

# BETO 2021 Peer Review Separations in Support of Arresting Anaerobic Digestion

March 9, 2021

Organic Waste

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Renewable Resources and Enabling  
Sciences Center

# Project Overview






- **Context:** Carboxylic acids are versatile intermediates for fuel and chemical production. They can be produced from wet waste through Arrested Anaerobic Digestion (AAD) making them carbon negative and cost advantaged
- **Project goals:**
  - Adapt microbial culture to VFA production at  $\text{pH} < 5$
  - Engineer robust *in situ* separations system that operates in high solids and multiple feedstocks
  - Produce more than 10 g of >95% pure VFA product
- **Heilmeier catechism:**
  - ***What are you trying to do?*** Produce purified carboxylic acids from wet waste through AAD
  - ***How is it done today and what are the limits?*** Current AAD processes operate with large energy consumption and are limited to liquid waste feedstocks
  - ***Why is it important?*** Carboxylic acids from wet waste through AAD provides a pathway to carbon negative and cost advantaged (even cost negative) biofuels and biochemicals
  - ***What are the risks?*** Energy consumption of separations must be  $< 20\%$  of the heating value of the carboxylic acids. Bioconversion take place at a  $\text{pH} < 5$ . System must handle solid food waste to access an appreciably sized feedstock market

# Market Trends




## Product

-  Anticipated decrease in gasoline/ethanol demand; diesel demand steady
-  Increasing demand for aviation and marine fuel
-  Demand for higher-performance products
-  Increasing demand for renewable/recyclable materials




## Feedstock

-  Sustained low oil prices
-  Decreasing cost of renewable electricity
-  Sustainable waste management
-  Expanding availability of green H<sub>2</sub>
-  Closing the carbon cycle

## Capital

-  Risk of greenfield investments
-  Challenges and costs of biorefinery start-up
-  Availability of depreciated and underutilized capital equipment

## Social Responsibility

-  Carbon intensity reduction
-  Access to clean air and water
-  Environmental equity

## NREL's Bioenergy Program Is Enabling a Sustainable Energy Future by Responding to Key Market Needs

### Value Proposition

- NREL's AAD technology is the first to produce carbon negative and cost advantaged carboxylic acids from wet and solid waste forming a platform for renewable diesel & aviation fuel, solvents, lubricants, and more.

### Key Differentiators

- First to handle solid food waste in addition to thin stillage and whey. This increases available feedstock by a factor of 2.
- New separation system enables first net positive AAD technology for product energy balance.

# Management

- **Members from NREL's separations and fermentation groups**
- **Monthly and Ad hoc meetings**
- **Work conducted in shared labspace**
- **Dedicated project manager Mrs. Michelle Reed**
- **Publish findings and IP<sup>1</sup>**
- **Collaborate with BETO projects**

## **Providing VFAs to make carbon negative fuels:**

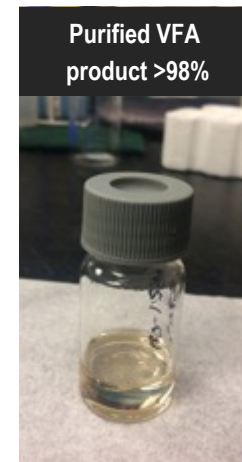
- NREL – Opportunities in Biojet WBS 3.7.3.306 (3/22 @1:35pm ET)
- NREL – Co-optima WBS 3.5.1.8 (3/15 1:30pm ET)
- LANL – Upgrading of biochemical intermediates WBS 2.3.1.103 (3/10 @ 10:00 am ET)

## **Providing process data:**

- NREL – TEA WBS 2.1.0.111 (3/9 @12:00pm ET)

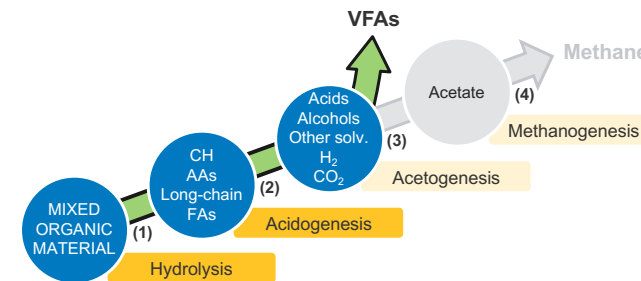
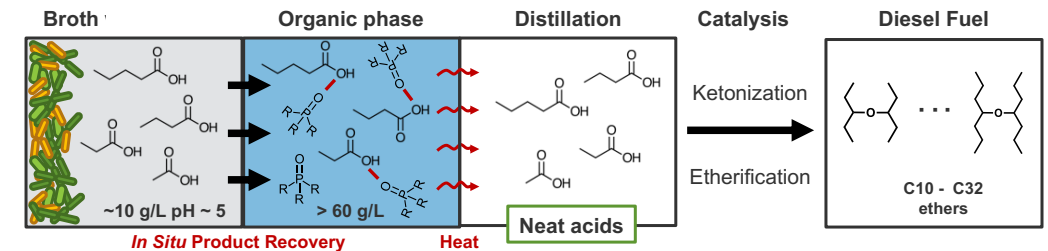
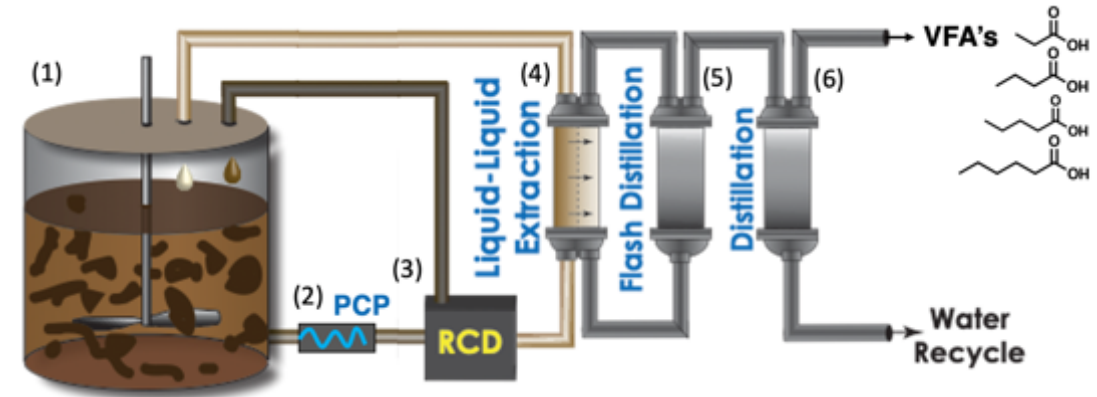
## **Sharing process optimization learning:**

- NREL – Biological Upgrading of Sugars WBS 2.3.2.105 (3/8 @4:40 pm ET)



# Approach

1. Identify, understand, and evolve robust microbial community for VFA production below pH 5
2. Engineer *in situ* separation technology to remove VFAs as they are produced to arrest methanogenesis
3. Demonstrate components of the system in batch mode at > 10wt.% solids loading
4. Demonstrate integrated system in continuous mode at > 10wt.% solids loading with minimum viable product > 10g of VFA's at > 95% purity
5. Demonstrate energy consumption < 50% of the HHV of the VFA product

