Computational modeling of an atmospheric pressure plasma containing CF_4: Unveiling the mechanism of fluorocarbon plasma-based depyrogenation

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Abstract: Low temperature plasmas have been widely explored for biomedical treatment. A recent study showed that fluorine bearing gases enhance endotoxin reduction efficiency in plasma-based depyrogenation. However, a thorough study on the specific species contributing to this effect is yet unknown. To analyze this phenomenon, we used a global model to study the fluorocarbon chemistry in an atmospheric dielectric barrier discharge plasma to explore the production pathways of various reactive species.

Keywords: atmospheric pressure plasmas, depyrogenation, global model, Boltzmann solver

1. Depyrogenation with Fluorocarbon Gases

Atmospheric pressure plasma is growing in importance in biomedical applications over the past few decades due to its ability to produce reactive species at low gas temperature. As a result, it has been widely used in sterilization of medical and pharmaceutical devices. Chitosan is a polymer used in medical applications such as wound healing and drug delivery. Depyrogenation or removing the pyrogen, endotoxin is a crucial step in maintaining patient safety while using chitosan. Recently, Bhatt et al. found that plasma processing chitosan in fluorine-containing containers accelerated the endotoxin level reduction [1]. While the experimentation has been validated with two different fluorine-based compounds, the actual mechanism of the depyrogenation due to fluorine-based compound has not been studied yet. Therefore, a thorough study on how each species evolves inside the atmospheric pressure dielectric barrier discharge (DBD) would reveal more about the mechanism of this phenomenon.

Motivated from this, we are studying a plasma containing CF_4 using a global model to draw a correlation to the chitosan reduction found in the experimentation. To investigate realistic timescales of reactive species formation and recombination while keeping the computation time realistic, a global model has been used. In this approach, the plasma volume is approximated as a well-stirred reactor, with a specified power deposition. While other models such as two-dimensional fluid models can model a system with high spatial and temporal resolution, the long processing time in the chitosan depyrogenation makes it unrealistic. In this global model, a multi-term Boltzmann solver has been used instead of the more traditional solver which uses a 2-term spherical harmonic expansion to provide with higher accuracy in obtaining the reaction rates and densities.

The structure of the abstract is as follows: In the first section, the model description, initial conditions and reactions are explained. Next, preliminary results of the global model with a simplified reaction mechanism have been analyzed. Further analysis that will be done is discussed to give some insights on how this study will be able to help explain which species may be present in the plasma-based depyrogenation treatment.

2. Global Model Description

A 0-dimensional well-stirred reactor model is used to investigate the production of reactive species in an Ar/CF_4 plasma [3]. Multibolt, a multi-term Boltzmann solver, is used to calculate electron energy distribution functions and reaction rates [2,4].

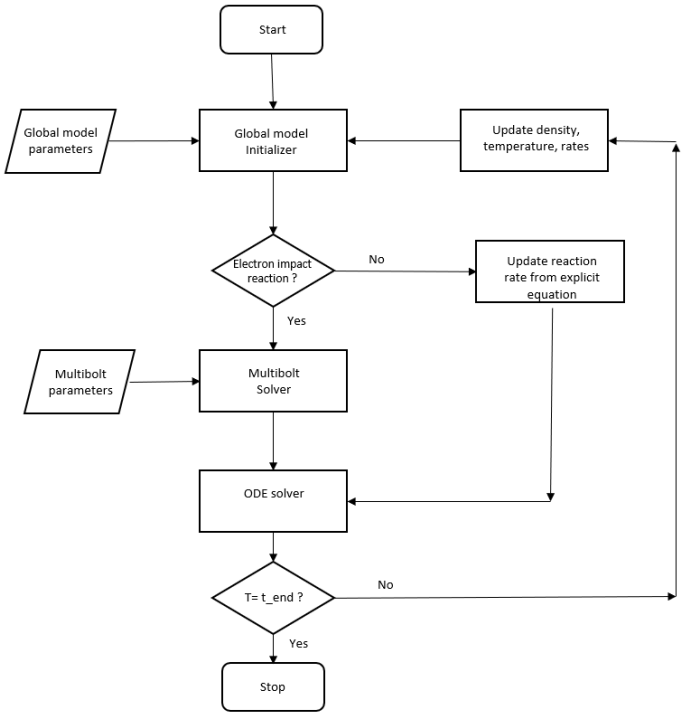

Fig. 1. Flow chart of the global model coupled with Multibolt.

The flow chart of the global model is shown in Fig. 1. First, the Global model is initialized with the plasma parameters and a list of reactions and species. After that, the reaction list is analyzed and only electron impact reactions are passed to Multibolt for calculating reaction rates, mobility, diffusivity and electron energy distribution functions (EEDF). For other reactions, these parameters are calculated from Arrhenius forms of the reaction rates. The global model parameters are fed using a yaml file for increased human readability and structured reading capability. Next, the rates corresponding to the appropriate average energy is used in the ODE solver that solves for the temperature and density for all species. The rates are updated according to the density and temperature by reading into the Multibolt data. This loop is repeated until the desired end time is achieved.

