Physico-chemical modeling of positive corona discharge in carbon dioxide

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***Abstract*—Positive wire-to-cylinder corona discharge in pure CO_2 has been simulated using a model that includes elementary plasma processes (ionization, electron attachment and detachment, ion recombination, etc.) and chemical reactions between neutral species. The plasma chemistry model is included in the continuity equations of species, which are coupled with Poissons equation for the electric field and the energy conservation equation for the gas temperature. The experimental values of voltage and current are used as input data into the numerical simulation, and the spatial distributions of electrons, ions, atoms and molecules are then predicted for different gas flow rates. The average concentrations of ozone and carbon monoxide inside the discharge reactor have been experimentally determined by means of ultraviolet and FTIR spectrometry, and their values are compared with the results of the numerical simulation.**

I. INTRODUCTION

As is well known, carbon dioxide is a green house gas that contributes to the global warming of Earth atmosphere. Therefore, many plasma studies have been aimed to investigate the decomposition of CO_2 by means of different electrical discharges, which could be used in CO_2 abatement technologies. The study of corona discharge in CO_2 and its mixtures with other gases has attracted the interest of many investigators. For example, Morvová [1] has investigated the formation of gas products after the action of positive and negative dc corona discharge in mixtures of CO_2 and humid air. Mikoviny et al. [2] have measured the generation of ozone and carbon monoxide in pure CO_2 and its mixtures with oxygen, using negative corona discharge in a system of coaxial cylindrical electrodes with axial gas flow. More recently, Horv´ath et al. [3] have performed an extensive experimental study of CO_2 decomposition in positive and negative dc corona discharges in pure CO_2, without gas flow. Generally, numerical simulation in these works are limited to one-dimensional models, where species concentrations are predicted as a function of time.

In this paper, a two-dimensional model of positive corona discharge in pure CO_2 is presented. The corona discharge is produced using a coaxial wire-cylinder electrode system, with gas flow in the axial direction. The equations governing the electric field distribution, the transport of charged and neutral species, and the temperature distribution, have been solved simultaneously. Therefore, the ionization and the drift regions arise naturally in the solution of these equations. The plasma chemistry model used in the transport equations includes elementary plasma processes (ionization, electron attachment, charge transfer reactions between ions, etc), electron induced reactions with neutral species and chemical reactions between neutral species. When appropriate, the electric field and thermal dependence of the reaction rate constants has been taken into account in the transport equations. The numerical work is complemented with the experimental measurements of the chemical species generated by the corona discharge, particularly O_3 and CO. The concentration of species are quantified by means of UV-VIS spectrophotometry (O_3) and FTIR spectroscopy (CO).

II. EXPERIMENTAL SETUP

The discharge reactor used in the experiments has already been described in past works [4]. The electrode system consists of a tungsten wire situated along the axis of symmetry of a stainless-steel cylindrical tube. Both the corona wire and cylinder have identical length, L =5 cm, and their radii are, respectively, r_0 =0.0125 cm and R =1.1 cm. Parallel windows were installed at ends of the cylindrical tube, to allow spectrophotometric measurements.

Positive dc high voltage was applied to the wire using a HV amplifier (Trek 610C), while the cylinder was connected to ground through a digital multimeter (Keithley 196). Prior to the application of the high voltage, the discharge reactor was purged with high purity carbon dioxide (99.995%) for sufficient time, and then the flow was adjusted to desired flow rate. In order to measure the average concentration of species generated by the corona discharge, the discharge reactor was situated inside the sample compartment of a ultraviolet-visible (Nicolet Evolution 300) or a FTIR (Bruker Vertex 70) spectrophotometer. Ozone was determined using the Hartley bands, in the ultraviolet region (200–300 nm), while carbon monoxide was obtained from its infrared spectrum (45004900 nm).

III. EQUATIONS

Corona discharge is simulated using a hydrodynamics model, where the density of species is governed by continuity equations, coupled with Poisson's equation and the temperature equation. The continuity equations include the effects of transport and chemical reactions induced by the electrical discharge. In the stationary state, these equations

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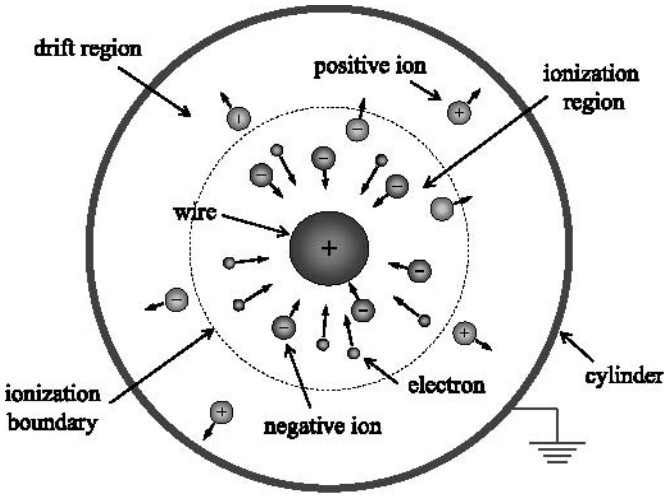

