

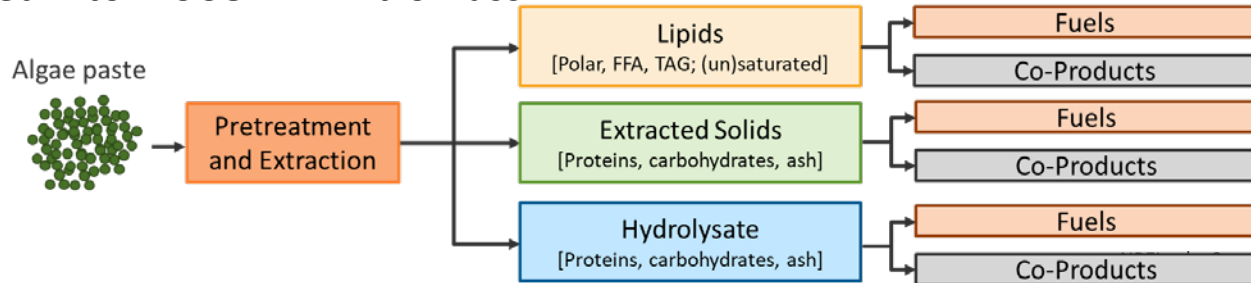
Combined Algal Processing for the Synthesis of Liquid Oleofuels and Products (CAPSLOC)

WBS 1.3.4.204

April 4th, 2023
Advanced Algal Systems
Tao Dong
National Renewable Energy Laboratory

Project Overview

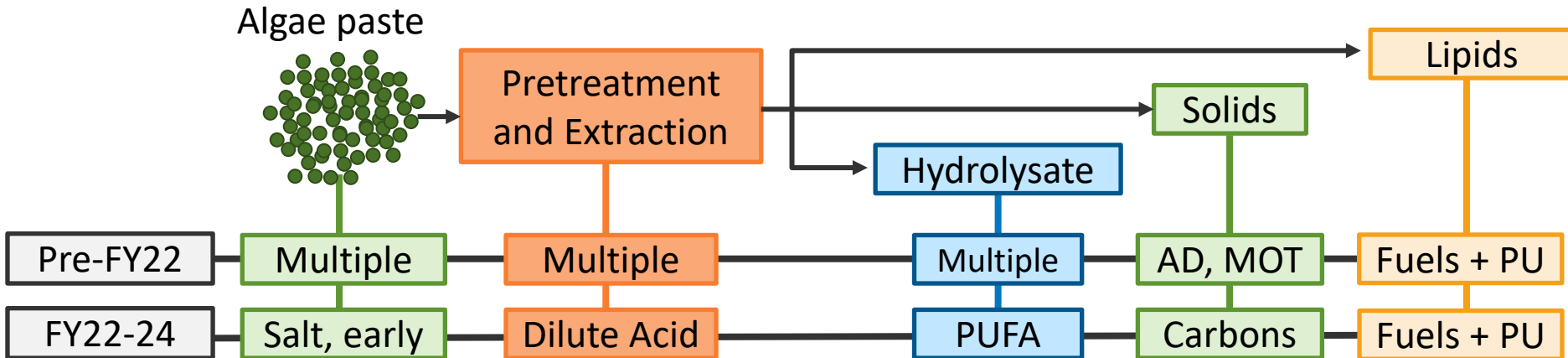
- **Aim:** Develop a composition-agnostic biorefinery concept that enables economically, environmentally, and socially-viable biofuel production by maximizing the value from each fraction.
- **Today:** Algal biorefining at commercial scale exists only for niche, high-value products, not fuels. There have been huge investment 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**. Algae biorefining 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 DISCOVER HP biomass.



