3.4.2.301 PNNL Hydrothermal PDUs

May 3, 2023

Systems Development and Integration

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Pacific Northwest National Laboratory

Process Overview for Hydrothermal Liquefaction (HTL): **Transforming Wet Wastes to Liquid Fuels**

HTL Plant

HTL Conditions
330-350°C / 2900 psig / 10-30 min
"Accelerating what the earth does"

HTL
Biocrude

Stable biocrude
60% C-yield
Thermally stable

Hydrotreater

Hydrotreater conditions
400°C / 1500 psig
"Standard refinery unit-op"

Hydrocarbon
blendstock
(Diesel, Jet, Naptha)

Fuel Blendstocks
(95%+ C-yield)
Predominantly high
cetane diesel (70%)

- **Conceptually simple (i.e., heated pipe), continuous process**
- **High carbon yields to liquid hydrocarbons (~78% GHG reduction)**
- **Tolerates dirty, wet feedstocks**

Project Overview: ***Adapt and apply PNNL PDU to enable production of biofuels from wet wastes***

Outcome

The project is enabling ***technology innovation, process integration*** and ***partnership projects*** to demonstrate ***scalable hydrothermal processing*** converting wet wastes into biofuels

Impact

- Benefit #1: Potential for ~6 billion gallon/year of fuel (U.S. wet wastes)
  - Modeled GHG emissions 81% less than petroleum[1]
- Benefit #2: Alternative disposal processes expensive (~$4/gal fuel produced)
  - 77 million dry tons/yr of wet wastes in the U.S.
  - Environmental, societal and waste management benefits

Directly supports BETO's SDI strategic goal:
By 2030, support scale-up of multiple biofuel production pathways with a focus on **sustainable aviation fuels** capable of **>70% GHG reduction** by enabling the construction and operation of **at least 4-5 demonstration**-scale integrated biorefineries

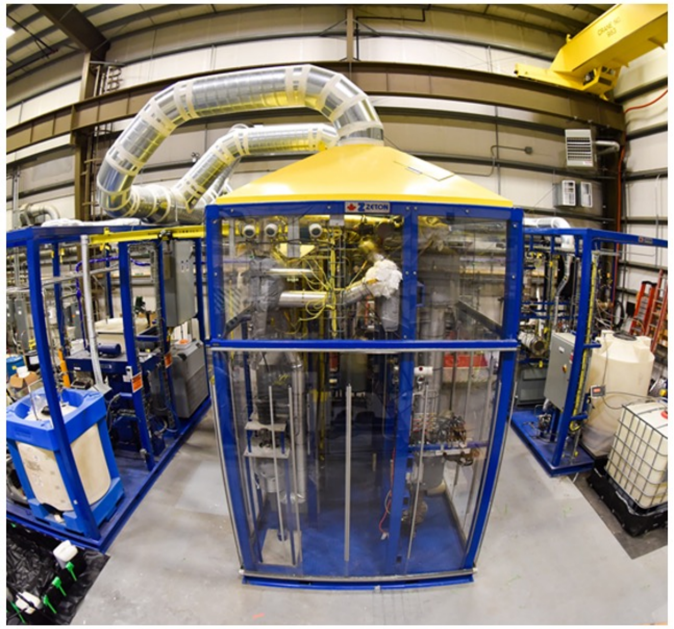
[1]Cai, Hao, et al. *Supply Chain Sustainability Analysis of Renewable Hydrocarbon Fuels via Indirect Liquefaction, Hydrothermal Liquefaction, Combined Algal Processing, and Biochemical Conversion: Update of the 2021 State-of-Technology Cases*. United States: N. p., 2022

Project Overview
PNNL PDU Hydrothermal Systems

Objectives: Enabling commercial deployment through engineering design and demonstration:

1. Identify the uncertainties for HTL deployment
2. Determine the pilot needs to address HTL uncertainties
3. Develop solutions for engineering, demonstration, and commercial scale systems

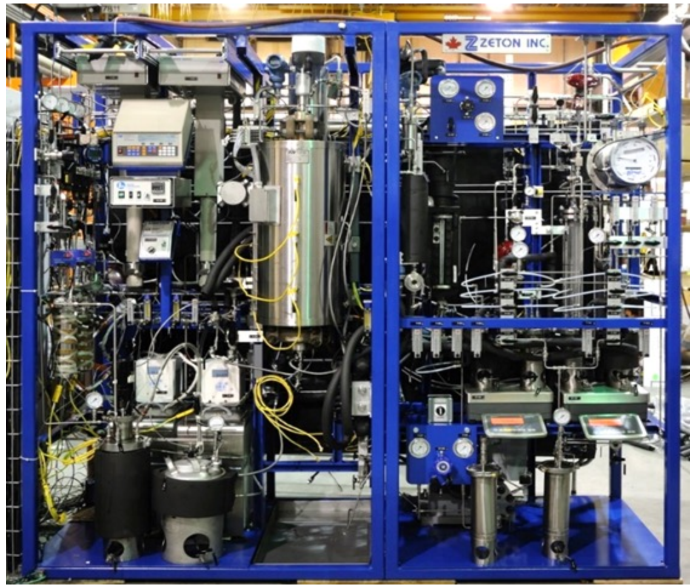
HTL



Engineering-Scale (1)
- Feed rate 12 to 18 L/h
- 3 integrated skids
  - Feed prep, HTL, product separations

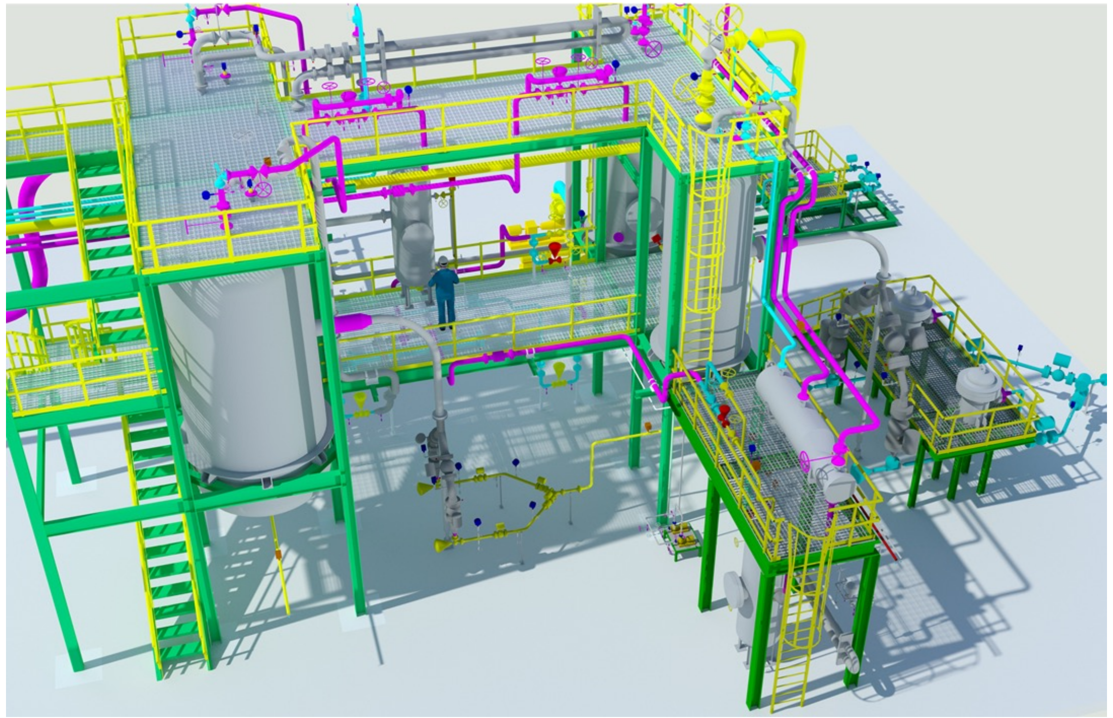
Bench scale (2)
- Feed rate 4-6 L/h

Upgrading



Bench-scale Hydrotreater (2)
- Reactor volume 0.4-1 L
- Fix and moving bed

Lab scale Hydrotreater (5)
- Fixed bed and CSTR
- Reactor volume 25-50 ml



1 – Approach: Key to HTL deployment is addressing uncertainty and technical challenges

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Partnerships:

Commercialization Entities

ALOVIAM
PyroEco Transforming waste to bioenergy
GLWA
Circlia NORDIC
Genifuel
Brown AND Caldwell
metrovancouver

Feedstock providers

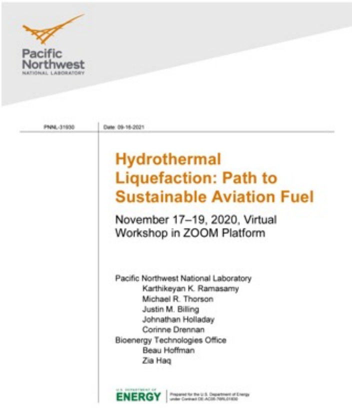
Central Contra Costa Sanitary District
Columbia Crest
PURDUE UNIVERSITY
GLWA
LambWeston SEEING POSSIBILITIES IN POTATOES
DARIGOLD
WM WASTE MANAGEMENT
ICE HARBOR BREWING COMPANY
WASHINGTON STATE UNIVERSITY
metrovancouver

