



BETO 2017 Project Peer Review Algal Biomass Conversion WBS 1.3.4.201

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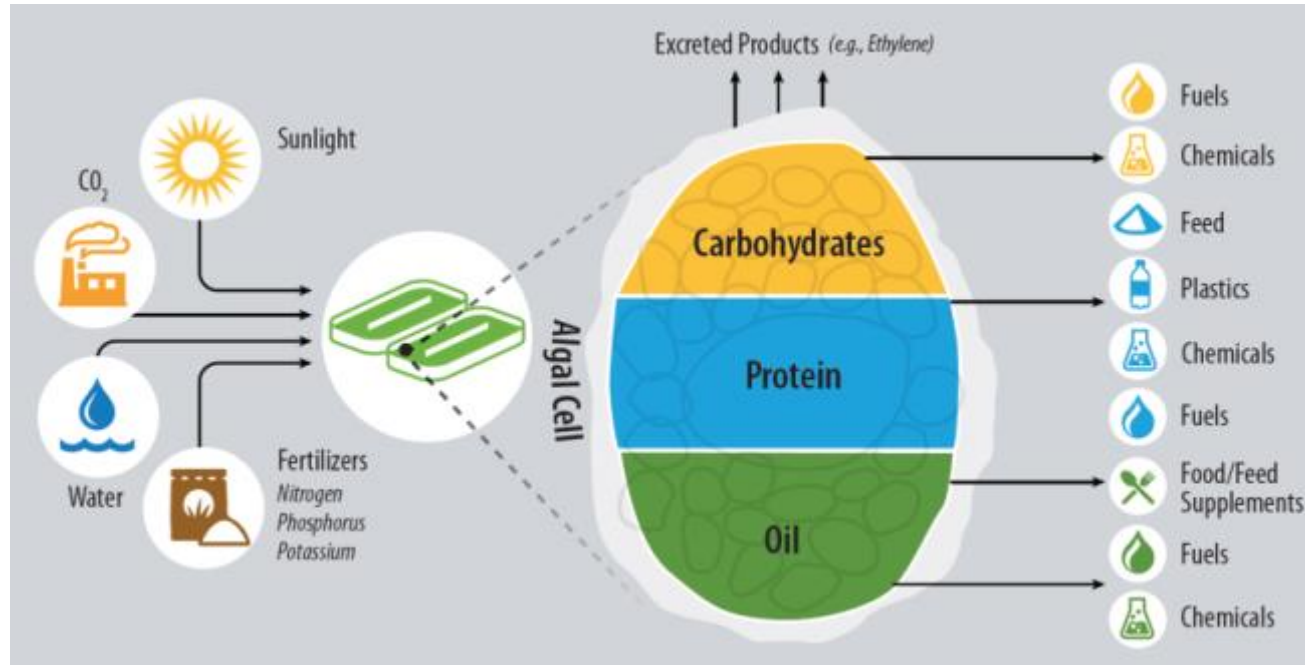
Advanced Algal Systems

Goal Statement and Outcomes

Goal: **Reduce algal biofuel production cost** by developing 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**.

Relevance: Modeled algal biomass production costs indicate that **algal biofuels cannot compete with petroleum without coproducts**.

Outcomes: **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

- Project start date: 10/1/15
- Merit review: 2015
- Project end date: 9/30/18
- Percent complete: 50%
- Existing project

Budget

	Total Costs FY10–FY14	FY 15 Costs	FY 16 Costs	Total Planned Funding (FY 17–Project End Date)
DOE-Funded	\$644,000	\$741,000	\$615,000	\$1,000,000

Barriers

Barriers addressed

- Aft-H. Overall Integration and Scale-Up
 - Identify unit ops for preprocessing to be co-located with algal farms
- Aft-I. Algal Feedstock On-Farm Preprocessing
 - Develop sustainable and energy efficient processing and fractionation
- Aft-J. Resource Recapture and Recycle
 - Evaluate impact of coproduct options on potential for nutrient recycle

Partners

Partners

- ATP³ for biomass supply

Other interactions/collaborations

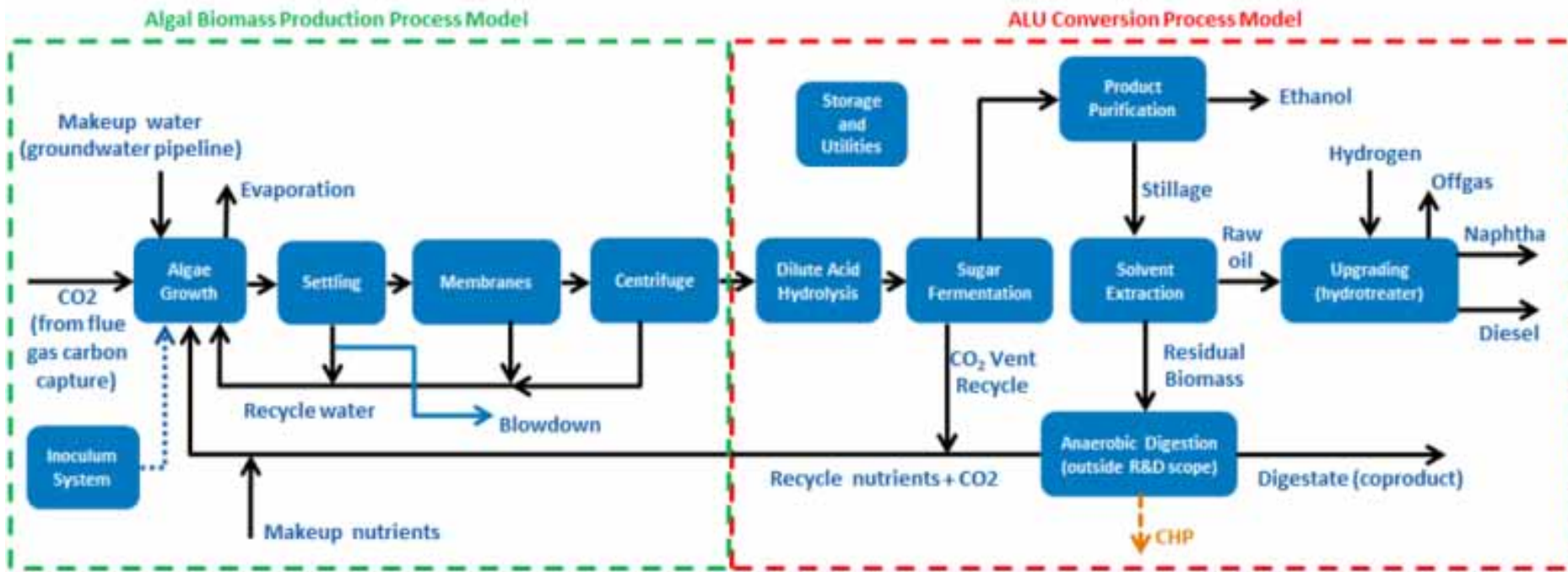
- NREL Algal Biomass Valorization, Techno-Economic Analysis, and Algae Biotech Partnership projects
- ANL for LCA modeling
- Algix, ASU, UIUC/CSM, and NRC for evaluation of protein
- DISCOVR and Separations Consortium

