DOE Bioenergy Technologies Office (BETO) 2023 Project Peer Review

Novel and Viable Technologies for Converting Wet Organic Waste Streams to Higher Value Products

April 7th, 2023
Technology Area Session

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The Research Foundation of SUNY, University at Albany

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Project Overview

Context

Food waste: 1) Only 8.5% is used for beneficial purposes. Annually, 56 million wet tons are landfilled or combusted; 2) Several states in the northeast have now banned the disposal of food waste in landfills.

Sewage sludge: 1) The US generated 14.8 million dry tons of wastewater residuals in 2016 with half landfilled; 2) Landfilling sludge has been discouraged by some states.

This project addresses BETO's interest in "Wet Waste-to-Energy". Organic waste-derived volatile fatty acids are a new platform for renewable fuels and chemicals production.

Project history

BP1: 10/1/2019-05/31/2020

BP2: 06/01/2020-11/30/2021

BP3: 12/01/2021-05/31/2023

The overarching goal

This project seeks to evaluate the whole process from wet wastes to high value products using a systematic approach.

Project overview (cont.)

Objectives

(1) Identification of the optimal pretreatment method for each target waste stream,

(2) Determination of the best process parameters for arrested methanogenesis (AM),

(3) Evaluation of product yield and titer of volatile fatty acids (VFAs) from the waste streams separately through Microbial Electrosynthesis (MES) with CO_2 capture and conversion,

(4) Developing an innovative membrane-based liquid-liquid extraction process for extracting VFAs out of the fermentation broth,

(5) Performing preliminary life-cycle analysis (LCA) and techno-economic analysis (TEA) for each process block,

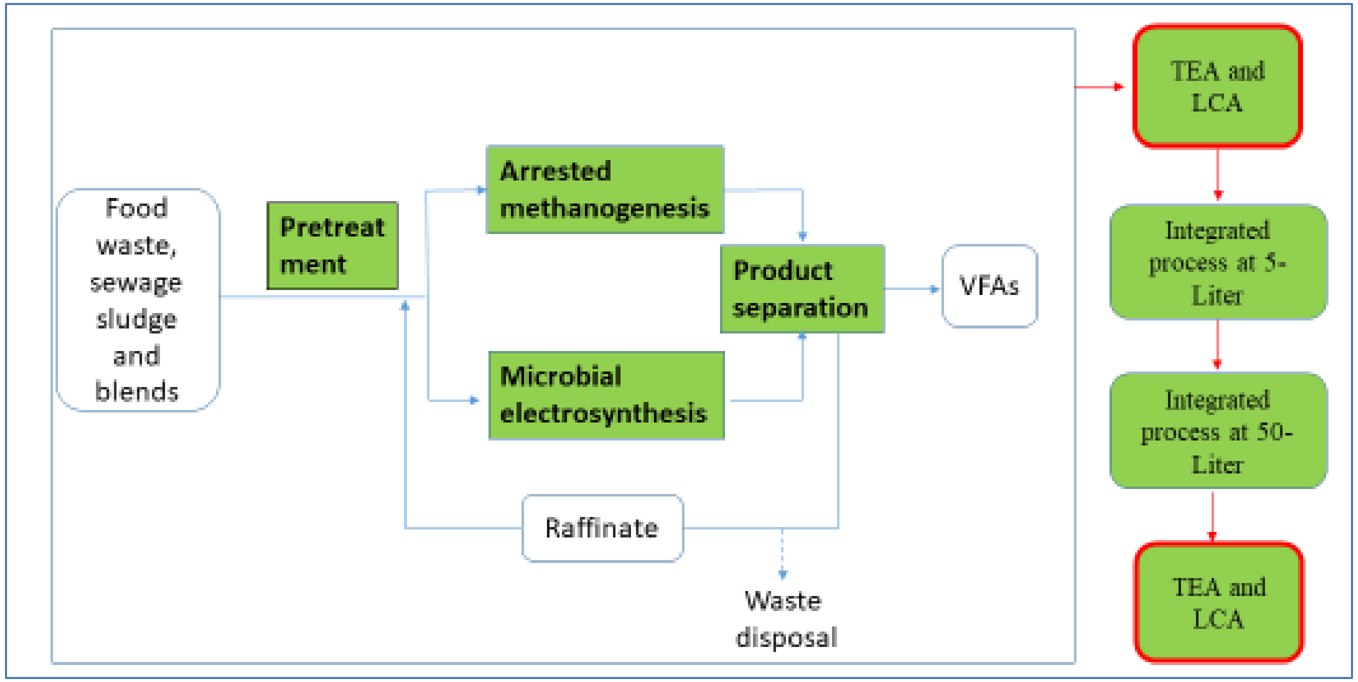
(6) Operating the integrated process continuously at a 5-Liter scale for at least 3 months,

(7) Operating the integrated process continuously at a 50-Liter scale for at least 100 hours.

1- Approach

The big challenges:

- Efficiency for converting wet organic wastes to VFAs is low.
- Titer of VFAs is not high.
- Separating VFAs from fermentation broth has not been cost-effective.
- CO_2 emitted from digestion needs to be converted to achieve carbon negative.
- A continuous process targeting VFAs production from organic wastes does not exist.



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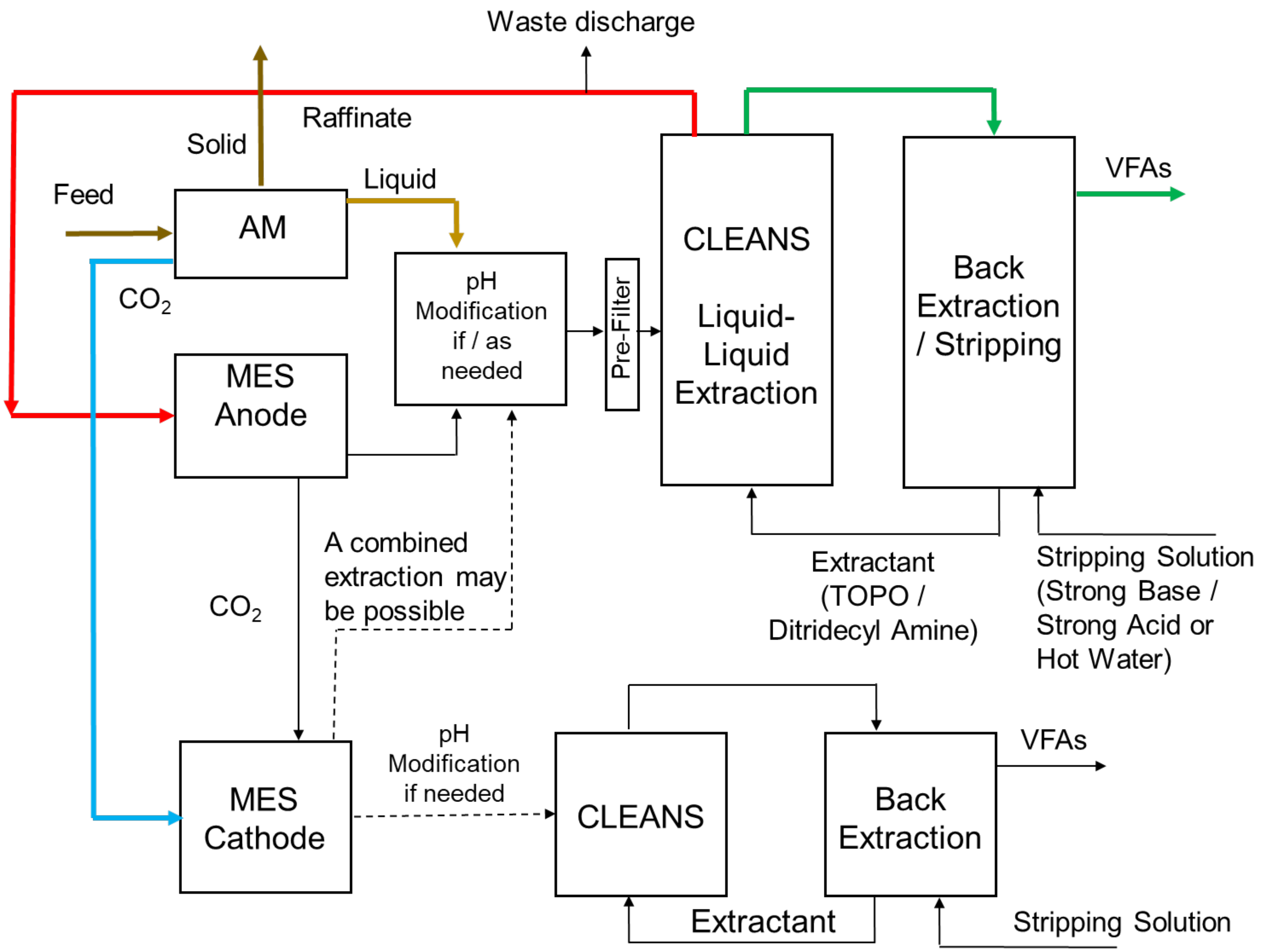
1- Approach- Updated



CLEANS – Continuous Liquid-liquid Extraction And iN-situ Separation

Management

Team members:

University at Albany, SUNY: **Task 1:** Initial Verification

Task 2: Pretreatment of feedstocks individually or combined

Task 7: Continuous operation at 5 Liter scale by the whole team

Task 8: Continuous operation at 50 Liter scale by the whole team

Argonne National Laboratory: **Task 3, 6, 7, and 8**: Use of AM to produce VFAs from untreated/ treated feedstocks, TEA and LCA

Princeton University: **Task 4, 7, and 8**: Use of MES to produce VFAs from wastes and CO_2

University of Michigan: **Task 5, 7, and 8**: Extracting VFAs from various fermentation broth

Communication:

Weekly lab meetings, monthly team meetings, other meetings scheduled as needed.

Stakeholder involvement:

Stakeholder inputs have been constantly sought.

2. Progress and Outcomes

2.1. Food waste pretreatment – Collection and handling

UAlbany dinning hall

Blended

Centrifuged

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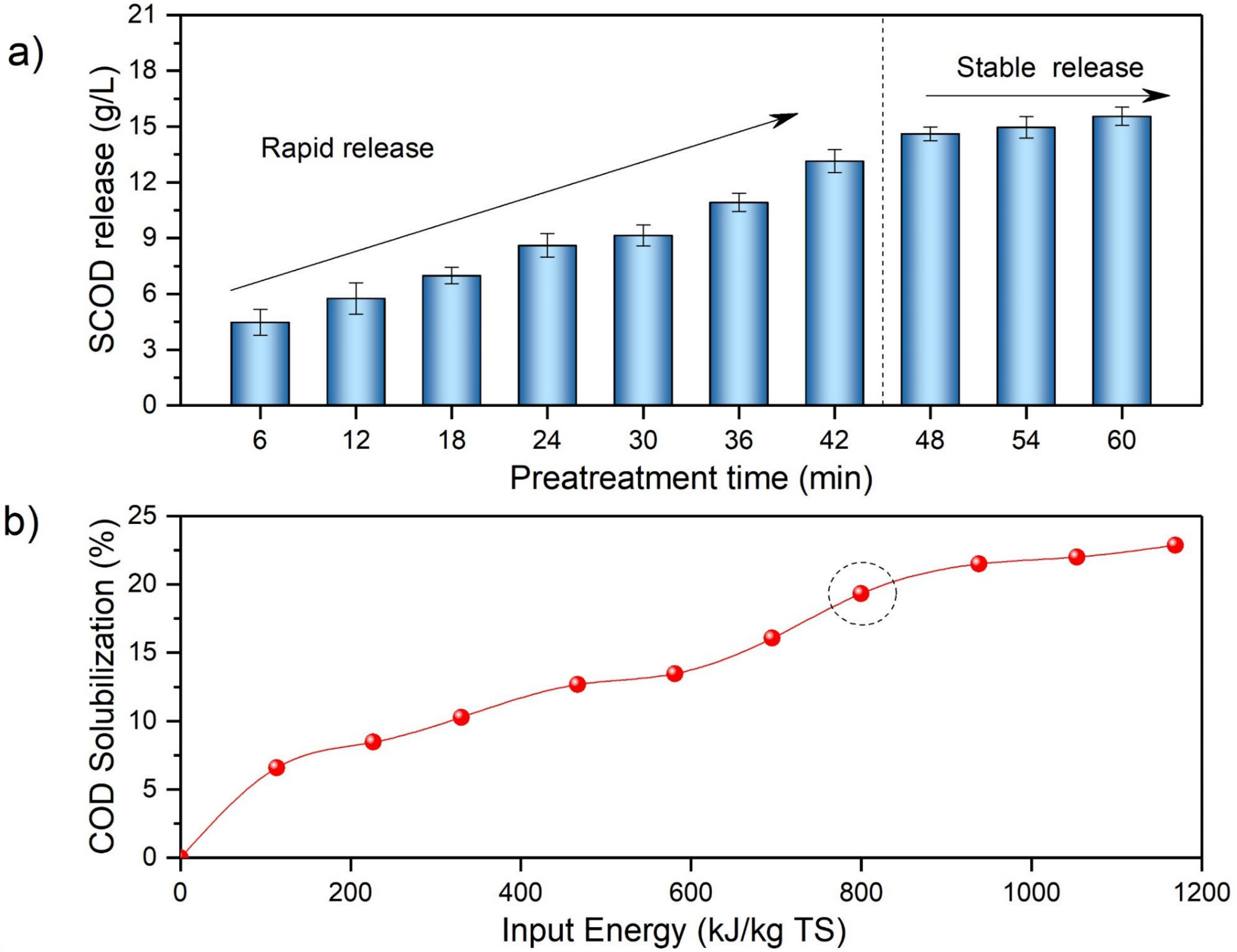
Ultrasonication on SCOD release and COD solubilization



Rapid increase of soluble COD (SCOD) took place during the first 42 minutes. The rate of increase leveled off after that time.

