



Bench Scale Hydrothermal Liquification of Wet-Wastes 2.2.2.302

February 18, 2021
Organic Wastes Review Panel

Mike Thorson
Principal Investigator
Pacific Northwest National Laboratory



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

This presentation does not contain any proprietary, confidential, or otherwise restricted information



77 million dry
tons of wet-
waste per
year

Hydrothermal Liquefaction (HTL): A sustainable solution for wet-wastes

Value of HTL

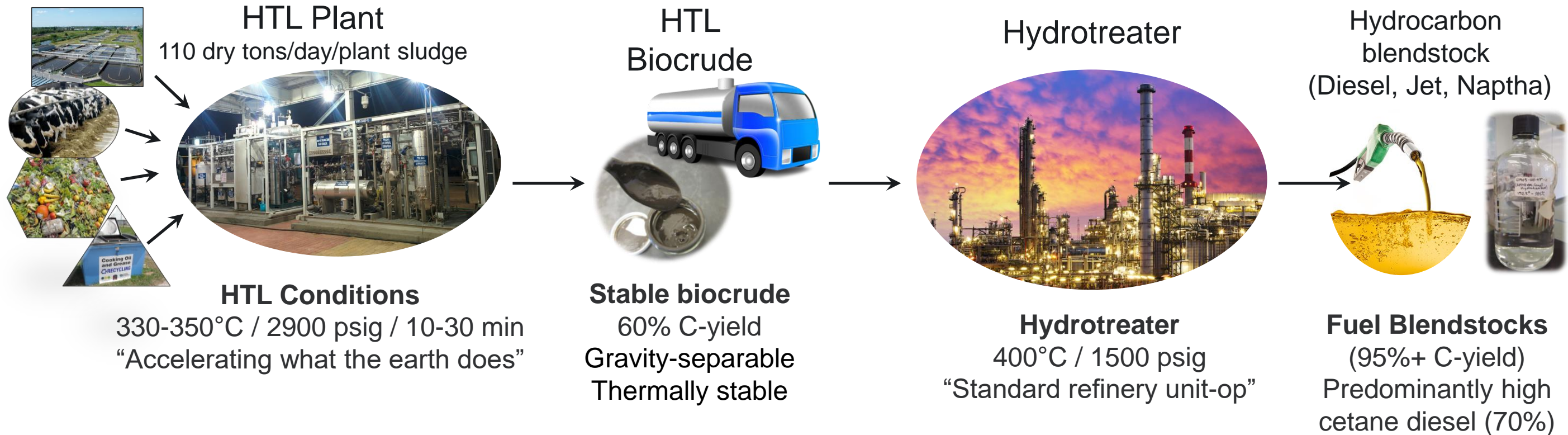
1. HTL solves a wet-waste problem by eliminating wet-wastes (convert wet-wastes to fuel)
2. There is potential for 5.5 billion gallon/year of fuel in the U.S. (diesel gallon_{eq}).

Robustness of HTL

- Tolerates high solid content
- Accepts tremendous feedstock diversity (no drying!)
- Consistent biocrude product



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



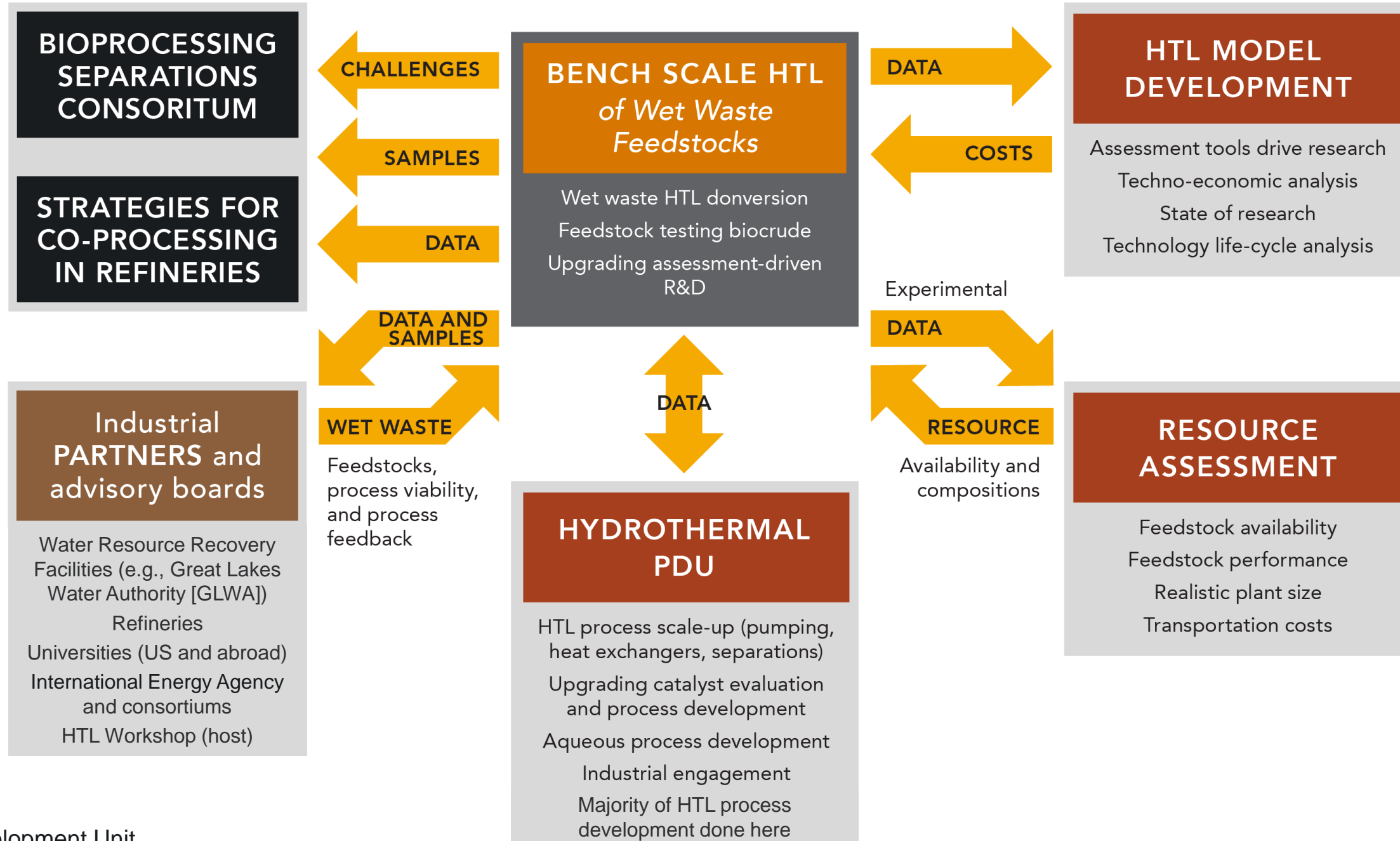
Primary Challenge: Reduce commercialization barriers

- Reducing uncertainty by retiring process assumptions (e.g., 500-hour catalyst life)
- Developing technology to reduce capital intensity of HTL (capital is the primary cost)