1 – Project Overview

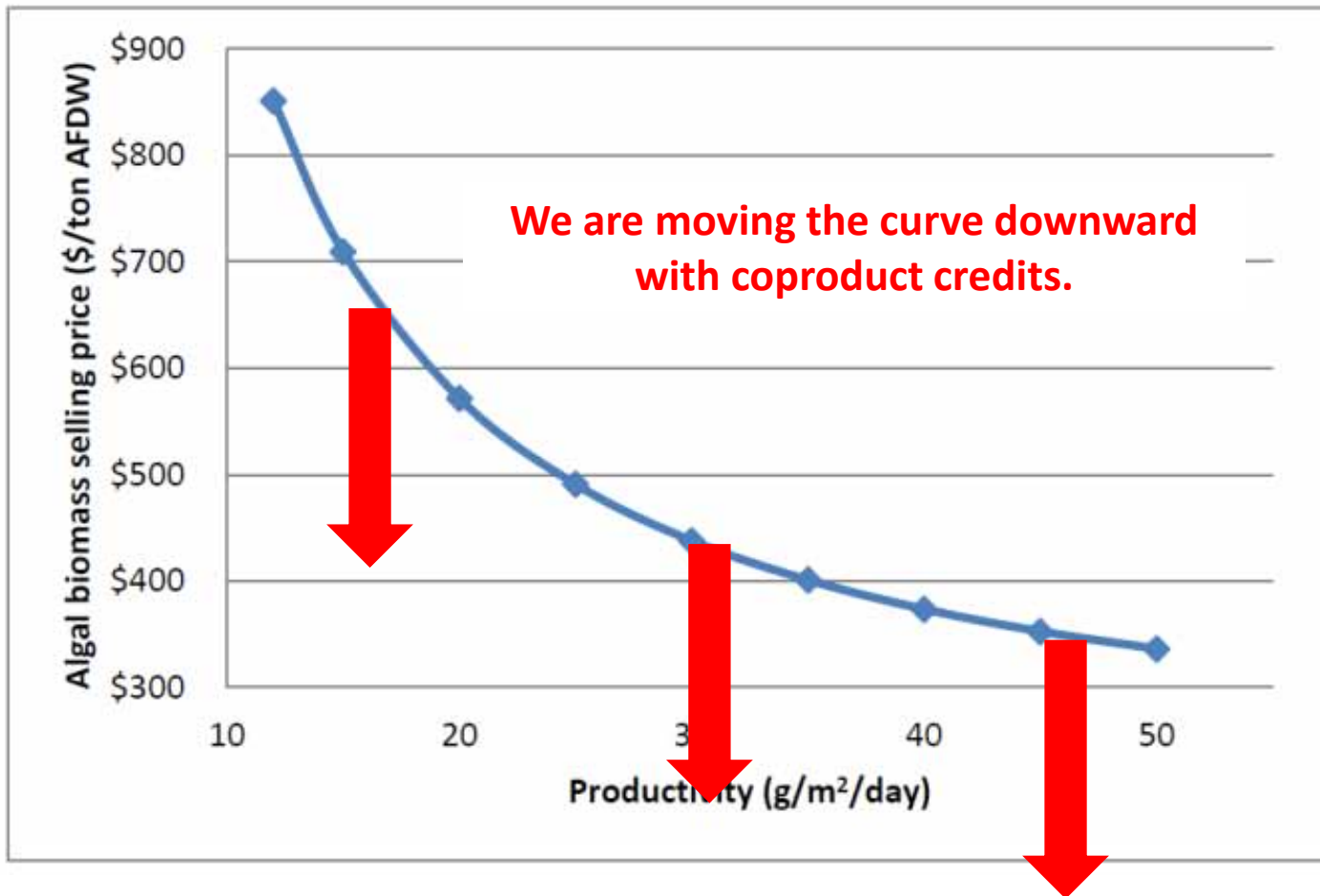
- In FY13, the Sustainable Algal Biofuel Consortium demonstrated the concept of reducing costs through algal biomass fractionation and individual component valorization to fuels and coproducts.
- The Combined Algal Processing (CAP) scheme became the basis for the Algal Lipid Upgrading (ALU) pathway, described in the FY14 Design Report and FY15 and FY16 State of Technology Reports.
- We work with Algal Biomass Valorization to develop new unit operations to incorporate their coproduct options into the CAP scheme.
- Further improvements in the CAP scheme are being evaluated and additional coproducts are being added to refine and expand our multiproduct biorefinery concept.

Combined Algal Processing (CAP)

- Allows valorization of both algal lipids and sugars
- High Technical Readiness Level: Concept has been demonstrated at scale by corn ethanol biorefineries

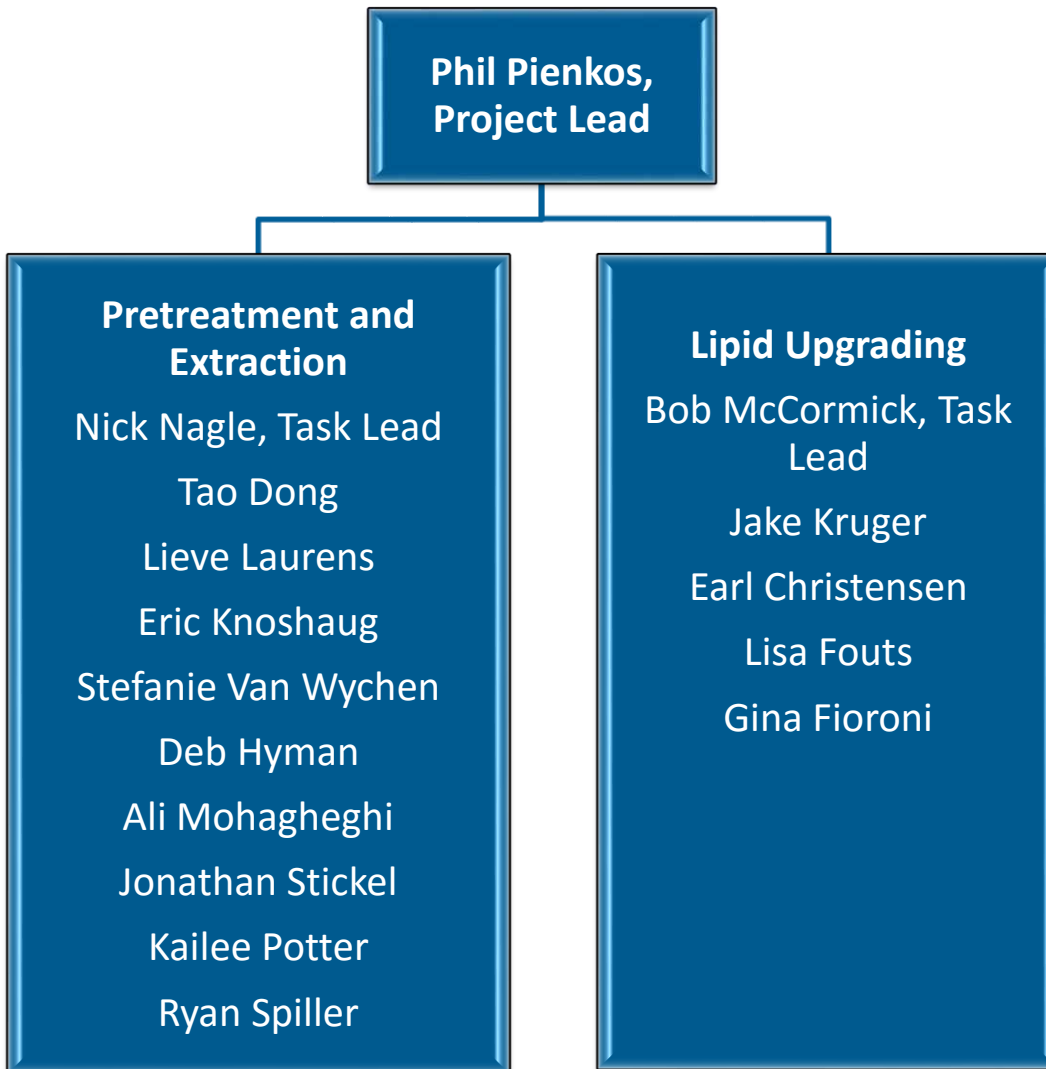


The \$3/GGE Challenge for Algae



**Both CAP and HTL pathways require biomass <\$300/ton for success.
Algal biomass cost reductions and algal biomass value enhancements:
Both are essential but neither is sufficient.**

2 – Approach (Management)



- Weekly progress update meetings
- Quarterly milestones to track progress
- Go/no go and merit review in past two years
- Regular discussions with Algal Biomass Valorization and TEA project personnel as well as ATP³
- Regular outreach to stakeholders

2 – Approach (Technical)

- Work with ABV and TEA 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.
- Obtain **samples of biomass with high value composition** from ATP³ and other suppliers
- Demonstrate **proof of concept** data for **targeted coproducts** to determine **feasibility and applicability**. Metrics include conversion **rates, yields and titers** as well as **process complexity**.
- Follow on work to be considered based on initial results and **TEA impact**.

