Integrated Biological Hydrogen Production

Alan Guwy

University of South Wales
Sustainable Environment Research Centre

H2FC SUPERGEN Conference

All-Energy AECC Aberdeen 21st May 2013
Hydrogen Energy Systems

Bioenergy Systems

Advanced Nanomaterials

Waste Water Treatment

Microbial Fuel Cells

Biohydrogen

Environmental Analysis

Anaerobic Digestion
Dark-Biohydrogen Fermentation

- Applicable for co-product/waste streams food industry and to energy crops
- Bacteria involved, particularly clostridia use the enzyme hydrogenase
- Use carbohydrates: glucose, sucrose, starch, cellulose, hemi-celluloses
- $H_2$ yield depends on fermentation products and amount of readily biodegradable carbohydrate
Dark fermentation - H₂ yield

Theoretical:

Hexose $\rightarrow$ CH₃COOH (acetic acid) + 4 H₂

*that is 4 mol H₂/mol hexose or 0.5 m³ H₂ / kg carbohydrate*

Hexose $\rightarrow$ CH₃CH₂CH₂COOH (butyric acid) + 2 H₂

*that is 2 mol H₂/mol hexose or 0.25 m³ H₂ / kg carbohydrate*

- A mix of acetate and butyrate is usual with H₂ yields approx. 1 to 2 mol H₂/mol hexose utilised

Significant energy remains in acetate and butyrate
**Integrated Biological Hydrogen Production Options**

- Biomass → Hydrogen fermentation → H₂ + CO₂
  - Methane fermentation → CH₄ + CO₂
  - Photo fermentation → H₂ + CO₂
  - MFC → e⁻ + H⁺ + CO₂
  - MEC → H₂ + CO₂
  - BES → Reduced Products (NaOH, Clean H₂O, HOCl, H₂O₂ etc.)


Biohydrogen Production in an Integrated Anaerobic system-(dark fermentation)

**Fermentation End Products**

- **Optimised Methanogenic Stage**
- Methane Reactor
  - $\text{CH}_4 + \text{H}_2$
  - $\text{pH}=5.2$
  - 33% conversion

- **Advanced water recycling**

**Soil Conditioner**

1. **Biomass feedstock**
2. $\text{H}_2 + \text{CO}_2$
3. Hydrogen Reactor
   - $\text{pH}=5.2$
   - 33% conversion
4. Fermentation End Products
5. Methane Reactor
   - $\text{pH}=7.0$
   - 90% energy conversion (substrate)
6. $\text{CH}_4 + \text{CO}_2$
7. Soil Conditioner
## SERC: Bio-H$_2$/Bio-CH$_4$

<table>
<thead>
<tr>
<th>Year</th>
<th>Authors</th>
<th>Research</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000</td>
<td>Mizuno et al</td>
<td>Glucose</td>
<td>Continuous H$_2$</td>
</tr>
<tr>
<td>2005</td>
<td>Hussy et al</td>
<td>Sucrose and sugar beet</td>
<td>Continuous H$_2$</td>
</tr>
<tr>
<td>2007</td>
<td>Hawkes et al</td>
<td>Flour milling co-product (Batch)</td>
<td>Batch H$_2$</td>
</tr>
<tr>
<td></td>
<td>Kyazze et al</td>
<td>Fodder maize</td>
<td>Continuous H$_2$</td>
</tr>
<tr>
<td>2010</td>
<td>Massanet-Nicolau et al</td>
<td>Sewage Biosolids</td>
<td>Continuous 2 stage H$_2$ + CH$_4$</td>
</tr>
<tr>
<td>2012</td>
<td>Massanet-Nicolau et al</td>
<td>Wheat feed pellets</td>
<td>Continuous 2 stage H$_2$ + CH$_4$</td>
</tr>
</tbody>
</table>
Direct fermentation of complex substrates to $H_2$

