bioprocessalgae
Valuing Carbon

Mixo-IBR BP1A Report

Report on Scale-up Efforts Based on
Data Collected During BP1A

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Summary

- The objective of the initial budget period was to determine whether BioProcess Algae (BPA) had all of the data, information, facilities, and agreements presented in its proposal response to DE-FOA-0000739. BPA was to demonstrate heterotrophic lipid production, demonstrate the production of fuels by metathesis of algal oils, and develop data to justify the scale-up effort proposed for the Pilot Mixotrophic Algae Integrated Biorefinery.

- Budget Period 1A activities supported assumptions in BPA's original application. Highlights include:
  - Successfully produced sufficient biomass and extracted oil for all planned activities
  - Achieved a cell density of 26 g/L with 63% oil content, compared to a target of 15 g/L and 60% for the Pilot Plant in the original application.
  - Achieved oil extraction efficiency of 84% compared to a 85% target for the Pilot Plant in the original application.
  - Catalyst usage in the metathesis process was 30-40ppm compared to 125ppm for previous algal oils and a target of 40-60ppm in the original application.
  - Successful evaluation of oils produced oils through hydrothermal liquefaction, which would eliminate the drying step (but may limit co-product opportunities). Conversion efficiency was as high as 71% of biomass to bio-oil for the high-lipid biomass.
  - Successful hydrotreating of various oil streams with yields of 86% or higher in all cases. Boiling points for all oil streams fell within targets for diesel but some may require further processing to meet drop-in fuel specifications.

- All budget period objectives were met. BPA produced the required biomass, extracted oils, and evaluated several options for oil extraction and conversion to fuels and/or fuel precursors during BP1A. BioProcess Algae used appropriate project management and reporting through the period, and all objectives were met on schedule and under budget.

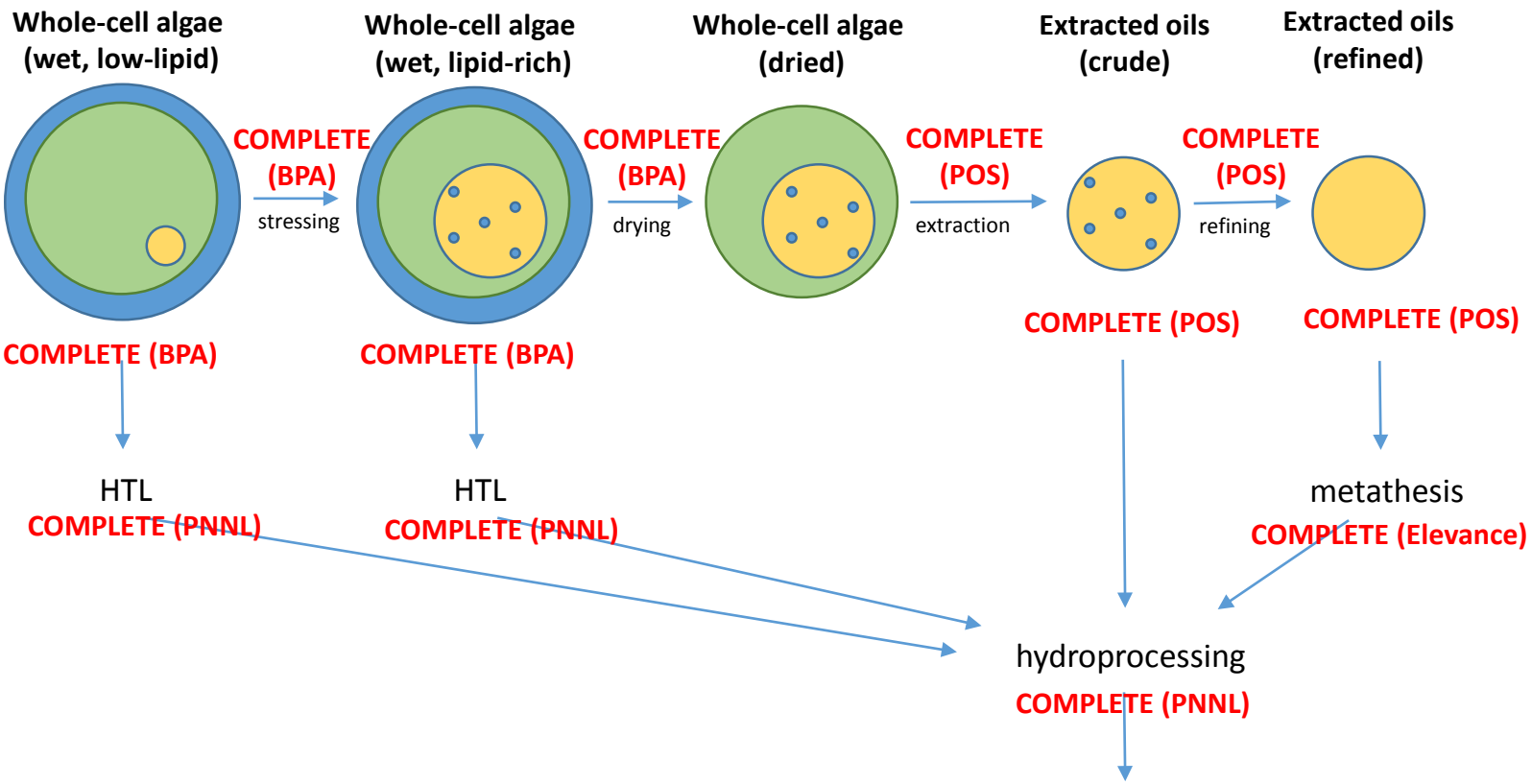
- The result of the go/no-go stage gate at the end of the validation period was a 'Go' decision by the Technical Project Officer and Contract Officer to proceed with the project.

