DOE Bioenergy Technologies Office (BETO)
2019 Project Peer Review

WBS 1.3.4.201 CAP Process Research

Advanced Algal Systems
March, 2019

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Background
**Goal Statement**

**Goals:** *Reduce algal biofuel production cost* by integrating advanced process options for the conversion of algal biomass into fuels along with *scalable, higher value bioproducts* based on *detailed knowledge of algal biomass composition* using *novel conversion pathways* leveraged with *technologies developed by the BETO Biochem Conversion Program*.  

**Relevance:** TEA modeling for algal biofuels indicate that *algal biofuels cannot achieve economic viability without coproducts*.  

**Outcome:** *Complement work on improved cultivation productivity to accelerate commercialization of algal biorefineries, leading to expansion of 21st century agriculture, high quality job creation, and energy independence.*
## Quad Chart Overview

### Timeline
- Start date: 1/30/13
- Merit Review: FY18
- End date: 9/30/21
- Percent complete: 17%

<table>
<thead>
<tr>
<th></th>
<th>Total Costs Pre FY17</th>
<th>FY 17 Costs</th>
<th>FY 18 Costs</th>
<th>Total Planned Funding (FY 19-Project End Date)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>DOE Funded</strong></td>
<td>$2.0M</td>
<td>$500K</td>
<td>$500K</td>
<td>$1.5M</td>
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<tr>
<td><strong>Cost Share</strong></td>
<td>NA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Partners</strong></td>
<td>None</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Barriers addressed
- Aft-E. Algal Biomass Characterization, Quality, and Monitoring
- Aft-F. Algae Storage Systems
- Aft-I. Algal Feedstock On-Farm Preprocessing
- Aft-J. Resource Recapture and Recycle

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

### End of Project Goal
Demonstrate integrated high protein biomass CAP process with data supporting <$3/GGE, with path to <$2/GGE
Project Overview

- **Context:** Leveraging Biochem Conversion Program processes for biomass with very different composition. Acid pretreatment enables wet lipid extraction and also efficiently hydrolyzes algal carbohydrates with no need for enzymes. Though verified cultivation productivity is increasing and cost of biomass production decreasing, the long term targeted cost for biomass will not allow economic production of algal biofuels without coproducts. Combined Algal Processing serves as basis for multiproduct biorefinery concept using lipids, carbs and proteins able to achieve MFSP goals despite high biomass cost.
Project Overview

Project Goals:

• Demonstrate integrated pathway for conversion of high lipid/carb algal biomass to a product portfolio with modeled MFSP <$2.50 per GGE.
  – Identify novel coproduct options
  – Mitigate feedstock costs by blending algal biomass with high lipid waste streams.
  – Mitigate cultivation challenges by adapting CAP process for use with high protein biomass.

Creative Advantage:

• Leverage work in Cellulosic Biochem Program to integrate conversion technologies for fuel and coproduct development to reduce MFSP.
  – The CAP multiproduct biorefinery concept is the only technology in BETO portfolio that has identified a path to reduce algal MFSP<$2.50/GGE.
  – Continued development of novel conversion operations for broad portfolio of products and inclusion of lower cost feedstocks can accelerate algal biofuel commercialization.

See Additional Slides 36-38
Approach - Management

- Biweekly progress update meetings
- Quarterly milestones to track progress
- Merit Review in FY18
- Go/no go scheduled for FY20
- Close Coordination with Algal Biomass Composition, RACER, Polyurethane TCF, TEA, DISCOVR, INL and SNL personnel
- Regular outreach to stakeholders

See Additional Slide 29
Technical Approach:

- Coordinate with other BETO projects to identify and develop processes for algal biofuels and bioproducts that can utilize all algal components, can be scaled to multiple unit farms, and can generate significant revenue to mitigate high cost of algal biomass.
  - Identify, develop and integrate new unit operations to expand product portfolio and evaluate TEA potential
  - Improve upon core unit operations (pretreatment, extraction, and lipid upgrading) to increase performance metrics and reduce MFSP
Potential Challenges:
• Establishment of coproduct options with significant TEA impact
• Development of unit operations for multiple products that can plug and play within CAP process
• Build a credible concept that requires simultaneous development of technology for multiple products
• Expansion of CAP process to include options for high protein biomass (FY20 Go/No Go)

Critical Success Factors:
• Bridge gap between business strategies involving high-value, small-market products and low-value, large-market products
• Engage companies interested in coproduct market opportunities
• Reduce risks for biorefinery startups through extensive portfolio of coproducts offering breadth of opportunities
Accomplishments

