Challenges and Opportunities for Hydrothermal Liquefaction of Macroalgae

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Richland, WA

ARPA-E Workshop, November 18, 2020
PNNL-SA-158056
What is HTL and why do we care?

Hydrothermal liquefaction (HTL) is…

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

It stands out among thermal conversion processes because…

• HTL is a conceptually simple (i.e., heated pipe), scalable, and robust continuous process that can accept a diverse range of wet feedstocks (no drying!)

• HTL results in high carbon yields to liquid hydrocarbons (up to 60%)

• HTL produces a gravity-separable biocrude with low oxygen content (5–15 %) that can be upgraded in a single stage hydrotreater

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

Hydrotreating Conditions
Temp: 400°C
Pressure: 1500 psig \( \text{H}_2 \)
Sulfided Catalyst

Wet biomass material (algae, sludge, manure) → Stable biocrude oil (up to 60% C-yield) → Fuel Blendstocks (95%+ C-yield)
HTL Process Development Timeline Spans Decades and Includes Wood, Algae, and Wet Waste

1970s Process Development
• Batch and Model Compounds

1980s Pilot Demonstrations for Woody Feedstocks
• Albany
• Shell HTU
• PERC, LBL

2008-2010 Renewed Process Development
• Continuous-Flow Process
• No Reducing Agent
• Agricultural Residues

2014-Present Process Scale-up
• Genifuel
• PNNL
• bio2oil
• Steeper
• Licella

US DOE Consortia
• 2011-2014 NABC for wood
• 2010-2013 NAABB for microalgae

2015-Present Expanded Range of Feedstocks
Wet wastes such as sludge, manure, food waste
We have successfully scaled the process from bench to engineering scale (~5x)

Bench-scale continuous HTL reactor system, slurry flow 2 to 6 L/h

Modular HTL system, slurry flow 12 to 16 L/h
Integrated cross-flow heat exchange
Continuous pressure letdown and separations
HTL of kelp led to lower biocrude yields but showed promise for nutrient recovery (N,P,K)

- Continuous HTL tests of 6 samples of Saccharina spp. collected by PNNL dive team
- Low starting solids concentration (5-10%) and high ash content (20-40%) led to low biocrude mass yields (<20%, daf)
- Thermal pretreatment at 175 °C allowed dewatering to 22% solids with a resulting biocrude mass yield of 27% (daf)
- Aqueous phase was treated with CHG
- Phosphorus precipitated in reactor solids and presumed to be recoverable (bio-available)
- Nitrogen split between products, but recoverable as ammonia from aqueous fractions; potassium remained in solution

Catalytic hydrothermal gasification (CHG) can treat the aqueous phase and recover energy and nutrients.

- Original integrated process included CHG for the HTL aqueous phase to recover fuel gas (CH$_4$/CO$_2$) and ammonia.
- CHG was determined to be cost-prohibitive for microalgae due to sulfur poisoning of the catalyst.
  - Sulfur-tolerant CHG catalysts are under development.
  - High Nitrogen?
Nutrient Recovery from Hydrothermal Processing

• **Nitrogen** primarily reduced to ammonium and partitions to the aqueous waste

• **Phosphorus** and **iron** precipitate into the solid phase waste fraction

Edmundson et al.  
Algal Research 26 (2017) 415–421
Results of Water and Nutrient Recycle Testing

• All Nitrogen, Phosphorus, and Iron can be replaced with nutrients derived from the by-products of HTL processing

• DIRECT recycle of HTL aqueous phase for N eliminates need for treatment of HTL aqueous phase (and thus, CHG)

• Over 350 days of continuous cultivation water recycle for *Chlorella sorokiniana*

• Additional algal strains have been screened for tolerance to direct recycle of HTL derived nutrients

<table>
<thead>
<tr>
<th>Strain (Genus species)</th>
<th>Relative HTL Tolerance</th>
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<tbody>
<tr>
<td><em>Chlorella sorokiniana</em> DOE1412.HTL</td>
<td>113.0</td>
</tr>
<tr>
<td><em>Nannochloropsis oceanica</em> CCAP849/10</td>
<td>108.5</td>
</tr>
<tr>
<td><em>Tetraselmis</em> sp. (LANL isolate)</td>
<td>87.0</td>
</tr>
<tr>
<td><em>Stichococcus minor</em> CCMP819</td>
<td>41.6</td>
</tr>
<tr>
<td><em>Chlorella vulgaris</em> LRB-AZ1201</td>
<td>27.2</td>
</tr>
<tr>
<td><em>Nannochloris sp.</em> NREL39-A8</td>
<td>20.7</td>
</tr>
<tr>
<td><em>Acutodesmus obliquus</em> UTEX393</td>
<td>17.4</td>
</tr>
<tr>
<td><em>Choelastrella</em> sp. DOE0202</td>
<td>14.9</td>
</tr>
<tr>
<td><em>Scenedesmus</em> sp. NREL46B-D3</td>
<td>3.5</td>
</tr>
<tr>
<td><em>Monoraphidium minutum</em> 26B-AM</td>
<td>3.4</td>
</tr>
<tr>
<td><em>Tisochrysis lutea</em> CCMP1324</td>
<td>2.4</td>
</tr>
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Initial Strain Screening Using HTL Derived Nutrients
But won’t it corrode the reactor?

