SULFIDE EFFECT ON BIOGAS UPGRADING WITH A BIOELECTROCHEMICAL SYSTEM

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**INTRODUCTION & BACKGROUND**

Anaerobic Digestion

Methane $\text{CH}_4$

Carbon Dioxide $\text{CO}_2$

Trace Gases (e.g., $\text{H}_2\text{S}$, $\text{H}_2$, $\text{N}_2$)

**Biogas Yield** (L/kg volatile solids)$^a$

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Biogas Yield (L/kg volatile solids)$^a$</th>
<th>Methane Content (%$\text{, v/v}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fat</td>
<td>1,000 – 1,250</td>
<td>70 – 75</td>
</tr>
<tr>
<td>Protein</td>
<td>600 – 700</td>
<td>68 – 73</td>
</tr>
<tr>
<td>Carbohydrate</td>
<td>700 – 800</td>
<td>50 – 55</td>
</tr>
</tbody>
</table>

$^a$At 25°C, 1 atm; Petersson and Wellinger, 2009. IEA Bioenergy.
Biogas Upgrading

- Absorption
  - Physical
  - Chemical
- Adsorption
  - Activated Carbon
  - Alumina
  - Zeolite
- Membranes
  - Gas separation
  - Gas adsorption
- Cryogenics
- Biological
  - Biomass Production (e.g., algae)
  - Bioelectrochemical Systems

- Energy intensive
- Carbon waste product
- Expensive consumables

Direct conversion of CO₂ to CH₄
BIOELECTROCHEMICAL SYSTEMS

**Oxidation**

Organics $\rightarrow$ CO$_2$/oxidized organics, H$^+$, e$^-$

**Reduction**

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

- Microbes are an inexpensive, self-renewing catalyst
- The potential applied at A (< 1 V) can be supplied by photovoltaics/renewables
- Optional proton exchange membrane, B
**HYDROGEN SULFIDE**

- Corrosive, toxic (NIOSH, IDLH = 100 ppm)
- Produced by sulfate-reducing bacteria during anaerobic digestion
- Inhibitory to methanogenesis during anaerobic digestion [1]
- Feedstock C:S ratio predicts biogas $H_2S$ [2]

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>C/S (g/g)</th>
<th>Theoretical Biogas $H_2S$ (%)</th>
<th>range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grease trap waste</td>
<td>798</td>
<td>0.0 – 0.1</td>
<td></td>
</tr>
<tr>
<td>Biological sludge</td>
<td>59</td>
<td>0.6 – 1.9</td>
<td></td>
</tr>
<tr>
<td>Industrial WW biological sludge</td>
<td>46</td>
<td>0.8 – 2.0</td>
<td></td>
</tr>
<tr>
<td>Pig bristles</td>
<td>19</td>
<td>2.0 – 4.9</td>
<td></td>
</tr>
<tr>
<td>Harvested green seaweed</td>
<td>7</td>
<td>5.5 – 17.7</td>
<td></td>
</tr>
</tbody>
</table>


RESEARCH OBJECTIVE
Determine how the presence of hydrogen sulfide (H\textsubscript{2}S), a common contaminant in anaerobic digester biogas, affects the conversion of carbon dioxide (CO\textsubscript{2}) to methane (CH\textsubscript{4}) in the cathode of a bioelectrochemical system (BES).

RESEARCH APPROACH
- Compare the mean initial 3-day CH\textsubscript{4} production rate following feeding
- Assess the effect of H\textsubscript{2}S on the full BES performance

Figure 1. Linear biocathode CH\textsubscript{4} production during the first 3 days of a feeding cycle
METHODS: BIOELECTROCHEMICAL SYSTEM

Anode
- 300 mL total, 250 mL liquid volume
- Carbon felt electrode with exoelectrogens
- Batch-fed acetate (4 g COD/L) weekly

Cathode
- 300 mL total, 250 mL liquid volume
- Carbon felt electrode with methanogens and SS collector
- Batch-fed CO$_2$ (g) (92 mL at 22°C, 1 atm) weekly
- Applied potential -0.8 V vs. SHE with Gamry Interface 1000 potentiostat
  - Continuously mixed with magnetic bars and stir plates at 22°C
  - Nafion 117 proton exchange membrane (PEM)
RESULTS: BIOCATHODE CH₄ PRODUCTION

- H₂S improves biocathode CH₄ production rate up to 2-3% initial H₂S
- Initial H₂S concentrations of 4-6% result in a decreased biocathode CH₄ production rate

- **Two competing effects:**
  - **Depress CH₄ production (≥4% H₂S):** Inhibition of methanogens?
  - **Improve CH₄ production (≤3% H₂S):** What is/are the process(es) involved?

