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3.4.2.301 PNNL Hydrothermal PDUs

February 18, 2021
Systems Development and Integration (SDI)

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PNNL

U.S. DEPARTMENT OF ENERGY BATTELLE

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Project Overview

Goal

Adapt and apply PNNL hydrothermal Process Development Unit (PDU) capabilities* to enable the production of biofuels and co-products from wet waste feedstocks

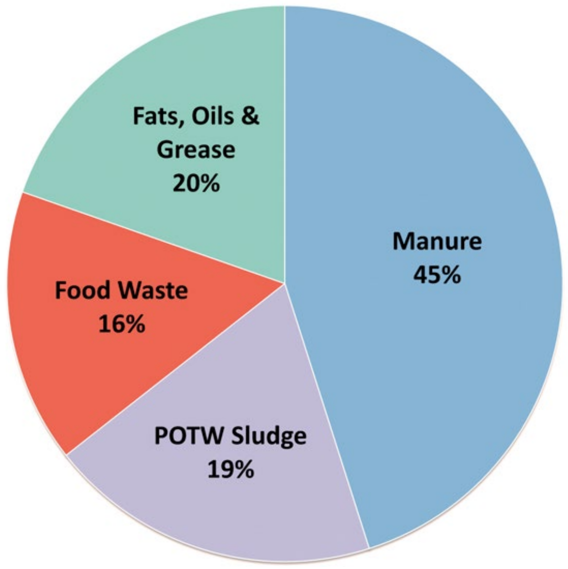
** Hydrothermal Liquefaction (HTL), Hydrotreating (HT), Catalytic Hydrothermal Gasification (CHG)*

Outcome

- The project is enabling ***technology innovation, process integration*** and ***partnership projects*** to demonstrate ***scalable hydrothermal processing methods*** for the conversion of wet waste feedstocks into biofuel and co-products

Impact

- 69.4 Million dry metric tons/year of wet waste feedstocks available
- Potential for 5.6 Billion gallons/year of renewable diesel blendstock
- Huge benefits in waste management and environmental protection



Directly supports BETO's SDI strategic goals:

- **By 2022**, verify integrated systems research at engineering scale for hydrocarbon biofuel technologies that achieve a mature modeled MFSP of \$3/GGE with a minimum 60% reduction in emissions relative to petroleum-derived fuels.
- **By 2030**, verify integrated systems research at engineering scale for hydrocarbon biofuel technologies that achieve a mature modeled MFSP of \$2.5/GGE with a minimum 60% reduction in emissions

Project Overview
PNNL PDU Hydrothermal Systems

HTL PDU

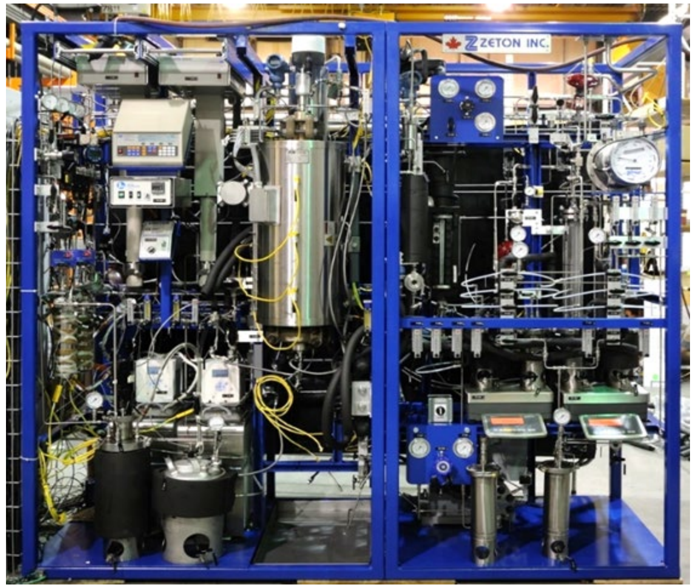
Engineering-Scale (1)

- Feed rate 12 to 18 L/h
- 3 integrated skids
    - feed prep, HTL, product separations

Bench scale (2)

- Feed rate 4-6 L/h

Upgrading PDU



Engineering-Scale Hydrotreater (2)

- Feed rate 100-500 ml/h
- Fix and moving bed

Lab scale Hydrotreater (5)

- Fixed bed and continuous stir tank reactors (CSTRs)
- Feed rate 1-100 ml/h

CHG PDU

Catalytic Hydrothermal Gasification

Engineering Scale (1)

- Feed rate 8-16 L/h, reactor volume 4L
- Mobile plug flow reactor system

Lab scale (3)

- Feed rate 20-200 ml/h, reactor volume 25 ml

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1 – Management Project Structure

BETO SDI
Liz Moore

BETO SDI PDU Working Group
NREL - TCPDU & IBRF
LBNL - ABPDU
INL - BFNUF
PNNL - HTL

Josh Messner

PNNL Hydrothermal PDU
Dan Anderson, PI/PM

Process Development

- **Feedstock Formatting and HTL Testing**
  Andy Schmidt
- **Rheology Impacts on Heat Exchanger (HX) Design**
  Lesley Snowden Swan
- **Separations**
  Alan Zacher
- **Biocrude Upgrading**
  Mike Thorson
- **Waste Stream Valorization**
  Mike Thorson

Scale-up Testing and Production

- **HTL Engineering Scale Campaigns**
  Andy Schmidt
- **Upgrading Scale-up Campaigns**
  Mike Thorson

PDU Systems Capability Management

- **Engineering Scale HTL Capability Operations and Maintenance**
  Lisa Middleton-Smith
- **PDU System Modifications and Upgrades**
  Lisa Middleton-Smith

PDU Utilization and Partnership Projects

- **PDU Working Group**
  Dan Anderson, Andy Schmidt
- **BETO R&D, Consortia, CRADAs and Industrial Partnerships**
  Dan Anderson

Project Structured to Address Technical Risks and Challenges

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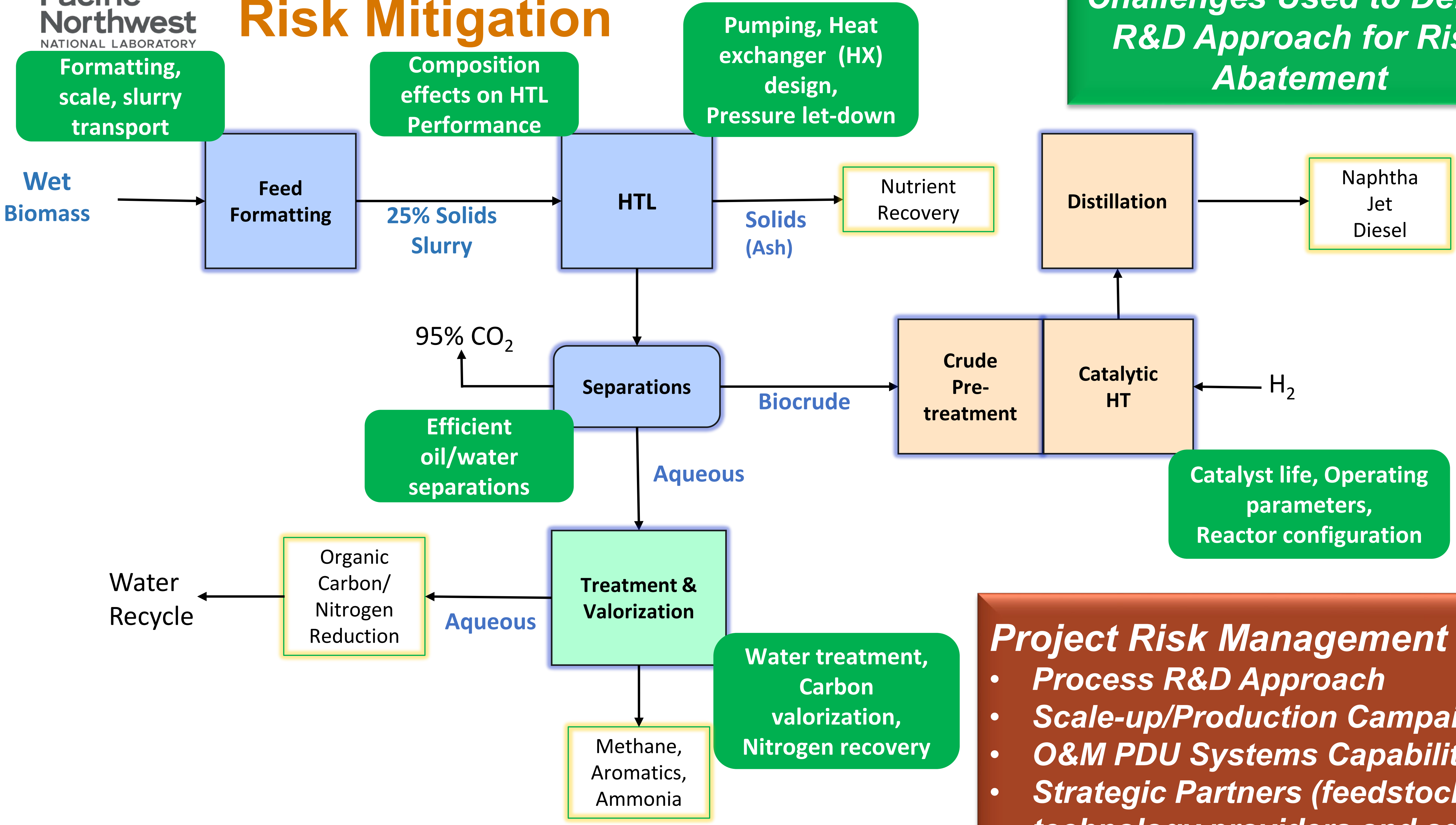
1 – Management Approach and Communication

- Detailed work breakdown structure (WBS) with experienced task leads
  - 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
- Regular Meetings with BETO (technical and progress updates)
- PDU Working Group Monthly Meetings
  - Coordination and Integration with Other PDUs
  - Utilization Tracking
  - Sharing Best Practices
- Management and Integration of Supporting Projects and Partners

► ***Structured Risk Based Plan***
► ***Integrated Project Team***
► ***Strong Project Management***
► ***Experienced Task Leads***
► ***Effective Communications***

1 – Management Risk Mitigation



Technical Risks & Challenges Used to Define R&D Approach for Risk Abatement

Project Risk Management Spans

- ***Process R&D Approach***
- ***Scale-up/Production Campaigns***
- ***O&M PDU Systems Capability***
- ***Strategic Partners (feedstocks, technology providers and adopters)***

2 – Approach

Tasks	Risks/Challenges	Objectives
Process Development	Formatting/HTL Processing Waste Feedstocks	Develop methods to format various wet waste feedstocks and blends **(ML)**
		Conduct benchscale HTL testing of various wet waste feedstocks and blends **(ML)**
	Rheology Impacts on HX Design and HTL Operations	Conduct rheology evaluations of feedstocks and products at process conditions
		Use data and modeling to develop HX designs and commercial scale equipment
	Enhance Biocrude Yield and Separations	Test separations methods to enhance biocrude separations at process conditions
		Identify a promising performance enhancing (catalytic) constituent **(ML)**
	Upgrading Processing of Biocrudes	Conduct pretreatment testing for clean-up of biocrude and process scale-up **(ML)**
		Demonstrate hydrotreating catalyst lifetimes relevant for commercialization **(ML)**
	Treatment/Volarization of HTL Waste	Develop and test thermochemical methods for HTL aqueous phase **(Go/No-Go)**
		Develop and test non-thermochemical methods for HTL aqueous phase
		Develop and test methods for extraction of HTL solids
Scale-Up Testing and Production	HTL Testing and Scale-Up	Conduct HTL scale-up testing at engineering scale with wet waste feed and blends, produce biocrude and HTL wastes for testing and evaluations **(ML)**
	Upgrading Testing and Scale-Up	Conduct upgrading scale-up testing at engineering scale with HTL biocrudes, produce fuel blendstocks for testing and evaluations **(ML)**
PDU Utilization and Partnership Projects	Improving PDU Operations and Utilization	Develop PDU business models, utilization tracking and strategies for collaborative projects
		Collaborate with other BETO PDUs on best operation practices and lessons learned
		Develop partnership projects for PDU utilization
PDU Systems Capability Management	PDU System Modifications	Plan and complete needed modifications to PNNL PDU systems
	Capability Management and Maintenance	Manage PDU and maintain PDU equipment and facilities
		Provide quality assurance for configuration control of systems, procedures, training, etc.

Focused on Addressing Risk/ Challenges with Defined Objectives and Milestones (ML)

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2- Approach
PDU/ Modeling Projects Integrated to Achieve Process Targets

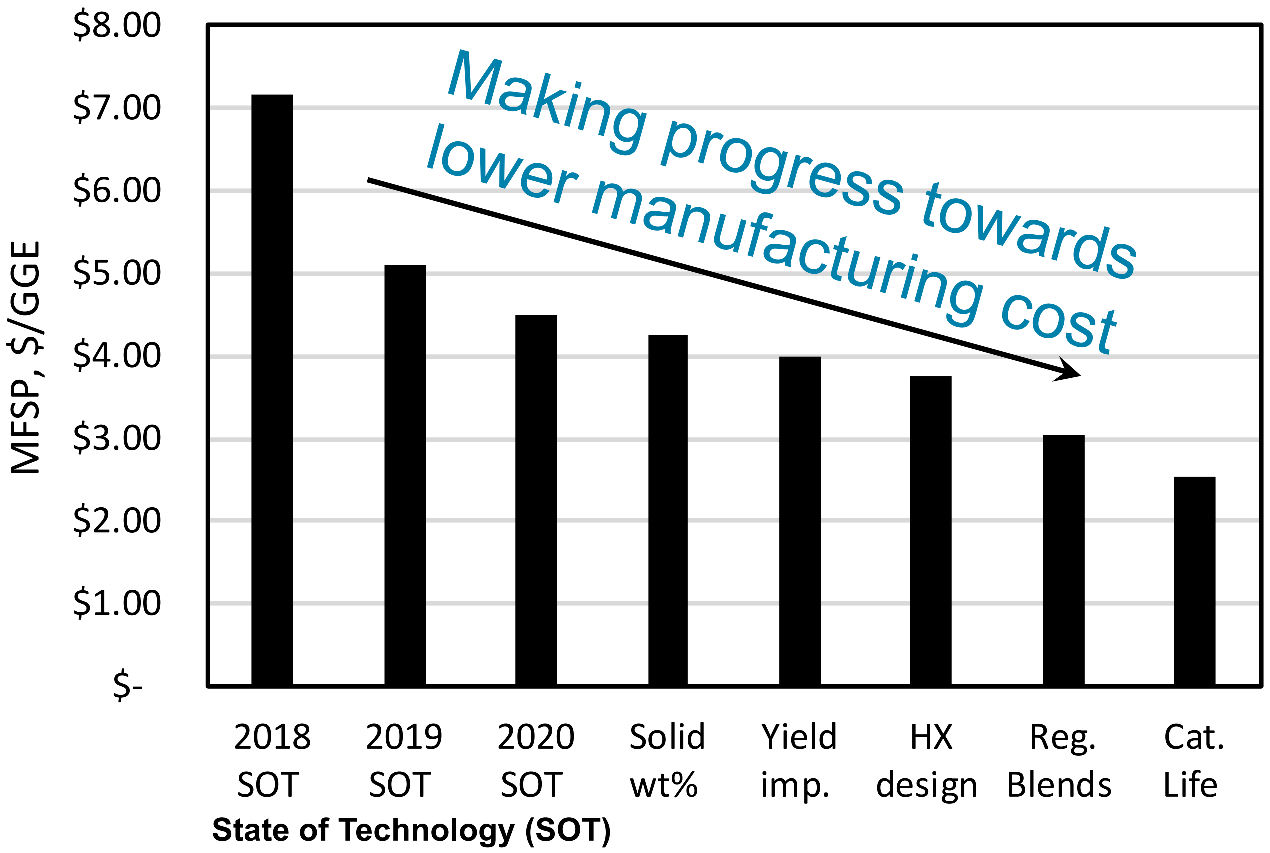
Assumption	Current	Target	Estimated Cost Reduction	Planned PDU Campaigns
HTL Feed Solids	20% wt%	25% wt%	$0.25/GGE	ML, 2021 (HTL Bench/PDU)
HTL Biocrude Yield	44% wt%	48% wt% (stretch goal)	$0.28/GGE	ML, 2021 / 2022 (HTL Bench/PDU)
Hydrotreater Catalyst Life	2000 hours	1 year	$0.51/GGE	ML, 2021 (PDU)
HTL Scale & Feedstock	110 TPD / Sewage Sludge	≥1000 TPD / Blended Waste	$0.56/GGE	ML, 2021 (PDU/HTL Bench and waste-to-energy teams)
HTL Aqueous Treatment	NH3 Stripping	Effective and lower cost 50% C and N removal for recycle	TBD	ML 2021 (PDU)
Heat Exchanger Design	Single Stage Shell/Tube	Two Stage Shell/Tube with core inserts	$0.50/GGE	2022 (PDU, Pilot Plant Project)

