DOE Bioenergy Technologies Office (BETO) 2023 Project Peer Review

Demonstration of continuous biobutanol fermentation integrated with membrane solvent extraction (FIMSE)

4/7/2023

Technology Area: Performance-Advantaged Bioproducts and Bioprocessing Separations

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ADM

Project Overview

SAF Grand Challenge – What's Important

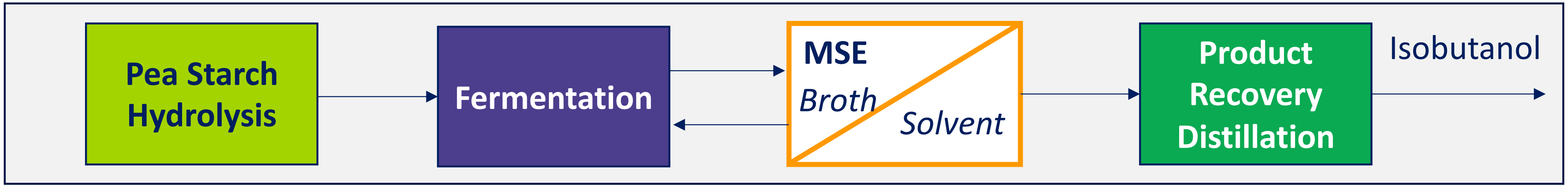
The **Sustainable Aviation Fuel (SAF) Grand Challenge** is a U.S. government-wide approach to achieve 3 bill gallons annual domestic SAF production - minimum of a 50% reduction in life cycle greenhouse gas emissions (GHG) compared to conventional fuel by 2030 and 35 bill gallons annual production by 2050[1].

Limitations – Why it is Hard

- Isobutanol (IBA), feedstock for an ASTM approved pathway for SAF production, can only be produced at low levels in fermentation (<2%) due to **toxicity**
- **Energy intensive recovery** – high heat input or high vacuum required to separate from aqueous broth

Opportunity

- **Decrease energy for recovery** of IBA using Fermentation Integrated Membrane Solvent Extraction (**FIMSE**)
- IBA preferentially partitions to Solvent side of MSE – **lower intensity recovery of IBA from solvent**
- With increasing vegetable protein production, waste streams will continue to become more available as a **sustainable feedstock**



Goal – What We are Trying to Do

Decrease energy use (by 50%) and cooling water use (by 30%) of IBA recovery while using low impact feedstocks to accelerate commercialization of SAF – by demonstrating process to produce 100kg with 100 h of continuous operation.

1. https://www.energy.gov/sites/default/files/2022-09/beto-saf-gc-roadmap-report-sept-2022.pdf

Approach – MSE and Project History

Previous Work

2008-2013	**DOE Funded Opportunity – ADM & 3M** Energy Reduction & Advanced Water Removal via ***Membrane Solvent Extraction*** Technology	**Ethanol Recovery** **25% Energy and 40% Water Savings**	**Available Equipment, Infrastructure** *Patent: US 10,752,875*
2019-2020	**Internal Development Project – ADM, University of Minnesota, MSE Tech** Lab-scale MSE process to recover aliphatic alcohols using hollow fiber membrane filtration	**n-Butanol Recovery** **50% Energy Savings**	**Predictive Energy Models, Initial direction for isobutanol recovery technology** *Provisional Patent App: CP0206US00*

Capability	Technical Know-how, lab equipment, directional process modeling, piloting equipment in place to support this work.

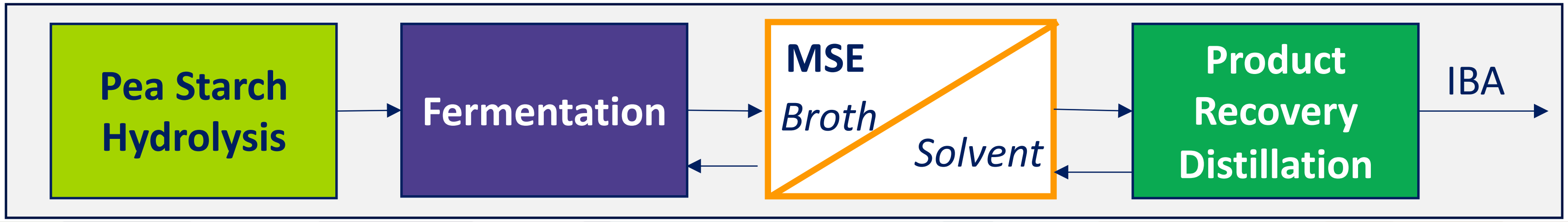
1000L Main Fermenter

Approach –Innovation Potential

Potential	**This technology has potential to substantially advance IBA recovery for SAF production. Initial TEA indicating *52% energy reduction***

