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2017 DOE Bioenergy Technologies Office (BETO) Project Peer Review

1.3.4.101 Thermochemical Interface

PNNL-SA-109025

DATE MARCH 8, 2017

TECHNOLOGY AREA REVIEW: ALGAE

DAN ANDERSON
ANDY SCHMIDT, JUSTIN BILLINGS, KARL ALBRECHT, SCOTT EDMUNDSON, SUE JONES, YUNHUA ZHU

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Goal Statement

Develop processing methods for the algae hydrothermal liquefaction *(HTL) Pathway* to reduce conversion cost, improve sustainability and enable commercialization of algal biofuels supporting BETO's MYPP strategic goals.

- **Technical improvements span the Entire Pathway**
  HTL processing, upgrading to finished fuels, water treatment, and nutrient recycle
- **R&D Targets based on data driven *Process Models* and *"State-of Technology" (SOT) Analysis***
- **Conversion Processing will be Validated at Engineering Scale**

Quad Chart Overview

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Timeline

- Project Start: 10/1/2016
- Project Finish: 9/30/2019
- Percent complete: 6%

Barriers

- Aft-H. Overall Integration and Scale-Up
  - Process integration/TEA; Engr. Scale HTP system being tested
- Aft-J. Resource Recapture and Recycle
  - Aggressively demonstrating reuse of HTL byproduct stream

Budget

	FY 17 Budget	FY 18 Budget	FY 19 Budget	Total Planned Funding (FY 17-Project End Date
DOE Funded	$1,591,520	$1,800,000	$1,800,000	$5,191,520

Partners

- Other interactions/collaborations
  - Algal Biofuel Techno-economic Analysis 1.3.1.200 (NREL)
  - BETO Algal Testbeds (UA RAFT and ASU ATP3)
  - Hydrothermal Processing of Biomass 2.2.2.301
  - Characterization and Valorization of Aqueous Waste 2.3.1.310
  - Microalgae Analysis 1.3.2.102
  - Waste-to Energy : Feedstock Evaluation 2.2.1.109
  - Genifuel, Reliance Industries

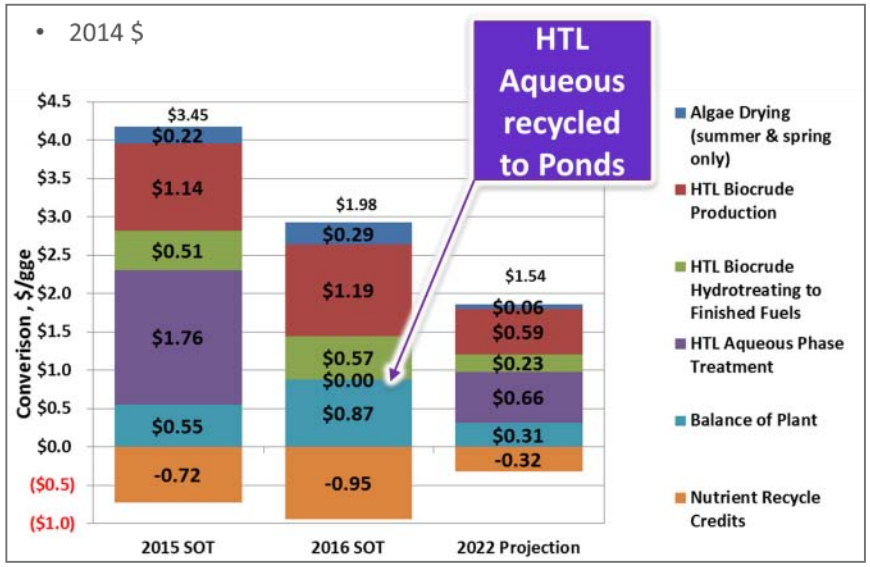
1 - Project Overview
Algae HTL Process

Chlorella Algae, 22wt%

HTL Biocrude (Chlorella)

Component	Weight %
Lipid Content of Algae	14%
Biocrude from HTL Wt% (DAF)	43%
Carbon Yield to Biocrude	60%

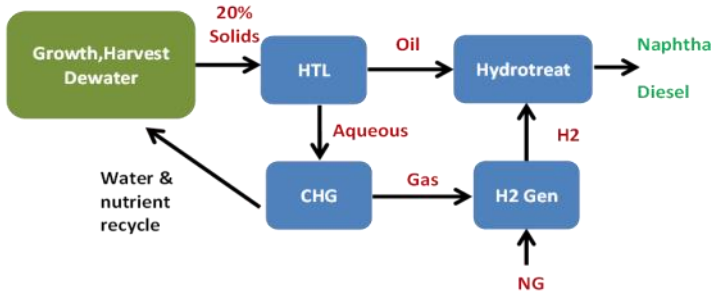
Wet Processing / High Carbon Yield



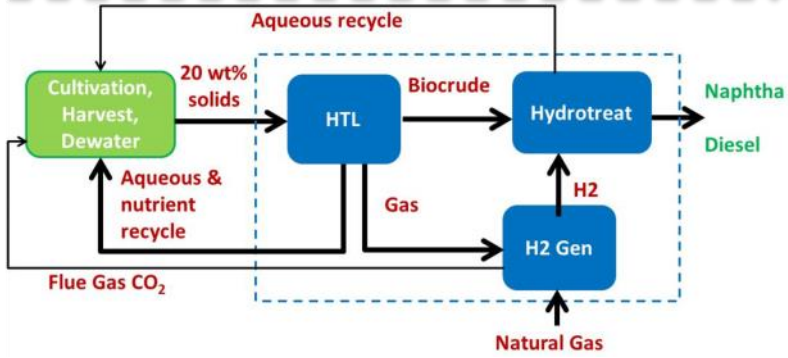
HTL accounts for ~60% of conversion cost

