Electrochemical Systems for Enhanced Product Recovery from Anaerobic Fermentations

Integration of Chemical, Biochemical and Thermal Process to Maximise Biomass Resource Potential

Joint AD Network/SUPERGEN Bioenergy Event
6th February 2018

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Long Term Energy and Chemical Landscape

• The UK is committed to reducing its greenhouse gas emissions by at least 80% by 2050, relative to 1990 levels.
• About 10% of fossil hydrocarbons are converted to chemicals.
• Energy “trilemma” (reduced carbon emissions vs energy cost vs security of energy supply).
• Demand for “sustainable products”
Potential Chemical Feedstocks From Mixed Anaerobic Fermentations

- Gaseous products such as H$_2$, CH$_4$ and CO$_2$
- Organic molecules such as volatile fatty acids (acetic acid, propionic acid, butyric acid, octanoic acid), acetone, butanol, lignins etc.
Biomass to biomethane: a mature technology

- Anaerobic Digestion is an established worldwide industry (52.3TWh cross EU, 1.5% of EU’s primary energy, 5% of natural gas consumption).

Great potential to produce other products via anaerobic fermentations?

H₂ and VFAs
Low Grade Biomass Feedstocks

Sustainable Production Routes for VFA

VFA Production Bioprocess

- Acetate
- Propionate
- Butyrate
- Valerate

Electrons and Hydrogen

Green Chemicals

- Plastic monomers
  - Vinyl acetate
- Terephthalic acid
- Food Preservatives
- Esters for flavourings and fragrances
## Chemical Uses of Volatile Fatty Acids

<table>
<thead>
<tr>
<th>Compound</th>
<th>Uses of Volatile Fatty Acids (VFAs)</th>
<th>Demand per annum (metric tonne)</th>
<th>Cost per tonne</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid (CH₃COOH)</td>
<td>Vinyl acetate monomer (33%), acetic anhydride (18%), terephthalic acid (17%), acetate esters (17%) and other products (15%) including monochloroacetic, ketene and diketene derivatives (19%)</td>
<td>10.7 million</td>
<td>$500-1300</td>
</tr>
<tr>
<td>Propionic acid (CH₃CH₂COOH)</td>
<td>Preservation of animal feed, grain and food, herbicides, diethyl ketone, cellulose acetate propionate, flavourings, fragrances, pharmaceuticals, dyes and esters.</td>
<td>400,000</td>
<td>$1250-1450</td>
</tr>
<tr>
<td>Butyric acid (CH₃CH₂CH₂COOH)</td>
<td>Cellulose acetate butyrate plastic, butyrate esters</td>
<td>40,000</td>
<td>NA</td>
</tr>
<tr>
<td>Valeric acid (CH₃CH₂CH₂CH₂COOH)</td>
<td>A range of esters, which can be used as lubricants, turbine oils, refrigeration oils, flavourings and fragrances, plasticisers as well as numerous speciality chemicals.</td>
<td>15,000</td>
<td>NA</td>
</tr>
</tbody>
</table>
Bioprocess Uses of VFA: Substrate Shuttle Bioreactor

Figure 1. Proposed Substrate Shuttle Reactor
Sustainable Products 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
- H₂ yield and targeted Volatile Fatty Acid (VFA) production depends on fermentation conditions and biodegradable carbohydrate feedstocks
Production of H₂ and VFAs by Mixed Culture 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 and VFA production (especially retention time, pH)
• a second anaerobic digestion stage
Biohydrogen Production in an Integrated Anaerobic system-(dark fermentation)

- \( \text{H}_2 + \text{CO}_2 \) to \( \text{CH}_4 + \text{H}_2 \) in Hydrogen Reactor (pH=5.2)
- VFAs produced
- \( \text{CH}_4 + \text{H}_2 \) to \( \text{CH}_4 + \text{CO}_2 \) in Methane Reactor (pH=7.0)
- 33% conversion
- 90% energy conversion (substrate)

Biomass feedstock

Soil Conditioner

Advanced water recycling

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Dark fermentation – H₂ & VFA yield

Theoretical:

**Hexose → CH₃COOH** (acetic acid) + 4 H₂

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

**Hexose → 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
Lab Integrated Bioreactors

- Model substrates e.g. sucrose, fructose
- Sewage sludge
- Food industry co products e.g. wheatfeed
- Rye grass
- Wheat Straw

CH₄ Bioreactor

H₂ Bioreactor
Maximising the Carboxylic Acid Production Platform from Food Waste

Reactor Operating Parameters

<table>
<thead>
<tr>
<th>HRT [days]</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>OLR [g l(^{-1}) d(^{-1})]</td>
<td>95</td>
<td>47.5</td>
<td>31.7</td>
</tr>
<tr>
<td>NaOH Buffer (a)</td>
<td>1a</td>
<td>2a</td>
<td>3a</td>
</tr>
<tr>
<td>NH(_4)OH Buffer (b)</td>
<td>1b</td>
<td>2b</td>
<td>3b</td>
</tr>
</tbody>
</table>