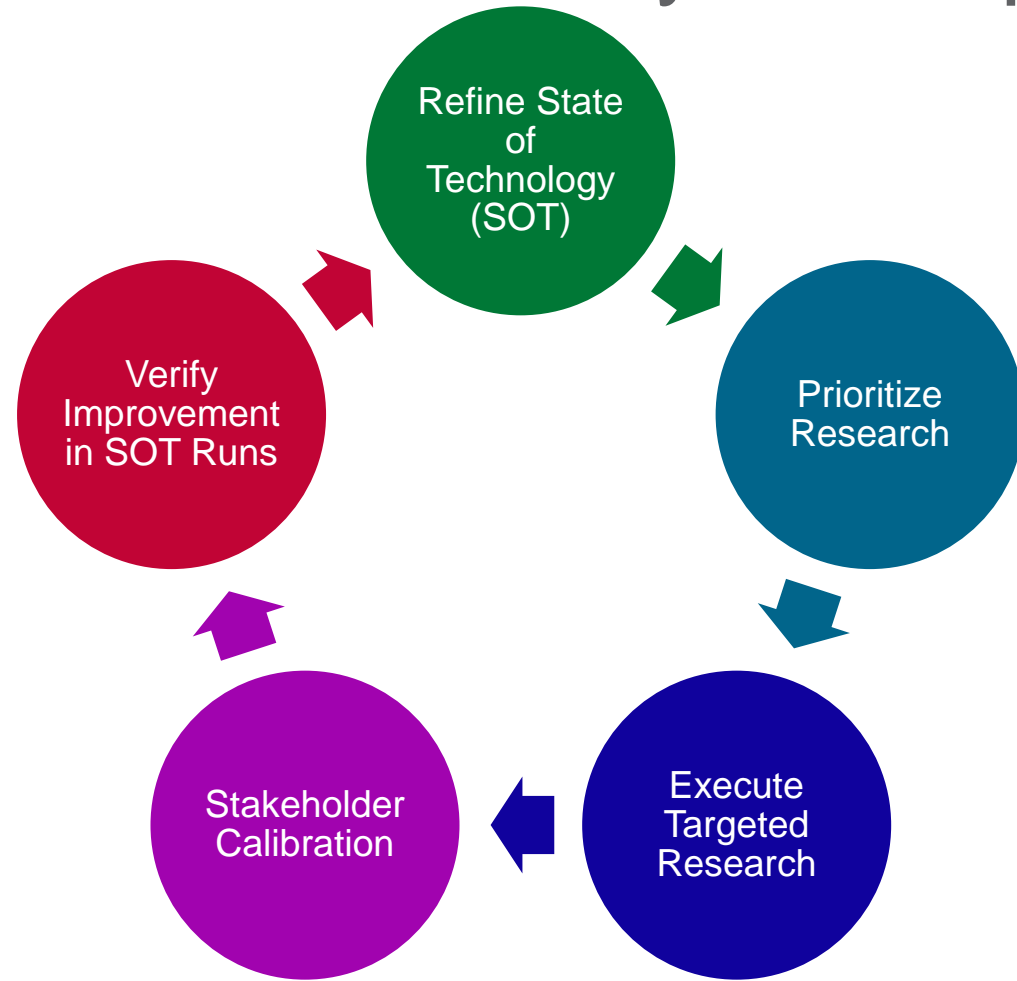
Approach: Targeted research based on shared learnings from PDU (3.4.2.301), Analysis (2.1.0.301) and Waste to Energy (2.1.0.113)

- Reduce cost of capital for HTL
- Improve hydrotreater catalyst activity and catalyst life

1 - Management: Project interfaces proactively with related projects to leverage learnings/maximize value.



1 - Management: Continuous iteration with economic analysis keeps focus on impactful research.

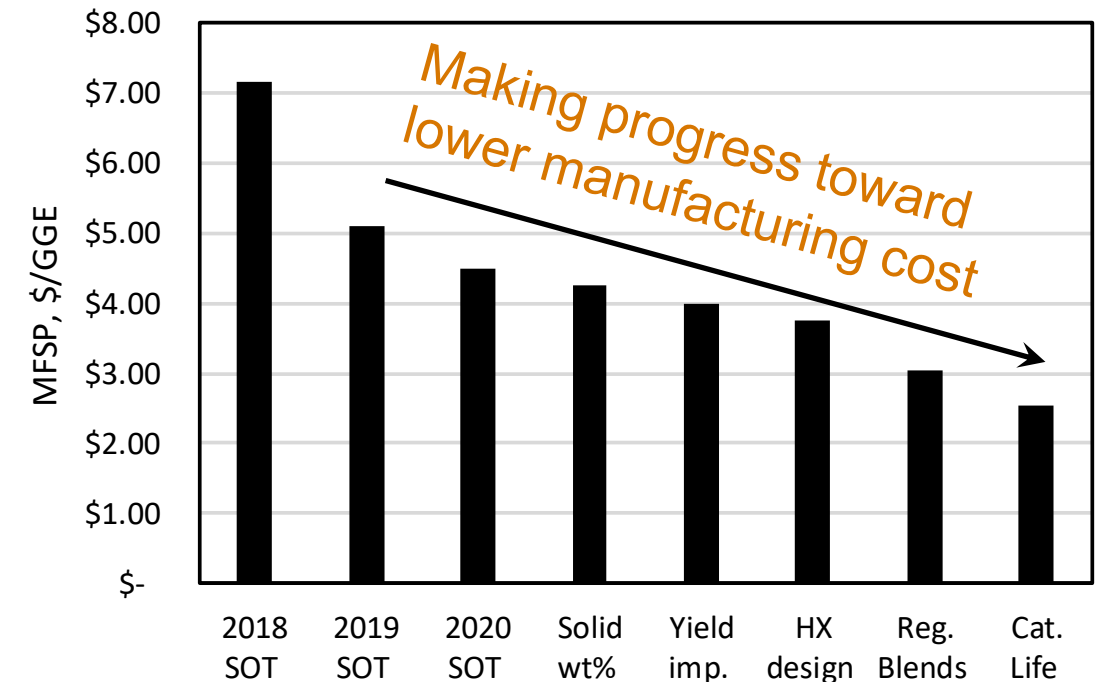


Regular Communications

- Monthly cross-team meetings, including process research updates and economic implications
- Quarterly updates with Bioenergy Technologies Office (BETO) (video and written)
- Frequent vetting of alternative process ideas PDU (3.4.2.301), Analysis (2.1.0.301), Waste to Energy (2.1.0.113), and industrial collaborators

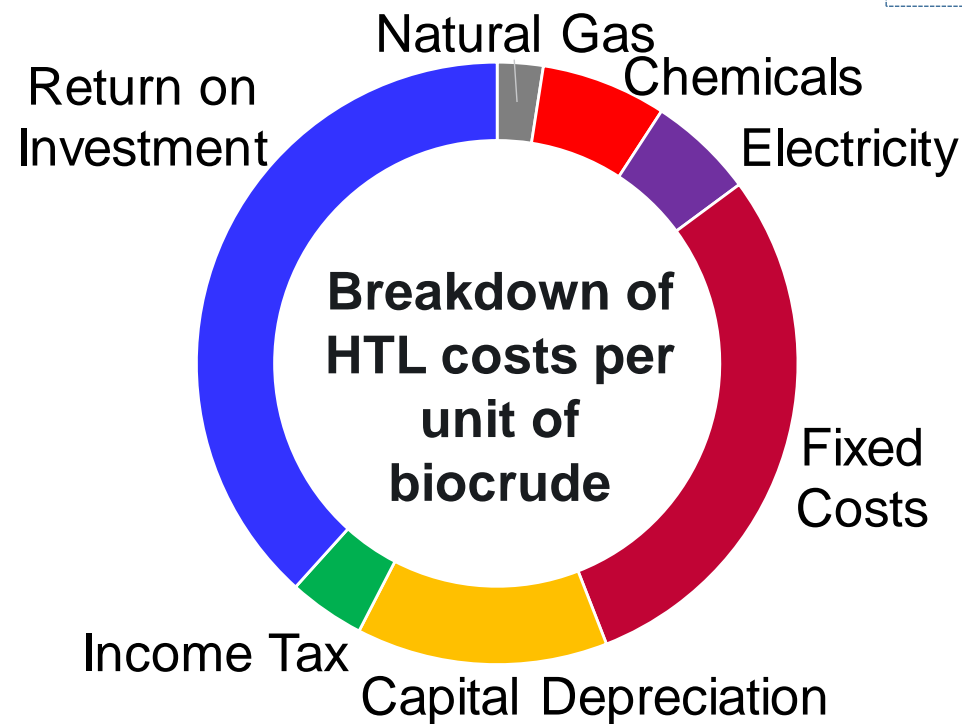
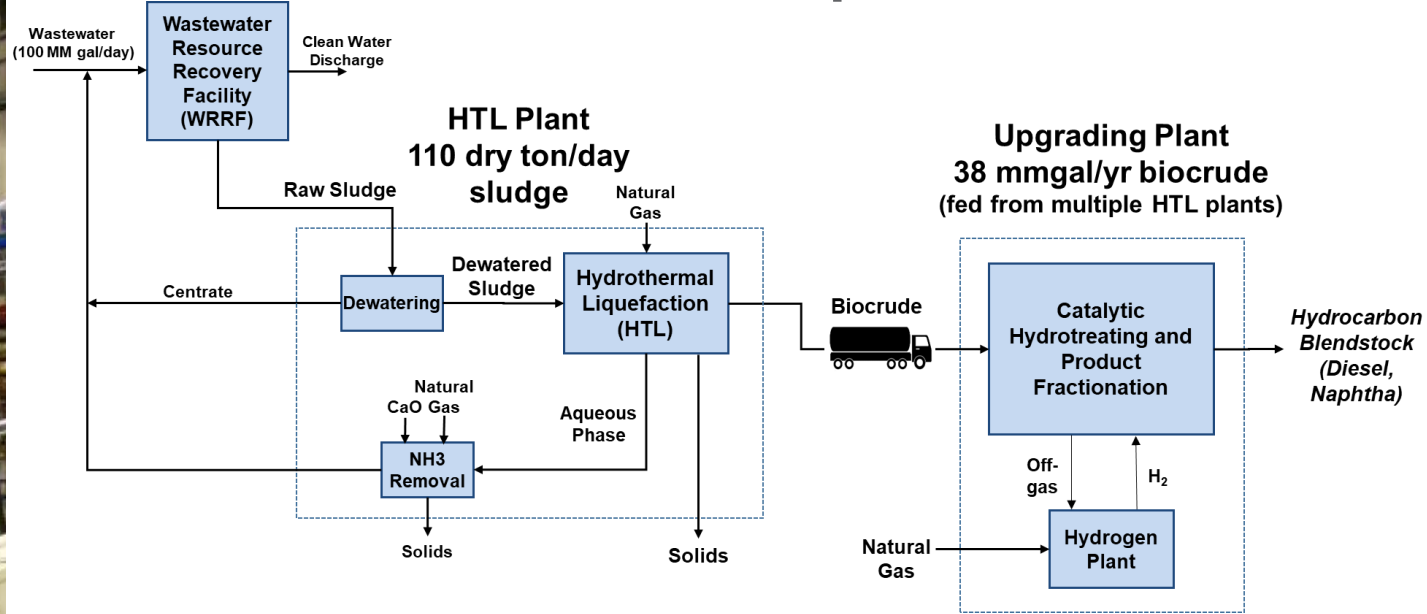
Key Research Areas