**Figure 2.** Mean initial 3-day biocathode CH₄ production rates following feeding with an initial headspace concentration of 0-6% H₂S (n, number of feeding cycles).
**CE, Coulombic Efficiency:** The ratio of total Coulombs actually transferred to the anode from the substrate, to maximum possible Coulombs if all substrate removal produced current. \(^1\)

**CCE, Cathode Capture Efficiency:** The ratio of total Coulombs actually transferred to the \(\text{CH}_4\) from the cathode, to maximum possible Coulombs if all current produced \(\text{CH}_4\). \(^2\)

\(^1\) Logan et al., 2006. ES&T
\(^2\) Villano et al., 2013. Bioresource Technol.
**H₂S WITHIN A METHANOGENIC BES**

Henry’s Law constant in catholyte medium
- CO₂: 32.7 mM/atm
- H₂S: 82.0 mM/atm
H₂S is the most toxic of the sulfide species.

H₂S IN THE CATHODE – INHIBITORY EFFECT

H₂S, CH₄, and CO₂ react to form HS⁻ and S²⁻.
H₂S IN THE CATHODE – INHIBITORY EFFECT

The methanogenic biocathode is semi-protected from sulfide inhibition by biofilm formation and a local high pH at the cathode surface.
H₂S IN THE ANODE – ENHANCEMENT EFFECT

- Low H₂S → more electrons donated to the anode → more biocathode CH₄ production
- High H₂S → stimulate SRB cycle → divert acetate eeq from the anode → less biocathode CH₄ production
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<table>
<thead>
<tr>
<th>Initial Cathode H₂S (%)</th>
<th>Acetate Removal (%)</th>
<th>Final Anode H₂S (%)</th>
<th>H₂S Recovery as Anode SO₄²⁻ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>91.4</td>
<td>0.00</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>99.6</td>
<td>0.18</td>
<td>24</td>
</tr>
<tr>
<td>5</td>
<td>91.7</td>
<td>0.17</td>
<td>18</td>
</tr>
<tr>
<td>6</td>
<td>91.0</td>
<td>0.20</td>
<td>18</td>
</tr>
</tbody>
</table>

Potential anode H₂S oxidation products:
- S⁰, Sₓ²⁻, S₄O₆²⁻, S₂O₃²⁻, SO₄²⁻

Sun et al., 2009. ES&T
## Biocathode H₂S Removal

<table>
<thead>
<tr>
<th>Initial Cathode H₂S (‰)</th>
<th>Acetate Removal (‰)</th>
<th>Final Anode SO₄²⁻ (mM)</th>
<th>H₂S Recovery as Anode SO₄²⁻ (‰)</th>
<th>Final H₂S in Catholyte (mM)</th>
<th>Final H₂S in Cathode Gas (‰)</th>
<th>H₂S Removal Efficiency (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>91.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>99.6</td>
<td>0.18</td>
<td>24</td>
<td>0.47</td>
<td>0.5</td>
<td>84.6</td>
</tr>
<tr>
<td>5</td>
<td>91.7</td>
<td>0.17</td>
<td>18</td>
<td>0.63</td>
<td>0.7</td>
<td>83.4</td>
</tr>
<tr>
<td>6</td>
<td>91.0</td>
<td>0.20</td>
<td>18</td>
<td>0.81</td>
<td>1.0</td>
<td>83.2</td>
</tr>
</tbody>
</table>
CONCLUSIONS

• Up to 3-4% H₂S in biogas can enhance biocathode CH₄ production by contributing electrons to the anode

• Above 4% H₂S, biocathode CH₄ production decreases due to: i) inhibition of methanogens at the cathode; ii) sulfide oxidation cycling in the anode, which diverts electron equivalents away from CH₄ production
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METHODS: ANALYTICAL

- Gas pressure → Pressure transducer
- Gas composition → Gas chromatography (GC) with Thermal Conductivity Detector (TCD)
- Acetate → GC with Flame Ionization Detector (FID)
- Dissolved CO₂, H₂S → Sample acidification (6 N H₂SO₄) followed by composition analysis of evolved gas (conditional calibration)
- Voltage
- Current
- Cyclic Voltammetry → Handheld multimeter and Gamry Interface 1000 potentiostat
RESULTS: SERUM BOTTLE TESTS

• Cathode inoculum: hydrogenotrophic, methanogenic, suspended growth culture fed with H₂/CO₂ (80:20) and catholyte medium with vitamins and trace metals

• Similar methane production at all initial gaseous H₂S concentrations up to 3% H₂S