

DOE Bioenergy Technologies Office (BETO) 2023 Project Peer Review

Electro-Enhanced Conversion of Wet Waste to Products Beyond Methane

April 7, 2023
Organic Waste Conversion

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Project Overview

- U.S. produces >77 MM dry tons of organic waste, including food waste and manure, every year
 - Most is landfilled or land applied, incurring disposal costs
 - Anaerobic digestion (AD) produces low-value methane and CO₂ ⇒ poor economics and risk of greenhouse gas emissions
 - Disposal costs are significant to dairies and other animal operations
- Organic waste has substantial energy content

Feedstocks	Annual Resource Generation		
	Estimated Annual Resources	Inherent Energy Content (Trillion Btu)	Fuel Equivalent (MM GGE) ¹
Wet Feedstocks	77.17 MM Dry Tons	1,078.6	9,290.8
Wastewater Residuals	14.82	237.6	2,046.6
Animal Waste	41.00	547.1	4,713.0
Food Waste ²	15.30	79.6	685.3
Fats, Oils, and Greases	6.05	214.3	1,845.9

Biofuels and Bioproducts from Wet and Gaseous Waste Streams: Challenges and Opportunities. 2017.

Project Overview

- The *technical* goal of this project is to **valorize wet organic waste by using renewable electrons to drive targeted pathways in AD and subsequent bioconversions to higher-value products**, including
 - Hexanoic acid: precursor to diesel-range blendstock and other products
 - Isobutanol and other alcohols: gasoline blendstock, upgradable to jet fuel
- **Benefits:**
 - Levelized cost of energy production will be improved by at least 25%
 - Net levelized cost of disposal (nLCOD) will be improved by at least 25%
- The *educational* goals are to train students in biological waste conversion technologies and to share innovative solutions with the public
- **Benefits:**
 - Train new STEM professionals to find new solutions to waste conversion

Project Overview

- Project award: October 2019
- Initial funding:
 - NREL: March 2020, then on reduced spend rate
 - Universities: December 2020
 - Timeline revised to account for delayed start and pandemic closures
- Go/No-Go #1 passed in December 2022, now in BP2

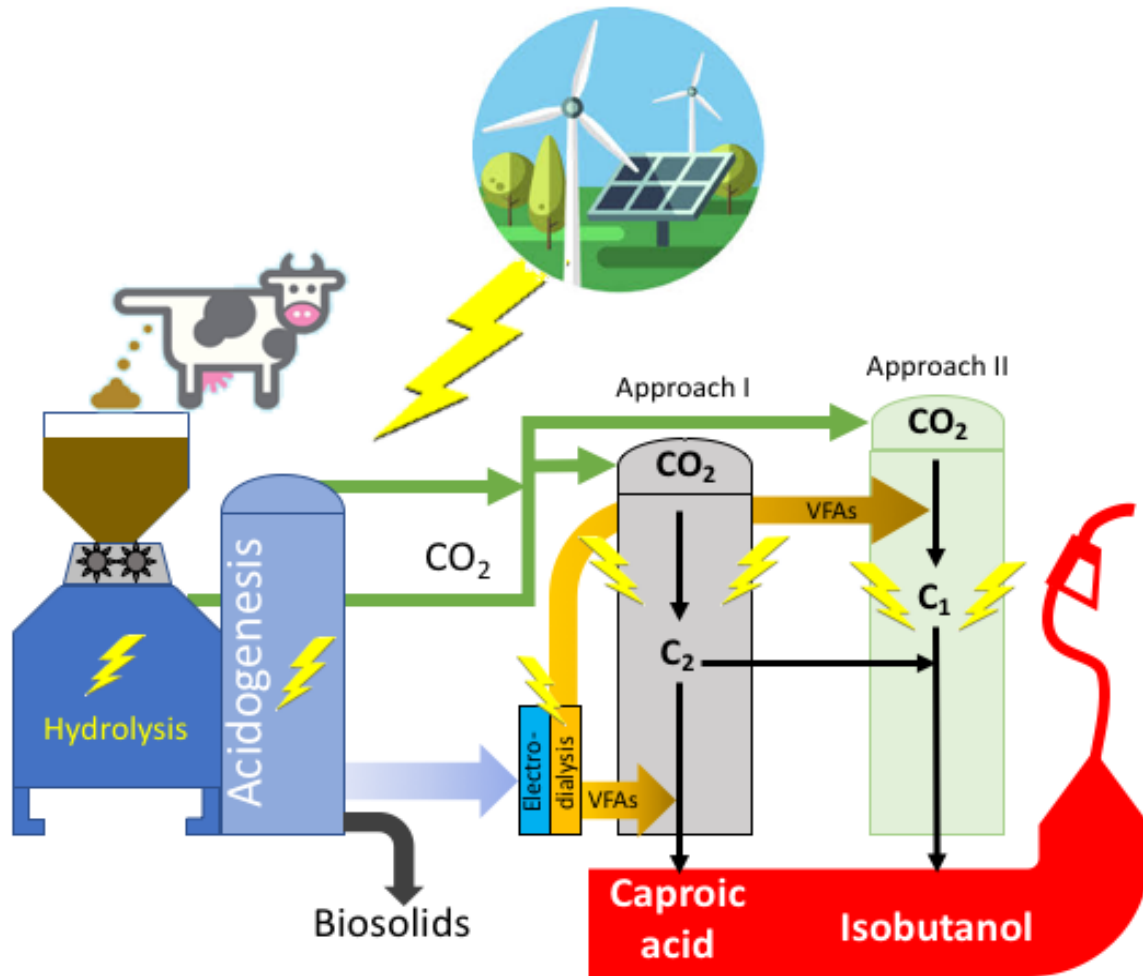
1 – Approach

To achieve the technical goal, need to

- Convert high levels of feedstock carbon to target products
(and away from methane and CO₂)
- Demonstrate scalability
- Demonstrate environmental and economic sustainability

1 – Approach

Volatile fatty acid = VFA



Task 1: Alter AD to enhance VFA production

Task 2: Upgrade AD product streams

Task 3: Process modeling and TEA

Task 4: Education and Outreach

Research is highly integrated, within and across tasks

1 – Approach

Task 1: Enhancement of Volatile Fatty Acids Production in AD

- Strategies to increase VFA production for economic sustainability:
 - Arrested methanogenesis (T, pH, microaeration)
 - Electro-enhanced AD
 - In-situ VFA extraction
 - Microbial consortium development
- ✓ **BP 1 Go/No-Go:** Demonstration of increased total VFA yield by at least 50% over baseline total VFA yields (g VFA/g TS) of 0.1 from manure and 0.3 from food waste
- BP 2 Go/No-Go: Select conditions for 2000-L digester from those demonstrated to achieve total VFA yields at the 20-L scale of 0.12 g/g manure or 0.36 g/g food waste.
- BP 3 Go/No-Go: Demonstrate AD total VFA yields at the 2000-L scale of at least 0.096 g/g manure or 0.29 g/g food waste.

1 – Approach

Task 2: Capturing and upgrading AD product streams

- Strategies to separate and upgrade for economic sustainability:
 - Development of VFA separation process
 - Microbial electrosynthesis for conversion of waste CO₂ to VFAs
 - Electro-elongation of microbial electrosynthesis (MES) products and VFAs to hexanoic acid and other medium-chain (MC) FAs
 - Bioconversion of VFAs to isobutanol and other MC alcohols
- BP 2 Go/No-Go: Demonstrate production of higher alcohols from engineered *E. coli*
- BP 3 Go/No-Go: Scale-up of the MES process to at least 1 L without significantly decreasing MES performance compared to pure CO₂ feed; Demonstrate total MC alcohol production with a final titer of 1.0 g/L at 20-L scale with continuous feeding.

MC FAs: higher value than VFAs

MC alcohols: higher value than VFAs; fuel blendstocks

1 – Approach

Task 3: System Evaluation and Optimization to Assess Economic Viability

- Engineering process modeling
 - Techno-economic analysis to quantify economic performance metrics
 - Sensitivity, scenario, and optimization
-
- BP 2 Go/No-Go: Demonstration via TEA of a pathway that meets a MFSP of less than \$5/GGE.
 - BP 3 Go/No-Go: Demonstration of a pathway that meets the DOE target of \$3/GGE and improvement of nLCOD to \$60/ton (25% improvement) or less for at least one configuration of the developed process.

1 – Approach

Task 4: Integrate Education and Outreach with Research

- Graduate student and post-doctoral researcher participation, with leadership roles
- Undergraduate internship programs with industry
- Intensive summer engagement programs for undergraduates
- Outreach programs to partner community college
- Education/outreach program at the CSU Spur campus

- Multi-disciplinary research engagement
- Stimulating and training the next generation of STEM professionals to transform waste valorization

- ✓ **BP 1 Go/No-Go:** Involvement of 4 graduate students and 1 postdoctoral researcher.
- **BP 2 Go/No-Go:** Completion of at least 4 forums for project participants to develop research skills and discuss challenges; Cumulative engagement of at least 12 undergraduate students.

