Hydrogen production from biomass by fermentation

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Renewable H₂ production routes (not considering nuclear or CO₂ sequestration)

- Electrolysis - electricity from wind, marine, hydro, solar pv
  \[ H_2 + O_2 \]

- Photolysis
  \[ H_2 + O_2 \]

- Pyrolysis/gasification - (woody biomass)
  \[ \text{syngas} - H_2 \]

- Biophotolysis by algae
  \[ H_2 + O_2 \]

- Photofermentation - (fermentable biomass)
  \[ H_2 + CO_2 \text{ (neutral)} \]

- Dark fermentation - (fermentable biomass)
  \[ H_2 + CO_2 \text{ (neutral)} \]
Hydrogen production from biomass by fermentation

**Photofermentation** -
Advantage: increased $H_2$ yield.
Disadvantage: photobioreactors in research stage

**Dark fermentation** - reactors similar to anaerobic digestion - process at research stage but reactors commercially available
Sustainable Environment Research Centre

Wastewater Treatment Research Unit

Specialising in:
• anaerobic digestion (30 year history)

Hydrogen Research Unit

Specialising in:
• fermentative H₂ production
• the transition to a H₂ economy
Sustainable Environment Research Centre

• Personnel ~25

• Wide range of inter-disciplinary skills

• Many collaborative projects with other institutions and industry

• Long experience of lab, pilot and full scale anaerobic digester plants operating on industrial, agricultural and domestic organic material
UK Sustainable Hydrogen Energy Consortium (SHEC)

Targeting research challenges in:

- sustainable hydrogen production
- hydrogen storage (5 university departments)
- social science and policy related to the hydrogen economy (2 universities)
Hydrogen production from crops by fermentation

Biomass → Optimised fermentative $H_2$ reactor → Acetic/butyric acids → Compression for transportation fuel $H_2 + CH_4$ → Transportation or reformer Fuel Cell $CH_4 + CO_2$ → Effluent for crop irrigation

Direct $H_2$ utilisation in Fuel Cells

$H_2 + CO_2$
SUPERGEN SHEC: Sustainable hydrogen production - hydrogen production from crops by fermentation

Experimental programme 2003-2008:
- Selection of most suitable crops
- Process optimisation at lab scale
- Pilot plant work on crops (sugar beet, maize, rye grass?)
- Process modelling, energy balance, LCA, EIA

 IGER, Aberystwyth
Hydrogen production from biomass by fermentation

- Applicable to crops and co-product/waste streams e.g. food industry, putrescible municipal solid waste, sewage sludge
- Property of various species of bacteria, particularly clostridia, involves the enzyme hydrogenase
- Uses carbohydrates: glucose, sucrose, starch, cellulose, hemi-celluloses - clostridia are versatile
- $\text{H}_2$ yield depends on fermentation products
Hydrogen production from biomass by fermentation

This approach uses:

- inoculum from natural sources
- non-sterile operation and mixed microflora
- batch start-up, then continuous operation
- temperature ~30°C, operational conditions selecting for H₂ production (especially retention time, pH)
- a second anaerobic digestion stage

Research on-going in UK, USA, Japan, Korea, Taiwan, PR China
Dark fermentation - limits on H$_2$ yield

Theoretical maximum:

**Hexose → CH$_3$COOH** (acetic acid) + **4 H$_2$**
(that is 4 mol H$_2$/mol hexose or 0.5 m$^3$ H$_2$ / kg carbohydrate)

**Hexose → CH$_3$CH$_2$CH$_2$COOH** (butyric acid) + **2 H$_2$**
(that is 2 mol H$_2$/mol hexose or 0.25 m$^3$ H$_2$ / kg carbohydrate)

A mix of acetate and butyrate is usual with H$_2$ yields approx. 1 to 2 mol H$_2$/mol hexose utilised

H$_2$ production is thermodynamically unfavourable as H$_2$ concentration rises - lower H$_2$ partial pressure can improve H$_2$ yield
Competing reactions

• Production of methane:
  \[ \text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \]
  avoid by pH around 5.2, retention time <24 hrs in CSTR

• Production of acetic acid from CO\(_2\) and H\(_2\):
  \[ 2 \text{CO}_2 + 4 \text{H}_2 \rightarrow \text{CH}_3\text{COOH} + 2\text{H}_2\text{O} \]
  avoid by lowering H\(_2\) partial pressure in continuous operation

• Production of reduced fermentation end products e.g. acetone, butanol, ethanol
  avoid by continuous operation
Hydrogen production from biomass by fermentation - examples:

**Wheat flour industry co-products:**
- Low grade flour, variable amounts, 0-1,000 tonnes/week in UK
- Wheatfeed (bran), UK production 1.2 million tonnes/year, worldwide 96 million tonnes/year

**Crops:**
- sugar beet
- fodder maize
- rye grass
H$_2$ production from wheat industry co-products

Low grade flour composition:
Starch 74%
Protein max. 5%
Water max. 10%

Wheatfeed composition:
Carbohydrates 78%
• Starch 24%
• Holocellulose 54%
  - Hemicellulose 44%
  - $\alpha$-cellulose 10%
Water 13% + protein (+ lignin?)
Continuous operation on 1% wheat starch, pH 5.2, 30°C, 18 h HRT

Days 7-9 1.3 mol H₂/mol hexose converted

![Graph showing gas production and hydrogen content over time]

- started feeding
- gas production
- hydrogen content [%]
Continuous operation on 1% wheat starch, pH 5.2, 30°C, 18 h HRT

![Graph showing acetate and n-butyrate production over time](image-url)
Continuous operation on 1% wheat starch, pH 5.2, 30°C, 15h HRT, N₂ sparging.
Days 6-20 H₂ yield 1.9 mol H₂/mol hexose converted.

![Graph showing gas production and hydrogen content over time.](image)
Continuous operation on 1% wheat starch, pH 5.2, 30°C, 15h HRT, N₂ sparging

hexose utilisation and end-products

started feeding

- acetate
- n-butyrate
- hexose
H₂ production from wheatfeed (bran)

Helen Forsey
unpublished results
Batch 10g/l wheatfeed, 35°C + nutrients: gas production, H₂ content
Estimate: 1 tonne wheatfeed gives $60 \text{m}^3 \text{ H}_2 \ 240 \text{m}^3 \text{ CH}_4$

- Sufficient $\text{H}_2$ to use as transport fuel in IC engines, replacing all diesel used in UK flour industry transport fleets.
- Sufficient $\text{CH}_4$ to run the process and compress $\text{H}_2$, could use excess with $\text{H}_2$ as transport fuel in IC engines (saving 1 million tonnes CO$_2$ pa).
Fermentative hydrogen production from energy crops: sugar beet

- Sugar beet (*Beta vulgaris*) harvested September-February in UK yields 54 tonnes (wet weight) hectare\(^{-1}\)
- Sucrose content 80% of dry weight
- >90% of sucrose is water extractable, 170g water-extractable sucrose/kg wet beet
- Batch experiments on pulped sugar beet, continuous experiments on sucrose and sugar beet extract (10gl\(^{-1}\) hexose) with manually-added extracted pulp
Continuous operation (15 hour HRT, pH 5.2, N₂ sparging) on sucrose and sugar beet extract
10g/l sucrose days 1-11 (A-B), 18-25 (C-B), sugar beet extract days 11-18 (B-C) and 25-32 (B-end)
Continuous operation (15 h HRT) on sucrose or pulped beet
10g/l sucrose day 0-33, 39-40 & pulped beet day 34-38 & 41-45
### H₂ yields from sugar beet

mol H₂ mol⁻¹ hexose consumed

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Sparging</th>
<th>H₂ Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sugar Beet (batch)</td>
<td>No</td>
<td>0.9</td>
</tr>
<tr>
<td>Sugar Beet (continuous)</td>
<td>No</td>
<td>0.9 ± 0.2</td>
</tr>
<tr>
<td>Sucrose (continuous)</td>
<td>No</td>
<td>1.0 ± 0.1</td>
</tr>
<tr>
<td>Sucrose (continuous)</td>
<td>Yes</td>
<td>1.9 ± 0.2</td>
</tr>
<tr>
<td>Beet extract (continuous)</td>
<td>Yes</td>
<td>1.7 ± 0.2</td>
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</tbody>
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Approx. 1900 m³ H₂ per hectare in UK

Estimated cost of H₂ = €7.2 - €9/GJ on basis of anaerobic digester technology

Ines Hussy
Conclusions

• H$_2$ can be produced continuously and stably using dark fermentation with mixed microflora in non-sterile conditions using easily available natural inocula
• H$_2$ production followed by anaerobic digestion uses available technology
• H$_2$ can be produced from low grade flour and wheatfeed (bran), sugar beet, grass, sewage sludge, bread, kitchen waste
• For wastes/co-products - economics promising
• For energy crops - techno-economic feasibility studies on-going
• For particulate feedstock, work is starting at pilot-scale