Fig. 1. Figure 1. Schematic of the structure of positive corona discharge between a wire and a cylinder.

can be written as

$$\frac{1}{r}\frac{\partial}{\partial r}\left[r\frac{e_i}{e_0}N_i\mu_i E\right] = S_i, \tag{1}$$

$$v_g\frac{\partial N_j}{\partial z} - \frac{1}{r}\frac{\partial}{\partial r}\left[rD_j\frac{dN_j}{dr}\right] = S_j, \tag{2}$$

$$\frac{1}{r}\frac{\partial}{\partial r}(rE) = \frac{1}{\epsilon_0}\sum_i e_i N_i, \tag{3}$$

$$v_g\frac{\partial}{\partial z}(\rho c_V T) = -\frac{1}{r}\frac{\partial}{\partial r}\left[rk\frac{T}{dr}\right] - EJ_{\text{ion}}, \tag{4}$$

where r and z are the radial and axial coordinate, Ni is the number density of charged species i (i = e,O^+,O^+_2,,O^+_3,O^-,O^-_2,O^-_3,CO^+_2,CO^-_3,CO^-_4), Nj is the number density of neutral species j (j =O, O2,O(^{1}D), O2($^1\Sigma$g), O2($^1\Delta$g), O3,O^*_2,O^*_3,CO2,CO, C, C2O), Si and Sj are the gain/loss rate terms due to chemical reactions, μi and Dj denote the mobility and diffusion coefficients, vg is the gas flow velocity, E is the electric field, 0 is the gas permittivity, ei and e0 are the charge of species i and the elementary charge, T is the gas temperature, ρ, cV and k are mass density, specific heat and thermal conductivity of CO2,and Jion is the current density due to ions. The electric field can be expressed as the gradient of the electrical potential φ, E =−dφ/dr.

The following approximations have been assumed in the above equations: (i) the electrical discharge has azimuthal symmetry around wire [5], (ii) the gas flow is incompressible and uniform, (iii) the transport of charged species is unaffected by the gas flow [6], and (iv) the material functions of the gas, such as drift velocities and reaction rate constants, are entirely determined by the local reduced electric field, E/N (N: gas number density) and the gas temperature.

Equations (1)-(4) must be integrated subjected to appropriate boundary conditions. Firstly, at the inlet of the cylinder (z =0), the densities of all neutral species (with the exception of CO2)are set to zero,

$$N_j(r,0) = 0. \tag{5}$$

On the electrode walls, the density of positive (negative) ions is zero on the anode (cathode),

$$\left.\begin{array}{ll} N_i(r_0,z) = 0, & \text{for positive ions,} \\ N_i(R,z) = 0, & \text{for negative ions.} \end{array}\right\} \tag{6}$$

For electrons, the experimental current intensity, I,isusedas a boundary condition that determines its number density on the wire,

$$I = 2\pi L e_0 r_0 \sum_i \mu_i N_i E, \quad \text{at } r = r_0. \tag{7}$$

The neutralization of charged species on the electrodes may constitute a source of other neutral species (e.g. O^- is converted into O on the anode). Therefore, the drift flux of such charged species must be equal to the diffusion flux of the corresponding neutral species,

$$e_0 D_j\frac{dN_j}{dr} = e_i\mu_i N_i E, \quad \text{at } r = r_0 \text{ and/or } r = R. \tag{8}$$

The diffusion flux of the remaining neutral species that do not have an associated ion must be null on the electrodes,

$$D_j\frac{dN_j}{dr} = 0, \quad \text{at } r = r_0 \text{ and/or } r = R. \tag{9}$$

On the cathode, ozone is produced by the neutralization of O^+_3, but it is also decomposed on the metal surface. This phenomenon is known to be controlled by a decomposition coefficient, δ [5]. The balance between O^+_3 ions and O3 molecules must therefore be modified to include this process,

$$-D_{O_3}\frac{dN_{O_3}}{dr} = \delta N_{O_3} + \mu_{O_3^+}N_{O_3^+}E, \quad \text{at } r = R. \tag{10}$$

The value δ =2.88× 10 cm/s was used in the numerical simulation.

For the electrical potential, boundary conditions are straightforward,

$$\phi(r_0,z) = V, \qquad \phi(R,z) = 0, \tag{11}$$

where V is the high voltage applied to the wire.

