Sustainable Aviation Fuel (SAF) from liquefaction

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Special thanks to Karthi Ramasamy, Beau Hoffman, Mike Thorson, Justin Billing, Josh Heyne, Steve Csonka
In November 2020, PNNL facilitated an international workshop on HTL for SAF production

Present an overview of findings
• Quick overview of HTL
• Details from the workshop – research opportunities
• Examples of pilot and demonstrations
• Conclusions

Take home message
• HTL has high promise
• Roughly 20% of fuel in SAF range
• Four areas of “research opportunities”
We thank those who organized and participated in the workshop.
Quick overview of HTL
Hydrothermal liquefaction is a means to convert wet carbon streams to biocrude oil

- Heat and pressure (300-350 °C, 16-22 MPa, 10-20 min)
- Produces a biocrude oil, thermally stable
- Biocrude can be upgraded to fuels, rich in diesel
- Need to optimize value from other HTL streams (aqueous, solids, gasses)
HTL expands feedstock from classical biomass to low-cost carbon-waste streams

- Municipal wastewater sludge, food waste, manures
- Classical biomass can be added as a mixture (or as the primary feed)
- Feedstock changes the composition of the biocrude
The biocrude can be upgraded to produce transportation fuels

- Co-processing in petroleum refineries, risk
- Hydrotreating, the biocrude removes O and N
- Fractionated into gasoline, diesel, and jet fuel
Valuing the economic services of treating carbon waste needs to be fully understood

- Social justice
- Pollution avoidance
- Economic services of cleaning up carbon sources
Hydrothermal liquefaction provides a means to convert wet carbon-rich waste into biocrude oil.
Details from the workshop
The carbon yield to fuels is among the highest in bioprocessing

**Typical**
- 58% to biocrude
- Biocrude is stable
- Rich in diesel hydrocarbons

*This analysis based on carbon basis*
Accessible municipal sludge, manure, food waste, and FOG could provide ~ 6 B gallons of biocrude (CONUS*).

- Greater than 70% of waste can be aggregated (50 mi radius) with a capacity of 1000 dry tons/day (TPD)
- Promising economic performance down to 5 TPD
- 76 MMT/y dry waste at 56,000 sites
- 5.6 Bgal/y biocrude potential

*CONUS – Continental United States
The wet resources are widely dispersed, with municipal sludge centered in urban areas.

Site-specific inventory of untreated sludge production at >15,000 municipal wastewater treatment plants (WWTPs) in the US.
Manures are dispersed in rural areas

Feedlot beef manure

Beef Manure (x000 T/y dry solids)
- < 5
- 5 - 15
- 15 - 30
- 30 - 95

States
- No Spatial Data
- Priority State

Market swine manure

Swine Manure (x000 T/y dry solids)
- < 5
- 5 - 15
- 15 - 30
- 30 - 100

States
- No Spatial Data
- Priority State

Dairy manure

Dairy Manure (x000 T/y dry solids)
- < 5
- 5 - 15
- 15 - 30
- 30 - 65

States
- No Spatial Data
- Priority State

Site-specific inventory of confined manure production at >32,000 feedlot beef, dairy, and market swine operations
Within a 50-mile radius, wet carbon waste can be blended for treatment

Urban wet waste composition:
- 40% food / 50% sludge / 10% FOG

Rural wet waste composition:
- 50% Manure / 20% food / 25% sludge / 5% FOG

Points
- Sludge makes a higher quality fuel than wood
- Sludge improves the processibility of wood
- Wood and stover increase the total fuel production potential
Europe has similar resource assessments

**HTL feedstock potentials, wastes and residues in EU**

- **Spatial analysis of residue and waste availability in Europe**
- **Feedstock density maps available for:**
  - Animal excretions (cattle, pigs, poultry), agricultural by-products (straws, sugar beet leaves, corn stover), sewage sludge, biowastes
- **Conversion to biofuels potentials (yield model)**
- **Theoretical fuel production potentials**
  - Agricultural by-products: 26-29 Mt
  - Animal excretions: 10-26 Mt
  - Sewage sludge: 3 Mt
  - Biowastes: 1.5 Mt

Potentials refer to mixture of liquid hydrocarbons!
Biocrude and jet fuel from wet waste

Typical

• 58% to biocrude
• Biocrude is stable
• Rich in diesel hydrocarbons

*This analysis based on carbon basis
Feedstock has an impact on the biocrude in terms of hydrocarbon type, N content, and aromatic content.