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)

PI: Jake Kruger/Tao Dong

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

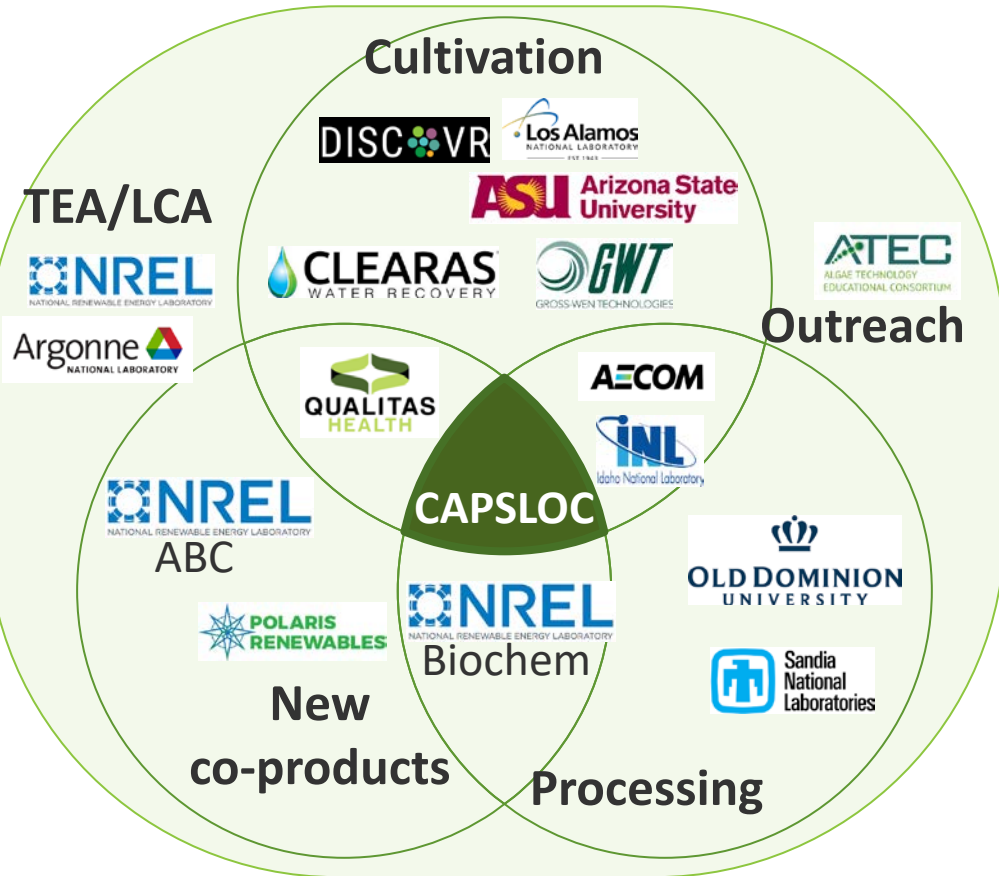
- **Algae Compositional and Product Analysis**
 - Stefanie Van Wychen, Bonnie Panczak, Alicia Sowell, Hannah Alt
- **Algae Pretreatment**
 - Matt Fowler, Tao Dong, Skylar Schutter
- **Hydrolysate Fermentation**
 - Eric Knoshaug, Ryan Spiller, Rob Nelson
- **Catalytic Upgrading**
 - Jake Kruger, Tobias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

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 DISCOVER, ABC, and 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 be 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



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Laboratory Analytical Procedures
Biomass Compositional Analysis
Bio-Oil Analysis
Microalgae Compositional Analysis

Microalgae Compositional Analysis Laboratory Procedures

NREL develops laboratory analytical procedures (LAPs) for microalgae. These procedures help scientists and analysts understand more about the chemical composition of algae as a feedstock to convert to biofuels.

Sample Reference Biomass Materials Available

A sample of a reference biomass material is available upon request for collaborating groups aiming to sign data between different procedures or fine-tuning the implementation of the microalgae compositional analysis methods.

