DOE Bioenergy Technologies Office (BETO) 2019 Project Peer Review

WBS 2.3.2.107
Separations in Support of Arresting Anaerobic Digestion

Waste to Energy

March 4-7, 2019

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National Renewable Energy Laboratory

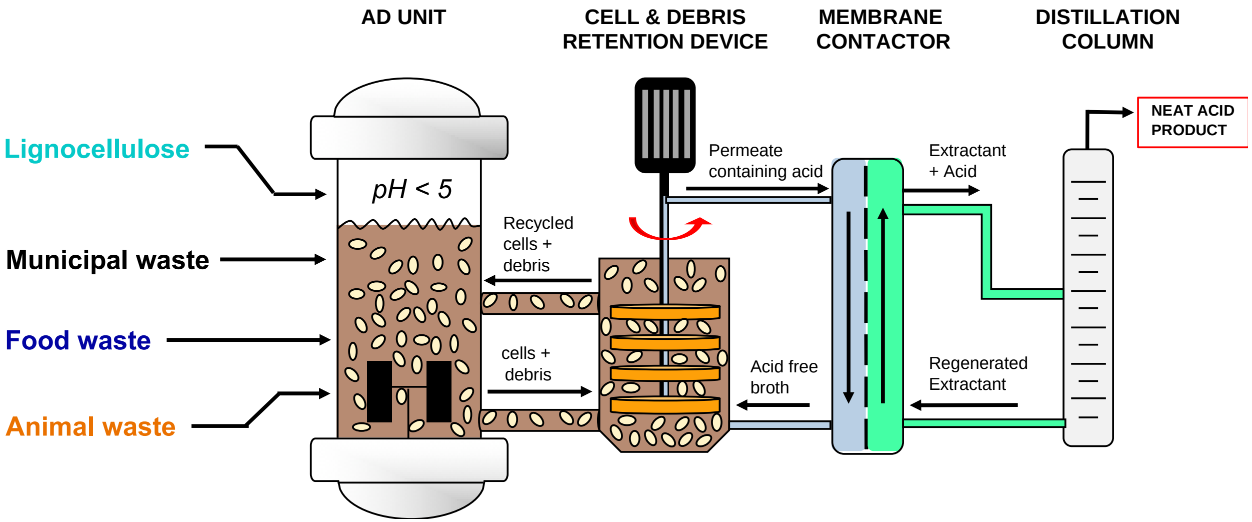
Goal Statement

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

- Contribute to 2022 BETO cost targets of $3/GGE for HC fuel production
- Leverages on-going work with other tasks for producing carboxylate platform chemicals

Aim 1: Mixed culture(s) for bio acid production from of waste feedstocks at pH < 5

Aim 2: In-situ separations to remove VFA's and arrest methanogenesis



Relevance: Fuels from wastes are major benefit to the U.S. biorefinery infrastructure

- Lower feedstock cost through the use of waste
- In situ separations broadens chemicals produced from AD units
- **Outcome:** Demonstrate, scalable In Situ Product Recovery process for converting waste to platform carboxylates

Quad Chart Overview

Timeline

- Start date: 10/2017 (FY 18)
- End date: 09/2020 (FY 20)
- Percent complete: 50%

Barriers Addressed

- Feedstock availability and cost (Ft-A)
  - Waste feedstocks are cost advantaged, modular deployment, on-site conversion
- Selective separation of organic species (Ct-O)
  - LLE selective to carboxylic acid removal
- First-of-a-kind technology development (ADO-F)
  - ISPR, arrested AD, solids handling of waste feedstocks

Budget

	FY 18 Costs	FY 19 Costs	Projected FY 20 Costs	Total Planned Funding (FY19–FY20)
DOE-funded	$250K	$250K	$250k	$750K

PARTNERS: Metro Wastewater Reclamation District (Denver), Coors Brewing Company, JBS USA, New Belgium Brewing Company, Agricultural Research Service USDA (Horticultural Research Laboratory), Del Monte, Harvest Power.

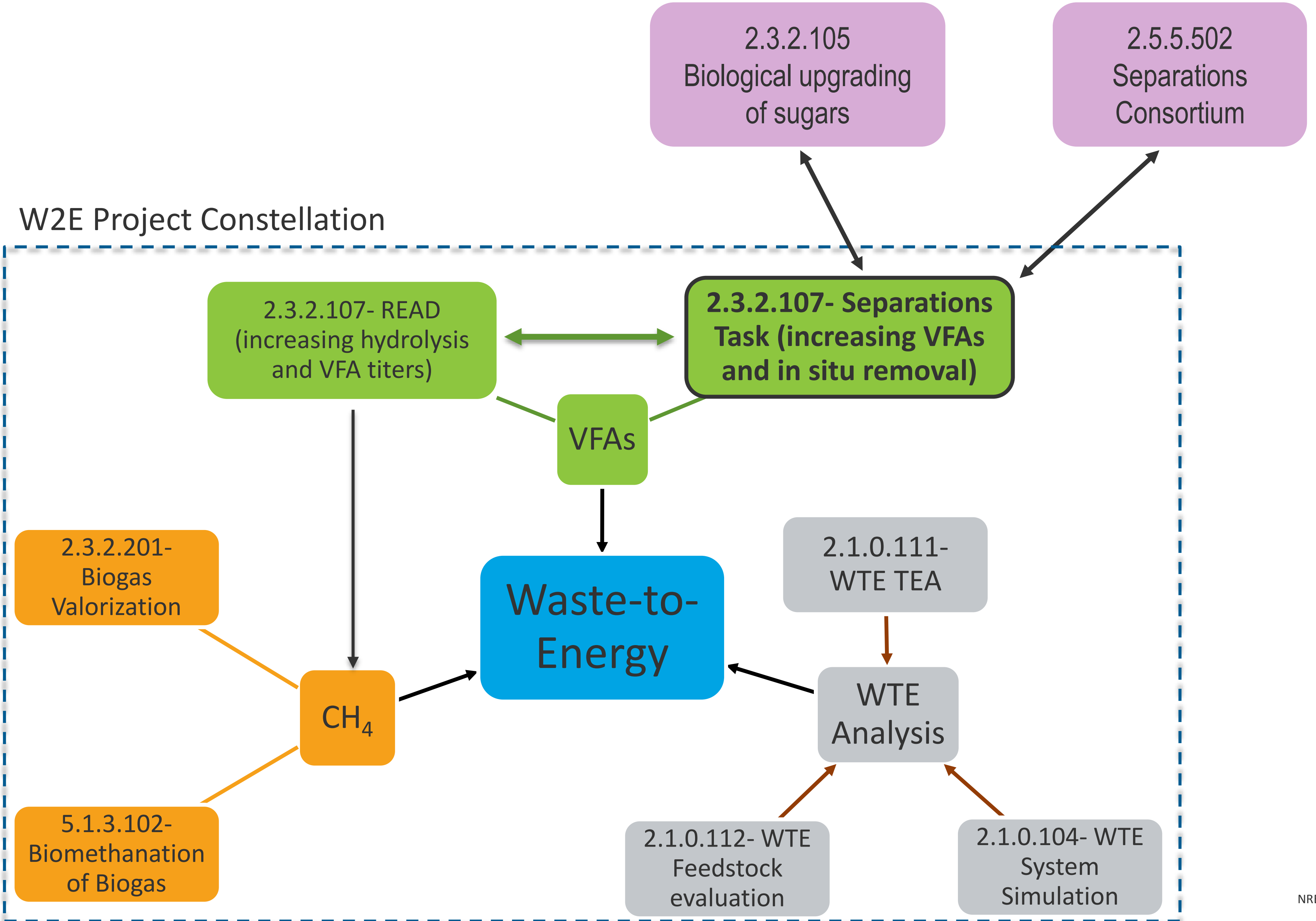
Objective

- Identify and appropriate microbiome & waste feedstock to produce VFA's below a pH of 5
- Engineer an *in situ* separations system to remove VFA's as they are produced
- Demonstrate an integrated AD unit to produce VFA's and effectively arrest methanogenesis

End of Project Goal

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

Interactions with Biochemical Conversion Projects



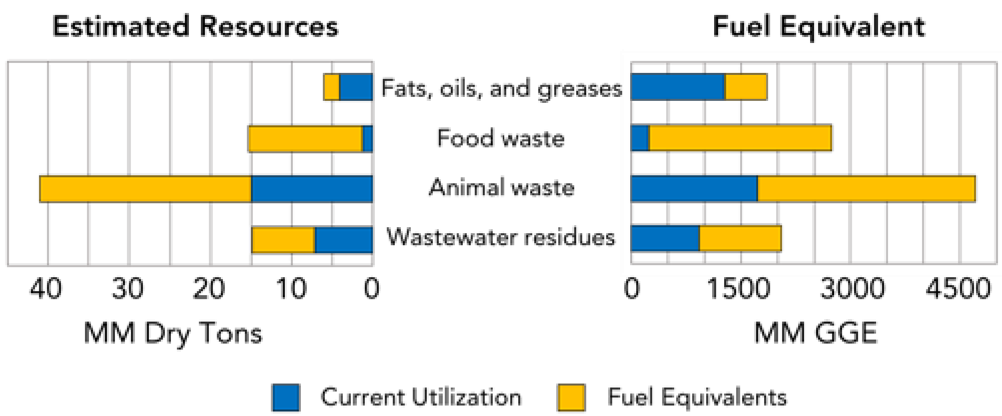
Project Overview

History: Biogas from AD has been around for centuries, only in the last decade has technology targeting other chemicals from AD units been investigated.

