Alternative Product Streams from Anaerobic Digestion

AD NETWORK RESEARCH COLLOQUIUM

University of Manchester

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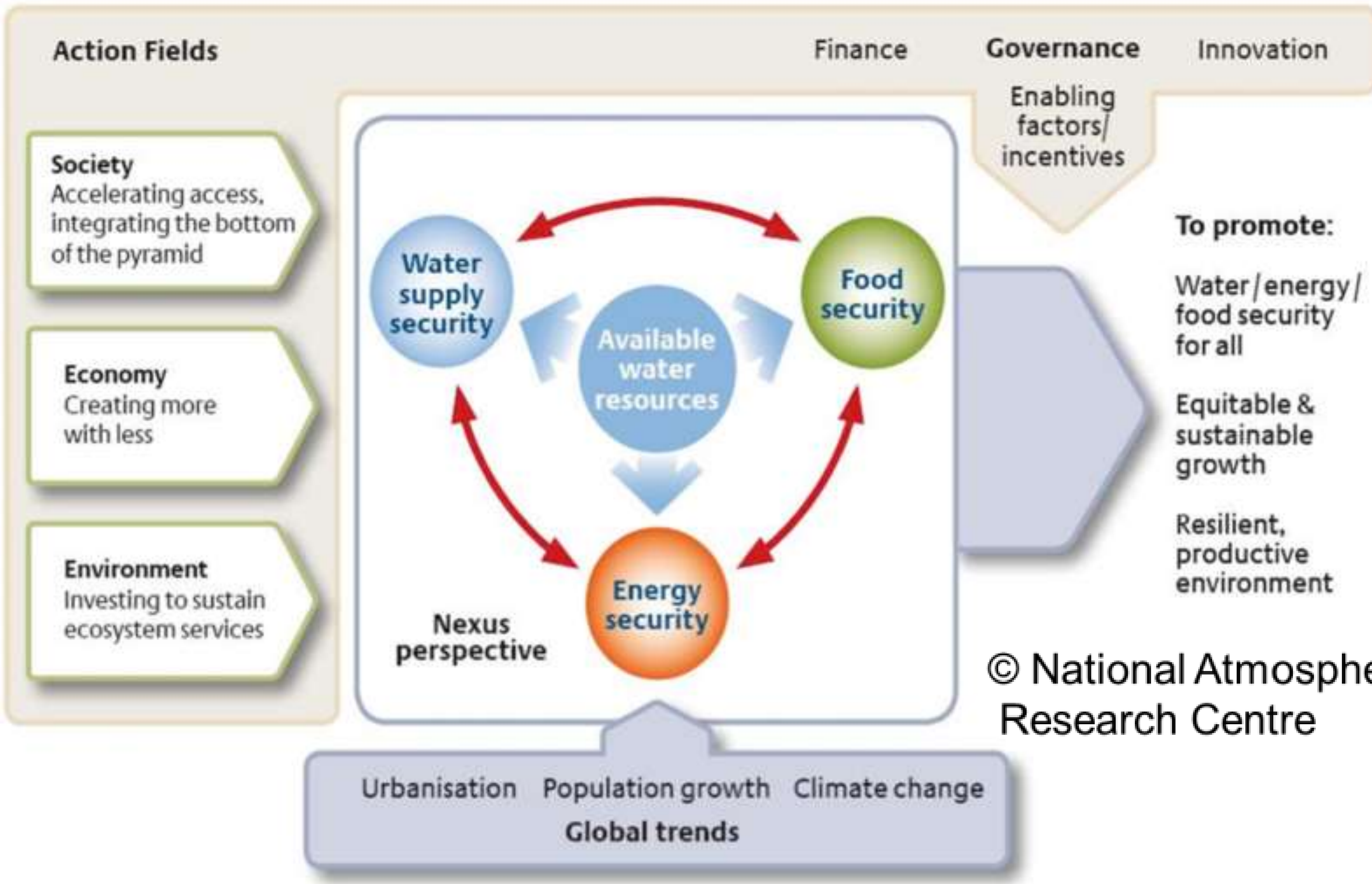
Global Challenges for 21st Century: "Water, Energy and Food Nexus"



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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”

