Pacific Northwest
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DOE Bioenergy Technologies Office (BETO)
2019 Project Peer Review

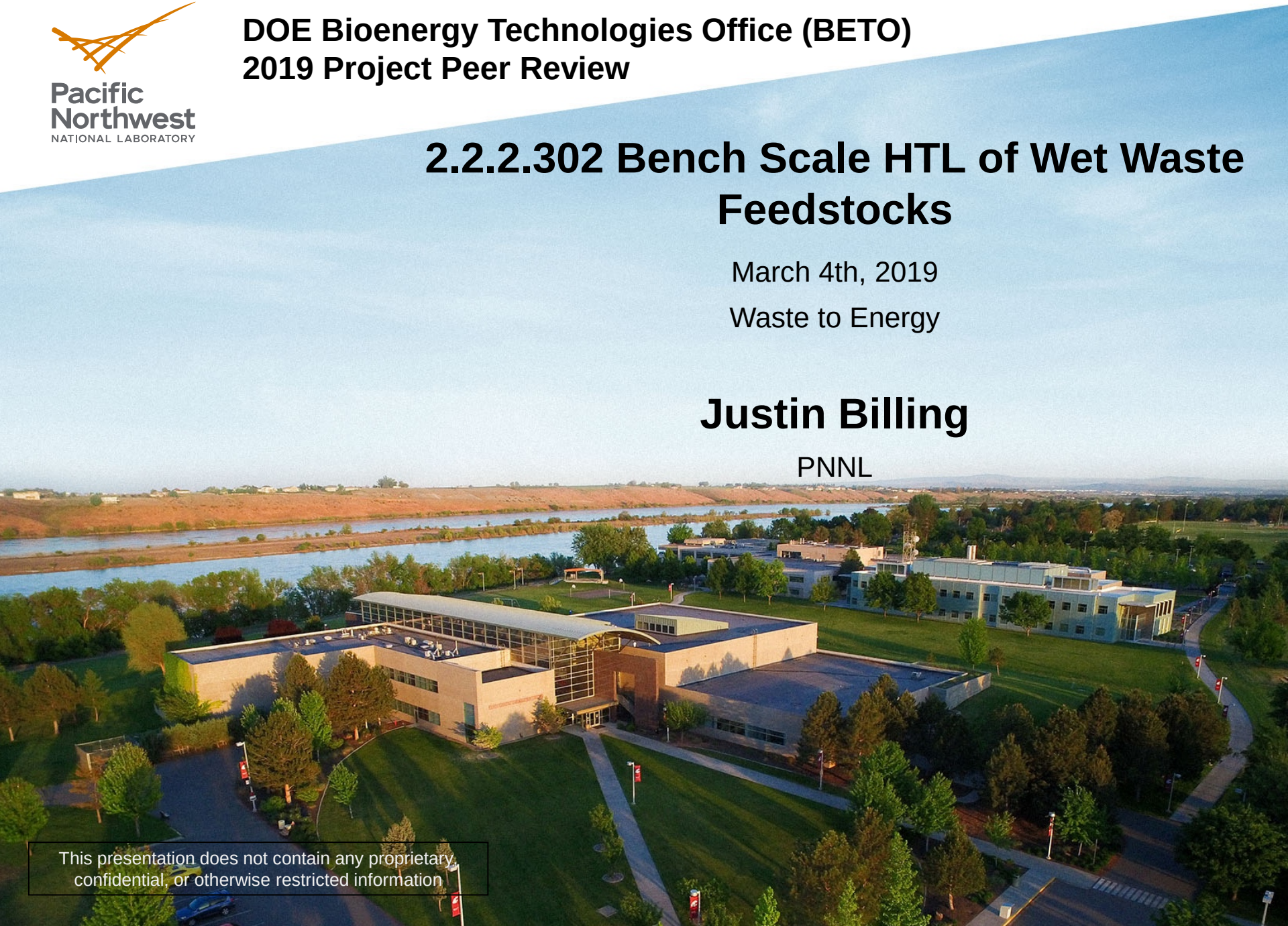
2.2.2.302 Bench Scale HTL of Wet Waste Feedstocks

March 4th, 2019

Waste to Energy

Justin Billing

PNNL



Acknowledgments

BETO sponsor, Technology Manager Beau Hoffman, and Waste to Energy Coordinator Mark Philbrick.

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy
Bioenergy Technologies Office

Wet Waste HTL is a team effort and we thank the following people:

- Andy Schmidt
- Todd Hart
- Sam Fox
- Lesley Snowden-Swan
- Rich Hallen
- Dan Anderson
- Teresa Lemmon
- Marie Swita
- Alan Cooper
- Miki Santosa
- Mike Thorson
- Igor Kutnyakov
- Tanner Schaub (NMSU)
- Jackie Jarvis (NMSU)
- Logan Krajewski (NMSU)

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Goal Statement

Goal

Establish hydrothermal liquefaction (HTL) as an advanced biofuel pathway for wet waste feedstocks

Challenge

High moisture content, compositional variation, and contaminants in wet waste feedstocks limit the application of conventional thermochemical processes (e.g., pyrolysis) while established biological processes such anaerobic digestion do not produce advanced liquid biofuels directly

Outcome

TEA-directed bench-scale research will lead to lower costs and decreased technical risks for the HTL wet waste pathway

Quad Chart Overview

Timeline

- New project created by separating bench scale wet waste HTL effort from engineering scale testing (PDU 2.2.2.301)
- Start: 10/01/2018 ▪ End: 09/30/2019 ▪ 50% complete

	Total Costs Pre FY17**	FY 17 Costs	FY 18 Costs	Total Planned Funding (FY 19-Project End Date)
DOE Funded				360K
Project Cost Share*				

•Partners: NMSU, Genifuel, WRF, MetroVancouver, Central Contra Costa Sanitary District, GLWA - City of Detroit, Aloviam

Collaborators: NREL/PNNL – WTE Resource Assessment, ORNL – Materials of Construction, Bioprocessing Separations Consortium, Strategies for Co-processing in Refineries, HYPOWERS team

Barriers addressed

Ct-I. Development of Processes Capable of Processing High-Moisture Feedstocks in Addition to Conventional Anaerobic Digestion

Ct-E. Improving Catalyst Lifetime

Objective

Improve impact and cost performance of the Hydrothermal Liquefaction (HTL) technology through targeted research and development. Using TEA and resource assessment tools to prioritize research, tasks for the current FY include:

1. Hydrotreating catalyst life and activity
2. Biocrude yield improvement through increased solids content, feedstock blending, and liquid phase separations
3. Improved ammonia removal from HTL aqueous

End of Project Goal

Reduce the modeled overall cost of upgraded biofuel blendstock by $1.00/gge from initial SOT

1 - Project Overview
What is HTL and why does it matter?

