DOE Bioenergy Technologies Office (BETO) 2021 Project Peer Review

Tailored Bioblendstocks With Low Environmental Impact To Optimize MCCI Engines

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Co-Optima Initiative

André L. Boehman

University of Michigan

Participants

DOE Project Management: Alicia Lindauer, Philip Lee, Evan Mueller

Co-PIs: André Boehman, Brad Cardinale, Dan Haworth, Phil Savage, Levi Thompson

Co-Optima Liaison: Robert McCormick

Michigan

- Research Scientist/Co-Investigator: Dr. Saemin Choi
- Post doctoral Fellow: Dr. Taehoon Han (now at Argonne National Lab)
- Ph.D. students: Muhammad Abdullah, Kaustav Bhadra
- M.S. students: Cansu Doganay, Spenser Widin, Kia Billings, Elena Miyasato
- Undergraduate students: Alexander Henry

Penn State University

- Ph.D. students: Jun Han, Alex Carley, Tim Shokri

Industry

- Steven McConnell, Dr. Diep Vu, Marathon Petroleum

Consultants/Advisors

- Dr. Charlie Westbrook (LLNL, retired)

Project Overview

- This projects seeks to overcome impediments to expansion of algae cultivation and conversion into fuels to displace petroleum and reduce greenhouse gas (GHG) emissions
- The overall objective of the project is to
  - develop and demonstrate a microalgae bio-blendstock with greater than 60% greenhouse gas reduction relative to petroleum diesel
  - reduce sooting propensity
  - increase cetane number
  - improve engine thermal efficiency relative to a baseline diesel engine operating on conventional fuel

Project Overview

- Applying cultivation of algae polycultures to achieve robustness and productivity
- Converting whole algae to bio-hydrocarbons via Hydrothermal Liquefaction (HTL) to make a biocrude and up-grading the biocrude via hydroprocessing to obtain tailored bioblendstocks for diesel fuel
- Optimizing diesel (MCCI) combustion through blending model compounds into diesel fuel to represent the tailored bioblendstocks through experiments and numerical simulation

Management

Link application of fuels in autoignition and mixing controlled compression ignition combustion to the processes for generating biocrude and upgrading the biocrude from algal feedstocks, wherein those algal feedstocks are cultivated using algal polycultures to maximize productivity and robustness

The management approach of this project directly aligns with the task structure

- Task 1: Demonstration Project (cultivation of algae)
- Task 2: Hydrothermal Liquefaction to Biocrude
- Task 3: LCA and TEA
- Task 4: Biocrude Upgrading to Tailored Fuels
- Task 5: Engine Studies and Simulation

Management

The management approach of this project directly aligns with the task structure

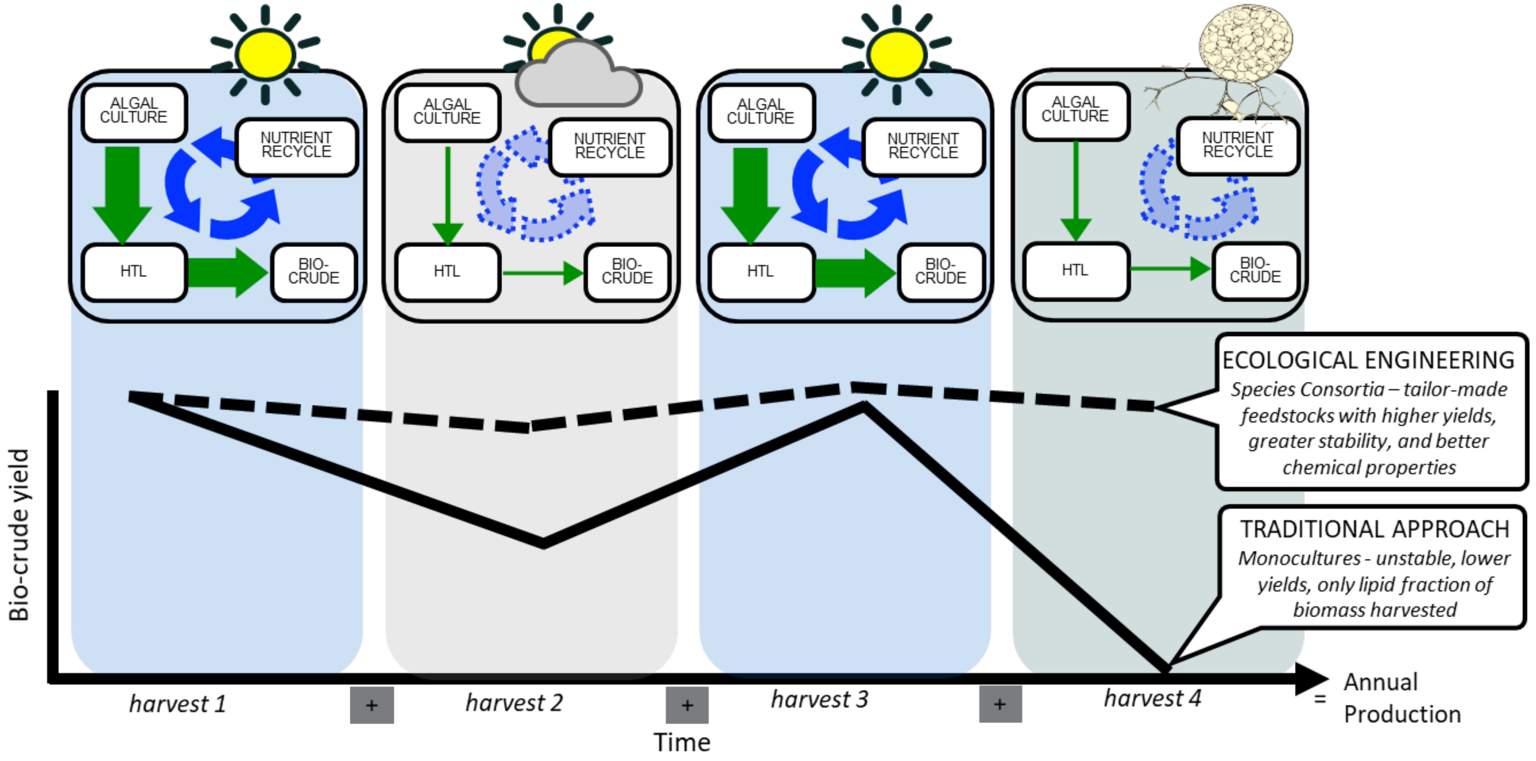
- B. Cardinale (UM→PSU): cultivation, LCA, TEA (Tasks 1 and 3)
- P. Savage (PSU): HTL, LCA, TEA (Tasks 2 and 3)
- Thompson (UM→UDel.): upgrading biocrude (Task 4)
- Haworth (PSU): MCCI engine CFD (Task 5)
- Boehman: autoignition, engine, fuel properties experiments (Task 5, PI)