1 – Approach

Changes made in light of 2021 Peer Review comments

No changes in approach were suggested following the 2021 Peer Review

1 – Approach

Potential challenges facing the technical approach

- Inocula variations
- Feedstock characterization

1 – Approach

Risk analysis and mitigation strategies

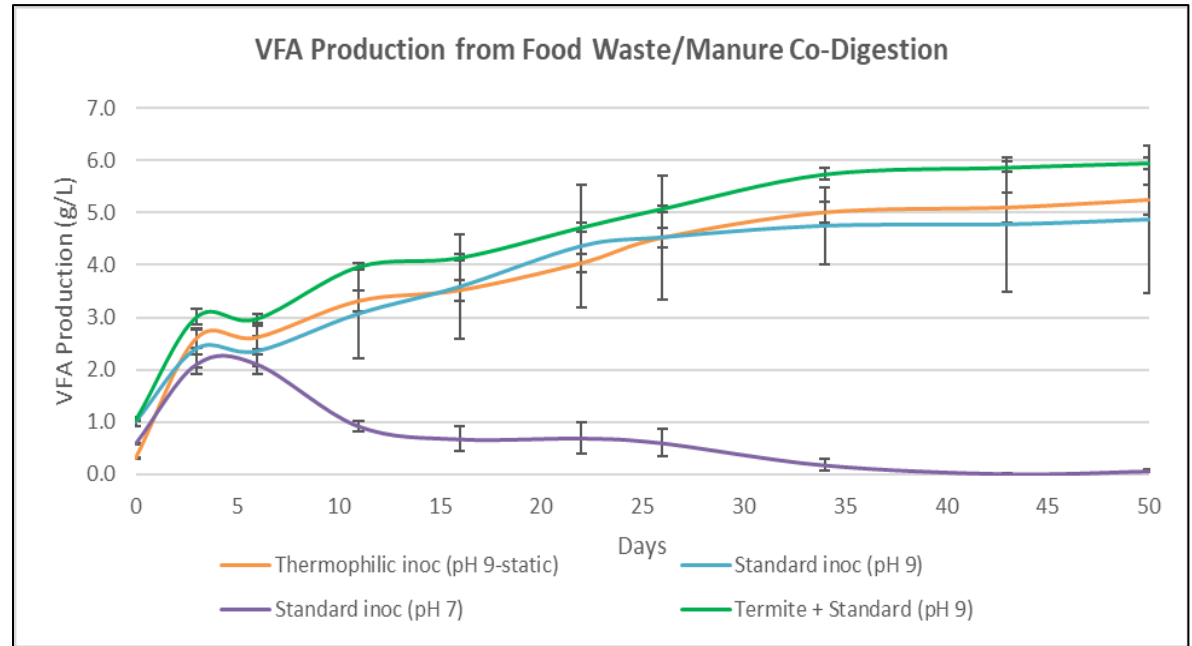
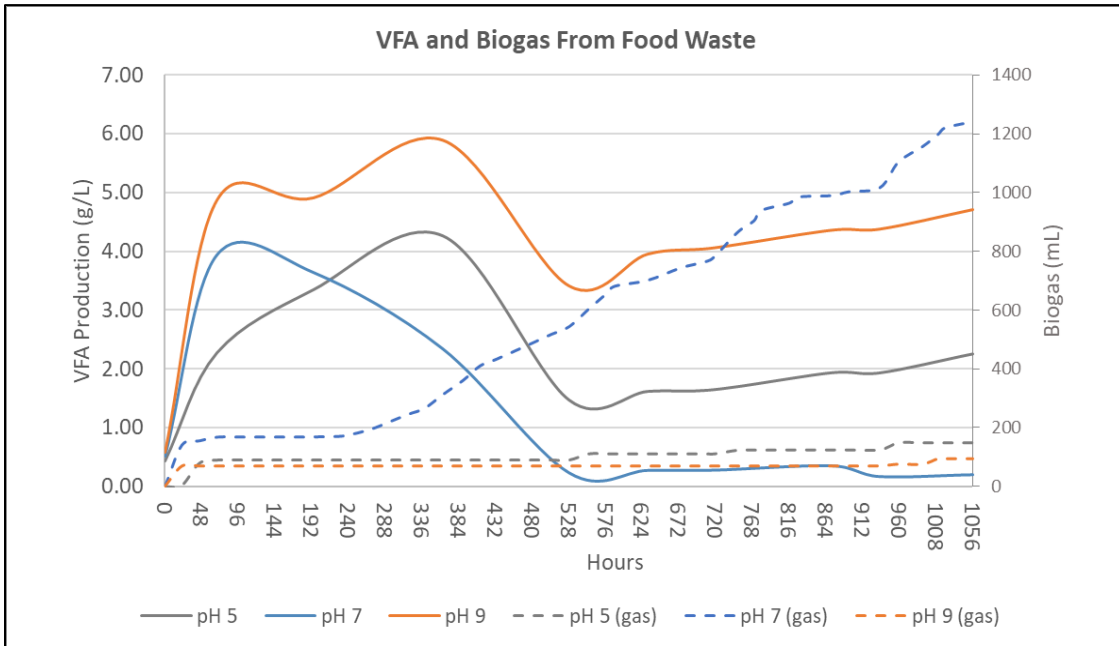
- **Risks:**
 - Divergent and/or duplicative efforts
 - Site-to-site reproducibility
 - Problems with process for upgraded product
- **Mitigation:**
 - Discussion and coordination
 - Shared analytical methods
 - Shared analysis of microbial community composition
 - Shared feedstock
 - Process model highlights knowledge gaps
 - Parallel efforts for upgraded products and VFA production

2 – Progress and Outcomes

Increase VFA production by altering AD conditions

Task 1.1: Arrested Methanogenesis

- **~150% increase in VFA production and titers** from food waste as a function of pH
 - Conditions: pH 5, 7, or 9; 16 g/L COD of food waste; 35 °C
- **>20% increased VFA production and titers** from food waste/manure co-digestion using higher termite gut consortia
 - Conditions: 50/50 food waste/manure; 15 g/L total COD; 35 °C

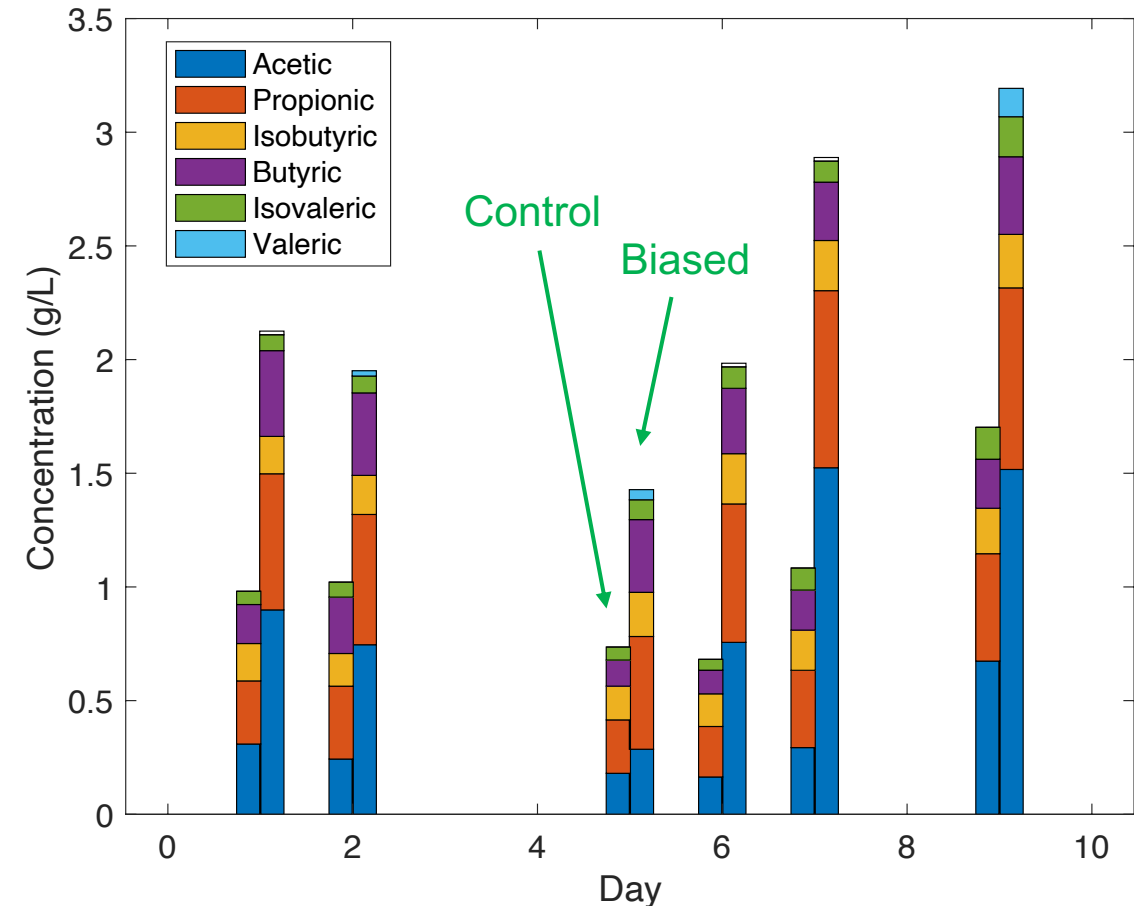


2 – Progress and Outcomes

Increase VFA production
by supplying electrons

Task 1.2: Electro-Enhanced AD

- Conditions:
 - Applied potential: -300 mV vs. Ag/AgCl applied (biased) and open circuit (unbiased control)
 - Inoculum: unacclimated wastewater sludge
 - Feedstock: Homogenized food waste
 - Initial: 10 g COD/L
 - Operating conditions:
 - Temp: 35 °C
 - pH: 7, automated control
- **88% increase in maximum VFA levels** over baseline (unbiased control) exceeds milestone (25% increase)