- No funds were used for subsequent budget periods or any continuation of the project.

Project Objectives

- The overall objective of the initial budget period was to determine whether BioProcess Algae (BPA) had all of the data, information, facilities, and agreements presented in its proposal response to DE-FOA-0000739. Specific project objectives included:
  - Finalize Partnership Agreement: BioProcess Algae will finalize all agreements and the proposed scope, schedule, and budget for participating companies.
  - Develop Data for Scale-up: BioProcess Algae and its team will demonstrate heterotrophic lipid production, demonstrate the production of fuels by metathesis of algal oils, and develop data to justify the scale-up effort proposed for the Pilot Mixotrophic Algae Integrated Biorefinery. The effort will include:
    - Selecting an algal strain and identifying initial operating conditions to determine the baseline performance of heterotrophic lipid production that meets the lipid production targets for production of fuels for the metathesis process.
    - Producing kilogram quantities of heterotrophic lipids using the mixotrophic algal growth platform and extracting lipids for subsequent pretreatment and conversion testing.
    - Processing kilogram quantities of algal oil to evaluate pretreatment methods to determine the steps that will be needed for the metathesis process.
    - Producing kilogram quantities of fuels and/or fuel precursors from algal oil using the metathesis process.
  - Technical Project Officer and Independent Engineer (IE) Process Validation: BioProcess Algae will provide the Technical Project Officer, Project Monitor, DOE's Independent Engineer, and other experts DOE deems appropriate access to information, data, agreements, and facilities necessary to verify claims made by BioProcess Algae in its application to DE-FOA-0000739. The FOA states that a Go/No Go Critical Decision is required to approve the BioProcess Algae performance baseline.
  - Project Management and Reporting: The project team shall conduct effective project management including required meetings and communication of results.

Oil Production and Conversion Options Tested



Fuels (F-76, JP-5, JP-8) and/or fuel precursors

Biomass production

Biomass production:

- Autotrophically-grown algae from BPA's adjacent facility was used to inoculate a newly-installed fermenter in Jan 2014
- Achieved a cell density of 26 g/L with 63% oil content, compared to a target of 15 g/L and 60% for the Pilot Plant in the original application.
- Centrifuged pastes were sent to PNNL for hydrothermal liquefaction
- Dried biomas was sent to POS Biosciences for solvent extraction

