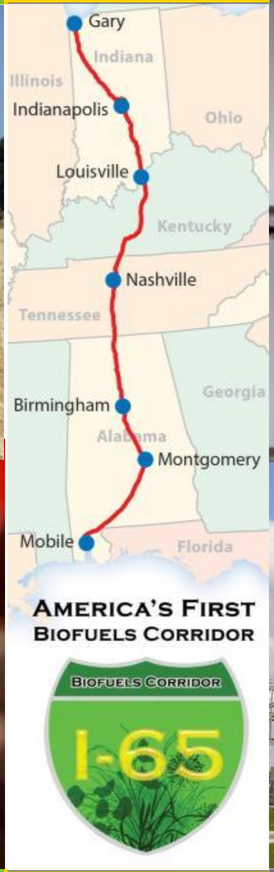
2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review

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




Pyrolysis Core R&D, Stabilized Oil Upgrading

May 21, 2013 Alan Zacher, Kristiina Iisa

Technology Area Review: Bio-oil Technology

Organizations: PNNL, NREL

PNNL-SA-95399

Goal Statement

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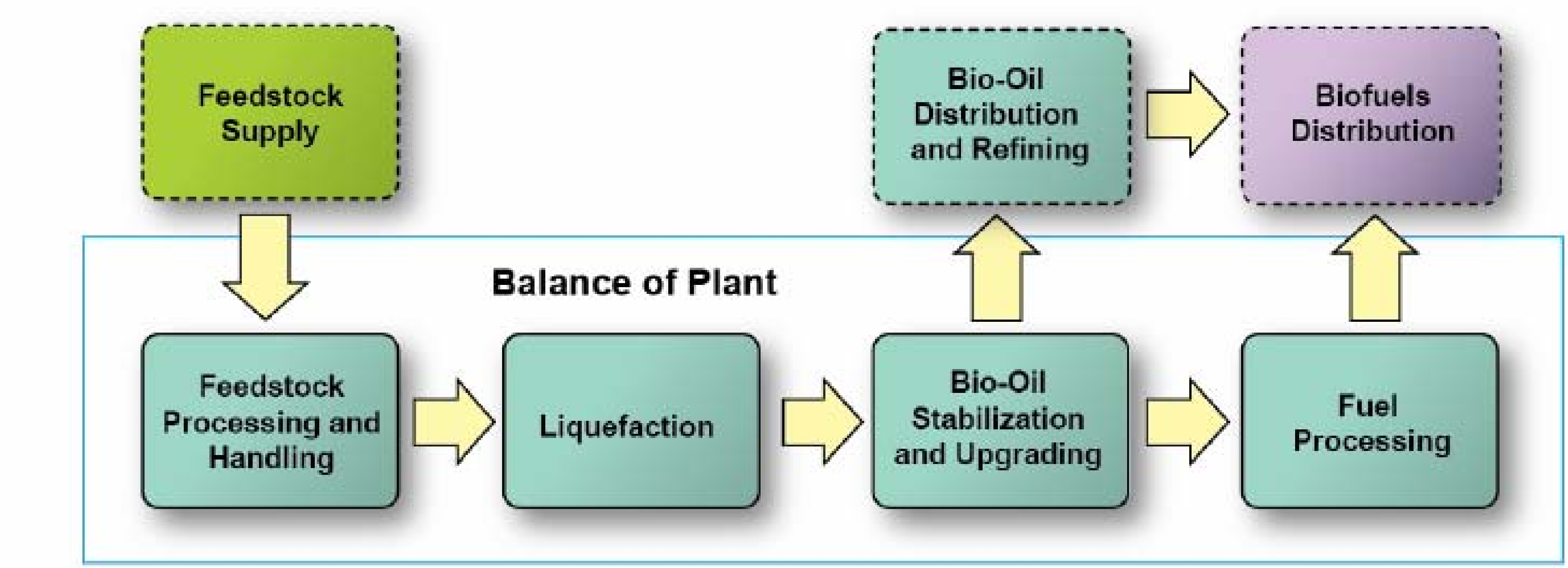
- Develop the science and engineering for production of liquid transportation fuels from biomass via pyrolysis (fast pyrolysis and catalytic pyrolysis) and bio-oil upgrading



Quad Chart Overview 3.2.2.4 /3.2.2.5/3.7.1.2

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Timeline

- Project start: October 1, 2006 (June 30, 2008)
- Project end: December 31, 2015
- Percent complete 75%

Budget

Total: PNNL $5.9M, (PNNL Equipment $5.4M), NREL $4.9M

DOE share: 100%

FY11: PNNL: $1M, ($1.65M), NREL: $1M

FY12: PNNL: $1M, ($850k) NREL: $1M

FY13: PNNL: $1M, ($850k)

Avg FY07 – FY13:

PNNL: $841k/yr,

(FY08-FY13 PNNL equipment: $1.07M/yr)

NREL: $841k/yr

Barriers

- Barriers addressed
  - Tt-E. Pyrolysis/Stabilization of biomass
  - Tt-G. Fuel Synthesis and Upgrading
  - Tt-K. Thermochemical Process Integration

Partners & Roles

Collaborations

- INL (feedstock interface)
- Technical Research Centre of Finland (VTT)
- Washington State University
- Kansas State University
- CanmetENERGY, Natural Resources Canada

Quad Chart Overview 3.2.2.32

Timeline

- Project start October 1, 2012
- Project end September 30, 2014
- Percent complete 5%
- New Project

Barriers

- Barriers addressed
  - Tt-E. Pyrolysis/Stabilization of biomass
  - Tt-G. Fuel Synthesis and Upgrading

Budget

Funding for FY2013:

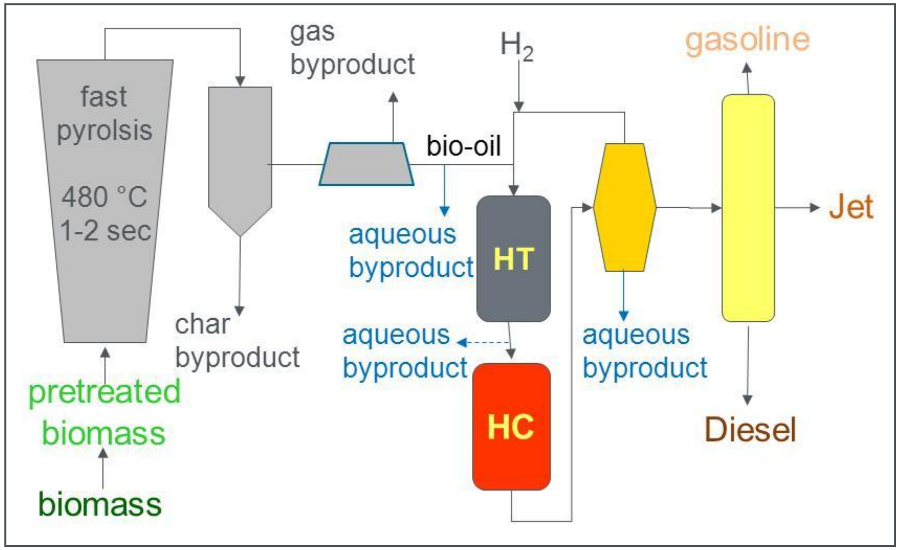
PNNL:$200K NREL: $200K

Partners & Roles

NREL: Production of physically stabilized oils

PNNL: Upgrading of oils

Project Overview



- Project addresses most aspects of the pyrolysis pathway
- Key technical barriers:
  - Bio-oil stability and lifetime of upgrading catalyst
  - Hydrogen efficiency
  - Impact of feedstock composition and pretreatments on pyrolysis and upgrading (yield and fuel speciation)
  - Quality of bio-derived fuels and how they fit into the existing refinery infrastructure.
  - Market acceptance of bio-derived compound suite

Historically, the results of this project have provided data, and identified barriers for the DOE for further development of fuels from pyrolysis and scale-up of the technology

