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DOE Bioenergy Technologies Office (BETO) 2015 Project Peer Review

Hydrothermal Processing of Biomass

March 26, 2015

Thermochemical Conversion

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Pacific Northwest National Laboratory

Goal Statement

- Advance HTL technology towards 2020 goal of $3/gge at 50% reduced GHG.
  - Improve overall process performance and economics
  - Determine the value and best pathway to market for the product
  - Demonstrate high process and carbon efficiencies for HTL with broad range of feedstocks and assess value of bio-crude for fuels and chemicals

  (By 2020, select another thermochemical pathway for integrated operations to validate the 2022 Office performance goal of $3/GGE by evaluating R&D data from bench-scale, semi-integrated thermochemical pathways that produce gasoline and diesel blendstock fuels.)

- Enable hydrothermal processing of biomass to provide sustainable production of hydrocarbon products for biofuels and bioproducts that reduce greenhouse gas emissions relative to petroleum-derived fuels, and displace petroleum-derived products to reduce U.S. dependence on foreign oil
  - Provide critical data needs for HTL for a wide range of biomass and waste feedstocks to support the creation of new domestic bioenergy and bioproduct industry
  - Provide feedstock agnostic pathway important to meeting the energy and sustainability challenges facing the nation

Quad Chart Overview

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Timeline

- November 2012 HTL detailed characterization funded
- June 2012 HTL demonstrates >50% carbon efficiency NABC
- October 2013 Improved and CAT HTL development funded
- September 2014 Merit reviews completed
- Combined Improved HTL and Hydrothermal Processing of Wet Waste for FY 15 - 17
- 15% complete

Budget

	FY 13 Costs	FY 14 Costs	Total Planned Funding (FY 15-Project End Date
DOE Funded	$88K*	$642K	FY15=$1.35M FY16-17=$3M

*HTL product characterization only.

Barriers Addressed

- Tt-F. Deconstruction of Biomass to Form Bio-Oil Intermediates
- Tt-J. Catalytic Upgrading of Bio-Oil Intermediates to Fuels and Chemicals
- Tt-C. Relationship between Feedstock Physical and Chemical Properties and Conversion Processes

Partners

- NMSU, biocrude characterization
- CSU, fuel evaluation
- WERF, waste feedstocks
- Food processors, waste feedstocks
- Genifuel, commercialization
- Other interactions/collaborations
- INL - Feedstock
- ORNL – Materials of Construction
- NREL – 4.1.3.30 Adv Biofuels and Bioprod Modeling
- Pall – Separations
- PNNL – 2.3.1.310 Charac. & Valor. of Aq. Phases
- PNNL – 1.3.4.101 Whole Algae HTL Model Devel.

HTL Technology Overview

Recent Advances

- ✓ *No reducing gas*
- ✓ *Recycle of aqueous byproduct*
- ✓ *Confirmed 1-stage upgrading*
- ✓ *Achieved > 50% Carbon efficiency in HTL*
- ✓ *95%+ carbon efficient upgrading step*
- ✓ Published processing papers and TEAs
- ✓ Assessment of reactor alternatives
- ✓ *Competitive with other conversion pathways*
- ✓ *Feedstock agnostic operating conditions*

Hydrothermal Liquefaction (HTL)

- Conversion of a biomass slurry (e.g., wood, algae, wet waste to biocrude and and aqueous product
  - ~ 350°C
  - ~ 3000 psig
  - 5 to 30 min

HTL

Slurry Feedstock

Biocrude Product

+

Aqueous Product (contains organics)

Biocrude product upgraded via Catalytic Hydrotreatment and fractionated by Distillation to gasoline, diesel, jet fuel and resid

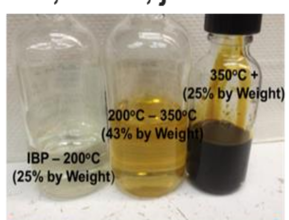
Catalytic Hydrotreatment

Catalytic Hydrothermal Gasification (CHG)

Hydrotreated Biocrude

Clean Aqueous Product

Distillation

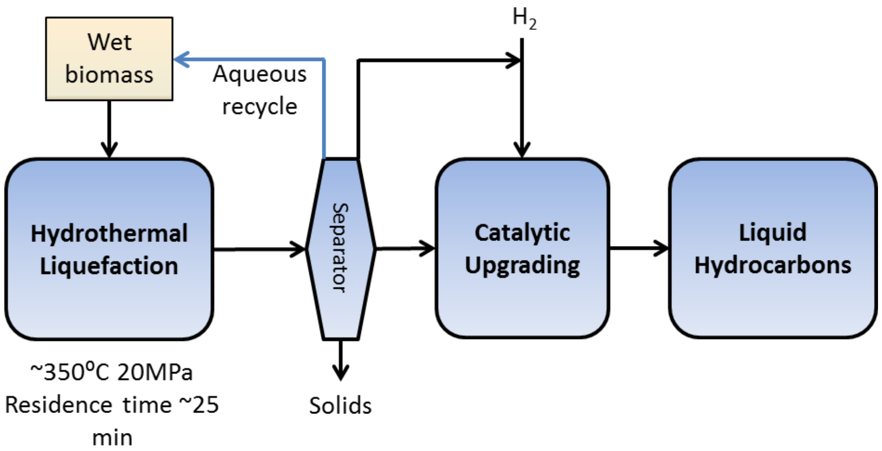


Fuel Fractions

Catalytic Hydrothermal Gasification (CHG) can convert aqueous byproduct to medium BTU gas and clean water

Overview - Why Invest in HTL?