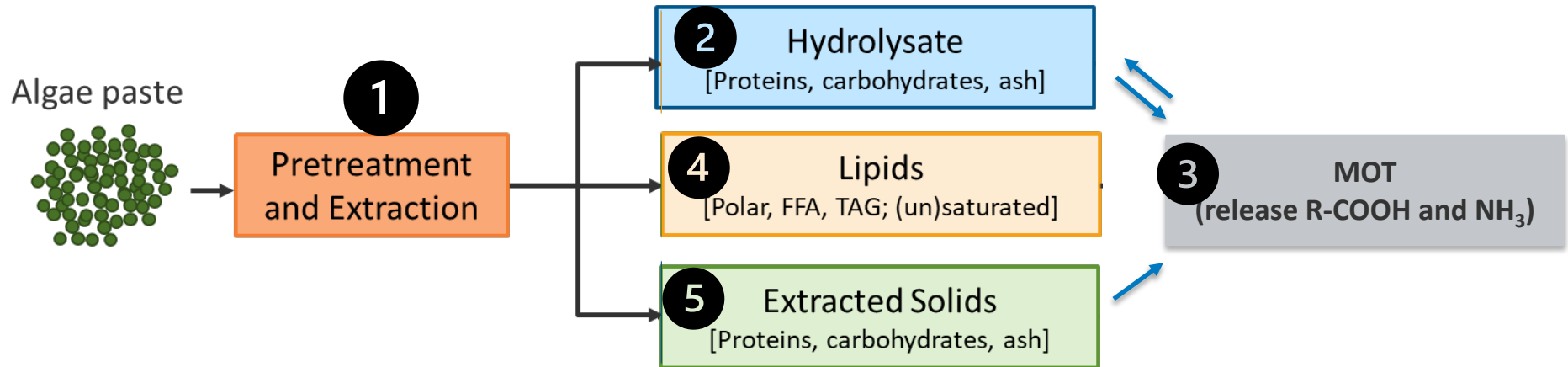
Two species of algae—*Nannochloropsis* and *Scenedesmus*—were harvested at the Arizona Center for Algae Technology and Innovation at Arizona State University resulting in biomass that was freeze-dried, certified by our team of analytical chemists, and vacuum-packaged for distribution.

Request a sample (as long as supplies last).

Examples of freeze-dried and vacuum-sealed packages of algae biomass. Photo by NREL.

2. Progress and Outcomes

Biorefinery Process



2. Progress and Outcomes

1

Pretreatment & Fractionation

Biomass Pretreatment and Fractionation

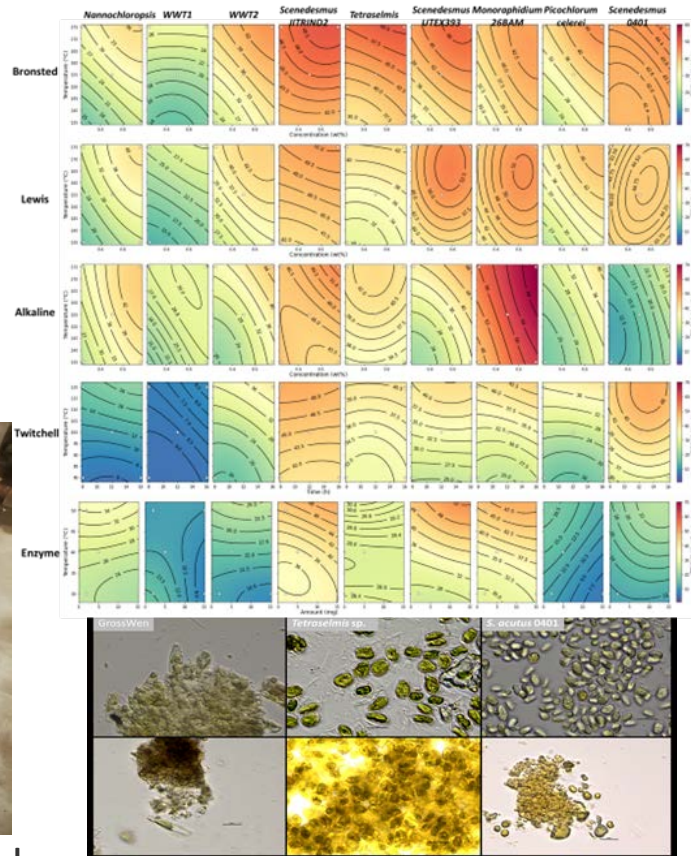
- Demonstrated dilute acid pretreatment as a robust method for a broad range of algae compositions
- Successfully scaled up from 5g to 100kg
- Generated pretreated biomass to support studies in fermentation, lipid extraction and catalytic upgrading.