Product Streams 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.,
- Plant Growth Promoting Soil Additives

Biomass to biomethane: a mature technology

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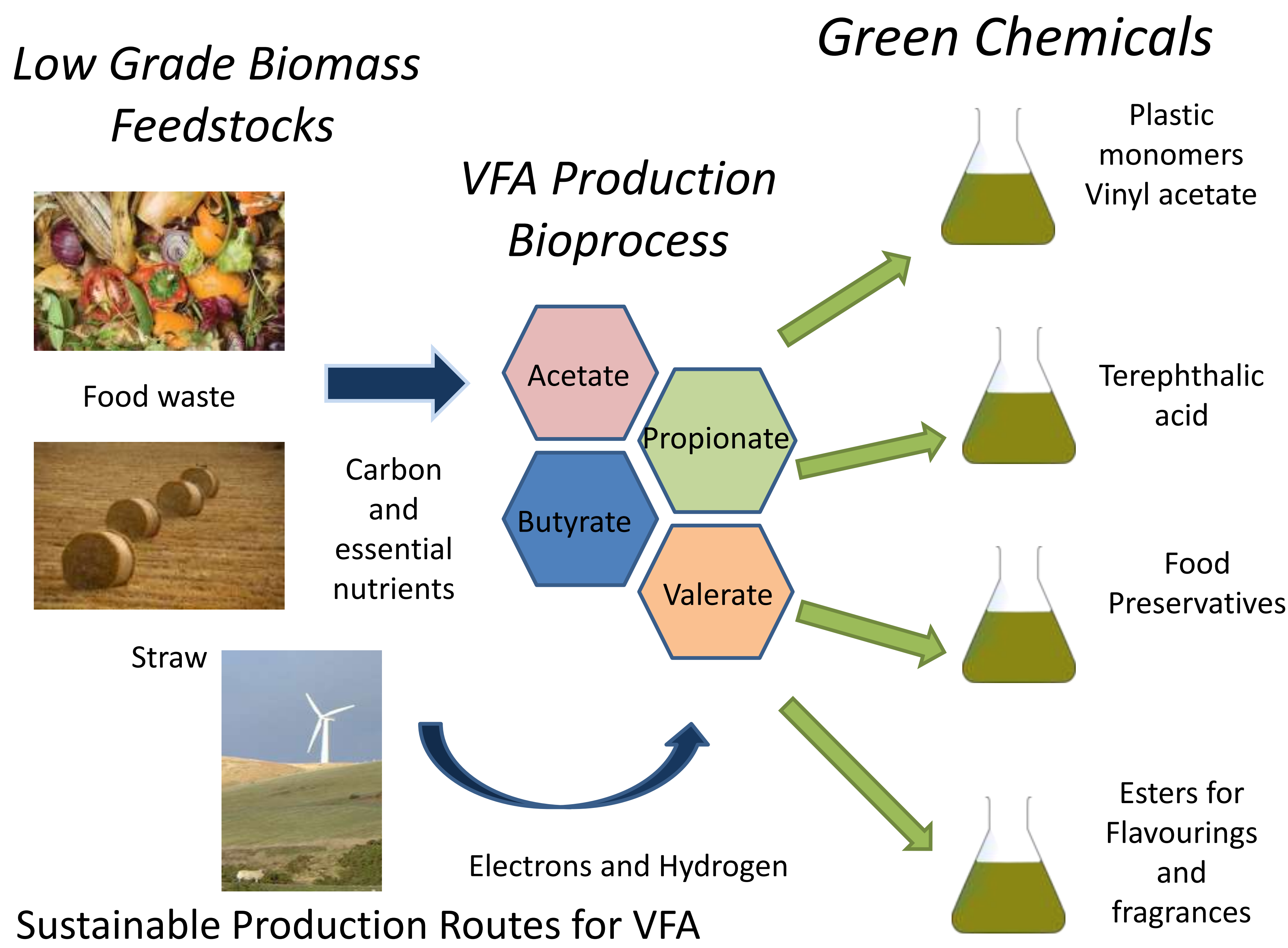
- Anaerobic Digestion is an established worldwide industry (52.3TWh cross EU, 1.5% of EU's primary energy, 5% of natural gas consumption).

