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In Situ Extraction of Volatile Fatty Acids from Anaerobic Digestion Systems

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CENTRE FOR RENEWABLE AND SUSTAINABLE ENERGY STUDIES

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Introduction

- What are volatile fatty acids (VFAs)?
  - Linear carboxylic acids containing C_2 – C_6 atoms
  - Average pKa value ≈ 4.7

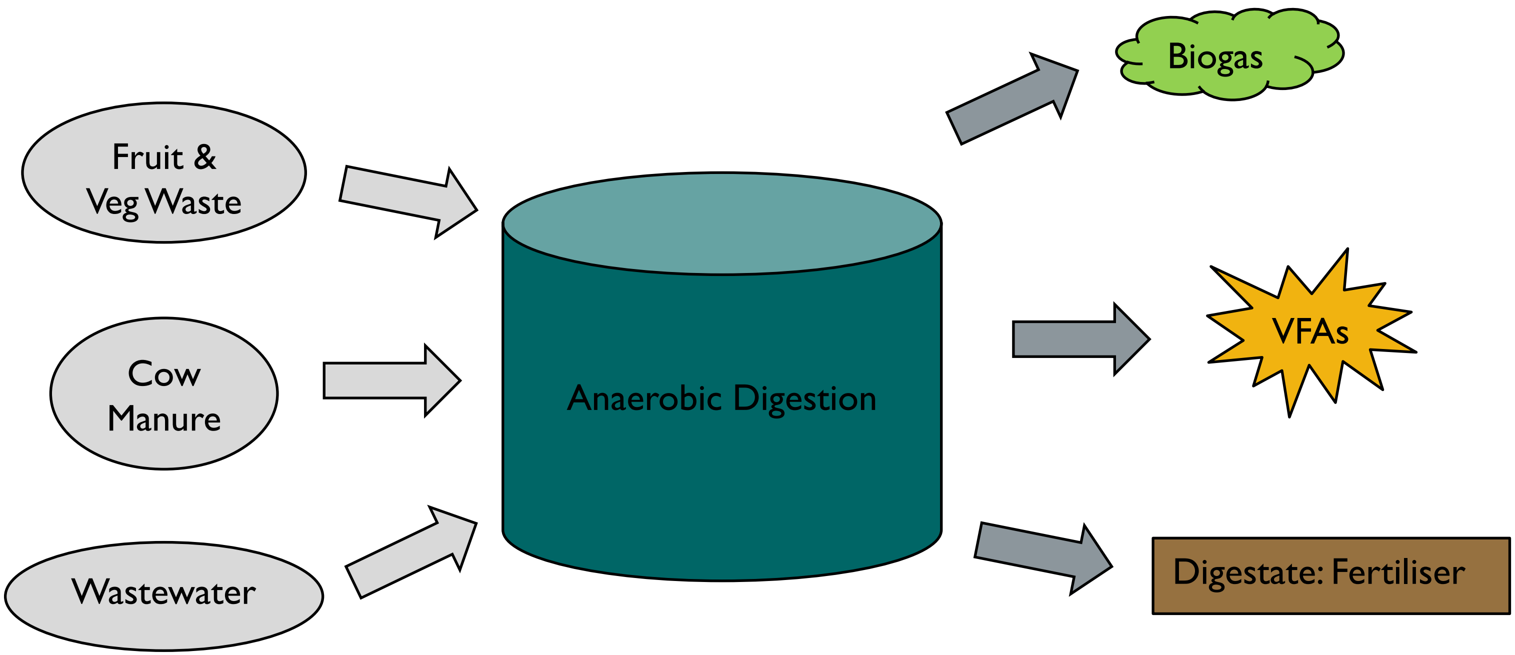
- VFAs are valuable products
  - Pharmaceutical
  - Food and beverage
  - Precursors for biodegradable polymers

Table 1: VFA commodity value and market size, (Zacharof and Lovitt, 2013)

