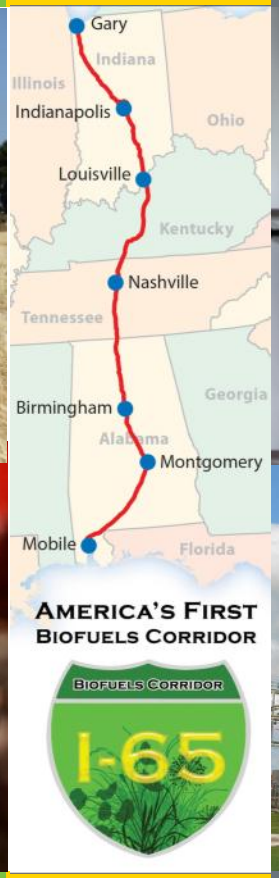
2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy



Production and Upgrading of Infrastructure Compatible Bio-Oil

3.2.2.26

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May 21, 2013

Technology Area Review: Bio-Oil

Organization: PNNL

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Goal/Objective Statement

Goal: Validate, in collaboration with an international process technology leader, an integrated conversion process for biomass to gasoline, diesel, or jet fuel by fast pyrolysis and hydrotreating.

Major Project Objectives:

- Process fast pyrolysis bio-oil using HT methods
- Analyze products and evaluate infrastructure compatibility
- Evaluate techno-economic assessment process model outputs based on input from process tests in HT bio-oil

PNNL will partner with the Technical Research Centre of Finland (VTT) in development of both the fuel production processes and the technoeconomic assessment of those processes.

Project Quad Chart Overview

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Timeline

- January 1st 2012
- February 28th 2015
- Percent complete 40%

Budget

- $1,500,000 ($1.2M + $300K Cost Share)
- $ 351,000 in FY 11
- $ 549,000 in FY 12
- $ 100,000 in FY 13
- $ 200,000 in FY 14

Funding Years FY 11 to 14

average DOE funding: $300K

Barriers

- Tt-E: Pyrolysis of Biomass and Bio-Oil Stabilization
- Tt-G: Fuel Synthesis and Upgrading – Pyrolysis
- Tt-K. Bio-oil Pathways Process Integration

