2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review

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

3.2.2.31-Improved Hydrothermal Liquefaction Bio-Oil Production

May 23, 2013

Principal Investigators:
Richard Hallen and Tanner Schaub

Technology Area Review: Bio-Oil Technology Area

Organizations: PNNL/NMSU
Presented by: Karl O. Albrecht

Goal/Objective Statement

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

- Develop a detailed understanding of the effect of key process parameters impacting the quality and yield of hydrothermal liquefaction (HTL) bio-oil
- Key process parameters for HTL include:
  - **Process configuration** (stirred tank, plug flow reactor)
  - **Conditions** (Temperature, residence time)
  - **Feedstock** (Wood, corn stover, etc.)
- Advanced characterization techniques will enable fundamental chemical research leading to optimization of HTL bio-oil yield and upgraded products, and facilitate overall plant operability
- Evaluate the impact of improved hydrothermal liquefaction (HTL) processing schemes on overall hydrocarbon fuel production costs.

Project Quad Chart Overview

Timeline

- Project start date
  - November 2012
- Project end date
  - September 2015
- 17% complete

Barriers

- Barriers addressed:
  - Tt-B. Feeding or Drying Wet Biomass
  - Tt-E. Liquefaction of Biomass and Bio-Oil Stabilization
  - Tt-G. Fuel Synthesis and Upgrading

Budget

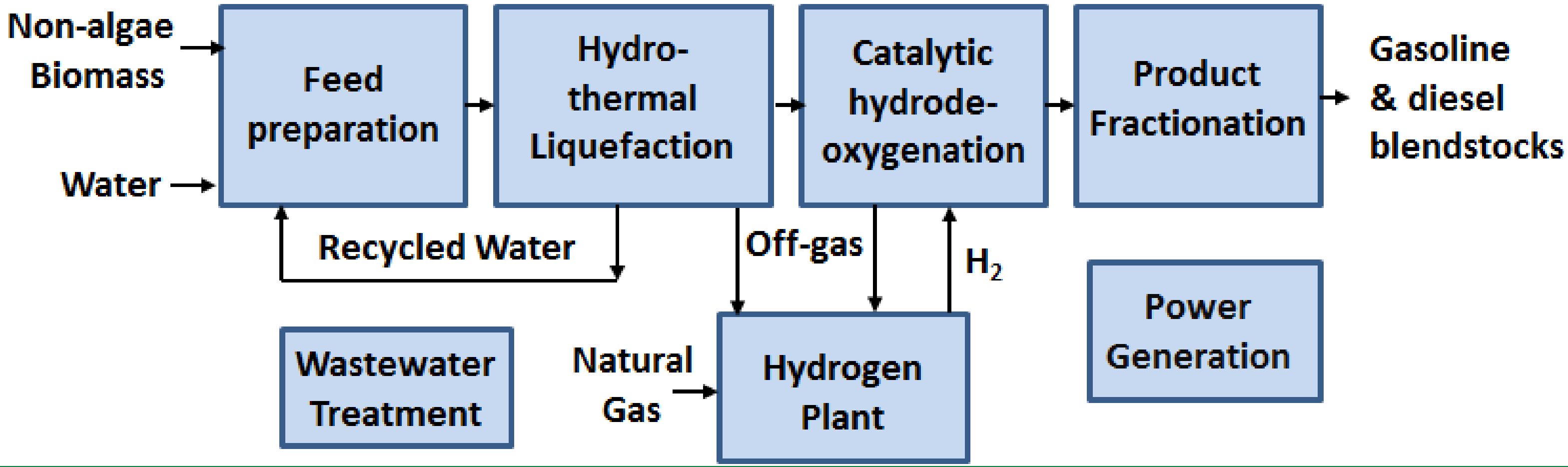
- FY 2013 new start
- Funding for FY13 = $200k

Partners

- New Mexico State University
  - Tanner M. Schaub (co-P.I.)
  - Nilusha Sudasinghe
- Project management
  - Richard T. Hallen, PNNL

Project Overview

- Provide fundamental understanding of HTL bio-oil production, specifically examining improved yield (carbon yield to bio-oil) and bio-oil quality.
- HTL bio-oil production varies with feedstock, processing conditions, and system design changes and impacts bio-oil production and quality.
- PNNL has continuous feed HTL systems with various reactor configurations for producing bio-oils from a wide range of feedstocks for study.
- Deploy state of the art analytical technique, Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR-MS), to understand the fundamental nature of chemical and physical property changes based upon process parameters.