1 - Approach

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3.2.2.4, 3.2.2.5 Core R&D

- Advanced analysis
  - Develop metrics for predicting and tuning performance in upgrading
  - Fuels and intermediate characterization
- Bench-Scale Pyrolysis and Bio-Oil Upgrading
  - Improved Pyrolysis Methods for Higher Quality Bio-oil
  - Improved Stabilization and Upgrading of Bio-oil
  - Bench-scale hydroprocessing to evaluate operating parameters, catalysts and bio-oil modifications
  - Determine requirements for refinery integration
- Informing the design case
  - Input to techno-economic assessment
  - TEA used to drive experiments
- Integration of the Pyrolysis Conversion Chain
  - Mixed biomass testing
  - Torrefied biomass evaluation (collaborations)

3.2.2.32 Hydrotreating of physically stabilized pyrolysis oils

- Production of hot vapor filtration pyrolysis oil
- Upgrading campaigns to assess fuel quality and performance

Management Approach:

- Project milestones, schedule, and risk mitigation via PMP approved by DOE
  - Weekly or monthly discussion and exchange with partners
  - Quarterly reviews to BETO

2 – Technical Progress: 3.2.2.4

Milestone	Planned Completion Date	Completion
Perform fundamental analysis on 4 pyrolysis/upgrading tests	30 Mar 12	✓
Complete 3 pairs of pyrolysis followed by upgrading demonstrations	1 Jun 12	✓
Complete publications advancing pyrolysis/upgrading knowledge	1 Aug 12	✓
Begin pyrolysis testing of new parametric feed study	30 Dec 12	✓
1-week fixed bed campaign supporting long catalyst life testing	28 Feb 13	✓
Fundamental analysis tests (4 experiments)	31 Mar 13	✓
Complete publications advancing pyrolysis/upgrading knowledge	30 Jun 13	Underway
1-week fixed bed campaign supporting long catalyst life testing	31 Jul 13	
Design report, justifications for equipment mods and testing program	30 Sep 13	Underway
Complete Pyrolysis/Upgrading SME review of TEA	30 Sep 13	
Report on fundamental analysis testing	30 Sep 13	
Report on feedstock parametric testing	30 Sep 13	Underway

2 – Technical Progress: 3.2.2.5

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Milestone	Planned Completion Date	Completion
Evaluate impact of pretreatment methods on catalytic pyrolysis of wood	Jun 2011	✓
Evaluate impact of catalyst type on oil yield and hydrogen consumption from mild hydrotreating	July 2011	✓
Select two best performing hydrogen donors for further catalytic pyrolysis tests	March 2012	✓
Characterization of upgraded bio-oils from catalytic pyrolysis and hydrotreating by GCxGC-TOFMS.	May 2012	✓
55% C conversion of bio-oil organic fraction to refinery intermediate in bench-scale hydrotreating tests	Sept 2012	✓
Catalytic deoxygenation of biomass pyrolysis vapors in the presence of co-reactants with 30% carbon conversion from biomass to refinery intermediate	Sept 2012	✓

2 – Technical Progress: 3.7.1.2

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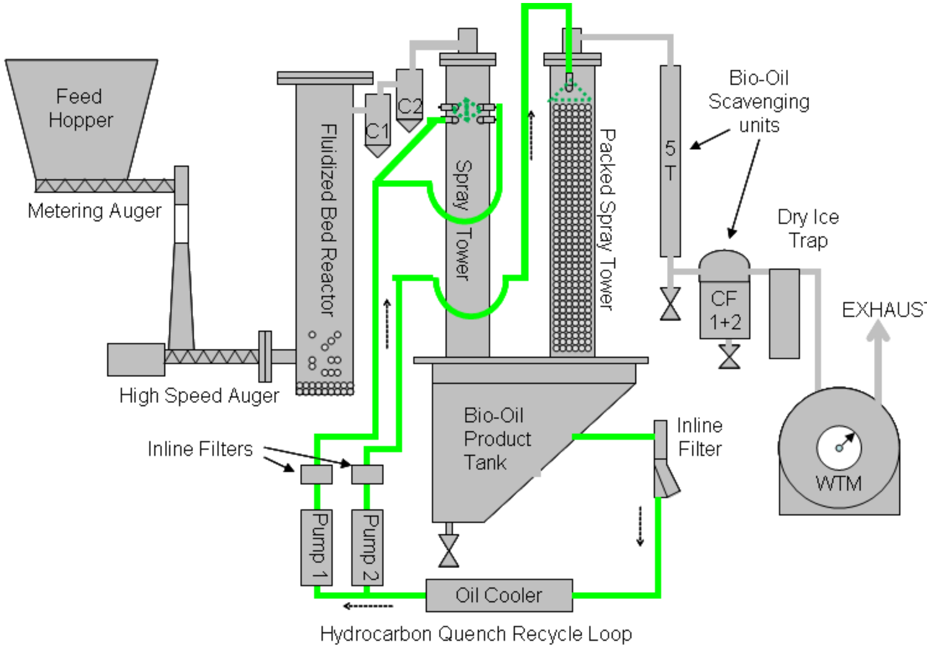
Milestone	Planned Completion Date	Completion
Initiate construction of large Class 1 Division safety enclosure for large hydrotreater	Sep, 2012	✓
Complete acceptance of large Class 1 Division safety enclosure for large hydrotreater	Jan, 2013	✓
Complete factory acceptance testing of large hydrotreater and separations system	Jan, 2013	✓
Receipt of large hydrotreater and separations system at PNNL	Feb, 2013	✓
Additional safety reviews to ensure safe start-up and operation of the system	May, 2013	Underway
Shakedown and produce first products from large hydrotreater and separations system	Jun, 2013	
Complete a full scale operation with actual bio-oil within R&D projects	Sep, 2013	

2. Technical Progress
Improved Pyrolysis Methods

Goal: Improve fast pyrolysis and impact national research efforts

Accomplishments:

- 51 pyrolysis tests performed since last platform review
  - 31 Tests in support of core R&D directly
  - 20 Tests in support of other DOE projects
- Bio-oil and aqueous samples generated to support other DOE research efforts, and university research collaborations
- Exchange of processing fundamentals operating experience with research collaborators to advance national research
- Improved pyrolysis oil collection, quench, and capture methods



1 kg/hr

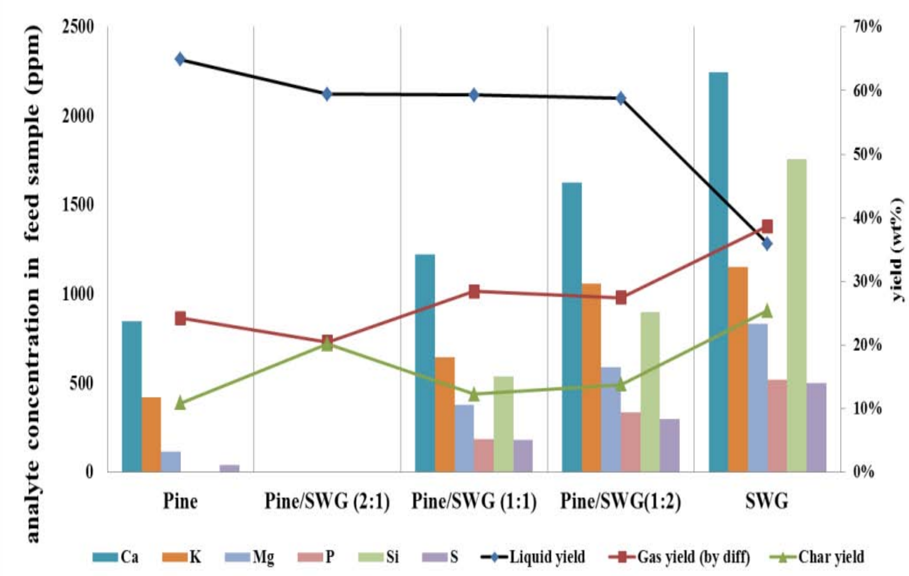
1-2 second vapor residence time

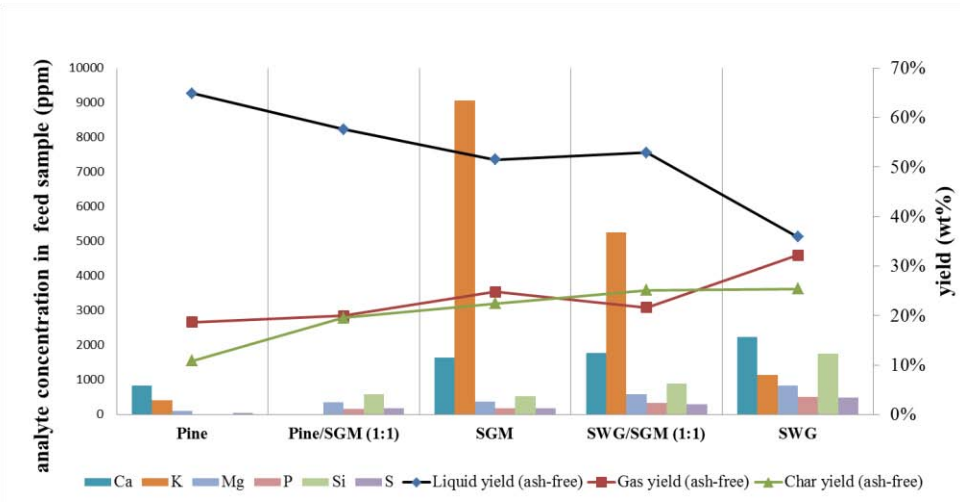
450 to 550 °C

Project has been broadly enabling to national and international research in fast pyrolysis