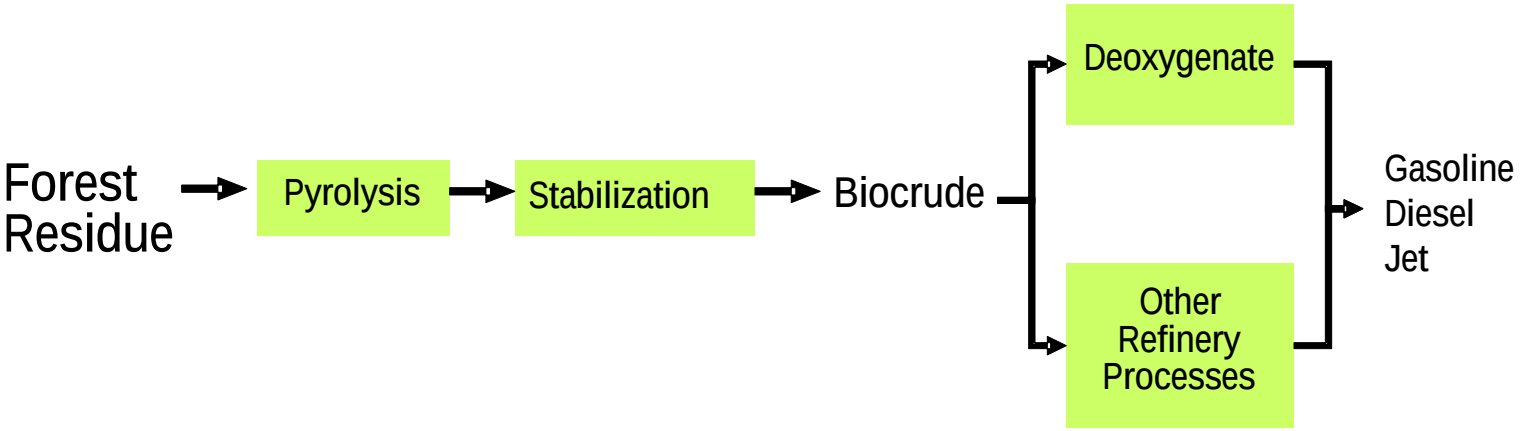
Partners & Roles

- VTT - Technical Research Centre of Finland

  Internationally known experts in biomass fast pyrolysis with laboratory and PDU units for production of bio-oil and documented skills in bio-oil analysis

Project Overview

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



- PNNL will conduct stabilization and upgrading tests on forest residue bio-oil produced by the international R&D leader, VTT, to produce a finished market ready fuel.
- Techno-Economic Analysis, TEA, of these processes will be conducted in this project.

1- Approach

- Leveraging PNNL and VTT long-established research partnership in pyrolysis oil stabilization and upgrading
  - VTT will be responsible for demonstration and PDU scale bio-oil production and delivery
  - PNNL's research will focus on the development of stabilized and fully upgraded finished fuels
- PNNL and VTT will jointly develop mass and energy (M&E) process models and economic analysis to demonstrate the economic viability of the liquefaction routes
- Project Monitoring:
  - International monthly conference calls, yearly in-person meetings
  - Analysis Task: international conference calls occur weekly
  - PNNL Team: weekly team updates and in-person meetings

Project Tasks and Results to Date:

Task A – Hydrotreating Bench-Scale Experimental Evaluation:

- **Low-severity stabilization**
- **HT experiments on improved bio-oils**

Task B – Techno-Economic Analysis:

- **Development of HT model for VTT Fast Pyrolysis (FP) TEA**
- **Economic comparison underway of complete HydroThermal Liquefaction (HTL) and FP and HT models**