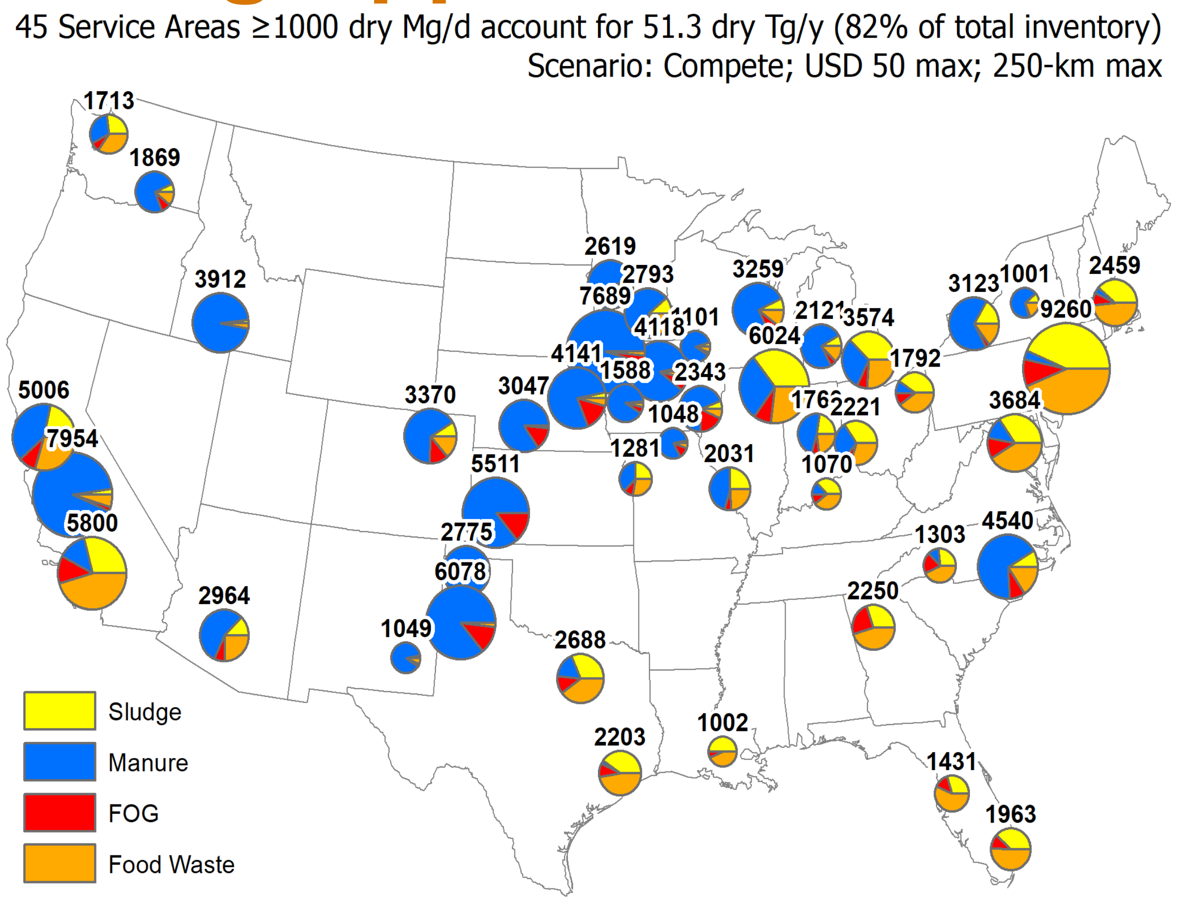
PDU Project is Retiring Assumptions and Technological Uncertainty for Scale-up and Commercialization

2- Approach
Future FY21 and Beyond

- Extend HTL processing and scale-up to blended wet waste feedstocks to enable 1000 ton/day scaling potential
- Incorporate new HX design into HTL pilot plant project
- Evaluate separation methods to improve scale-up and process performance
- Determine potential catalytic component in waste sludge that improves process performance and yields
- Develop and test additional HTL aqueous phase treatment and valorization processes (thermochemical, biological, separations)
- Determine upgrading catalyst deactivation mechanisms and mitigation to achieve 1 year catalyst life
- Conduct scale campaigns HTL and upgrading using feedstocks blends to produce fuels for testing

3 – Impact
Reducing Cost and Expanding Applications





82% **of the total resource could be collected at sites ≥ 1000 ton/day!**

Fats, oils and grease (FOG)

PDU Process Development is Driving Down Costs for HTL Processing and Upgrading to Achieve $2.50/GGE Cost Target

PDU Process Development is Expanding the Range and Quantities of Wet Waste Feedstocks for HTL Processing at 1000ton/day Scale

3 – Impact
PDU Utilization

- **PNNL Projects**
  - 2.2.2.302 Bench Scale HTL of Wet Waste Feedstocks (direct SOT support)
  - 1.3.4.101 Algae HTL for Fuels and Co-products – Sharing applicable learnings
  - 2.1.0.301 Analysis & Sustainability Interface, (Modeling and techno-economic analysis (TEA)
  - 2.1.0.113 Waste-to-Energy Cost-Benefit Analyses (PNNL/NREL)
- **Consortia Projects**
  - Separations Consortium (PNNL/ORNL/ANL/LBNL) *Aqueous Phase Treatment*
  - Refinery Co-Processing Strategy (PNNL/NREL) *Upgrading/TEA*
  - Co-optima (PNNL/NREL) *Fuel Production for Engine Testing*
- **CRADA Projects with Industry**
  - Great Lakes Water Authority (GLWA) HTL/ anaerobic digestion (AD) Integration
  - SoCal Gas HTL Aqueous Valorization to Methane
- **Developing Partnerships/Collaborations**
  - HTL/Feedstocks (Gibby Group, Waste Management, Water Resource Foundation (WFR), multiple Water Resource Recovery Facility (WRRF), DoD)
  - Upgrading (Kern, Chevron, Marathon, SunCor, Haldor Topsoe).
- **HTL Pilot Projects with DOE and Industry**
  - DOE HYPOWERs, Water Resource Recovery Facility (WRRF)
  - Metro Vancouver, WRRF

PDU Supports Multiple Collaborations with Related DOE Projects and Industry

3 – Impact
Technology Transfer

- Project has developed enabling **HTL and upgrading process technology** for **wet waste feedstocks** to produce **biofuels** and **provide environmental solutions**
- Project **providing HTL PDU scale-up capabilities for DOE and others**
- Project is supporting **collaborative AOP & competitive projects** with DOE
- Project is supporting production of data and knowledge that **Industrial Partners are using to raise capital**
- Project is supporting development of **pilot plant projects**
- Project has resulted more than **20 publications** and **20 presentations**
- Project has supported the development of **two patents and licensing agreements**

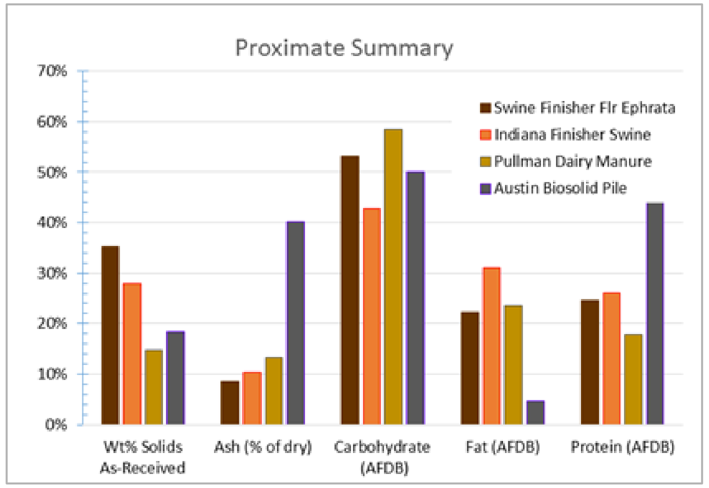
FY19 Peer Reviewer Quote

"The impact and support to the industry at large cannot be underestimated. Of particular relevance is the effort to make this facility flexible and capable to provide engineering data of immediate use for scale up activities."

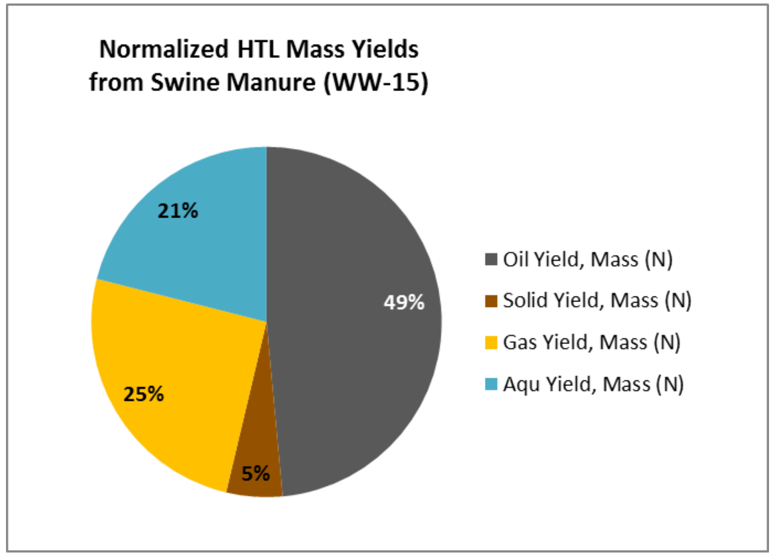
4 – Progress and Outcomes FY19 Summary

Outcomes:

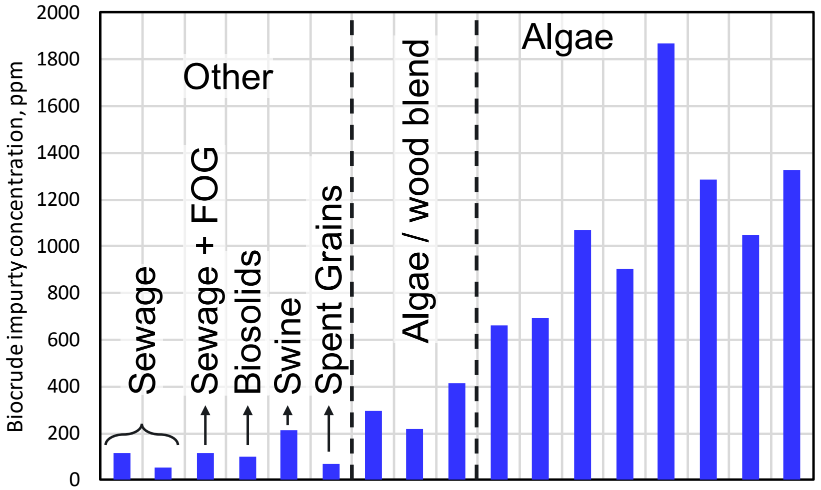
- Demonstrated bench scale HTL processing and biocrude upgrading for 4 wet wastes
  - AD biosolids, swine manures, brewery waste and sewage sludge
- Demonstrated engineering scale HTL processing for 2 wet wastes
  - brewery waste and sewage sludge
- Develop pretreatment IP for biocrude upgrading to remove metals
- Scaled up upgrading processes producing several liters of diesel range blendstock for engine testing
- PDU Working Group established
- Completed upgrades and maintenance of PDU systems and procedures



Proximate Analysis Wet Waste Feedstocks



Mass Yields HTL Processing Swine Manure



Biocrude Impurities for Various Feedstocks

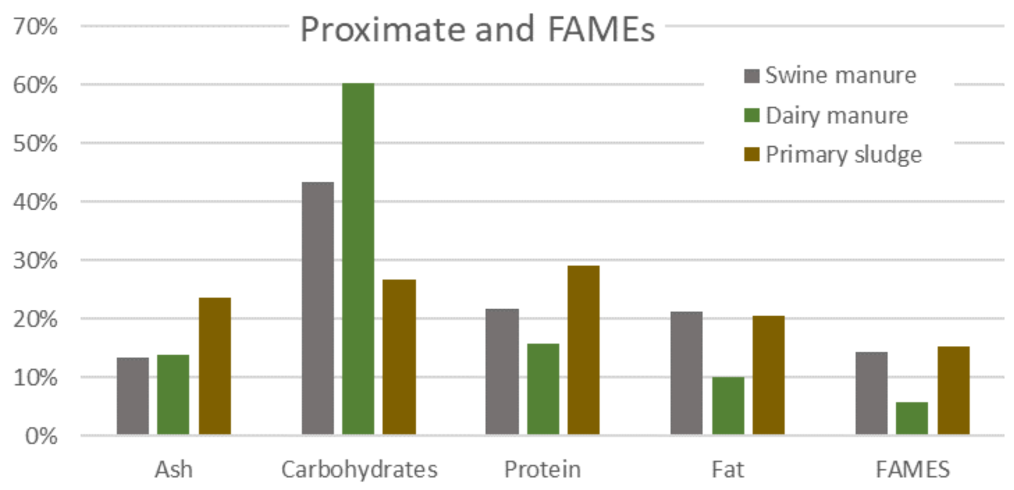
Brewery Waste Feed Formatting

4 – Progress and Outcomes FY20
HTL Process Development for New Feedstocks

FY20 Milestone

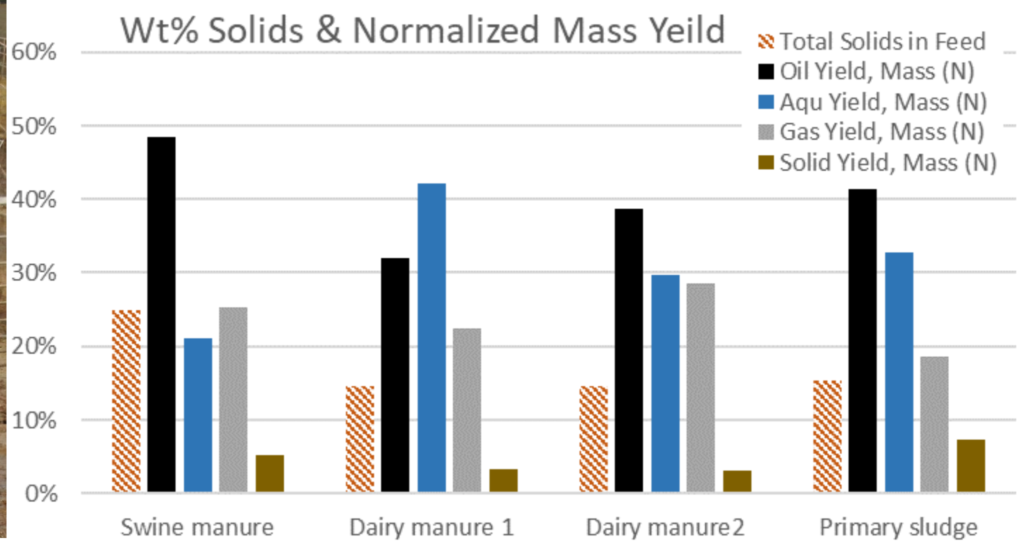
Acquire, format and test 2 distinct manure streams in the HTL bench system to determine impacts on process yields and biocrude quality

- Approximately 10 dairy and swine manures were collected and analyzed. High fat concentrations (>10%) found in most manures.
- Many had ash contents greater 40% (rocks, grit, sand) even though all were acquired from covered/indoor operations.
- Conducted bench scale HTL runs with swine and dairy manure



Outcomes:

- ► Successful benchscale HTL runs conducted with swine and dairy manure.
- ► Demonstrated processing swine manure at 25% solids; yield to biocrude was almost 50%
- ► Need improved formatting approach remove rocks/grit

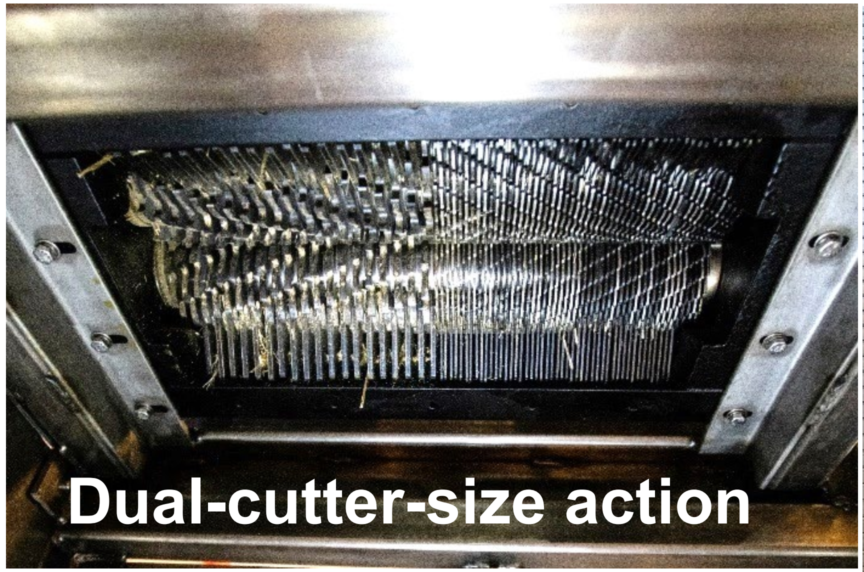


4 – Progress and Outcomes FY20
HTL Process Development Feedstock Formatting

FY20 Milestone (Stretch)

Complete safety approvals and approved SOP for Wet Grinder to be used to format animal manures and other wet or dry wastes for bench-scale HTL and M engineering scale HTLS testing

- SOP approved by a dozen SME and management staff.
- Custom guards and interlocks
- DOE and PNNL worker safety officials witnessed the processing food waste.
- System successfully used on dairy manures, food waste streams, and water bottles.



