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DOE Bioenergy Technologies Office (BETO) 2015 Project Peer Review

Production and Upgrading of Infrastructure Compatible Bio-Oil with VTT

March 25, 2015
Thermochemical Conversion

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Goal Statement

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- Problem Statement: Methods with higher yields or less expensive operation are needed to produce liquid fuels from biomass
- Goal: Validate, in collaboration with international process technology leaders, integrated conversion processes for biomass to liquid fuels by thermochemical liquefaction and hydrotreating.
- Major Project Objectives:
  - Low-severity hydrotreating (HT)
    - Stabilize bio-oil for fuel oil application
    - Produce blendable home heating oil (HHO) components
  - HT bio-oils to produce more hydrocarbon-like products
    - Fractional condensation low-moisture bio-oil (from VTT)
    - *In situ* catalytic pyrolysis bio-oil (from VTT)
  - Evaluate techno-economic assessment process model outputs based on input from process tests in HT bio-oil and HTL/HT
- Benefit to the U.S.: Improved process development effort working with international experts.

Quad Chart Overview

Timeline

- Project start date 1/1/2012
- Project end date 2/28/2015
- Percent complete 100%

Budget

	Total Costs FY 10 –FY 12	FY 13 Costs	FY 14 Costs	Total Planned Funding (FY 15-Project End Date
DOE Funded	211,061	1,003,890	501,387	83,337
Project Cost Share (Comp.)	0	3,978	93,899	12,878

Barriers

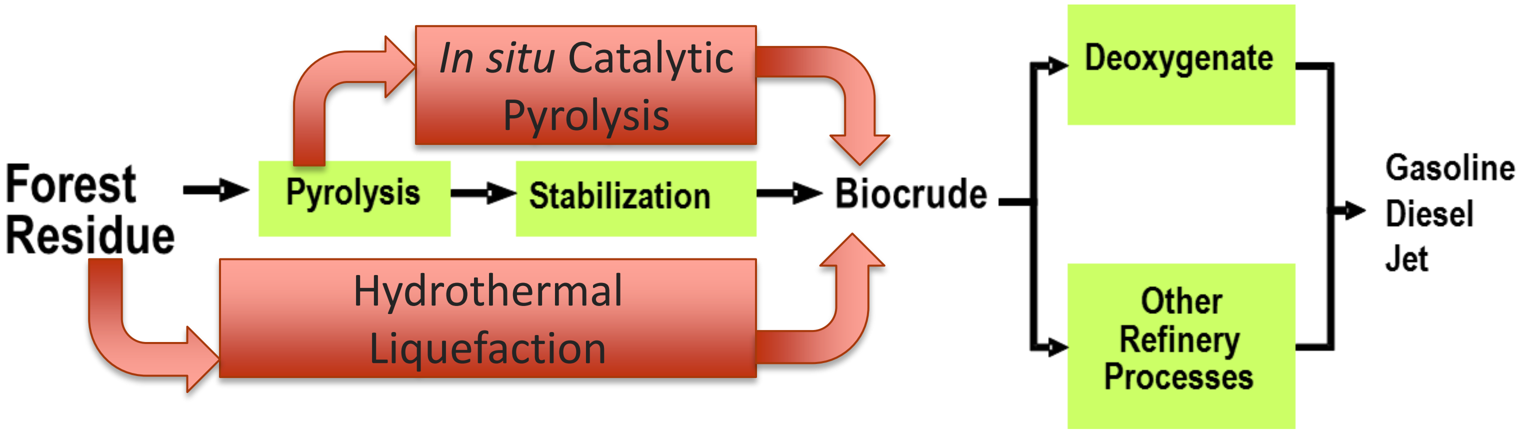
- Tt-F. Deconstruction of Biomass to Form Bio-Oil Intermediates:
- Tt-J. Catalytic Upgrading of Bio-Oil Intermediates to Fuels and Chemicals:
- Tt-R. Process Integration:

Partners

- VTT Finland: Experts in biomass fast pyrolysis with 20 kg/h PDU for production of bio-oil and documented skills in bio-oil analysis
- Zeton Canada: Process equipment designers and fabricators with particular expertise in pyrolysis and HT
- BNL: blended fuel evaluation
- ORNL: corrosion assessments

1 - Project Overview

- Stabilization and upgrading of pyrolysis bio-oils to a finished fuel is largely dependent on the Hydrotreating (HT) process.



- PNNL conducted stabilization and upgrading tests on forest residue bio-oil produced by the international R&D leader, VTT, to produce fuel components with identifiable markets.
- Techno-Economic Analysis and Life-Cycle Assessments of these processes were conducted in this project.