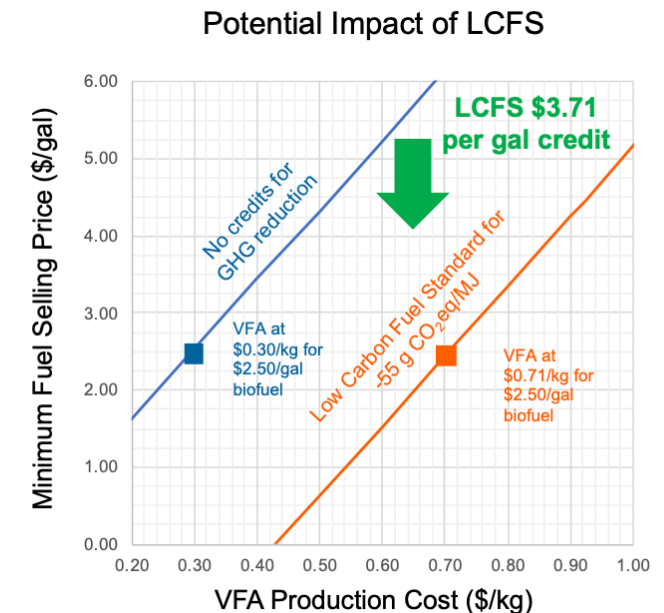
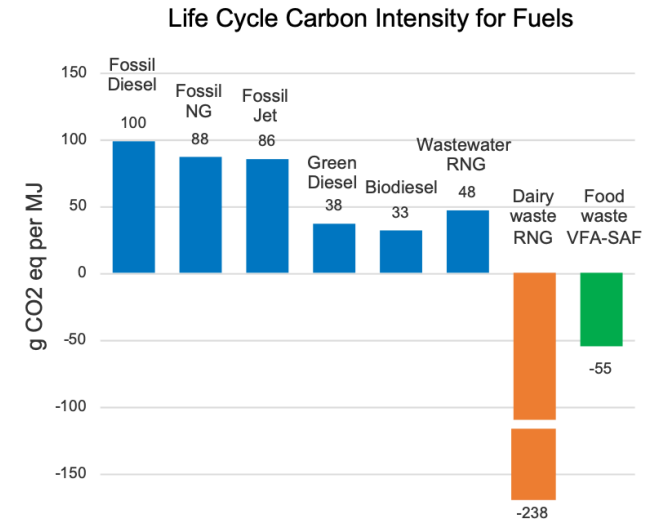


**Go/No-Go decision point:** Project has been sunset

# Impact

## Solves problems inherent in today's AAD technology

- 1. Demonstrated first separations system that is net positive in energy balance**
  - ~22% of the HHV
  - Truly carbon negative
  - Literature systems are NOT carbon negative (slide 17)
- 2. Demonstrated first system that is flexible to multiple feedstocks**
  - Current systems limited to whey and thin stillage at U.S. 33.5 kTA
  - Enables solid food waste at U.S. 66.5 kTA
  - Even CBP of lignocellulose
- 3. In collaboration demonstrated conversion to multiple carbon negative chemicals and fuels**
  - Diesel
  - Sustainable aviation fuel (Biojet consortium talk)
  - Solvents
  - Plastics



# Progress and Outcomes

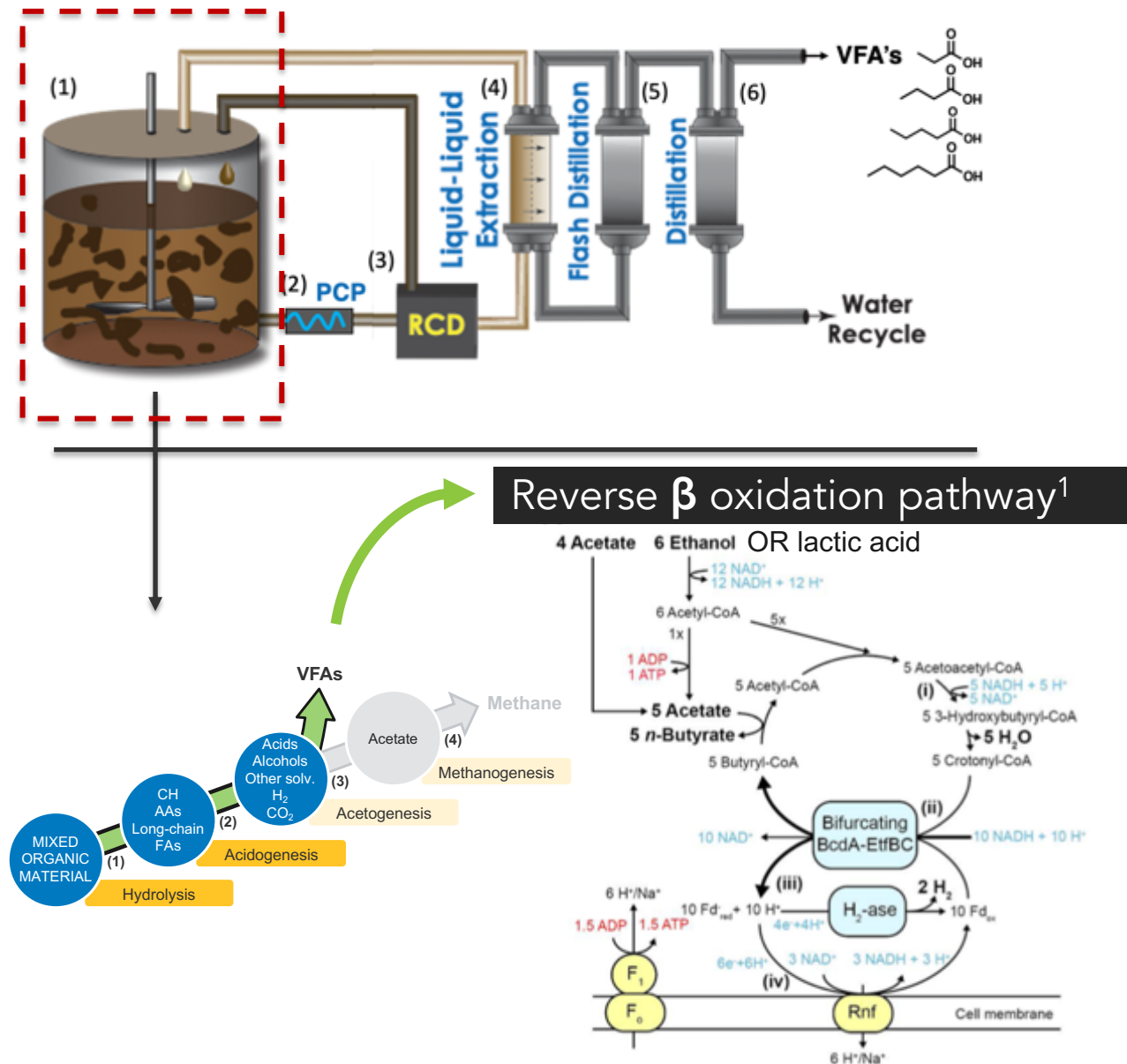
## Principle of operation

### 1. Wet waste is converted to VFAs through

- Acidogenesis to produce short chain carboxylic acids (SCCAs)
- Chain elongation to medium chain carboxylic acids (MCCAs)
- Methanogenesis arrested by *in situ* extraction

### 2. Only carbohydrates enter this pathway

- Food waste and why make best wet waste feedstock for high yield
- Hydrolysis is likely the rate limiting step



