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Electron kinetics in mixtures of CH_4, CO_2 and He, with formation of H_2 and CO: the effects of composition and vibrational temperature

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TÉCNICO LISBOA

Introduction:

The present work studies the electron kinetics in He/CH_4/CO_2 and He/CH_4/CO_2/H_2/CO mixtures relevant for the production of Syngas or higher hydrocarbons. This study contributes to the interpretation of experimental results and allow us to identify the main processes and energy transfer channels.
This work expands a preliminary study [1], a) considering the effect of vibrational populations such as in "warm" plasma conditions and, b) considering the influence of dissociation products in the electron kinetics, adding H_2 and CO to the mixture.

Cross Sections:

The electron collision cross sections used are based on published ones from different authors, mostly developed on the two-term angular expansion approximation. Modifications were introduced on the cross sections to ensure the coherence of the set with our Boltzmann solver with a density gradients representation for the evdf, validated by comparing results with experimental transport parameters. Initial cross-sections: He [3]; CO_2 4, 5]; CH_4 [1]; H_2 [6]; CO (http://www.lxcat.laplace.univ-tlse.fr).

Computational details:

Solution of Boltzmann equation:

Boltzmann equation for an electron swarm in hydrodynamic regime. Electron distribution function expanded on the electron density gradients.

$$f(\vec{r},\vec{v},t) = \sum_{k=0}^{\infty} F^{[k]}(\vec{v}) \otimes (-\nabla)^k n(\vec{r},t)$$

Solutions by a discrete ordinates method [2] in a (v, θ) grid.

Superelastic collisions:

We assume that vibrational modes are independent of each other. Vibrational levels: harmonic approximation, with a Boltzmann population with temperature T_v. We then assume that the vibrational excitation cross sections depend only on the mode and the number of transitions. These assumptions allow a considerable simplification on the superelastic collision terms.

Stepwise excitation and ionization:

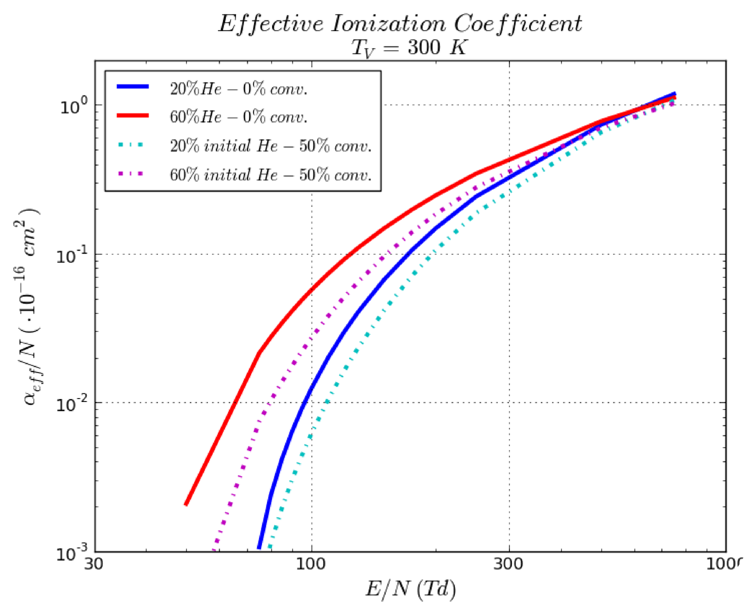
We take into account ionization and electronic excitation from vibrational excited states. The cross section for the transition to a level *x* (ionization or electronic excitation) is defined through a scaling law (adapted from [7]) for the transition from the fundamental level as:

$$\sigma^{v\to x}(\varepsilon) = \sigma^{0\to x}(\varepsilon \Delta^{v\to x})[\Delta^{v\to x}]^{2(1+\gamma)} \frac{\sum_{v=0}^{v_{max}}[\Delta^{v\to x}]^{-2(1+\gamma)}}{(1+v_{max})}$$

with: $\Delta^{v\to x} = \varepsilon_x/(\varepsilon_x - v\varepsilon_m)$

Results and discussion:

We have explored the effects of the electric field, He concentration, products formation, and vibrational temperature.
In real discharges, reagents conversion and products formation change the gas mixture. We compare initial He/CH_4/CO_2 mixtures with post-discharge He/CH_4/CO_2/H_2/CO mixtures. 0% conversion refers to initial conditions with a CH_4/CO_2 ratio of 1 on a fixed He dilution. 50% conversion refers to post-discharge conditions where half of CH_4 and CO_2 being converted to H_2 and CO, with a H_2/CO ratio of 1. As more molecules of products are formed than reagents consumed, there's also a dilution of gases, including He.
Atmospheric pressure DBD is a common discharge for Syngas production from methane. We compare results at 75 Td and 750 Td (around the disruption field, and those obtained in streamers).