- High carbon efficiency to product; greater than 50% to HC product
- Robust and can be applied to wide range of feedstocks at similar identical processing conditions
- Conceptually simple (feed preparation, pump, heated pipe, gravity separable biocrude)



- HTL biocrude is thermally stable and can be readily upgraded
- Economics compare favorably with other biomass conversion technologies in head to head comparisons (NABC)
- Wet feedstocks (ag resids, sludges, algae) exploit HTL attributes and minimize deployment challenges associated with pumping
- HTL has not been commercially deployed. Impediments to overcome include pumping to high pressures, scalable reactor configurations, and high capital cost estimates

2 – Approach (Technical)

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Advancement of Lignocellullosics HTL: → move technology towards 2020 goal of $3/GGE at 50% reduced GHG.

- Testing with continuous flow reactor designs → Scalable reactor designs and higher volumetric efficiencies reduce $/GGE and commercial barriers
- Feedstock testing → HTL is feed agnostic, but specific yields of diverse feeds must be determined to unravel chemistry and assess economics.
- Detailed characterization of biocrudes → understand impacts of feedstock and process conditions on quality
- Characterize upgraded product for evaluation as blendstock and/or for refinery insertion

Technical Feasibility & Process Economics of HTL of Wet Waste

- Resource inventory and characteristics (agriculture residuals, WWT sludges etc.)
- Working with industrial partners (regional, WERF and licensee)
- HTL biocrude yields and CHG of aqueous byproduct
- Yield and quality of upgraded product

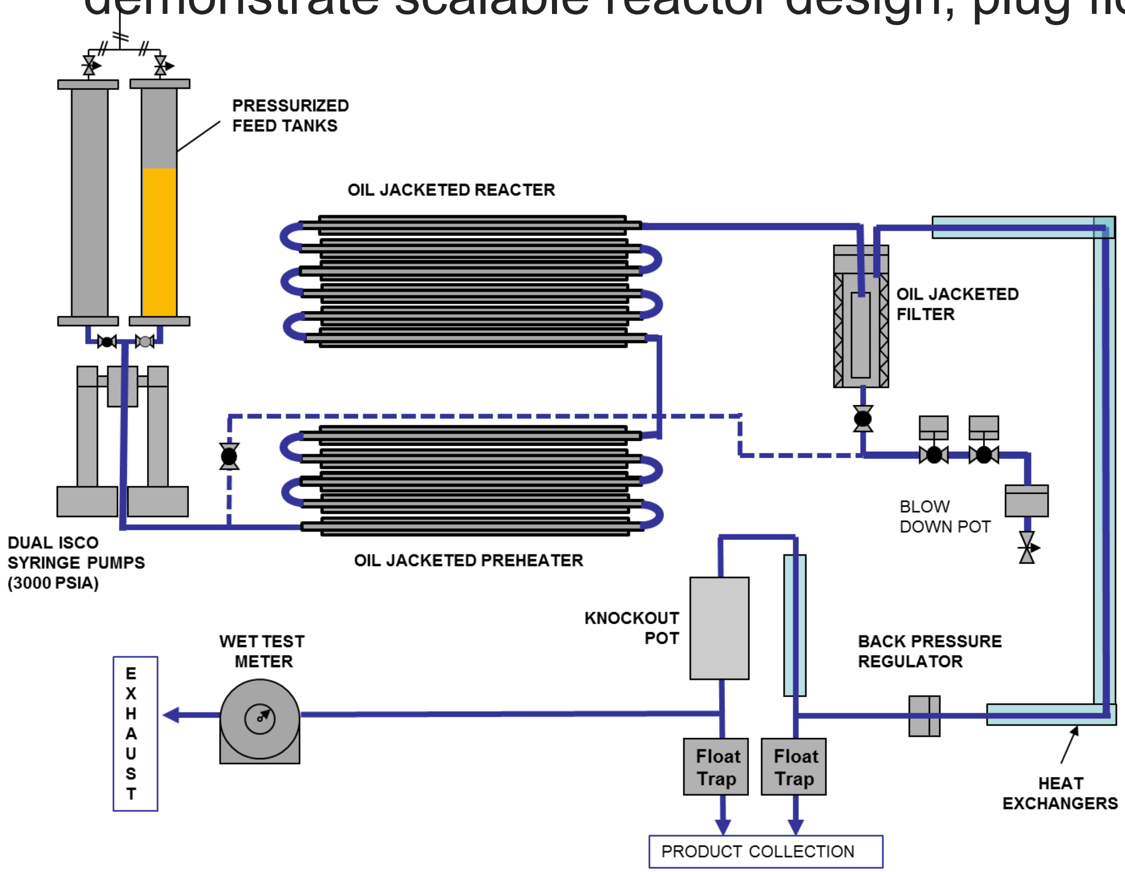
2 – Approach (Management)