2 – Approach (Technical)

- Leverage PNNL and VTT long-established research partnership in pyrolysis oil stabilization and upgrading
- VTT was responsible for PDU scale bio-oil production and delivery
  - Base-line fast pyrolysis bio-oil (for this project and others at PNNL)
  - Improved pyrolysis bio-oils—fractionated, catalytic pyrolysis
- PNNL's research focused on the experimental development of stabilized and fully upgraded finished fuels in continuous-flow reactors
  - Low-severity hydrotreating for stabilization of heavy fuel oil
  - Minimal upgrading for fuel oil blending – products evaluated at BNL for fuel properties and at ORNL for materials compatibility issues
  - One- and two-stage hydrotreating of bio-oil to hydrocarbon liquid fuels
- PNNL and VTT jointly developed ASPEN-Plus-based mass and energy process models and economic analysis to compare the economic viability of the biomass liquefaction routes

2 – Approach (Management)

- Project Challenges:
  - Identify improved bio-oil through "hydrotreatability" assessments
    - Operation with reduced number of temperature stages
    - Extended on stream operation without bed fouling
    - Improved yields or product properties
  - Produce a uniform basis for process assessments
    - Feedstock specifics
    - Equipment specifics
    - Unit operation limits
    - Model management
- Project Monitoring:
  - International monthly conference calls, yearly in-person meetings
  - Analysis Task: international conference calls occurred more often
  - PNNL Team: weekly team updates and in-person meetings
  - Quarterly reporting addressing AOP with Milestones & Deliverables
  - Dialogue with BETO to enable them to have an active role in project direction

3 – Technical Accomplishments/ Progress/Results

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Hydrotreating Bench-Scale Experimental Evaluation:

- Low-severity stabilization
- HT experiments on improved bio-oils
    - Fractionated bio-oil
    - Catalytic pyrolysis

Techno-Economic Analysis:

- Development of ASPEN-Plus models for Fast Pyrolysis and Upgrading and Hydrothermal Liquefaction and Hydrotreating
- Development of model for low-severity hydrotreating for producing stable fuel oil from bio-oil

Life Cycle Assessment :

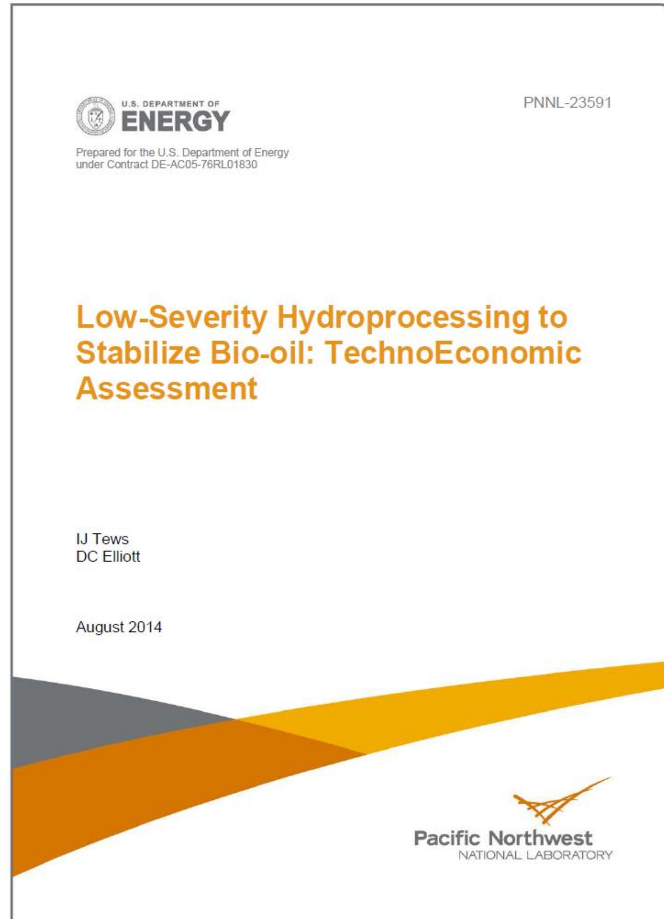
- Life-cycle assessments of Fast Pyrolysis and Hydrothermal Liquefaction pathways

Home Heating Oil:

- Minimal upgrading by hydrotreating using either sulfided or precious metal catalysts
- 20% blended fuels produced, analyzed and assessed

Low-Severity Hydrotreating of Bio-oil for Stable Fuel Oil

- Experimental testing of low-severity conditions validated bio-oil stabilization, as expressed by reduced viscosity increase, allowing longer term storage of fuel oil.
- TEA suggests
  - Efficiency reduced by <2 points
    - 60.2% → 58.4%
  - Cost increased by 20%
    - $16/GJ → $19.3/GJ
- Report PNNL-23591