Risks include the challenge of algae instability (crashing of ponds) during cultivation and challenges with processing and upgrading

- Risk is mitigated by following a “BACI” (Before, After, Control, Impact) approach
- Risk in processing was mitigated by seeking advice from BETO researchers also pursuing HTL processing strategies

Approach

Innovation → Applying Ecological Engineering to Improve Stability and Robustness of Algae Cultivation



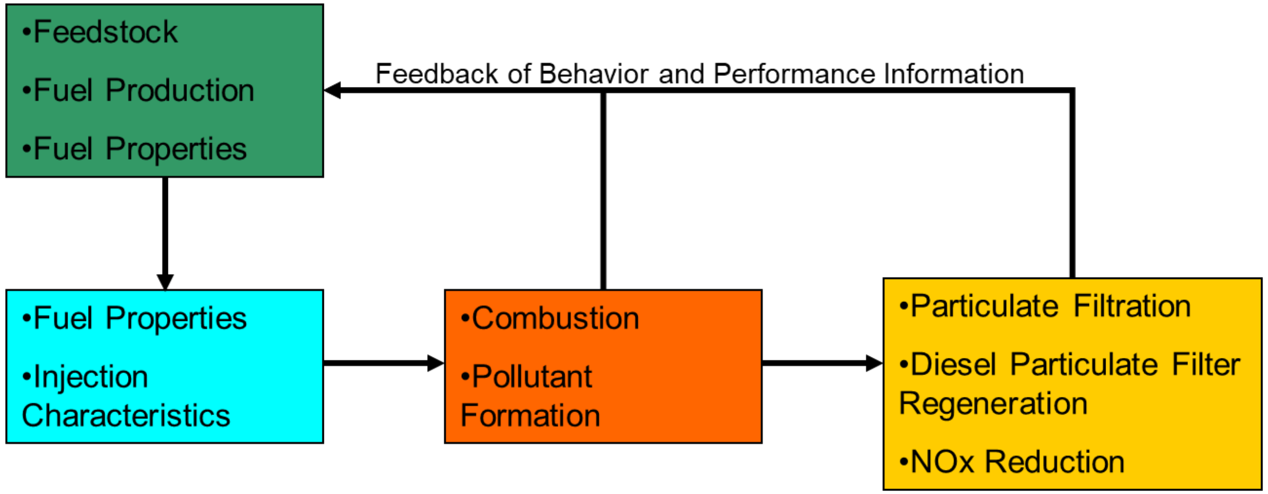
Traditional approaches to development of algal feedstocks versus Ecological Engineering → The goal of Ecological Engineering is to design multi-species algal feedstocks that are more stable, more resistant to pests and disease, and thus achieve greater annual production of biocrude with fewer crop loss events.

Approach

Our approach is to create a feedback loop and linkage from algae cultivation, through conversion to biocrude and upgrading of biocrude to an optimized fuel blendstock for diesel (MCCI, mixing controlled compression ignition) engines.

Innovation → Optimize the Hydrothermal Liquefaction and Upgrading Steps to Obtain Highly Desirable Biofuel to Blend into Diesel Fuel

Innovation → Focus on Downstream Fuel Performance in Sooting Tendency and Cetane Number

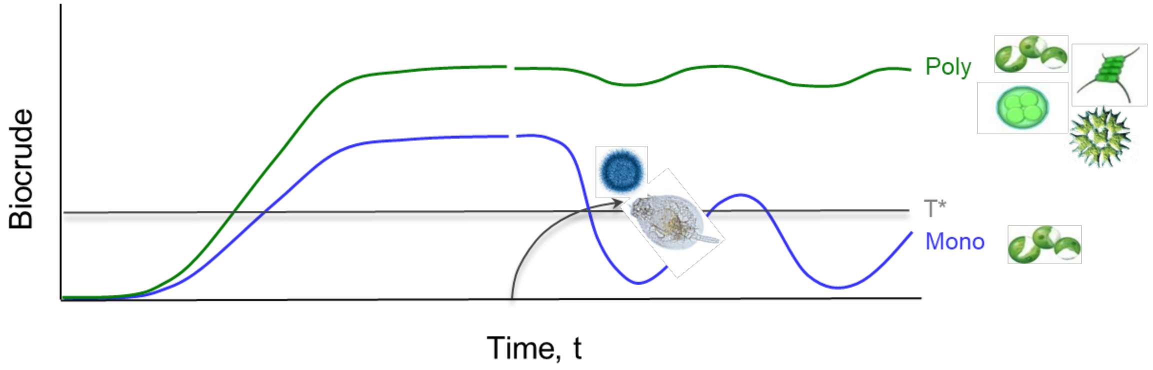


Overall "feedback" scheme → primary feedback that we will execute is with the **biocrude production and refining steps**

Approach

Link application of fuels in autoignition and mixing controlled compression ignition combustion to the processes for generating biocrude and upgrading the biocrude from algal feedstocks, wherein those algal feedstocks are cultivated using algal polycultures to maximize productivity and robustness

Algal polycultures (species 'consortia') can achieve higher yield and greater stability than the best algal monocultures.