- Management Approach – Approved Project Management Plan
- Incorporate strategic partners—Genifuel, WERF, University analysts
- AOP with scheduled regular Milestones and Deliverables
- Go/No Go in Q2 FY16 for assessment of CAT HTL pathway via updated TEA

Quarter	Due Date	Status	Narrative
Q1	**12/31/14**	**Complete**	**Produce >1L of HTL biocrude from forest residual to demo continuous catalytic HTL and feedstock for upgrading.**
Q2	**3/31/15**	**Complete**	**Acquire wet waste feedstock from 3 industrial partners and complete bench-scale HTL tests for product analysis.**
Q3	**6/30/15**	**Complete**	**Upgrade >1L of HTL biocrude to assess yields and generate samples for characterization and fuel property testing.**
Q4	**9/30/15**	**On Schedule**	**Demonstrate by TEA, viable business case (including potential volumetric impact) for wet waste HTL/CHG of $3/GGE.**

3 – Technical Accomplishments/ Progress/Results

- Most HTL R&D conducted by others using batch reactors
- Continuous flow HTL necessary to obtain relevant biocrude samples and generate relevant engineering & TEA input data.
- New modular HTL system commissioned in FY14 and used to demonstrate scalable reactor design, plug flow

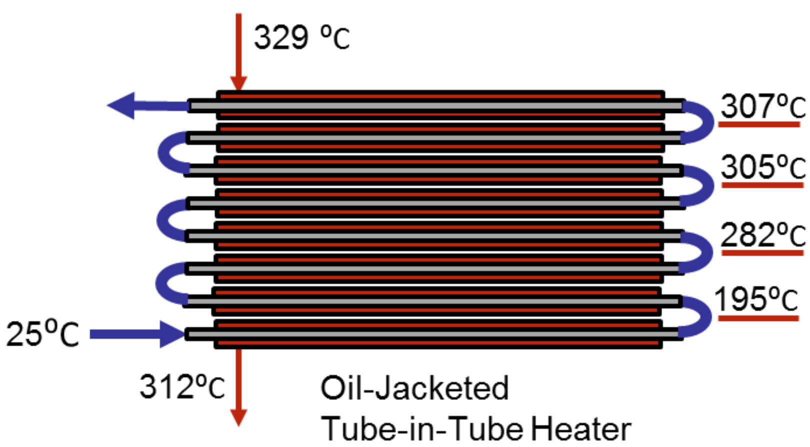


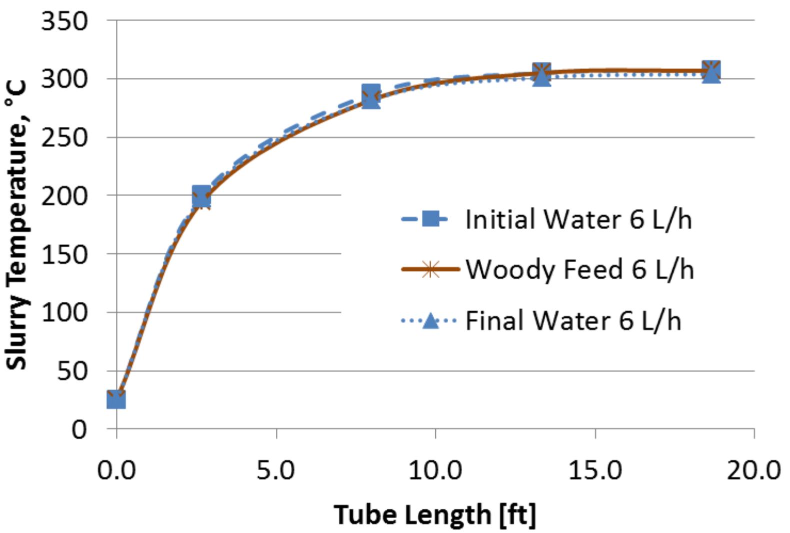
- Linear velocity increased to prevent plugging
- 4-fold increase in throughput with continuous pumping and pressure letdown

3 – Technical Accomplishments/ Progress/Results

Significant Impacts to Scale-up and Process Economics

- *HTL Commercial Scale Design Report performed by Harris Group*
- *Sensitivity analyses provided top priority areas for research*
  - "experimentally determine the expected heat transfer coefficients"
- *Testing in bench scale system at high feedrates (6 L/h) provided the experimental data to estimate heat transfer rates for FPR slurry*
- *Estimate = 50 BTU/h-ft^2, indistinguishable from water in same system*





