Hydrothermal Processing for Algal Based Biofuels and Co-Products 1.3.4.101

February 15, 2021
Advanced Algal Systems Program

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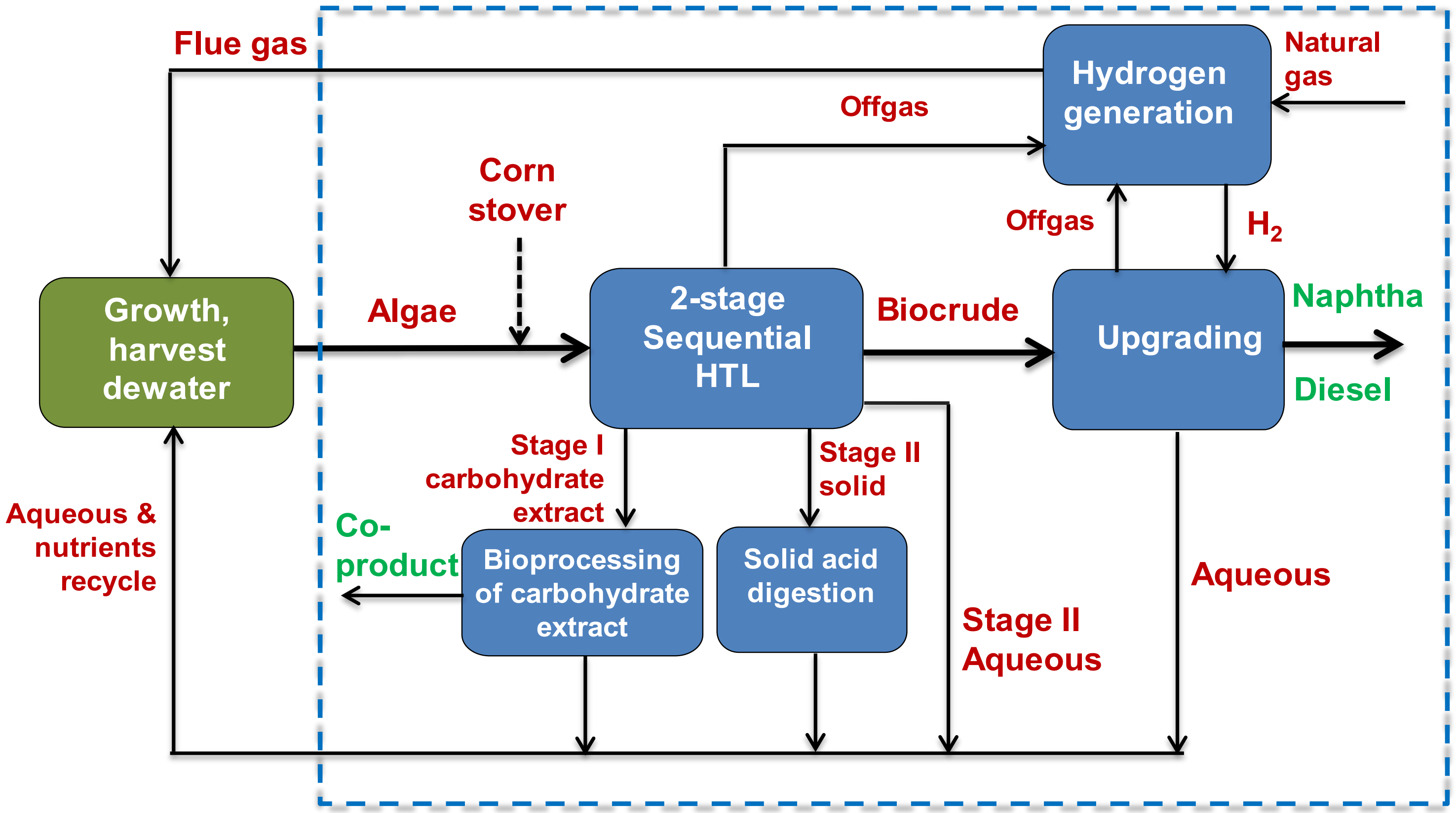
Pacific Northwest National Laboratory (PNNL)

PNNL is operated by Battelle for the U.S. Department of Energy

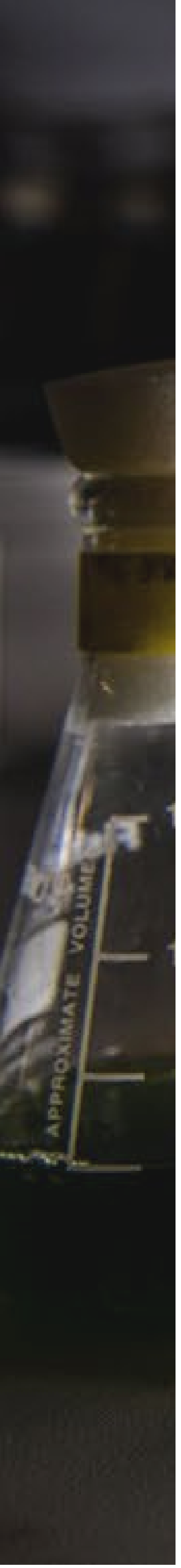
Project Overview

- New Start Annual Operating Plan (AOP) in Fiscal Fear (FY) 2020:
  - Builds on algae hydrothermal liquification (HTL) pathway to fuels (Peer Reviewed FY 2019)
  - Focused on **sequential hydrothermal liquefaction (SEQHTL)** processing to enable the **production of fuels and co-products**
- Developed SEQHTL processing and provided data for FY 2020 state of technology (SOT).
  - Reduced fuel costs by $0.50 to $4.48/ gasoline gallon equivalent (GGE).
  - Algae feedstocks account for 82% of production cost.
- Project has pivoted in FY 2021-2022.
  - Adapted SEQHTL process to low-cost waste algal feedstocks as recommended by the FY 2019 Peer Review Panel.



Sequential HTL with Co-Products

Directly supports Bioenergy Technologies Office (BETO) mission: “By 2030, deliver technologies that can enable the verification of technical performance of algae cultivation, harvesting, and conversion processes at engineering scale capable of converting algal feedstocks to biofuels and bioproducts in support of BETO’s goals for mature modeled minimum fuel selling price of $2.5/GGE for biofuels”



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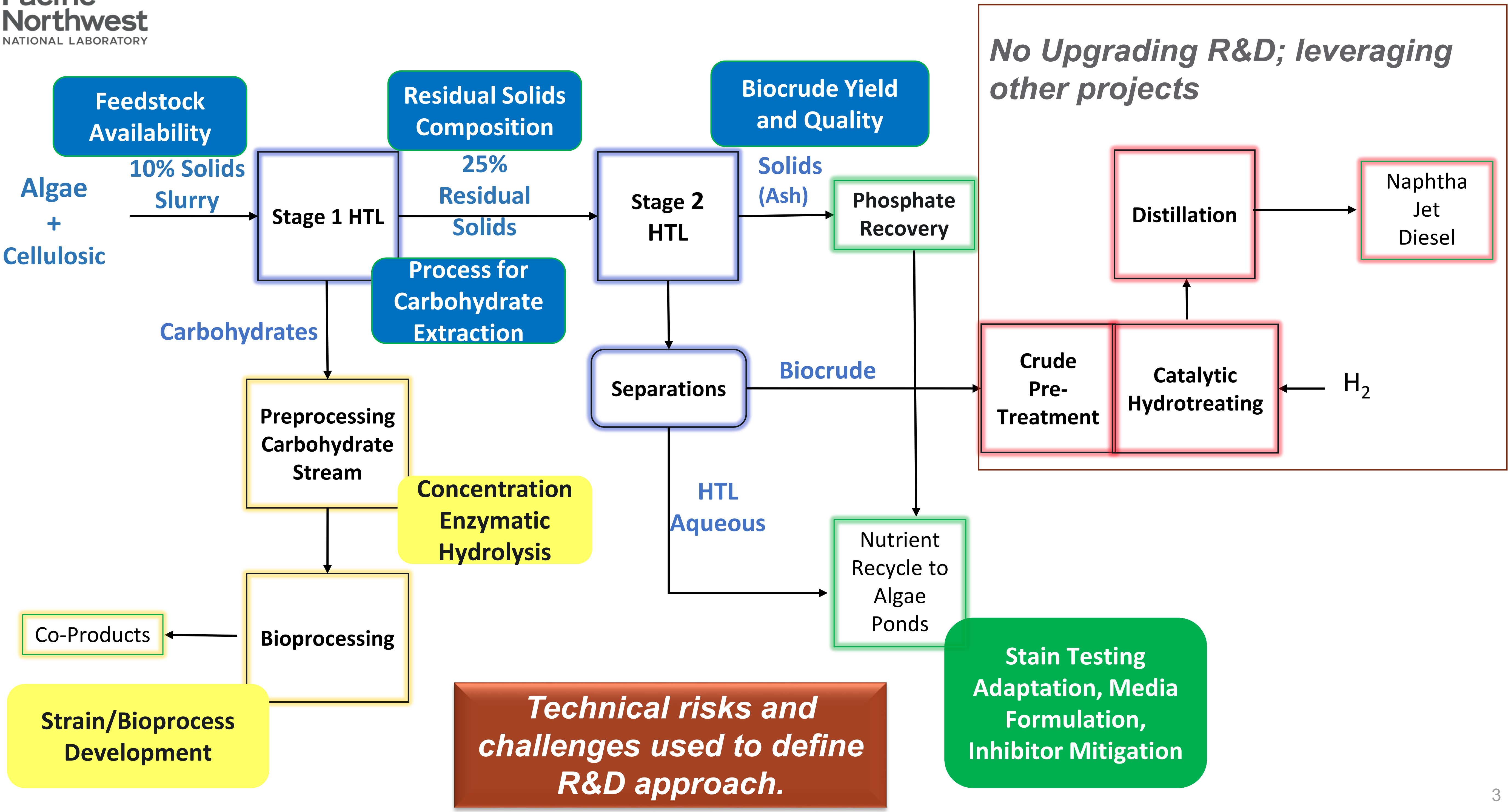
1 – Management Risk Mitigation



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1 – Management
Project Structure FY 2020

BETO Algae
Dan Fishman

BETO Algae DISCOVR Project
PNNL/Arizona State University
Michael Huesemann/ Arizona State University

Algae HTL Modeling
PNNL
Yunhua Zhu, Lesley Snowden-Swan

PNNL Hydrothermal Processing for Algal Based Biofuels and Co-Products
Dan Anderson, Principal Investigator /Project Manager