2 – Approach (Technical)

- **Potential challenges**

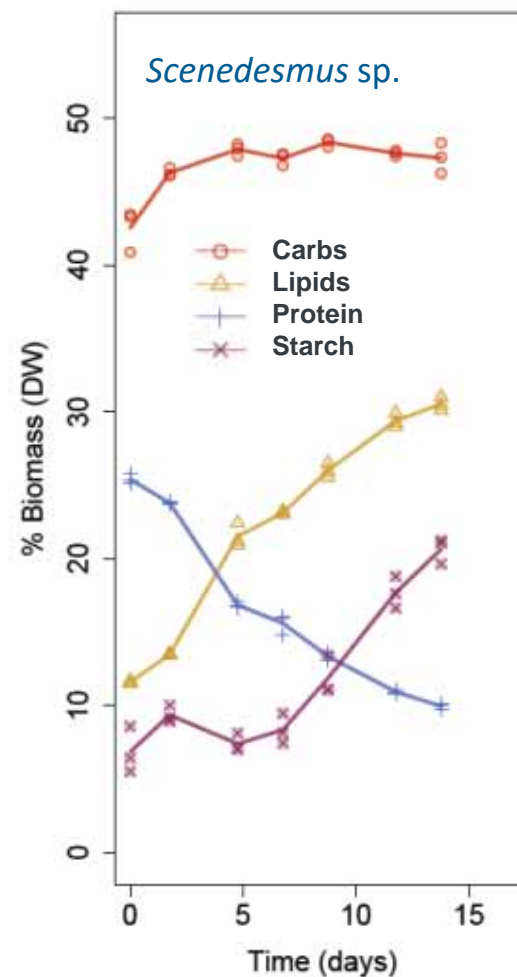
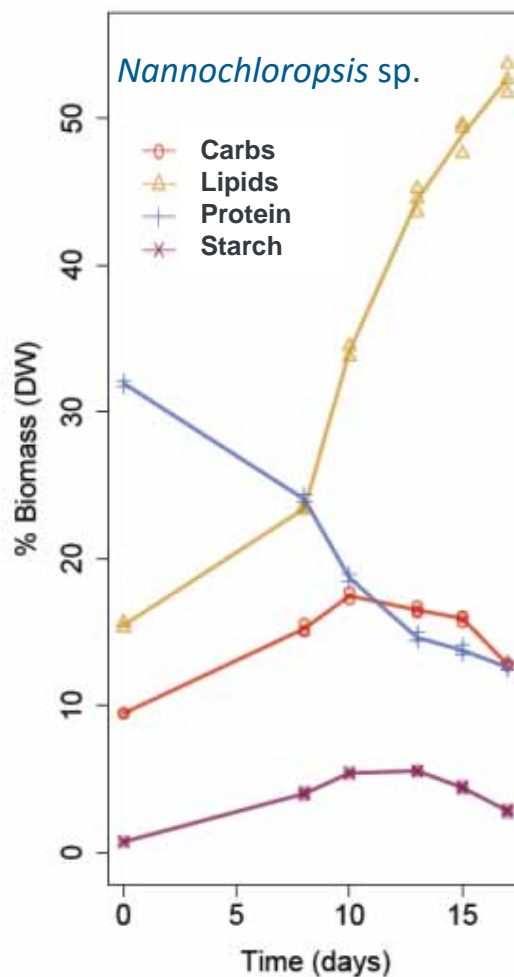
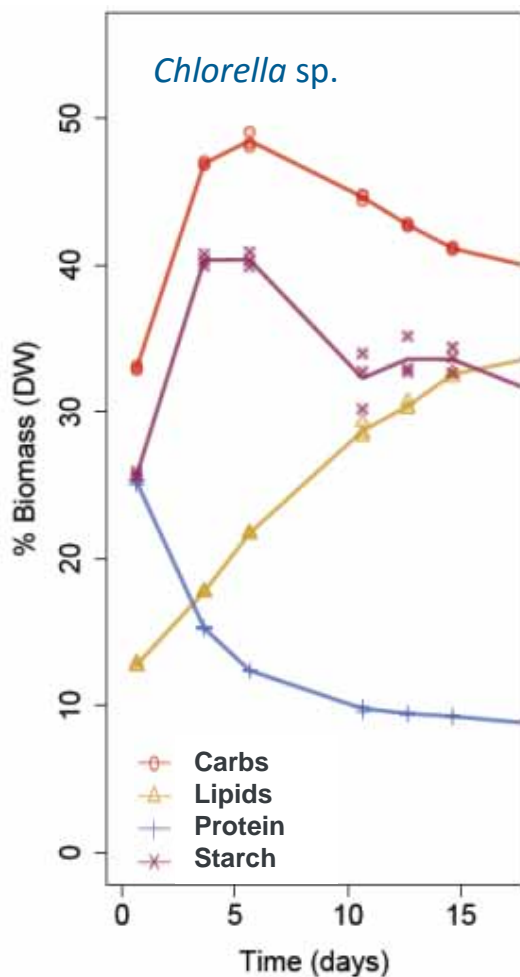
- Identification of commercially relevant algal strains with composition consistent with CAP process
- Establishment of coproduct options with significant TEA impact
- Development of unit operations for multiple products that can plug and play within CAP process

- **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

3 – Technical Accomplishments/Progress/Results

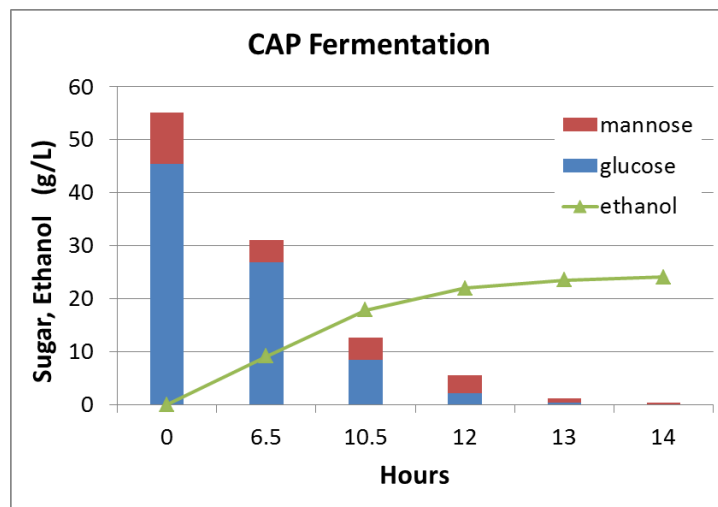
**Underlying principle:
Algal biomass is expensive; don't throw any of it away**



Go/No Go Milestone: Integrated CAP Run

Composition of <i>Scenedesmus</i> Biomass Used in this Demonstration (% DW)						
Ash	Starch	Non-starch glucose	Mannose	Other carbs	Protein (N)	Lipids (FAME)
1.4	8.1	18.0	11.8	1.3	8.9	40.9

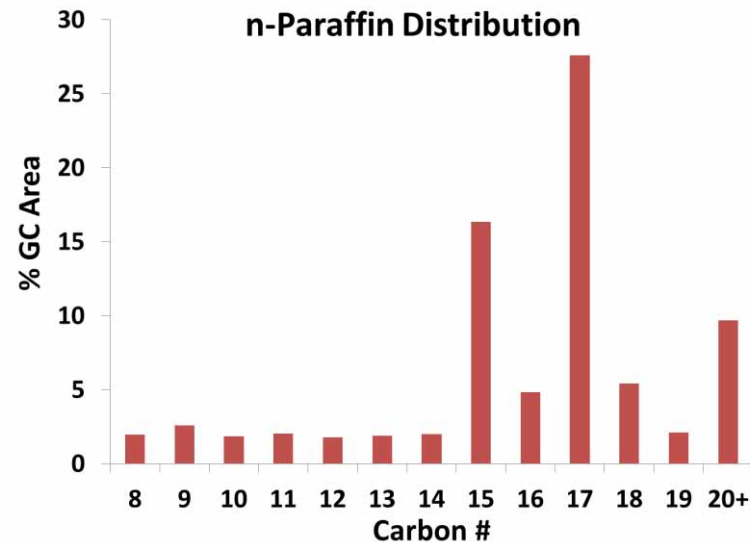
Run #	Time (min)	Temperature (C°)	Pretreatment severity (Ro)	Glucose (g/L)	Mannose (g/L)	Combined sugar yield (%)
1	5.0	195.0	3.50	58.7	15.0	82.0
2	15.5	146.0	2.54	49.3	12.9	80.4
3	2.0	175.0	2.51	61.4	15.6	78.0
4	15.0	155.0	2.81	51.1	13.2	72.6
5	15.0	155.0	2.81	47.7	12.8	73.9
6	15.0	155.0	2.81	47.8	12.3	71.8