- Perennial rye grass ($21.8 \pm 8 \, cm^3 \, H_2/g \, dry \, matter$)
- Fructo-oligosaccharides ($218 \pm 28 \, cm^3 \, H_2/g \, chicory$)
- Fodder maize ($62.4 \pm 6.1 \, cm^3 \, H_2/g \, dry \, matter$)
- However, most of the insoluble polymeric components remains unutilised
  - pre-treatment could improve further the energy recovered
Hydrogen Production from Wheat Feed

- Manually fed continuous operation
- 15 hour HRT
- 10 litre bioreactor inoculate with anaerobes in sewage sludge
- pH 5.5 and 35°C
- Lab trials showed that $64\text{m}^3\ H_2 +$ potentially $244\text{m}^3\ CH_4$ could be produced from 1 tonne wheatfeed (20% v/v H$_2$ and 80% CH$_4$)

Biohydrogen Pilot Scale

R&D scaling up to pilot scale
• Industrial systems
• Energy balance
• System control & optimistion

Pilot scale biohydrogen and biomethane plant using rotated crops

Pilot scale biohydrogen and biogas plant using wheatfeed
GHG Saving

Scenario 3: 2 stage AD with gas upgrading to hythane

- 98% H₂ 20.1 m³
- 98% CH₄ 247 m³
- CO₂ 180 m³
- 40% H₂ 51 m³
- 60% CH₄ 583 m³

Gas upgrading – Gas upgrading

400 m²

CHP

183 m³

CO₂ 183 m³

Hythane 101 m³

BioCNG 167 m³

1.4 t CO₂ eq t⁻¹ carbon saving

Wheatfeed 1 tonne
Water 24 m³

Hydrogen reactor

Methanogenic AD

Digestate 25 m³

Heat 530 kWh
Electricity 447 kWh
Parasitic load 6 kWh
Electricity exported 441 kWh
Bio-H₂/Bio-CH₄
Comparison of single BioCH$_4$ with Two stage BioH$_2$/BioCH$_4$

**Substrate:** Wheat feed  
**Pretreatment:** 24 h @ pH 11  
**Hydrogen reactor pH:** 5.5  
**Methane reactor pH:** 7.0  
**Temperature:** 35°C

---

Hydrogen Production

Increased methane production when coupled with biohydrogen reactor

**Figure:**

- **Production Rate**
- **Yield**

**Table:**

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Effluent (Reduction percentages are in parentheses)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Single-stage 20 day HRT</td>
</tr>
<tr>
<td><strong>CH₄ Yield</strong></td>
<td>261.14</td>
</tr>
<tr>
<td><strong>Volatile Solids (g L⁻¹)</strong></td>
<td>48.02</td>
</tr>
<tr>
<td><strong>COD (g L⁻¹)</strong></td>
<td>58.61</td>
</tr>
<tr>
<td><strong>Carbohydrate (g L⁻¹)</strong></td>
<td>26.24</td>
</tr>
<tr>
<td><strong>VFA (mg L⁻¹)</strong></td>
<td>572</td>
</tr>
</tbody>
</table>

### Energy Yields

<table>
<thead>
<tr>
<th>Process</th>
<th>Energy Yield (MJ kg(^{-1}) VS)</th>
<th>Increase (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single stage 20 day</td>
<td>8.73 (+17.9%)</td>
<td></td>
</tr>
<tr>
<td>Two Stage 12 day</td>
<td>10.30 (+38.5%)</td>
<td></td>
</tr>
<tr>
<td>Two Stage 20 day</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- 38% increase in energy yields
- 18% increase in energy yields even when reducing residence time
- Relatively small difference in VS reduction between single and two stage digestion

Further Work - Molecular

The next phase of research:

• Identifying the microbial differences between single stage CH$_4$ and two stage H$_2$/CH$_4$ fermenters using a variety of substrates

• Quantifying these differences using molecular tools such as pyrosequencing
Biogas Utilisation Options