Sequential HTL

Stage 1: Batch Testing
Heather Job

Stage 1: Continuous Bench Testing
Andy Schmidt

Stage 2: Continuous Bench Testing
Andy Schmidt

Co-Products Production

Carbohydrate Preprocessing and Characterization
Jim Collett

Bioprocess Development
Jim Collett

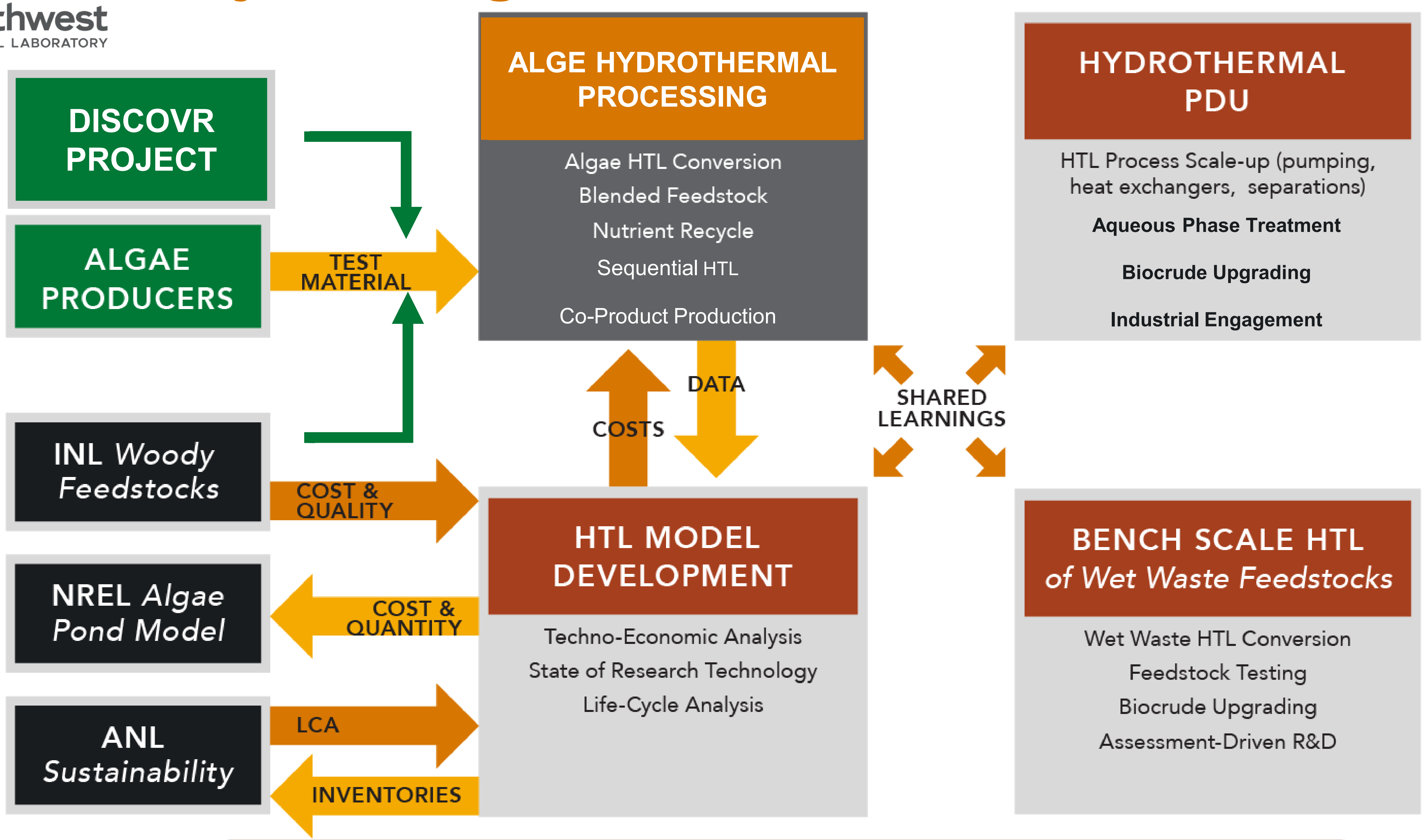
Nutrient and Carbon Recycling

Demonstrate HTL Nutrient Recycle with DISCOVR Strains
Scott Edmundson

Feedstock Production for Sequential HTL Testing
Scott Edmundson

Project structured to address technical risks and challenges.

1 – Management
Project Integration & Collaboration



Project is integrated with modeling and other related projects to promote communication and collaboration.

1 –Management Approach and Communication

- Detailed work breakdown structure (WBS) with experienced task leaders.
  - Well-defined scope/deliverables structured to address risk/challenges
  - Funding authorizations
- Defined AOP Milestones (1/Quarter) and Deliverables
  - Quarterly Reports
- Formal monthly project team/modeling team meetings
  - Review progress, schedule, and budget
  - Discuss issues, risks, mitigation plans, and task integration
- Informal weekly discussions at task level
- Regular Meetings with BETO (technical and progress updates)
- Management and integration of supporting projects and partners

► ***Integrated Project Team***
► ***Strong Project Management***
► ***Experienced Task Leaders***
► ***Structured Plan and Communications***

2 – Approach
FY 2020 Technical Objectives

Tasks	Risk/Challenges	Technical Objectives
Sequential HTL Processing	**Developing HTL Stage 1 Carbohydrate Extraction**	Optimize process conditions for carbohydrate extraction **(ML)**
		Evaluate effect of processing blended feedstocks (algae + stover)
	Verifying HTL Stage 2 Biocrude Production	Maximize residul solids and composition from Stage 1
		Optimize process conditions for biocrude yield **(ML)**
		Determine biocrude composition for upgrading and fuel quality
Co-product Production	**Pre-processing of Carbohydrate Extract to Enable Bioconversion**	Concentration of carbohydrate stream
		Carbohydrate hydrolysis to fermentable sugars
	Developing a Bioprocess to Produce Co-products	Strain development and screening
		Bioprocess development for co-product production **(ML)**
Nutrient Recycle	**Recycle and Reuse HTL Waste Streams for Algae Cultivation**	Validate HTL aqueous recycle to support DISCOVR strains
		HTL filter solids reuse (P and other minerals)
		Confirm sustainable cultivation of DISCOVR strains **(ML)**
Provide Process Data	**Developing Targeted Comprehensive Data Sets**	Provide mass balance data for each segment to modeling team **(ML)**
		SOT Updates/Pathway Options Analysis
		Adjust R&D Focus

Approach is focused on addressing key challenges with defined objectives and milestones (ML).

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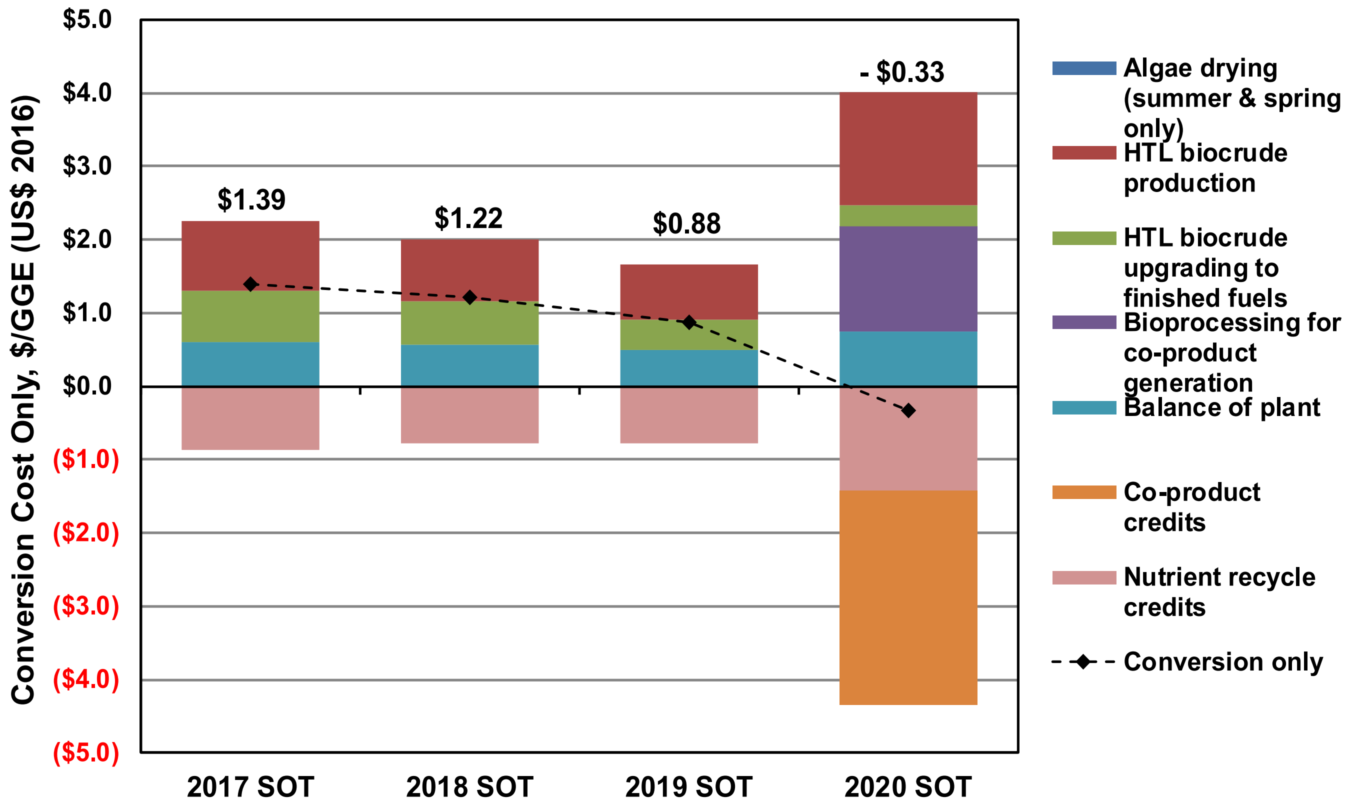
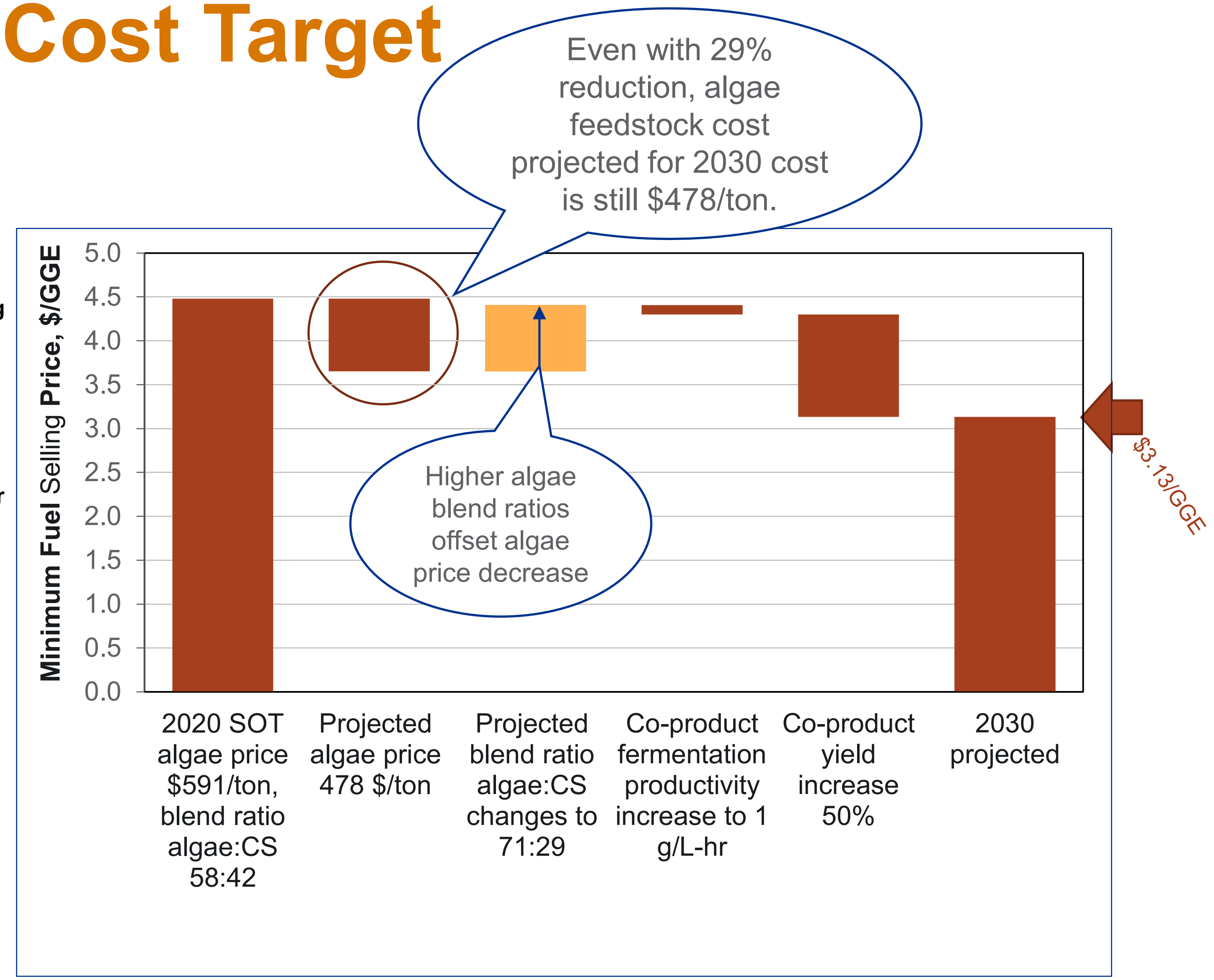
2 – Approach
Assumptions and Technical Targets