Dry biomass sent for extraction to POS for oil extraction

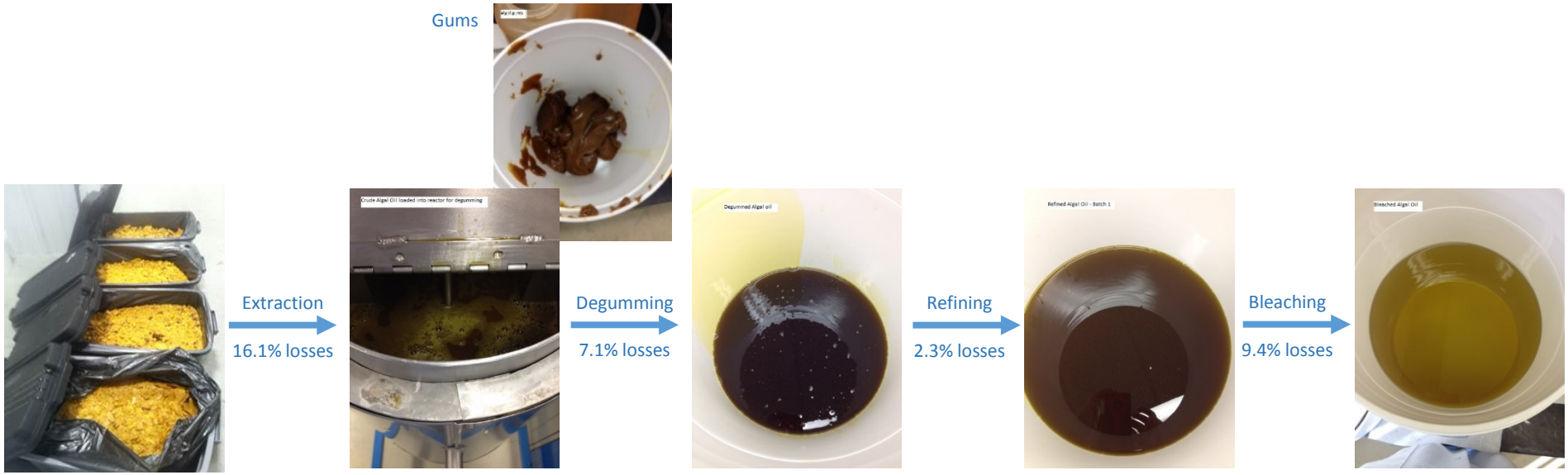
High lipid (top) and low lipid (bottom) wet biomass sent to PNNL for hydrothermal liquefaction

Fermenter Installation: Green Plains, November, 2013

Solvent-based Oil Extraction and Processing

Oil extraction:

- POS Biosciences extracted and refined oils from the dried biomass
- Extraction efficiency was very close to the target for the Pilot Plant (84% achieved compared to 85% target for the Pilot Plant)
- Losses in refining totaled 18.8%, but results from subsequent metathesis conversion suggested that the bleaching step may be able to be skipped, which would cut losses in half to 9.4%. Direct hydrotreating would not require any degumming or refining.



Notes on Refining Steps:

Degumming: Removes more polar compounds (eg polar lipids) as well as some metals through an acidification (to hydrate the gums) and washing step.
Refining: Primarily removes free fatty acids by forming soaps when the oils are neutralized with caustic.
Bleaching: To remove color and metals by adding chelating and bleaching agents. Residual soaps can also be removed in this step.

Bio-oil Production via Hydrothermal Liquefaction

- Hydrothermal liquefaction performed by PNNL
- Mass yield to bio-oil for high lipid was exceptionally high (71%), with low yield to aqueous phase
- Mass yield to bio-oil for low lipid was also good compared to previous results
- Much of this effort was published in *Algal Research*:
  - Albrecht, K., Y. Zhu, A. Schmidt, J. Billing, T. Hart, S. Jones, G. Maupin, R. Hallen, T. Ahrens, and D. Anderson. 2016. Impact of heterotrophically stressed algae for biofuel production via hydrothermal liquefaction and catalytic hydrotreating in continuous-flow reactors. *Algal Research*, 14: 17-27.

Mass Yields (Dry, Ash Free, Normalized)			
Parameter	Unit	High Lipid	Low Lipid
Mass Balance	%	99%	100%
Oil Yield, Mass (N)	g_{oil}/g_{fd}	**71%**	35%
Solid Yield, Mass (N)	g_{solid}/g_{fd}	1%	1%
Gas Yield, Mass (N)	g_{gas}/g_{fd}	4%	9%
Aq. Yield, Mass (N)	g_{aq}/g_{fd}	**25%**	55%

Bio-oil water separation with high lipid (left) and low lipid (right) BPA feed. Very clean separation achieved in both cases.

Metathesis Results (Elevance Renewable Sciences)

Metathesis Results:

- Used the BPA/POS solvent-extracted, refined algal oils as the feedstock

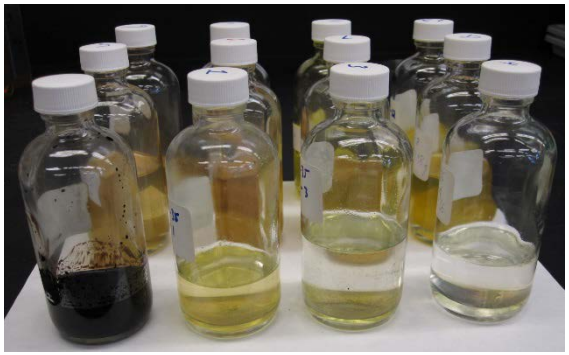
- Good agreement between actual and modelled results
  - Stripped product recovered 75.6% of the feed with very good agreement in profile with predicted results for C7 & above, indicating the yield loss was likely due to the loss of butene and hexene during depressurization and stripping. After accounting for these losses, the yield was close to 95.4%.