- Regional wet-waste blending to increase plant size
- Process high wt% solids feedstock to reduce capital and increase process yield
- Increase hydrotreating catalyst activity and lifetime





2 - Approach: Example of leveraging techno-economic analysis (TEA) and resource assessment to drive process research



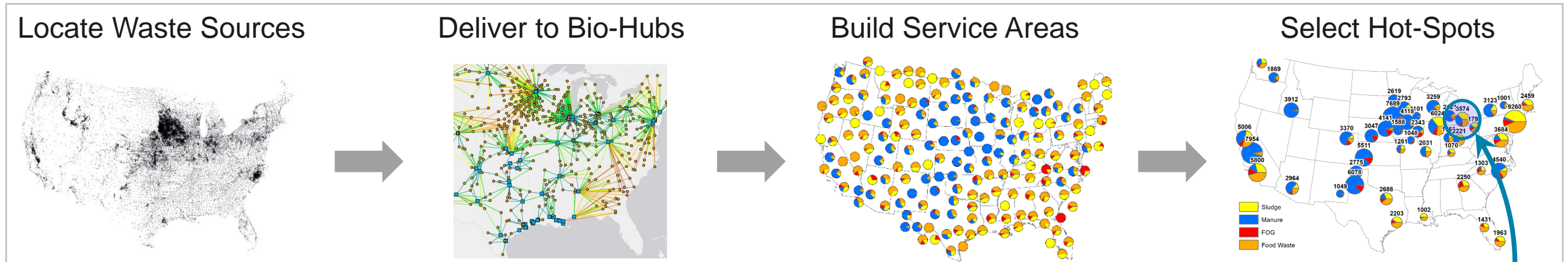
Collaboration: Analysis team (WBS 2.1.0.301) identified the majority of HTL costs lie in capital costs.

- Drives brainstorming on ways to reduce capital
 - Example: Increasing plant size to 1,000 dry tons/day (from 100 dry tons/day) decreases minimum fuel selling price (MFSP) by \$0.69/ gas gallon equivalent (GGE) (WBS 2.1.0.301).

Outcomes:

- Motivates realistic transportation costs, plant sizes, and wet-waste compositions for regional HTL plants (WBS 2.1.0.113).
- Evaluate impact of regional wet-waste blends on HTL and upgrading process performance and yields.

2 - Approach: Example of leveraging techno-economic analysis and resource assessment to drive process research

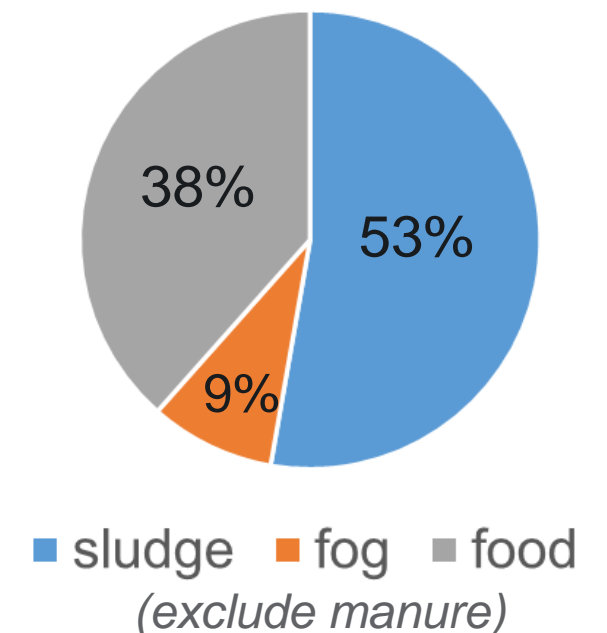


Collaboration: The “Waste to Energy” Team (WBS 2.1.0.113) modelled feedstock supply to determine realistic blending ratios.

- 82% of total wet organic feedstocks in the U.S. can be processed at HTL conversion hot spots (≥ 1000 dry metric t/d) with transportation costs of \$50 per dry metric ton.
- Detroit, MI, selected as a representative blending profile at a ratio of 53:38:9 sludge-food-FOG.

Outcome: Experimental plans to characterize HTL conversion efficiency for a “typical” metro area with potential for significant reduction in modelled HTL fuel price.

Detroit, MI wet-waste profile (observed):



2- Approach: Regional wet-waste blends

Objective: Use realistic regional wet-waste blends to increased HTL plant size

- Increasing plant size to 1,000 dry tons/day (from 100 dry tons/day) decreases MFSP by \$0.69/GGE.

Approach: Test representative wet-waste blends for regional hot spots as compared to stand-alone wet-wastes.

- Real and representative feedstocks sourced from partners and collaborators.
 - Addressing real-world formatting challenges
 - No model or simulated feeds
- Use continuous flow tubular reactors which scale directly from bench to engineering reactors.

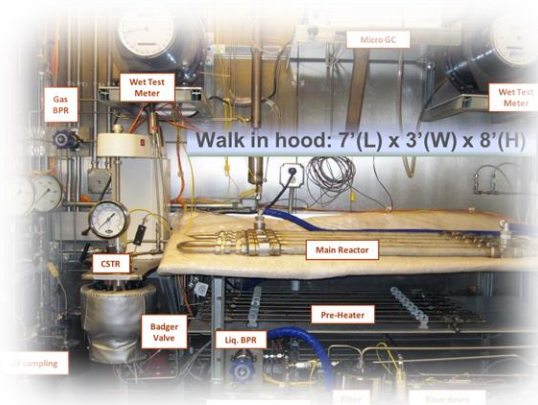
Risks to experimental approach:

- Feedstock Availability:** Foster relationships with real-world waste generators [e.g., GLWA]. Coordinate early with resource assessment team and real waste generators to define realistic regional blend "hot spots".
- Negative Impacts of Blended Wastes:** Evaluate HTL of individual wet-waste streams (e.g., sludge, food) to biocrude and upgrading to fuel blendstocks.

2021 Milestones

- Test at least one blend to support a 9x increase in the scale of HTL plant size compared to the design case (110 dry tons/day) while maintaining the design case biocrude yield of 44%.
- Quantify and report the yield of plastic to fuel when blended and co-processed with a wet-waste stream

Bench-Scale



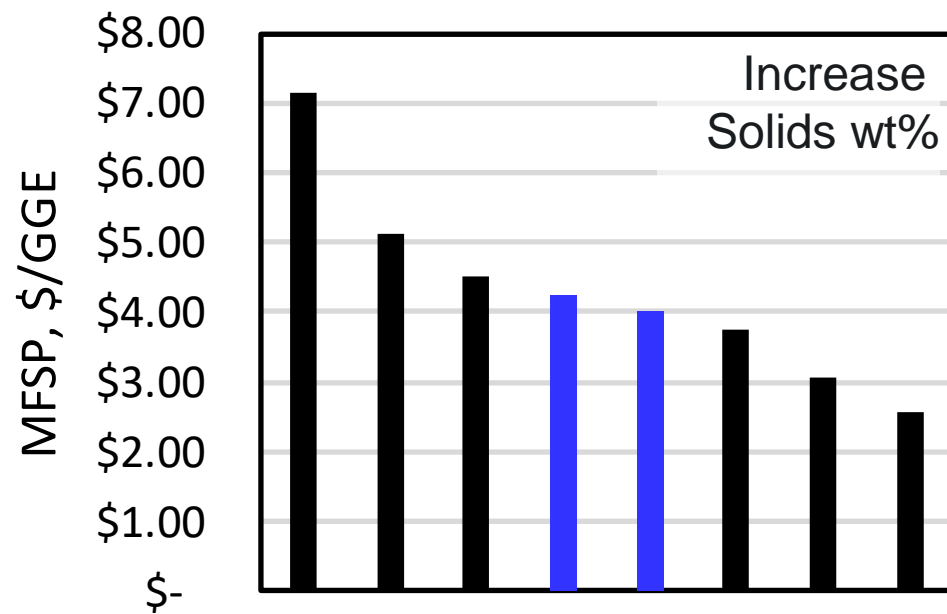
Engineering-Scale



2 - Approach: Process wet-wastes with high solids content to reduce capital costs and improve yields

Objective: Increase HTL process yield and reduce HTL capital costs by processing wet-waste feedstocks with elevated solids content.