State of the Art – Bio-Isobutanol Production	Project Goals
Batch Fermentation from ***Corn*** Feedstocks with distillation of IBA from Broth – with ***significant steam use*** or with ***electrically-intensive*** vacuum	Leverage ***Membrane Solvent Extraction*** to enable **1) *Continuous Fermentation***, with **2) *Decreased Energy Intensity*** due to increased concentration and better separation with IBA in Solvent, using ***non-conventional, food-waste feedstocks***

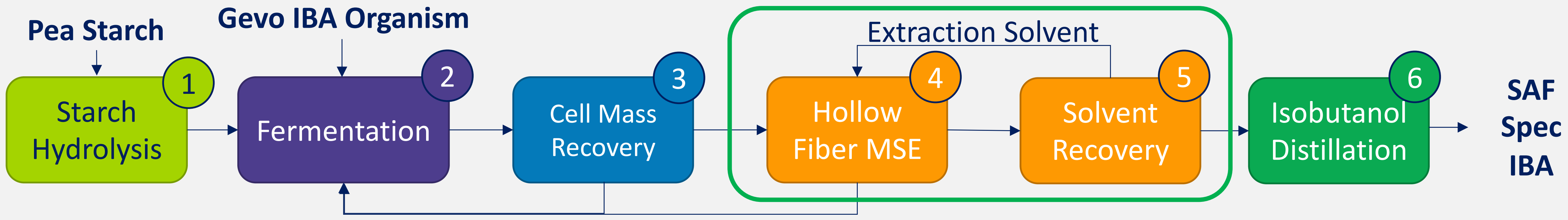
Industrial IBA Recovery Challenges	Innovation
IBA Toxicity – ***Low Titers***	Continuous removal improves volumetric productivity, decreasing Capital Cost for Fermentation by 10-30%
High Boiling Point (8 °C higher than water) – ***High Energy to Recover***	Continuous recovery of extractant with lowers separation energy and OPEX by up to 50%
IBA forms ***intractable emulsions with solvents***	MSE provides benefits of Liq-Liq Extraction, without emulsion



Approach – Integrated Plan

Management	**Project is following an integrated management plan,** with Bi-weekly meetings between institutions following an in-person Kick-Off, IP sub-committee, and shared Data repository

Fermentation Integrated Membrane Solvent Extraction (FIMSE)



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Fermentation Technology:
- Organism and Fermentation Process
- Technology Transfer to ADM
- Toxicity studies for impact of solvent on fermentation

Membrane Fouling and Recovery:
- Solvent stability
- Fouling and mitigation
- ***Life Cycle Analysis***

Liquid-Liquid Equilibrium and Membrane performance:
- Solvent screening – LLE partitioning
- Membrane performance characterization
- Lab distillation

Ownership & Integration:
- Established IP around MSE
- Hydrolysis technology
- Feedstocks
- Continuous fermentation
- Distillation
- Technoeconomic Analysis
- Piloting and Demonstration

1 2 3 4 5 6

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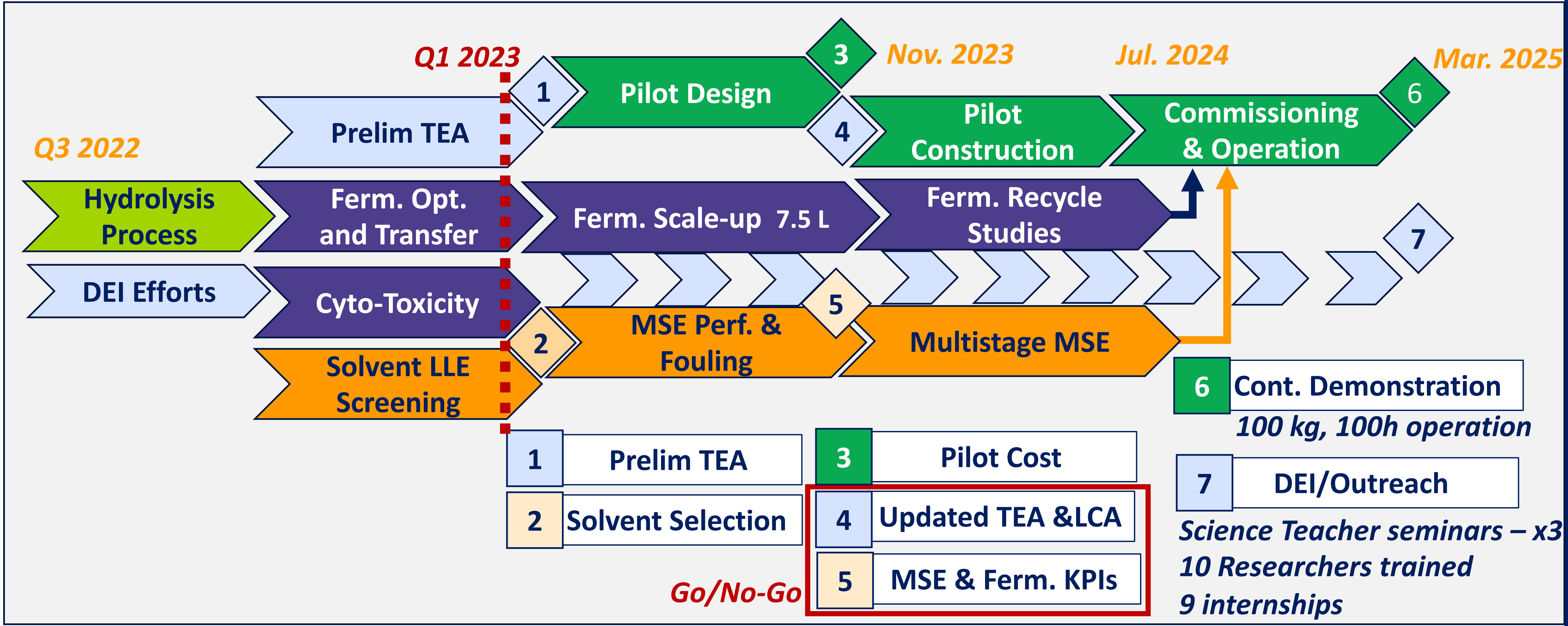
Approach – Select Decision Points

