Plasma-catalytic reforming of biogas into renewable and clean hydrogen (ECR Flexible Funding)

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Biogas: A promising renewable energy source

United Kingdom is currently the second largest biogas producer in Europe.

Primary production of biogas in the European Union in 2012 and 2013 (in ktoe); Green figures show total biogas production in ktoe.

Sources: EurObserv’ER 2014
Biogas: A promising renewable energy source

- Biogas mainly consists of methane (50–75%) and carbon dioxide (25–50%), and can be produced from the anaerobic digestion of biomass, landfill, and wastewater treatment.

- Biogas can be used for the generation of electricity and heating but suffers from high emissions and a low heating value due to its high CO₂ content.

- CH₄-rich biogas obtained by removing CO₂ can be used as a substitute for natural gas in a wide range of applications. However, separating CO₂ is an energy intensive and costly process.

- Catalytic reforming of biogas without prior CO₂ separation (also called dry reforming of methane) could effectively and sustainably produce syngas (CO and H₂).

\[ \text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2 \]

High temperature, high energy cost

Carbon deposition, catalyst deactivation

Thermal catalytic process
Non-thermal plasmas

- low temperature (as low as room temperature)
- generation of highly energetic electrons (1-10 eV)/chemically reactive species (free radicals O, OH, excited atoms, molecules and ions)
- fast instant reactions/fast start-shut down – distributed system
- size: microsystem – large scale; compact and mobile system
- flexibility to combine with other technologies, e.g. plasma/UV, plasma/catalysis, plasma/adsorption, plasma/biochemical

Plasma-catalysis (advantages)

- synergistic effect (interactions between plasma and catalysts)
- reduced metal particle size and enhanced metal dispersion
- improved selectivity, yield and energy efficiency
- minimise the formation of unwanted by-products

Coaxial DBD
Packed Bed DBD
Gliding Arc (GA)
Rotating GA
Plasma-catalytic reforming of biogas

DBD Reactor
- Gas gap: 2.5 mm
- Discharge length: 10 cm

Power supply
- Frequency: 10 kHz
- Voltage: 7 kV

Working gas
- Flow rate: 25-150 ml/min
- \( \text{CO}_2/\text{CH}_4 \) (1/1)

Dielectric barrier discharge (DBD) plasma reactor
Effect of Ni-Co bimetallic catalysts

- **Catalyst**
  0.5 g 10 wt.%Ni-\(x\) wt.% Co/γ-Al₂O₃ (\(x = 1, 3, 5, 7.5, 10\) ) : 10NixCo

- In-situ reduced in 20%H₂/Ar plasma before reaction
- No extra heating

- Flow rate: 50 ml/min, CO₂/CH₄ molar ratio: 1:1;
- -1 stands for the plasma reaction without a catalyst.
Thermodynamic equilibrium conversion rates of \( \text{CH}_4 \) and \( \text{CO}_2 \) as a function of temperature with \( \text{CH}_4/\text{CO}_2 \) molar ratio of 1 at 1atm (without plasma)

At 150 °C, very low conversions of reactants

Synergistic effect of plasma-catalysis
**Catalyst characterisation**  
**CO$_2$-TPD (left) and BET (right)**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ (m$^2$g$^{-1}$)</th>
<th>Pore volume (cm$^3$g$^{-1}$)</th>
<th>Pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10Ni</td>
<td>268.0</td>
<td>0.393</td>
<td>3.798</td>
</tr>
<tr>
<td>10Ni1Co</td>
<td>256.0</td>
<td>0.394</td>
<td>3.809</td>
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<tr>
<td>10Ni3Co</td>
<td>250.4</td>
<td>0.375</td>
<td>3.821</td>
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<tr>
<td>10Ni5Co</td>
<td>246.5</td>
<td>0.349</td>
<td>3.834</td>
</tr>
<tr>
<td>10Ni7.5Co</td>
<td>228.7</td>
<td>0.330</td>
<td>3.841</td>
</tr>
<tr>
<td>10Ni10Co</td>
<td>221.3</td>
<td>0.312</td>
<td>3.846</td>
</tr>
</tbody>
</table>

