Development of HTL Global Commercialization Possibilities

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ETBC

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Brussels
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Presentation Outline

- Process overview
- HTL development by Genifuel/PNNL
  - Range of feedstocks
  - Project specifics
- Commercialization and future work

Box Flow for Algae Application at PNNL
Hydrothermal Liquefaction in the U.S.

Albany, Oregon 1977-1982

Slow pyrolysis in pH-moderated, pressurized water

1 t/d Douglas fir wood
Since 2008, Use With Wet Biomass

Wastewater Solids
Food and Drink Processing
Animal Waste

And many others, including corn stover and co-processing with lignocellulosics

Algae
Technology Status

- Process clearly works and scales well
  - Hundreds of tests on dozens of feedstocks
  - Extensively published in journals and DOE publications
- Quality of raw and upgraded HTL biocrude fully documented
- Catalytic Hydrothermal Gasification process works and provides the aqueous “cleanup” step
  - Catalyst life needs further improvement
- The remaining step to full commercialization is to show industrial reliability in 24/7 operation at operating sites

Project 1: Original Genifuel Scale-Up Processing Algae Since 2017 at RIL

Project 2: Containerized System, 2019

Onsite tests with various wastes—e.g. dairy cow manure

Project 3: 2020 Startup

Wastewater processing
Vancouver, BC Canada
2 dry tonnes per day

MetroVancouver refining partner is Parkland Fuel

Project 4: 2021 Startup

Central Contra Costa Sanitary District, Martinez, CA
3 dry tonnes per day

## Regulatory Status Proceeding Well

<table>
<thead>
<tr>
<th>Regulation</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEQA</td>
<td>California Environmental Quality Act will use existing permit</td>
</tr>
<tr>
<td>Air Quality</td>
<td>Information provided and preliminary meeting scheduled</td>
</tr>
<tr>
<td>Water Quality</td>
<td>Testing shows no adverse environmental effects, but UV issues</td>
</tr>
<tr>
<td>Site</td>
<td>Soil samples taken; no current issues</td>
</tr>
<tr>
<td>Blowdown Solids</td>
<td>Take to fertilizer manufacturer</td>
</tr>
<tr>
<td>Fuel Credits</td>
<td>Eligible for D3 RINS and LCFS—Carbon Index 23</td>
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Raw and Hydrotreated HTL Biocrude

Raw
HTL Biocrude

Upgraded
HTL Biocrude
High Quality Upgraded Biocrude from Wastewater Solids

<table>
<thead>
<tr>
<th></th>
<th>Unit</th>
<th>Upgraded Product</th>
<th>Biocrude</th>
</tr>
</thead>
<tbody>
<tr>
<td>H:C Ratio</td>
<td>Mol ratio</td>
<td>2.03</td>
<td>1.6</td>
</tr>
<tr>
<td>O</td>
<td>Wt%</td>
<td>1.0%</td>
<td>6.2%</td>
</tr>
<tr>
<td>N</td>
<td>Wt%</td>
<td>&lt;0.05%</td>
<td>4.7%</td>
</tr>
<tr>
<td>S</td>
<td>ppm</td>
<td>9</td>
<td>11,000</td>
</tr>
<tr>
<td>TAN</td>
<td>mgKOH/g</td>
<td>&lt;0.01</td>
<td>59</td>
</tr>
<tr>
<td>Density</td>
<td>g/cm³</td>
<td>0.79</td>
<td>0.98</td>
</tr>
<tr>
<td>Viscosity</td>
<td>cSt @ 40°C</td>
<td>2.7</td>
<td>400</td>
</tr>
</tbody>
</table>

J. Billing et al. ACS NORM 2018, Richland, WA June 26, 2018; PNNL-SA-136090
Engineering Scale HTL Skid at PNNL

System Features

- Modular/relocatable
- Feed prep for all feedstocks
- HTL modes - PFR or CSTR/PFR hybrid
- Heat recovery
- Capacity 12-18 L/hour feed
- Ash solid separations
- Flexible product separations unit ops

Scaled-up Catalytic Hydrotreater at PNNL

- 9-zone fixed-bed catalytic hydrotreater (19 L)

- Atmospheric distilling column for fuel fraction collection
Recent and Future Work at PNNL

- Algal biomass: all types
- Wet waste: grape pomace, sugar beet tailings, waste-water treatment sludge mixtures
- Operation of the 12 L/h engineering scale reactor system
- Enhanced recovery of organics from aqueous phase – TEA indicates that process economics are most sensitive to this variable
- Longer-term demonstrations of HT catalyst activity and stability (>200 hr)
- Optimize fuel finishing to meet refinery insertion points
HTL Addresses PFAS, PPCP

- HTL substantially destroys PFAS (per/poly-fluorinated alkyl substances)
- HTL substantially destroys PPCP (pharmaceutical and personal care products)
- Final certification awaits publication of standards and testing methods
- Siloxane destruction was earlier verified in WERF-sponsored study
Recent Fundamental Research

- **Zhoukou Normal University China**
  - Catalysts, cosolvents, batch, rice straw
  - CuO + NaOH, batch, corn stover

- **China Agricultural University**
  - Spirulina biocrude aging – oxidation shell

- **Savage’s group Pennsylvania State University**
  - Review of feedstock effects on biocrude composition
    * Also China Agricultural University
Summary Conclusions

- A range of wet biomass feedstocks can be converted to a gravity separable biocrude by continuous-flow hydrothermal liquefaction.
- Variations in composition of biocrude products result from differences in feedstock composition.
- Biocrude products can be directly processed in single-stage, fixed bed catalytic hydrotreatment to liquid fuel-range hydrocarbons.
Acknowledgements

- Genifuel is a process licensee of PNNL and leads the commercialization efforts
- Staff in the Chemical and Biological Process Development Group at PNNL continue with bench-scale process development and demonstration
- U.S. Department of Energy funding from the Bioenergy Technologies Office funds the PNNL work