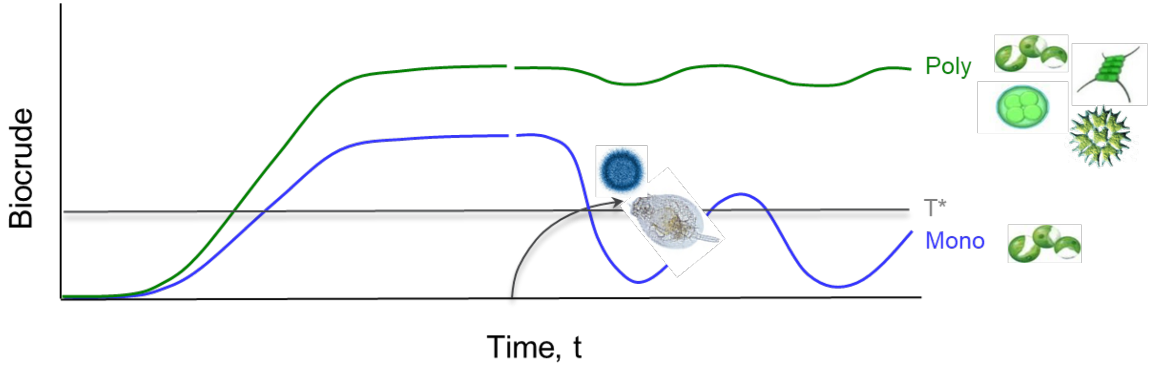


- Cultivation was our first major challenge → BP1 Go/No-Go Decision Point
- Mitigated by starting in smaller 4.5 m^2 ponds at AzCATI in summer 2019 with fresh water algae studied in Michigan

Approach – Task 1

Link application of fuels in autoignition and mixing controlled compression ignition combustion to the processes for generating biocrude and upgrading the biocrude from algal feedstocks, wherein those algal feedstocks are cultivated using algal polycultures to maximize productivity and robustness

Algal polycultures (species ‘consortia’) can achieve higher yield and greater stability than the best algal monocultures.

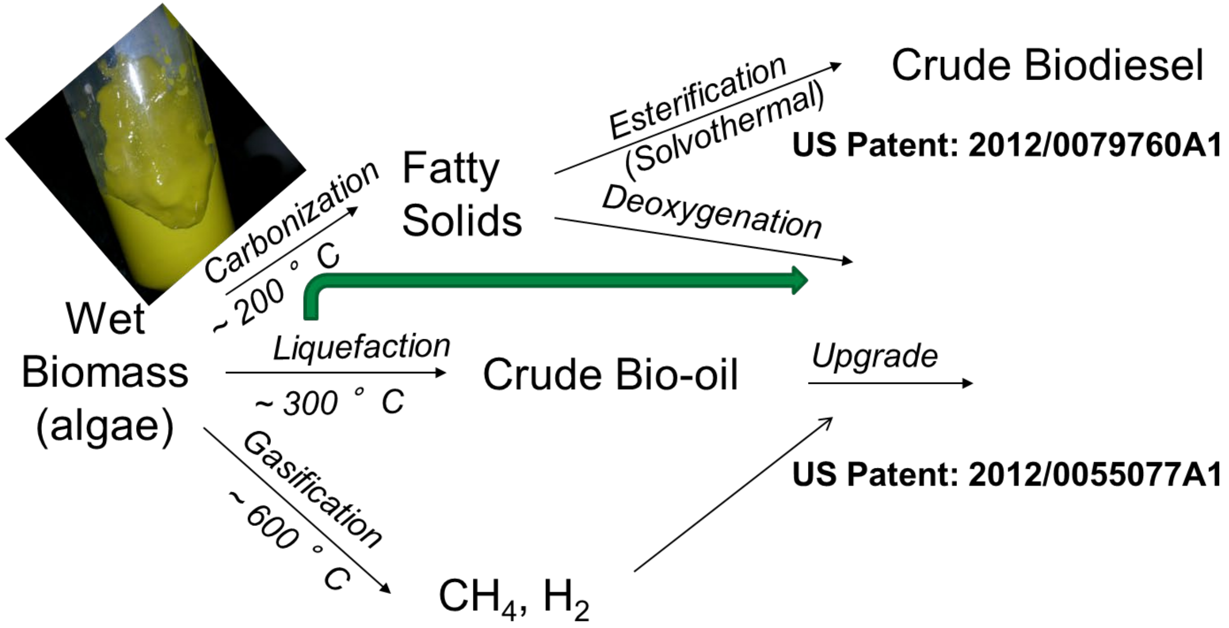


“Ecological Engineering” → Stability Leads to Productivity

- Cultivation was our first major challenge → BP1 Go/No-Go
- Mitigated by starting in smaller 4 m^2 ponds at AzCATI in summer 2019 with fresh water algae studied in Michigan

Approach – Task 2

Efficient conversion to desirable compounds

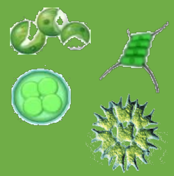


Processes that work with ***wet biomass*** (its natural state) and avoid organic solvents could be less costly, more energy efficient, and more environmentally sustainable.