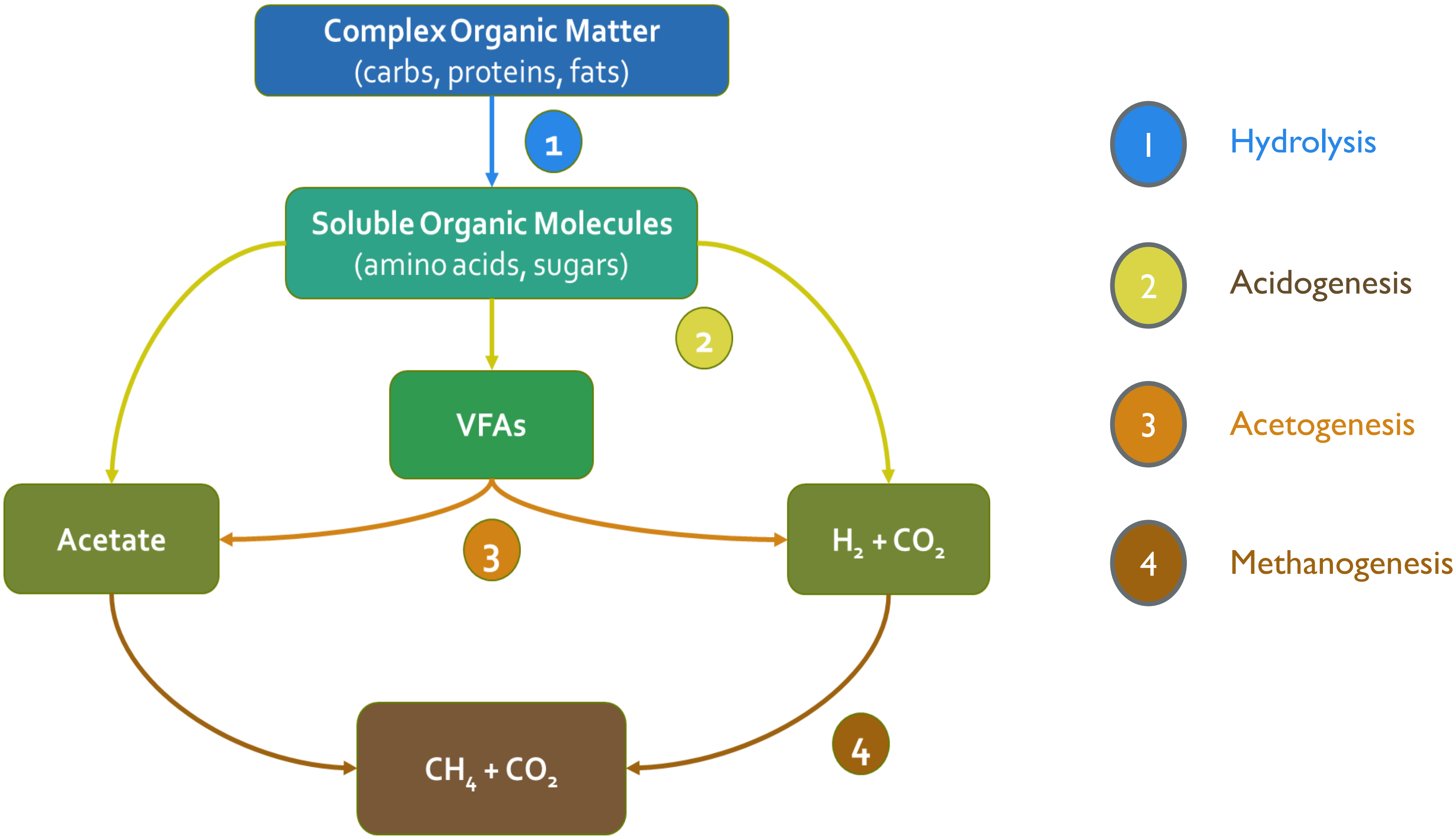
Volatile fatty acid	Chemical formula	Market size (tons/year)	Price per ton (USD, $)
Acetic	CH_3COOH	3 500 000	400 – 800
Propionic	CH_3CH_2COOH	180 000	1500 – 1650
Butyric	$CH_3(CH_2)_2COOH$	30 000	2 000 – 2 500
Caproic	$CH_3(CH_2)_4COOH$	25 000	2 250 – 2 500

Introduction

- Currently VFAs are produced by petrochemical-based processes
- Fermentation processes can be used to produce VFAs
- Anaerobic digestion is a fermentation process widely used to treat waste and could be used as a VFA source



Anaerobic Digestion (AD) Microbial Pathways



Introduction

- Several downstream processes
  - Expensive
  - Energy intensive
  - Use of chemicals that hinder the anaerobic process

- *In situ* extraction
  - Improved recovery efficiency for VFAs
  - Prevent inhibitory effects of VFAs
  - Higher VFA production rates

- Ataei & Vasheghani-Farahani, 2008; Roume et al., 2016; Ge et al., 2015)
  - These studies focussed on VFA production by acidification of the AD process
  - No biogas production

Project Scope

Aim

- Develop an *in situ* extraction method for the continuous recovery of VFAs in an anaerobic digester that co-produces biogas and VFAs

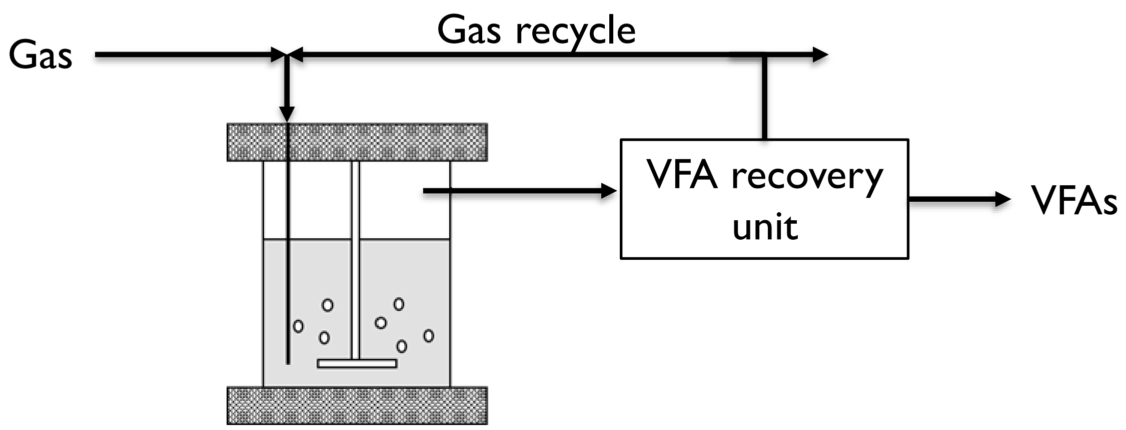
Objectives

- Identify the separation processes that can be used for an *in situ* extraction process scheme
- Determine the AD parameters that will affect the extraction method
- Determine a suitable recovery method for the extracted VFAs
- Design and construct a unit capable of continuously extracting VFAs from an AD reactor and evaluate the unit

Gas Stripping

Several Advantages

- Operation at fermentation temperature
- Fermentation gas used as a stripping agent in ABE fermentation
- Process of broth with/without the presence of solids