- BETO has historically identified cost advantages for waste feedstocks over lignocellulosic feedstocks[1]
- Feedstock cost identified as a major cost driver for HC biofuels[2,3]

Context: Differences over agricultural residues

- Cost advantaged feedstock(s) over lignocellulosic agricultural residues
- Non-sterile cultures
- Require modular manufacturing approach → Faster market adoption
- Significant infrastructure already in place



Project Objectives:

- Identify and appropriate waste feedstock to produce VFA's below a pH of 5
- Engineer an *in situ* separations system to remove VFA's as they are produced
- Demonstrate an integrated AD unit to produce VFA's and effectively arrest methanogenesis

(1) Biofuels and Bioproducts from wet and gaseous waste streams: Challenges and opportunities, BETO, 2017

(2) S. Chu & A. Majumdar, *Nature*, 2012, **488**, 294

(3) Ryan Davis et. al., Technical report # NREL/TP-5100-71949, 2018

APPROACH

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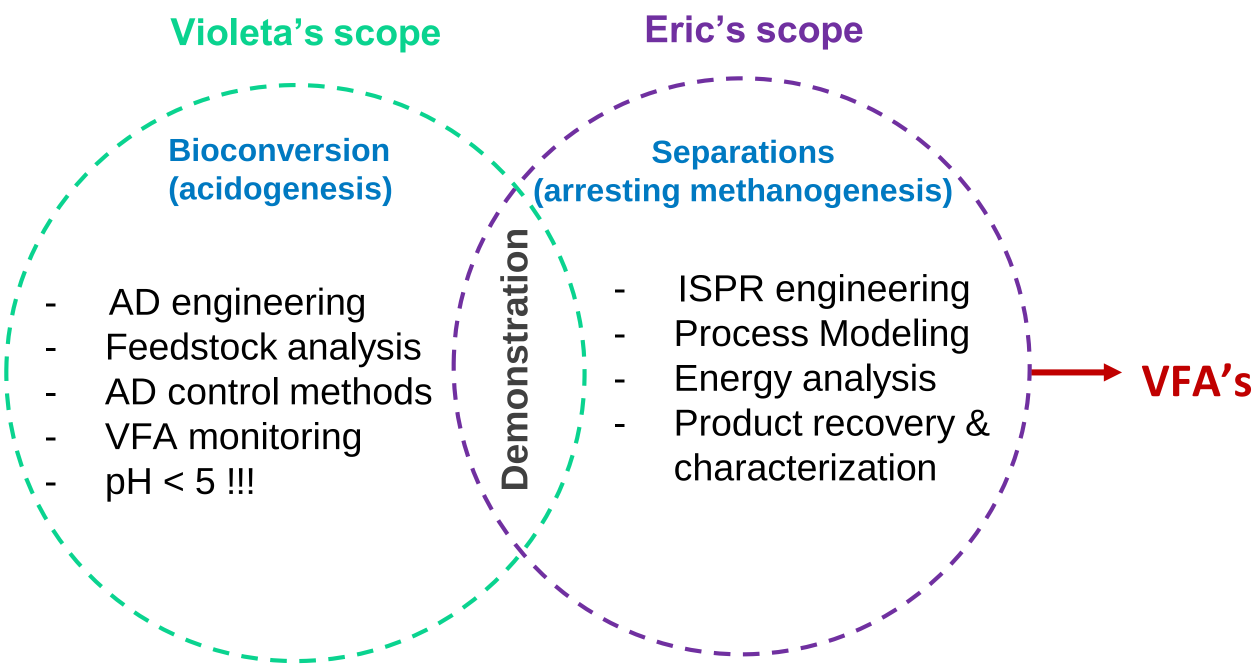
Management Approach

- *Develop culture / AD unit to digest a waste feedstock at pH < 5*
- *Engineer in situ separations system*
- *Demonstrate integrated unit to produce VFAs and effectively arrest methanogenisis*



Experienced task leads in Bioconversion and Separations

Collaborations with
- Separations Consortium (WBS 2.5.5.502)
- Analytical development and support
- Reverse engineering AD (WBS 2.3.2.108)
- TEA team (WBS 2.1.0.111)

Approach:

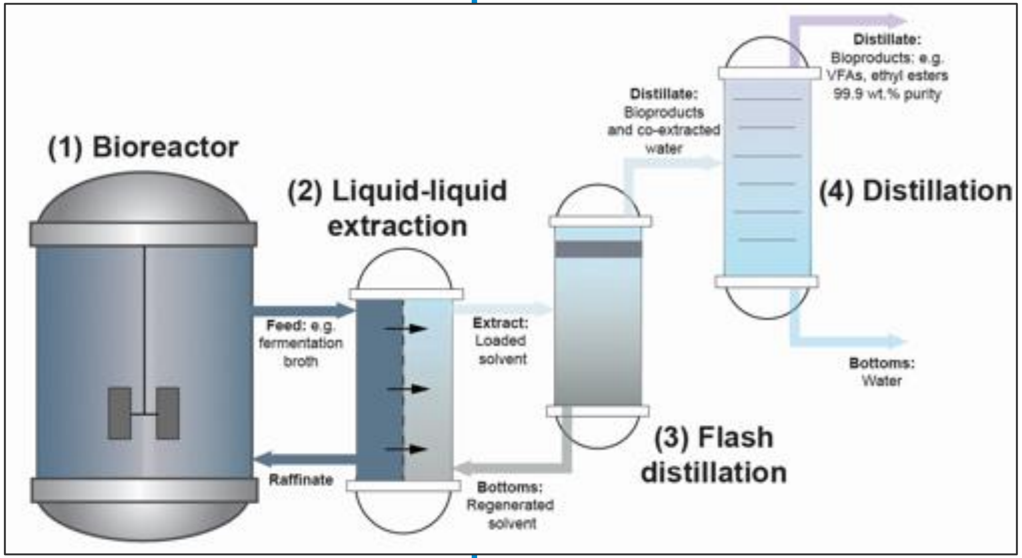
PI's
- Reports / slides
- Design experiments / systems
- Prospecting
- Publish work

Scientists / interns (1 postdoc, 2 interns)
- Collect data
- Maintain / build equipment
- Carry out experiments
- Data workup

Technical Approach

Aim 1: Identify, understand, and evolve robust microbial community for VFA production below pH 5

Aim 2: Engineer in situ separation technology to remove VFA's as they are produced to arrest methanogenesis.



Critical success factors
- Obtain multiple consortia for screening
- Understand rate limiting steps

Primary challenges:
- Maintain VFA production below a pH of 5 for ISPR
- Methods for feedstock analysis not yet developed

Critical success factors:
- Keep steady state acid titer below toxicity level
- Expand system developed in SepCon[1] to operate with mixed slate of VFAs

Primary challenges:
- Must handle solids present in AD units
- Extractant can not be toxic to consortia

(1) Saboe, Karp et al., *Green Chem*, 2018, 20 (8), 1791

TECHNICAL ACCOMPLISHMENTS

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Consortia AD Biology

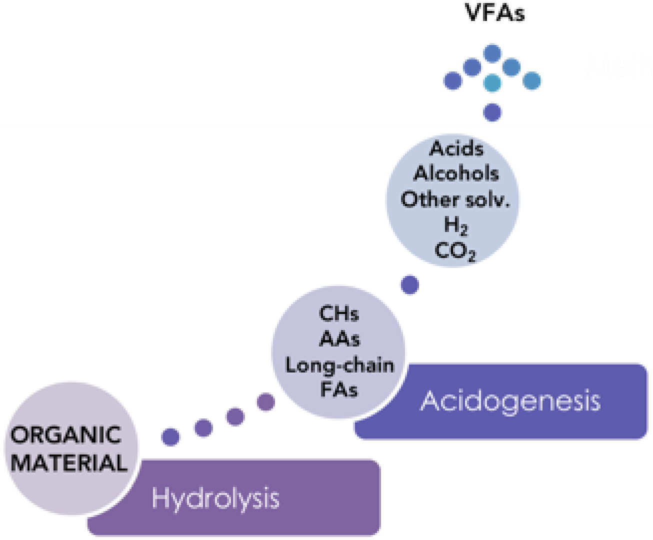
- Feedstock analysis (Cake & Rumen fiber)
- Feedstock digestions
- Identifying rate limiting steps
- Semi-continuous culture

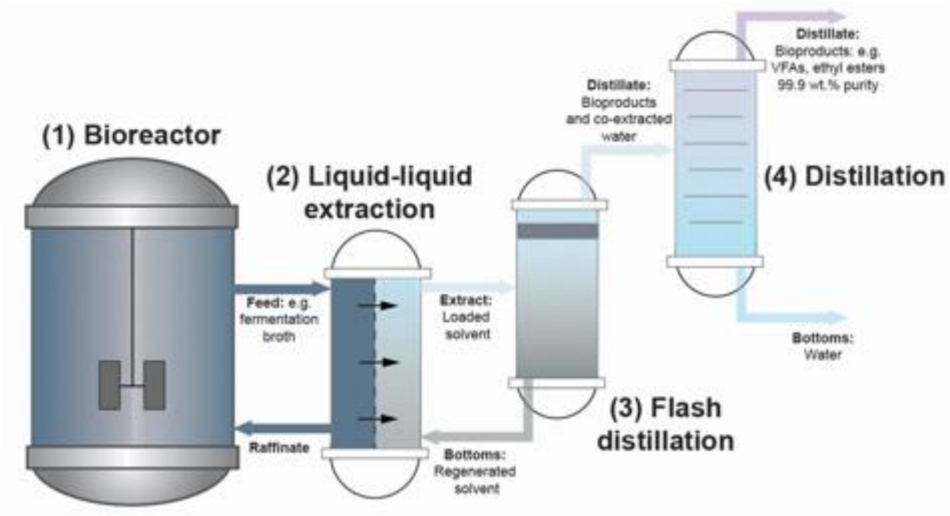
In situ separations system

- Calculating needed VFA titers and pH requirements
- Demonstration of VFA recovery
- Handling solids
- Engineering of in situ separations system
- Energy analysis

Demonstration / Integration

- Year 3 plans for integration





Technical Accomplishments – Feedstock Analysis

Hypothesis

We can modify current NREL analytical methods to determine compositional analysis of wet waste feedstocks

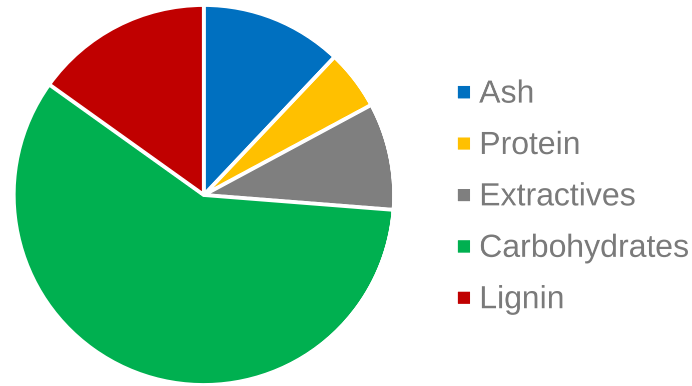
Cake

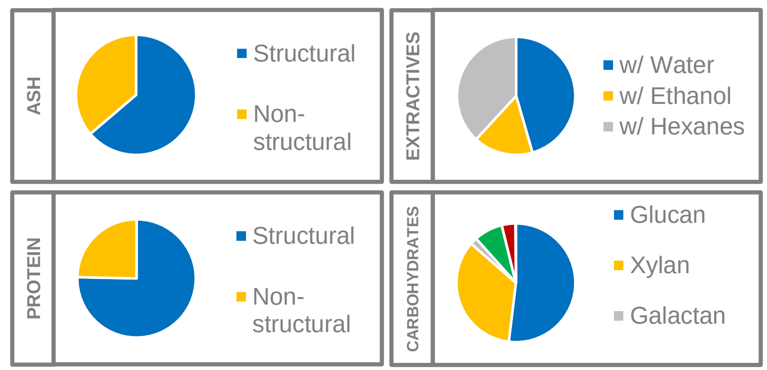
Rumen fiber

Outcome

- We can now perform a basic compositional analysis on non–conventional feedstocks
- Feedstocks highly different
  - Cake: Extractives, protein, and ash > 75%
  - Rumen fiber: Carbohydrates > 50%