Heating Profile; Water & Wood are equivalent

3 – Development of CAT HTL

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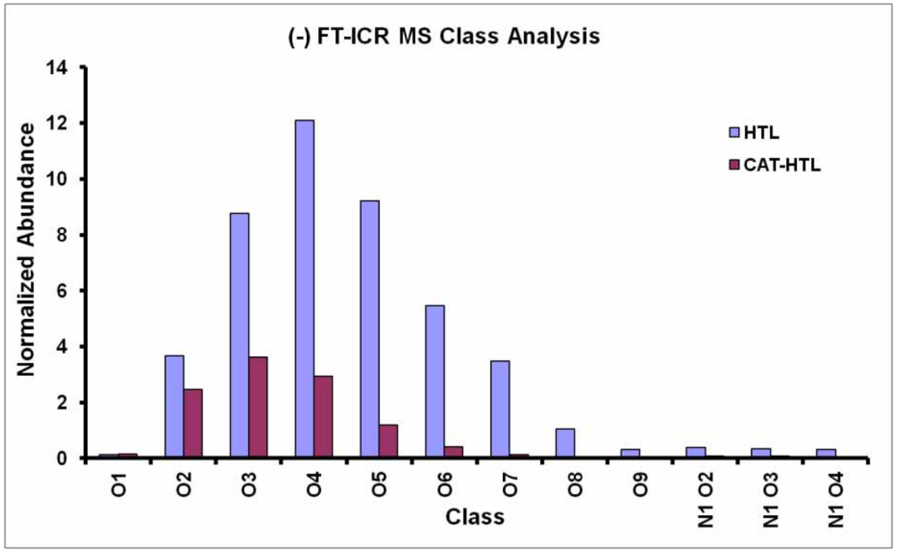
- Hydrothermally stable catalyst testing conducted to screen and identify potential catalysts, CombiCAT and Avantium screening
- Small lab scale system developed to screen catalyst operating parameters and activity over longer time on stream
- CAT bed incorporated into new bench-scale modular HTL system
- Multiple bench-scale runs completed and >1L of CAT HTL bio-crude generated for upgrading
- Demonstrated feasibility, the economic impact via TEA TBD



- Reforming of select aqueous organic compounds
- Reduction in bio-crude viscosity
- Some deoxygenation occurs during HTL process
- Reduction in relative concentration of highest molecular weight compounds

3 – Detailed Characterization of HTL Bio-crude Samples

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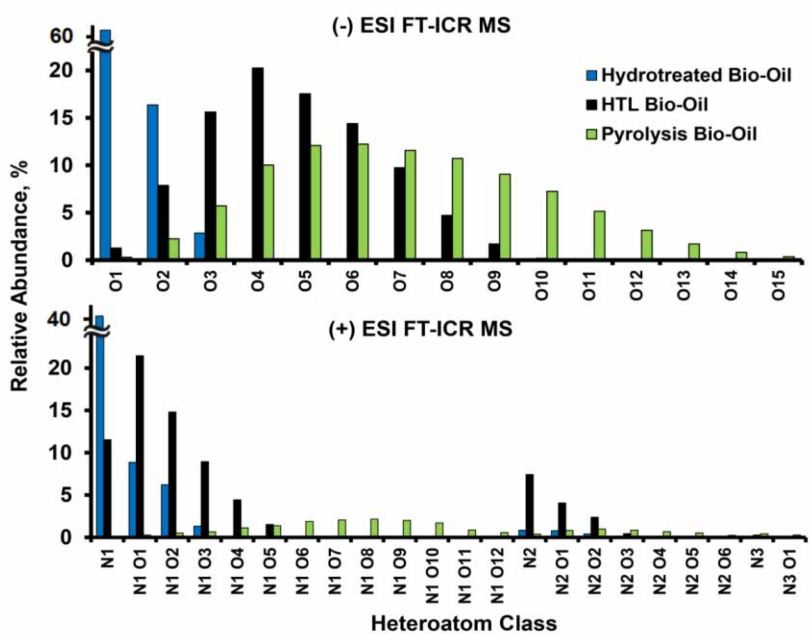
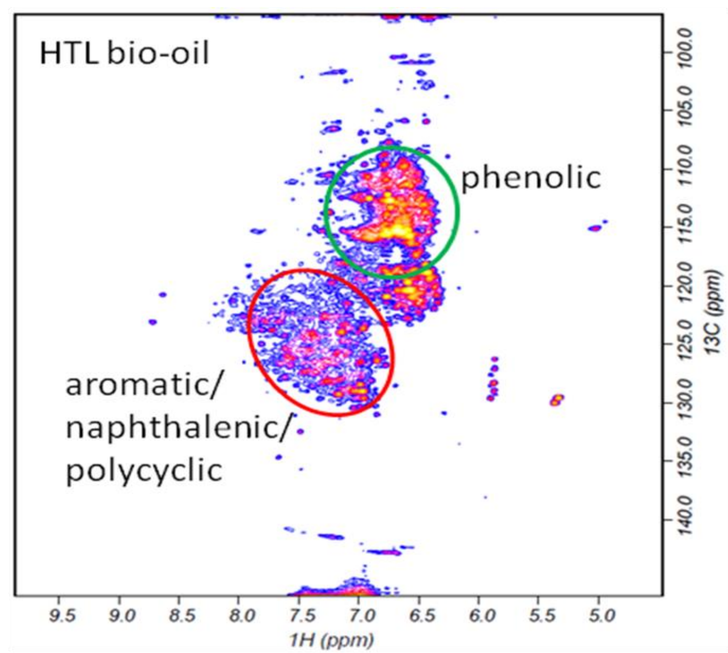
- Major FY14 milestone completed for demonstrating FT-ICR-MS as a characterization tool for HTL bio-crude samples
- FT-ICR-MS has high mass resolution and elemental composition and degree of unsaturation assigned for compositional comparisons
- Coupled with 2-D NMR detailed characterization of HTL biocrude publication completed, including comparison to fast pyrolysis bio-oil