1 - Approach

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

- Obtain HTL bio-oil samples for a range of feedstocks and processing conditions which provide various chemical and physical properties. HTL is relatively feedstock agnostic, demonstrated as part of the NABC, but the quality of the bio-oil product can change dramatically with feedstock

- Use state-of-the-art technology (FT-ICR-MS) to understand the differences in elemental and molecular weight distribution of bio-oil components as a function of feedstock and process parameters – includes low concentration components difficult to evaluate with complimentary techniques (e.g. NMR, GC/MS)

- Develop correlations of bio-oil properties with HTL process parameters for optimization and improvement in upgradability or direct refinery insertion

- Management Approach – Approved Project Management Plan
  - Regular Milestones (1/Quarter) and Deliverables
  - Go/No Go in Q2 FY14 to asses the FT-ICR MS analysis and HTL processes optimization

2 - Technical Accomplishments / Progress / Results

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

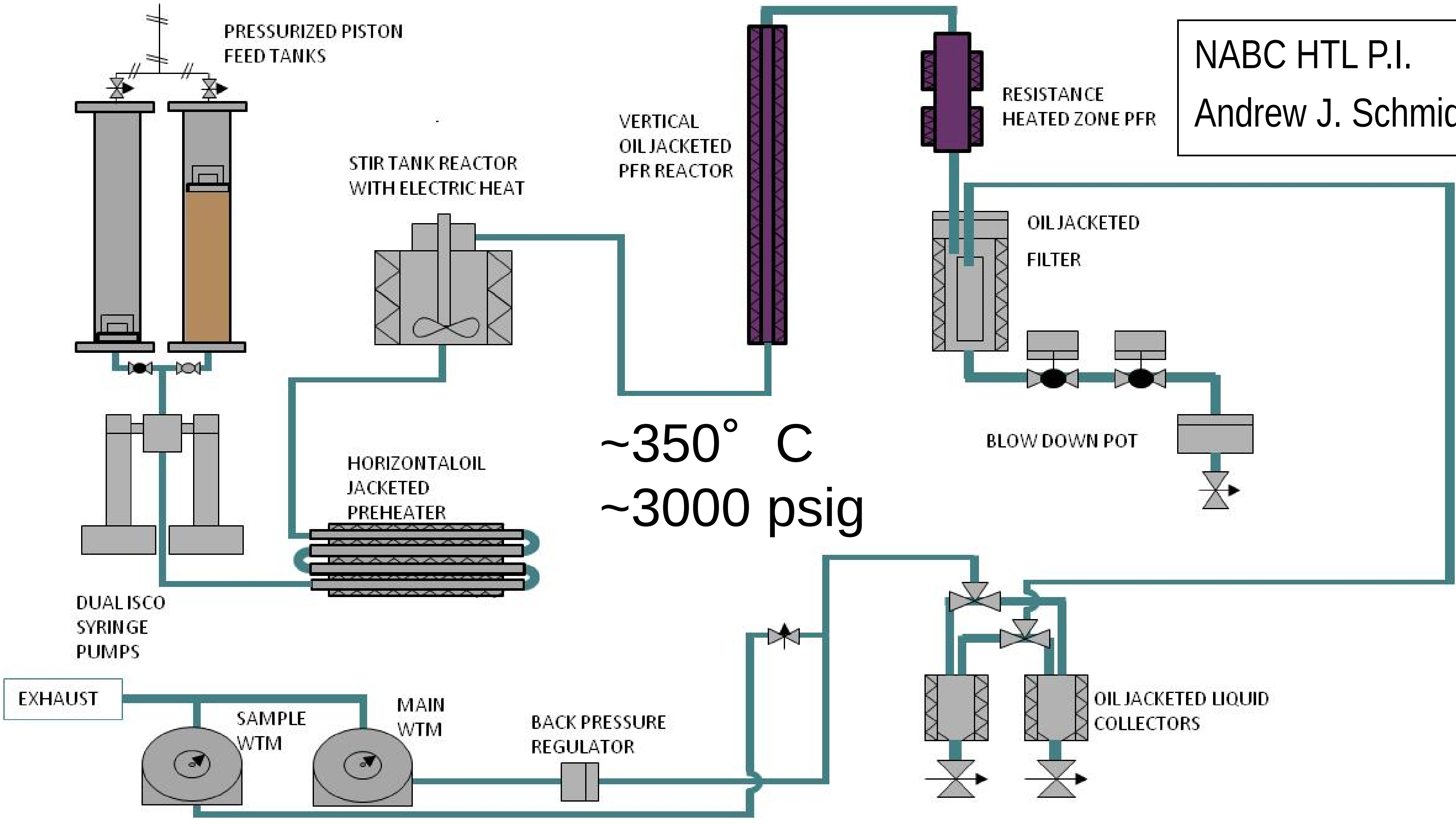
Milestone	Planned Completion Date	Completion
Subcontract issued to Professor Tanner Schaub at NMSU for FT-ICR-MS characterization of HTL bio-oil samples	31 Dec, 2012	✓
Provide baseline samples of HTL bio-oil from various feedstocks and process conditions to NMSU for evaluation, characterization	31 Mar, 2013	✓
HTL bio-oil characterization initiated at NMSU	30 Apr, 2013	✓
Characterization complete for initial feedstocks	30 June, 2013	Underway
Characterize HTL bio-oils generated in various reactor configurations	30 Sept, 2013	On schedule