Assumption	Achieved	Target
Algae/Corn Stover Blend Stocks	50:50 Blend	50:50 Blend
Stage 1 HTL Plug Flow Reactor (PFR) Carbohydrate Extraction	65%	60%
Stage 2 HTL Biocrude Yield	50%	57%
Carbohydrate Conversion to Co-products	LA yield: 0.37 g/g total carbohydrates	LA yield: 0.55 g/g total carbohydrates
HTL Nutrient Recycle	3 DISCOVR Strains Same productivity as defined media	3 DISCOVR Strains Same productivity as defined media

Project is retiring assumptions and technological uncertainty for scale-up and commercialization.

3 – Impact
Enabling DOE Biofuel Cost Target





- ***Fuel conversion cost reduced from $0.88/GGE in FY 2019 to $-0.33/GGE in FY 2020.***
- ***Projected improvements in key cost factors still do not meet the BETO’s $2.5/GGE 2030 goal.***
- ***Shifting to lower cost algae feedstocks provides major impact (e.g., eutrophic algae <$100/ton vs. $478/ton).***

3 – Impact
Technology Transfer

- Project has developed **HTL technology** that is being **leveraged** for other **wet waste feedstocks,** providing **environmental solutions** in addition to **biofuel and co-products.**
- Project has led the way in demonstration of full nutrient recycle.
- Project has led to several **collaborative competitive projects** with U.S Department of Energy (DOE).
- Project has led to several **industrial collaborations** and projects.
- Project has resulted more than **20 publications** and **20 presentations.**
- Project has supported the development of **several patents.**
- Technology was awarded the **2015 FLC technology transfer excellence award** and the **2015 R&D 100 Award** “Hydrothermal Processing to Convert Wet Biomass into Biofuels.”

Project is providing impact for DOE, research community, and technology commercialization.

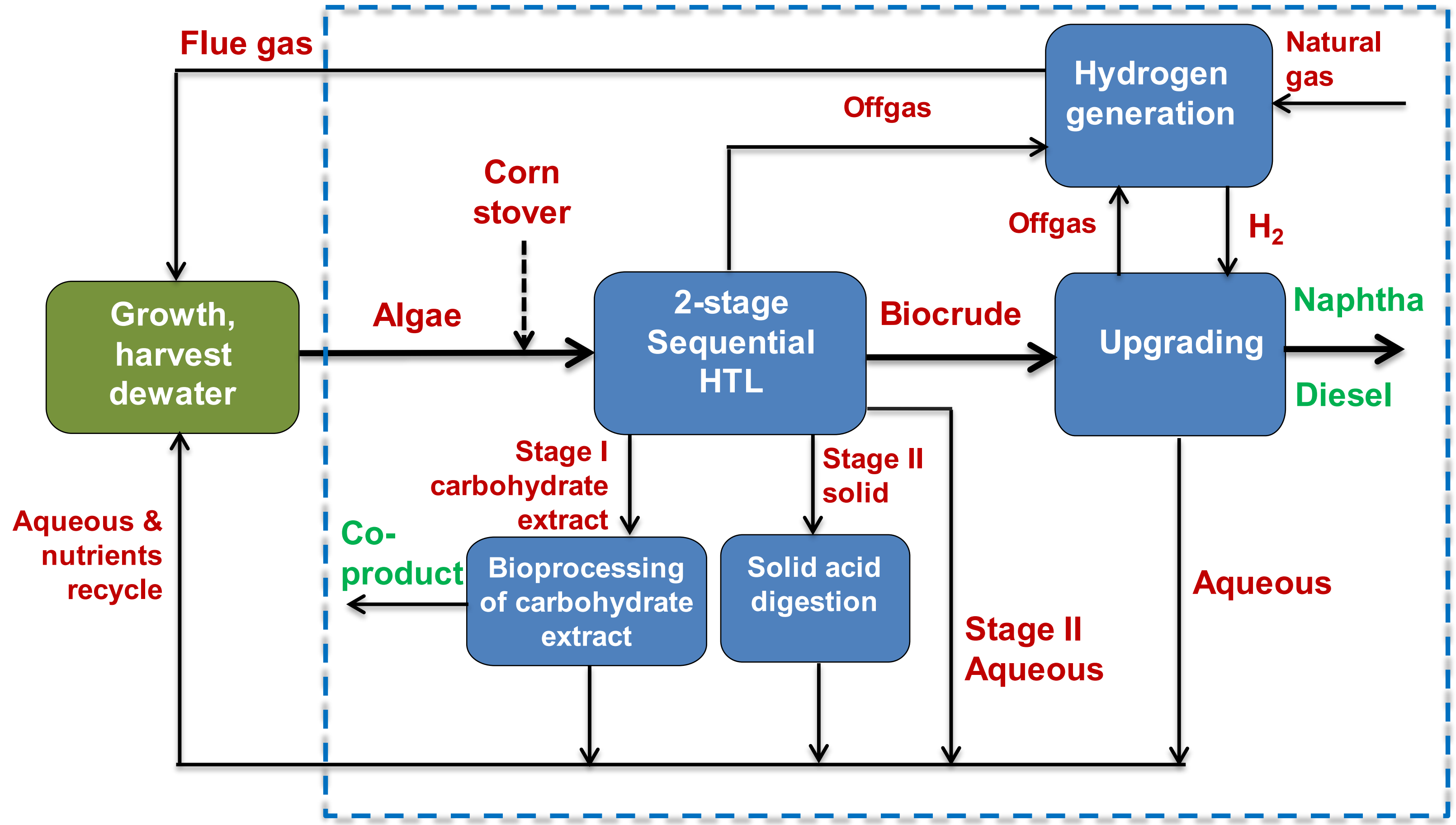
4 – Progress and Outcomes
SEQHTL and Co-Products included in FY 2020 SOT

FY 2020 Milestone

Complete and deliver data packages on hydrothermal processing of corn stover: DISCOVR algae feedstock blend to fuel blend stocks.

- **Processing experiments were completed and data packages were delivered to modeling team.**
  - Stage 1 HTL process conditions/mass balances
  - Stage 2 HTL process conditions/mass balances
  - Co-product bioprocessing conditions/mass balances
  - HTL nutrient recycle

SEQHTL, Bioprocessing and, Nutrient Recycle Process Data Developed



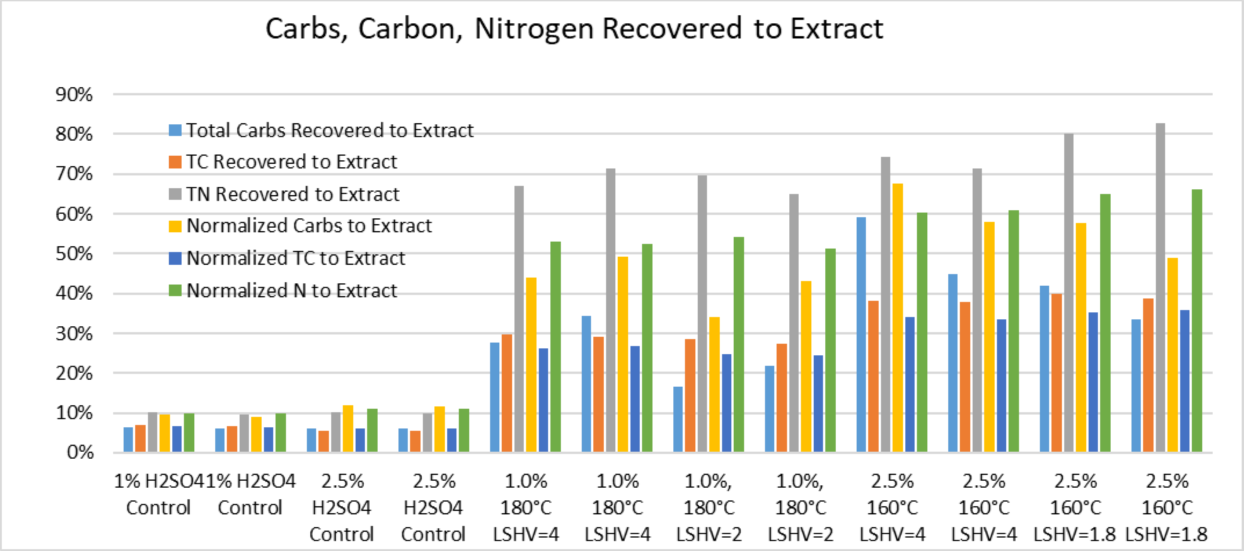
- Low temperature 1st stage combined with acid addition produces a carbohydrate-rich aqueous phase with high concentrations of simple sugars that can be used to produce co-products.
- High temperature 2nd stage processes 1st stage solids into biocrude that is upgraded to fuel.
- HTL waste streams used for nutrient recycle.