Refinery / Catalyst Partners

KERN ENERGY We Fuel the Future
TOPSOE

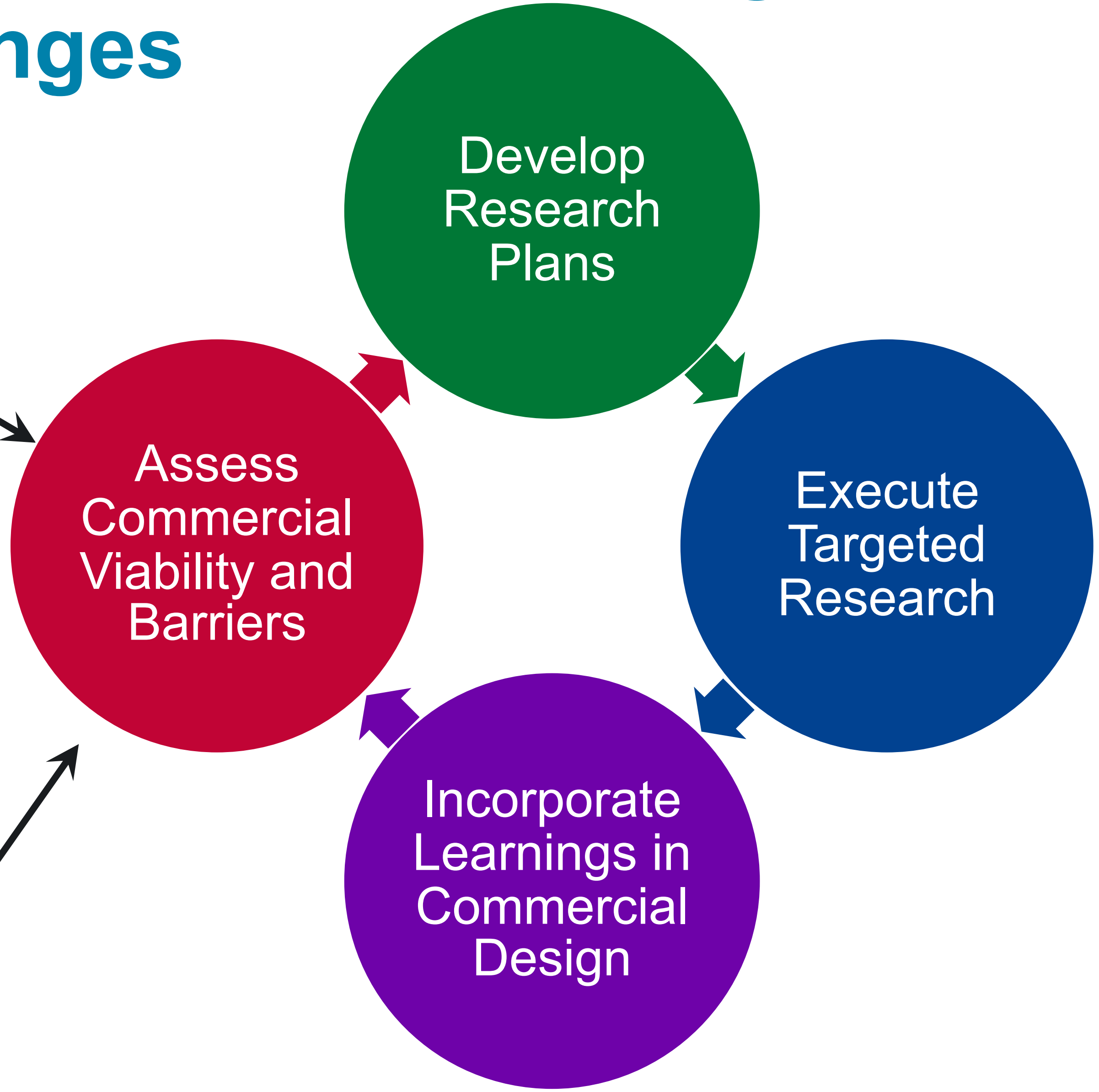
International Collaborators

HyFlexFuel
Water Environment Federation the water quality people
IEA Bioenergy Technology Collaboration Programme
AARHUS UNIVERSITY
WPI



Monitor commercialization efforts

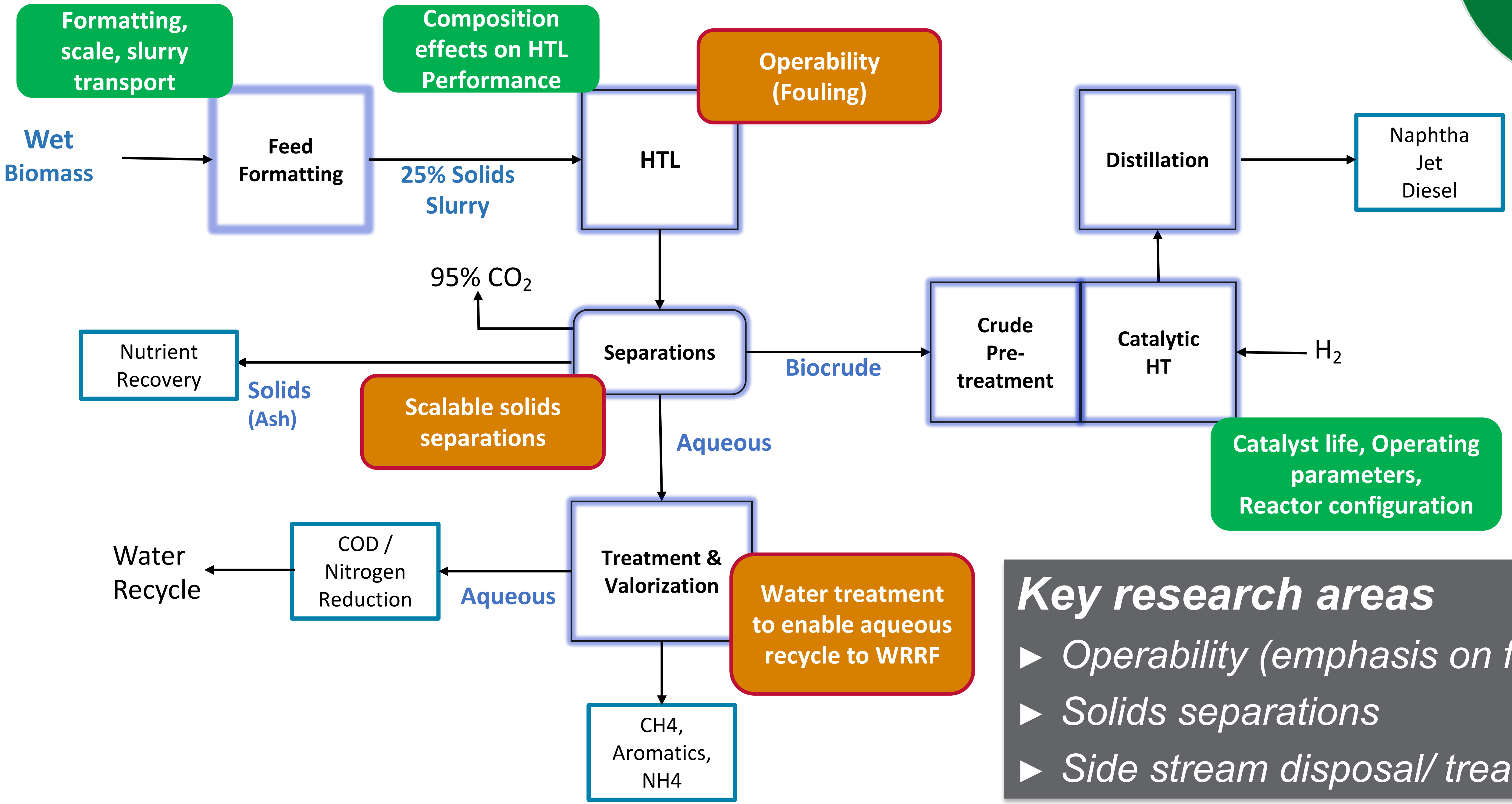
steeper ENERGY
ARBIOS BIOTECH
Licella™



Continual feedback loop key to address real-world barriers with implementable solutions

1 – Approach: Technical Risks & Challenges Used to Define R&D Approach

Develop Research Plans



Key research areas

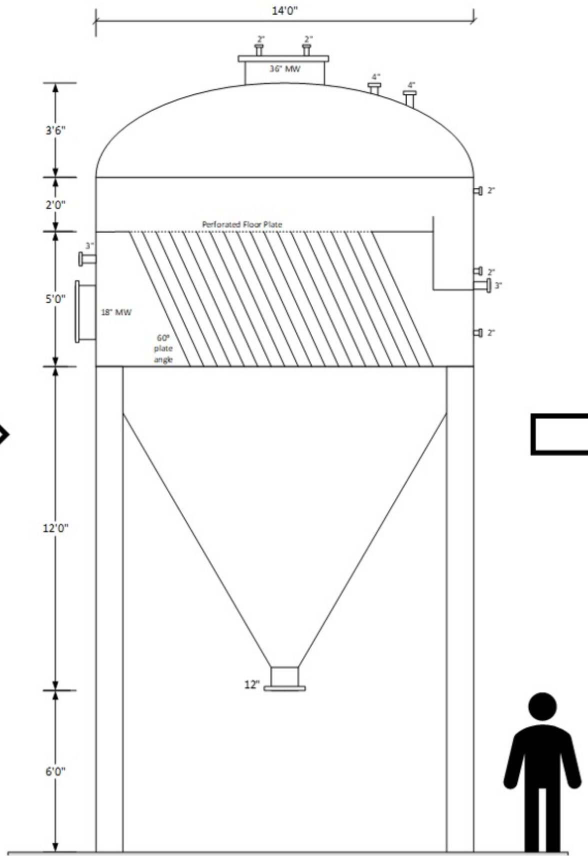
- Operability (emphasis on fouling)
- Solids separations
- Side stream disposal/ treatment

1 – Approach: **Execute Targeted Research Aligned to Commercial Embodiment**

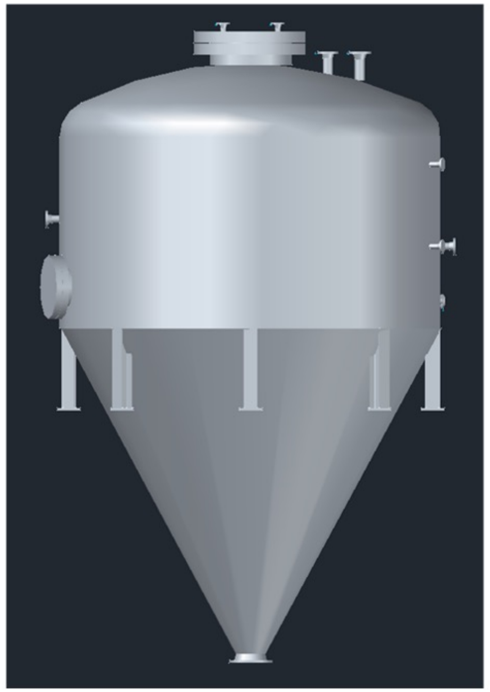
Critical success metrics:
- Assess the commercial challenges with fouling AND develop technology solutions to address fouling
- Develop scale-able solids separation approach
- Demonstrate industrially relevant processing time on stream