1. L.T. Angenent, Env. Sci. & Tech., (2016), 50, 2796

# Progress and Outcomes

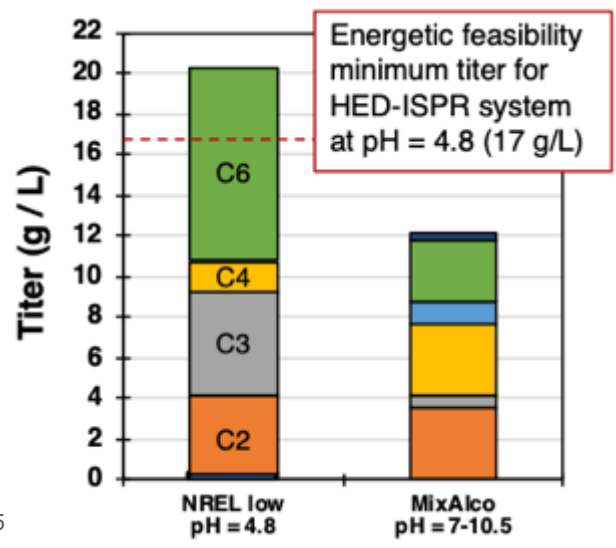
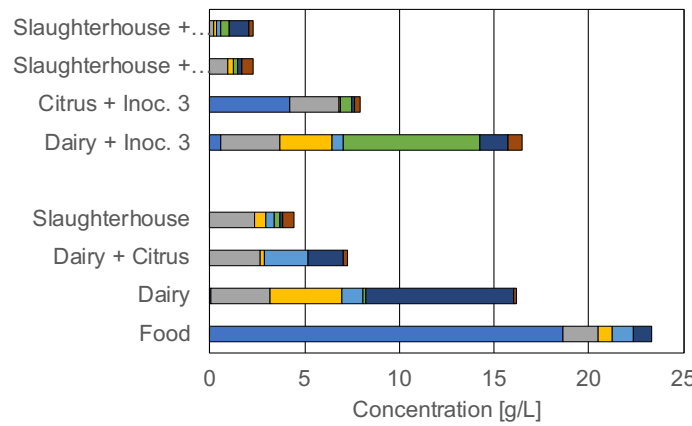
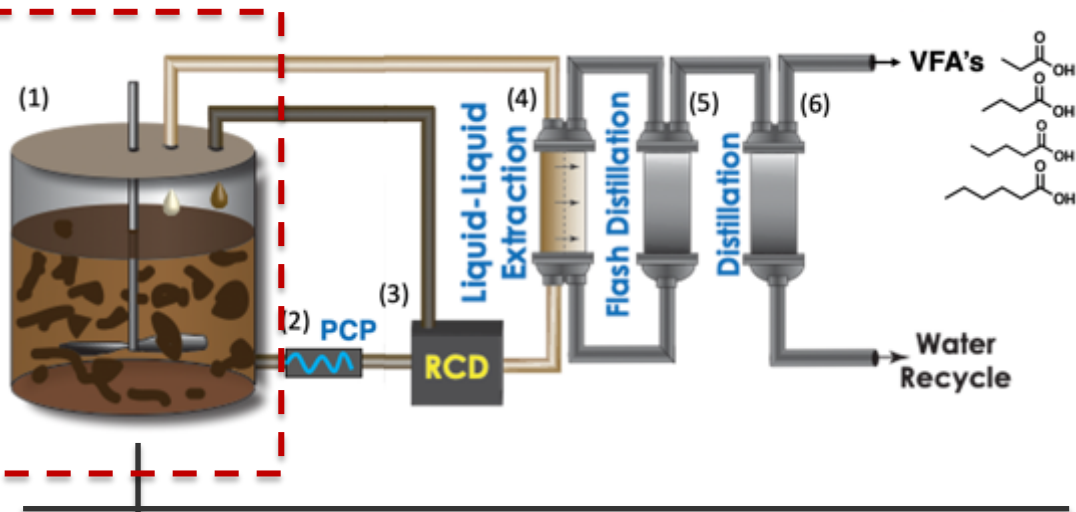
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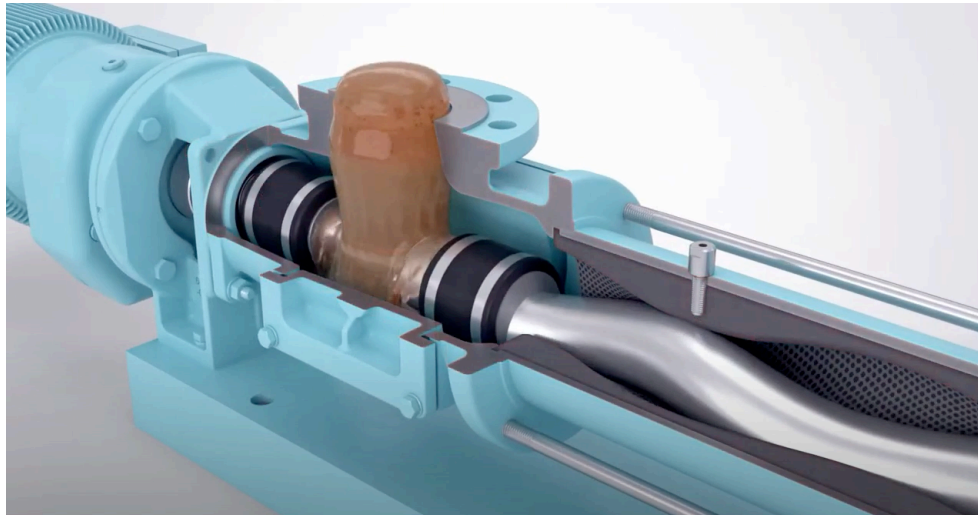
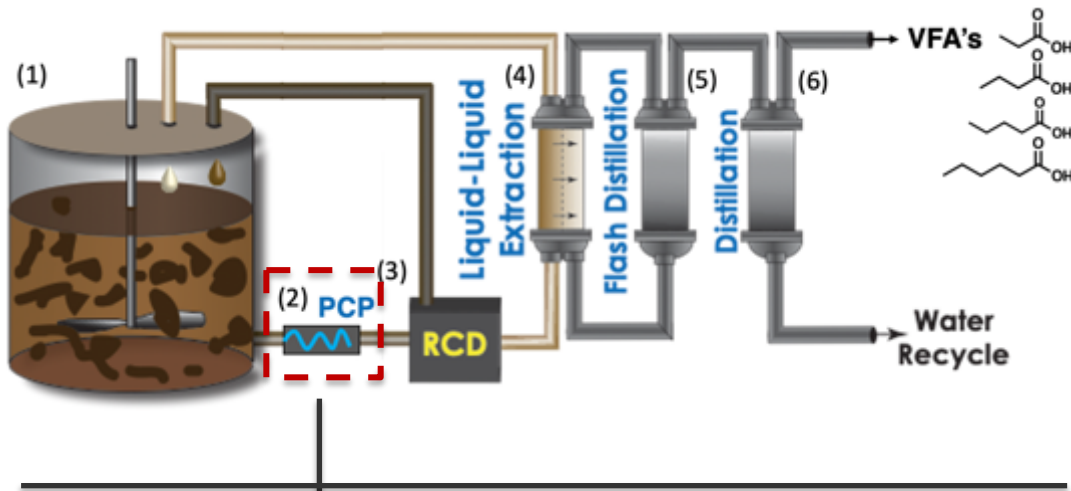
### 2. Only carbohydrates enter this pathway

- Food waste and whey make best wet waste feedstock for high yield
- Hydrolysis is likely the rate limiting step





# Progress and Outcomes



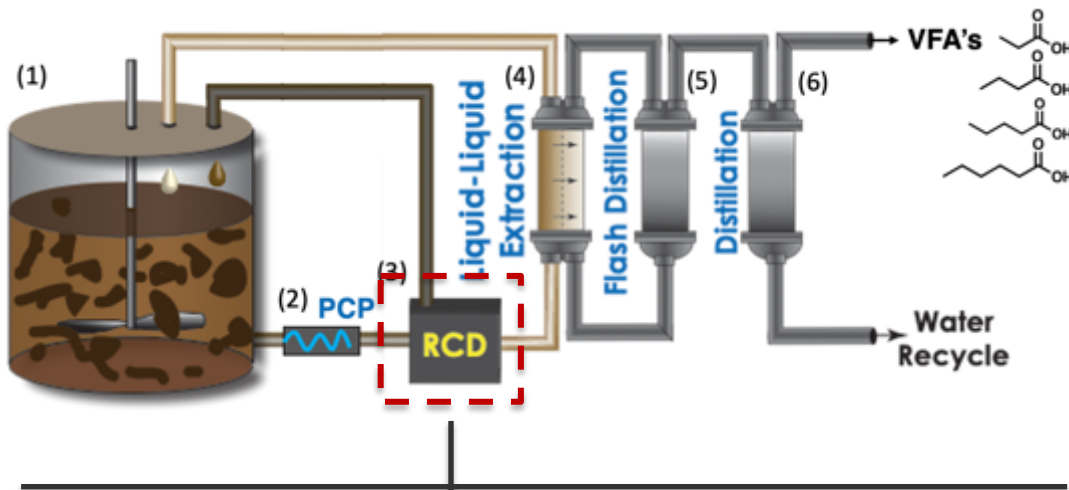
## Principle of operation

### 1. Progressing Cavity Pump (PCP)

- Circulates sludge around loop past the cell and debris retention device
- Used for high solids slurries much greater than 20 wt.%