PNNL Continuous Feed HTL System for Bio-oil Production

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

Continuous Bench Scale HTL Hybrid Reactor System Developed under NABC

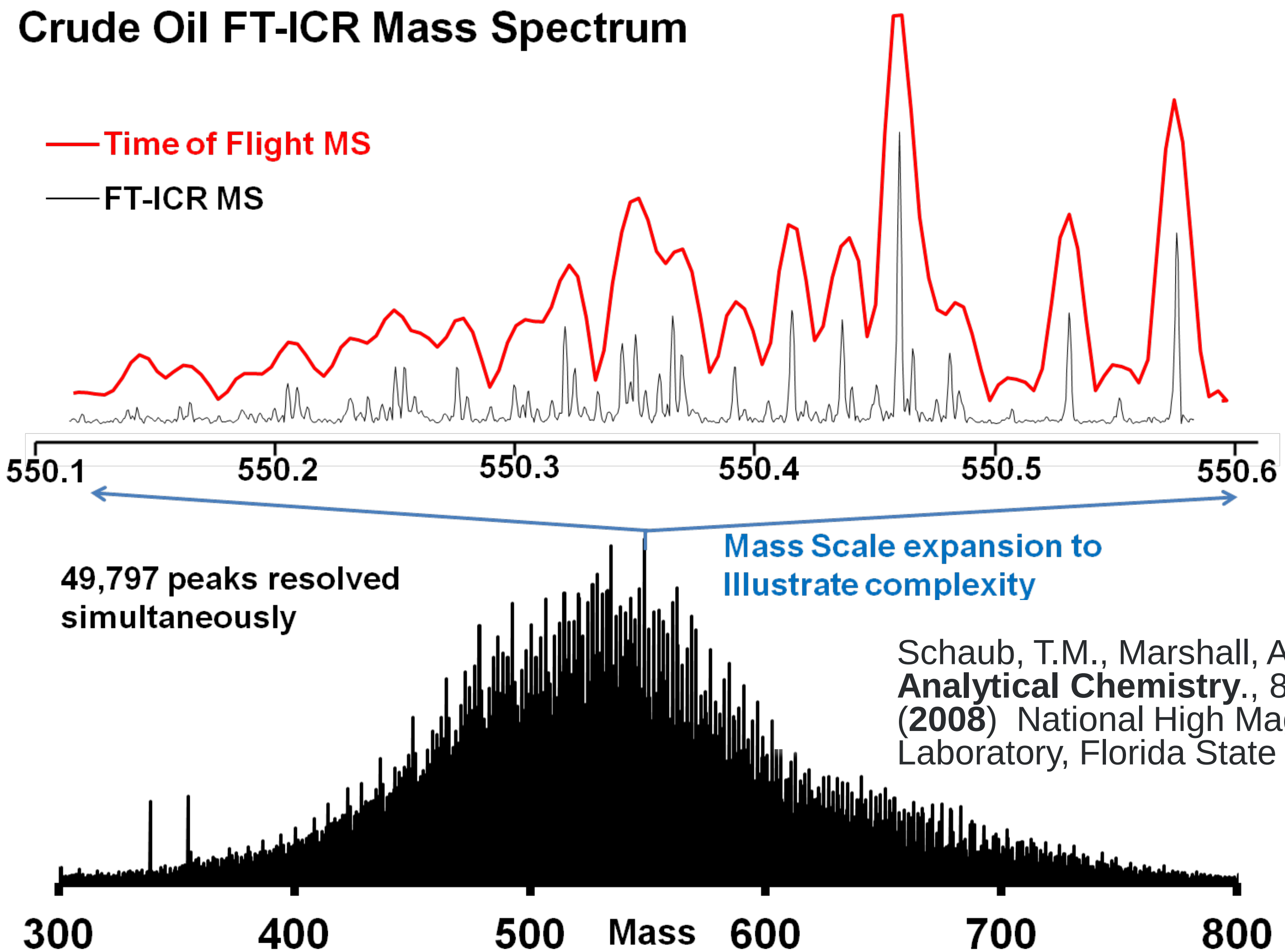
NABC HTL P.I.
Andrew J. Schmidt



Continuous feed system with various engineering options

Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR-MS)

Features of FT-ICR that are absolutely critical for complex mixture analysis 1) resolving power (resolution) and 2) mass measurement accuracy – hundreds of ppb (4th-5th decimal place)



Schaub, T.M., Marshall, A.G. et. al, **Analytical Chemistry**., 80, 3985-3990. (**2008**) National High Magnetic Field Laboratory, Florida State University

NMSU has experience characterizing many petroleum and bio-oil samples

Initial HTL Bio-oil Samples Provided to NMSU for Characterization

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

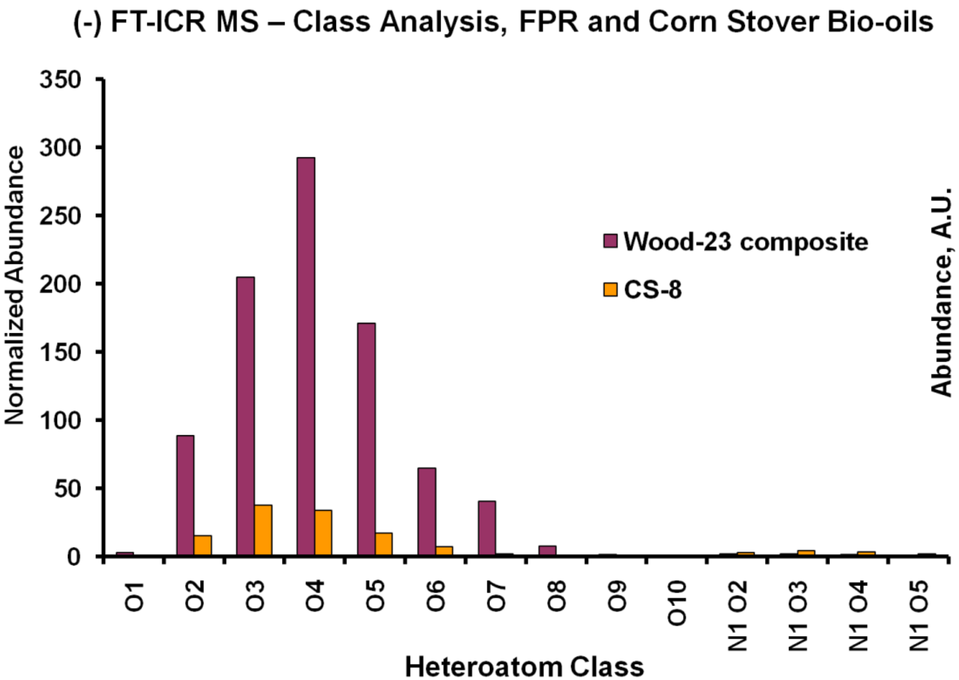
Sample ID	Matrix	Approx Mass, g	Date	Descriptions