Example compositional analysis: Rumen fiber





Technical Accomplishments – Feedstock Digestions

Hypothesis

Different process components will affect VFA production levels and composition

Strategy

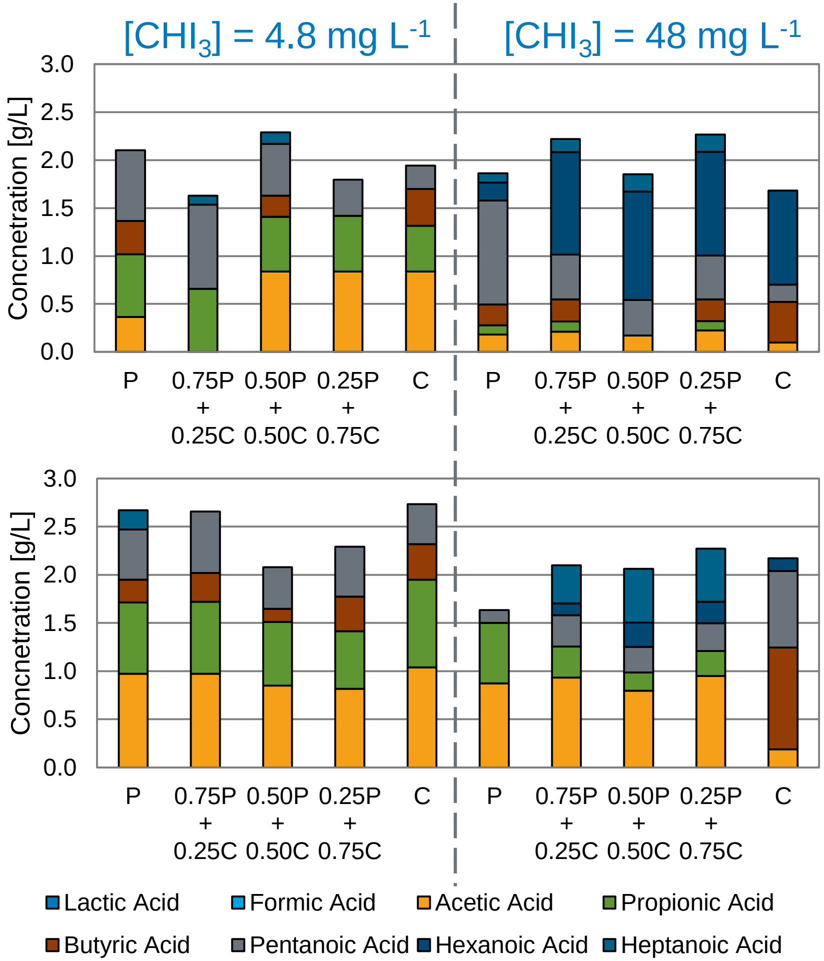
- Small vials
- Increase throughput
- Evaluated variables
  - Feedstock
  - Inocula
  - Iodoform

Outcome

- Similar levels of VFA production regardless of feedstock
- Higher iodoform promotes longer chain VFA production
- Stalled VFA production after an initial constant VFA production rate

Final stage AD sludge (~ pH 7)

Acid stage AD sludge (~ pH 5)



Technical Accomplishments – Rate Limiting Steps

Hypothesis

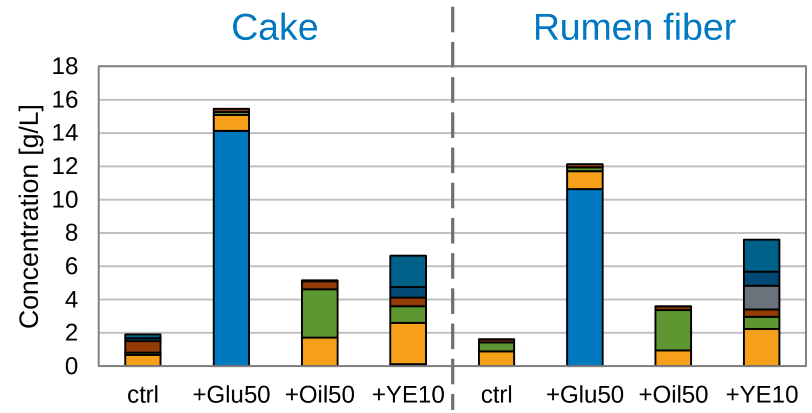
VFA production is limited by fermentability of feedstock or low microbiome activity

Strategy

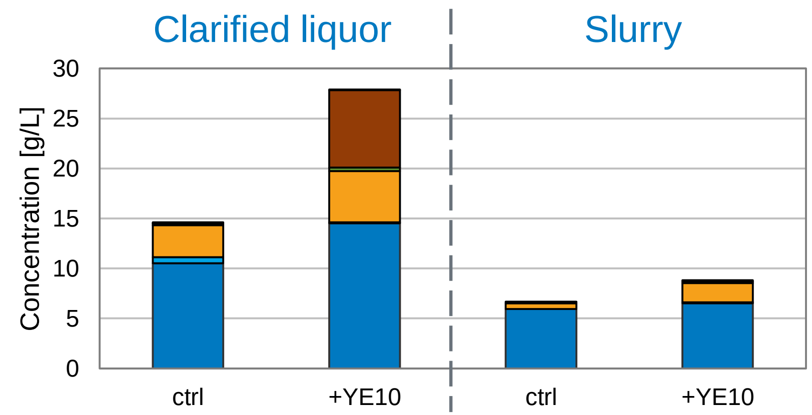
- Small vials
- Cake or Rumen fiber supplemented
    - Glucose
    - Vegetable oil (Oil in chart)
    - Yeast extract
- Performance of AD Inocula evaluated in lignocellulosic substrates
    - Clarified liquor (w/o solids)
    - Slurry (with solids)

Outcome

- Hydrolysis is the rate limiting step
- Bioconversion using AD microbial consortia can occur at pH < 5



Final pH	5.3	3.1	4.5	6.1	5.2	3.1	4.4	5.9



Final pH	3.12	3.27	2.98	3.64

Lactic Acid
Formic Acid
Acetic Acid
Propionic Acid
Butyric Acid
Pentanoic Acid
Hexanoic Acid
Heptanoic Acid

Technical Accomplishments – Semi-continuous Culture

Hypothesis

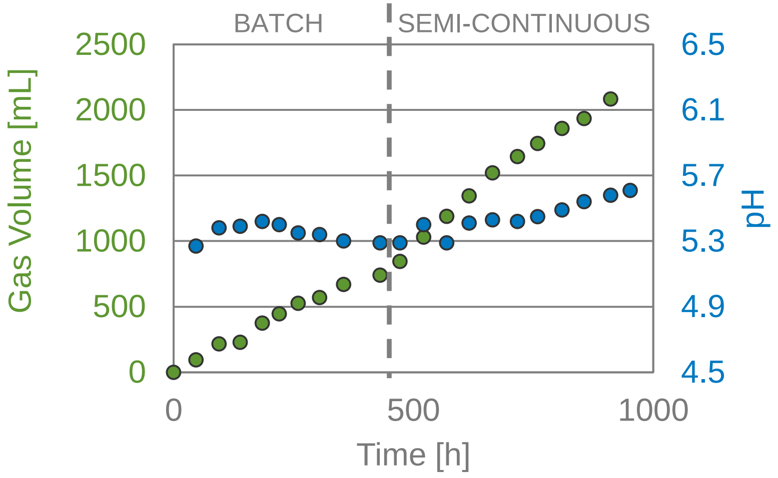
Scaling up the bioconversion step will improve VFA production

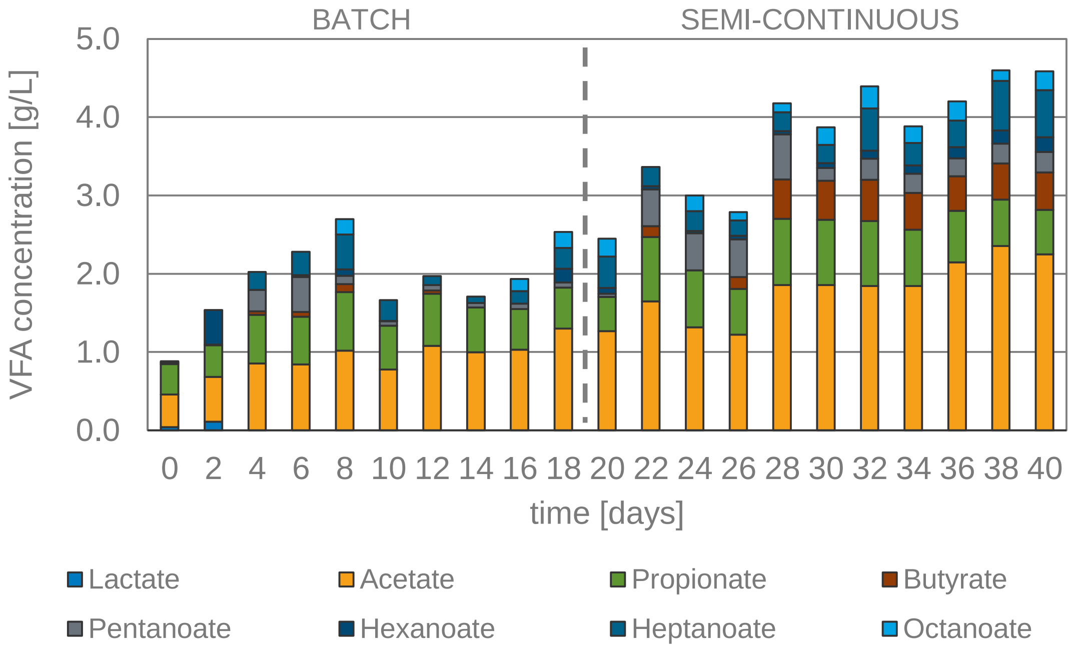
Strategy

- 2L bioreactor (scale-up to integrate with ISPR system)
- Cake and rumen as feedstock
- Semi-continuous mode
- Feed data to TEA team

Outcome

- Transition from batch to semi-continuous mode improved VFA titers
- Blending more fermentable feedstocks required to improve VFA production





Technical Accomplishments – pH and Titer Requirements

Hypothesis

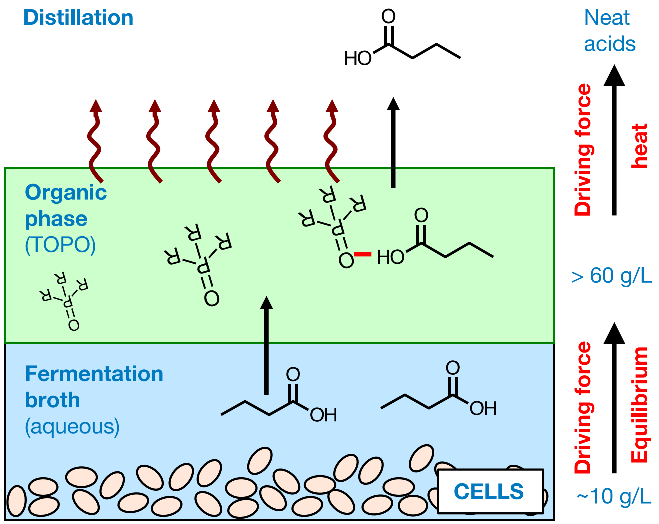
- Modeling extraction physics key to determining ISPR system viability
- Will define needed pH and titer requirements of AD unit.