- Very good catalyst performance
  - Achieved the goal of ≤125ppm of catalyst, actual results were far better
  - Much better performance than previous algal oils
    - As received, the refined/bleached algal oil (before thermal and chemical pretreatment) performed at least 33% better than past best results with an algal oil after thermal and chemical pretreatment.
    - Thermal plus chemical pretreatment of the refined/bleached processed BPA algal oil further reduces the catalyst usage by more than 50%, which meets the target we had set for catalyst performance.
  - Could likely skip the bleaching step in the refining, which would reduce refining losses

Hydrotreating Results

- Hydrotreating performed by PNNL
- In general, good yields exceeding 86% for all four streams
- The low lipid HTL bio-oil consumed significantly more H_2 and produced more gas compared with either the high lipid HTL bio-oil or lipid extract.

	High Lipid HTL Bio-Oil	Low Lipid HTL Bio-oil	High Lipid Lipid Extract	Metathesized High Lipid Extract
LHSV, hr^{-1}	0.20	0.20	0.20	0.20
Mass Balance, %	104	109	105	101
Yield to Organic, (g/g dry feed)	**0.90**	**0.86**	**0.88**	**0.86**
Yield to Aqueous, (g/g dry feed)	0.12	0.11	0.13	0.10
Yield to gas, (g/g dry feed)	0.03	0.13	0.06	0.05
H_2 Consumption, g H_2/g dry feed	**0.026**	**0.051**	**0.030**	**0.026**
Organic Product Density @ 40°C, g/mL	0.7757	0.7747	0.7618	0.7303
Normalized Carbon Yield to Organic Product, %	97	92	94	95



