



Development of HTL Global Commercialization Possibilities

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ETBC

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.



Slow pyrolysis in pH-moderated, pressurized water



Since 2008, Use With Wet Biomass



Wastewater Solids



Food and Drink Processing



Animal Waste



Algae

And many others, including corn stover and coprocessing with lignocellulosics

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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

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



Raw and Hydrotreated HTL Biocrude



Raw HTL Biocrude



Upgraded HTL Biocrude



High Quality Upgraded Biocrude from Wastewater Solids

	Unit	Upgraded Product	Biocrude
H:C Ratio	Mol ratio	2.03	1.6
0	Wt%	1.0%	6.2%
Ν	Wt%	<0.05%	4.7%
S	ppm	9	11,000
TAN	mgKOH/g	<0.01	59
Density	g/cm ³	0.79	0.98
Viscosity	cSt @ 40°C	2.7	400

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



A.J. Schmidt, tcbiomass2017, Chicago, IL, September 21, 2017, PNNL-SA-129182



Scaled-up Catalytic Hydrotreater at PNNL

- 9-zone fixedbed 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 WERFsponsored study



Analysis of Perfluorinated, Pharmaceutical, Personal Care Compounds and Heavy Metals in Waste Water Sludge using GC-MS/MS and Multicollector ICP-MS

November 2018

AV Mitroshkov, L Zhong, M-L Thomas



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Recent Fundamental Research

Zhoukou Normal University China

• Catalysts, cosolvents, batch, rice straw Y-J Ding et al. Bioresource Technol. 294 (2019) 122097

 \circ CuO + NaOH, batch, corn stover

Y-X Chen et al. Bioresource Technol. 294 (2019) 122148

• China Agricultural University

• Spirulina biocrude aging – oxidation shell Y-X Wang et al. Energy & Fuels, 33 (2019) 9870-9878

• Savage's group Pennsylvania State University

• Review of feedsock effects on biocrude composition

J-W Lu* et al. Indus. & Eng. Chem. Res. 58 (2019) 13971-13976

* 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



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