Plasma–assisted conversion of methane and carbon dioxide: myths, challenges and opportunities

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Outline

Availability of conventional fuels

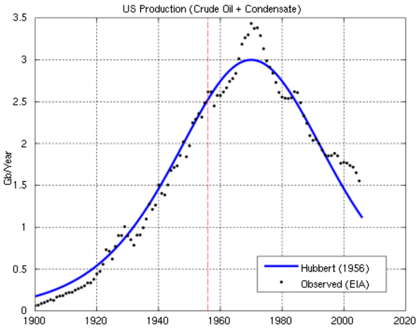


Figure: Hubbert peak of US oil production

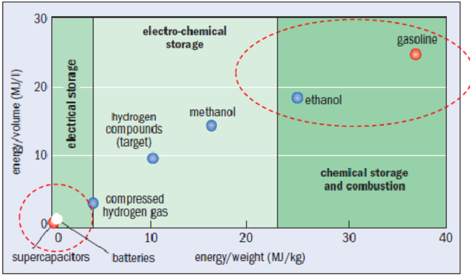
World:

- Oil: peak in 2015 (?)
- Gas: peak in 2030–2035 (?); $\approx$ 100 years of consumption
- 85% of global energy is transported by liquid fuels

Z.Jian et al. *Petr. Sci.* (2010)7:136-146

Storage of Energy: energy density

- **Electrical**
  - Batteries
  - Super capacitors



How to store it Chemicals like gasoline and ethanol store energy at much higher densities than batteries. With scientific advances, the gap can be filled with electro-chemical storage where chemical energy is converted to electricity in fuel cells.

- **Chemical storage**
  - H_2
  - Fuels (>10 more energy density)

Chemical conversion of methane

- CH_4 + oxidant (O_2, CO_2, H_2O) → H_2 + CO (Syngas)
  - Syngas → H_2
  - Syngas ⇒ Fisher-Tropsch ⇒ synthetic fuels
- CH_4 + oxidant ⇒ CH_3OH (methanol)

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Perspectives

- *Conversion of natural gas into liquid fuels → large-scale plants;*
- *Hydrogen for fuel cells → compact and small syngas units.*

Non-thermal plasmas for conversion of CH_4

Main plasma sources used in the conversion of CH_4:

- Dielectric Barrier Discharges
  1. Atmospheric pressure (normally in the filamentary mode);
  2. High electron density and energy;
  3. Easy to scale up;
  4. Coupling between the plasma and a catalyst facilitated.
  5. But... works at low gas flux
  6. But... low electrode spacing
- Gliding arc: $T_e = 1 - 3\,eV \gg T_g \sim 2000\,K$ and $T_v \sim 2T_g$.
- Microwave discharges

1. Background
   - Energy: An urgent problem to mankind
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   - Experimental results with $CH_4/CO_2/He$ mixtures
   - Application of over-voltages
3. A model of the discharge
   - Electron kinetics in $CH_4/CO_2/He$ mixtures
   - A model for breakdown
   - A model for CH_4 and CO_2 conversion
4. Summary

Experimental set-up

Diagnostics:

- Conversion and selectivity: GC-FID/TCD
- Power, breakdown voltage: Q-V plots

$CH_4/CO_2/He$ mixtures: Breakdown voltage

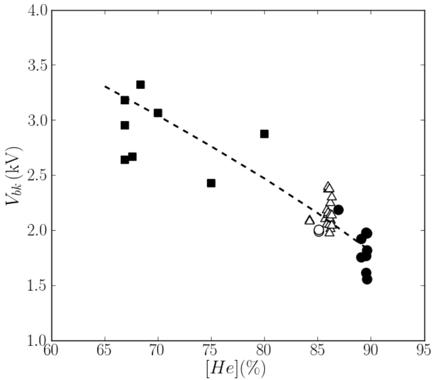


Figure: Gas breakdown voltage for $CH_4/CO_2/He$ mixtures and $[CH_4]$:$[CO_2]$=1