Outcomes:

- ▶ Added New Feedstock Formatting Capability to PDU
- ▶ JWC Shredder (Muffin Monster) is an industrial standard for sludges, food waste

4 – Progress and Outcomes FY20
HTL Scale-up Testing and Production

FY20 Milestone (Stretch)

Q3 Complete Complete at least one run in MHTLS PDU using swine or dairy manure. Process 300 L of feed slurry (24 hour TOS) and produce > 10L biocrude for subsequent evaluations. Biocrude will be upgraded at PNNL or provided to a refinery partner.

- Conducted 2 engineering scale HTL runs FY20
  - Primary sludge run met all objectives
  - Manure run terminated due to feeding and plugging issues in front end of system.
- Conducted engineering scale HTL FY21Q1
  - 50:50 primary:secondary sludge
  - Produced > 15L diesel fuel for engine testing

Engineering-Scale HTL Testing

Feed	Primary Sludge	Dairy Manure
Date	Jan-20	20-Sep
Feed Solids, wt%	15.3%	15.5%
Ash in dry feed, wt%	25.6%	20.6%
Slurry Processed, L	520 L	26 L
Time on Stream, h	44 h	3 h
Biocrude produced, L	26 L	> 1 L
Biocrude disposition	engine testing	N/A
All test objectives met?	Yes	No

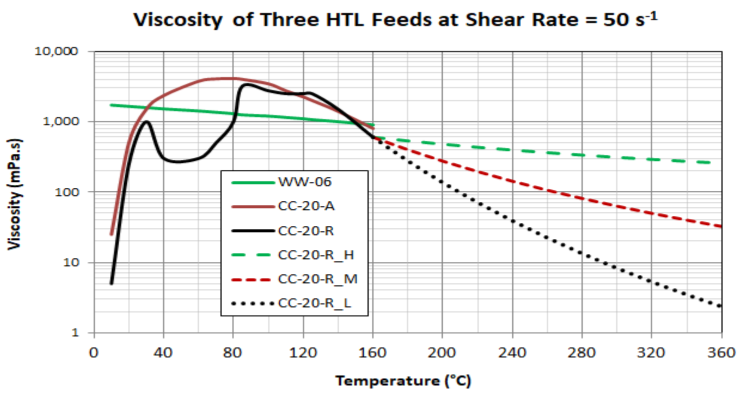
Outcomes:

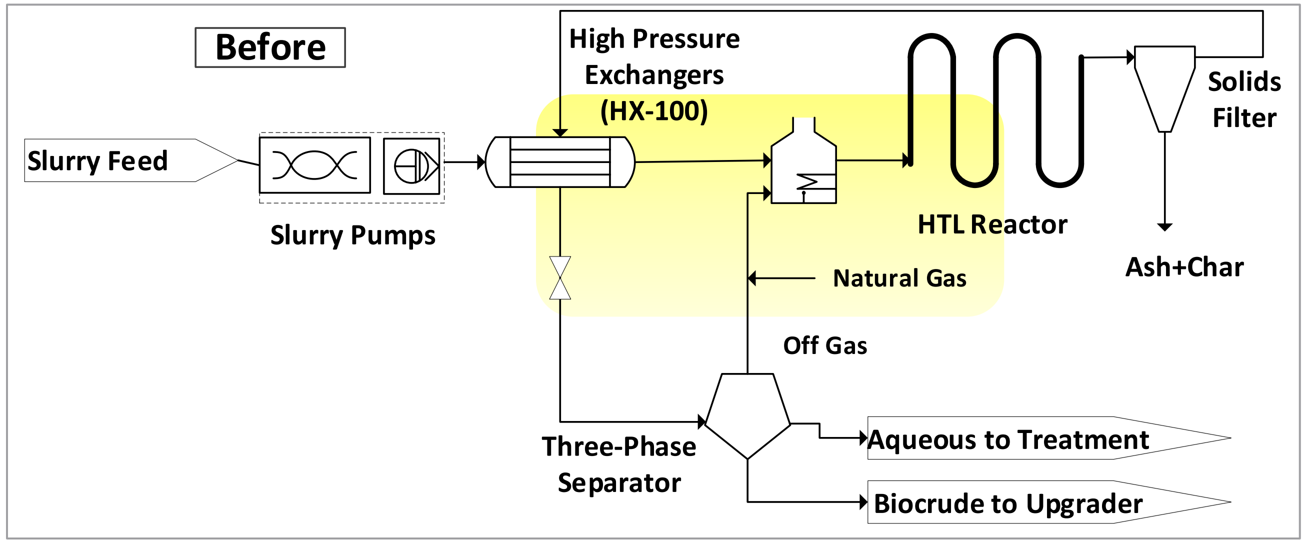
- Produced ~60L of biocrude for upgrading and engine testing (Co-Optima)
- Rheological data used for optimal operation of feeding system, heat exchanger, pressure control and biocrude separations
- Foreign materials (grit, straw, woody bits, fuzz/hair) present significant challenges to processing dairy manure

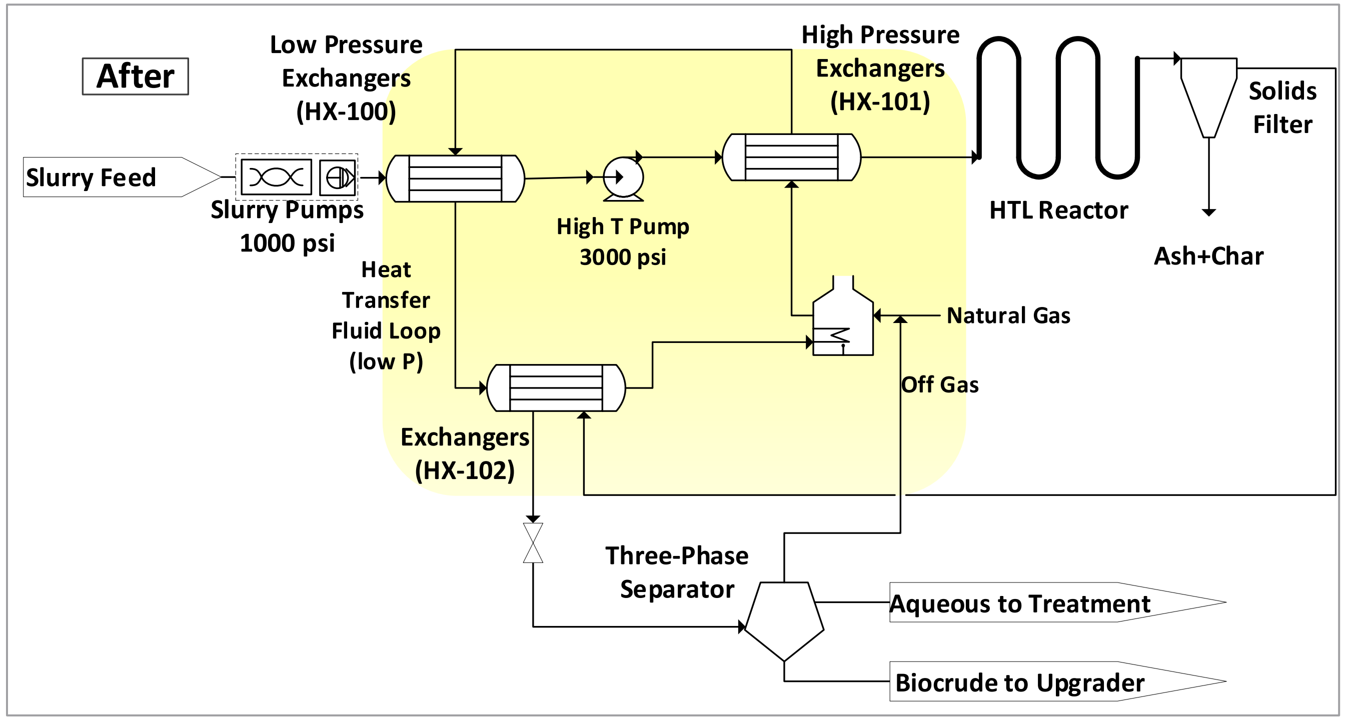
4 – Progress and Outcomes FY20 HX Detailed Design for HTL Scale-up

Goal: Investigate alternative heating/pumping configurations that can reduce CAPEX/OPEX

- **Heat exchangers are ~50% of the 2020 SOT HTL capital cost**
- Split HX design concepts evaluated
- Viscosity data for sludge was generated to improve fidelity of the designs







Outcomes:

- New design reduces the HTL installed capital cost by 13%
- New design is more scalable with regard to fabrication limitations (standard pipe thickness)
- Patent application filed; licensing agreement completed
- Plans for piloting new technology underway

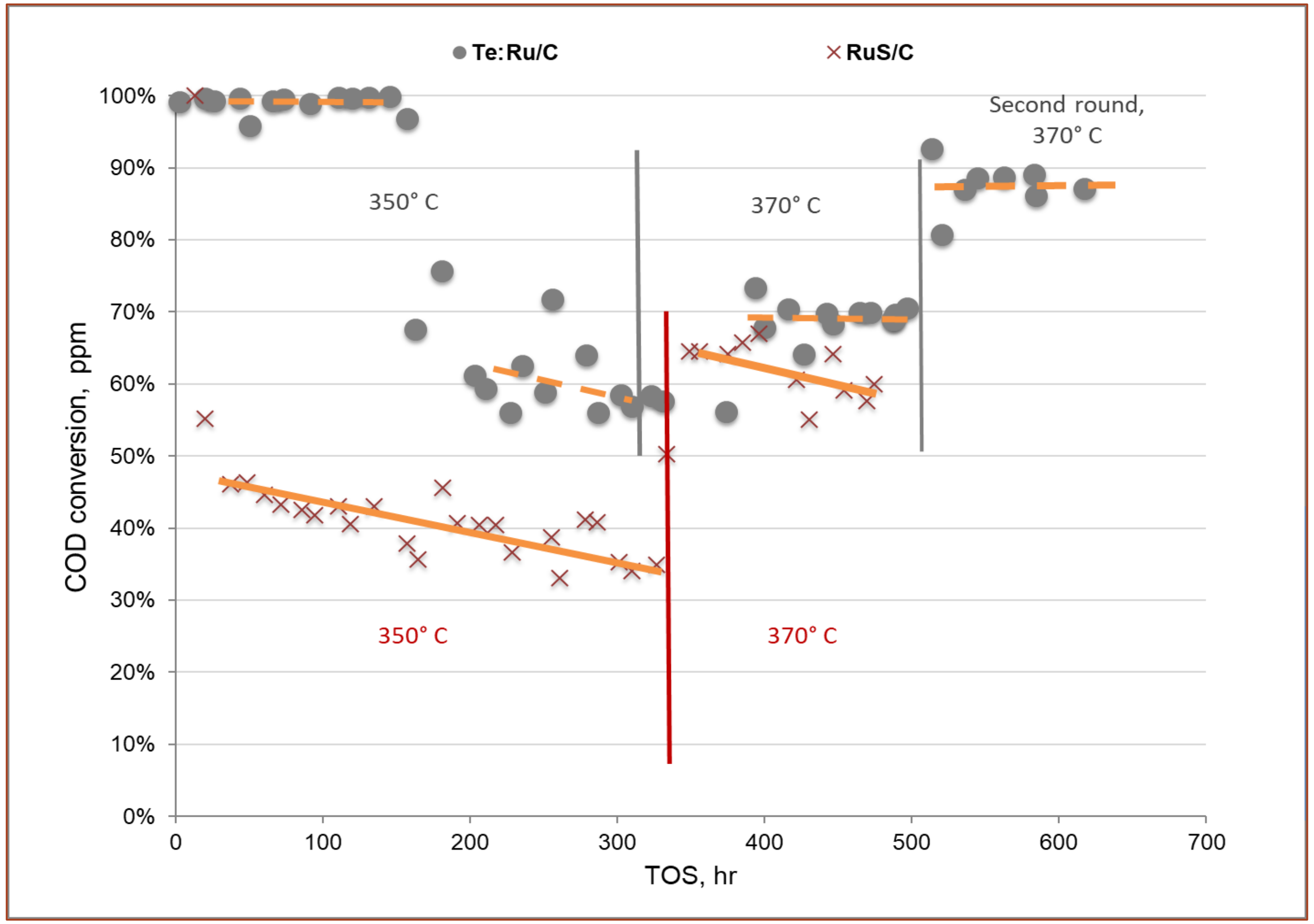
4 – Progress and Outcomes FY20
HTL Aqueous Waste Treatment/Valorization - CHG

***Go/No-Go*: Catalytic Hydrothermal Gasification (CHG) Operate at the lab scale unit for > 200 h with an aqueous product stream from HTL of WRRF sludge. COD reduction > 90%.**

- Conducted about 18 continuous catalyst tests.
- Identified a Te-doped Ru/C catalyst that is robust, 620 hours TOS

Outcomes:

- Initial 100% COD reduction was achieved for the first 180 h on stream.
- Highest follow-on conversion reached was ~87% at 370°C after a second pass treatment of the earlier treated effluent at 370°C (~120 h)
- Go/No-Go metrics were not achieved
- All CHG work has shifted to a CRADA Project focused development of sulfided gasification catalysts



Chemical Oxygen Demand (COD), Time on Stream (TOS)

4 – Progress and Outcomes FY20 HTL Aqueous Waste Treatment/Valorization - ZnZr

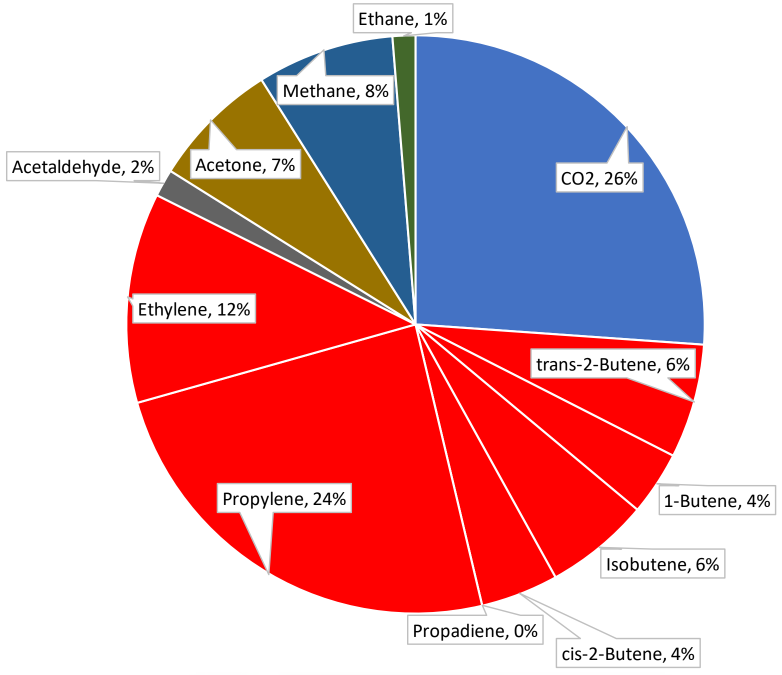
Goal: Zinc Zirconia and Zeolite Conversion to Ketones and Alkenes

- Catalytic treatment of HTL aqueous phase using zinc zirconia and zeolites 350 – 425°C

Operating Conditions			Carbon yield				Reduction in Aqueous	
Temp °C	WHSV hr-1	Pressure psig	CO_2 yield %	CH_4 yield %	Alkene yield %	Total gas yield %	%C reduction %	COD Reduction %
400	0.1	110	38%	6%	14%	76%	78%	92%
425	0.1	110	6%	38%	18%	82%	77%	94%
375	0.1	110	26%	3%	8%	45%	60%	65%
375	0.2	110	11%	2%	6%	25%	50%	51%