Total COD solubilization increased as a result of increasing energy input.

Ravi, YK., Zhang, W., Liang, Y.-N. 2023. Effect of Surfactant Assisted Ultrasonic Pretreatment on Production of Volatile Fatty Acids from Mixed Food Waste. Bioresource Technology. 368, 128340.

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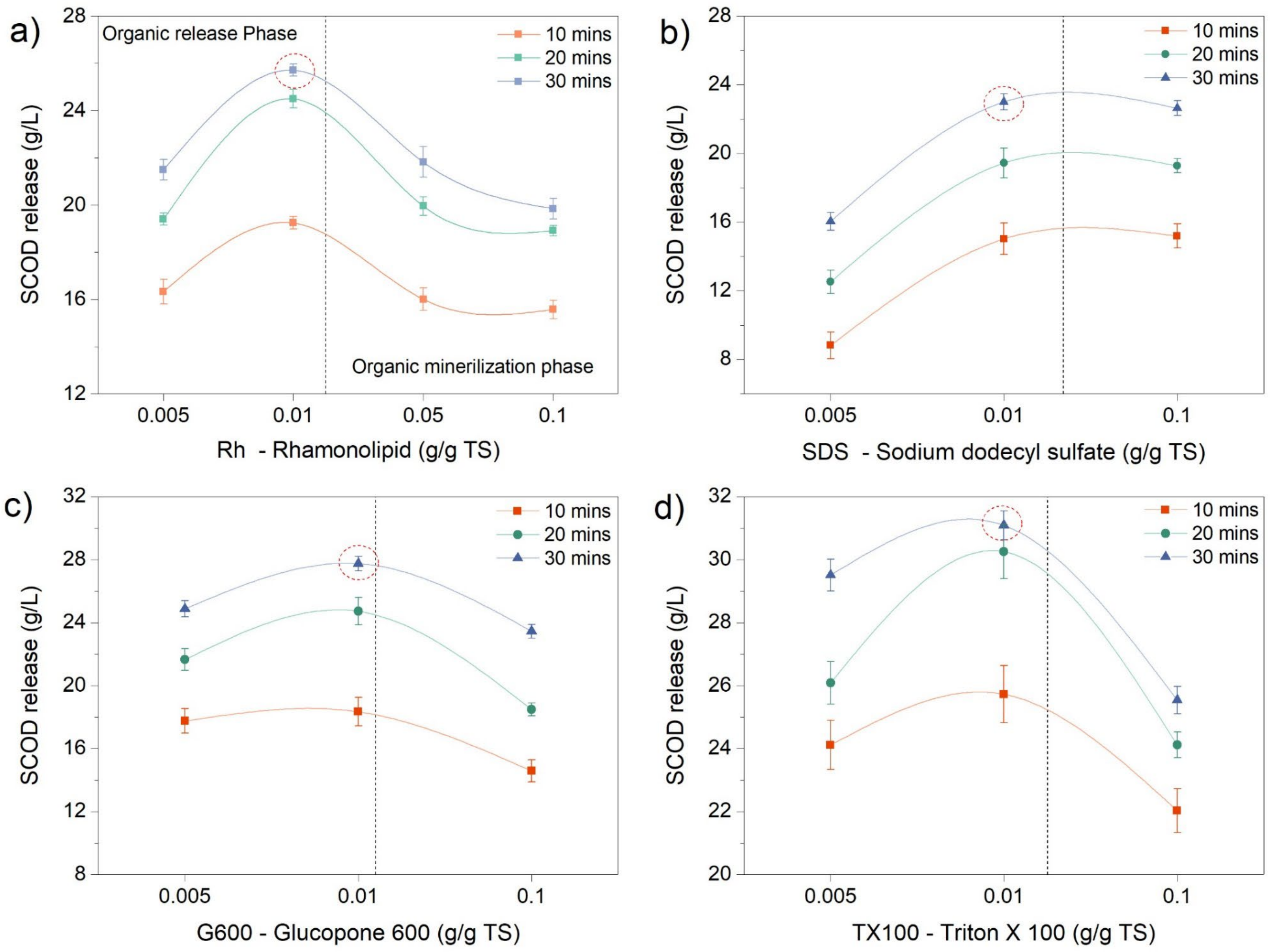
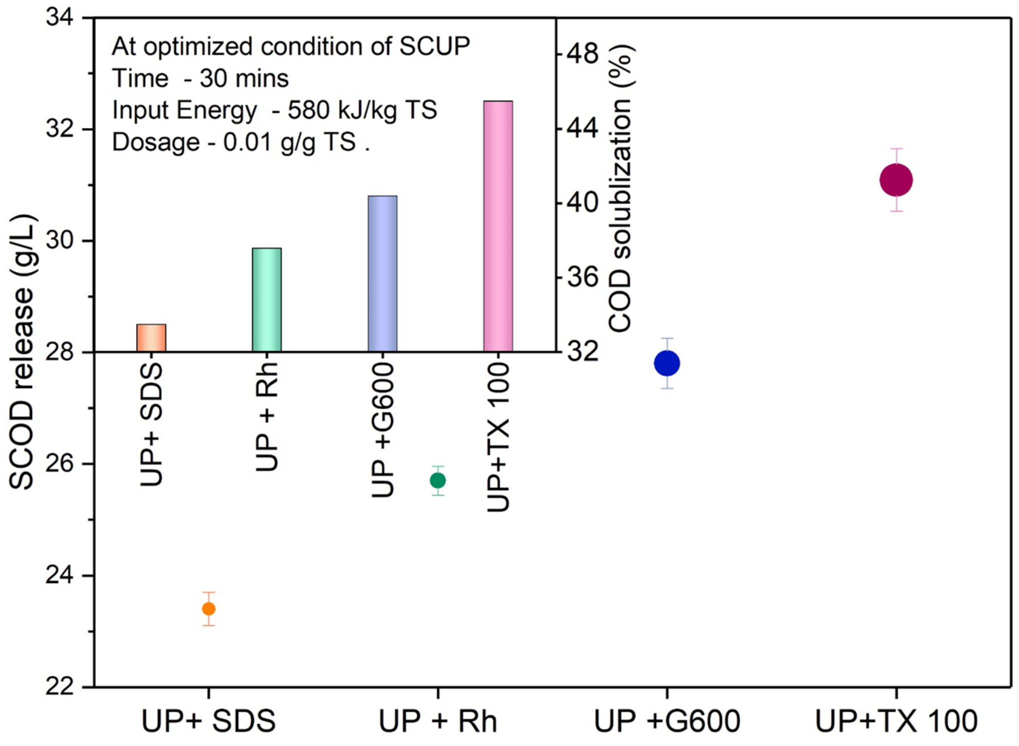
Effect of surfactant-assisted ultrasonication on SCOD release and COD solubilization





Effect of surfactant assisted ultrasonication (SAUP) is affected by time and dose of the surfactant.
Triton X100 was the best among the four surfactants tested and led to 45% of total COD solubilization in 30 min.

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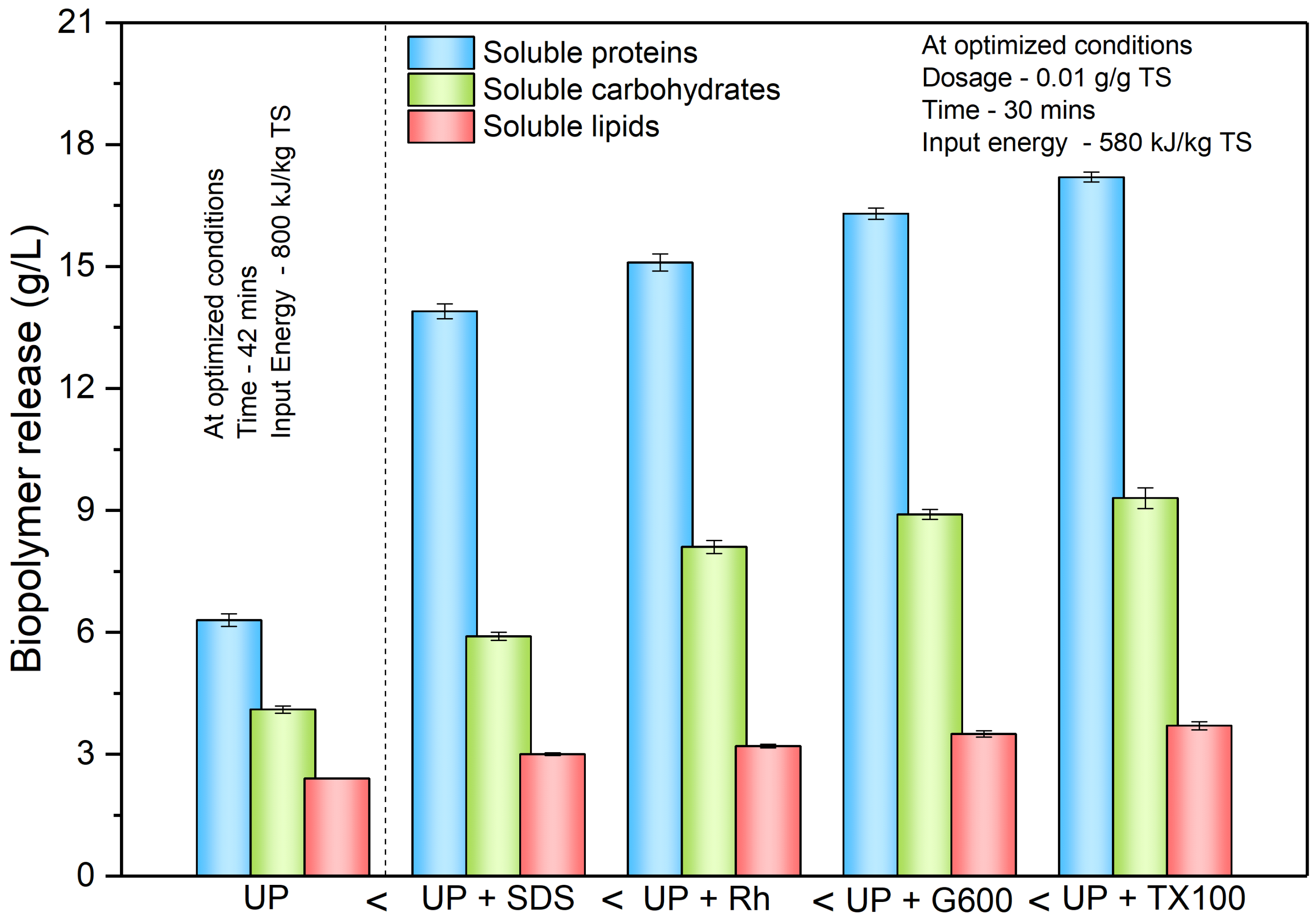
Effect of surfactant on biopolymer solubilization



Compared to ultrasonication alone, the addition of a surfactant led to increased solubilization of proteins, carbohydrates and lipids and consumed less energy.

Among the four surfactants tested, TX100 was the best.