Hydrothermal liquefaction (HTL) is…

the thermochemical conversion of biomass in a hot, pressurized water environment to break down the solid biopolymer structures to predominantly liquid components

It matters because…

- HTL is a conceptually simple (i.e., heated pipe), scalable, and robust continuous process that can accept a diverse range of wet waste feedstocks
- HTL results in high carbon yields to liquid hydrocarbons (up to 60%)
- HTL produces a gravity-separable biocrude with low oxygen content (5–15 %) that can be upgraded in a single stage hydrotreater

HTL Conditions
Temp: 330-350°C
Pressure: 2900 psig
t_{res}: 10-30 min

Hydrotreating Conditions
Temp: 400°C
Pressure: 1500 psig H_2
Sulfided Co-Mo on Al

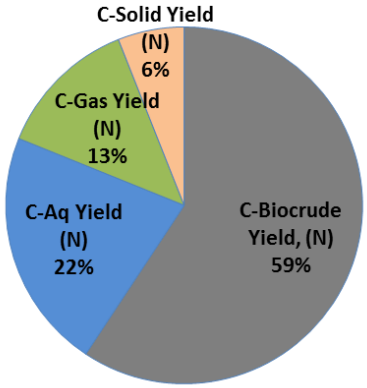
Wet biomass material (sludge, manure, algae) → Stable biocrude oil (up to 60% C-yield) → Fuel Blendstocks (95%+ C-yield)

1 - Project Overview
HTL is the most promising pathway for wet wastes

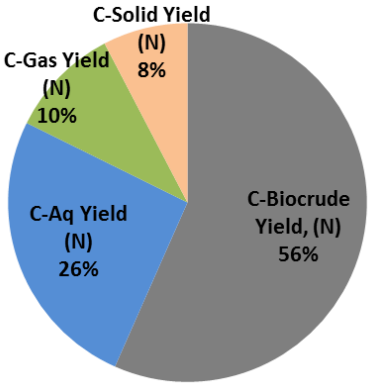
How did we get here?

- HTL emerged as a leading conversion pathway for whole algae (NAABB)
- Initial testing with WWTP sludge resulted in biocrude yield and quality comparable to algae feedstocks
- A design case was performed to define the pathway and research targets for wet waste HTL

WWTP Primary Sludge

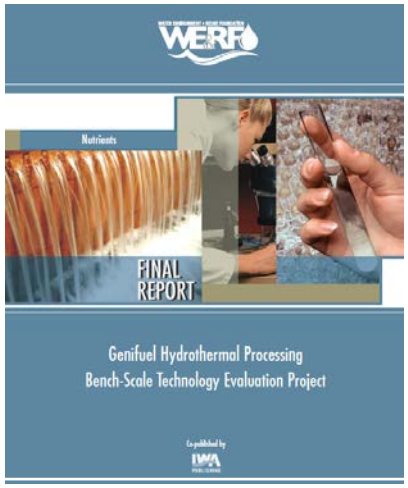


Tetraselmis Marine Algae



Normalized carbon yield on a dry, ash-free basis

Algae HTL



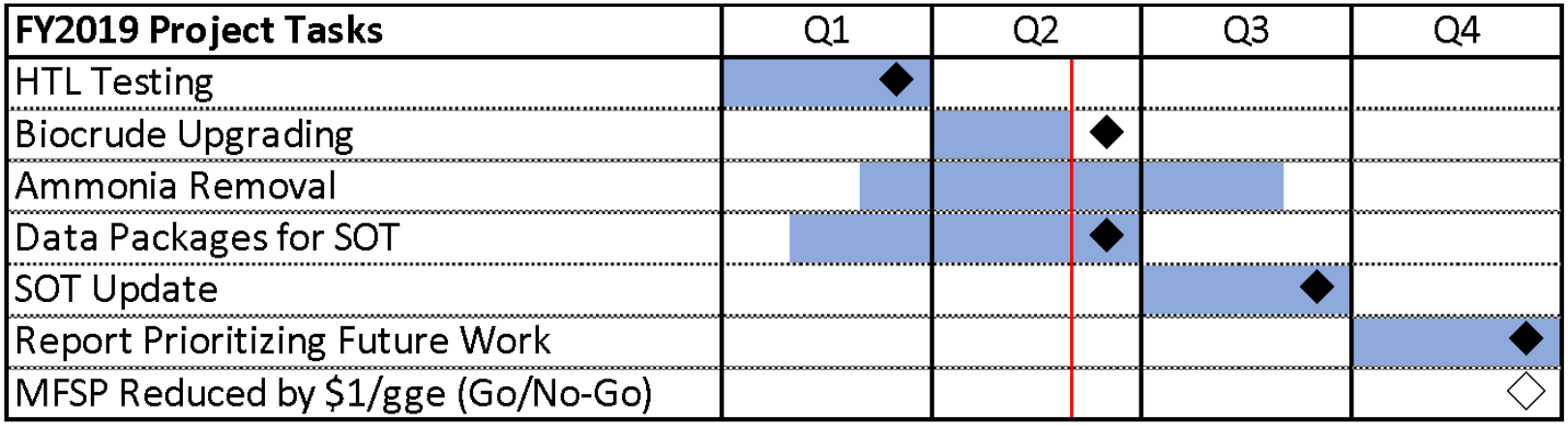
Initial Sludge Testing

Design Case

2 – Approach (Management)

