Enabling Hydrothermal Liquefaction for Fuels and Sewage Sludge Disposal

March 13, 2023

Organic Waste Conversion Technology Area

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

- **HTL Plant**
- **HTL Biocrude**
- **Hydrotreater**
- **Hydrocarbon blendstock (diesel, jet, naptha)**

**HTL Conditions**
330-350°C / 2900 psig / 10-30 min.  
“Accelerating what the Earth does”

**Stable biocrude**
60% C-yield  
Thermally stable

**Hydrotreater conditions**
400°C / 1500 psig  
“Standard refinery unit-op”

**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% greenhouse gas (GHG) reduction].
- Tolerates dirty, wet feedstocks.

**Benefit #1:** Potential for ~6 billion gallon/year of fuel in the U.S.
**Benefit #2:** Alternative disposal processes expensive (~$4/gal fuel produced).
Project Overview: Addressing Barriers to Deployment

Big Picture: HTL is attractive for sludge disposal, but key barriers remain for deployment.

Research Focus: Targeted research de-risking HTL to convert wet wastes to fuels.

1. **Aqueous treatment**: Enable sustainable recycle.
2. **Per- and polyfluoroalkyl substances (PFAS)**: Life cycle throughout HTL and upgrading.
3. **Nutrient recovery**: Recover phosphorus and nitrogen as fertilizer.
   - **Solids**: Ensure solids can be land applied.
4. **Low-grade feedstocks**: Expand feedstocks for regional wet waste processing (larger facilities).
   - **Improved HX**: Sustainable, cost-effective heat recovery.
   - **Reactor Plugging**: Correlation to predict plugging.
   - **Reliable Operation**: >500-hr time-on-stream w/o plug.
   - **Scale-up testing**: Testing at scale.
   - **Blow down system life**: Engineering robustness.
5. **Catalyst life**: Achieve >1yr performance.
   - **Efficient guard bed**: Prevent plugs: ebullated/slurry reactor.

Sustainable aviation fuel (SAF):
- **Nitrogen content in fuel**:
  - Reduce the nitrogen in the fuel to <10 parts per million.
  - Understand the nitrogen-sulfur interactions on fuel thermal stability.
- **Advance HTL towards SAF approval process**

Diesel:
- **Blend level limits**: Isomerization for cold temperature properties.
- **Fuel Stability**: Understand and address fuel oxidation.

Key:
- This project
- Scale-up project
- HDN project
1 – Approach: **Key to HTL Deployment is Addressing Uncertainty and Technical Challenges**

**Partnerships:**

- **Commercialization Entities**
  - ALOVIAM
  - Circlia Nordic
  - Genifuel
  - metrovancouver
  - Kern Energy
  - TOPSOE

- **Feedstock Providers**
  - PyroEco
  - GLWA
  - Lamb Western
  - Brown and Caldwell
  - HyFlexFuel

- **Refinery / Catalyst Partners**
  - Washington State University
  - Aarhus University

- **International Collaborators**
  - Water Environment Federation
  - IEA Bioenergy
  - WPI

**Monitor commercialization efforts**

**Continual feedback loop** key to address real-world barriers with implementable solutions and implement learnings with commercialization entities.

**Develop Research Plans**

**Execute Targeted Research**

**Assess Commercial Viability and Barriers**

**Incorporate Learnings in Commercial Design**

- Research Plans
- Incorporate Learnings in Commercial Design
- Assess Commercial Viability and Barriers
- Execute Targeted Research
- Continual feedback loop
## Approach: Develop SMART Research Plans

Focused on addressing risk/challenges with defined objectives and milestones.

<table>
<thead>
<tr>
<th>Task</th>
<th>Risk / Opportunity</th>
<th>Objective</th>
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<tbody>
<tr>
<td>Biocrude Upgrading</td>
<td>Jet fuel applicability</td>
<td>Achieve alpha and beta testing of SAF product</td>
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<tr>
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<td>Stable process</td>
<td>&gt;2000 hours of stable hydrotreating performance with on-spec fuel.</td>
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<tr>
<td>Feedstock R&amp;D</td>
<td>Impact of solids content</td>
<td>Improve HTL yield &gt;2% by increasing HTL solids content (20 to 25wt%).</td>
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<td>Regional impacts</td>
<td>Test regional feedstock HTL blend to increase the design HTL plant size 9X.</td>
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<tr>
<td>Nutrient Recovery</td>
<td>Phosphorous recovery</td>
<td>Demonstrate extraction of 75% of phosphorous from residual solids.</td>
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<tr>
<td>Tracking Forever Chemicals</td>
<td>Effective treatment</td>
<td>Verify at least 50% cumulative destruction of five PFAS compounds.</td>
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<tr>
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<td>Impact of entire process</td>
<td>Track PFAS destruction through HTL, hydroprocessing, mild oxidation, and struvite extraction.</td>
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<tr>
<td>Aqueous Treatment</td>
<td>Real-world application</td>
<td>Assess aqueous product by waste recovery resource facility (WRRF) to ensure recyclability.</td>
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<td>Effective treatment</td>
<td>Demonstrate &gt;50% carbon and COD reduction.</td>
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<td>Cost-effective</td>
<td>Demonstrate a cost-advantaged mild oxidation process (vs CHG).</td>
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<td>Process stability</td>
<td>&gt;2000 hours continuous operation while meeting partner WRRF specifications.</td>
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<td>Diversity, Inclusion</td>
<td>Effective team</td>
<td>All task leads complete Diversity, Inclusion, and Belonging training.</td>
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<td>Impact students</td>
<td>Hire at least one student from an underrepresented group in STEM</td>
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<td>Impact next generation</td>
<td>Reach one classroom/year through outreach.</td>
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FY21, FY22