Wood 23 composite	**HTL Bio-oil**	**10**	**2/4/13**	Composite for all of Wood 23, representative of 3-L sent for upgrading -- **Baseline**
CS-5/7	**HTL Bio-oil**	**10**	**8/20/2012**	HTL Bio-oil from **Cornstover**, single pass, composite of 2 runs at same operating condition
CS-8	**HTL Bio-oil**	**10**	**11/15/12**	HTL of **Cornstover**, feed prepared with aqueous phase from CS-5/7 (**recycle test**)
Wood-18	**HTL Bio-oil**	**10**	**6/4/12**	HTL of **forest product residual (FPR) pine**, single pass.
Wood-22	**HTL Bio-oil**	**10**	**12/6/12**	HTL of FPR, single pass, HTL conditions were same as Wood 18 **(reproducibility)**
Wood-21	**HTL Bio-oil**	**10**	11/2/12	HTL of FPR, **lower severity conditions,** single pass.
Wood 23A	**HTL Bio-oil**	**10**	**1/29/13**	HTL of FPR, **aqueous phase recycle, 1X**
Wood 23B	**HTL Bio-oil**	**10**	**2/4/13**	HTL of FPR, **aqueous phase recycle, 2X**
HT-130221 a3	**Hydro-treated bio-oil**	**2**	**2-22-13**	**Mildly upgraded bio-oil** from Wood 22. Sample was dried by RT Hallen on 3-22-13