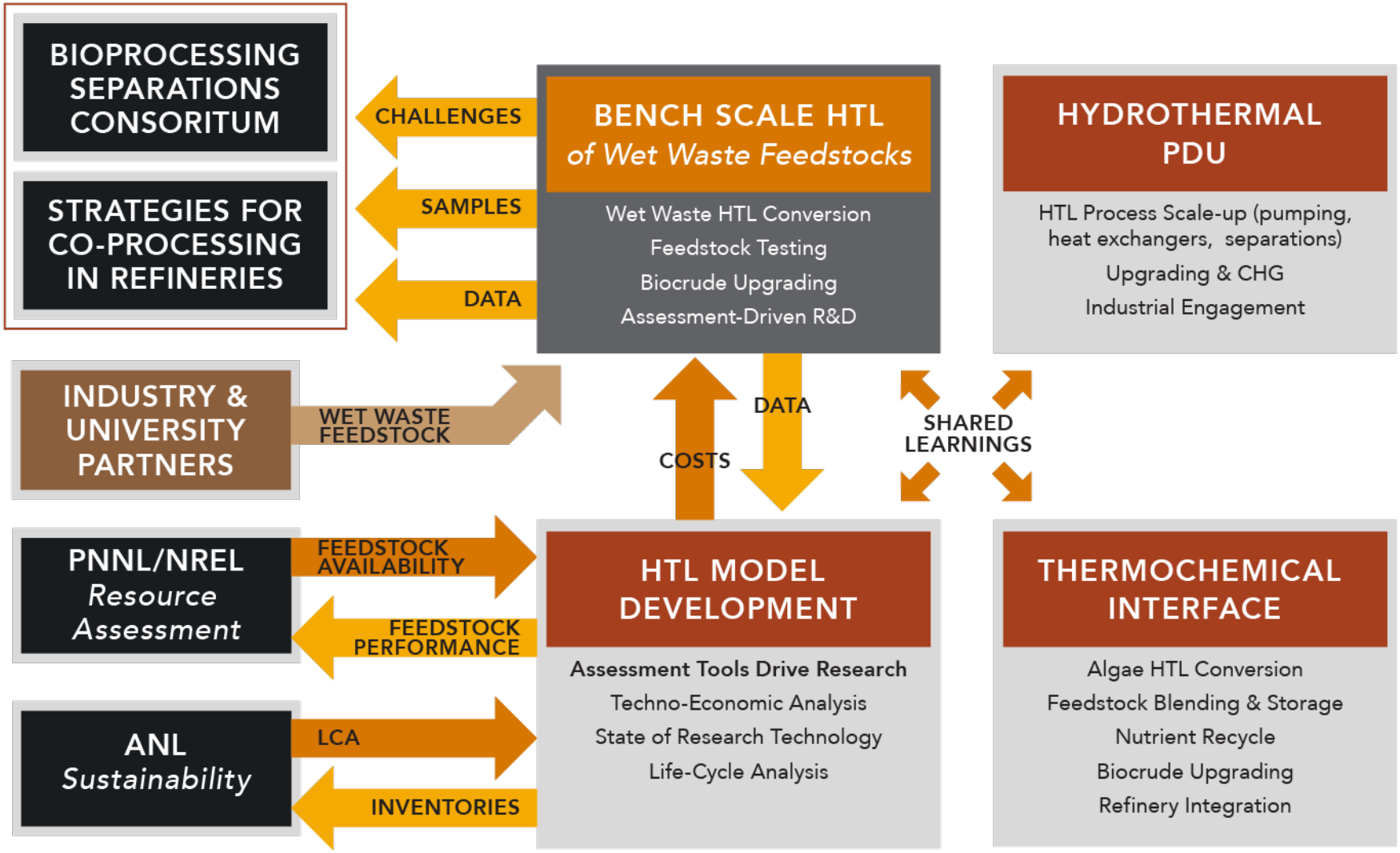
Strategy, communication, and collaboration are the pillars of the management approach

- Well-defined AOP to execute the strategy developed by PI with the Technology Manager, with scheduled milestones and deliverables
- Bi-weekly project meetings, regular updates to BETO
  - Quarterly Reports, Highlights Conversion Call, Deep Dives
- Integration with Co-Processing in Refineries, Bioprocessing Separations Consortium, Hydrothermal PDU and Thermochemical Interface AOPs
- Dissemination through publications, presentations, press releases



2 – Approach (Management)

Project interfaces naturally with related projects to provide maximum impact of bench-scale R&D



2 – Approach (Technical)

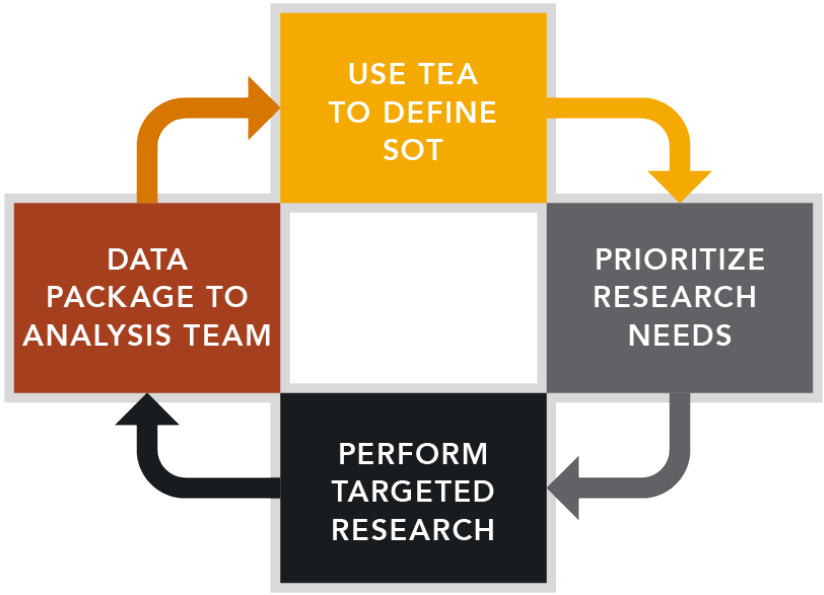
Bench-scale research is driven by TEA sensitivity analysis

Research Outputs

- Provide data packages for SOT modeling, drive down the modeled cost
- Support PDU testing

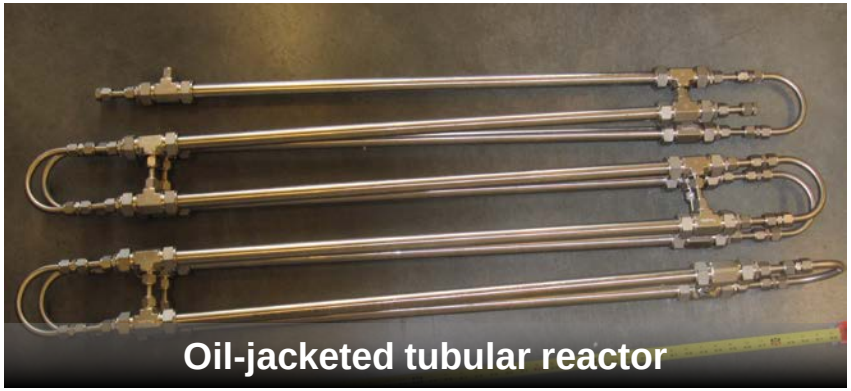
Experimental Criteria

- Real and representative feedstocks sourced from partners and collaborators; selection guided by resource assessment
- Continuous flow tubular reactors that can be modeled and scaled up



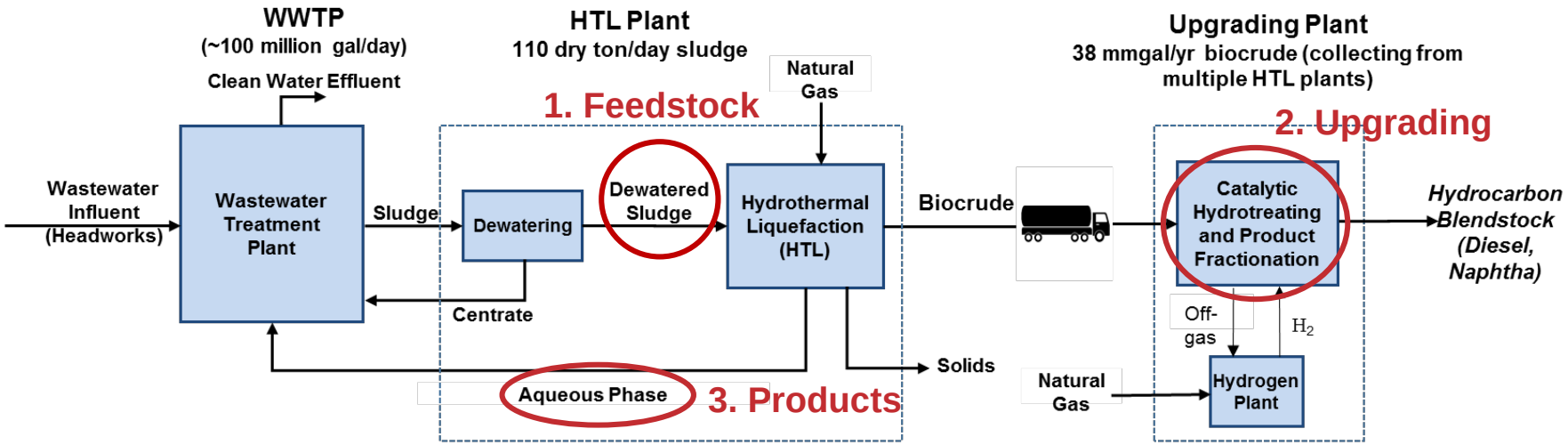

Biosolids


WWTP Scum


Oil-jacketed tubular reactor

2 – Approach (Technical)