- CO$_2$-TPD results indicate that the **basicity** of the catalysts increases with Co loading (enhances CO$_2$ adsorption and O production);
- The increase of Co content decreased the specific surface area and the pore volume of the catalysts;
- The superior performance of the catalyst with 5 wt.% Co results from the combined effect (**trade off**) between basicity and specific surface area.
Effect of promoted Ni catalysts

- **Catalyst**
  0.4 g 10 wt.%Ni/γ-Al₂O₃
  10 wt.%Ni - 2 wt.% X/γ-Al₂O₃ (X = K, Mg and Ce)
  10 wt.%Ni - y wt.% K/γ-Al₂O₃ (y = 4, 6 and 8)

Effect of different promoters (K, Mg and Ce)

Effect of different K loadings
Process optimisation using ANN

The optimal structure of the ANN model

Comparison of the predicted and experimental values in the optimised ANN model.
Effect of discharge power
Kinetic modelling of plasma reforming of biogas

We have developed a 0-dimension time-resolved model for plasma reforming of biogas in a DBD plasma reactor under ambient temperature and atmospheric pressure.

<table>
<thead>
<tr>
<th>Ground-state Neutrals &amp; Radicals (72)</th>
<th>CH₄ CH₃ CH₂ CH C C₂H₆ C₂H₅ C₂H₄ C₂H₃ C₂H₂ C₂H C₂ C₃H₈ C₃H₇ C₃H₆ C₃H₅ C₃H₄ C₃H₂ C₄H₂ CO₂ CO H₂ H O₂ O H₂O HO₂ OH H₂O₂ CH₂O CH₃CHO CH₂CHO CH₂CO C₂HO CH₃OH CH₃CO CH₂OH CH₃O HCO CH₃O₂ CH₃COOO C₂H₅O₂ CH₃COOOH CH₃COOH C₂H₅OH CH₃CHOH CH₃COCH₃ C₄H₁₀ HCOOH COOH CH₃COCH₂ CH₃COO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excited Neutrals &amp; Radicals (73)</td>
<td>CH₄(v) CO₂(v₁,8) CO₂(e₁,2) C(1D) C(1S) CO(v₁,10) CO(e₁,5) H₂(j₀,2) H₂(j₁,3) H₂(v₁,3) H₂(e₁,2) H₂(Σ) H₂(Π) O₂(v₁,4) H₂(r₁,2) O(1D) O(1S) H₂O(v₁,3) C₂H₂(v₂,5,3) C₂H₂(e₁,2) C₂H₄(v₁,2) C₂H₄(e₁,2) C₂H₆(v₁₃,2₄) C₃H₆(v) C₃H₆(v₁,2) C₃H₆(e)</td>
</tr>
<tr>
<td>Charged Species (29)</td>
<td>CH₄⁺ CH₃⁺ CH₂⁺ CH⁺ C⁺ C₂⁺ C₂H₆⁺ C₂H₅⁺ C₂H₄⁺ C₂H₃⁺ C₂H₂⁺ C₂H⁺ C₃H₈⁺ C₃H₇⁻ C₃H₆⁺ C₃H₅⁻ O₂⁺ O₂⁻ O⁺ O⁻ H₂⁺ H⁺ H⁻ H₂O⁺ CO₂⁺ CO⁺ OH⁻</td>
</tr>
</tbody>
</table>

297 electron-impact reactions; 300 neutral-neutral reactions; 67 ion-neutral/radical/ion reactions
Dominant gas phase reaction pathways
Rotating gliding arc reforming of CO$_2$ rich biogas
Effect of gas flow rate

(a) Conversion rates for CH$_4$ and CO$_2$:
- CH$_4$: 52.6%
- CO$_2$: 39.2%

(b) Selectivity for different products:
- H$_2$: 33.4%
- CO: 56.8%

(c) Yield and H$_2$/CO ratio:
- Yield decreases with increasing flow rate.
- H$_2$/CO ratio remains relatively constant.
### Energy Efficiency