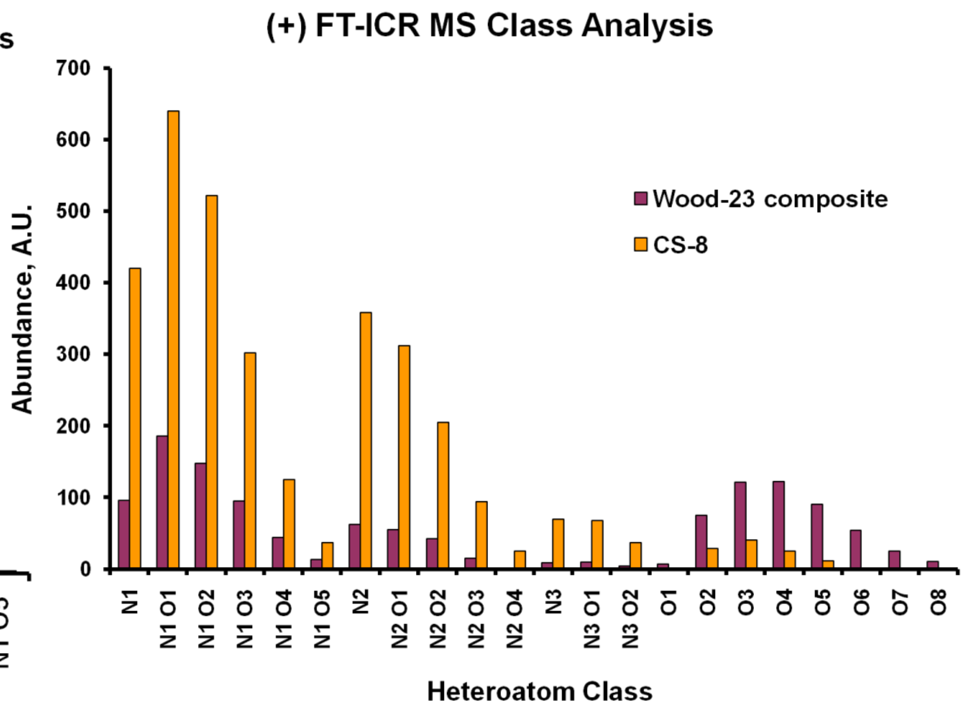
Broad range of HTL samples including various feedstocks, reactor configurations, and a mild hydrotreated sample provided to NMSU

Initial Feedstock Comparison: Compound Class Analysis

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

Negative (-) and positive (+) ion mode data are used to assign elemental composition (~10K compounds), then compounds are sorted by class for comparison