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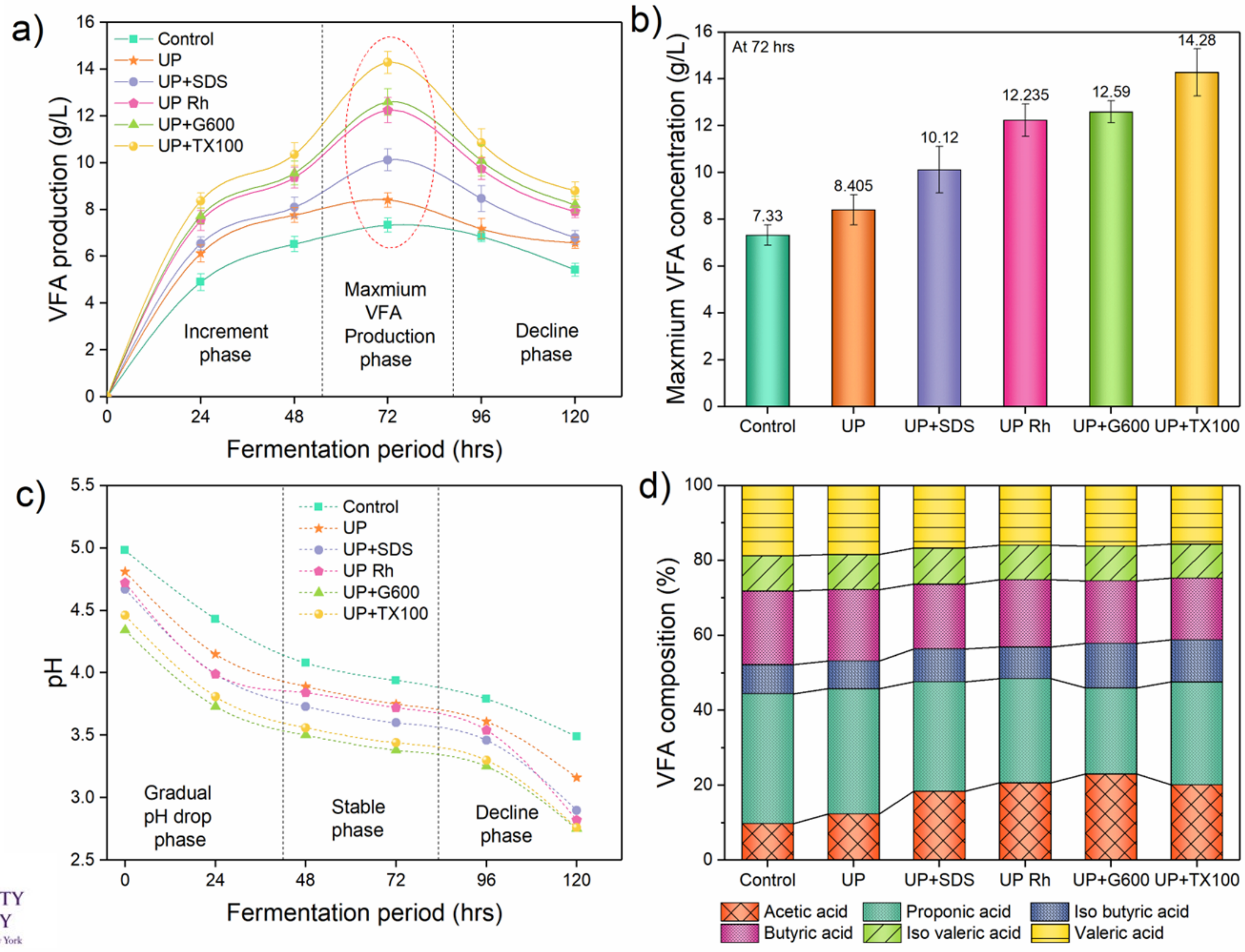
Effect of surfactant-assisted ultrasonication on VFA production-serum bottle experiment



During serum bottle experiment, VFA concentrations peaked at 72h, then decreased.

Although the pH was not controlled and adjusted, ultrasonication with TX100 resulted in 2-fold increase of VFA titer compared to those without pretreatment.

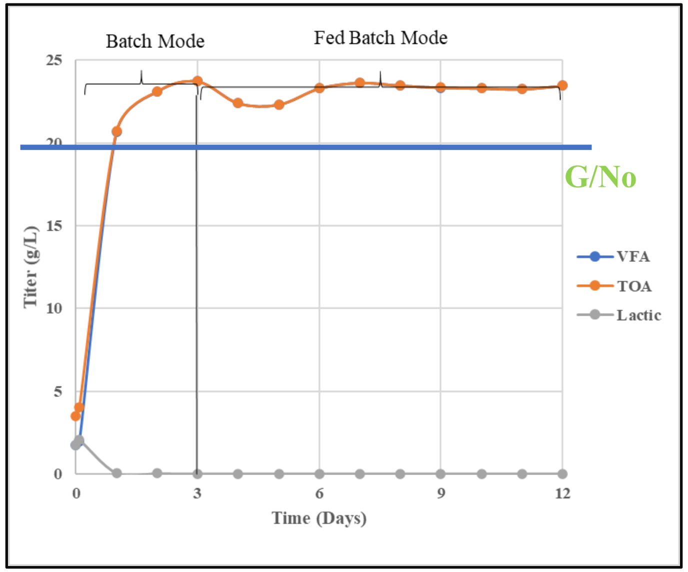
The main VFA was propionic acid followed by acetic acid.

2.2. Progress and Outcomes - Arrested Methanogenesis

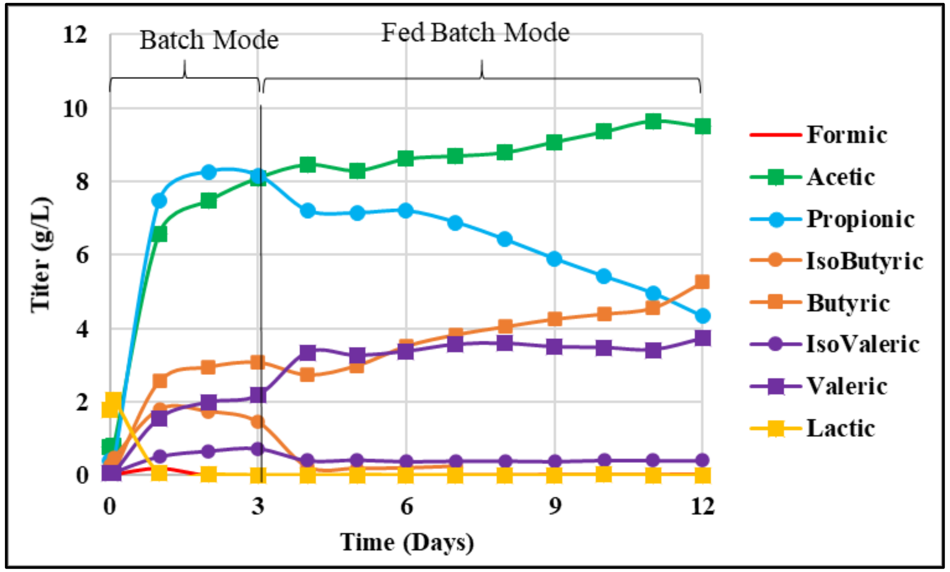
14-liter Fermenter Operation Conditions: untreated food waste

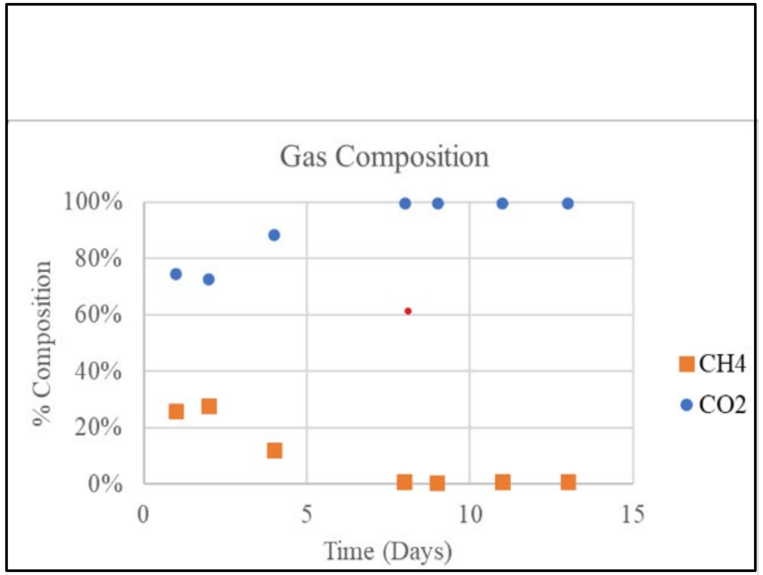
- Target pH 6.3 - 6.5 | Agitation 350 RPM | HRT 5 days
- Target TS 7% | OLR ~19.92 g COD/L Day

Organic Acid Production



Organic Acid Profile





- Met and exceeded G/No Criteria: VFA titer > 20 g/L and average methane content in biogas <10%
- AM process reached to the steady state on day 6 and stayed constant (change in performance is < 5%)

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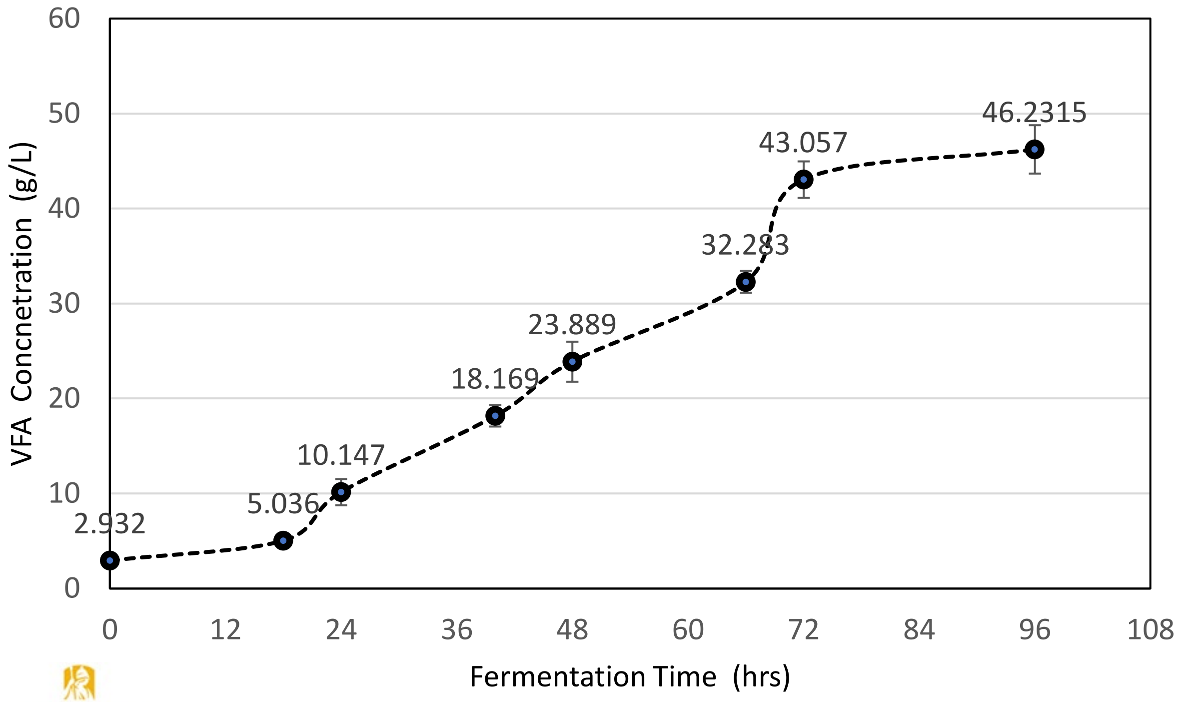
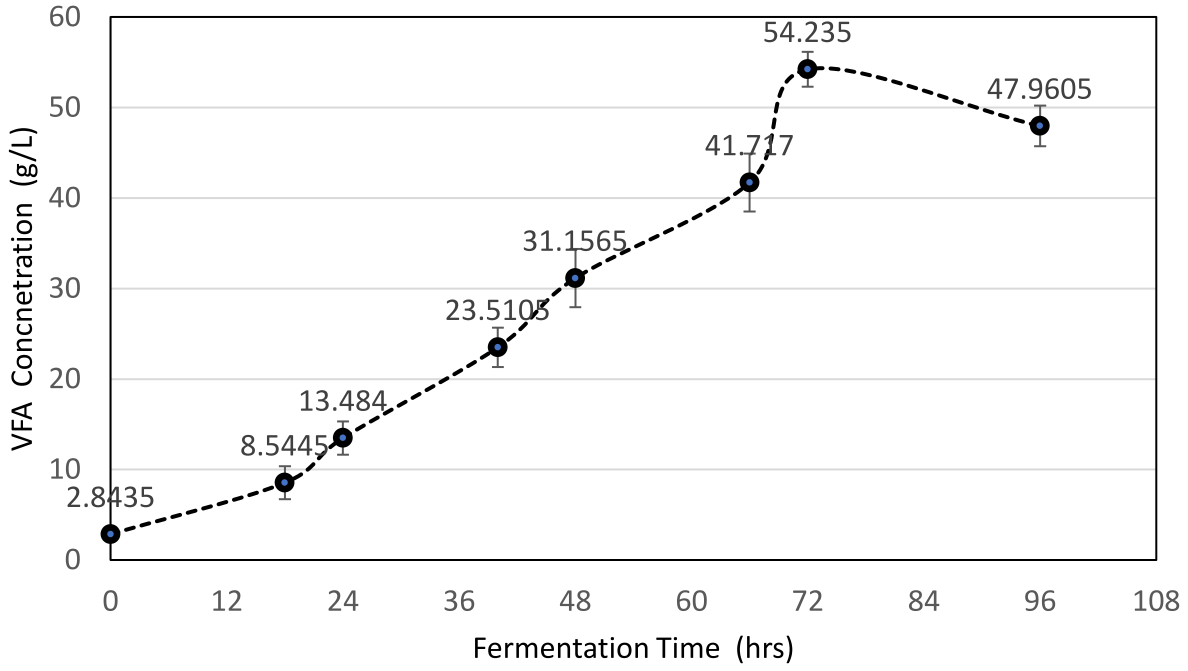
VFAs –Food waste + sludge with biochar and NPs

TS: 7 ± 0.5 %
Temp.: 37 ± 2 °C

Untreated in a 10-L fermentor
Biochar @ 100 mg/L, Iron oxide nanoparticles at 75 mg/L