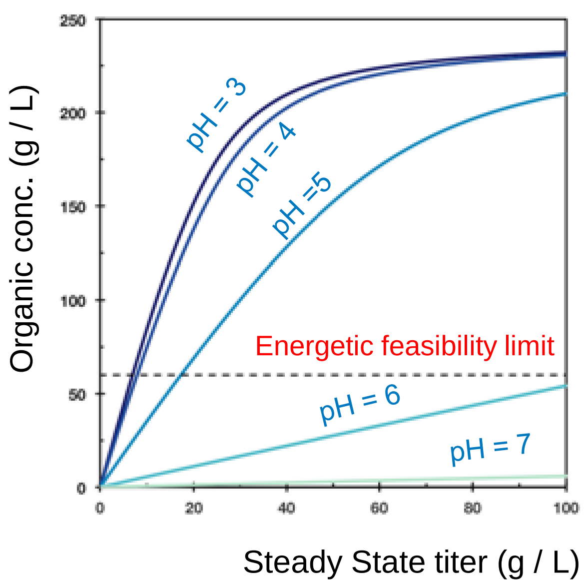
Strategy

- Mathematical model originally developed in SepCon[1,2] was adapted for mixed VFA profiles
- Applied using VFA profile measured in semi-continuous culture

Outcome

- Using measured ratio of VFA's
- Requires 17.8 g / L VFA's at pH = 5
- Requires 9.5 g / L VFA' at pH = 3
- **With easily hydrolysable substrate culture is already there!!**





(1) Saboe, Karp et al., *Green Chem*, 2018, 20 (8), 1791 (2) https://github.com/NREL-SEPCON/LLE_Model_ISPR

Technical Accomplishments – Engineering ISPR System

Hypothesis

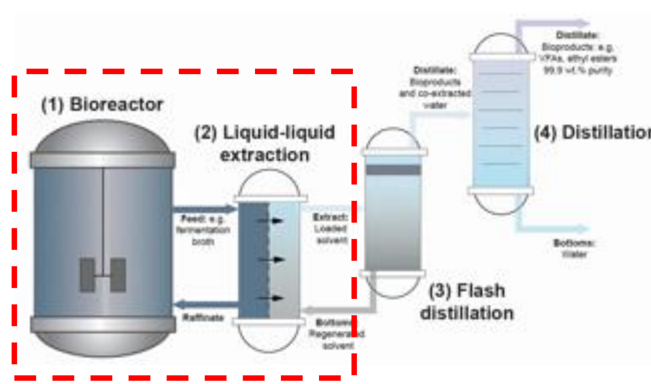
- ISPR system can be engineered to handle long run times, solids, and variabilities present in AD units

Strategy

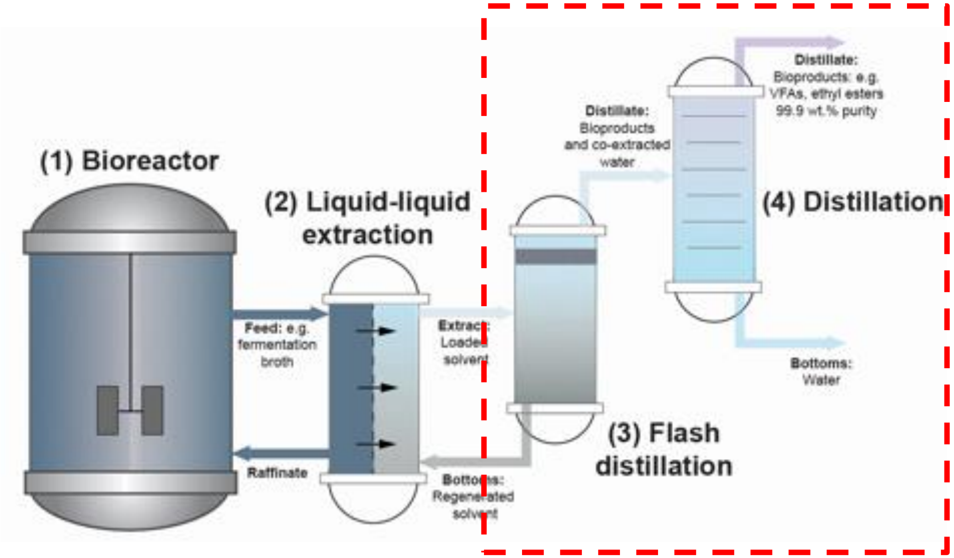
- Custom buildout of ISPR system specifically for AD units

Outcome

- Designed to handle solids up to 20 wt.%
- Gear pumps
- Pressure control
- Temperature control with heat tracing



Technical Accomplishments – ASPEN Modeling

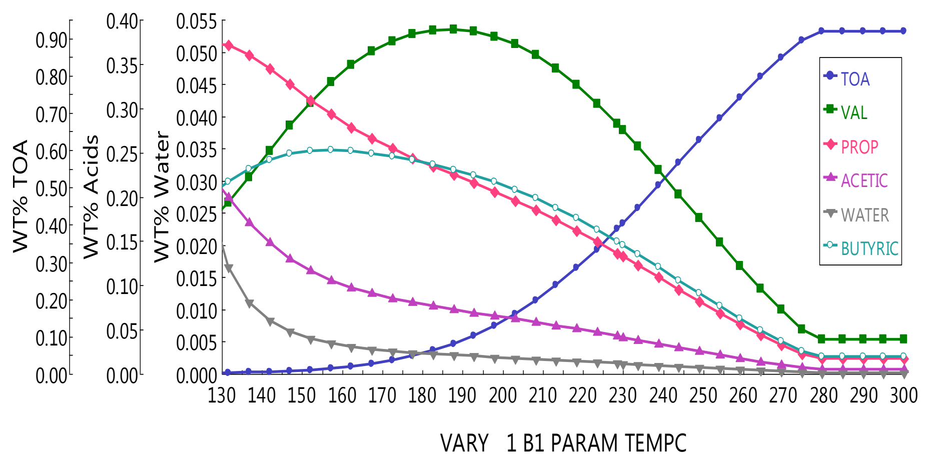


Hypothesis

- ASPEN models are key to building first of a kind integrated ISPR – Distillation system

Strategy

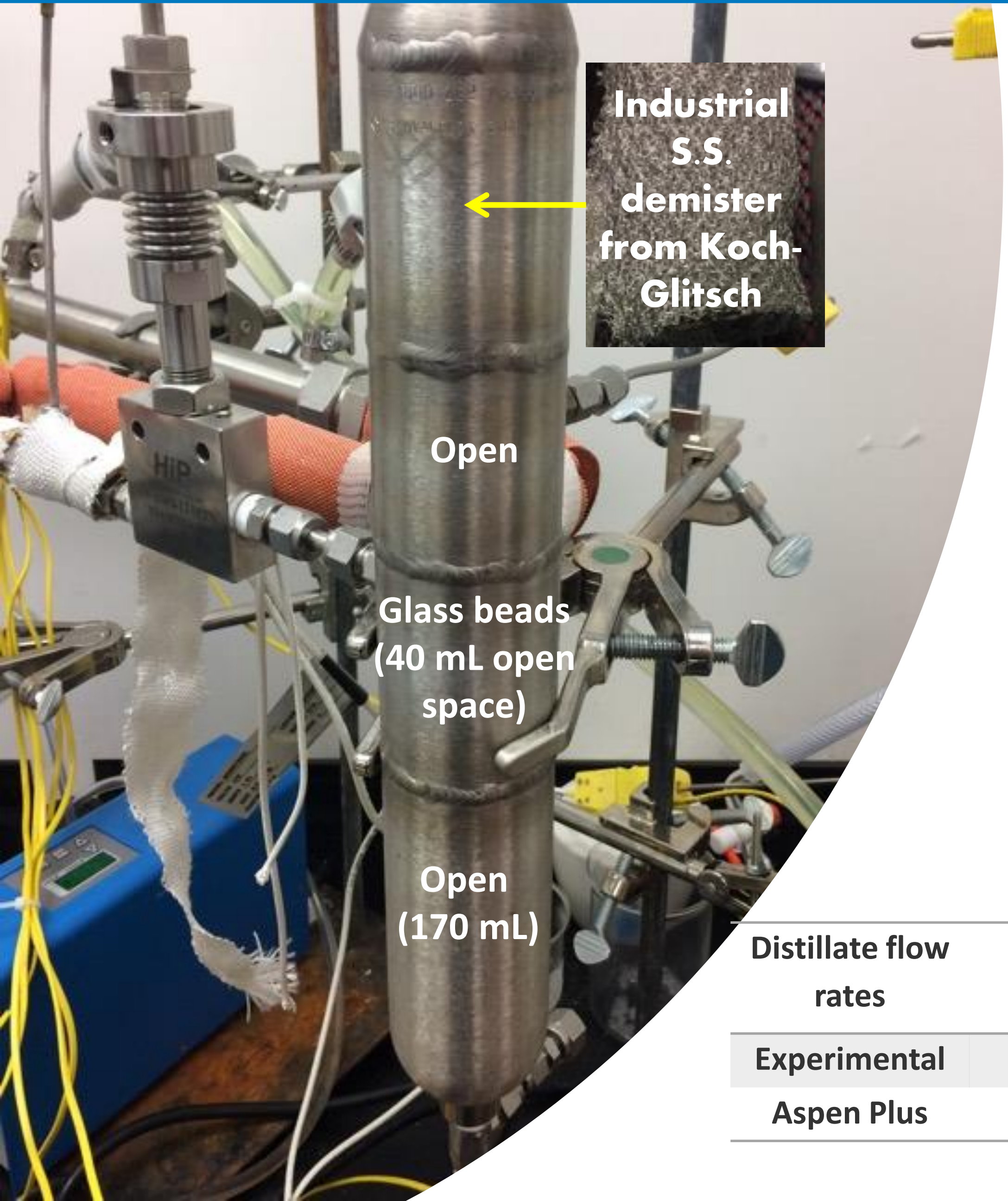
- Using loading factors calculated from mathematical model an ASPEN process model was built



Outcome

- Co-extracted water into organic phase is a key energy driver of the system
- Optimal flash drum conditions
  - 230 °C at 0.16 atm
- Requires energy footprint of < 20% of the heating value of the VFA's
- Recovers 90 % of VFAs in single pass

Technical Accomplishments – Engineering Flash Drum



Hypothesis

- Can build bench scale flash drum that matches ASPEN

Strategy

- Custom drum with 4 sections (right)

Outcome

- Distillate composition and rate matches ASPEN thermodynamically ideal system

Distillate flow rates	C2 (g/hr)	C3 (g/hr)	C4 (g/hr)	C5 (g/hr)
Experimental	0.31	1.00	1.02	2.03
Aspen Plus	0.31	1.00	1.10	2.07

RELEVANCE

Separations in Support of Arresting Anaerobic Digestion

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Relevance

Technology that converts a heterogenous waste feedstock to platform chemicals for liquid fuel production solves a major cost hurdle for the BETO 3$/GGE target

Relevance to bionenergy industry:

- Diversifies the slate of renewable chemicals and fuels that can be produced from an AD unit
- Industrial and academics can leverage the unique ISPR system
- Large existing infrastructure in industry for tech adoption

Project success:

- Provides a paradigm shift in routes to renewable platform chemicals for fuels and other specialty chemicals. Non-sterile cultures, waste feedstocks, fast market adoption through modular manufacturing

Tech transfer & marketability:

- Technology enables ”modular” adoption approach to existing AD unit infrastructure in industry
- 1 ROI filed, patent application expected in year 3

Contributions to BETO goals:

- **Utilizing cost advantage waste feedstock directly address a key cost barrier towards the 3$/GGE target. Note lignocellulosic feedstock accounts for ~60-67% of a biofuel cost.**[1]

(1) S. Chu & A. Majumdar, *Nature*, 2012, **488**, 294.