- New products for the CAP portfolio
- Improved efficiency of lipid extraction upgrading
- Modeled cost reductions to achieve <$2.50/GGE
- CAP process with biomass from halotolerant algae
- High protein biomass

CAP configuration 2019
# Carboxylate-Based Fuel Coproduct

**Filtered liquor with algal sugars**

**Flocculated and vacuumed algal solids**

**Clostridium butyricum**

<table>
<thead>
<tr>
<th>Media</th>
<th>Time (h)</th>
<th>Titer (g/L)</th>
<th>Productivity (g/L/h)</th>
<th>Yield (g/g sugar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Algae Liquor</td>
<td>12</td>
<td>12.15 ± 1.21</td>
<td>1.01 ± 0.10</td>
<td>0.29 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>56</td>
<td>17.23 ± 1.05</td>
<td>0.31 ± 0.02</td>
<td>0.41 ± 0.03</td>
</tr>
<tr>
<td>Control</td>
<td>12</td>
<td>11.62</td>
<td>0.97</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>56</td>
<td>15.07</td>
<td>0.27</td>
<td>0.32</td>
</tr>
</tbody>
</table>

Productivity and yields comparable to that seen with cellulosic hydrolysate.
Fully Renewable **Polyurethane Plastics** from unsaturated lipids and protein-derived amine cross linkers - *replacing toxic isocyanates*

Resins prepared from:
- Soybean oil
- Linseed oil
- Fish oil
- Two algal oils
- Two different amino acid based crosslinkers
- Two peptide based crosslinkers

Polymer properties linked to level of unsaturation of initial oil and nature of amine-cross linker. The potential number of possible polymers is nearly limitless.

*Dong et al. USPTO provisional patent: 62/482238*

Subject of Technology Commercialization Fund project FY19

See Poster #64 March 5 for more information about Technology Commercialization Fund Project NL00TCF1 (6.6.0.1), “Fully Renewable Polyurethane Resins Produced from Algae and other Feedstocks”
Volatile Compounds in Algal Biomass

Determine if high value coproducts can be recovered from pretreatment vapor phase

Interesting compounds identified but concentrations too low to warrant further work.
Progress in Lipid Extraction and Upgrading

<table>
<thead>
<tr>
<th>Solvent System</th>
<th>Total FAME Recovery (%)</th>
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</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>87.4 ± 6.0</td>
</tr>
<tr>
<td>Hexane/EtOH</td>
<td>96.0 ± 0.4</td>
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<tr>
<td>Naphtha/EtOH</td>
<td>95.7 ± 1.7</td>
</tr>
</tbody>
</table>

Improvements in lipid extraction and upgrading included in FY18 SOT resulted in 12% improvement in MFSP
Halotolerant Strains

Improve sustainability of algal biofuel process by reducing freshwater usage

<table>
<thead>
<tr>
<th></th>
<th>FAME (%)</th>
<th>Total Carb (%)</th>
<th>Glucose (%)</th>
<th>Mannose (%)</th>
<th>Protein (%)</th>
<th>Ash (%)</th>
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<tbody>
<tr>
<td>Desmodesmus</td>
<td>30</td>
<td>37.7</td>
<td>24.8</td>
<td>12.1</td>
<td>10.2</td>
<td>7.6</td>
</tr>
<tr>
<td>Nannochloris</td>
<td>16.5</td>
<td>38.3</td>
<td>27.2</td>
<td>3.4</td>
<td>15.6</td>
<td>12.5</td>
</tr>
<tr>
<td>Scenedesmus (freshwater benchmark)</td>
<td>30.8</td>
<td>44.3</td>
<td>34.9</td>
<td>8.8</td>
<td>10.9</td>
<td>1.6</td>
</tr>
</tbody>
</table>

- **Ethanol**
  - **Desmodesmus**
  - **Nannochloris**
  - **Scenedesmus**
  - **Sugar control**

- **Succinic acid**
  - **Desmodesmus**
  - **Nannochloris**
  - **Scenedesmus**
  - **Sugar control**

<table>
<thead>
<tr>
<th></th>
<th>FAME Yield</th>
<th>FAME Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Desmodesmus</td>
<td>82.6 +/- 6.8</td>
<td>101.6 +/- 1.0</td>
</tr>
<tr>
<td>Nannochloris</td>
<td>104.2 +/- 4.7</td>
<td>90.5 +/- 0.3</td>
</tr>
<tr>
<td>Scenedesmus</td>
<td>96.7 +/- 14.1</td>
<td>101.4 +/- 0.3</td>
</tr>
</tbody>
</table>
Mild Oxidative Treatment (MOT)

- Focus on conversion of carboxylates to hydrocarbons
- Yields to hydrocarbons will be critical metric

Mild Oxidative Treatment (MOT) is promising pathway for conversion of CAP residuals to biofuels and ammonia for recycle to algae ponds.
Relevance

- **Goals:** Reduce biofuel production costs through development of multiproduct biorefinery concept with integrated conversion of all major algal components.

