

Study of the electron kinetics and modeling of discharges used for methane conversion

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- 1 Background
 - Methane reforming in DBD with admixtures of rare gases
 - Experimental results on CH₄/CO₂/He mixtures
- 2 Study of the electron kinetics
 - Cross sections
 - Electron kinetics in CH₄/CO₂/He mixtures
- 3 Modeling the discharge
 - A model for breakdown
 - A model for CH₄ and CO₂ conversion

From the literature:

Effect dilution of methane with rare gases:

- *A significant increase in conversion with the rare gas concentration;*
- *No significant difference between helium, argon and neon;*
- *Results explained by Penning ionisation.*

Experimental results

Some definitions:

- $\alpha = \phi_{out} / \phi_{in}$
- Conversion of a reactant X: $C_X = \frac{[X]_0 - \alpha[X]}{[X]_0}$
- Selectivity for a product Y: $S_Y = \frac{\alpha n_Y [Y]}{\sum_X ([X]_0 - \alpha[X])}$
- Specific input energy: $\mathcal{S} = P / q_V$

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Conditions:

- DBD, AC power supply, (5–10) kHz, (room temperature);
- Electric diagnostics, GC;

N.Pinhão, A.Janeco and J.Branco *Plasma Chem. Plasma Process* (2011) 31:427-439

CH₄/CO₂/He mixtures: Breakdown voltage

`../Figuras/Vbkfit_bw.png`

Figure : Gas breakdown voltage for CH₄/CO₂/He mixtures and [CH₄]:[CO₂]=1

CH₄/CO₂/He mixtures: Conversion

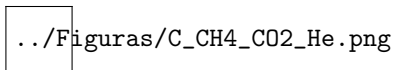
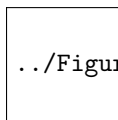
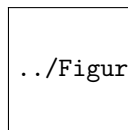


Figure : Conversion of (a) CH₄ and (b) CO₂ for mixtures with different helium mole fractions of 55%, 70%, 80% and 90% ([CH₄]:[CO₂]=1).

CH₄/CO₂/He mixtures: Selectivity



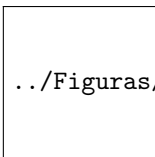
../Figuras/Selectivity2.png



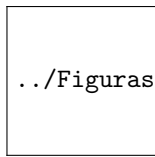
../Figuras/Selectivity1

Selectivity for H₂ and CO for mixtures with different helium mole fractions of 55%, 70%, 80% and 90% ([CH₄]:[CO₂]=1).

CH₄/CO₂/He mixtures: Selectivity



`../Figuras/S_other1.png`



`../Figuras/S_other2.png`

Selectivity for C₂H₆ and C₃H₈ for mixtures with different helium mole fractions of 55%, 70%, 80% and 90% ([CH₄]:[CO₂]=1).

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e-collision cross sections

../Figuras/CH4_new.png ../Figuras/CO2_new.png ../Figuras/He_BeDance_10

Legend:

- momentum transfer; — vibrational excitation; — electronic excitation;
- ionisation; — attachment.

Difficulties...

- CH₄, CO₂, CO: large $\sigma_v/\sigma_m \Rightarrow$ higher anisotropy of the *evdf*

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- Multi-step excitation and ionisation \Rightarrow Cross sections?

Treatment of vibrational levels: Approximations

- We neglect anharmonicity: SHO !

Further discussion in *ESCAMPIG 2014, Greiswald*

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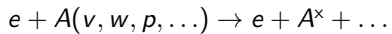
Further discussion in *ESCAMPIG 2014, Greiswald*

Methane intra- and inter-mode transition cross sections

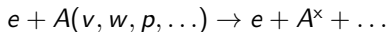
../Figuras/cs-eps-converted-to.pdf

Figure : Lowest intra- and inter-mode v -cross sections for CH₄: – A: $\sigma_{0,1;0,1}^{ij}$, B: $\sigma_{1,0;0,1}^{ij}$, C: $\sigma_{0,1;1,0}^{ij}$, D: $\sigma_{1,0;1,0}^{ij}$. σ_m is the momentum transfer cross section and the index S identifies superelastic cross sections.