100kg scale pretreatment



>80kg hydrolysate produced



2. Progress and Outcomes

2

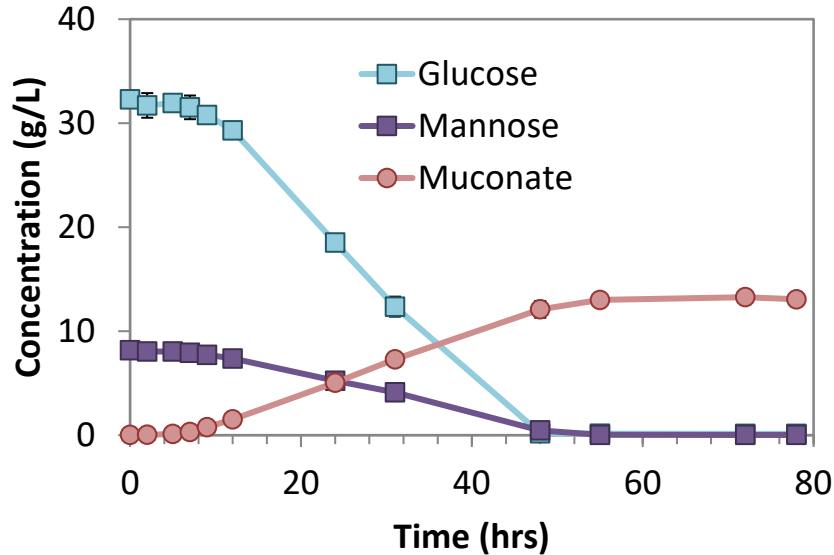
Hydrolysate

Fuels

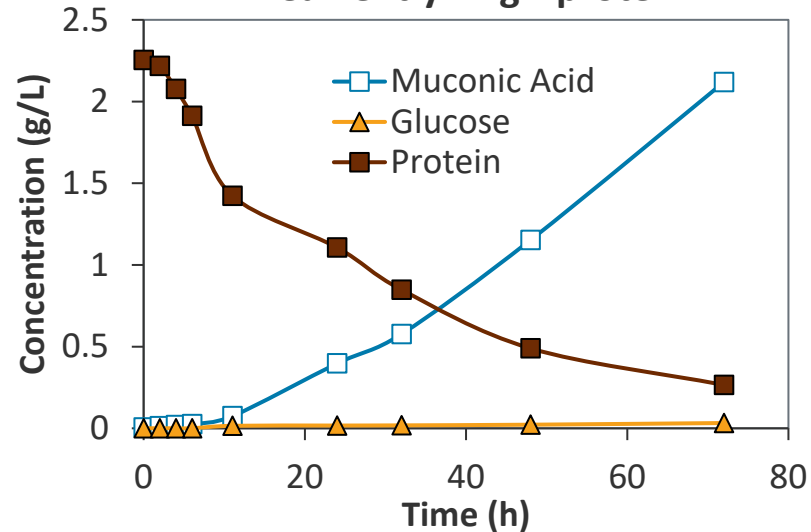
Co-Products

Hydrolysate fermentation

Previously: High-carb



Currently: High-protein



Flexible hydrolysate fermentation

- High-carbohydrate CAP hydrolysates support fermentation to multiple products and fuel precursors
 - 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