HTL Pathway Model

FY15 with CHG then recycle to pond



FY16 with untreated recycle to pond



Model Evolution

CHG eliminated / Direct recycle

$/gge reduced by 40% 2015 to 2016

2 - Approach Technical
FY17- FY19

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Focus Area	Technical Objectives
Improved HTL Capacity/Capital Cost	Increase LHSV Evaluate Blended Feedstocks (Cost, scale and capacity) Scale-up Validation at Engineering Scale
Improved Biocrude Yield	Improve Separations (solids/liquids and liquid/liquid) PFR scale-up improved conversion efficiency Use of blended feedstocks (wet wastes/lignocellulosics)
Improved Fuel Yield and Quality	Catalytc HTL Refinery Integration Options with Improved Biocrude
Water Treatment/Reuse	Direct recycle to Algae Ponds Concentration/Recovery Aqueous Phase Carbon for Fuel and Co-products Conversion to methane (CHG or AD)
Nutrient Recovery and Recycle for Algal Cultivation	HTL filter solids reuse (P and other minerals) Direct HTL water recycle (Carbon, N, P and Minerals)
Distributed Small–scale Upgrading Process for HTL Biocrude	Increased LHSV, Fe mitigation, Catalyst and Process Development LHSV and Reactor Economy of Scale Scale-up Validation at Engineering Scale
Updated Process Models, TEA and LCA	Integrate Conversion Models with Algae Farm (nutrient/water recycle) Use of blended feedstocks (wet wastes/lignocellulosics) Processing Improvements Validated at Engineering Scale SOT Updates/Pathway Options Analysis
Scaled-up Fuel Production and Characterization	Integrated engineering scale HTL, HT and distillation processing at best conditions

2 - Approach (Management)

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- ***Critical Success Factors***
  - *Decreasing HTL Conversion Costs*
  - *Nutrient Recycle*
  - *Scale-up Validation*
  - *Fuel Validation*

- ***Top Potential Challenges***
  - *HTL Capital and Operating Costs*
  - *Process Turndown (seasonal productivity effects)*

- ***PM Approach***
  - *Regular Milestones (1/Quarter) and Deliverables, Data Input for Process Model and Validation of SOT Technical Targets*
  - *Go/No Go Decision Points based SOT*
  - *Regular Meetings with BETO*
  - *Management and Integration of Supporting Projects and Partners*

3-Technical Accomplishments/Progress/Results

Algal HTL Process Development

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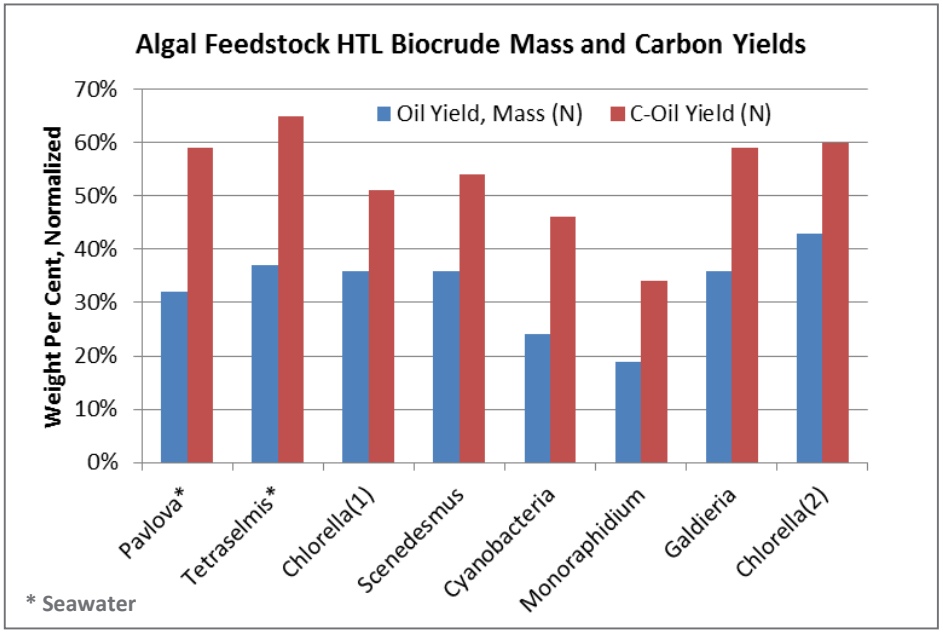
- **Evaluated Multiple Algal Feedstocks in Plug Flow HTL**

  Feedstock composition and solids impact biocrude yield

  (Milestone)

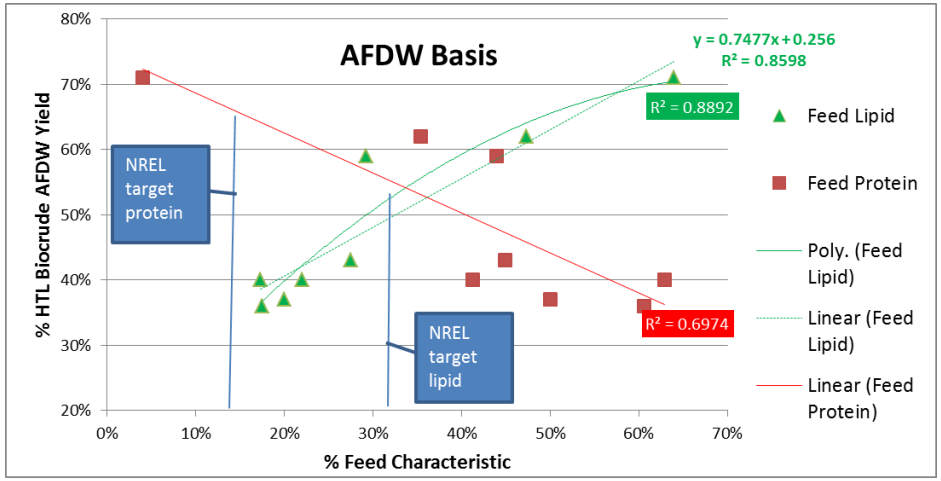
  Karl O. Albrecht, Daniel B. Anderson, Justin M. Billing, Douglas C. Elliott, Richard T. Hallen, Todd R. Hart, and Andrew J. Schmidt. **Progress in Hydrothermal Liquefaction of a Variety of Species of Microalgae, Algal Research, in progress**