Fatty acid purity (%)	Total FAME recovery (%)
91.9 ± 0.2	85.3 ± 1.9

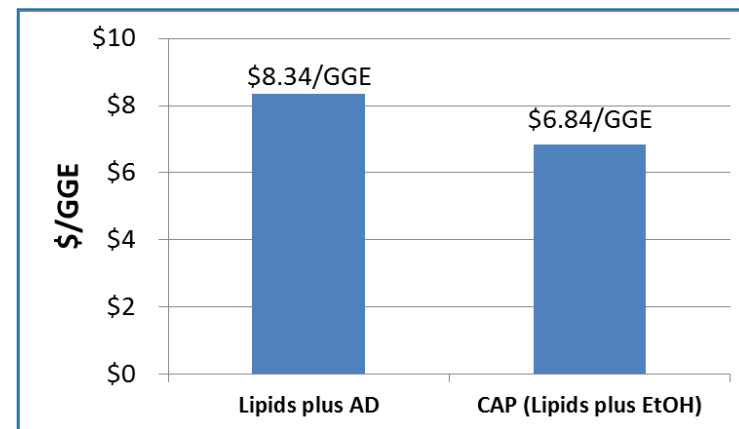
Integrated CAP Run: Met/Exceeded Goals

Product	Yield, wt% of oil feed
Total reactor product yield	94.24%
H ₂ consumption	1.90%
Reactor product composition	
Fuel-range hydrocarbons	82.08%
Diesel-range	62.1%
Naphtha-range	10.0%
CO ₂ (g/g oil)	2.19%
CO (g/g oil)	5.62%
H ₂ O (g/g oil)	6.30%
Off-gas (C _{≤5} H _{≤12})	4.35%



Go-No Go Milestone criteria and experimental results

Criteria	Target	Experimental
Recovery of fermentable sugars after pretreatment	80%	82.0%
Sugar utilization by <i>S. cerevisiae</i>	100%	98.5%
FAME lipid recovery	85%	85.3%
RDB yield after hydroprocessing (HDO)	60%	80%



Modeled MFSP based on biomass at \$490/ton

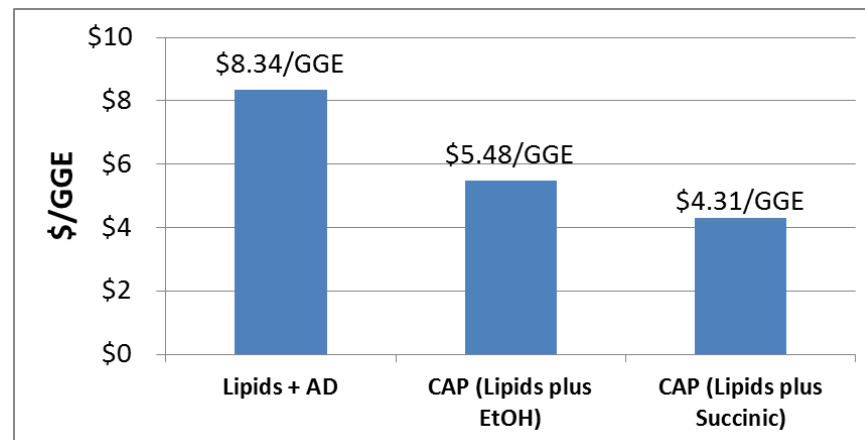
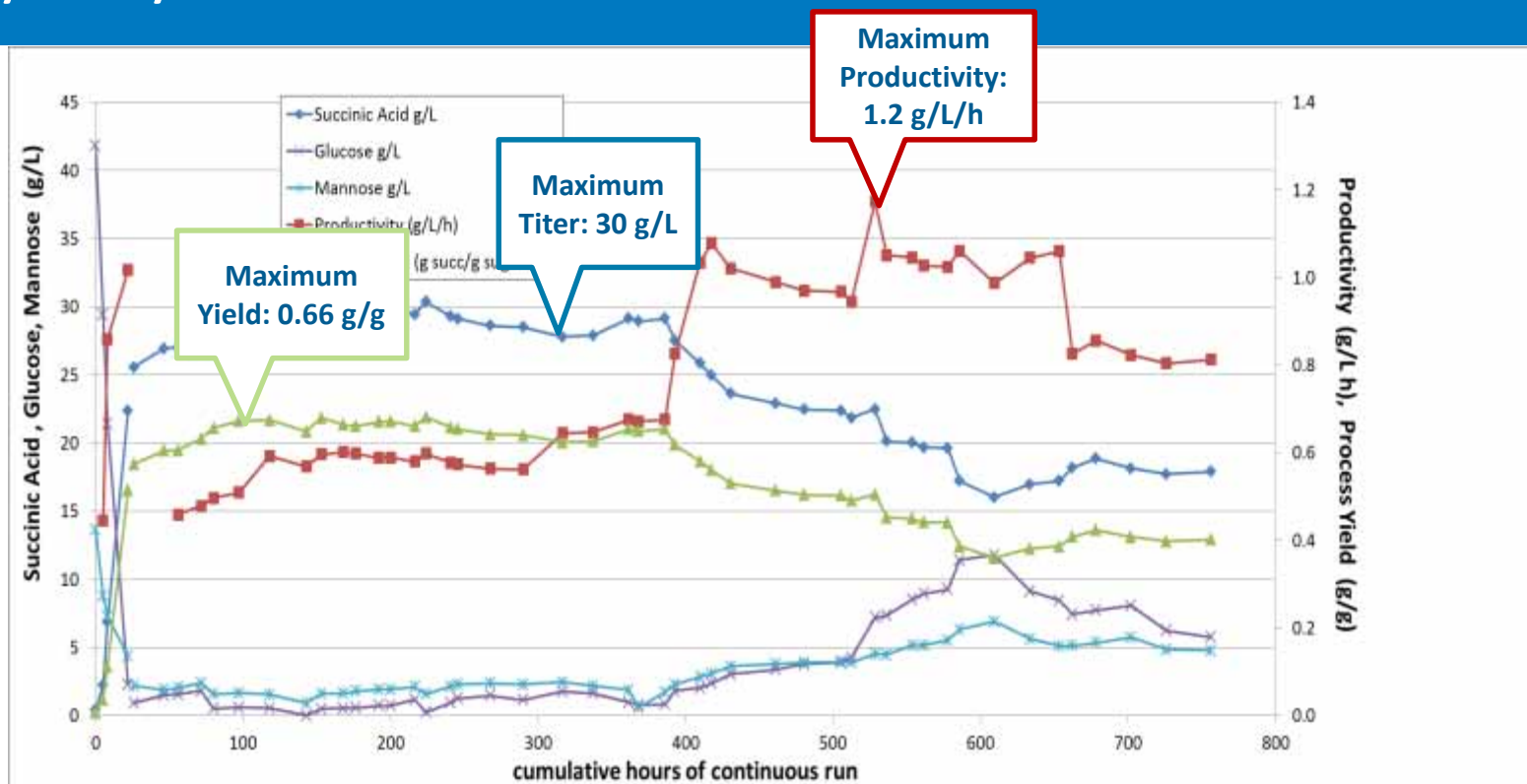
Algal Biorefinery Product Options

Product	Revenue Potential (\$MM/yr)	Yield (ton/yr)	Global Market Volume (ton/yr)	Process Complexity	Industry Involvement
Primary fuel product for reference					
Hydrocarbon fuels (from lipids)	\$40.7	12.8 MM gal/yr	56,900 MM gal/yr (U.S. Consumption)	Low	Cellana, GAI
Sugars					
Succinic acid (from sugars + glycerol)	\$136.3	78,000	441,000	High	Myriant, Bioamber, Succinity/BASF, Reverdia
Hydrocarbon fuels (from sugars + glycerol)	\$20.7	6.4 MM gal/yr	56,900 MM gal/y (U.S. Consumption)	Medium	Amyris, LS9
Lipids					
Surfactants from sterols	\$16.6	7,000	6,414,000	Medium	BASF, TerraVia
Polyols via polyunsaturated fatty acids	\$24.1	15,200	8,047,000	High	Cargill, Dow, Urethane Soy Systems, Bio-Based Technologies, Algenesis
Protein					
Protein → C4+ OH (SNL/Liao process)	\$9.7	9,100	734,400 as isobutanol 36,400 as plasticizer	Medium	Early R&D
Animal/fish feed	\$4.0 - \$16.0	45,700	16,538,000 - 190,126,000	Low	Mars, GAI, Cellana
Bioplastics	\$41.8	69,900	1,545,000	Medium	Algix
<i>Galdieria</i> via mixotrophic growth on protein stillage + HTL	\$20.3	6.4 MM gal/year	56,900 MM gal/year (U.S. Consumption)	Medium	Early R&D

*Based on unit farm and mid-harvest *Scenedesmus* biomass and demonstrated composition