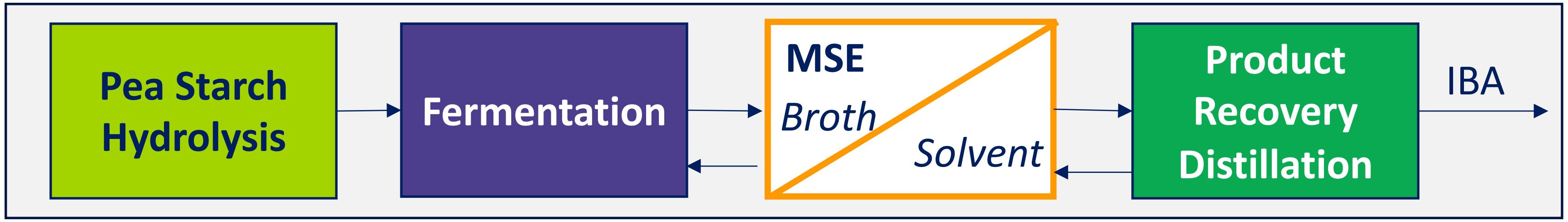


Go/No-Go - To Demonstrate *Nov. 2023*	***Hydrolysis of Pea Starch*** – 550-650 g/kg dextrose ***Fermentation meeting targets*** at 2 to 10L (0.36 g IBA/g dextrose, 10-15 g IBA/L, 1.0±0.1 g IBA/L-hr) ***Demonstrated potential energy savings*** (50%) with TEA informed from scale-up data

Approach – Key Performance Parameters

KPP Approach	**Fermentation KPPs chosen based on best performance with conventional feedstock** • Target – demonstrate best performance with more complex, waste feedstock • The same Culture Productivity will translate to better overall productivity through FIMSE continuous fermentation **MSE KPPs chosen informed from previous work, TEA** • Previous trials with n-butanol demonstrated 70% efficiency is achievable • Initial TEA work indicated 50% energy reduction is possible with this target

Key Performance Parameters			***Drivers***
Conv. & Yield	**0.36 g/g**	→	**Feed Costs**
Productivity	**1.0 g/L/h**	→	**Capital**
Titer	**10 g/L**	→	**DSP Energy**
Memb. Eff.	**70%**	→	**Memb. Costs**



Approach – Diversity, Equity, Inclusion

Professional Development:
Recruiting underrepresented & underserved Ph.D. students and postdocs
Goal: 10 students/postdocs trained

Internships:
Recruiting underrepresented & underserved students
Goal: 9 internship opportunities

Education/Outreach:
Education workshops for >10 K-12 science teachers per year, impacting >500 students
Goal: 3 teacher workshops held

Progress

ANL: Student Research hired

ADM: Two Interns onboarded through ADM Modeling Center at University of Illinois to train in TEA development

ANL: Mentoring two students through Illinois Math and Science Academy

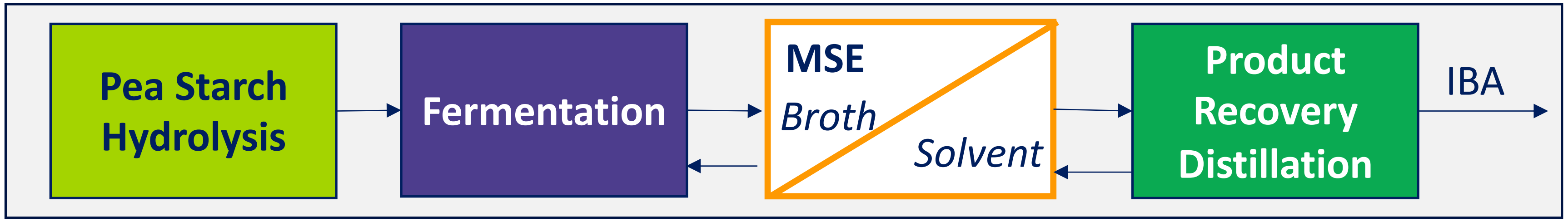
ANL: provided tours of ANL to students in the Chicago Initiative

UofM: 2022 Workshop held with feedback received from attending teachers

Diversity, Equity, and Inclusion	Leverage existing diversity efforts at each institution to engage underrepresented communities in science, technology, engineering, and mathematics (STEM) disciplines through student recruiting, internships, and local school programs.