Multi-step processes



Multi-step processes

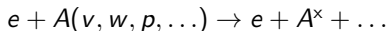


Defining $\Delta_w^{x,i} = \varepsilon_x / (\varepsilon_x - w\varepsilon_i)$, we use

$$\sigma_v^{x,i}(\varepsilon) = \sigma_0^x (\varepsilon \Delta_v^{x,i}) \left[\Delta_v^{x,i} \right]^{2(1+\gamma)} \frac{\sum_{w=0}^{w_M} \left[\Delta_w^{x,i} \right]^{-2(1+\gamma)}}{(1+w_M)}$$

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and

$$\sigma_{w\dots p}^x(\varepsilon) = \frac{1}{m} \left[\sigma_w^{x,i}(\varepsilon) + \dots + \sigma_p^{x,m}(\varepsilon) \right]$$

Adapted from Celiberto, R. and Capitelli, M. and Janev, R.K., Chem. Phys. L., 6 (1996) 575–580

Electron kinetics

Gas mixtures:

- Input: $\eta\text{He}/\frac{1}{2}(1 - \eta)\text{CH}_4/\frac{1}{2}(1 - \eta)\text{CO}_2$;

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- Hydrodynamic regime, non-conservative processes, multiterm;
 - Results: f_0 , α/N , $\nu_i/N = [M_i] \times k_e^X$, with $M_i = \text{CH}_4, \text{CO}_2, \text{He}$;

A.Janeco, N.Pinhão, and V.Guerra *Plasma Sources Sci. Tech.* (submitted)

a) Electron energy distribution function

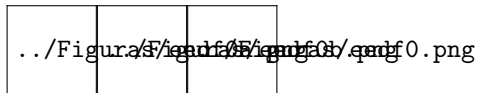


Figure : Isotropic component of the eedf for three values of reduced field, (a) 10 Td, (b) 74 Td and (c) 736 Td, and different combinations of (η, C) : — (0, 0); - - - (0.6, 0); — · — (0, 0.3); · · · · (0.6, 0.3).

b) Ionization coefficient

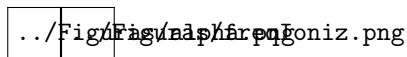


Figure : [left] Effective ionization coefficient as a function of E/N and for different values of (η, C) : — (0, 0); - - - (0.6, 0); - · - (0, 0.3); · · · (0.6, 0.3). [right] Ionization reduced frequencies for — He, □ CH₄, — CO₂, - · - CO and · · · H₂ as a function of the reduced field for a $(\eta, C) = (0.6, 0.3)$.

c) Vibrational excitation frequencies

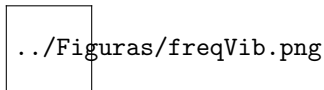


Figure : Total vibrational reduced collision frequencies in (a) CH₄ and (b) CO₂ as a function of the reduced field and for different values of (η , C): [same codes as before].

d) Ionization and excitation of He metastable levels

../Figuras/freqHe.png

Figure : (a) Electron collision reduced frequencies for helium ionization and (b) excitation of helium metastables as a function of the reduced field and for different values of (η, C) . Ionization or 2^1S level: — (1, 0); - - - (0.6, 0); — · — (0.4, 0). For 2^3S : dotted curves (· · ·) with the same colors as before.

e) Fractional energy losses

../Figuras/powerLosses.png

Figure : Fractional power losses for each type of process and mixtures component: (a) He, (b) CH₄, (c) CO₂ and, (d) the whole mixture. — momentum transfer; — vibrational exc.; - - - electronic exc.; — · — ionization. Calculations made for $(\eta, C) = (0.6, 0)$, with the exception of the dotted curves (· · · ·) in (d), corresponding to $(\eta, C) = (0, 0)$.