Gas Stripping

Preliminary Aspen Model

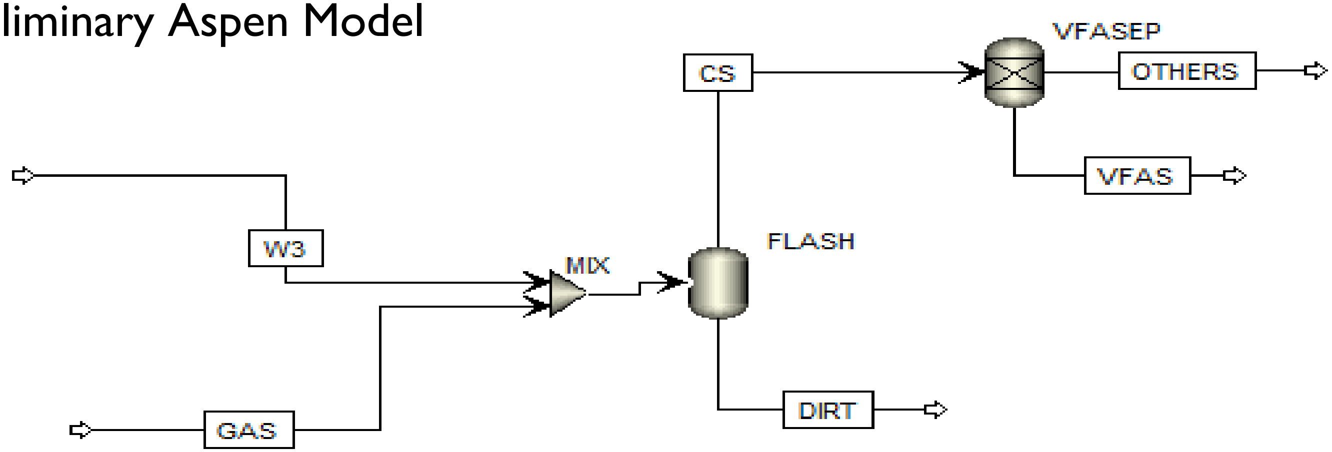


Table 2: Required amount of gas needed to strip x% of VFAs

Mass ratio of gas to VFAs [gas:VFAs]	**VFAs extracted using CO_2 gas [%]**	**VFAs extracted using equimolar CO_2 and CH_4 gas [%]**
90	19.7	33.4
130	32.6	73.8
150	41.3	100
230	100	100

Equilibrium Gas Stripping Experiments

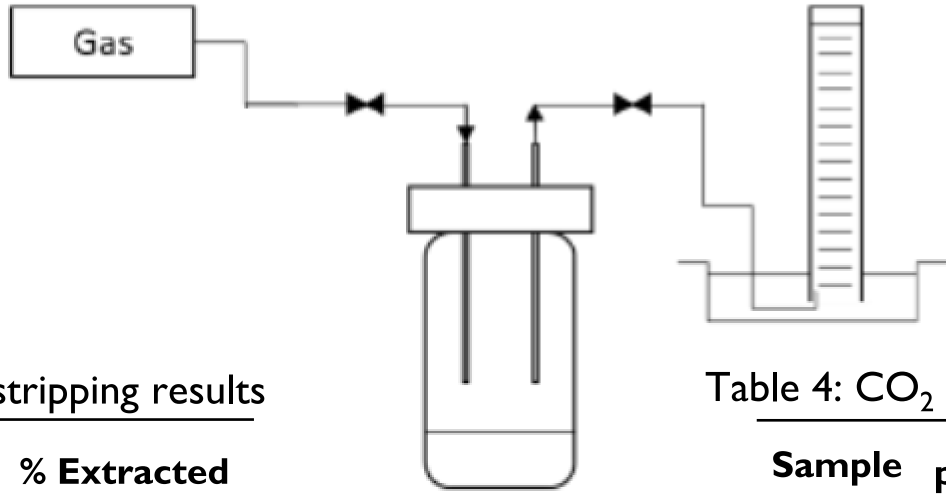


Table 3: CO_2 stripping results

Sample	pH	% Extracted
1	2.0	0.18 ± 0.95
2	3.5	-0.12 ± 0.70
3	4.5	0.30 ± 0.13
4	5.0	-0.03 ± 0.55
5	6.0	0.91 ± 1.42
6	7.0	-0.08 ± 0.29

Table 4: CO_2 & CH_4 stripping results

Sample	pH	% Extracted
1	2.0	0.18
2	3.5	0.55
3	4.5	0.09
4	5.0	-0.19
5	6.0	-0.76
6	7.0	-0.92

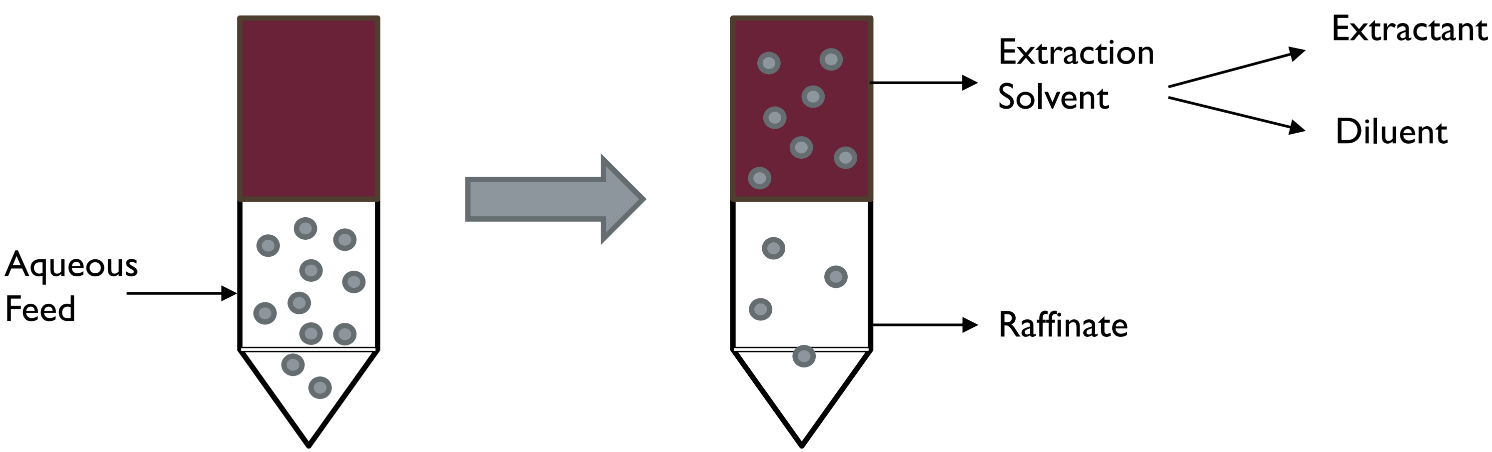
- Continuous gas stripping extracted 0.013 g of VFAs (4.48%) using 40.2 L of equilmolar CO_2 & CH_4 at 1.2 vvm