Pretreated in a 10-liter fermentor
Biochar and nanoparticles both @ 5 mg/L



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Carbon conversion efficiency (CCE) comparison

Untreated in a 10-L fermentor

Biochar @ 100 mg/L, Iron oxide nanoparticles at 75 mg/L

	Formic acid	Acetic acid	Propionic acid	n-butyric acid	n- Valeric acid	TOTAL
0	0.355	1.7615	0.61	0.075	0.1305	2.932
72	1.3585	16.9105	1.3715	0.9295	22.487	43.057
Net VFAs	1.0035	15.149	0.7615	0.8545	22.3565	40.125
% of total VFAs	2.50	37.75	1.90	2.13	55.72	
VFA to COD conversion factor	0.348	1.066	1.512	1.816	2.037	
VFA as COD	0.349218	16.148834	1.151388	1.551772	45.5401905	64.7414
VFA as COD	64.7414025					
TCOD	121.9					
CCE	0.53					

Pretreated in a 10-liter fermentor

Biochar and nanoparticles both @ 5 mg/L

	Formic acid	Acetic acid	Propionic acid	n-butyric acid	n- Valeric acid	TOTAL
0	0.162	1.6055	0.06	0.119	0.897	2.8435
72	3.069	26.8895	0.8985	2.7635	20.6145	54.235
Net VFAs	2.907	25.284	0.8385	2.6445	19.7175	51.3915
% of total VFAs	5.66	49.20	1.63	5.15	38.37	
VFA to COD conversion factor	0.348	1.066	1.512	1.816	2.037	
VFA as COD	1.011636	26.952744	1.267812	4.802412	40.1645475	74.1991 5
VFA as COD	74.1991515					
TCOD	116.1					
CCE	0.64					

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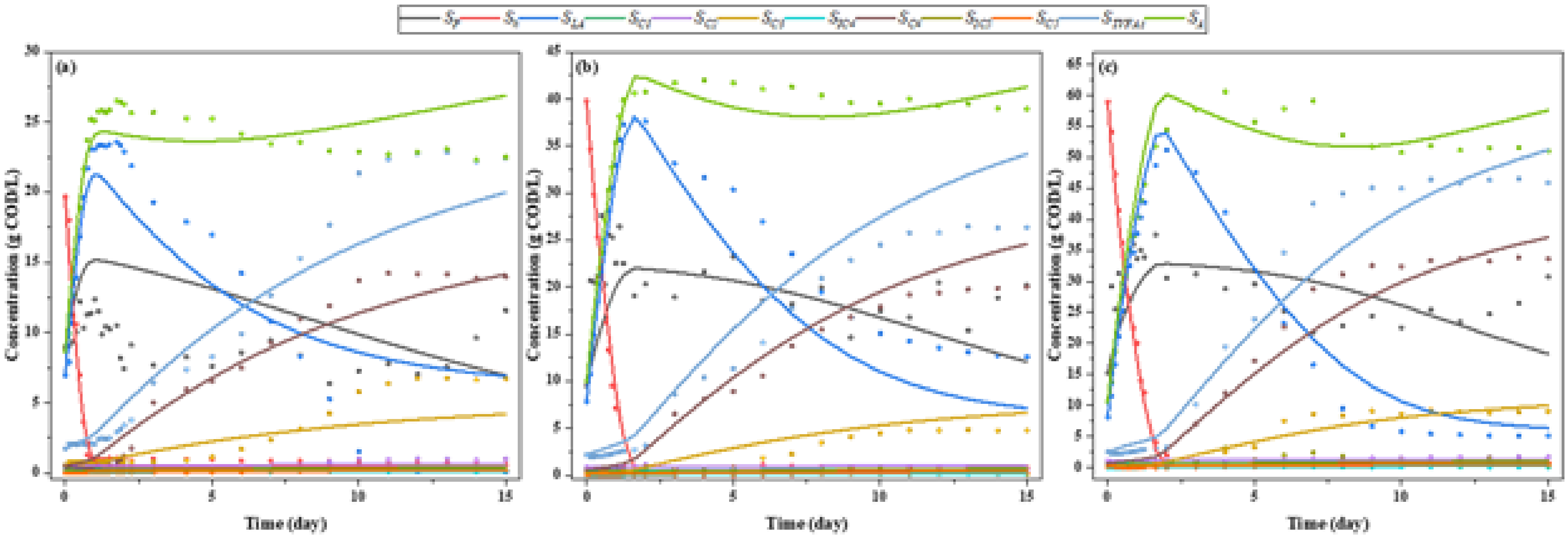
Process modeling

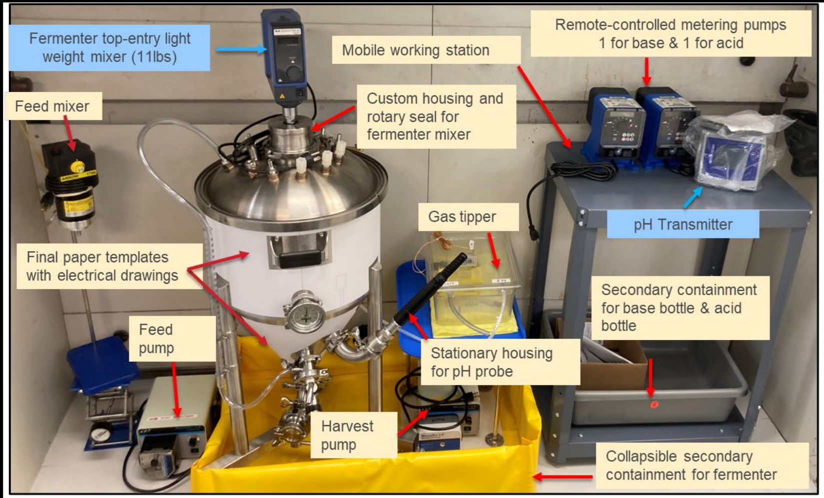


Comparison of experimental values (points) and kinetic models simulated values (lines) for the batch Arrested Methanogenesis Digester Operation (data from digesters run with cheese whey/brewery waste streams with three substrate concentrations)

Kinetic models adequately describe the digestion performance of batch AM process and accurately predict the transitory nature of the soluble hydrolysate and lactic acid in AM, and eventually produce VFAs ($R^2 \geq 0.95$)

Arrested Methanogenesis
Process Scale-up from 14 liters to 50 liters

- The project team worked with Argonne Environmental Safety Health (ESH) team and received the authorization to run the 50-liter (14-gal) fermenter with food waste.
- The team conducted dry-run experiments with water at 37-55 °C
- The project team is ahead of the scheduled activities and started to run 50-liter fermenter with food waste at different organic loading rates and retention time (February 2023).

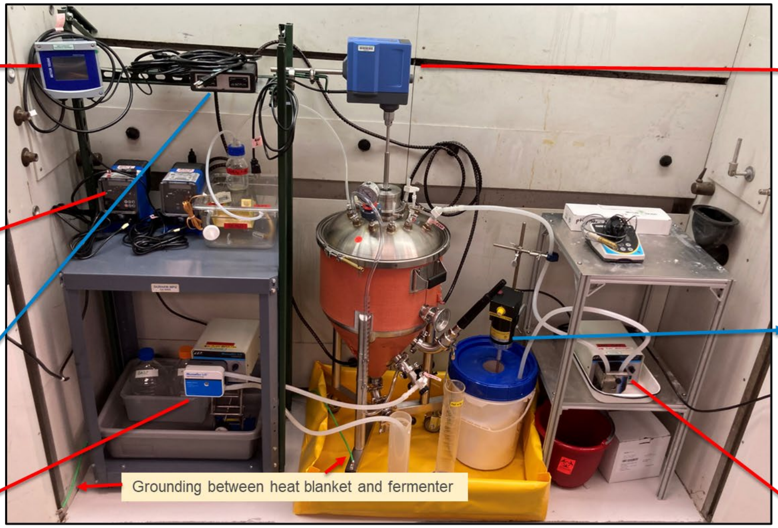


Set-up of 50L operation inside designated fume hood of BSL-2 lab

**All items in blue (fermenter mixer, PID controller, transmitter) will be mounted on custom frame manufactured by Argonne Central Shop. Aim is to have all parameter controller (pH, mixing RPM, and temperature) visible, accessible and separated from set-up to avoid damage and electrical complication.*

Custom Made Silicone Rubber Heater & PID controller.

**Heaters are kept flat until ready to peel off backing paper for installation.*



Final set-up of 50L operation inside designated fume hood of BSL-2 lab

**All electrical auxiliary devices are connected and turned on to check integrity (side pictures and videos). Heater PID controller (15 amps) turned on after grounding work. All devices plugged in at the same time after electrical work to increase power voltage (scheduled).*

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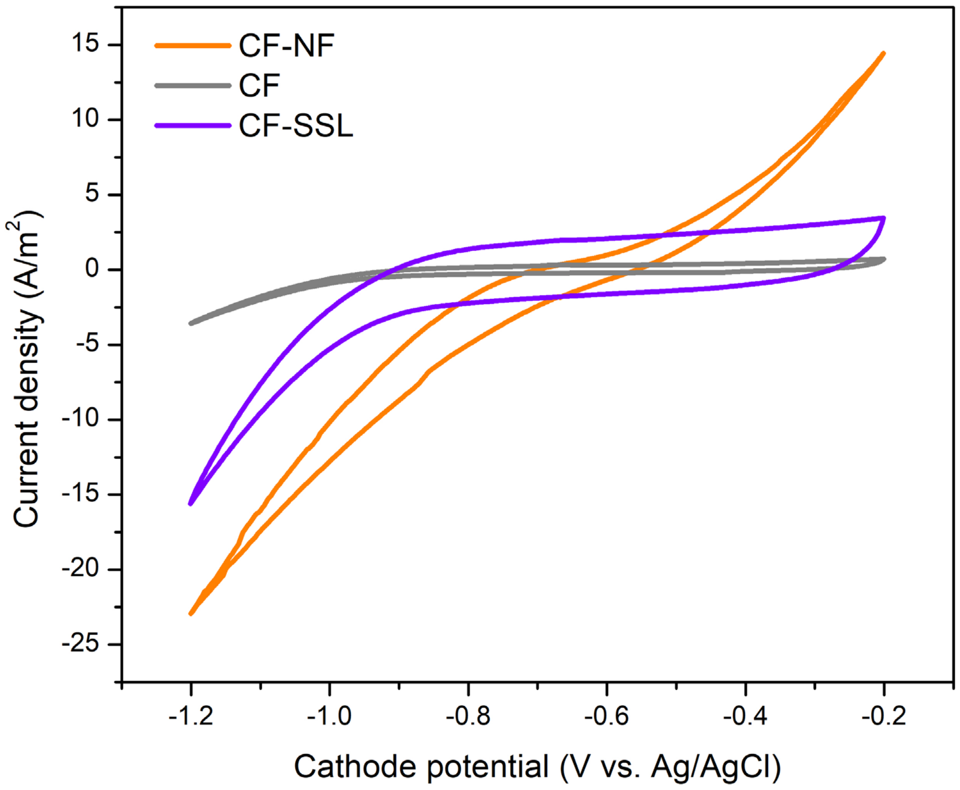
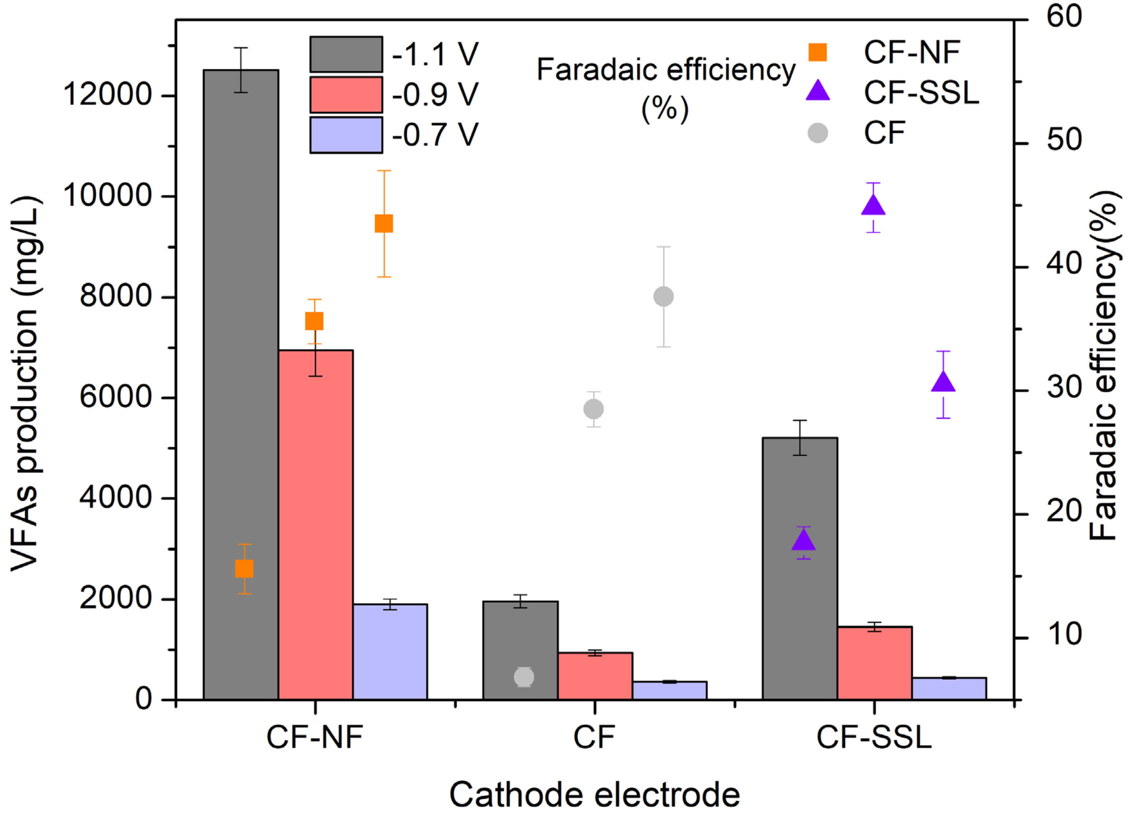
2.3. Progress and Outcomes - Microbial Electrosynthesis