- TEA shows solids content significantly impacts HTL conversion costs.
- 25 wt% is a realistic solids feedstock conc.



Approach: Modify process equipment to handle high solid wt%.

- Demonstrate pumpability with multiple 25 wt% feeds.
- Commercial pumps can pump 25 wt% wet-waste streams.

Process a wet-waste stream at solids contents between 20 to 25wt% to make clear correlations.

- Use continuous, scalable HTL system and real waste streams.

Risks to Experimental Approach:

Pumpability: Laboratory equipment can't pump high solids feed.

- Modify equipment and replace pumps, if necessary.

Improved Yield: No yield improvement from increased solids wt%.

- HTL wood data indicates yield correlated to solids content.

2021 Milestone: Modify experimental equipment and demonstrate pumping of feedstocks with solids content of 25% at a rate of 4L/hr for four hours.

2021 Go/No-Go (Q1): Determine the impact of increased solids content (25%) on HTL and upgrading to fuels.

2- Approach: Improve hydrotreater catalyst activity and lifetime.

Objective: Reduce upgrading costs by increasing hydrotreater catalyst activity (catalyst development) and extending hydrotreating life.

Approach: Leverage catalyst development and learnings from PDU (3.4.3.201) to improve hydrotreating catalyst activity and life.

- All testing done on whole pill extrudates to ensure scale-able data
 - Satisfy criteria necessary to ensure data quality (Mear's criteria, Gierman criteria, etc.)
- >20x scale-up from bench to engineering hydrotreater demonstrates scaleability performance

Risks to Experimental Approach: *Catalyst Activity:* Upgraded fuel does not meet fuel blendstock specifications at elevated flow rates.

- Partner with industrial catalyst suppliers
- Evaluate multiple catalyst types (NiMo, CoMo) and extrudate sizes on partnership project (PDU, 3.4.3.201)

Catalyst Life: Catalyst deactivation limits life.

- Develop guard bed reactors to pre-treat biocrude (slurry and fixed-bed reactors) to on PDU (3.4.3.201)

2020 Milestone: Increase catalyst weight hour space velocity (WHSV), a measure of reaction rate or catalyst activity, from 0.3hr^{-1} to 0.5 hr^{-1}

2022 Milestone: Achieve 2,000 hours of stable hydrotreating performance at a WHSV of 0.75 hr^{-1} (2022)

3 - Impact: Clear path to improving economic viability of HTL

Aligned with BETO Conversion Goals:

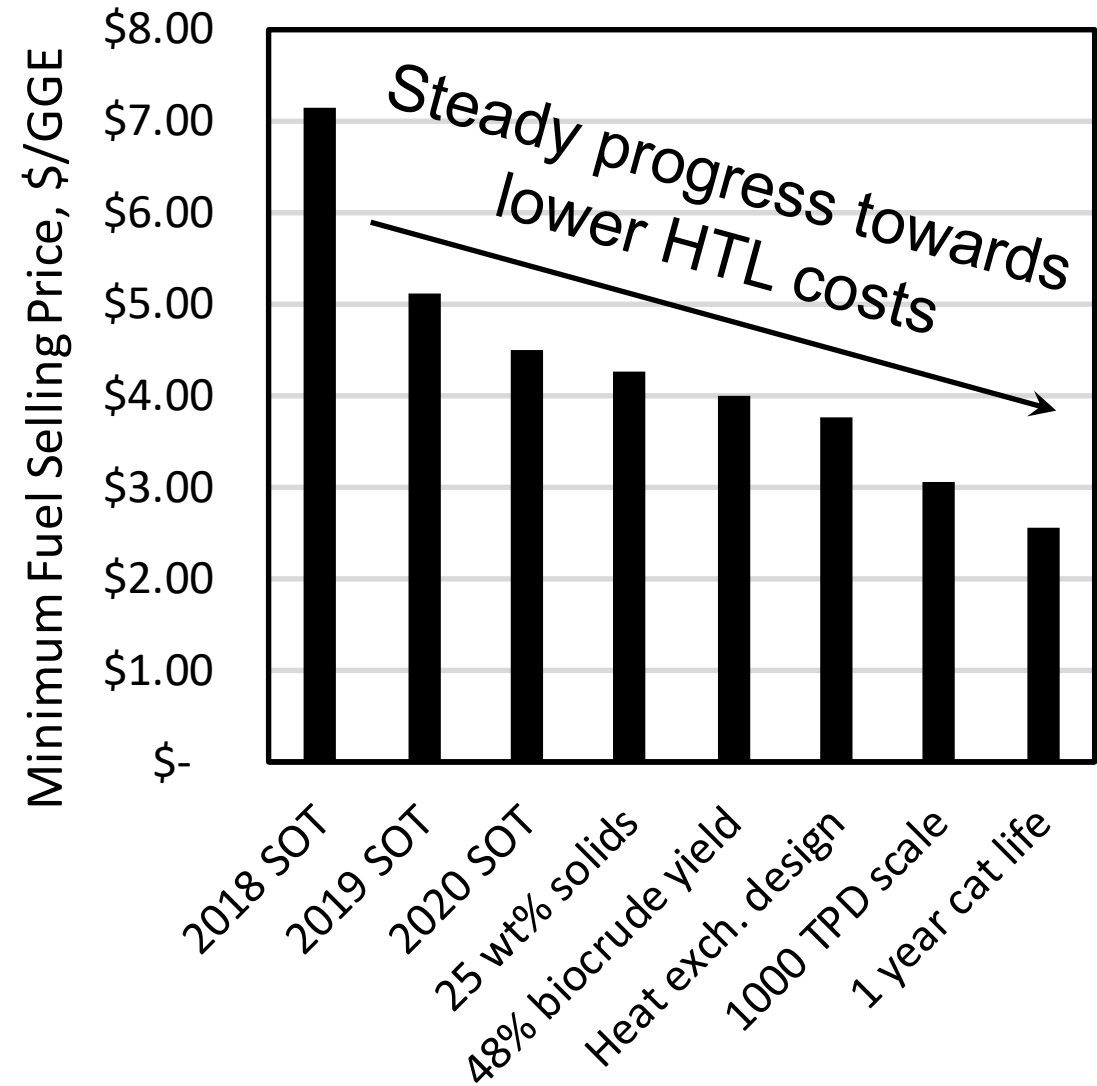
Planned improvements provide clear path to \$3/GGE in 2022 and \$2.5/GGE in 2030.

2021 GPRA Goal Aligned to this Project:

Provide final SOT achieving a modeled cost of \$3.03/GGE.

Impactful Improvements:

- Reduced the cost of NiMo hydrotreater catalyst and increased catalyst activity, including:
 - Extended hydrotreater catalyst life beyond 500 hours; and
 - Increased catalyst activity over 3x.
- Increase solids loading for process intensification.
 - Improvement in process yield via increased solids loading.
- Demonstrated viability of multiple high-impact wet-wastes
 - Regional wet-waste blending to increase plant size to 1000 TPD.

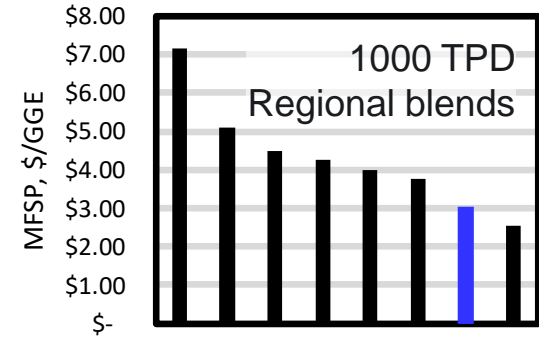


3 - Impact: Providing impact towards HTL commercialization

- Advancing HTL technology to reduce technology uncertainty
 - Providing a sustainable means of **converting wet-waste streams** to fuels
 - Advanced **HTL and upgrading process technology** for **wet-wastes**
 - Providing **scale-able**, commercially relevant HTL and upgrading data
 - **Retiring process assumptions** to reduce modelled HTL conversion costs
- Advancing HTL knowledge sharing and collaboration
 - Project is supporting **collaborative annual operating plan and competitive projects** with the U.S. Department of Energy (DOE).
 - Hosted internationally attended **HTL workshop** focused on jet fuel.
 - **Invited as advisor for international projects**, including International Energy Agency Bioenergy Task 34: Direct Thermochemical Liquefaction, HyFlexFuel: HTL Consortium.
- Advancing the prospects for HTL commercialization
 - Project has led to several **industrial collaborations** and projects
 - Supporting **pilot plant project opportunities**

Project provides impact for DOE, the research community, and opportunities for technology commercialization.