U.S. DEPARTMENT OF ENERGY

PNNL-23591

Prepared for the U.S. Department of Energy under Contract DE-AC05-76RL01830

Low-Severity Hydroprocessing to Stabilize Bio-oil: TechnoEconomic Assessment

IJ Tews
DC Elliott

August 2014

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3 – Technical Accomplishments/ Progress/Results (cont'd)

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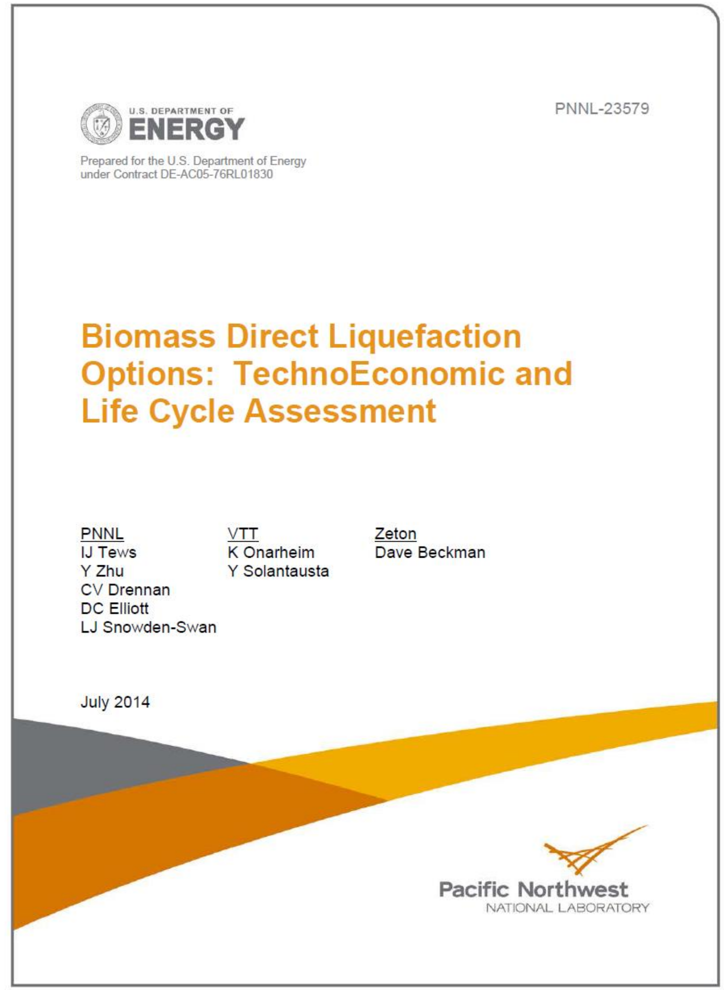
Hydrotreating VTT improved bio-oil

- Low-moisture bio-oil collected at VTT by fractional condensation. (FY2012-13, previous peer review)
  - 2-stage hydrotreating used with sulfided catalyst
  - Quality products produced with high yield and H_2 consumption
  - Catalyst bed fouled leading to over-pressure shutdown in 18 h
  - Similar or worse than whole bio-oil
- Catalytic pyrolysis bio-oil (FY2014-2015)
  - Single-stage hydrotreating used with sulfided catalyst
  - Quality products produced with high yield and moderate H_2 consumption
  - Catalyst bed plugging due to particulate, as opposed to fouling
  - Filtration of bio-oil down to 1 micron allowed 57 h on stream
  - Significant improvement relative to fast pyrolysis bio-oil

Techno-Economic Assessment

- VTT experimental data and ASPEN-Plus model for fast pyrolysis merged with hydroprocessing data and hydrothermal liquefaction data from PNNL.
- Comparative TEA the two pathways for biomass to liquid hydrocarbon fuels
- Report PNNL-23579


U.S. DEPARTMENT OF ENERGY

PNNL-23579

Prepared for the U.S. Department of Energy under Contract DE-AC05-76RL01830

Biomass Direct Liquefaction Options: TechnoEconomic and Life Cycle Assessment

PNNL
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Y Zhu
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DC Elliott
LJ Snowden-Swan

VTT
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Dave Beckman

July 2014

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Comparison of the Results for Fast Pyrolysis versus Hydrothermal Liquefaction

	FP	FP + Upgrading	HTL	HTL + HT
Energy efficiency to liquid fuel, LHV	60.2	54.4	64.5	62.3
Fixed Capital Investment, $M	231	358	195	244
Liquid fuel mass yield, % feed, dry basis	51.2	24.2	35.1	27.4
Liquid fuel product cost, $/GJ	16.0	26.3	14.5	16.9
Liquid fuel product cost, $/metric ton	231	1103	449	712
Liquid fuel product cost, $/gallon gasoline equivalent	NA	3.09	NA	2.00

- Updated hydrothermal liquefaction including upgrading to liquid hydrocarbon fuels compares favorably with fast pyrolysis and upgrading
- HTL is higher efficiency and lower cost to similar fuel mix.

