Combined Algal Processing for the Synthesis of Liquid Oleofuels and Products (CAPSLOC)

WBS 1.3.4.204

April 4th, 2023

Advanced Algal Systems

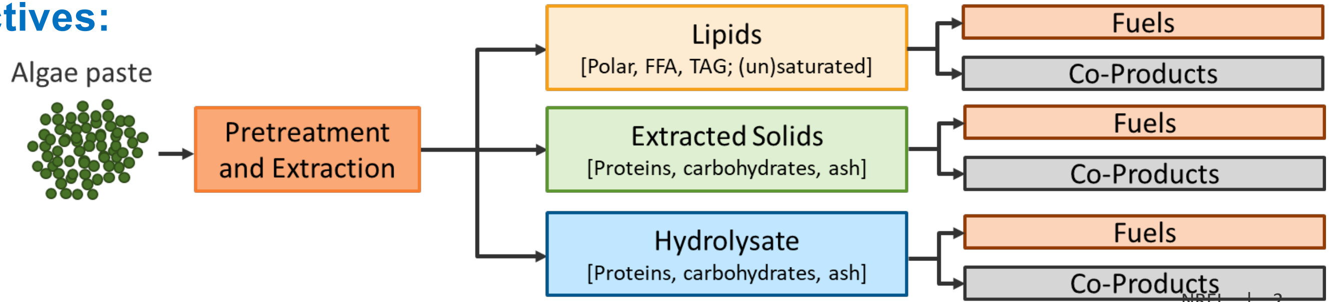
Tao Dong
National Renewable Energy Laboratory

Project Overview

- **Aim:** Develop a composition-agnostic biorefinery concept that enables economically, environmentally, and socially-viable biofuel production by maximizing the value from each fraction.
- **Today:** Algal biorefining at commercial scale exists only for niche, high-value products, not fuels. There have been huge investments for understanding and improving algal biology and cultivation, but relatively little work done on conversion processes.
- **Importance:** **Unique** in BETO portfolio to deliver an **integrated biorefinery** that is critically needed by **industry** for **commercialization**; will boost **bioeconomy**, advance **decarbonization**, and create **jobs**.
- **Risks:** Algae feedstocks have variable/complex composition; feedstock costs limit product slate to maintain economic viability; tied into DISCOVR HP biomass.

Aligns with BETO's objectives:

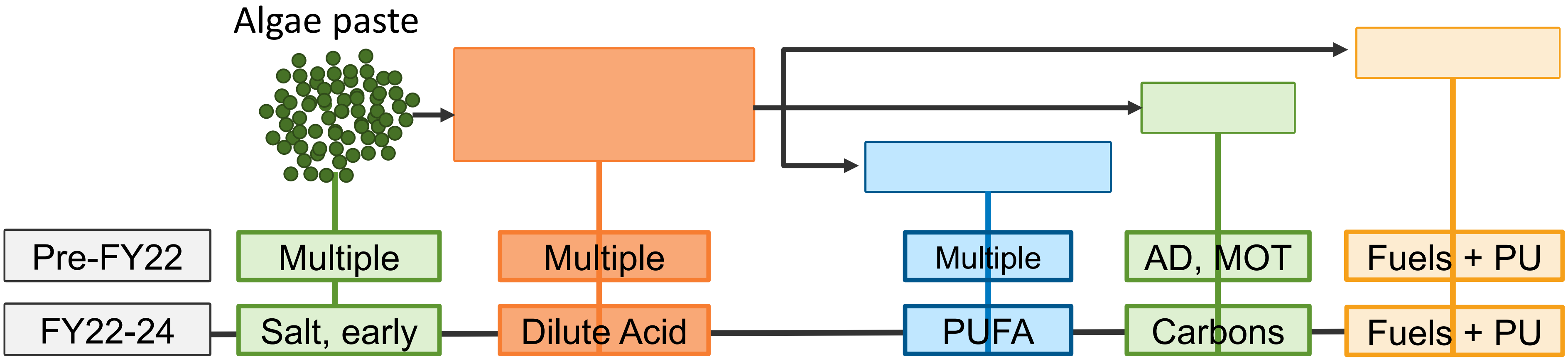
- Reduce GHG emissions
- Industrially viable "drop-in" biofuels and bioproducts
- Compatible with existing infrastructure and vehicles



Approach (Technical)

Technical Approach

- Develop robust technologies for a source-agnostic biorefinery (representative biomass from various partners).
- Document interplay of product yields and properties across different compositions and process configurations.
- Iterative approach R&D consulting with TEA/LCA to establish process targets and quantify improvements in MFSP, reducing in carbon intensity, and supporting state of technology (SOT)



Approach (Technical)

Potential Risk and Mitigation Strategies

Risks	Mitigations
Feedstock composition is complex and variable.	Develop robust “funneling” conversion technologies.
Biorefinery steps are interdependent.	Flexibility in valorization of each fraction as well as pathway redundancy allows strategic pivot points if one operation underperforms.
Simultaneous development of multiple new products from changing algae composition challenges quantification of project progress.	Ongoing dialogue with SOT/TEA/LCA produces traceable metrics (e.g., MFSP, GHG emissions), and allows timely feedback on new concepts.

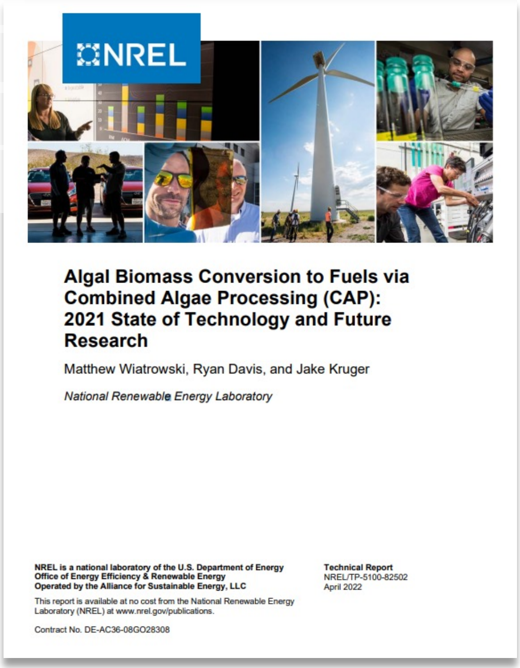
Approach (Management)

Task 1: TEA/LCA Support (Eric Knoshaug)
Generate data for SOT and Design Reports

Task 2: CAP Expansion (Jake Kruger)
Identify new process and co-product opportunities

Task 3: Algae-Based Polymers (Tao Dong)
Novel polymer-based co-products

- **Algae Compositional and Product Analysis**
  - Stefanie Van Wychen, Bonnie Panczak, Alicia Sowell, Hannah Alt
- **Algae Pretreatment**
  - Matt Fowler, Tao Dong, Skylar Schutter
- **Hydrolysate Fermentation**
  - Eric Knoshaug, Ryan Spiller, Rob Nelson
- **Catalytic Upgrading**
  - Jake Kruger, Tobias Hull
- **Product Formulation and Characterization**
  - Tao Dong, Lieve Laurens, Ali Chamas


NREL

Algal Biomass Conversion to Fuels via Combined Algae Processing (CAP): 2021 State of Technology and Future Research

Matthew Wiatrowski, Ryan Davis, and Jake Kruger

National Renewable Energy Laboratory

NREL is a national laboratory of the U.S. Department of Energy
Office of Energy Efficiency & Renewable Energy
Operated by the Alliance for Sustainable Energy, LLC

This report is available at no cost from the National Renewable Energy Laboratory (NREL) at www.nrel.gov/publications.

