generated by the corona discharge. The numerical modeling is complemented with the experimental measurements of species, like carbon monoxide, ozone and nitrogen oxides, by means of UV and FTIR spectrophotometry.

2. Experiment

The corona discharge is generated by a thin tungsten wire, with radius r_0 = 62.5 μm, which is situated along the axis of a stainless steel cylinder, with inner radius 0.85 cm. The length of the wire and of the cylinder was L = 5 cm. Negative high voltage was applied to the wire in the range -5.5 kV to -7.5 kV using a Trek 610 HV amplifier, and the cylinder was grounded through a Keithley 196 digital multimeter. Before the start of experiments, the corona reactor was filled with a mixture of pure CO_2 (99.995% purity) and N_2 (99.999% purity). The two ends of the stainless steel cylinder were closed with parallel BaF_2 windows, in order to allow spectrophotometric measurements. The corona discharge reactor was then placed inside the sample compartment of a Bruker Vertex 70 FTIR spectrophotometer or a Thermo Nicolet UV/VIS spectrophotometer, and periodic absorption measurements were performed during the application of the high voltage. All experiments were carried out at atmospheric pressure and ambient temperature.
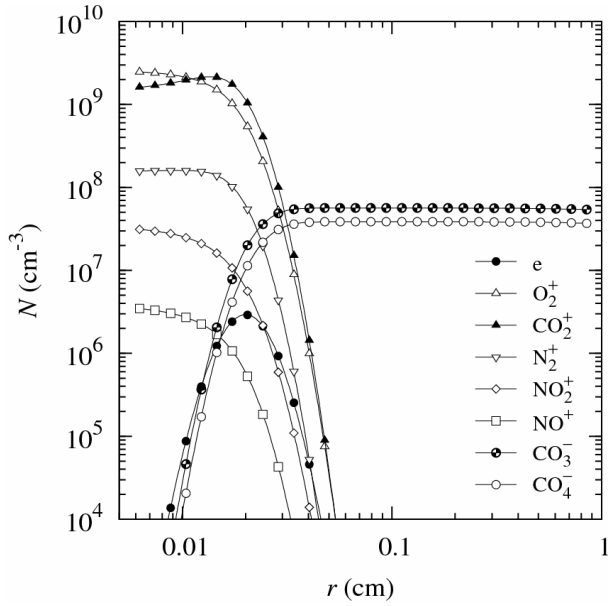
Figure 1. Number density of electrons and ions as a function of the radial distance to the wire surface in a gas mixture of 10% N_2 and 90% CO_2 (numerical). $V = -6.5$ kV, $I = -54$ μA.
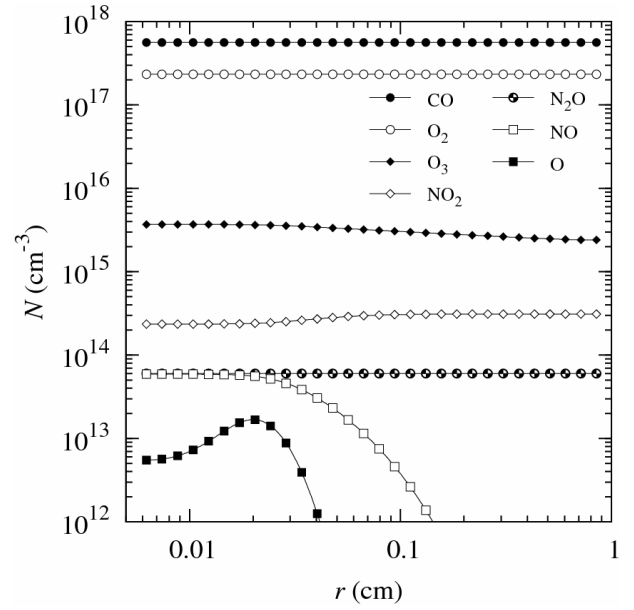

Figure 2. Number density neutral species as a function of the radial distance to the wire surface in a gas mixture of 10% N_2 and 90% CO_2 (numerical). $V = -6.5$ kV, $I = -54$ μA.

3. Numerical Model

For simplicity, the electrical discharge is assumed to have cylindrical symmetry and translational symmetry in the direction of the wire. Therefore, the corona discharge can be modeled as a 1D problem where the spatial distribution of species, temperature and electric field can be described in terms of the radial coordinate, r. The governing equations can then be written as [5]

$$\frac{1}{r}\frac{d}{dr}\left[r\frac{e_i}{|e_i|}\mu_i N_i E\right] = S_i, \qquad (1)$$

$$-\frac{1}{r}\frac{d}{dr}\left[D_j\frac{dN_j}{dr}\right] = S_j, \qquad (2)$$

$$\frac{1}{r}\frac{\partial}{\partial r}\left[rk\frac{\partial T}{\partial r}\right] = EJ_{\text{ion}}, \qquad (3)$$

$$\frac{1}{r}\frac{d}{dr}(rE) = \frac{1}{\varepsilon}\sum_i e_i N_i, \text{ with } E = -\frac{d\phi}{dr}, \qquad (4)$$

where N_i is the number density of the i-th charged species, N_j is number the density of j-th neutral species, S_i and S_j are the gain/loss rate terms due to the chemical reactions, μ_i and D_j denote the mobility and diffusion coefficients, e_i is the charge of i-th

charged species, E is the electric field, ε, k and T are the permittivity, thermal conductivity and temperature of the gas mixture, and the term EJ_{ion} corresponds to Joule heating due to the ion current density.