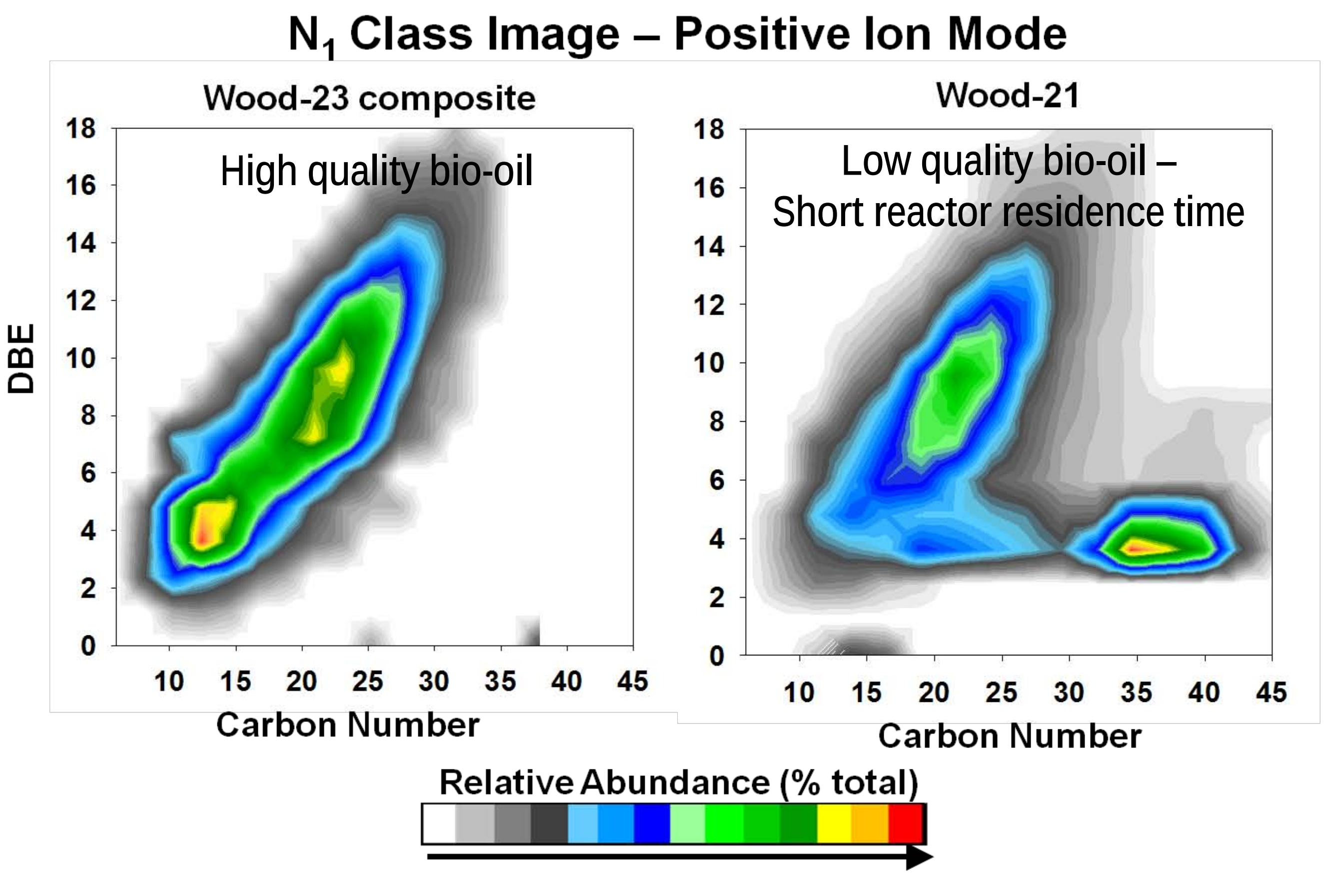
Each ionization mode highlights different classes of compounds

Corn stover feedstock contains higher nitrogen levels and more nitrogen is incorporated into the bio-oil. Nitrogen is a concern for upgrading and refinery insertion as acid sites on hydrocracking catalysts can be poisoned by nitrogen compounds.