R. Davis et al. FY16 Q1 Milestone Report, NREL

Algal Hydrolysate As Feedstock for Value Added Chemicals



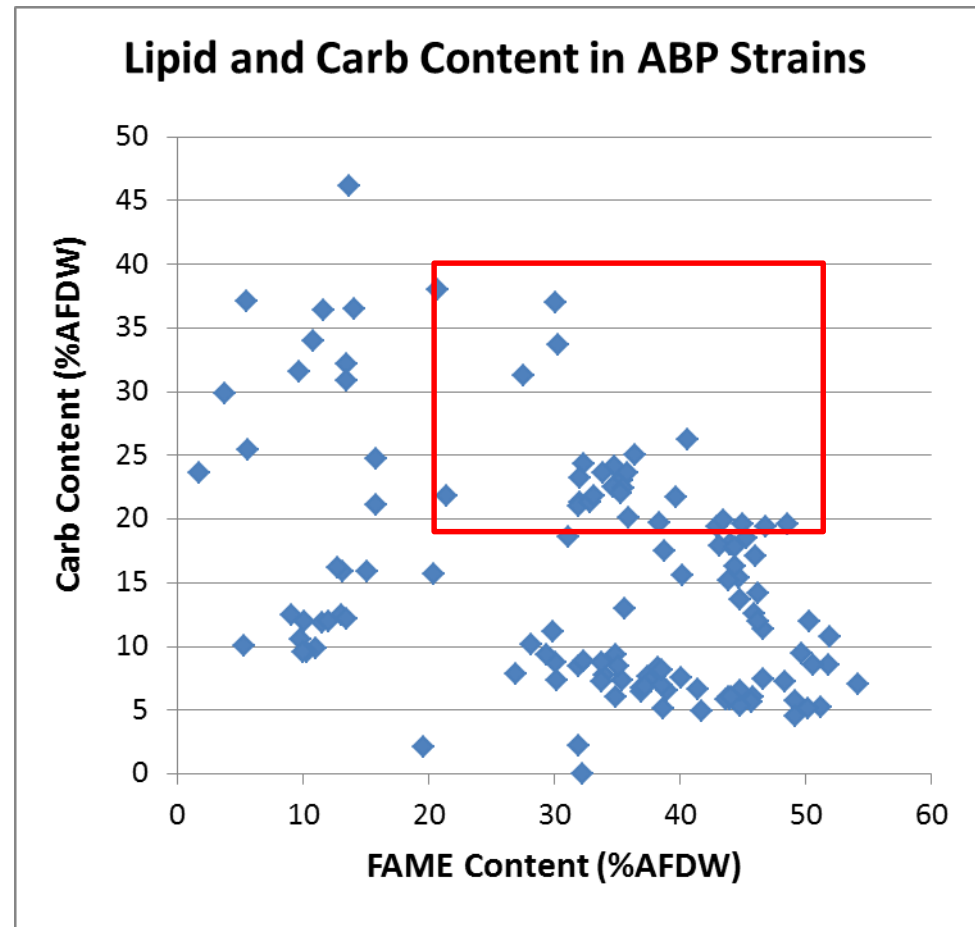
New Coproducts Can Provide Significant Revenue Relative to Biofuel Options

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

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

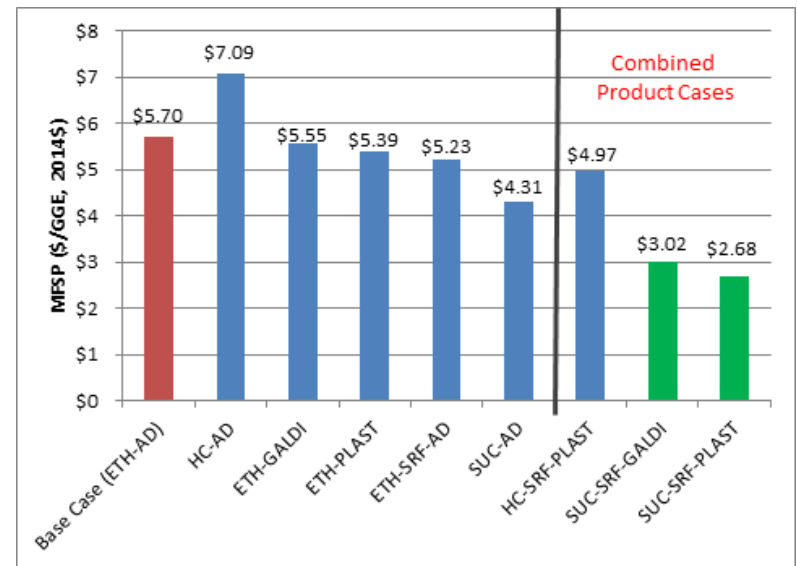
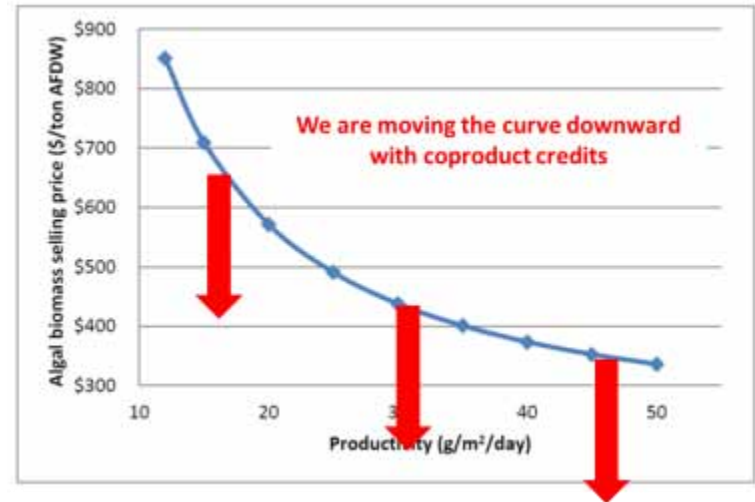
Saltwater Strains As Feedstock for CAP

- Cultivation in saline or brackish media important consideration for sustainability
- Most of our work has been done with freshwater high-lipid/high-carb strains of *Scenedesmus* and *Chlorella*
- Marine strain *Nannochloropsis* is high lipid but low carb
- Many salt water strains with high-lipid/high-carb phenotype
 - Algal Biotech Partnership culture collection
 - Strains used in other BETO projects
- Cultivation at larger scale by ATP³



4 – Relevance

- The ABC project is developing coproduct processes in partnership with ABV to enable commercial viability despite high biomass costs.
- A portfolio of fuels and coproducts from algal lipids, sugars, sterols, and proteins provides a route to <\$3/GGE.
- Both freshwater and saltwater algae exhibit compositional makeup necessary for CAP scheme.
- Shared technology development (pretreatment, extraction, upgrading) with Biochemical Conversion Program saves R&D costs and accelerates progress.



Future Work

- **FY17**
 - Reduce salt introduced by pretreatment process to improve conversion productivities.
 - Demonstrate pretreatment process for CAP scheme with freshwater and saltwater biomass.
 - Demonstrate one-step process for algal lipid upgrading to RDB to match refinery specs.
- **FY18**
 - Demonstrate all unit operations for conversion of algal biomass to optimal fuels and coproduct portfolio for 20% reduction in modeled MSFP relative to FY16 SOT.
 - Identify additional high-value, scalable coproducts that can help attain MFSP targets while minimizing process complexity.
- **FY19 and beyond**
 - Provide data to secure role for CAP process in BETO MYPP demonstrations.

Summary

- Go-No Go Milestone for fully integrated CAP Process completed with metrics met or exceeded.
- Algal oils can be deoxygenated with no cleanup steps to provide renewable diesel blendstock
- Conversion of algal sugars to succinic acid demonstrated in continuous process
- Algal sterols converted to surfactants through PEGylation process
- Algal proteins in waste stream offer significant coproduct opportunities
 - Biogas from anaerobic digestion
 - Additional biomass from mixotrophic algae cultivation
 - RDB from hydrothermal liquefaction
 - Bioplastics based on Algix technology
- Saltwater strains shown to have composition relevant for CAP, offering algal biofuel processes with minimal freshwater impact
- **Fuel and coproduct portfolio can beat \$3/GGE target even with biomass at \$490/ton**

Acknowledgments

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- **Algix**
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 - Ashton Zeller
- **UIUC/CSM**
 - Jeremy Guest
 - Timm Strathmann
 - Moses Leow
 - Yalin Li

Questions?