CH_4/CO_2/He mixtures: Conversion

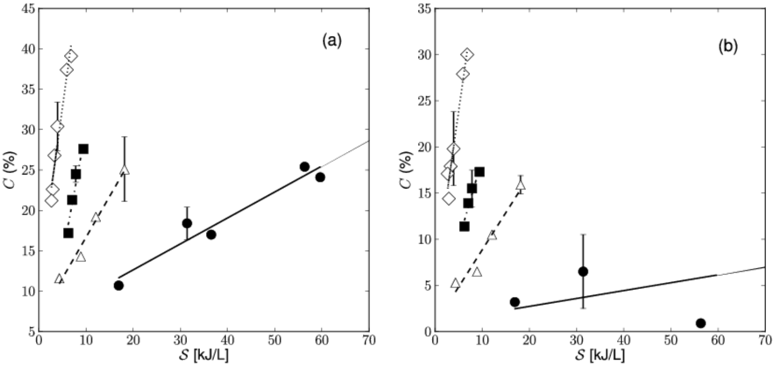
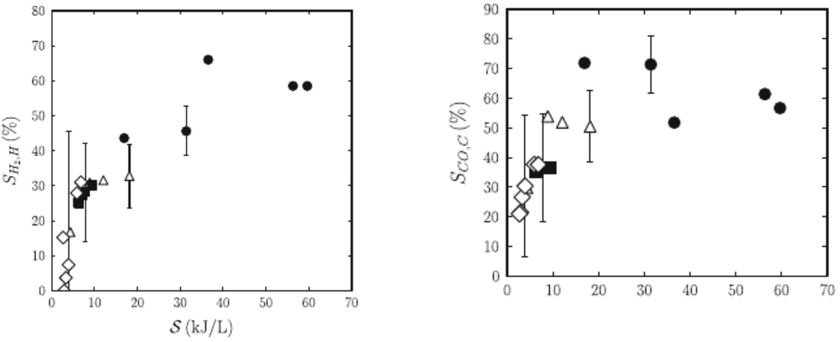


Figure: Conversion of (a) CH_4 and (b) CO_2 for mixtures with different helium mole fractions of 55%, 70%, 80% and 90% ($[CH_4]:[CO_2]=1$).

CH_4/CO_2/He mixtures: Selectivity



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/rare gas mixtures: Summary

Table: Products and energy efficiency for CH_4 conversion in a DBD

Reference value[a] (H_2): 1.13 eV/molec.

Admixture		pure CH_4	+ O_2 or CO_2	+ He, Ar, Ne
Products		H_2, C_xH_y, solid-C	H_2, CO, CO_2[a], CH_3OH, $C_xO_yH_z$	
Conv. ab.	[total]	40	8.6	5.7
(MJ/mol)	[CH_4]	40	15	9
	[CO_2]	-	20	14
E. eff. (H_2)	eV/molec.	-	-	17
Comment		C-deposits	H_2O[b], liquid products	

[a] Gutsol et al., *J. Phys. D: Appl. Phys.* **44** (2011) 274001

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

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Challenge:

How to explain the results?
How to increase the energy efficiency?

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Results with a rectangular power supply

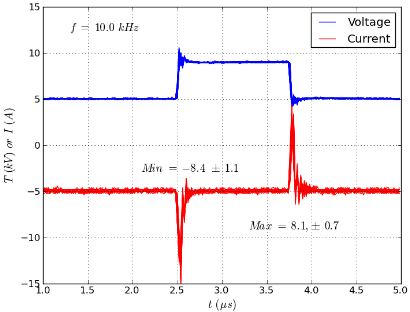

Figure: Voltage and current signals with a rectangular power supply on mixtures of CH_4/CO_2 with 60% He.

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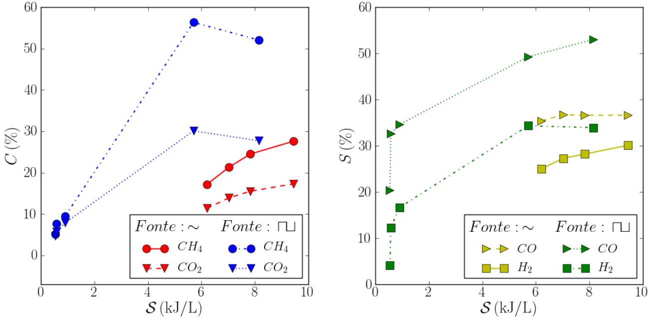

Figure: Conversion and selectivity results obtained with sinusoidal or rectangular power supplies on mixtures of CH_4/CO_2 with 80% He. Conversion ability: $(5.7 \rightarrow 1.8)$ MJ/mol (H_2 : 6 $eV/molec.$)

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Boltzmann equation for an electron swarm:

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- Parameters: initial helium concentration and conversion: (η, C)

a) Electron velocity distribution function

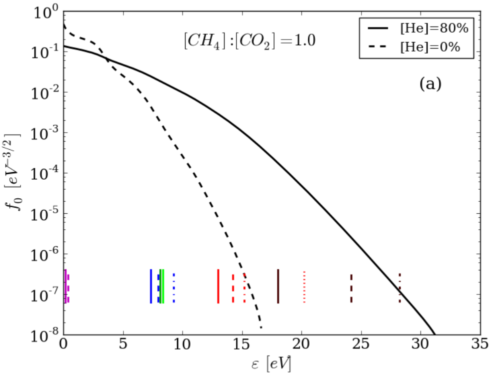


Figure: Isotropic component of the $F^{[0]}$ expansion coefficient of the electron velocity distribution function for $E/N = 5 \cdot 10^{-16}$ Vcm^2. The vertical lines are the thresholds for inelastic processes in methane.