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Impact</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fats</td>
<td>Increased long n-alkane (cetane)</td>
<td><img src="image1" alt="Fats structure" /></td>
</tr>
<tr>
<td>Lignin</td>
<td>Increased aromatic content</td>
<td><img src="image2" alt="Lignin structure" /></td>
</tr>
<tr>
<td>Protein</td>
<td>Increased N content, does form oil</td>
<td><img src="image3" alt="Protein structure" /></td>
</tr>
<tr>
<td>Cellulose</td>
<td>Increased C to aqueous phase, does form oil (Maillard reaction with protein)</td>
<td><img src="image4" alt="Cellulose structure" /></td>
</tr>
</tbody>
</table>
Biocrude has higher O and N content and higher acidity than petroleum crude oil

<table>
<thead>
<tr>
<th></th>
<th>O%</th>
<th>N%</th>
<th>S%</th>
<th>TAN*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petroleum*</td>
<td>0.5</td>
<td>0.1-2</td>
<td>0.05 - 6</td>
<td>0.2 - 5</td>
</tr>
<tr>
<td>Biocrude</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sludge</td>
<td>8</td>
<td>4</td>
<td>1</td>
<td>65</td>
</tr>
<tr>
<td>Chlorella</td>
<td>4</td>
<td>6</td>
<td>1</td>
<td>53</td>
</tr>
<tr>
<td>Pine</td>
<td>10</td>
<td>0</td>
<td>0.01</td>
<td>53</td>
</tr>
</tbody>
</table>

* The heteroatom content into unit operations (after atmospheric distillation) is much lower

- N content is an issue if cracking is needed (cracking catalysts have acidic sites)
- The heteroatom content is outside of what refiners are comfortable, so they dilute

Organic N is in two forms

Amides (easily hydrogenated)

Cyclic amines (more difficult to hydrogenate)

*TAN = Total acid number
Today two alternative feedstocks have ASTM D1655 approval for co-refining, yet little product is jet fuel

Co-refining
• Interesting to refiners
• Two feedstocks are approved at 5% renewable blend
  ▪ Vegetable oils
  ▪ Fischer-Tropsch liquids
• Little product from co-refining goes into the jet fraction
Upgrading biocrude from wet waste yields 20% in the jet range, more could be produced if heavies were cracked

Biocrude upgrading challenges
- Poisoning of catalyst (alkali, Fe…)
- Increasing jet fraction (cracking)
- Improving low temperature properties, diesel (isomerization)
- Processing of heavier oil (>350 °C)

Biocrude upgrading achievement
- Achieved 2000 h on untreated biocrude
- Biocrude from municipal sludge, food waste

Jet fuel properties met
- Viscosity (-40°C, -20°C)
- Density (15°C and 22°C)
- Flash point
- Heat of combustion (HOC)
- DCN

Properties to monitor
- Freeze-point (high n-alkane content)
- Stability (trace N content)
Initial testing of HTL SAF from wet sludge is promising

- Composed of well distributed carbon numbers and a range of hydrocarbon types
- Likely to provide adequate blend properties for Jet A
- Initial swell testing with fluorosilicone o-ring material suggests acceptable swelling behavior of neat HTL products
- Impact of nitrogen content on thermal stability and other items need to be investigated
- Prescreening of HTL fuels with blends of wet waste and wood or other biomass sources is needed

Josh Heyne,
University of Dayton
Jet fuel fraction from sewage sludge/FOG is well distributed range of hydrocarbons

<table>
<thead>
<tr>
<th>Biocrude</th>
<th>Hydrotreating</th>
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<tr>
<td>Sewage Sludge mixed with FOG*</td>
<td>Sulfided NiMo (single stage, 400 °C)</td>
</tr>
<tr>
<td></td>
<td>Fractionated 160-240 °C</td>
</tr>
</tbody>
</table>

- Likely to provide adequate blend properties for Jet A
- Fuel thermal stability needs to be studied as N content, although low, is higher than Jet A
- N content in fuel 0.3-0.4% (recent)

*FOG = fats, oils and greases
Light hydrotreatment of the jet fraction shifts aromatics to cycloalkanes