<table>
<thead>
<tr>
<th>No</th>
<th>Type</th>
<th>Plasma reactor</th>
<th>SED (kJ/l)</th>
<th>Total feed flow rate (ml/min)</th>
<th>CO₂/CH₄ molar ratio</th>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>EC₇₂ (MJ/mol)</th>
<th>FPE (%)</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>CH₄</td>
<td>CO₂</td>
<td>Total</td>
<td>H₂</td>
<td>CO</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>1</td>
<td>DC pulse</td>
<td>46.4</td>
<td>45</td>
<td>1:1</td>
<td>-</td>
<td>52.7</td>
<td>42.7</td>
<td>47.7</td>
<td>75.0</td>
<td>70.8</td>
<td>2.6</td>
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<tr>
<td>2</td>
<td>DBD</td>
<td>50</td>
<td>600</td>
<td>1:1</td>
<td>Zeolite NaY</td>
<td>34.7</td>
<td>15.2</td>
<td>25.0</td>
<td>23.2</td>
<td>45.0</td>
<td>13.9</td>
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<td>3</td>
<td>DBD</td>
<td>150</td>
<td>200</td>
<td>1:3</td>
<td>Zeolite A</td>
<td>54.8</td>
<td>25.3</td>
<td>47.4</td>
<td>48.1</td>
<td>26.8</td>
<td>8.5</td>
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<tr>
<td>4</td>
<td>DBD</td>
<td>60</td>
<td>50</td>
<td>1:1</td>
<td>10 wt.% Ni/γ-Al₂O₃</td>
<td>56.4</td>
<td>30.2</td>
<td>43.3</td>
<td>31.0</td>
<td>52.4</td>
<td>7.7</td>
</tr>
<tr>
<td>5</td>
<td>DBD</td>
<td>28</td>
<td>3</td>
<td>1:2</td>
<td>20 wt.% Ni/γ-Al₂O₃</td>
<td>35.9</td>
<td>20.0</td>
<td>30.6</td>
<td>57.1</td>
<td>37.0</td>
<td>2.3</td>
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<td>6</td>
<td>DBD</td>
<td>120</td>
<td>30</td>
<td>1:1</td>
<td>12 wt.% Ni-12 wt.% Cu/γ-Al₂O₃</td>
<td>69.8</td>
<td>75.3</td>
<td>72.6</td>
<td>56.6</td>
<td>76.0</td>
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<td>7</td>
<td>DBD</td>
<td>225</td>
<td>40</td>
<td>1:1</td>
<td>LaNiO₃@SiO₂</td>
<td>88.3</td>
<td>77.8</td>
<td>83.0</td>
<td>83.7</td>
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<td>8</td>
<td>DBD</td>
<td>66.7</td>
<td>22.5</td>
<td>2:3</td>
<td>Perovskite LaNiO₃</td>
<td>54.5</td>
<td>73.0</td>
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<td>9</td>
<td>Corona</td>
<td>18</td>
<td>60</td>
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<td>Ni/Al₂O₃</td>
<td>43.8</td>
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<tr>
<td>10</td>
<td>GA</td>
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<td>7:3</td>
<td>-</td>
<td>19.3</td>
<td>11.5</td>
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<td>25.8</td>
<td>63.0</td>
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<tr>
<td>11</td>
<td>DBD</td>
<td>36</td>
<td>50</td>
<td>1:1</td>
<td>10 wt.% Ni-5 wt.% Co/γ-Al₂O₃</td>
<td>30.0</td>
<td>21.0</td>
<td>25.5</td>
<td>40.2</td>
<td>54.4</td>
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</tr>
<tr>
<td>12</td>
<td>Rotating GA</td>
<td>4.4</td>
<td>6000</td>
<td>7:3</td>
<td>-</td>
<td>52.6</td>
<td>39.2</td>
<td>43.2</td>
<td>33.4</td>
<td>56.8</td>
<td>0.9</td>
</tr>
</tbody>
</table>

**EC₇₂**: Energy cost for H₂ production

\[
EC_{H_2} (MJ mol^{-1}) = \frac{\text{Discharge power (kW)}}{1000 \times \text{H₂ produced (mol s⁻¹)}}
\]

**FPE**: Fuel production efficiency

\[
FPE(\%) = \frac{\sum \text{fuel produced (mol s⁻¹)} \times \text{LHV (kJ mol⁻¹)}}{\text{CH₄ converted (mol s⁻¹)} \times \text{LHV of CH₄ (kJ mol⁻¹)} + \text{Discharge power (kW)}} \times 100
\]
Acknowledgement
THANK YOU