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

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1 Background
   - Energy: An urgent problem to mankind
   - An opportunity for plasma systems?

2 Conversion of CH\textsubscript{4} in a DBD
   - Experimental results with CH\textsubscript{4}/CO\textsubscript{2}/He mixtures
   - Application of over-voltages

3 A model of the discharge
   - Electron kinetics in CH\textsubscript{4}/CO\textsubscript{2}/He mixtures
   - A model for breakdown
   - A model for CH\textsubscript{4} and CO\textsubscript{2} conversion

4 Summary
1. **Background**
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   - Experimental results with CH₄/CO₂/He mixtures
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4. **Summary**
Availability of conventional fuels

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


**Figure:** Hubbert peak of US oil production
Storage of Energy: energy density

- **Electrical**
  - Batteries
  - Super capacitors

- **Chemical storage**
  - $\text{H}_2$
  - Fuels (>10 more energy density)
Chemical conversion of methane

- $\text{CH}_4 + \text{oxidant (O}_2, \text{CO}_2, \text{H}_2\text{O)} \rightarrow \text{H}_2 + \text{CO (Syngas)}$
  - Syngas $\rightarrow$ $\text{H}_2$
  - Syngas $\Rightarrow$ Fisher-Tropsch $\Rightarrow$ synthetic fuels
- $\text{CH}_4 + \text{oxidant} \Rightarrow \text{CH}_3\text{OH (methanol)}$
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**Perspectives**

- *Conversion of natural gas into liquid fuels $\rightarrow$ large-scale plants;*
- *Hydrogen for fuel cells $\rightarrow$ 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**
  - Atmospheric pressure (normally in the filamentary mode);
  - High electron density and energy;
  - Easy to scale up;
  - Coupling between the plasma and a catalyst facilitated.
  - But... works at low gas flux
  - But... low electrode spacing

- **Gliding arc**: $T_e = 1 - 3$ eV $\gg T_g \sim 2000$ K and $T_v \sim 2 T_g$.

- Microwave discharges
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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
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).
Selectivity for $H_2$ and CO for mixtures with different helium mole fractions of 55%, 70%, 80% and 90% ([CH$_4$]:[CO$_2$] = 1).
Table: Products and energy efficiency for CH$_4$ conversion in a DBD

Reference value$^a$ (H$_2$): 1.13 eV/molec.

<table>
<thead>
<tr>
<th>Admixture</th>
<th>pure CH$_4$</th>
<th>+ O$_2$ or CO$_2$</th>
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<tbody>
<tr>
<td>Products</td>
<td>H$_2$, C$_x$H$_y$, solid-C</td>
<td>H$_2$, CO, CO$_2$$^a$, CH$_3$OH, C$_x$O$_y$H$_z$</td>
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<tr>
<td>Conv. ab. [total]</td>
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<td>8.6</td>
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$^b$with O$_2$

CH₄/CO₂/rare gas mixtures: Summary

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Challenge:

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

ᵇwith O₂

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.
Results with a rectangular power supply

![Graph showing conversion and selectivity results](image)

**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 → 1.8) MJ/mol (H$_2$: 6 eV/molec.)
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Electron kinetics

Boltzmann equation for an electron swarm:
- expansion on the electron density gradients / non-conservative processes;
- multi-term expansion on $\theta$ required by CH$_4$ and CO$_2$;

Gas mixtures:

Input: He/CH$_4$/CO$_2$, with $[CH_4]/[CO_2] = 1$;
... + Products: H$_2$, CO
Stoichiometry: $CH_4 + CO_2 \rightarrow 2CO + 2H_2$
Parameters: initial helium concentration and conversion: $(\eta, C)$

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Plasma conversion of CH$_4$ and CO$_2$
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- Parameters: initial helium concentration and conversion: ($\eta$, C)
Figure: Isotropic component of the $F^{[0]}$ expansion coefficient of the electron velocity distribution function for $E/N = 5 \cdot 10^{-16} \text{ Vcm}^2$. 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 function of the initial helium concentration ($\eta$) and methane conversion, $C$. 