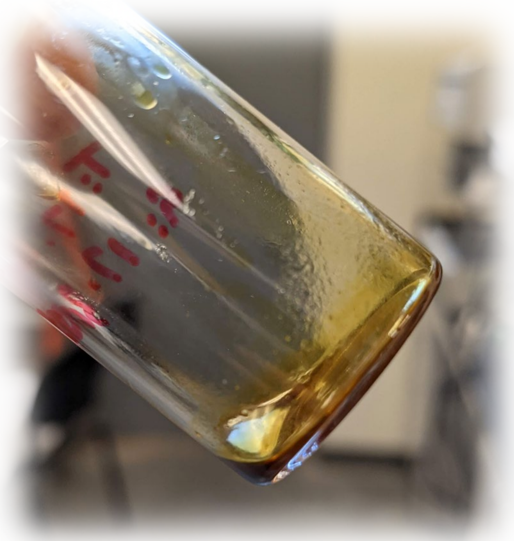
Weight Hourly Space Velocity (WHSV)

Gas Products from ZnZr/Zeolite



Outcomes:

- Demonstrated a path to produce alkenes using either a ZnZr or a ZnZr and Zeolite catalyst with stable performance for >400 hours
- High COD removal
- Partial conversion of the organic stream into a crude oil



4 – Progress and Outcomes FY20 Upgrading Process Development

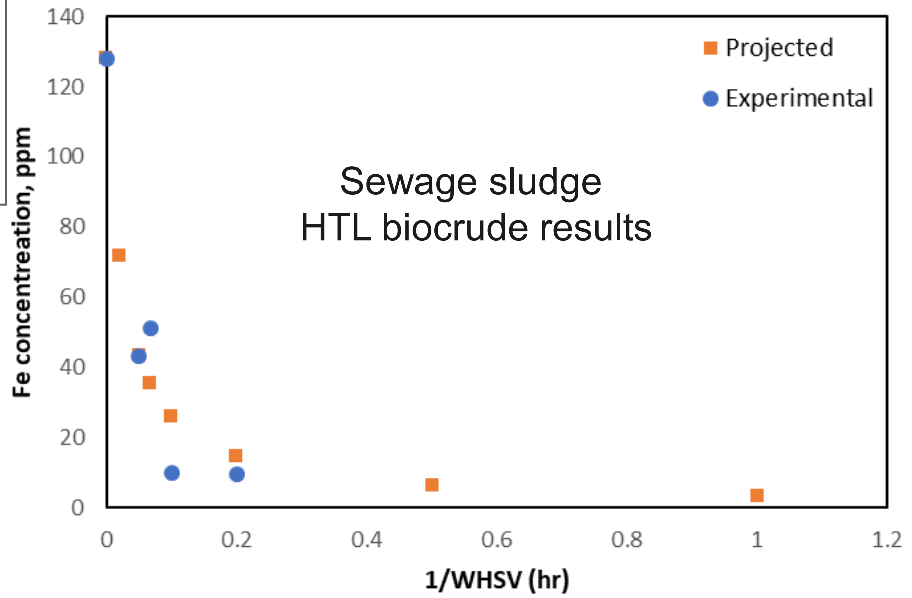
FY20 Milestone

Demonstrate a novel CSTR to simulate a slurry bubble column guard bed reactor for scale-up

- Built small-scale slurry stirred-reactor to evaluate slurry chemistries for continuous slurry hydrogenation, including hydrodemetallization (HDM)
- Used slurry chemistry to pre-treat HTL biocrudes to reduce the individual metal contaminants to <20ppm from sewage sludge and algae (over 1L each)

Algae HTL biocrude results

WHSV hr^{-1}	Fe removal wt%	Na removal wt%	K removal wt%	S removal wt%	Light gas yield loss %
1	94.3	90.0	56.1	69.3	2.9
2	86.7	87.8	53.9	70.7	2.3
5	79.9	-	-	49.6	1.5



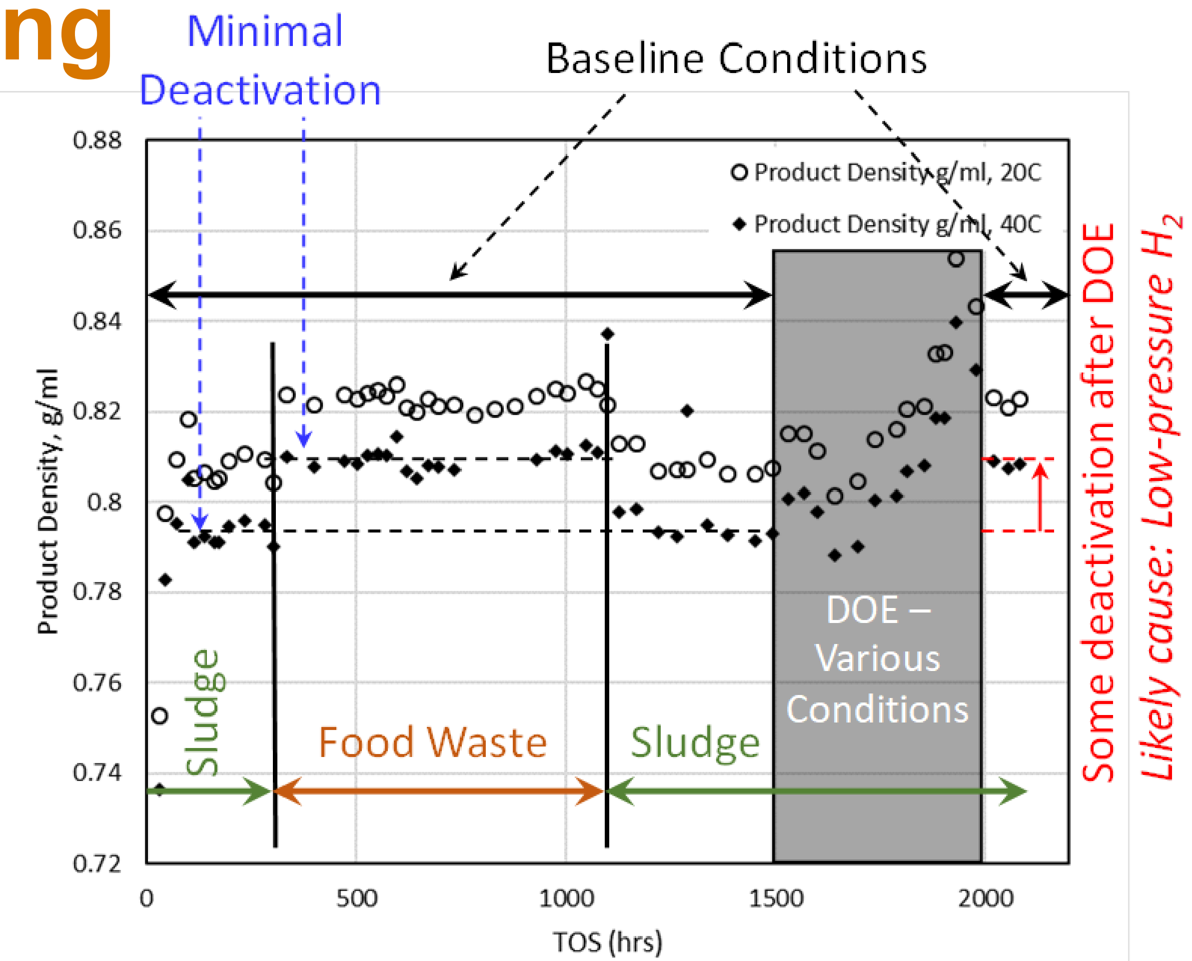
Outcomes:

- Built and tested new small-scale slurry reactor for guard bed processing
- Provides longer guard-bed catalyst lifetimes and smaller guard-bed reactors
- Developed and demonstrated a kinetic model for predicting Fe and S removal in the pretreatment CSTR

4 – Progress and Outcomes FY20-21
HTL Biocrude Hydrotreating

FY20 Milestone: Quantify the main-bed hydrotreating catalyst activity for HTL biocrude upgrading over 1000 hours

- Evaluated 4 commercial CoMo and NiMo hydrotreating catalysts
  - NiMo: superior performance and lower cost
  - Completed all testing with whole pill catalysts
    - Quantified pore diffusion limitations
- 3x increased in hydrotreating WHSV (from 0.3 hr^{-1} to 1 hr^{-1})



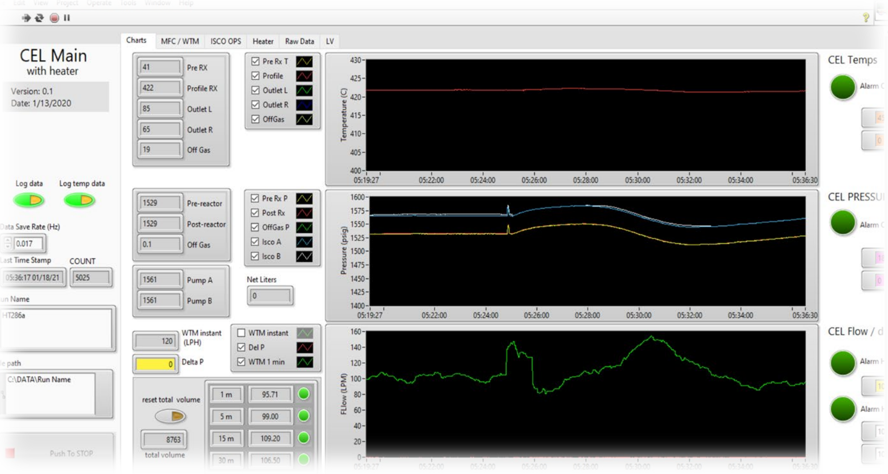
Outcomes:

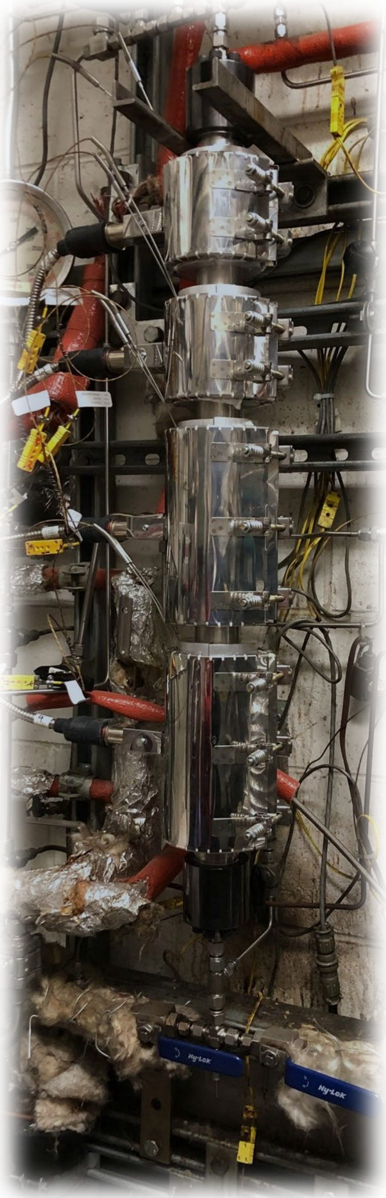
- ***Demonstrated <u>2000hrs</u> of continuous operation with stable hydrotreating performance***
  - Continuous (1 interruption for <4 hours)
  - Stable oxygen content ~0.2 wt% and C to H ratio
- Used biocrude from sludge and foodwaste
- Liquid product primarily high cetane diesel (70% diesel)

4 – Progress and Outcomes FY20-21 PDU HT Capability Improvement

Goal: Upgrade bench scale 400 mL hydrotreater with electrical heating

- Improvement includes installation of dedicated electrical cabinet and update to LabView controller interface





Outcomes:

- Upgraded 400 mL hydrotreater reactor now has both oil and electrical heat capabilities
- Multiple zones (4) with independent controls
- Heater sequence/arrangement is flexible
- **Used to Produced 20L of diesel blendstock**

4 – Progress and Outcomes FY20 Upgrading Scale-up and Production

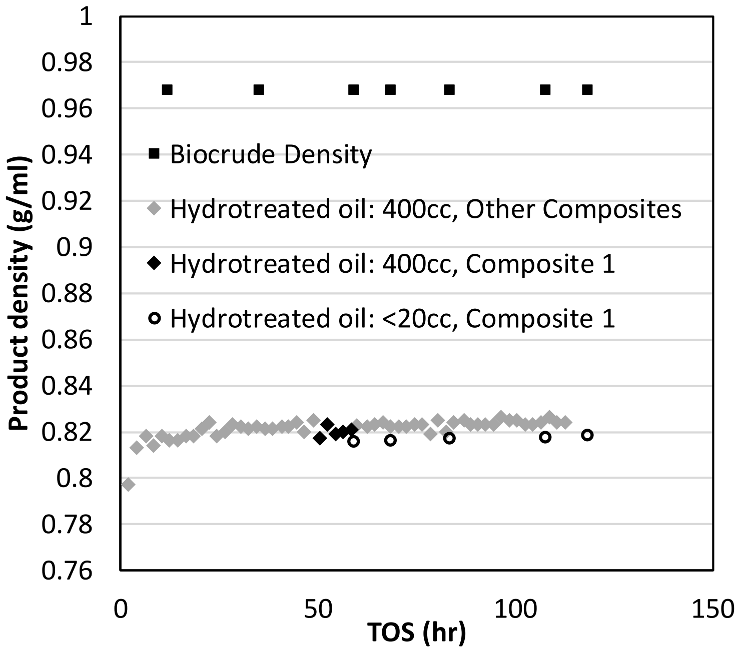
FY20 Milestone

Upgrade greater than 10L of HTL biocrude at the small engineering scale (400ml) reactor. Quantify the scalability from lab-scale (<50ml) of the upgraded fuel based on the upgraded fuel properties and process conditions.

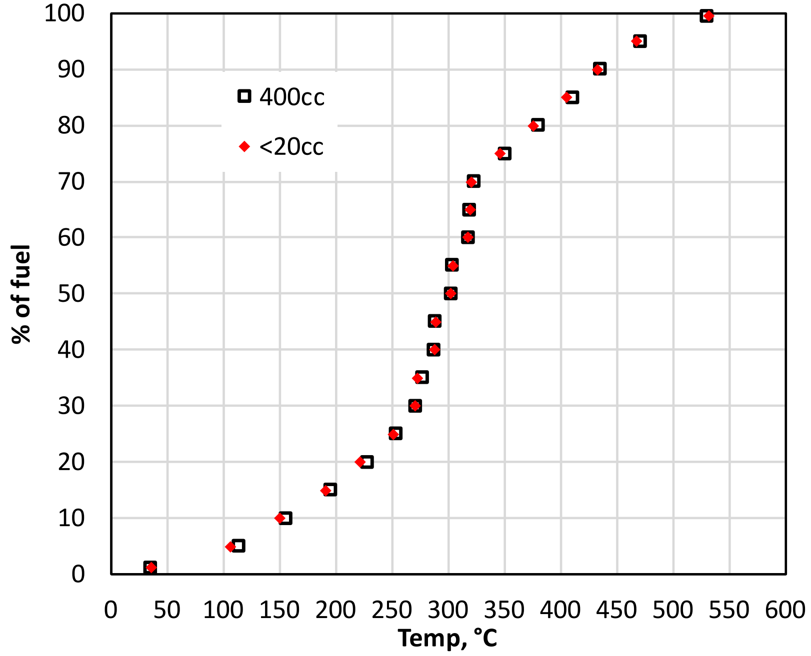
Outcomes:

- **Produced over 15L of upgraded oil and >11L of distilled diesel blendstock**
- **Demonstrated excellent scalability between bench and engineering scale hydrotreaters**