Summary

Role of helium:

- Significant shift of the evdf to higher energy;
- Responsible for an increase of the electronic ext. and ionization frequencies in CH₄ and CO₂;
- Responsible for a shift of the α/N curve to lower E/N values;
- The excitation and ionization frequencies in He are negligible;
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Effect of conversion:

- Depends on process and E/N range;
- Process with ε_0 low, increase at low E/N and decrease afterwards;
- Process with ε_0 high are relatively insensitive and $\nu \propto [M]$;

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Breakdown voltage

Model: Townsend regime

- 1 Discharge starts as a Townsend avalanche;
- 2 Electric field undisturbed: $E(r) \propto U_{bk,g}/r$;
- 3 $1/\nu_{inel} < 0.1 \text{ ns} \Rightarrow f_e(\mathbf{r}, \mathbf{v}, t)$ in local field equilibrium;
- 4 Initial development sustained by photo-electric effect;
- 5 Breakdown criteria: $\int_{r_0}^R \alpha_{eff}(E(r)/N)dr = \log(1 + \gamma^{-1})$

Breakdown voltage

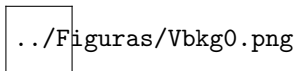


Figure : Gas breakdown voltage for CH₄/CO₂/He mixtures and [CH₄]:[CO₂]=1.
Experimental (points) and model (lines) results.

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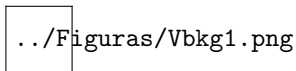


Figure : Gas breakdown voltage for $\text{CH}_4/\text{CO}_2/\text{He}$ mixtures and $[\text{CH}_4]:[\text{CO}_2]=1$.
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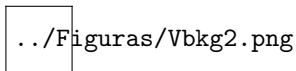


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../Figuras/DBD_simulado.png

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- 5 $\overline{E/N} \Rightarrow \overline{K_e^*}$;

Equivalents E/N and discharge length


 ../Figuras/figure_EbyNLeq.png

Figure : [Left] Equivalent field and [right] equivalent length as a function of helium concentration for two values of conversion.

Model equations and species

Model species:

CH₄: CH₄v_i, CH₃, CH₂, CH, CH₃⁺, CH₂⁺, CH⁺, C⁺, H₂⁺, H⁺,
CH₄⁺, CH₃⁺, CH₂⁺, CH⁺;

CO₂: CO₂v_i, CO₂^{*}, CO₂^{**}, CO, O(¹S), CO₂⁺, O⁺, CO⁺, C⁺

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In steady state, for species lost (or produced) on the streamers:

$$\frac{d}{dz} [v_{gas}(z)n_i(z)] = -f_T f_V n_i(z) \left(\frac{Q_i}{q_e \bar{\alpha}(z) \xi} \right) \sum_j \bar{K}_{ei}^j(z) + S_i,$$

Model results – Densities

../Figuras/figure_nz.png

Figure : Density of selected species along the reactor length for an initial helium concentration of 55% and SIE = 30 kJ/L.

Model results – Conversion

`../Figuras/fig_Ccvib.png`

Figure : Conversion of CH₄ and CO₂: [points] experimental results, [lines] model results.

Model results – Selectivities


 ../Figuras/figure_S_1order.png

Figure : Selectivity for H₂ and CO production as a function of SIE for different values of initial helium concentration.

Conclusions

Conclusions:

- The role of helium in the mixtures was clarified;
- Cross sections for inter- and intra-vibrational excitation and multi-step processes were developed;
- Simple models for the discharge breakdown and the chemical kinetics explain qualitatively the experimental results.

Perspectives:

- Refine the chemical kinetics model;
- More realistic $E/N(r, t)$ and $n_e(r, t)$.

New E/N

`../Figuras/new_EbyN.png`

Figure : Reduced field along the streamer axis for different instants, $dt = 5$ ns.