Finally, the gas temperature on the cylinder surface is assumed to be constant and equal to the ambient temperature. On the wire, the gas is assumed to be in thermal equilibrium with the electrode,

$$T(R,z) = 298\,K, \qquad \left.\frac{dT}{dr}\right|_{r0,z} = 0. \tag{12}$$

IV. RESULTS AND DISCUSSION

The structure of positive corona discharge in wire-cylinder geometry is well established (see figure 1). Positive ions and electrons are confined within a narrow region around the corona wire (ionization or plasma region), and they drift towards the anode. Secondary electrons, which sustain the discharge, are generated by photoionization of the gas outside

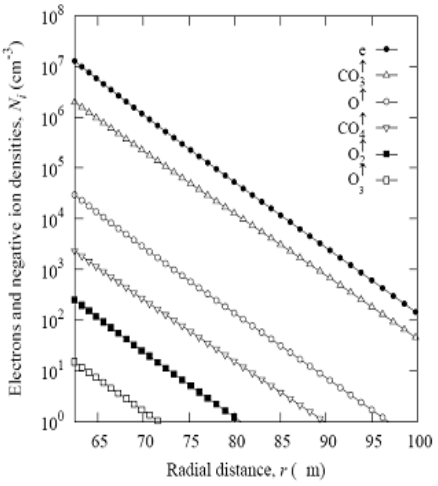

Fig. 2. Radial distribution of electrons and negative ions at the exit of the discharge reactor (z =5 cm) for a gas flow rate of 20 cm^3 /min. Applied voltage: 7 kV, current intensity: 24.6μA.

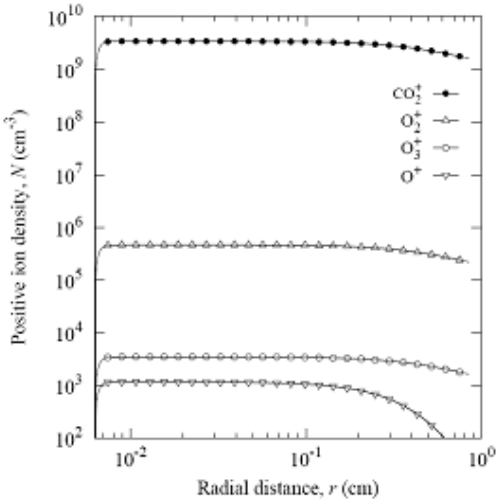

Fig. 3. Radial distribution of positive ions at the exit of the discharge reactor (z = 5 cm) for a gas flow rate of 20 cm^3 /min. Applied voltage: 7 kV, current intensity: 24.6μA.

the plasma region. The photons are mainly emitted from the plasma region as a result of de-excitation processes. Under the effect of the electric field, positive ions leave the plasma region and enters into the unipolar drift region, where they slowly migrate towards the cathode.

The radial distributions of electrons, ions and neutral species predicted by the numerical simulation are shown in .gures 2–4. These distributions where computed for V = 7kV and I =24.6μA, which are the voltage and current intensity experimentally registered when the .ow rate was 20 cm^3/min. The axial coordinate was chosen to be z =5cm, that is, the exit of the discharge reactor.

Clearly, electron and negative ion densities increase ex-ponentially in the direction of the wire and the length of the plasma region is of the order of ten micrometers (see figure 2). The predominant negative ion is CO_3^- a three-body charge transfer reaction with O^- ,

$$O^- + CO_2 + CO_2 \rightarrow CO_3^- + CO_2. \qquad \text{(R1)}$$

Negative oxygen atom ions are mainly formed by dissociative attachment of electrons to CO_2 molecules,

$$e + CO_2 \rightarrow CO + O^-. \qquad \text{(R2)}$$

The number densities of the rest of negative ions are signicantly smaller.

Positive carriers are predominantly formed by CO_2^+ ions essentially linked to the electric (see figure 3), which are formed by ionization of CO_2 molecules

$$e + CO_2 \rightarrow CO_2^+ + 2e. \qquad \text{(R3)}$$

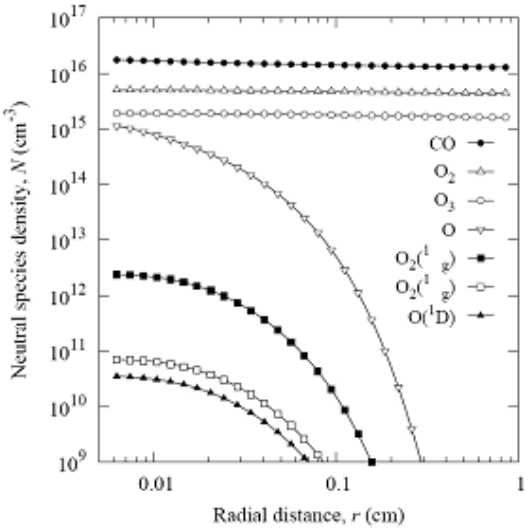

Fig. 4. Radial distribution of neutral species at the exit of the discharge reactor (z = 5 cm) for a gas flow rate of 20 cm^3 /min. Applied voltage: 7 kV, current intensity: 24.6μA.