Great potential to produce other products via anaerobic fermentations?

H_2 and VFAs



Low Grade Biomass Feedstocks
Food waste
Straw
Carbon and essential nutrients
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
Sustainable Production Routes for VFA

Chemical Uses of Volatile Fatty Acids

Compound	Uses of Volatile Fatty Acids (VFAs)	Demand per annum (metric tonne)	Cost per tonne
Acetic acid (CH_3COOH)	Vinyl acetate monomer (33%), acetic anhydride (18%), terephthalic acid (17%), acetate esters (17%) and other products (15%) including monochloroacetic, ketene and diketene derivatives (19%)	10.7 million	$500-1300
Propionic acid (CH_3CH_2COOH)	Preservation of animal feed, grain and food, herbicides, diethyl ketone, cellulose acetate propionate, flavourings, fragrances, pharmaceuticals, dyes and esters.	400,000	$1250-1450
Butyric ($CH_3CH_2CH_2COOH$)	Cellulose acetate butyrate plastic, butyrate esters	40,000	NA
Valeric ($CH_3CH_2CH_2CH_2COOH$)	A range of esters, which can be used as lubricants, turbine oils, refrigeration oils, flavourings and fragrances, plasticisers as well as numerous speciality chemicals.	15,000	NA

Bioprocess Uses of VFA: Substrate Shuttle Bioreactor

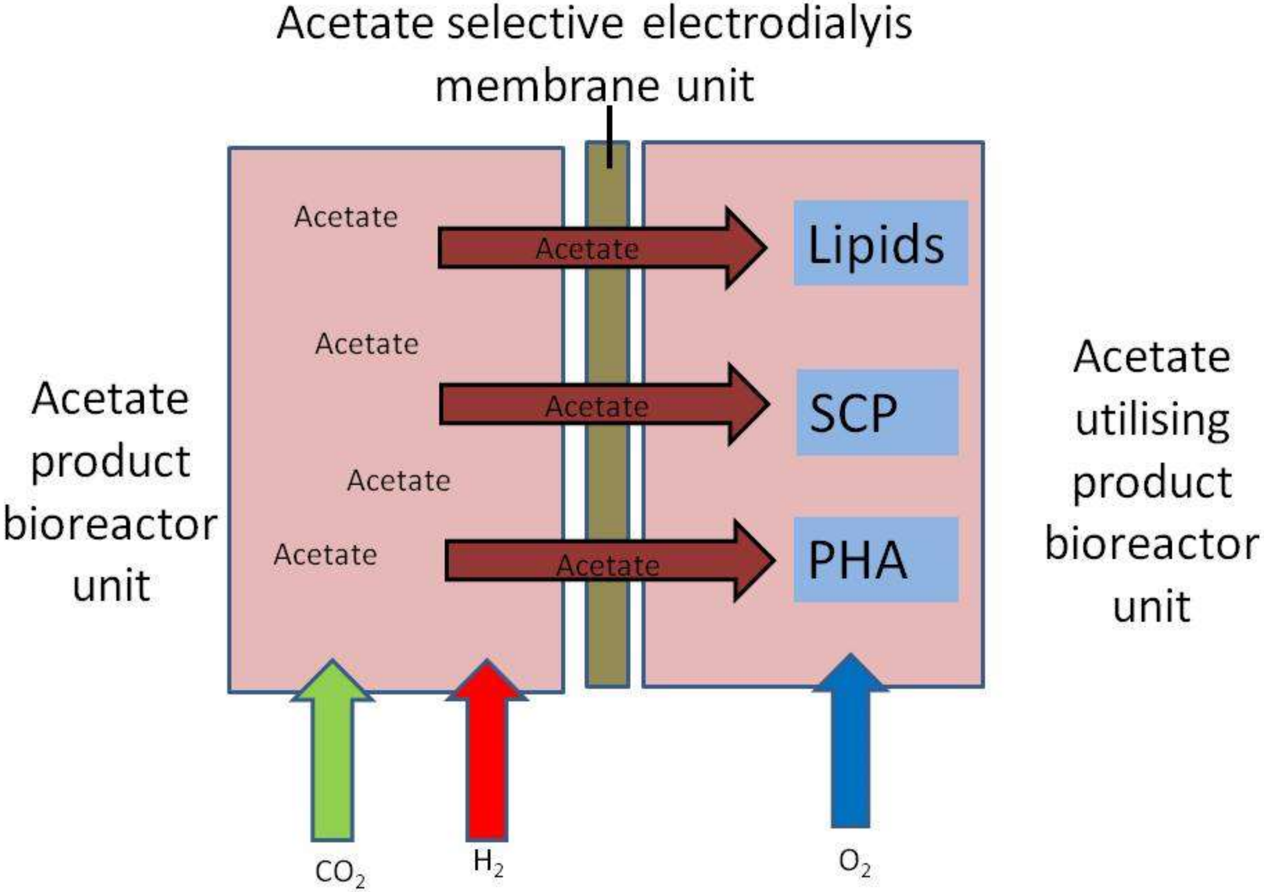
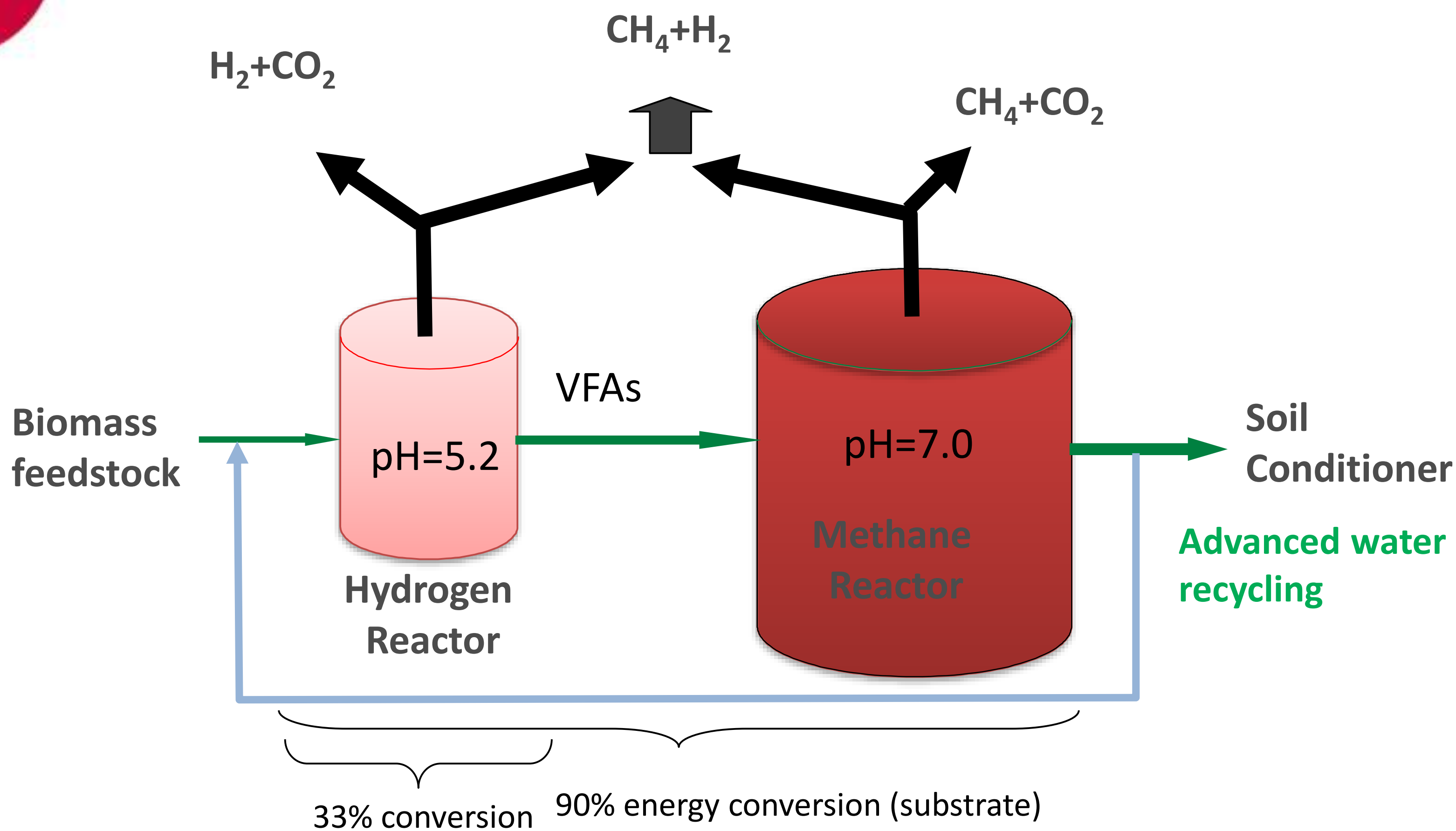