Blended Feedstock Pyrolysis

Goal: Correlate pyrolysis performance with feedstock composition





Accomplishments:

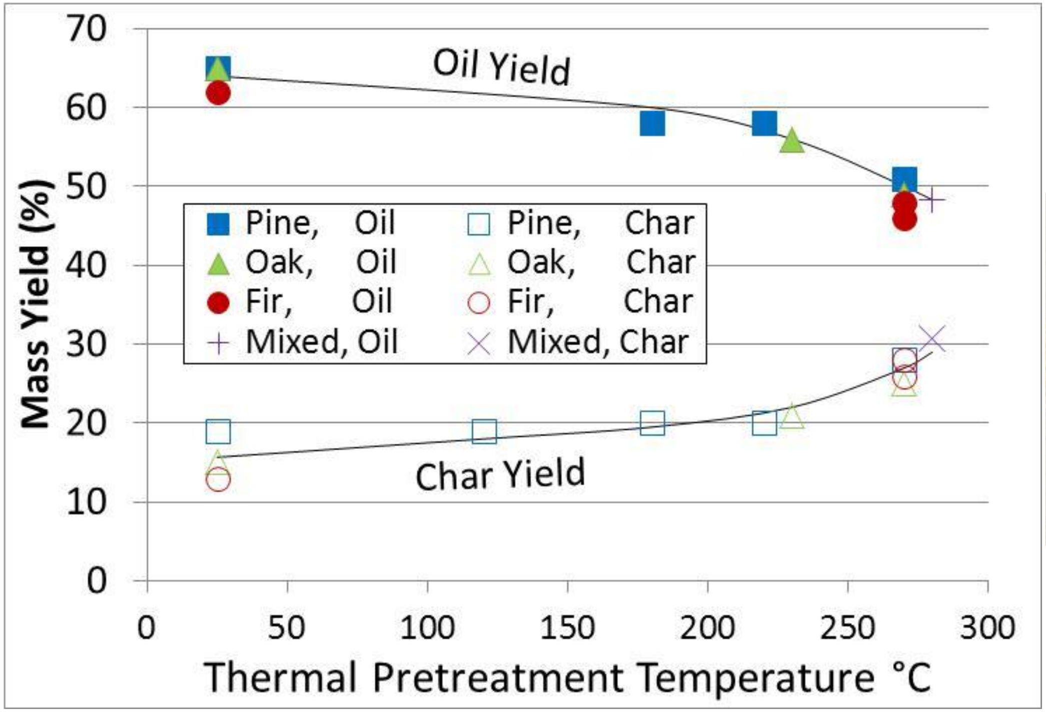
- Pyrolyzed blends of pine, switchgrass, and sorghum stover
- Blending improves performance of lower yield feeds
- Determined that inorganic content dominates performance
- Feedstock composition may have positive impacts on bio-oil composition

Critical first step towards understanding the pyrolysis impact of low-cost blended feedstock

Collaborative effort with Feedstock Interface: Dan Howe, PNNL; Tyler Westover, INL

2. Technical Progress
Pyrolysis of Thermal Pretreat

Goal: Evaluate performance of thermal pretreatment on pyrolysis yields



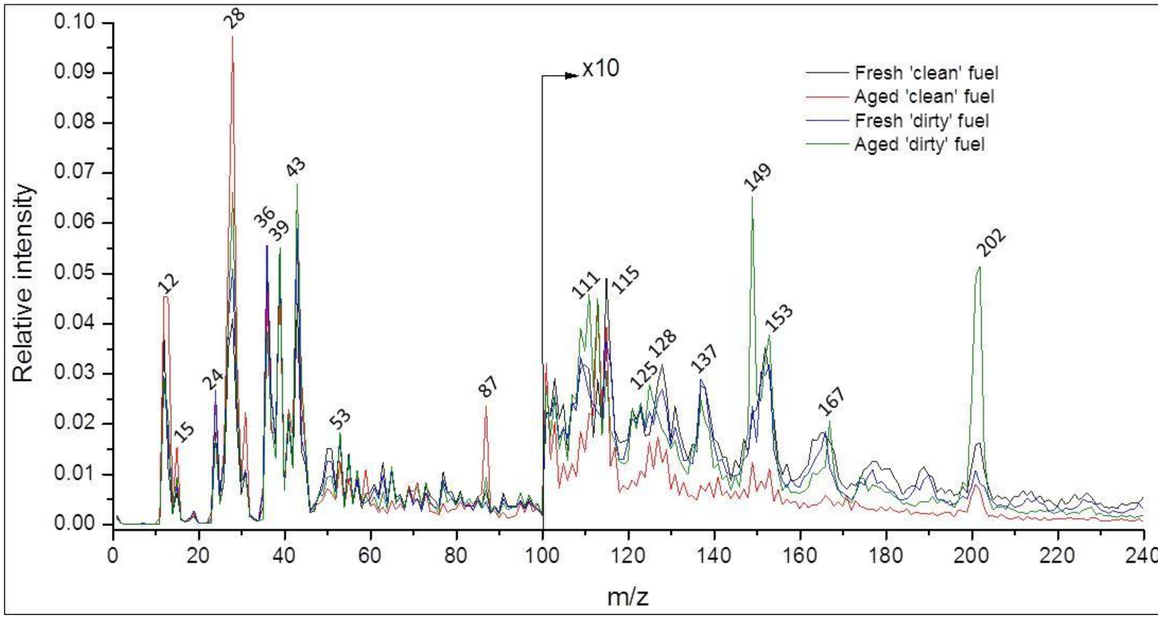
Accomplishments:

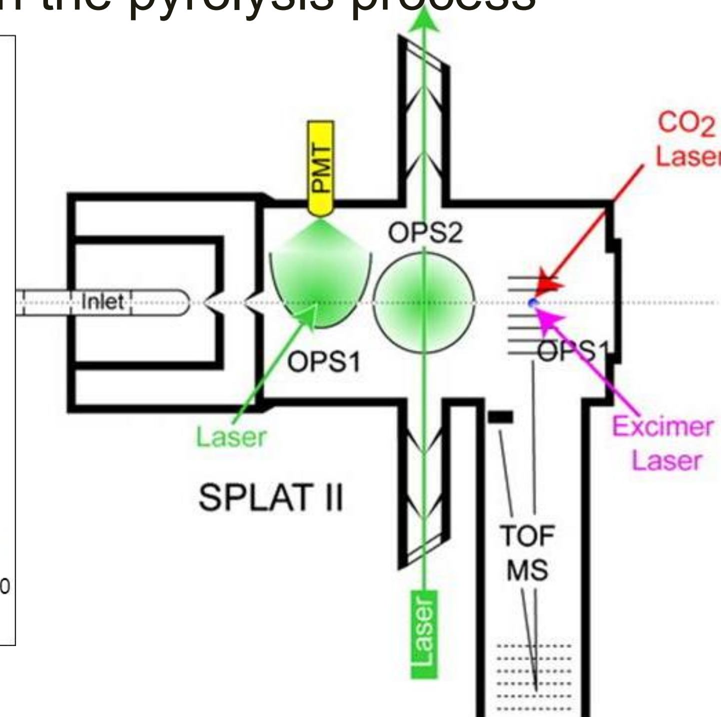
- Pyrolysis of multiple pretreated woody biomass feeds between 480-500 ºC
- Demonstrated pyrolysis performance impact for various woody biomass