- Low-cost scalable nickel foam cathode to enable H_2 evolution for acetogen growth
- H_2-mediated electron transfer is more efficient than direct contact
- VFAs production and current density increased significantly with lower cathode potential





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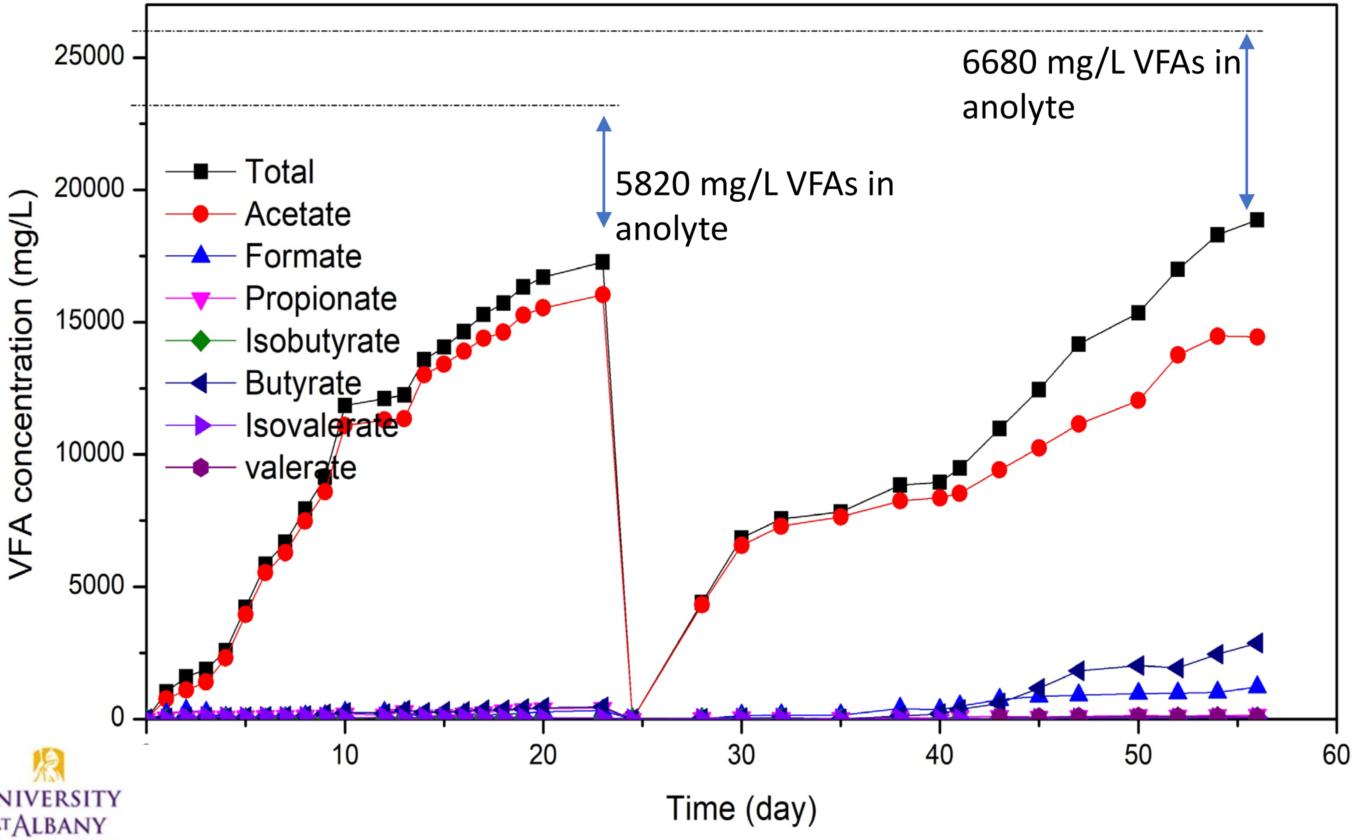
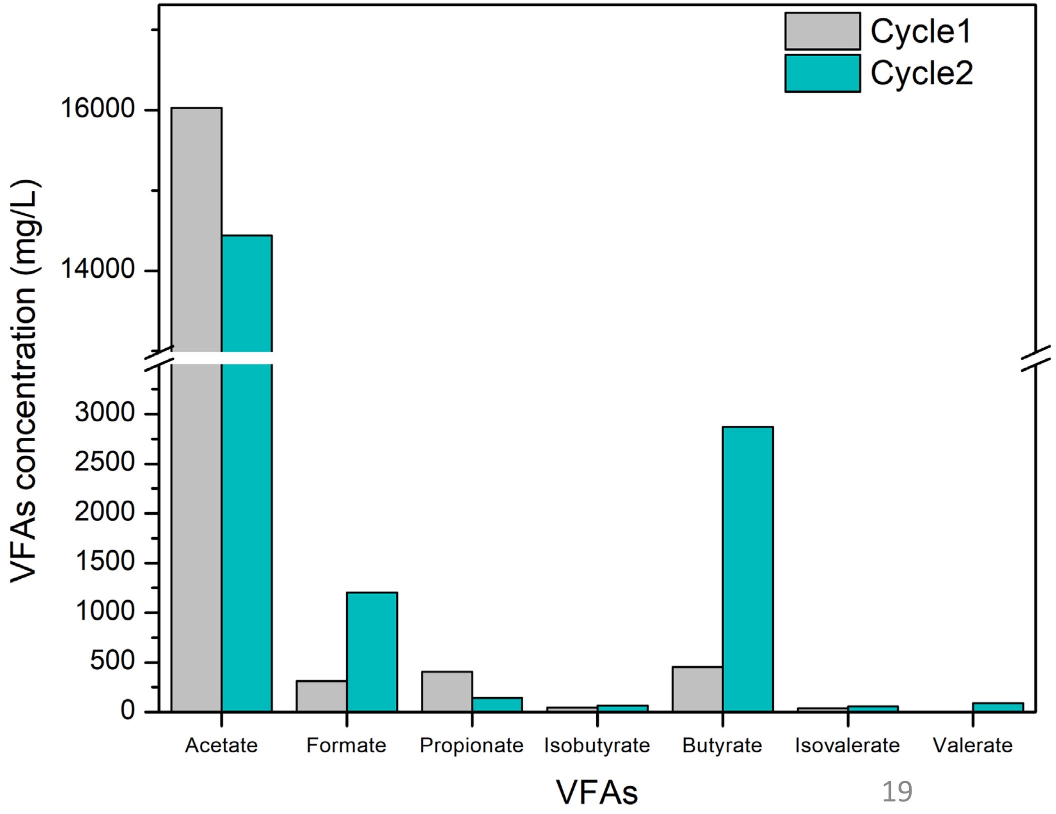
High titer VFAs were generated during long term operation of MES with nickel foam cathode

- Applied cathode potential: -1.1 V vs. Ag/AgCl (3M KCl)
- VFAs titer in final catholyte is 17,270 ~18,870 mg/L.
- VFAs diffusion was found in anolyte (5,820~6,680 mg/L in final anolyte).





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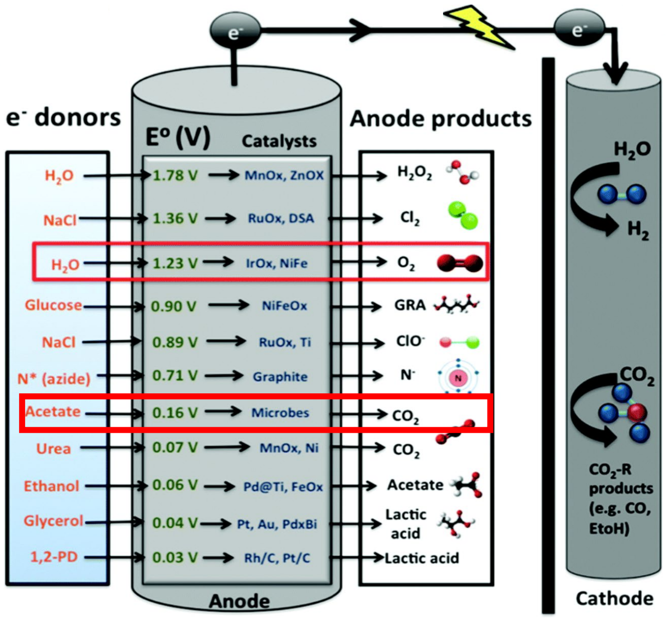
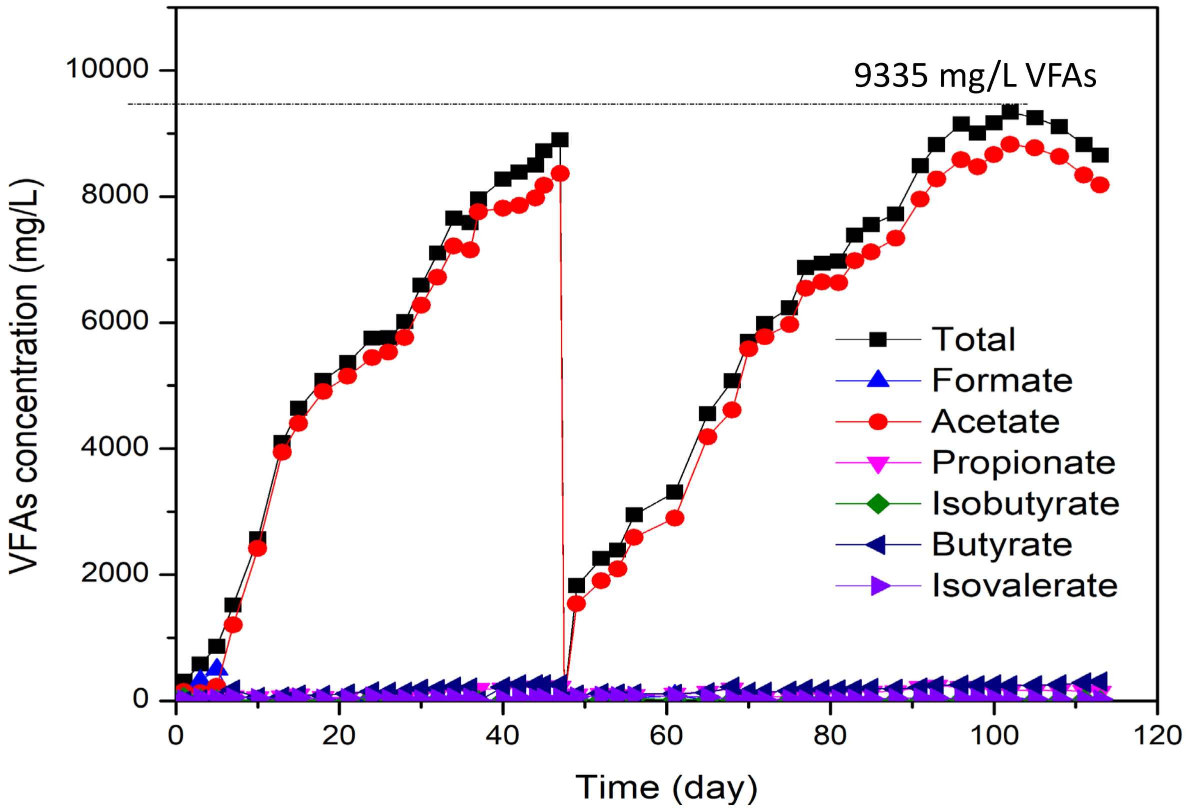
Bioanode MES for food waste treatment + biocathode for VFAs production from CO_2

- Most MES used abiotic anode, while we tried bioanode-biocathode coupled reactions that reduced electricity consumption.
- The highest VFAs titer in bioanode MES was 9,335 mg/L, the energy consumption for acetate production was ~9.95±0.4 kWh/kg (saves ~70% electric energy compared with abiotic anode MES).