- **Importance and Alignment with BETO Goals:** This project supports the MYP Goals for 2019, 2020, 2024, and 2030 regarding biofuel and bioproduct in support of BETO’s goals for mature modeled MFSP of $2.5/GGE for biofuels.

- **Relevance to the bioenergy industry:** The algae industry has largely shifted away from biofuels in favor of higher value products. However, the coproducts generated by CAP process options, especially our novel polyurethane chemistry, can significantly reduce MFSP and is gaining traction with industry as noted by TCF partnership with Patagonia and Algix.

- **State of technology and commercial viability:** Advances in biomass conversion play a key role in BETO’s annual SOT analysis, and CAP process improvements are integrated into that analysis. By advancing the state of technology, this project could and positively impact the commercial viability of algal biomass technologies.

- **Tech transfer:** Both Patagonia and Algix received licensing rights for NREL novel polyurethane chemistry.

![Biofuel Cost Reduction with CAP](image-url)
Future Work

FY19 (Begin transition to high protein biomass)
- Integrated CAP processing of halotolerant algal biomass and biomass/brown grease blend pretreated in Q2 to provide data for FY19 SOT
- Evaluate process options for conversion of high protein biomass to establish modified CAP process focusing on high carbon conversion efficiency of proteins to biofuels

FY20 (Focus on high protein biomass)
- Integrate at least one new fuel/coproduct option for high protein biomass based on new information from detailed compositional analysis and provide data for TEA.
- Work with Old Dominion University to compare efficacy of flash hydrolysis vs. dilute acid pretreatment for disruption of high protein biomass.
- Go/No Go: Compare modeled MFSP for high protein biomass conversion approaches under development at NREL and SNL based on projected feedstock costs, processing costs, biofuel intermediate yields, and coproduct contributions.
- Establish basecase biofuel production cost of <$5/GGE from high protein algal biomass using validated aspirational MBSP (for open ponds, $490/ton AFDW) with >50% of algal carbon slated for biofuels
High Protein CAP Process

- Polyurethanes
- Novel Fuel Options
- Fertilizers

See Additional Slide 29
1. **Overview:** Combined Algal Processing provides a flexible approach to identifying low cost/energy routes to a wide portfolio of biofuels and bioproducts using all main algal components.

2. **Approach:** CPR works closely with other BETO projects to integrate with multiple stakeholders providing synergies across the project portfolio.

3. **Technical Accomplishments:** Several new product options were identified since last peer review and critical path operations such as lipid extraction and upgrading have been improved. The biomass feedstocks have been expanded to include halotolerant algal strains as well as algal/wet waste blends.

4. **Relevance:** CPR is critical to the AAS portfolio providing process options and data for SOT analyses. TEA modeling has identified a set of CAP product options with potential for MFSP<$2.50/GGE.

5. **Future work:** Complete CAP process development with high carb/lipid biomass with integrated production run to provide data for production of fuels and coproducts using lipids, carbs, and proteins. Incorporate waste streams such as brown grease to mitigate seasonal cultivation variation. Adapt CAP process for use with high protein biomass to mitigate the challenges of providing consistent high carb/lipid biomass.
Thank You