Collaborative effort with Tyler Westover, INL; Hanwu Li, WSU; RFT

2. Technical Progress
Pyrolysis Aerosol Analysis

Goal: Understand the nature of aerosols formed in the pyrolysis process





Accomplishments:

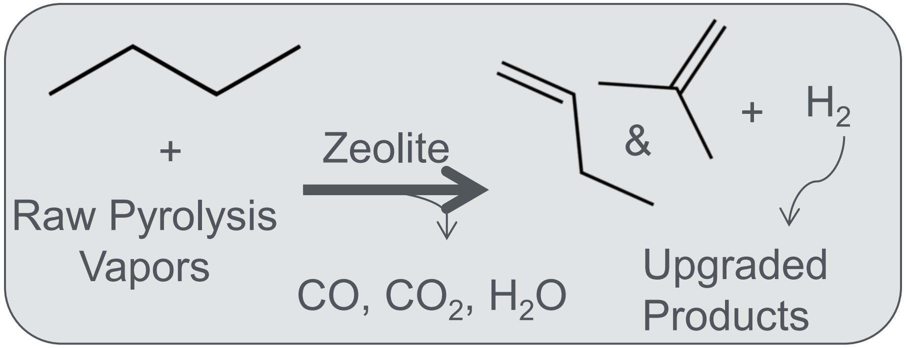
- Used single particle laser ablation mass spectrometry to look at individual aerosols in the pyrolysis reactor, liquid quench, and oil scrubbers
- Detected increase is aerosol size, and compound mass in aerosol handling units
- Observed compound mass increases with < 24h aging tests
- Determined that bio-oil from wood residue ages faster than from clean wood

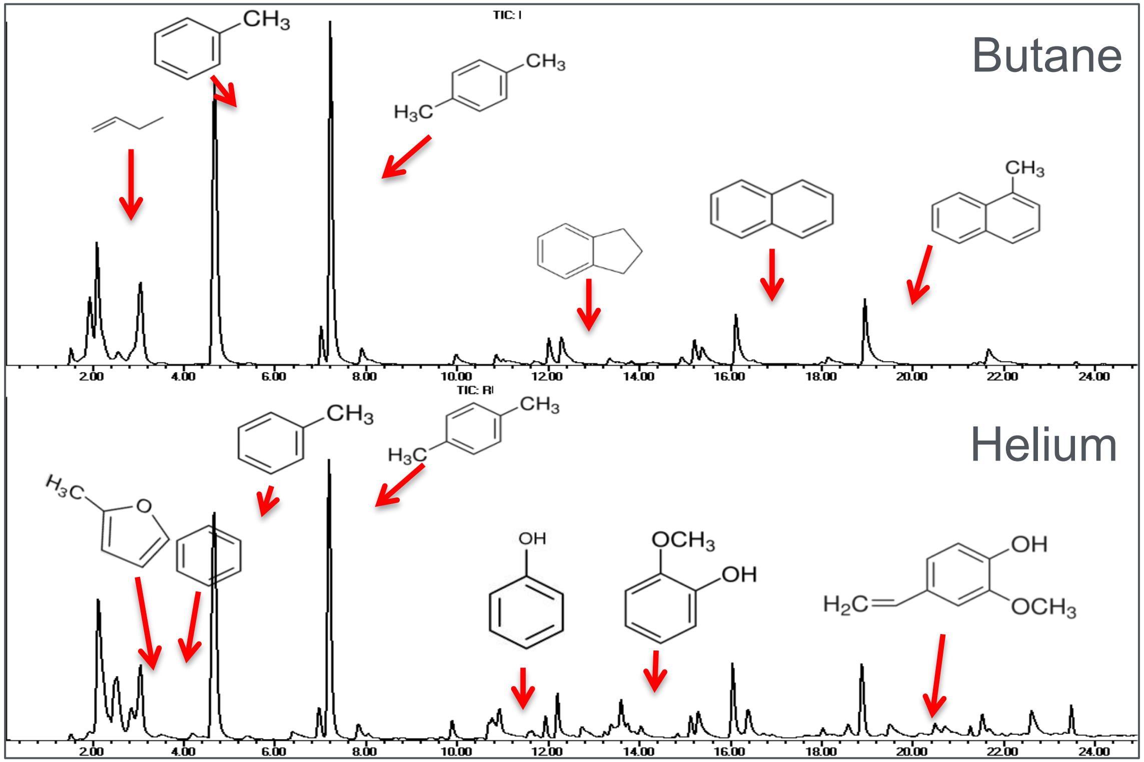
Bio-oil aging effects may appear in under 24 hours

2. Technical Progress: Catalytic Pyrolysis in the Presence of Hydrogen Donors

Goal: Evaluate light hydrocarbons as hydrogen donors

- Tested in micro scale (pyroprobe-GCMS) and bench scale (2-in fluidized bed reactor)





Catalyst:Pine = 0.9

2. Technical Progress: Catalytic Pyrolysis in the Presence of Hydrogen Donors

Accomplishments:

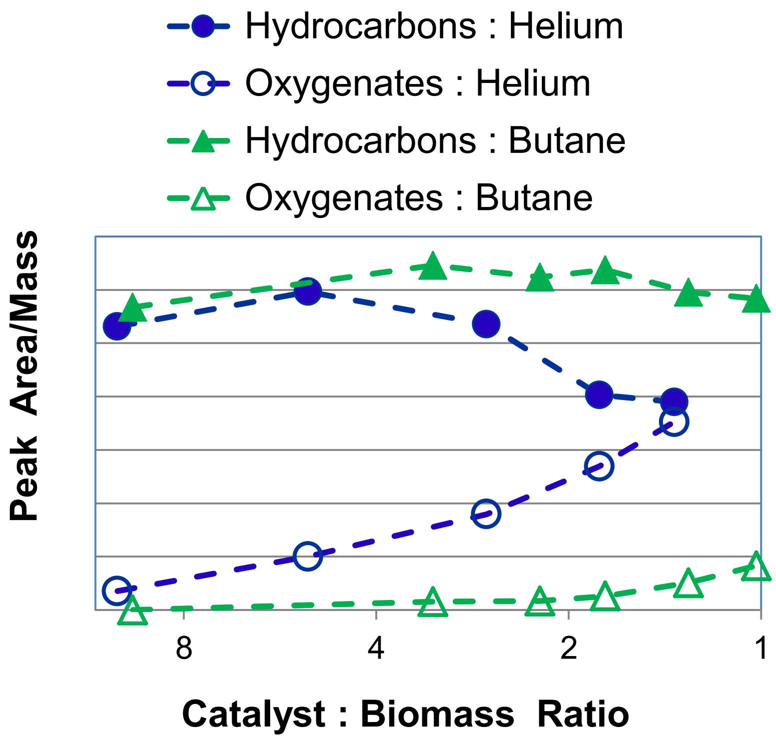
Demonstrated that addition of light hydrocarbons to catalytic pyrolysis delays catalyst deactivation and suppresses oxygenates formation

Potential to reduce costs by reducing need for catalyst regeneration, improving product quality, and/or increasing product yield

Fluidized Bed Results

	N_2	Propane
Oil Yield	8.2%	9.2%
Oil C Yield	16.4%	18.4%
Oil O content	4.3%	0.5%
Char+Coke	20.9%	19.6%

Micro-Scale Results



2. Technical Progress
Upgrading Catalytic Pyrolysis Oil

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Goal: Determine upgrading requirements for catalytic pyrolysis oil

Bio-oil	Product Oil				H_2 used (g/100g oil)	TOS (h)
	H/C	O	Density	TAN		
Pine, Baseline, no pretreatment	1.79-1.48	0.57-1.87	0.80-0.92	0.35-0.59	4.4 – 3.5	19.5 fouled
Pine, Baseline, prehydrotreated	1.78-1.61	0.21-0.75	0.80-0.83	0.21-0.81	4.6 – 4.8	>115
MCFP Oil, no pretreatment	1.65	0.26	0.82	<0.01	2.9	>13