J. Jack, et al. Green Chemistry,2021



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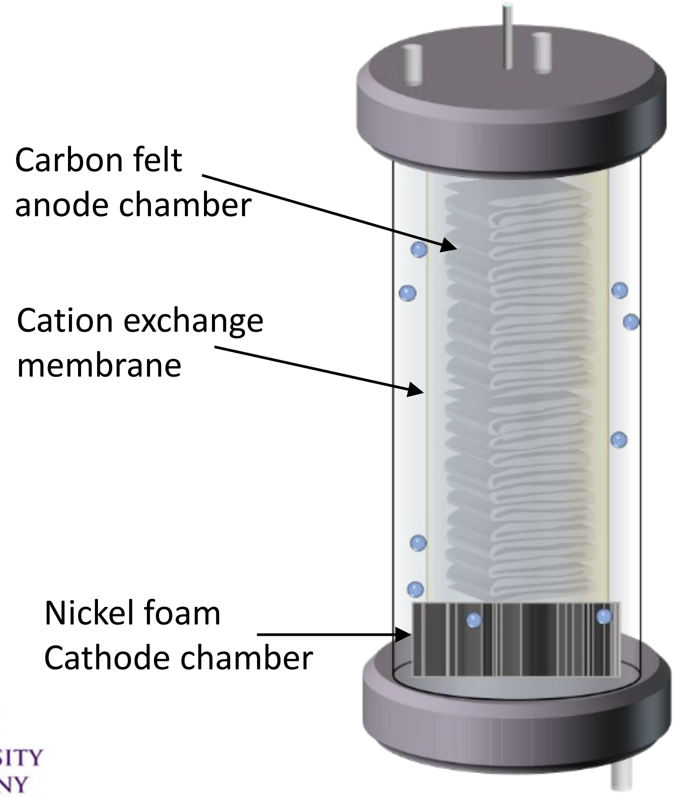
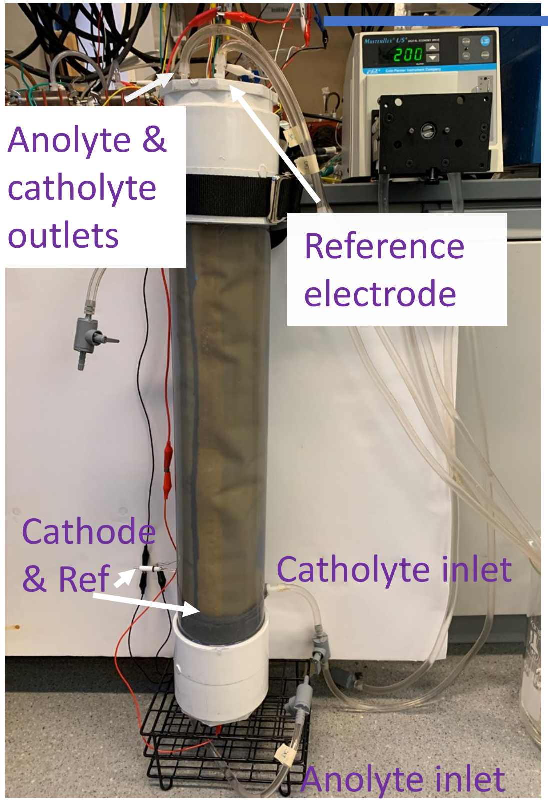
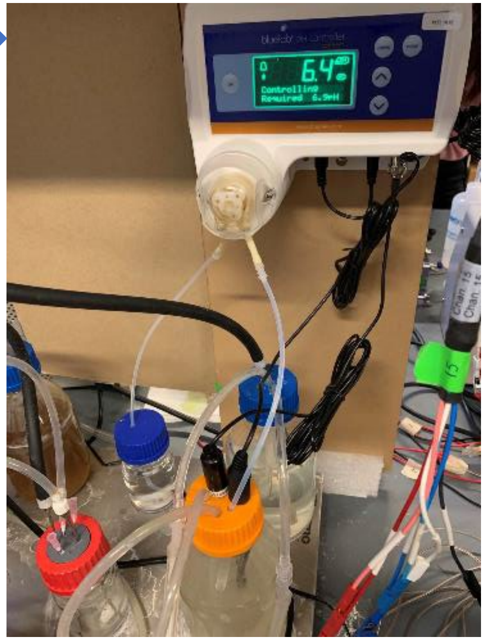
A 6L bench pilot tubular MES was operated for food waste treatment and VFAs production

- A 6 L tubular MES was built for scale up
- Carbon felt was used as anode in the inside chamber and nickel foam as cathode in the outside chamber.
- pH auto-controller was set for maintaining optimal condition.







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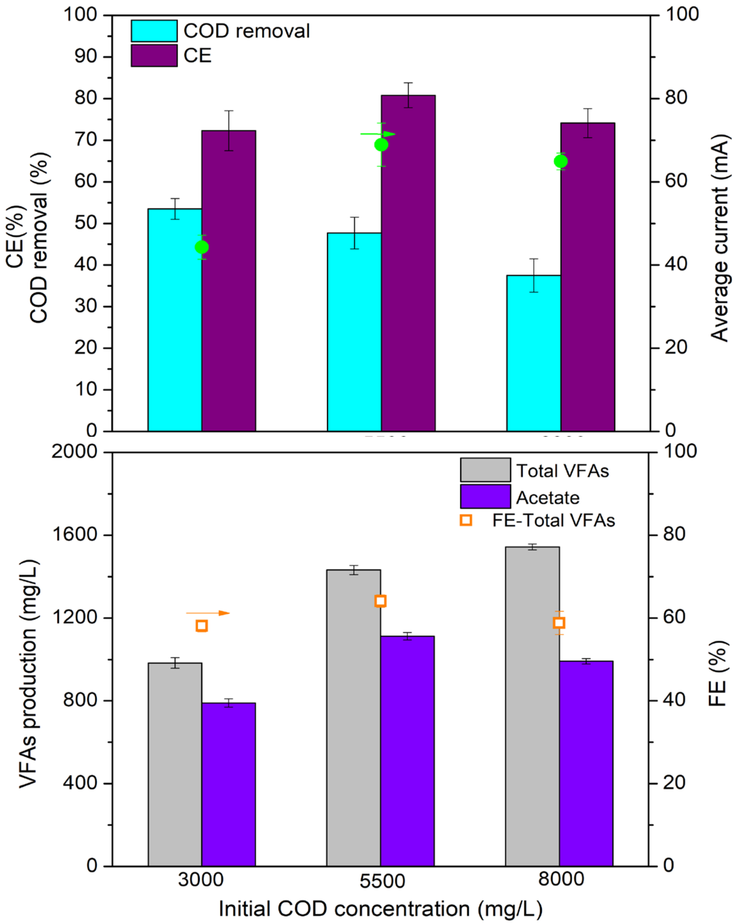
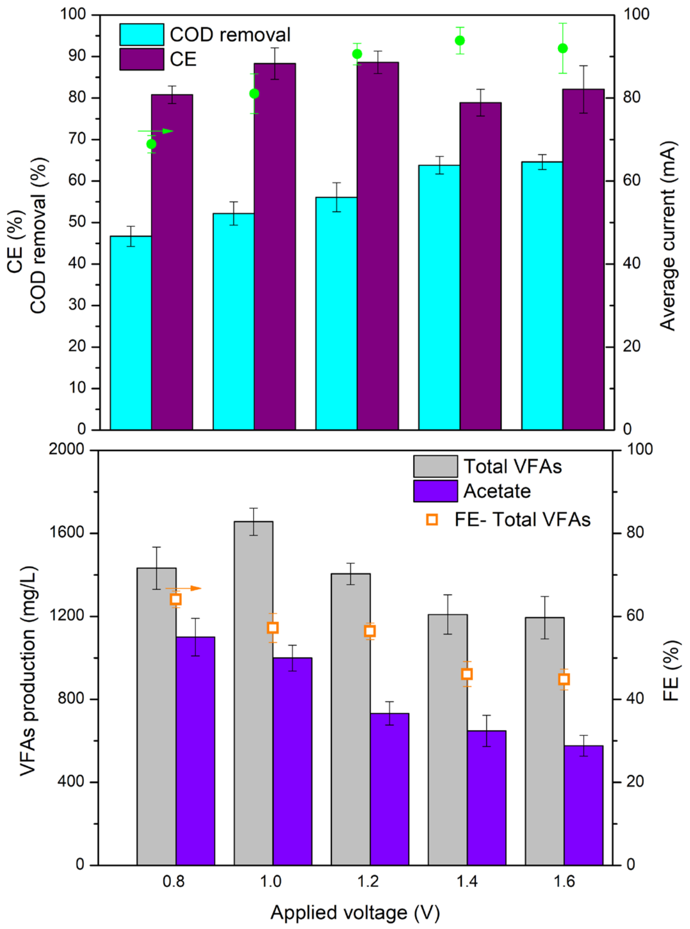
Optimized initial food waste COD and applied voltage

- Operational parameters including initial food waste COD and applied voltage were optimized.
- Optimal condition was obtained with initial COD concentration of 5,500 mg/L and 1.0 V.
- The highest VFAs titer of 1,656 mg/L was obtained in 10 days batch mode.

Optimize food waste COD concentration (applied 0.8 V)



Optimize applied voltage (COD concentration 5500 mg/L)



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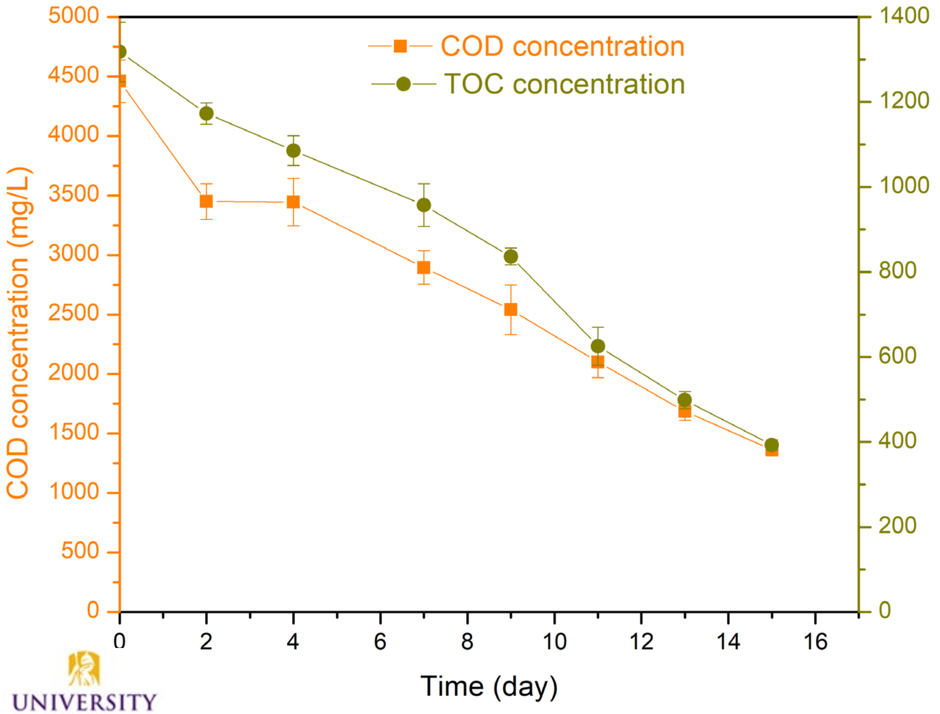
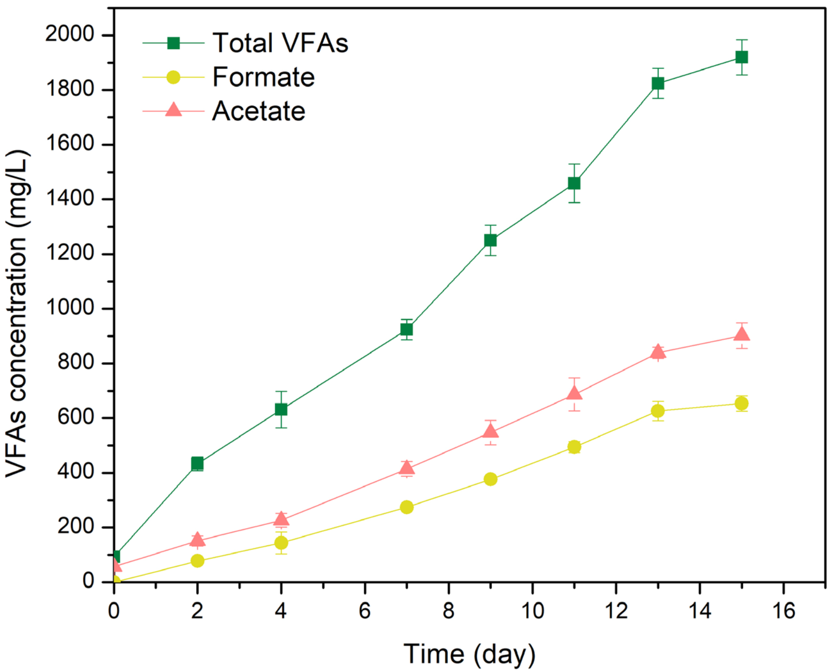
Apply permeate solution from CLEANS in the MES anode

- Applied voltage 1.0 V, averaged current 83 mA
- COD removal : 69.4% (vs. 53% for food waste with similar initial COD and cell voltage)
- VFAs production (1,920 mg/L) was obtained in cathode with carbon conversion efficiency of 119% in 15 days batch mode.