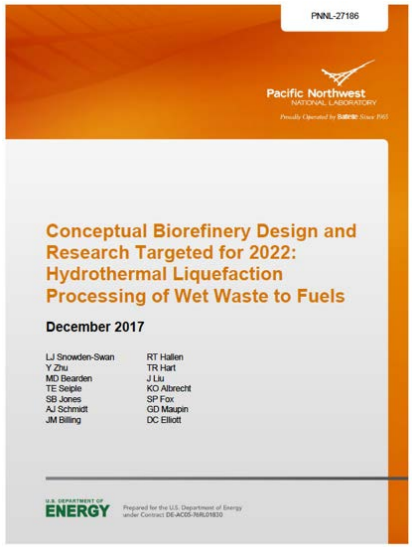
Priorities for FY2019 research driven by Design Case/SOT in three categories: feedstock, upgrading, and products



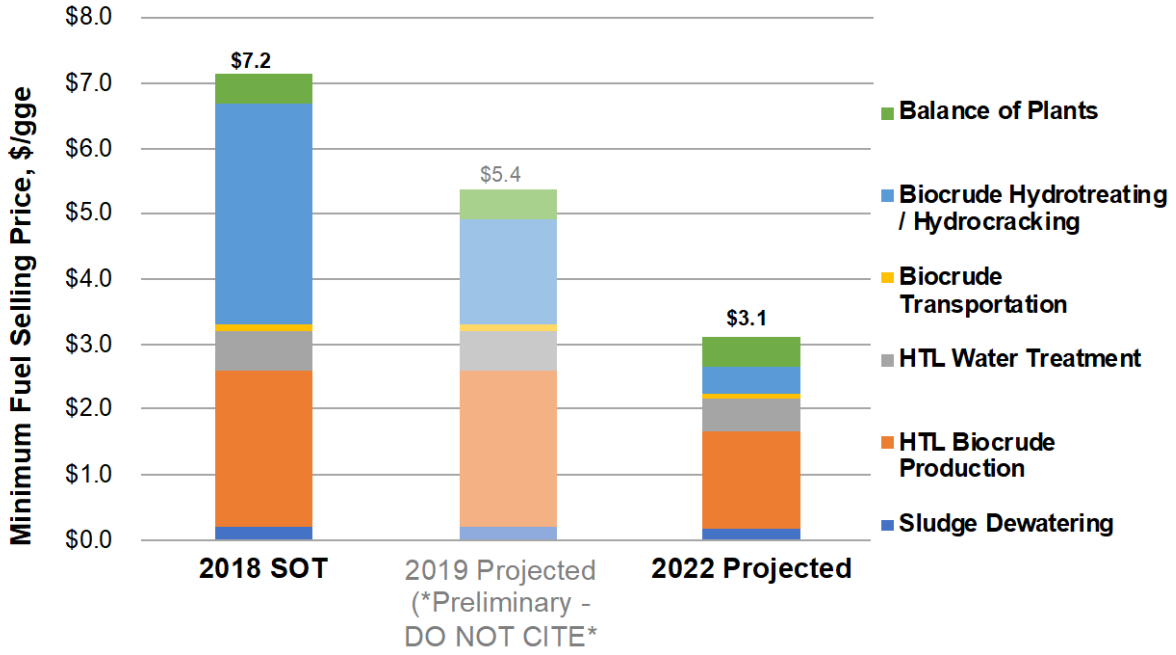
Feedstock	Upgrading	Products
Blend fats, oils, and grease (FOG) stream into POTW sludge to improve HTL yield and biocrude quality Increase the resource base	Demonstrate improved hydrotreating catalyst lifetime and throughput via (a) biocrude pre-treatment (b) use of a guard bed (c) higher-activity catalysts	Collect empirical bench-scale ammonia stripping data to improve flowsheet modeling assumptions

3 – Technical Accomplishments

Experimental data enabled the establishment of the wet waste HTL pathway and publication of the design case



Design Case
PNNL-27186
doi: 10.2172/1415710



Initial SOT Analysis (FY2018)

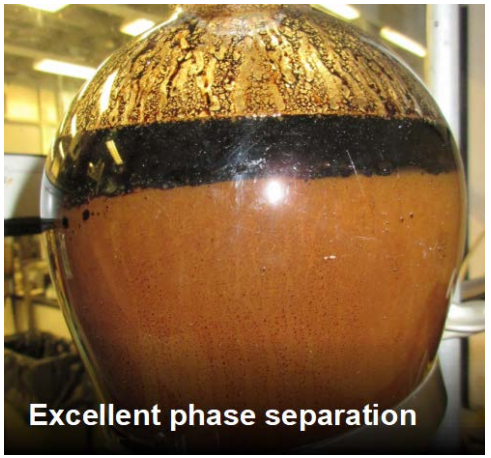
- Wet waste HTL design case was published in December 2017
- Initial state of technology (SOT) analysis completed in June 2018
- Key principles: **1/20th of typical BETO nth plant scale**, **no avoided disposal credit claimed**, feedstock is 50:50 blended of primary:secondary WWTP sludges, 10 HTL units supply one upgrading unit

3 – Technical Accomplishments

Addition of scum boosts biocrude yield

Preliminary data – DO NOT CITE

- Central Contra Costa Sanitary District (CCCSD) decanted scum (FOG) blended at 20 wt% target with CCCSD sludge (dry, ash-free basis)
- **54 L** slurry processed (17 wt% solids) at 4 L/h (conditions: T=350 °C, P=2900 psig)
- **4.2 L** of biocrude produced
- **Mass yield to biocrude: 50%**
- This compares to **37%** biocrude yield for CCCSD sludge only (no scum), representing an approximate 1:1 yield boost for scum addition