4 - Progress and Outcomes: HTL of food waste, a wet-waste blendstock

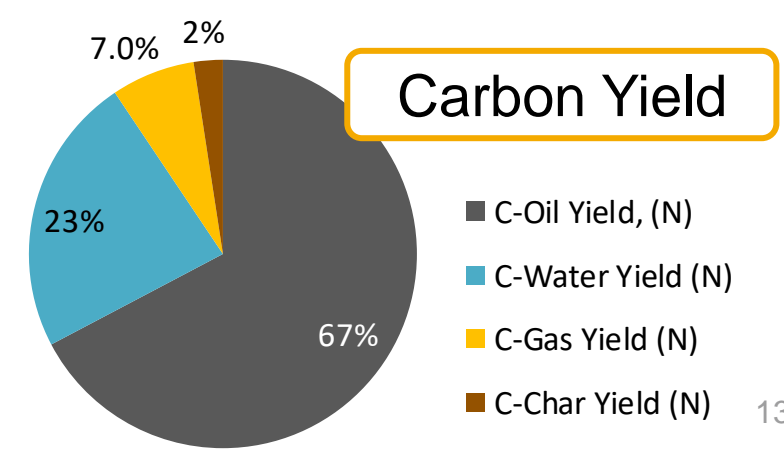
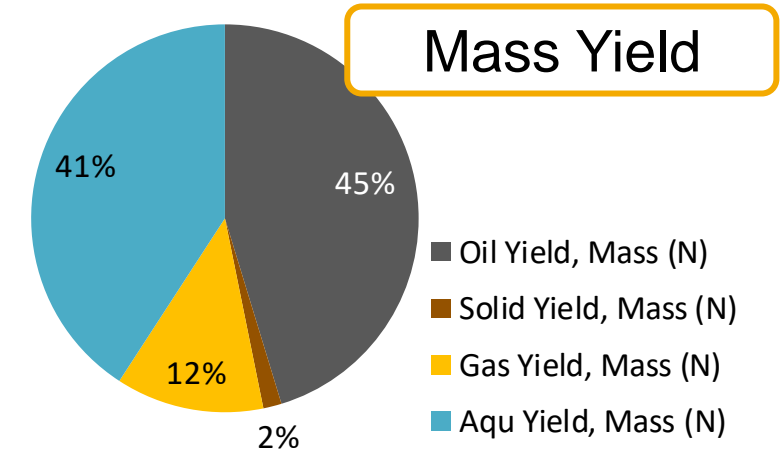
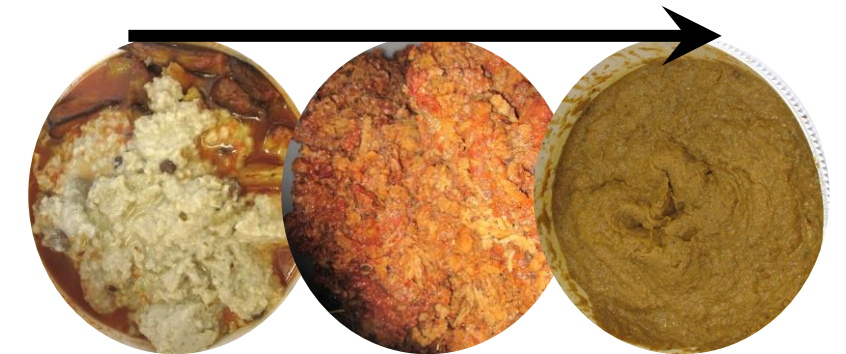


Objective: Test a regional wet-waste blend to support a 9x increase in HTL plant size while maintaining a biocrude yield of 44% (2021 milestone)

Progress: Tested individual components of regional wet-waste blend

- Testing HTL of food waste from a regional prison cafeteria in a continuous, plug-flow HTL reactor gives similar performance to HTL of sewage sludge.
 - *Quality Feedstock Attributes:* High solids without concentration (23%), low ash (<5 %), and high fat (18%)
 - *Good Process Performance:* Improved HTL yields (45%), carbon yields (67%), and above average biocrude
- Promising hydrotreating results of the HTL biocrude
 - Low density (0.81g/ml) of upgraded product
 - Similar upgraded oil oxygen content (0.23% vs 0.18% for sewage sludge)

As Received → Feed to Reactor

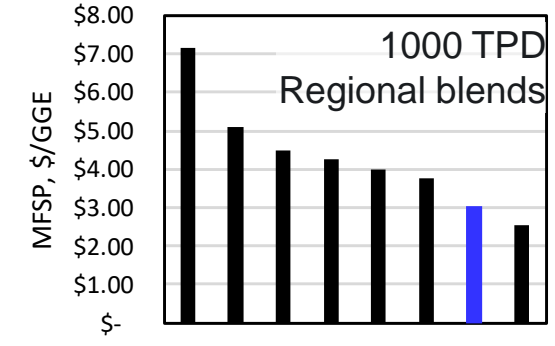
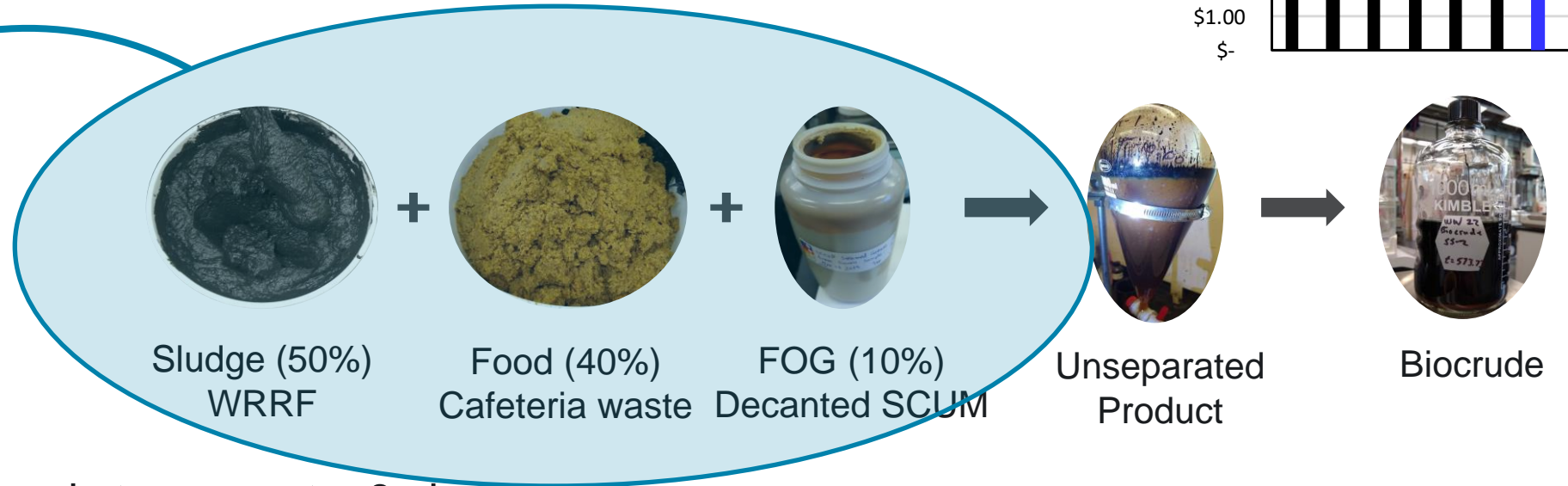
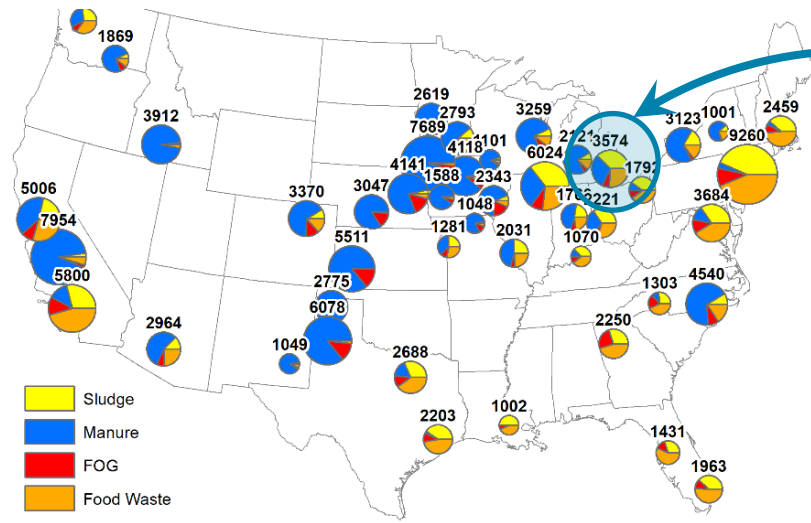


Key Learning:

Food waste makes an excellent HTL feedstock.