Equations (1)-(4) are integrated subjected to the usual boundary conditions. At the anode (cathode), the density of positive (negative) ions must be zero. However, the electron density on the cathode is non zero, due to the secondary emission caused by the impact of positive ions. Instead, its number density is fixed through the experimental current intensity,

$$I_{\text{exp}} = 2\pi r_0 Le_0\sum_i \mu_i N_i E, \quad \text{at } r = r_0. \qquad (5)$$

Regarding neutral species, molecular diffusion is taken as zero at the electrode walls. Finally, for gas temperature, isothermal and adiabatic boundary conditions are assumed, respectively, on the cylinder ($T = 298$ K) and on the wire.

The chemical model is formed by 37 chemical species, including electrons, ions (O^+, O_2^+, O_3^+, CO_2^+, CO^+, N^+, N_2^+, NO^+, NO_2^+, O^-, O_2^-, O_3^-, CO_3^- and CO_4^-) and neutral species (O, O_2 O_3, O(^{1}D), $O_2(^1\Delta_g)$, O_2 ($^1\Sigma_g^+$), $O_2(v)$, $O_3(v)$, CO_2, CO, C,
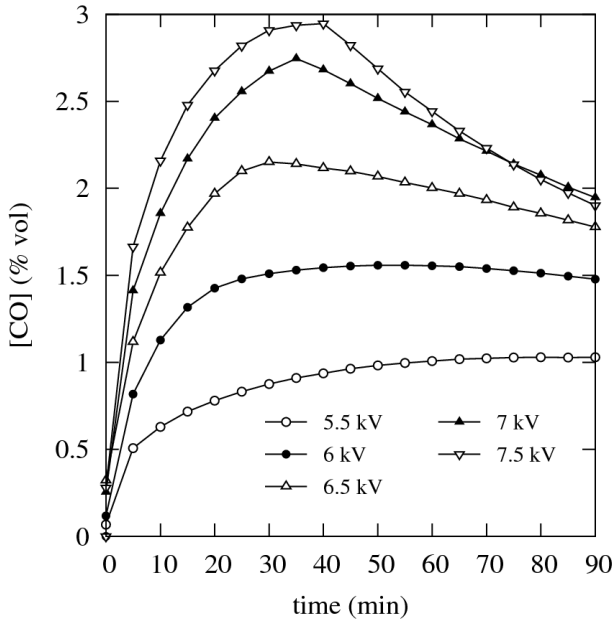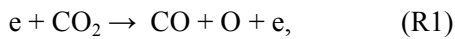
Figure 3. *Averaged concentration of carbon monoxide inside the corona discharge reactor as a function time (experimental). Initial gas composition: 30% N_2 and 70% CO_2.*
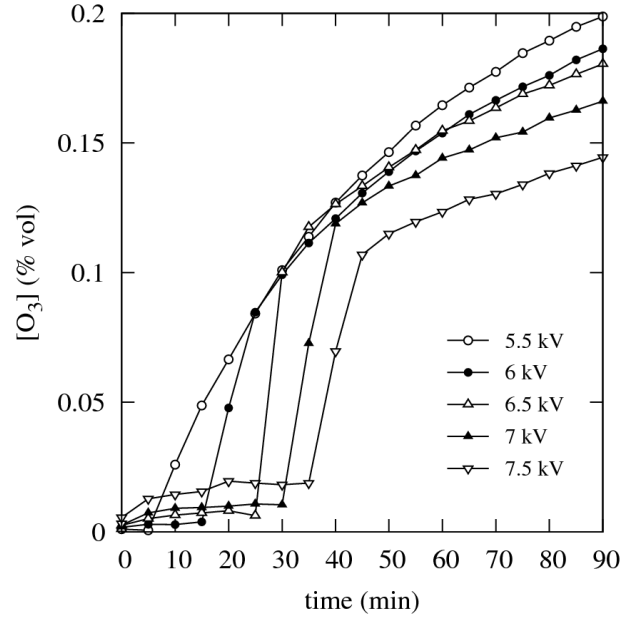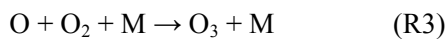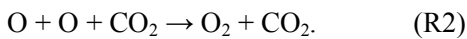

Figure 4. *Averaged concentration of ozone inside the corona discharge reactor as a function time (experimental). Initial gas composition: 30% N_2 and 70% CO_2.*

C_2O, N_2, $N_2(A^3\Sigma_u^+)$, $N_2(a'^1\Sigma_u^-)$, N, $N(^2D)$, NO, NO_2, N_2O, NO_3 and N_2O_5)..