4 – Progress and Outcomes Sequential HTL Stage 1 Testing

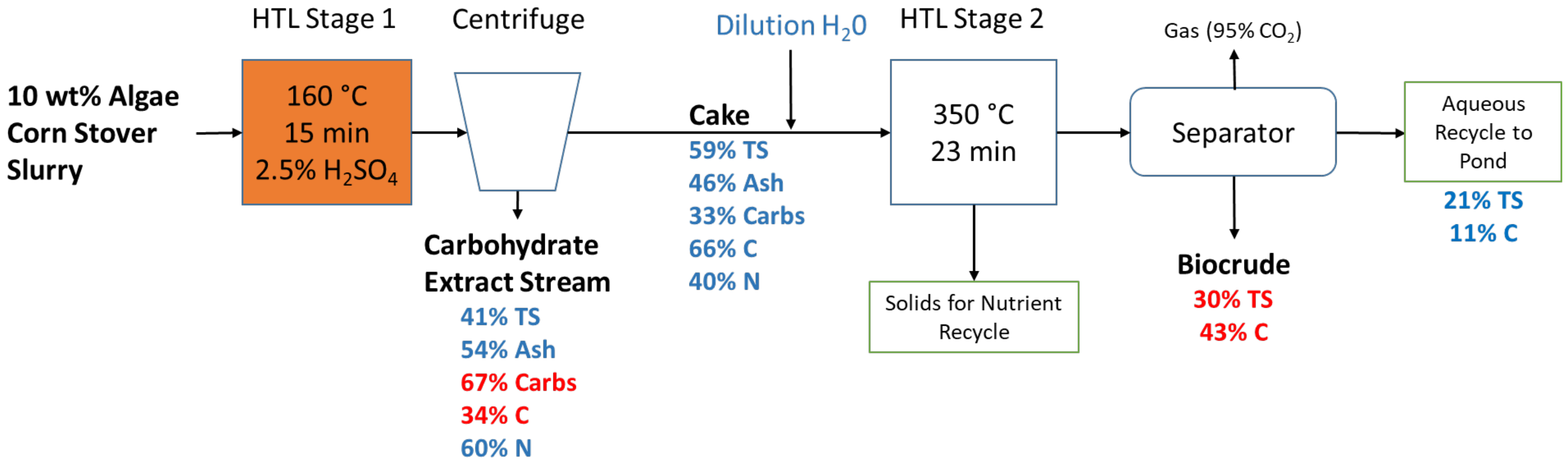
FY 2020 Milestone

Complete the integrated sequential HTL test (Stage 1 and Stage 2), processing greater than 80-L of corn stover/algae blend in Stage 1 at best stage 1 conditions and processing the residual in Stage 2.

- **Processed greater than 80-L of corn stover/algae blend in Stage 1** at best stage 1 conditions and processing the residual in Stage 2.
- Continuous flow Stage 1 HTL was successfully **transitioned** from a continuous stirred tank reactor **to a PFR**.
- Algal biomass was **DISCOVR algae strain** (Acutodesmus obliquus UTEX393).
- **Carbohydrate extract** from the Stage 1 testing was **provided for co-product fermentation to produce a product (lactic acid).**



Demonstrated >65% carbohydrate extraction in Stage 1 PFR process.



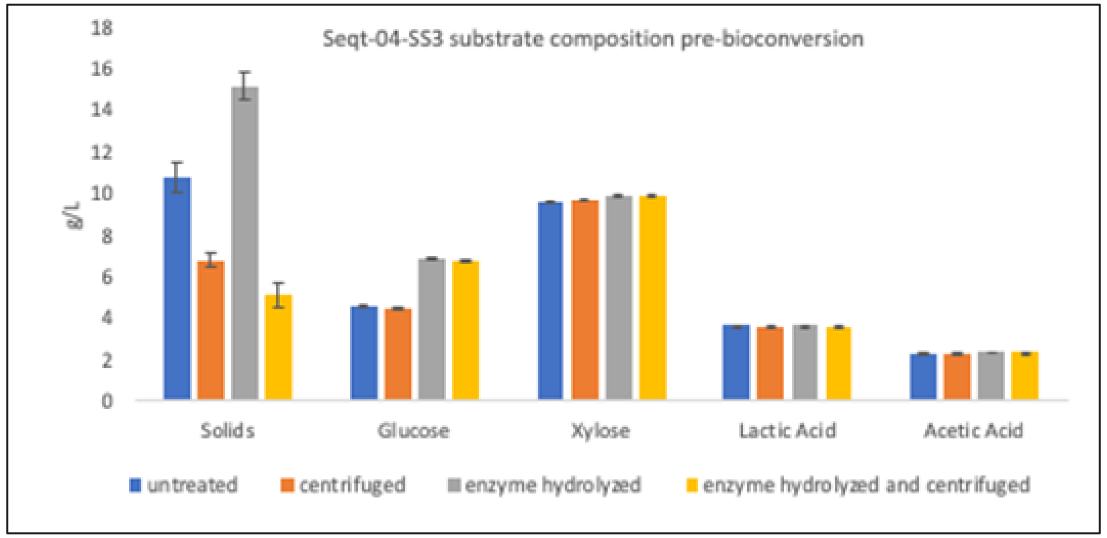
4 – Progress and Outcomes
Bioconversion of Carbohydrate Stream

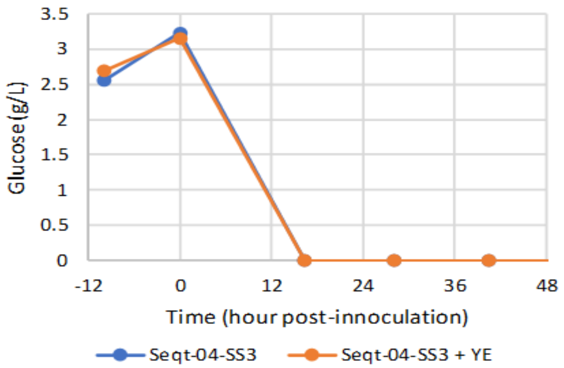
FY 2020 Milestone

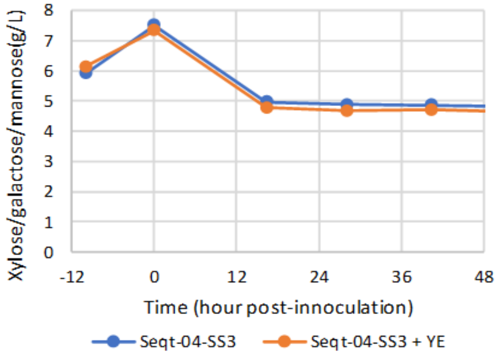
Quantify the production of a co-product from 1st stage HTL carbohydrate extract from a feedstock blend of algae and corn stover.

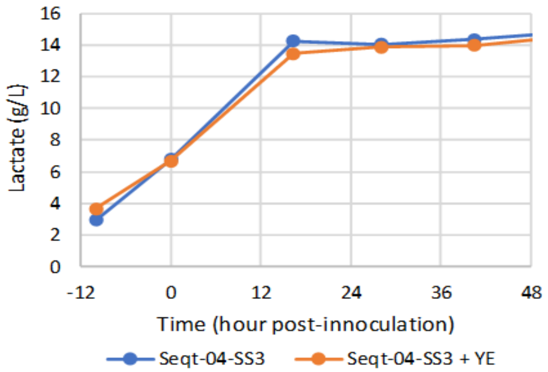
- **An initial bioprocessing study was completed.**
- Stage 1 carbohydrate extract was concentrated by evaporation.
- Concentrated extract was treated by enzymatic hydrolysis to release sugar monomers.
- ***Lactobacillus pentosus*** **and** ***Lactobacillus rhamnosus*** **were tested for direct conversion of carbohydrate extract to lactic acid in bioreactors.**
- Glucose was rapidly converted to lactic acid. Conversion of xylose, galactose, and mannose was incomplete and produced acetic acid as a side product.
- Additional bioprocess development will be required for optimization.

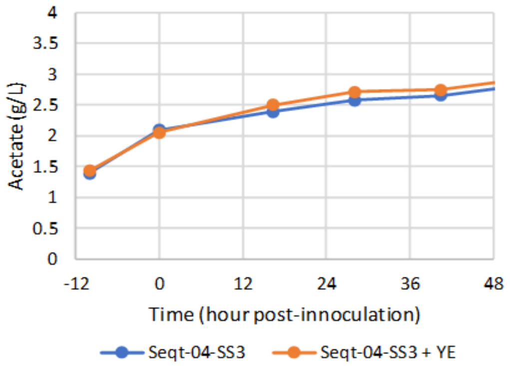
Demonstrated lactic acid co-product production from SEQHTL.











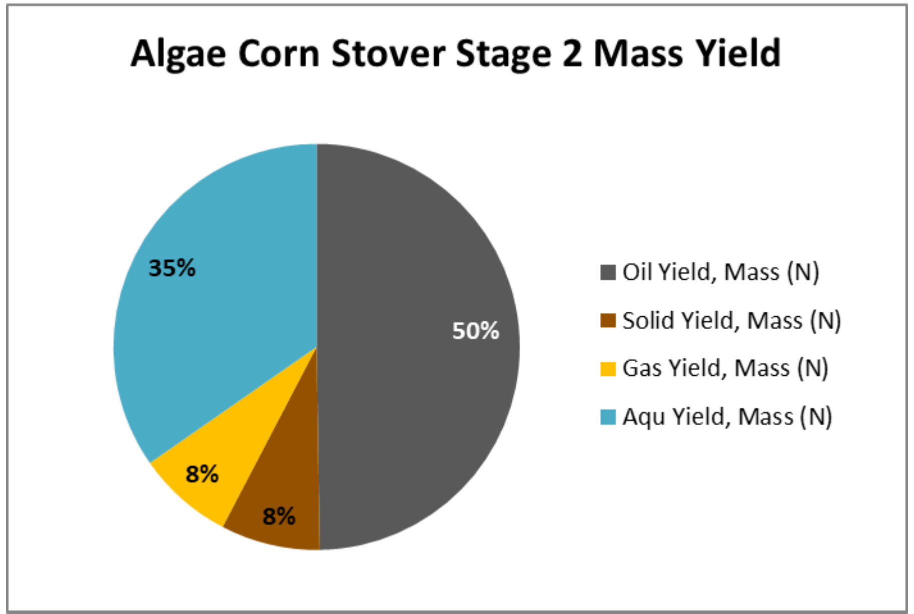
4 – Progress and Outcome SEQHTL Stage 2 Processing

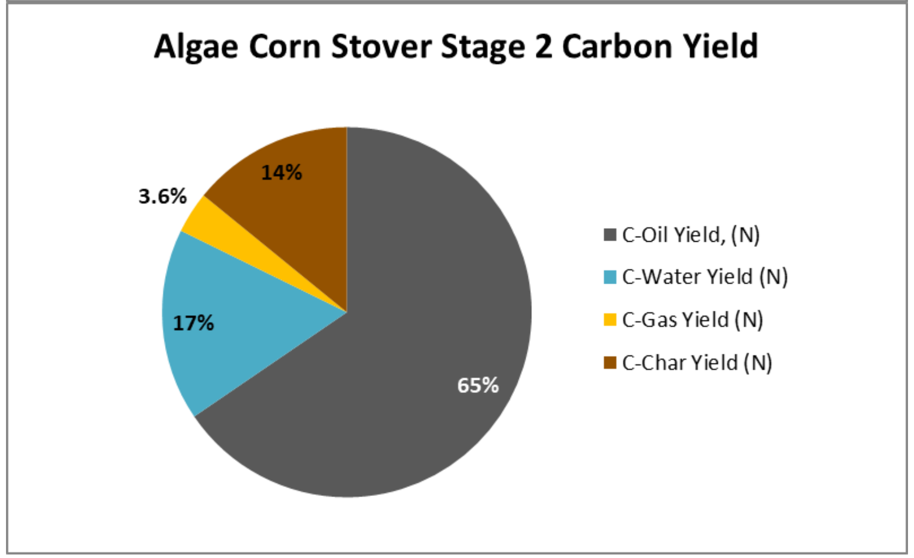
FY 2020 Milestone

Complete the integrated SEQHTL test (Stage 1 and Stage 2) processing. Meet SEQHT technical target of 50% biocrude yield from Stage 2 HTL processing of residual solids.

- Continuous Stage 2 HTL processing was conducted using Stage 1 residual solids.
- Process conditions were 3000 psia, 350^{o}C, LHSV 4/
- **Target biocrude yield of 50% (around 2nd Stage) was demonstrated.**
- HTL aqueous phase and ash solids provided for nutrient recycle evaluation.

Demonstrated 50% biocrude mass yield for Stage 2 SEQHTL processing of residual solids.