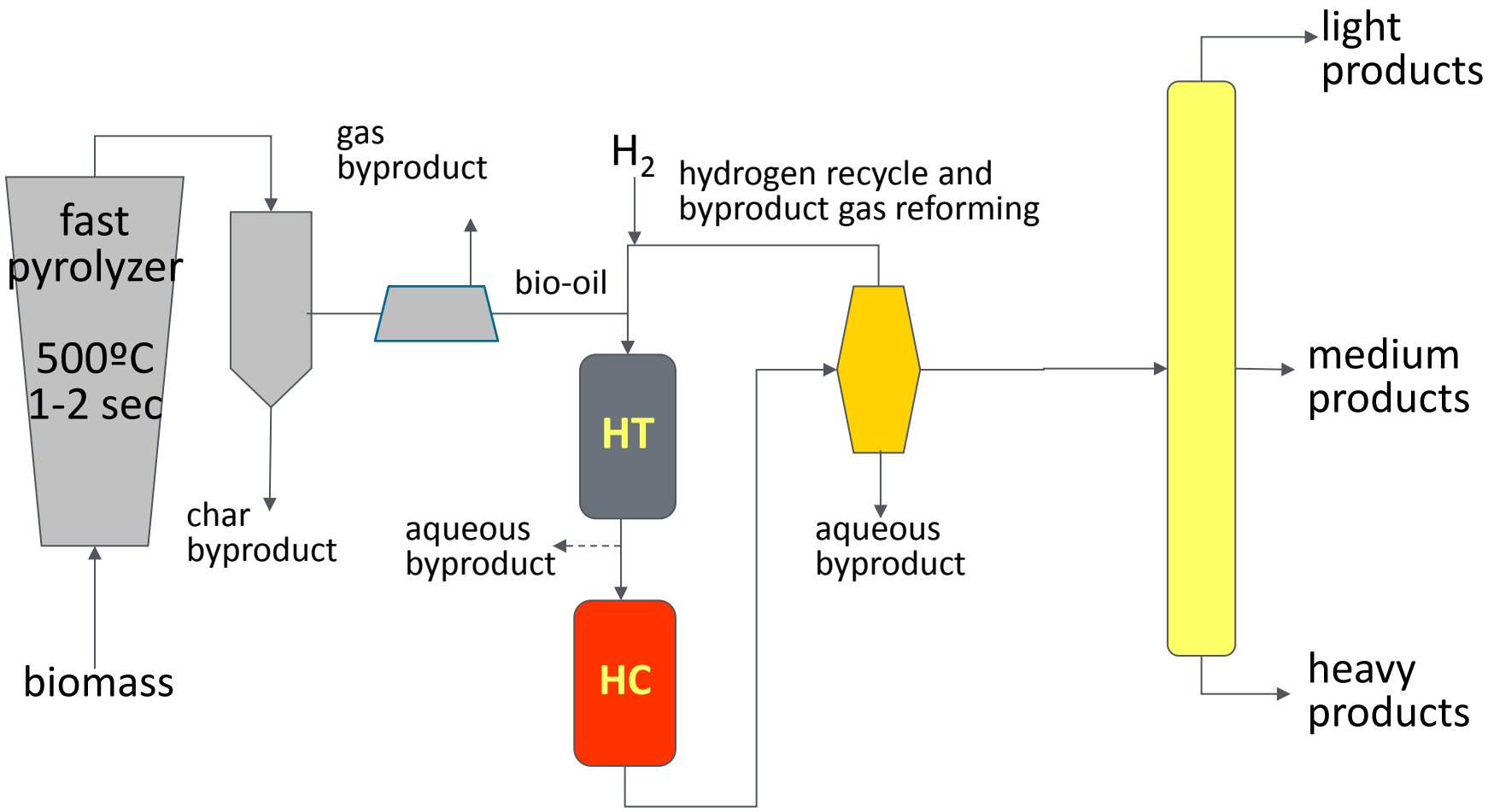
Task C – Life Cycle Assessment :

- Start FY 13 Q4 continued into FY 14

Task D – Working Meetings:

- Successful completion of project kickoff in August 2012 (Helsinki, FI)
- Working meeting at PNNL (10/12)
- Monthly conference calls

Hydrotreating of Fast Pyrolysis Bio-Oil



- Low Severity HT Tests

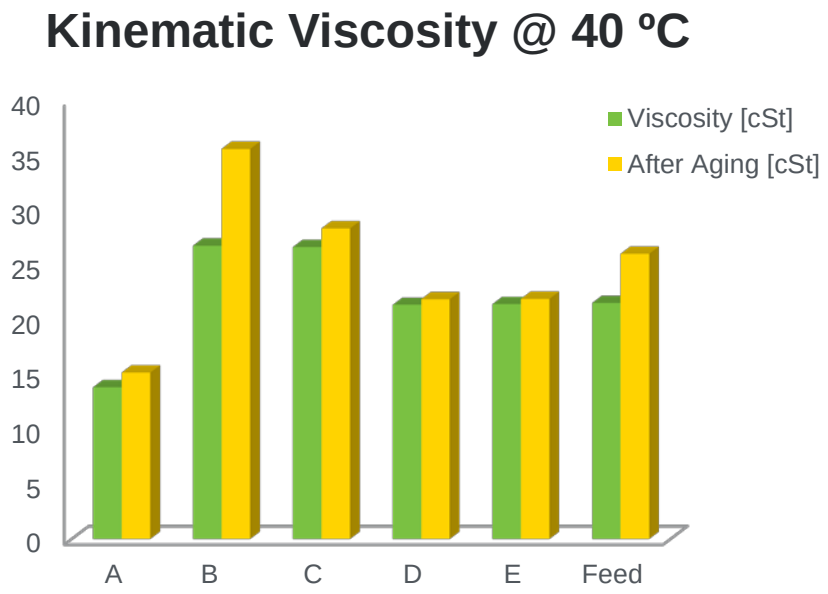
  (HT 177 and HT 181)