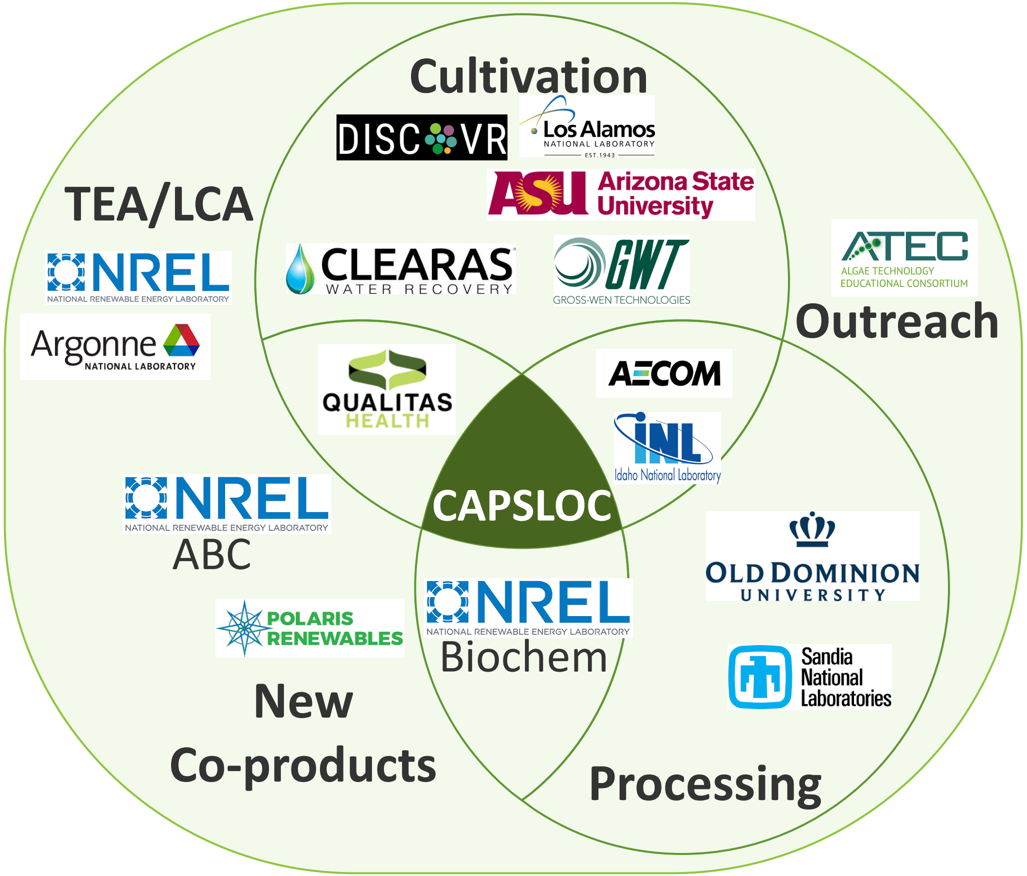
Contract No. DE-AC36-08GO28308

Technical Report
NREL/TP-5100-82502
April 2022

Management Approach

- Monthly meetings with BETO, bi-weekly meetings with project team, 1-on-1 meetings with team members as needed
- Milestones structured to support process modeling, which quantifies project progress via improvement in TEA and LCA outcomes **(success metrics #1 and #2)**
- Disseminate results via publications, presentations, patent applications, technical reports **(success metric #3)**
- Leverage expertise of collaborating partners and projects to develop new concepts

Approach (collaboration)



Collaboration and coordination with other national lab research, industry, academia

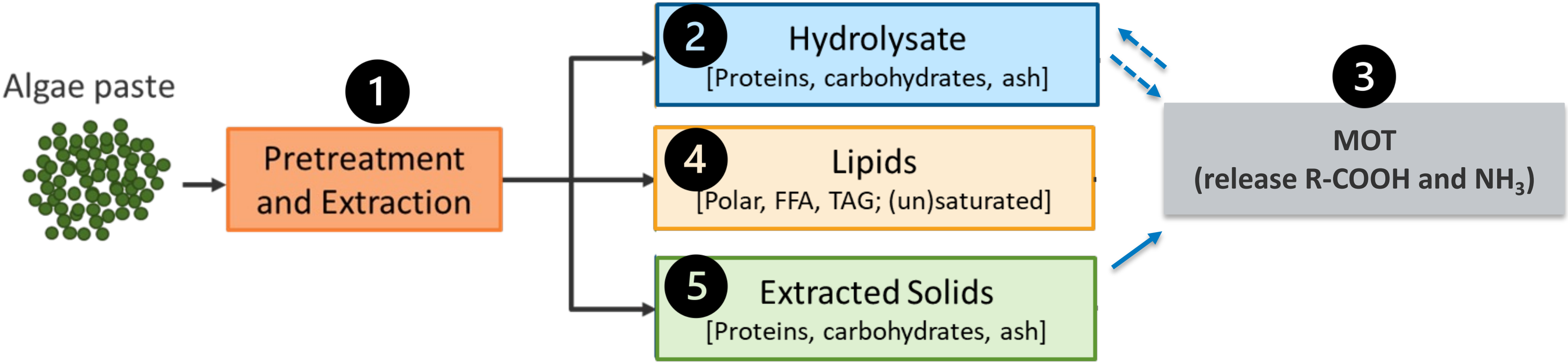
- Understand algae composition via coordination with DISCOVR, ABC, RACER, industry
- Guide product development via industry outreach
- Guide process development via collaboration with TEA and LCA teams

Diversity, Equity, Inclusion

- Developing approaches that can be implemented in communities that may exposed to excess waste biomass for energy justice.
- Hosted 3 interns through DOE programs supporting underrepresented groups (e.g., MEISPP)
- Energy Justice online training for key project personnel
- Algae conversion technology course development with ATEC
- Algae compositional analysis training development

2. Progress and Outcomes

Biorefinery Process

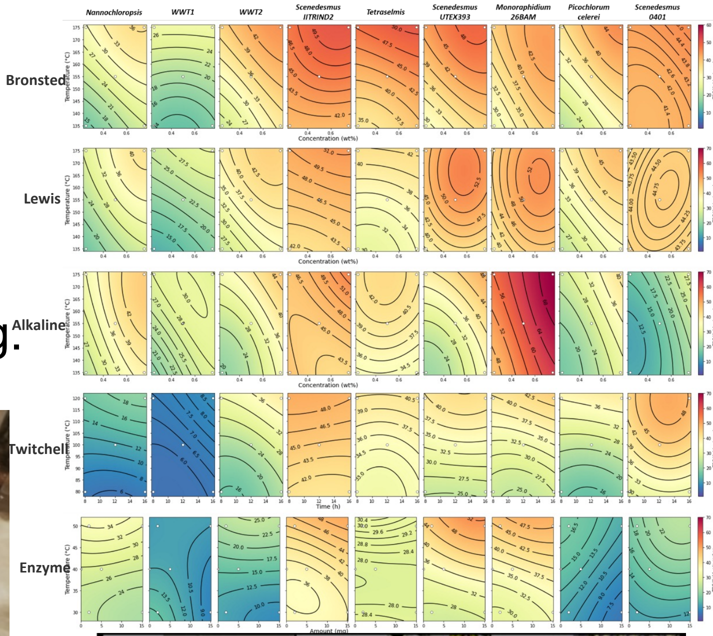


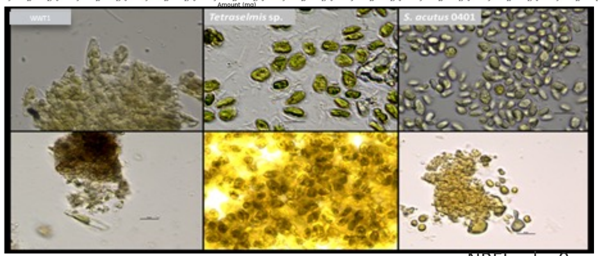
2. Progress and Outcomes

❶ Pretreatment & Fractionation

Biomass Pretreatment and Fractionation

- Demonstrated dilute acid pretreatment as a robust method for a broad range of algae compositions
- Successfully scaled up from 5 g to 100 kg
- Generated pretreated biomass to support studies in fermentation, lipid extraction and catalytic upgrading.