Stage 2 HTL Product Yields
Algae/corn stover (50/50)

4 – Progress and Outcomes HTL Nutrient Recycle with DISCOVR Strains

FY 2020 Milestone

Demonstrate that 3 DISCOVR algal strains can be grown in recycled media derived from HTL wastewaters without reduced productivity.

- Completed screening DISCOVR strains in photobiorectors. **Eight strains showed strong growth in HTL derived media.**
- Recycle of HTL aqueous phase from a wood: algae blend stock had an inhibitory effect. **Inhibitory impacts were mitigated by simple filtration of char particles and micronutrient addition.**

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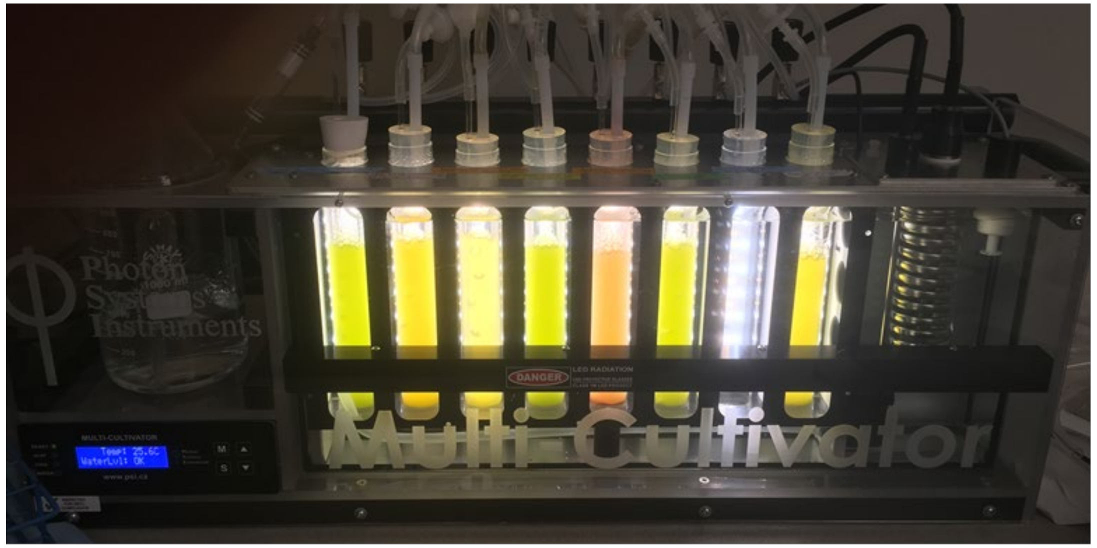

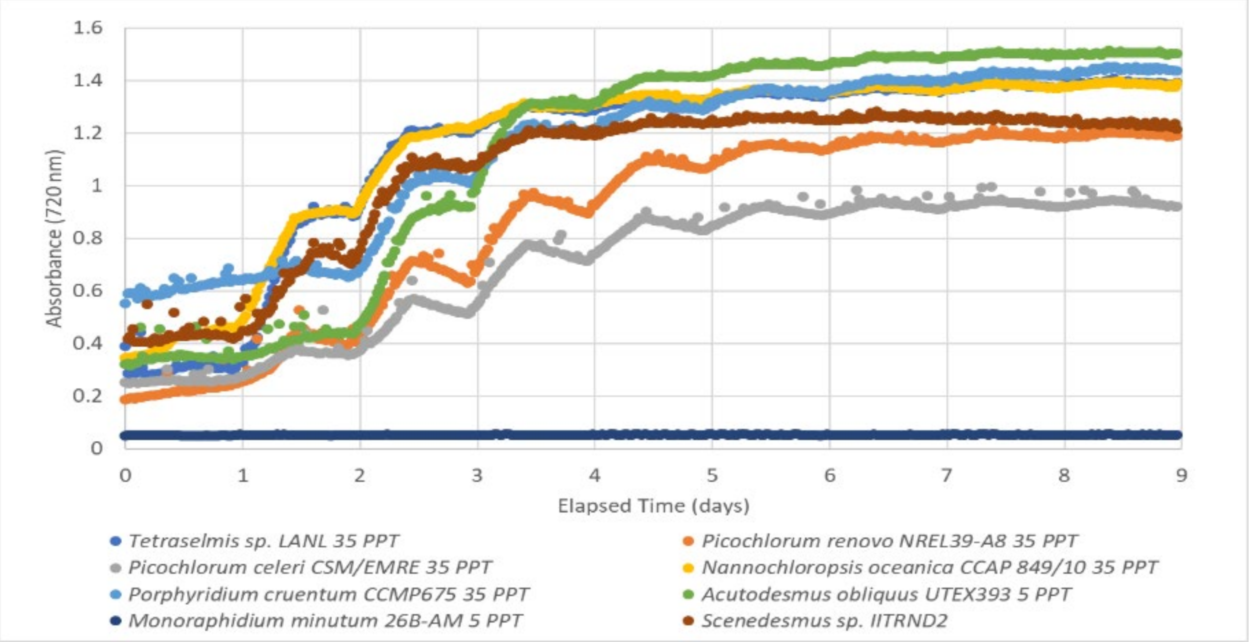

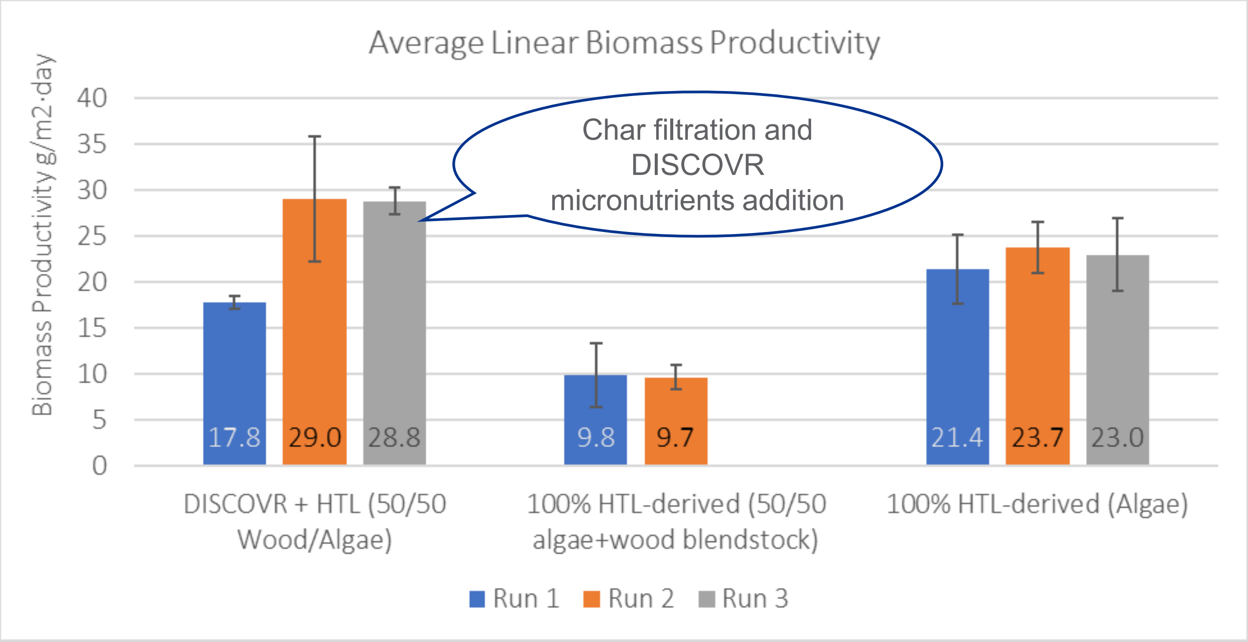

Demonstrated nutrient recycle using SEQHTL derived media with DISCOVR strains.

FY 2021 – 2022 Project Pivot

Objective: Adapt SEQHTL to low-cost algae feedstocks

Management: Same Team, New Risks, and New WBS

- New Risks and Challenges
  - High ash, dirt, and moisture content
  - Slurry prep and separations challenging
  - High carbohydrate/low lipid
  - Harvesting and transport costs may be significant

Approach: Revised R&D Plan

- Task 1 - Selection and Sourcing of Target Algae Feedstocks for Characterization and Testing
  - (coastal kelp farms, turf-scrubber remediation projects, tertiary wastewater treatment, etc.)
- Task 2 - Develop Processing Scenarios and Experimental Plan for Macroalgae and Scrubber Algae Feedstocks
  - (thermal hydrolysis below 200 °C to hydrothermal carbonization, HTL, SEQHTL, and co-product production
- Task 3 - Hydrothermal Process Development for Targeted Algae Feedstocks
- Task 4 - Provide Process Data for Modeling/Techno-Economic Analysis (TEA) to Focus R&D on the Most Promising Pathways

Impacts: Process economics, environmental benefits, and technology adoption

Progress: Task 1 and 2 underway (Q2 MLs); Task 3 beginning in Q3

Objectives

- ***Demonstrate hydrothermal processing methods for low-cost, high ash algae feedstocks.***
- ***Evaluate co-product product options and biocrude production.***
- ***Provide process data to modeling team for conducting TEA.***
- ***Go/No-Go 9/30/22***

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Acknowledgements

- Daniel Fishman – BETO Technology Manager
- Project Team
    - Dan Anderson
    - Andy Schmidt
    - Justin Billing
    - Sam Fox
    - Todd Hart
    - Rich Hallen
    - Scott Edmundson
    - Heather Job
    - Lesley Snowden-Swan
    - Yunhua Zhu
    - Kyle Pomraning
    - Jim Collett

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Summary

1 - Management

- Project WBS structured to address technical risks and challenges
- Integrated project team with strong project management, experienced task leaders, and structured communications

2 - Approach

- Based on key risks and technical challenges
- Clear R&D objectives and milestones

3 - Impact

- Developed fully-integrated SEQHTL process to produce fuel and co-products
  - ✓ Potential to meet BETO FY 2030 goal of $2.50/GGE
  - ✓ Potential to be adapted to low-cost algae feedstocks and other wet wastes
- Publications, presentations, awards, and collaborations

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Summary

4 - Progress and Outcomes

- SEQHTL, bioprocessing, and nutrient recycle process data developed
- Demonstrated >65% carbohydrate extraction in Stage 1 PFR process
- Demonstrated lactic acid co-product production from SEQHTL
- Demonstrated 50% biocrude mass yield for Stage 2 SEQHTL processing of residual solids
- Demonstrated nutrient recycle using SEQHTL derived media with DISCOVR strains
- Provided process data for modeling/TEA and SOT
- Pivoted direction in FY 2021 – 2022 to focus on SEQHTL processing of low-cost algae

Quad Chart Overview

Hydrothermal Processing for Algal Based Biofuels and Co-Products 1.3.4.101

Timeline

- 10/1/2019
- 9/30/2022

	FY20	Active Project
DOE Funding	(10/01/2019 – 9/30/2020) *$525,000*	(negotiated total federal share over active project) *$1,575,000*

Related/Leveraged Projects

- 1.3.5.202 HTL Model Development
- 1.3.2.501 Algae DISCOVR Project
- 2.2.2.301 PNNL Hydrothermal Process Development Units

Barriers Addressed

Aft-H. Overall Integration and Scale-Up

Process integration (HTL, Upgrading, Recycle), TEA; Engr. Scale HTP system being tested

Aft-J. Resource Recapture and Recycle

Aggressively demonstrating reuse of HTL byproduct stream

Project Goal

Develop/adapt hydrothermal process technology to enable the commercialization of algal-based biofuels and co-products from lower-cost algae feedstocks derived from nutrient remediation in wastewater treatment and marine macroalgal farms.

