One-dimensional hydrodynamical kinetics model of a cylindrical DBD reactor with \( \text{N}_2 \)

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Abstract. A numerical 1-D model of the chemical kinetics related hydrodynamics of room pressure \( \text{N}_2 \) plasma at 25 \( ^\circ \)C is reported. This generic discharge is assumed to take place between two cylindrical concentric electrodes, coated in a dielectric material, biased between 1 kV and 10 kV at 60Hz - 3kHz. The model includes the integration of particles conservation and the momentum equations as well as the local field approximation and the Poisson equations for the sake of completeness. The outcome shows that an accumulation of electrons takes place in the close vicinity of the higher voltage electrode, due to the electric field convergence to the internal electrode. Thus, this is a region of intense ionization whereas the generation of free radicals would occur away from the internal electrode. The model predicts no significant influence of the electric field on the heavier particles whose density remains practically constant.

1. Introduction

The dielectric barrier discharge (DBD) is one of the most popular techniques for non-thermal plasma industrial production, given its versatile configuration and the convenience of operating at room pressure. DBDs have been applied to ozone production [1], treatment of live tissue [2], biomaterial modification for implant production [3], bacteria elimination [4], surface conditioning [5], atmospheric pollution control [6] and so on.

The cylindrical geometry being the most applied, e.g., in the experimental degradation of toxic gas [7],[8], waste water treatment [9], it is also the less theoretically studied geometry, especially from the point of view of hydrodynamics, albeit some advances in its electrodynamics have been recently achieved. In some particular cases, a few cylindrical geometry models have been proposed [10],[11]. Nevertheless, there is a need for understanding the chemical behavior and generation mechanisms of the chemical species, including the effects of the electric field, both in time and space.

The model presented here is structured on the continuity and momentum equations. The closure of the equation system is provided by the Poisson equation. Despite its simplifications, the model is able to predict the space-time distribution of electrons, ions, and neutrals as well as the evolution of the electric field.
2. The model
The model has been conceived to apply within the 1−10kV and 60Hz−3kHz power supply ranges. The AC power source is connected to the electrodes while keeping the external one grounded. The reactor is considered as an open system as it is continuously circulated by a 1L/min nitrogen flow of nitrogen at atmospheric pressure.

2.1. DBD cylindrical reactor
A generic reactor has been assumed with both electrodes insulated with Pyrex\textsuperscript{TM} glass, $8 \times 10^{-4}m$ thick at the inner electrode and $1 \times 10^{-3}m$ at the external one. Thus, the gap discharge becomes $3 \times 10^{-3}m$, figure 1.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig1.png}
\caption{Cross sectional view of the cylindrical double dielectric barrier reactor.}
\end{figure}

The applied potential behaves sinusoidally and can be represented by the expression:

$$V_S(t) = V_0 \sin(\omega t),$$

where $\omega$ is the angular frequency, $t$ time in seconds and $V_0$ is the maximal amplitude provided by the power supply. The potential difference through the dielectric barriers ($V_W$) and through the discharge gap ($V_G$) are expressed respectively as [12]:

$$V_W(t) = V_{DI} + V_{DE} = -\int_{r_a}^{r_b} E_r(r, t)dr - \int_{r_b}^{R} E_r(r, t)dr,$$

$$V_G(t) = -\int_{r_a}^{r_b} E_r(r, t)dr,$$

where $V_{DI}$ is the voltage through the internal dielectric, $V_{DE}$ through the external one and $E_r(r, t)$ is the electric field as a function of radial distance and time. The discharge current ($i_T$) has been calculated as the algebraic sum of the conduction ($i_C$) and displacement ($i_D$) currents [12]:

$$i_T(t) = i_C(t) + i_D(t),$$

where the conduction one is given by [12]

$$i_C(t) = \frac{eS}{R} \int_0^R [\Gamma_+(r, t) - \Gamma_e(r, t)] dr,$$

Here $e$ is the elementary charge, $S$ is the discharge cross section, $\Gamma_+, \Gamma_e(r, t)$ are the ion and electron fluxes, as functions of the radial position and time. The displacement current can be expressed as [13]:

$$i_D(t) = \frac{\sigma S}{R} \int_0^R \partial_r E_r(r, t) dr,$$

where $\sigma$ is the conductivity of the discharge gas.
\[ i_D(t) = \sum \frac{i_C(r, t) dr}{d_G + d_D} + \epsilon_0 S \frac{dV_G}{d_G + d_D} dt, \]

where \( i_C(r, t) = eS[\Gamma_+(r, t) - \Gamma_-(r, t)] \) is the net current, \( \epsilon_0 \) is the permittivity of vacuum, \( d_G \) is the gap space between insulated electrodes, \( d_D = (d_{DI}/\kappa) + (d_{DE}/\kappa) \) is the electrode dielectric thickness, \( \kappa \) being the dielectric constant of the barrier.