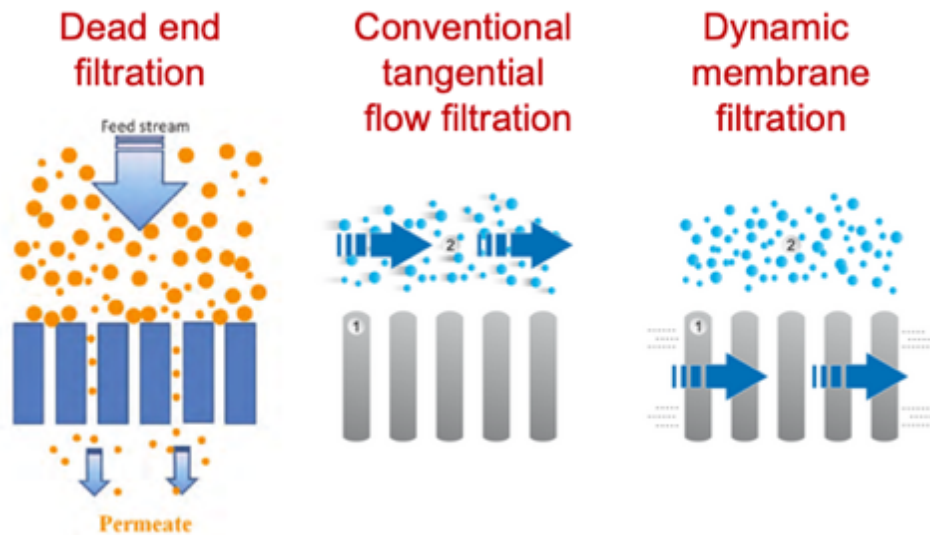


# Progress and Outcomes

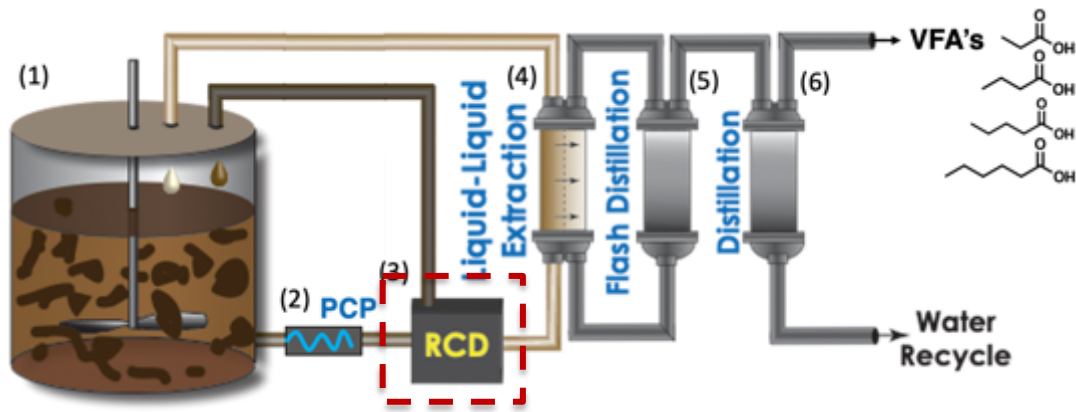


## Principle of operation

- Dynamic membrane used as a robust cell and debris retention device**
  - Rotating Ceramic Disk (RCD)
  - Increased shear rate allows appreciable flux in high solids solutions
  - Turns 6L bioreactor over every 23 hr
  - 0.2  $\mu\text{m}$  pore size. Permeate is sterile
- RCD + PCP consume relatively low amount of energy  $\sim 0.1$  kWh/kg VFA product**
- Crux of separations advance**
  - Allows permeate withdrawal in high solids solutions opening new bioprocessing doors
  - CBP, SSF for low volatility products

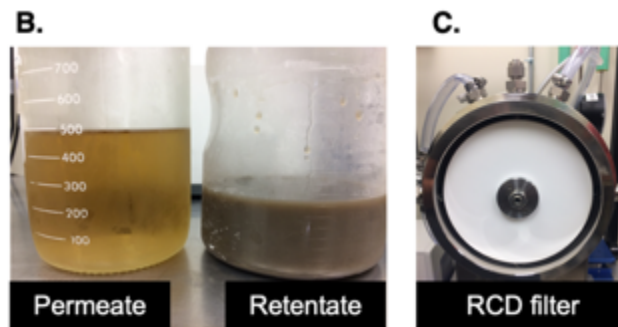
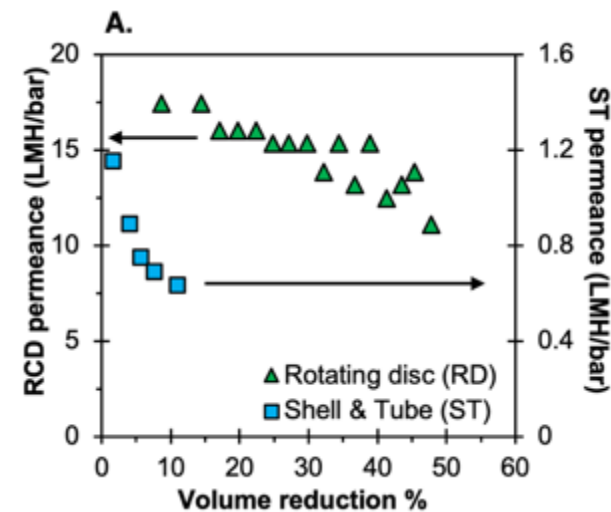


# Progress and Outcomes

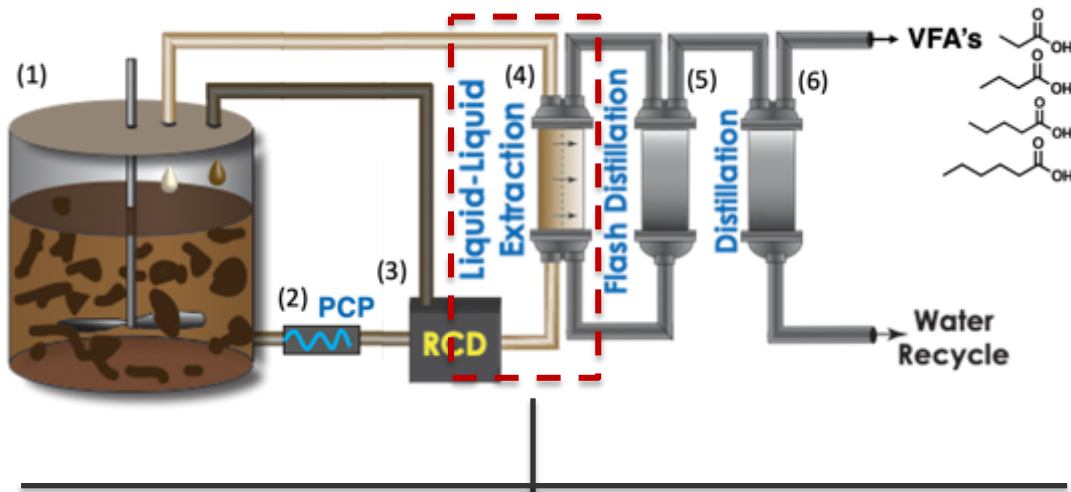


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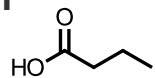
# Progress and Outcomes



## Principle of operation

1. **Extraction system is a continuous LLE**
  - Phosphine oxide extractants
  - Hydrogen bond to acidic proton
  - Highly pH dependent (pH must be  $< 5$ )
2. **Originally developed in separations consortium work**
3. **Energy analysis shows concentration of VFAs must be  $> 4$  wt.% in the organic phase for  $< 20\%$  HHV energy consumption in the distillation train**
  - Achieving that  $> 4$  wt% concentration is dependent on titer and pH