FT-ICR MS negative ion mode highlights the oxygen compound classes and positive ion mode highlights the nitrogen compound classes



The aromatic region of the 2-D NMR spectra of HTL bio-oil showing high levels of phenol and other aromatic/polycyclic compounds

3 – HTL of additional feedstocks

- 6 feedstock continuous-flow tests completed in FY15 to assess HTL technology applicability and chemistry
  - Cellulose
  - Wheat Straw
  - Switch Grass
  - 2 different Winery wastes
  - Sugar beet waste
- No issues feeding or pumping at pressure for feedstocks
- No issues with system plugging or fouling
- All feedstocks produced phase separable biocrude

Wheat Straw | **Switchgrass** | **Grape Pomace**

Biocrude product characterization, upgrading, and aqueous byproduct CHG wet waste underway.

3 – Upgrading Forest Product Residual CAT HTL Bio-crude

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- Single stage hydrotreater with baseline Co/MoS catalyst
  - Biocrude LHSV: 0.208 L/L-cat/h; H_2/biocrude: 1276 L H_2/L biocrude
  - Pressure: 1540 psi; Temperature: 400°C
- Upgrading run >200 hours, >1L biocrude upgraded to hydrocarbons
- No catalyst deactivation
- H_2 consumption averaged over run, 0.0422 +/- 0.0036 g H_2/g biocrude
- Product: Mass yield = 0.86g/g, C yield = 0.97g/g, volume yield = 1.07L/L

	Biocrude Feed	TOS = 34 hr	TOS = 118 hr	TOS = 208 hr
Density*, g/mL	1.102	0.891	0.893	0.897
Viscosity*, cSt	2109	3.33	3.94	4.34
C, wt%	73.0	89.00	88.82	88.80
H, wt% (Dry Basis)	7.7	11.73	11.92	11.75
N, wt%	0.2	<0.05	<0.05	<0.05
O, wt% (Dry Basis)	13.5	0.81	0.85	0.86
S, ppm (ASTM D5453)		31	13	7
H/C Atomic Ratio	1.2	1.57	1.60	1.58

***Biocrude at 40°C and product at 20°C**

3 – Characterization of Upgraded and Fractionated Samples

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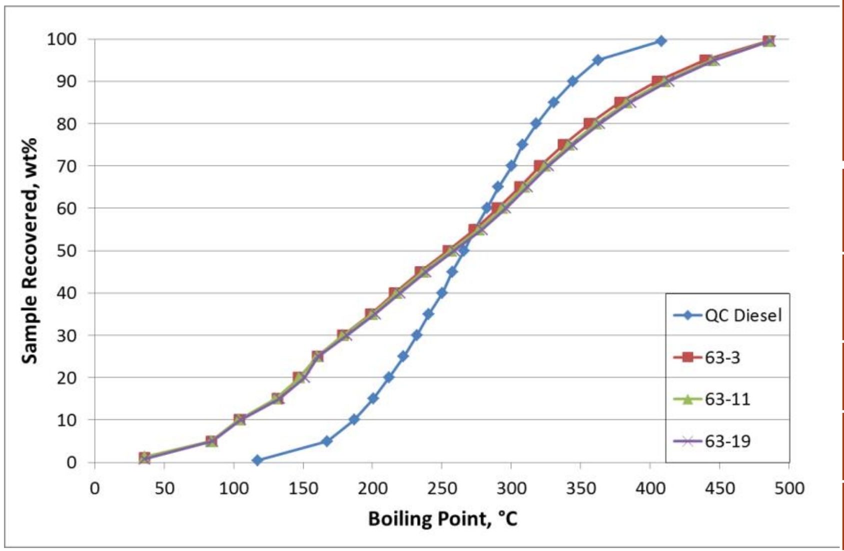
- Detailed characterization data package assembled for blendstock and refinery integration evaluation
- Chemical and physical property characterization
- Fractionation and characterization of fuel properties (underway)



Simulated Distillation Boiling Point Distribution

Batch Distillation Temperature Range, °C	Yield, wt%	Fraction	Density*, g/cc	API Gravity, 15°C	Viscosity*, cSt
HT Composite		feed	0.8909	27.33	3.8877
20-150	20.05	naphtha/ gasoline	0.7554	55.82	0.5477
150-250	25.82	jet	0.8473	35.50	1.4794
250-350	34.99	diesel	0.9395	19.11	11.369
>350	19.15	bottoms	1.0348	5.25	5839

* fuel cut data at 20°C, bottoms data at 40°C

4 – Relevance

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HTP Project alignment with Bioenergy Technologies Office goals:

"The strategic goal of Thermochemical Conversion R&D is to develop commercially viable technologies for converting biomass into energy-dense, fungible, finished liquid fuels, such as renewable gasoline, jet, and diesel, as well as biochemicals and biopower"– 2014 MYPP

MYPP Barriers addressed:

- Tt-F. Tt-J. Tt-C.