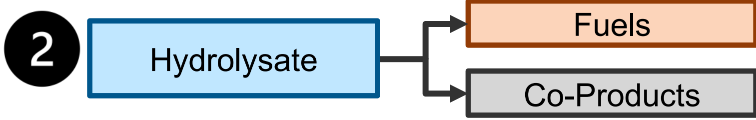


100kg scale pretreatment

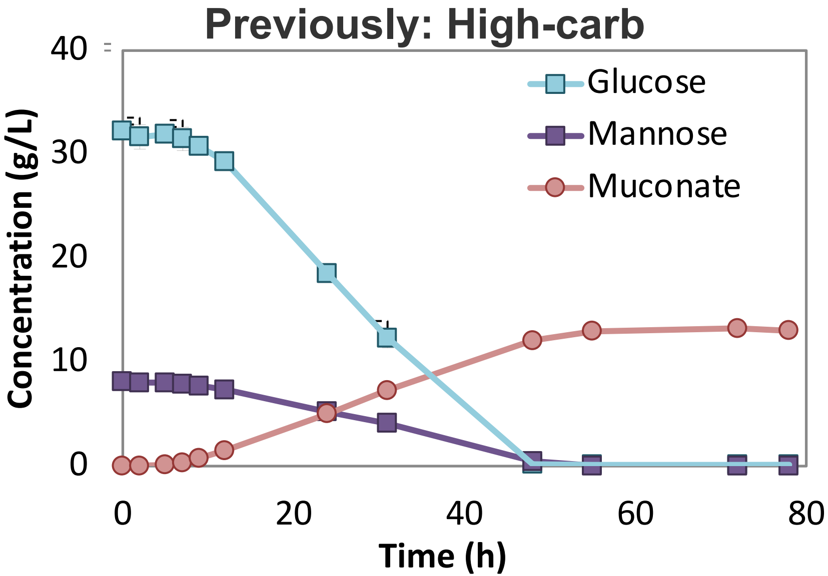
>80kg hydrolysate produced

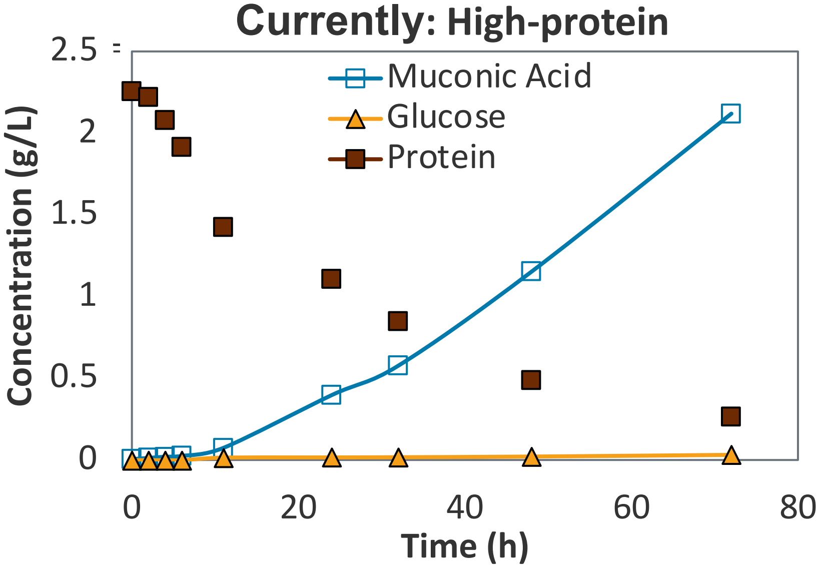
Kruger et al., submitted, **2023**. [FY22 Q1 Milestone.]

2. Progress and Outcomes



Hydrolysate fermentation



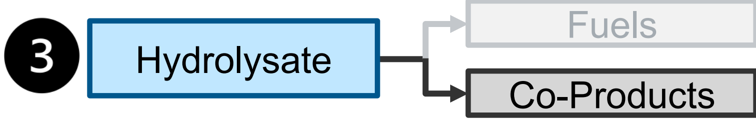


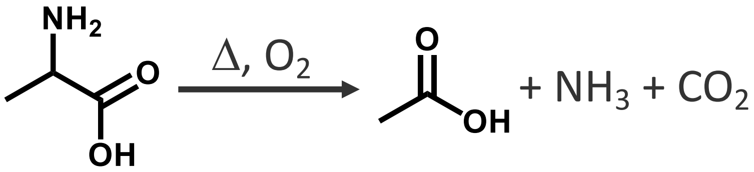
Flexible hydrolysate fermentation

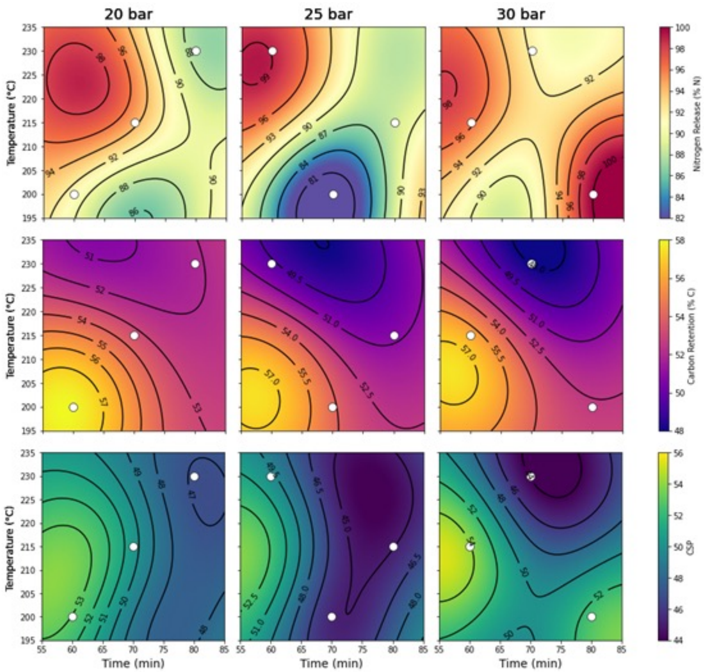
- High-carbohydrate CAP hydrolysates support fermentation to multiple products and fuel precursors (e.g., ethanol, succinic acid, butyric acid, muconic acid)
- Transition toward high-salt and high-protein biomass necessitates halotolerant and protein-utilizing organisms or chemo-catalytic protein conditioning to enable robust fermentation

Quiroz-Arita et al., *Sus Energy Fuels*, **2022**, 6:2398-2422; Spiller et al., *submitted*, **2023**.