Savage, *Science*, 2012

- Hydrothermal liquefaction → mass and carbon efficiency are coupled between cultivation and HTL steps via nutrient recycling

Approach – Task 3



Life-cycle assessment and techno-economic analysis → approach is based on incorporating GREET into algae production framework

Biodiversity Improves Life Cycle Sustainability Metrics in Algal Biofuel Production

David N. Carruthers,[†] Casey M. Godwin,[‡] David C. Hietala,[†] Bradley J. Cardinale,[*,§] Xiaoxia Nina Lin,[*,†] and Phillip E. Savage[*,†,‖]

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[‡]University of Michigan – Ann Arbor, Cooperative Institute for Great Lakes Research, School for Environment and Sustainability, Ann Arbor, Michigan 48109 United States
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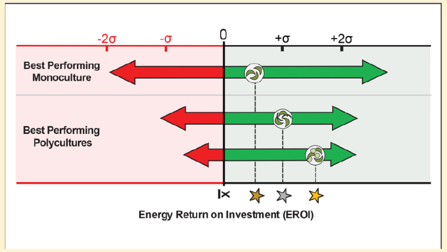
Supporting Information

ABSTRACT: Algal biofuel has yet to realize its potential as a commercial and sustainable bioenergy source, largely due to the challenge of maximizing and sustaining biomass production with respect to energetic and material inputs in large-scale cultivation. Experimental studies have shown that multispecies algal polycultures can be designed to enhance biomass production, stability, and nutrient recycling compared to monocultures. Yet, it remains unclear whether these impacts of biodiversity make polycultures more sustainable than monocultures. Here, we present results of a comparative life cycle assessment (LCA) for algal biorefineries to compare the sustainability metrics of monocultures and polycultures of six fresh-water algal species. Our results showed that when algae were grown in outdoor experimental ponds, certain



Environ. Sci. Technol. 2019, **53**, 9279–9288

- LCA completed and published
- TEA is in progress with March 31, 2021 deadline for report on outcomes from 4.5 m^2 pond studies → BP2 Go/No-Go Decision Point

GREET: Greenhouse Gases, Regulated Emissions, and Energy Use in Technologies

MICHIGAN ENGINEERING
UNIVERSITY OF MICHIGAN

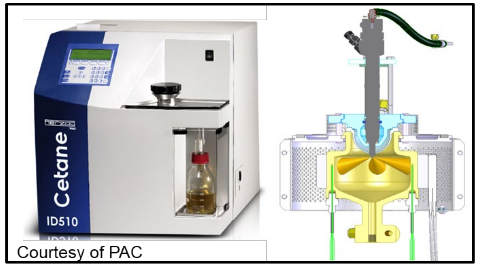
PennState
College of Agricultural Sciences

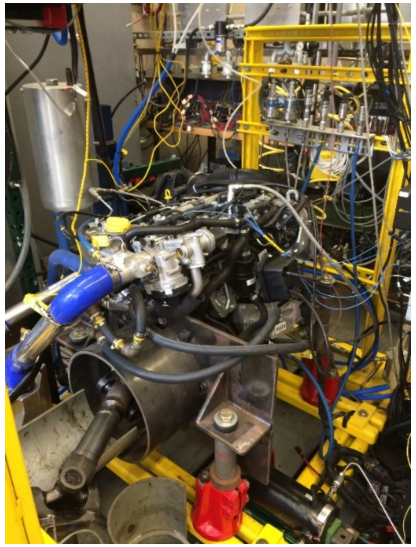
PennState
College of Engineering

Approach – Tasks 4 and 5

- Task 4: Hydroprocessing to target desirable bio-hydrocarbon species
- Task 5: Using most abundant compounds as “models” for engine and fuel property studies
- Overall – mode to 1.8L twin scale-up reactors when the “recipe” for HTL and upgrading are ready

Bench-scale hydroprocessing to screen catalysts and process conditions





Studies of ignition quality, low temperature behavior, smoke point, ignition kinetics and diesel (MCCI) combustion

Impact

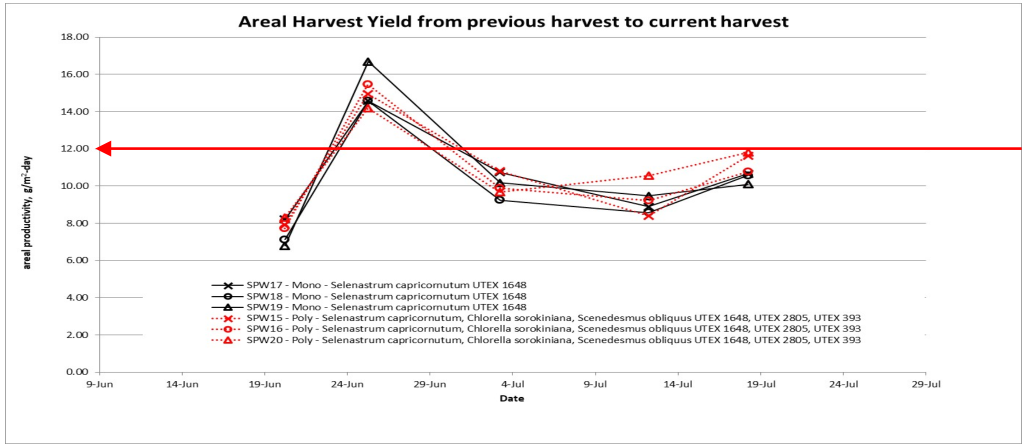
- Demonstrate benefits of polycultures for enhancing stability and robustness in algae cultivation
- Demonstrate effective catalytic processes to make biocrude and tailored fuel blendstocks
- Demonstrate improved properties of diesel fuel with the algal bio-blendstock
- Demonstrate optimized engine performance and emissions with model algal bio-blendstock
- Confirm greenhouse benefits and effective mass efficiency, to yield a promising potential fuel cost
- Collaborate with an energy company to explore the tech transfer possibilities for refinery integration of algae biocrude