Execute Targeted Research → **Incorporate Learnings in Commercial Design**

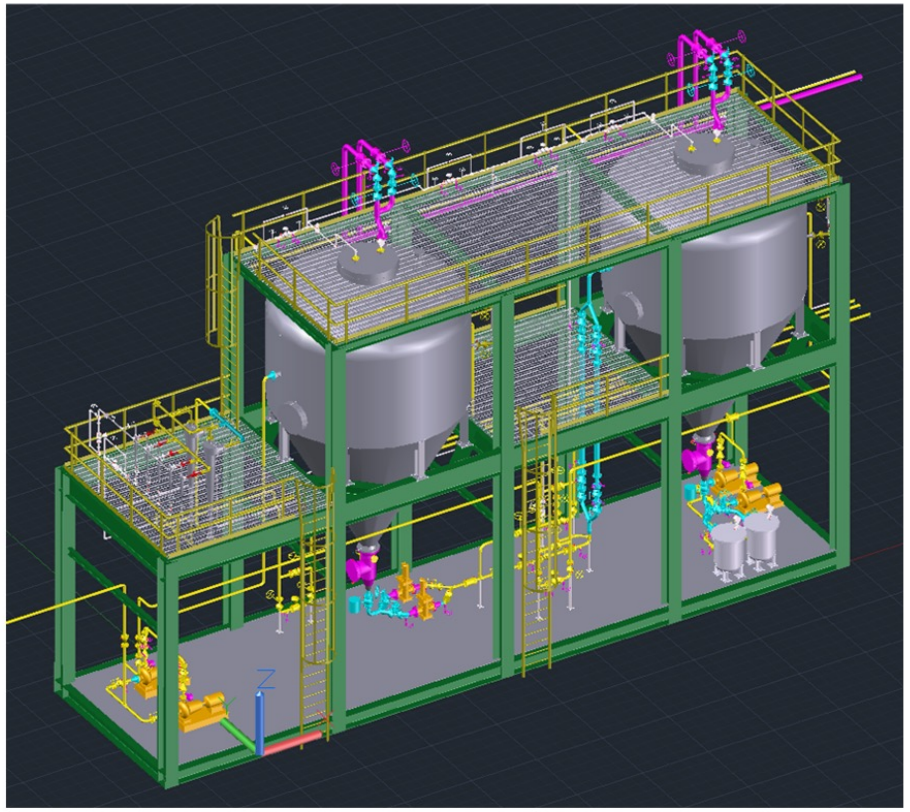
Bench Experiments



Conceptual Scale-up



Equipment Design



Process Integration

1 – Approach
Project Structure

BETO SDI
Ben Simon
Mark Shmorhun

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

PNNL Hydrothermal PDU

Basic Engineering
- Commercial Plant Design

Process Development
- Reactor Fouling
- Heat Exchanger and Heat Integration
- Solids Disposal and Separations
- Basic Engineering
- Biocrude / Aqueous Separations

Scale-up Testing and Production
- HTL Engineering Scale Campaigns
- Upgrading Scale-up Campaigns

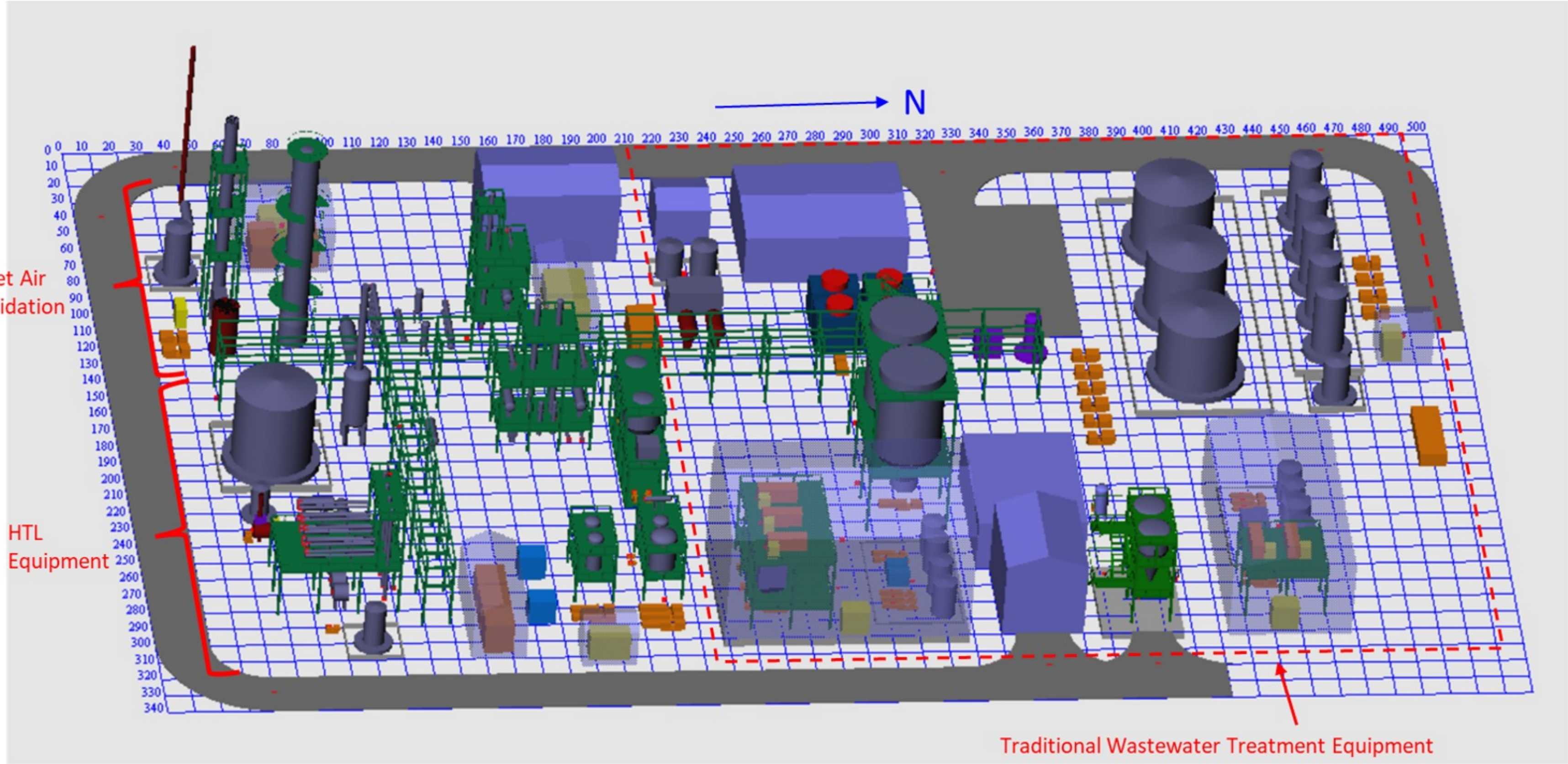
PDU Systems Capability Management
- Engineering Scale HTL Capability Operations and Maintenance
- PDU System Modifications and Upgrades

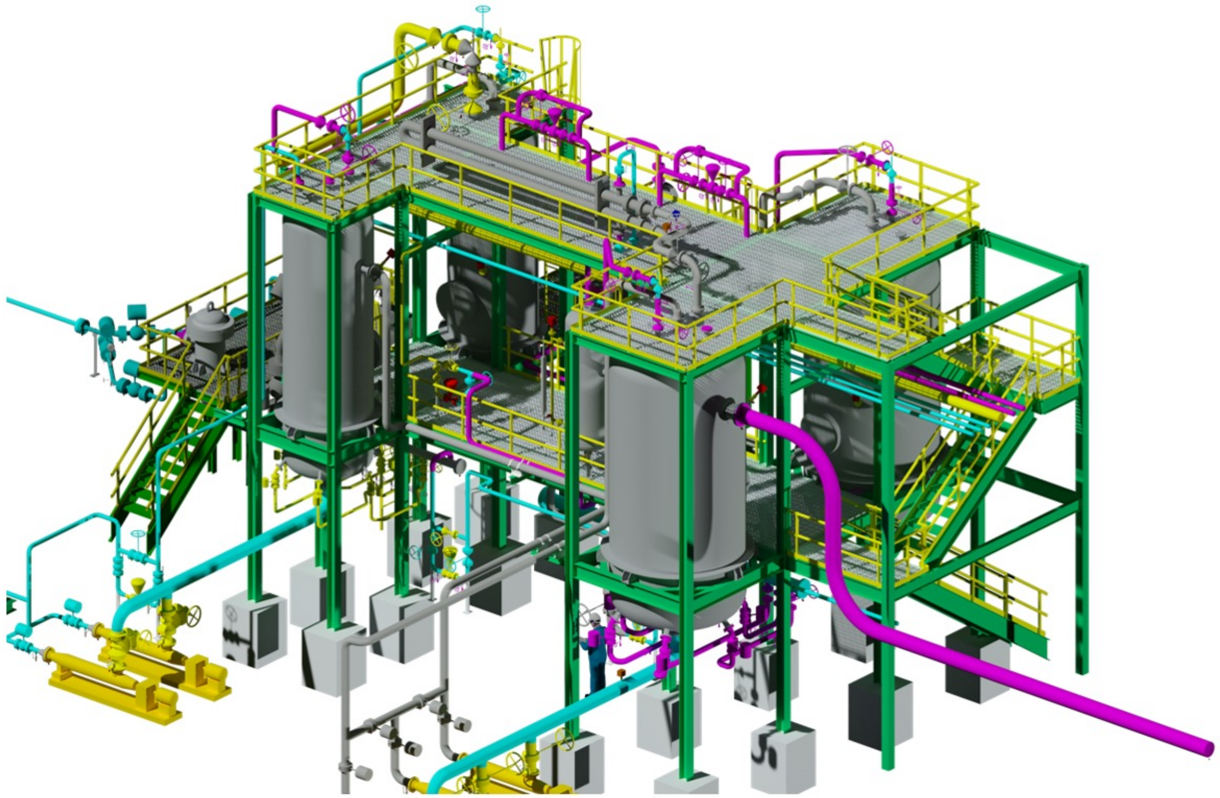
PDU Utilization and Partnership Projects
- PDU Working Group
- BETO R&D, Consortia, CRADAs and Industrial Partnerships
- Project STEM Outreach