Conclusions: Gas Stripping

- VFAs: Don't be fooled by the name!
  - VFAs are not as volatile as the name suggests
  - VFAs are hydrophilic compounds
  - Tremendous amounts of gas required to strip relatively small amounts of VFAs
- Gas stripping was not a viable extraction method
- An alternative and more efficient extraction method was required
  - Extraction Fermentation?

Liquid-Liquid Extraction

- Separation technique to extract components dissolved in liquid feed solution
- Feed contacted with second liquid known as the solvent
- Solvent is immiscible or partially miscible: used to create a second liquid phase
- Solvent comprised of extractant and diluent



- Extractant: strong interactive interaction with solute
- Diluent: improve surface properties of extractant

Liquid-Liquid Extraction

- Influential Parameters
  - pH
  - Loading ratio
  - Distribution coefficient
  - Properties of the solvent
  - Temperature

- Solvents
  - Extractants
    - Tributyl Phosphate (TBP)
    - Trioctylamine (TOA)
  - Diluents
    - Oleyl Alcohol
    - Kerosene
    - Canola Oil

Results: Total VFA extraction using Canola Oil

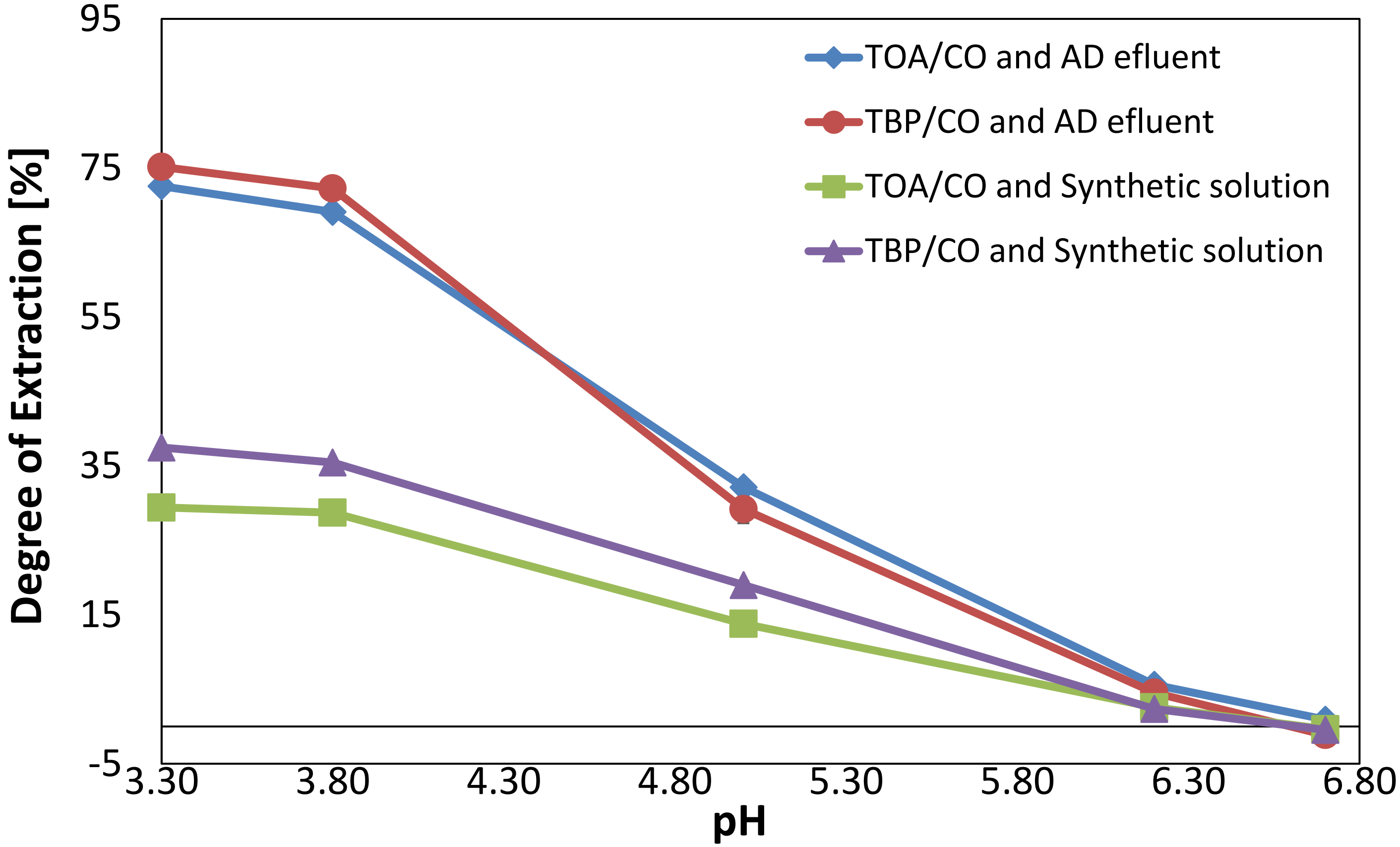


Figure 1: LLE of AD effluent and synthetic solution using 20 vol% TOA or 20 vol% TBP in canola oil. Experiments were done in triplicate at pH 5.0