Area%	Upgraded	
	PO	MCPO
Paraffinic	28.4%	14.6%
Olefinic	2.2%	2.4%
Cyclic HC	50.6%	50.6%
Hydro-aromatic	2.7%	7.4%
Aromatic	15.8%	25.0%

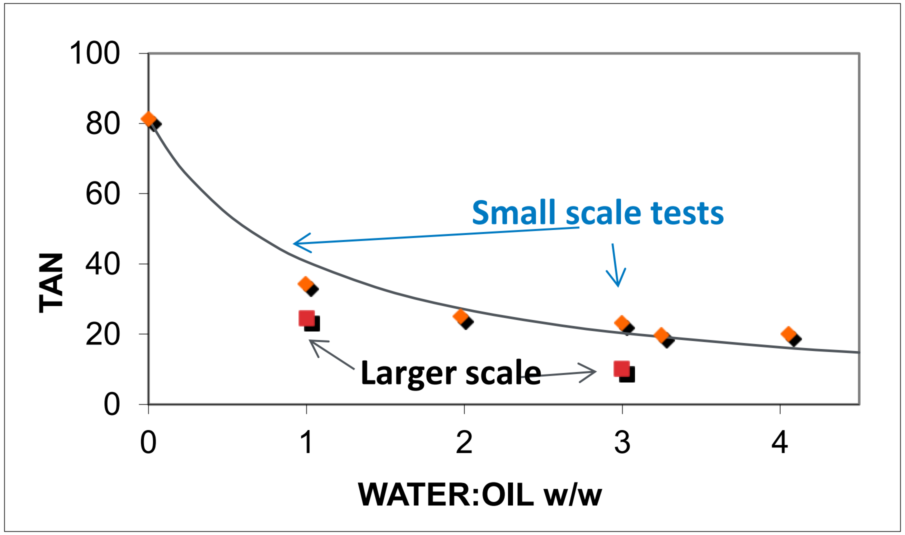
Accomplishments:

- Successfully upgraded mild catalytic pyrolysis oil to liquid transportation fuels
    - *In-situ* mild CPO with short exposure time to ZSM-5 at 480 ºC
- Demonstrated that upgrading requirements and fouling potential are reduced
- Discovered higher aromatic and lower paraffinic composition than baseline upgraded oils

2. Technical Progress: Mild Hydrotreating of Pyrolysis Oil Organic Fraction

Goal: Hydrotreat pyrolysis oil organic fraction & use aqueous fraction for H_2 generation

- Separated organic fraction by water addition



Oil:cat	P, psi	Stab. T, °C	Final T, °C
10:1	1000	150	340
10:1	2450	280	370
10:1	2450	280	400

H_2O:Oil	C, wt%	H, wt%	O, wt%	H2O, wt%	Volatile	CAN
0:1	38.9	7.3	53.7	30		81
1:1	57.8	6.7	35.9	17.2	55.6	24
3:1	59.4	6.6	34.6	10.8	62.6	10

Catalysts
$NiMoS/Al_2O_3$
Pd/C
Pt/Char

Microscale results confirmed at bench scale

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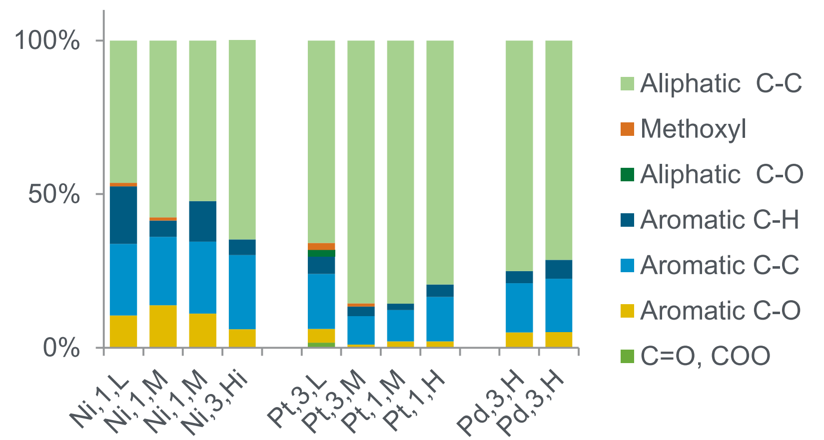
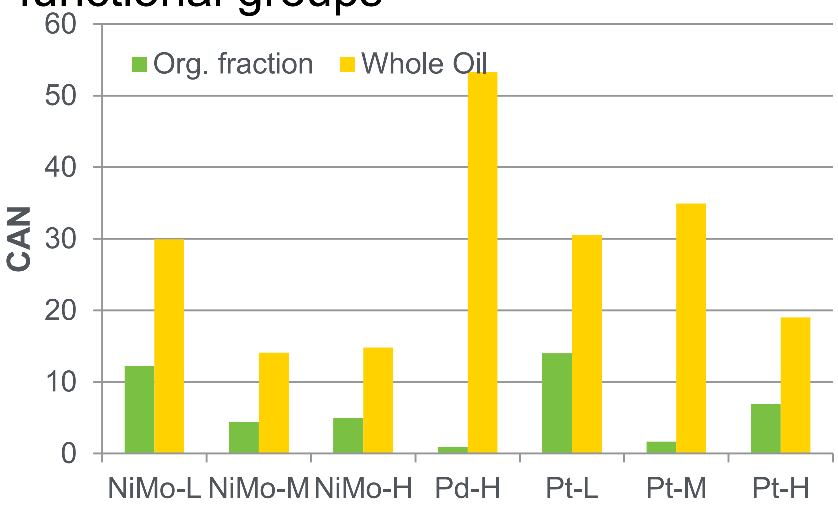
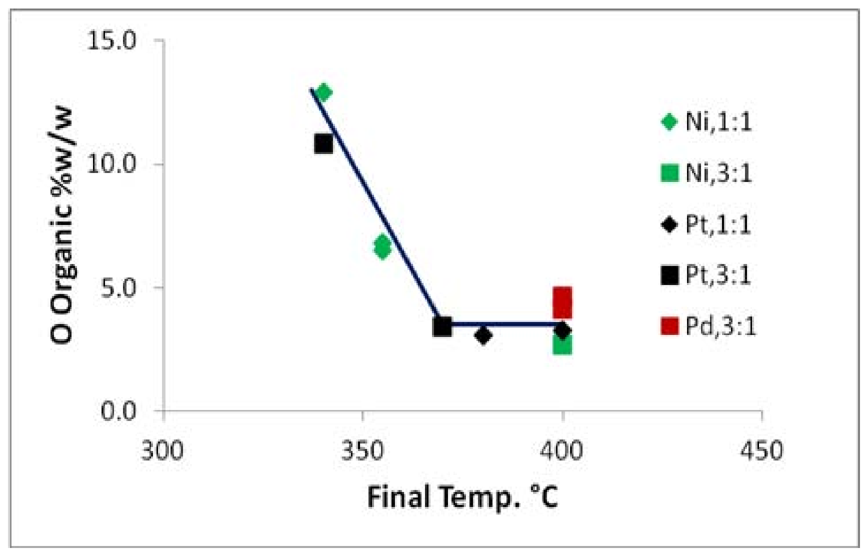
Accomplishments:

- Produced oil with better properties than by hydrotreating of whole oil with similar yields
- Identified impact of main process parameters
- Categorized relationship between operating conditions and residual oxygen functional groups