Figure 1. Proposed Substrate Shuttle Reactor

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
- H_2 yield and targeted Volatile Fatty Acid (VFA) production depends on fermentation conditions and biodegradable carbohydrate feedstocks

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



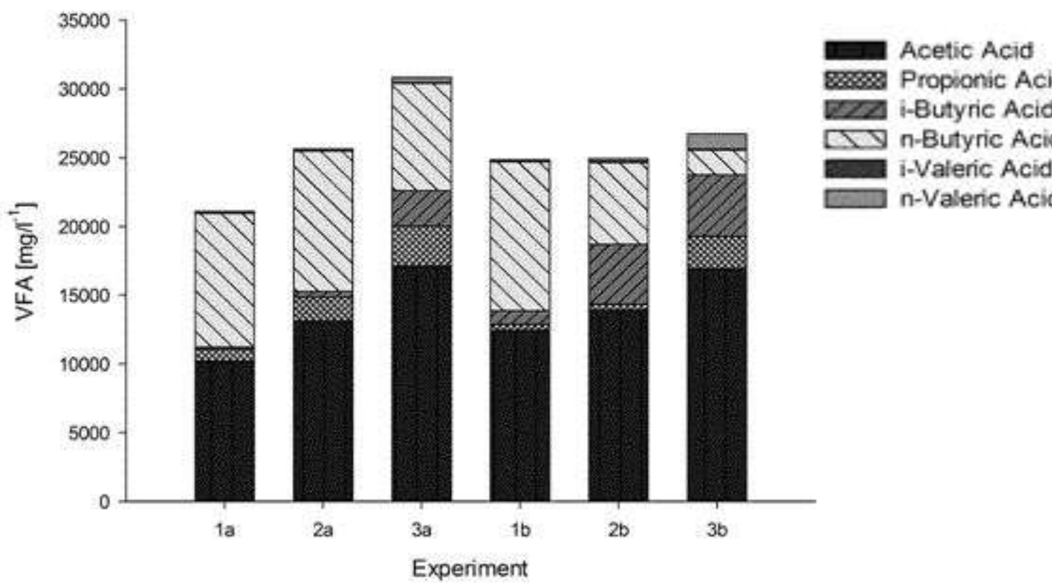
Maximising the Carboxylic Acid Production Platform from Food Waste