Results: Total VFA extraction using Oleyl Alcohol

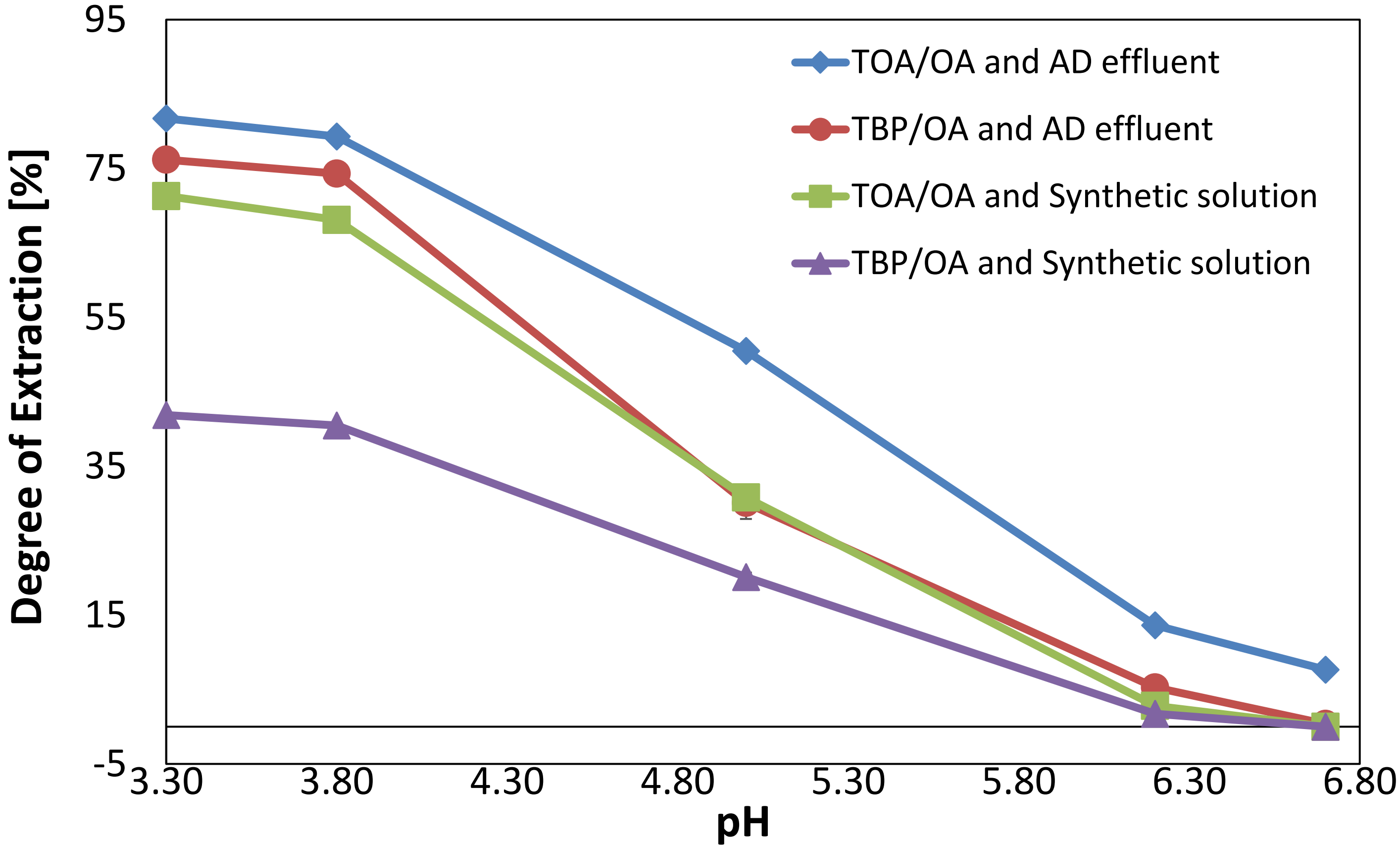


Figure 2: LLE of AD effluent and synthetic solution using 20 vol% TOA or 20 vol% TBP in oleyl alcohol. Experiments were done in triplicate at pH 5.0