Progress and Outcomes – Task 1

- Algae Cultivation Demonstration with “BACI” design: successful polyculture versus a monoculture comparison

Algae Yields, kg

Date	Mono	Poly	Total
6/20/2019	5.5	3.0	8.5
6/25/2019	3.0	2.0	5.0
7/3/2019	5.5	4.0	9.5
7/12/2019	6.3	4.5	10.8
7/18/2019	4.6	4.8	9.4
7/25/2019	4.6	3.9	8.5
Average per harvest	4.9	3.7	8.6
Sum of all harvests	34.4	25.8	60.2



Target

Collaboration with AzCATI

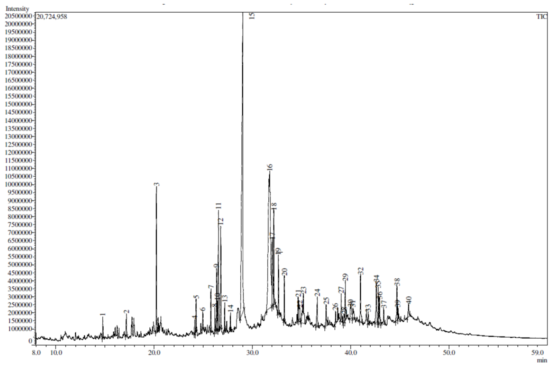
- Summer 2019
- Two 4.5 m^2 ponds
- Met areal productivity
- Met harvest mass target

Our ponds

Their ponds

Progress and Outcomes – Tasks 2 and 4

Monoculture



n-hexadecane identified as a major component of the HTL product → model compound to study in engine and fuel property experiments

Polyculture

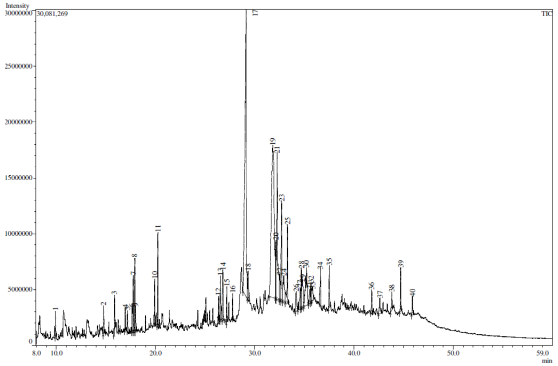


Table 1. Monoculture *S. capriconutum* GCMS Results

Peak Number	Elution Time	% Area	Likely Compound	Similarity Index
3	20.232	3.99	1-Pentadecene	96
9	26.354	1.89	3,7,11,15-tetramethyl-hexadecyl acetic acid	89
11	26.543	4.48	R,R,R,R-3,7,11,15-E-2-tetramethylhexadecene	93
12	26.778	3.81		92
15	29.008	23.03	n-hexadecanoic acid	97
16	31.756	21.84	Oleic acid	90
17	32.025	3.42	Octadecanoic acid	90
18	32.177	3.19	Hexadecanamide	95
19	32.645	1.90	N-methyl-myristamide	92
23	35.186	2.66	N-butyl-dodecanamide	81
29	39.449	1.47	3-amino-3-(4-octyloxy-phenyl)-propionic acid	75
30	39.983	1.41	Tetracosanoic acid	66
32	41.002	2.31	O-methyl-delta,tocopherol	83
34	42.604	2.18	Octadecanamide	73
38	44.704	1.51	4-pentenoic acid, 2,2-diethyl-3-oxo-5	79

Table 2. Polyculture *S. capriconutum, C. sorokiniana, S. obliquus* GCMS Results

Peak Number	Elution Time	% Area	Likely Compound	Similarity Index
8	17.905	1.84	3-methyl-indole	96
11	20.232	1.94	1-pentadecene	96
14	26.784	1.74	R,R,R,R-3,7,11,15-E-2-tetramethylhexadecene	86
17	29.138	23.00	n-hexadecanoic acid	95
19	31.829	23.11	E,E,Z-1,3,12-nonadecatriene-5,14-diol	89
20	32.120	2.05	Octadecanoic acid	90
21	32.266	7.36	Hexadecanamide	95
22	32.520	1.36	3,9-dodecadiyne	61
23	32.704	3.90	N-methyl-myristamide	92
24	32.934	2.09	(Z,Z)-9,12-octadecadienoic	75
25	33.300	2.66	N,N-dimethyldodecanamide	90
27	34.573	1.35	N-propylmyristamide	75
28	34.697	1.44	(Z)-9-octadecenamide	83
29	34.853	1.74	9,12,15-octadecatrienoic acid	84
30	35.224	3.30	N-butyl-dodecanamide	82

Progress and Outcomes - Other Tasks

- Task 2: HTL studies are now coupled to upgrading to explore pretreatment strategies and conversion efficiency of combined processes
- Task 3: TEA on 4.5m^2 ponds nearing completion
- Task 4: Linkage to Task 2 and preparation for transition to 1.8L scale-up reactor operation
- Task 5: Engine studies are preparing for optimization studies in 1.9L turbodiesel test engine with *n*-hexadecane blended into diesel fuel as a model of the algal bio-blendstock