Relevance – Stakeholder Outreach and Engagement

Feedstock Supply

- Routine visits & interactions:
  - JBS beef supplies cake and paunch material
  - Denver waste water treatment

Consortia Prospecting

- Denver waste water treatment
- Harvest Power in Orlando
  - Unique AD unit process array of wastes
- Coors & New Belgium
- CSU – cow rumen microbiome

Bioconversion + ISPR Engineering

- Scaleup equipment discussions with
  - Belach Bioteknik AB – AD custom-made bioreactors
  - Andritz – cell retention
  - Pope Scientific – distillation units
  - Bürkert – membrane contactors

Meetings

- Mini-Workshop on Anaerobic Digestion of Wet Waste organized by Violeta Sànchez i Nogué & Steve Decker. Participants from national laboratories (18), industry (12), academia (7), and DOE (5).

FUTURE WORK
Separations in Support of Arresting Anaerobic Digestion

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Future Work – Biology and Separations

Bioconversion (this year)

- Engineer semi-continuous culture to obtain process-relevant VFA titer and pH
- Evaluate alternative waste feedstocks to optimize and improve VFA production
- Continue advancing analytical methods for both VFA and feedstock composition analysis

Handling solids with ISPR (this year)

- Need to be able to pump solutions with 10-20 wt.% solids (gear pumps)
- Cell and debris removal prior to LLE (Rotating disc membrane)
- Operate in lower pH range 3 - 5

Quantifying energy footprint (this year)

- ASPENplus modeling of the systems separation energy footprint

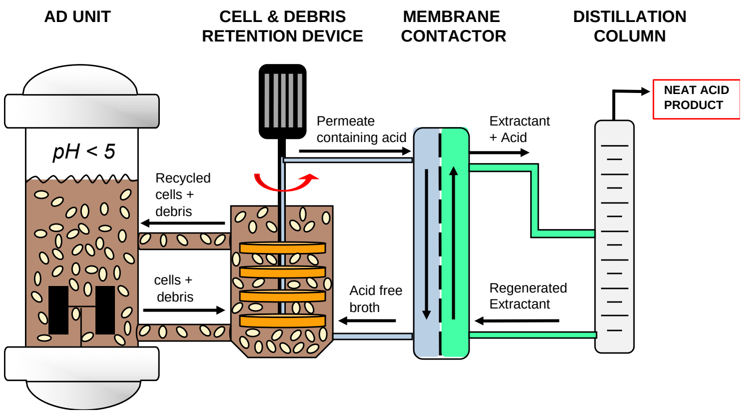
Integration / demonstration (year 3)

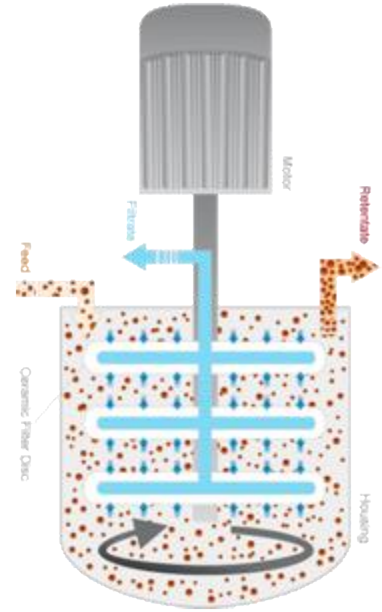
- Test and validate ISPR system
- Integrate/demonstrate with live semi-continuous AD culture at >5 wt. % solids
- Report results, paper targeting EES

Future Work – ISPR System Engineering

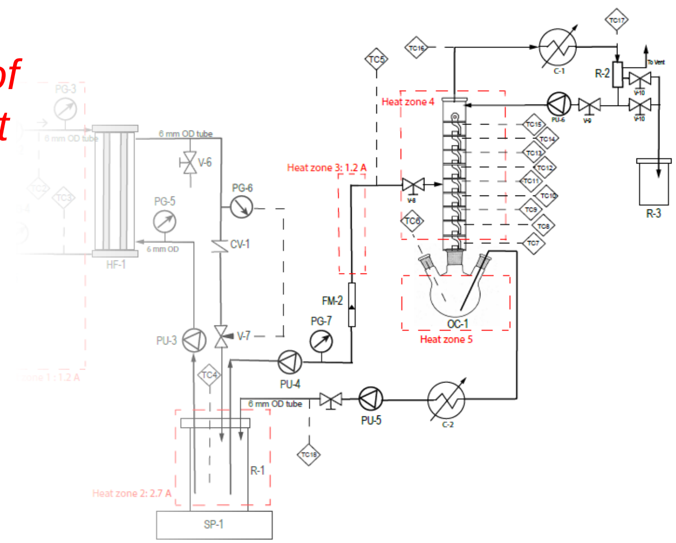
Upcoming milestones in FY!9

- Go/No-Go (End Q2): *recover VFAs at least at a 30% recovery level from a mock AD culture at titers of ~20 g/L in the presence of partially digested, sterilized lignocellulose*





- Annual Milestone (end Q4): *Demonstration > 30% recovery of VFAs at > 80% purity from a mock solution mimicking AD unit composition WITH online distillation*



Integration / demonstration (FY20, year 3)

- Annual milestone: *Demonstrate fully integrated unit with live semi-continuous AD culture*

Summary

1) Approach:
   - Aim 1: Identify, understand, and evolve robust microbial community for VFA production below pH 5
   - Aim 2: Engineer in situ separation technology to remove VFA’s as they are produced to arrest methanogenesis.

2) Technical accomplishments:
   - Demonstrated production of VFA from waste feedstocks in batch mode
   - Established a semi-continuous culture for VFA production
   - Calculated necessary titer and pH of AD unit (9.8 g/L VFAs at pH 3, and 17.8 g/L at pH 5)
   - Demonstrated ability to recover 90% of VFAs from extractant via single pass flash distillation
   - Built ISPR system with gear pumps, and flash drum for bench scale demonstrations in year 3.

3) Relevance:
   - **Utilizing cost advantage waste feedstock directly address a key cost barrier towards the 3$/GGE target. Note lignocellulosic feedstock accounts for ~60-67% of a biofuel cost.[1]**
   - Diversifies the slate of renewable chemicals and fuels that can be produced from an AD unit

5) Future work:
   - ISPR engineering:
     - Complete installation of the solids handling components to the ISPR system.
     - Demonstrate system with low pH AD culture in FY19

(1) S. Chu & A. Majumdar, *Nature*, 2012, **488**, 294.

Acknowledgments

- **BETO**: Beau Hoffman and Mark Philbrick

- Brenna Black
- Steve Decker
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- Justin Sluiter
- Venkat Subramanian
- Dylan Thomas
- Todd Vander Wall
- Todd Vinzant

Eric Karp

Violeta Sànchez i Nogué

Patrick Saboe

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Industrial collaborators

- Christina Dorado - Agricultural Research Service USDA (Horticultural Research Laboratory)
- Gary Aguinaga & Javier Corredor - Harvest Power
- Mark Risema, JBS USA
- Mark Fischer – New Belgium Brewing Company
- Jeremy Woolf – Coors Brewing Company
- Quintin Schermerhorn & Jim McQuarrie - Denver Metro Wastewater Reclamation District

Thank You

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Publications

1. P.O. Saboe, D.C. Thomas, L. Manker, H. Monroe, G.T. Beckham, E.M. Karp*, V. Sànchez i Nogué*,

   "Platform Chemicals from the Anaerobic Digestion of Waste", ***In prep.***

Presentations

1. SIMB Annual Meeting (August 12 – 16 2018 · Chicago, IL – USA) **V Sànchez i Nogué**, E M Karp, P O Saboe, L P Manker, D J Peterson, W E Michener and G T Beckham. Production of volatile fatty acids through arresting anaerobic digestion. *Invited oral presentation*

2. SBFC Annual Meeting (April 28- May 1 2019 · Seattle WA – USA) **V Sànchez i Nogué**, DC Thomas, PO Saboe, HR Monroe, GT Beckham, and EM Karp, *submitted for oral presentation*

ADDITIONAL SLIDES

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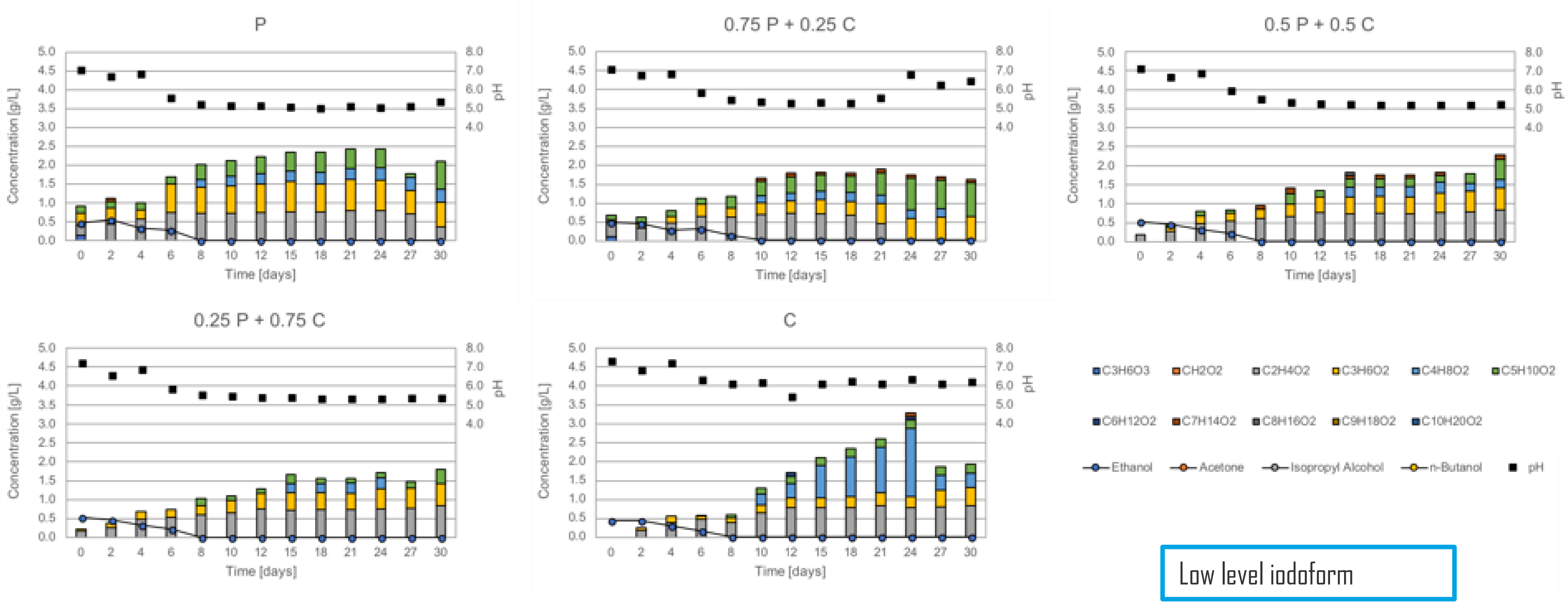
Additional Slides – Initial screening: Feedstock digestions