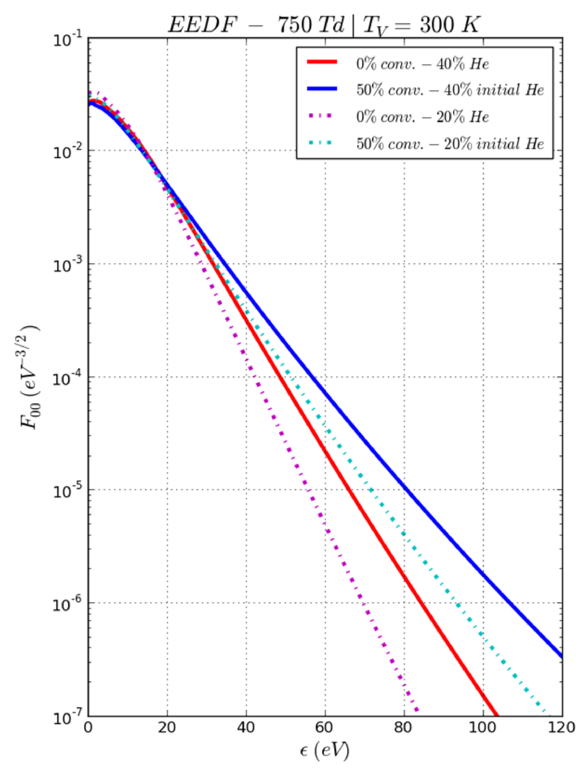


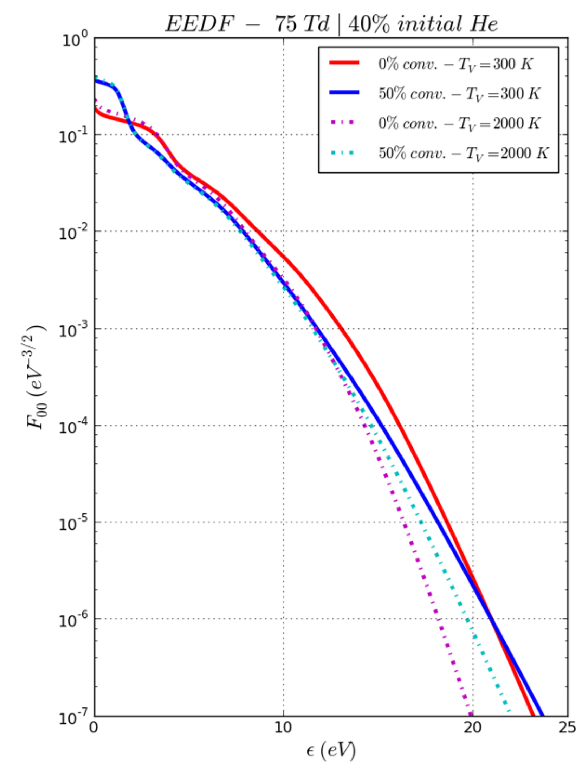
On disruption:

- Discharge breakdown voltage is lower on higher He concentrations (higher effective ionization coefficient).
- The presence of H_2 and CO, with slightly higher ionization thresholds (compared to CH_4 and CO_2), and also with the dilution of He, determines a lower ionization coefficient.

On dissociation:

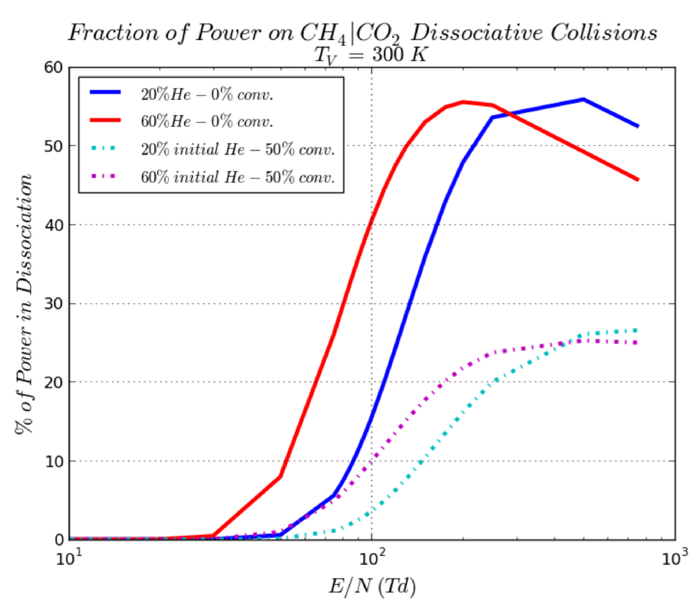
- With dilution in He, higher electron energies competes with less inelastic collisions. For reduced fields around the disruption field, He increases the fraction of power on the dissociation of CH_4 and CO_2. For higher fields, as found in streamers' ionization waves, He slightly decreases this efficiency.
- Stepwise ionization and excitation effect on the collision frequencies is more pronounced for lower fields where the shift of inelastic cross sections to lower energies facilitates the processes and raises dissociation.
- The production of H_2 and CO determines the dilution of the other gases and the lower relative power losses for CH_4 and CO_2 dissociation.