2. Progress and Outcomes







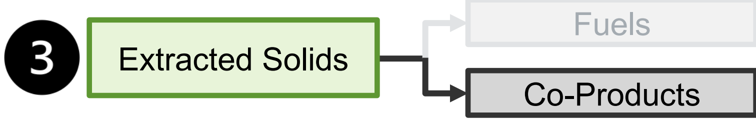
Mild Oxidative Treatment (MOT) with Ion Exchange Conditions High Protein Hydrolysates

- Optimized MOT for nitrogen release and carbon retention via Design of Experiments and Machine Learning
- Conditioned hydrolysate improves lipid production at bioreactor level
- Lipid product decreases capital costs because oleaginous biomass can be processed with incoming algae
- MOT also enables nutrient recovery and recycle

Strain (Media)	FAME (mg/L @ t_0)	FAME (mg/L @ t_f)	Fold Change
C. oleaginosus (Control)	67	1136	16.8
C. oleaginosus (IX1)	67	1210	17.9
C. oleaginosus (IX2)	67	2703	40.1

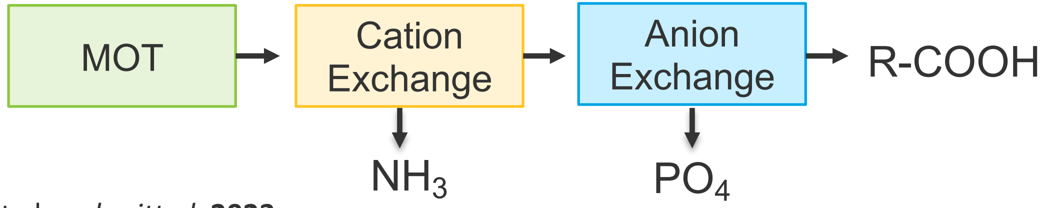
Hull et al., *in prep.*, **2023**. [FY22 Q2 and Q3 milestones.]

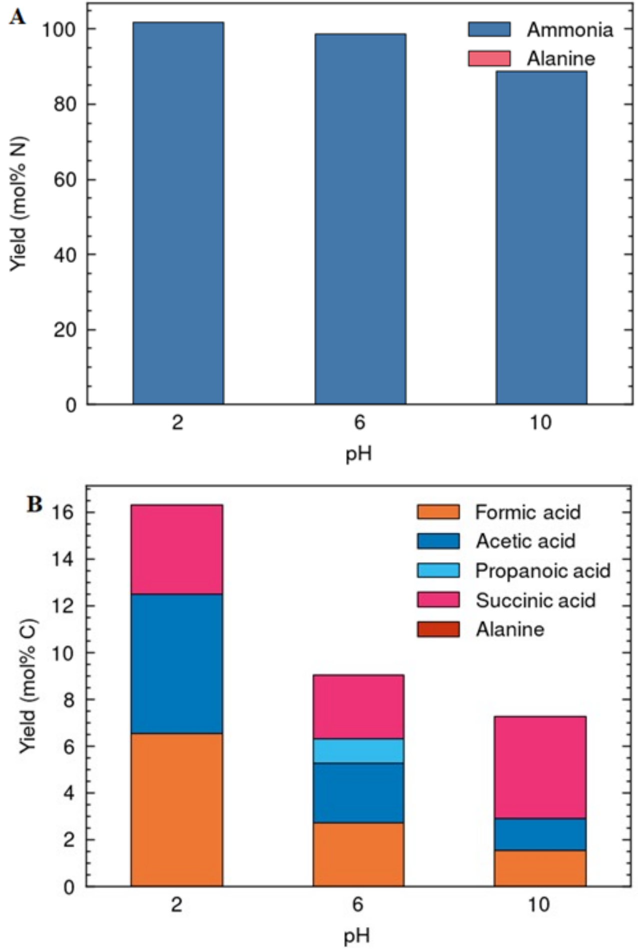
2. Progress and Outcomes



MOT of Extracted Solids Enables Further Nutrient Recovery

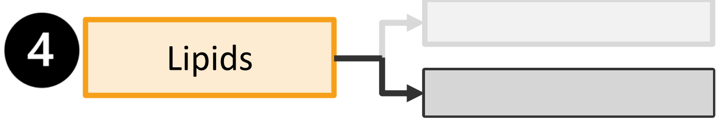
- Demonstrated >95% nitrogen release as NH_3 with up to 16% R-COOH yield with selective recovery of NH_3 and PO_4
- Hydrolysate and extracted solids can be co-processed by MOT
- Improved performance under acidic conditions integrates well with pretreatment and lipid extraction
- MOT allows flexible conditioning of extracted solids for further conversion





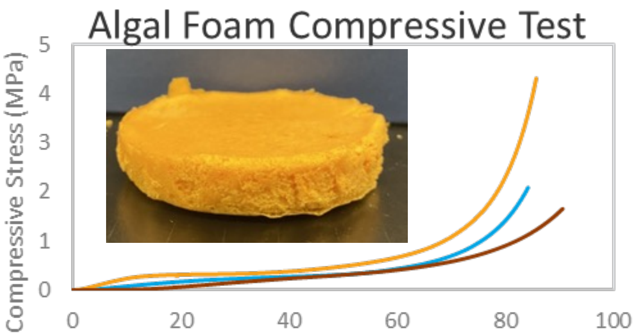
Hull et al., *submitted*, **2023**.

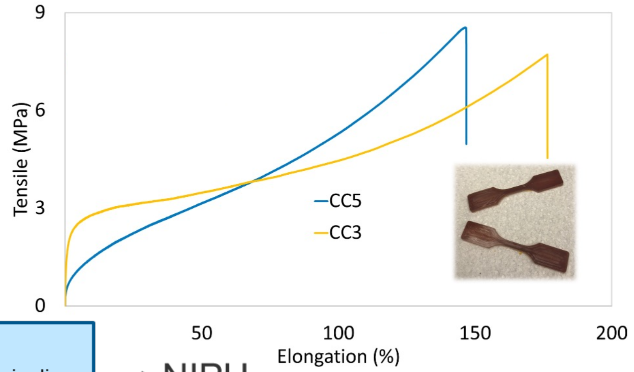
2. Progress and Outcomes

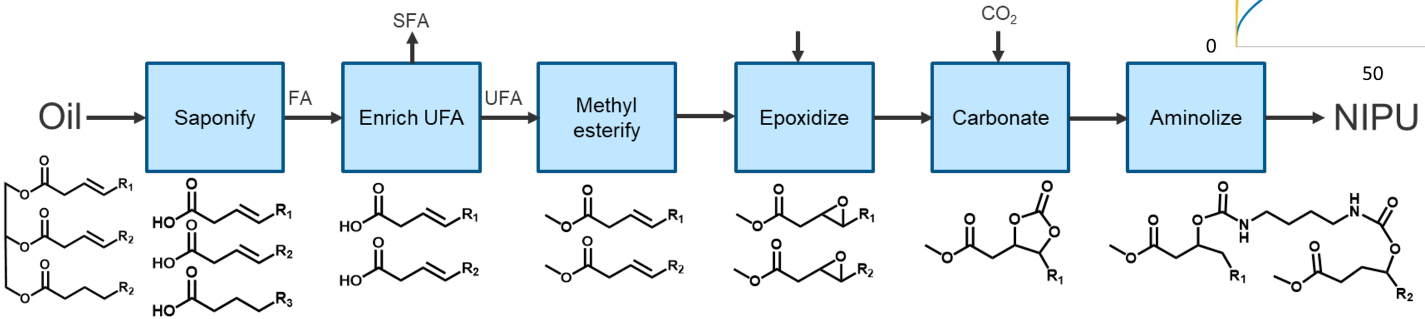


Algal Polymers

- Leverage high degree of unsaturation in algal lipids to produce polyurethane without using isocyanate
- Wide range of applications, such as foam (insulation) and elastomer (textile)
- NREL's bio-NIPU technology has been licensed to Polaris Renewables
- Potential to reduce MFSP by more than $5/GGE with algae oils of favorable composition