Final stage AD unit inoculum: low level iodoform

pH: pH 7 after inoculation
Evolution to 5.4 – 5.2

VFAs: Acetic
Propionic
Butyric
Pentanoic

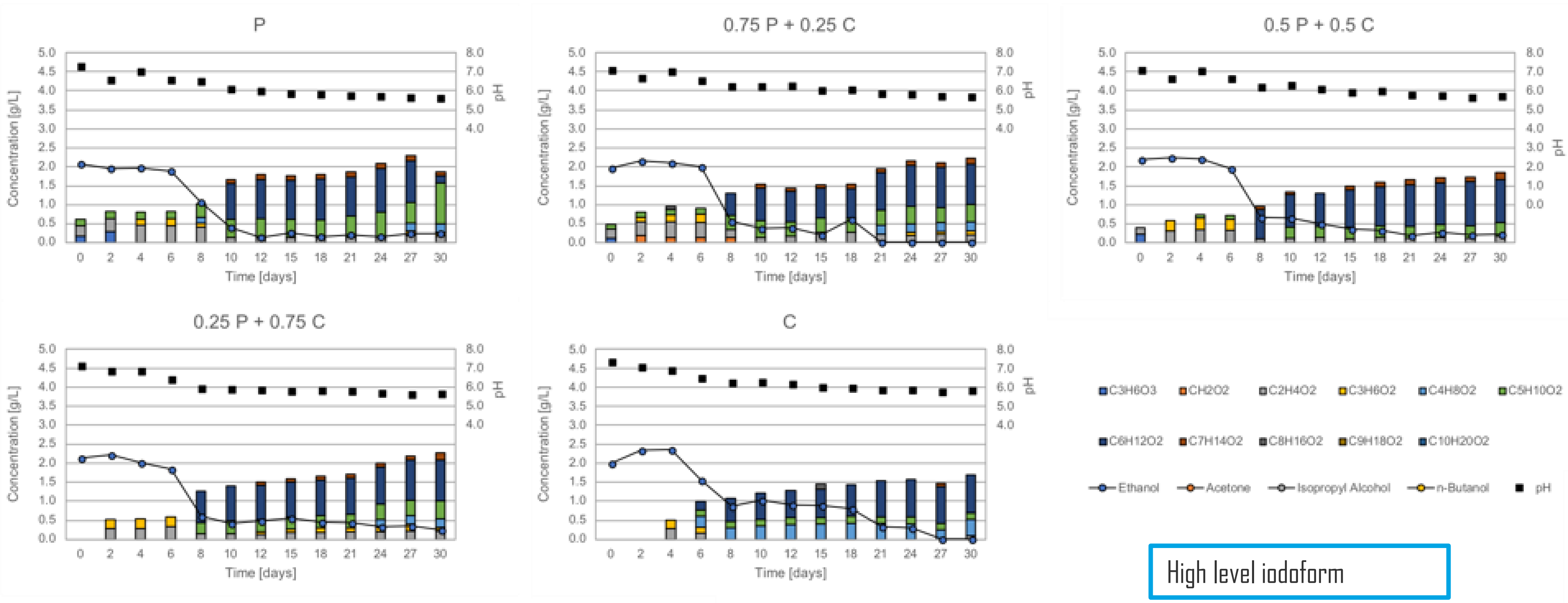


Additional Slides – Initial screening: Feedstock digestions

Final stage AD unit inoculum: high level iodoform

pH: pH 7 after inoculation
Evolution to 5.4 – 5.2

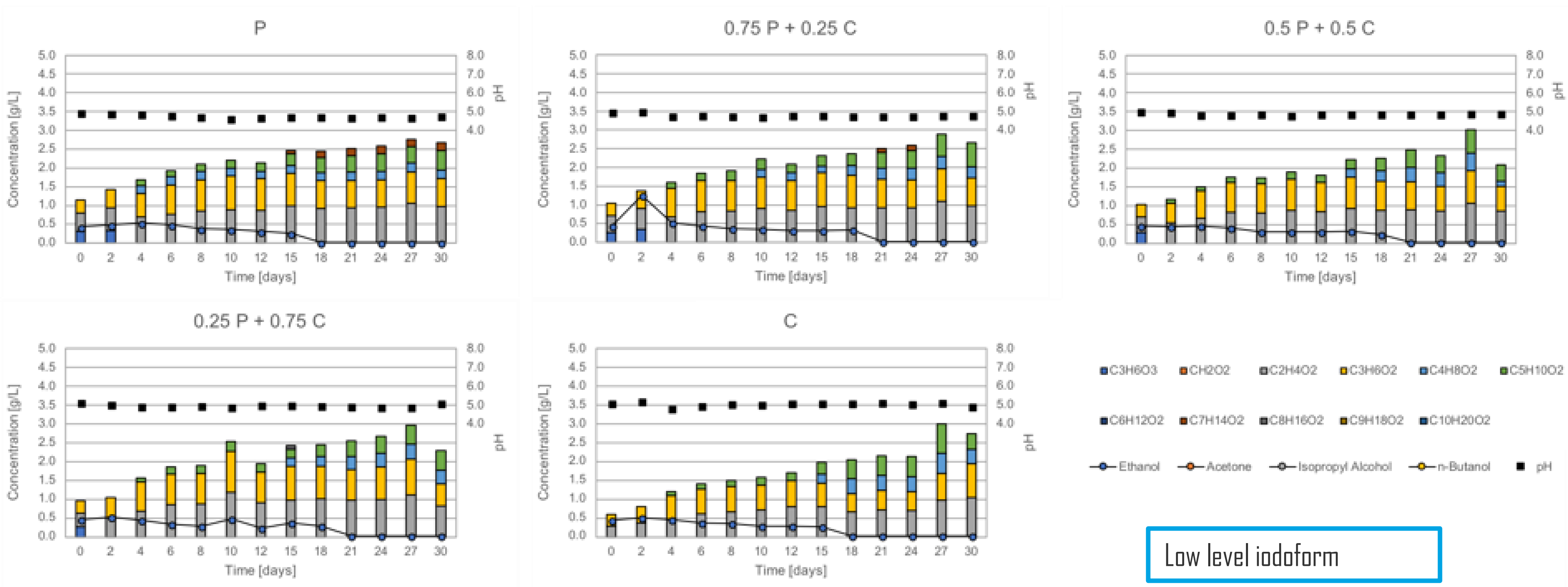
VFAs: Hexanoic
Heptanoic



Acid stage AD unit inoculum : low level iodoform

pH: maintained at around 5 during cultivation

VFAs:
Acetic
Propionic
Minor: Butyric and pentanoic

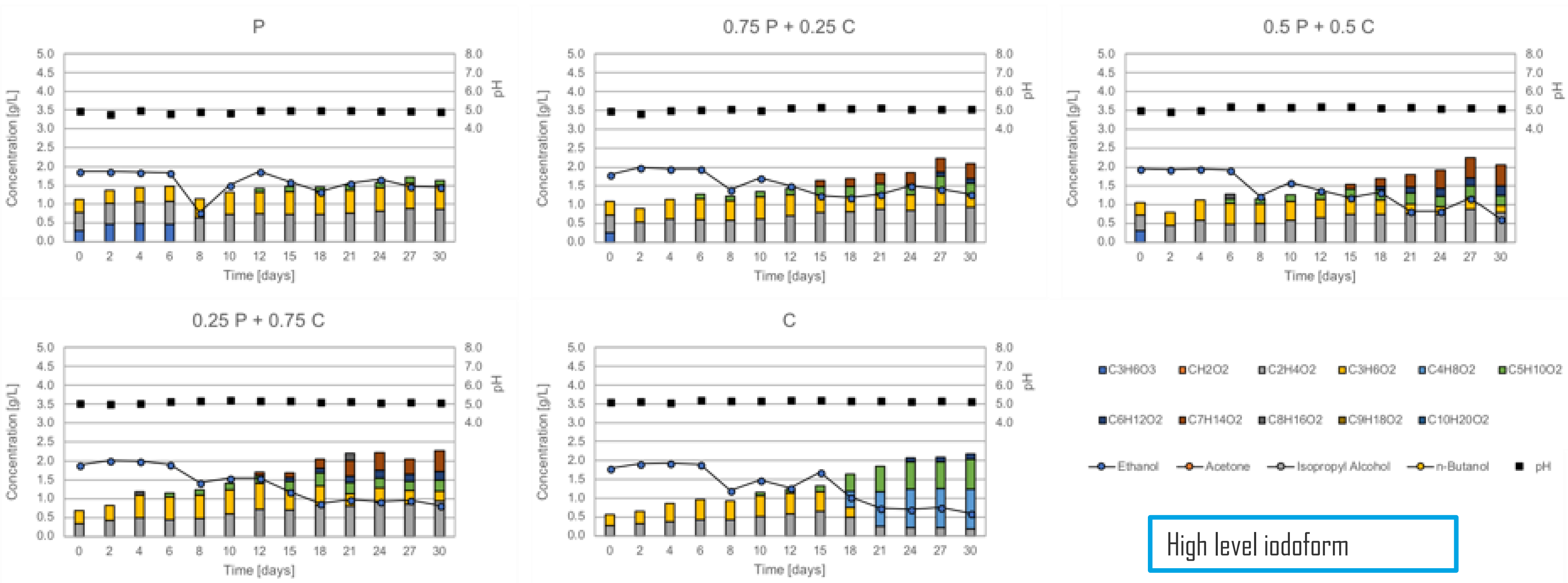


Additional Slides – Initial screening: Feedstock digestions

Acid stage AD unit inoculum: high level iodoform

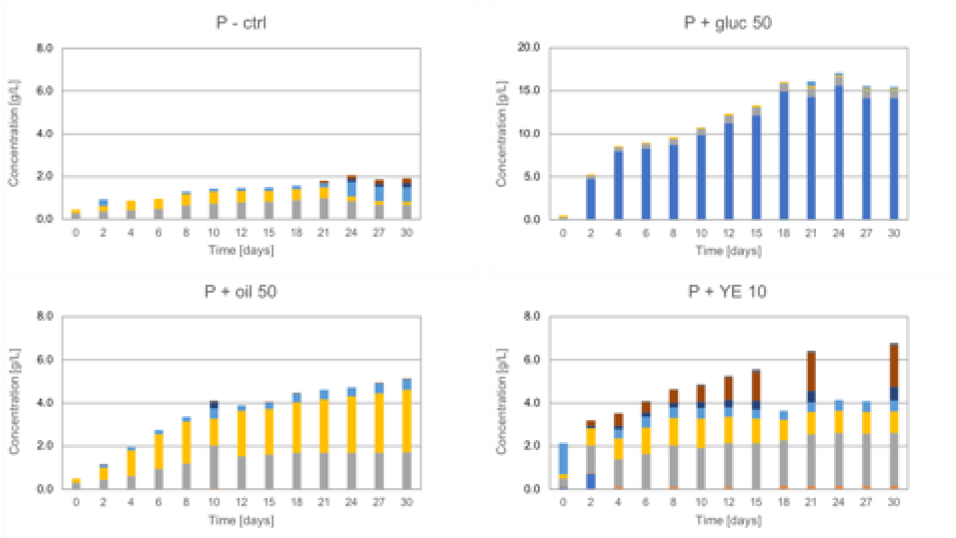
pH: maintained at around 5 during cultivation

