Dry reforming in $He/CH_4/CO_2$ mixtures: the role of the rare gas

N. Pinhão

Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Lisboa, Portugal

This work focuses on the role of the rare gas component in $He/CH_4/CO_2$ mixtures used for plasma production of *Syngas* in dielectric barrier discharges. The model comprises coupled avalanche and afterglow phases each with different time scales, electron and chemical kinetics. Rare gas processes include electron excitation and ionisation, radiative transitions with resonance radiation trapping, Penning ionization and other heavy species collisions. Results show that the main contribution of the rare gas is in the avalanche phase where it shifts the electron energy distribution (*eedf*) to higher energies, while the contribution to the chemical kinetics is negligible.

1. Introduction

The use of plasmas for dry reforming of methane, either for the production of *Syngas* (a CO/H_2 mixture) or as a source of methanol or other hydrocarbons is an active field of research. Several authors have reported an increase in conversion and, in selected conditions, of energy efficiency in CH_4/CO_2 mixtures with the admixture of rare gases [1-3]. It has been argued that this effect results from Penning ionization and Penning dissociation with the rare gas metastable species [1,2]. In a recent paper on the electron kinetics in $He/CH_4/CO_2$, it was shown that elastic collisions in helium is responsible for a large shift of the electron energy distribution to higher energies. In spite of dilution, this shift contributes to large increase in the electron collision frequencies with the molecular gases [4]. At the same time, the excitation frequencies in helium are very low, raising doubts on the importance of Penning processes to explain the findings.

2. Model

In order to clarify the role of the rare gas in DBD discharges with these mixtures we have developed a 1D steady-state model. The model applies to cylindrical reactors in a plug-flow configuration powered by a sinusoidal voltage and a filamentary discharge regime. Neglecting diffusion and assuming a constant concentration in the plane perpendicular to the reactor axis, the time-dependent kinetic equations for the species are converted into 1D space-dependent equations for the concentrations along the reactor length. The model does not depend on experimental parameters and allows estimating the equilibrium concentrations along the reactor and the conversion, selectivity and yield.

In each half-cycle of the applied voltage the discharge is composed of a streamer shower and afterglow phases. In the streamer phase, the volume covered by the streamers is only a fraction

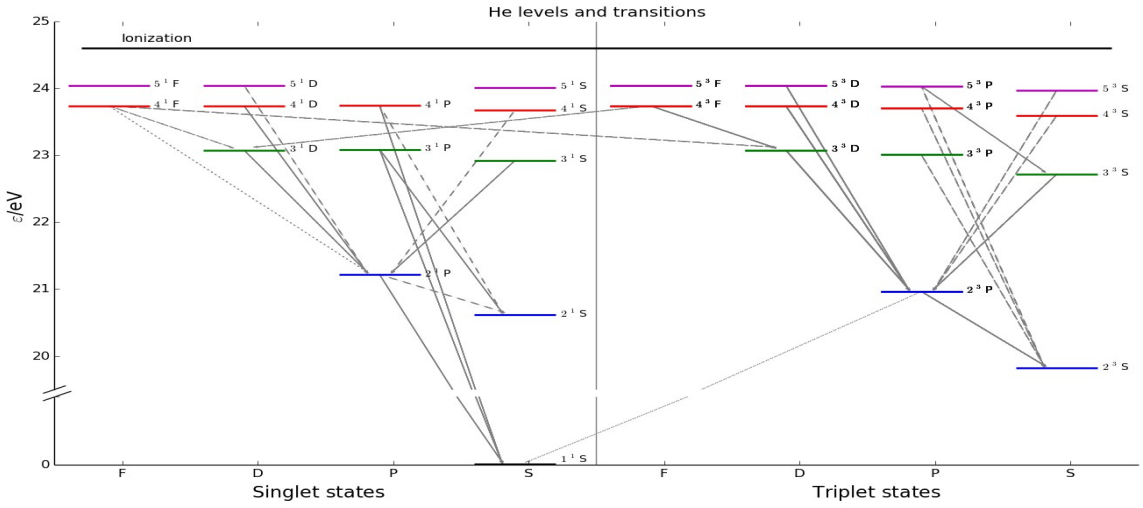

Figure 1 - Helium levels and radiative transitions included in the model.

of the total. The model accounts for this in the following ways:

a) The net effect of streamers on charge build-up, dissociation and production of excited species depends on the specific energy deposited in the gas and is estimated with a simplifying model for this phase;
b) Reactions that occur only during the active phase (mainly electron collision reactions) are multiplied by two factors, (i) the time fraction of the streamer phase and, (ii) the ratio between the volume occupied by streamers and the total volume.