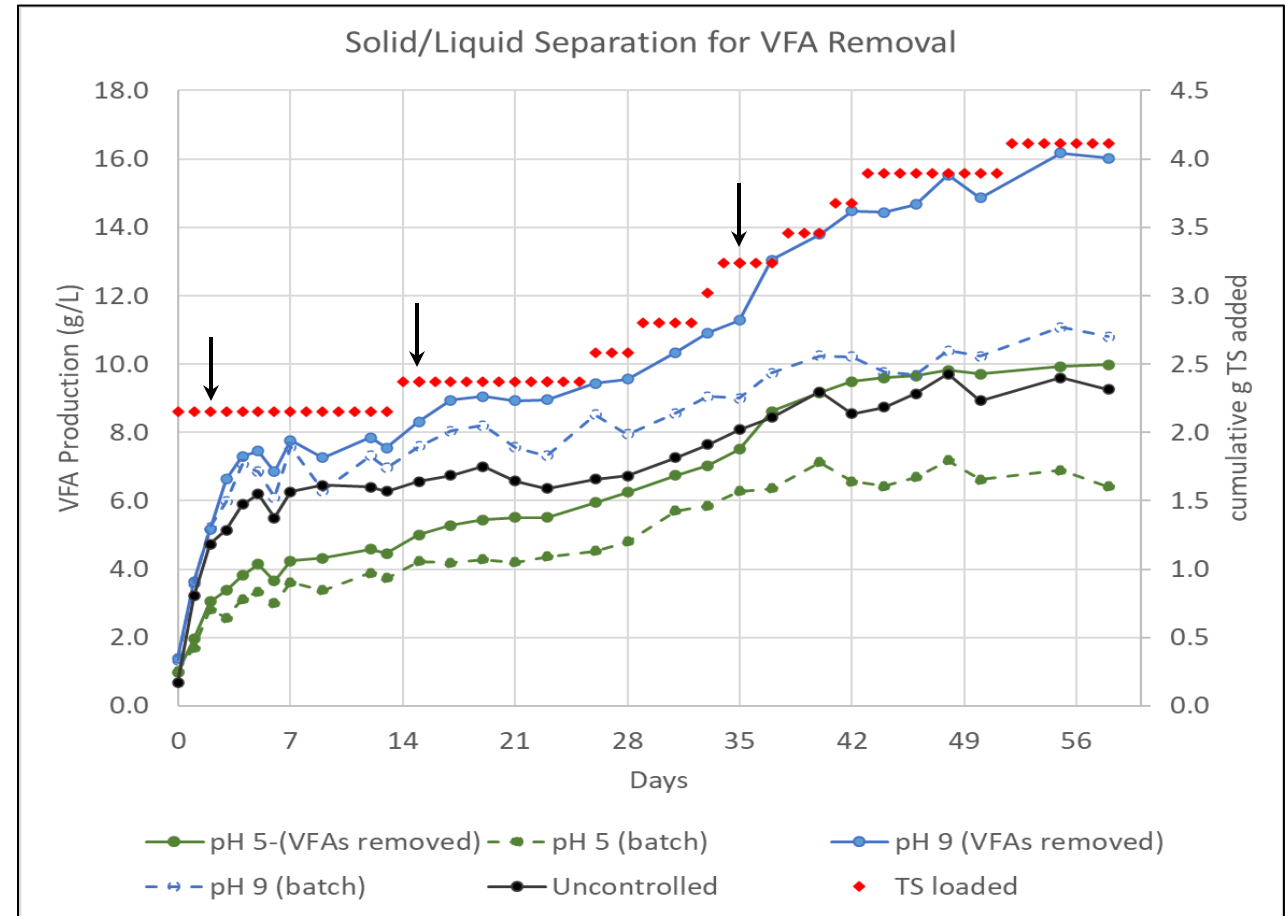


2 – Progress and Outcomes

Increase VFA production by removing inhibition

Task 1.3: In-Situ VFA Extraction

- Solid/liquid separation by centrifugation
- **>48% increase** in VFA titers by removal of VFAs during AD
- VFA removal (↓) at day 2, 15, 35
- pH 5, 9, and uncontrolled
- 32 g COD + periodic feeding



	Day 58 cumulative VFAs (g/L)	Increase in VFA production (%)
pH 5-(VFAs removed)	9.98	56%
pH 5 (batch)	6.41	-
pH 9 (VFAs removed)	16.02	48%
pH 9 (batch)	10.79	-
Uncontrolled	9.25	-

2 – Progress and Outcomes

Increase C4 VFA
production by improving
microbiome

Task 1.4: Microbial Consortium Development

- Designed/constructed a 30 continuously-mixed, pH-stat reactor system enabling microbiome development experiments
- Identified the microbial inoculum source and conditions for producing **up to 10X increased titers of butyric acid** from food waste.
- Identified a novel microbial inoculum source and conditions for maximizing butyric acid titers from manure
- Produced a substantial body (>600 samples) of coupled fatty acid profile and microbiome structure data
- Developed metagenomics-based software for relating microbiome structure to VFA production

2 – Progress and Outcomes

Increase C6 VFA production and scale AD process

Task 1.5: Baseline AD performance for 2 – 2000 L

Semi-continuous AD milestones: Yield = 0.3 g tVFA/g TS; Productivity= 0.56 g tVFA/L/d

- Achieved high caproic acid productivity through strain enrichment
 - Maximum caproic productivity = 0.48 g C6/L/d
- Demonstrated that digester agitation level has a significant impact on VFA production
 - Increase from 400 to 700 rpm decreased caproic productivity by 50%
- Demonstrated that lactic acid is a key caproic acid precursor
 - Lactic spike (5 g/L) increased caproic level by 330% compared to FW spike (control)
- Found no significant scale-up effect from 2- to 600-L bioreactors
 - Given same feedstock, feed rate, HRT, T, and pH; P/V = 5 to 8 kW/m³
- Food waste pre-fermentation to lactic acid improved productivities and tVFA yields
 - **With pre-fermentation, achieved 106% of yield milestone and 340-390% of productivity milestone**

2 – Progress and Outcomes

Separate VFAs from AD mixture to remove inhibition and facilitate upgrading steps

Task 2.1: Development of VFA separation process

- Demonstrated VFA separation by electrodialysis (ED) from AD
 - Batch: 63% of produced VFA transferred to anode compartment at pH 9, at 0.7 g/L·h; 3-7 kWh/kg specific energy consumption
 - Milestone: 70% VFA transfer
- Demonstrated production of higher alcohols with ED stream
- Transitioning to continuous separation

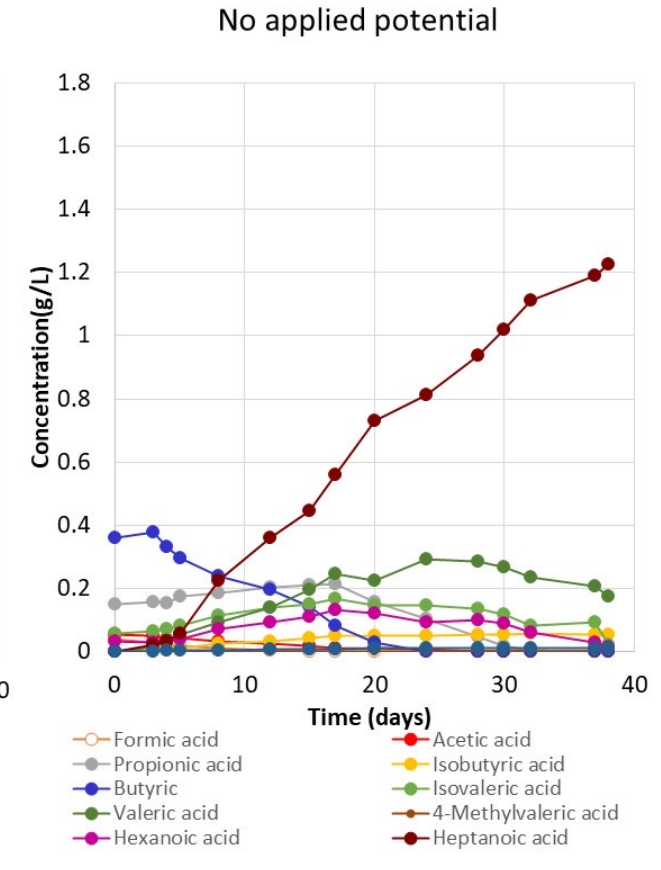
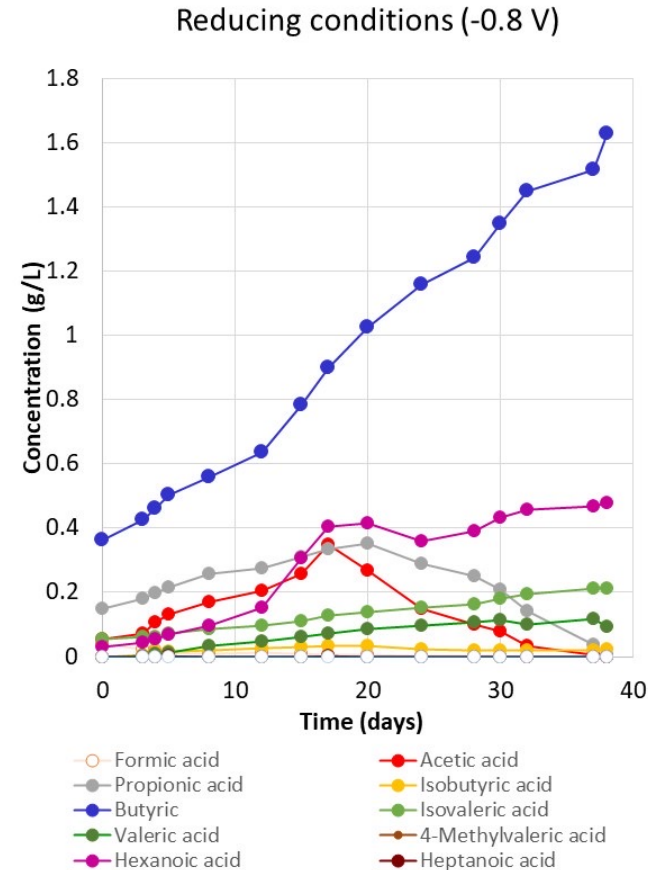
→ Demonstrated ED to be viable for VFA separation and upgrading