Support MYPP critical, near- to mid-term issues:

- Understand the relationship between feedstock quality and conversion
- Develop strategies for conserving carbon and hydrogen in conversion and upgrading processes
- Enable high-performance separations technologies to improve yields
- Work with petroleum refiners to address integrating biofuels into refinery processes.

Applications of the expected outputs from this project:

- New data to support TEA and state of the technology assessment, goal case $3.00
- Validating additional feedstock blends and innovative conversion processes that can meet long-term cost goals and maximize the volume of U.S. biomass resources that can be accessed for biofuels production.
- Provide data for environmental sustainability assessments, and
- Provide data for assessing upgraded HTL bio-crude quality and assign value as fuel blendstock and for refinery insertion.

4 – Relevance; Partnerships

- HTL advances in lignocellulosics utilized for algae and vis versa
- Paradigm change in algae to fuels conversion pathway (HTL of whole algae vs. lipid extraction approach)
- Working with licensee (Genifuel) to identify opportunities, speed commercialization and investment/scale-up by others.
- PNNL HTL skid to Algenol Biofuels Inc. (500 L/day) – ongoing collaboration
- Partnership with Water Environmental Research Foundation (WERF) to assess WWTP stream opportunities and HTL test materials

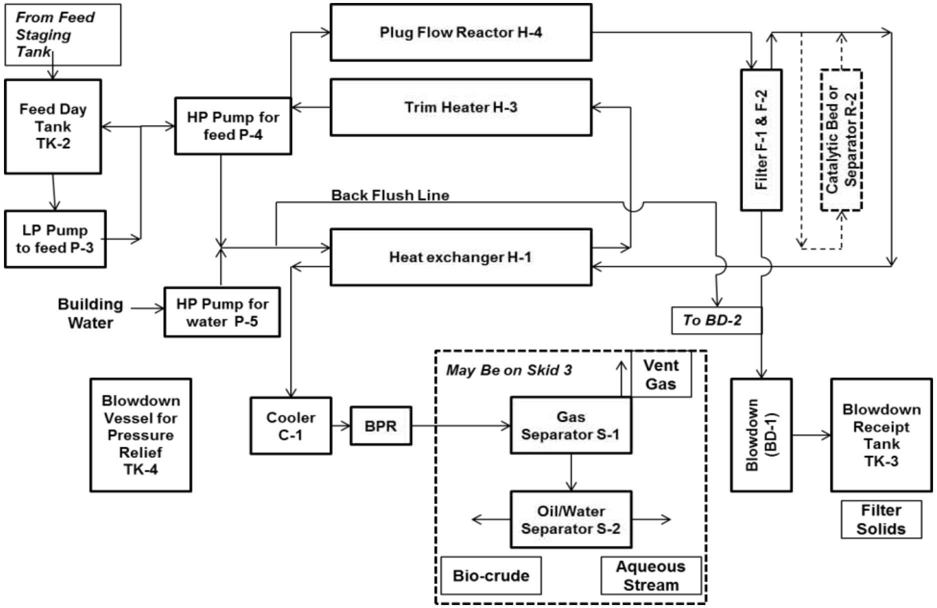
2015 Federal Laboratory Consortium Award Winning Team, 1000 L/day (20 wt% BDAF) system Reliance-PNNL-Genifuel HTL/CHG System

FLC NATIONAL AWARDS

- HTL Reactor Design Assessment by third party (Harris Group) http://www.nrel.gov/docs/fy14osti/60462.pdf
- Assessment of Commercial Vendors for Feeding and Pumping Biomass Slurries for HTL http://www.pnnl.gov/main/publications/external/technical_reports/PNNL-21981.pdf

5 – Future Work

- Complete HTL processing of baseline feedstocks and determine biocrude properties.
- Upgrade select biocrude samples and evaluate hydrocarbon products as blendstock or for refinery integration.
- Expand bench-scale HTL capabilities to allow processing wide range of feedstocks, additional process parameters, and improved separations.
- Provide additional supporting chemical and physical analyses for development of data correlation.
- Determine overall impact on economics and GHG
- Utilize process models, TEA, and LCA for implementing improved HTL conversion process and feedstocks.
- Go/No Go decision point at 18 months with regards to CAT HTL
- Support development of HTL Engineering Scale System



Block Flow Diagram Engineering Scale HTL

Summary

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1) Advanced Hydrothermal Processing Technologies for Biomass Conversion
    1) Expanded feedstocks.
    2) Improve biocrude yield and quality via CAT HTL.
    3) Advance reactor designs and separation improvements
    4) Improved biocrude for upgrading to blendstock or for refinery insertion.
2) Addresses Technical Barriers: *Tt-F, Tt-J, Tt-C*
3) Critical Success Factors
    1) Developed modular, continuous HTL system for data generation and process validation.
    2) Produced biocrude from wide range of feedstocks.
    3) Demonstrated ease of HTL biocrude upgrading and provided critical data.
4) Future Work
    1) Convert additional feedstocks to biocrude samples, provide engineering data, and assessments including quantifying feedstocks resources.
    2) Extended upgrading campaign with HTL biocrude samples.
    3) Expand hydrothermal processing to lignocellulosic biorefinery waste streams.