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<th>Biocrude</th>
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<tbody>
<tr>
<td>Sewage Sludge + FOG</td>
<td>Sulfided NiMo (single stage)</td>
</tr>
<tr>
<td></td>
<td>Fractionated</td>
</tr>
<tr>
<td></td>
<td>160-240°C</td>
</tr>
</tbody>
</table>

- Operability properties are in range
- Initial swell testing with fluorosilicone o-ring material suggests acceptable swelling behavior of neat HTL products
- Hydrocarbon variance similar to Jet A

*FOG = fats, oils and greases
SAF samples from Aalborg (Europe) have similar properties to the U.S. samples

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<tbody>
<tr>
<td>Sewage sludge</td>
<td>sulfided NiMo catalysts (4 stages with different catalysts), ranging from 260-400 °C</td>
</tr>
<tr>
<td>Fractionated 160-240 °C</td>
<td></td>
</tr>
</tbody>
</table>

- Similar compositions to PNNL
- Aromatics and high cycloalkane content
- Relatively high n-alkane content
- Bulk properties look promising (Blend of the two GCxGC profiles used for property measurements)
Need to get value from each HTL fraction

Typical
• Gases concentrated in CO$_2$
• Aqueous phase carbon
• Solids
Research opportunities on the solid stream include P recycling and biocrude recovery

Issue
• Solids can either be removed at process temperatures/pressure or after the reactor
• Ash stream is rich in phosphorous and may contain trapped biocrude
• Phosphorus recovery is a concern for the wastewater community
  ▪ Land-applied biosolids can lead to nutrient run-off and ecological harm to surface waters

R&D opportunities
• Phosphorus recovery is an opportunity and benefit of HTL
• Opportunity to recover biocrude trapped on solids
Research opportunities on the aqueous phase can be to recover energy or produce H$_2$

Issue

• One third of carbon is in aqueous phase (O-rich, low molecular weight compounds such as carboxylic acids, alcohols, and carbonyls)

• But the compounds are dilute, collective concentration of 2-3%

• Water resource recovery facility (WRRF)
  ▪ interfere with UV sanitation,
  ▪ elevated nitrogen levels can push a wastewater treatment facility beyond their discharge limits
  ▪ or the components of the aqueous stream can interfere with the treatment facilities’ other treatment processes.
While one third of the carbon ends up in the aqueous phase, the species are dilute.

Carbon in the aqueous phase

- Acetic acid and other small alcohols, polyols, carbonyls, and phenols
- 2-3% collective concentration
There is not enough value to try to capture components

• C compound concentration is 2-3%
• Purification of individual chemicals is not cost effective (Sherwood plot)
R&D opportunities for the aqueous phase need to be low cost and reduce COD, N, and UV Vis absorbance

**Needs**

- low cost
- reduce the chemical oxygen demand (COD) and N content
- reduce the UV Vis absorbance

**Options**

- Separations
- Biological routes - clean up the stream and generate higher purity products - challenge, inhibitors
- Partial oxidation combined with biological or catalytic conversion
- Thermochemical routes (wet gasification or H₂ production) – challenge, catalyst life (S poisoning)
In conclusion, we have identified critical research opportunities for SAF to jet fuel.

- **Materials**
  - **Feedstocks**
    - Sewage sludge
    - Food waste
    - Manure
  - **Intermediates**
    - Biocrude
    - Aqueous
    - Gases
    - Solids
  - **Final Products**
    - SAF
    - Marine
    - Diesel

- **Research Areas**
  - Sourcing, Transporting, and Formatting

- **Major* R&D Gaps**
  - Feedstock availability
  - Feedstock quality
  - Feedstock blending
  - Reactor interface

- **Liquefaction**
  - Long-term operation
  - Heat integration
  - Scale/modularization
  - Higher liquid yields

- **Upgrading and Refining**
  - Demineralization
  - Denitrogenification
  - Catalyst life
  - ASTM specification

- **Sustainability**
  - Social
  - Environmental
  - Economic

- **Value Added**
  - Nutrient recovery
  - Water clean-up
  - Avoiding landfill
  - Eliminate pathogens

*Not full list of gaps
Examples of pilot and demonstrations
A partial overview of the players in the field include demonstrations and piloting.
MetroVancouver points out the need for water management, understanding opportunity cost

Objectives/questions:
• Can HTL perform better than AD?
• TEA considerations for full scale?