Direct distillation of organic phase



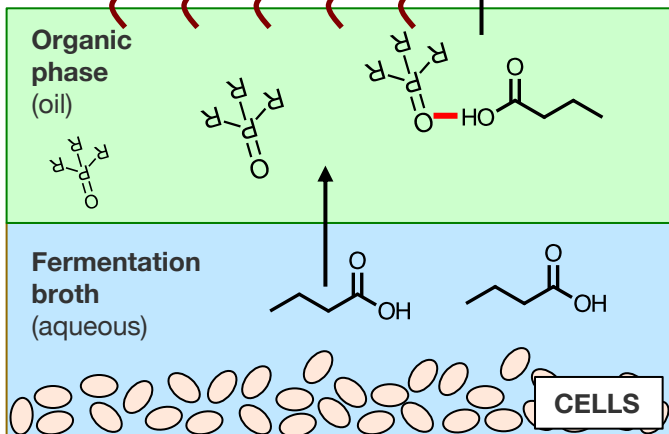
Neat acids

Driving force  
↑  
heat

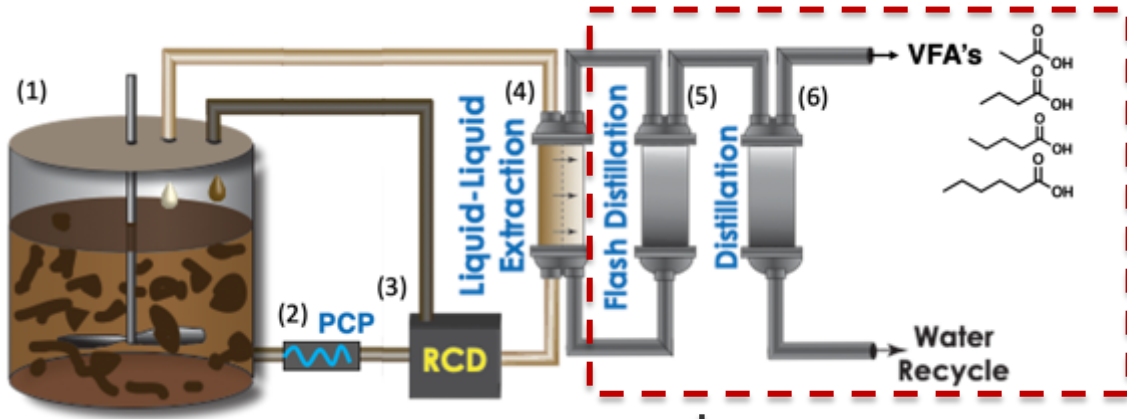
$> 40$  g/L

Driving force  
↑  
Equilibrium

$\sim 10$  g/L



# Progress and Outcomes

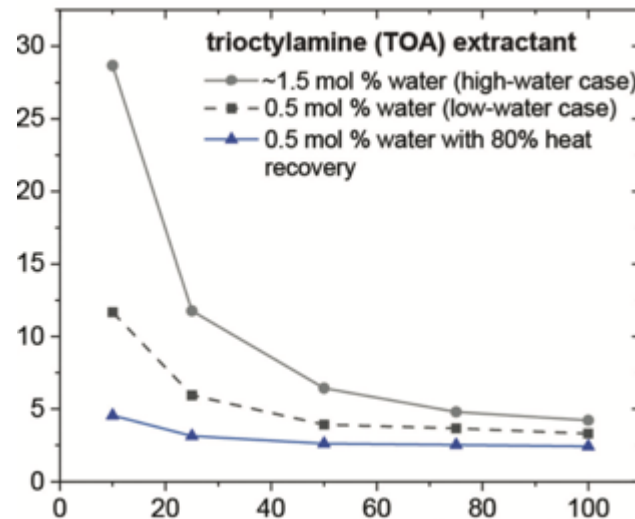
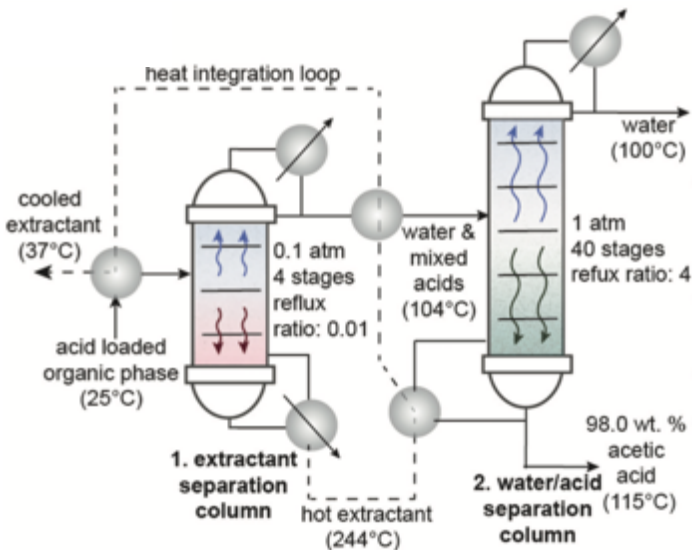


## Principle of operation

1. Energy analysis shows concentration of VFAs must be  $> 4\text{wt.}\%$  in the organic phase for  $< 20\%$  HHV energy consumption in the distillation train<sup>1</sup>

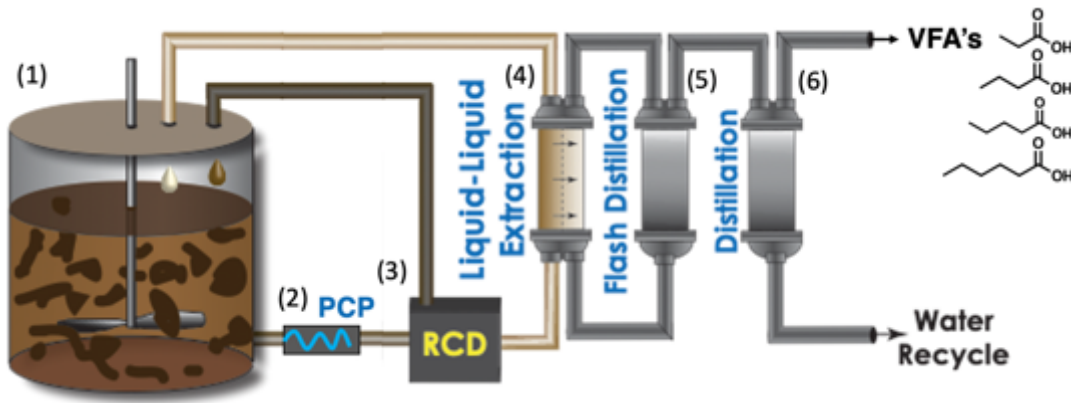
- Achieving that  $> 4\text{ wt}\%$  concentration is dependent on titer and pH
- $\text{pH} < 5$
- Titer  $\sim > 15\text{ g/L}$
- Titer requirements are lowered as pH drops
- Water is recycled back to bioreactor

Direct distillation of organic phase



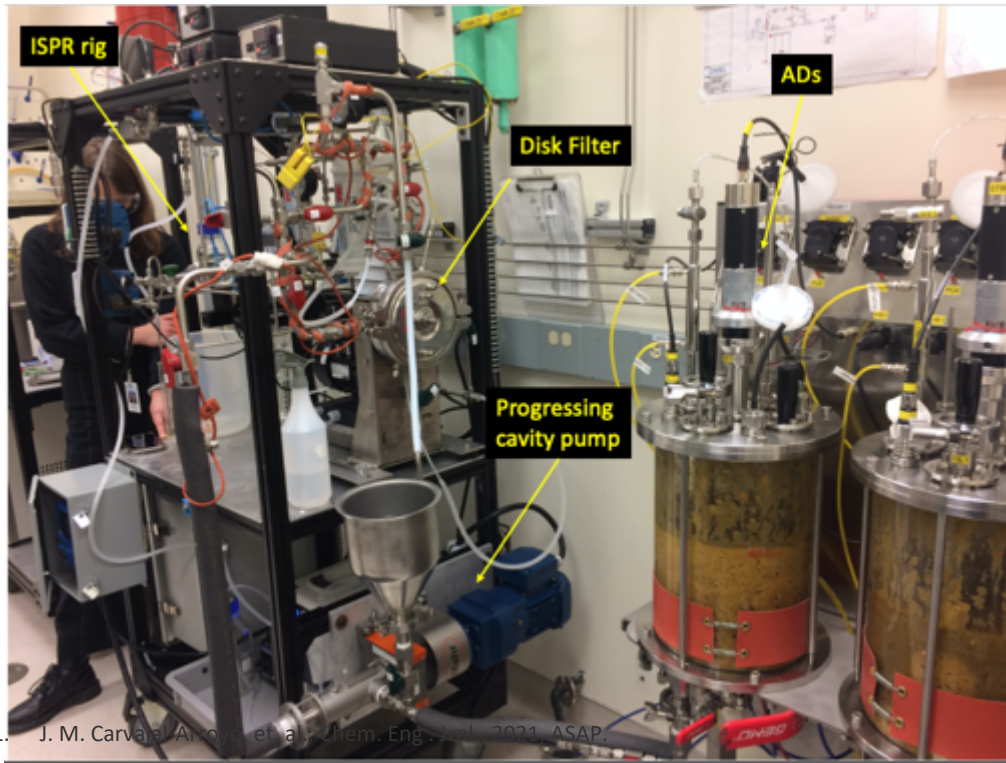
1. P.O Saboe Green Chem., (2018), 20 (8), 1791