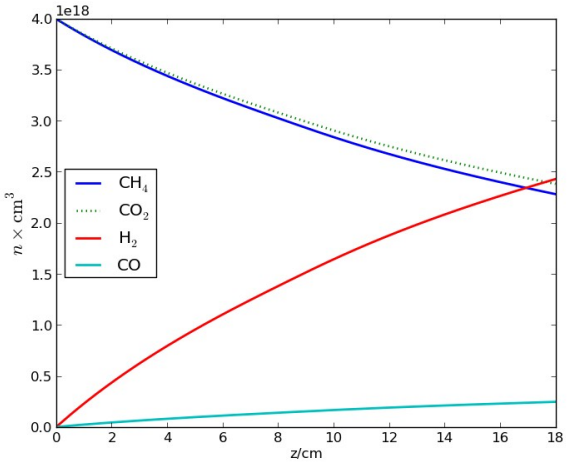

Figure 2 – Equilibrium distribution of reactant and main products for c_{He} = 80% and SIE = 30 kJ/L.

2.1. Streamer phase

Instead of simulating the streamer development, we use simplifying approximations to estimate the electron density and the electron collision rate coefficients for the chemical kinetics model. As a preliminary step, the reduced ionization coefficient, α_{Eff}/N, and rate coefficients, K_{ei}, for electron collision processes are obtained by solving the electron Boltzmann equation in $He/CH_4/CO_2/CO/H_2$ mixtures as a function of the helium concentration, $c_{He,}$ conversion, C, (assumed the same for CH_4 and CO_2) and reduced field, E/N. The cross sections and method used to solve the Boltzmann equation are discussed in [4]. The α_{Eff}/N values are used to compute the gas breakdown voltage V_{bk}, along the reactor assuming an exponential development of the discharge in a non-perturbed electric field. This value is used to compute the peak voltage as a function of the specific energy deposited, SIE, using

$$V_{max} = \frac{C_d + C_g}{C_d} V_{bk} + \frac{SIE \cdot Q_v}{4 C_d V_{bk} f}, \quad (1)$$

where C_d and C_g are the dielectric and gas capacities, respectively, and f the frequency. The number of streamers is calculated from

$$n_s = \left\{ \frac{1}{4} - \frac{\arcsin\left(V_{bk}/V_{max}\right)}{2\pi} \right\} / \left(f \cdot \delta t\right) \quad (2)$$

where δt is the duration of a streamer. From these results and the value of charge deposited by a streamer, we estimate the value of homogeneous field necessary to produce the same number of electrons. This field is then used to estimate the electron collision rate coefficients for the chemical kinetics model.

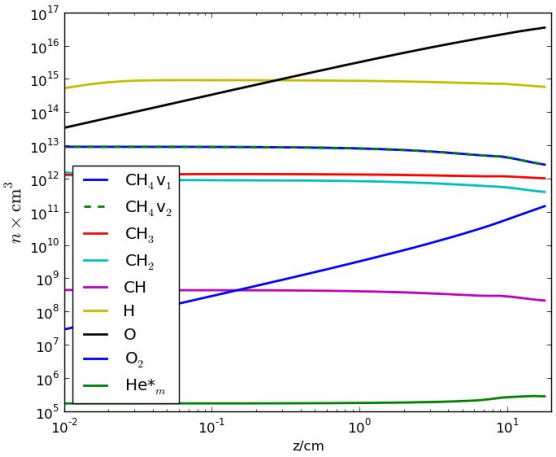

Figure 3 – Equilibrium distribution for other products. Same conditions as in Figure 2.

2.2. Chemical kinetics

The helium model is based on [5] and considers all helium levels until n=5. Besides the electronic excitation and ionization process of section 2.1, the model includes (i) radiative transitions with resonance radiation trapping through Doppler and collisional broadening, (ii) Penning collisions, (iii) associative ionization and, (iv) 3-body ionic conversion. The levels and radiative transitions are shown in Figure 1.