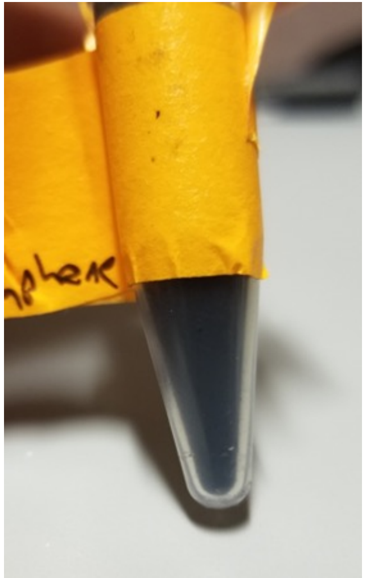




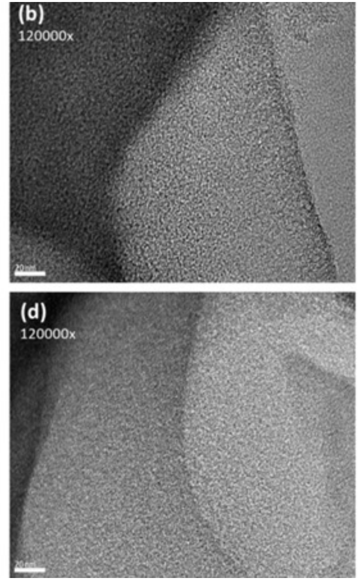
Technology Commercialization Fund

U.S. DEPARTMENT OF ENERGY | OFFICE OF Technology Transitions

2. Progress and Outcomes



Graphene

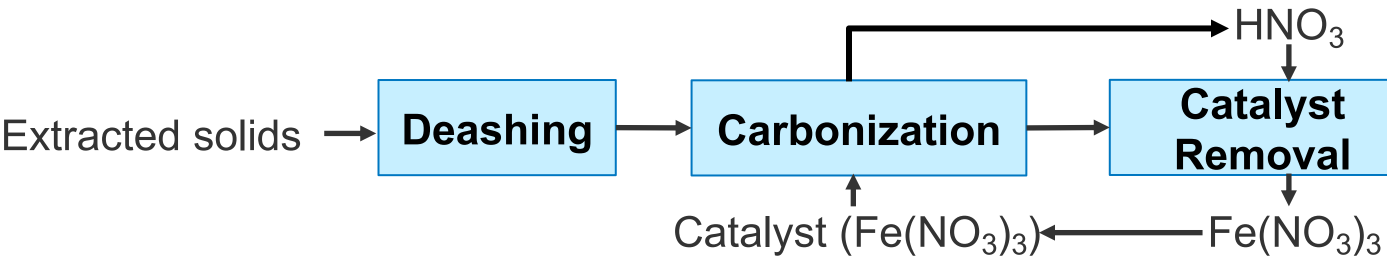


Activated Carbon

Graphite

Insoluble Solids to High-Value Conductive Carbons

- Developed purification procedure to reduce ash content to < 0.1 %
- High purity graphitic carbons represent new high-value co-product ($10+/kg) that fixes carbon long-term

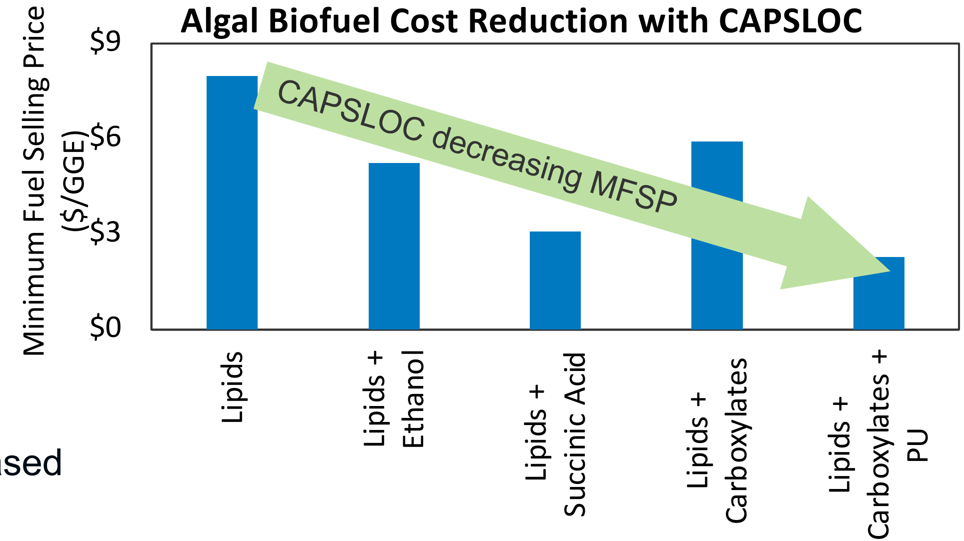


Thakkar et al., *Biomass Conv Biorefin*, **2022**; Chamas et al., *in prep*, **2023**. [FY22 Q4 Milestone]

Impact

Technical and Science Impact

- Demonstrated pre-pilot scale algae pretreatment to de-risk commercialization
- Demonstrated new pathways for nutrient recycle, high-protein hydrolysate conversion, and carbon-sequestering co-products.
- Publications, presentations, patents detailing promise of CAPSLOC



Industrial Impact

- Lack of conversion process in the current biobased products and biorefinery industry.
- One of two pathways included in the annual SOT.
- NIPU technology has been licensed.
- Development of robust, high-protein processing concept enables use of “secondary product” algae from WWT, algal blooms
- TEA suggests pathway to produce $2.50/GGE fuels from $400+/ton biomass

Environmental Impact

- Algae are powerful carbon capture tool
- Multiple carbon co-products that fix CO_2 long-term

DEI Impact

- Enabling future algae researchers from diverse backgrounds through training and outreach

Kruger et al., *Front Chem Eng*, **2022**, 3:803513

Summary

Overview: CAPSLOC aims to generate drop-in algal jet- and diesel-range biofuels at modeled cost of < $2.50/GGE and > 50% GHG emissions reduction versus fossil incumbents.

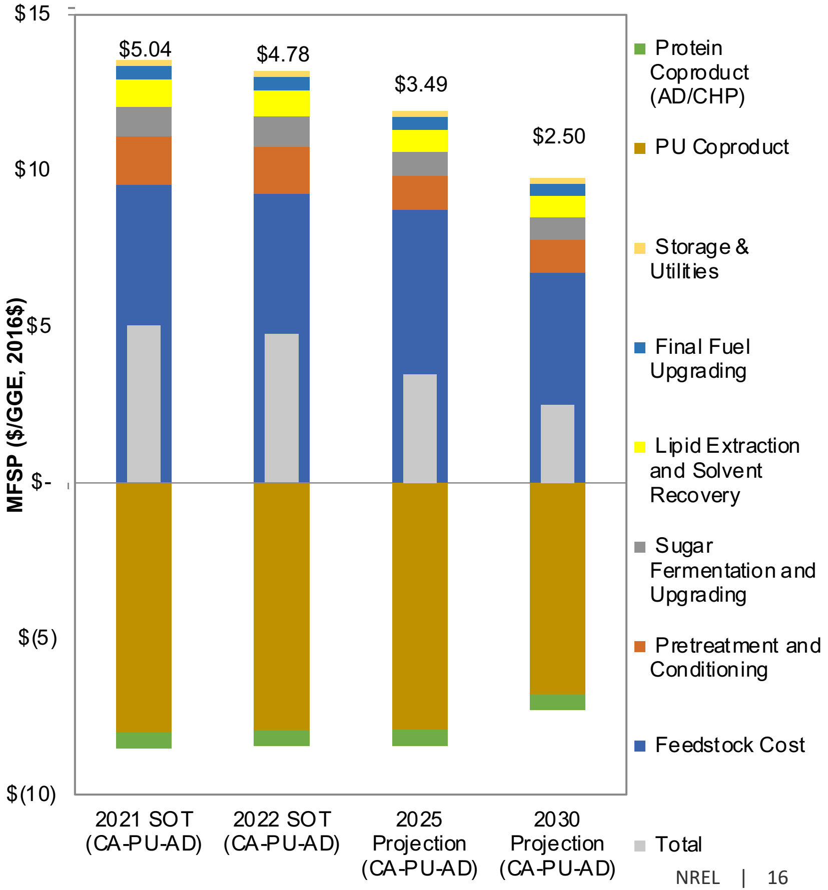
Management: Provide quantitative data to analysis teams to measure improvements via TEA and LCA metrics.