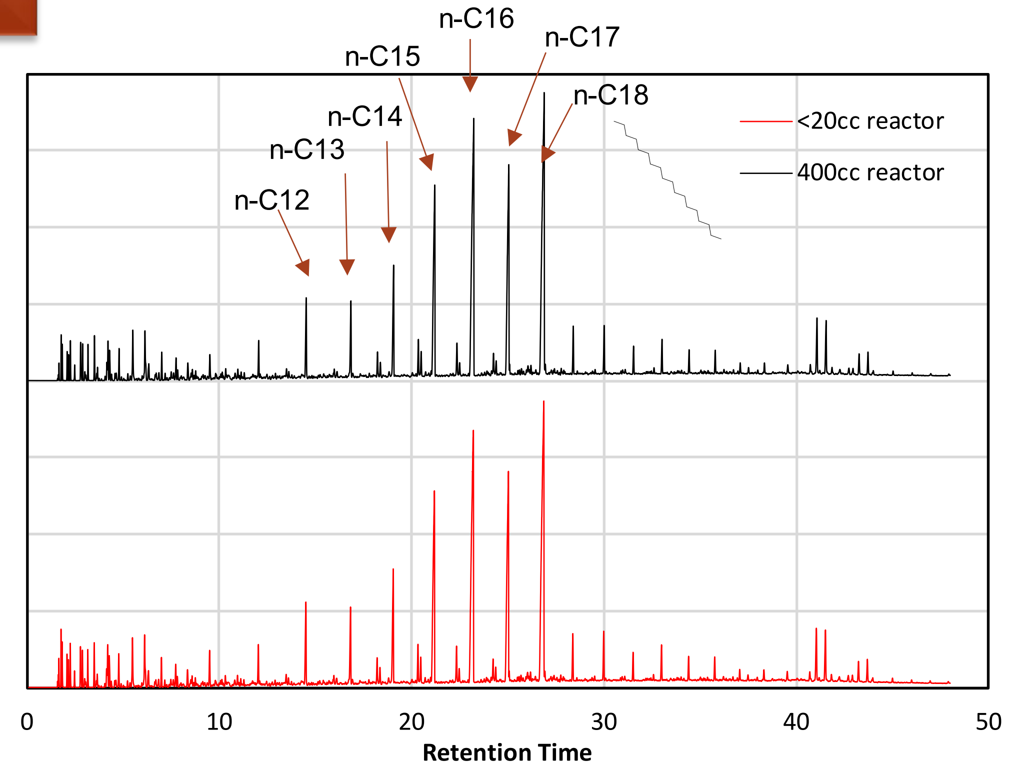
Product Density



Simulated Distillation

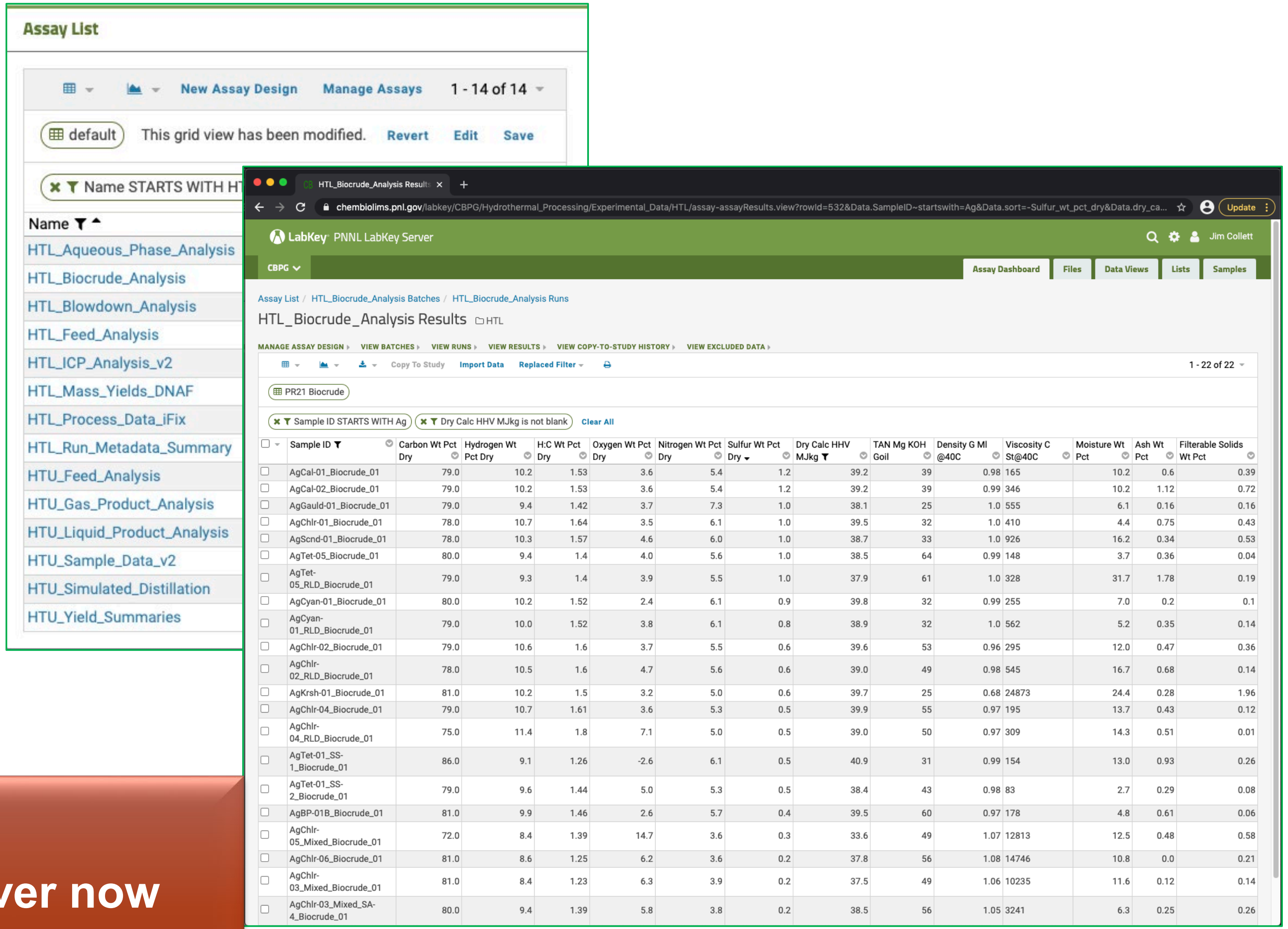


GCMS Overlay from Two Scales of Hydrotreaters



4 – Progress and Outcomes FY20 PDU Data Sets into LabKey

- Several years of HTL and hydrotreater data were standardized and loaded into **PNNL's LabKey Server** to ensure that they remain **F**indable, **A**ccessible, **I**nteroperable, and **R**eusable (**FAIR**) as mandated by DOE.
- The LabKey database holds high quality, manually curated datasets that currently include:
  - Feedstock analysis and provenance data from a wide range of algal and wet waste sources.
  - 62 bench scale HTL runs including, biocrude, aqueous phase, and reactor performance data
  - Hydrotreater performance and material analysis data for 70 fuel



Outcomes:

▸ **The standardized datasets on the LabKey server now facilitate a range of "Feedstock to Fuel" statistical analyses to inform R&D on process scale-up.**

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Thank you

Acknowledgements

- Liz Moore– BETO Technology Manager
- Hydrothermal PDU Team
  - Dan Anderson
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  - Michel Gray
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  - Gary Neuenschwander
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  - Alan Zacher
  - Jim Collett
  - Yunhua Zhu
  - Karthi Ramasamy
  - Dan Howe

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Summary

Overview: The PDU project is enabling technology innovation, process integration and partnership projects to demonstrate scalable hydrothermal processing methods for the conversion of wet waste feedstocks into biofuel and co-products

Management: The PDU project has a risk-based project plan, integrated project team, strong project management, experienced task leads & effective communications

Approach: The PDU project has established defined objectives and milestones (ML) to address risk/challenges for 4 task areas; Process Development, Scale-up and Production, PDU Systems Capability Management, PDU Utilizations and Partnership Projects

Impact: The PDU project is providing 1) process technology to enable HTL commercialization, 2) DOE PDU capability utilization supporting multiple collaborations with DOE related projects and industry, and 3) technology transfer through publications, presentations, the development of IP licensing agreements, and partnership projects

Progress and Outcomes: The project has made tremendous progress and has achieved significant outcomes;

- Met key technical objectives, milestones and retired technical risk related to process development, scale-up and production.
- Improved the PDU capabilities through system modifications, acquisition of new equipment and operational management practices.
- Enhanced PDU utilization by supporting multiple collaborative projects and partnerships and participation in SDI's PDU Working Group.

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Quad Chart Overview

Timeline
- Project start date: 10/1/18
- Project end date: 9/30/21

	FY20	Active Project
DOE Funding	(10/01/2019 - 9/30/2020) *$3,000,000*	(negotiated total federal share over active project) *$8,260,000*

Collaborations: Waste to Energy Resource Assessment Project (WBS 1.0.113), PNNL 1.3.5.202 PNNL HTL Model Development; NREL/ PNNL 2.4.2.302 Strategies for Co-processing in Refineries; PNNL 4.1.1.51 Refinery Integration; Separations Consortium; HYPOWERs PD2B3 project, INL Feedstock Interface, Hydrothermal Processing for Algal Based Biofuels and Co-Products 1.3.4.101 , Co-Optima

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

Project Goal:
Adapt and apply PNNL hydrothermal PDU capabilities to enable the production of biofuels and co-products from wet waste feedstocks

End of Project Milestone:
Demonstrate improved processing methods for scale-up of HTL, upgrading and HTL waste stream processing. Provide data and basis for improved HTL wet waste process model, TEA/LCA. Establish partnerships for PDU utilization

Funding Mechanism:
Lab Call 2018

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Additional Slides

Responses to Previous Reviewers' Comments

Reviewer Comments
Transitioning from Conversion to ADO this year. 10/18 start, 10% spent? Conduct process development research to evaluate feedstock impact on HTL yields, valorization of waste streams, PDU ops, scale-up challenges. Upgrading required (HT) because of heteroatoms (ONS), direct blendable with diesels. Catalytic HT gasification has been applied to other streams, this project trying to apply it toward HTL streams. BFD shows lots of issues to resolve.
This project is aimed at development and commercialization of PNNL's hydrothermal processing to convert wet feedstocks into transportation fuels. This PDU capability has been developed over last 30 years and its use is now extended to process wet solids.
Overall appears to be well thought through targeting a less developed process with the unique skills and equipment available or to be available to the National labs. Discussion of using a centrifuge to separate similar density liquids did not make sense and would not be equipment used in industry for such a task. Seems there must be better equipment to address this separation even going after the last bit.
Clear and well organized presentation, did a good job of describing technology and plans for continued hydrothermal processing technology development. Approach and planned work is well thought out and focused in value added areas. System design with focus on skidding and mobile units adds value and flexibility.
Laudable anticipated and continung use of existing facilities.
The development of a pilot/demo facility for a technology of such a potential impact is a critical activity and clearly an important mission for a national lab. The impact and support to the industry at large cannot be underestimated. Of particular relevance is the effort to make this facility flexible and capable to provide engineering data of immediate use for scale up activities. Only area of concern is the reliance on catalytic technologies that may be of limited scalability and questionable economics. Nonetheless this is a good platform for a variety of hydrothermal processing R&D activities.

RESPONSE TO COMMENTS
The Hydrothermal Processing team greatly appreciates the input from the Peer Review team. Many of the comments affirm the value of the project to BETO and reinforce our R&D and project management approach. There were also two important areas where a number of comments were directed that will be briefly discussed here: 1) our approach to industrial engagement, and 2) what are we doing different vs. our focus in previous years. From the onset, this project heavily relies on industry to provide candidate feedstocks and generally the feed suppliers have a vested interest in the application of HTL to their "wet waste". Through our collaborative work with Water Research Foundation, member municipalities (more than 15) are tracking the progress of our work at PNNL and the work on the HYPOWERs HTL demonstration project (FOA) at Contra Costa County, California. As a result, municipalities are reaching out to us along with about half a dozen entities working with venture capitalists. Additionally, BETO has set aside funds and it working to put out a broad solicitation for industrial engagement with the PDUs. With respect to a new focus and as we advance HTL and test at larger scales, the project has identified a number of technoeconomic and engineering challenges and uncertainties from feedstock assessments and formatting to HTL scale-up (pumping, heat exchanger evaluation, continuous oil/water separation) through water treatment and upgrading (metal removal, catalyst life, and throughput). While we have improved in many of these areas over the past 5 years, the TEA along with interactions with AECs are helping us establish priorities on the R&D for further improvements

Recent Publications

- Zacher, A.H. and A.J. Schmidt. July 2020. “Brief Update on Advancements by Commercial Vendors/Options for Feeding and Pumping Biomass Slurries for Hydrothermal Liquefaction.” Technical Report. PNNL-30107
- Santosa D.M., L. Wendt, B.D. Wahlen, A.J. Schmidt, J.M. Billing, I.V. Kutnyakov, and R.T. Hallen, et al. 2020. "Impact of Storage and Blending of Algae and Forest Product Residue on Fuel Blendstock Production." Bioresource Technology. PNNL-SA-158757. [Submitted]
- Cordova L.T., B.C. Lad, S.A. Ali, A.J. Schmidt, J.M. Billing, K. Pomraning, B. Hofstad, M.S. Swita, J.M. Collett, and H.S. Alperad, “Valorizing a hydrothermal liquefaction aqueous phase through co-production of chemicals and lipids using the oleaginous yeast Yarrowia lipolytica” Bioresourcd Technology, V 313, 2020. https://doi.org/10.1016/j.biortech.2020.123639
- Collett, J.R., J.M. Billing, P.A. Meyer A.J.Schmidt, A.B. Remington, E.R. Hawley, B.A. Hofstad, E.A. Panisko, Z. Dai, T.R. Hart, D.M.Santosa, J.K.Magnuson, R.T. Hallen, S.B. Jones, “Renewable diesel via hydrothermal liquefaction of oleaginous yeast and residual lignin from bioconversion of corn stover”, Applied Energy, V 233-334, 2019. https://doi.org/10.1016/j.apenergy.2018.09.115
- Marrone P.A., D. C. Elliott J. M. Billing R. T. Hallen T. R. Hart P. Kadota J. C. Moeller M. A. Randel A. J. Schmidt, “Bench-Scale Evaluation of Hydrothermal Processing Technology for Conversion of Wastewater Solids to Fuels” Water Environment Research, 2018 - Wiley Online Library https://doi.org/10.2175/106143017X15131012152861
- Fernandez S, K. Srinivasa, A.J. Schmidt, M.S. Swita, B.K.Ahring, “Anaerobic digestion of organic fraction from hydrothermal liquefied algae wastewater byproduct” Bioresource Technology, V247, 2018, https://doi.org/10.1016/j.biortech.2017.09.030
- Lesley should provide this one “Techno-economic uncertainty analysis of wet waste-to-biocrude via hydrothermal liquefaction” https://doi.org/10.1016/j.apenergy.2020.116340

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Past PDU Related 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
- 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]
- Zhu Y., S.B. Jones, A.J. Schmidt, K.O. Albrecht, S.J. Edmundson, and D.B. Anderson. 2018. "Techno-Economic Analysis of Alternative Aqueous Phase Treatment Methods for Microalgae Hydrothermal Liquefaction and Biocrude Upgrading System." *Algal Research*. PNNL-SA-137970. [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.
- 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.
- 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
- "Performance of a Compression Ignition Engine Fueled with Renewable Diesel Blends Produced from Hydrothermal Liquefaction, Fast Pyrolysis, and Conversion of Ethanol to Diesel." Jessica Tryner, Karl Albrecht, Justin Billing, Richard T. Hallen, and Anthony J. Marchese. 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
- "FT-ICR MS analysis of blended pine-microalgae feedstock HTL biocrudes." Jacqueline M Jarvis; Justin M Billing; Yuri E Corilo; Andrew J Schmidt; Richard T Hallen; Tanner Schaub, Ph.D. **Fuel**, Volume 216, 15March 2018, Pages 341-348. (https://doi.org/10.1016/j.fuel.2017.12.016)

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- 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.
- 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

- 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

- Maddi B, EA Panisko, TW Wietsma, TL Lemmon, MS Swita, KO Albrecht, and DT 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.” Accepted, in press. doi: 10.1021/acssuschemeng.6b02367
- Panisko EA, TW Wietsma, TL Lemmon, KO Albrecht, and DT Howe. 2015. "Characterization of the Aqueous Fractions from Hydrotreatment and Hydrothermal Liquefaction of Lignocellulosic Feedstocks." Biomass & Bioenergy 74:162-171. doi:10.1016/j.biombioe.2015.01.011

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Recent 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." Presented by D.M. Santosa at TC Biomass, Chicago, Illinois. PNNL-SA-147949.
- Santosa D.M, Thorson, M. 10/7/2020. Improving Scalability Of Hydrotreating Reactor: Upgrading Of Biocrude To Fuel Blendstocks. Presented by D.M. Santosa at TCS virtual symposium, Richland, WA.
- Santosa D.M., and M.R. Thorson. 10/07/2020. "Improving Scalability Of Hydrotreating Reactor: Upgrading Of Biocrude To Fuel Blendstocks." TCS, 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, Rosemont, Il, Illinois.

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Past PDU Related Presentations

- 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, RT Hallen, and DC Elliott. 2015. "Continuous Hydrothermal Liquefaction of Cellulosic and Lignocellulosic Biomass." Presented by Justin M. Billing at ACS 249th National Meeting, Denver, CO on March 25, 2015.
- 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.
- “Performance of a Compression Ignition Engine Fueled with Renewable Diesel Blends Produced from Hydrothermal Liquefaction, Fast Pyrolysis, and Conversion of Ethanol to Diesel.” Jessica Tryner, Karl Albrecht, Justin Billing, Richard T. Hallen, and Anthony J. Marchese. 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.
- “Characterization of Fuel Properties and Engine Performance of Renewable Diesel Produced from Hydrothermal Liquefaction of Microalgae and Wood Feedstocks.” Jessica Tryner, Karl Albrecht, Justin Billing, Richard T. Hallen, and Anthony J. Marchese. Algal Biomass Summit, Salt Lake City UT, October 30, 2017. PNNL-SA-126131.

- 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.

Past PDU Related Presentations (cont.)