www.nrel.gov



Additional Slides

Responses to Previous Reviewers' Comments

- *One perceived problem with this approach is that producing ethanol from terrestrial feedstock is very inexpensive, and the additional overall costs for processing algal biomass to generate relatively small amounts of ethanol may void any advantages of recovering ethanol from algal carbohydrates in the first place. It may be more useful to study ways to increase the lipid profile of algae, as well as the lipid extraction processes, than to study ways of generating product from the carbohydrates. TEA results indicate that lipids to biofuels alone will not be sufficient to allow algae to compete with petroleum. Higher value lipid products, if scalable, are of interest to us. We are evaluating the opportunities under development by Algenesis for algal lipid-based polyurethanes.*
- *Consistent quality of feedstock for the algal lipid upgrading (ALU) pathway will continue to be a challenge until productivity kinetics are optimized. However, bottlenecks exist in this project concerning the scale of biomass intake (i.e., how to process 10 st at a time). It seems nearly impossible to deliver such a quantity of microalgae to this group so that the work can progress. It may be necessary to optimize scale-dependent processes using an alternate feedstock for the time being. Issues surrounding scaling are always on our minds and that is why we make use, as much as possible, of high TRL processes in our work. We are indeed limited by the amount of biomass available, though we expect that to change in the near future. We believe that doing scaling work with non-algal feedstocks is a step in the wrong direction and that the information that could be obtained from that approach is already available in the literature. Your comment does suggest that other feedstocks with composition similar to algae (especially food wastes) may be available at large scale and may provide both opportunities for blending studies with algal biomass as well as separate processes.*

Responses to Previous Reviewers' Comments

- *Developing higher fuel yield from fixed algal biomass is an interesting option. The strategy needs careful comparison to alternative down stream approaches. The added complexity may limit adoption. This point is well taken. Though many industries (e.g. petroleum refineries and biorefineries) make use of, and to a large extent, depend on multi-product portfolios to maintain profit margins, they all started with a single product and incorporated new products to expand upon profitability. They did not require multiple products for initial profitability. And while some algae companies hope to achieve profitability with nutraceuticals and expand into fuels, we do not see a clear path to make that transition in terms of cost reductions and scale mismatches. Thus we see no real option for algal biofuels outside of development of product portfolios. We will look to find coproduct processes that are high TRL level to minimize the R&D challenges and high value and volume to minimize the process complexity needed for economic viability.*
- *This is a very important part of the program, being carried out in a well-coordinated way. As they point out, the issue is the cost of algal production, so this work will only be truly useful if that is reduced. It is very appropriate that this “deconstruction” approach be done in parallel with the brute force thermochemical route; both have potential advantages and disadvantages that need to be considered and addressed. This is an important point. Not all biomass will work with the CAP process and some biomass has too much intrinsic value for HTL. We recognize the importance of HTL as a conversion process and in fact have begun to explore uses for the this technology to bring extra value to our overall process.*

Publications

- Tao Dong et al. (2016) Lipid recovery from wet oleaginous microbial biomass for biofuel production: a critical review. Applied Energy
- Tao Dong et al. (2016) “Combined Algal Processing: A novel integrated biorefinery process to produce algal biofuels and bioproducts” Algal Research, doi:10.1016/j.algal.2015.12.021
- Tao Dong et al. (2016) “Impact of Biochemical Composition on Susceptibility of Algal Biomass to Acid-Catalyzed Pretreatment for Sugar and Lipid Recovery” Algal Research, 18, 69-77 doi:10.1016/j.algal.2016.06.004
- Tao Dong et al. A novel integrated biorefinery process for diesel fuel blendstock production using lipids from the methanotroph, *Methylomicrobium buryatense*. Submitted 2016.
- Eric Knoshaug et al. Production of renewable diesel intermediate and succinic acid by parallel algal processing.. Submitted 2017.
- Jacob Kruger et al. Bleaching and Hydroprocessing of Algal Biomass-derived Lipids to Produce Renewable Diesel Fuel.. Submitted 2017
- Shijie Leow et al. Integrating varying biomass compositions with different aqueous conversion technologies as a strategy towards economical microalgae biofuels. Submitted 2017.

Posters

- Catalytic Upgrading of Algae Oils to Hydrocarbon Fuels; Jacob S. Kruger, Earl D. Christensen, Robert L. McCormick, Philip T. Pienkos; ACS Spring Meeting, 22 Mar 2015
- Catalytic Upgrading of Algae Oils to Hydrocarbon Fuels; Jacob S. Kruger, Earl D. Christensen, Robert L. McCormick, Philip T. Pienkos; ACS Spring Meeting, 16 Mar 2016
- Catalytic Upgrading of Algae Oils to Hydrocarbon Fuels; Jacob S. Kruger, Earl D. Christensen, Robert L. McCormick, Philip T. Pienkos; AIChE Annual Meeting, 17 Nov 2016
- Dong, T., Laurens, L., Pienkos, P. Recovery of Fatty Acids from Methanotrophic Bacteria via an Efficient Pretreatment Approach. 106th American Oil Chemists' Society (AOCS) Annual Meeting, Orlando, 2015
- Dong, T., Laurens, L., Sweeney, N. Pienkos, P. Screening Potential Fuel Precursors from Microalgae to Improve Engine Performance for the Next Generation of Vehicles. Algae Biomass Summit (ABO), Phoenix, AZ 2014
- Dong, T., Nagle, N., Pienkos, P., Laurens, L., Sweeney, N. Evaluation of algal biomass from a variety of sources for biofuel potential based on Combined Algal Processing. 5th International Conference on Algal Biomass, Biofuels & Bioproducts (ABBB), San Diego, 2015
- Development of a Novel Biorefinery Concept for Acceleration of Algal Biofuel Commercialization Philip T. Pienkos. Poster presented at SBFC, 2016, Philip T. Pienkos

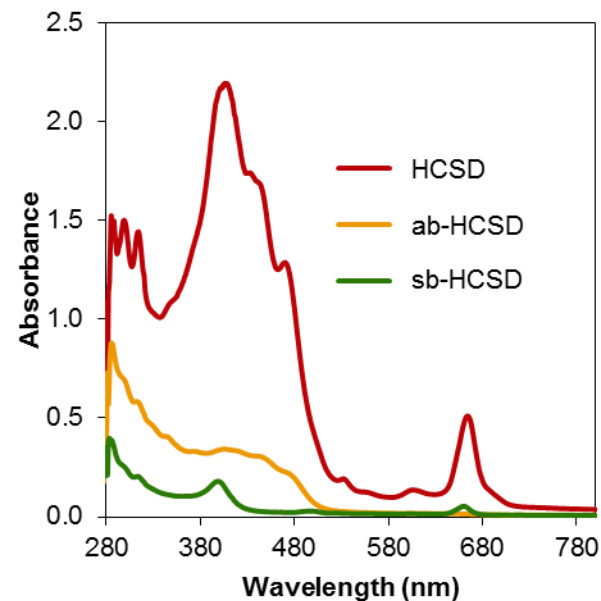
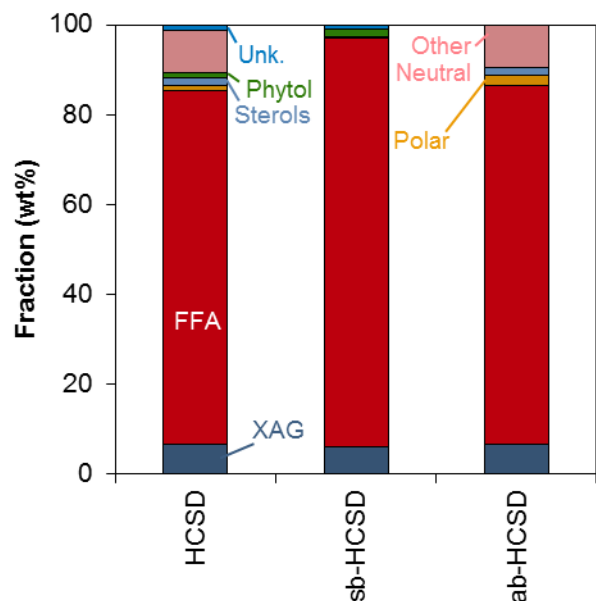
Oral Presentations

- Path to Commercial Algal Biofuels Through Combination of Process Cost Reductions and Identification of Novel Coproducts. Philip T. Pienkos, Biofuels 2015, Valencia Spain.
- Combined Algal Processing: A Novel Process for Biofuel and Bioproducts from Algal Biomass. P. Pienkos, T. Dong, E. Knoshaug, L. Laurens, R. Davis, N. Nagle. ABBB 2015. San Diego, CA
- A Biorefinery Concept for Accelerated Commercialization of Algal Biofuel Production. Philip T. Pienkos. Algae Biomass Summit, 2015, Washington DC
- Full Circle: How to Bring Algae Back into Biofuels. Philip T. Pienkos. Algae Biomass Summit 2016, Phoenix, AZ
- A Biorefinery Concept for Accelerated Commercialization of Algal Biofuel Production. Philip T. Pienkos. AOAI 2016, Wuhan China
- Recovery of Fatty Acids from Methanotrophic Bacteria via an Efficient Pretreatment Approach. Dong, T., Laurens, L., Pienkos, P. 106th American Oil Chemists' Society (AOCS) Annual Meeting 2015, Orlando.
- Algal Production System Design/SOT. Philip Pienkos and Ryan Davis. BETO Quarterly Meeting 2017, Washington DC.
- Biofuels at the Nexus of Climate Change and National Security. Philip Pienkos. Climate Change and National Security Interagency Roundtable, 2016. Washington DC.
- Co-products Value Proposition" Laurens, L. Oral presentation, DOE BETO Algae Biology Toolbox Workshop, San Diego, CA
- "Algae Biorefinery Development for Biofuels and Bioproducts" Laurens, L. Oral presentation, DOE Bioenergy 2016, Washington DC
- "Sterol Molecular Fingerprinting for High-Value co-Product Synthesis" Palardy, O., Laurens, L. Oral presentation at 7th Algae Biomass Summit, Phoenix, AZ