Project Structured to Address Technical Risks and Challenges

2 – Progress and Outcomes

Basic engineering to identify scale-up challenges





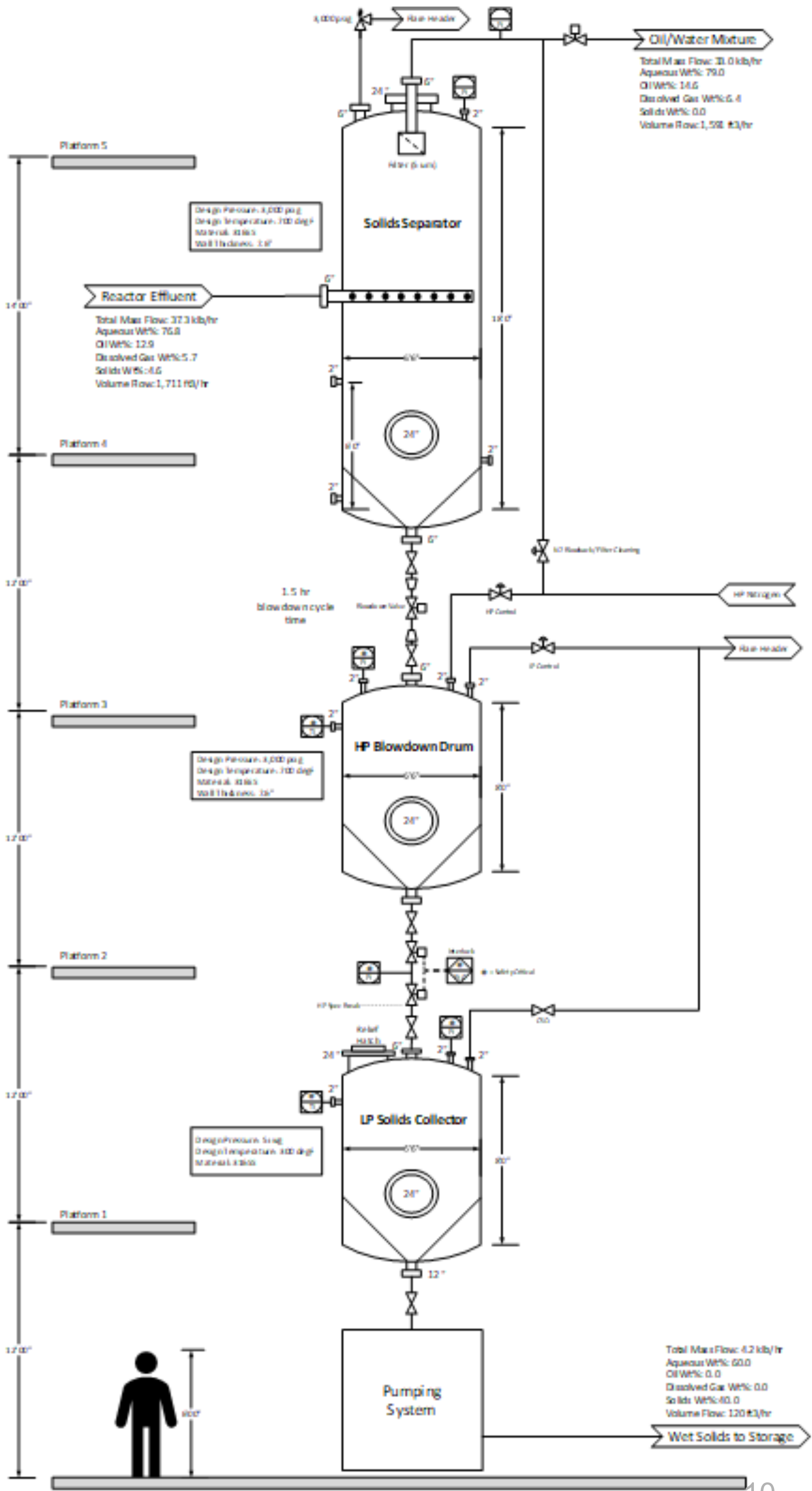
- Completed design of an integrated commercial scale HTL facility
- High level design for uncertain components

2 – Progress and Outcomes
Solids separations, a key scale-up risk

- Solids separations identified as a key process uncertainty
  - Operability and safety needs differ across process scales
  - Important considerations: Reliability and safety

INCLINED PLATE SEPARATORS UNDER CONSTRUCTION AT THE HORIZON FROTH TREATMENT FACILITY (PHOTO COURTESY CANADIAN NATURAL RESOURCES)

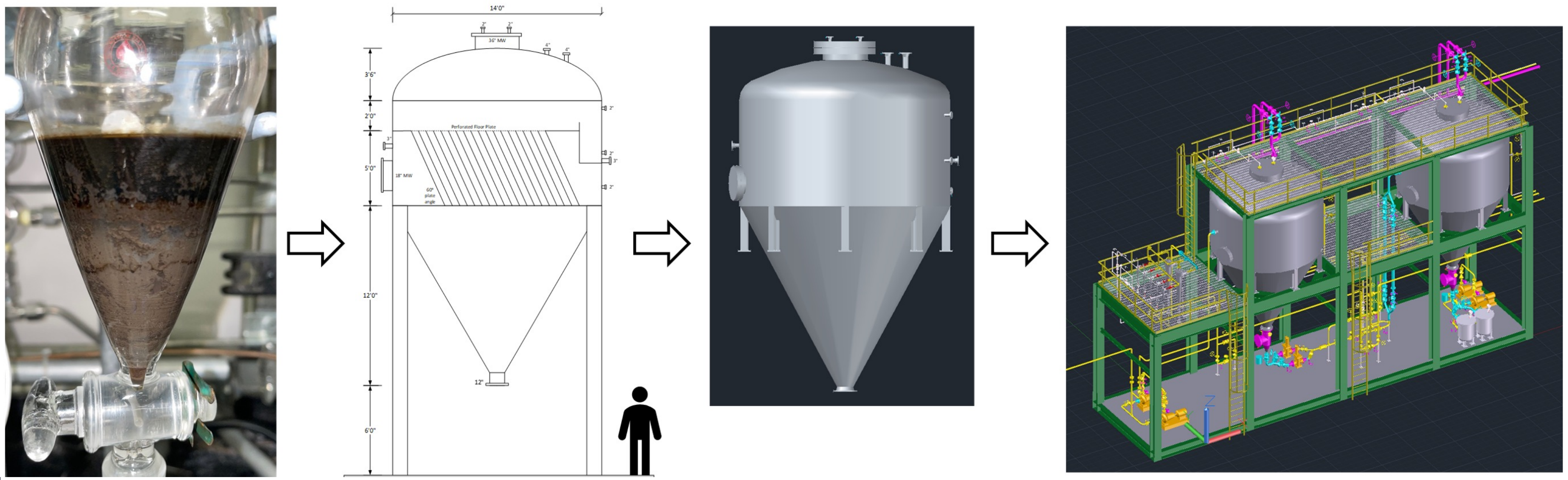
Leveraging oils sands process technology
- Bitumen has similar physical properties to biocrudes
- Commercially implemented by many major oil companies
- Removes solids and improves oil quality



2 – Progress and Outcomes
Solvent extraction effective for solids removal

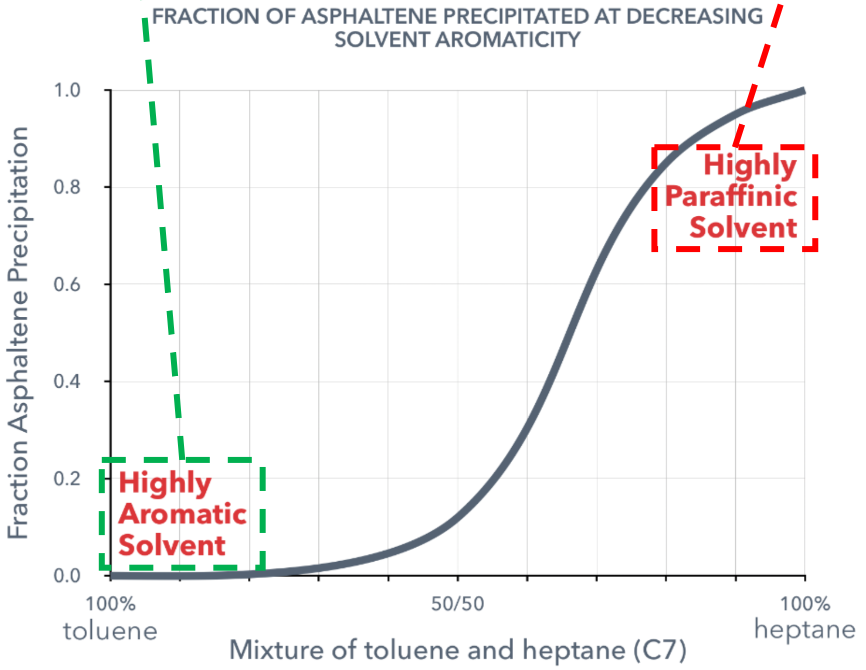
- Extraction processing: *Bitumen* process effective
  - Results match tar sands extraction process
- Adapting and miniaturizing the oil sands extraction process for biofuels production

De-risking commercial deployment through integrated process



Biocrude in Toluene

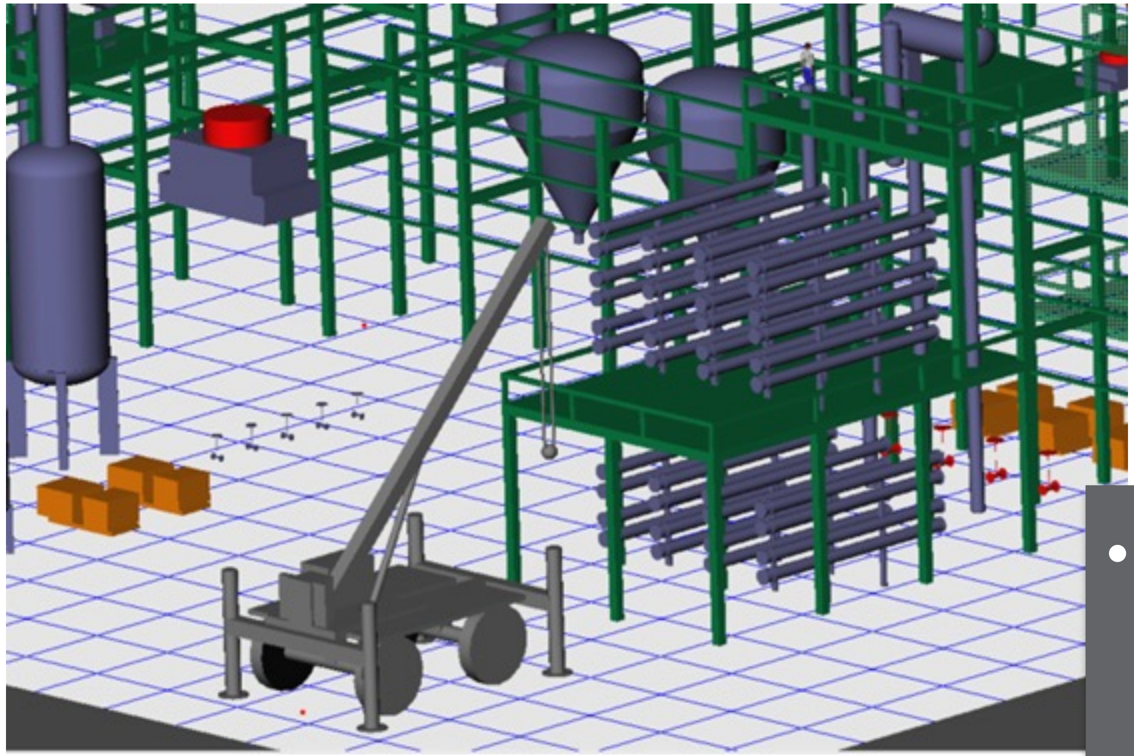
Biocrude in Decane



A more aromatic solvent increases the solubility of asphaltenes. As aromaticity of the solvent decreases (i.e., more paraffinic), more asphaltenes will precipitate.