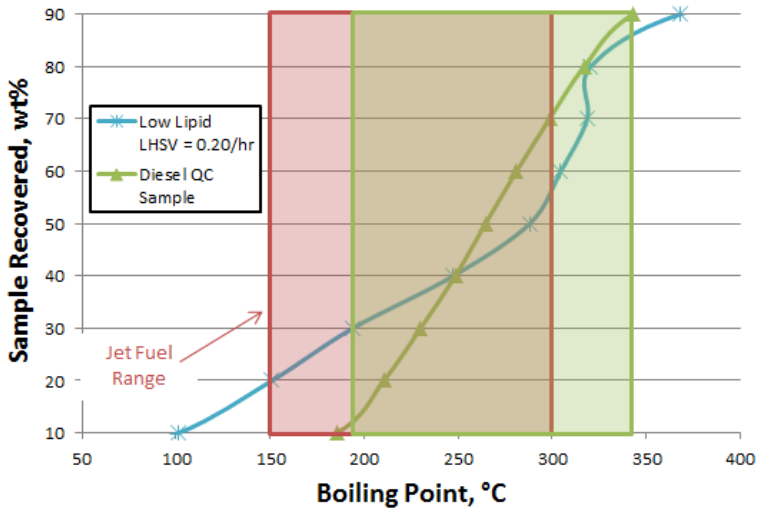
Upgraded HTL bio-oils

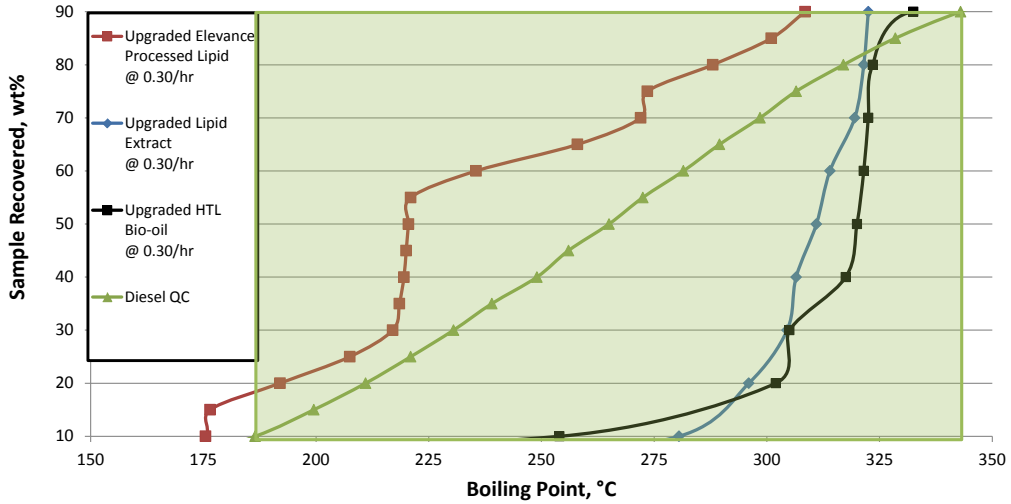
Upgraded extracted oils

Upgraded metathesized extract

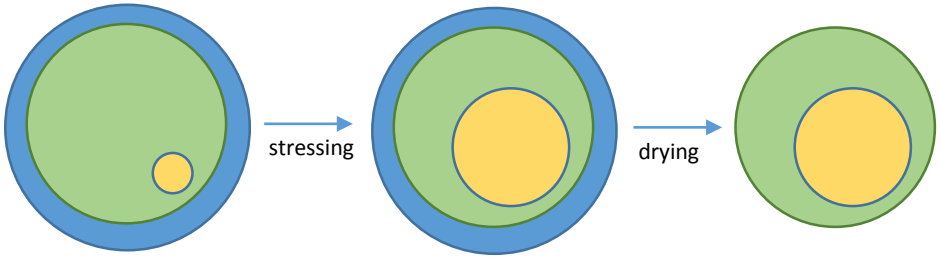
Upgraded Oil Analysis: SimDis of Organic Fraction

- Boiling points for all oil streams fell within targets for diesel. The low-lipid HTL bio-oil is shown on the top right and the other three oils are shown on the bottom right.
- Some products may require further processing to meet drop-in fuel specifications. For example, hydroisomerization to increase branching could improve cold flow properties (not measured) in the upgraded HTL bio-oil and upgraded lipid extract.





4 Fuel Conversion Options: Summary of Results



Whole-cell algae (wet, low-lipid)	Whole-cell algae (wet, lipid-rich)	Whole-cell algae (dried)	
1000 g algae	1000 g algae	1000 g algae	1000 g algae
HTL -65%	HTL -29% (B)	extraction -47%	extraction -47%
350 g bio-oil	710 g bio-oil	529 g crude oil	529 g crude oil
hydroprocessing -14% (A)	hydroprocessing -8% (C)	hydroprocessing -12%	degumming & refining -18.8% (E)
301 g jet & diesel	653 g diesel (D)	465 g diesel (D) + 470 g co-product	429 g refined oil
			metathesis -4.6% (F)
			409 g metathesized oil
			hydroprocessing -14%
			352 g diesel (G) + 470 g co-product

Fuels (F-76, JP-5, JP-8)

(A) Higher N has detrimental effect on catalyst lifetime
(B) Hydrogen consumption ~50% lower for high lipid feed compared to low lipid feed and would likely lead to a significant cost savings
(C) Higher O has detrimental effect on catalyst lifetime
(D) The upgraded material likely has an excellent (100+) cetane rating and by using the material as a blend stock 100% of the upgraded organic fraction could go into the diesel fuel and improve the value (i.e. overall cetane value) of the diesel blend
(E) Could likely skip the bleaching step in future runs, which would reduce losses to 9.4%
(F) Actual recovery of the stripped product resulted in a loss of 25.6%, but the match to modeled results for C7 and above implied that the loss of butene and hexene during stripping accounted for most of the difference. The 95.4% efficiency corrects for the butene and hexene that could be recycled.
(G) Increase to 393 g if bleaching step is removed

Conclusions

- All budget period objectives were met. BPA produced the required biomass, extracted oils, and evaluated several options for oil extraction and conversion to fuels and/or fuel precursors during BP1A. Data collected supported the original application as well as proposed scale-up efforts. The result of the go/no-go stage gate at the end of the validation period was a 'Go' decision by the Technical Project Officer and Contract Officer to proceed with the project. BioProcess Algae used appropriate project management and reporting through the period, and all objectives were met on schedule and under budget.

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- No funds were used for subsequent budget periods or any continuation of the project. BPA came to the conclusion that its award for the Pilot Mixo-IBR (DE-FOA-0000739) would not accelerate its commercialization efforts, and as a result, BPA requested to discontinue its financial assistance package (Award #EE0006245).

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