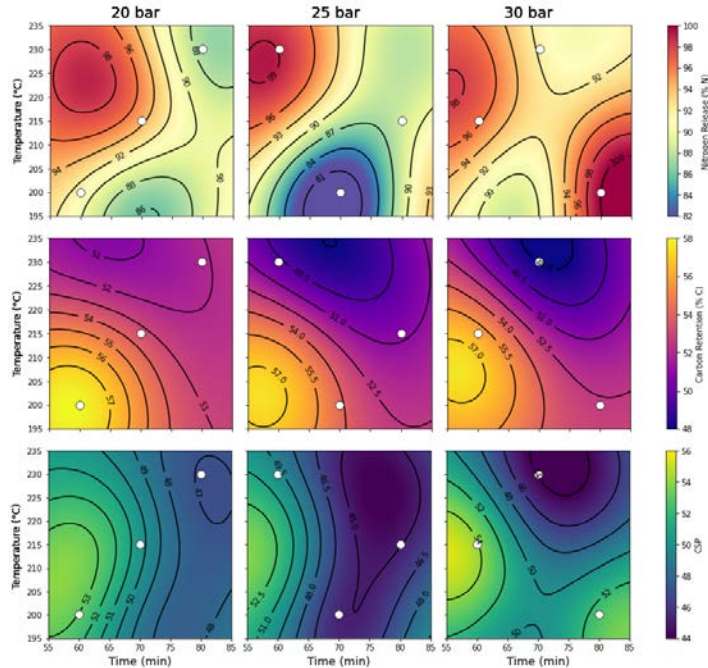
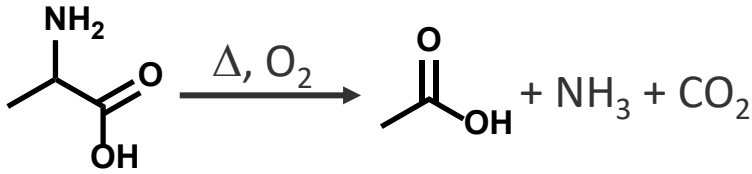
2. Progress and Outcomes

3

Hydrolysate

Fuels

Co-Products



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

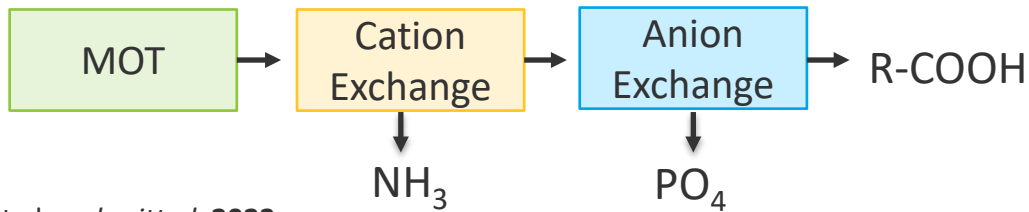
- Optimized MOT for nitrogen release and carbon retention via Design of Experiments and Machine Learning
- Conditioned hydrolysate improves lipid production at bioreactor level
- Lipid product decreases CAP capital costs because oleaginous biomass can be processed with incoming algae
- MOT also enables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

| Strain (Media) | FAME (g/L @ t ₀) | FAME (g/L @ t _f) | Fold Change |
|---------------------------------|------------------------------|------------------------------|-------------|
| <i>C. oleaginosus</i> (Control) | 67 | 1136 | 16.8 |
| <i>C. oleaginosus</i> (IX1) | 67 | 1210 | 17.9 |
| <i>C. oleaginosus</i> (IX2) | 67 | 2703 | 40.1 |

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

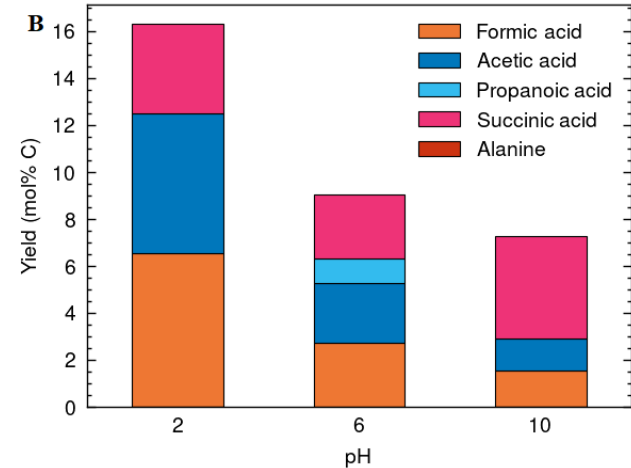
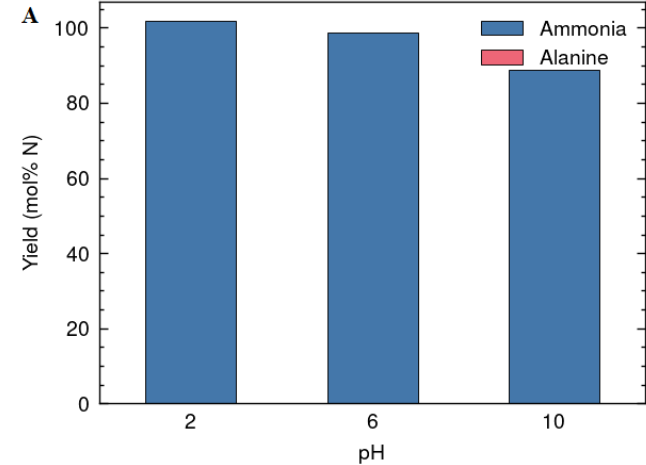