2 – Progress and Outcomes
Reactor fouling, an important consideration

PNNL 2021 HX design:
Use of heat exchangers (like all other HTL designs)



Plug: rich in inorganics

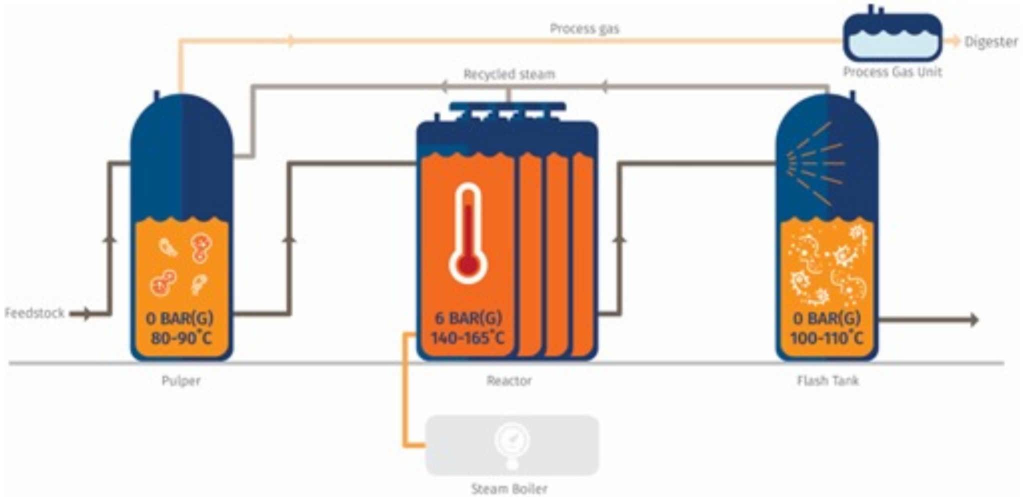
- 30 unique plugging events (1 - 110 hours TOS)
  - Frequent plugging in preheater (215-250°C)
  - Hard-plug compositional changes:
    - Reduced C content – up to 40%
    - Increased **Ca**, Fe, Mg, **P**, Si, & **S** content

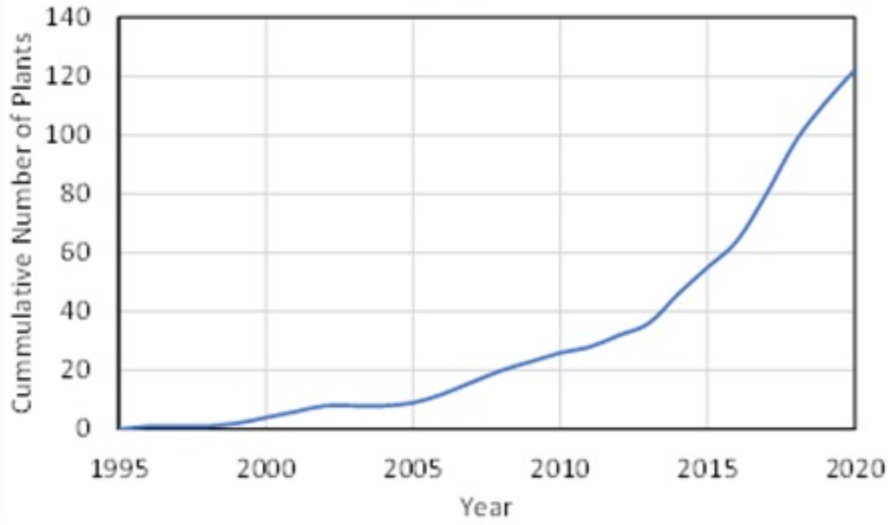
- ***Fouling expected to significantly hinder operability of commercial plants***
- ***Commercial design must minimize use of heat exchangers & "hot spots"***

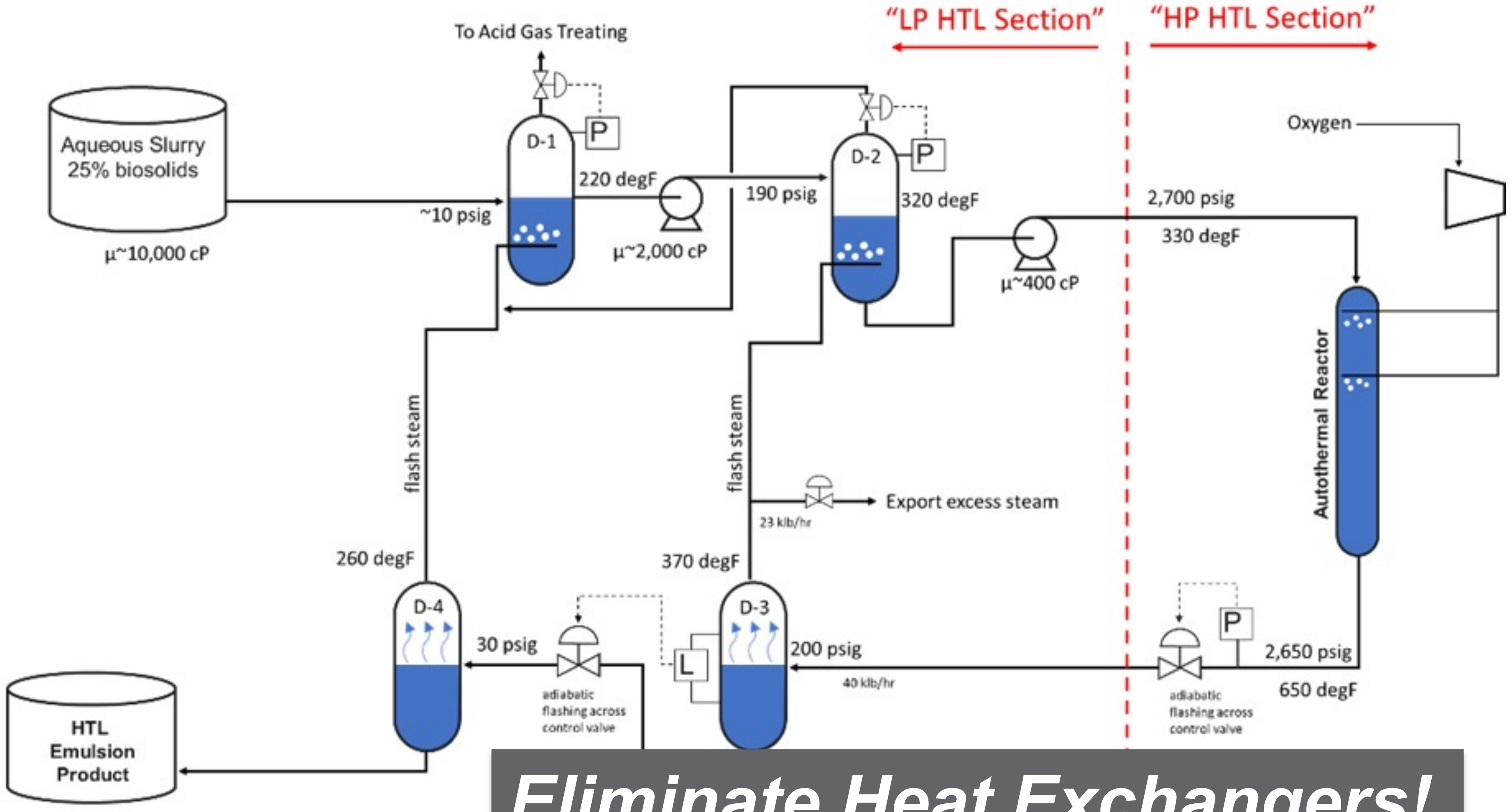
2 – Progress and Outcomes

Waste-water treatment plant have the solution!