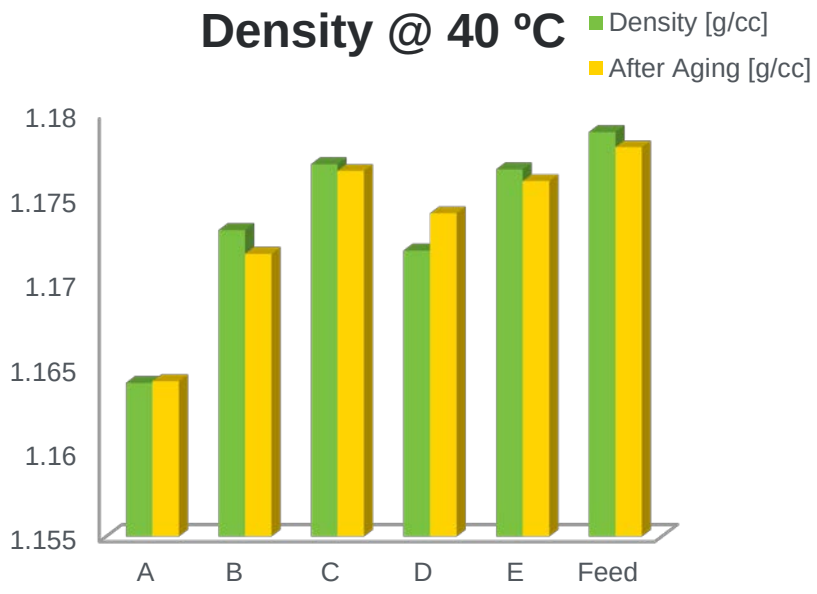
  – Run conditions matrix:
    - Temperature: 80 ºC, 90 ºC
    - Pressure: 1200 psig, 900 psig
    - H_2 flow rate: 25 L/h, 50 L/h
    - Bio-oil flow rate: 200 mL/h, 300 mL/h
    - Samples were collected every 2 h and upon change of conditions
  – Elemental analysis, water content, NMR, and accelerated aging tests (24h @ 80 ºC) were conducted on the collected product.

PNNL bench-scale, continuous-flow, fixed-bed, catalytic hydrotreater

Marginal change is seen in density and viscosity between the feed bio-oil and various products