VFAs: Less Propionic
Presence of: Hexanoic and Heptanoic

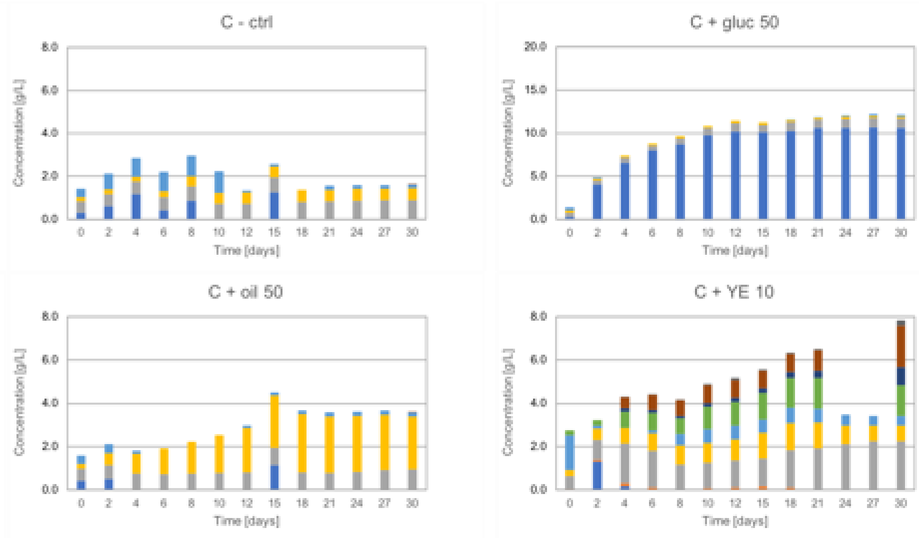


Additional Slides – Initial screening: Identifying Rate Limiting Steps

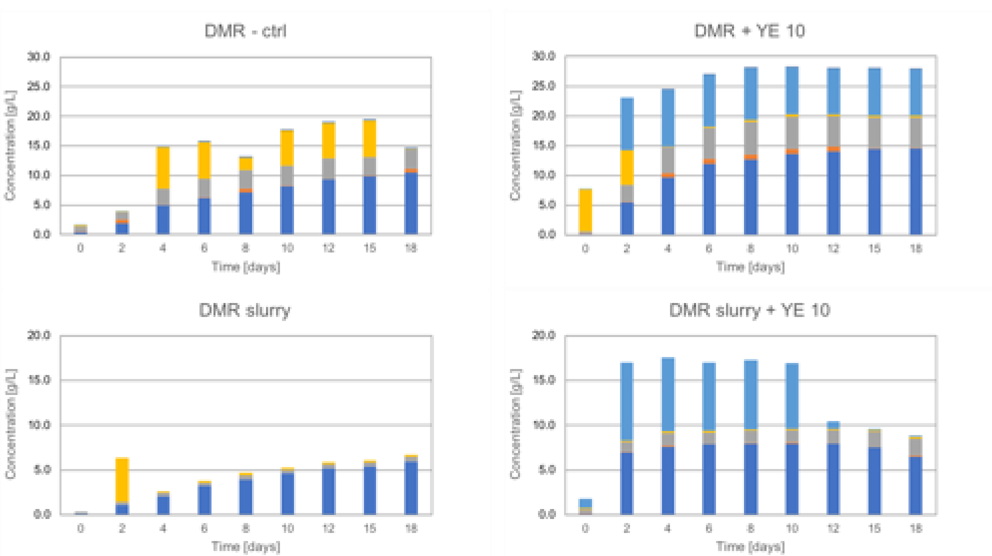
PAUNCH



CAKE



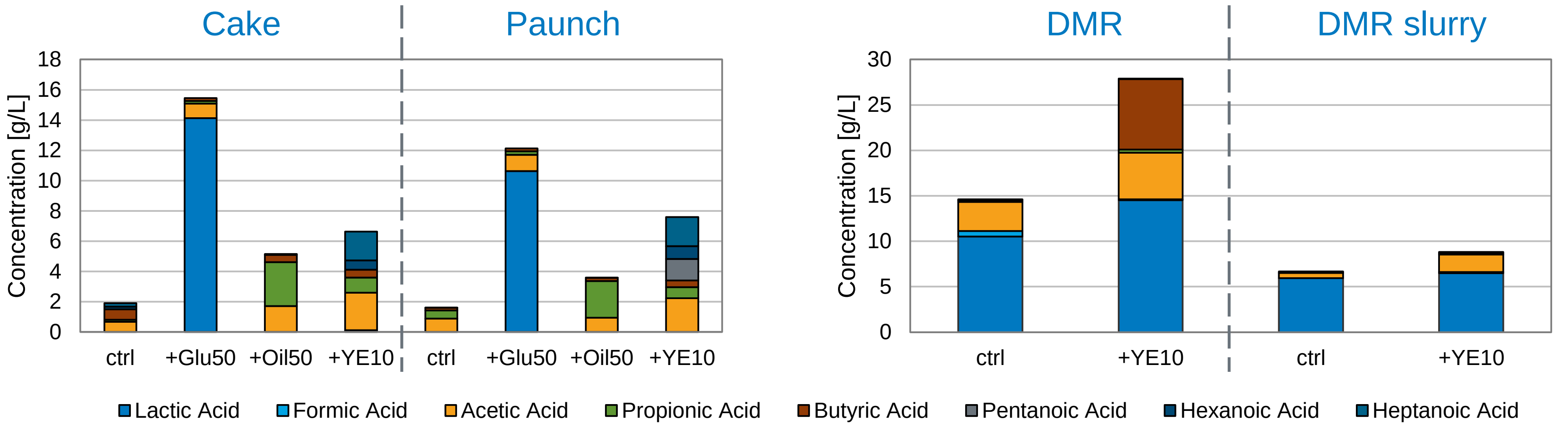
DMR

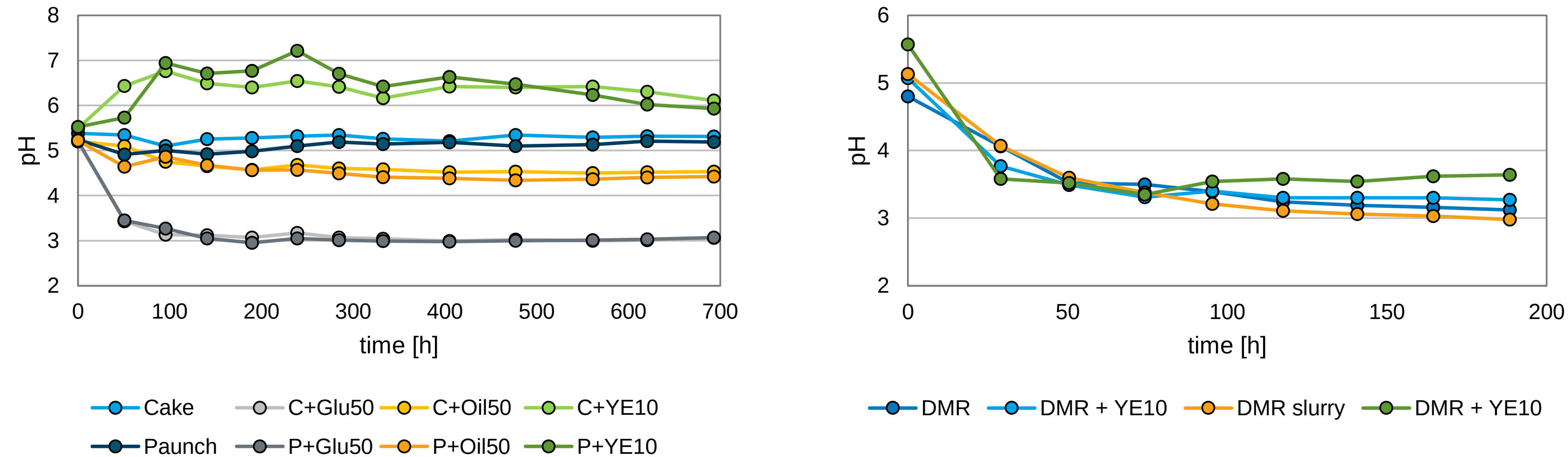


Feedstock pH_0 = 5.0; 5% (w/v)
Acid AD activated sludge (Denver WWTP); 10% (v/v)
High level of iodoform
35 ˚C, 150 rpm

$C_3H_6O_3$ | CH_2O_2 | $C_2H_4O_2$ | $C_3H_6O_2$ | $C_4H_8O_2$ | $C_5H_{10}O_2$ | $C_6H_{12}O_2$ | $C_7H_{14}O_2$ | $C_8H_{16}O_2$ | $C_9H_{18}O_2$ | $C_{10}H_{20}O_2$

Technical Accomplishments – Identifying Rate Limiting Steps



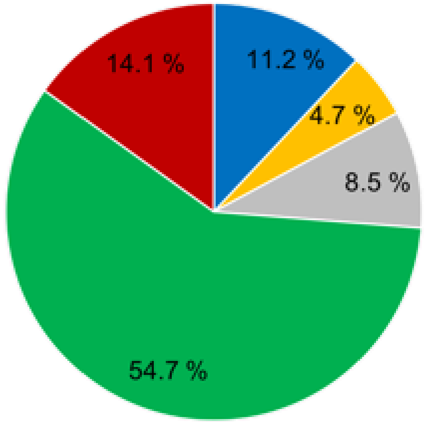


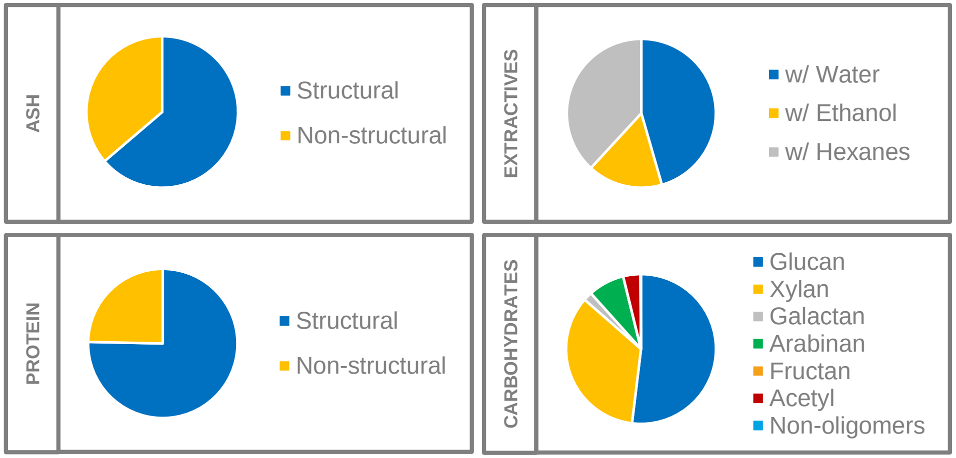
Outcome:

- Fermentability of feedstocks is crucial to increase VFAs production
- Bioconversion using AD microbial consortia can occur at pH < 5

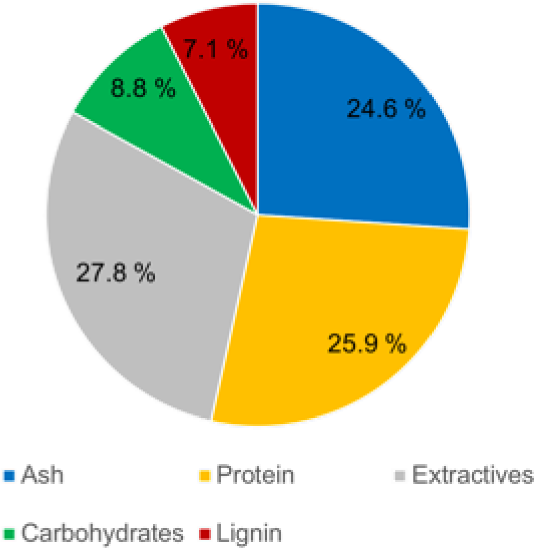
Technical Accomplishments – Feedstock Analysis

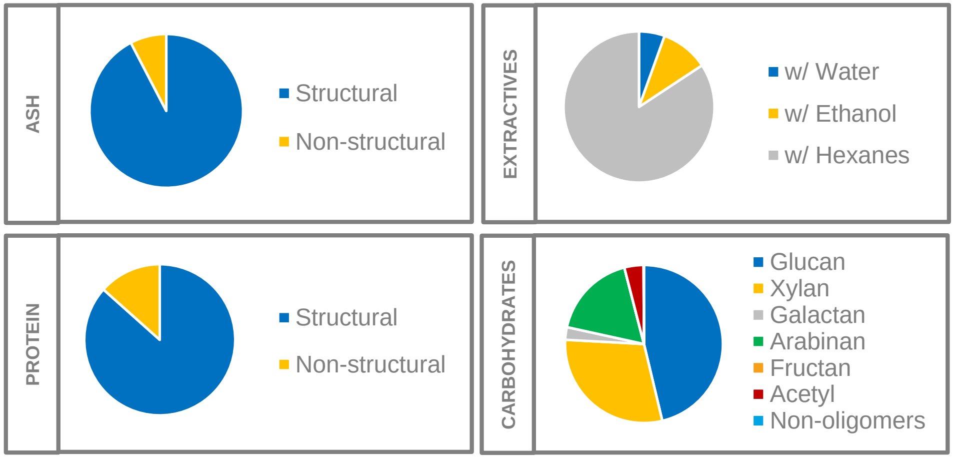
Rumen fiber





Cake

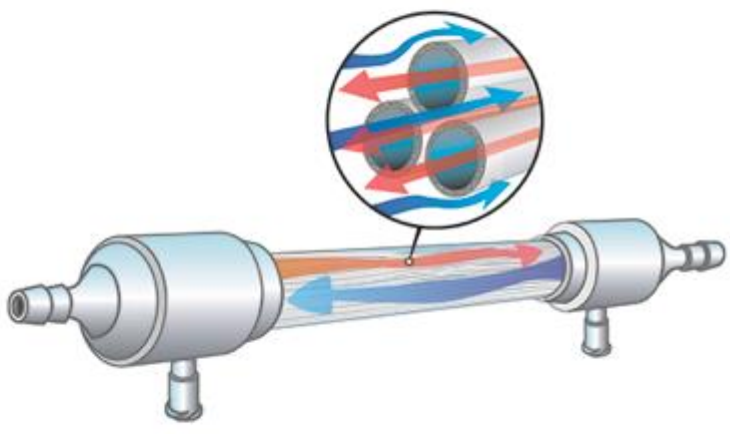


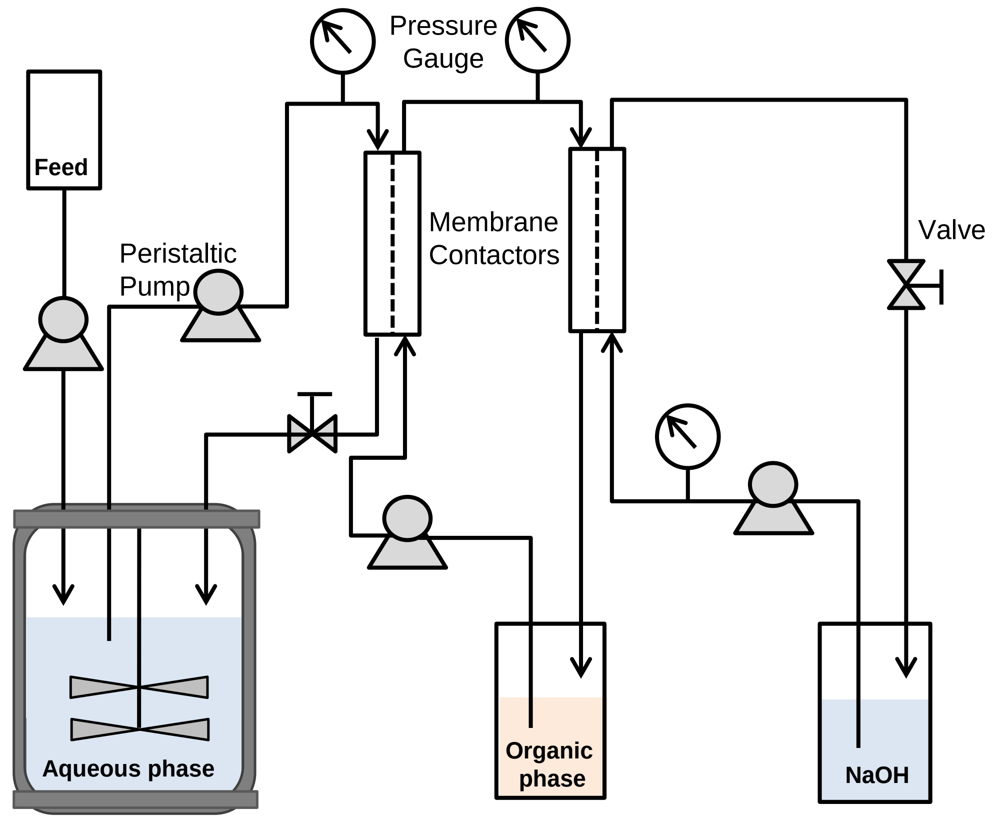


Additional Slides – What is ISPR?

Typical ISPR systems

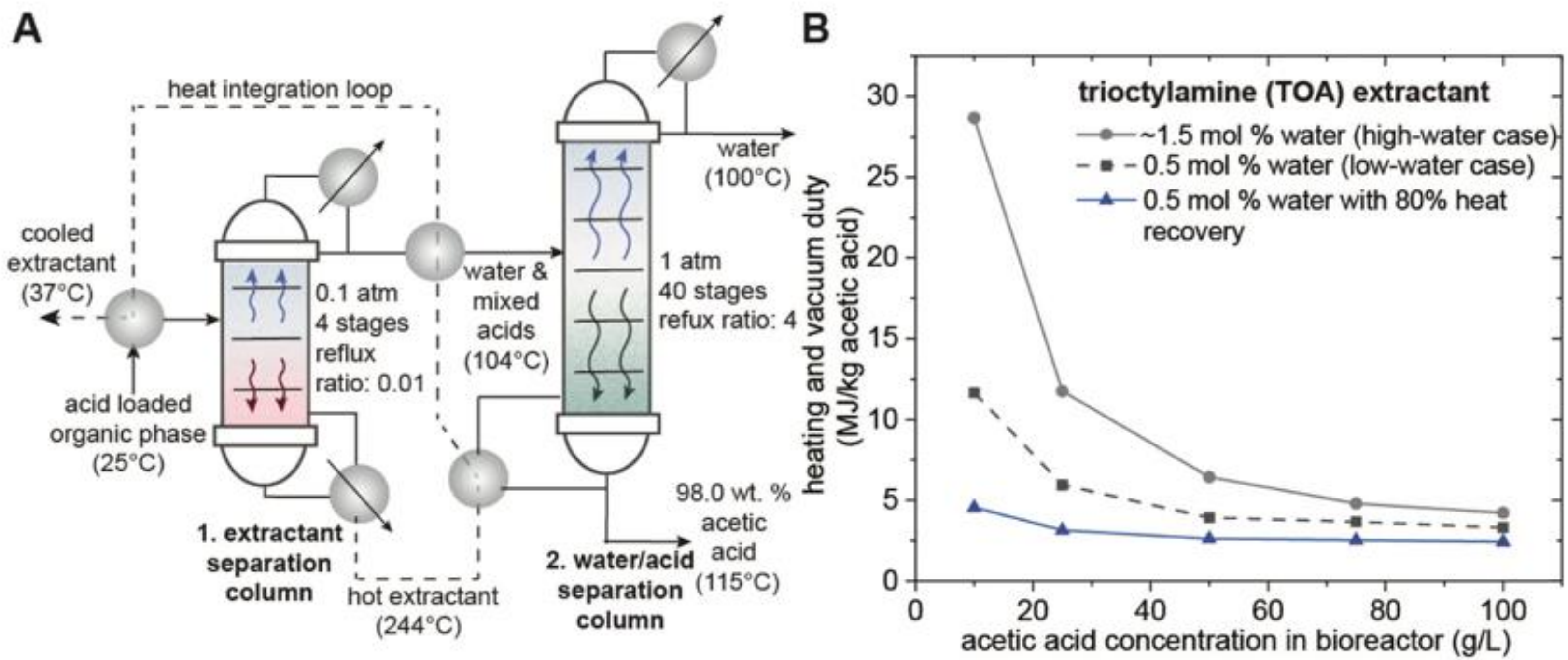
- Utilize membrane contacting units to mitigate the toxicity of the organic extractant
- Systems commonly look like that to the right.[1]
- Scalable equipment





1. RS Nelson, DJ Peterson, EM Karp, GT Beckham, D Salvachúa Fermentation 3 (1), 10

Additional Slides – ISPR Energy Footprint



- **Background:** Energy footprint of ISPR must not be more than the $\Delta H_{combustion}$ of target product
- **Hypothesis:** heat integration in downstream distillation can reduce energy footprint
- **Result:** ASPEN models calculate ISPR system energy footprint to be < 20% of the heat of combustion of the separated acid (targets > 98% purity)
- **Outcome:** Full ASPEN models for ISPR system to size equipment and calculate energy footprint[1]

(1) Saboe, Karp et al., *Green Chem*, 2018, 20 (8), 1791

Additional Slides – Cell + Debris Retention Device

Rotating disc ceramic membranes

- Low pH tolerant (or high pH)
- Can operate in > 30 wt.% solids environments
- May be able to filter down to 60 nm
- Retentates can be as viscous as peanut butter