www.nrel.gov
www.nrel.gov/bioenergy/algal-biofuels.html

Philip.pienkos@nrel.gov
## Responses to Previous Reviewers’ Comments

<table>
<thead>
<tr>
<th>Comment</th>
<th>Response</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification of potential algal species in order to meet commercial relevance could be a challenge.</td>
<td>Future work will involve biomass from high productivity strains identified by DISCOVR</td>
</tr>
<tr>
<td>Market sensitivity for potential co-products not considered.</td>
<td>This has become a more important role for TEA group; their guidance on market size for coproducts is a critical path element in evaluation.</td>
</tr>
<tr>
<td>I would have liked to hear more information on how the project envisioned controlling the culture to optimize their intended composition.</td>
<td>Though other projects are addressing this issue in a variety of ways, the CPR project will be focusing adapting the CAP process for high protein biomass.</td>
</tr>
<tr>
<td>Demonstration of pretreatment process with fresh and salt water species will help to provide clarity on the ability to achieve target goals.</td>
<td>The preliminary demonstration of the CAP process with saltwater biomass was competed in FY18 and a fully integrated process demonstration is planned for FY19.</td>
</tr>
<tr>
<td>It is not clear what if anything will be done in protein valorization under this project</td>
<td>Protein valorization became a key element in FY18 with the implementation of Mild Oxidative Treatment. This operation and additional biochemical conversion approaches are planned for FY19 and beyond.</td>
</tr>
<tr>
<td>It is unclear whether the fermentation portions of the CAP process will be competitive in the marketplace with competing technologies that utilize concentrated glucose feedstocks.</td>
<td>The fermentation processes were never meant to compete with pure sugars but rather to valorize the sugars made available by pretreatment, which would otherwise be sent to anaerobic digestion. The impact of this is reflected in reduced MFSP seen with integration of sugar-based coproducts along with lipid-based RDB.</td>
</tr>
</tbody>
</table>


Publications


Patents and Records of Invention

- P. Pienkos. Novel food-grade surfactants from algal components. Record of Invention. 2018
- J. Kruger. E. Christensen, G. Beckham, P. T. Pienkos, and T. Dong. Mild oxidative treatment of Biomass. Record of Invention. 2018
Presentations

Posters


BETO Project Interactions

- Identify novel coproducts and composition-conversion interactions
  - Algal Biomass Composition (NREL)
  - Biological Upgrading of Sugars (NREL)
- Identify critical cost elements and key process opportunities
  - Algal Biofuels TEA (NREL)
  - Bench Scale Integration (NREL)
- Develop high-value coproducts from lipid and protein fractions
  - Polyurethanes TCF (NREL)
  - Targeted Microbial Development (NREL)
- Evaluate storage and blending effects on conversion processes
  - Algal Feedstock Logistics (INL)
  - Lignin First Biorefinery Development (NREL)
- Coordinate work with other algae project operating in same space
  - Bioconversion of Algal Carbs and Proteins (SNL)
  - Biological Lignin Valorization (NREL)
- Obtain biomass samples from highest productivity strains cultivated for SOT runs
  - DISCOVR (PNNL, LANL, SNL, NREL)
  - Lignin Utilization (NREL)
FY18 SOT inputs reflect:

- Wet seasonal storage of biomass (inputs from INL)
- New 2-solvent extraction with light naphtha product + ethanol (from CPR) → **96% extraction yield**
- Sugars-to-HC fuels via acid fermentation (from CPR)
- Sugars-to-HC fuels via BDO fermentation (from RACER)
TEA modeling is highly relevant to industry and BETO goals:

- **Guides R&D/DOE decisions, sets targets**
  - Technical targets (yields, process performance)
  - Cost targets (basis for BETO MYPP goals)
- **Identifies key R&D directions** (pathways, coproduct opportunities, etc.)
- **Facilitate interaction between stakeholders in industry, research, DOE**
  - Example: Outreach to GAI, MicroBio, Algenol, Clearas, Algenesis for TEA discussions

- **Foster collaboration** with other modeling groups (ANL, PNNL, ORNL, INL), BETO consortia (ATP3, DISCOVR, Sep-Con)

- **Public dissemination** of models:
  - e.g. Excel-based algae farm TEA tool now available publicly:
  
  https://www.nrel.gov/extranet/biorefinery/aspen-models/
• Evaluated CAP conversion potential to achieve <$2.5/GGE for selected coproduct examples
• Evaluated over various market limit scenarios (reverted back to fuels after reaching saturation)
• ~1-4 BGGE/yr fuel potential is possible while supporting MFSP goals (for freshwater example) based on market scenarios
• Other coproduct options may further alleviate market limitation concerns – key point highlights ability to achieve MFSP goals with scalable coproducts beyond “niche” markets for a single proof-of-concept coproduct example
New Coproducts Can Provide Significant Revenue Relative to Biofuel Options

Protein-rich extracted stillage from CAP-ethanol go/no go provided to stakeholders for conversion feasibility studies