- Thermal Hydrolysis is operationally robust because is has no heat exchangers
  - Resulted in exponential growth within WRRF community
- We developed a process to incorporate steam flashing energy recovery in HTL







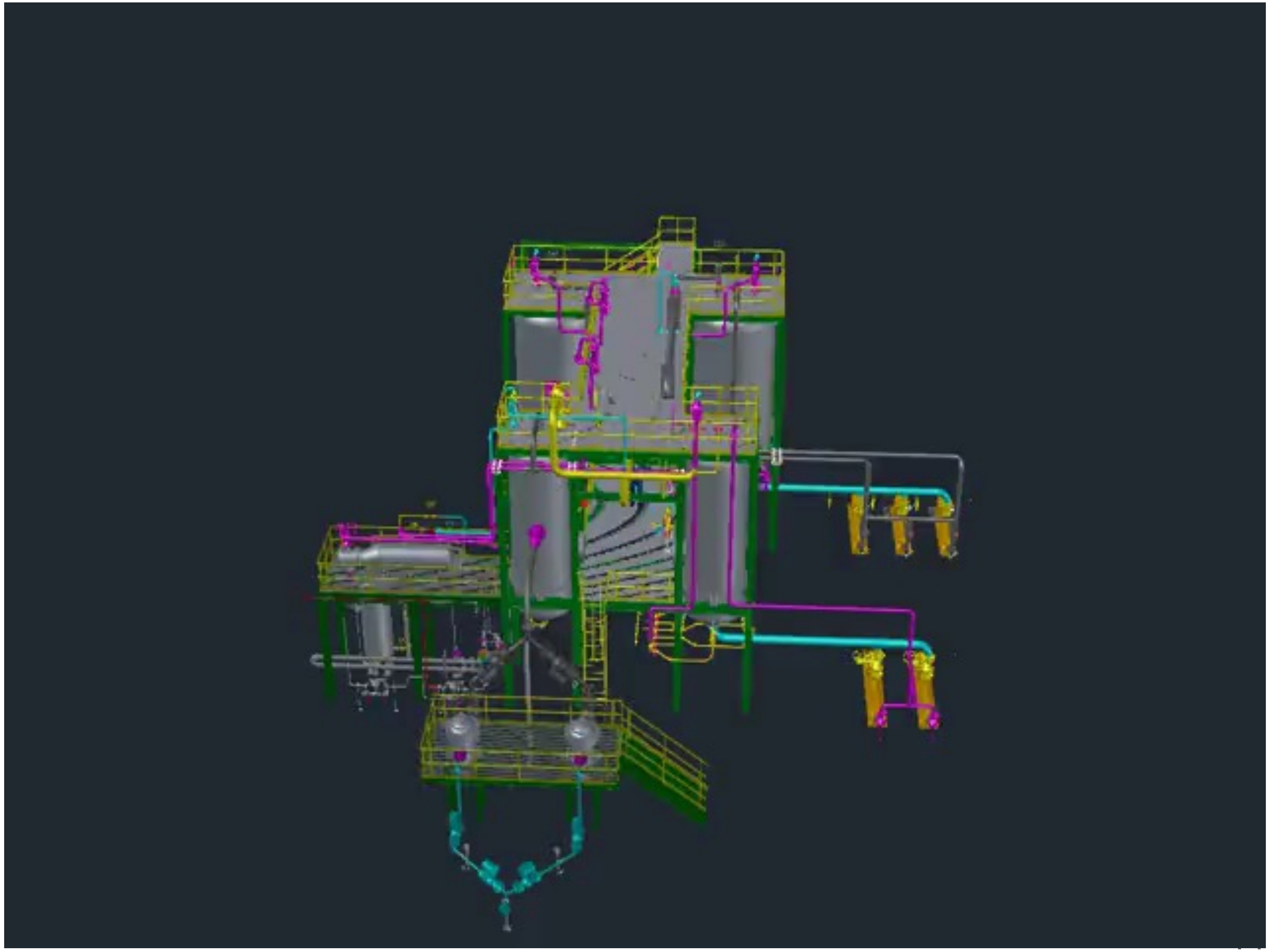
Eliminate Heat Exchangers!

2 – Progress and Outcomes
Heat Integration for reduced fouling

Objectives: Cost-effective, ***reduced-fouling*** heat integration

- Operationally robust because is has no heat exchangers
- Conceptual design used to identify technology gaps and set future research objectives
- Eliminate fouling by avoiding any hot heat exchange surfaces

Novel heat recovery process for reduced fouling: Patents filed



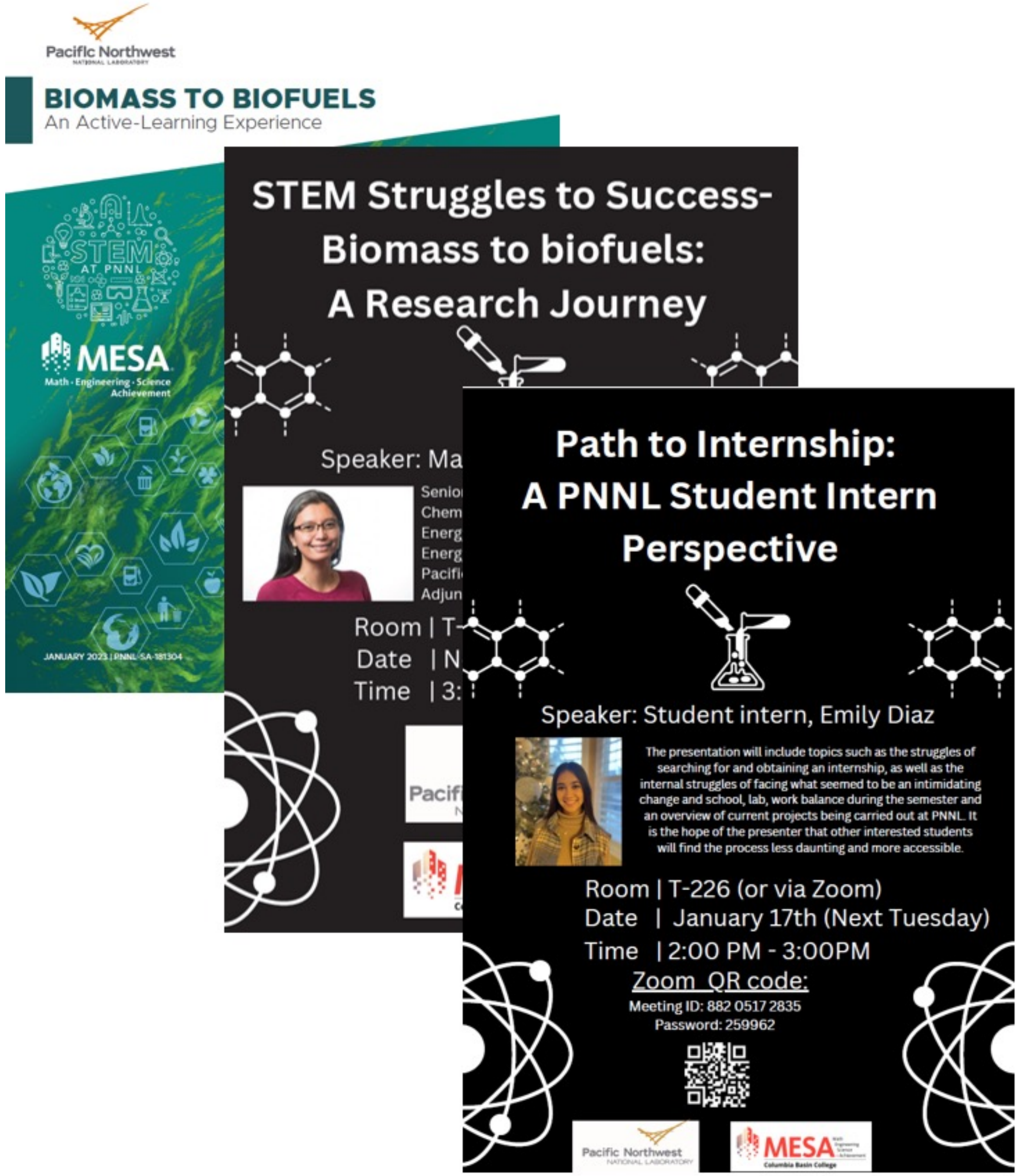
2- Progress and Outcomes:
Local Diversity, Equity and Inclusion Impacts

OBJECTIVES:

- Provide accessible DEI training to project leaders
- Engage future STEM workers in K-12 and college

PROGRESS:

1. Task leads trained on PNNL course 2983 (*Diversity, Inclusion and Belonging)*
2. Hired an undergraduate intern
3. Outreach with Columbia Basin College, a minority-serving institution. Seminars with PNNL full-time and tech intern staff
4. Development of lesson plan to be used by middle school science teacher in partnership with PNNL Office of STEM Education



3 – Impact
Meaningful Collaborations

Provides materials and insights to numerous BETO projects and teams

- *Supports Internal and External Projects*
- *Supports Multiple Collaborations with Related DOE Projects and Industry*

CRADA projects with Industry
- >50 gallons of HTL aqueous to a CRADA (SoCal gas)
- GLWA: HTL products and process data

HTL Pilot Projects with DOE and Industry
- DOE HYPOWERs, WRRF
- Metro Vancouver, WRRF

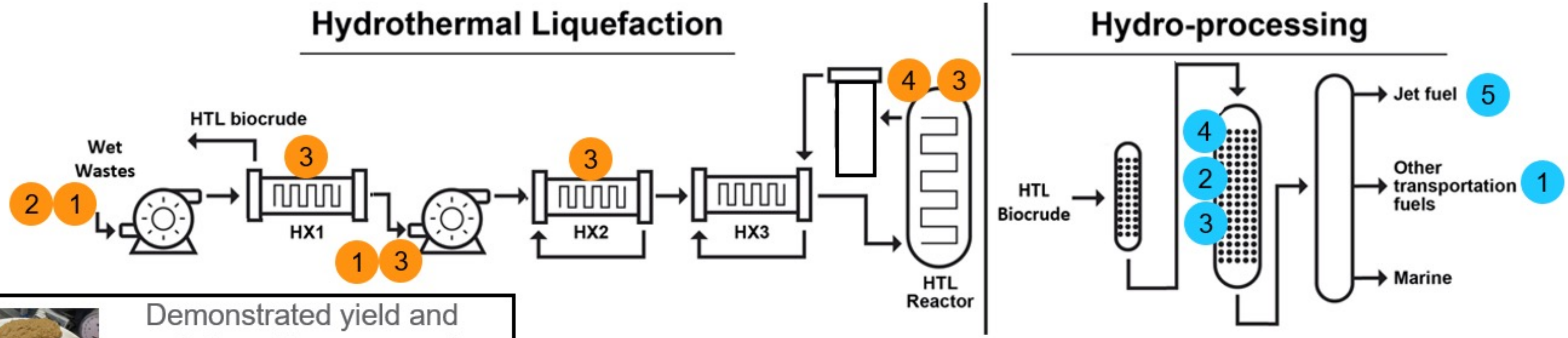
Partnerships/Collaborations
- HTL Feedstocks (Gibby Group, Waste Management, WRF, multiple WRRF utilities, DOD)
- Upgrading (Kern)

PNNL projects
- Bench Scale HTL of Wet Wastes Feedstocks (2.2.2.302): HTL products
- Bio-Hydroprocessing (BHP) Project (2.3.4.106): Formatted, autoclaved sewage sludge
- Waste-to-Energy (2.1.0.113) & Analysis Supporting Conv. for Fuels and Products (2.1.0.301): Process performance data
- Determination of the Feasibility of Biofuels in Marine Applications (3.1.4.007): Biocrude for marine fuel