Results: Total VFA extraction using Lamp Oil

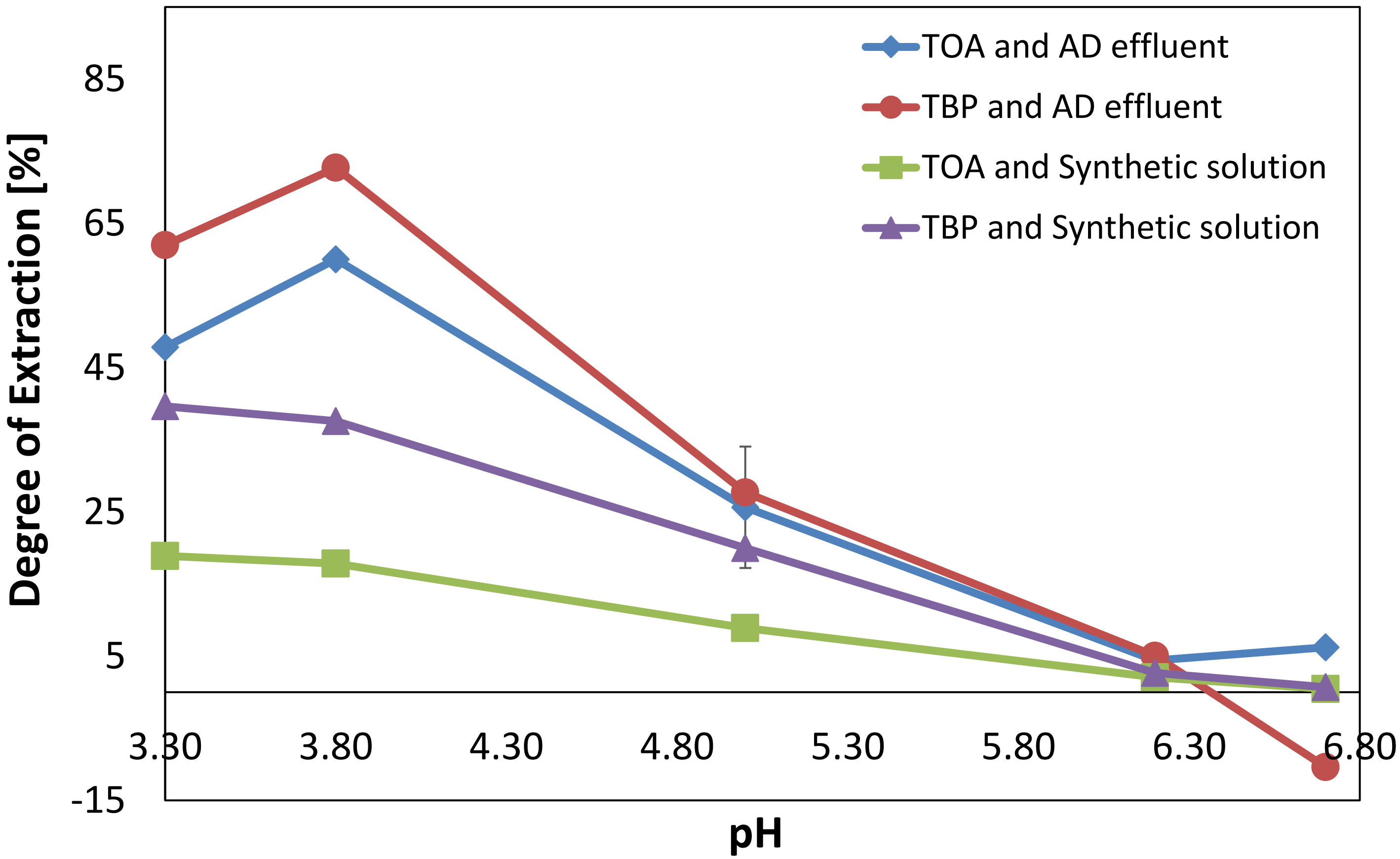


Figure 3: LLE of AD effluent and synthetic solution using 20 vol% TOA or 20 vol% TBP in lamp oil. Experiments were done in triplicate at pH 5.0