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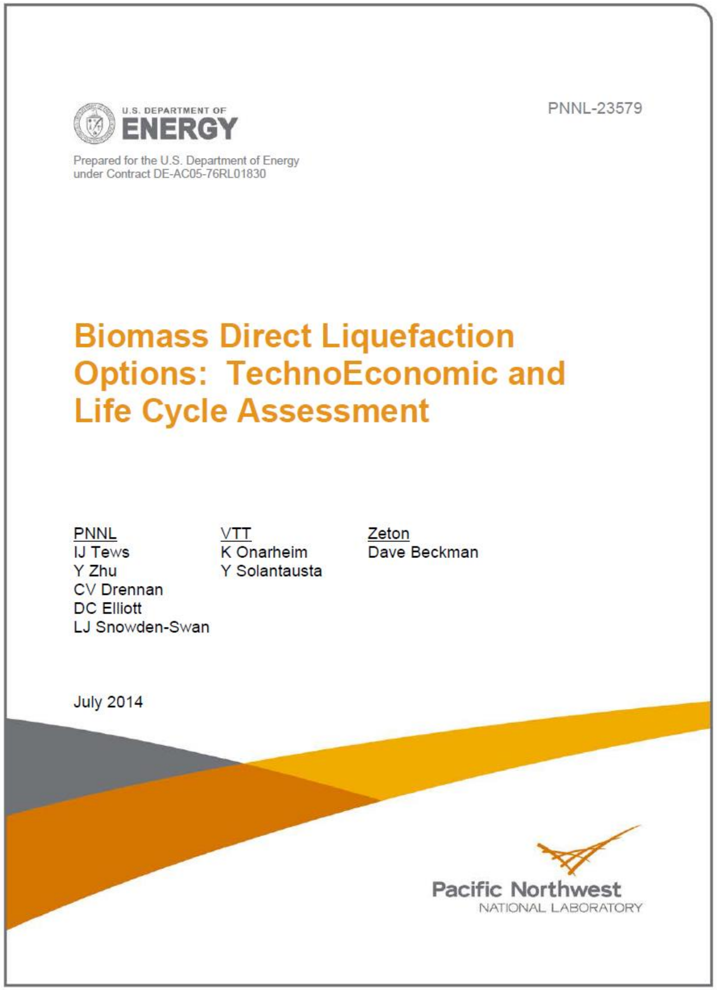
Life Cycle Assessment

- ASPEN-Plus modeling was the basis for the LCA
- Comparative LCA the two pathways for biomass to liquid hydrocarbon fuels
  - HTL has lower CO_2 emissions in the conversion step
  - Overall, FP path has 64% GHG reduction while HTL path has 71% reduction relative to fossil
- See also report PNNL-23579



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3 – Technical Accomplishments/ Progress/Results (cont'd)

Home Heating Oil

- Experimental testing of catalysts and conditions to determine minimally upgraded bio-oil properties.
- Precious metal catalyst deactivation over time
- Sulfided catalyst products unblendable

	water	TAN	C	H	N	O	S	Viscosity	density
	Wt%	mgKOH/g	Wt%	Wt%	Wt%	Wt%	Wt%	cSt	g/mL
#2 oil	<0.03	<0.01	85.9	12.8	ND	1.3	ND	2.9	0.83
Bio-oil	22.2	143	47.8	7.5	0.08	44.7	<0.1	105	1.24
MOx	1.05	47	79.0	11.3	0.08	9.5	<0.1	3.1	0.89
HOx	1.23	50	78.8	9.7	0.13	11.3	<0.1	17.7	0.96
MOx blend	0.03	8.3	85.1	12.7	<0.05	2.2	<0.1	2.7	0.84
HOx blend	0.08	8.6	85.2	12.4	<0.05	2.3	<0.1	3.2	0.85

ND = not determined

4 – Relevance

- The project develops new technology for advanced processes that address the barriers to commercialization of fast pyrolysis of biomass for production of infrastructure compatible liquid fuels
- Home heating oil for the U.S. Northeast was identified as an important issue during 2013 by DOE directive
- The inclusion of international leaders in the technology development as partners helps insure leading edge R&D
- The participation of industrial partners in the review of task activities validates the utility of the effort and guides the scope of work
- The use of techno-economic modeling to identify process advantages and to help focus research on important process development issues is a key element of this project