Approach: Leverage network of collaborators to define lowest cost and most sustainable algae compositions, develop and adapt fuel and co-product technology to optimize valorization.

Impact: TEA models suggest pathway from $400+/ton biomass to $2.50/GGE fuels and market-competitive co-products. Environmental benefits from CO_2-fixing co-products.

Progress and Outcomes: Demonstrated significant improvements in understanding key aspects of algae processing, especially:

- Pretreatment technologies suitable for variable composition
- Co-products available from lipid and extracted solid streams
- Conditioning and fermenting high-protein hydrolysates
- Recovering N and P nutrients for recycling to cultivation ponds



Quad Chart Overview

	FY22 Costed	Total Award
DOE Funding	(10/01/2021–9/30/2022) $651,065	$2,100,000
Project Cost Share*		

TRL at Project Start: 2-4
TRL at Project End: 4-6

Project Goal

Reduce biofuel production costs through development of multiproduct biorefinery concept involving integrated conversion of all major algal components.

End of Project Milestone

Demonstrate integrated CAP processing at pilot plant (500 L) scale.

Funding Mechanism

BETO AOP

Project Partners*

- **National Labs:** Sandia, Los Alamos, Idaho, DISCOVR, Algal Biomass Composition, Algal Biofuels TEA
- **Universities:** Arizona State University

Only fill out if applicable.

Acknowledgements

BETO
Christy Sterner
Phil Lee
Dan Fishman

NREL Contributors:
Jake Kruger, Lieve Laurens,
Eric Knoshaug, Matt Fowler, Rob Nelson, Bonnie Panczak, Stefanie Van Wychen, Alicia Sowell, Hannah Alt, Ryan Spiller, Tobias Hull, Ali Chamas, Ryan E. Davis, Matt Wiatrowski, Phil Pienkos, Earl Christensen, Cameron Hays

External Collaborators:
John McGowen (ASU), Sandeep Kumar (ODU), Jakob Nalley (Qualitas), Dan Levy (AECOM), Martin Gross (GWT), Jordan Lind (Clearas), Phil Pienkos (Polaris), Lynn Wendt (INL), Amanda Barry (SNL), Claire Sanders (LANL), Jenna Schaumbach (LANL), Ryan W. Davis (SNL), Meltem Urgun Demirtas (ANL), Kevin Wyss (Rice U),

Thank You!

www.nrel.gov

This work was authored by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. Funding provided by U.S. Department of Energy Office of Energy Efficiency and Renewable Energy BioEnergy Technologies Office. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.