VFA Yield at Different HRT`s and Different pH Control Agents

<table>
<thead>
<tr>
<th>Experiment</th>
<th>tVFA (mg l(^{-1}))</th>
<th>tVFA-COD/sCOD Ratio</th>
<th>VFA Yield (g tVFA / g VS(_{\text{added}}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>21083 (1174)</td>
<td>0.63</td>
<td>0.215</td>
</tr>
<tr>
<td>2a</td>
<td>25643 (564)</td>
<td>0.76</td>
<td>0.258</td>
</tr>
<tr>
<td>3a</td>
<td>30837 (1616)</td>
<td>0.99</td>
<td>0.309</td>
</tr>
<tr>
<td>1b</td>
<td>24850 (640)</td>
<td>0.74</td>
<td>0.269</td>
</tr>
<tr>
<td>2b</td>
<td>24947 (1700)</td>
<td>0.79</td>
<td>0.283</td>
</tr>
<tr>
<td>3b</td>
<td>26730 (1418)</td>
<td>0.83</td>
<td>0.255</td>
</tr>
</tbody>
</table>
H₂ and VFAs from wastes and co-products 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

Sewage Biosolids

Putrescible Fraction of Municipal Solid Waste
VFAs produced in hydrogen fermentation from food processing by-product

Theoretical:

**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
Electrodialysis
Conventional Electrodialysis of VFA typically present in fermentation systems

Changes in VFA concentration in concentrate and diluate streams during CED
Degrees of dilution: 95% AA removal; 95% PA removal; 94% iBA removal; 93% nBA removal; 92% iVA removal; 92% nVA removal; 93% total VFA removal. Reduction in VFA concentrations: 848 mg∙l⁻¹ AA; 964 mg∙l⁻¹ PA; 996 mg∙l⁻¹ iBA; 958 mg∙l⁻¹ nBA; 920 mg∙l⁻¹ iVA; 782 mg∙l⁻¹ nVA; 5,468 mg∙l⁻¹ total VFA.
Integration Dark Fermentation + Electrodialysis

Feed → H₂ Bioreactor → Electrodialysis → Effluent
Dark Fermentation Apparatus

Continuously fed bioreactor

- Four Litre working volume
- 24h HRT
- 40g L sucrose (10g L\(^{-1}\) d\(^{-1}\))
- pH 5.5
- Temperature 35\(^\circ\)C
Preliminary findings from combining ED and continuous fermentation:

- VFAs successfully transferred to concentrate stream (concentrations over 6300 mg L\(^{-1}\) achieved).
- Passive removal of VFAs to concentrate stream occurred (osmosis) but removal rate increased when voltage was applied (3566 mg L\(^{-1}\) 0V, 6324 mg L\(^{-1}\) 18V)
- Minimal transference of carbohydrate to concentrate stream (<500 mg L\(^{-1}\) in concentrate stream detected vs 10,000 mg L\(^{-1}\) in the feed).
- Positive effect on hydrogen yields.

Added benefit of 30% increase in H\(_2\) yields
Integration DF + H₂ Separation + ED

H₂ Separation and Sparging

Feed → H₂ Bioreactor → Effluent

Electrodialysis

VFA

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Hydrogen Separation

HyET Process

- DC current pulls protons through a catalyzed membrane
- Efficient
- High selectivity
- Scalable
- High pressure side can reach pressure of 1000 bar.
Possible Effect of Lowering Acetate Concentration on Homoacetogenesis

Homoacetogenesis

\[ 4 \text{H}_2 + 2 \text{CO}_2 \rightarrow \text{CH}_3\text{COOH} + 2 \text{H}_2\text{O} \]

Lowering [AC] in the bioreactor makes Homoacetogenesis thermodynamically favourable at a lower [H\textsubscript{2}]
DF + Hydrogen Separation

Two experimental conditions evaluated:
Recycling of headspace (Control)
• Recycling of headspace with active H2 removal (HYET process)
• Concentration of H₂ in head space reduced from 60% to 20%
• **23.5% increase in H₂ yields**
H2020 REsources from URban Blo- waSte (RES Urbis)

- Total Value 2.6M Euro-USW £280K, optimisation of dark fermentation (biohydrogen) for the production of VFAs as part of a urban biowaste biorefinery for green chemicals.

3 year project with 21 Partners
Led by University of Roma
- 10 Academics Partners
- 7 Private partners
- 3 Public authorities
- 1 Industrial Assoc.

* The acid fermentation step could be splitted into separate reactors for fine tuning of C and N balance in the process and/or sludge pretreatment could be also included

waste biorefinery of urban bio-waste and possible integration into existing wastewater treatment plant
Online VFA measurement

“…precise evaluation organic acid production patterns…”

- VFAs separated via capillary electrophoresis
- Gold electrode coated with electroactive polymer used for detection
- Differential penetration of acids into the polymer coating modifies current of the electrode at specific intervals
- Analysis can performed in just a few minutes and will ultimately be deployed as an online instrument
- Working prototype has been successfully completed and manual sampling will be available soon.
Summary

- Volatile fatty acids (VFAs) can easily be produced from wastes and low grade biomass
- Using mixed microflora “wild-type” AD systems rather than genetically manipulated cultures avoids the need for expensive sterilization of feedstock and effluent
- Increased production of key VFAs such as acetic acid can be achieved by removing H₂ and VFAs from the fermentation liquor.
- H₂ recovered can be used to further produce products such as lipids, single cell protein and bioplastics as well as powering gas separation.
Summary

- Produces a range of green chemical feedstocks, (H₂, CO₂, CH₄ and C2-C5 carboxylic acids).
- Can use complex substrates e.g. starches, unrefined sugar beet, grass, maize, wheat feed and wastes (NOT dependant on refined sugars)
- Continuously fed reactors over long terms of operation (>100 days).
- Up to 90g/l feedstocks used at hydraulic retention times of 0.5 to 3 days at OLRs of up to 90 g/l/d.
- Can integrate technologies removing product inhibition to supplying electrons to bind CO₂ to improve yields.