Science needs (Univ. British Columbia)
• Impact of HTL aqueous returned to i) headworks, ii) AD, iii) other?
• Required HTL aqueous pretreatment for i) NH$_4^+$, ii) phenols, iii) other?
• Required management of HTL precipitate
• Efficient phosphorus recovery or disposal?
• Fate of compounds of environmental concern (e.g. PFAS, other)?
Steeper Energy Norway (wood) and Calgary (sewage sludge) point to H₂ use and links to refining

Questions to be answered:

- Attributes and direct markets for Hydrofaction® Oil
- In situ renewable H₂ for upgrading
- Integration of bio-crude into refineries
- Chemical-linkers that improve compatibility of Hydrofaction® Oil with existing fuels
- Economic pathways to 100% renewable: gasoline, diesel, jet-fuel, marine fuels, and fine chemicals.

Perry Toms
Northern and Southern Oil Refineries (Australia), note capital and operating cost both need to come down

“It is not the return on my investment that I am concerned about; it's the return of my investment” - Will Rogers

- Completed detailed design of a 1t/h HTL process ($7M CAPEX)
- Financial model 16ML/annum, $28M CAPEX
- Feedstock tipping fee $160 – 285/dry tonne

David Lewis
Licella catalytic HTL (Australia, UK and N. America) noted the importance of collaboration

Current focus
- End-of-Life Plastics in the UK with Mura
- Post consumer biomass in North America with Arbios.

Importance of collaboration
- Access to large amounts of low-value feedstock without creating bidding wars
- Technology development companies and operational companies require different mindsets.
- Allows for synergies as each company can focus on their core competencies.
Reliance (India) point at the need to demonstrate robustness at scale to reduce risk

Next Steps

• Technology and Engineering robustness at scale

• Roadmap for Economical viability

• Investor confidence in building “First of it’s kind” precommercial plant

RE-CORD (Politecnico di Torino) notes the need for co-liquefaction as well as co-refining

Co-Liquefaction
• Enhanced feedstock availability

Water management
• Recycle, Cat HTG, AD, H₂ production

Co-refining
• Stabilization + HDO + co-refining

Biocrude sCO₂ fractionation
• extraction yields above 50%, low water and metal content, reduced acidity, moderate oxygen content reduction

David Chiaramonti
HyFlexFuel note, among other things the need for understanding feedstock supply chain and valorization

- Spatial analysis of residue and waste availability in Europe
- Feedstock density maps
- Energetic valorization of aqueous phase
- Nutrient recovery (phosphates)

HTL pilot reactor at Aarhus University

Valentin Batteiger
PNNL notes the importance of blends (urban and rural), as well as increasing catalyst life in upgrading

Address capital
• 50% of capital cost is in heat exchangers—big opportunity

Feedstock
• blends based on different regions

Co-refining
• refiners question using feed with the N-content of biocrude

Processing
• Improved HTL efficiency and hydrotreater catalyst life
• greatly improved catalyst life (untreated biocrude)

Current state on upgrading
• Major strides in biocrude upgrading
• Hydrothermal gasification remains a challenge
As the next step, we are preparing a roadmap identifying key research opportunities and needs.

* Not full list of gaps
Key Results of HTL for Sustainable Aviation Fuels Workshop

• Need to analyze feedstock pre-processing cost to produce uniform quality bio-crude from mixed feedstocks. Feedstock consistency (temporal, seasonal) needs to be analyzed.

• Small decentralized plants could produce bio-crude moved via rail, pipeline, or trucks to processing plant for upgrading and hydro-treatment to finished fuels.

• Aqueous product management, ash removal, and solids removal are key issues. Ability to recover chemicals and dissolved metals from aqueous phase could add to financial viability of project.

• Nitrogen in jet fuel is a key issue. Sewage sludge and waste-water treatment effluent might have high N levels. Interaction between nitrogen and sulfur needs to be better understood.

• Hydrogen requirement for HTL processes needs to be analyzed. Variability of cost and greenhouse gas emissions depends on source of hydrogen.

• Industry needs to produce bio-crude with required specifications on a reliable basis in order to facilitate ASTM approval.

• ASTM Marine diesel could be produced with minimal upgrading of HTL bio-crude. Integration of bio-jet, renewable diesel, and naptha/gasoline in single facility need to be explored.
Questions
We thank those who organized and participated in the workshop.
Thank you