- 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.
- Billing JM, DC Elliott, RT Hallen, TR Hart, AJ Schmidt, PA Marrone, JC Moeller, and P Kadota. 2017. "Bench-Scale Evaluation of the Genifuel Hydrothermal Processing Technology for Wastewater Solids." Presented by Philip A Marrone at WEFTEC 17 Conference, Chicago, IL on September 30, 2017.
- 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.
- 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.
- Holladay JE, and C Drennan. 2015. "Waste to Energy." Presented by John Holladay at Mass Production of Biomass Refineries Workshop, Broomsfield, CO on May 11, 2015.
- Maddi B, EA Panisko, TW Wietsma, TL Lemmon, MS Swita, KO Albrecht, and DT Howe. 2016. "Quantitative Characterization of Aqueous Byproducts from Hydrothermal Liquefaction of Municipal Wastes, Food Industry Wastes, and Biomass Grown on Waste." Presented by Balakrishna Maddi at TCS 2016, Chapel Hill, NC on November 1, 2016.

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

- US Pat Appl 31594/ 9760 (filed December 2019) “MOVING BED PRETREATMENT FOR IRON-CONTAINING BIOCRUDE.” Mike Thorson, Rich Hallen, Justin Billing, Andy Schmidt, Todd Hart, and Teresa Lemmon
- US Pat Appl 31697 / 9854 (filed January 2020) “Split Heat Exchanger Design for HTL.” Mike Thorson, Lesley Snowden-Swan, Andy Schmidt, Todd Hart, Justin Billing, Dan Anderson and Rich Hallen
- 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.

PDU Related Press Releases and Social Media

- 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, estimated 16.2M people who saw the link on Reddit or other social media.
- “From the Toilet to the Tank,” YouTube video. 2016. https://youtu.be/ER4C6EapZQ4, accessed 03 February 2017. Currently 97K 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 03 February 2017.

Abbreviations and Acronyms

- ACU: aqueous phase catalytic upgrading
- AD: anaerobic digestion
- ANL: Argonne National Laboratory
- AOP: Annual Operating Plan
- BETO: Bioenergy Technologies Office
- CHG: catalytic hydrothermal gasification
- COD: chemical oxygen demand
- CSTR: continuous stirred tank reactor
- DOE: U.S. Department of Energy
- FY: fiscal year
- GGE: gasoline gallons equivalent
- HT: hydrotreater
- HTL: hydrothermal liquification
- HXL heat exchange
- MHTLS: Modular hydrothermal liquefaction system
- MT: metric ton
- NREL: National Renewable Energy Laboratory
- PDU: process development unit
- PFR: plug flow reactor
- PNNL: Pacific Northwest National Laboratory
- SDI: Systems Development and Integration
- SOP: Standard Operating Procedure
- SOT: State of Technology
- TEA: techno-economic analysis
- TPD: ton per day
- WHSV: weight hourly space velocity
- WRRF: Water Resource Recovery Facility

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Project Risk Matrix

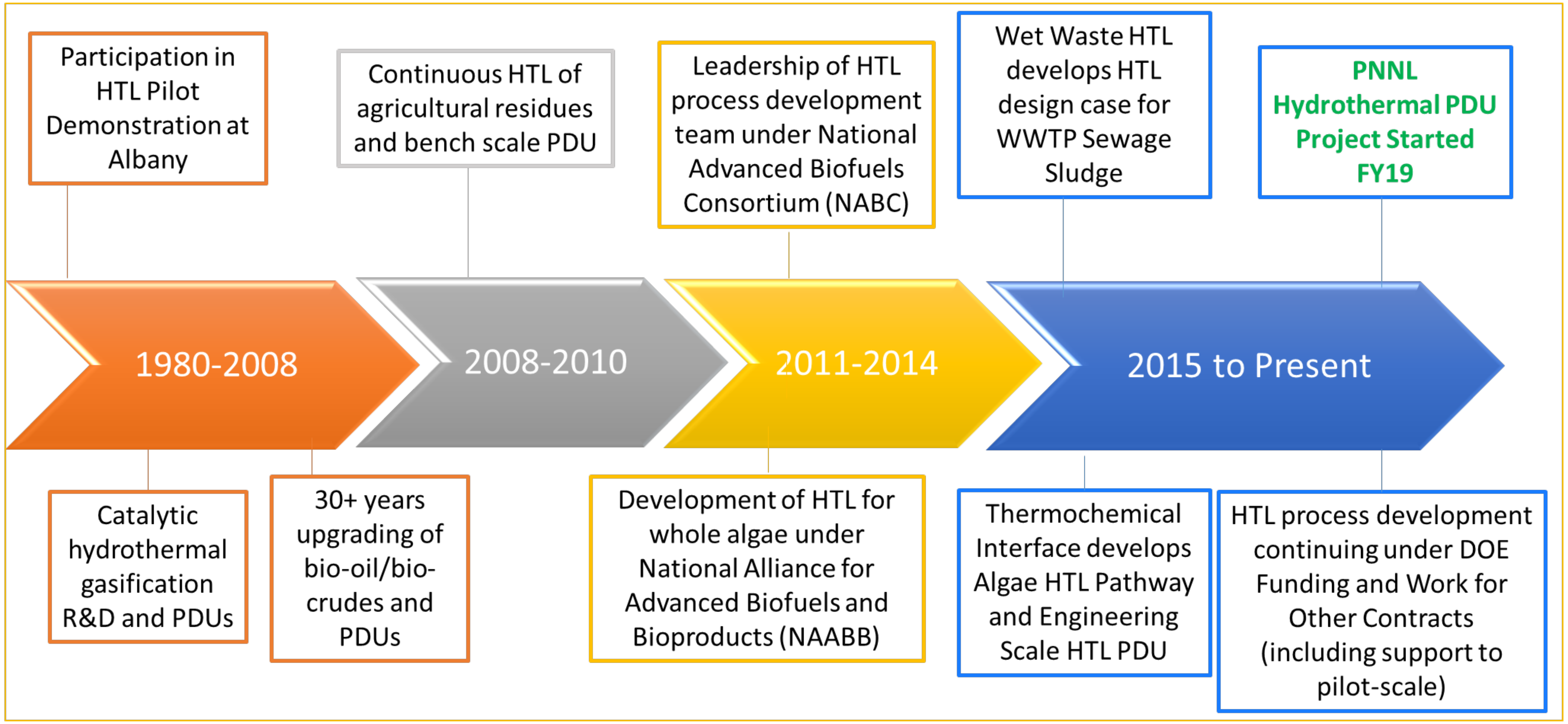
Name	Status	Target Completion Date	Severity	Response	Description
Aqueous Product Disposition	Known	9/30/2021	High	Mitigate	Depending upon the HTL application, the HTL aqueous stream will require some level of treatment to reduce COD, nitrogen, color bodies, toxicity. In FY2021, AP treatment using advanced AD will be the focus of a new CRADA
Pressure Let-down, Pressure control valve (PCV)	Complete	9/30/2019	Medium	Mitigate	MHTLS scale too small to allow demonstration of robust pressure letdown. FY2020 Progress: careful temp control around PCV has enabled stable pressure control in the MHTLS.
Oil/Water separation	Analyzed	9/30/2020	High	Mitigate	MHTLS runs hampered/shut down due to oil/water separation challenges. FY2020 Progress: excellent performance of oil/water separation demonstrated in MHTLS with sludge.
Heat Exchanger (HX) Design/Cost	Complete	9/30/2020	Medium	Mitigate	HX is the most expensive unit op in the process. FY2020 Progress: patent filed for HX design concept. AE firm engaged to model and cost design concept.
Hydrotreater Modifications	Complete	9/30/2020	Medium	Mitigate	Intermediate-scale hydrotreater system modifications to solve process challenges completed in FY2020.

Project Risk Matrix (cont.)

Name	Status	Target Completion Date	Severity	Response	Description
Lack of Feedstock	Known	9/30/2020	High	Avoid	Lack of availability of strategic feedstocks to support R&D studies. FY2020 Progress: Covid exacerbated feed stock acquisition challenges. We expanded our sphere of feedstock resources.
Feedstock Formatting	Known	9/30/2021	High	Mitigate	Manure compositions are complex and often include foreign material that can challenge formatting and pumping. FY2020 progress: An industrial shredder was added to our formatting capabilities.
Feedstock Properties	Known	9/30/2021	Medium	Mitigate	Feedstock properties not well characterized and/or not suited for processing in MHTLS. FY2020 progress: we increased pretest analytical and rheology characterization of incoming feedstock.
Upgrading Catalyst Lifetime	Analyzed	9/30/2021	Medium	Mitigate	Insufficient catalyst longevity/activity for biocrude upgrading. FY2020 progress: improvements in pretreatment and upgrading tactics have made.
CHG Catalyst Lifetime	Analyzed	6/30/2020	High	Mitigate	High sulfur levels in wet waste feedstocks poison current gasification catalyst. FY2020 progress: We have moved to sulfided catalyst development with lower but stable activity. This work will go forward on CRADA project.
Fuel Blendstock Testing	Ongoing	9/30/2020	Medium	Avoid	Fuel blendstock testing constrained by availability of blendstocks produced or subcontractor schedule. FY2020 progress: We have partnered with Co-Optima for advance engine testing of HTL-derived diesel.

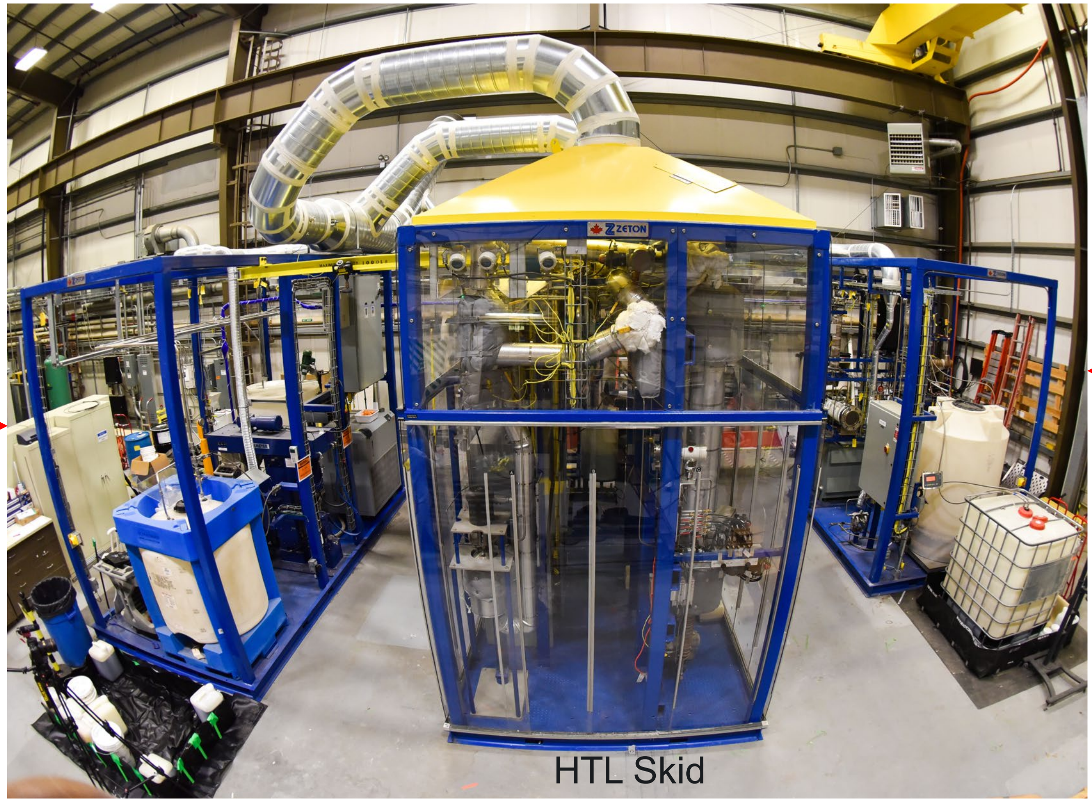
Project Overview

How Was the PDU Capability Developed?

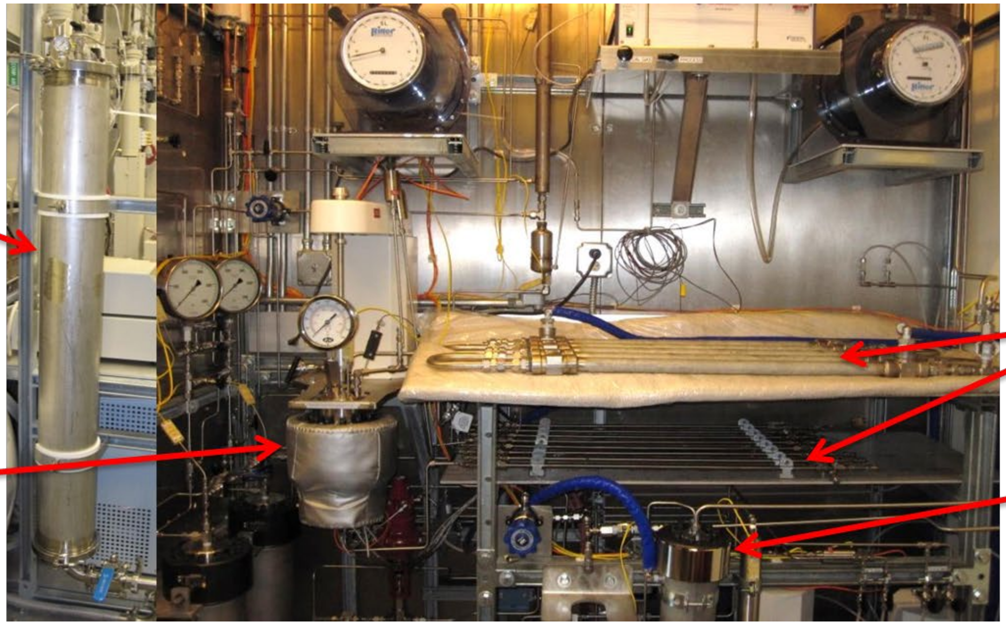


Leverages >$3M BETO Capital Investments

HTL PDU Systems



(1) Engineering Scale HTL System
16 L/hr



(2) Bench Scale HTL Systems
2- 4 L/hr

System Scale

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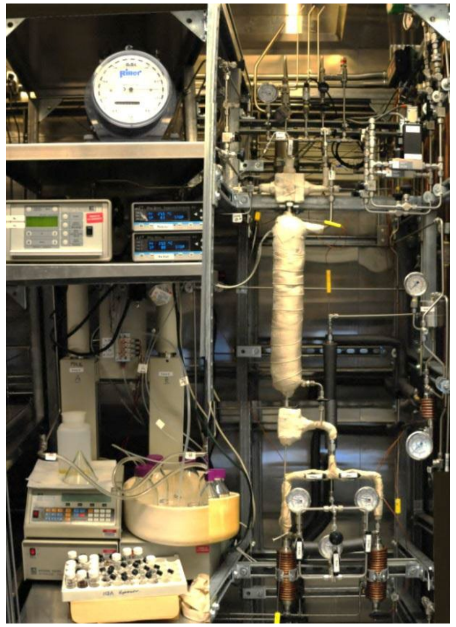
Upgrading PDU Systems

(1) 25ml CSTR HT
(1) 10ml PFR HT



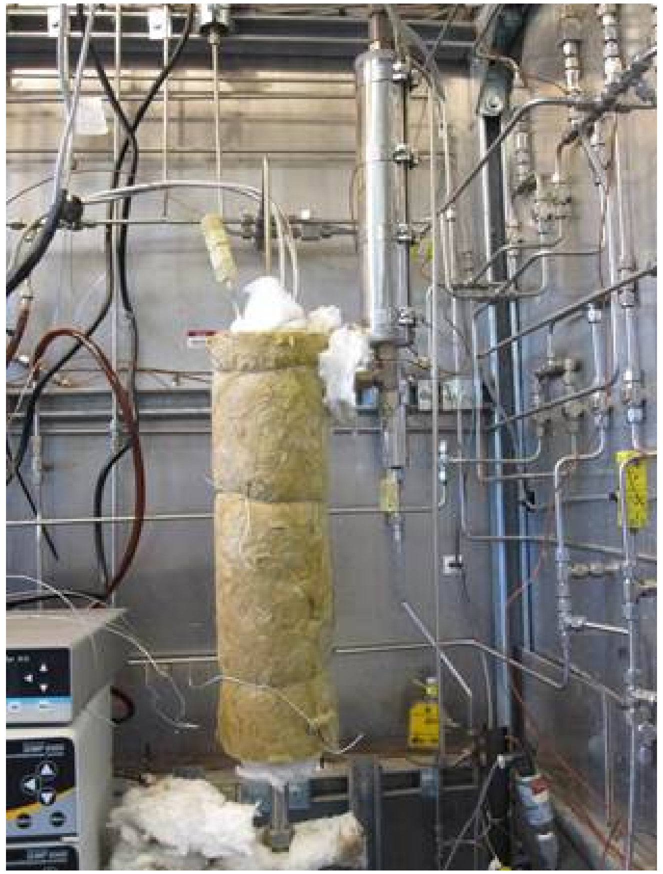
(3) 50ml PFR HT

(1) 400ml CSTR HT
Pretreatment System

(1) 400-800ml PFR HT

System Scale

CHG PDU Systems



(3) Micro Scale CHG Systems
30ml Catalyst Bed
60ml/hr

(1) Engineering Scale CHG System
16 L Catalyst Bed
20 L/hr

System Scale

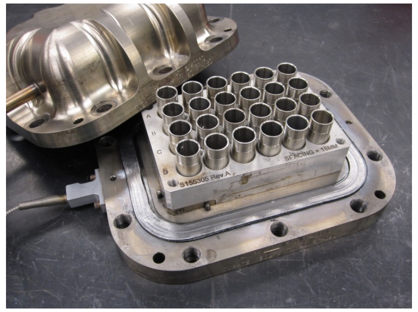
High Throughput Center (HTC) Systems

HIGH THROUGHPUT MATERIAL HANDLING

- Catalyst Preparation
- Ambient pressure reaction screening
  - »Kinetic studies
- Analytical sample preparation
  - »Dilutions
  - »Derivatizations
  - »Plate daughtering
  - »Filtration