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Product</th>
<th>Volume Product Per Unit Farm Per Year</th>
<th>Revenue Per Unit Farm Per Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lipid</td>
<td>RDB from Lipids (NREL)</td>
<td>16M GGE</td>
<td>$47M</td>
</tr>
<tr>
<td>Carbohydrate</td>
<td>Ethanol (NREL)</td>
<td>5.5M GGE</td>
<td>$16M</td>
</tr>
<tr>
<td>Extracted stillage</td>
<td>Biogas (NRC)</td>
<td>12,500 tonnes methane</td>
<td>$4.3M</td>
</tr>
<tr>
<td>Extracted stillage</td>
<td>Cultivation medium for G. sulphuraria (ASU)</td>
<td>65,000 tonnes biomass</td>
<td>$34M</td>
</tr>
<tr>
<td>Extracted stillage</td>
<td>RDB from HTL biocrude (CSM)</td>
<td>9.3M GGE</td>
<td>$28M</td>
</tr>
<tr>
<td>Extracted stillage solids</td>
<td>Bioplastic blendstock (Algix)</td>
<td>32,000 tonnes</td>
<td>$23M–$39M</td>
</tr>
</tbody>
</table>

Li et al. Demonstration and Evaluation of Hybrid Microalgae Aqueous Conversion Systems for Biofuel Production. Submitted
Cost Reduction Scenarios

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Algae Farms Supported</th>
<th>Tons of Biomass Supported</th>
</tr>
</thead>
<tbody>
<tr>
<td>Utilize 50% of US Spent coffee grounds as biomass blendstock</td>
<td>6</td>
<td>1.1M</td>
</tr>
<tr>
<td>Utilize 50% of US brown grease as biomass blendstock</td>
<td>11</td>
<td>2.0M</td>
</tr>
<tr>
<td>Capture 50% of US market for succinic acid as coproduct</td>
<td>13</td>
<td>2.4M</td>
</tr>
<tr>
<td>Capture 50% of US market for polyurethane as coproduct</td>
<td>38</td>
<td>7.1M</td>
</tr>
</tbody>
</table>

Source: R. Davis and J. Markham. National scale potential for algal coproducts to achieve $2/GGE. Go/No Go Milestone. June, 2018
Wet Wastes As Substitute for Algal Biomass

Compositional analysis of fresh and spent coffee grounds (NREL unpublished data)

<table>
<thead>
<tr>
<th>Sample</th>
<th>% Total Ash</th>
<th>% Total Protein</th>
<th>% Lignin</th>
<th>% Fermentable Sugars</th>
<th>% FAMEs</th>
<th>% Sterols</th>
</tr>
</thead>
<tbody>
<tr>
<td>Algal Biomass</td>
<td>2.4</td>
<td>13.2</td>
<td>0.0</td>
<td>47.8</td>
<td>27.4</td>
<td>1-2</td>
</tr>
<tr>
<td>Fresh Coffee Grounds</td>
<td>4.4</td>
<td>11.5</td>
<td>15.9</td>
<td>29.2</td>
<td>14.9</td>
<td>0.12</td>
</tr>
<tr>
<td>Spent Coffee Grounds</td>
<td>1.6</td>
<td>10</td>
<td>22.6</td>
<td>38.8</td>
<td>18.1</td>
<td>0.15</td>
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<tr>
<td>Brown Grease</td>
<td>1.6</td>
<td>11</td>
<td>ND</td>
<td>7.7</td>
<td>63.2</td>
<td>ND</td>
</tr>
</tbody>
</table>

- Potential to use waste streams to generate portfolio of fuels and coproducts at a fraction of the feedstock costs.
- Keep waste streams from entering landfills
Table 2. Lipid and monomeric sugar recovery from the original brown grease samples without pretreatment.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>FAME yield</th>
<th>Monomeric sugar yield</th>
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<tbody>
<tr>
<td>BG #1</td>
<td>91.9 ± 2.2</td>
<td>6.3 ± 0.3</td>
</tr>
<tr>
<td>BG #2</td>
<td>84.2 ± 3.0</td>
<td>27.3 ± 0.6</td>
</tr>
</tbody>
</table>

Figure 1. Carboxylic acid yield from *Scenedesmus* and brown grease extracted solids on mol% C basis.
Fermentation of Sugars from Spent Coffee Grounds

![Graph showing the fermentation of sugars from spent coffee grounds compared to a sugar control. The graph plots ethanol concentration (g/L) against time (hours). The spent coffee grounds show a significant increase in ethanol production compared to the sugar control.]