b) Ionization coefficient

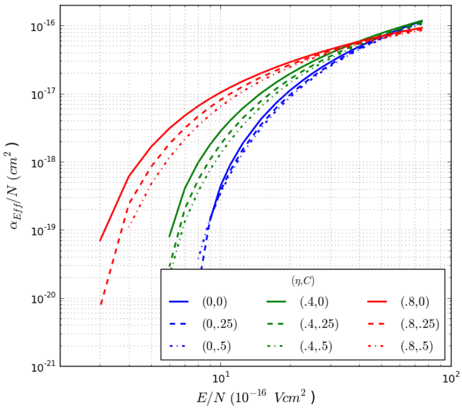


Figure: Ionisation coefficient in CH_4/CO_2/He mixtures as a funcion of the initial helium concentration (η) and methane conversion, C.

c) Dissociation frequencies

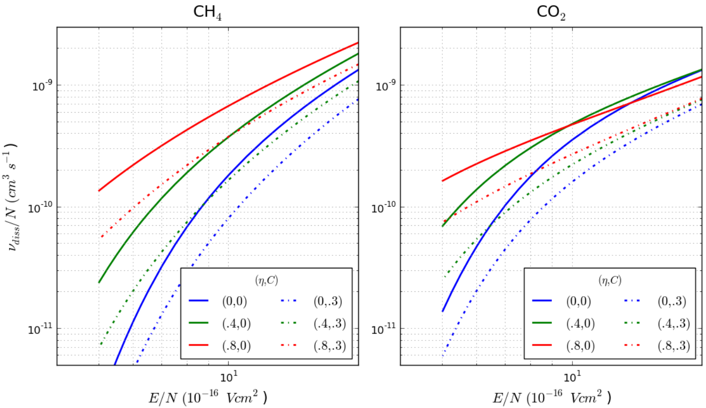


Figure: Dissociation frequencies in CH_4/CO_2/He mixtures as a function of the initial helium concentration (η) and methane conversion (C).

d) Excitation of helium metastable levels

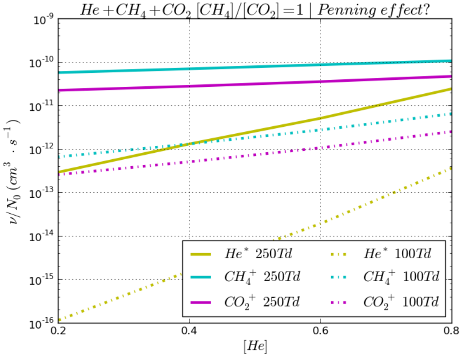


Figure: Comparison of ionization frequencies and excitation frequencies for the helium metastable levels in $CH_4/CO_2/He$ mixtures, as a function of the initial helium concentration.

e) Fractional energy losses

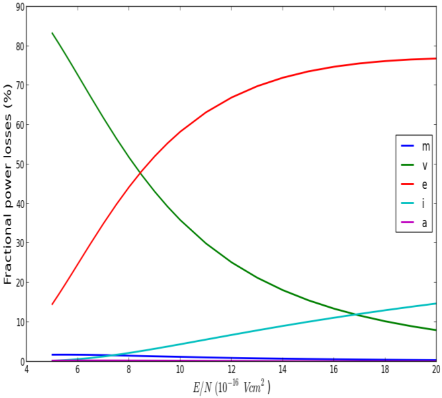


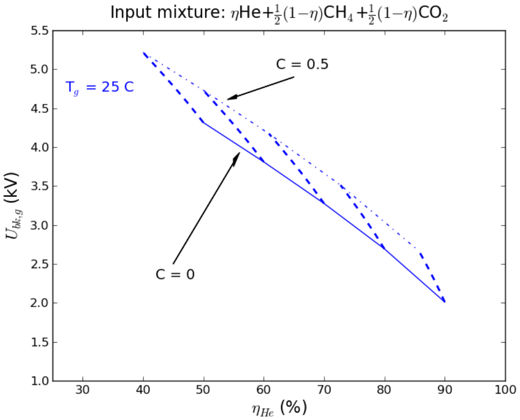
Figure: Fractional electron energy losses per type of process in CH_4/CO_2/He mixtures with [He]=60%.