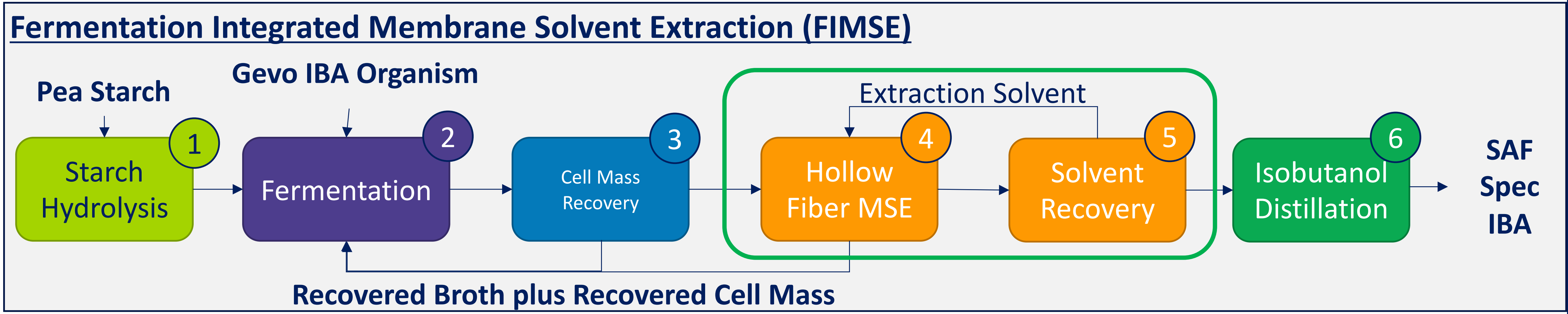
Approach – Key Risks & Mitigations

Risk Approach	• Risk workshops generating a risk register and risk management plan – reviewed and updated regularly, with mitigation plans identified to address high ranking risks across the project scope



Risk	Driver	Potential Impact	Mitigation(s)
Solvent Toxicity	Solvent in aqueous phase from MSE is recycled to fermentation	Decreases in yeast performance in continuous operation	• Back extraction of returning broth with secondary solvent • Periodic reinoculation to maintain performance
Energy Use too High	Additional recovery steps or processing of purge streams requires more energy than initially anticipated	Energy use does not meet project success criteria (<50%)	• Detailed TEA modeling using Aspen Plus® - impacts and levers • Integrated solvent selection and ferm. optimization to assess impacts
Byproduct Accumulation	Generated byproducts have lower partitioning through membrane	Decreases in yeast performance in continuous operation	• Impact of continuous recycling and partitioning through MSE • Tune purge rates to optimize process

Progress and Outcomes - Overview



Milestone	Status	Target Date
Hydrolysis Process Validation	*Complete*	Oct. 2022
Fermentation Tech Transfer to ADM from Gevo	*Complete*	Dec. 2022
Preliminary TEA – based on Hydrolysis, Fermentation, Initial LLE	*On Track*	Mar. 2023
Solvent Specs for Broth - Cytotoxicity	*Complete - Early*	Jul. 2023
Equilibrium Partitioning Defined	In Progress	Jul. 2023

Key Results	*Milestones planned for project to date have been met or are on track. Milestones for the next 6 months are in progress and on track.*

Progress - Hydrolysis

Lead: ADM

Results	• **Pea starch hydrolysis process successfully defined** • **Moisture and Protein content of Pea Starch shows minor variability based on in-plant sampling over ~6 months** *(<10% variation over key parameters)*

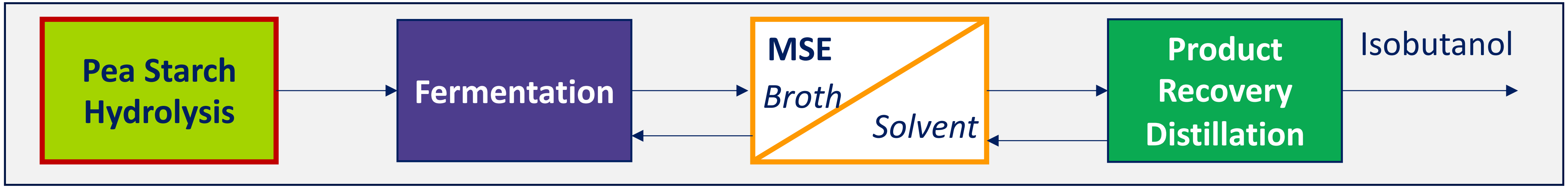
ADM Jet Cooker

- ***Composition:*** Waste pea starch resulting from the isolation of pea protein was analyzed for protein, fat, fiber, recalcitrant starch and other trace materials.
- ***Variation:*** Samples were collected over time and compared to understand variation in the composition.
- ***Impact***: Understand effects of feed variability on the KPIs of the hydrolysis products to ensure a robust process.

