Anodic vs cathodic potentiostatic control of a tubular pilot scale MEC for biogas upgrading

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Anaerobic digestion and biogas

BIOGAS

- CH$_4$: 50 - 75%
- CO$_2$: 25 - 45%
- H$_2$: 1 - 10%
- N$_2$: 0.5 - 3%

DIGESTATE

- NH$_4^+$: 1 - 4 g/L
- COD: 4 – 10 g/L
- sCOD: 1 – 2 g/L

COGENERATION
Heat & Power
(40% electricity)

UPGRADING
BIOMETHANE
(CH$_4$ >95%)
- Physical Adsorption
- Chemical Adsorption
- Membrane technologies
  (among which bioelectrochemical systems)

Wastewater treatment

Fertilizer
CO₂ rich gaseous streams (waste gases):
- Urea production (100% CO₂)
- Fermentation waste gas (100% CO₂)
- Cement (20% CO₂)
- Anaerobic digestion (25-45% CO₂)

Bioelectrochemical Methanation

Energetic overproduction from renewable resources

Distribution network (Domestic use; transports)

CH₄

Storage

A Microbial electrolysis cell (MEC) is a particular application of bioelectrochemical systems (BES) in which an electric potential is applied.

Using a MEC is possible to couple the CO₂ reduction to CH₄ with the oxidation of waste COD.

A MEC could be used for upgrading Biogas into Biomethane while the digestate could be used as COD source furnishing electrons to the reaction.
The bioelectromethanogenesis

- Direct Extracellular Electron Transfer (EET)
- Hydrogen mediated mechanism

**Bioelectromethanogenesis**

\[ \text{CATHODE} \]

\[ e^- \rightarrow \text{Reduced Compound} \rightarrow \text{CO}_2 \rightarrow e^- \]

\[ \text{CO}_2 \rightarrow \text{CH}_4 \text{COOH} \rightarrow \text{CO}_2 \]

**Hydrogenotrophic methanogenesis**

\[ \text{CATHODE} \]

\[ 8e^- + 8H^+ \rightarrow 4H_2 \]

\[ \text{CO}_2 \rightarrow \text{CH}_4 + 2H_2O \]

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CO₂ removal mechanisms inside a biocathode

- The progress of the reactions generates alkalinity inside the cathodic chamber favoring the CO₂ sorption

\[ \text{CO}_2 + 8e^- + 8H^+ \rightarrow \text{CH}_4 + 2H_2O \]
CO$_2$ removal through alkalinity production

CO$_2$ + 8H$^+$ + 8e$^-$ $\rightarrow$ CH$_4$ + H$_2$O

For every mole of produced CH$_4$, 8 moles of monovalent ions have to be transported through the ion exchange membrane in order to maintain the electroneutrality; for every species transported different from the hydroxyl, an equivalent of alkalinity is generated inside the cathodic chamber.

If 8 moles of HCO$_3^-$ are transported for the electroneutrality maintenance.

For every produced mole of CH$_4$, a maximum of 9 moles of CO$_2$ is removed.
Integration of a MEC with a two-stage anaerobic digestor

- One (or more) tubular MEC placed after a two-stage anaerobic digestor
- First scale up of this type of MEC
Experimental apparatus: Tubular microbial electrolysis cell

- 1.5 m high
- 12 L total volume
- Granular graphite
  **Anode**
  Inoculum activated sludge
  Volume: 3.14 L
  Fed with mix VFA (Acetate, propionate e butyrate)

  **AEM membrane**

  **Cathode**
  Inoculum anaerobic digestate
  Volume: 8.83 L
  Fed with gaseous mix (30% v/v CO₂)

**Polarization through three-electrode configuration**
- Control of the anodic potential + 0.2 V vs SHE
  Changing the OLR 2.55; 3.82; 5.11 gCOD/Ld
- Control of the cathodic potential -1.3; - 1.8; - 2.3 V vs SHE
  With an OLR of 2.55 gCOD/Ld
The electric current increased with the increase of the OLR. The increase of the produced electric current was not as high as the increase of the OLR. For this reason, the CE is lower for higher OLR.

- The reason of the little increase is a kinetic limitation of the biofilm to convert COD into electric current.
CO₂ production and CH₄ production

- The CO₂ abatement did not change significantly.
- The AEM membrane permits the migration of the anion bicarbonate.
- The CH₄ production did raise with the enhancement of the electric current but not as much as expected. For this reason, the CCE is significantly lower for the last period.

<table>
<thead>
<tr>
<th>OLR</th>
<th>2.55 gCOD/Ld</th>
<th>3.82 gCOD/Ld</th>
<th>5.1 gCOD/Ld</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔCO₂ (mmol/d)</td>
<td>243 ± 15</td>
<td>224 ± 11</td>
<td>270 ± 33</td>
</tr>
<tr>
<td>CH₄ production rate (mmol/d)</td>
<td>26 ± 4</td>
<td>27 ± 5</td>
<td>31 ± 4</td>
</tr>
<tr>
<td>CCE %</td>
<td>41 ± 1</td>
<td>59 ± 1</td>
<td>25 ± 1</td>
</tr>
</tbody>
</table>

- The CO₂ abatement did not change significantly.
- The AEM membrane permits the migration of the anion bicarbonate.

- The CH₄ production did raise with the enhancement of the electric current but not as much as expected. For this reason, the CCE is significantly lower for the last period.
The electric current increases with the decrease of the cathodic potential. The increase did not enhance the performance. 

<table>
<thead>
<tr>
<th>$E_{\text{cat}}$ vs. SHE</th>
<th>-1.3 V</th>
<th>-1.8 V</th>
<th>-2.3 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average electric current (mA)</td>
<td>91 ± 5</td>
<td>148 ± 5</td>
<td>277 ± 8</td>
</tr>
<tr>
<td>ΔCO$_2$ (mmol/d)</td>
<td>276 ± 16</td>
<td>215 ± 13</td>
<td>199 ± 12</td>
</tr>
<tr>
<td>CH$_4$ production rate (mmol/d)</td>
<td>12 ± 1</td>
<td>32 ± 2</td>
<td>15 ± 1</td>
</tr>
</tbody>
</table>

$E_{\text{an}} = +1.46 \pm 0.05$ V vs. SHE

Increase of the anodic potential to sustain the cathodic reaction:

$\downarrow$

water oxidation
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Potentiostatic control

<table>
<thead>
<tr>
<th>Stream</th>
<th>kWh/kgCOD</th>
<th>kWh/Nm³CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.55 gCOD/L d</td>
<td>10.7</td>
<td>2.4</td>
</tr>
<tr>
<td>3.82 gCOD/L d</td>
<td>5.6</td>
<td>3.3</td>
</tr>
<tr>
<td>5.11 gCOD/L d</td>
<td>14.1</td>
<td>7.7</td>
</tr>
<tr>
<td>-1.3 V vs. SHE</td>
<td>1.2</td>
<td>0.6</td>
</tr>
<tr>
<td>-1.8 V vs. SHE</td>
<td>1.4</td>
<td>1.7</td>
</tr>
<tr>
<td>-2.3 V vs. SHE</td>
<td>10.9</td>
<td>6.2</td>
</tr>
</tbody>
</table>
Take home message

• The micro pilot scale reactors are a promising first step towards an eco-friendlier biogas upgrading.

• A higher OLR is not the better solution to enhance the current density.

• From a higher electric current production derives a higher CH$_4$ production rate.

• Controlling the cathodic potential minimizes the overpotential even in a micro pilot reactor.

• Further studies will be conduct using a CEM membrane.
Thank you for the attention!

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