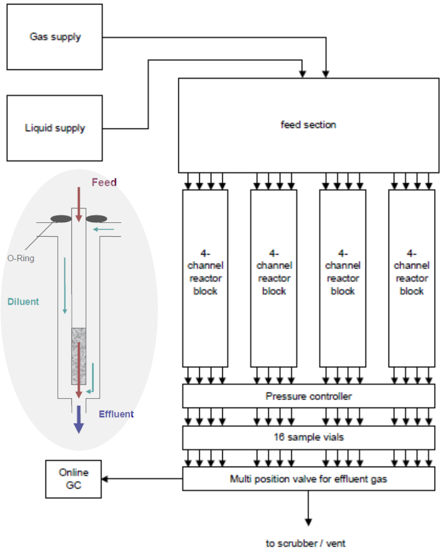
HIGH THROUGHPUT BATCH REACTOR

- Hydrogenation reactions
- Hydroformylation reactions
- Oxidation reactions
- Carbonylation reactions
- Catalyst Stability Testing



HIGH THROUGHPUT FLOW REACTORS

- Trickle bed reactions
- Fixed bed, vapor phase reactions
- Absorption studies
- H_2 or CO_2 capture
- Solubility testing



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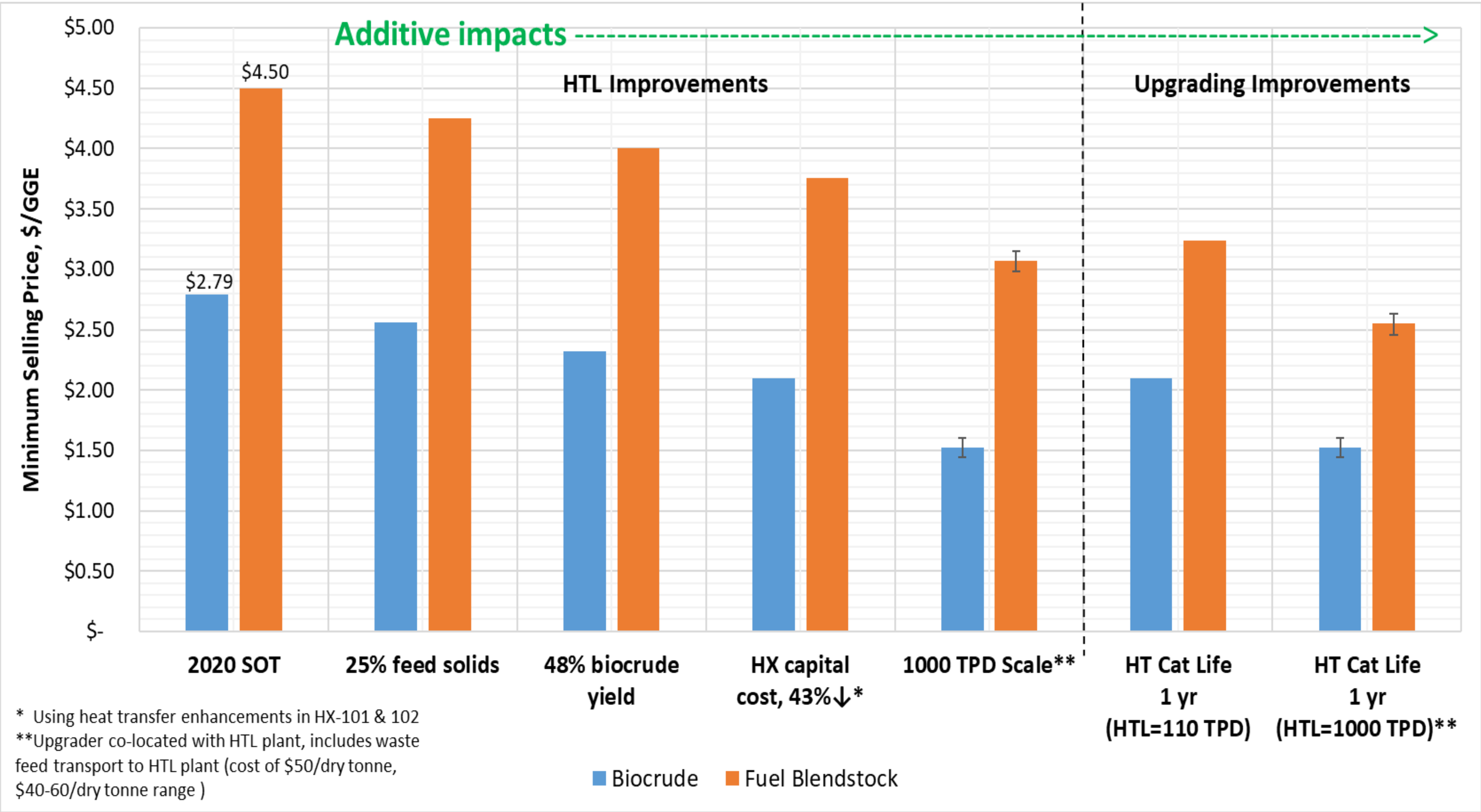
2- Approach Future Work

Integrated analysis, R&D, and resource assessment is creating a vision for regional waste-to-energy hubs



- Improved HTL efficiency and hydrotreater catalyst life can get us to the $3.3/GGE range
- Blending and co-processing could get us to the $2.5/GGE range
- 1000 TPD case
  - 105-mile collection radius, truck capacity of 35 m3, truck cost of $2.86/mile ($45/ton)

- Planned improvements **lead to $3/GGE 2022 and $2.5/GGE 2030** program goals

4 – Progress and Outcomes FY20
Feedstock Rheology at Elevated Temperature

Elevated Temperature / High-Pressure Cell

This specialized cell enables measurement of feedstock rheology at elevated temperature (25 to 300°C). Specific feedstock flow parameter measured are:

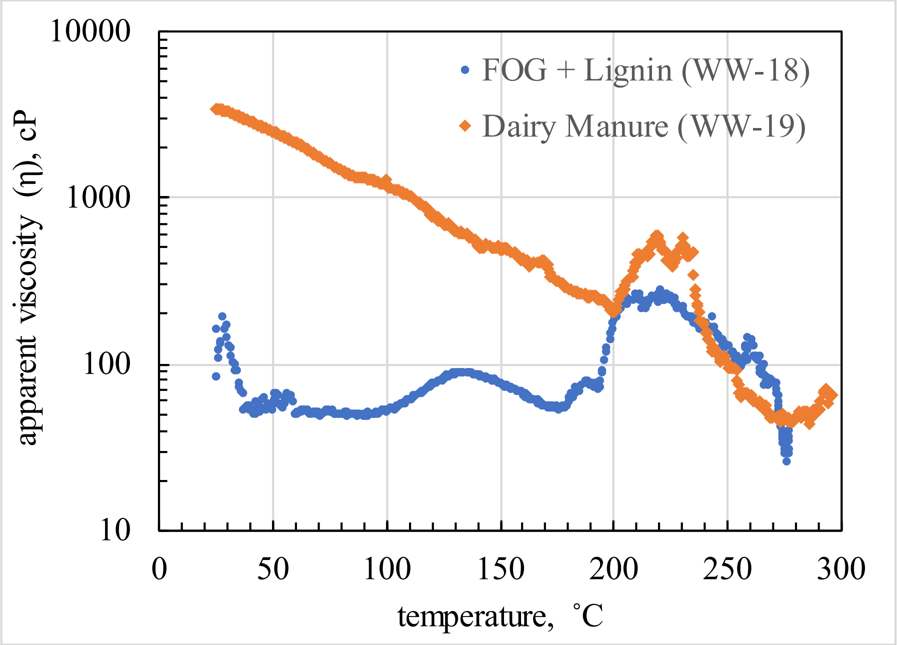
- constitutive parameters (yield stress / consistency) at HTL process relevant temperatures
- apparent viscosity as a function of temperature (again at HTL process relevant temperatures)

PNNL high-precision rheometer with glass-wool-wrapped elevated temperature measuring cell (left). Measuring cell DIN geometry after measuring WW-22 (25% solids) feed at 300°C (right).

Outcome:

Measured feedstock specific rheology data enable

- design and optimization of heat exchangers
- improved TEA of feedstock conversion processes
- increased knowledge of bounding feedstock rheology
- identification of process/flow-limiting rheology conditions



Apparent viscosity of WW-18 (FOG + Lignin) and WW-19 (dairy manure, 15-wt% solids) feeds measured from 25 to 300°C (at a fixed shear rate of 50 s^{-1}).

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4 – Progress and Outcomes FY20
HTL Process Development for Enhanced Separations

Goal: Developed design for proof-of-concept designs for oil/water separators

- Modified design based on industrial oil/water scavenging
- Tested at bench-scale HTL to refine concept
- Designed to manage separation challenges:
  - Biocrude density is lighter and/or heavier than water
  - Gas/liquids entrained in biocrude
  - Polarity of biocrude too close to water

Oil scavenging separator

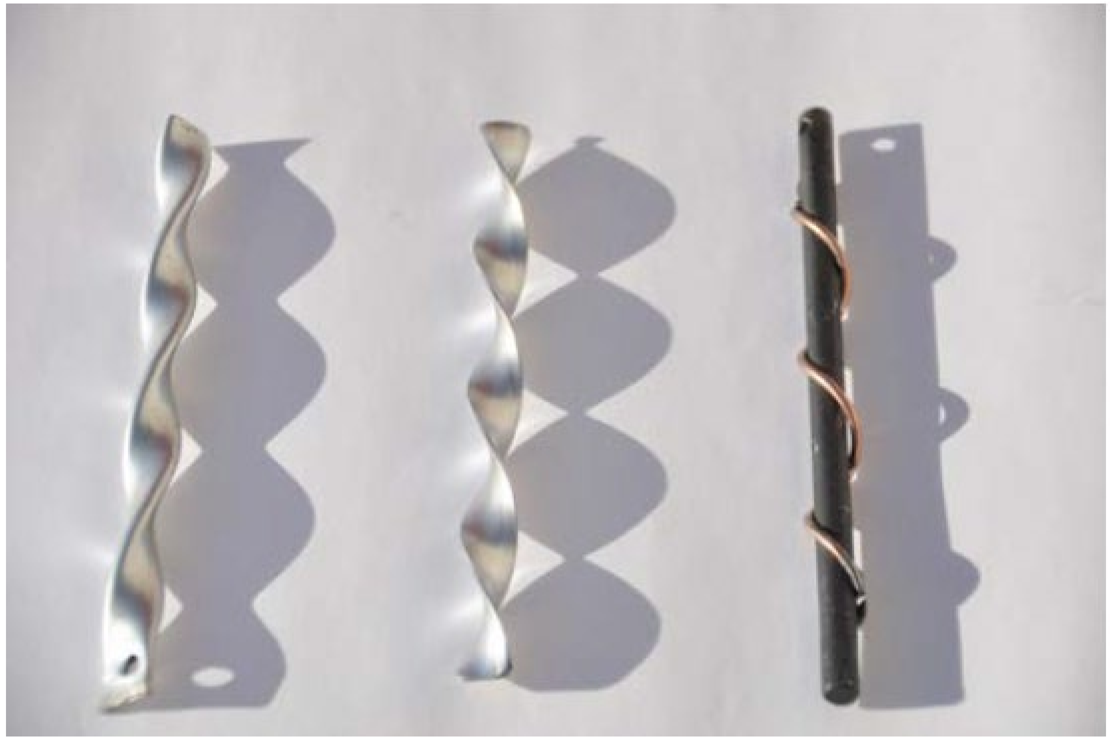
2nd Prototype Testing

Partially Separated Oil Recovery

Outcome:

- ▸ Prototype improves robustness for separation of biocrude and aqueous
- ▸ Potential improvement on quality and biocrude recovery

4 – Progress and Outcomes FY21
HX Equipment Enhancements



Outcome:

- Could reduce heat exchanger capital further by 35-45%
- Core inserts (KochTM) improve heat transfer coefficients by reducing flow area, increasing mixing, and increasing tube velocity
- Also can act as lancing devices for improving cleanability of exchanger tubes

4 – Progress and Outcomes FY20
HTL Aqueous Waste Treatment/Valorization - SCREW

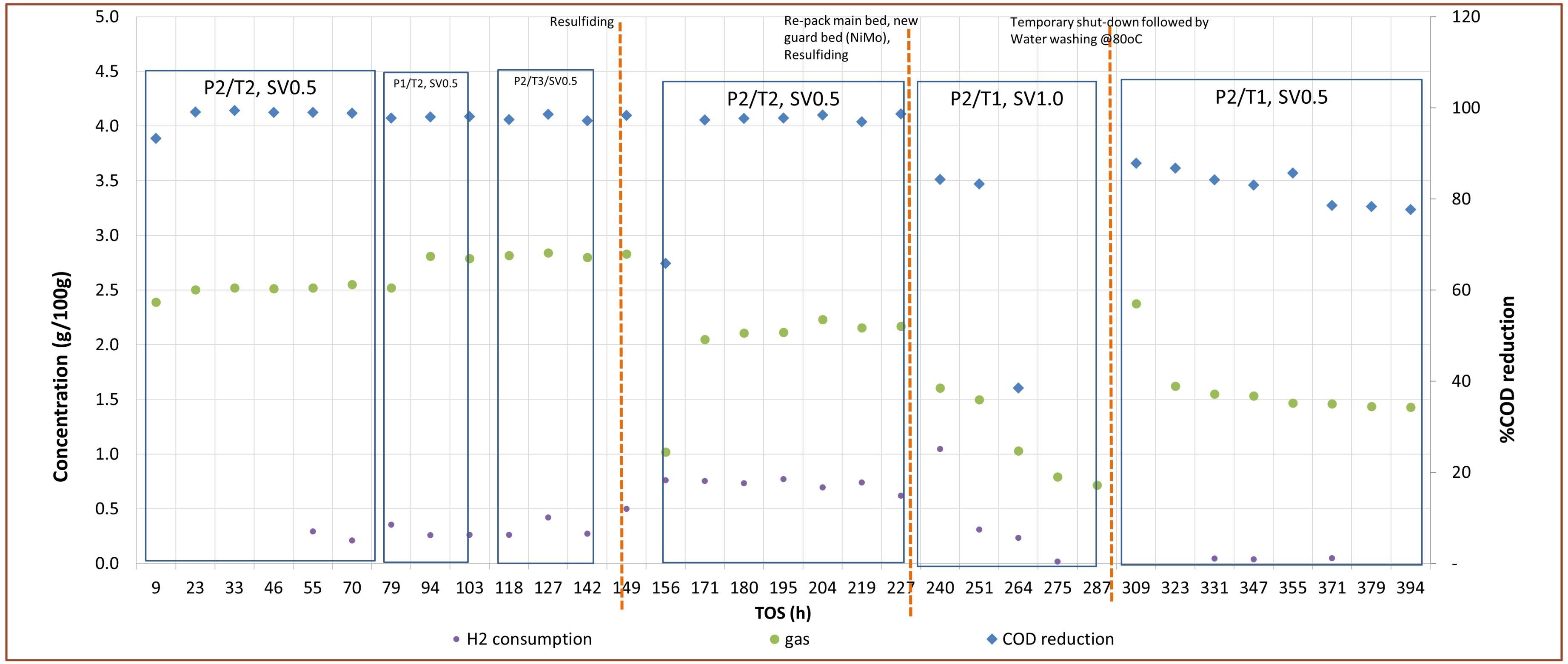
Superheated Catalytic Reduction of Effluent Water (SCREW)

- Parallel route considered to achieve CHG milestone
- Catalytic treatment of HTL aqueous phase using sulfided catalyst on carbon at T_1 to T_3°C in the presence of flowing H_2 at P_1 – P_2 psig.