End of Project ML

Provide conversion pathways and associated data for processing two low-cost algae feedstocks to the PNNL HTL Model Development project (WBS 1.3.1.202) for completion of a new design case or the FY 2022 SOT for HTL of a down-selected, low-cost algae feedstock.

Funding Mechanism

Lab Call 2019

Additional Slides

Responses to Previous Reviewers' Comments
2019 Peer Review Report

Reviewers' Comments	PNNL Response
This project demonstrates further progress in optimizing hydrothermal liquefaction (HTL) process technology with the goal of meeting the BETO liquid biofuel cost target. Results achieved over this review period have shown how increases in feed solids loading for biocrude production and pre-treatment and an improved catalyst for upgrading are helping to drive down the overall cost towards the BETO goal. PNNL staff have continued to investigate methods of improvement to the HTL process from many angles, as shown by the results of blending tests and nutrient recycle tests. While it is understood that the HTL algae work has laid the groundwork for subsequent tests with real wet wastes (e.g., sludge), the algae used in these tests are not waste and therefore this project may not really belong in this group (though this is a BETO decision). However, eutrophic algae would qualify as a waste and its negative feedstock cost would further help meet the BETO biofuel cost target, so it should be considered as a future feedstock. The only major concern with the work shown is the apparent disconnect in the modeling cost results between that shown in this project and in the formal TEA modeling project (2.1.0.301), also performed by PNNL staff. Future modeling work in any of the PNNL HTL projects should all be performed on the same basis with the same cost categories to avoid confusion.	We thank the reviewers for their thoughtful comments. This project is part of the Algae Program at BETO specifically focused to develop an HTL conversion pathway for algal biomass to produce biofuels. BETO decided to conduct the peer review of this Algae Program project as part of the Waste to Energy Program and this resulted in some confusion for Waste to Energy reviewers. On the positive side we were able to show the reviewers how this algae HTL project had laid the technical groundwork for establishing the HTL conversion and Modeling projects focused on wet wastes. However, there was disconnect with algae project and its relationship to the wet waste process/TEA since the associated Algae HTL Process Model project was reviewed in the Algae program session. This project has a direct connection with HTL Algae Model/TEA project from the very beginning, but it was not presented to the reviewers. So, there is direct connection between the Algae HTL Conversion project and the Algae HTL Modeling effort as the reviewers suggest. We do agree that focusing on eutrophic algae as a potential negative cost feedstock makes sense and we are pursuing project opportunities in that area.

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Recent Publications

- Zhu Y, SB Jones, AJ Schmidt, KO Albrecht, SJ Edmundson, and DB Anderson. 2019. "Techno-economic analysis of alternative aqueous phase treatment methods for microalgae hydrothermal liquefaction and biocrude upgrading system." *Algal Research* 39:101467.
- Zhu Y, SB Jones, AJ Schmidt, JM Billing, MR Thorson, DM Santosa, RT Hallen, and DB Anderson. 2020a. "Algae/Wood Blends Hydrothermal Liquefaction and Upgrading: 2019 State of Technology." PNNL-29861. Pacific Northwest National Laboratory, Richland, WA.
- Zhu Y, SB Jones, AJ Schmidt, JM Billing, DM Santosa, and DB Anderson. 2020b. "Economic impacts of feeding microalgae/wood blends to hydrothermal liquefaction and upgrading systems." *Algal Research* 51:102053.

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Past Publications

- Pegallapati, AK, J Dunn, E. Frank, S. Jones, Y Zhu, L Snowden-Swan, R Davis, C Kinchin. April 2015. “Supply Chain Sustainability Analysis of Whole Algae Hydrothermal Liquefaction and Upgrading.” ANL/ESD—13/8 https://www.osti.gov/src/details.jsp?query_id=1&Page=0&osti_id=1183770.
- Davis R., A. Coleman, M.S. Wigmosta, J. Markham, Y. Zhu, S.B. Jones, and J. Han, et al. 2018. “2017 Algae Harmonization Study: Evaluating the Potential for Future Algal Biofuel Costs, Sustainability, and Resource Assessment from Harmonized Modeling.” PNNL-27547. Richland, WA: Pacific Northwest National Laboratory.
- Zhu Y., S.B. Jones, and D.B. Anderson. 2018. “Algae Farm Cost Model: Considerations for Photobioreactors.” PNNL-28201. Richland, WA: Pacific Northwest National Laboratory.
- Jiang Y., S.B. Jones, Y. Zhu, L.J. Snowden-Swan, A.J. Schmidt, J.M. Billing, and D.B. Anderson. 2018. "Techno-Economic Uncertainty Quantification of Algal-derived Biocrude via Hydrothermal Liquefaction." *Algal Research*. PNNL-SA-138139. [submitted]
- Jiang Y., S.B. Jones, Y. Zhu, L.J. Snowden-Swan, A.J. Schmidt, J.M. Billing, and D.B. Anderson. 10/29/2018. "Techno-Economic Uncertainty Quantification of Algal-derived Biocrude via Hydrothermal Liquefaction." Pittsburgh, Pennsylvania. PNNL-SA-139100.
- Anderson D.B., J.M. Billing, S.J. Edmundson, A.J. Schmidt, and Y. Zhu. 04/29/2019. "Demonstration of the Hydrothermal Liquefaction Pathway for Conversion of Microalgae to Biofuels with Integrated Recycle of Nutrients." Abstract submitted to Biofuels and Bioenergy Conferences, San Francisco, California. PNNL-SA-139499.
- Jessica Tryner, Karl Albrecht, Justin Billing, Richard T. Hallen, and Anthony J. Marchese. 2017. “Performance of a Compression Ignition Engine Fueled with Renewable Diesel Blends Produced from Hydrothermal Liquefaction, Fast Pyrolysis, and Conversion of Ethanol to Diesel.” Paper accepted for presentation and publication in Conference Proceedings of the Western States Section of the Combustion Institute Meeting at the University of Wyoming, October 3, 2017.

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Past Publications (cont.)

- Jessica Tryner, Karl Albrecht, Justin Billing, Richard T. Hallen, and Anthony J. Marchese. 2017. “Performance of a Compression Ignition Engine Fueled with Renewable Diesel Blends Produced from Hydrothermal Liquefaction, Fast Pyrolysis, and Conversion of Ethanol to Diesel.” Paper accepted for presentation and publication in Conference Proceedings of the Western States Section of the Combustion Institute Meeting at the University of Wyoming, October 3, 2017.
- Edmundson S.J., M. Huesemann, R. Kruk, A. Schmidt, T. Lemmon, J. Billing, and D. Anderson. “Phosphorus and Nitrogen Recycle Following Algal Bio-crude Production via Continuous Hydrothermal Liquefaction.” *Algal Research*, 26, 415-421. https://doi.org/10.1016/j.algal.2017.07.016
- Edmundson S.J., R. Kruk, K. Pittman, M. Huesemann, A. Schmidt, T. Lemmon, and D. Anderson. “Water and Nutrient Recycling in Algal Biomass Production.” *Nature Scientific Reports*, In preparation.
- Edmundson S.J., M. Huesemann, R. Kruk, A. Schmidt, T. Lemmon, J. Billing, and D. Anderson. “Phosphorus and Nitrogen Recycle Following Algal Bio-crude Production via Continuous Hydrothermal Liquefaction.” *Algal Research*, 26, 415-421. https://doi.org/10.1016/j.algal.2017.07.016.
- Jacqueline M Jarvis; Justin M Billing; Yuri E Corilo; Andrew J Schmidt; Richard T Hallen; Tanner Schaub, Ph.D. “FT-ICR MS analysis of blended pine-microalgae feedstock HTL biocrudes.” *Fuel*, Volume 216, 15March 2018, Pages 341-348. (https://doi.org/10.1016/j.fuel.2017.12.016).
- Edmundson S.J., R. Kruk, K. Pittman, M. Huesemann, A. Schmidt, T. Lemmon, N. Schlafer, J. Wood, and D. Anderson. “Water and Nutrient Recycling in Algal Biomass Production.” In preparation.
- Edmundson S.J., M. Huesemann, R. Kruk, A. Schmidt, T. Lemmon, J. Billing, and D. Anderson. “Phosphorus and Nitrogen Recycle Following Algal Bio-crude Production via Continuous Hydrothermal Liquefaction.” *Algal Research*, in progress.
- Karl O. Albrecht, Daniel B. Anderson, Justin M. Billing, Douglas C. Elliott, Richard T. Hallen, Todd R. Hart, and Andrew J. Schmidt. “Progress in Hydrothermal Liquefaction of a Variety of Species of Microalgae.” *Algal Research*, in progress.
- Jarvis JM, N Sudasinghe, KO Albrecht, AJ Schmidt, RT Hallen, DB Anderson, JM Billing, and T Schaub. 2016. "Impact of Iron Porphyrin Complexes when Hydroprocessing Algal HTL Biocrude." *Fue*l 182:411-418. doi:10.1016/j.fuel.2016.05.107.
- He Y, X Li, X Xue, MS Swita, AJ Schmidt, and B Yang. 2017. "Biological Conversion of the Aqueous Wastes from Hydrothermal Liquefaction of Algae and Pine Wood by Rhodococci." *Bioresource Technology* 224:457-464. doi:10.1016/j.biortech.2016.10.059.

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Past Publications (cont.)

- Elliott, D.C. 2016. “Review of Recent Reports on Process Technology for Thermochemical Conversion of Whole Algae to Liquid Fuels.” *Algal Research* 13, 255-263, web published: December 17, 2015, DOI: 10.1016/j.algal.2015.12.002.
- Albrecht, K.O. 2016 “Impact of Heterotrophically Stressed Algae for Biofuel Production via Hydrothermal Liquefaction and Catalytic Hydrotreating in Continuous-Flow Reactors” *Algal Research* 14, 17-27, web published: January 8, 2016, DOI: 10.1016/j.algal.2015.12.008.
- Frank E, AK Pegallapati, R Davis, J Makrham, A Coleman, SB Jones, MS Wigmosta, and Y Zhu. 2016. “Life-cycle analysis of energy use, greenhouse gas emission, and water consumption in the 2016 MYPP algal biofuel scenarios.” https://www.osti.gov/src/details.jsp?query_id=3&Page=0&osti_id=1281137.
- Maddi, B.; Panisko, E.; Wietsma, T.; Lemmon, T.; Swita, M.; Albrecht, K.; Howe, D. 2016. “Quantitative characterization of the aqueous fraction from hydrothermal liquefaction of algae.” *Biomass and Bioenergy*, 93, 122-130.
- Pegallapati, AK, J Dunn, E. Frank, S. Jones, Y Zhu, L Snowden-Swan, R Davis, C Kinchin. April 2015. “Supply Chain Sustainability Analysis of Whole Algae Hydrothermal Liquefaction and Upgrading.” ANL/ESD—13/8 https://www.osti.gov/src/details.jsp?query_id=1&Page=0&osti_id=1183770.