4 - Progress and Outcomes: Representative real-world regional blend



Objective: Test regional wet-waste blends to support a 9x increase in HTL plant size while maintaining a 44% yield (2021 milestone).

Progress: Tested representative, real-world regional blend using real-world wet-waste streams (food waste, sludge, FOG).

- Resource-informed HTL feedstock composition

HTL Performance:

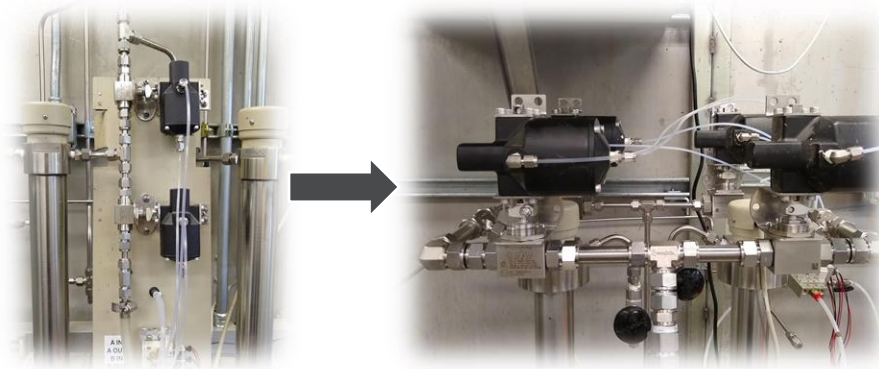
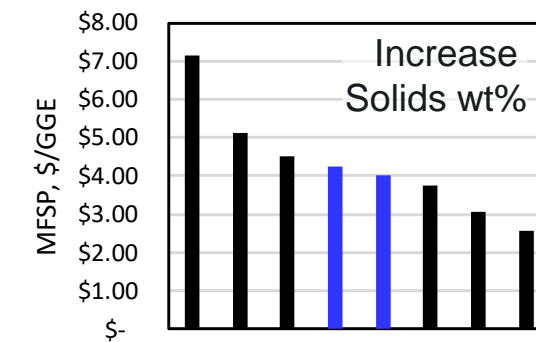
- Consistent biocrude yield / properties
- Pending hydrotreating results

Impact: Blended wet-wastes = excellent HTL feedstock

Bonus: HTL of PET has promising results as a blendstock

Biocrude Properties		Food Waste	Consistent Regional Blend	Sewage Sludge
Carbon	wt%	75.9%	74.8%	78.0%
Hydrogen	wt%	11.2%	11.5%	10.6%
dry calc HHV	MJ/kg	38.7	38.8	39.1
Oxygen	wt%	8.6%	8.0%	5.3%
Nitrogen	wt%	4.3%	4.8%	5.0%
Sulfur	wt%	0.0%	0.7%	1.0%
TAN	mgKOH/goil	110	98	52
Density	g/ml	1.00	0.96	0.98
Filterable Solids	wt%	0.08%	0.14%	0.15%

4 - Progress and Outcomes: Increase solids content in HTL wet-waste blends



Pumping is only a challenge at the laboratory scale. Existing pumps exist at commercial scale.

Impact: Increased solids content improves yield and reduces HTL capital costs.

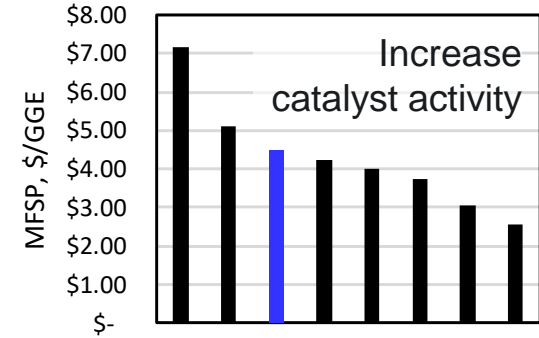
Objective:

- **2021 Milestone:** Modify experimental equipment and demonstrate pumping of feedstocks with solids content of 25% at a rate of 4L/hr for four hours.
- **2021 Go/No-Go (Q1):** Determine the impact of increased solids content (25%) on HTL and upgrading to fuels.

Progress:

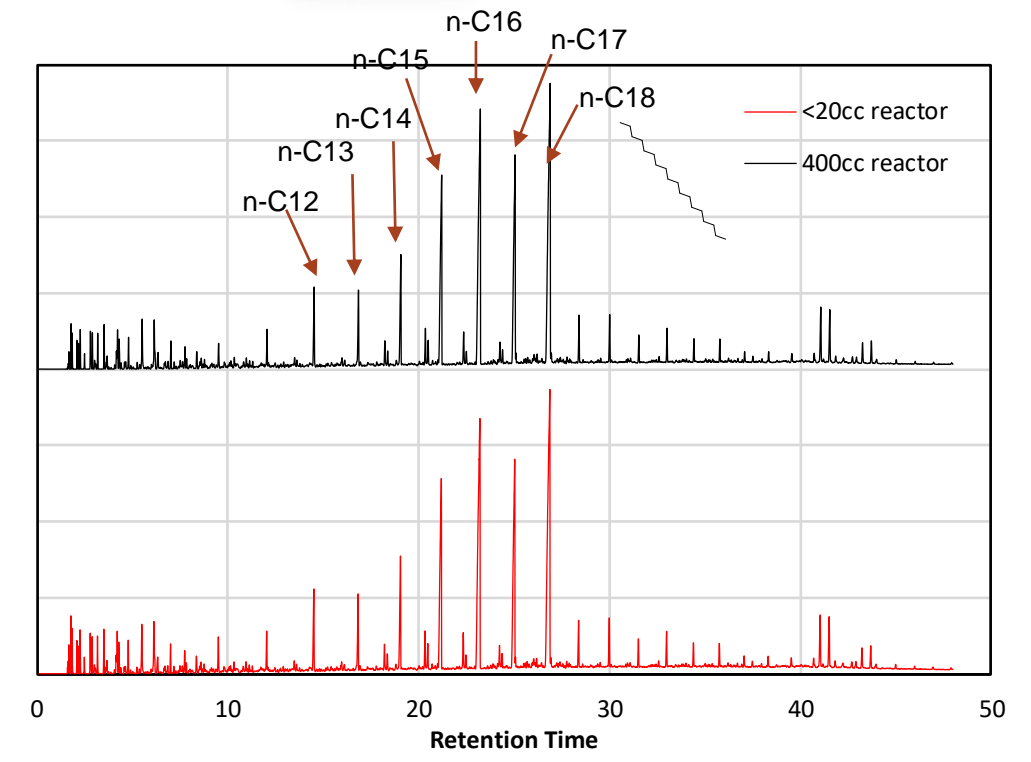
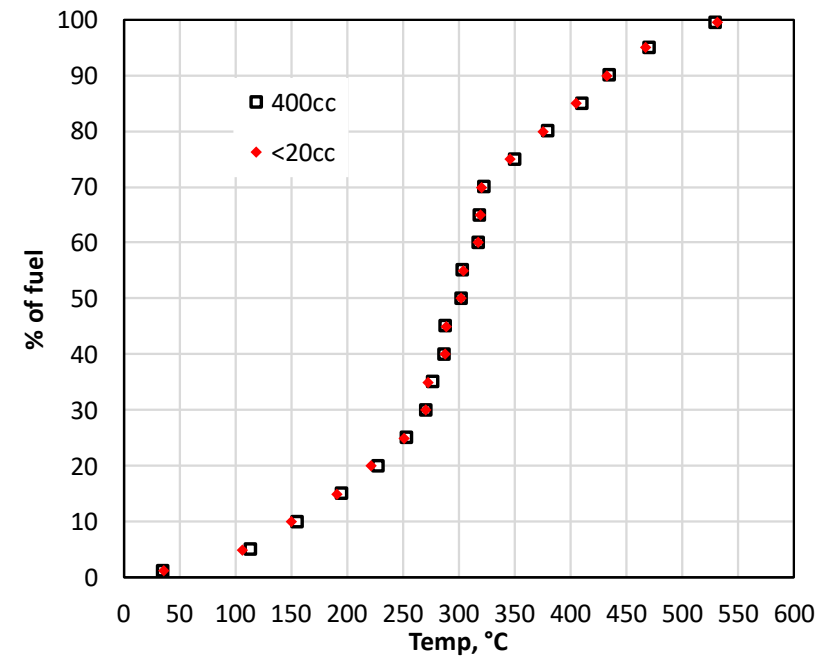
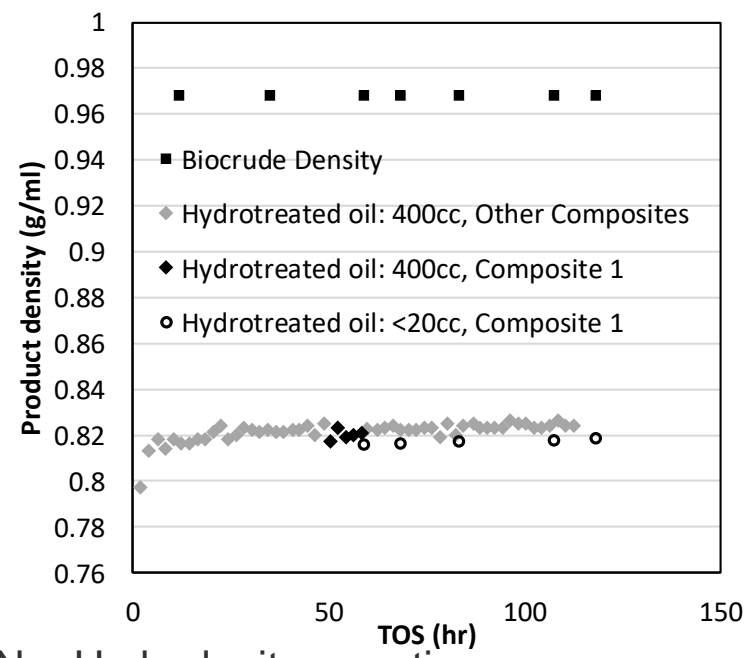
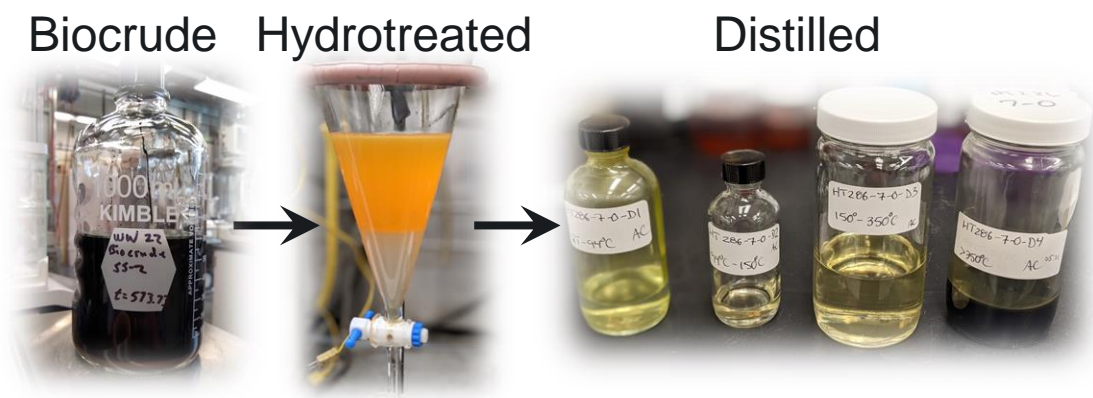
- Modified process equipment to enable pumping higher solids content using laboratory equipment
- Demonstrated pumping 25 wt% solids feedstocks and tested pump modifications with for >4 hours at >4L/hr (2 feedstocks)
- Processed regional “hot-spot” blend with real-world wet-waste streams at 20 and 25 wt% solids
 - Increase in biocrude yield (>2%) from high solid content
 - 46+% yield at 25 wt% (vs 44% in design case)
 - >60% carbon yield to biocrude
- Consistent biocrude quality
 - Low viscosity, density
 - Consistent ash, oxygen, sulfur, and nitrogen %
- Concurrent efforts under way to scale-up process with higher solids systems in the scaled-up system (PDU, 3.4.2.301)