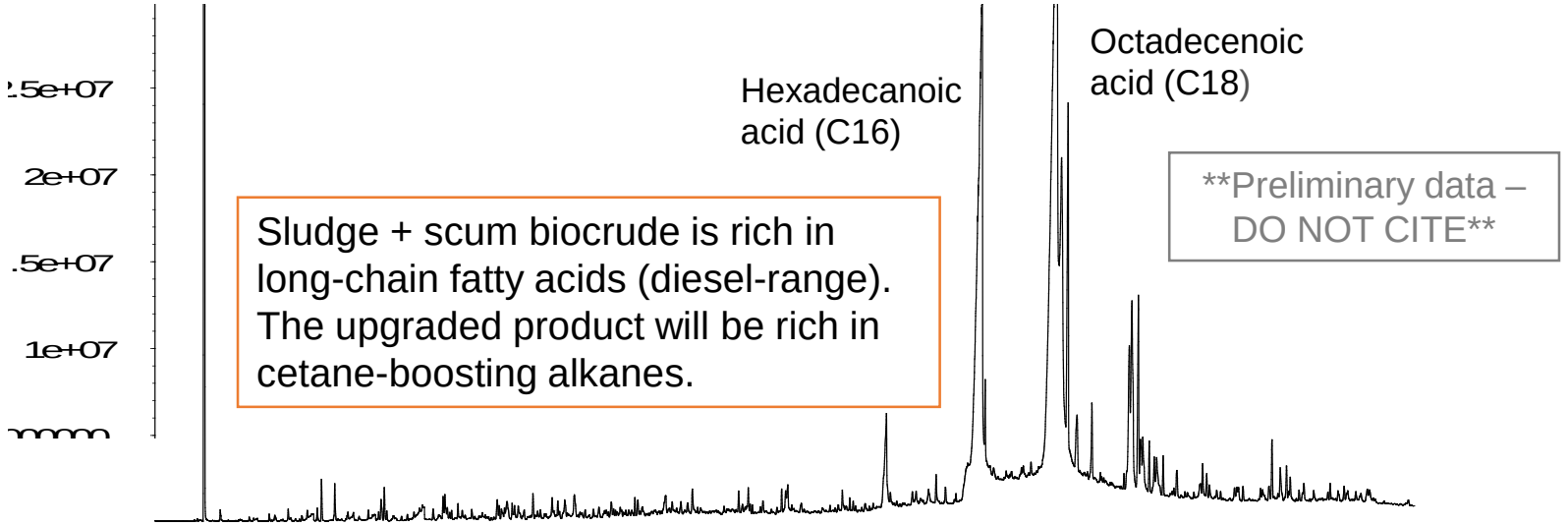
3 – Technical Accomplishments

Addition of scum makes a higher quality biocrude

- Lower biocrude density leading to enhanced phase separation
- Lower nitrogen in biocrude due to lower nitrogen in feed
- Lower moisture content leading to improved heating value

Property	CCCSD Sludge	CCCSD Sludge + Scum
Density [g/cm^3]	0.99	0.95
Nitrogen [wt%]	5.2%	3.6%
Moisture* [wt%]	10.2%	2.9%
Heating Value* [Btu/lb]	13,340	15,790

*Based on continuous product letdown samples



4 – Relevance

HTL conversion of wet wastes supports the BETO mission and meets the technology development timeline

Wet waste HTL is aligned with Bioenergy Technologies Office mission and the MYP for Waste to Energy

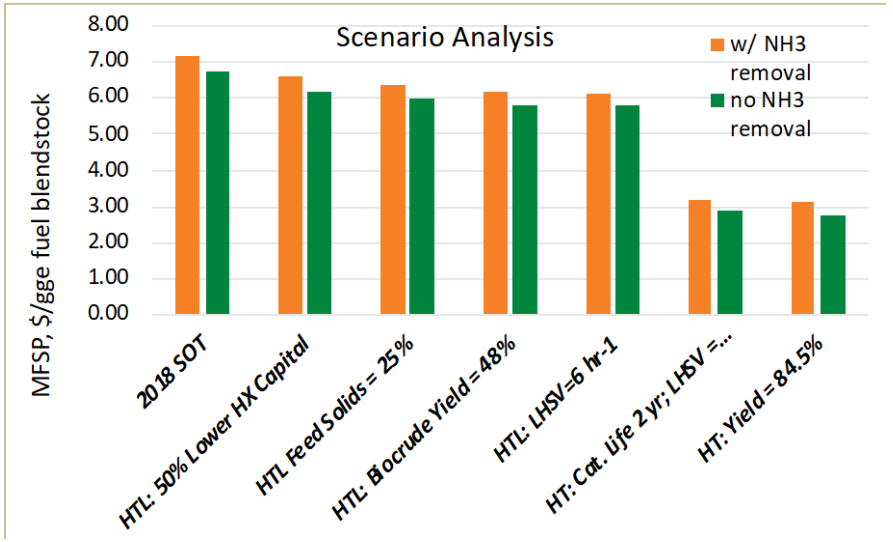
- "Mission: Develop and transform domestic renewable biomass resources into commercially viable, high-performance biofuels, bioproducts, and biopower through targeted RD&D supported by public and private partnerships."
- "Wet wastes are underutilized feedstocks that could feed an emerging pathway to advanced biofuels. They have the potential to make a significant contribution toward achieving the Office's near-term and long-term advanced biofuel and bioproduct goals." (Waste to Energy MYPP 2016)

Wet waste HTL supports the MYP Technology Development Timeline

Conversion: By 2022, validate an n^{th} plant modeled MFSP of $3/GGE for two additional conversion pathways to hydrocarbon biofuel with GHG emissions reductions of 50% or more compared to petroleum-derived fuel.

HTL is featured in reports and roadmaps

- Biofuels and Bioproducts from Wet and Gaseous Waste Streams: Challenges and Opportunities (BETO, January 2017)
- Technology Roadmap – Delivering Sustainable Bioenergy (IEA 2017)



SOT Scenario Analysis (FY2018) Showing Improvements Leading to 2022 Goal Case

4 – Relevance

PNNL's leadership in this area is externally recognized

Working with licensee (Genifuel) to speed commercialization

- MetroVancouver Annacis Island pilot HTL system (design phase)
- WRF-led HYPOWERS pilot HTL system design for Central Contra Costa Sanitary District
- Strategic relationships with utilities, universities, consultants, and industry partners for feedstock evaluation and supply, aqueous phase treatment, and product evaluation

Recognition by wastewater industry
Selected as cover article for WEFTEC 2017 proceedings in Water Environment Research

Independent technology validation

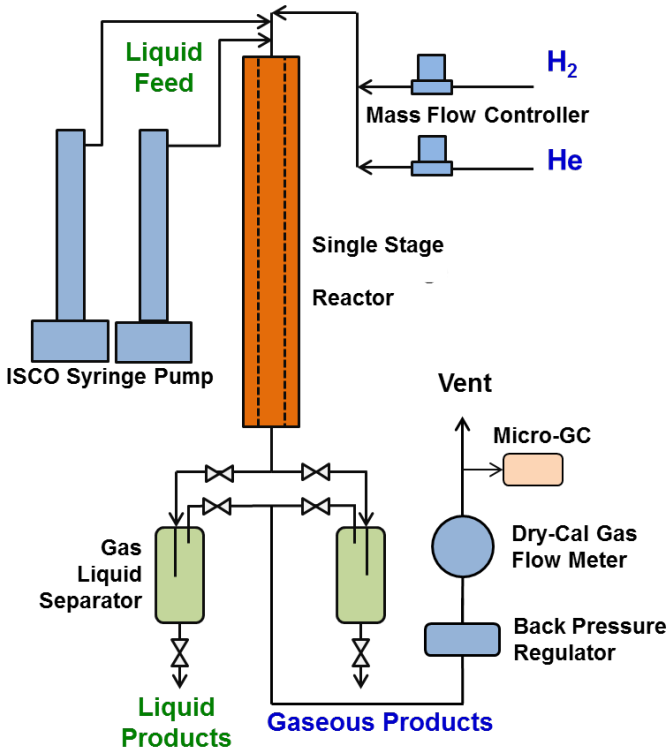
- Leidos for WRF LIFT project
- DOE for HYPOWERS