MYPP 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-R. Process Integration:

5 – Future Work

- Transition to new project is underway
  - Close-out of project and funds-in contract from VTT
  - Start 10/1/2014 **2.3.1.312 *In situ* Catalytic Pyrolysis and Product Bio-Oil Upgrading**
- Recent Milestones
  - Implement sub contract with Utah State University
    - Prof Foster Agblevor
    - Catalytic pyrolysis catalyst development and testing
  - Continue with catalytic hydrotreating of catalytic pyrolysis bio-oil
    - *In situ* catalytic pyrolysis bio-oil from VTT, including new funds-in contract
    - Continuous-flow reactor systems at PNNL
- Go/No-Go in FY 2016 to proceed to larger scale operations based on successful bench-scale development of catalysts and HT processing

Summary

- Relevance: PNNL has partnered with VTT to bring the strengths of each to bear on the development issues for thermochemical processing to liquid fuels
- Approach: Both process testing and modeling were used to identify and resolve barriers to direct liquefaction of biomass
- Improved bio-oil properties, specifically from *in situ* catalytic pyrolysis may facilitate hydrotreating to infrastructure compatible fuels
- TEA with LCA completed comparing FP and HTL
- HHO production by minimally upgrading bio-oil

Additional Slides

Responses to Previous Reviewers' Comments

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- More clarification was needed of the unique aspects of this project relative to other PNNL HT work.
  - New bio-oil products were received from VTT and tested at PNNL, including fractionated bio-oil and catalytic pyrolysis bio-oil not otherwise available in the U.S.
  - Utilization of the expertise in process modeling at VTT was valuable.
  - Production of partially upgraded bio-oil and blending with home heating oil was unique.
- Difficulties in the long distant relationship and transportation of bio-oils were identified.
  - The stability of fresh bio-oil during trans-Atlantic shipment made it difficult to consistently evaluate low-severity upgrading. Otherwise, it was not an issue.
  - Communications and project coordination were not a problem.

Publications and Commercialization

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- Oasmaa, A.; Kuoppala, E.; Elliott, D.C. “Development of the Basis for an Analytical Protocol for Feeds and Products of Bio-oil Hydrotreatment.” **Energy & Fuels**, *2012* **26** 2454-2460; web published 19 March 2012.
- Elliott, D.C.; Hart, T.R.; Neuenschwander, G.G.; Rotness, L.J.; Olarte, M.V.; Zacher, A.H.; Solantausta, Y. “Catalytic Hydroprocessing of Fast Pyrolysis Bio-oil from Pine Sawdust.” **Energy & Fuel** *2012* **26** 3891-3896. web published May 29, 2012.
- Elliott, D.C. “Transportation fuels from biomass via fast pyrolysis and hydroprocessing.” **Wiley Interdisciplinary Reviews (WIREs) Energy and Environment** *2013*. doi: 10.1002/wene.74; web published February 25, 2013.
- Elliott, D.C. “Biofuel from fast pyrolysis and catalytic hydrodeoxygenation.” invited submission to **Current Opinion in Chemical Engineering**, Editor-in-Chief: Kamalesh K. Sirkar, Energy and Environmental Engineering / Reaction Engineering and Catalysis, Volume 9: Energy and Environmental Engineering.

- Tews, I.J., Elliott, D.C., “Low-Severity Hydroprocessing to Stabilize Bio-oil: TechnoEconomic Assessment” PNNL-23591, August 2014.
- Tews, I., Elliott, D.C., Zhu, Y., Drennan, C.V., Snowden-Swan, L.J., Onarheim, K., Solantausta, Y., Beckman, D. “Biomass Direct Liquefaction Options: TechnoEconomic and Life Cycle Assessment” PNNL-23579, July 2014.

- The efforts in Finland have resulted in an operating commercial integrated fast pyrolysis plant. The consortium is now moving into catalytic pyrolysis as the next step in the development. Our collaboration plays a key role in the developments there.
- The optimistic comparison of hydrothermal liquefaction relative to fast pyrolysis has provided further incentive to Genifuel, who has licensed the hydrothermal technology from PNNL.