Past Presentations

- An oral presentation entitled “Complete NPK Recycle following Algal Bio-crude Production via Hydrothermal Liquefaction” was presented by Scott Edmundson at the 7th International Conference on Agal Biomass, Biofuels, and Bioproducts in Miami, FL on June 21st, 2017.
- A poster entitled “Climate simulated biomass productivities of Chlorella sorokiniana DOE 1412 using recycled nutrients derived from hydrothermal liquefaction processing” was presented by Robert Kruk at the 7th International Conference on Agal Biomass, Biofuels, and Bioproducts in Miami, FL on June 19th, 2017.
- Jessica Tryner, Karl Albrecht, Justin Billing, Richard T. Hallen, and Anthony J. Marchese. 2017. “Performance of a Compression Ignition Engine Fueled with Renewable Diesel Blends Produced from Hydrothermal Liquefaction, Fast Pyrolysis, and Conversion of Ethanol to Diesel.” Paper presented and publication in Conference Proceedings of the Western States Section of the Combustion Institute Meeting at the University of Wyoming, October 3, 2017.
- Jessica Tryner, Karl Albrecht, Justin Billing, Richard T. Hallen, and Anthony J. Marchese. 2017. “Characterization of Fuel Properties and Engine Performance of Renewable Diesel Produced from Hydrothermal Liquefaction of Microalgae and Wood Feedstocks.” Algal Biomass Summit, Salt Lake City UT, October 30, 2017. PNNL-SA-126131.
- Edmundson S.J., R. Kruk, K. Pittman, M. Huesemann, A. Schmidt, and D. Anderson. 2018. “Sustained Algal Biomass Productivities in Continuously Reused Cultivation Water with Nutrients Derived from the Waste Products of Algal Biocrude Production by Hydrothermal Liquefaction.” Presentation at the 2018 International Conference on Algae Biomass, Biofuels, and Bioproducts. Seattle, WA.
- Edmundson S.J., R. Kruk, K. Pittman, M. Huesemann, A. Schmidt, T. Lemmon, N. Schlafer, J. Wood, and D. Anderson. 2018. “Water and Nutrient Recycling in Algal Biomass Production for Biofuels.” Presentation at the 2018 Algal Biomass Summit Houston, TX.
- Kruk R, SJ Edmundson, and MH Huesemann. 2017. "Climate simulated biomass productivities of Chlorella sorokiniana DOE 1412 using recycled nutrients derived from hydrothermal liquefaction processing." Presented by Robert Kruk at The 7th International Conference on Algal Biomass, Biofuels and Bioproducts, MIAMI, FL on June 19, 2017. PNNL-SA-126819.
- Edmundson SJ, R Kruk, MH Huesemann, TL Lemmon, JM Billing, AJ Schmidt, and DB Anderson. 2017. "Complete NPK recycle in algal cultivation after hydrothermal liquefaction of algal biomass." Presented by Scott J Edmundson at 7th International Conference on Algal Biomass, Biofuels, & Bioproducts, Miami, Florida, FL on June 21, 2017. PNNL-SA-126818.

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Past Presentations (cont.)

- Robert Kruk. 2016. “Completing the Nutrient Cycle in Algae Biomass Production” at the 28th Northwest Algae and Seagrass Symposium, on Whidbey Island, WA, May 8th, 2016.
- Scott Edmundson. 2016. “Phosphorus Recycle following Algal Biocrude Production via Hydrothermal Liquefaction” at the 6th International Conference on Algal Biomass, Biofuels and Bioproducts in San Diego, California, June 27th, 2016.
- Albrecht KO, RT Hallen, AJ Schmidt, JM Billing, MA Lilga, AR Cooper, JE Holladay, and DB Anderson. 2016. "Waste Streams as Economic Feedstocks for the Production of Sustainable Liquid Fuels." Presented by Karl O Albrecht at 2nd CRC Advanced Fuel and Engine Efficiency Workshop, Livermore, CA on November 2, 2016.
- Billing JM, AJ Schmidt, TR Hart, GD Maupin, KO Albrecht, H Wang, DB Anderson, RT Hallen, and DC Elliott. 2015. "Continuous Flow Hydrothermal Liquefaction of Biomass Feedstock." Presented by Justin Billing at tcbiomass 2015, Chicago, IL on November 4, 2015.
- Billing JM, DB Anderson, RT Hallen, TR Hart, GD Maupin, AJ Schmidt, and DC Elliott. 2016. "Design, Fabrication, and Testing of the Modular Hydrothermal Liquefaction System (MHTLS)." Presented by Justin M Billing at TCS 2016, Chapel Hill, NC on November 3, 2016.
- Elliott DC, DB Anderson, RT Hallen, AJ Schmidt, and JM Billing. 2016. "Recent Developments in Hydrothermal Processing of Wet Biomass." Presented by Douglas C. Elliott (Invited Speaker) at South Dakota School of Mines and Technology, Rapid City, SD on March 22, 2016.
- Drennan C. 2016. "Hydrothermal Liquefaction - a new paradigm for sustainable bioenergy." Presented by Corinne Drennan at Bioenery Australia 2016, Brisbane, Australia on November 14, 2016.
- Jones SB, Y Zhu, LJ Snowden-Swan, and DB Anderson. 2015. "HTL Model Development." Presented by Susanne B. Jones (Invited Speaker) at DOE Bioenergy Technologies Office (BETO) 2015 Project Peer Review, Washington DC, DC on March 24, 2015. PNNL-SA-108674.
- Zhu Y., S.B. Jones, A.J. Schmidt, J.M. Billing, K.O. Albrecht, R.T. Hallen, and D.B. Anderson. 06/12/2018. "Co-feeding of algae/wood blend feedstock for hydrothermal liquefaction (HTL) and upgrading – a techno-economic analysis." Presented by Yunhua Zhu at The 8th International Conference on Algal Biomass, Biofuels and Bioproducts, Seattle, Washington. PNNL-SA-135398.
- Zhu Y, SB Jones, DB Anderson, RT Hallen, AJ Schmidt, KO Albrecht, and DC Elliott. 2015. "Techno-Economic Analysis of Whole Algae Hydrothermal Liquefaction (HTL) and Upgrading System." Presented by Zhu, Yunhua (Invited Speaker) at Algae Biomass Summit, Washington, D.C., DC on October 2, 2015. PNNL-SA-112790.

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Patents, Awards, and Commercialization

Awards

- 2015 FLC technology transfer excellence award
- 2015 R&D 100 Award “Hydrothermal Processing to Convert Wet Biomass into Biofuels”

Patents

- Mike Thorson, Rich Hallen, Justin Billing, Andy Schmidt, Todd Hart, and Teresa Lemmon. Filed December 2019. “MOVING BED PRETREATMENT FOR IRON-CONTAINING BIOCRUDE.” US Pat Appl 31594/ 9760.
- Mike Thorson, Lesley Snowden-Swan, Andy Schmidt, Todd Hart, Justin Billing, Dan Anderson and Rich Hallen. Filed January 2020. “Split Heat Exchanger Design for HTL.” US Pat Appl 31697 / 9854.
- Elliott, D.C.; Oyler, J.R. Issued on November 4, 2014. "Methods for Sulfate Removal in Liquid-Phase Catalytic Hydrothermal Gasification of Biomass." U.S. Patent #8,877,098.

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Project History

- FY 2013: Algal **HTL potential demonstrated** as part of the National Alliance of Advanced Biofuels and Bioproducts.
- FY 2014 - 2019: Thermochemical Interface project focused on developing **algae HTL pathway** for fuel production.
  - Project conducted process R&D and developed **HTL design case** and **SOT** outlining cost reduction targets for the 2022 timeframe.
  - **Conversion cost were driven down from $3.02/GGE in FY 2015 to $.88/GGE in FY 2019.**
  - Demonstrated fuel production costs of $4.98/GGE for FY 2019 SOT. (Modeled algae **feedstock cost** at $670/US ton dry ash free basis **accounts for 82% fuel production cos**t).
- FY 2020: Began the current project to further drive down minimum fuel selling price $/GGE.
  - Focused on microalgae with terrestrial feedstocks supplement in non-summer seasons and **sequential HTL** to produce both fuels and co-products.
  - FY 2020 SOT **demonstrated potential to drop fuel production costs to $4.48/GGE.**
  - **Conversion cost were driven down from $0.88/GGE in FY 2019 to $-0.33/GGE in FY 2020.**
- FY 2021 - 2022: BETO requested a change in project approach focusing on hydrothermal processing of **low-cost** algae feedstocks.

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1- Management: FY 2021 Milestones

Provide all remaining process data from FY 2020 to the modeling team for completing a final SOT for publication. (QPM)

Prepare and present the scenario analysis with experimental plan for both a marine macroalgae and another wastewater algae used for nutrient remediation to BETO. (AMR)

From batch testing results, select a processing strategy for the second low-cost algae feedstock and develop an approach for implementing the strategy in a continuous process. (QPM)

Q1 | Q2 | Q3 | Q4 | FY 2022

Compile resource availability reporton low-cost algae feedstock from wastewater treatment and marine macro algae farming. Obtain materials needed for characterization and bench-scale processing work. (QPM)

From batch testing results, select a processing strategy for one of the low-cost algae feedstocks and develop an approach for implementing the strategy in a continuous process. (QPM)

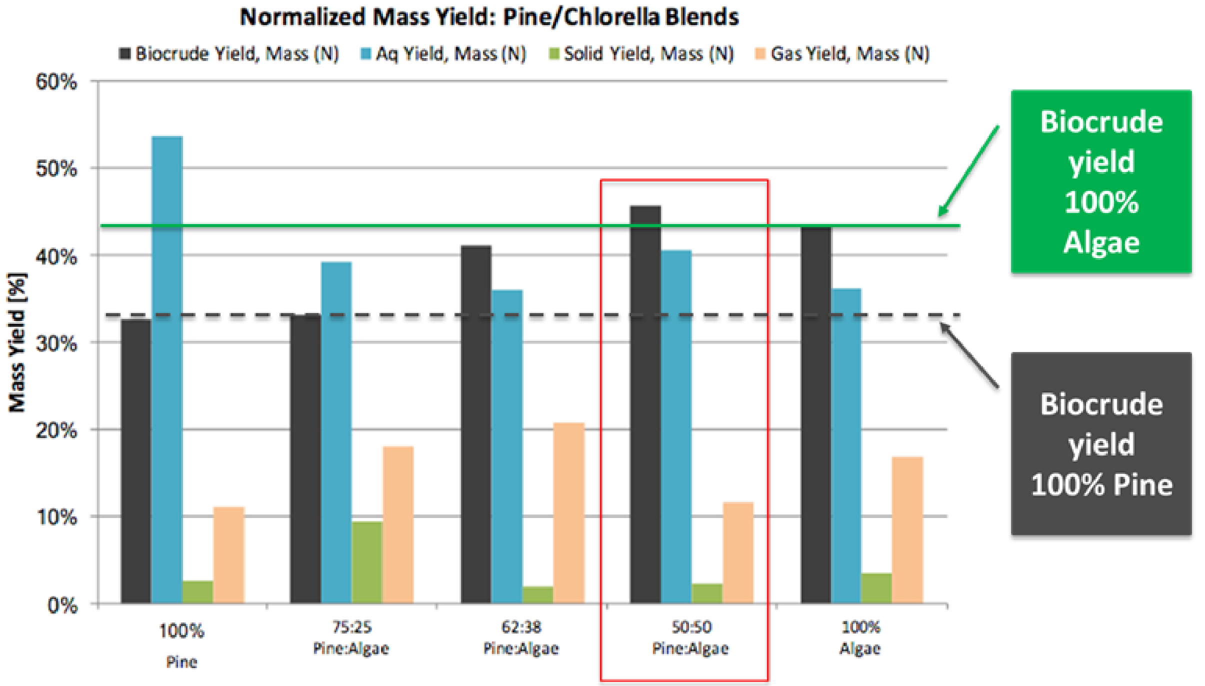
Provide performance data form continuous processing experiments to modeling/TEA team. (QPM)