PNNL invited as advisor for international projects

- IEA Bioenergy Task 34: Direct Thermochemical Liquefaction
- HyFlexFuel: HTL Consortium, European Commission Horizon 2020 Programme
- ISO/PC 318 Community Scale Resource Oriented Sanitation Treatment Units

5 – Future Work

Strategy for catalytic upgrading of sludge + scum biocrude will lead to a substantial reduction of modeled costs



Reactor: ½" ID, ¾" OD, 25" long, 3/16" thermal well
Heater block: aluminum sheath (3" OD, 9" length) wrapped with heating tape; insulated.

Objectives

- Objectives are increased catalyst life and higher throughput
  - Time-on-stream (TOS) > 300 hr, target is 500 h
  - Liquid hourly space velocity (LHSV) > 0.30 L/L/h
  - Commercial NiMo catalyst in place of the baseline CoMo
- Effect of scum addition on properties of upgraded product
- Advanced characterization at New Mexico State University

Impact on Upgrading Cost

- Achieving the target TOS of 500 h at LHSV > 0.30 L/L/h will lead to a projected **$1.80/gge** cost reduction

5 – Future Work

Defining a technical basis for ammonia stripping from the HTL aqueous phase will lead to more accurate modeled costs

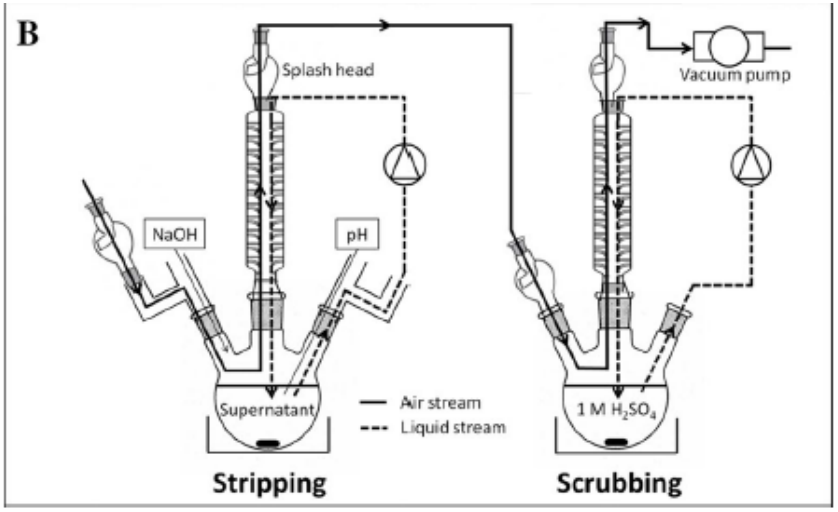


Fig. 2 **a** Picture of the complete self-developed laboratory-scale setup used for the ammonium removal and recovery and **b** schematic drawing of the stripping and scrubbing process

From Ghyselbrecht et al., (2018) IJEEE
doi: 10.1007/s40095-018-0283-7

- Bench-scale ammonia stripping tests at lower pH and temperature than assumed by design case
  - Fate of sulfur and light organic compounds

Other strategies for future work

- Demonstration of membrane technology for ammonia separation
- Demonstration of Anammox technology for baseline comparison
- Test the efficacy of various sorbents on the carbon and nitrogen in the aqueous phase: zeolites, activated carbon
- Engage Bioprocessing Separations Consortium (2.5.5.502-507)

5 – Future Work

Remaining FY2019 tasks will set the stage for FY2020 and beyond in the areas of feedstock, upgrading, and products

- Complete data packages from bench-scale testing to support SOT update for wet waste HTL pathway (joint Q3 milestone with 1.3.1.202 PNNL HTL Model Development)
- Go/No-Go Decision (Q4) is the reduction of the modeled overall cost by $1.00/gge from initial SOT

- Expand the resource base through additional wet waste feedstocks such as manure, food waste, MSW, and bagasse based on resource assessment and determine the best approach for modelling process performance of individual feedstocks and blends
- Using the FY2019 SOT update, prioritize future bench-scale research needs and propose tasks for FY2020 and beyond
  - Biocrude upgrading, aqueous phase treatment, other high-impact topics

Summary

HTL is the most promising pathway to advanced biofuels from wet waste feedstocks

1. **Overview:** Success of the HTL platform with algae feedstocks led to its successful application to wet waste feedstocks.
2. **Approach:** TEA and resource assessment drives research priorities leading to reduced modeled costs. Working with real, representative feedstocks using scalable reactor designs eases technological risks.
3. **Progress:** The HTL testing with scum (FOG) addition is complete, work on upgrading this biocrude is in progress, ammonia stripping tests are underway, additional feedstock has been secured. The project is on schedule to meet all milestones and objectives.
4. **Relevance:** This project supports the BETO mission and addresses a critical need in the Waste-to-Energy portfolio. Collaborators, sponsors, and the wastewater industry recognize the significance of this work.
5. **Future work:** Feedback from the FY2019 SOT update will prioritize the remaining technical challenges and direct future research.

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Additional Slides

- Abbreviations and Acronyms
- Responses to Previous Reviewers' Comments
- Recent Publications
- Key Presentations
- Awards and Patents
- Press Releases and Social Media
- HTL Simplified Process Flow Diagram
- WWTP Diagram and Scum Photos

Abbreviations and Acronyms

- AOP: annual operating plan
- BAT: Biomass Assessment Tool
- BETO: Bioenergy Technologies Office
- CHG: catalytic hydrothermal gasification
- GGE: gasoline gallon equivalent
- HTL: hydrothermal liquefaction
- LCA: life-cycle analysis
- MFSP: minimum fuel selling price
- MYP: multi-year plan
- PDU: process development units
- PNNL: Pacific Northwest National Laboratory
- POTW: publicly owned treatment works
- SCSA: supply chain sustainability analysis
- SOT: state of research technology
- TEA: techno-economic analysis
- WRF: Water Research Foundation
- WWTP: waste water Treatment Plant

Responses to Previous Reviewers' Comments

- Reviewers expressed concerns about recycle of HTL aqueous phase to the POTW headworks and listed this as an example of how additional wastewater industry engagement was needed going forward

  Response: The sludge HTL design case was reviewed by a cross-section of industry experts (over 500 comments) and the current flow sheet includes a commercial ammonia stripping process to address concerns of HTL aqueous phase recycle.