Summary

- This project links the cultivation and processing of algae to fuel performance in diesel engines
- Cultivation using algal polycultures can maximize productivity and robustness
- This team is meeting milestones and collaborating across tasks to pursue the project's major objectives
- Exciting next steps include a planned return to AzCATI to explore saline-tolerant algae cultivation
- Engine studies are poised to demonstrate substantial engine efficiency improvements
- Bench-scale studies will soon transition to scale-up reactor operation

Quad Chart

Timeline

- Project Start Date: 10/01/2018
- Project End Date: 12/31/2021

	FY20 Costed	Total Award
DOE Funding	(10/01/2019 – 9/30/2020) $573,999	$2,000,000
Project Cost Share	$231,628	$602,446

Project Partners*

- Marathon Petroleum
- Charlie Westbrook (LLNL, retired)

Project Goal

Develop and demonstrate a microalgae bio-blendstock with greater than 60% greenhouse gas reduction potential relative to petroleum diesel, that can reduce sooting propensity, increase cetane number and improve engine thermal efficiency relative to a baseline diesel engine operating on conventional fuel

End of Project Milestone

Demonstrate improvements in key fuel properties, sooting propensity and cetane number, with improvement in engine performance and emissions for the algal bioblendstock. Complete LCA and TEA demonstrating >60% reduction in GHG emissions relative to diesel fuel and a potential MFSP of $3/gallon of fuel.

Funding Mechanism

DE-FOA-0001919, AOI 5b, 2018

Additional Slides

Responses to Previous Reviewers' Comments

From BETO Review Meeting Poster Presentation, March 2019

Reviewer Comments	Responses
The approach of using algal biomass to produce bio-blendstock and then eventually test it on MCCI engine is the right and strong approach to take. Technically this project is good with right combination of experts running the project. This project aligns with BETO goals and objectives, by taking steps towards more bio-based compounds in the fuel. The successful completion of this project would help fuel industry to introduce the outcomes in commercial diesel production with bio-blendstock. It is observed that the team will aim for producing about 10 lt of algal biomass-based bio-blendstock. From an overall prospective it would be good to evaluate feasibility and economics of mass production of bio-blend bio-blendstock.	Thank you for this encouragement. By both incorporating LCA/TEA and engaging with Marathon Petroleum to explore refinery integration of algae, we are evaluating the feasibility and economics of this approach.
This project is focused on using algal feedstocks for bio-oil and subsequent fuel production. The composition of mixtures of algal species will be optimized for maximum production and combustion performance. This approach can reach a 60% reduction in greenhouse gas production, exceeding the requirements of the FOA. If successful, this project will contribute to the sustainable production of biofuels and to reduce pollution from combustion engines used for transportation.	Thank you for this encouragement.

Publications, Patents, Presentations, Awards, and Commercialization

Journal Articles:

- D.N. Carruthers, C.M. Goodwin, D.C. Hietala, B.J. Cardinale, X. N. Lin and P.E. Savage, “Biodiversity improves life cycle sustainability metrics in algal biofuel production,” *Environ. Sci. Technol.*, **53**, 9279–9288 (2019).
- (*in preparation*) Widin et al. Biodiversity does not enhance algal feedstock production when exposed to fungal infection: An experimental test in outdoor ponds using a before-after-control-impact (BACI) design. Target journal: *Environmental Science and Technology*.

Presentations:

- Dow Sustainability Program Distinguished Scholars and Faculty Dinner, “Toward sustainable transportation”. February 20, 2019.
- Chalmers University of Technology, Combustion Engine Research Center Annual Seminar, “Autoignition Characteristics of Alternative Fuels”. May 28, 2019.
- August 2020 ACS National Meeting, Symposium on *Chemistry of Fuel Properties, Combustion & Fuel-Engine Interactions*, “Tailored Bioblendstocks with Low Environmental Impact to Optimize MCCI Engines”