- **Initial Data Analysis of Algae Composition vs. Biocrude Yields**

  Inverse correlation between lipid and protein

  NREL algal feedstock compositional targets could enable high yields



3-Technical Accomplishments/Progress/Results
Plug Flow HTL Processing

- **Demonstrated Dramatic Increase in HTL Throughput**
  - 2X increase in LHSV = ***50% Reduction in Capital Cost***

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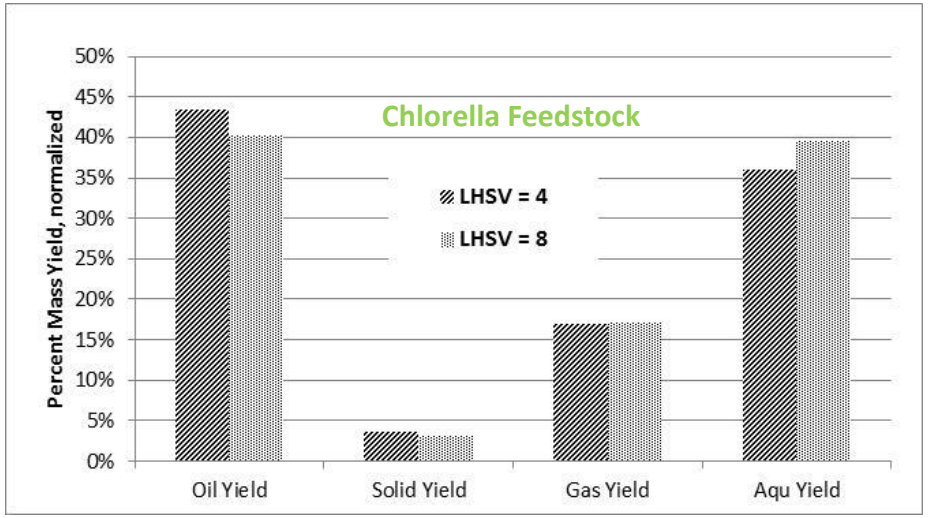
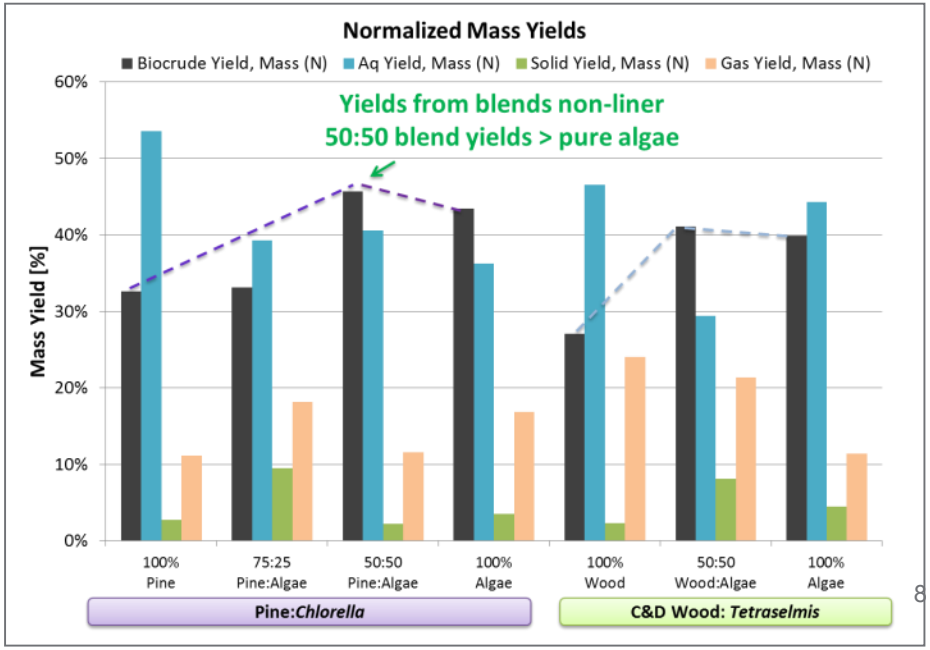
- **Catalytic HTL Evaluated**
  - TEA suggests no improvement over SOT for algal feedstocks ***(Milestone)***

- **Feedstock Blends Proof-of - Concept**
  - Higher biocrude yields observed with blended feedstocks ***(Milestone)***