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Extracted Solids

Fuels

Co-Products



2. Progress and Outcomes

4

Lipids

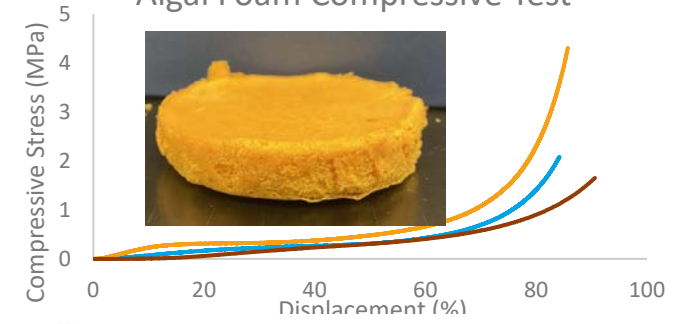
Fuels

Co-Products

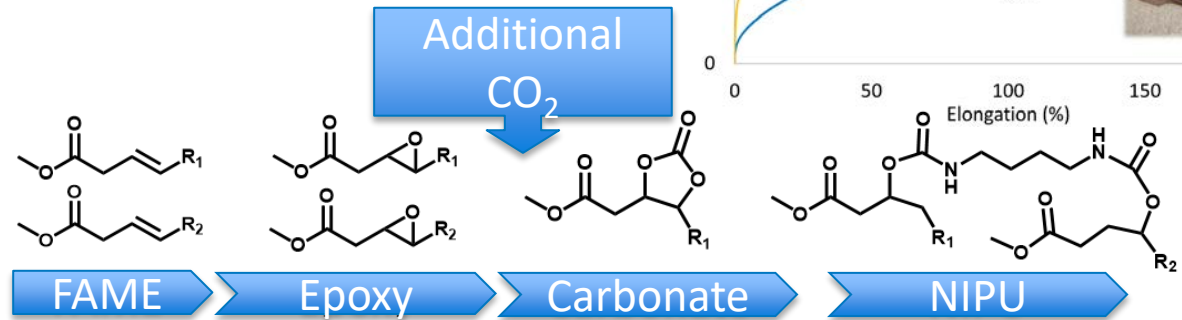
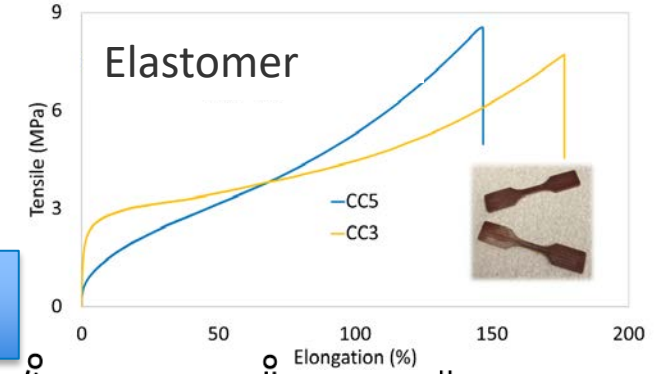
Algal Polymers