4 - Progress and Outcomes: Increased reactor WHSV with scale-able data



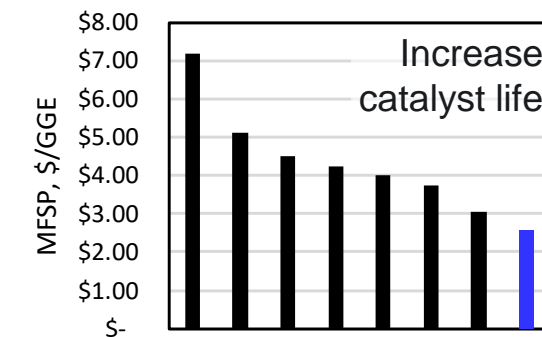
Objective: Increase catalyst WHSV from 0.3 hr⁻¹ to 0.5 hr⁻¹ (2020 milestone).

- **3x increase in hydrotreater catalyst activity** (WHSV: 0.3 → 1.0 hr⁻¹)
 - Improved HDN catalyst (NiMo); lower cost catalyst
 - High cetane diesel product; diesel cut: 72%
- **Scalable results**
 - Leveraged industrial practices of co-packing with inert material
 - Matched scale-up performance (HTL PDU, 204.4.301)
 - Good agreement in density, GCMS, and SIMDIS



HDN = Hydrodenitrogenation

4 - Progress and Outcomes: Increase hydrotreater catalyst lifetime

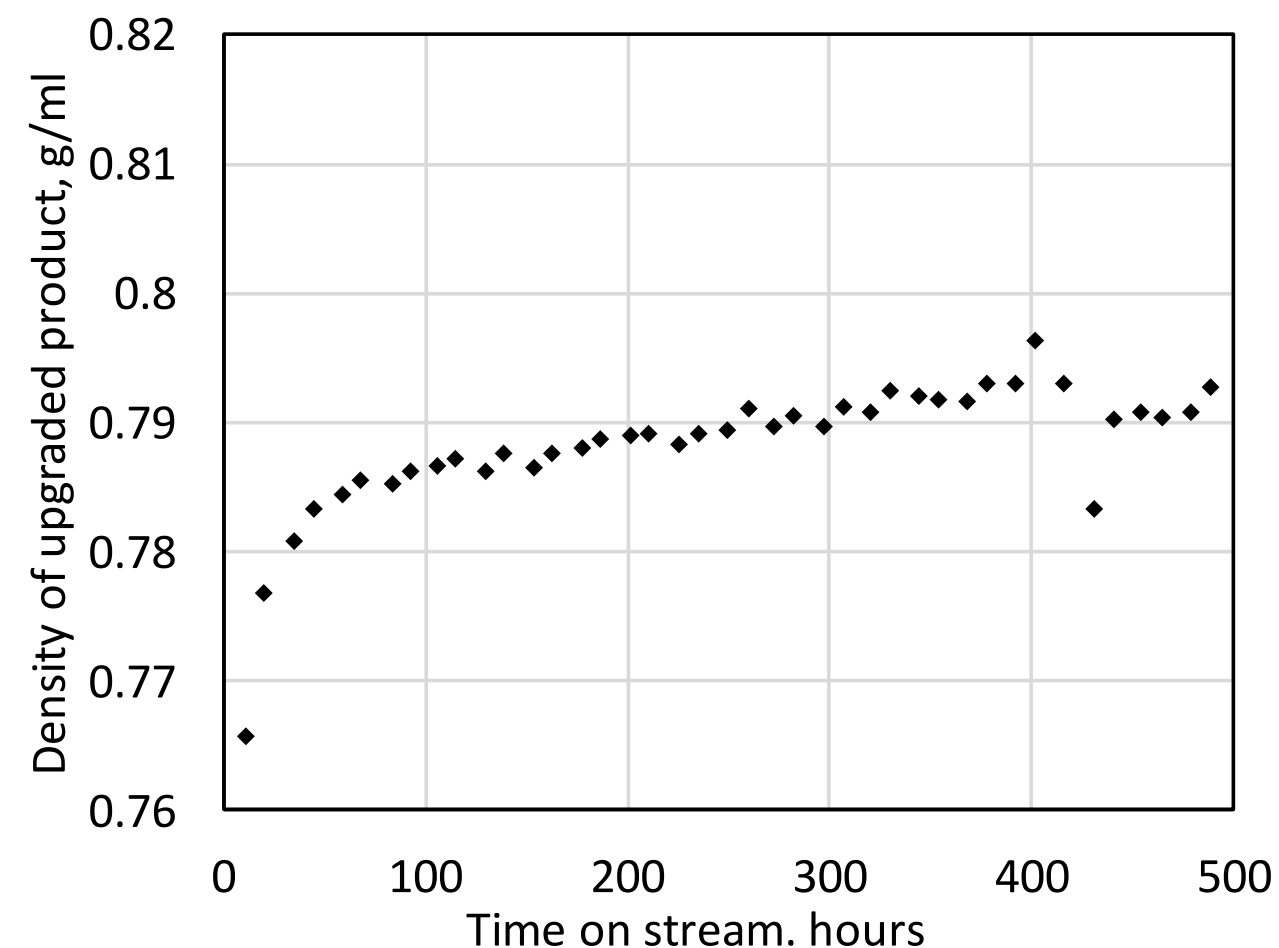


Objective: Achieve 2,000 hours of stable hydrotreating performance at a WHSV of 0.75 hr⁻¹ (2021 milestone).