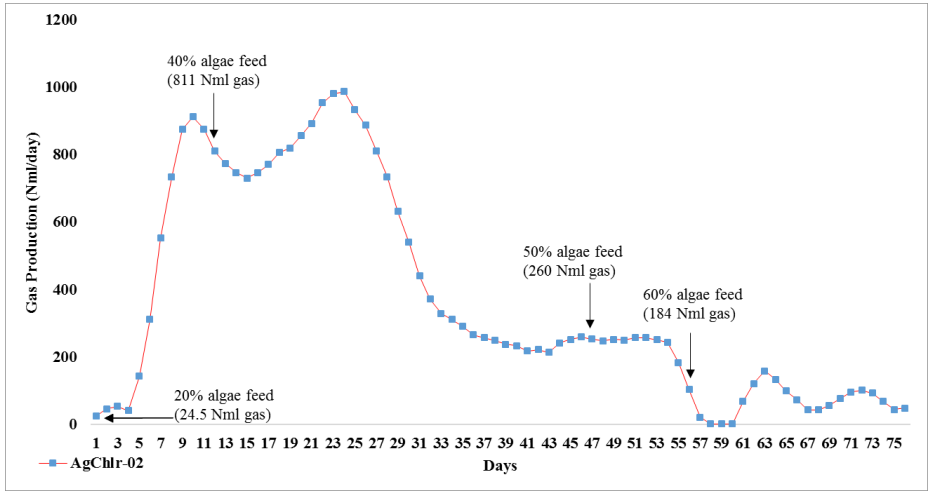


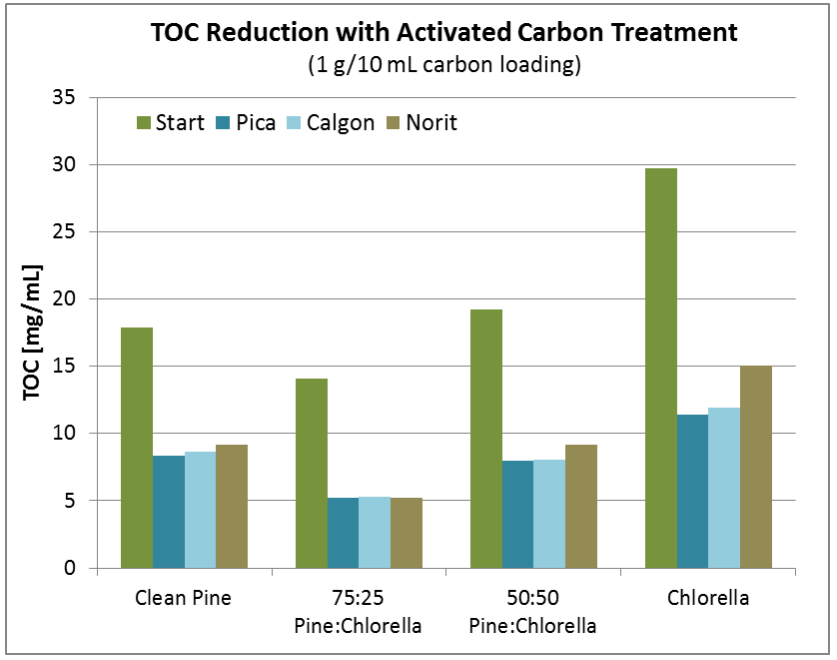
3-Technical Accomplishments/Progress/Results
Aqueous Phase Treatment & Valorization

- **Evaluated AD Treatment**
  HTL aqueous phase (WSU subcontract) ***(Go/No-Go)***

- **Extended CHG Catalyst Life**
  Sulfur removal below 10ppm for freshwater strains only
  (Go/No-Go)

- **Demonstrated 60%TOC Reduction Aqueous Phase**
  Developing aqueous product recovery and valorization methods





3-Technical Accomplishments/Progress/Results
Upgrading and Fuel Characterization

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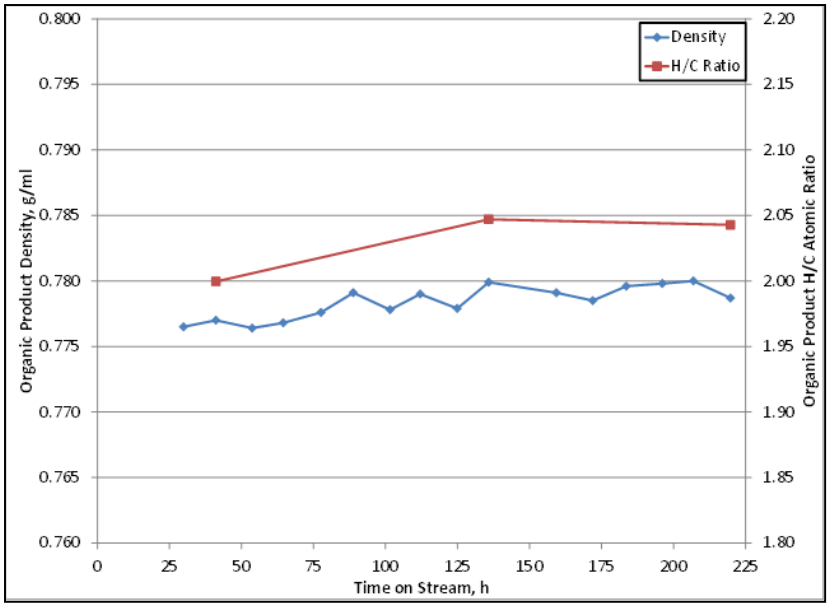
- **Developed Guard Bed Mitigation**
  Iron plugging from algal biocrude porphyrins ***(Milestone)***

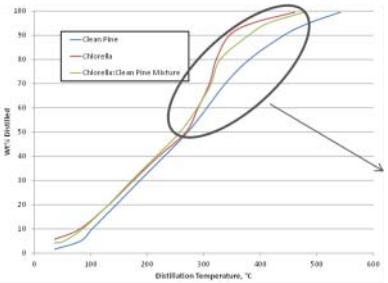
  Jarvis JM, N Sudasinghe, KO Albrecht, AJ Schmidt, RT Hallen, DB Anderson, JM Billing, and T Schaub. 2016. **"Impact of Iron Porphyrin Complexes when Hydroprocessing Algal HTL Biocrude."** Fuel 182:411-418. doi:10.1016/j.fuel.2016.05.107

- **Demonstrated 200+ Hrs Hydroprocessing**
  Algal HTL biocrude upgrading stability and fuel characterization ***(Milestone)***



- **Completed Blended Feedstock Upgrading and Fuel Characterization**
  Blends improved diesel fuel properties ***(Milestone)***

	Chlorella	Clean Pine	50% *Chlorella* 50% Clean Pine Mixture (wt%)
Density, g/mL	0.78	0.9	0.82
H_2 Consumption, g H_2/g dry biocrude	0.047	0.057	0.045
H/C Ratio	2.1	1.6	1.9
Diesel Fraction Cetane Index	>40	28.5	42.6
Diesel Fraction Cloud Point, °C	3	-33	-11