- Biocrude Upgrading
- Feedstock R&D
- Nutrient Recovery
- Tracking Forever Chemicals
- Aqueous Treatment
- Diversity, Inclusion

FY23+

- Biocrude Upgrading: On track
- Feedstock R&D: On track
- Nutrient Recovery: On track
- Tracking Forever Chemicals: On track
- Aqueous Treatment: On track
- Diversity, Inclusion: On track

Demonstrate a cost-advantaged mild oxidation process (vs CHG).
1 – Approach: **Execute Targeted Research Aligned to Commercial Embodiment**

Critical success metrics:
- Cost-effective HTL aqueous stream disposal.
- Quantitate *destruction* of forever chemicals.
- Effective *residual solids* treatment for disposal.

Addressing FY21 peer review feedback:  
*Don’t trade one waste problem for another, more challenging one.*
Objectives:
- Assess using regional wet-waste blends to support 9x increase in HTL plant size (2021 milestone).
- Assess impact of increasing feedstock solids content up to 25%.

Key outcomes:
1. Resource-informed, real-world regional blends have high yields and outstanding quality.¹,²
2. Increasing solids content from 15 to 25 wt% increased biocrude yield (46% vs 44%).¹
3. Funded competitive project with Great Lakes Water Authority assessing HTL for their site.

2 – Progress and Outcomes:

**Demonstrate Stable, Scalable Hydrotreating**

Assessed extended time-on-stream hydrotreating of biocrudes from mixed fuels.

**Key outcome:**
- Stable continuous hydrotreating: 1500+ hours
  - World record!
  - Industrially relevant catalyst lifetimes.
2 – Progress and Outcomes: HTL of Wet Wastes Produces a High-Quality SAF

- ~25% of upgraded fuel in jet range.
- Similar mix of cycloalkanes, n-alkanes, iso-alkanes, aromatics to traditional jet.
- Positive Tier α and β jet fuel properties.¹
- Main concern is nitrogen in the jet fuel.

Objective: Develop process to extract valuable fertilizer co-products from HTL side stream.
- Concentrated, phosphorus-containing fertilizer.
- Reduction in NH$_3$N content in HTL aqueous.

Purified phosphorous product

Early progress:
- >75% extraction of phosphorus from HTL solids as an impure struvite.
- Removal of ~50% NH$_3$N from HTL aqueous.
2 – Progress and Outcomes: Tracking Destruction of Forever Chemicals – New Task in FY23

**Background:** PFAS pollution is an environmental concern.
- U.S. Environmental Protection Agency (EPA) Guidance (2016): “Established the health advisory levels at 70 parts per trillion.”
- EPA (2022): “Propose to designate two PFAS as hazardous substances under CERCLA, or Superfund.”

**Objectives:** Study the impact of HTL processing on forever chemicals.
- Track PFAS/perfluorooctane sulfonic acid (PFOS) from the feedstock via all processes: HTL, aqueous oxidation, struvite recovery, and hydrotreating.

**Early Progress:**
- Demonstrated high level of PFAS/PFOS destruction in HTL.
- Identified major PFAS/PFOS compounds of concern in HTL aqueous stream.
- Demonstrated >10,000x reduction in PFAS/PFOS chemicals through hydrotreating (3 spiked samples)
2 – Progress and Outcomes: **Mild Oxidation to Enable Recycle of HTL Aqueous to a WRRF**

**Motivation:** HTL aqueous phase is full of recalcitrant compounds, limiting recycle to WRRFs.

**Approach:** Mild oxidation can clean up aqueous phase.
- Completed screening, semi-batch, and CSTR demonstration of technology.