Commercialization

- **Discussions with algae companies regarding application of pretreatment and extraction for omega-3 fatty acids**
- **Discussions with corn biorefineries for integration of CAP process with corn ethanol/oil process**
- **Evaluation of algal protein with Algix**
- **Discussions with Algenesis regarding renewable polyurethanes from algal biomass**
- **Discussions with Clearas Water Systems for valorization of low cost waste-water based algal biomass**

Oil Bleaching Removes Nitrogen and Pigments, But Doesn't Improve Hydrodeoxygenation

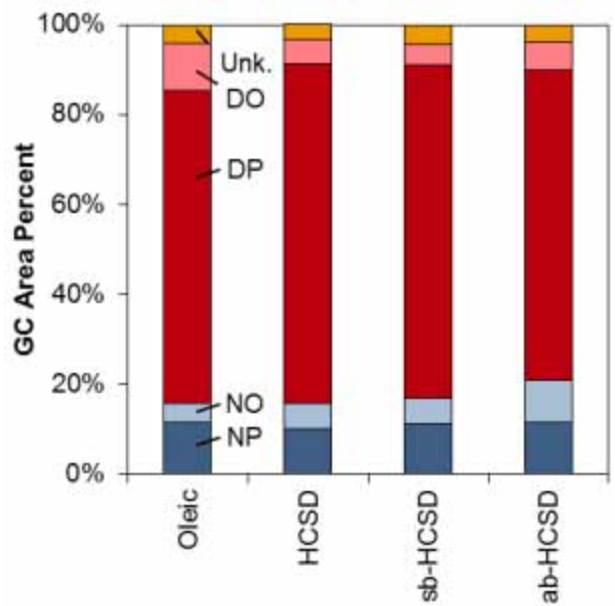


Element	Crude HCSD	sb-HCSD	ab-HCSD
Carbon, wt%	76.6		
Hydrogen, wt%	11.9		
Oxygen, wt%	11.9		
Nitrogen, ppm	1644	254	138
Sulfur, ppm	72		
Phosphorus, ppm	18	4	349
Calcium, ppm	17	372	296
Iron, ppm	6	1	2
Magnesium, ppm	5	50	26
Potassium, ppm	26	< 5	< 5
Sodium, ppm	17	119	< 5
Silicon, ppm	36	13	12

Product	Crude HCSD	sb-HCSD	ab-HCSD
Fuel-range hydrocarbons	73.9%	73.2%	74.0%
Naphtha-range (C7-C12)	15.9%	16.9%	20.9%
Diesel-range (C12+)	80.8%	78.7%	75.3%
CO ₂ (g/g oil)	2.2%	2.0%	2.0%
CO (g/g oil)	5.4%	4.3%	5.9%
H ₂ O ^a (g/g oil)	6.4%	7.1%	6.3%
Off-gas (C ₂₅ H ₅₁₂)	4.5%	2.5%	4.8%
Overall mass balance	92.5%	89.2%	93.0%

The DO catalyst was 5 wt% Pd/C, which was used as-received from Johnson Matthey, except for crushing and sieving to obtain particles in the 125-250 μm (60-120 mesh) range. The catalyst was reduced for at least one hour in flowing hydrogen at pressures over 100 psi and temperatures over 100 °C in the process of bringing the reactor up to operating conditions.

Algae Oil Can Be Upgraded to High Quality RDB Through Hydrodeoxygenation and Hydroisomerization



	Oil N (ppm)	DO N (ppm)	Bleaching N Conv	DO N Conv	Total N Conv
HCSD	1644	140		91.5%	91.5%
sb-HCSD	254	83	84.5%	67.5%	95.0%
ab-HCSD	138	16	91.6%	88.2%	99.0%

	HI Mass Yield	Approximate Isoparaffin Content	Cloud Point (°C)
Hexadecane	57.9%	78.7%	-20
Oleic Acid	71.6%	58.6%	-3
HCSD	79.4%	41.1%	-15
sb-HCSD	81.1%	31.6%	-12
ab-HCSD	77.3%	50.7%	-21

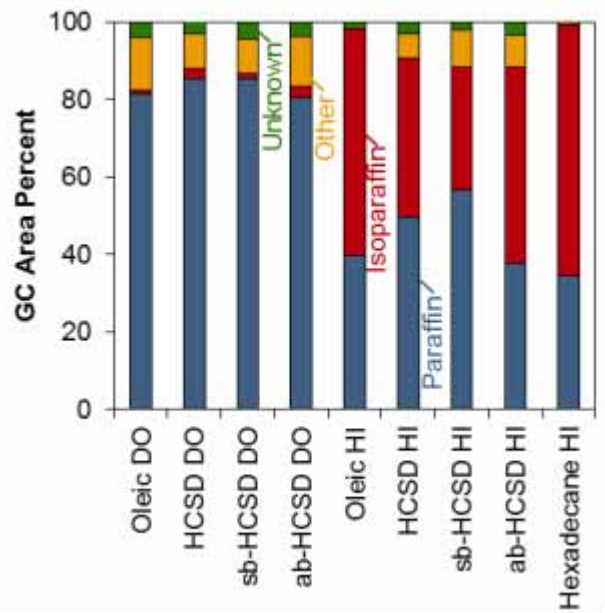
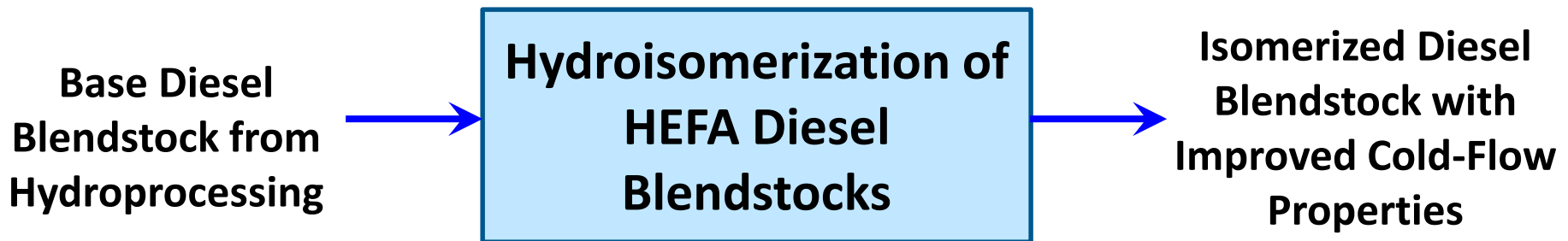


Table 5. Results from HI of hexadecane and DO products over 1 wt%Pt/SAPO-11. Conditions: 350 °C, 500 psi, LHSV = 0.5 hr⁻¹, H₂/feed = 2375 Nm³/m³. Samples taken at 10 h TOS. Approximate isoparaffin content expressed as percent of total GC-MS area.

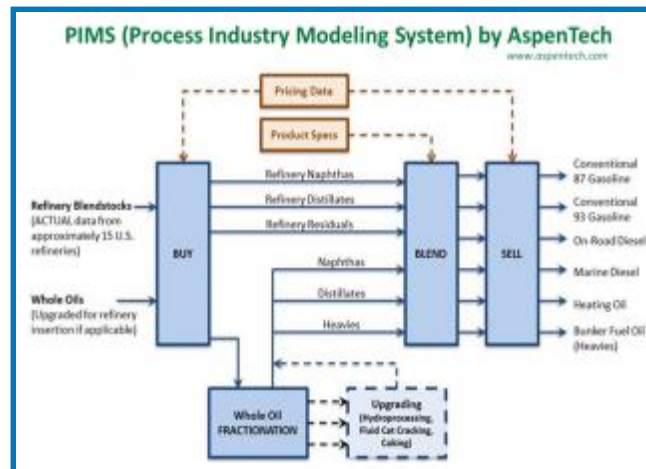
Hydroisomerization Can Produce a Higher Value RDB with Greater Blending Properties

TEA calculates the cost of adding hydroisomerization process to the pathway. The Biofuels Blending Model is utilized to assess the increase in value and blendability.