Materials of construction evaluation with ORNL

- In-situ: reactor parts, rings, coupons for hundreds of hours
- Ex-situ: coupons and U-bend pieces (stress) in liquid and vapor space
- Findings: little corrosion for 304L, 316L, and 321 stainless steels, no evidence of Cl-stress corrosion cracking

Rings of 304L, 310, 316L and 321 stainless steels and alloy 825

Glass system with reflux used for 50 and 75°C → Coupons located in immersed aqueous and in vapor phase

Rings installed in HTL CSTR Reactor

316-L U-bends on preheater removed from service
Technoeconomic analysis shows that 2025 and 2030 projected HTL conversion cost targets have already been met.

- Biomass conversion costs are based on PNNL research into HTL conversion, biocrude upgrading, and HTL aqueous testing.
- Demonstrating full nutrient recycling and avoiding water treatment by CHG (2016) led to deep net cost reductions.
- Where to go next?

- Out-year cost targets from the HTL Design Case published in 2014 have already been met.
- A new design case outlining strategies for additional cost reductions slated for FY20 publication.
Sequential HTL enhances biocrude yield from algae residuals and produces carbohydrate stream

- **Stage 1 Extraction**
  - Yields usable sugars for co-product production
  - Provides improved residual biomass for fuel conversion

- **Stage 2 Conversion**
  - Results in higher biocrude yields and quality from higher solids feed, lower ash and carbohydrates

- **Sequential HTL Processing Progress**
  - Technical feasibility proven
  - Update of the algae HTL design case (2020) is based on sequential HTL

**General Process Flow Diagram**

- **Stage 1 Feed**: Chlorella from ATP, 27 wt%
- **Stage 1 Feed, Diluted to 9.9 wt% solids**: Carbohydrate extract from Stage 1 (5.3 wt% solids)
- **Biocrude from Stage 2**: 19 wt% solids
- **Residuals Solids from Stage 1 Feed for Stage 2**: Carbohydrate extract from Stage 1
- **Carbohydrate Stream from Stage 1**: 10% Algae Slurry
- **Centrifuge**: 180 °C 30 min.
- **HTL Stage 1**: 25% Residual Solids Slurry
- **HTL Stage 2**: 350 °C 15 min
- **Gas (95% CO2)**
- **Separator**: Solids for Nutrient Recycle
- **Aqueous Recycle to Pond**
- **Biocrude from Stage 2**
Algae HTL 2020 design case features sequential HTL to meet programmatic cost targets

- Initial algae HTL based on single-stage high-temperature conversion.
- Further cost improvements for the single-stage HTL system are limited.
- PNNL proposed and tested two-stage sequential HTL to meet future cost targets.
Sequential HTL co-products help offset feedstock costs

<table>
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<tr>
<th>Processing Area Cost Contributions</th>
<th>2020 design case (SEQHTL-2025 projection)</th>
<th>Single-stage HTL (blended feed, 2025 projection)</th>
<th>2014 design case (algae only, single-stage HTL, 2025 projection)</th>
</tr>
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<tbody>
<tr>
<td>Feedstock</td>
<td>$4.57</td>
<td>$3.85</td>
<td>$3.87</td>
</tr>
<tr>
<td>Algae Drying (summer &amp; spring only)</td>
<td>$0.00</td>
<td>$0.00</td>
<td>$0.11</td>
</tr>
<tr>
<td>HTL Biocrude Production</td>
<td>$0.73</td>
<td>$0.55</td>
<td>$0.47</td>
</tr>
<tr>
<td>HTL Biocrude Upgrading to Finished Fuels</td>
<td>$0.21</td>
<td>$0.28</td>
<td>$0.23</td>
</tr>
<tr>
<td>HTL Aqueous Phase Treatment</td>
<td>$0.00</td>
<td>$0.00</td>
<td>$0.66</td>
</tr>
<tr>
<td>Bioprocessing of HTL Stage I extract</td>
<td>$3.10</td>
<td>$0.00</td>
<td>$0.00</td>
</tr>
<tr>
<td>Balance of Plant</td>
<td>$0.58</td>
<td>$0.38</td>
<td>$0.28</td>
</tr>
<tr>
<td>Co-product and Byproduct Credit</td>
<td>($5.58)</td>
<td>$0.00</td>
<td>$0.00</td>
</tr>
<tr>
<td>Nutrient Recycle Credits</td>
<td>($0.52)</td>
<td>($0.37)</td>
<td>($0.32)</td>
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<tr>
<td>Minimum Fuel Selling Price, $/GGE</td>
<td>$3.09</td>
<td>$4.70</td>
<td>$5.30</td>
</tr>
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Sequential HTL can be applied to macroalgae feedstocks

• Based on earlier work on kelp (Elliott et al. 2013), thermal pre-treatment improves dewatering and pumpability leading to higher yields

• Thus, algae HTL research in FY 2021 and beyond will focus on applying sequential HTL to macroalgae and turf scrubbers

• Optimization of fuel, starch and nutrient outputs informed by process modeling
Remaining barriers to commercialization

• Develop and demonstrate the following at pilot scale:
  ▪ Robust solutions for aqueous phase treatment
  ▪ Feedstock formatting and slurry pumping to high pressure; pressure let-down
  ▪ Efficient heat exchange to reduce capital and operating expenses
  ▪ Equipment for continuous separation of solid, oil, and aqueous phases
  ▪ Long-term corrosion and material compatibility testing

• Pilot-scale systems have been fully designed and are nearing procurement and construction

PNNL’s engineering scale HTL system
Acknowledgements

DOE Bioenergy Technologies Office (BETO)
• Dan Fishman, Technology Manager

PNNL Thermochemical Interface Team
• Dan Anderson, Project Manager
• Andy Schmidt
• Scott Edmundson
• Todd Hart
• Sam Fox
• Teresa Lemmon
• Heather Job
• Sue Jones
• Yunhua Zhu
• Rich Hallen

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