$TOC_{VFA\ cathode} / TOC\ change_{anode} = 119\%$





Performance	
COD removal	69.4%
TOC removal	70.2%
Coulombic efficiency	89.2%
VFAs production	1920 mg/L
Faradaic efficiency	51.5%
Carbon conversion efficiency	119%

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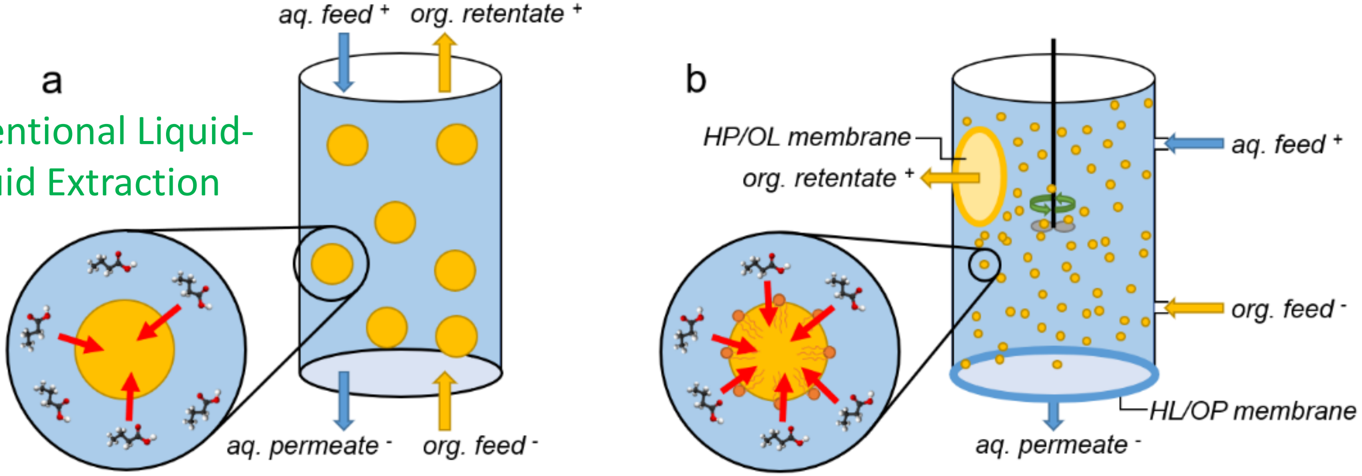
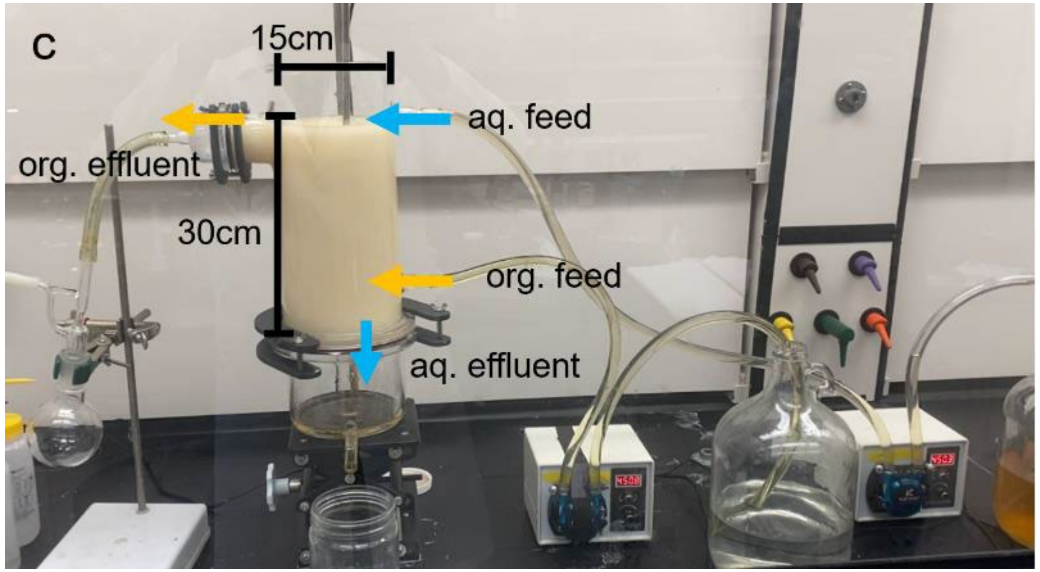
2.4. Progress and Outcomes - Product separation

Novel CLEANS Process

Conventional Liquid-Liquid Extraction





Scaled up CLEANS process for continuous extraction

We developed a continuous liquid-liquid extraction system termed CLEANS that utilizes emulsions to significantly enhance extraction efficacy.

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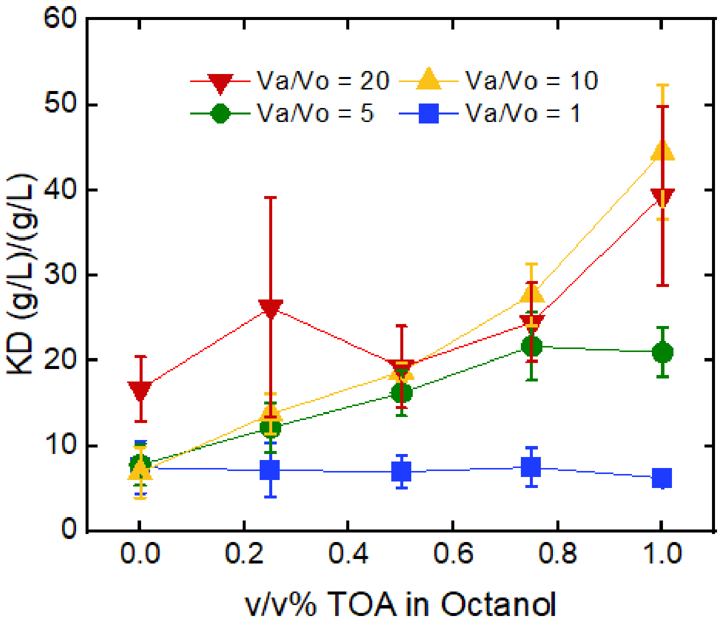
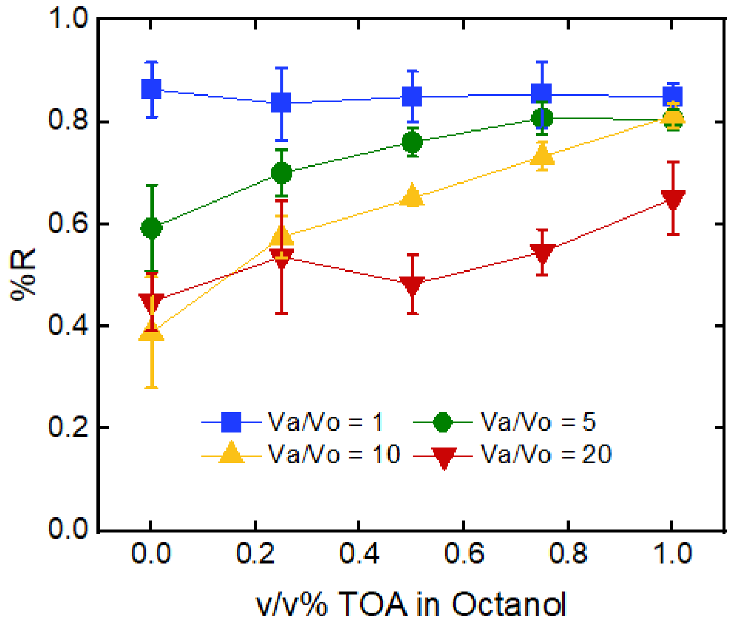
2.4. Product separation-cont.





K_D = g/L of VFAs in extractant /g/L of VFAs in the raffinate

V_a / V_o: Ratio between the aqueous (feed) and organic (extractant) phases.

- Demonstrated K_D values > 40 for all VFA's using actual samples from ANL under continuous operation (Flux > 100 L / m^2/ hr) at the 5 liter scale. This is an order of magnitude improvement over what was proposed in our work (K_D = 4)
- This K_D value exceeds the highest ever reported separation efficiencies for VFA extraction by over an order of magnitude
- The system allows for ~ 80% VFA removal in a single pass, even with a feed to extractant ratio of 10:1.
- We identified trioctyl amine as the ideal extractant to achieve high recovery in a single CLEANS pass. The large boiling point differences between trioctyl amine and different VFA's allow for low-cost, low-energy distillation for extractant recovery (stripping).

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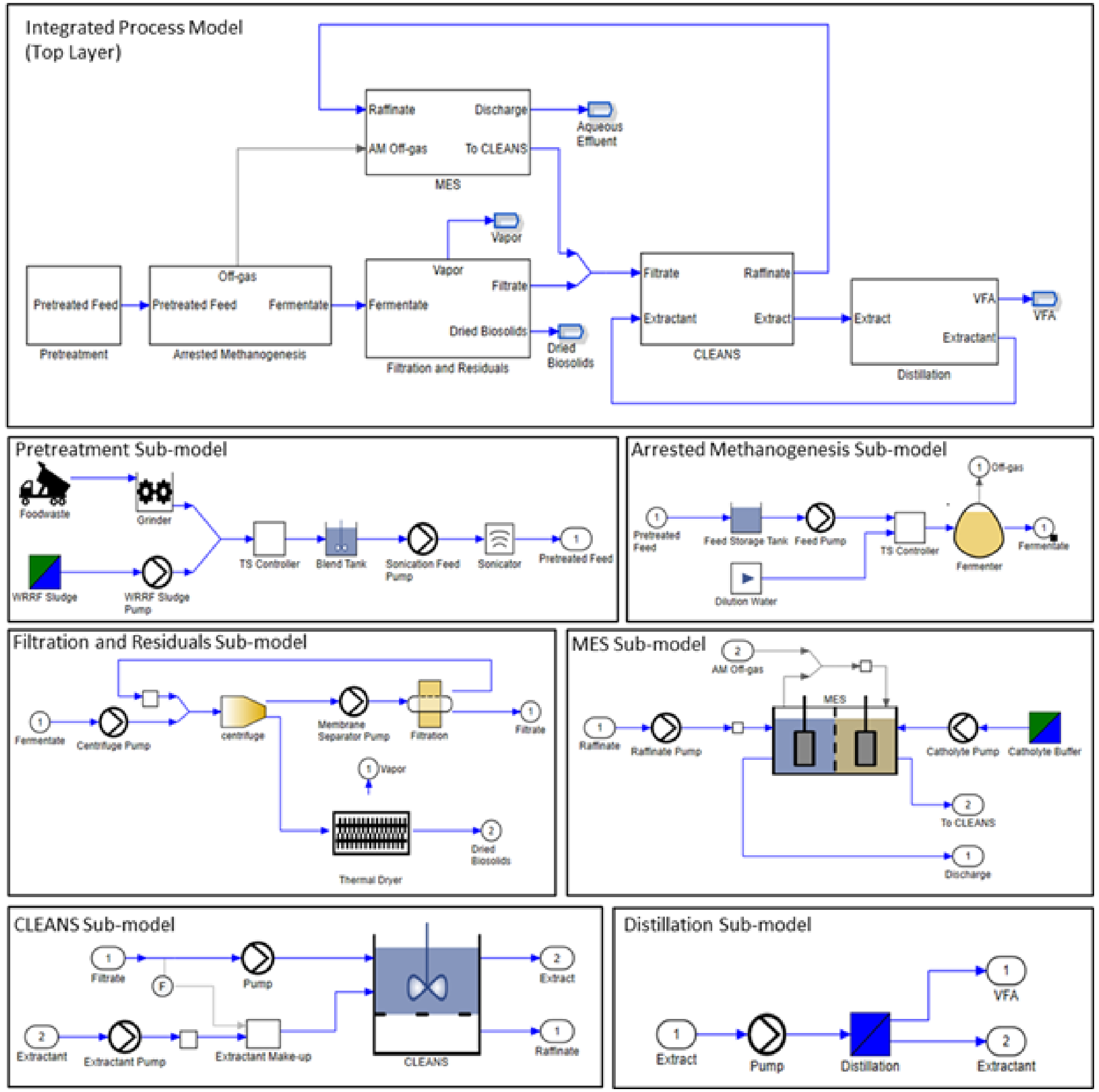
2.5. Progress and Outcomes -TEA and LCA Task

- The top layer of the model shows the flow paths of material between each unit process.
- Each block of the top layer contains a more detailed sub-model that includes individual equipment blocks connected into any reasonable configuration.
- Each piece of equipment includes embedded code for calculation of mass/energy balances, operating/capital resource requirements, and associated costs.