Results: LLE of Individual VFAs

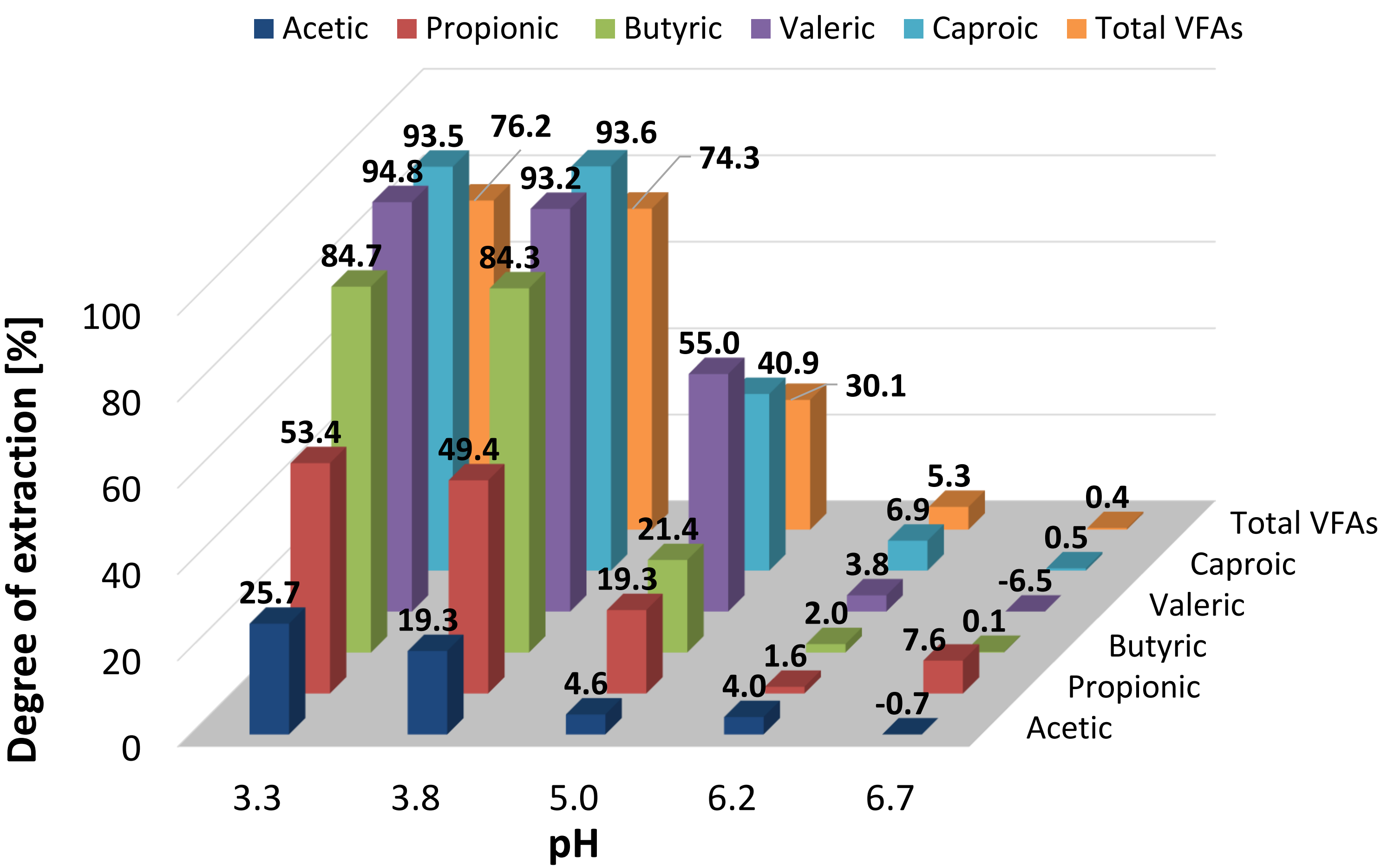
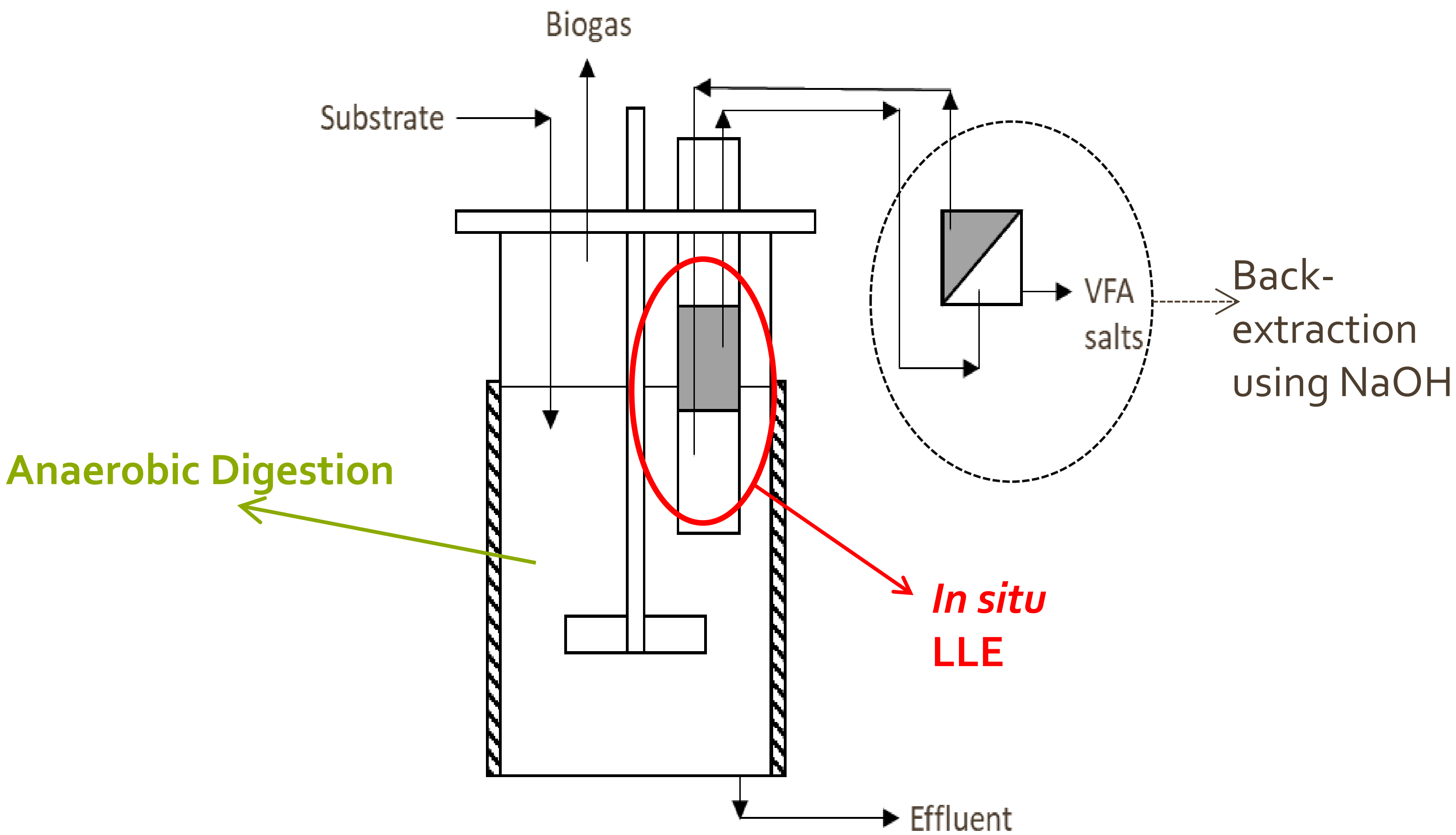


Figure 4: Degree of extraction of individual VFAs from LLE using 20 vol% TBP in oleyl alcohol on AD effluent for a range of pHs at 37°C

Conclusions: LLE

- TBP and TOA performed similar in canola oil
- TBP / lamp oil performed significantly better than TOA
- TOA / oleyl alcohol had the best degree of extraction
- Better extractions were observed for actual AD effluent
- Higher degrees of extractions were observed when the pH of the system was below the pKa value of the VFAs
- BUT AD usually operates between a pH of 6 - 8