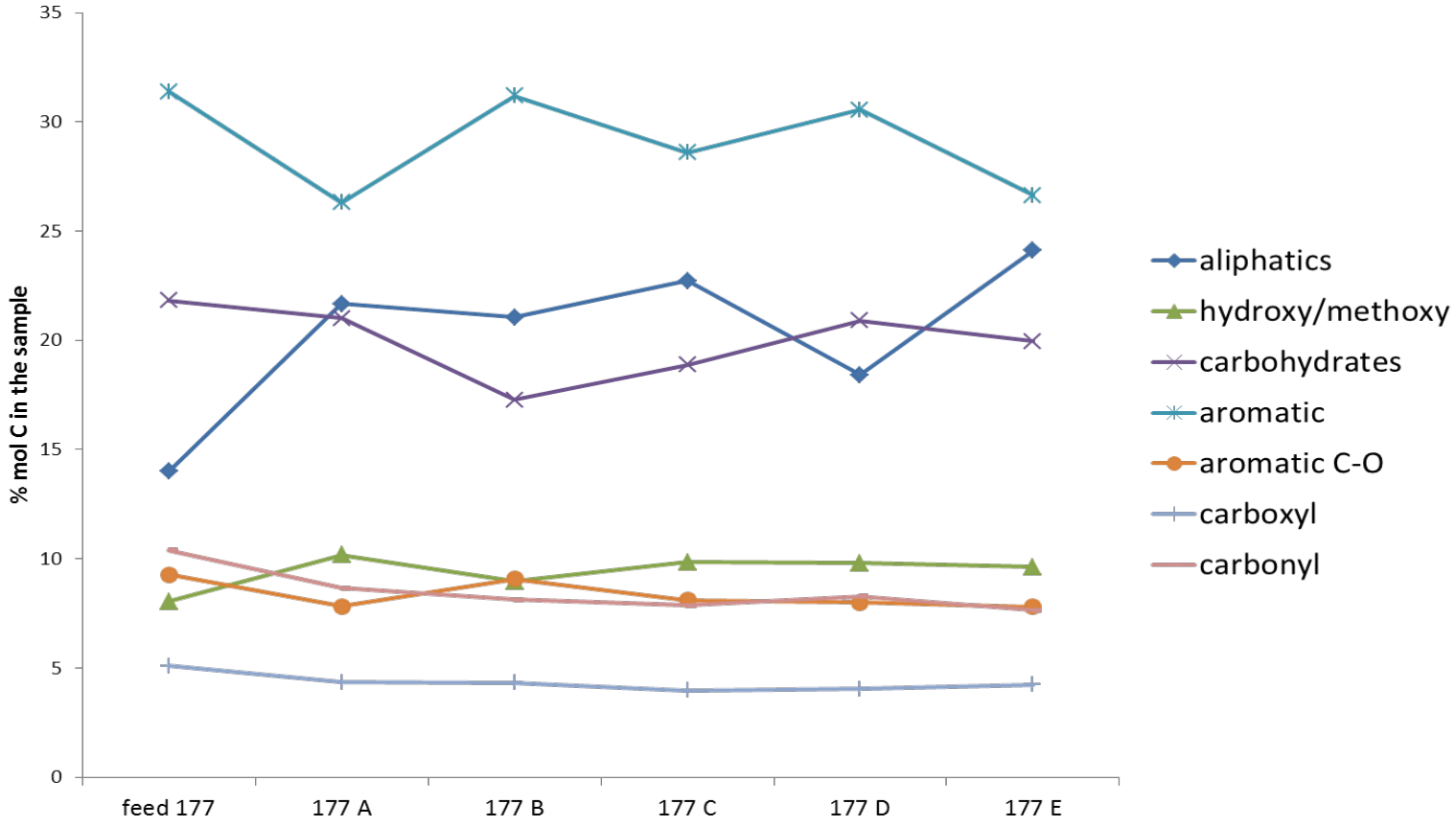
standard aging test of 24h @ 80 ºC





NMR studies were conducted for further proof of change in the product

^{13}C NMR Results in Low-Severity HT



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

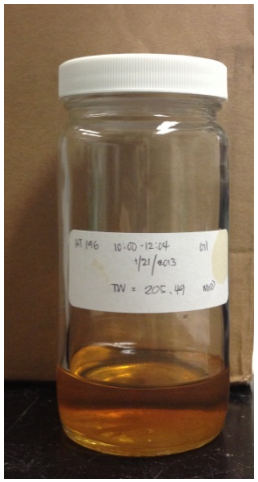
- Little to no change was seen in HT 177
  - Reason: Bio-oil used was produced at the VTT/Metso Pilot Plant and was treated with addition of isopropyl alcohol (IPA)
  - IPA as a solvent stabilizes the raw pyrolysis bio-oil and therefore no change is seen at the lower severity hydrotreating conditions.