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Selected Process Model and TEA Findings

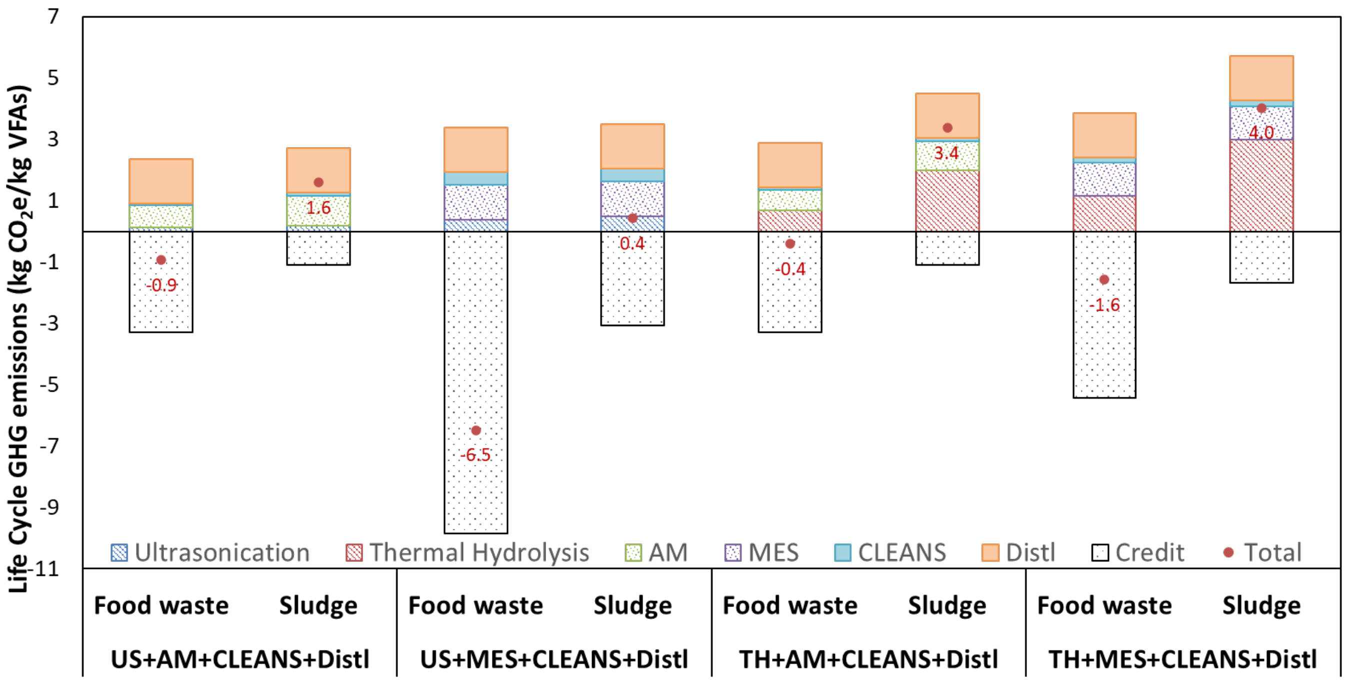
- Inclusion of MES (as shown in previous slide) improves COD removal, direct CO_2 emissions, and VFA production

- Distillation of volatile fatty acids from CLEANS extractant is predicted to be feasible:
  - Efficient recovery of VFA in the light phase
  - Efficient recovery of extractant in the heavy phase
  - Capital and operating costs are on the same order as the other unit processes

- Inclusion of thermal drying results in a lower predicted 30-year Net Present Cost at land application costs greater than $70/tonne

Life cycle GHG Emission Comparison of Different Pathways

- TEA and LCA results are used to guide experimental decisions
  - Feedstock selection:
    - **Food waste** could provide higher avoided emission credit than wastewater sludge. Using food waste as the feedstock to produce VFA could potentially have lower GHG emissions due to the high credit by reducing food waste in landfill
  - Pretreatment technology selection:
    - Hydrothermal and ultrasonic treatments are two candidates we investigated. LCA results show that **ultrasonication** is less energy intensive than hydrothermal treatment. Therefore, ultrasonication is selected in the integrated system



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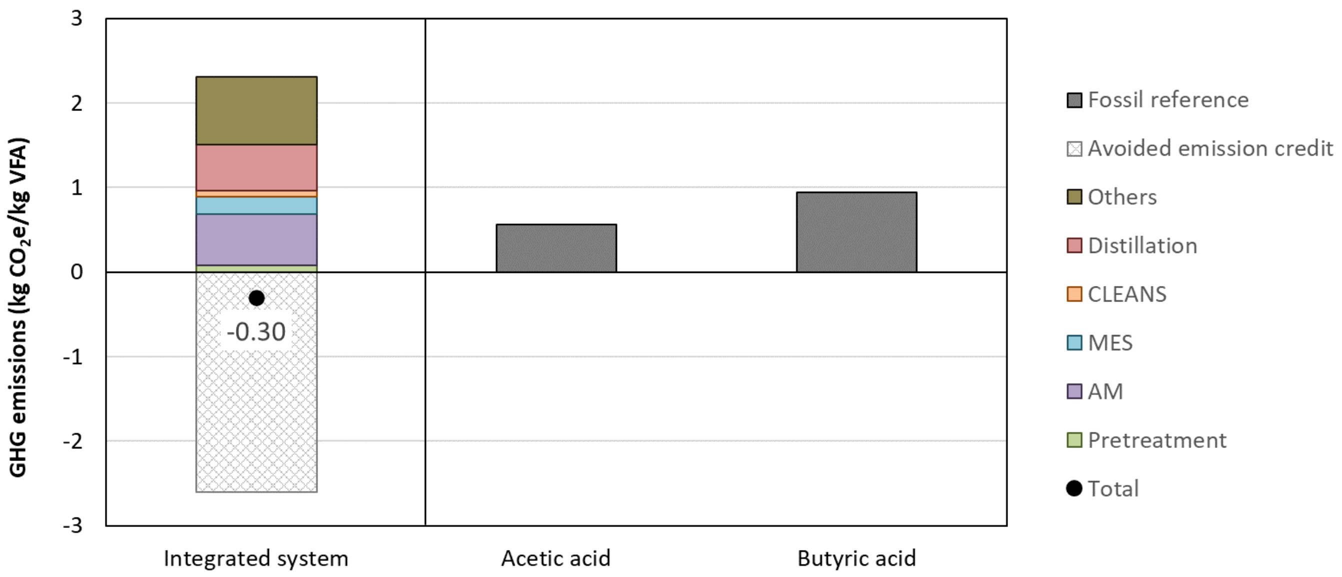
GHG Emissions From Integrated System

- The integrated system configuration:
  - MES is integrated in-series after AM to convert remaining organic carbon to VFA product to boost overall carbon conversion efficiency
- The integrated system, which generates VFA mixture, has **lower GHG emissions** when compared to acetic acid and butyric acid production, which are two major components of VFA mixture.



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3 – Impact

- Success of this project will contribute significantly to DOE BETO's mission to develop and transform domestic renewable biomass resources into commercially viable, high-performance biofuels, bioproducts, and biopower.
- Utilization of organic wastes for VFAs production diverts these materials from being disposed at landfills.
- Integration of all process blocks successfully will lead to a carbon-negative process that can be operated continuously.
- A cost-effective modular system can be developed and deployed at where wastes are generated.
- Results from this project will be disseminated through peer-reviewed publications, conference presentations, seminars and conferences organized by the team to the scientific community and broad stakeholders.

Summary

- The optimal pretreatment of the mixture of food waste and sludge using ultrasonication and Triton X100 led to 2-fold increase of VFA titers.
- Compared to untreated feedstocks, the pretreated feedstocks yielded higher VFA titers and higher carbon conversion efficiency, but demanded less amendment of biochar and nanoparticles.
- The highest VFAs titer in abiotic anode MES was obtained at 17.3 ~18.9 g/L with carbon felt/nickel foam composite electrode.
- 6-L tubular MES reactor was built and operated parameters were optimized; the VFAs production in MES treating permeate solution from CLEANs was 1.9 g/L with carbon conversion efficiency of 119%.
- All milestones and Go/No go decision points are met.
- The whole project in on track.

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Quad Chart Overview

Timeline

- *Project start date: 10/01/2019*
- *Project end date: 05/31/2023*

	FY22 Costed	Total Award
DOE Funding	*(10/01/2021 – 9/30/2022)* $684,315.00	*$2,698,541.00*
Project Cost Share *	$179,880.00	$709,550.00

TRL at Project Start: 2

TRL at Project End: 4

Project Goal

The overarching goal of this project is to develop an integrated and efficient process for converting wet organic wastes to volatile fatty acids (VFAs).

End of Project Milestone

The conversion efficiency of carbon in food waste and sewage sludge is enhanced by at least 50% and/or the disposal costs of these two wet waste streams are decreased by at least 25%.

Funding Mechanism

FOA: DE-FOA-0002029

Topic area: AOI 9: Rethinking Anaerobic Digestion Year: 2019

Project Partners*

- Partner 1: Argonne National Laboratory
- Partner 2: Princeton University
- Partner 3: University of Michigan

*Only fill out if applicable.

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Acknowledgment

- **BETO:** Drs. Chenlin Li, Katie Davis
- **UAlbany**: Yasir Muhammad; Drs. Yukesh Ravi, Quan Zhang, Weilan Zhang
- **ANL**: Drs. Meltem Urgun Demirtas, Haoran Wu, Troy Hawkins, Hui Xu, Uisung Lee, Yuan Li, Jingyi Zhang
- **Princeton University:** Dr. Jason Ren, Yanhong Bian
- **University of Michigan**: Dr. Anish Tuteja, David Speer
- **City College of New York**: Dr. Alex Rosenthal

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Additional Slides

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Responses to Previous Reviewers' Comments

1. Fate of digestate from the AM process: presence of organic content and PFAS.

Response: The digestate after AM could be converted to fertilizer after thermal drying; Treatment of PFAS in digestate through thermal hydrolysis, ultrasonication and stabilization was studied. Results were published already.

2. Inclusion of side streams and waste products into TEA and LCA.

Response: various streams from the whole process have been considered for TEA and LCA.

3. VFAs separation and the resulting aqueous phase.

Response: we have been exploring obtaining pure VFAs through distillation and optimizing the extractant. The residual aqueous phase turned out to be a good substrate for the anode of MES.

Publications, Patents, Presentations, Awards, and Commercialization

Peer-reviewed publications

1. Ravi, YK., Zhang, W., **Liang, Y.-N**. 2023. Effect of Surfactant Assisted Ultrasonic Pretreatment on Production of Volatile Fatty Acids from Mixed Food Waste. Bioresource Technology. 368, 128340.
2. Liang. Y-N. 2021. A Critical Review of Challenges Faced by Converting Food Waste to Bioenergy Through Anaerobic Digestion and Hydrothermal Liquefaction. Waste and Biomass Valorization. 1-16.
3. Zhang, W.L., Zhang, Q., **Liang. Y-N.** 2022. Ineffectiveness of ultrasound at low frequency for treating per- and polyfluoroalkyl substances in sewage sludge. Chemosphere. 286, 131748.
4. Zhang, W.L., Tao, J., **Liang. Y-N.** 2022. Stabilization of per- and polyfluoroalkyl substances (PFAS) in sewage sludge using different sorbents. Journal of Hazardous Materials Advances. 6, 100089.
5. Zhang, W.L., **Liang. Y-N.** 2022. Performance of different sorbents toward stabilizing per- and polyfluoroalkyl substances (PFAS) in soil. Environmental Advances. Volume 8, 100217.
6. Zhang, W.L., Liang. Y-N. 2021. Effects of Hydrothermal Treatments on PFAS in sewage sludge. Environmental Pollution. 285, 117276.
7. Zhang W.L., Cao H.M*., **Liang, Y.-N.** 2021. Optimization of thermal pretreatment of food waste for maximal solubilization. Journal of Environmental Engineering. 147 (4), 04021010.
8. Kwon, G., Post, ER., Kota, AK., Li, C., Speer, DL., Guenthner, AJ., Reams, JT., Lamison, KR., Mabry, JM., and Tuteja, A. 2021. Continuous Liquid–Liquid Extraction and in-Situ Membrane Separation of Miscible Liquid Mixtures”, Langmuir, 37, 46, 13595–13601.

Publications, Patents, Presentations, Awards, and Commercialization

Conference Presentations:

1. Weilan Zhang, **Yanna Liang**. Performance of different sorbents toward stabilizing PFAS in sewage sludge. ACS, Aug. 22-24th, 2022, Chicago, IL.
2. **Yanna Liang,** Meltem Urgun Demirtas, Troy Robert Hawkins, Hui Xu, Zhiyong Jason Ren, Anish Tuteja, Alex Rosenthal. 2022. An Integrated Process for Converting Food Waste to Value-added Products. 44th Symposium on Biomaterials, Fuels and Chemicals. May 2-4th. New Orleans, LA.
3. Tao Jiang, Weilan Zhang, Aswin Kumar Ilango, Jeremy I. Feldblyum, Zheng Wei, Haralabos Efstathiadis, Mehmet V. Yigit, **Yanna Liang**. Innovative green and sustainable sorbents for removing or stabilizing PFAS in different environmental matrices. 2022 SERDP & ESTCP and OE-Innovation Symposium. Nov. 29-Dec. 2, 2022.

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