2 – Progress and Outcomes

Increase VFA production by using waste CO₂

Task 2.2: Microbial electrosynthesis to convert waste CO₂ to VFAs

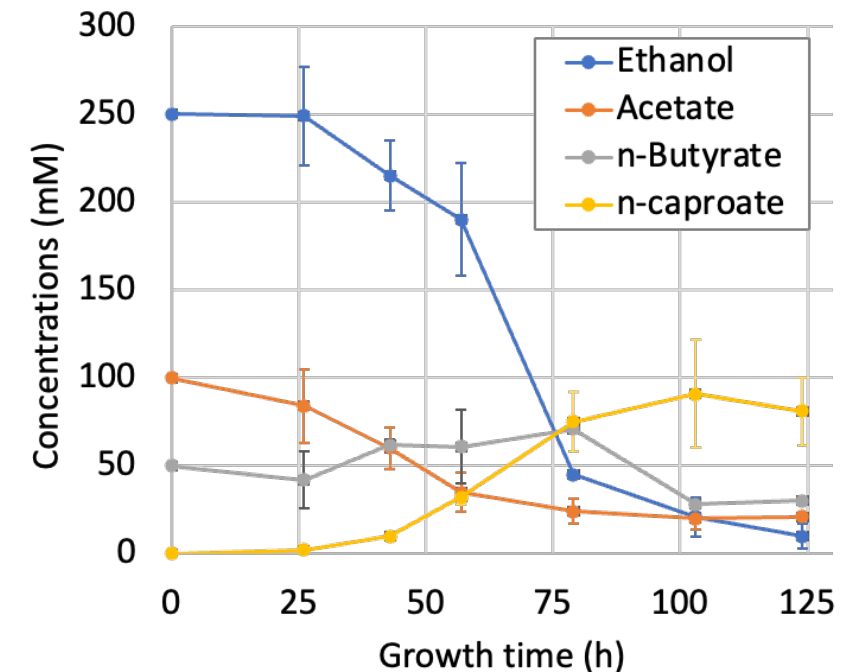
- ✓ **Achieved milestone:**
18 g acetate/m²/day at 80% Faradaic efficiency
- Observed increased VFA production and chain elongation in AD culture in presence of *C. ljungdahlii* and applied potential
- Current work: integration of MES, AD, and chain elongation



2 – Progress and Outcomes

Task 2.3: Electro-elongation of MES products and VFAs to MCFAs

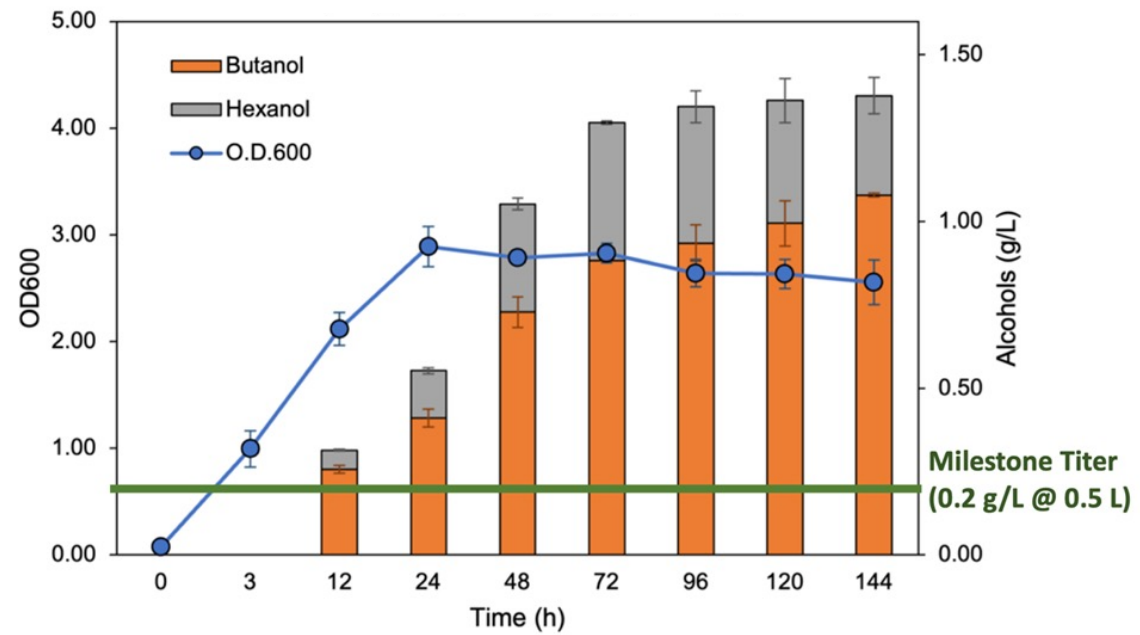
- Investigating use of acetate and ethanol for caproic (hexanoic) acid production
- Caproate production by *C. kluyveri*
 - Caproate yield: 9.4 g/L
 - Carbon conversion from C2 to C6: 48%
- Milestone: demonstrate conversion of VFAs from AD liquid stream to C6-C8 acids with at least 60% carbon conversion efficiency (M60)
 - To date, caproate production demonstrated in *C. kl.* optimal medium
- Current work: integration of AD, MES and chain elongation



2 – Progress and Outcomes

Task 2.4: Bioconversion of VFAs to isobutanol and other MC alcohols

- Constructed *E. coli* capable of converting C4-C6 acids to alcohols at >0.2 g/L at 0.5-L scale with mock AD solutions
- **Achieved 7X intermediate milestone for alcohol production**
- Demonstrated higher alcohol production and no growth inhibition with processed AD solutions



2 – Progress and Outcomes

Conduct TEA and LCA to track sustainability and identify opportunities

Task 3: System Evaluation and Optimization to Assess Economic Viability

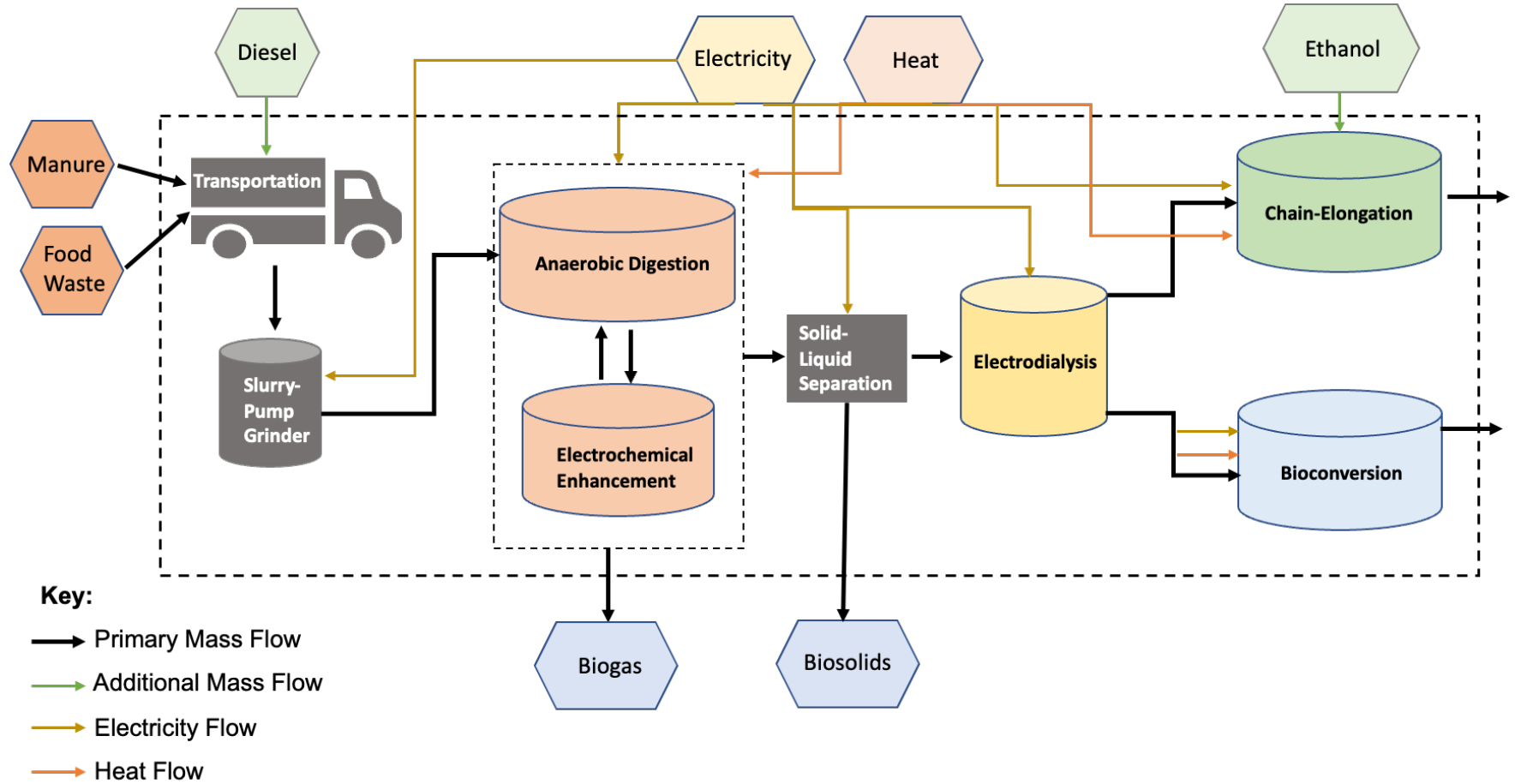
- Developed and validated an engineering process model representing the two production pathways
- Generated sustainability results including economic viability and environmental impact
- Provided data feedback to experimental teams on progress and needs to achieve performance targets