Task 2 HTL of Wet Algae to Biocrude

Examples of Biocrude Samples from Algae from the Demonstration Project

Monoculture

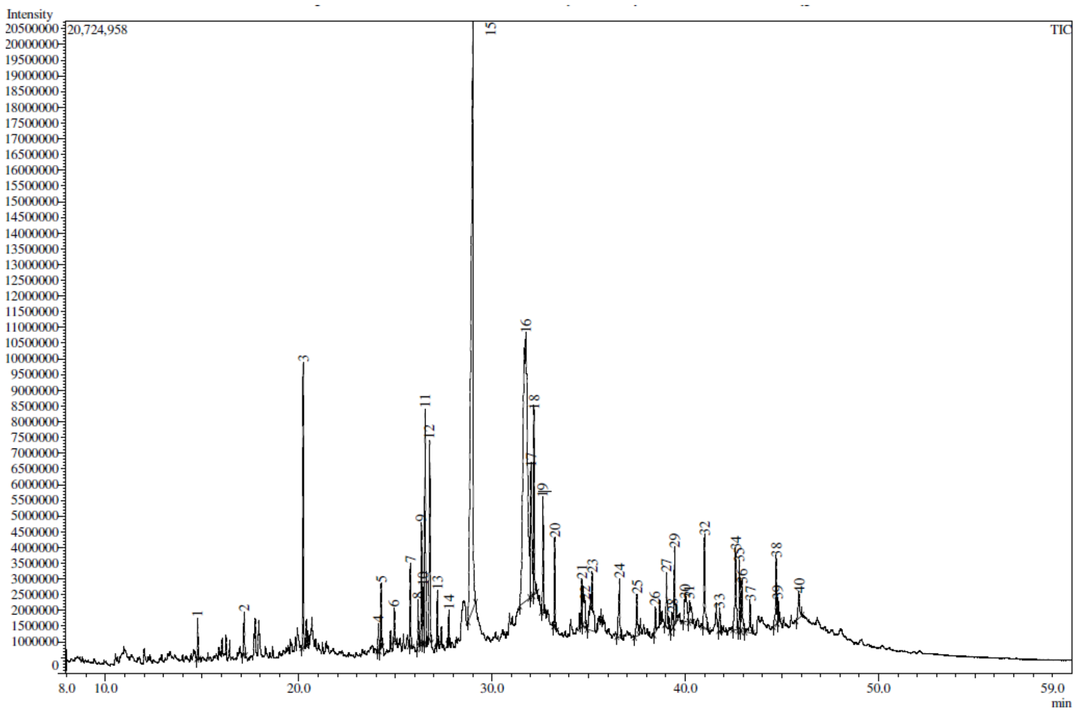


Figure 1. Total Ion Chromatogram of HTL biocrude from monoculture *S. capriconutum,* ran 10/28/19

Polyculture

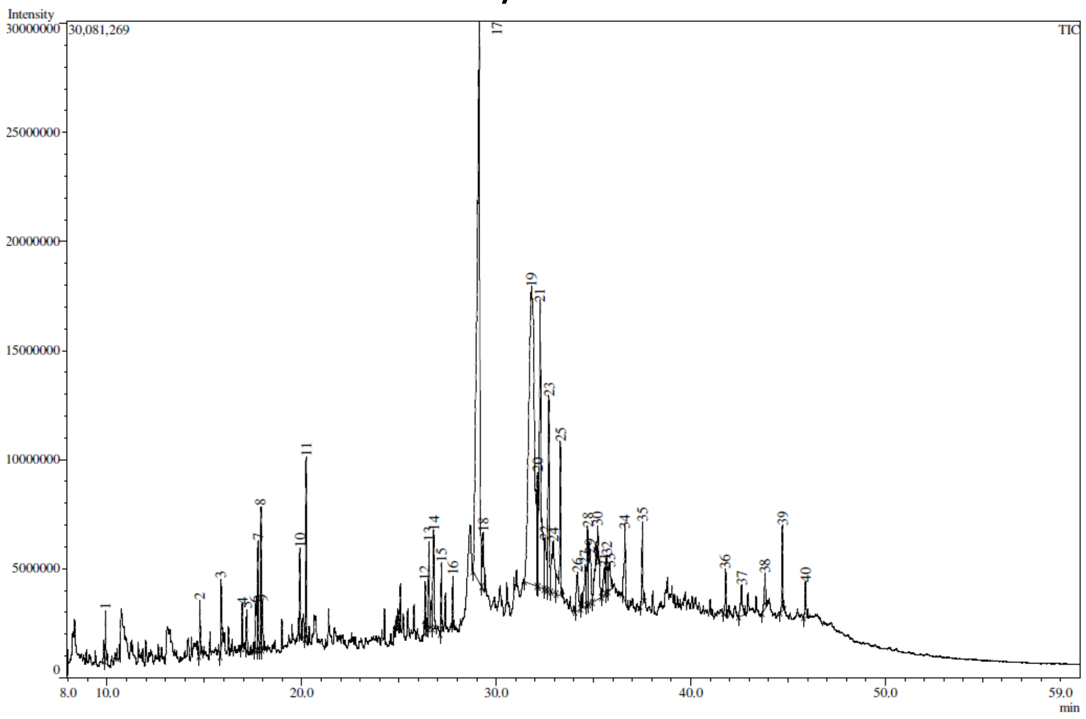


Figure 2. Total Ion Chromatogram of HTL biocrude from polyculture *S. capriconutum, C. sorokiniana, S. obliquus,* ran 10/28/19

Task 4 Biocrude Upgrading to Tailored Fuels

Studies of Hydrodeoxygenation of Major Components of the Biocrude

- Using oleic acid as the surrogate compound, and Ru/C as the catalysts under the above conditions, the resulting solid products were fully hydrogenated C14-C18 paraffin mixture without any trace of oleic acid. The degree of deoxygenation (DoD) of the reactant was 100%.
- The GC MS results showed 5 major products, and the type of compounds are summarized in Table 3. Over 77% of the solid portion of the product was *n*-heptadecane ($C_{17}H_{36}$).

Table 3. Summary of solid product for oleic acid conversion over Ru/C

Peak	RT (min)	Compound	Area %
1	10.619	Tetradecane ($C_{14}H_{30}$)	7.7
2	11.976	Pentadecane ($C_{15}H_{32}$)	9.5
3	12.594	Hexadecane ($C_{16}H_{34}$)	2.4
4	13.189	Heptadecane ($C_{17}H_{36}$)	77.2
5	13.735	Octadecane ($C_{18}H_{38}$)	3.1

Table 4. Summary of liquid product for oleic acid conversion over Ru/C

Peak	RT (min)	Compound	Area %
1	3.370	Pentanoic acid ($C_5H_{10}O_2$)	32.9
2	4.021	4-butoxy-2-butanone	21.8
3	4.266	Hexanoic acid ($C_6H_{12}O_2$)	25.9
4	4.516	2-tert-butoxyethanol	10.1
5	5.308	Heptanoic acid ($C_7H_{14}O_2$)	6.0
6	10.172	TBD	3.3