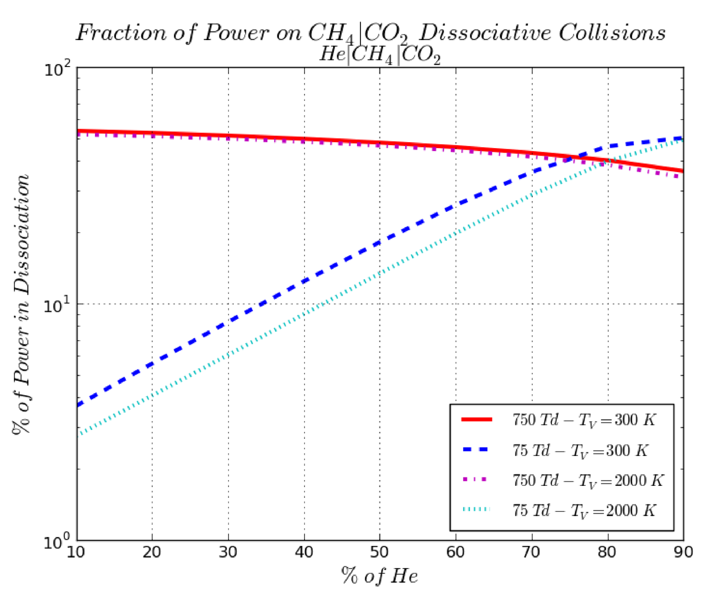


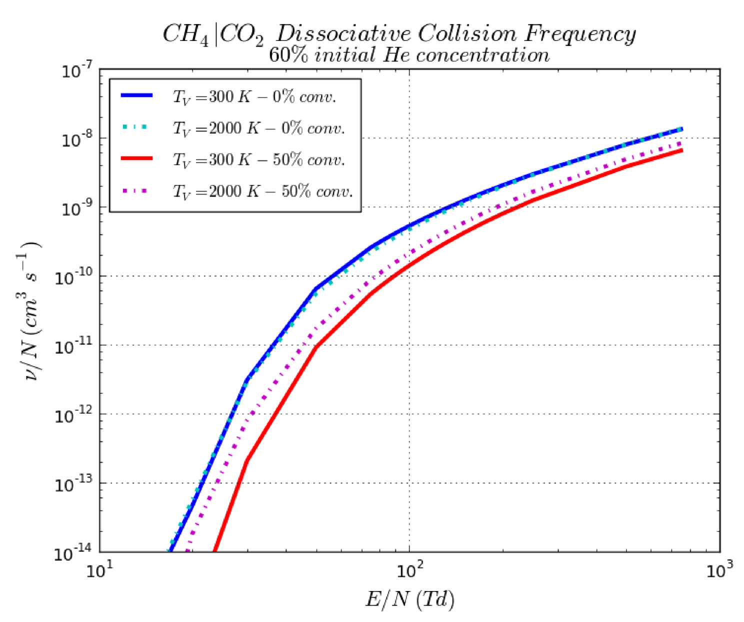


On Electron Energy Distribution Function:

- Dilution in He reduces inelastic collisions and thus raises the electron mean energy and the tail of the EEDF.
- Products formation lowers the EEDF below 20 eV because of the important CO vibrational excitations. Above 20 eV, with less overall inelastic collisions, it allows increased high-end tails of the EEDF.
- Superelastic collisions and stepwise ionization and electronic excitation have competing effects on the EEDF. Superelastic collisions raise electron energy while stepwise excitation depopulate the tail of the EEDF as they introduce additional energy losses at lower energies. This negative effect is dominant.







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