Initial Process Severity Comparison: Deep Dive into Specific Class

For each compound class, such as N1 shown below, carbon number and double bond equivalence can be compared for various process conditions.

DBE = number of molecular rings and/or double bonds

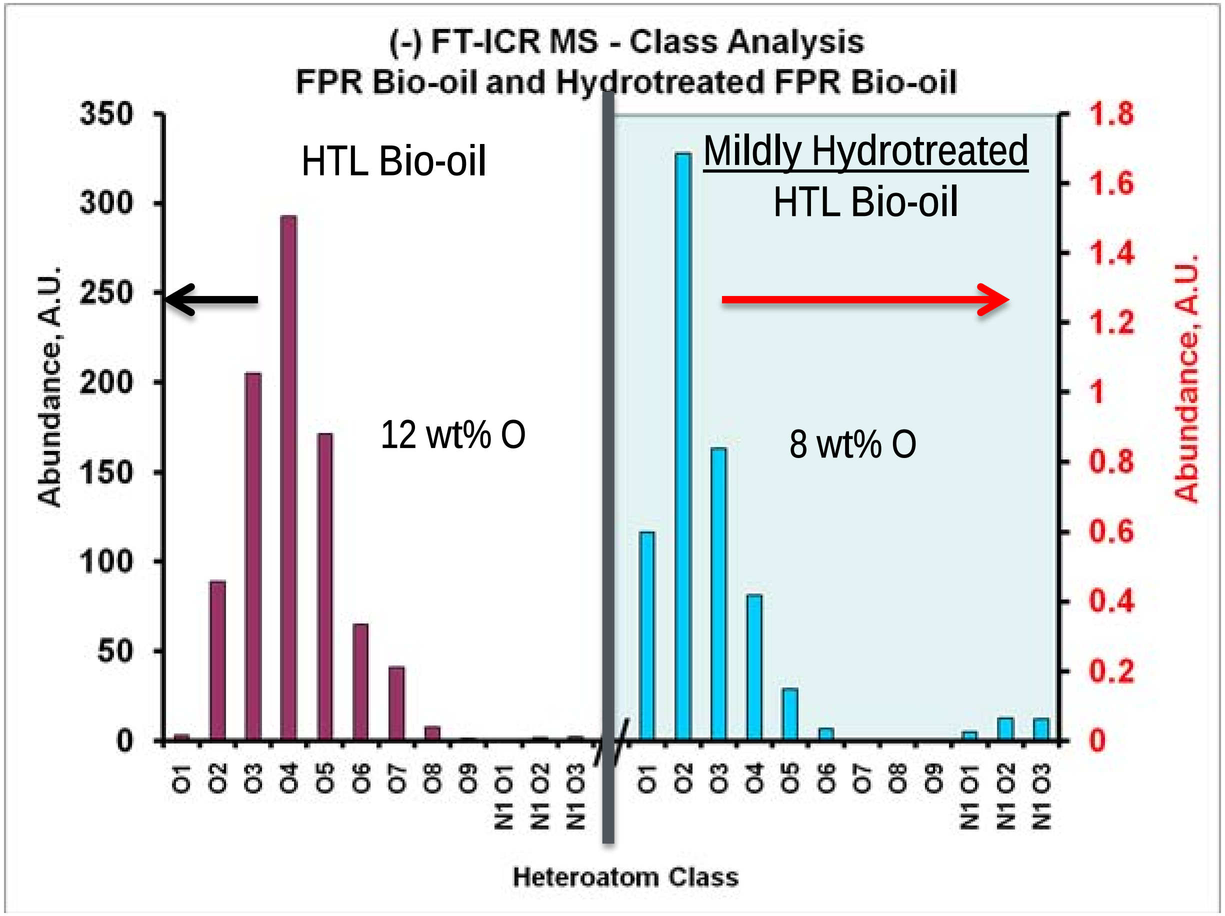


Wood-21 sample showed a class of compounds with high carbon number but low DBE, uncharacteristic of the higher quality Wood-23 composite sample

Expanding Comparisons to Upgrading: Answer Important Refinery Questions

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

Bio-oil upgrading for direct refinery insertion is an important pathway to drop-in transportation fuels. Key questions: 1) How much upgrading is needed? 2) What are the remaining oxygen and nitrogen compounds.