Presentations

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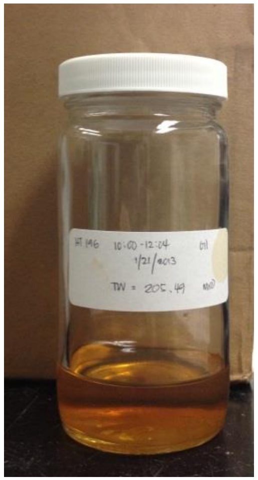
- Elliott, D.C., Solantausta, Y., Onarheim, K., Tews, I., Beckman, D. and Snowden-Swan, L.J. “Biomass Conversion to Liquid Hydrocarbon Fuels by Alternative Processes” presented at the TCS2014 conference, 9/3/2014, Denver, CO.
- Elliott, D.C., Solantausta, Y., Onarheim, K., Tews, I., Beckman, D. “Biomass Conversion to Liquid Hydrocarbon Fuels by Alternative Process Routes.” invited plenary presentation at the 22nd European Biomass Conference and Exhibition, Hamburg, Germany, June 25, 2014.
- Elliott, D.C. and Zacher, A.H. “Upgrading Fast Pyrolysis Liquids to Biofuels” PYRO 2014 20th international Symposium on Analytical and Applied Pyrolysis, Birmingham, UK, May 19, 2014.
- Elliott, D.C. and Zacher, A.H. “Upgrading Fast Pyrolysis Liquids to Biofuels” International Bioenergy Conference 2014, Manchester, UK, March 12, 2014.
- Padmaperuma AB, DM Santosa, DC Elliott, SB Jones, PA Meyer, H Wang, SJ Lee, GG Neuenschwander, MV Olarte, LJ Rotness, Jr, AH Zacher, IJ Tews, and C Drennan. 2014. "Technical and economical challenges in the production of renewable home heating oils." at 247th ACS National Meeting, Dallas, TX on March 17, 2014.
- Padmaperuma, A.B.; Santosa, D.M.; Elliott, D.C.; Male, J.L.; Valkenburg, C.; Zacher, A.H.; Neuenschwander, G.G.; Olarte, M.V.; Rotness, L.J.; Lemmon, T.L.; Burton, S.D.; Tews, I.J. 2013. "Chemical characterization of liquid fuels derived from Northeast-US hardwood for potential application in residential heating." at 246th ACS National Meeting, Indianapolis, IN on September 9, 2013.
- Santosa, D.M.; Padmaperuma, A.B.; Male, J.L.; Elliott, D.C.; Valkenburg, C.; Zacher, A.H.; Neuenschwander, G.G.; Olarte, M.V.; Rotness, L.J.; Lemmon, T.L.; Burton, S.D.; Tews, I.J.; Nichol, C.; Westover, T.; Boardman, R.D.; Muth, D. 2013. "Renewable home heating oils (HHO): Pyrolysis and upgrading of bio-oils derived from US Northeast hardwood." at TC Biomass 2013, Chicago, IL on September 3, 2013.
- Tews, I.J.; Onerheim, K.; Elliott, D.C.; Solantausta, Y; Beckman, D. “Technoeconomic Assessment of Direct Biomass Liquefaction Processes” Presented by Iva Tews at the 21st European Biomass Conference and Exhibition, Copenhagen, Denmark, June 2013.
- Tews, I.J.; Kinchin, C.; Iisa, K.; Solantausta, Y "Use of TEA in Fast Pyrolysis Research for Economic Process Development and Technology Deployment." Bioenergy from Forest, Jyväskylä, Finland. August 2013.
- Male, J. L; Jones, S. B.; Jacobson, J.; Searcy, E. “A Qualitative Discussion on Conversion, Stabilization, and Upgrading versus Infrastructure Compatibility and Retrofit Requirements”. at Technical Information Exchange on Pyrolysis Oil: Potential for Renewable Heating Oil Substitution Fuel in New England, 5/9-10/2012 Manchester, NH.

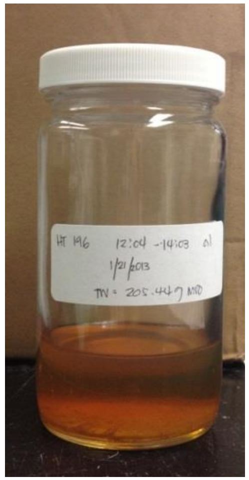
Hydrotreating VTT improved bio-oil (HT 195)

- VTT fractionated bio-oil condensed at 6% H_2O moisture
  - more viscous (529 cSt@40 ºC) and had to be filtered before processing
- HT Run Conditions:
  - Temperature Profile: Split bed (25%:75%) at 250 ºC:390 ºC
  - Pressure: 2000 psig
  - Flow rates: 120 L H_2 /h, 53 mL bio-oil/h
  - Catalyst: sulfided CoMo on alumina
- Results:
  - 6h run before a pressure build-up >100 psi occurred and shutdown
  - Plugging in catalyst suggested little improvement
  - The run was re-scheduled with a different catalyst configuration