Residual Solids After (left) and Before (right) autoclaving Pea Starch Hydrolysate

Challenges Identified:

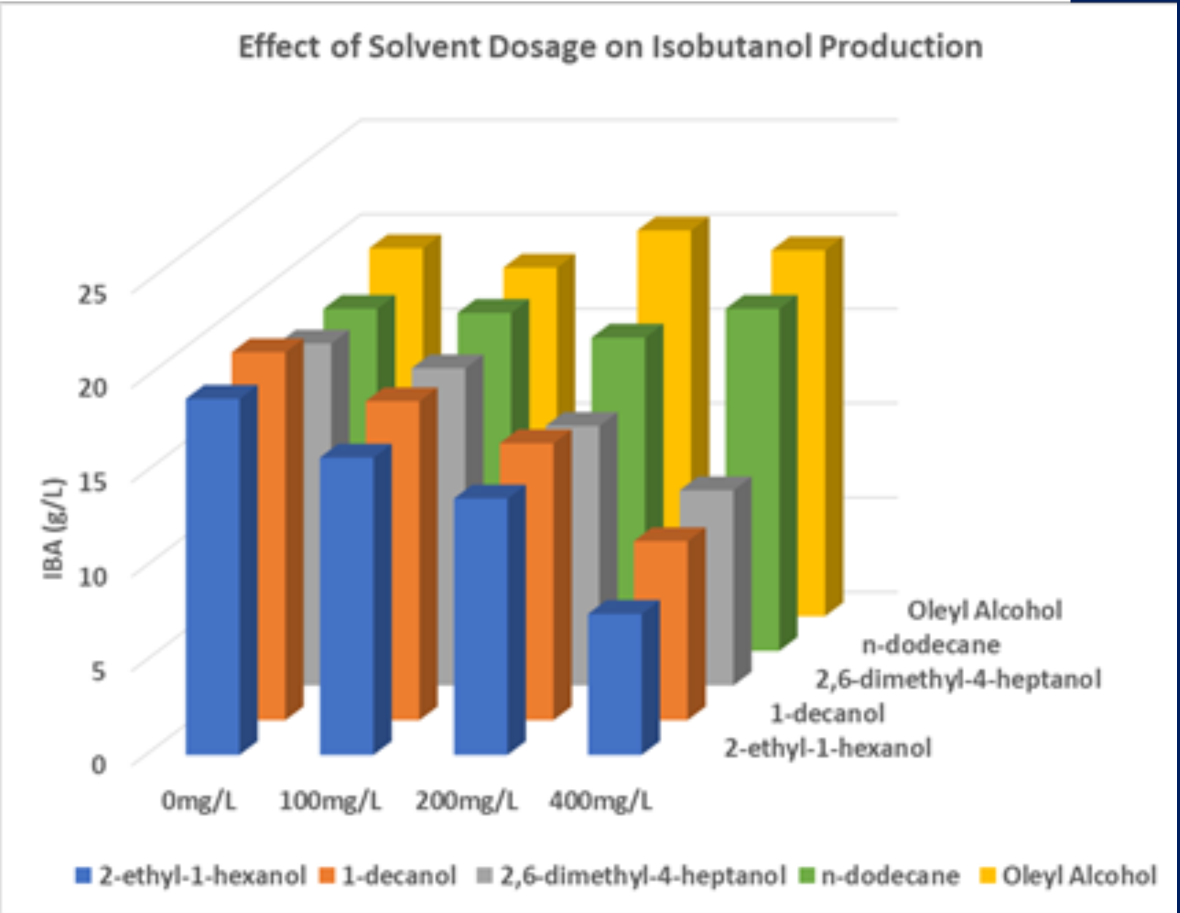
- ***Feedstock Solids:*** High insoluble solids in hydrolysate samples - hydrolysate may require processing before feeding to Fermentation