- Replacement bio-oil was received from VTT and processed under same conditions (HT 181):
  - Again, no change was seen in the accelerated aging tests conducted on the feed and products
  - Apparently, due to uncontrolled temperature in shipping this bio-oil was stabilized (aged) as-received at PNNL

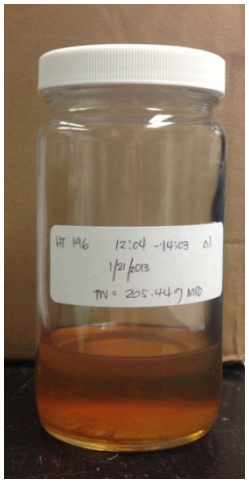
Hydrotreating VTT improved bio-oil (HT 195)

- 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

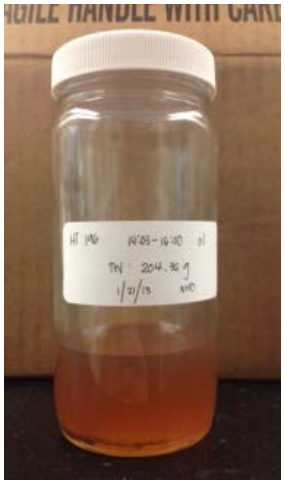
Fractionated bio-oil HT processing – 2nd attempt (HT196)



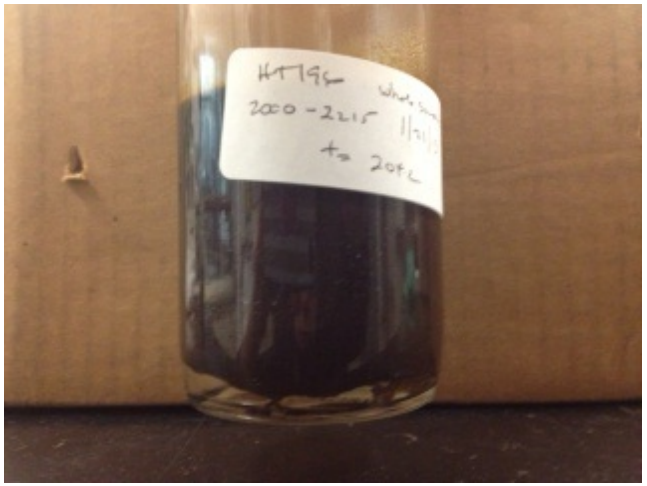
HT 196 1000-1204



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 (HT 195, HT 916)

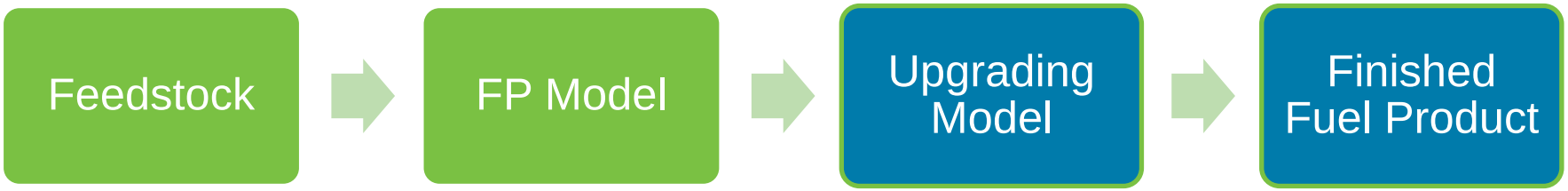
Oil sample	C	H	O	moisture	density	TAN	viscosity
	wt%			wt%	g/mL	mg KOH/g	cSt@40C
feed	53.2	6.9	35.3	6.1	1.24	132	529
HT195	83.4	12.8	1.3	<0.01	0.80	<0.01	1.1
HT196 early	84.8	11.8	1.6	0.04	0.84	<0.1	1.3
HT196 late	84.9	11.2	2.0	0.04	0.87	<0.1	1.7