# Progress and Outcomes

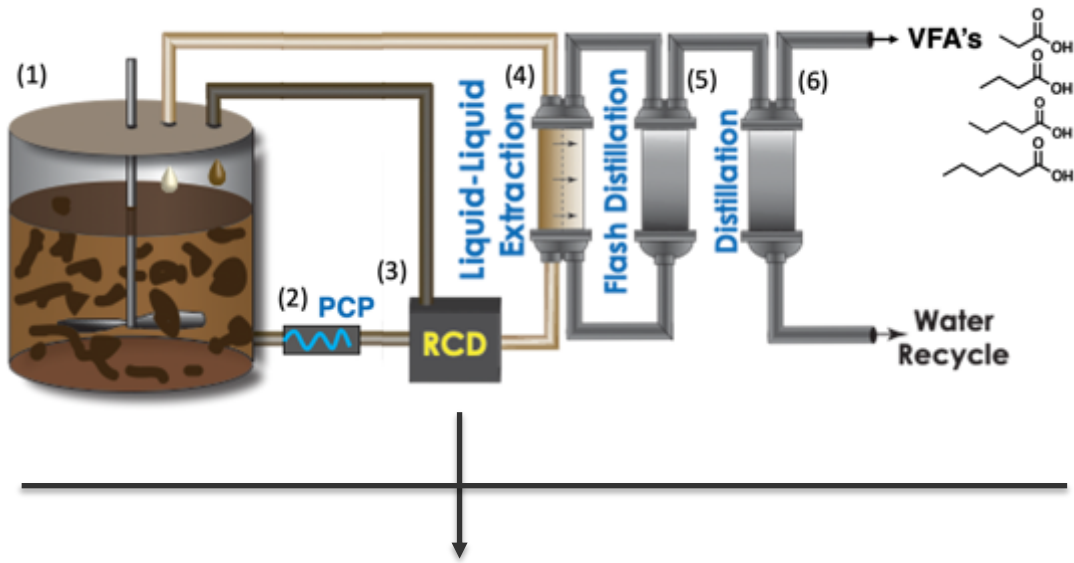


## Integrated run (summary)

- First demonstration of Short Chain and Medium Chain Carboxylic acids (SCCAs and MCCAs) production from solid food and dairy waste at 13-15 wt.% solids loading
- Only system in the world that can decouple HRT and SRT at solids >5 wt.%
- First demonstration at pH < 4.5 (pH 3.7-3.8)
- Rate = 0.589 g / L day of VFAs
- Need optimization of process conditions for biology to utilize the chain elongation pathway more effectively

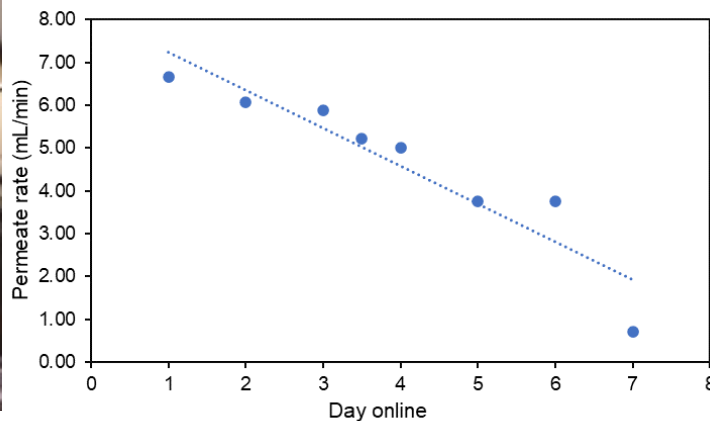


# Progress and Outcomes

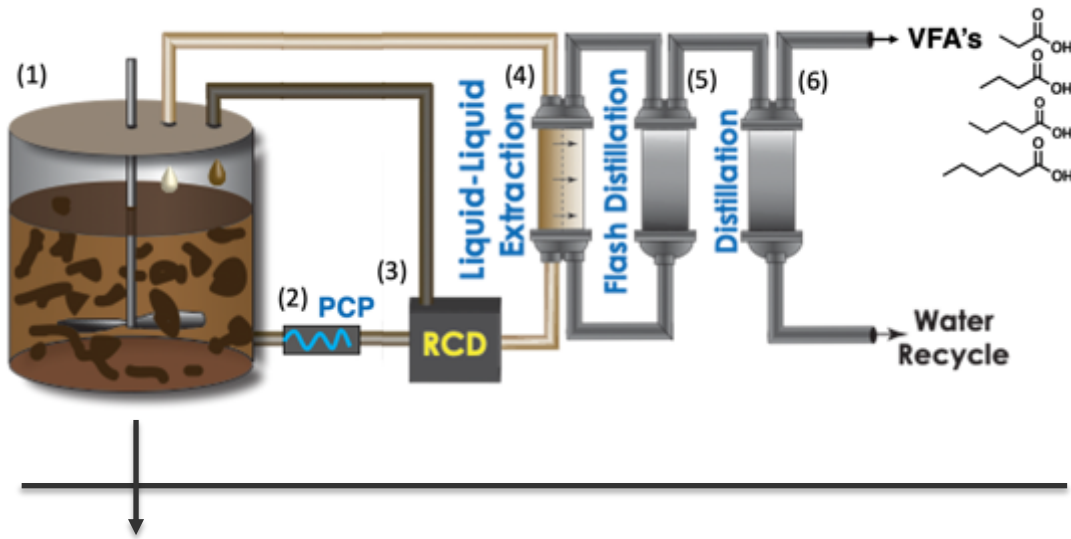


## Integrated run (disk filter)

- System is sterile past disk
- Permeate rate  $\sim 4$  ml/min = 1 bioreactor every  $\sim 25$  hours
- Washed with water at day 6 to restore flux
- ***Operated for 7 days at 13.8 wt.% solids***