- All technical targets presented in 2013 Peer Review were met
- Have published processing results and technoeconomic assessments

Additional Slides

Responses to 2013 Peer Reviewers' Comments

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Summary of Reviewer Comments Related to Commercial/Industrial Involvement/Impact::

- "Unlikely ever to catch up to or surpass the industrial and academic work already underway"
- "The CSF's are nominally linked to process improvements, but industry innovation will progress at a greater rate, based on mainly empirical work, so by the time the Lab work is completed and published, the baseline it was built around will have moved on (most likely). Developing or improving technology for commercial application in this fashion has severely limited potential in the absence of at least one commercialization partner."
- "There is collaboration between an established lab with biomass processing expertise & equipment and a lab with a powerful analytical method, but with no direct industry link, the likely outcome will be a journal article that may or may not be published in time to be relevant to commercial activity."
- "Shares the strengths and weaknesses of most of the Lab projects -- sound scientific work, utilizing new techniques and investigating the fundamentals in far greater depth than is likely in the commercial world, but little or no link to the commercial world, so limited chance for impact and virtually no chance for feedback."
- "The work is of good fundamental relevance, but with no partnership in the commercial sector, the likelihood is that the results will find their way into peer-reviewed articles too late to be of use in optimizing commercial technologies. This is yet another example of scientifically excellent work in the Labs having little commercial relevance because of this time lag."
- "The results would have tech transfer potential relating to conversion of moist biomass."

Response

- PNNL is the leading national laboratory in continuous processing HTL, and other industrial entities (domestic and foreign) and other national labs continue to reach out to us for our HTL expertise and support.
- Since the 2013 peer review, two skid-mounted engineering scale HTL systems have been designed and constructed for industrial application with our support and that of our Licensee.

Responses to 2013 Peer Reviewers' Comments

Summary of Reviewer Comments Related to Technical Work

- "Need to be able to compare to other biomass processing technologies."
- "This project is limited by these existing samples. No new HTL bio-oil will be produced by this project."
- "Characterization of HTL bio-oil samples is worthy exercise which should add to the HTL database. On the other hand, this project is tainted somewhat by the use of old potentially degraded samples which are representative of limited operating conditions and feedstocks."
- "Expand to more feedstocks and process conditions, and upgraded BO properties."
- "This project has the potential to contribute to the goals of the bio-oil technology area and provide data for HTL modeling. It may not be complete because the samples used are old and limited to those already on hand."

Response

- Under the NABC, a head to head comparison with 5 other conversion strategies was performed; HTL was favorable on a $/GGE basis. Several HTL TEA papers published since last peer review.
- Many HTL samples (and upgraded HT products) from many feedstocks have been and continue to be subjected to detailed characterization. Several characterizations papers have been published and we expect to publish several more in 2015.

Publications, Patents, Presentations, Awards, and Commercialization

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Awards

- 2014 FLC technology transfer excellence award
- PNNL Energy Technology Division – Paper of the year

Patents

- Elliott, D.C.; Oyler, J.R. "Methods for Sulfate Removal in Liquid-Phase Catalytic Hydrothermal Gasification of Biomass." U.S. Patent #8,877,098, issued on November 4, 2014.

Publications

- Elliott, D.C.; Biller, P.; Ross, A.B.; Schmidt, A.J.; Jones, S.B. 2014. "Hydrothermal liquefaction of biomass: Developments from batch to continuous process" invited submission to Special Issue: Thermo-chemical conversion, **Bioresource Technol.** *178* **2014***,* 147–156.
- Elliott, D.C. 2015. "Catalytic Hydrothermal Gasification." In: Power from Biomass, W.P.M. van Swaaij and S.R.A. Kersten, eds., in press, Pan Stanford Publishing, Singapore.
- Nilusha Sudasinghe, John R. Cort, Richard Hallen, Mariefel Olarte, Andrew Schmidt, and Tanner Schaub. *Hydrothermal liquefaction oil and hydrotreated product from pine feedstock characterized by heteronuclear two-dimensional NMR spectroscopy and FT-ICR mass spectrometry.* **Fuel** *137* **2014**, 60-69**.**
- Zhu, Y.; Biddy, M.J.; Jones, S.B.; Elliott, D.C.; Schmidt, A.J. Techno-Economic Analysis of Liquid Fuel Production from Woody Biomass via Hydrothermal Liquefaction (HTL) and Upgrading. **Applied Energy** *129* **2014,** 384-394,.
- Berglin, EJ; Enderlin, CW; Schmidt, AJ. Review and Assessment of Commercial Vendors/Options for Feeding. Pacific Northwest National Laboratory (November 2012). PNNL-21981
- Elliott DC, TR Hart, AJ Schmidt, GG Neuenschwander, LJ Rotness, MV Olarte, AH Zacher, KO Albrecht, RT Hallen, and JE Holladay. Process Development for Hydrothermal Liquefaction of Algae Feedstocks in a Continuous-Flow Reactor. **Algal Research** *2*(4) **2013**, 445-454.