BETO and other DOE and DOD projects
- Electrochemical (T-MEC) Approach for Drop-In Fuel Production from Wet Waste (2.3.4.609): HTL aqueous
- Harvesting Energy from Waste-Water by Converting Sewage (1.6.1.3) (led by WPI) >20L of HTL products
- Expertise, feedstocks, and materials, where beneficial (5.1.3.202)
- Hazardous Algae Blooms (US Army Core of Engineers)

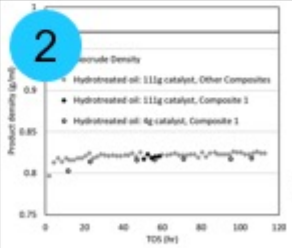
Consortia and other National Laboratories
- Separations Consortium (2.5.5.503): HTL products
- Bio-Oil Co-Processing with Refinery Streams (3.4.3.301): Biocrude
- Autoclaved Pig Manure (10-gallons) in addition to handling protocols to INL

3 – Impact: **Addressed numerous barriers towards commercialization (subset here)**



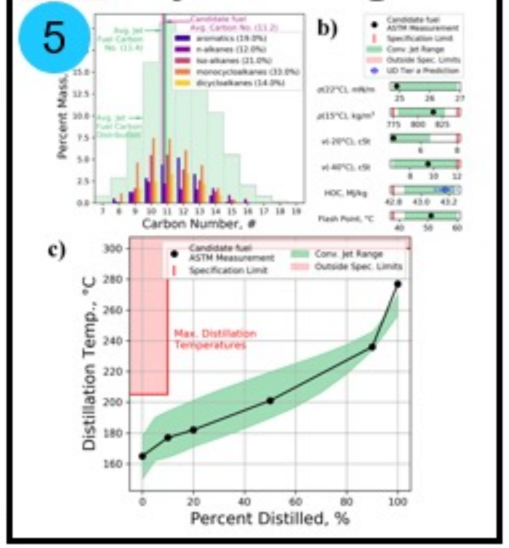
1 Demonstrated yield and capital cost improvements with increased solids content[4]

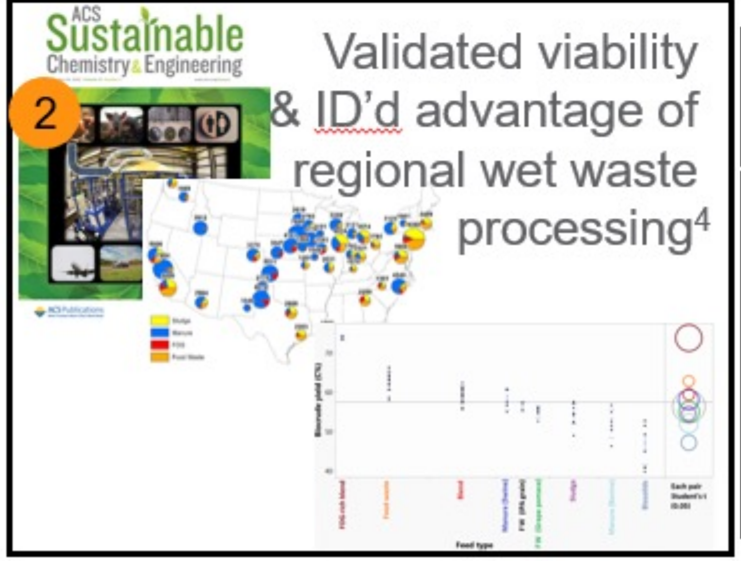
4 ID'd real world challenges with HTL of plastics 4



2 Scalable hydrotreating >20x scale-up[5]

Excellent Tier α and β SAF Properties[1] & ID'd key challenges[1,2]

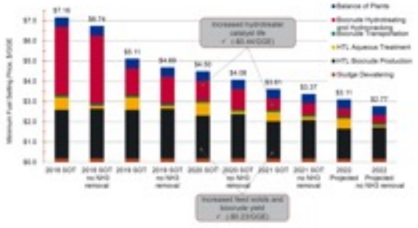




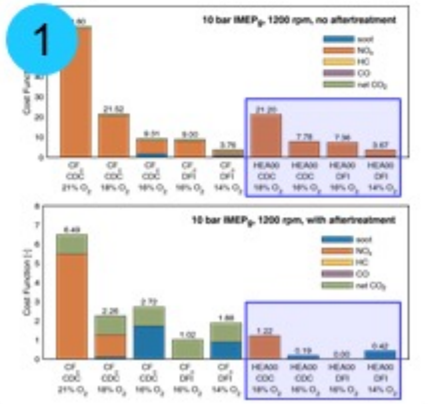
Validated viability & ID'd advantage of regional wet waste processing[4]

Quarterly GPRA updates to BETO (FY21)

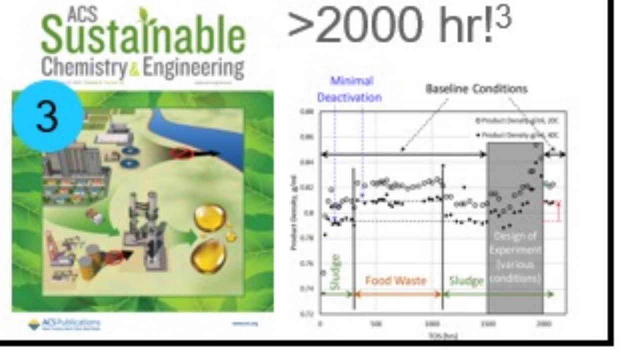
3 Significant SOT cost reductions[6]



Excellent diesel engine test results



Stable hydrotreating >2000 hr![3]



[1]Cronin, D. J., Subramaniam, S., Brady, C., Cooper, A., Yang, Z., Heyne, J., ... & Thorson, M. R. (2022). Sustainable Aviation Fuel from Hydrothermal Liquefaction of Wet Wastes. *Energies*, 15(4), 1306.

[2]Kallupalayam Ramasamy, K., Thorson, M. R., Billing, J. M., Holladay, J. E., Drennan, C., Hoffman, B., & Haq, Z. (2021). *Hydrothermal Liquefaction: Path to Sustainable Aviation Fuel* (No. PNNL-31930). Pacific Northwest National Lab.(PNNL), Richland, WA (United States).

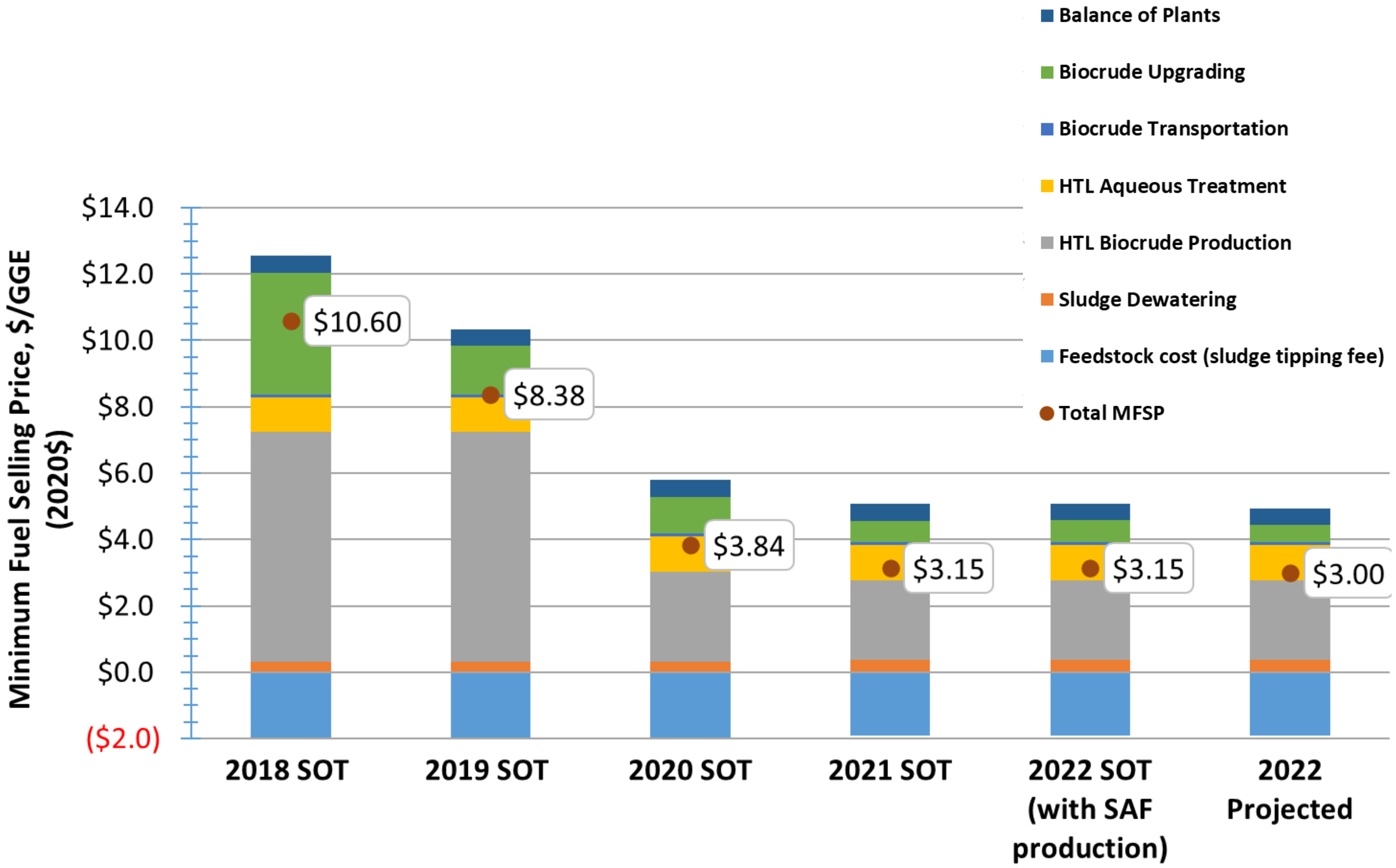
[3]Subramaniam, S., Santosa, D. M., Brady, C., Swita, M., Ramasamy, K. K., & Thorson, M. R. (2021). Extended Catalyst Lifetime Testing for HTL Biocrude Hydrotreating to Produce Fuel Blendstocks from Wet Wastes. *ACS Sustainable Chemistry & Engineering*, *9*(38), 12825-12832.