Mixing pine with algae improves cold flow properties

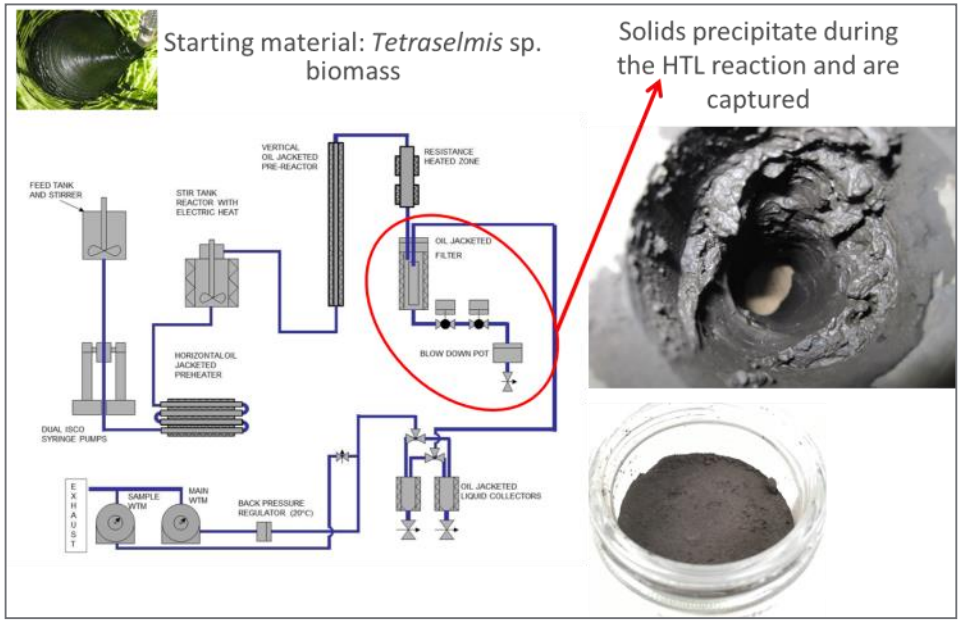
Mixing algae with pine improves diesel cetane index

Straight chain alkanes from lipids are apparent in the feeds containing algae

3-Technical Accomplishments/Progress/Results
Phosphate Recovery and Recycle

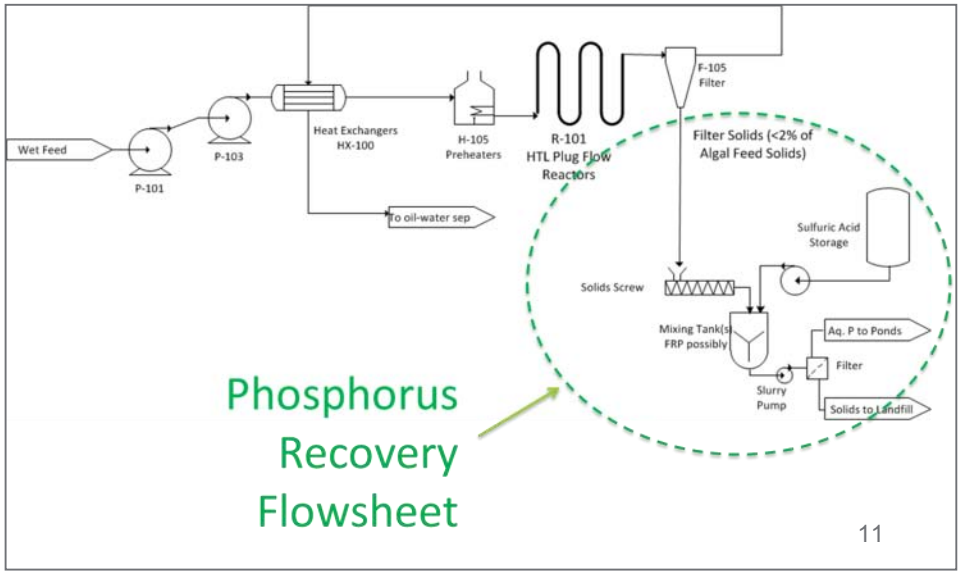
- **Developed HTL Solids Separation for Phosphate Recovery**

  P and other minerals captured for nutrient recycle ***(Milestone)***



- **Demonstrated Phosphorus Recovery Process**

  Dilute sulfuric acid recovery process flowsheet developed for HTL process model ***(Milestone)***



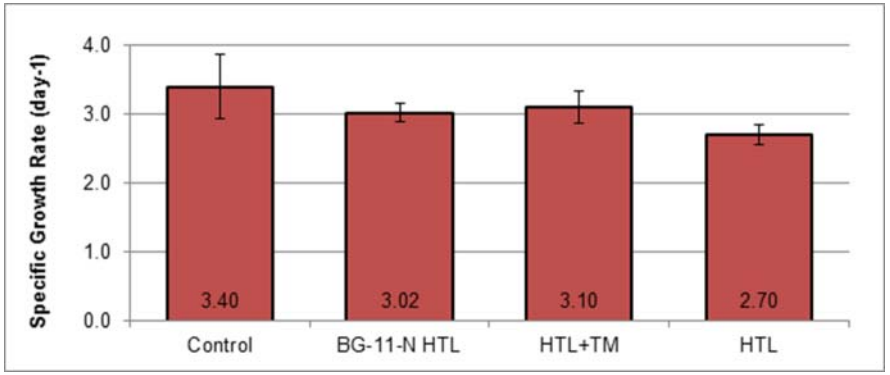
3-Technical Accomplishments/Progress/Results
Nutrient Recycle

- **Demonstrated Complete Nutrient Recycle using HTL Process Wastes**
  - **P** and (Ca, Mg, and S) derived from the acid extracted solids
  - N and P derived from the HTL-aqueous phase