2. Technical Progress: Comparison of Catalysts for Hydrotreating

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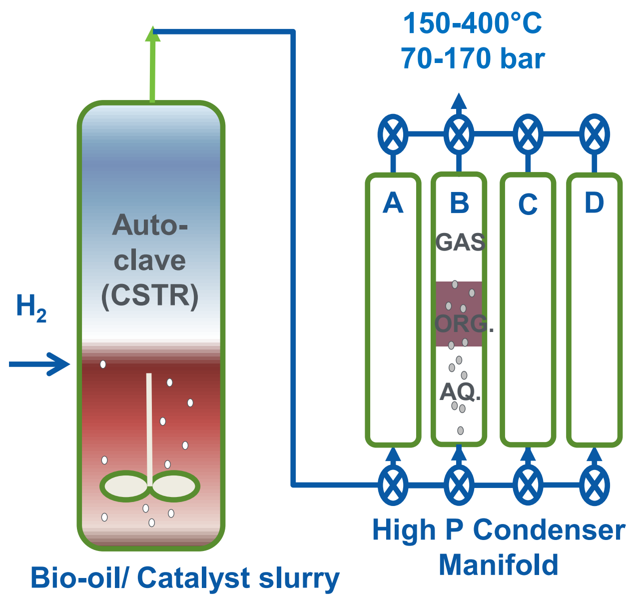
Goal: Compare precious metal and traditional hydrotreating catalysts for production of oil with compatibility with crude oil

- **Targets:** Oxygen <7 wt%, CAN <15, Carbon conversion > 55%, Volatility >95%, Complete miscibility in hydrocarbons



Oak oil (550°C)	
C	42%
H	4%
Org O	20%
H_2O	33%
CAN	87

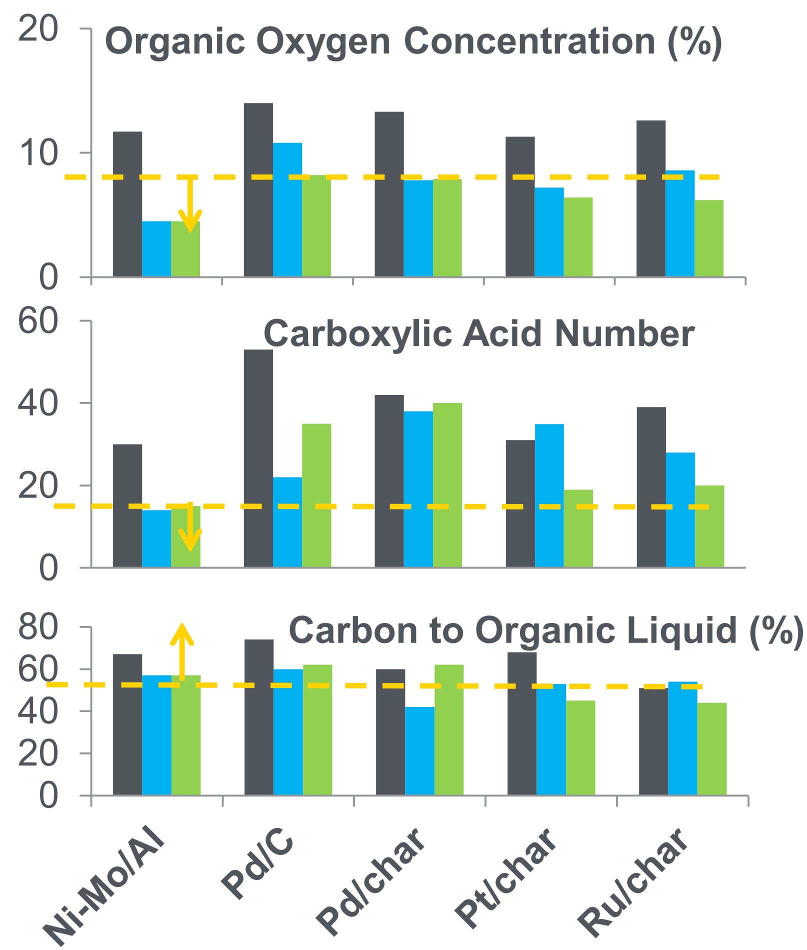
Catalysts
$NiMoS/Al_2O_3$
Pd/C
Pd/Char
Pt/Char
Ru/Char

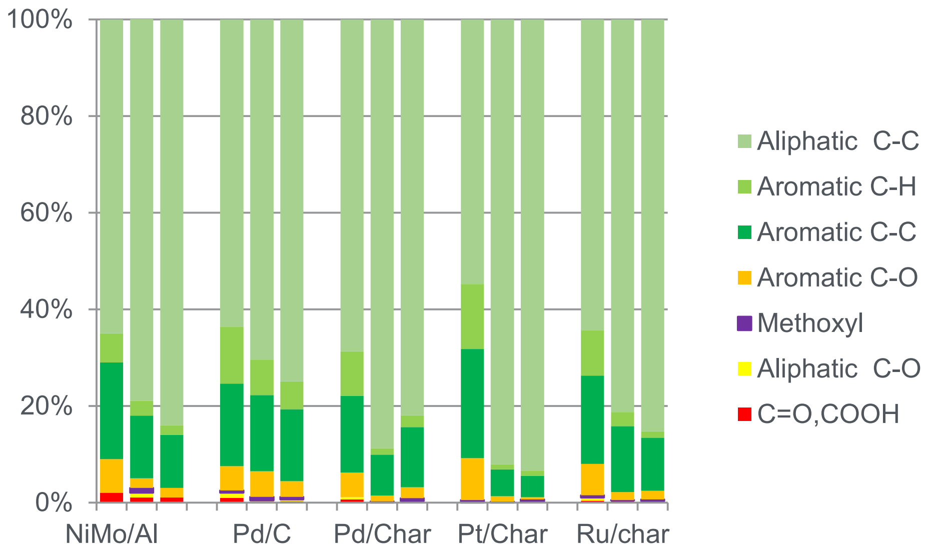
Oil:cat	P, psi	Stab. T, °C	Final T, °C
10:1	1000	150	340
10:1	1725	215	370
10:1	2450	280	400

Comparison of Catalysts for Hydrotreating

Accomplishments:

- Demonstrated production of intermediate oil with reduced H_2 consumption (~2.2%)
- Identified major differences in catalyst performance





2. Technical Progress
Advanced Analytical: ATR-IR, ^{13}C NMR

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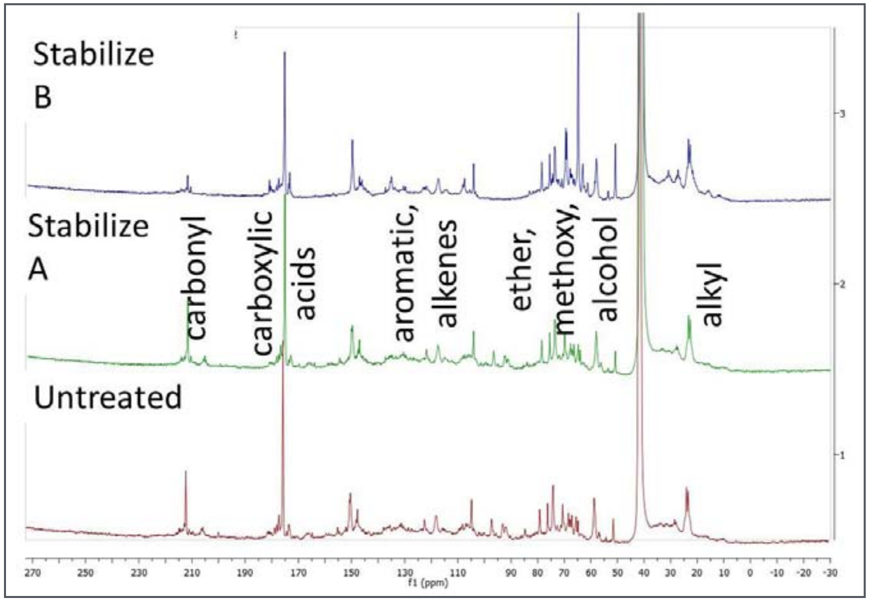
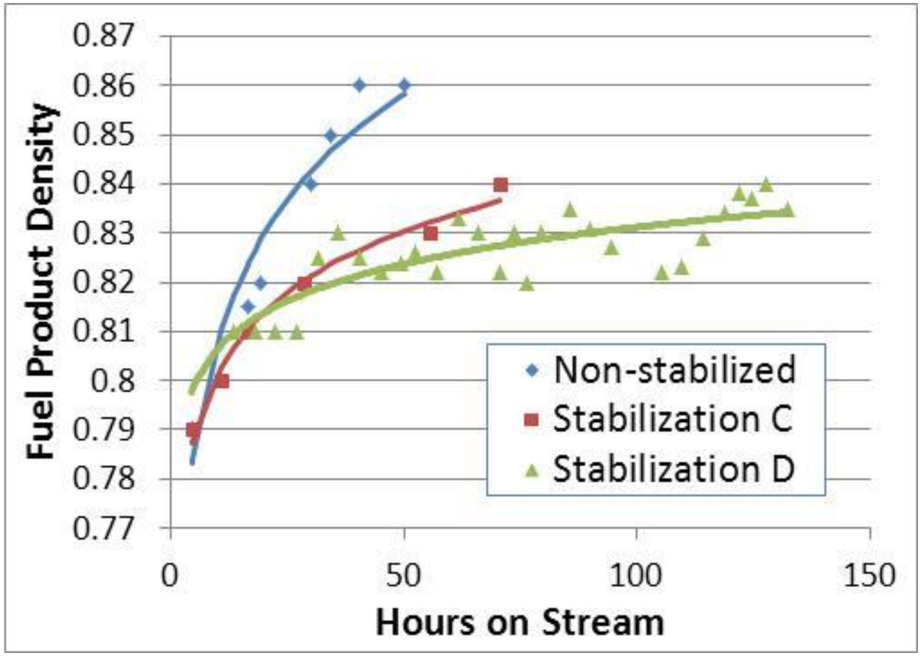
Goal: Apply fundamental pyrolysis oil understanding to empirical upgrading success