- Hydrogen consumption and oil product yield relatively high

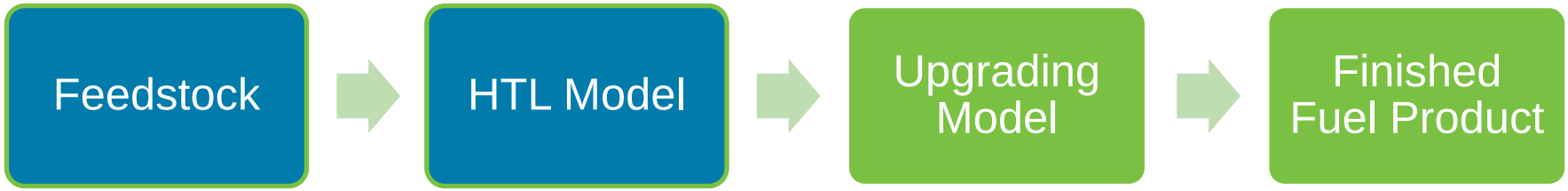
Techno-economic Analysis (TEA) Task B:

- Task Purpose:
  - Develop mass and energy models for techno-economic analysis to help inform on the economics of researched liquefaction routes
  - Liquefaction routes to be evaluated: Fast Pyrolysis (FP), Hydrothermal Liquefaction (HTL) and all subsequently followed by Hydrotreating
- Work to Date:
  - Aspen Plus models for HTL and FP developed previously by PNNL and VTT were identified as the basis for new modeling efforts
  - Criteria, assumptions, and modeling techniques for future model development was identified such that all model comparisons are on similar basis
  - Feedstock composition and user defined compounds were input

FP + Upgrading Model



HTL + Upgrading Model



Blue: TEA modules to be developed with major modifications and re-design

Green: TEA modules already available with minor changes and modifications

- FY 13 major changes modeling accomplishments:
  - HT module design for the Fast Pyrolysis case developed by VTT
  - Feedstock upgrade in the HTL model
- FY 13: both model routes and economics will be complete and presented at TC Biomass 2013.

2 – Project Milestones/ Deliverables

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Number	Title	Completion	Status
A	**HT Experimental Evaluation**		
A.1.ML.1	Low Severity HT Run	31-Dec-12	Complete
A.1.ML.2	First “improved” Bio-oil HT Run	31-Mar-13	Complete
A.1.DL.1	First Round Analysis Report	30-Sep-13	In Progress
B	**Techno-economic Analysis**		
B.ML.1	HTL and Fast Pyrolysis Model modifications for comparison	30-Jun-13	In progress
B.ML.2	E&M Balances and Preliminary Sensitivities	30-Sep-13	In progress
D	**Working Meetings**		
D.ML.2	Working Meeting VTT	30-Sep-12	Completed
D.ML.3	Working Meeting PNNL	30-Sep-13	Planned

3 - 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
- The inclusion of a leader in the technology development as a partner insures leading edge R&D
- The participation of industrial partners in the review of task activities validates to 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-E: Pyrolysis of Biomass and Bio-Oil Stabilization
- Tt-G. Fuel Synthesis and Upgrading
- Tt-K. Bio-oil Pathways Process Integration

4 - Critical Success Factors

- Successful HT experiments can depend on the processed oil received. VTT provides bio-oil of several grades for HT tests at PNNL
- Establishing sets of criteria upon which TEA models are developed can be challenging considering international partners needs
- Long distance collaborations with a large time difference is a challenge but one that can be overcome through consistent online and phone meetings and alternating in-person working meetings
- Strong connection to industrial leaders in bio-oil production
  - Yrjo Solantausta and Jani Lehto (formerly Metso) from VTT in Finland
  - Consortium of Metso, UPM, Fortum, and VTT
    - Building a commercial biomass fast pyrolysis plant, operating a scaled-up demonstration plant

5. Future Work

- Further upgrading campaigns on improved VTT bio-oils, scale-up runs
- Finish HTL and FP with upgrading TEA models
- Develop TEA model and analysis for Catalytic Fast Pyrolysis
- Conduct Life Cycle Assessment on all TEA models developed
- Hydrotreating of other “improved” bio-oils