2 – Progress and Outcomes

Conduct TEA and LCA to track sustainability and identify opportunities

Task 3: System Evaluation and Optimization to Assess Economic Viability

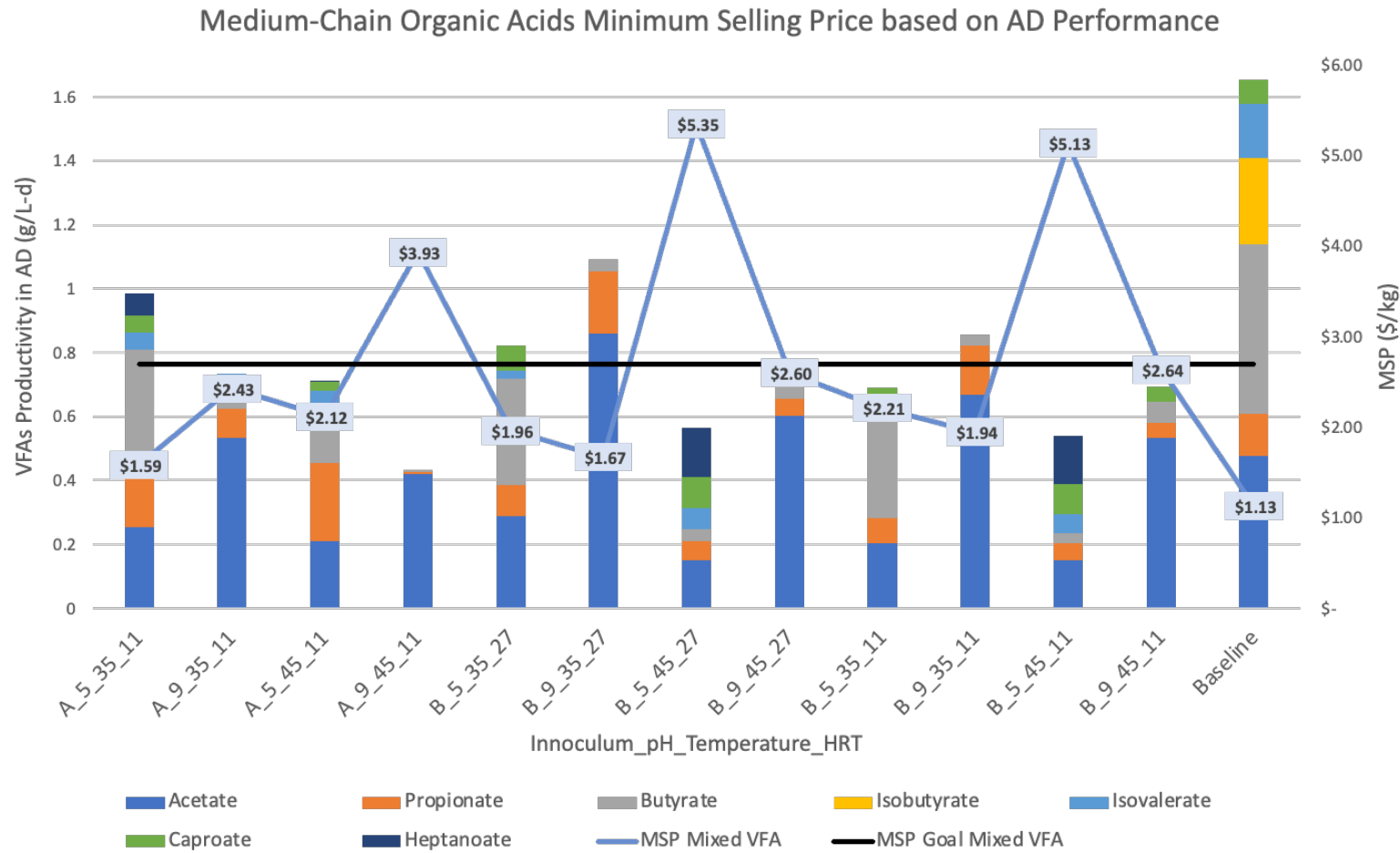
✓ **Achieved milestone:** Developed and validated an engineering process model



2 – Progress and Outcomes

Task 3: System Evaluation and Optimization to Assess Economic Viability

Generate economic viability results as feedback to experimental team



Economic Assumptions:

- Tipping Fee: \$30 per ton
- Facility Scale: 154 m³/h
- Final Product: VFA mixture
 - VFA Mix Goal (\$2.70/kg)
 - VFA Mix (Calculated) consists of:
 - Propionate (\$1.00/kg)
 - Isobutyrate (\$1.69/kg)
 - Isovalerate (\$1.69/kg)
 - Heptanoate (\$2.00/kg)
 - Caproate (Calculated)

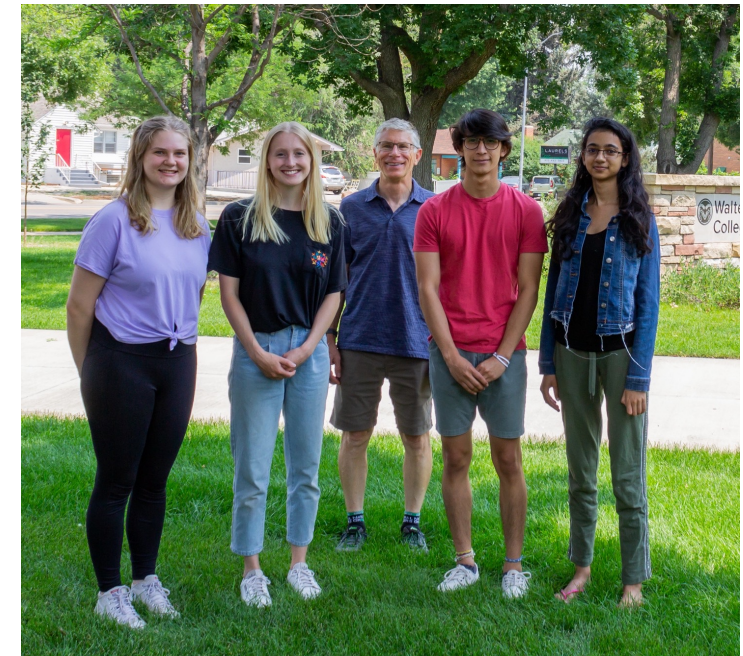
VFA Production Assumptions:

- Electrochemical enhancement increases AD VFAs by a factor of 2.9
- Electrodialysis has 84% VFA removal efficiency at pH 5 and 60% at pH 9
- Chain-elongation converts 79% of acetate and 77% of butyrate to caproate

2 – Progress and Outcomes

Task 4: Integrate Education with Research

- Involvement of 10 graduate students and 3 postdoctoral researchers
- Involvement of 13 undergraduate students
- Conducted outreach at CSU Spur in January 2023



3 – Impact

- U.S. produces >77 MM dry tons of organic waste every year:
 - Valorizing biomass carbon (vs. GHGs) is high impact
 - Hexanoic acid is a precursor to fuels and other chemicals
 - Isobutanol and MC alcohols are gasoline/diesel blendstocks and upgradable to jet fuel
- Contribute to development of renewable electrons as process input
- Technoeconomic impacts:
 - Levelized cost of energy production will be improved by at least 25%
 - Net levelized cost of disposal will be improved by at least 25%
- Valuable engagement with industry
 - Leprino Foods, others TBD
- Dissemination
 - Publications, patent applications planned
- Education and outreach to train a new generation in innovative waste conversion

Summary

- Important technical achievements toward project goal
 - Several approaches successful for increasing VFA yields and productivity
 - Medium-chain acid production demonstrated
 - Medium-chain alcohol production demonstrated
 - TEA and LCA models established
- Current research
 - Improved connection of microbiome composition to VFA production
 - Integration of VFA production, chain elongation, and separation

Project Team

Colorado State University

Danielle Bartholet, Joshua Chan, Susan De Long, Parsa Ghadermazi, Jocelyn Hittle, Jason Quinn, Ken Reardon, Jorge Rico, Abdo Soliman, Kathryn Venzor, Smith Pittman

National Renewable Energy Laboratory

Steve Decker, Venkat Subramanian, Drazenka Svedruzic, Chris Urban

South Dakota School of Mines & Technology

Patrick Gilcrease, Shyanne Lambrecht, Dan Cerfus, Mike Hickey

University of California, Irvine

Plamen Atanassov, Han Li, Will Black, Jim Kim

Quad Chart Overview

Timeline

- 10/01/2019
- 10/31/2025

	FY22 Costed	Total Award
DOE Funding	(10/01/2021 – 9/30/2022) \$1,102,105	(negotiated total federal share) \$5,067,538
Project Cost Share	\$293,062	\$1,267,907

Project Goal

Re-engineer anaerobic digestion to divert C from low-value methane into chemicals other than methane, upgrade these precursors to displace petroleum-based products, and enhance waste conversion efficiencies.

End of Project Milestones

Demonstration of a pathway that meets the target of \$3/GGE and improvement of nLCOD to \$60/ton; Scale-up MES to at least 1 L without significantly decreasing performance; Demonstrate total higher alcohol production with a final titer of 1.0 g/L at 20-L scale with electro dialysis-purified AD and MES effluent; Demonstrate AD total VFA yields at the 2000-L scale of at least 0.096 g/g manure or 0.29 g/g food waste.

Funding Mechanism

DE-FOA-0002029, FY19 Bioenergy Technologies Office Multi-Topic
Topic Area 6 – Renewable Energy from Urban and Suburban Wastes

TRL at Project Start: 2

TRL at Project End: 5

Project Partners

- NREL
- UC-Irvine
- South Dakota School of Mines & Technology
- Leprino Foods

Additional Slides

Responses to Previous Reviewers' Comments

- The 2021 Peer Review presentation took place in the very early stages of the project
- Review comments were positive about initial progress
- Some comments reflected lack of information:
 - NREL is involved
 - Education/outreach was a requirement of the FOA
 - TEA/LCA is part of the project (Task 3) and incorporates side streams and waste products, as well as electricity and disposal costs
- Concern about project breadth: this is being managed by task coordination
- Increased industry participation was suggested and is a priority

Publications, Patents, Presentations, Awards, and Commercialization

- Li et al. Extracellular electron transfer across bio-nano interfaces for CO₂ electroreduction. *Nanoscale* 2021,13, 1093-1102. <https://doi.org/10.1039/D0NR07611B>
- Guo et al. Catalytic Hybrid Electrocatalytic/Biocatalytic Cascades for Carbon Dioxide Reduction and Valorization. *ACS Catal.* 2021, 11, 5172-5188
- In preparation: Review of effects of operating conditions on VFA production
- Reardon, K.F., Bartholet, D.L. Electro-fermentation for enhanced product yields. *Frontiers in Biorefining*; 2022 Oct 24; St. Simons Island, GA
- Cutting, H., Arends, E. “Optimizing Volatile Fatty Acid Production in Anaerobic Digestion”. December 8, 2002. NREL intern poster session
- Lambrecht, S., Gilcrease, P., Cerfus. D., Hickey, M. Effects of Retention Time and Agitation on the Anaerobic Digestion of Food Waste for Caproic Acid Production. Poster presented at: SBE 5th International Conference on Microbiome Engineering; 2022 Dec 9-11; Boston, MA.