This presentation contains the results of work performed under Contract No. DE-AC05-76RL01830 from the United States Department of Energy. As such it may contain subject inventions exempted from public disclosure under 35 USC 205 et. seq., Public disclosure of this information without permission is prohibited.

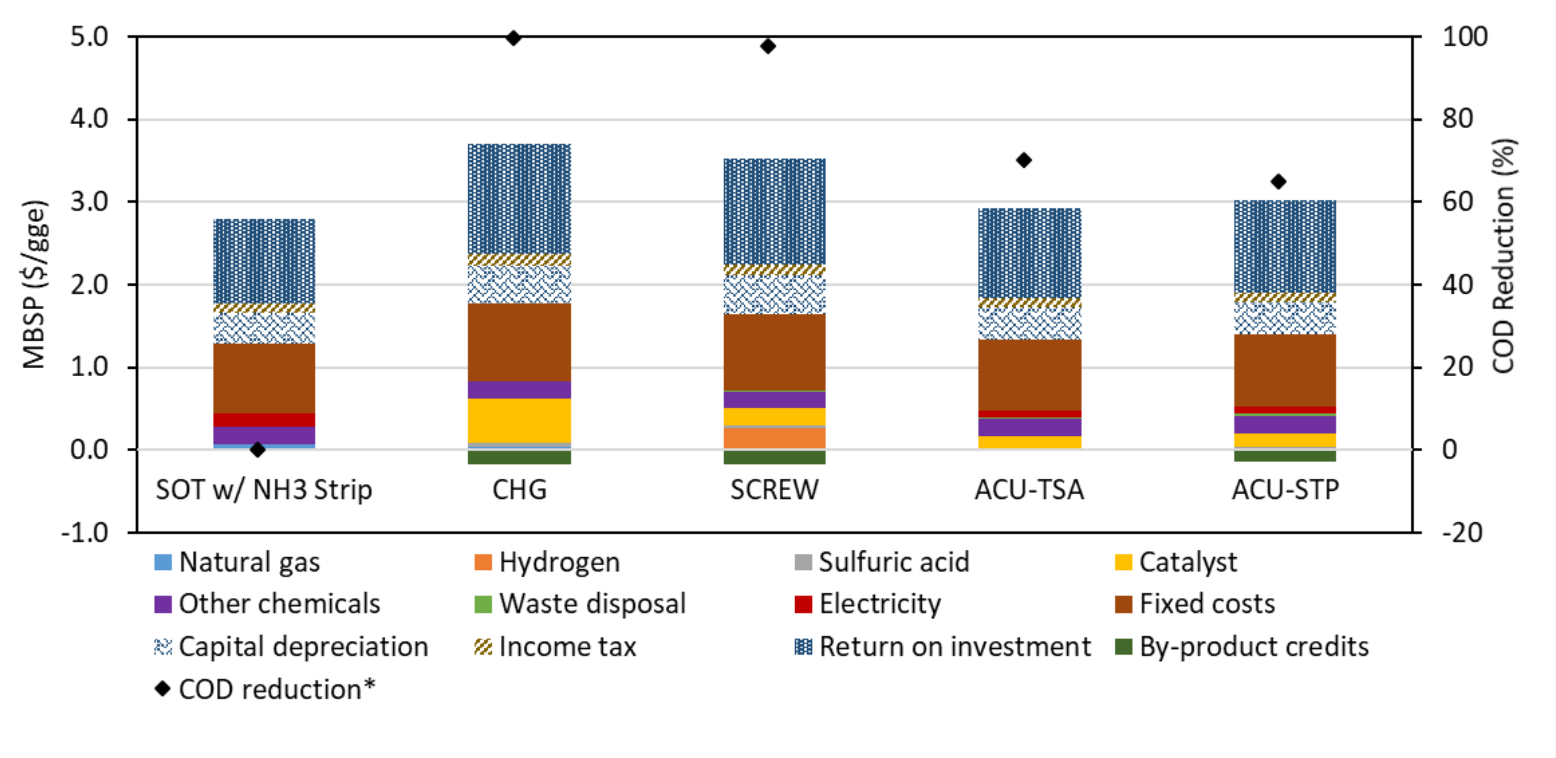
Accomplishments:

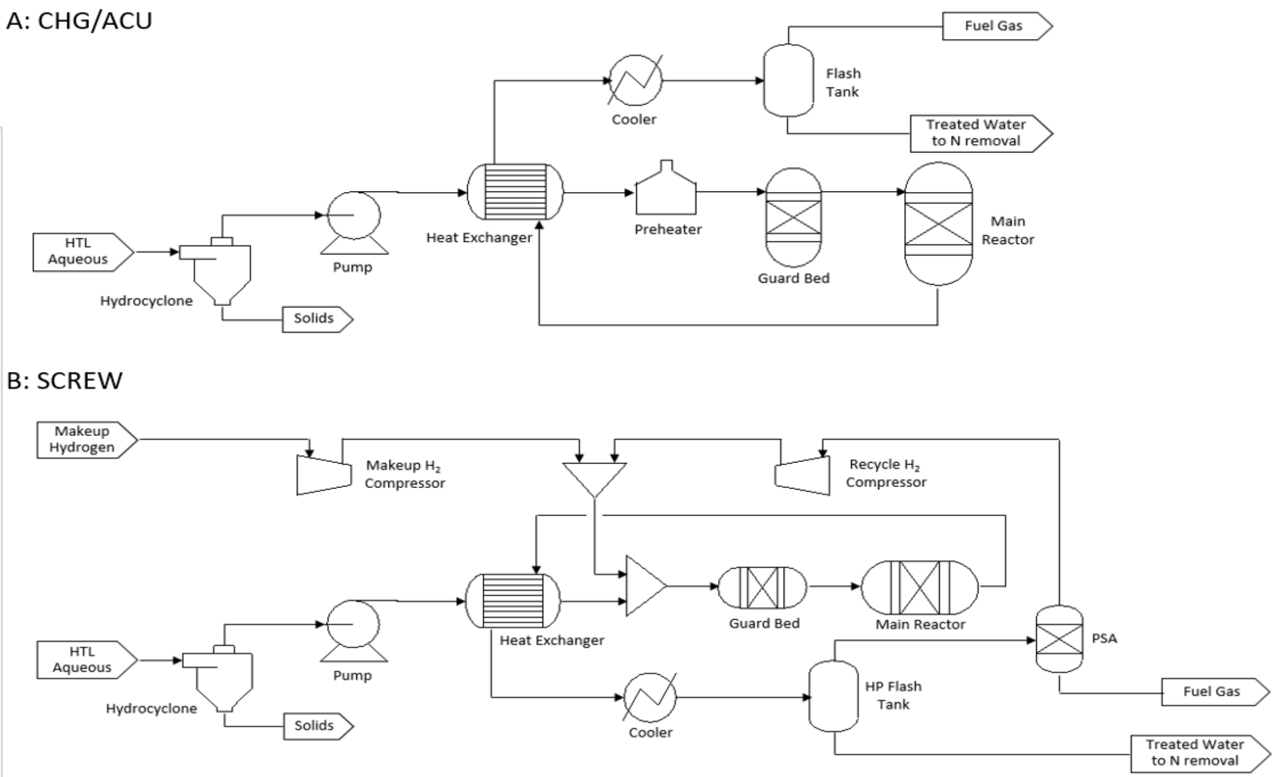
- Conducted 3 campaigns.
- Catalyst was mechanically stable up to 400 h between P_1 – P_2 psig.
- **Catalyst showed excellent COD removal at T_2 °C (> 96%) for 220 h.** However, carbon deposition and eventual plugging, resulted in repacking and addition of new catalysts in the upper catalyst bed.
- Lower reaction temperature (T_1 C) yielded lower % COD conversion (77 – 87%).



4 – Progress and Outcomes FY20 Thermochemical Aqueous Phase Treatment

Task Goal: Estimate initial economics for screening of treatment methods tested in FY20





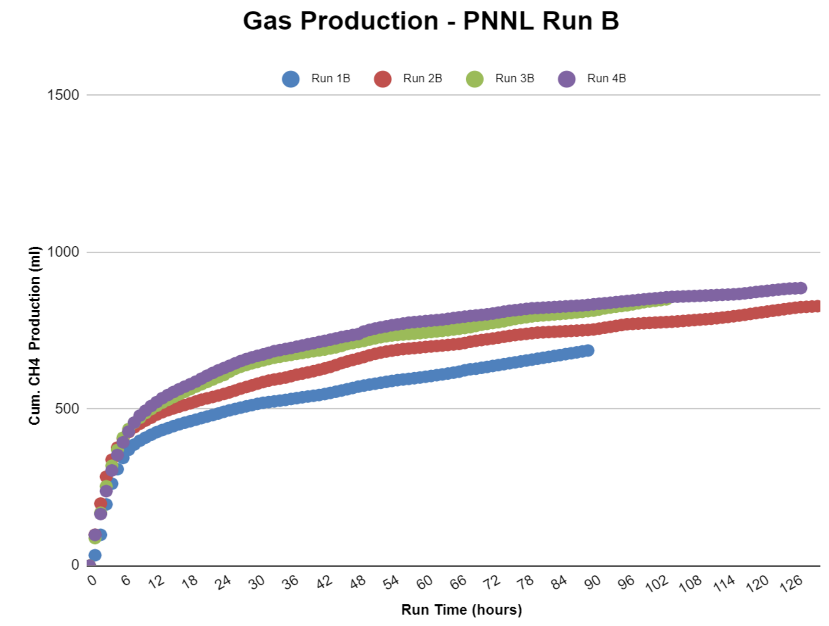
Outcomes:

- High-level modeling and techno-economic analysis (TEA) was performed using experimental testing data for catalytic hydrothermal gasification (CHG), aqueous phase catalytic upgrading (ACU), and steam phase catalytic reduction of wastewater (SCREW)
- When used in conjunction with ammonia stripping, these methods may provide 65-100% COD removal and 80-100% NH3 removal
- Initial TEA indicates that an additional cost of $0.47-0.74/gge for high COD removal and $0.08-0.14/gge for medium COD removal methods can be expected

4 – Progress and Outcomes FY20
AD Aqueous Phase Treatment

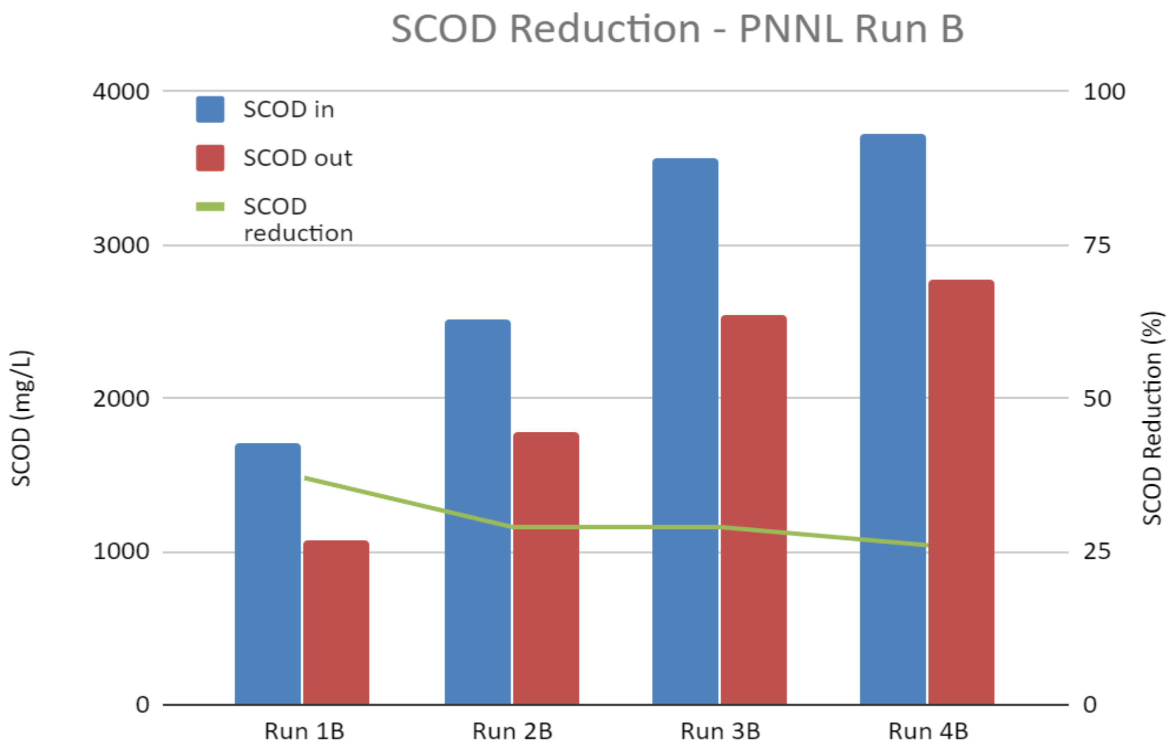
Goal: Conduct batch treatability testing of AD by Veolia as a first step in a proposed AD-annamox treatment process

- AD testing was initially done at 6.5X and then 28X dilution of the aqueous phase



Outcome:

- At normal system loading, aqueous phase contains compounds that are severely inhibitory to the AD microorganisms.
- More diluted sample somewhat mitigates inhibition, but COD reduction is still low
- **AD tests conducted by WSU showed significant COD reduction and gas production with 4 months of culture adaptation**



4- Progress and Outcomes MHTLS Assessment Requirements

- DOE O 422.1, Conduct of Operations is flowed down to PNNL through our contract.
  - It is applicable to Hazard Category 1, 2 & 3 nuclear facilities and when designated by DOE Line Management to accelerator, explosives, laser, nanotechnology, biohazard, chemical, or other facilities.
- PNNL complies by having designated Complex Projects evaluate the applicability of each element from the order.
  - This is accomplished through PSB-004, Managing Complex Projects. Projects determine the applicability of the 18 elements of the Order commensurate with project operational risk.
- MHTLS capability was designated a complex project because of risk associated with high pressure and high temperature operations with BLEVE potential.
- PNNL's Plan, May 2019, outlines an annual self-assessment of MHTLS operations will be conducted
  - The focus of the annual self-assessment will be on configuration management, maintenance, calibrations, training, operator proficiency, and management structure.

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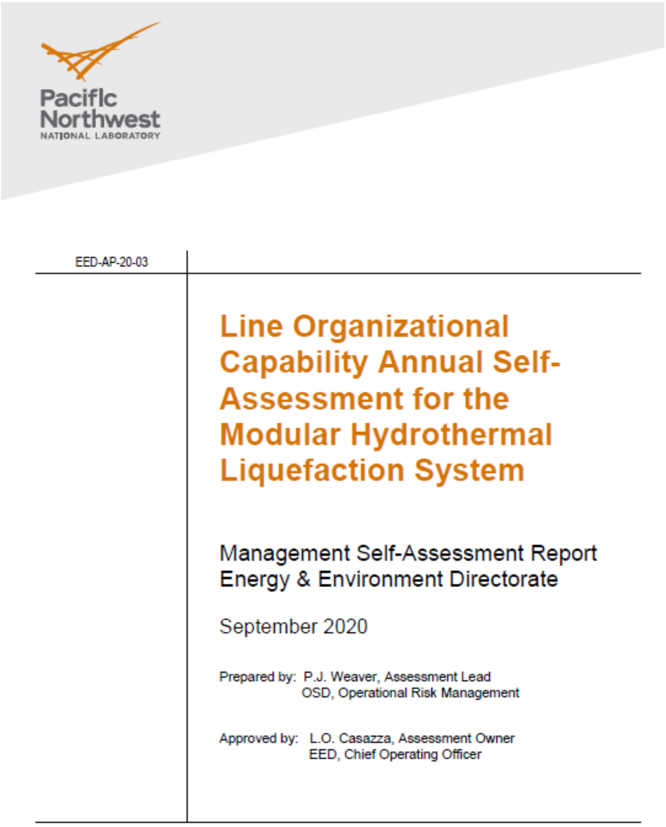
4- Progress and Outcomes Independent Assessment of MHTLS Operations

- Assessment performed by 7 independent observers (PNNL), with addition DOE PNNL Oversight; Observations during MHTLS test with Cow Manure
- Charter: Evaluate Sustainability of High Level of Operational Rigor (i.e., conduct of operations)
- Lines of inquiry included:
  - Change and Configuration Control
  - Maintenance and Calibrations
  - Operator training and proficiency
  - Adherence of operators to procedures
  - Shift Turnovers,
  - Implementation of Covid Controls
  - Safety culture of the team.



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EED-AP-20-03

Line Organizational Capability Annual Self-Assessment for the Modular Hydrothermal Liquefaction System

Management Self-Assessment Report
Energy & Environment Directorate

September 2020

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OSD, Operational Risk Management

Approved by: L.O. Casazza, Assessment Owner
EED, Chief Operating Officer