Reactor Operating Parameters

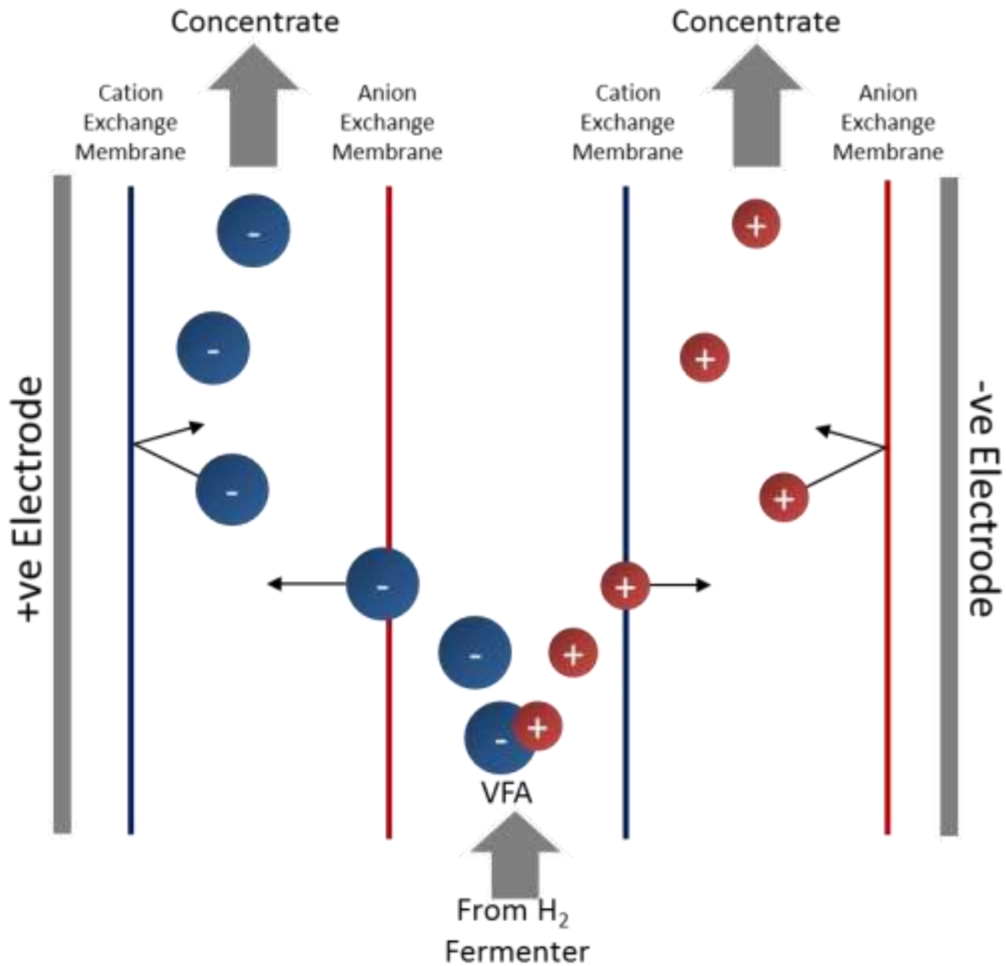
HRT [days]	1	2	3
OLR [$g\ l\ d^{-1}$]	95	47.5	31.7
NaOH Buffer (a)	1a	2a	3a
NH_4OH Buffer (b)	1b	2b	3b

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

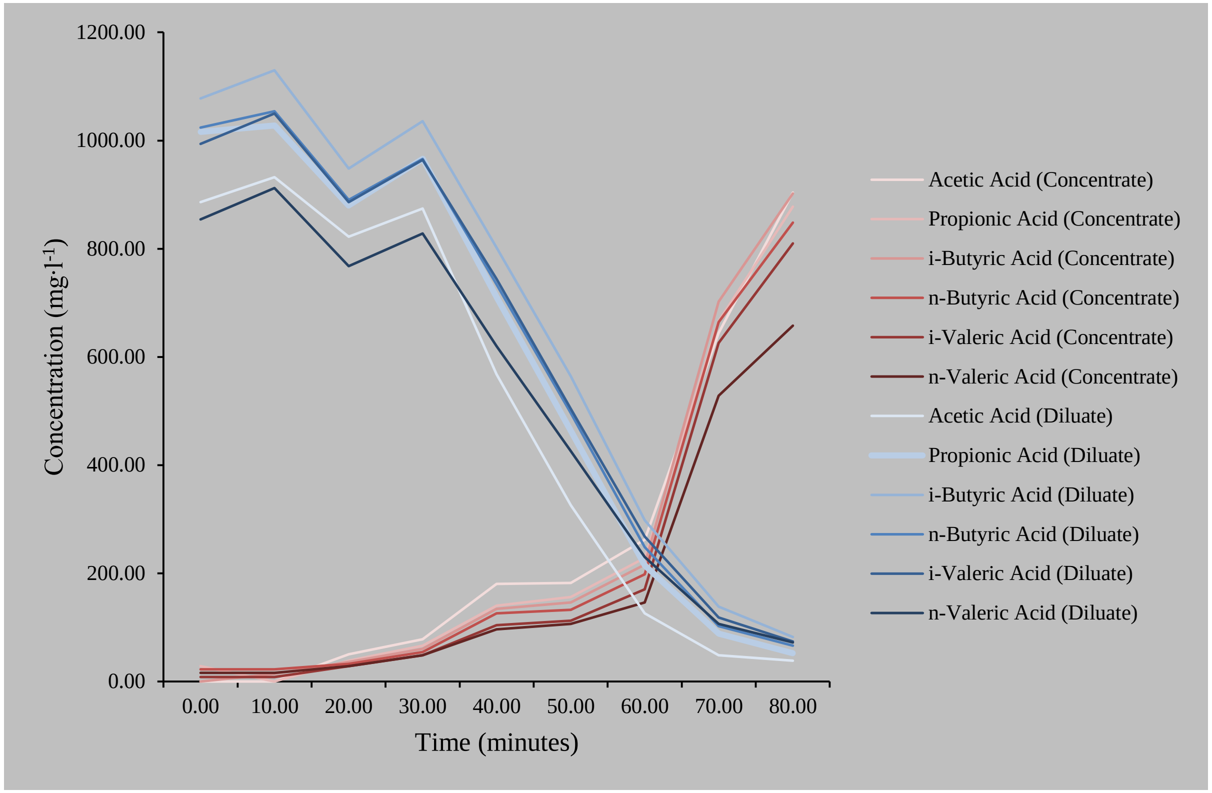
Experiment	tVFA (mg l)	tVFA-COD/ sCOD Ratio	VFA Yield (g tVFA / g VS_{added})
1a	21083 (1174)	0.63	0.215
2a	25643 (564)	0.76	0.258
3a	30837 (1616)	0.99	0.309
1b	24850 (640)	0.74	0.269
2b	24947 (1700)	0.79	0.283
3b	26730 (1418)	0.83	0.255