Progress - Fermentation

Lead: gevo

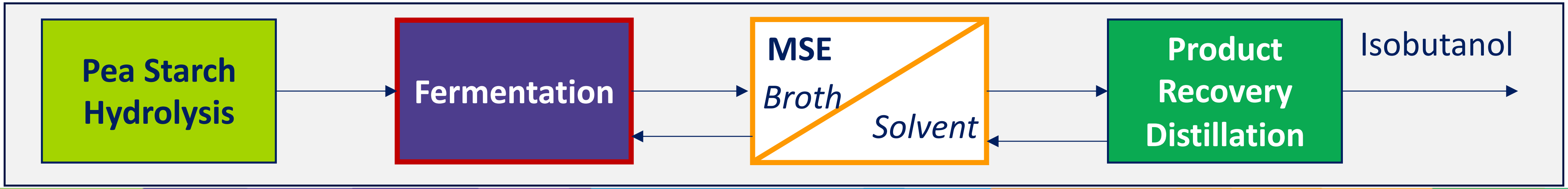
Results	• ***Validation & Tech. Transfer:*** Demonstrated performance of organism using pea starch • ***Cytotoxicity***: Based on initially defined potential extraction solvents – quantified impact and ***MSE targets for residual solvent*** in broth on organism productivity and health



- ***Optimization (in progress):*** defining nutrient package, ferm. targets, propagation schemes to maximize performance

Challenges:

- ***Cytotoxicity***: with fermentation integration, broth is returned to fermenter(s) after contact with solvent – at >100 ppm of 3 of 5 solvents tested, yeast performance is impacted
- ***Propagation configuration***: potential reinoculation strategies to be investigated to mitigate solvent impact



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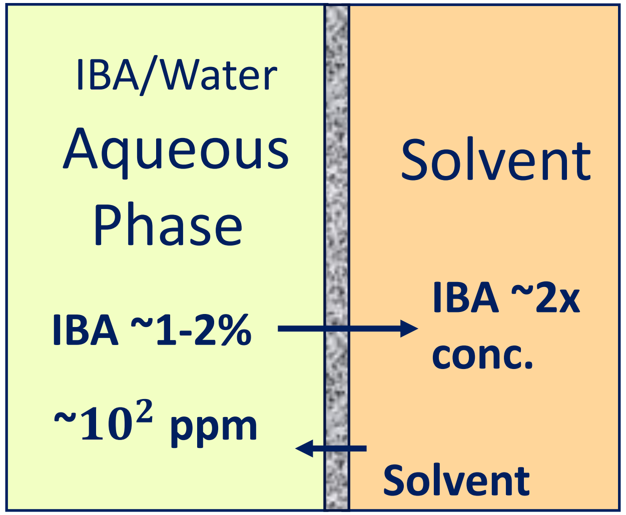
Progress - MSE

Lead: University of Minnesota

Results	***Solvent Screening:*** Determined the liquid-liquid ***equilibrium partition coefficients and selectivity*** of aqueous and model mixtures with selected solvents using shake flask LLE partition experiments and theoretical modeling – ***significant benefit from concentrating IBA in solvent***

- ***Understand byproduct partitioning (in progress)***: Analytical Characterization of aqueous phase and organic phase components using GC/HPLC
- ***MSE Performance (planned)***: Determine MSE performance characteristics using aqueous and broth mixtures with selected solvent using membrane solvent extraction experimental setup at various flow rates – including ***long term*** changes

Porous Membrane

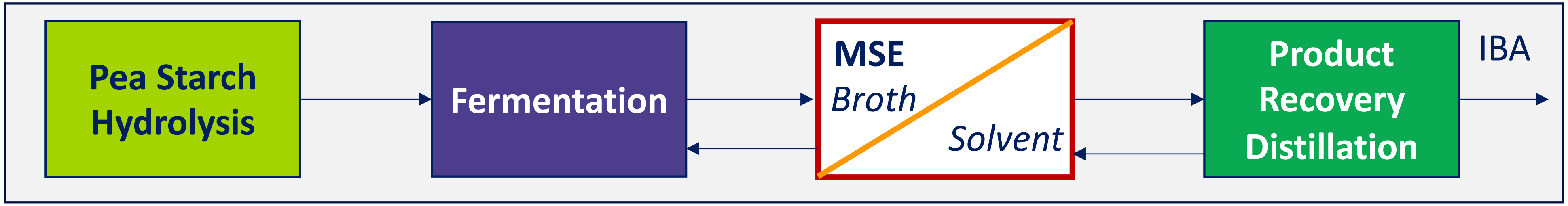


*Membrane provides contact between phases **prevents emulsion formation***

Challenges:

- ***Byproducts:*** Glycerol, Isobutyrate Partitioning – appears to have lower transfer rates through membrane to solvent

Hollow Fiber Cartridge



Progress – Solvent Selection

Lead: University of Minnesota

Solvent Screening:

Based on the comparison of partition coefficient, selectivity and other properties, ***2,6-dimethyl-4-heptanol has the most favorable characteristics***

Solvent	Boiling Point at 1 atm (°C)	Density (kg/m3) at 37°C (Aspen Plus)	Viscosity, mPas	Kd	Selectivity
2,6-dimethyl-4-heptanol	177.85	797.222	5.53	4.62-5.41	203.8-264
Oleyl alcohol	349.13	845	15.98	2.8-3.6	270-350
1-decanol	229.85	812.795	7.32	3.9- 5	71.7-102.4
2-Ethyl-1-hexanol	183-186	833	10.3	4.6-6.3	135.3-171.8