Publications, Patents, Presentations, Awards, and Commercialization (continued)

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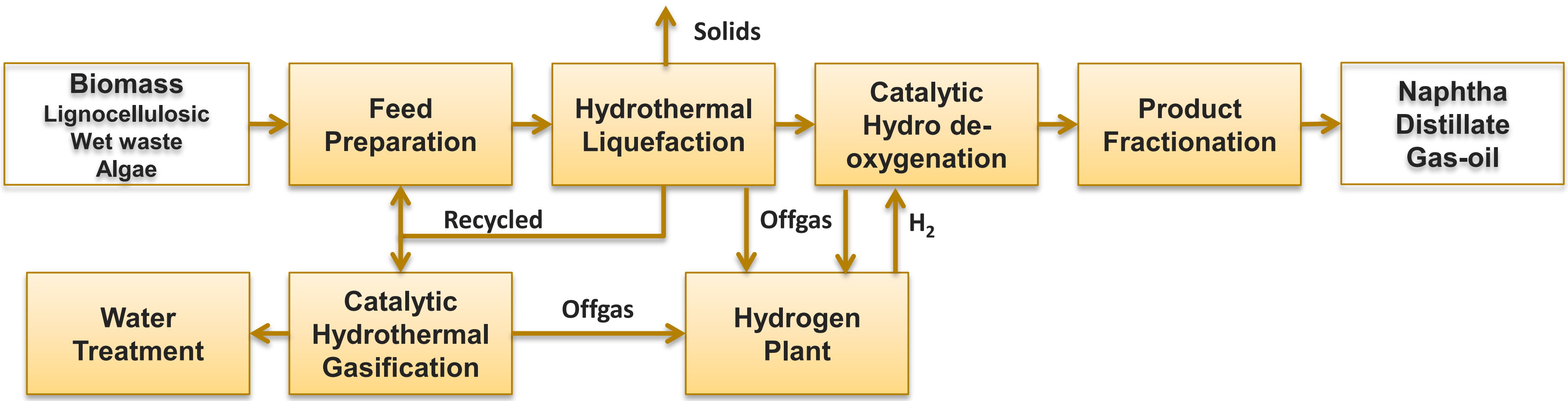
.**Key Presentations**

- Elliott, D.C. Conversion of Algal Biomass to Liquid Fuels by Hydrothermal Processing in Continuous-Flow Reactors. invited seminar, Aarhus University, Aarhus, Denmark, October 3, 2014.
- Albrecht, K.O., J.E. Holladay, and D.C. Elliott. Advanced Biofuel and Biochemical Production at Pacific Northwest National Laboratory. Presented (Invited Speaker) at Bioenergy at CSU Seminar, Ft. Collins, CO on December 3, 2014. PNNL-SA-106969.
- Elliott, Doug, Rich Hallen, Karl Albrecht, Andy Schmidt, Todd Hart, Gary Neuenschwander, Mariefel Olarte, L.J. Rotness, and Gary Maupin. Conversion of Algal Biomass to Liquid Fuels by Hydrothermal Processing in Continuous-Flow Reactors. Presented at tcbiomass2013, Chicago, Illinois, September 2013.
- Holladay, J.E. and K.O. Albrecht. Hydrothermal Processing of Algae. Presented by Karl Albrecht (Invited Speaker) at 3rd International Conference on Algal Biomass, Biofuels and Bioproducts, June 17, 2013, Toronto, Canada.
- Elliott, D.C. Conversion of Algal Biomass to Liquid Fuels by Hydrothermal Processing in Continuous-Flow Reactors. Joint Engineering and Science Seminar, Washington State University/Tri-Cities, Richland, Washington, March 28, 2014.
- Elliott, D.C. Conversion of Algal Biomass to Liquid Fuels by Hydrothermal Processing in Continuous-Flow Reactors. Portland Section meeting, American Chemical Society, Reed College, Portland, Oregon, April 10, 2014.
- Elliott, D.C. Conversion of Algal Biomass to Liquid Fuels by Hydrothermal Processing in Continuous-Flow Reactors. Southern California section meeting, American Institute of Chemical Engineers, Anaheim, California, April 15, 2014.
- Holladay, J.E. Liquefaction Technologies for Producing Biocrude for Jet, Diesel and Gasoline. Presented (Invited Speaker) at Northwest Wood-based Biofuels and Products, April 29, 2014, Seattle, WA.
- Holladay, J.E. Technical and Economic Aspects for Hydrothermal Liquefaction of Algae. Presented (Invited Speaker) at Algae Biomass Summit, October 2, 2013, Orlando, FL.

Back up


Solids
Biomass
Lignocellulosic
Wet waste
Algae
Feed Preparation
Hydrothermal Liquefaction
Catalytic Hydro de-oxygenation
Product Fractionation
Naphtha
Distillate
Gas-oil
Recycled
Offgas
H_2
Water Treatment
Catalytic Hydrothermal Gasification
Offgas
Hydrogen Plant