[4]Cronin, D., Schmidt, A. J., Billing, J., Hart, T. R., Fox, S. P., Fonoll, X., ... & Thorson, M. R. (2021). Comparative Study on the Continuous Flow Hydrothermal Liquefaction of Various Wet-Waste Feedstock Types. *ACS Sustainable Chemistry & Engineering*.

[5]Thorson, M. R., Santosa, D. M., Hallen, R. T., Kutnyakov, I., Olarte, M. V., Flake, M., ... & Swita, M. (2021). Scaleable Hydrotreating of HTL Biocrude to Produce Fuel Blendstocks. *Energy & Fuels*, *35*(14), 11346-11352.

[6]Snowden-Swan, L. J., Billing, J. M., Thorson, M. R., Schmidt, A. J., Jiang, Y., Santosa, D. M., ... & Taylor, M. A. (2021). Wet Waste Hydrothermal Liquefaction and Biocrude Upgrading to Hydrocarbon Fuels: 2020 State of Technology (No. PNNL-30982). PNNL, Richland, WA

3 – Impact: **Addressing uncertainty barriers while improving economic viability**



PDU Process Development is Driving Down Costs for Wet Waste Conversion to Fuels

3 – Impact: **HTL solves two crucial challenges to society:** *Sustainable Aviation Fuel & Sewage Sludge Disposal*

Value #1: Low GHG fuels

- Potential of 6 billion gal/year of fuel (U.S.)[1]
- 78% reduction in GHG

Value #2: Sludge disposal

- Sludge disposal represents ~50% of wastewater costs
- Partitioning forever chemicals out of water
- Costs expected to continue to increase as land application becomes illegal

3.1 M gal fuel/yr
$12M/yr[2]

Two potential revenue streams
Example:100 dry tons/day plant

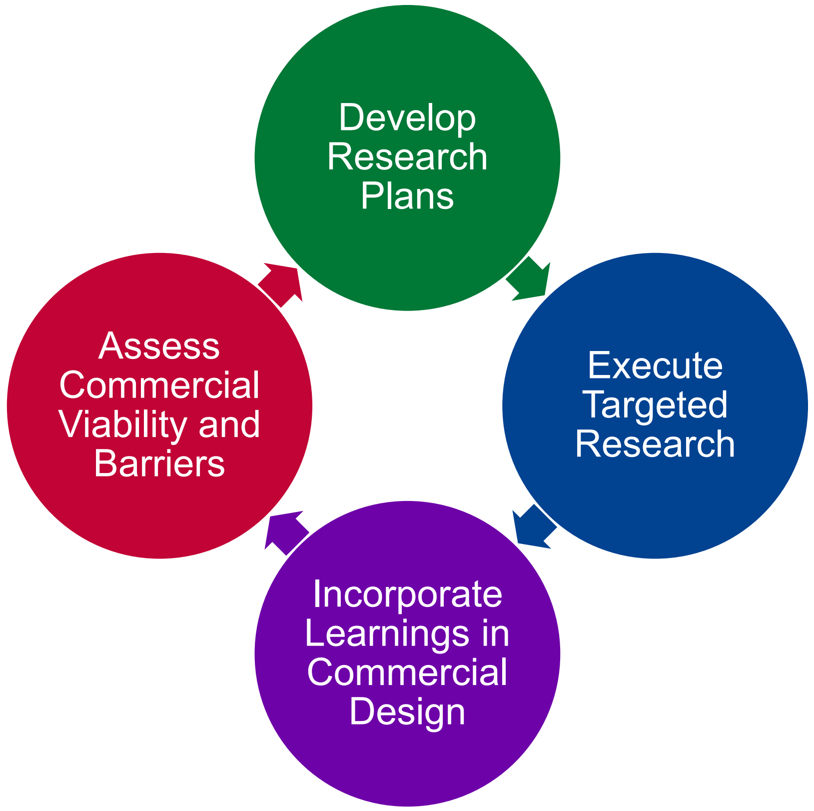
HTL provides a disposal solution in addition to sustainable fuel production

Offset sludge disposal costs:
$7-15M /yr[1]

[1]Basis of disposal costs: $200-400/dry ton or $40/wet ton @ 10-20 wt% solids, [2]Assumed fuel value of $4/gal

Summary

- **Overview:** Targeted research to enable the deployment of HTL to convert wet wastes to fuels
- **Approach:** Close partnership with industry, TEA and resource assessment teams to prioritize and target research. SMART milestones and GNGs to ensure successful impact of developments.
- **Progress and Outcomes:** Addressing commercial deployment barriers with commercially deployable technical solutions for:
  - Solids separation at scale
  - Reducing fouling in commercial embodiment
  - Hydroprocessing of biocrude
- **Impact:** The PDU project is providing
  - Process technology to enable HTL commercialization
  - DOE PDU capability utilization supporting multiple collaborations with DOE related projects and industry
  - Technology transfer through publications, presentations, the development of IP licensing agreements, and partnership projects



Quad Chart Overview

Timeline
- Project start date: Oct 1, 2021
- Project end date: Sept 30, 2024

	FY 22	Total Award
DOE Funding	10/1/2022-9/30/2023 $1,985,000	$6,255,000 (10/1/2021-9/30/2024)
Project Cost Share*	$0	$0

TRL at Project Start: 5
TRL at Project End: 6

Project Goal
Develop technology innovation, process integration and partnership projects to demonstrate scalable hydrothermal processing for the conversion of wet waste feedstocks into biofuel and co-products

End of Project Milestone
Demonstrate over 500 hours of continuous HTL operation without plugging with a wet organic waste feedstock to demonstrate reliable operation and de-risk HTL commercialization and investment

Funding Mechanism
Lab Call

Project Partners
- Great Lakes Water Authority
- MetroVancouver
- Aloviam
- Circlia Nordic

*Only fill out if applicable.

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Acknowledgements

- Beau Hoffman, BETO Technology Manager

Experimental Team:

- Andy Schmidt
- Ben Spry
- Mike Thorson
- Dan Anderson
- Mariefel Olarte
- Todd Hart
- Sam Fox
- Miki Santosa
- Senthil Subramanian
- Igor Kutnyakov
- Matt Flake
- Dylan Cronin
- Uriah Kilgore
- Lisa Middleton Smith

Analysis Team:

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

Waste Resource Team:

- Tim Seiple
- Andre Coleman

Additional Slides

Responses to Previous Reviewers' Comments

Feedback: "Does PNNL intend to scale up this technology themselves to the commercial scale? What is the strategy to do that?":

PNNL's strategy is to work with both technology end users/adopters and commercialization partners to scale up and commercialize the technology. We have established strategic partnerships with users that are generating and managing wet-waste feedstocks, and we have licensing agreements with commercialization partners that are raising capital for scale-up and commercialization. Our goal is to de-risk commercial deployment.

Feedback: Regarding the reviewer's recommendation on the pursuit of modeling to understand the impacts of feedstock composition on the upgrading process and final product properties, we agree that being able to systematically correlate incoming biomass composition with the upgraded fuel blendstock product properties is of great value. Toward this effort, we have developed reduced-order models based on PNNL's extensive library of continuous HTL processing data to predict biocrude yield and quality. Extending the models to predict the upgraded fuel properties based on biocrude quality is the next logical next step that should be worked into our future plans. We have since published a paper quantifying the impacts of feedstock composition on product yields and quality (ACS Sustainable Chem. Eng. 2022, 10, 3, 1256–1266).

Publications, Patents, Presentations, Awards, and Commercialization (since FY21 Review)

Publications:

1. Subramaniam S., Kilgore, U.K., Fox, S.P., Cronin, D.J., Guo, M.F., Schmidt, A.J. Ramasamy, K., Thorson, M.R., "Catalytic Wet Air Oxidation of Hydrothermal Liquification Aqueous Stream." 2022 ,Submitted to: Water Research.
2. Cronin, D. J.; Subramaniam, S.; Brady, C.; Cooper, A.; Yang, Z.; Heyne, J.; Drennan, C.; Ramasamy, K. K.; Thorson, M. R., Sustainable Aviation Fuel from Hydrothermal Liquefaction of Wet Wastes. Energies 2022, 15 (4), 1306.
3. Snowden-Swan, L. J.; Li, S.; Jiang, Y.; Thorson, M. R.; Schmidt, A. J.; Seiple, T. E.; Billing, J. M.; Santosa, D. M.; Hart, T. R.; Fox, S. P. Wet Waste Hydrothermal Liquefaction and Biocrude Upgrading to Hydrocarbon Fuels: 2021 State of Technology; Pacific Northwest National Lab.(PNNL), Richland, WA (United States): 2022.
4. Santosa, D. M.; Wendt, L. M.; Wahlen, B. D.; Schmidt, A. J.; Billing, J.; Kutnyakov, I. V.; Hallen, R. T.; Thorson, M. R.; Oxford, T. L.; Anderson, D. B., Impact of storage and blending of algae and forest product residue on fuel blendstock production. Algal Research 2022, 62, 102622.
5. Choi, H.; Soland, N. E.; Moss, M. R.; Liu, J.; Prestangen, R. R.; Katahira, R.; Lee, S.-J.; Thorson, M. R.; Freeman, C. J.; Karp, E. M., The cell utilized partitioning model as a predictive tool for optimizing counter-current chromatography processes. Separation and Purification Technology 2022, 285, 120330.
6. Subramaniam, S.; Santosa, D. M.; Brady, C.; Swita, M.; Ramasamy, K. K.; Thorson, M. R., Extended Catalyst Lifetime Testing for HTL Biocrude Hydrotreating to Produce Fuel Blendstocks from Wet Wastes. ACS Sustainable Chemistry & Engineering 2021, 9 (38), 12825-12832.

Patents:

1. Thorson, M. R.; Snowden-Swan, L. J.; Schmidt, A. J.; Hart, T. R.; Billing, J. M.; Anderson, D. B.; Hallen, R. T., Hydrothermal liquefaction system. US Patent 11,279,882: 2022. - **Licensed**

Presentations

1. TCBiomass, Denver, CO, 04/2022
2. WEF Process Innovations, 06/2022
3. HTL workshop, MetroVancouver, 06/2022
4. WEFTEC, 10/2022
5. AIChE, 11/2022
6. ACS, 08/2022

Commercialization Efforts of PNNL IP:

1. Metro Vancouver is building a demonstration HTL plant (PNNL technology
2. Aloviam is scaling up the HTL process via an awarded FOA based on PNNL technology

Thank you