2 – Approach

	Y1	Q1	Q2	Q3	Q4	Y2	Q1	Q2	Q3	Q4	Y3	Q1	Q2	Q3	Q4	Y4	Q1	Q2	Q3	Q4	Y5	Q1	Q2	Q3	Q4		
Task/Subtask										G/NG									G/NG							G/NG	
Task 1: Enhancement of VFA Production in AD																											
Task 1.1: Arrested methanogenesis				M1.1.1				M1.1.2					(depends on down-selection)														
Task 1.2: Electro-enhanced AD								M1.2.1					(depends on down-selection)														
Task 1.3: In-situ VFA extraction				M1.3.1									(depends on down-selection)														
Task 1.4: Microbial consortium development										M1.4.1			(depends on down-selection)														
Task 1.5: Baseline AD performance and scaleup																											
Task 1.6: Enhanced AD – 2 to 20L scaleup																M1.6.1											
Task 1.7: Enhanced AD – 20 to 2000L scaleup																										G/NG 3	
Task 2: Capturing and upgrading AD product streams																											
Task 2.1: Development of electrodialysis for VFAs																			M2.1.1								
Task 2.2: MES for conversion of CO2		M2.2.1																					M2.2.2			G/NG 3	
Task 2.3: Electro-elongation of VFAs to MCFAs																									M2.3.1	M2.3.2	
Task 2.4: Bioconversion of VFAs to higher alcohols																										G/NG 3	
Task 3: System Evaluation and Optimization																											
Task 3.1: Engineering process modeling					M3.1.1																						
Task 3.2: Techno-economic analysis																										M3.3.2	G/NG 3
Task 3.3: Sensitivity, scenario, and optimization																											
Task 4: Integrate education with research																											
Task 4.1: Student and PD researcher participation																											
Task 4.2: Internship programs for undergraduates																										M4.2.1	
Task 4.3: Cross-disciplinary forums																											
Task 4.4: Outreach programs to partner universities																											
Task 4.5: Summer engagement programs																											
Task 4.6: Education at CSU Spur Campus																											

Project Overview

Volatile fatty acid = VFA

- Project structure
 - Task 1 (alter AD to enhance VFA production)
 - Task 2 (upgrade AD product streams)
 - Task 3 (process modeling and TEA)
 - Task 4 (integrate education with research)

Research is highly integrated, within and across tasks

Project Overview

Volatile fatty acid = VFA

- Project structure

- Task 1 (alter AD to enhance VFA production)

- Arrested methanogenesis (NREL)
 - Electro-enhanced AD (CSU, SDSM&T)
 - In-situ VFA extraction (NREL, SDSM&T)
 - Microbial consortium development (CSU)
 - Scaleup of enhanced AD (SDSM&T)

Collaboration within task:

- Measurement methods
- Inoculum development and sharing
- Experimental design
- Shared sample analysis

Project Overview

VFA = Volatile fatty acid
SC = short chain (C2-C4)
MC = medium chain (C5-C8)

- Project structure

- Task 1 (alter AD to enhance VFA production)
- Task 2 (upgrade AD product streams)
 - Develop VFA separation process (UCI, NREL)
 - Microbial electrosynthesis for conversion of CO₂ to VFAs (NREL, UCI)
 - Electro-elongation of VFAs to MC FAs (NREL)
 - Bioconversion of VFAs to MC alcohols (UCI, CSU)

Collaboration within task:

- Measurement methods
- Shared sample analysis
- Data interpretation

Project Overview

- Project structure

- Task 1 (alter AD to enhance VFA production)
- Task 2 (upgrade AD product streams)
- Task 3 (process modeling and TEA)
- Task 4 (integrate education with research)
 - Student and postdoc participation (all)
 - Cross-disciplinary training (all)
 - Vocational/JC connections (CSU)
 - Education/outreach at CSU Spur campus (all)

Collaboration within task:

- Shared training methods
- Joint effort to create outreach program

Project Overview

- Project structure

- Task 1 (alter AD to enhance VFA production)
- Task 2 (upgrade AD product streams)
- Task 3 (process modeling and TEA)
- Task 4 (integrate education with research)

Collaboration across tasks

- Electrobiochemical methods
- Data for all modeling
- Input and output stream composition and samples
- TEA guidance for experiments
- Research output to education and outreach

Additional task-specific information

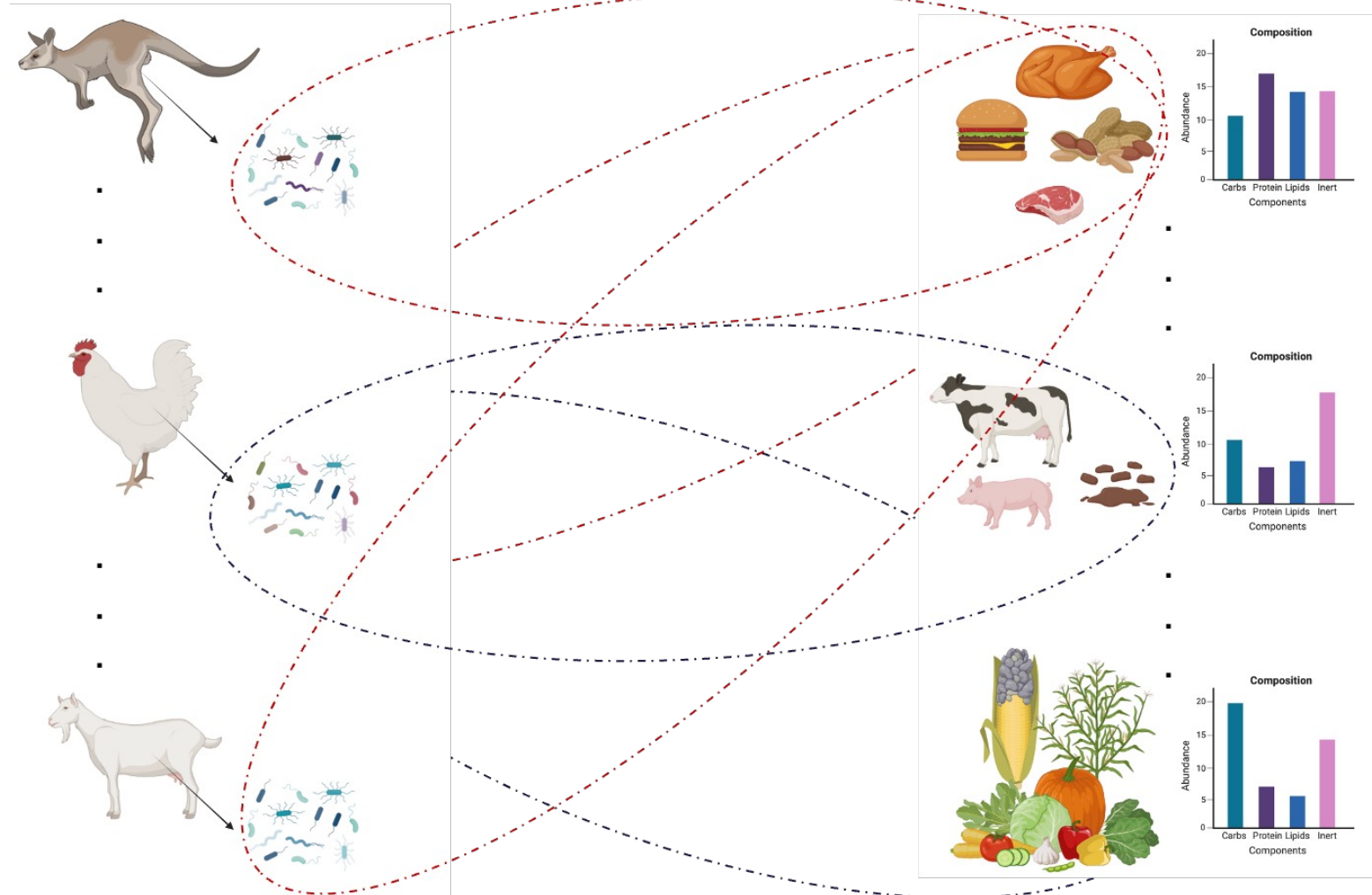
Task 1: Alter AD to enhance VFA production