ML or DL or Go/No Go	Description	FY13 Q3	FY13 Q4	FY14 Q1	FY14 Q2	FY14 Q3	FY14 Q4	FY15 Q1	FY15 Q2	FY15 Q3	FY15 Q4
B.ML.1	HTL and Fast Pyrolysis Model modifications for comparison										
A.1.DL.1	First Round Analysis Report										
B.ML.2	E&M Balances and Preliminary Sensitivities										
D.ML.3	Working Meeting PNNL										
A.1.ML.1	Bench scale process optimization										
B.ML.3	Complete Economic Assessment of Comparison										
C.ML.1	Model updates to SimaPro										
A.1.ML.2	Bench-scale testing improved bio-oil										
A.2.ML.1	Scale-up testing of stabilized pyrolysis bio-oil										
B.ML.4	Low Severity Sensitivity Model										
C.ML.2	Complete collection of data and integration into model										
C.ML.3	Complete GHG assessment and uncertainty analysis										
A.1.ML.3	Bench-scale testing of catalytic pyrolysis bio-oil										
A.1.DL.2	Second Round Analysis Report										
C.DL.1	Publish LCA in final report										
D.ML.4	Final Working Meeting										
D.DL.1	Working Meeting Minutes in Final Report										
A.2.ML.2	Extended Scaled-up testing of pyrolysis bio-oil										
A.DL.1	Final Report										
D.ML.1	Planning of working meetings										

Summary

Relevance: Supports the Bioenergy Technologies Office's Multi Year Program Plan (MYPP)

Approach: Both process testing and modeling are being used to identify and resolve barriers to direct liquefaction of biomass

Hydrotreating of bio-oil can be a useful route to infrastructure compatible fuels

PNNL has partnered with VTT to bring the strengths of each to bear on the development issues for such processing

Success factors and challenges: Successful HT experiments can depend on the processed oil received. VTT provides bio-oil of several grades for HT tests at PNNL

Technology transfer and future work: Scale-up of the processing options is planned

This project is a successful outgrowth of the Core Pyrolysis project presented at the 2011 Platform Review

Additional Slides

Responses to Previous Reviewers' Comments

In the previous 2011 peer review the PNNL-VTT collaboration was included as a part of the Core Pyrolysis project 3.2.2.4.

A separate project was initiated since that time, at least in part, because of the positive reviewer comments relative to the interaction—as related below:

"The PIs are working with leading international labs, industry and different national industries which is really important. The whole conversion chain is addressed which is appreciated."

"Excellent collaboration with labs and industry partners, and international partner VTT."

Publications and Presentations

- 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.

5 – Project Milestones - Future

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Number	Title	Completion	Status
A	**HT Experimental Evaluation**	**28-Feb-15**	
A.1.ML.1	Bench scale process optimization	31-Dec-13	
A.1.ML.2	Bench-scale testing improved bio-oil	30-Apr-14	
A.1.ML.3	Bench-scale testing of catalytic pyrolysis bio-oil	30-Sep-14	
A.2.ML.1	Scale-up testing of stabilized pyrolysis bio-oil	30-Jun-14	
A.2.ML.2	Extended Scaled-up testing of pyrolysis bio-oil	31-Dec-14	
B	**Techno-economic Analysis**	**28-Feb-15**	
B.ML.3	Complete Economic Assessment of Comparison	31-Dec-13	
B.ML.4	Low-Severity HT Sensitivity Model	30-Jun-14	

5 – Project Milestones

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Number	Title	Completion	Status
C	**Life Cycle Assessment**	**28-Feb-15**	
C.ML.1	Model updates to SimaPro	30-Jan-14	
C.ML.2	Complete collection of data and integration into model	1-Apr-14	
C.ML.3	Complete GHG assessment and uncertainty analysis	30-Jun-14	
D	**Working Meeting**	**28-Feb-15**	
D.ML.1	Planning of working meetings	30-Jan-15	
D.ML.4	Final Working Meeting	30-Sep-14	