4. Results

Figures 1 and 2 show, respectively, the radial distribution of charged and neutral species for a gas mixture of 10% N_2 and 90% CO_2 and an applied voltage of -6.5 kV. For clarity, only the chemical species with higher number densities have been included in these figures. The ionization region around the wire is dominated by CO_2^+ and O_2^+, which are formed by ionization of CO_2 and O_2 molecules. Nitrogen based ions are of secondary importance for this gas composition. Regarding negative ions, the drift region is dominated by CO_3^- and CO_4^-, which are mainly formed by charged transfer reaction of O^- and O_2^- with CO_2.

Carbon dioxide is decomposed by electron impact dissociation,

$$e + CO_2 \rightarrow CO + O + e, \qquad (R1)$$

and the recombination of oxygen atoms in neutral molecule reactions,

$$O + O + CO_2 \rightarrow O_2 + CO_2. \qquad (R2)$$

$$O + O_2 + M \rightarrow O_3 + M \qquad (R3)$$

leads to the formation of molecular oxygen and ozone. These are the most important species resulting from the decomposition of CO_2. However, the number densities of different nitrogen oxides, like NO_2, N_2O and NO, become significantly important as the initial concentration of N_2 in the gas mixture increases.

The concentrations of CO and O_3, determined by spectrophotometric measurements, are shown in Figures 3 and 4 as a function of time for a gas mixture of 30% N_2 and 70% CO_2. During the experiments, each applied voltage was kept for 90 minutes, and spectra were recorded every 5 minutes. According to the observations, the concentration of CO increases sharply with time during the first 30 to 40 minutes, and the higher the applied voltage the faster the rate of increase of CO,. However, after this initial period, the concentration of CO tends to saturate or starts declining. This change in the time evolution of CO is particularly marked at 6.5 kV and above. Ozone concentration also exhibits a significant increase with time, but only after some time has elapsed. The fast growth of O_3 seems to be triggered by the start of the declining of CO. During the initial time lag, the preponderant nitrogen oxides
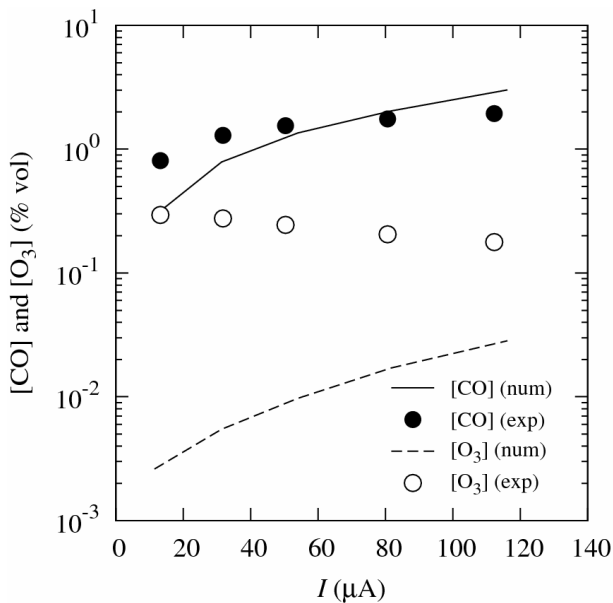
Figure 6. *Averaged concentration of CO and O₃ as a function of current intensity for a gas mixture of 10% N₂ and 90% CO₂ (numerical and experimental).*

are NO and NO_2, which are known to efficiently inhibit the formation of ozone [6].

In Figure 5, the maximum concentration of CO and O_3 predicted by the numerical modeling (solid lines) and measured during the experiments (dots) are compared with each other as a function of current intensity for a mixture of 10% N_2 and 90% CO_2. The agreement between simulation and experiment is quite satisfactory for carbon monoxide, since both the order of magnitude of CO concentration and its trend with current intensity are correctly predicted. However, the concentration of ozone is underestimated by the numerical simulation.

5. Conclusions

The decomposition of carbon dioxide with admixtures of nitrogen in wire-to-cylinder negative corona discharge has been investigated experimentally and numerically. The numerical modeling has shown that for N_2 admixtures up to 10%, ions are still preponderantly associated to CO_2. However, the decomposition of CO_2 into CO and O_3 is strongly influenced by the presence of nitrogen oxides, since they delay the formation of ozone and stop the growth of CO with time during the application of the high voltage. Numerical

predictions of carbon monoxide are in agreement with the measured data, but the numerical modeling, in its present stage, tends to underestimate the generation of ozone.

Acknowledgments

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