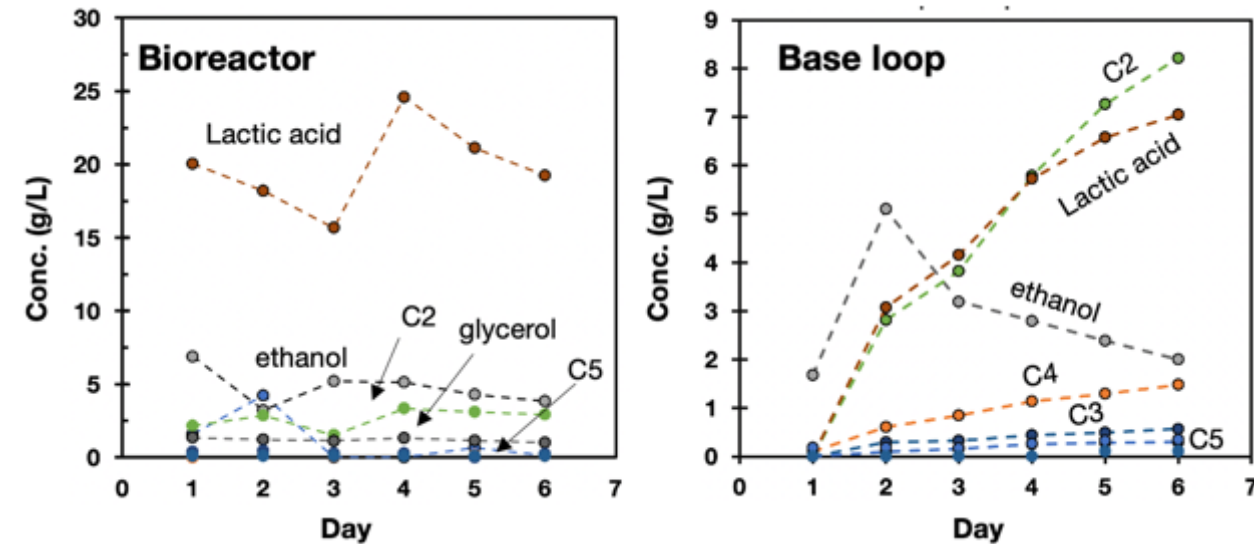


# Progress and Outcomes



## Integrated run (bioconversion)

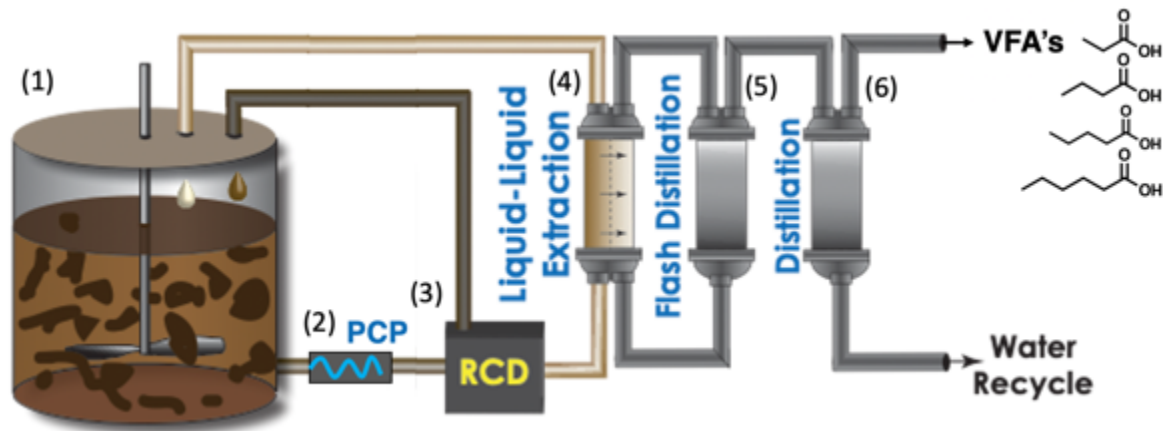
- Extracted profiles show:
  - Efficient extraction of lactic, C2, C4, and C5.
  - Ideally would not extract C2 and lactic
  - Estimate a C to VFA % of ~26-35%<sup>1</sup>
- All ingredients for chain elongation are there
- Extracting SCCA too fast
- Optimal pH is ~4.5 (where C2 and lactic are not extracted)
- CHN compositional analysis



1. J. M. Carvajal-Arroyo, et. al., Chem. Eng. J., 2021, ASAP

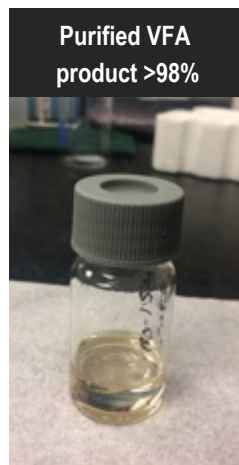


# Comparison to the State of the Art

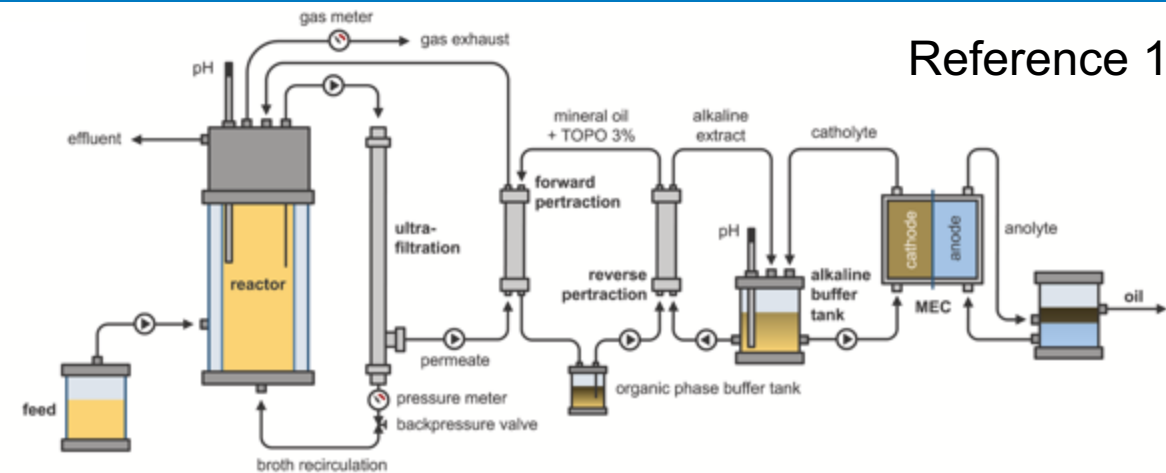


pH = 3.7      Feedstock = food waste      Solids = ~13.8 wt. %

	Rate g/L/d
Lactic	0.27
C2	0.25
C3	0.025
C4	0.044
TOTAL	0.589 g/ L / day



- Energy consumption 0.72 kWh/kg
- ~18-22% of HHV of the VFA product
- Demonstrated solid feedstock conversion!



pH = 5      Feedstock = Thin stillage      Solids = ~1-3 wt. %

	Rate g/L/d
Lactic, C2, C3	N.D.
C4	0.16
C5	0.21
C6	0.89
C7	0.1
C8	0.13
Total	1.49 g/L/day

• Excellent chain elongation

• Limited to solids < 3 wt. %

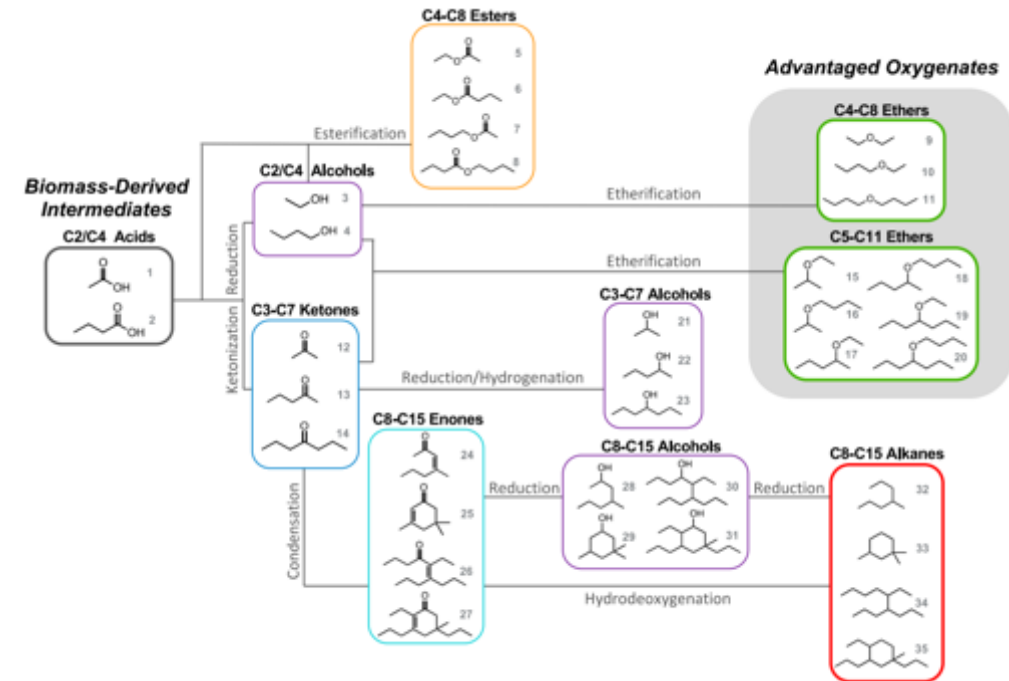
• Oil not pure and contains grease & coextracted salts

• 160 kWh/kg is 222x energy consumption of NREL system

# Biorefinery of the future

## Potential concept for the biorefinery of the future

- **Solids handling means flexibility in feedstock**
  - In addition to the current use of whey and thin stillage (33.5 kTA in U.S), NRELs technology accesses another 66.5 kTA in U.S. of food waste
  - Open to other applications where scale and solids loadings are a currently a challenge: SSF & CBP
- **Minimal Sterility requirements**
- **Separations are first positive energy balance on VFA production**
  - Truly carbon negative (EER is at best carbon neutral)
  - Literature systems are NOT carbon negative
- **Traditional bioprocess more cost effective**
  - CBP of lignocellulose removes ~\$1/kg of production cost
  - Solids handling has been a limiting hurdle for scaling
- **VFAs are a flexible product well beyond ethanol (collaboration with other BETO projects at NREL and LANL)**
  - SAF • Surfactants • Solvents
  - Diesel • Lubricants • Monomers



# Quad Chart Overview

## Timeline

- Project start 10-1-2018
- Project end 12-31-2020

	FY20	Active Project
DOE Funding	10/01/2019 – 9/30/2020	\$250k/yr (\$750k total over 3 years)

## Project Partners (unfunded collaborations)\*

- Colorado State University
- Rocky Mountain Composting
- Denver Metro WW Reclamation District
- Coors
- Leprino Foods
- Harvest power

## Barriers addressed

1. Feedstock availability and cost (Ft-A)
2. Selective separation of organic species (Ct-O)
3. First-of-a-kind technology development (ADO-F)

## Project Goal

- Develop robust ISPR system to remove VFAs from AD units and to pursue enabling understanding of how microbial communities respond to *in situ* separations and arrested methanogenesis, towards improved inoculum

## End of Project Milestone

*Demonstrate an integrated AD unit with online separations to produce carboxylic acids from the bioconversion of waste feedstocks*

## Funding Mechanism

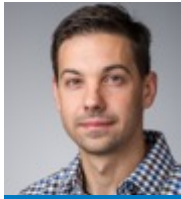
AOP funded project

\*Only fill out if applicable.