- 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

Algal Foam Compressive Test



Elastomer



Acrylated photo polymer

2. Progress and Outcomes

5

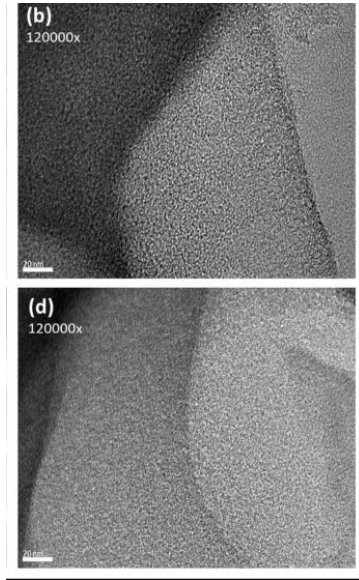
Extracted Solids

Fuels

Co-Products



Graphene



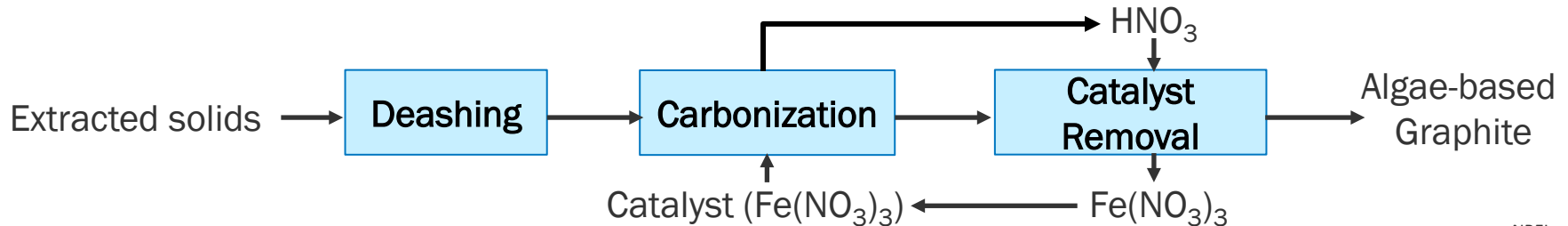
Activated Carbon



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 ($\$10+/\text{kg}$) that fixes carbon long-term



Impact

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

Technical and Science Impact

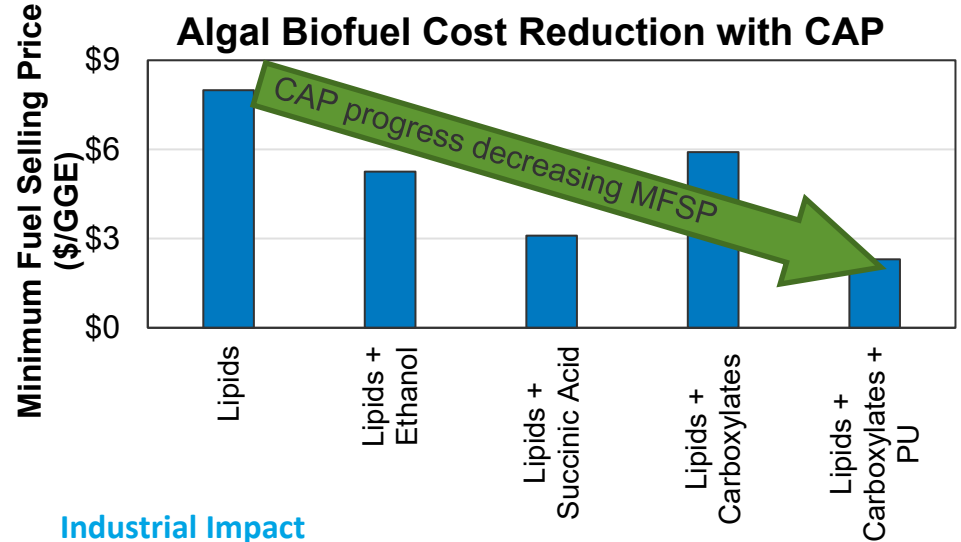
- Demonstrated pre-pilot scale algae pretreatment to de-risk commercialization
- Demonstrated new pathways for nutrient recycle, high-protein hydrolysate conversion, and carbon-sequestering co-products.
- Publications, presentations, patents detailing promise of CAP