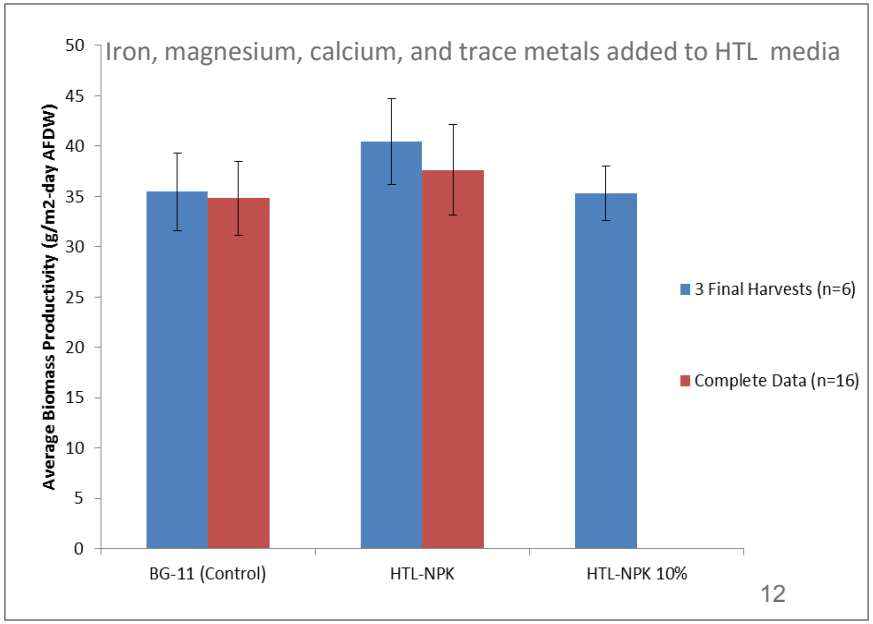
- **Demonstrated Recycle for Semi-continuous Pond Simulation**
  - 80% dilution, alternating days for 16 cycles with no loss in productivity ***(Milestone)***

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

Bioavailability of HTL Recovered Nutrients



Recycled HTL Nutrients in Semi-continuous Culture



3-Technical Accomplishments/Progress/Results
HTL Process Model, TEA/LCA, and SOT

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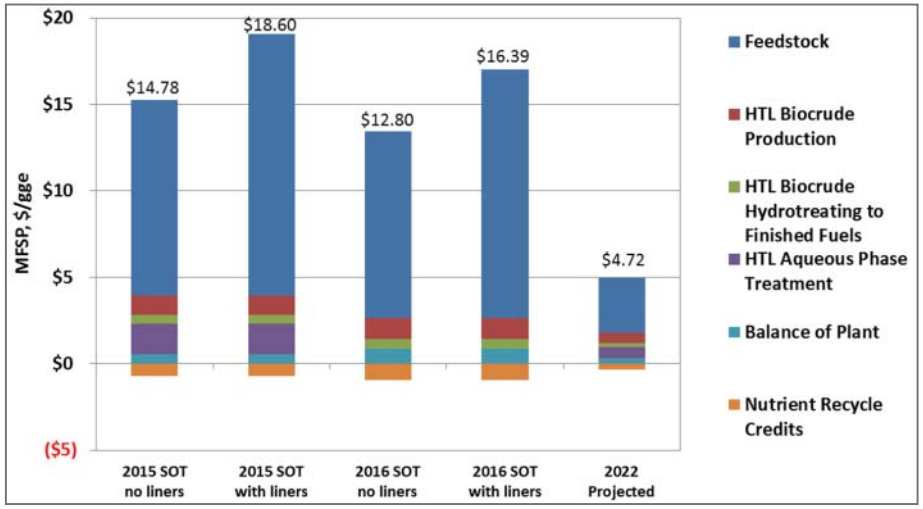
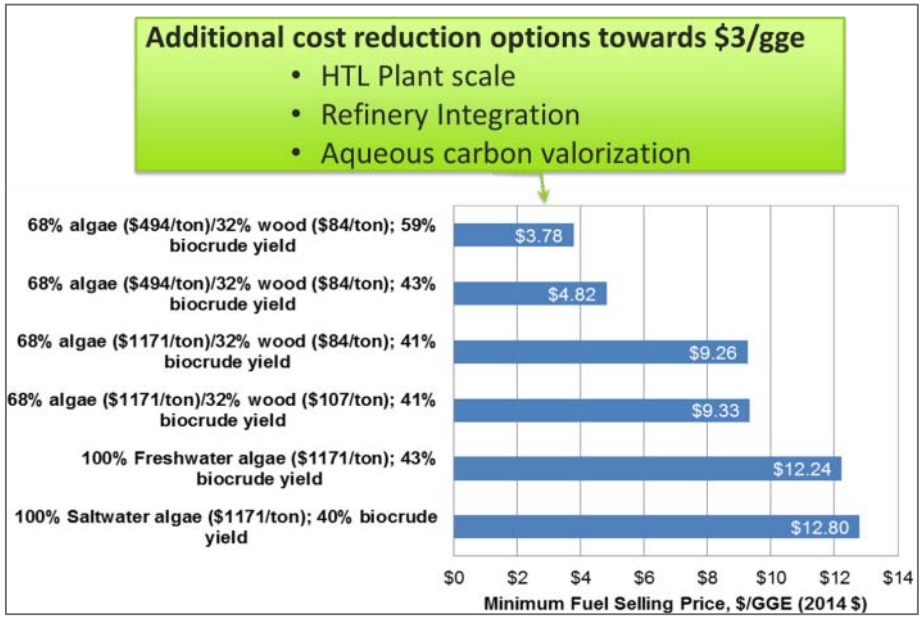
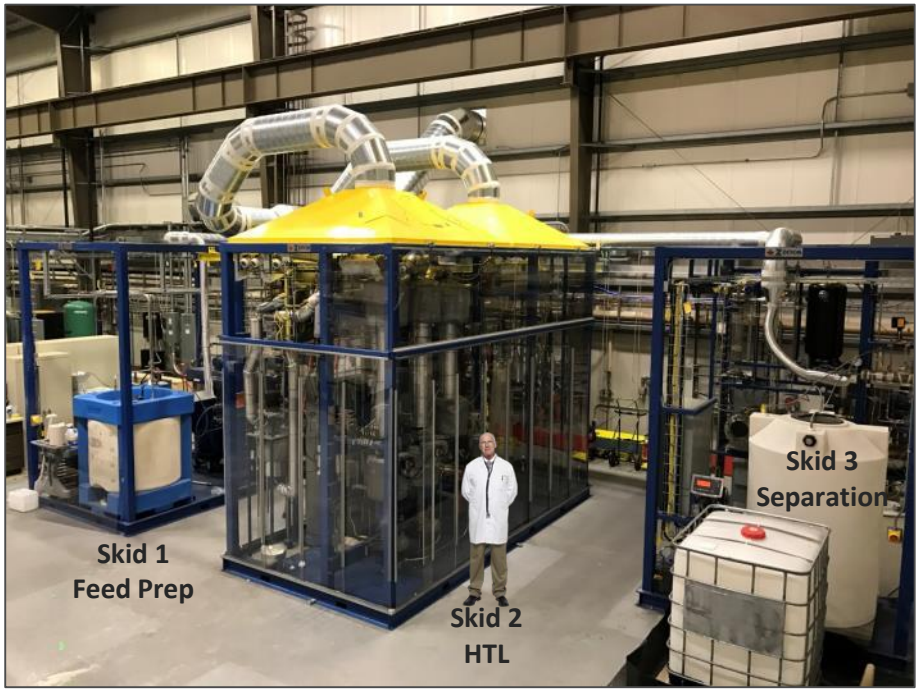
- **Updated Process Model and SOT (*Milestone*)**
  - NREL CAP feedstock and farm scale
  - Remove CHG/ Add direct recycle
  - Add phosphate recovery recycle
  - Regional Upgrading
- **Completed PBR Cost Model (*Milestone*)**
  - vetted by an industrial entity
  - 800 to 1200 $/US ton (AFDW basis)
- **Modeled Blended Algal and Terrestrial Feeds Path to $3/gge (*Milestone*)**