The global model was initialized with atmospheric pressure, 300 K gas temperature and $5x10^{18}$ W/m^3 of power deposition for 10,000 ns. Simulation was run for 1000 timesteps with 10 ns time step. The initial gas density is taken to be 10^{20} m^{-3} and the electron density is 10^{10} m^{-3}. Multibolt was run for values of the reduced electric field from 0.1 to 1500 Td. For these preliminary results, only electron impact reactions of CF_4 in Table 1 were considered.

Table 1. List of electron impact reactions for CF_4.

Electron Attachment	$e + CF_4 \rightarrow CF_4^-$
Elastic Collision	$e + CF_4 \rightarrow e + CF_4$
Excitation	$e + CF_4 \rightarrow e + CF_4(V24)$
Excitation	$e + CF_4 \rightarrow e + CF_4(V13)$
Excitation	$e + CF_4 \rightarrow e + CF_4^*(7.86eV)$
Excitation	$e + CF_4 \rightarrow e + CF_4^*(12.85eV)$
Ionization	$e + CF_4 \rightarrow e + e + CF_4^+$

3. Results from global model analysis

Multibolt was used with 2, 4, 6 and 8 terms with a mixture of Ar/CF_4 = 80/20 to get an insight on the effect of changing the number of terms of the solver. Increasing the number of terms increases the computational complexity. However, it is evident from Fig. 2 that 2-term solvers deviate from higher term solvers. However, the difference in the EEDF and other plasma parameters for 6 terms and 8 terms are within error limit. Therefore 6 terms were used for the simulations. There is some variation between 2 term and 8 term solvers. However, the 6 terms and 8 term results are mostly identical in the regime of 0.1 Td to 1000 Td.

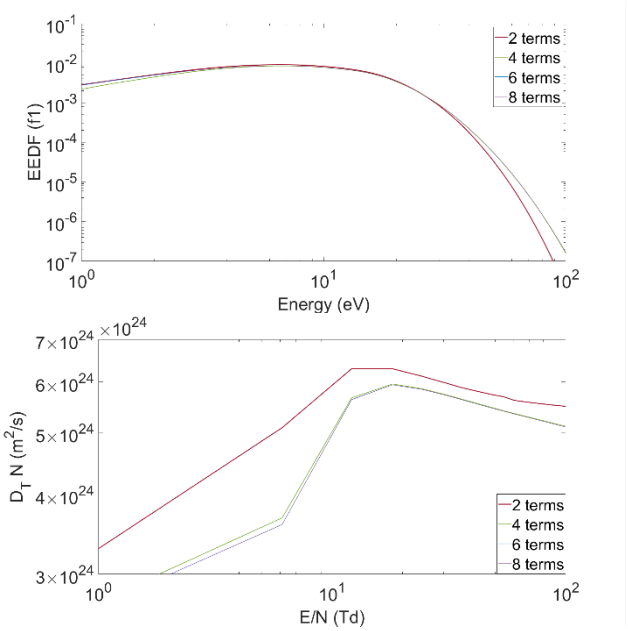

Fig. 2. (upper) The anisotropic component of the electron energy distribution EEDF when considering a different number of terms in the spherical harmonic expansion with a reduced electric field of 1000 Td. (lower) The transverse diffusion coefficient for varying values of reduced electric field (E/N) for Ar/CF_4 = 80/20.

Multibolt was used with 6 terms to calculate the electron energy distributions (EEDFs) for various mixtures of CF_4 in Ar shown in Fig. 3 [5,6]. For larger CF_4 mole fractions, the mean electron energy is lower due to increased energy losses from inelastic processes such as vibrational excitation. As expected, the ionization rate increases monotonically with E/N. The 2-body attachment rate has a maximum at approximately 100 Td for 20% CF_4 and 200 Td for 50% CF_4.

These reaction rates are used in a global model of a plasma with CF_4 admixtures. The volumetric power deposition was chosen as a reasonable value for the power deposition during the discharge pulses in an atmospheric pressure dielectric barrier discharge (DBD). The primary reactive species produced will be studied as the CF_4 concentration and power deposition is varied.