2.2. Equations of the model

The main body of equations results from simplifying the moments of the Boltzmann equation. Thus, from the first moment one obtains the species continuity equation, (7), and the equation of momentum, derived from the second Boltzmann moment and neglecting inertia. The simultaneous solution to both equations enables to specify the species distribution in time and space. The general 1-D expressions of the equations of continuity and momentum in cylindrical coordinates are, after [14],

\[ \frac{\partial n_i(r, t)}{\partial t} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \Gamma_i(r, t) \right) = S_i, \]

\[ \Gamma_i(r, t) = n_i(r, t)v_r - D_{i,eff} \left[ \frac{\partial n_i(r, t)}{\partial r} \right], \]

where \( n_i \) is the density of species \( i \) (electrons, ions and neutral particles), \( S_i \) is the source term, \( v_r \) is the radial flux velocity of the neutrals and \( D_{i,eff} \) is the effective diffusion coefficient of species \( i \) and can be calculated from the gas kinetic theory. The radial velocity is assumed to be zero and only the second term relating the diffusion and gradient of density were considered. In the case of charged particles, the equation of motion is given by [14]:

\[ \Gamma_{+,e}(r, t) = \pm n_{+,e}(r, t)\mu_{+,e}E_r(r, t) - D_{+,e} \left[ \frac{\partial n_{+,e}(r, t)}{\partial r} \right], \]

where \( \mu_{+,e} \) is the (ion, electron) mobility and \( D_{+,e} \) is the diffusion coefficient of the charged species and \( (\pm) \) refers to the respective polarity of the charge.

The transport coefficients \( \mu_e \) and \( D_e \) are evaluated from BOLSIG+ [15] whereas \( \mu_+ \) and \( D_+ \) are available in [16],[17]. The electric field of equation (9) results from:

\[ E_r(r, t) = -\frac{d\phi(r, t)}{dr}, \]

where the radial potential \( \phi \) can be obtained from the Poisson equation

\[ \nabla^2 \phi(r, t) = -\frac{\rho(r, t)}{\epsilon_0}, \]

2.3. Reaction processes

Ten chemical species have been considered relevant for the model, namely \( e^- \), \( N^+ \), \( N_2^+ \), \( N_4^+ \), \( N(2D) \), \( N(2P) \), \( N \), \( N_2(A) \), \( N_2(a') \) and \( N_2 \) involved in 11 main reactions summarized in table 1.

2.4. Numerical method

The solution to equations (7) to (8) was achieved by the finite volume technique [23]. A 200 cell mesh has been considered. \( 1.0 \times 10^{-11} \) to \( 1.0 \times 10^{-9}s \) time increments were applied bearing in mind the Courant-Friedrich-Lewy condition [24]. The initial density profile was specified on the Townsend discharge criterion. The solution to the Poisson equation adopted the form of a three point finite difference [25].
Table 1. Chemical reactions of $N_2$ and their respective reaction rate coefficient values

| No. | Reaction                                   | $k$ [cm$^3$s$^{-1}$] | Reference |
|-----|--------------------------------------------|-----------------------|-----------|
| 1   | $e^- + N_2 \rightarrow 2e^- + N^+ + N$     | $4.29 \times 10^{-12}\sqrt{\varepsilon}(1 + 6.76 \times 10^{-6})\exp(-2.96 \times 10^5 T_e^{-1})$ | [18]      |
| 2   | $e^- + N_2 \rightarrow 2e^- + N_2^+$        | $5.05 \times 10^{-11}\sqrt{\varepsilon}(1 + 1.10 \times 10^{-5})\exp(-1.82 \times 10^5 T_e^{-1})$ | [18]      |
| 3   | $e^- + N_2 \rightarrow e^- + N_2(A)$       | $6.21 \times 10^{-11}\sqrt{\varepsilon}(1 + 2.46 \times 10^{-5})\exp(-8.21 \times 10^4 T_e^{-1})$ | [18]      |
| 4   | $e^- + N_2 \rightarrow e^- + N_2(a')$      | $\log(-8.8 - 17.7)/(E/N) + \log(-8.5 - 17.4)/(E/N)) + \log(-8.7 - 17.5)/(E/N))$ | [19]      |
| 5   | $e^- + N^+ \rightarrow N$                  | $3.5 \times 10^{-12}$ | [20]      |
| 6   | $e^- + N_2^+ \rightarrow N_2$              | $4.0 \times 10^{-12}$ | [20]      |
| 7   | $e^- + N_2^+ \rightarrow N^2(D) + N$       | $2.0 \times 10^{-7}(300 T_e^{-1})^{0.50}$ | [19]      |
| 8   | $N_2^+ + N_2 \rightarrow N_2^+ + 2N_2$     | $2.4 \times 10^{-15}$ | [21]      |
| 9   | $N_2(A) + N_2(a') \rightarrow N_2^+ + e^-$ | $5.0 \times 10^{-11}$ | [22]      |
| 10  | $N_2(a') + N_2(a') \rightarrow N_2^+ + e^-$ | $2.0 \times 10^{-10}$ | [22]      |
| 11  | $N^2(D) + N^2(P) \rightarrow N_2^+ + e^-$  | $2.4 \times 10^{-14}$ | [22]      |