Outside the plasma region, the radial distribution of CO_2^+ is essentially linked to the electric field distribution. Hence, the presence of positive space charge reinforces the electric field in the vicinity of the cathode and, consequently, the number density of CO_2^+ decreases.

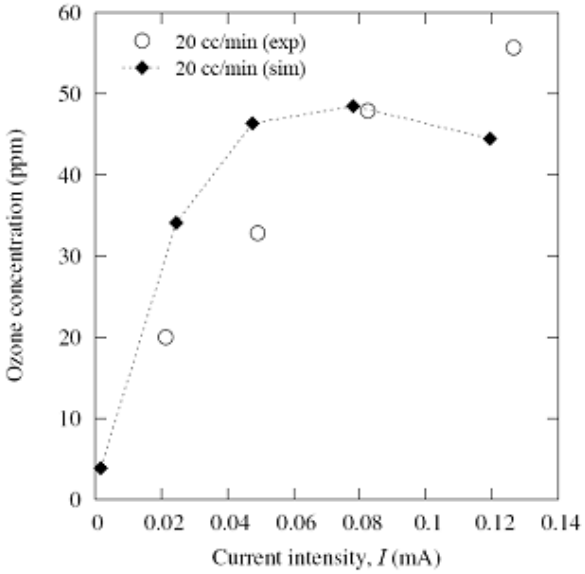

Fig. 5. Spatial average of O3 density inside the discharge reactor as a function of current intensity. Exp: experimental results, sim: numerical simulation.

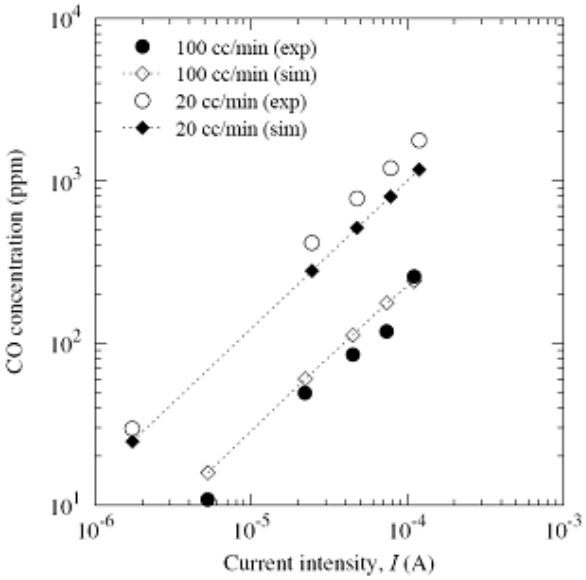

Fig. 6. Spatial average of CO density inside the discharge reactor as a function of current intensity. Exp: experimental results, sim: numerical simulation.

Carbon monoxide, molecular oxygen and ozone are the major constituents of neutral species generated by the corona discharge (see .gure 4), and they are distributed in the whole discharge gap. In addition to (R2), CO is mainly formed by electron impact decomposition of CO2 molecules,

$$e + CO_2 \rightarrow CO + O + e. \qquad \text{(R4)}$$

Oxygen molecules and ozone are formed in three body reactions with CO2,

$$O + O + CO_2 \rightarrow O_2 + CO_2. \qquad \text{(R5)}$$

$$O + O_2 + CO_2 \rightarrow O_3 + CO_2. \qquad \text{(R6)}$$

The average concentrations of CO and O3 within the discharge reactor have been determined by means of spec-troscopic techniques, and they are compared with the results of the numerical simulation in .gures 5 and 6. The average densities are presented as a function of current intensity, which was obtained from the current-voltage characteristic. For carbon monoxide, results are presented for two different .ow rates: 20 cm3/min and 100 cm3/min. The agreement between experiment and simulation is quite acceptable.

V. Conclusions

The spatial distributions of electrons, ions and radicals, generated by a positive wire-cylinder corona discharge in pure carbon dioxide, has been obtained using a physico-chemical model that includes the most important plasma chemistry processes. The numerical simulation predicts that the dominant charged species inside the plasma region are constituted by electrons, CO- 32 and CO+, while in the drift region CO+2 is the principal ion. Neutral species produced by the corona are mainly CO, O2 and O3. This prediction is quantitatively con.rmed by spectroscopic measurements of ozone and carbon monoxide in the ultraviolet and infrared regions.

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