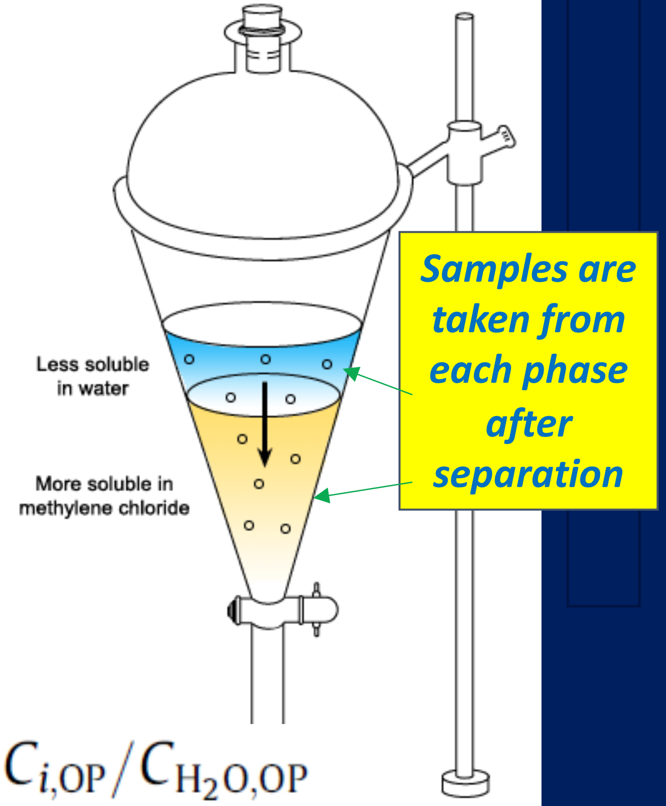
High BP and high viscosity are not desired

Partition Coefficient:

$$K_{Di} = \frac{C_{i,OP}}{C_{i,AP}}$$

Selectivity:

$$S_i = \frac{K_{Di}}{K_{D,H_2O}} = \frac{C_{i,OP}/C_{H_2O,OP}}{C_{i,AP}/C_{H_2O,AP}}$$



Higher K_{Di} and higher S_i, higher the concentration of component ("i") and lower the concentration of water in the organic (extract) phase, indicating that we are mostly separating the desired component "I" (i.e., ethanol, butanol)

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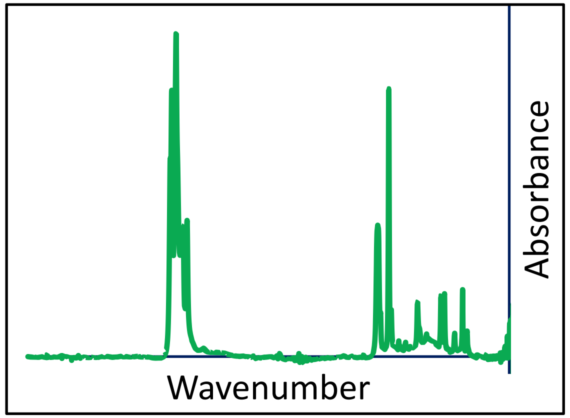
Progress - Membrane

Lead: Argonne NATIONAL LABORATORY

Approach

- ***Compatibility and stability (in progress):*** Evaluate the chemical compatibility of polypropylene with candidate extractant solvents and in the presence of cleaning agents through batch testing, under flow conditions, and through post-mortem analysis.
- ***Fouling and Fouling Control (planned):*** Identify potential fouling agents (colloidal, organic, inorganic, biological) in fermentation broth and through membrane characterization; develop efficient mitigation/control strategies.



Sample FTIR spectrum

Results

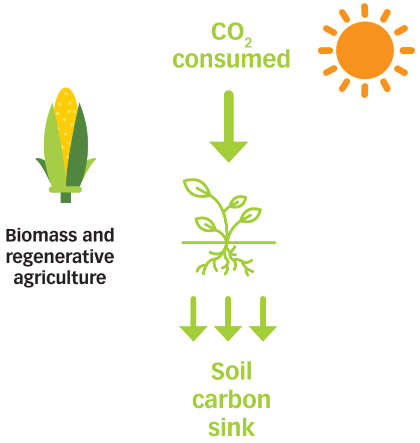
- ***Established baseline physicochemical characterization***
  - Fourier Transform Infrared Spectroscopy (FTIR) - chemical functional groups
  - Contact angle – hydrophobicity/hydrophilicity
  - Scanning Electron Microscopy (SEM) - surface morphology and topology
  - Thermogravimetric analysis (TGA) - polymer integrity
- ***Optimized pre-treatment requirements*** to remove mineral oil (residual from thermally induced phase separation manufacturing process)
- ***Initiated membrane/chemical batch testing***