**Biogas**

- **Gas Clean-up / Desulfurisation**
  - **CO₂ Removal: biomethane**
  - **Steam Reforming: Syngas**
    - **Fischer-Tropsch Synthesis and Separation**
    - **MeOH / DME synthesis**
      - **MeOH**
  - **Water Gas Shift and CO₂ Removal: H₂**
    - **SOFC 500-1000 C**
      - **Gas Engine**
    - **Gas Clean-up / Desulfurisation**
      - **DC and Heat**
        - **PEMFC < 10 ppm CO 70-90 C**
          - **DC**
Using Biogas from BioH$_2$/BioCH$_4$

Similar power output for hydrogen and simulated biogas

i-V Plot of SOFC operating at 850°C on
• H$_2$ (2 cm$^3$ min$^{-1}$)
• and simulated biogas (CH$_4$:CO$_2$ 1:0.5 cm$^3$ min$^{-1}$)

Laycock et al., Dalton Transactions, 2011 40 (20), pp. 5494-5504.
Hydrogen fermentation
-Microbial Electrolysis Cells (MEC)

Guwy et al. Bioresource Technology 2011

Reduced Products
NaOH, Clean H₂O₂, HOCl, H₂O₂ etc
Dark fermentation BioH$_2$/Microbial Electrolysis Cells (MEC)

Fermentation + microbial catalysed electrolysis

Using Acetate

\[ C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2 \]
\[ CH_3COOH + 2H_2O \rightarrow 2CO_2 + 4H_2 \]

Theoretically 12 mol H$_2$/mol
Microbial Electrolysis - Functionality

$V_{\text{applied}} \geq 118 \text{ mV (lower than water electrolysis = 1230 mV (pH7))}$

e$^{-}$

Acetate & Butyrate From dark fermentation

Anode

$2\text{HCO}_3^- \rightarrow \text{H}_2 + \text{H}_2 \text{O}$

Biofilm

Electrode

Microorganisms

Membrane

Cathode

H$_2$ H$_2$ H$_2$
Challenges for MECs

• Low CE (substrate to electrons)
  • Competing biological pathways-Methanogenesis
  • Maximise substrate availability to biofilm
  • Utilisation of both acetate and butyrate from dark biohydrogen fermentation stage
  • Substrate migration to cathode

• Poor cathodic H$_2$ efficiency (electrons to H$_2$)
  • H$_2$ diffusion to anode (worse at low current densities)
  • Efficient evolution of hydrogen from the cathode chamber
Monolithic carbon foam electrode
- Increasing flowrate
- Not much mixing
- Shear does exist

Carbon fiber veil and former
- Increasing flowrate
- Better mixing with velocity

Anode Systems for Tubular Microbial Fuel Cells (MFC)

3D arrow plots showing fluid particle velocities (with arrows showing velocity field direction and their tone indicates magnitude); zoomed in on helical flow path MMCC (a) – (c); and LVSF (a) – (c).
Inlet velocities and flow rates:
(a, d) $V_{in} = 1.67 \times 10^{-9}$ m$^3$s$^{-1}$ [0.1 mL min$^{-1}$],
(b, e) $3.33 \times 10^{-8}$ m$^3$s$^{-1}$ [2 mL min$^{-1}$],
(c, f) $1.25 \times 10^{-7}$ m$^3$s$^{-1}$ [7.5 mL min$^{-1}$].

(a) Tubular microbial electrolysis cell schematic, (b) drawing of cathode and anode chamber assembly and (c) anode chamber membrane and cathode sleeve assembly

Summary

• Fermentative hydrogen production can be integrated with biomethane systems to increase energy recovery.

• Acetate and butyrate co-products can be utilised in microbial electrolysis cells for increased hydrogen production.

• Further work is needed for BioH2/MEC systems to out compete BioH2/bioCH4 systems.
Acknowledgements

Alan Guwy
Sustainable Environment Research Centre
University of South Wales
alan.guwy@southwales.ac.uk