In order to study the reaction paths and the contribution of each species to the experimental results, we limit the number of species included in the model (Table 1). Starting with the initial mixture we only include those formed in electron collisions (1st order) and from reactions with the latter (2nd order). The reactions and reaction coefficients closely follow [6].

Table 1 - Species included in the model.

Order	Molecule	Radical	Charged
0	He, CH_4, CO_2		e
1	He(m), He(n,l,s) $CH_4(v_{13})$, $CH_4(v_{24})$, $CO_2(v_i)$, $CO_2(*)$, CO, O_2, H_2	CH_3, CH_2, CH, C_2H_5, C_3H_3, C_2H, C, H, O	He^+, CH_4^+, CH_3^+, CH_2^+, CH^+, C^+, CO_2^+, CO^+, O^+
2	C_2H_4, C_2H_6, C_2H_2, H_2O, H_2O_2, CH_2O,	OH, HO_2, CHO	O^-, O_2^+, OH^-, He_2^+

The reactions change the number of molecules which, under isobaric and isothermal conditions, implies a change in the volumetric flux of gases along the reactor. Accordingly, the gas velocity is corrected at each point. The results were obtained with the *PlasmaKin* software package [7].

3. Results

The equilibrium distribution of selected species along the reactor are shown in Figures 2 and 3 for c_{He} = 80% and SIE = 30 kJ/L.

The CH_4 and CO_2 concentrations at the exit of the reactor are used to compute the conversion and compare with experimental values from [3]. These last results, like the present model, include the effect of gas expansion. In this case the conversion is computed as

$$C = 1 - \beta \frac{c_{out}}{c_{in}} \quad (3)$$

where β is the gas expansion obtained from the ratio between the volumetric fluxes exiting and entering the reactor. The agreement with the experimental results for CH_4 is very good (Figure 4) but less satisfactory for CO_2 (Figure 5).

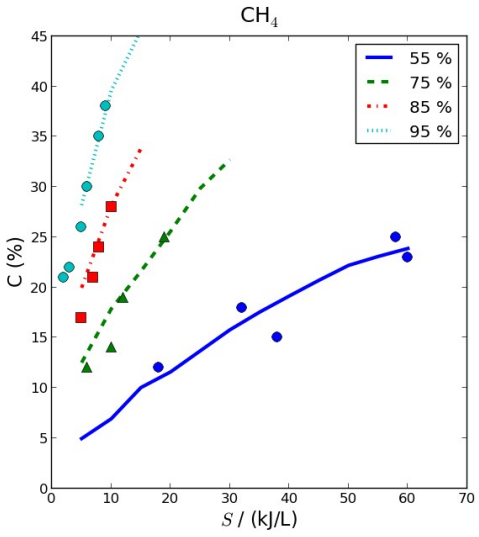

Figure 4 – Experimental (points) and model results (lines) for methane conversion.

The density of helium excited states is always very low (Figure 3). Although radiation imprisonment increases the population of n=2 levels, the total density of excited states is still very low. Penning ionization and excitation are important loss processes for these levels but the overall effect on the discharge is small. The model results confirm that the main effect of the rare gas component in these conditions is the increase in energy of the *eedf* as discussed in [4].

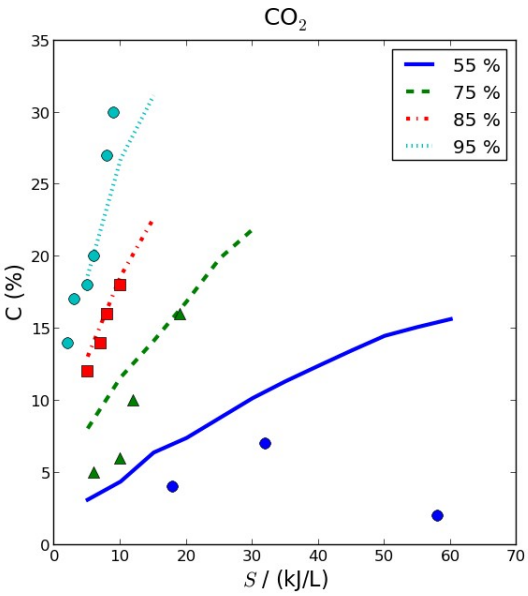

Figure 5 - Experimental (points) and model results (lines) for CO_2 conversion.

Acknowledgements

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3. References

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