Category	Exposure chemical
Extraction solvents	2,6-dimethyl-4 heptanol
	Decanol
	2-ethyl-1-hexanol
	Oleyl alcohol
Fermentation product	Isobutanol
Control	Milli-Q water
Cleaning agents	0.1N NaOH

Impact

Net-Zero Plant Concept

Carbohydrate Rich Plant-Based Feedstocks

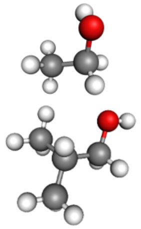


Climate Smart Ag enables low or negative carbon intensity feedstocks

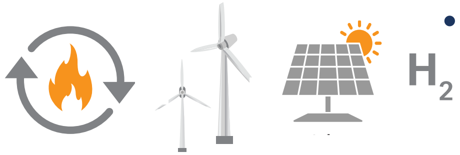
Fermentation Process Technology

- **Naturally derives carbohydrate energy as alcohols**
- **Concentrates biogenic CO2 that can be captured and stored.**
- **Recover high-quality protein and oil for pet, aquaculture and animal nutrition**

Intermediate Alcohols



Efficient intermediate for catalytic conversion drop-in products



Catalytic Transformation

- **Novel application of catalytic transformations commonly used in the petroleum industry.**
- **Optimization and integration enable lower carbon intensity.**

Drop-In SAF, Renewable Fuels and Sustainable Chemicals

Enables existing transportation, petroleum and petrochemical infrastructure to become net-zero and beyond based on the Argonne GREET model

Gevo and ADM continue to **advance partnerships in SAF** space with capital planned and in execution.

Impact

Commercial Potential	• Should FIMSE be proven viable through this project, it will be **incorporated as a technology option for future expansion and energy reduction**, with potential for IP to be generated • **FIMSE enables IBA for SAF** to become operationally viable, lowering Carbon Intensity of separations

DEI Impact	We are engaging underrepresented communities in science, technology, engineering, and mathematics (STEM) – training **15-20 researchers and students** from underrepresented backgrounds and supporting teacher education which could impact more than **500 students per year** from underrepresented backgrounds

Commercial Impacts
Continuous removal improves volumetric productivity, decreasing **Capital Cost** for Fermentation by ***10-30%***
Continuous recovery of extractant with lowers **separation energy** up to ***52%***

ADM, Gevo Sign MoU to Produce up to 500M Gallons of Sustainable Aviation Fuel

https://www.globenewswire.com/news-release/2021/10/25/2319898/23976/en/ADM-Gevo-Sign-MoU-to-Produce-up-to-500M-Gallons-of-Sustainable-Aviation-Fuel.html

Summary

Technical Approach	**Integrated risk management approach guided by TEA and LCA through:** 1. **Conversion Process Definition** (Pea Starch Hydrolysis) 2. **Fermentation Transfer**, Validation and Optimization with Pea Starch Feedstock 3. **Solvent Screening** – Membrane Performance and Fermentation Impact 4. **MSE Performance and Fouling Characterization** 5. **Continuous Fermentation** Characterization 6. **Demonstration** at Pilot Scale
Impact	Integration of Key Industry SAF production and fermentation leaders in project guides technical direction. Potential energy reduction from FIMSE process can be included in future options for SAF expansion.
Progress	**Milestones have been achieved to plan.** **Recent and Upcoming:** 1. **(Complete)** Conversion Process Defined 2. **(Complete)** Fermentation Process Validated and Transferred to ADM 3. ***(In Progress)*** Definition of Solvent impacts on fermentation, determining process needs for Solvent recovery and propagation configuration *4.* ***(Upcoming)*** Initial TEA completion based on Conversion and Fermentation Results

Quad Chart Overview

Timeline

- *Project Start Date: 10/01/2021*
- *Project End Date: 5/31/2025*

	FY22 Costed	Total Award
DOE Funding	*(10/01/2021 – 5/31/2025)*	*$3,341,844*
Project Cost Share *		$875,000

TRL at Project Start: 4

TRL at Project End: 6

*Only fill out if applicable.

Project Goal

Demonstrate Fermentation Integrated with Membrane Solvent Extraction for Isobutanol recovery to decrease recovery energy requirements and costs for Sustainable Aviation Fuel fermentation feedstocks.

End of Project Milestone

Demonstrate at least a 50% reduction in energy and water usage compared to recovering isobutanol directly from fermentation broth, >100h of stable operation of the continuous fermentation-FIMSE unit and recover at least 100kg of product. Achieve fermentation yeast efficiency of 0.36 g IBA/g glucose with Pea starch hydrolysate feed; volumetric productivity of 1.0 ± 0.1 g/L-h, 70% extraction of IBA into ternary solvent and 95% yield of IBA in distillation.

Funding Mechanism

FY21 BETO Scale-up and Conversion FOA – Subtopic Area 3b: Separations to Enable Biomass Conversion (Bioprocessing Separations Consortium)

Project Partners

- ADM
- Gevo
- University of Minnesota
- Argonne National Lab