2.5. Boundary conditions

For the continuity equation (7):

$$n_e(r_a, t) = n_+ (r_a, t) = 0,$$

$$n_e(r_b, t) = n_+ (r_b, t) = 0,$$

The condition for Poisson equation (11) is set by the Gauss law [26] whereby

$$V_{rb} = \frac{\lambda}{2\pi \varepsilon_0} \int_{r_R}^{r_b} \frac{dr}{r},$$

where $\lambda$ is the charge density per length unit (C/m) given by

$$\lambda = \frac{2\pi \varepsilon_0 V_0 \sin(\omega t)}{T_a} \ln \left( \frac{T_b}{r_R} \right) + \ln \left( \frac{T_a}{r_b} \right) + \frac{1}{\kappa} \ln \left( \frac{T_a}{r_a} \right) + \frac{1}{\kappa} \ln \left( \frac{T_b}{r_b} \right).$$

3. Results

Figures 2 to 5 shown below have been obtained in the following conditions: 3kHz, 10kV power supply.

3.1. Voltage and current in the discharge

The waveforms corresponding to $V_S(t)$, $V_W(t)$, $V_G(t)$ and $i_T(t)$, all shown in figure 2.

In a cylindrical configuration discharge, contrary to a flat parallel plate one [12], the potential through the barriers $V_W(t)$ is not out of phase with respect to the supply $V_S(t)$. The voltages $V_W(t)$ and $V_G(t)$ follow the same sinusoidal wave and the gap potential $V_G(t)$ is the main component of $V_S(t)$. This fact implies a greater potential fall, $V_G(t)$, and a smaller dielectric one, $V_W(t)$, for the cylindrical discharge case.

Figure 2 presents the $V_S(t)$ and $i_T(t)$ curves with a mutual $\omega t = \pi/2$ shift, which confirms the capacitive property of a DBD reactor. Clearly the potential reaches its maxima at $\pi/2$, $3\pi/2$, $5\pi/2$ and $7\pi/2$, while the current curve shows no distortions, suggesting a discharge more homogeneous than filamentary.
The evolution of the electric field can be observed in figure 3. The extent of the field variation reaches ±4000 kV/m. The field value at the left side extreme of the radial domain, \( r = 1.5 \times 10^{-3} \) m, is the maximal one, corresponding to the point of greatest potential, namely, the energized electrode.

### 3.2. Space-time distribution of the species density and electric field

Figures 4 and 5 describe the behavior, in time and space, of the electrons and neutrals species respectively. The neutral species have been added together and can be seen in figure 5. All the distribution functions have been considered on the discharge gap only.

The electron radial distribution is displayed in figure 4 to \( \omega t = 4 \pi \). The illustrated time-space evolution differs considerably from that of the flat plate case [12]. At \( \pi/2, 3\pi/2, 5\pi/2 \) and \( 7\pi/2 \), when the potential reaches its maxima, the greatest electron concentration is found near the inner electrode. When the voltage goes to zero \( (\pi, 2\pi, 3\pi \) and \( 4\pi) \) the electron concentration is in the order of \( 10^7 \) \( \text{m}^{-3} \). This rather low value can be attributed to the lack of an electric field that promotes the generation of the species referred to in table 1. Nevertheless, the residual electron concentration facilitates the ionization process during the following voltage increase. The high density of this species suggests the existence of a negative charge concentration towards the inner electrode. Electrons presents a minimal density close to the external electrode when the potential vanishes.

Figure 5 displays the neutral species density, with the exception of molecular nitrogen. The neutral species are unaffected by the electric field, their only density variations within the inner electrode vicinity are due to ionization processes derived from electron impacts.

### 4. Conclusions

The 1-D model of an AC nitrogen plasma discharge in a double dielectric barrier reactor with cylindrical configuration has been developed with satisfactory results. The evolution in time and space of the chemical species densities, along with the respective electric potential and field distributions, has been obtained.

In a cylindrical DBD reactor with an active inner electrode, the chemical processes tend to take place in the close proximity to it, whereby the species concentration exhibits an exponentially increasing profile towards the inner electrode. These profiles are clearly distinct from those of the flat parallel plate DBD case.
Within its own region in the variable space, the model constitutes not only an effective approximation to the experimental behavior of DBD cylindrical plasma but also a solid basis for the development of more complex models including characteristics such as higher dimensionality or additional species and chemical reactions.

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