NREL
Transforming ENERGY

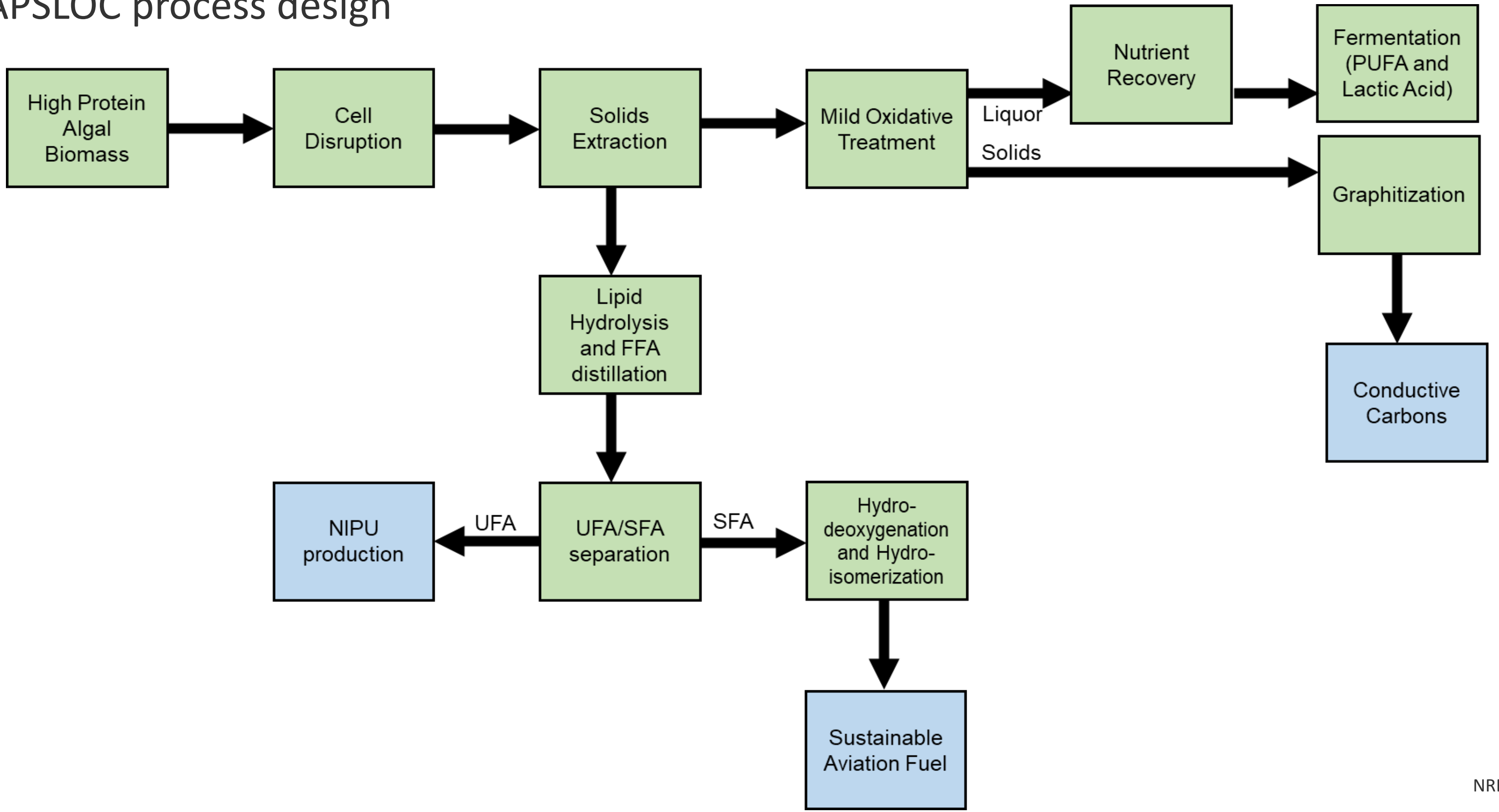
Additional Slides

Response to Reviewer Comments

Comment	Response
The team should consider progressing the understanding on yield and losses in the different steps involved in the production of NIPU and upgrade the model to reflect this. The team should provide more clarity on CAPEX required for this process.	While process losses in each step depend on algae and lipid composition, we have worked with Qualitas to understand the mass balances in their optimized commercial process, and include these losses in the process models used for TEA and LCA. Similarly, the TEA models include the CAPEX costs for the NIPU production, which are described in detail in our manuscript currently under review at Green Chem. Additionally, the CAP approach includes pathways to make use of these "losses," including fuel production from less saturated lipids, and fermentation of glycerol produced during saponification.
The fractionation technologies and incorporation of other processes should be detailed in this discussion. Incorporation of impacts to BETOs targets and goals would enhance the presentation. The presentation can be enhanced by providing a quantitative assessment of milestones achieved and future work to be developed.	The fractionation technology is a key aspect of this project moving forward, and our FY21 Q4 milestone (slide 27) contains some details of what we are targeting in the fractionation step. We have met all 17 milestones planned on this project to date (through FY21 Q2) in this project cycle, though a few were delayed due to COVID. Regarding future work, the MFSP graph shows improvements in MFSP (to $2.50/GGE) out to 2030 mainly reflecting reductions in cultivation costs. Our remaining two milestones for FY21 target additional coproducts from phytol that is co-extracted with lipids but inhibits NIPU production (slide 23), and improvements in the pretreatment step that we expect will further decrease MFSP. We believe there is significant potential for graphene as well.
The go/no go described uses quantifiable metrics to assess success. Risks and mitigation plans in this project do not seem well described.	Risks (and mitigation) considered include poor performance of NIPU (which can be improved by esterifying or crosslinking with different reagents), poor fermentation yields (which can be improved by adapting/engineering the microbes or relegating unused substrates to MOT or graphene), low pretreatment yields at large scale (which can be mitigated by validating at multiple smaller scales before scaling up), poor residue upgrading performance (which can be mitigated by considering multiple upgrading approaches, such as MOT and graphitization), and none of the new pretreatment configurations outperforming the baseline, resulting in no MFSP reductions from improved pretreatments (which can be mitigated by expanding the pretreatment approaches surveyed and improving MFSP through incorporation of new coproducts).

Progress and outcomes

CAPSLOC process design



Progress and Outcomes

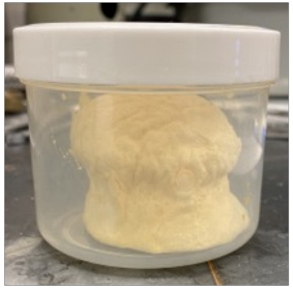
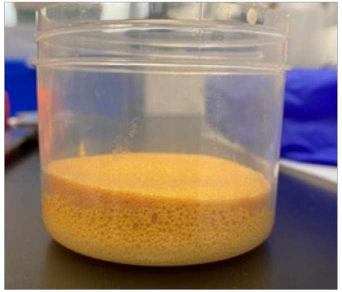
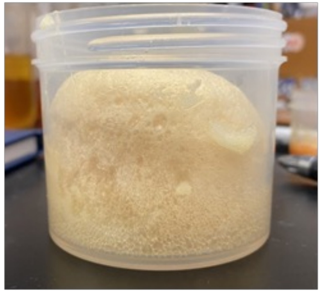
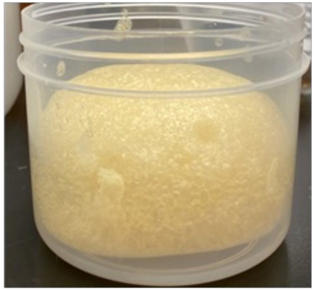
Microalgal lipid fractionation by short path distillation

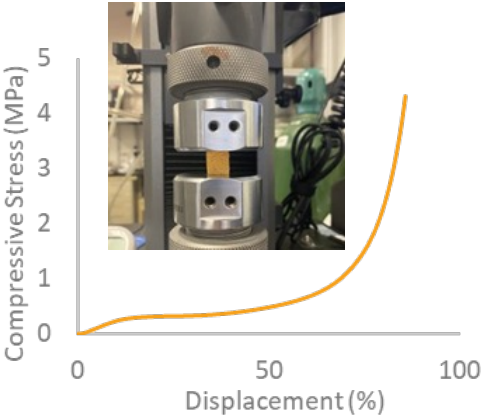
FAME recovery in each fraction (%)	Fraction at different temperature (°C)									
	80	100	120	140	160	180	200	220	240	leftover
C14:0	40.2	42.5	4.7	0.4	0.4	0.3	0.4	0.2	0.3	10.2
C16:0	15.4	37.5	31.4	2.2	1.1	0.9	1.6	0.2	0.2	10.5
C16:1n11	30.2	19.7	7.5	1.8	2.0	1.7	2.1	0.7	1.1	10.9
C16:1n7	18.0	35.3	29.3	1.7	0.8	0.7	1.2	0.2	0.2	10.4
C18:1n9	4.2	19.6	28.7	14.3	8.0	4.8	4.2	0.9	1.0	12.5
C18:2n6	4.4	19.9	28.7	13.9	7.6	4.5	4.0	0.8	0.9	11.9
C20:4n6	1.4	9.6	16.9	11.3	10.1	9.8	6.0	3.1	3.8	17.9
C20:5n3	1.3	9.2	16.5	10.9	9.9	9.7	5.9	3.1	3.8	17.5
FAME content (%)	75.9	94.5	98.1	94.9	91.9	91.2	88.9	84.2	83.5	24.0
FAME recovery (%)	11.7	24.4	23.5	6.5	5.0	4.5	3.3	1.3	1.7	13.6

- Microalgal fatty acids can be separated based on chain length.
- Distillation might be an efficient way to fractionate lipids and remove impurities for SAF production.

Progress and outcomes

Effect of surfactant on NIPU foam production

Linseed Density= 0.18 g/cm^3 	Petro based Density= 0.11 g/cm^3 	Algae lipid Density= 0.13 g/cm^3 
Linseed + surfactant (2%) Density= 0.07 g/cm^3 	Petro + surfactant (2%) Density= 0.05g/cm^3 	Algae + surfactant (2%) Density= 0.13 g/cm^3 



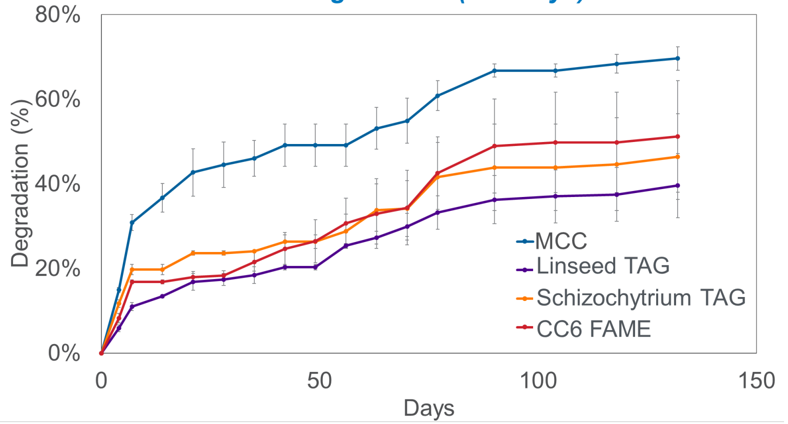
- Novel approach to produce NIPU foam using a bifunctional blowing agent
- Surfactants can affect morphology and density
- Low thermal conductivity 0.05W/(mK) for insulation application.