Mild hydrotreating of HTL bio-oil reduced the oxygenated compounds signal by 200 fold as well as shift to lower total oxygen number.

3 - Relevance

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

Project relevance to Bioenergy Technologies Office goals:

- *"The Bio-Oil Pathways R&D strategic goal is to develop commercially viable technologies for converting biomass feedstocks into energy dense, fungible liquid fuels, such as renewable gasoline, jet fuel, and diesel, bioproducts and chemical intermediates, and bioenergy."– 2012* MYPP

MYPP Barriers addressed:

- Tt-B. Feeding or Drying Wet Biomass
- Tt-E. Liquefaction of Biomass and Bio-Oil Stabilization
- Tt-G. Fuel Synthesis and Upgrading

MYPP Tasks supported:

- R 3.6.1.4.M.1 : Cost, energy and atom efficiencies of new concepts presented as needed on a comparable basis. 2013: Updated. 2015: Updated.

Applications of the expected outputs from this project:

- Further the understanding of constituents present in HTL derived bio-oil for project optimization and for BETO programmatic economic analyses
- Production of a raw HTL bio-oil of improved stability relative to raw fast pyrolysis oil through understanding of the molecular species present in order to enable process control and ultimately assign quality.

4 - Critical Success Factors and Challenges

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

Critical success factors which will define technical and commercial viability:

1. Improve the overall carbon liquid fuel yield and reduce subsequent upgrading processing costs by understanding HTL derived Bio-oil constituents and correlating them to processing parameters.
2. Reduce H_2 requirements for bio-oil hydrotreating through process optimization which improve HTL bio-oil quality and improve upgrading to fuel blendstock or direct refinery insertion.
3. Develop a correlation between feedstock components and HTL Bio-oil quality to enable low cost blended feedstocks.

Potential challenges to overcome in order to achieve successful project results:

1. Ability to provide a sufficiently broad parametric sweep of process conditions and feedstocks.
2. Establish key classes of compounds for focused analysis.

Hydrothermal liquefaction of biomass is demonstrating traction, as denoted by its progress in NABC. Understanding of the species present in this bio-oil will be critical in comparing to other technologies and for integration into refineries and markets.

5 - Future Work

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

ML, 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
ML	Complete characterization of baseline samples.	■	■								
DL	Annual Report and Manuscript Preparation		■								
ML	Develop correlations of bio-oil properties to compound class and product distributions, including DBE and carbon number.		■	■	■						
ML	Expand bio-oil sample characterization to other feedstocks, process parameters, and upgraded bio-oils products.			■	■	■	■				
Go/No Go	Decision point to continue FT-ICR-MS characterization				← Go/No Go						
ML	Provide additional supporting chemical and physical analyses for development of data correlation (e.g. GCxGC MS; NMR)					■	■	■			
DL	Annual Report and Manuscript Preparation						■				
ML	Determine overall impact on economics and GHG, utilize process models, TEA, and LCA for implementing improved HTL conversion process and feedstocks.								■	■	■
DL	Final Report										■

Summary

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

1) Use advanced characterization techniques to study HTL bio-oils
    1) Expand fundamental understanding of bio-oil composition impact on properties to guide process and engineering improvements.
    2) Improve bio-oil yield and quality for wide range of feedstocks.
    3) Improved bio-oil for upgrading and refinery insertion.
2) Addresses Technical Barriers: *Tt-B, Tt-E, Tt-G*
3) Critical Success Factors
    1) Develop fundamental understanding of process to improve bio-oil yield.
    2) Correlate process and feedstock variations to bio-oil quality.
    3) Demonstrate impact on bio-oil upgrading and provide critical refinery data.
4) Future Work
    1) Characterize additional HTL bio-oil samples from a wide range of process conditions, engineering designs, and feedstocks.
    2) Extend characterization to upgraded HTL bio-oil samples.
    3) Correlate characterization to process improvements and demonstrate the impact on overall process performance, feedstock through fuel.

Additional Slides

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

Responses to Previous Reviewers' Comments

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

- This project is a new start in FY2013 and was not peer reviewed in FY2011