- Reviewers had several comments about refinery integration and whether the current stand-alone upgrading strategy was the best or only route to convert HTL biocrude into a fungible liquid transportation fuel

  Response: It is clear from the FY18 SOT that catalytic upgrading can be a costly step in the process and it is a focus of the R&D effort. We have shown compatibility of the upgraded product by engine testing a 5% blend at Colorado State University. We are exploring other routes by leveraging the Strategies for Co-Processing in Refineries project.

- Comments captured in the 2017 Project Peer Review Report that were related to TEA modeling and resource assessment and have been addressed by those projects

Recent Publications

- Marrone P.A., D.C. Elliott, J.M. Billing, R.T. Hallen, T.R. Hart, P. Kadota, and J.C. Moeller, et al. 2018. "Bench-Scale Evaluation of Hydrothermal Processing Technology for Conversion of Wastewater Solids to Fuels." Water Environment Research 90, no. 4:329-342. doi:10.2175/106143017X15131012152861
- Snowden-Swan L.J., Y. Zhu, M.D. Bearden, T.E. Seiple, S.B. Jones, A.J. Schmidt, and J.M. Billing, et al. 2017. Conceptual Biorefinery Design and Research Targeted for 2022: Hydrothermal Liquefacation Processing of Wet Waste to Fuels. PNNL-27186. Richland, WA: Pacific Northwest National Laboratory.
- Elliott D.C., A.J. Schmidt, T.R. Hart, and J.M. Billing. 2017. "Conversion of a wet waste feedstock to biocrude by hydrothermal processing in a continuous-flow reactor: grape pomace." Biomass Conversion and Biorefinery 7, no. 4:455-465. doi:10.1007/s13399-017-0264-8
- Tryner J., K.O. Albrecht, J.M. Billing, R.T. Hallen, and A.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." In proceedings of the Western States Section of the Combustion Institute – Fall Technical Meeting (WSS/CI 2017), October 2-3, 2017, Laramie, WY.

Recent Publications (cont.)

- Collett J.R., J.M. Billing, P.A. Meyer, A.J. Schmidt, A.B. Remington, E. Hawley, and B.A. Hofstad, et al. 2019. "Renewable diesel via hydrothermal liquefaction of oleaginous yeast and residual lignin from bioconversion of corn stover." Applied Energy 233. doi:10.1016/j.apenergy.2018.09.115
- Jarvis J.M., J.M. Billing, R.T. Hallen, A.J. Schmidt, and T. Schaub. 2017. "Hydrothermal Liquefaction Biocrude Compositions Compared to Petroleum Crude and Shale Oil." Energy and Fuels 31, no. 3:2896–2906. doi:10.1021/acs.energyfuels.6b03022
- Maddi B., E.A. Panisko, T.W. Wietsma, T.L. Lemmon, M.S. Swita, K.O. Albrecht, and D.T. Howe. 2017. "Quantitative Characterization of Aqueous Byproducts from Hydrothermal Liquefaction of Municipal Wastes, Food Industry Wastes, and Biomass Grown on Waste." ACS Sustainable Chemistry & Engineering 5, no. 3:2205-2214. doi:10.1021/acssuschemeng.6b02367
- Mitroshkov A.V., L. Zhong, and L. Thomas. 2019. Analysis of Perfluorinated, Pharmaceutical, Personal Care Compounds and Heavy Metals in Waste Water Sludge using GC-MS/MS and Multicollector ICP-MS. PNNL-28216. Richland, WA: Pacific Northwest National Laboratory.

Key Presentations

- Marrone P.A., D.C. Elliott, J.M. Billing, R.T. Hallen, T.R. Hart, P. Kadota, and J.C. Moeller, et al. 9/30/2017. "Bench-Scale Evaluation of the Genifuel Hydrothermal Processing Technology for Wastewater Solids." Presented by Philip A Marrone at WEFTEC 17 Conference, Chicago, Illinois.
- Billing J.M., D.B. Anderson, R.T. Hallen, T.R. Hart, A.J. Schmidt, and L.J. Snowden-Swan. 09/23/2019. "Development of an Integrated Process for the Hydrothermal Conversion of Wastewater Sludge to Recover Energy, Recycle Nutrients, and Destroy Contaminants." Abstract submitted to WEFTEC 2019, Chicago, Illinois.
- Elliott D.C. 12/05/2018. "Hydrothermal Liquefaction as a Means for Resource Recovery from Wet Waste." Presented by D.C. Elliott at SPS'18: Innovations in Transforming Waste to Value-Added Products, Somerset, New Jersey.
- Billing J.M., K.O. Albrecht, T.R. Hart, A.J. Schmidt, S.P. Fox, D.B. Anderson, and R.T. Hallen. 06/26/2018. "Brown gold: producing hydrocarbon fuel blendstock from municipal sewage sludge via hydrothermal liquefaction (HTL)." Presented by J.M. Billing at ACS NORM 2018, Richland, Washington.
- Schmidt A.J., J.M. Billing, K.O. Albrecht, S.P. Fox, T.R. Hart, G.D. Maupin, and L.J. Snowden-Swan, et al. 09/21/2017. "Conversion of Blended Primary and Secondary Sewage Sludge into Biofuels by Hydrothermal Liquefaction and Catalytic Hydrotreatment." Presented by Karl O Albrecht at tcbiomass2017, Chicago, Illinois.

Key Presentations (cont.)

- Snowden-Swan L.J., J.M. Billing, A.J. Schmidt, R.T. Hallen, K.O. Albrecht, T.E. Seiple, and M.D. Bearden, et al. 04/11/2017. "Techno-Economic Analysis of Renewable Hydrocarbon Fuel from Municipal Sludge." Presented by Lesley J Snowden-Swan at Residuals and Biosolids: The Future of Biosolids and Bioenergy, Seattle, Washington.
- Billing J.M., A.J. Schmidt, T.R. Hart, S.P. Fox, G.D. Maupin, R.T. Hallen, and D.B. Anderson. 10/09/2018. "Scale-Up Testing of the Modular Hydrothermal Liquefaction System." Presented by J.M. Billing at Thermal & Catalytic Sciences Symposium (TCS), Auburn, Alabama.
- Albrecht K.O., R.T. Hallen, A.J. Schmidt, J.M. Billing, L.J. Snowden-Swan, M.A. Lilga, and A.R. Cooper, et al. 03/28/2017. "Waste Streams as Economic Feedstocks for the Production of Sustainable Liquid Fuels." Presented by Karl O Albrecht at AIChE 2017 Spring Meeting, San Antonio, Texas.
- Padmaperuma A.B., L.J. Snowden-Swan, T.E. Seiple, Y. Zhu, M.D. Bearden, S.B. Jones, and J.M. Billing, et al. 06/19/2018. "Petroleum Blendstocks from Wastewater Treatment Sludge: A Techno-Economic and GHG Analysis." Presented by Asanga B Padmaperuma at ACS - Green Chemsitry and Engineering, Portland, Oregon. PNNL-SA-135636.
- Cort J.R., A.K. Bingol, J.T. Bays, A. Heredia-Langner, A.H. Zacher, J.M. Billing, and M.V. Olarte. 06/27/2017. "Characterizing composition and properties of bio-oils with 2-D heteronuclear NMR spectroscopy." Corvallis, Oregon. PNNL-SA-127176.