Progress:

- **>500 hours on stream** with on-spec product at a WHSV of 0.75 hr⁻¹
- **4.2 L** of biocrude from a sludge + FOG feedstock were upgraded catalytically in a trickle-bed bench-scale hydrotreater
- Low product density (<0.80g/ml)
 - FOG decreases the upgraded fuel density
- High diesel yield (70%)
- 2022 Plans: 2000-hour hydrotreater run
 - 2000-hr run completed to understand catalyst deactivation (via PDU, 3.4.2.301)

Impact: **Significant progress extending hydrotreater catalyst lifetime**



Summary



- **Overview:** Executing on strategy to meet SOT target of \$3/GGE in 2022
- **Approach:** Carry out targeted research prioritized based on TEA
- **Impact:** De-risk commercialization of HTL by advancing the technology to enable an economically viable pathway to fuel for <\$2.50/GGE by 2030
- **Progress and Outcomes:**
 - ✓ Reduced hydrotreating costs via improved catalyst with increased WHSV
 - ✓ Intensified HTL process and improved process yield via increase solids loading
 - ✓ Demonstrated viability regional HTL processing by converting high-impact, regional wet-wastes to quality HTL biocrudes. This will enable increased plant size.
- **Forward Looking Plans:**
 - ✓ Upgrade biocrudes derived from regional “hot-spot” blend and high solid content to determine the impact of the entire HTL waste to fuel process (2021)
 - ✓ Evaluate regional waste “hot-spot” blend high in manure (2021)
 - ✓ Achieve modelled hydrotreater catalyst lifetime of one year through long TOS (2,000 hours+) testing and effective guard bed utilization (2022)

Acknowledgements

- Beau Hoffman, BETO Technology Manager
- Mark Philbrick, BETO Waste-to-Energy Coordinator

Experimental Team:

- Andy Schmidt
- Justin Billing
- Mike Thorson
- Dan Anderson
- Rich Hallen
- Todd Hart
- Sam Fox
- Miki Santosa
- Senthil Subramanian
- Igor Kutnyakov
- Matt Flake

PDU Team

Analysis Team:

- Yuan Jiang
- Shuyun Li
- Yunhua Zhu
- Aye Meyer
- Lesley Snowden-Swan

Waste Resource Team:

- Tim Seiple
- Andre Coleman



Quad Chart Overview

Timeline

- Project start date: 10-01-2019
- Project end date: 9-30-2022

	FY20	Active Project
DOE Funding	\$360K	\$1,080K

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

Collaborators: National Renewable Energy Laboratory/PNNL – Waste To Energy Resource Assessment, Bioprocessing Separations Consortium, Oak Ridge National Laboratory – Materials of Construction, 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

Project Goal

Improve impact and cost performance of the HTL technology through targeted research and development. Using TEA and resource assessment tools to prioritize research; tasks for the current fiscal year include:

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

End of Project Milestone

Exceed the 2022 goal case for upgrading wet-waste derived HTL biocrude. Demonstrate catalytic upgrading of wet-waste derived HTL biocrude with improved scalable reactor design, higher activity catalyst, and biocrude pretreatment.

Achieve a WHSV of 0.75 h⁻¹ and an extended TOS of 1,000 hours.

Funding Mechanism

Laboratory Call Annual Operating Plan 2019

Additional Slides



Responses to Previous Reviewers' Comments

Weakness: The project did not yet quantify progress to improve cost performance from hydrotreating catalyst life, increased solids content, feedstock blending and liquid phase separations or ammonia removal.

- The reviewers were correct to identify the need to improve the hydrotreating performance which have a significant impact on the modelled minimum fuel selling price (MFSP)
- Significant strides were made in increasing the hydrotreating catalyst life and activity since the last peer review. Much of the cost reduction from the 2018 SOT (\$7.16/GGE) through the 2020 SOT (\$4.50/GGE) was due to hydrotreater improvements in both activity and life of the catalyst (both main hydrotreater and the guard-bed).
 - Collaborations were made to test commercial hydrotreater catalysts
 - Hydrotreater activity of was increased more than 3x
 - Catalyst life was demonstrated beyond 500 hours
 - ✓ Data from the process development unit (3.4.2.301) shows stable catalyst performance in a 2000 hour run

Publications, Patents, Presentations, Awards, and Commercialization

- Publications and Patent Applications

- JM Jarvis, KO Albrecht, JM Billing, AJ Schmidt, RT Hallen, TM Schaub. “Assessment of hydrotreatment for hydrothermal liquefaction biocrudes from sewage sludge, microalgae, and pine feedstocks.” *Energy & Fuels* 32 (8), 8483-8493.
- JR Collett, JM Billing, PA Meyer, AJ Schmidt, AB Remington, ER Hawley, et al. “Renewable diesel via hydrothermal liquefaction of oleaginous yeast and residual lignin from bioconversion of corn stover.” *Applied Energy* 233, 840-853.
- LJ Snowden-Swan, JM Billing, MR Thorson, AJ Schmidt, DM Santosa, et al. “Wet-Waste Hydrothermal Liquefaction and Biocrude Upgrading to Hydrocarbon Fuels: 2019 State of Technology.” PNNL. Richland, WA.
- Dan Anderson, Justin Billing, Richard Hallen, Todd Hart, Andrew Schmidt, Lesley Snowden-Swan and Michael Thorson. Filed January 10, 2020. “Hydrothermal Liquefaction System.” US Pat Appl 16/740,339.
- Zacher A.H., D.C. Elliott, M.V. Olarte, H. Wang, S.B. Jones, and P.A. Meyer. 2019. “Technology Advancements in Hydroprocessing of Bio-oils.” *Biomass & Bioenergy* 125, 151-168.

Publications, Patents, Presentations, Awards, and Commercialization

• Presentations

- Santosa D.M., A.J. Schmidt, J.M. Billing, D.B. Anderson, and Y. Zhu. 10/07/2019. "Evaluating effect of silaging of Pine/Chlorella Blend via Hydrothermal Liquefaction (HTL) and hydrotreating (HT) pathway." TC Biomass 2019, Chicago, Illinois.
- Santosa D.M., and M.R. Thorson. 10/07/2020. "Improving Scalability Of Hydrotreating Reactor: Upgrading Of Biocrude To Fuel Blendstocks." TCS 2020, Richland, Washington.
- Thorson M.R., R.T. Hallen, K.O. Albrecht, J.M. Jarvis, T. Schaub, T.L. Lemmon, and J.M. Billing, et al. 10/07/2019. "Challenges Upgrading HTL Biocrudes." TC Biomass 2019, Rosemont, IL, 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." Presented by J.M. Billing at WEFTEC 2019, Chicago, Illinois.
- Padmaperuma A.B., C. Drennan, and L.J. Snowden-Swan. 12/15/2020. "Distillate fuels from waste." Presented by A.B. Padmaperuma at Pacifichem 2020, Honolulu, Hawaii.
- Billing J.M., L.J. Snowden-Swan, A.J. Schmidt, M.R. Thorson, R.T. Hallen, and D.B. Anderson. 06/16/2020. "Successful scale-up of continuous hydrothermal liquefaction (HTL) systems to enable resource recovery from wet organic wastes." Presented by J.M. Billing at ACS Green Chemistry & Engineering Conference, Online, United States.
- Billing J.M., A.J. Schmidt, L.J. Snowden-Swan, T.R. Hart, D.B. Anderson, and R.T. Hallen. 09/08/2019. "Hydrothermal Liquefaction of Wastewater Sludge: Process Overview." Presented by J.M. Billing at Pacific Northwest Clean Water Association Pre-Conference Workshop, Portland, Oregon.

Abbreviations and Acronyms

- BETO: Bioenergy Technologies Office
- DOE: U.S. Department of Energy
- FOG: Fats, Oils, and Grease
- GGE: gasoline gallons equivalent
- GLWA: Great Lakes Water Authority
- HTL: hydrothermal liquification
- MFSP: PDU: process development unit
- PFR: Plug Flow Reactor
- PNNL: Pacific Northwest National Laboratory
- SOT: State of Technology
- TEA: techno-economic analysis
- TPD: Dry Tons per Day
- WHSV: Weight Hour Space Velocity

Thank you