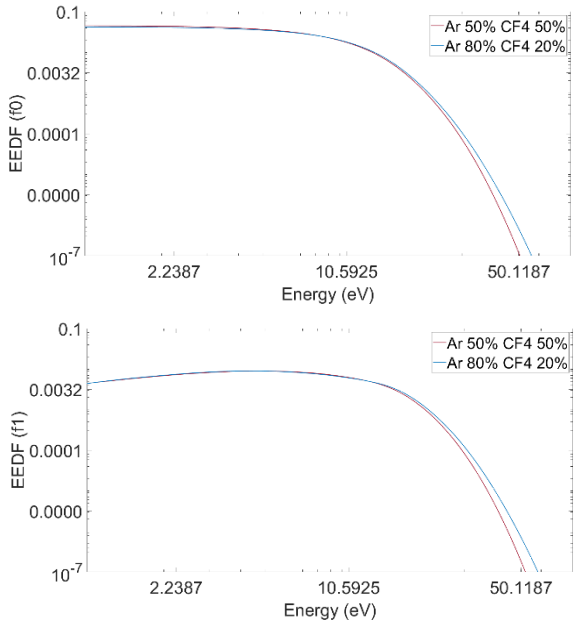

Fig. 3. Electron energy distribution functions calculated in Ar/CF_4 mixtures with 20% and 50% CF_4 at 301 Td. The EEDF is divided into (upper) the isotropic component and (lower) the anisotropic component.

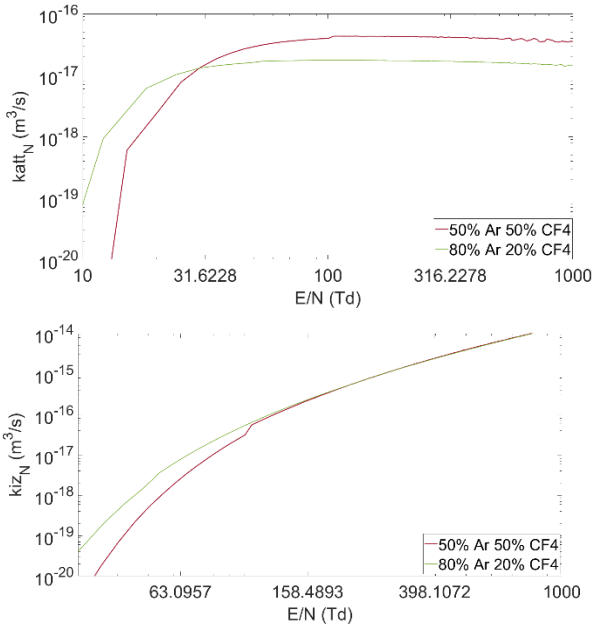

Fig. 4. Reaction rates of electron impact processes at various reduced electric field (E/N) values. (upper) k_{att} refers to attachment and (lower) k_{iz} refers to ionization. Results are shown for 20% and 50% CF_4.

For transient analysis, only a preliminary calculation with a simplified reaction mechanism and reduced pressure in pure CF_4 is shown. This calculation includes only the electron impact reactions shown in Table 1, and a discharge power which is constant rather than pulsed, as it would be for the dielectric barrier discharge. As the complete reaction process is not present here, this test case results only demonstrate the employed methodology and foreshadow the results that are going to be obtained from a full mechanism. From table 1 we can deduce that CF_4 should be gradually converted to other species as in all the reactions it is used as reactant. On the other hand, the excited states and ions should see an increased density profile as time advances. This shows that the simulation follows the reaction mechanism and with the full mechanism enlisted in [7] will be used to simulate the reaction rates and density of the species.

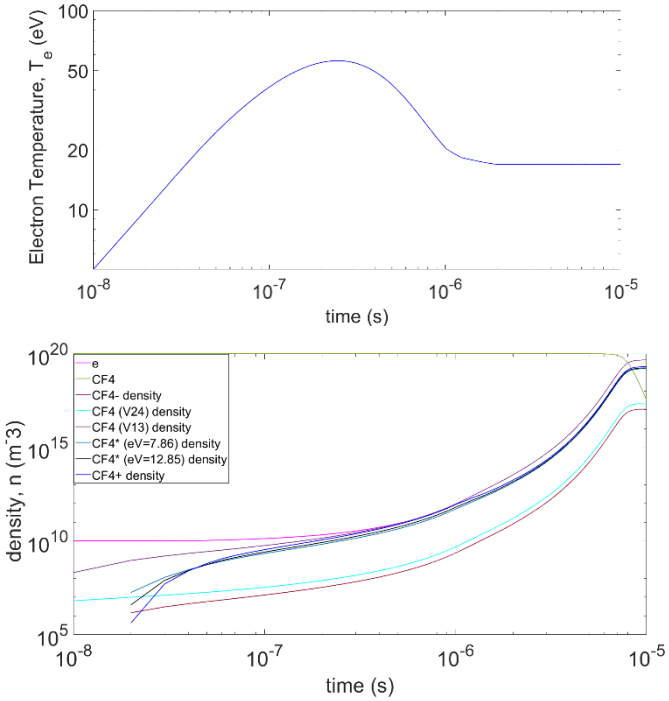

Fig. 5. (upper) Electron temperature vs time, and (lower) the density for all gas species in Table 1. The system is 100% CF_4 and includes only electron-impact reactions.

With the simulated time evolution of the full Ar/CF_4 mechanism, we will be able to observe how the reaction rates and densities of each species evolves with time and infer more about which species may be causing the increased depyrogenation effect.

4. References

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