**Key accomplishments:**
- Numerous catalysts (e.g., HTL solids) effective for mild oxidation.
- Oxidizes nitrogen organics to carboxylic acids (>2x increase in acids).
3 – Impact: **HTL solves two crucial challenges to society:**
Sustainable Aviation Fuel and Sewage Sludge Disposal

**Value #1: Low GHG fuels**
- Potential of 6 billion gal/year of fuel (U.S.).
- 78% reduction in GHG.

<table>
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<tr>
<th>Two potential revenue streams</th>
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<td>Example: 100 dry tons/day plant</td>
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| 3.1 M gal fuel/yr | $12.4M/yr. |

**Value #2: Sludge disposal**
- Sludge disposal represents ~50% of wastewater costs.
- Provides destruction of forever chemicals.
- Costs expected to continue to increase as land application becomes illegal.

HTL provides a disposal solution in addition to sustainable fuel production.

Offset sludge disposal costs¹: $7.3-14.6M /yr.

¹Basis of disposal costs: $200-400/dry ton or $40/wet ton @ 10-20 wt% solids, ²Assumed fuel value of $4/gal.
3 – Impact: HTL Addresses Environmental and Social Justice Issues Worldwide

Need processes to cost effectively destroy PFAS.

Maine passes first PFAS biosolids ban, taking stand against forever chemicals

BANGOR, Maine (UPI) -- Maine has become the first state to ban fertilizer using sewage sludge containing “forever chemicals”...

May 4, 2022

EPA Moves To Regulate Toxic PFAS Chemicals

PFAS chemicals have been linked to illnesses, including cancer, but there remain a lot of questions about how they affect people’s health and in...

May 4, 2022

States take on PFAS ‘forever chemicals’ with bans and lawsuits

Colorado, for example, passed a law this year covering many products, ... And California passed laws this year to ban PFAS in cosmetics and...

Nov 5, 2022

Latest impact of PFAS contamination: Rising sewer rates

This spring, Maine banned the reuse of sewage sludge as fertilizer ... And those costs are only expected to rise as disposal rules get more...

Jul 10, 2022

Fertilizer recovery can reduce foreign dependance.

Fertilizer prices just hit a record high sparking fears of global starvation and the worst food insecurity level since World War II

Russian fertilizers are everywhere - A global food supply crisis.

Mar 21, 2022

Fertilizer Prices Surge as Ukraine War Cuts Supply, Leaving ...

FORTUNE

Mar 24, 2022

‘A perfect storm for the whole food system right now’:
One of the world's largest fertilizer companies warns that every country—even those in Europe—is facing a food crisis

Mar 23, 2022

Putin is weaponising food, says boss of fertiliser giant Yara

Mar 22, 2022

High sludge disposal costs are born by local communities.

Metro Vancouver's new sewage treatment plant near YVR Airport to cost over $10 billion

July 23, 2023
## Summary: Targeted Research to Accelerate HTL Deployment to Convert Wet Wastes to Fuels

### Approach
- Close partnership with industry and technoeconomic analysis and resource assessment teams to (a) prioritize research and (b) provide industrially viable solutions.
- SMART milestones to ensure successful impact.

### Progress and Outcomes
- Assessed key levers impacting conversion costs (solids content, regional blends).
- Advanced hydroprocessing of biocrude to produce SAF:
  - >2000 hours of stable hydroprocessing
  - Excellent Tier $\alpha$ and $\beta$ properties of SAF fraction.
- Progress towards FY23 tasks and milestones:
  - Initial assessment of PFAS compounds in HTL aqueous and solids stream
  - >75% extraction of phosphorous
  - Development of mild oxidation process for HTL aqueous cleanup.

### Impact
- Produce SAF.
- Disposing of sludge (including PFAS removal) and extracting fertilizer.

### Future Outcomes
- Aqueous treatment: Use mild oxidation to enable recycle of aqueous stream.
- PFAS: Assess PFAS partitioning and destruction throughout HTL and upgrading.
- Nutrient recovery: Recover phosphorus and nitrogen as fertilizer while enabling land application.
Quad Chart Overview

Timeline
• Original project start date: Oct 1, 2019
• Project renewal start date: Oct 1, 2022
• Project end date: Sept 30, 2025

<table>
<thead>
<tr>
<th>FY 22</th>
<th>Total Award</th>
</tr>
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<tbody>
<tr>
<td>DOE Funding</td>
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<tr>
<td>10/1/2021-9/30/2022</td>
<td>$1,200,000 (10/1/2022-9/30/2025)</td>
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<td>$360,000</td>
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Project Cost Share* $0 $0

TRL at Project Start: 2
TRL at Project End: 4

Project Goal
Develop mild oxidation to enable recycle of the aqueous stream, develop a process for concentrated phosphorous extraction, and track forever chemical destruction through HTL.

