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

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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;

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CH_4/CO_2/He mixtures: Breakdown voltage

../Figuras/Vbkfit_bw.png

Figure : Gas breakdown voltage for CH_4/CO_2/He mixtures and $[CH_4]:[CO_2]=1$

CH_4/CO_2/He mixtures: Conversion

../Figuras/C_CH4_CO2_He.png

Figure : Conversion of (a) CH_4 and (b) CO_2 for mixtures with different helium mole fractions of 55%, 70%, 80% and 90% ([CH_4]:[CO_2]=1).

CH_4/CO_2/He mixtures: Selectivity

../Figuras/Selectivity2.png ../Figuras/Selectivity1

Selectivity for H_2 and CO for mixtures with different helium mole fractions of 55%, 70%, 80% and 90% ([CH_4]:[CO_2]=1).

CH_4/CO_2/He mixtures: Selectivity

../Figuras/S_other1.png ../Figuras/S_other2.png

Selectivity for C_2H_6 and C_3H_8 for mixtures with different helium mole fractions of 55%, 70%, 80% and 90% ($[CH_4]$:$[CO_2]$=1).

1. Background
   - Methane reforming in DBD with admixtures of rare gases
   - Experimental results on CH_4/CO_2/He mixtures
2. Study of the electron kinetics
   - Cross sections
   - Electron kinetics in CH_4/CO_2/He mixtures
3. Modeling the discharge
   - A model for breakdown
   - A model for CH_4 and CO_2 conversion

e-collision cross sections

../Figuras/CH4_new.png ../Figuras/CO2_new.png ../Figuras/He_BeDance_1(

Legend:

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

Difficulties...

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

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- We neglect anharmonicity: SHO !

Further discussion in *ESCAMPIG 2014, Greiswald*

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Methane intra- and inter-mode transition cross sections

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

Figure : Lowest intra- and inter-mode v-cross sections for CH_4: – A: $\sigma^{ij}_{0,1;0,1}$, B: $\sigma^{ij}_{1,0;0,1}$, C: $\sigma^{ij}_{0,1;1,0}$, D: $\sigma^{ij}_{1,0;1,0}$. σ_m is the momentum transfer cross section and the index S identifies superelastic cross sections.

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and

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

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

Electron kinetics

Gas mixtures:

- Input: $\eta He/\frac{1}{2}(1-\eta)CH_4/\frac{1}{2}(1-\eta)CO_2$;

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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 $M_i = CH_4, CO_2, He$;

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

../Figures/alpha.png ../Figures/freqIoniz.png

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, □ CH_4, — — — CO_2, — · — CO and · · · · H_2 as a function of the reduced field for a (η, C) = (0.6, 0.3).

c) Vibrational excitation frequencies

../Figuras/freqVib.png

Figure : Total vibrational reduced collision frequencies in (a) CH_4 and (b) CO_2 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 ^{1}S level: —— (1, 0); – – – (0.6, 0); — · — (0.4, 0). For 2 ^{3}S: dotted curves ($\cdots$) 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) CH_4, (c) CO_2 and, (d) the whole mixture. —— momentum transfer; —— vibrational exc.; – – – electronic exc.; — · — ionization. Calculations made for $(\eta, \mathrm{C}) = (0.6, 0)$, with the exception of the dotted curves $(\cdot\cdot\cdot\cdot)$ in (d), corresponding to $(\eta, \mathrm{C}) = (0, 0)$.

Summary

Role of helium:

- Significant shift of the evdf to higher energy;
- Responsible for an increase of the electronic exct. and ionization frequencies in CH_4 and CO_2;
- Responsible for a shift of the α/N curve to lower E/N values;
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Effect of conversion:

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

Breakdown voltage

Model: Townsend regime

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

Breakdown voltage

../Figuras/Vbkg0.png

Figure : Gas breakdown voltage for CH_4/CO_2/He mixtures and $[CH_4]$:$[CO_2]$=1. Experimental (points) and model (lines) results.

Breakdown voltage

../Figuras/Vbkg1.png

Figure : Gas breakdown voltage for CH_4/CO_2/He mixtures and $[CH_4]:[CO_2]=1$. Experimental (points) and model (lines) results.

Breakdown voltage

../Figuras/Vbkg2.png

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Model for a DBD discharge

What we know

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../Figuras/DBD_simulado.png

CH_4 and CO_2 conversion

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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:

CH_4: $CH_4 v_i$, CH_3, CH_2, CH, CH_3^+, CH_2^+, CH^+, C^+, H_2^+, H^+, CH_4^+, CH_3^+, CH_2^+, CH^+;

CO_2: $CO_2 v_i$, CO_2^*, CO_2^{**}, CO, $O(^1S)$, CO_2^+, O^+, CO^+, C^+

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He: $He(2^3S)$, $He(2^1S)$

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

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

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 CH_4 and CO_2: [points] experimental results, [lines] model results.

Model results – Selectivities

../Figuras/figure_S_1order.png

Figure : Selectivity for H_2 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.