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c) Dissociation frequencies

\[ \nu_{\text{diss}} / N \left( \text{cm}^3 \text{s}^{-1} \right) \]

\[ E/N \left( 10^{-16} \text{ Vcm}^2 \right) \]

**Figure:** Dissociation frequencies in CH\(_4\)/CO\(_2\)/He mixtures as a function of the initial helium concentration \((\eta)\) and methane conversion \((C)\).
d) Excitation of helium metastable levels

Figure: Comparison of ionization frequencies and excitation frequencies for the helium metastable levels in CH₄/CO₂/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. \( 1/\nu_{inel} < 0.1 \text{ ns} \Rightarrow f_e(r, v, t) \) in local field equilibrium;
4. Initial development sustained by photo-electric effect;
5. Breakdown criteria: \( \int_{r_0}^{R} \alpha_{\text{eff}}(E(r)/N) \, dr = \log(1 + \gamma^{-1}) \)

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Plasma conversion of CH\(_4\) and CO\(_2\)
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**Figure:** Gas breakdown voltage for CH$_4$/CO$_2$/He mixtures and [CH$_4$]:[CO$_2$]$=1$. Experimental (points) and model (lines) results.
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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 \(^a\): \[ Q^i(\delta t) = (C_d + C_g) \Delta U_{fs}^i + C_d (U_e^i(t + \delta t) - U_e^i(t)) \]

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1. \( Q^i = Q^j, \Delta U^i_{fs} = \Delta U^j_{fs} \quad \forall i, j; \)
2. Consecutive microdischarges: \( U^{i+1}_e(t) = U^i_e(t + \delta t); \)
3. Each point in space has a maximum of one microdischarge.

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\[ \Rightarrow Q_{gas}(T/2) = (C_d + C_g)m\Delta U_{fs} + C_d(U_{max,e} - U_{bk,e}) \]

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**Figure:** Gas breakdown voltage for CH$_4$/CO$_2$/He mixtures and [CH$_4$]:[CO$_2$]=1. Experimental (points) and model (lines) results.
CH₄ and CO₂ conversion

Model

1. Consumption of CH₄ and CO₂ only by e-collisions or Penning ionz.;
CH$_4$ and CO$_2$ conversion

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### CH$_4$ and CO$_2$ conversion

#### Model

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How to estimate $n_e(r, t)$ and the source terms from collisions with electrons?
CH$_4$ and CO$_2$ conversion

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CH₄ and CO₂ conversion

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How to estimate nₑ(r, t) and the source terms from collisions with electrons?

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1. Qᵢ ∝ exp(α × lₑquiv);
2. α ⇒ E/N ⇒ Kₑ*.
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How to estimate $n_e(r, t)$ and the source terms from collisions with electrons?

Equivalent field

1. $Q^i \propto \exp(\overline{\alpha} \times l_{equiv})$;
2. $\overline{\alpha} \Rightarrow E/N \Rightarrow K_e^*$;
3. $l_{equiv} \sim v_d \delta t_{microdisc}$.
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$_2^-$; 
CO$_2$: O($^1$S), $O^+$, CO$^+$, C$, O^-$
**Model equations and species**

### Products involved in conversion:

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<td><strong>CH$_4$</strong></td>
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<tr>
<td><strong>CO$_2$</strong></td>
<td>O($^1$S), O$^+$, CO$^+$, C$^+$, O$^-$</td>
</tr>
<tr>
<td><strong>He</strong></td>
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<td><strong>He</strong>: He((^2)(^3)S), He((^2)(^1)S)</td>
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In steady state:

\[
\frac{d \rho v_{gas}}{dz} = 0
\]

\[
\frac{d}{dz} \left[ n^i(z)(v_{gas} + V_D) \right] = -f_T f_V \frac{Q_{gas}}{q_e} c^i(z) \sum_j \frac{K_{e,j}^i(z)}{\alpha(z)/N_\xi} - K_P n^i(z) n_{He^*}(z), \quad i = CH_4, CO_2
\]
Model results

**CH\(_4\)**

- Blue line: 55%
- Green dashed line: 75%
- Red dotted line: 85%
- Cyan dotted line: 95%

**CO\(_2\)**

- Blue line: 55%
- Green dashed line: 75%
- Red dotted line: 85%
- Cyan dotted line: 95%
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- Role of helium:
  - shifts the \( eedf \) to higher energy;
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  - low He excitation or ionization rates: Negligible Penning ionization
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- Conversion of CH$_4$ and CO$_2$ by electron collisions;
- 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 \textit{Syngas} production.