VFA Removal by Sequential Membrane Separation with Electrodialysis



Conventional Electrodialysis of VFA Typically Present in Fermentation Systems

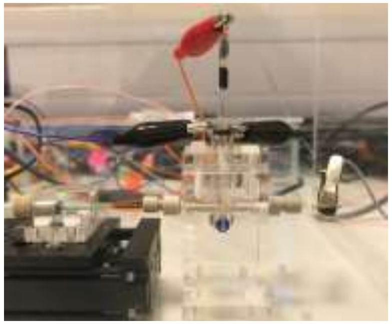


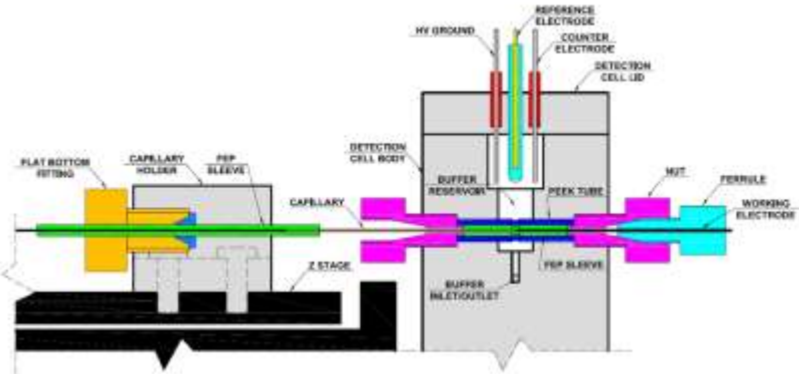
Changes in VFA concentration in concentrate and diluate streams during CED
Degrees of dilution: 95% AA removal; 95% PA removal; 94% iBA removal; 93% nBA removal; 92% iVA removal; 92% nVA removal; 93% total VFA removal. **Reduction in VFA concentrations:** 848 $mg \cdot l^{-1}$ AA; 964 $mg \cdot l^{-1}$ PA; 996 $mg \cdot l^{-1}$ iBA; 958 $mg \cdot l^{-1}$ nBA; 920 $mg \cdot l^{-1}$ iVA; 782 $mg \cdot l^{-1}$ nVA; 5,468 $mg \cdot l^{-1}$ total VFA.

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.**





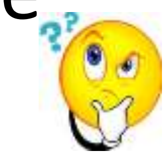
Summary

- 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 H_2 and VFAs from the fermentation liquor.
- VFA can be recovered can be used to further produce products such as lipids, single cell protein and bioplastics.