3-Technical Accomplishments/Progress/Results
Engineering Scale HTL Skid

Modular Hydrothermal Liquefaction System (MHTLS)



System Features

- Modular/Relocatable
- Feed Prep for All Feedstocks
- HTL Modes - PFR or CSTR/PFR Hybrid
- Heat Recovery
- Capacity 12-18 L/hour Feed
- Ash Solid Separations
- Flexible Product Separations Unit Ops

Operational Status

- System Fabrication and FAT completed July 2016
- PNNL Facility Mods & Installation completed October 2016
- Operational Readiness Testing/Documents/Training underway
- 100 Hour Run using Algae Feedstock scheduled March 2017 (***Milestone***)

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.

3-Technical Accomplishments/Progress/Results

FY 17 Milestones

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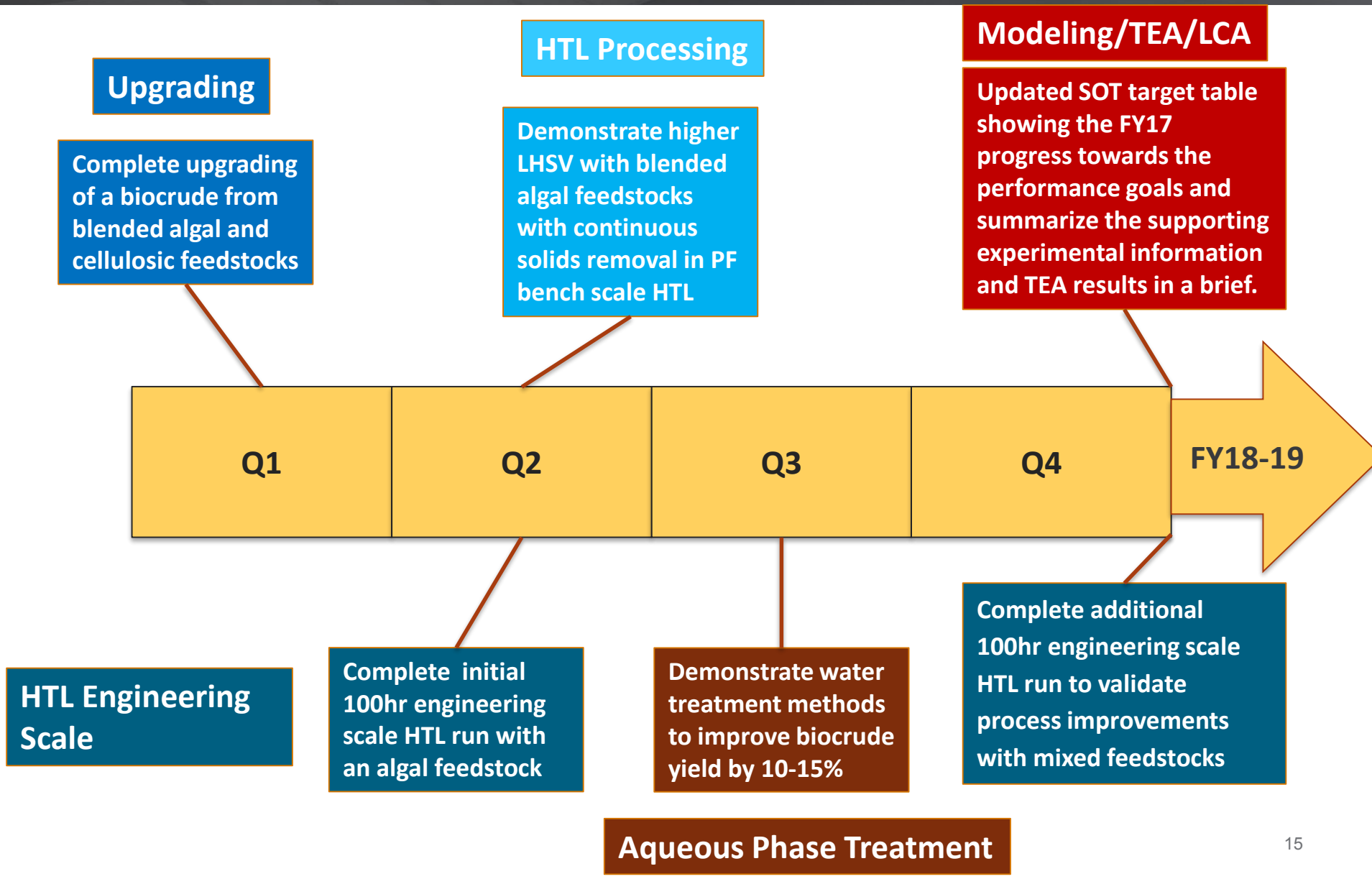