Awards and Patents

Awards

- 2015 FLC Excellence in Technology Transfer Award
- EERE “Recognition of Innovation” for HTL technology transfer to Genifuel Corporation, presented to the team by DOE Assistant Secretary David Danielson. March 2015.
- 2015 R&D 100 Award “Hydrothermal Processing to Convert Wet Biomass into Biofuels”

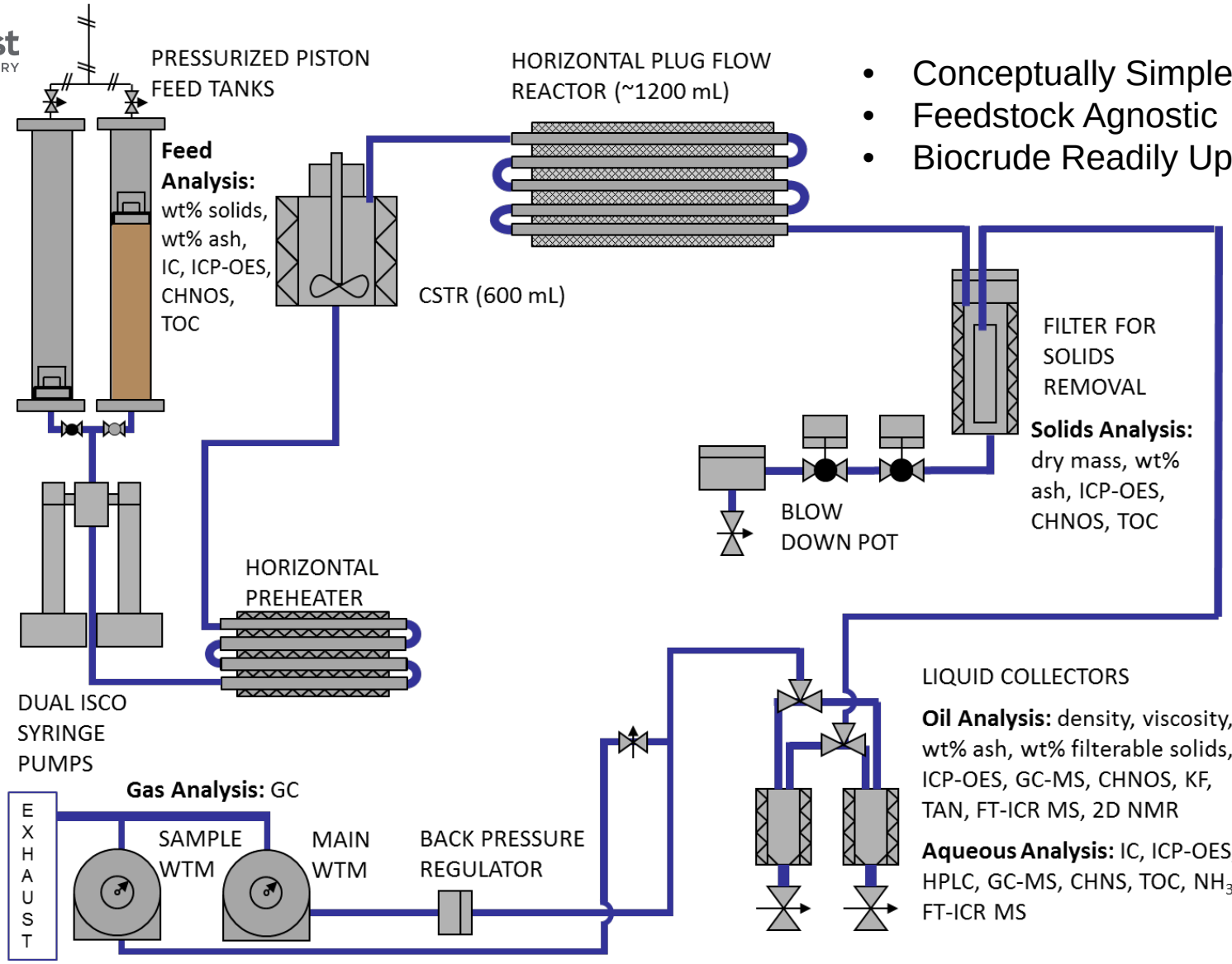
Patents

- Hart, TR, DC Elliott, AJ Schmidt, RT Hallen. “Catalytic hydrothermal liquefaction for bio-oil production.” US Patent No. 9,758,728
- Elliott DC, GG Neuenschwander, TR Hart. “Combined hydrothermal liquefaction and catalytic hydrothermal gasification system and process for conversion of biomass feedstocks.” US Patent No. 10,138,426
- Schmidt AJ, TR Hart, JM Billing, GD Maupin, RT Hallen, DB Anderson. “Liquefaction processes and systems and liquefaction intermediate compositions.” US Patent No. 9,388,364
- Elliott DC, TR Hart, GG Neuenschwander, JR Oyler, LJ Rotness, AJ Schmidt, AH Zacher. “System and process for efficient separation of biocrudes and water in a hydrothermal liquefaction system.” US Patent No. 9,404,063

Press Releases and Social Media

- “From Breakfast to Biocrude: Study Identifies Production Potential across Nation” PNNL Research Highlight. May 2018. https://energyenvironment.pnnl.gov/highlights/highlight.asp?id=3022, accessed 14 February 2019.
- “Turning Goo to Fuel - Hydrothermal Liquefaction at Pacific Northwest National Laboratory.” YouTube video. 2018. https://youtu.be/vmrO3O6pUnc, accessed 14 February 2019.
- Reddit Ask Me Anything (AMA) live event with Justin Billing. “Human Waste to Biofuels” in r/Science category. Archived questions and responses at The Winnower. doi: 10.15200/winn.148060.00259. Stats: Most popular biofuels AMA, 10,031 user click-throughs, 7,576 up-votes.
- “From the Toilet to the Tank,” YouTube video. 2016. https://youtu.be/ER4C6EapZQ4, accessed 14 February 2019. Currently 106K views.
- “Fuel from sewage is the future – and it's closer than you think.” PNNL News Center. November 2, 2016. Story adapted by dozens of national and international media outlets including Popular Science and the Huffington Post UK. http://www.pnnl.gov/news/release.aspx?id=4317, accessed 14 February 2019.

HTL Simplified Process Flow Diagram



- Conceptually Simple
- Feedstock Agnostic
- Biocrude Readily Upgraded

Elliott et al. (2015) *Bioresource Technology*
doi:10.1016/ j.biortech.2014.09.132

Diagram of a typical wastewater treatment plant with photos of scum streams