Dong et al. US 17/398.760

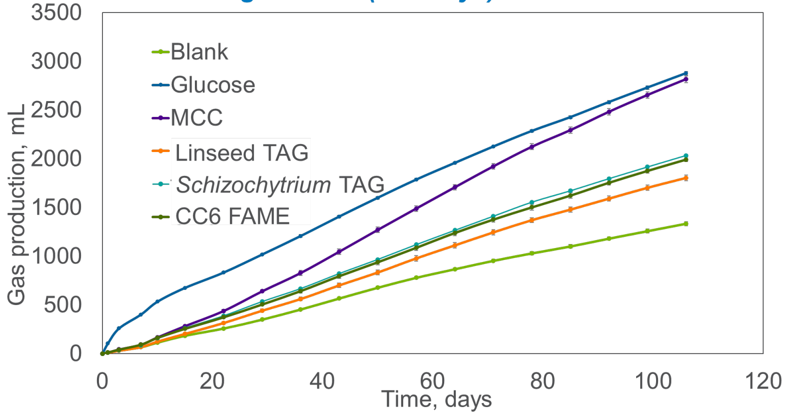
Progress and outcomes

Biodegradation tests of algal NIPU

Freshwater biodegradation (132 days)



Soil biodegradation (106 days)



Freshwater biodegradation model

sample	50%	Real 50%	90%	Fit
	Days			
MCC	50	50	271	93.6%
Linseed TAG	172		632	96.0%
Schizochytrium TAG	137		550	93.9%
CC6 FAME	114	119	418	95.0%

MCC: Microcrystalline cellulose;

CC6 FAME: Docosahexaenoic acid methyl ester derived cyclic carbonates

Soil biodegradation model

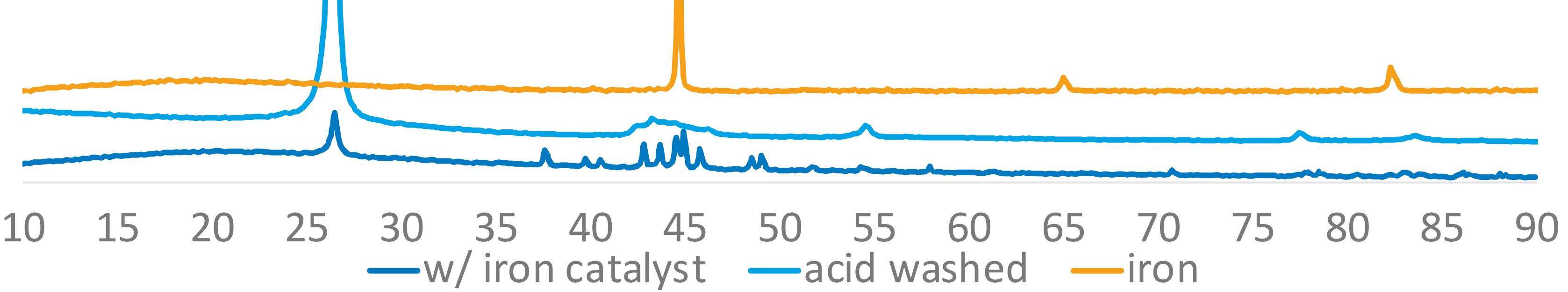
sample	50%	Real 50%	90%	Real 90%	Fit
	Days				
MCC	22	30	57	49	80.8%
Linseed TAG	68	75	196		92.9%
Schizochytrium TAG	36	54	87	85	74.5%
CC6 FAME	38	58	91	91	71.1%

Predicted Material half-lives and 90% biodegradation based on 1st order kinetics.

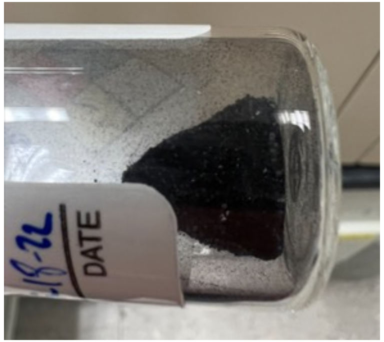
- Algal NIPU samples show good biodegradability.

Progress and outcomes

Effective catalyst removal after carbonization (XRD)



Catalyst removal was completed by stirring the iron catalyst containing graphite in HCl at 40 °C for 3hr.



Publications

1. Kruger, J. S.; Knoshaug, E. P.; Dong, T.; Hull, T. C.; Pienkos, P. T.; Renewables, P.; Drive, S. C., Catalytic Hydroprocessing of Single-Cell Oils to Hydrocarbon Fuels. Johnson Matthey Technology Review 2021, 65 (2), 227-246.
2. Dong, T.; Dheressa, E.; Wiatrowski, M.; Pereira, A.; Zeller, A.; Laurens, L.; Pienkos, P. Assessment of Plant and Microalgal Oil Derived Non-isocyanate Polyurethane Products for Potential Commercialization. ACS Sustainable Chemistry & Engineering 2021, 9(38), 12858–12869
3. Kruger, J. S.; Wiatrowski, M.; Davis, R. E.; Dong, T.; Knoshaug, E. P.; Nagle, N. J.; Laurens, L. M. L.; Pienkos, P. T., Enabling Production of Algal Biofuels by Techno-Economic Optimization of Co-Product Suites. Frontiers in Chemical Engineering 2022, 3. 83
4. Thakkar, A.; Pienkos, P. T.; Nagle, N.; Dong, T.; Kruger, J.; Kumar, S., Comparative Study of Flash and Acid Hydrolysis of Microalgae (Scenedesmus sp.) for the Recovery of Biochemicals and Production of Porous Biocarbon Nanosheets. Biomass Conversion and Biorefinery 2022. 1-10
5. Quiroz-Arita, C.; Shinde, S.; Kim, S.; Monroe, E.; George, A.; Quinn, J.; Nagle, N. J.; Knoshaug, E. P.; Kruger, J. S.; Dong, T.; Pienkos, P. T.; Laurens, L. M. L.; Davis, R. W., Bioproducts from High-protein Algal Biomass: An Economic and Environmental Sustainability Review and Risk Analysis. Sustainable Energy & Fuels 2022, 6 (10), 2398-2422.
6. Chamas, A. Sustainable Carbonization of Algal Proteins to High-Purity Graphite. In preparation
7. Chamas, A. Leveraging Iron for CO_2 Reduction into Carbons with Electro-conductivity. In preparation
8. Dong, T. Non-isocyanate Polyurethane Foam Produced from Algal Lipids. In preparation.
9. Nelson, R. Muconic Acid Production from Algae Hydrolysate. In preparation
10. Kruger, J. De-Risking Pretreatment of Microalgae to Produce Fuels and Chemical Co-Products. In preparation.
11. Hull, T. Nutrient Recovery from Algae Using Wet Oxidation and Ion Exchange. In preparation.

Presentations

1. Dong, T. Non-isocyanate Polyurethane Produced from Biobased Lipids and Amines. Thermoset Resin Formulators Association conference. 2021
2. Spiller, R. Muconic Acid Production from P. putida using High Protein Algae Hydrolysate. 44th Symposium on Biotechnology for Fuels and Chemicals (SBFC). 2022.
3. Kruger, J. Pretreatment of Algae for the Production of Fuels and Chemical Coproducts. 44th SBFC 2022
4. Dong, T. Non-isocyanate Polyurethane Produced from Algal Lipids. 44th SBFC 2022
5. Dong, T. Development of Biobased Non-isocyanate Polyurethane for Industrial Applications. American Oil Chemists' Society conference. 2023 Abstract accepted.
6. Chamas, A. Carbonization of extracted algal solids to high-quality conductive carbon. Algal Biomass, Biofuels, and Bioproducts conference. 2023 Abstract accepted.

Patents and Records of Invention

1. T. Dong. R. Allen. LML. Laurens. Phytol-based surfactants and methods therefor. US Patent App. 17/970,938
2. T. Dong. C. Zhang. Monomers for non-isocyanate polyurethanes App. 63/323,950
3. T. Dong. P. Pienkos. Non-isocyanate polyurethane products and methods of making the same App. 17/398.760