3 – Impact FY 2021 - 2022 Pivot
Adapting SEQHTL for Low-Cost Algae Feedstocks

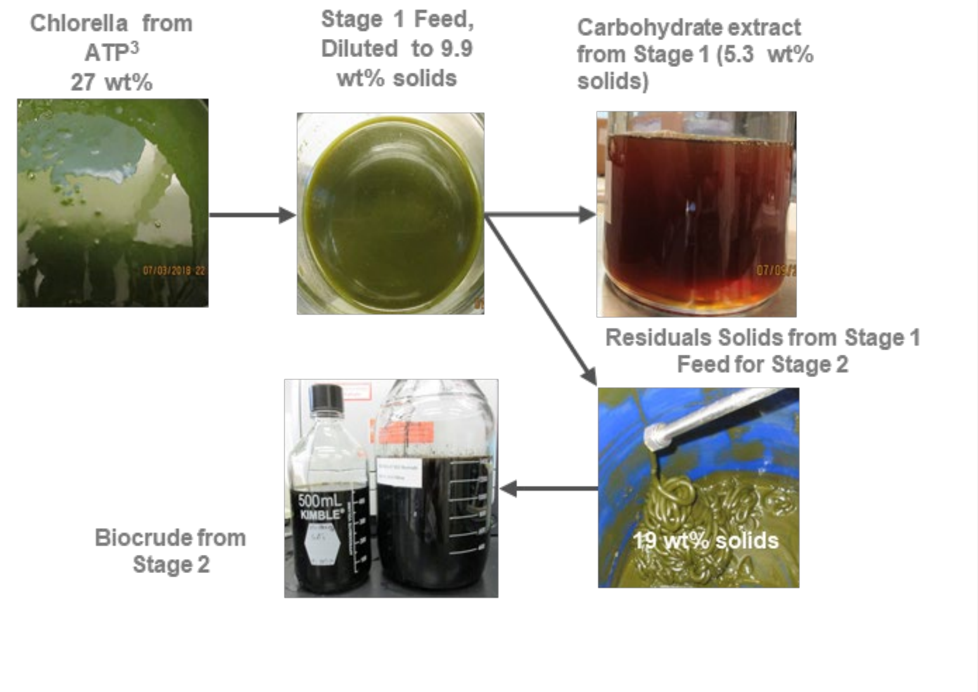
- SEQHTL has potential to enable processing low-cost feedstocks (<$100 vs. $670 per DMT).
- Micro- and macroalgae wastes could be processed into fuel and products.
- SEQHTL could provide mitigation of environmental problems.
  - Nutrient recovery, metals recovery, etc.
- Nearer term commercial application of the SEQHTL possible with existing waste/low-cost algae feedstocks.

4 – Progress and Outcomes: FY 2019 Lessons Learned

- Synergistic biocrude yields achieved using algae/wood blends.
- Algae/wood silage storage blends feasible for long-term storage of a blended feedstock.
- Sequential HTL conditions identified to produce:
  - carbohydrate stream for co-product production in Stage 1, and
  - residual stream that is 25 wt% solids increasing Stage 2 throughput and higher biocrude yields of 50%.
- Initial testing of blended feedstocks for sequential HTL showed likely blended feedstocks will yield more carbohydrates.
- Methods identified enabling hydrotreating algal biocrudes at industrial relevant conditions.
- HTL aqueous recycle and HTL derived nutrients work with multiple DISCOVR algal strains.



Blending to Level Seasonal Algae Production Provides Improved Biocrude Yields



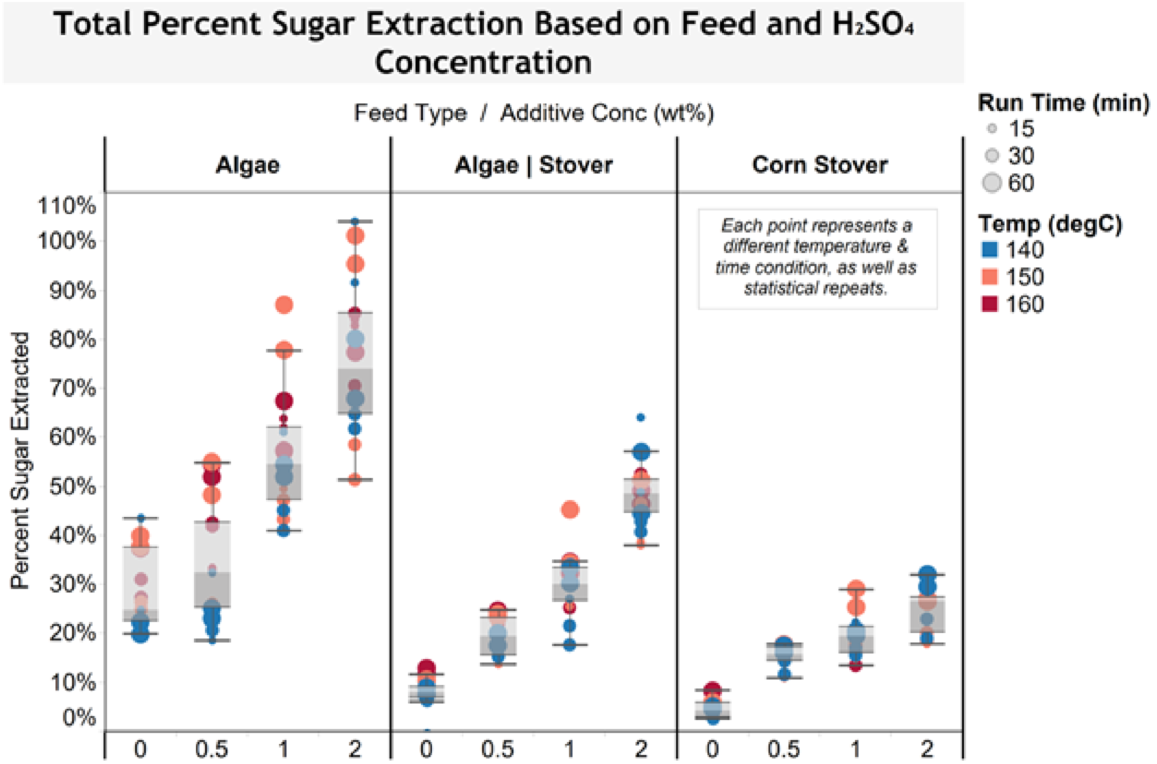
Material Flow in Sequential HTL

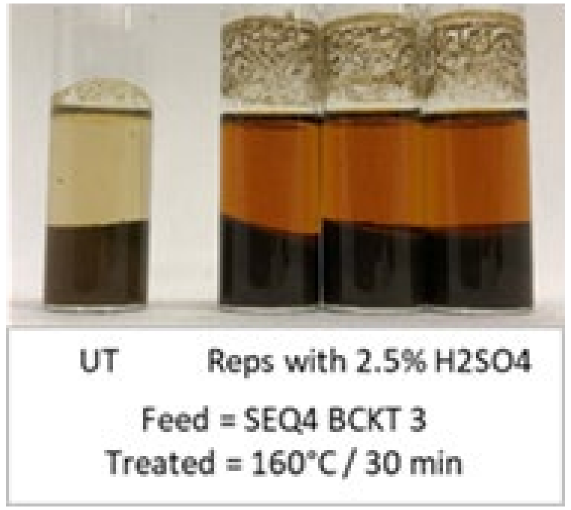
4 – Progress and Outcomes FY 2020: Batch Sequential HTL

FY 2020 Milestone

Determine conditions for recovery of up to 60% of total carbohydrates from algae/corn stover blended feedstocks.

- Stage 1 extraction studies were completed in high throughput center.
- A range of process conditions were evaluated, including:
  - temperature, acid concentration, residence time, and temperatures
  - 60% recovery achieved
- Residual solids recovery for Stage 2 conversion were determined:
  - 50-60% yield dry wt. basis
  - 20% solids





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FY 2020 Risk Matrix

Name	Status	Target Completion Date	Severity	Response/Progress	Description
Access to Algal Biomass		9/30/2022	High	Mitigate In 2020, we worked with AzCat in Arizona and GAI out of Hawaii to supplement algae supply.	Lack of algae feedstock availability for integrated sequential HTL testing (need about 10 kg dry per test)
Access to formatted Forest Product Residual	Known	9/30/2022	High	Mitigate We will work with Idaho National Laboratory in FY 2020 Q-4 to allow rapid start in FY 2021 Q-1.	Lack of forest product residual feedstock availability for integrated sequential HTL testing (need about 15 kg dry per test)
Stage 1 Plug Flow Processing	Closed	6/30/2021	Medium	Mitigate Through experience, this risk has been reduced; higher linear velocity reduces plugging.	Failure to successfully conduct Stage 1 HTL in pure PFR mode (e.g., persistent plugging)
Stage 1 Additives to Boost Carbohydrate Extraction	Response Selected	6/30/2021	Medium	Mitigate H_2SO_4 is inexpensive and relatively effective.	Failure to identify Stage 1 additive that boosts carbohydrate recovery.
Recycle Toxicity from Blended Feeds	Known	9/30/2022	Medium	Mitigate	Toxicity of combined feedstocks is increased and inhibits algal growth.
Bacterial/Fungal Contamination of Algal Cultures	Analyzed	9/30/2022	Medium	Mitigate	Bacterial/fungal contamination of algal cultures.
Bioconversion Metabolic Inhibitors	Partially understood. Established mitigation measures.	9/30/2022	Medium	Mitigate. Evolve strains to tolerate higher concentration of inhibitors. Search of alternative strains with higher tolerance.	Varying metabolic inhibitors in carbohydrate extract from feedstock blends

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Risk Matrix FY 2021 - 2022

Name	Status	Target Completion Date	Severity	Response	Description
Access to Algal Biomass	Known	9/30/2022	High	Mitigate	Lack of algae feedstock availability for integrated sequential HTL testing (need about 10 kg dry per test).
Hydrothermal Processing High Ash Feedstocks	Known	9/30/2022	High	Mitigate	High ash feedstocks require new sequential HTL processing methods to enable separations and processing.
Adapt Batch Processing to Plug Flow Processing	Known	9/30/2022	Medium	Mitigate	Processing in pure PFR mode may lead to plugging and/co-product degradation.
Additives to Enable Extraction Co-Product Biopolymers	Known	9/30/2022	High	Develop H	Failure to identify additive that boosts co-product recovery in plug flow processing.
Direct Conversion High Ash Algae Biomass to Fertilizer	Known	9/30/2022	Medium	Develop	Carbonization requires new plug flow process.

Abbreviations and Acronyms

- AMR: Annual Milestone Regular
- AOP: annual operating plan
- BETO: Bioenergy Technologies Office
- DOE: U.S. Department of Energy
- FY: fiscal year
- GGE: gasoline gallon equivalent
- HTL: hydrothermal liquefaction
- PDU: Process Development Unit
- PFR: plug flow reactor
- PNNL: Pacific Northwest National Laboratory
- QPM: Quarterly Progress Measure
- SEQHTL: sequential hydrothermal liquefaction
- SOT: state of technology
- TEA: techno-economic analysis
- WBS: Work Breakdown Structure

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