Accomplishments:

- Identified specific functional groups that correlate to empirically successful upgrading
- Determine conditions for successful conversion to finished fuel
- Developed operating strategy for longer upgrading catalyst lifetime

Enabled the hydrotreater to meet the technical targets for catalyst lifetime

2. Technical Progress Hydrocarbon Fuels Analysis

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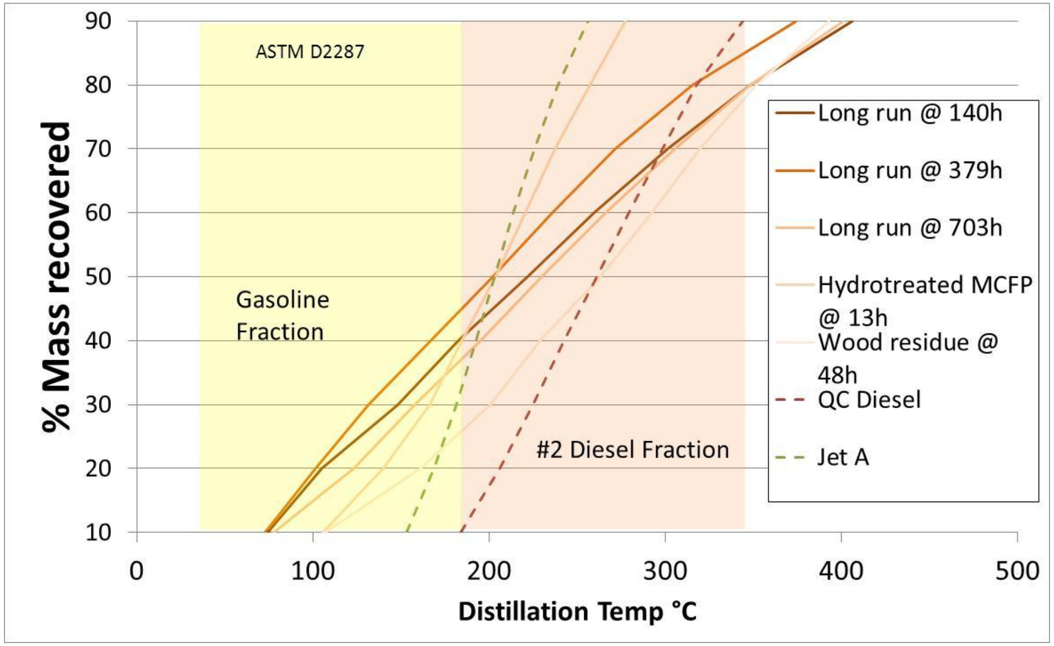
Goal: Characterize hydrotreated fuels as gasoline, diesel, and jet distillates



Fraction (BP range)	Long Run			MCFP	Wood Residue
	140h	379h	703h	13h	48h
Gasoline IBP-184°C	40%	45%	37%	40%	26%
Diesel 184-344°C	39%	41%	42%	60%	52%
Heavies > 344°C	21%	14%	20%	<1%	22%
Jet A (overlap) 153-256°C	27%	29%	29%	56%	30%

Accomplishments:

- Characterization of distillation range for various hydrotreated fuels
- Underscores the difference between bio- and petro-derived distillation cuts
  - MCFP “diesel” versus reported high aromatic content
  - Will need to understand equivalence to petroleum cuts

2. Technical Progress: Upgrading Catalyst Lifetime Improvement

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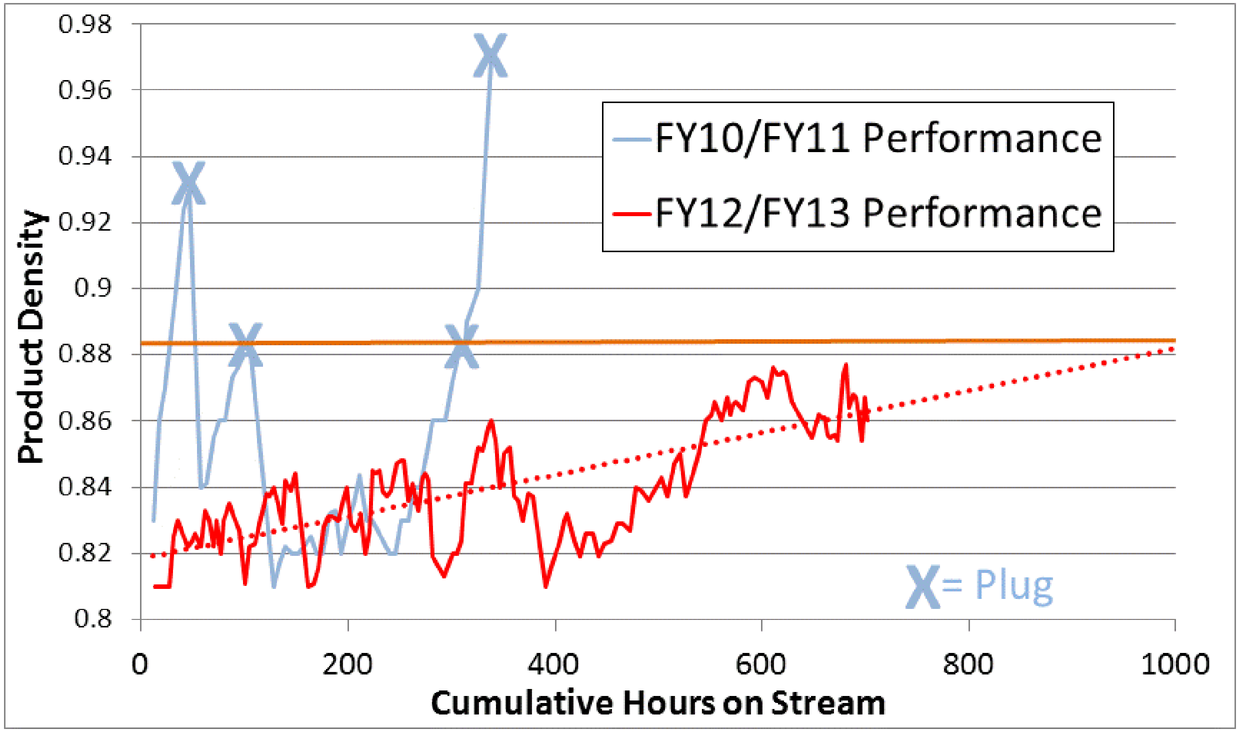
Goal: Advance the technology for making liquid transportation fuels from fast pyrolysis and upgrading



Accomplishments:

- Developed process for upgrading for 700 to 1000 hours without plugging
- Consistent fuel yield of 0.42 g/g of bio-oil, oxygen content < 3%
- Catalyst lifetime and operation greatly improved over FY2011 benchmark