Environmental Impact

- Algae are powerful carbon capture tool
- Multiple carbon co-products that fix CO₂ long-term

DEI Impact

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



Industrial Impact

- Lack of conversion process in the current biobased products and biorefinery industry.
- One of two pathways included in the annual SOT updates.
- NIPU technology has been licensed to Polaris Renewables.
- 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

Summary

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

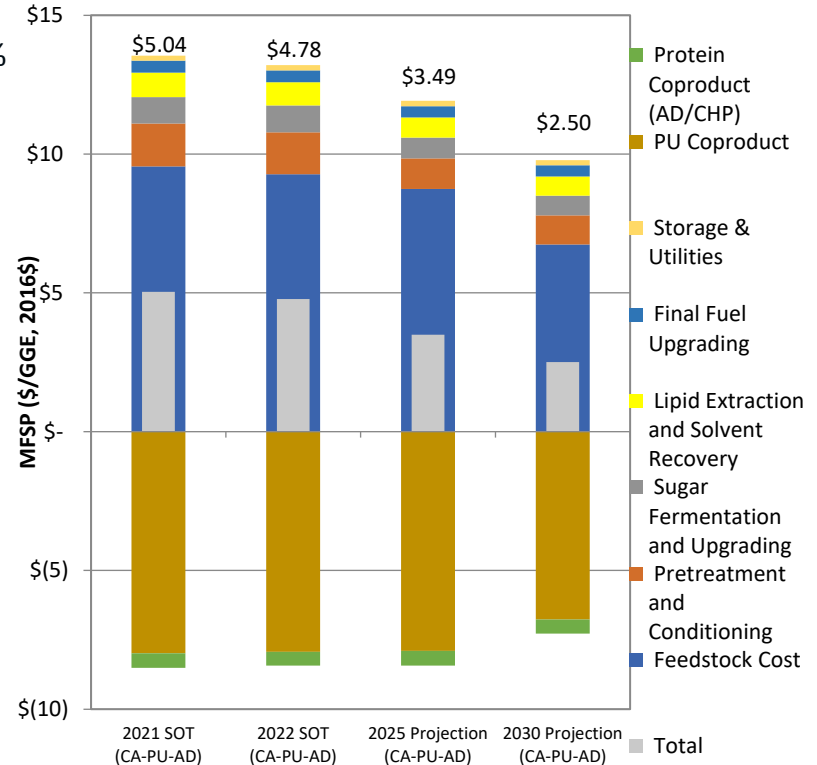
Management: Provide quantitative data to analysis teams to measure improvements via TEA and LCA metrics.

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 CO₂-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

Timeline

- Project start date: 10/1/2021
- Project end date: 9/30/2024

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

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, DISCOVER, Algal Biomass Composition, Algal Biofuels TEA
- **Universities:** Arizona State University

*Only fill out if applicable.

Acknowledgements

BETO

Christy Sterner

Phil Lee

Dan Fishman

Thank You!

NREL Contributors:

Jake Kruger, Lieve Laurens,

www.nrel.gov

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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), Jenna Schaumbach (LANL),

Ryan W. Davis (SNL), Kevin Wyss (Rice U)



Additional Slides

Response to Reviewer Comments

| Comment | Response |
|---|--|
| <p>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.</p> | <p>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.</p> |
| <p>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.</p> | <p>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.</p> |
| <p>The go/no go described uses quantifiable metrics to assess success. Risks and mitigation plans in this project do not seem well described.</p> | <p>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).</p> |

Publications

1. 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.
2. 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.
3. 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**.
4. 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.
5. A. Chamas. Sustainable Carbonization of Algal Proteins to High-Purity Graphite. In preparation
6. A. Chamas. Leveraging iron for CO₂ reduction into carbons with electro-conductivity. In preparation

Presentations

- T. Dong. Non-isocyanate Polyurethane Produced from Algal Lipids. 44th SBFC **2022**
- T. Dong. Non-isocyanate Polyurethane Produced from Biobased Lipids and Amines. TRFA **2021**

Patents and Records of Invention

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