Proposed Prototype: *In Situ* Extractive Fermentation



Results: Biochemical Methane Potential Tests

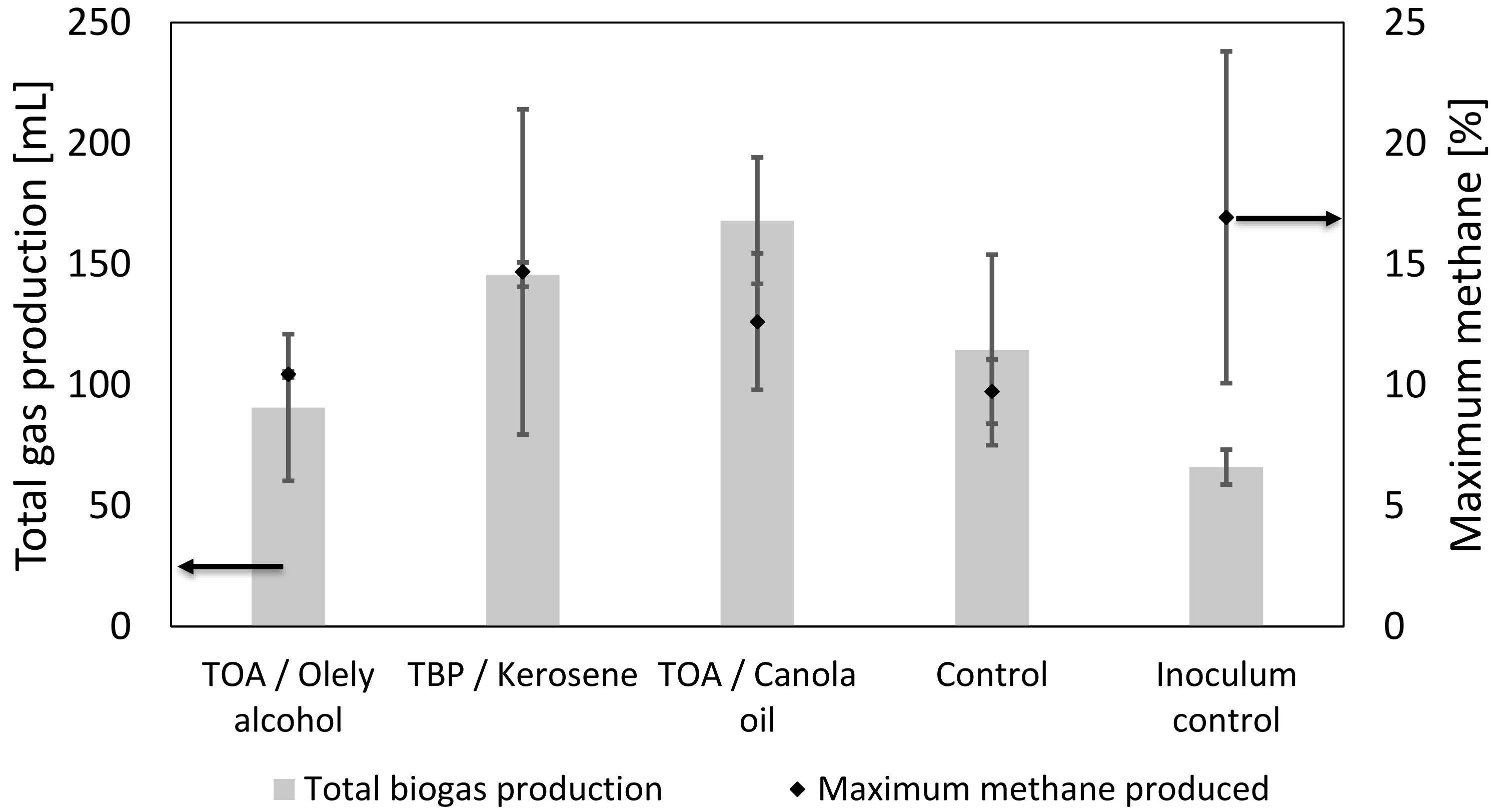


Figure 5: Biocompatibility test of solvents in BMPs by measuring the total biogas production and maximum methane percentage observed in a 28 day digestion period. Solvents consisted of 20 vol% extractant and diluent. 20 vol% TOA was in oleyl alcohol and canola oil, and TBP in lamp oil (kerosene).

Results: Biochemical Methane Potential Tests (BMPs)

Table 5: Total VFAs before and after digestion from the BMP test and VFAs in the solvent

	Pre-digestion [g/L]	Post-digestion [g/L]	Net VFAs produced [g/L]	VFAs in solvent [g/L]*
TOA and canola oil	7.80 ± 0.15	12.90 ± 0.29	5.10 ± 0.33	n/a **
TBP and lamp oil	7.80 ± 0.15	9.51 ± 0.56	1.71 ± 0.58	2.40 ± 0.30
TOA and oleyl alcohol	7.80 ± 0.15	8.83 ± 0.48	1.03 ± 0.50	5.84 ± 0.36
Control	7.80 ± 0.15	11.07 ± 0.29	3.27 ± 0.33	n/a
Inoculum control	0.10 ± 0.01	0	-0.10 ± 0.01	n/a

* VFAs measured after the digestion period through back-extraction using 1 M NaOH solution

** Could not be determined due to the formation of an emulsion with the solvent

1st 17 L Run

Table 6: Parameters and results obtained from 17 L run

Solvent flowrate:	4 mL/min
ISR:	2.5
Cow manure to apple pomace:	4:1
Solvent in bioreactor:	70 mL of 20 vol% TBP in lamp oil
Temperature:	37°C
Initial pH:	7.37
Buffer:	120 g of calcium carbonate
VFAs extracted in solvent:	0 g/L
Methane composition:	38%

2nd 17 L Run

Table 7: Parameters and results obtained from 17 L run

Solvent flowrate:	52 mL/min
ISR:	2.0
Cow manure to apple pomace:	2:3
Solvent in bioreactor:	70 mL of 20 vol% TOA in oleyl alcohol
Temperature:	37°C
Initial pH:	7.23
Buffer:	n/a
VFAs extracted in solvent:	0.186 g/L
Gas production:	6.71 L
Methane composition:	43%

Conclusions

- Gas stripping and LLE was identified as potential *in situ* extraction methods
- Gas stripping was inefficient in extracting VFAs
- LLE is strongly dependent on the solvent and the pH of the system
- pH-swing back-extraction using 1 M NaOH was suitable for the recovery of VFAs
- *In situ* LLE can be used to continuously extract VFAs for the co-production of biogas and VFAs

Thank You