Subtask 3.1 – Develop biomass sensors

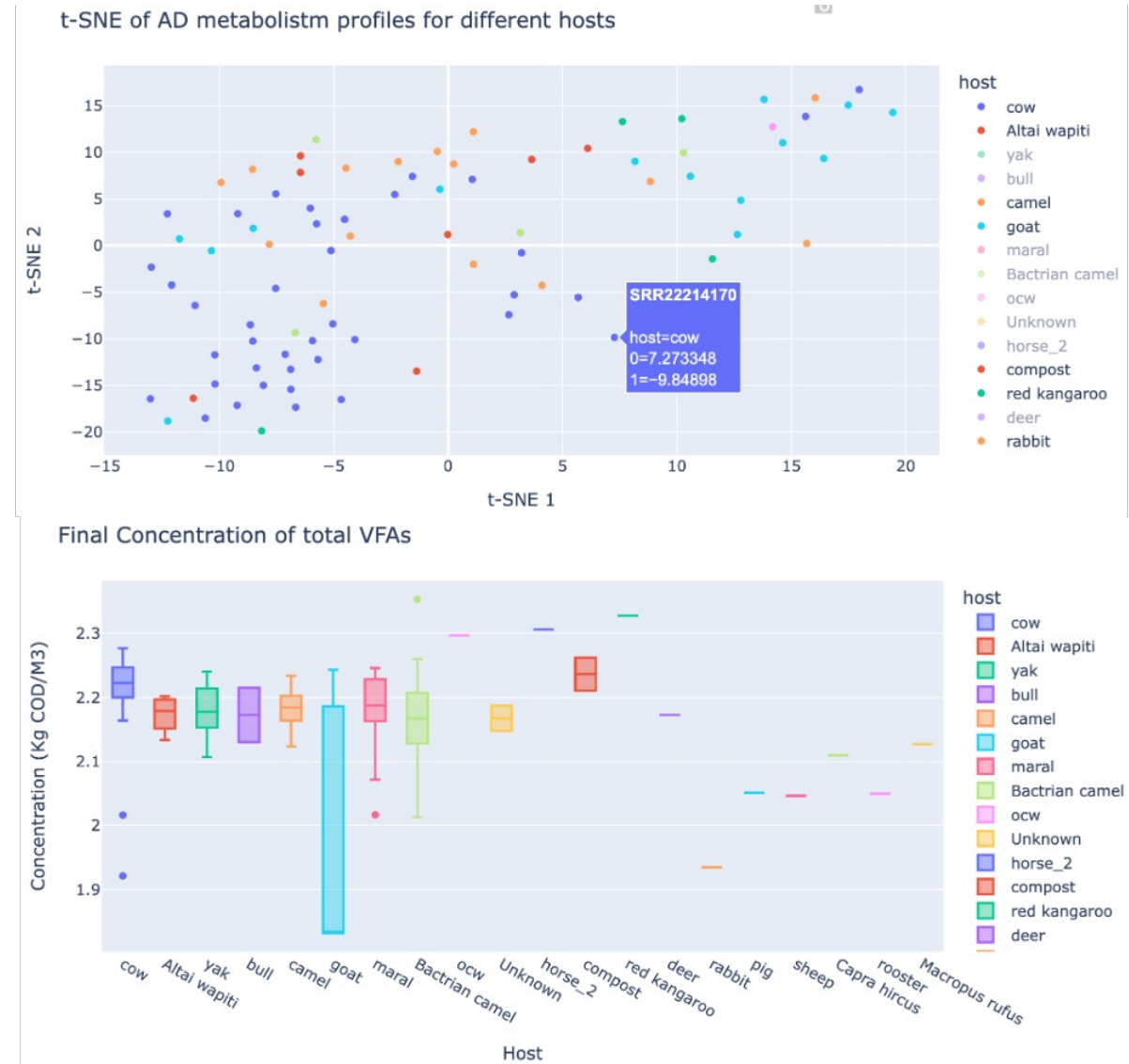
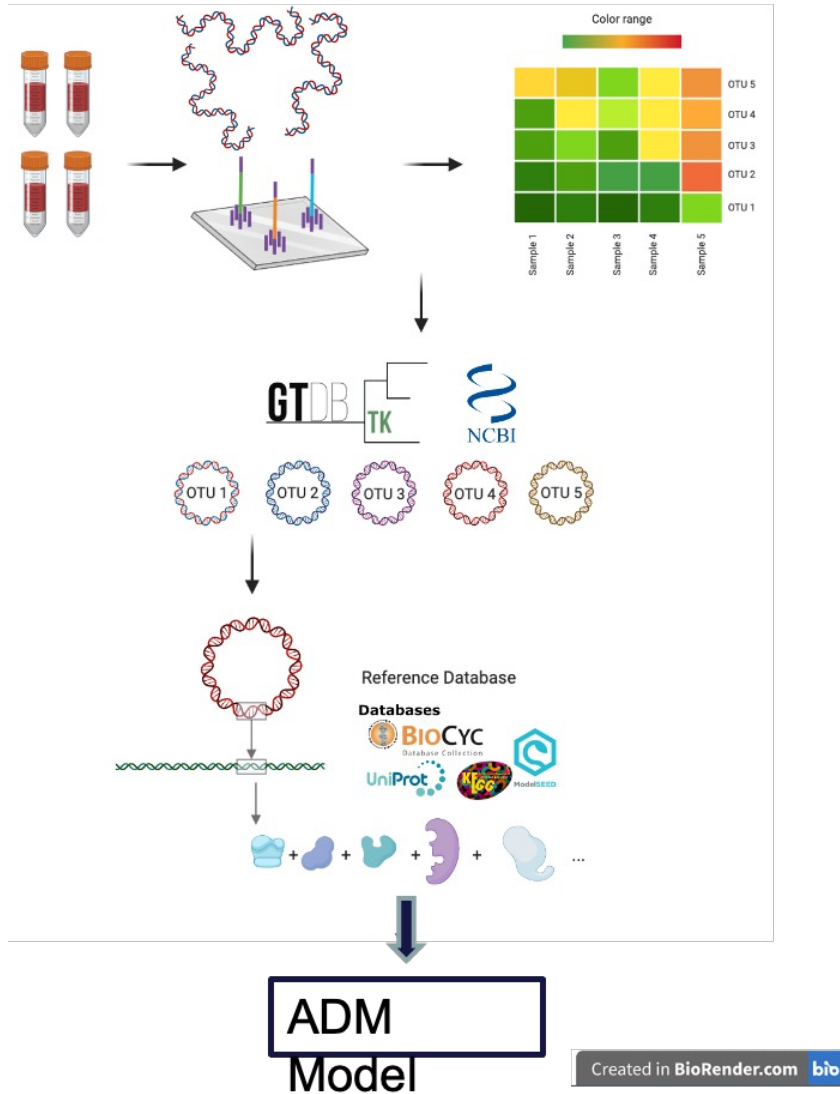
Subtask 1.4: Inoculum development. What is the right combination?

Inocula

Feedstocks

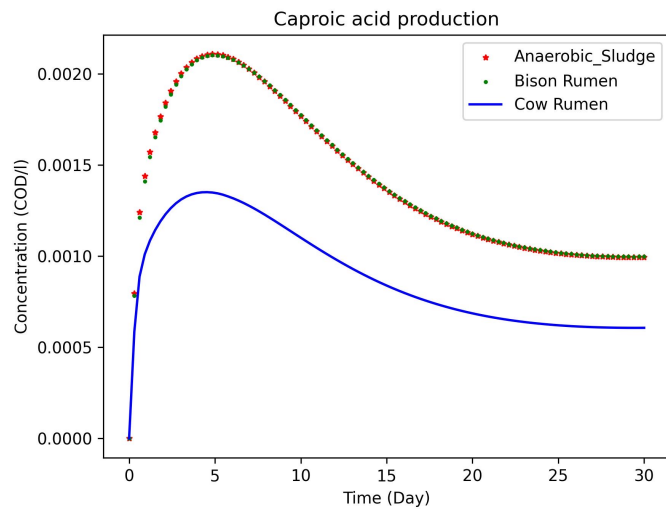
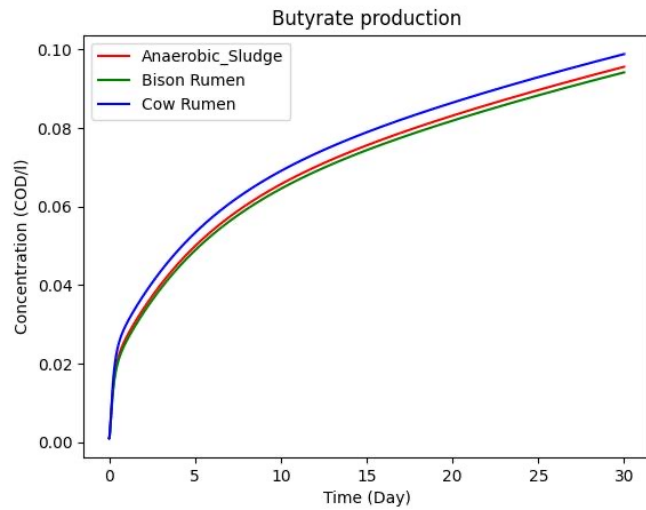