Digestate Premium ™

The phytoactive properties of digestates could be due to the following :

- Inorganic nutrients such N, P and K.

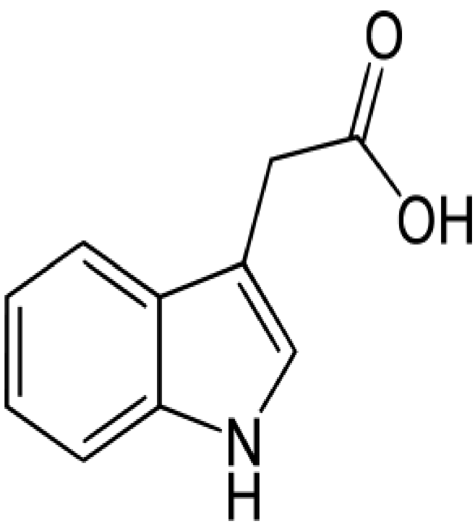
- Can the bacteria present in digestates produce plant hormones?

- Microbial release of phytoactive compounds (humic acids/soluble lignins)?

- Can plant growth promoting bacteria or microbial plant disease inhibitors grow in digestates?


Do the bacteria present in digestates produce plant hormones?

- One group of phytoactive compounds (plant hormones) have been detected in a number of microbial media. Not all have been identified but include :
  - Auxins
  - Ethylene
  - cytokinins
- Microbial isolates from soils have been shown to produce plant hormones.

Auxin



- Regulates and promotes plant growth
- Most important natural auxin is indole-3-acetic acid (IAA).
- Consists of a aromatic ring and a carboxylic acid group.
- Promotes plant growth at low levels but then becomes inhibitory

Developed a Range of Analytical Procedures for Auxins in Digestates

- Bioassay
  - Based on plant model *Arabidopsis thaliana*
- Chemical Analysis
  - UVVis Spectrophotometeric Method
  - HPLC/Uvvis
  - UPLC ESI-MS/MS and GC/MS

Screening Analysis of Auxins and Confirmatory Analysis by HPLC

- Salkowski's procedure was used with a colour change at 530nm
- A reverse phase HPLC method with auxin detection at 274 nm.
- Spot samples confirmed with UPLC ESI-MS/MS

Auxin Analysis Results

			Salkowski		HPLC	
Site	Type	Sample	mg/L	uM	mg/L	uM
A	Food Waste	Raw Feed	1.2	6.7	1.1	6.1
A	Food Waste	Digestate	10.7	60.9	3.6	20.1
A	Sewage Sludge	Raw Feed	nd	-	nd	-
A	Sewage Sludge	Digestate	8.7	24.5	2.2	12.5
B	Sewage Sludge	Raw Feed	nd	-	nd	-
B	Sewage Sludge	Digestate	4.3	24.5	3.1	17.7
C	Maize	Feed	nd	-	nd	-
C	Maize	Digestate	10.3	58.9	14.2	81.1
C	Maize	Digestate (dewatered)	nd	-	nd	-

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Inoculation with Plant Growth Promoting Bacteria

- A number of pure cultures from a range of plant growth promoting bacteria associated with soil/plant systems were selected.
- Used to inoculate autoclaved food waste/digestate/sewage sludge mediums.
- Some mediums were also supplemented with a auxin precursor.
- Increases in auxin levels were associated with the inoculation with *Bradyrhizobium japonicum, Pseudomonas fluorescens* and *Ensifer meliloti.*

Summary

- In total 21 samples from commercial anaerobic digesters were analysed.
- The increased presence of auxin was found in anaerobic digestates of food waste, sewage sludge, mixed crop and whole crop maize digestion compared to the incoming feed.
- The level of auxin could be effected by reactor operation, inoculation with plant growth promoting bacteria and chemical supplementation.

Conclusions

- Anaerobic processes can be used to produce a range of gases not only for energy uses but also chemical uses.
- Biomass can be converted to a range of volatile fatty acids (VFA)which can be extracted for use as a “green” chemical feedstock or converted to other bioproducts.
- Residual digestates could be used as a enhanced plant growth media and soil conditioner.

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