4 - Relevance

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- **Targeted R&D focused on BETO primary technology pathway**
  - HTL pathway technical needs and cost targets identified
  - Developing new enabling technology for critical elements of the pathway
- **Project has resulted new IP**
- **Project is supporting technology transfer**
  - 2015 FLC Award, 2015 R&D100 Award
  - Multiple collaborations with industrial partners and BETO IBRs
- **Project is leveraging synergies with Thermochemical Platform**
  - HTL process development, upgrading and fuel characterization
  - Establishment of engineering scale HTL capability
- **Project has already contributed to multiple publications and invited presentations**

5- Future Work
FY17- FY19

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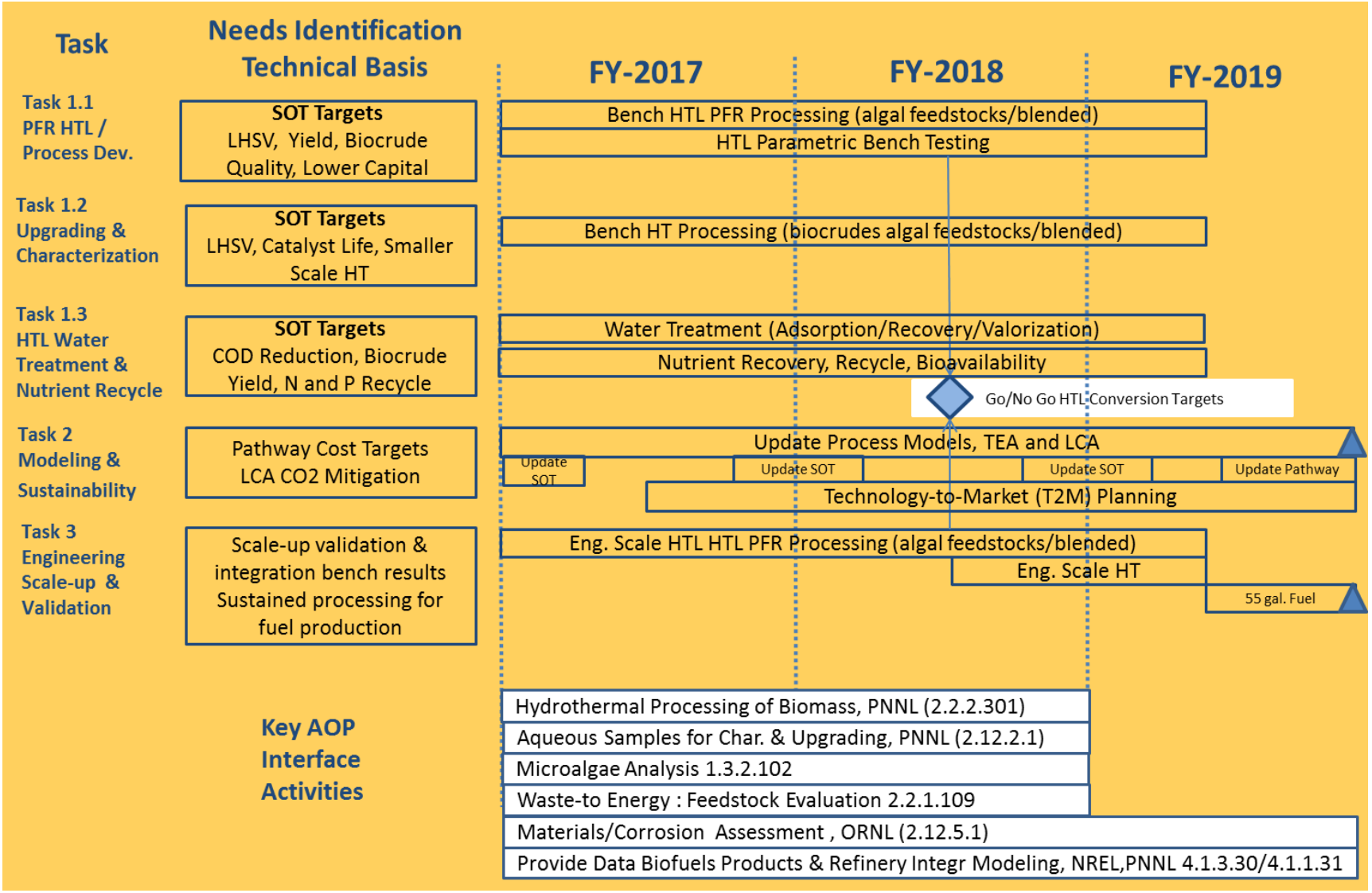

Summary

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- **Relevance:** Project directly contributes to meeting the goals and objectives of BETO's Advanced Algal Systems R&D (HTL Pathway)
- **Approach:** HTL pathway process development and scale-up base on process modeling and SOT technical and cost targets
- **Technical Accomplishments:** Significant advancements made in HTL processing, nutrient recovery/recycle, upgrading/fuel characterization and process scale-up
- **Future Work:** The project will conduct targeted research in FY17-19 based on SOT targets to significantly reduce HTL conversion cost, validate at engineering and enable commercialization
- **Success Factors and Challenges**: The critical success factors and challenges for the project have been identified and are being addressed
- **Technology Transfer**: The project is actively supporting technology transfer to industry through collaborations, IP development and licensing, publications and presentations. Received FLC Award and R&D 100 Award in 2015. Industrial collaborations underway.

Additional Slides

Publications, Patents, Presentations and Awards

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Publications

- 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." Fuel 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
- 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., Quantitative characterization of the aqueous fraction from hydrothermal liquefaction of algae. Biomass and Bioenergy 2016, 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

Publications, Patents, Presentations and Awards

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Presentations

- Robert Kruk. “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. “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, 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.

Publications, Patents, Presentations, Awards, and Commercialization

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Awards

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

Patents

- Elliott, D.C.; Oyler, J.R. "Methods for Sulfate Removal in Liquid-Phase Catalytic Hydrothermal Gasification of Biomass." U.S. Patent #8,877,098, issued on November 4, 2014.