Fractionated bio-oil HT processing – 2nd attempt (HT196)

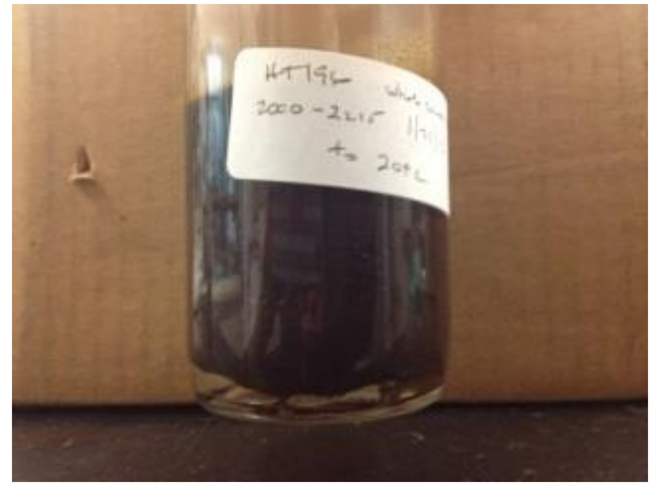


HT 196 1000-1204



HT 196 1204-1403

HT 196 1403-1600



HT 196 2000-2215 emulsion

- Run Conditions : reduced oil flow rate to improve conversion
  - Changed catalyst, temperature profile
  - Temperature, pressure settings and H_2 flow were unchanged.
- Results: successful production of 4 oil fractions
  - 18h processing run until >100 psi pressure drop occurred and shutdown.
  - Last three samples came out as an emulsion, which was hard to split

Feed/Product Analysis – VTT Fractionated Bio-oil

Oil sample	C	H	O	moisture	density	TAN	viscosity
	wt%			wt%	g/mL	mg KOH/g	cSt@40C
feed	53.2	6.9	35.3	6.1	1.24	132	529
HT195	83.4	12.8	1.3	<0.01	0.80	<0.01	1.1
HT196 early	84.8	11.8	1.6	0.04	0.84	<0.1	1.3
HT196 late	84.9	11.2	2.0	0.04	0.87	<0.1	1.7

- Hydrogen consumption and oil product yield relatively high

Biomass Conversion to Liquid Hydrocarbon Fuels by Alternative Processes

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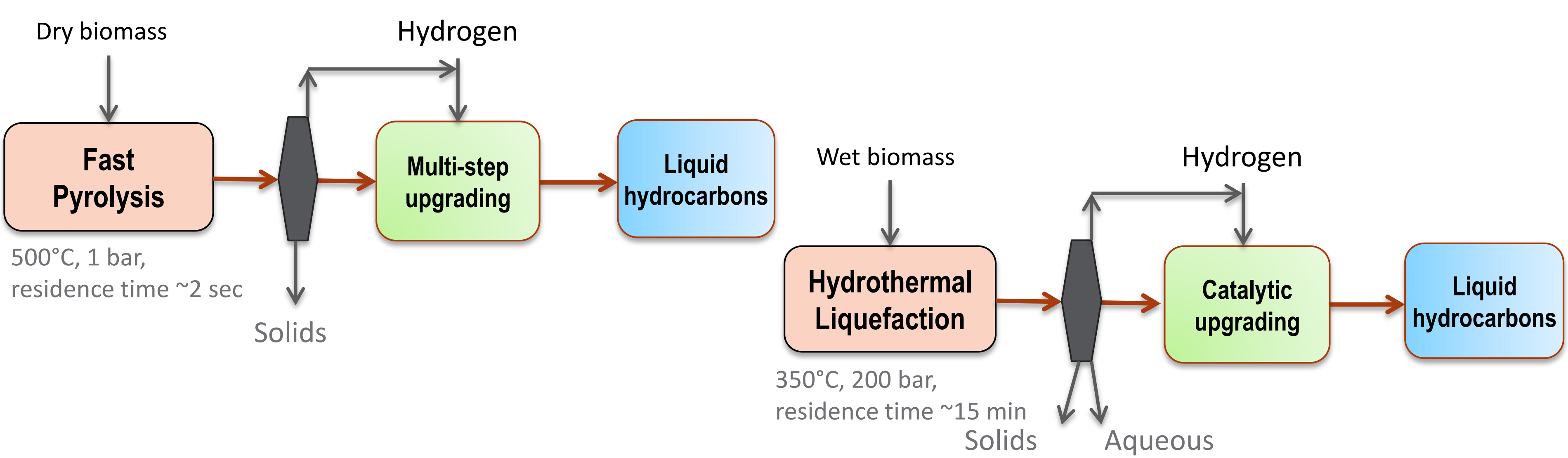
- Biomass liquefaction and product upgrading
- New developments in hydrothermal liquefaction
- Model development
- Comparison and evaluation of results