End of Project Milestone
Develop an aqueous and solids treatment process (mild oxidation and struvite precipitation) that meets solids disposal requirements and aqueous recycle requirement at partner WRRFs.

Funding Mechanism
Lab Call

Project Partners
• Great Lakes Water Authority
• MetroVancouver
• Aloviam
• Circlia Nordic
Acknowledgements

• Beau Hoffman, Technology Manager, Bioenergy Technologies Office

Experimental Team:
• Mike Thorson
• Andy Schmidt
• Uriah Kilgore
• Todd Hart
• Sam Fox
• Miki Santosa
• Senthil Subramanian
• Igor Kutnyakov
• Matt Flake
• Mariefel Olarte
• Lisa Middleton Smith

Analysis Team:
• Yuan Jiang
• Shuyun Li
• Yunhua Zhu
• Aye Meyer
• Lesley Snowden-Swan

Waste Resource Team:
• Tim Seiple
• Andre Coleman
Addressed numerous barriers towards commercialization (subset here)

**Hydrothermal Liquefaction**

1. Demonstrated yield and capital cost improvements with increased solids content
2. Validated viability & ID’d advantage of regional wet waste processing
3. Significant SOT cost reductions
4. ID’d real world challenges with HTL of plastics
5. Scalable hydrotreating >20x scale-up
6. Excellent diesel engine test results
7. Stable hydrotreating >2000 hr

**Hydro-processing**

1. Excellent Tier \(\alpha\) and \(\beta\) SAF Properties
2. ID’d key challenges

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Responses to Previous Reviewers’ Comments

**Feedback:** The reviewers expressed interest in “Understand[ing] any issues with disposal of solids” … “and any recycle stream to the WRRF” & “Liability/utility of waste/byproduct streams will be important”

**Response:** We agree that the disposal or treatment strategy for full-scale integration within a WRRF is needed for the HTL aqueous and solids streams. PNNL is developing multiple promising commercially viable treatment solutions for the aqueous streams including catalytic hydrothermal gasification, anaerobic digestion, wet air oxidation, and other processes to clean up the stream. The ultimate goal is for all or part of the aqueous stream to be recycled to the headworks of WRRF. While the solids stream may meet landfill or land applications specifications, we believe there is an opportunity to improve the overall process yield by extracting residual oil from the solids stream.

**Feedback:** “It is not clear what the approach to actually extending the catalyst lifetime is”

**Response:** To extend the hydrotreater catalyst life, we used a guard bed to remove the Fe and other metals (hydrodemetallization) from the biocrude and thereby, reduce catalyst poisoning in the main hydrotreater due to metal deposition. We evaluated two guard-bed configurations, a slurry bubble column and a trickle-bed hydrotreater to reduce the metal content <10ppm before the main hydrotreater. The use of a guard bed enabled us to achieve a modeled hydrotreater catalyst life of 1 year by doing long-term catalyst lifetime testing for over 2000 hours.
Publications, Patents, Presentations, Awards, and Commercialization (since FY21 Review)

Publications:

Patents:

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

Commercialization Efforts:
1. Metro Vancouver is building a demonstration HTL plant based on PNNL's technology
2. Aloviam is scaling up the HTL process via an awarded FOA
Objectives:
Advance mild oxidation to treat the HTL aqueous phase, and thereby enable sustainable recycling of this stream to the headworks of a water resource recovery facility (WRRF)

Motivation:
• HTL Aqueous phase if full of recalcitrant compounds limiting recycle to WRRFs
• Commercial process with multiple licensors with modular designs
• Widely used in refining, petrochemicals, and wastewater treatment

Milestones:
• FY23Q2 (6/2023): Reduce the residual solids volume >50%. Track the residual organic nitrogen with 90% mass balance. Partner with WRRF to assess the recyclability of this stream at their WRRF.
• FY23Q4 (9/2025): Develop a process for aqueous and solids treatment via wet air oxidation (>2000 hr of continuous operation) with sufficient treatment to meet solids disposal requirements and aqueous recycle at a WRRF
2 – Progress and Outcomes
Task 5 – Aqueous Treatment

Key accomplishments:
• Identified numerous catalysts effective for mild oxidation of the HTL aqueous stream
  • Residual solids from HTL proves to be a particularly effective catalyst
  • Demonstrated the ability to oxidizes the nitrogen organics to carboxylic acids (>2x increase in acids)

Next Steps:
• Transfer batch process to a continuous process (CSTR) to understand deactivation
• Determine the optimal temperature (⩽300°C), pressure, residence time, HTL residual solids addition (and recycle ratio) and heat integration
• Develop utilization strategy for carboxylic acids
• Determine the solids dewatering strategy following oxidation
• Develop strategy for heat integration in HTL
Thank you