# Acknowledgments



**Beau Hoffman and Mark Philbrick**



Eric M.  
Karp



Patrick O.  
Saboe



Violeta  
Sánchez i Nogué

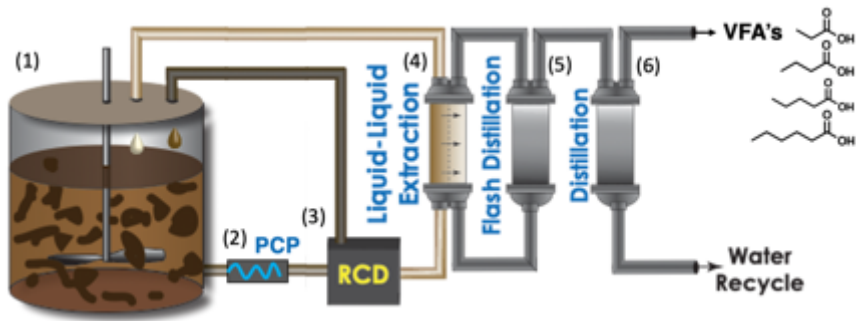
Colin Kneucker  
Dylan C. Thomas  
Hanna Monroe  
Gregg T. Beckham  
Stefan Haugen

Sean Woodworth  
Justin B. Sluiter  
Steve R. Decker  
Venkat Subramanian  
Todd Vinzant

## Industrial collaborators

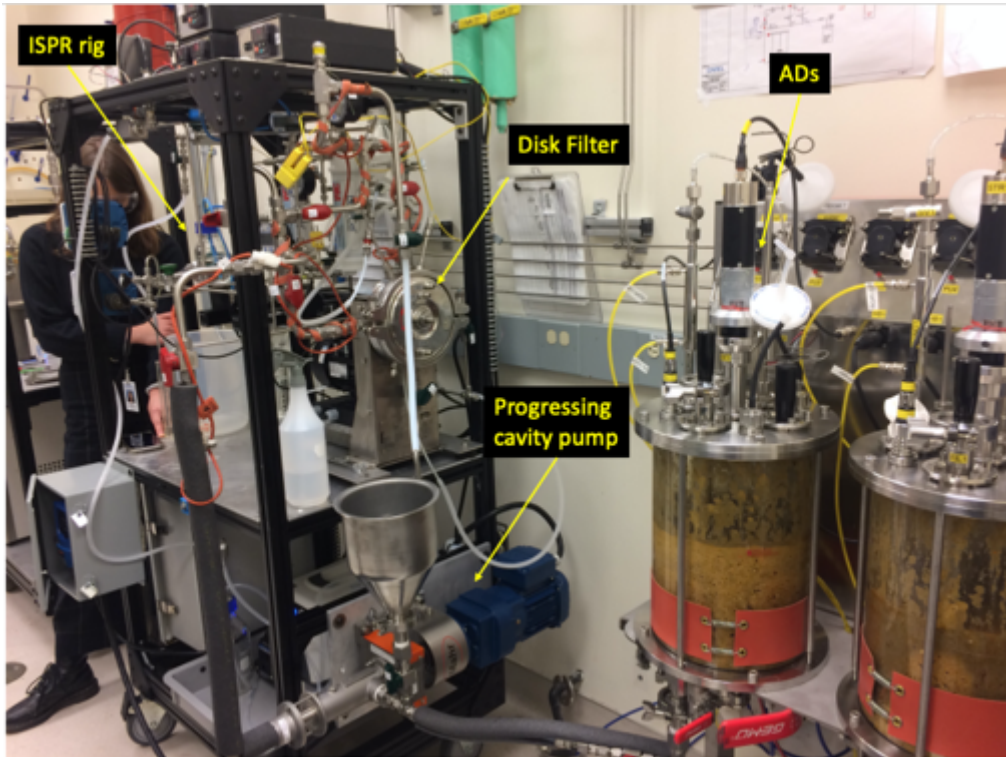
- **Rocky Mountain Composting** – Eric Kenna
- **Leprino Foods** – Joseph Herrud, James Frazier & Christopher Dorcey
- **Denver Metro Wastewater Reclamation District** – Isaac Avila, Quintin Schermerhorn & Jim McQuarrie
- **Coors Brewing Company** – Jeremy Woolf & Kevin Dickerson
- **JBS USA** – Mark Risema
- **Colorado State University** – Marcia Stille
- **ARS-USDA (Horticultural Research Laboratory)** – Christina Dorado
- **New Belgium Brewing Company** – Mark Fischer
- **Harvest Power** – Gary Aguinaga & Javier Corredor





# Questions?

[www.nrel.gov](http://www.nrel.gov)



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25 minutes with 10 minutes of Q&A

# Response to previous reviewer comments

Weakness	Response
<p>Weakness: In the world of technical accomplishments, feedstock analysis for composition does not rank amongst the top. It would have been more surprising if there were technical hurdles to this. In understanding the rate limiting steps in VFA production from cake, rumen fiber, clarified liquor, and slurry, the yield of VFA from the added supplement (glucose, oil, or YE) was not noted. If the goal was to determine stalled VFA production due to feedstock fermentability or low microbial activity the reader needs to know to what level the added carbon compounds were degraded.</p>	<p>There definitely are major challenges associated with developing general compositional analysis methods for waste feedstock fed into AD units and for the outputs of these units. Developing those methods, however, is outside the scope of this project. We fully realize the shortcomings of traditional methods and are working with outside tasks to address this as much as possible. However, simple methods will be utilized during the demonstration of the system such as total carbon and VFA concentration in the distillate.</p>
<p>Weakness: At this stage is not clear if the process is scalable and if can achieve economics enabling deployment. The ISBR reactor will need considerable validation at scale for long period of time with "real" high ds feedstock. Economics of mixed organic acids may not be very attractive.</p>	<p>In this presentation we demonstrate continuous operation at the minipilot scale validating all unit operations and net positive energy consumption.</p>
<p>Weakness: It is not clear what the value of the target VFAs are relative to upgraded biogas. If the relative value of a specific VFA is not high enough, it won't be worth putting in the considerable effort to develop this process for that VFA species. The project claims that the technology solves a major cost hurdle for meeting the BETO \$3/gge biofuel cost target, but it is not clear why. The \$3/gge target applies to fuels, whereas the intent of this project is to generate renewable intermediate chemicals.</p>	<p>The aim is not to have the VFAs as the final product but send them to upgrading processes being developed in the ChemCatBio portfolio for fuel production. Reactions such as ketonization and condensation reactions can be applied to generate a mixed fuel product suitable for light or heavy duty vehicles. Post demonstration of this ISPR arrested AD technology those conversion pathways will likely be investigated.</p>

# Publications, patents, and commercialization

## **PATENTS**

1. Advanced Anaerobic digestion to carboxylic acids U.S. Patent App. No. 63/020,598

## **PUBLICATIONS**

1. Arrested Anaerobic Digestion in High Solids Environments, *in prep.*



# Disk filter scalability



## Very large units available

- Andritz, Spintek, Kerafol, etc.
- Disk overlap increases CIP, flux, and uptime before cleaning needed