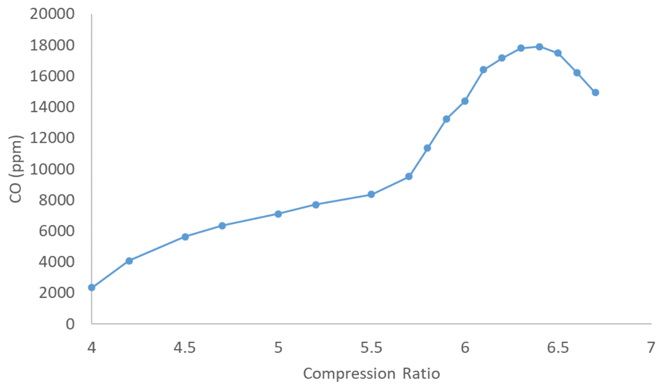
Task 5 Engine Studies and Simulation

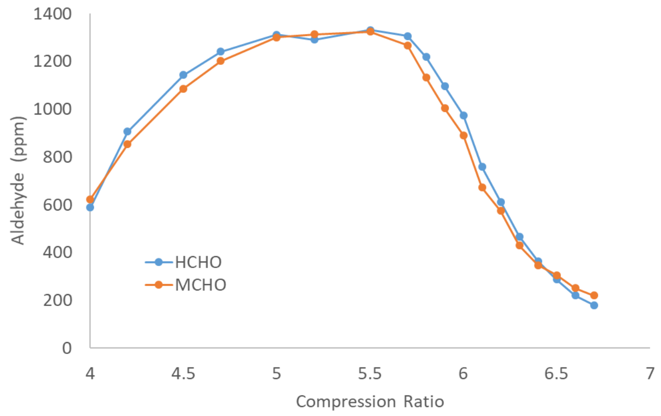
- Multizone simulations of *n*-cetane and other model algal blendstock components
- CFR engine experiments to determine critical ignition phenomena (CCR – critical compression ratio) and intermediate species
- Screening mechanisms to see which yield good predictions
- Then apply those mechanisms in MCCI simulations and work with Westbrook to improve mechanisms

Intake Temp 155C Phi=0.25	CCRs at intake pressures of 1 bar	
	n-cetane	n-heptane
Exp	6.50	6.80
C49	8.60	---
A66	---	6.80

Trends in CO emissions from modified CFR Octane Rating engine used to study critical ignition phenomena

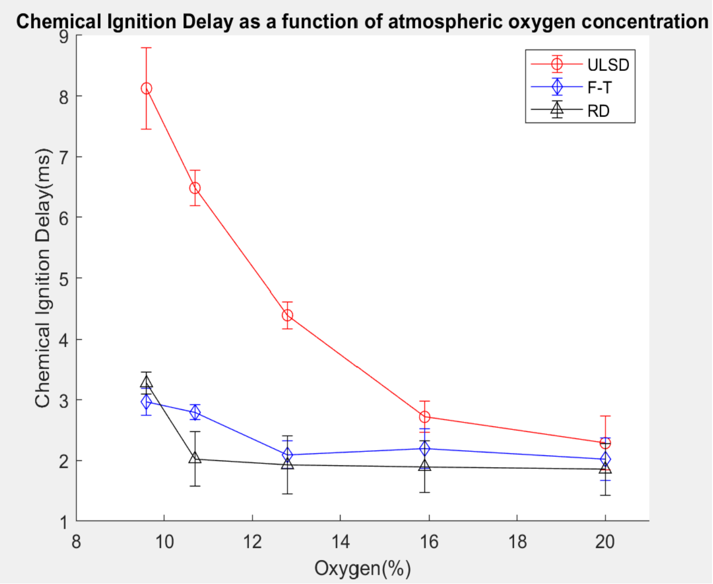
n-cetane, P_{int} = 1 bar, T_{int} = 155°C, ϕ = 0.25

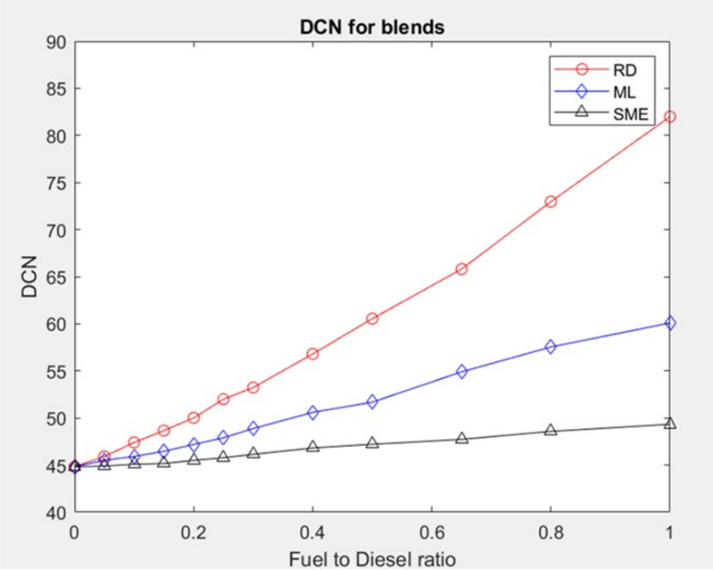




Task 5 Engine Studies and Simulation

- Key decision is whether to preserve oxygen functional groups or eliminate them
- Consensus seems to be that making “bio-hydrocarbons” from HTL biocrude is preferable
- Our preliminary fuel property studies support that approach





RD = camelina renewable diesel fuel
F-T = Fischer-Tropsch diesel fuel
SME = soy methyl ester
ML = methyl laurate

Ignition studies and derived cetane number measurements confirm value of seeking to make long-chain hydrocarbons, based on trial studies with “renewable diesel” fuel