Subtask 1.4: Inoculum development. Functional insights from metagenomics

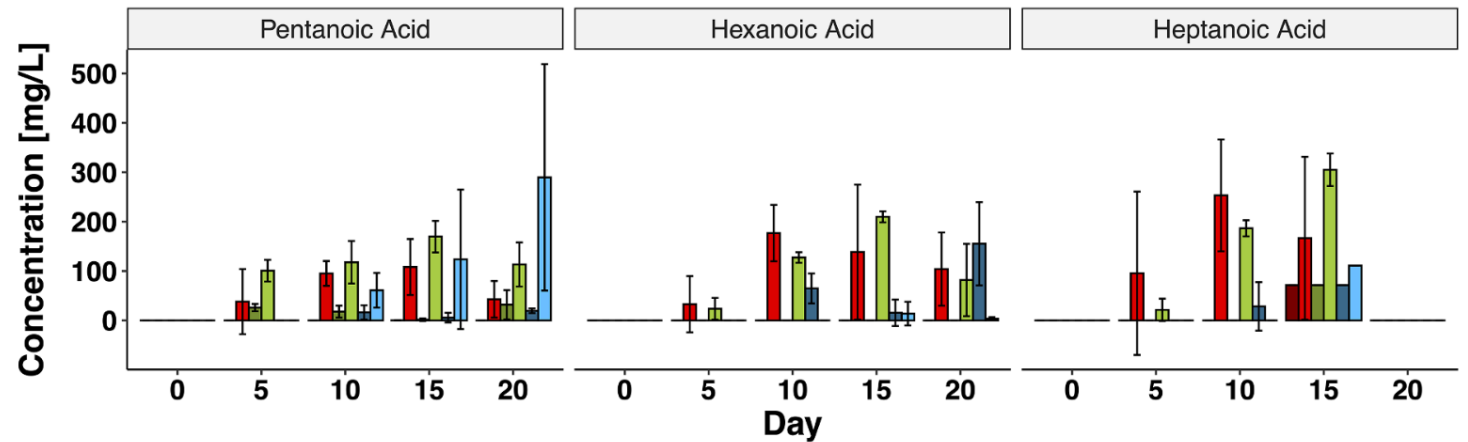
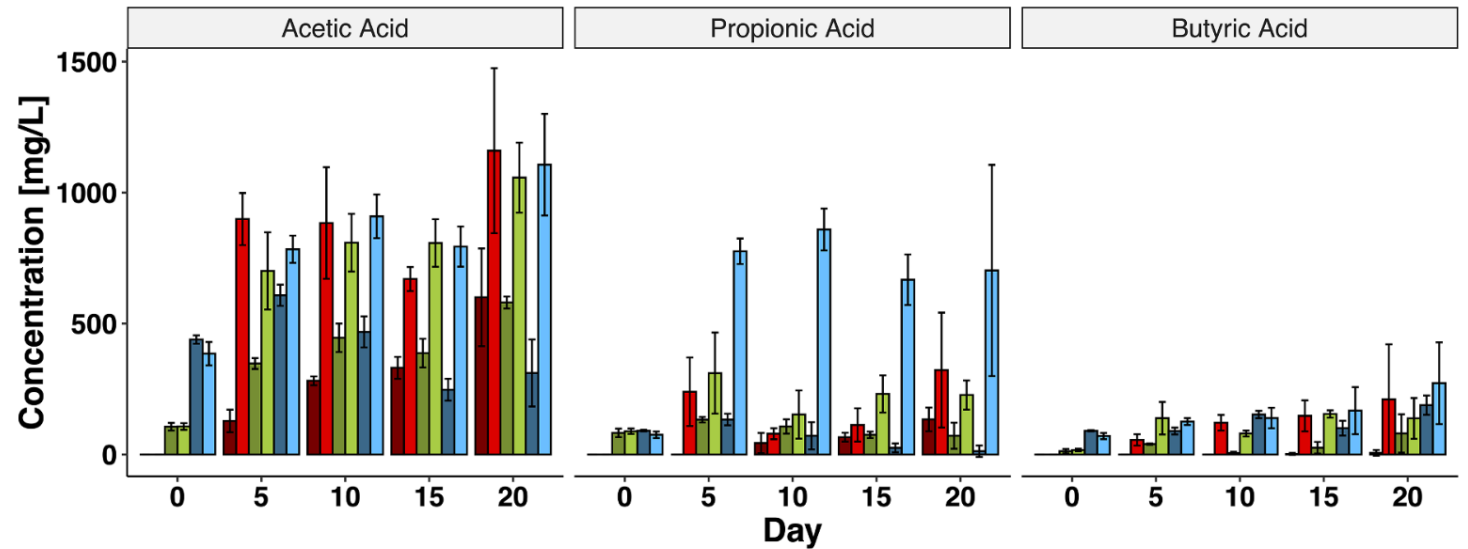


Subtask 1.4: Inoculum development. Functional insights from metagenomics

Simulation



Experimental Data



Treatment

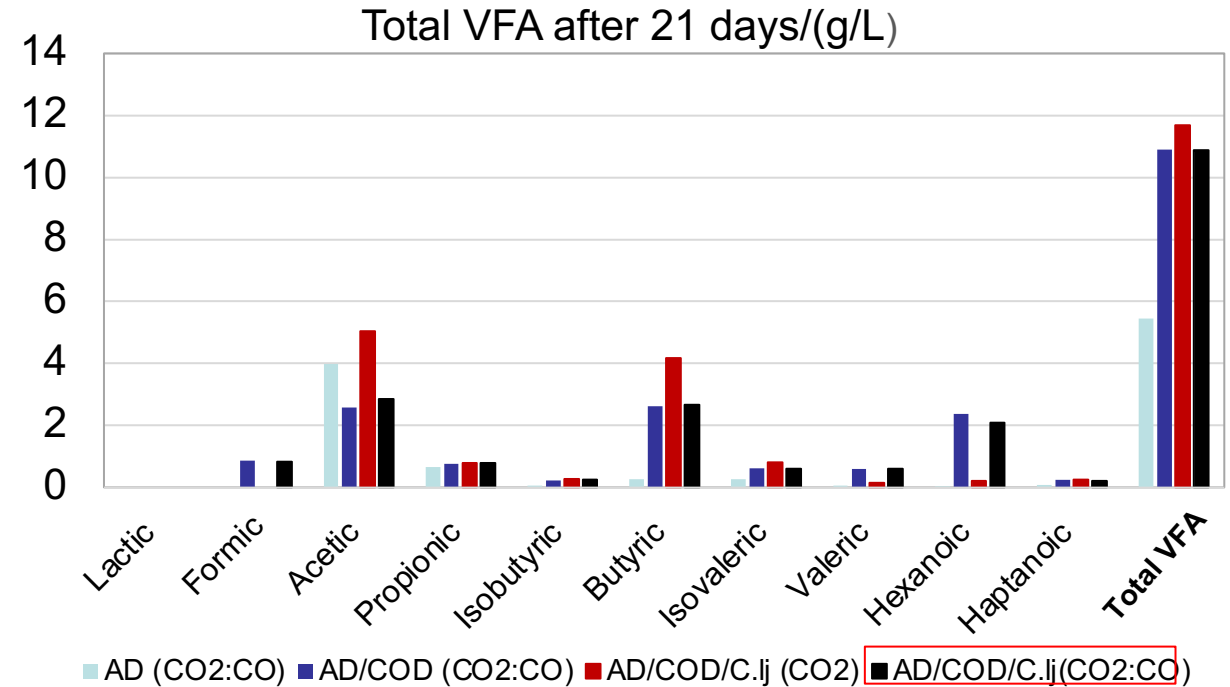
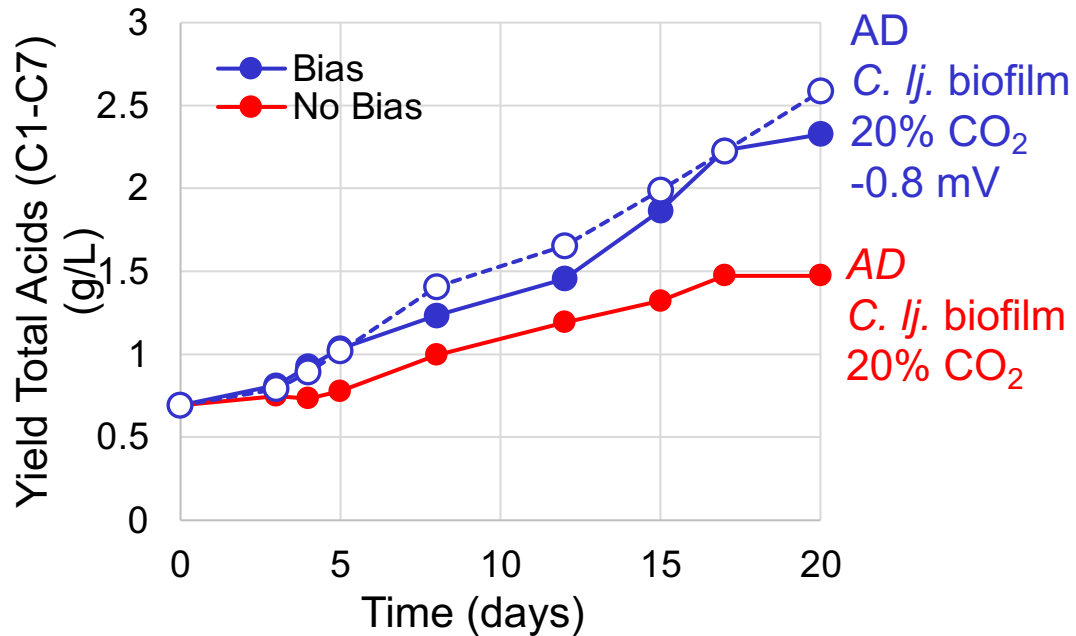
■ A_Fed	■ B_Fed	■ C_Fed
■ A_Control	■ B_Control	■ C_Control

Task 2: Upgrade AD product streams

2 – Progress and Outcomes

Task 2.2: Capturing and upgrading AD product streams

- CO₂ utilization and chain-elongation in AD



- Increased VFA production and chain elongation in AD culture in presence of *C. ljungdahlii* and applied potential.
- Electrons provided electrochemically

In situ production of ethanol for chain elongation:

- Electrons provided as CO
- CO:CO₂ = 20:80 headspace composition is optimal for *C. ljungdahlii* growth and ethanol production
- Controls: no COD added, no *C. ljungdahlii*, 100% CO₂

Task 3: Process modeling and TEA

2 – Progress and Outcomes

Task 3: System Evaluation and Optimization to Assess Economic Viability

Information on Major Model Assumptions

Overall Process

- Operating Time: 8000 hr/yr
- Feedstock is 2.48% Food Waste and 97.52% Manure

Transportation

- 100 trucks travel 160 miles per day and have fuel consumption of 4.4 miles per gallon diesel fuel

Anaerobic Digestion

- 2.4 g/L-d NaOH addition is required to raise AD pH from 5 to 9
- AD is cylindrical CSTR composed of carbon steel and insulation with a centered impeller rotating at 254 rpm with a 10 day HRT
- Biogas composition is 50% H₂, 3% CH₄, and 47% CO₂

Electrochemical Enhancement

- CSTR composed of concrete and insulation, 29 day HRT
- Working and counter electrode (total area required=72 m²), separated by cation exchange membrane (total area required= 95 m²)

Solid-Liquid Separation

- Composed of hydro cyclone solid-liquid separation followed by microfiltration, which removes 95% of biosolids

Electrodialysis

- Energy required is 0.395 kWh per kg VFA
- HRT=105 min, Total Volume: 230 m³, Total Anode Area: 77 m², Total Cathode Area: 77 m², Total Ion-exchange Membranes Area: 77 m²

Chain-Elongation

- 96% of ethanol input reacts
- 100% of acetate that reacts with ethanol becomes butyrate
- 82% of butyrate that reacts with ethanol becomes caproate
- CSTR composed of concrete and insulation with centered impeller
- HRT = 480 hr, Mixing Speed = 100 rpm, Total Volume = 6787 m³

Task 4: Education and Outreach

Task 4: Integrate Education and Outreach with Research



CSU new Spur campus
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