Breakdown voltage

Model: Townsend regime

1. Discharge starts as a Townsend avalanche;
2. Electric field undisturbed: $E(r) \propto U_{bk,g}/r$;
3. $1/\nu_{inel} < 0.1\,ns \Rightarrow f_e\left(\mathbf{r}, \mathbf{v}, t\right)$ 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



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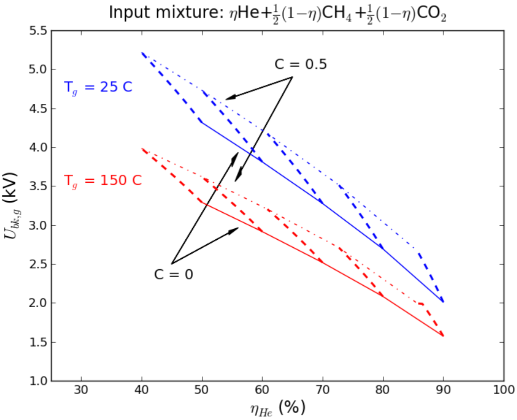

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Breakdown voltage

$$U_{bk,g} = \frac{C_d}{C_d + C_g} U_{bk,e} + \frac{1}{2} \frac{Q_{gas}(T/2)}{C_d + C_g}$$

$$Q_{gas} = \sum_{i}^{m} Q^i$$

with[a]: $Q^i(\delta t) = (C_d + C_g)\Delta U^i_{fs} + C_d(U^i_e(t + \delta t) - U^i_e(t))$

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2. Consecutive microdischarges: $U^{i+1}_e(t) = U^i_e(t+\delta t)$;
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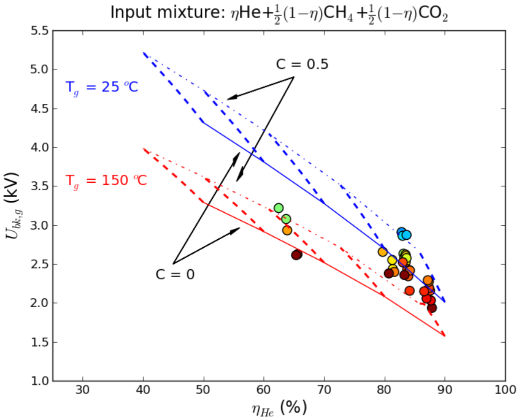

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CH_4 and CO_2 conversion

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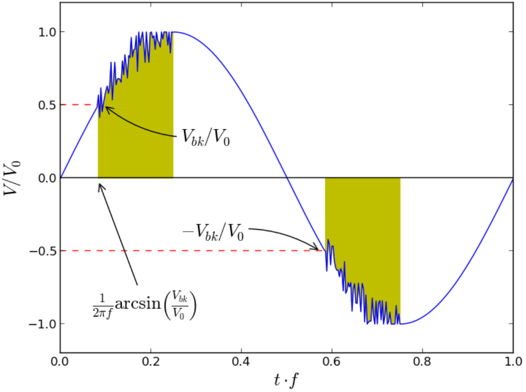
1.0
0.5
0.0
−0.5
−1.0
0.0
0.2
0.4
0.6
0.8
1.0
V/V_0
$t \cdot f$
V_{bk}/V_0
$-V_{bk}/V_0$
$\frac{1}{2\pi f}\arcsin\left(\frac{V_{bk}}{V_0}\right)$

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Model equations and species

Products involved in conversion:

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

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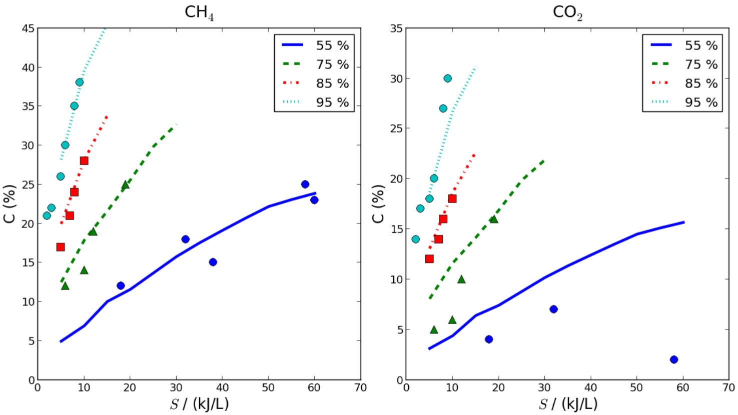
He: $He(2^3S)$, $He(2^1S)$

In steady state:

$$\frac{d\rho v_{gas}}{dz} = 0$$

$$\frac{d}{dz}\left[n^i(z)(v_{gas}+V_D)\right] = -f_T f_V \frac{Q_{gas}}{q_e} c^i(z) \sum_j \frac{\overline{K_e^{ij}}(z)}{\overline{\alpha}(z)/N\xi} - K_P^i n^i(z) n_{He^*}(z)\,, \qquad i = CH_4, CO_2$$

Model results



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- Model based on the measured charge and an "equivalent field" is useful to explain the conversion results;
- Use of DBD discharges for dry reforming of CH_4/CO_2 is not yet competitive for *Syngas* production.