Comparative Energy Balances

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Fast Pyrolysis Energy Flows, LHV, MW	IN	OUT
Feedstock	387.5	
Power	27.0	
Gasoline		139.4
Diesel		55.5
Heavy hydrocarbon		30.5
Heat loss		189.1
TOTAL	414.5	414.5

HTL Energy Flows, LHV, MW	IN	OUT
Feedstock	387.5	
Power	23.7	
Gasoline		121.7
Diesel		97.6
Heavy Oil		36.8
Heat Loss		155.1
Total	411.2	411.2

Comparative Capital Costs

Fast Pyrolysis Process	PID	Installed	Uninstalled	
Feedstock Handling and Prep	A100	$ 21.4	$ 8.7	6%
Fast Pyrolysis	A100	$210.0	$ 61.9	59%
FP Oil Hydrotreating	A310	$ 76.3	$ 35.6	21%
Hydrogen Plant	A400	$ 41.1	$ 21.4	11%
Utilities	A700	$ 9.2	$ 3.2	3%
Total		$358.0	$130.8	100%

Hydrothermal Liquefaction Process	PID	Installed	Uninstalled	
Feedstock Handling and Prep	A100	$ 22.5	$ 9.8	9%
HTL Oil Production	A200	$150.8	$ 75.0	62%
Wastewater Treatment	A240	$ 22.0	$ 8.9	9%
HTL Crude Upgrading	A310	$ 21.6	$ 20.9	9%
Hydrogen Plant	A400	$ 19.5	$ 10.1	8%
Utilities	A700	$ 7.9	$ 1.0	3%
Total		$244.3	$125.7	100%

Comparison of Previous and Current Studies

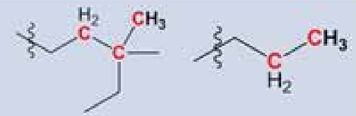
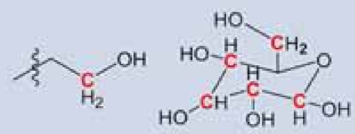
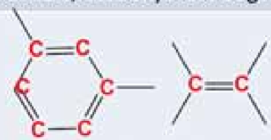
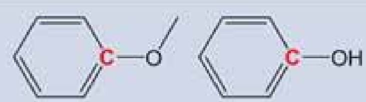
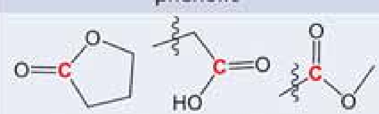
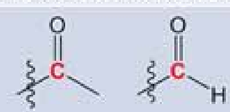
	IEA DBL Process Models[1]		Current Study	
	AFP Potential	LIPS Present	FP & Upgrade	HTL & HT
Total energy efficiency to product, LHV	52	41	50	57
Fixed Capital Investment, $M	AFP	AFP x 1.9	358	244
Product mass yield, % dry feed	25	23	24	27
Ratio of Product cost to value	1.2	2.0	1.2	0.8

Total energy efficiency assuming 40% conversion efficiency for $MW_{th} \rightarrow MW_e$

1 Beckman, D., et al. Techno-Economic Assessment of Selected Biomass Liquefaction Processes. Final Report of IEA Cooperative Project Direct Biomass Liquefaction. VTT Research Reports 697 Technical Research Centre of Finland, Espoo **1990**.

^{13}C NMR Analysis of HHO, Bio-oil, and HT Products

- Feed is raw bio-oil
- HHO #2 is home heating oil/#2
- MOx is moderately upgraded, while HOx is higher oxygen content, moderately upgraded
- Obvious changes through hydrodeoxygenation
- Significant residual aromatic content

Chemical Shift range (ppm)	Carbon assignment	Feed	MOx	HOx	HHO #2
0 – 53	 Short, long, and branched aliphatics	14.22	72.16	66.19	88.48
53 – 62	 Ethers, methoxy groups	3.25		1.01	
62 – 95	 Alcohols, carbohydrate sugars	27.46	0.33	3.31	
95 – 142	 Aromatic, olefins	22.54	18.17	19.04	11.01
142 - 170	 phenolic	15.3	3.43	4.04	0.51
170 – 190	 Carboxylics, ethers, lactones	8.56	1.96	2.98	
190 – 220	 Ketones, aldehydes	8.68	3.95	3.42	