Blendstock Value **Base**

Blended Volume **< 10%**

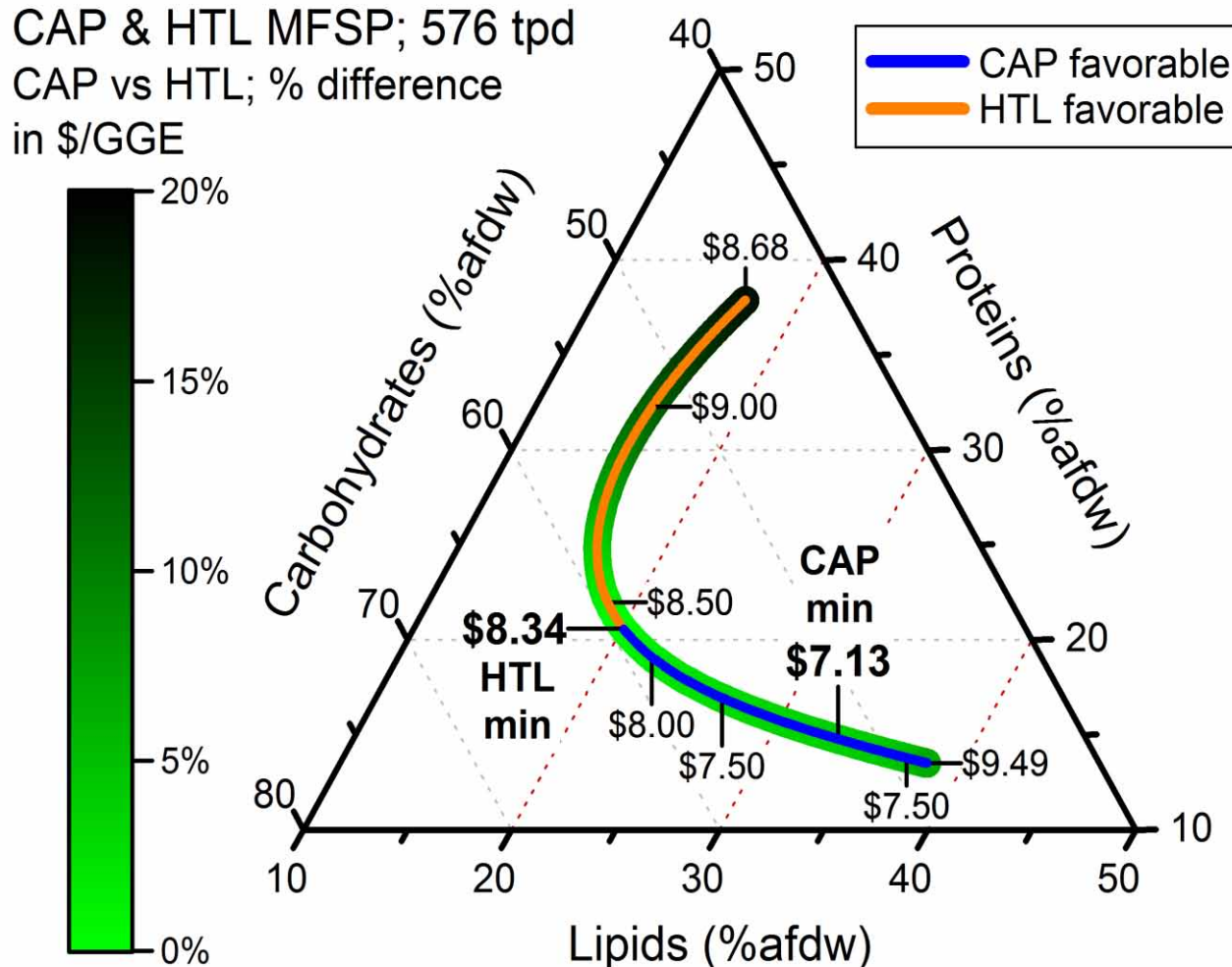


Base + \$0.25 / Gallon

> 90%

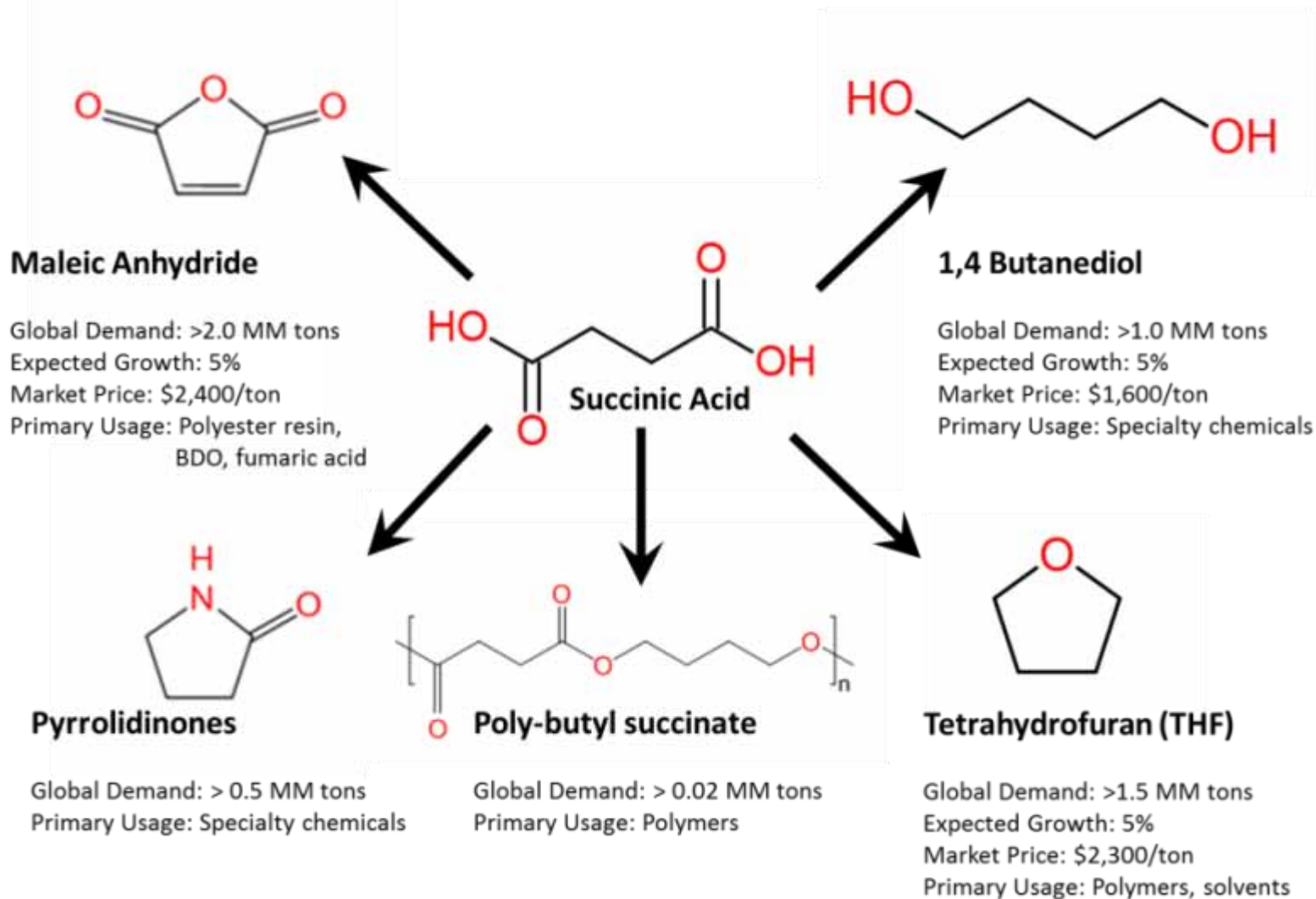
From Strategic Modeling Project

Robustness in microalgae biofuel systems can be achieved by leveraging varied biomass composition and conversion pathways



Figures from Leow S, et al. (Presented at Algae Biomass Summit 10/25/16. Manuscript in Preparation)

Potential Products from Succinic Acid



Biddy, Mary J., Ryan Davis, David Humbird, Ling Tao, Nancy Dowe, Michael T. Guarnieri, Jeffrey G. Linger et al. "The techno-economic basis for coproduct manufacturing to enable hydrocarbon fuel production from lignocellulosic biomass." ACS Sustainable Chemistry & Engineering 4, no. 6 (2016): 3196-3211.