2. Technical Progress: Upgrading Catalyst Lifetime Improvement

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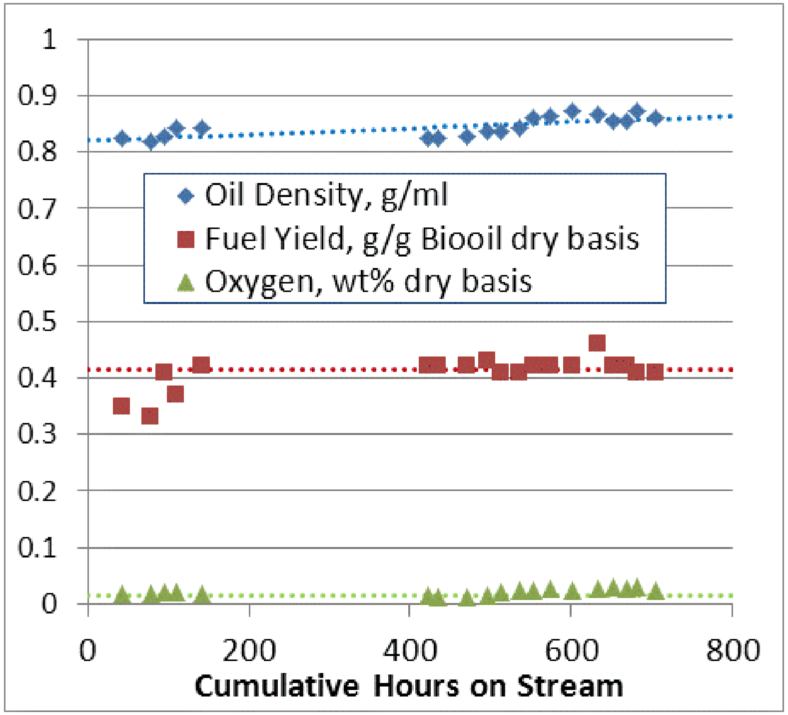
Goal: Evaluate stability of catalyst performance during bio-oil upgrading



Fraction (BP range)	Upgraded Bio-Oil (hrs on stream)								
	41h	140h	190h	237h	323h	379h	649h	667h	703h
Gasoline IBP-184°C	45%	40%	42%	42%	41%	45%	39%	37%	37%
Diesel 184-344°C	40%	39%	40%	41%	43%	41%	43%	41%	42%
Heavies > 344°C	15%	21%	17%	17%	16%	14%	19%	21%	20%
Jet A (overlap) 153-256°C	28%	27%	28%	29%	30%	29%	29%	28%	29%

Accomplishments:

- Fuel yield relatively constant over 700h even with changes in catalyst
- Simulated distillate cuts shift away from gasoline, towards fuel oils. Jet and diesel constant
- Impact of changes in hydrocracking function and residual oxygen content

2. Technical Progress: Ebullated Bed Hydrotreater CapEx

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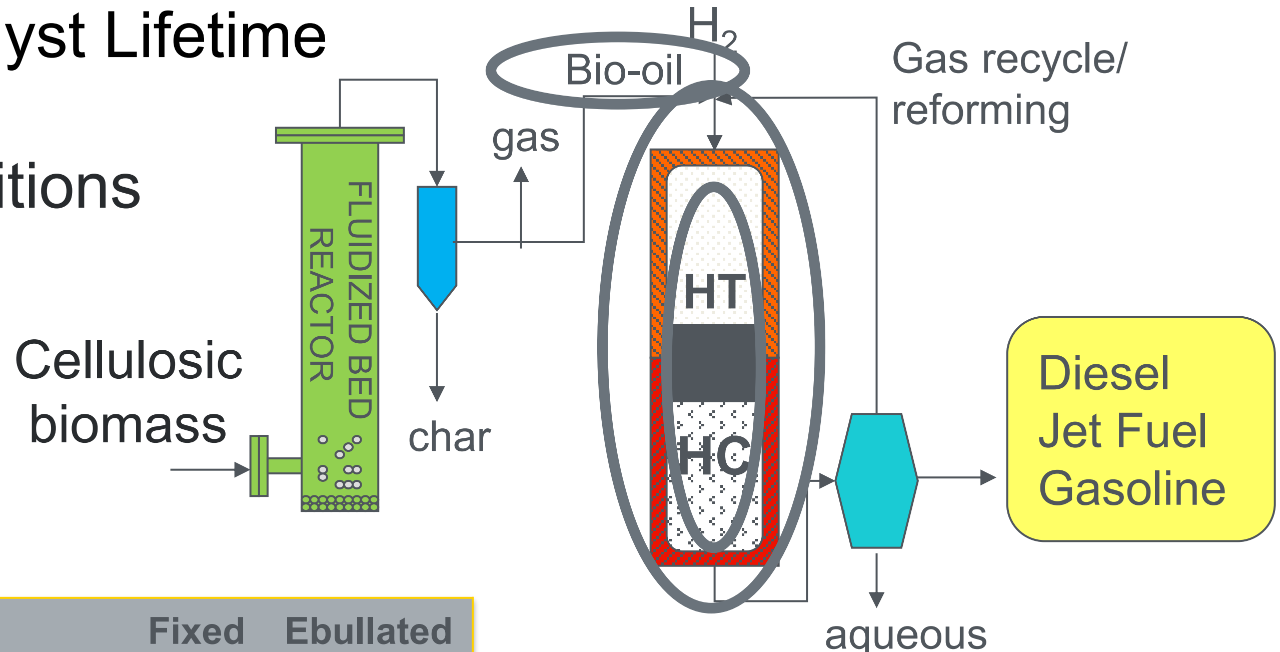
Challenge: Catalyst Lifetime

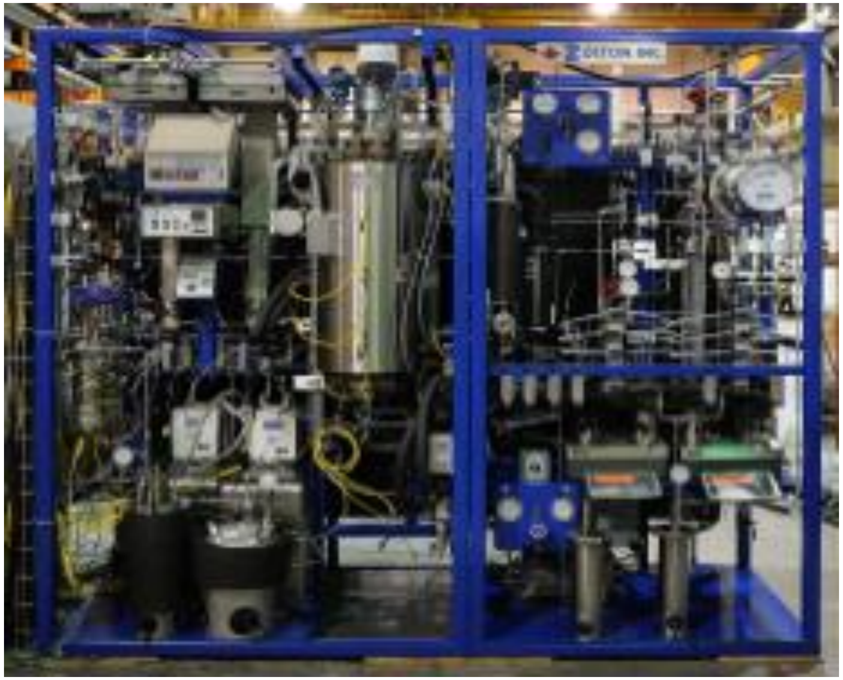
- Catalyst/Conditions
- Bio-Oil
- Reactor



	Fixed	Ebullated
Prevent Fouling		√
Manage Fouling		√
Manage Exotherm		√
Online Catalyst Replacement		√
Final Oxygen Content in Oil	√	?
Catalyst Attrition	√	
Catalyst Compatibility	√	?

Increased rates [of bio-oil upgrading] can also be achieved by better catalyst contacting to reduce diffusional limitation and reduce catalyst deactivation due to surface fouling. An ebullated-bed reactor should be considered for hydrotreated biomass-derived oils. (Baker and Elliott, 1988)

Goal: Construct novel bio-oil hydrotreater based on petroleum hydrotreater for processing similarly difficult petroleum oils



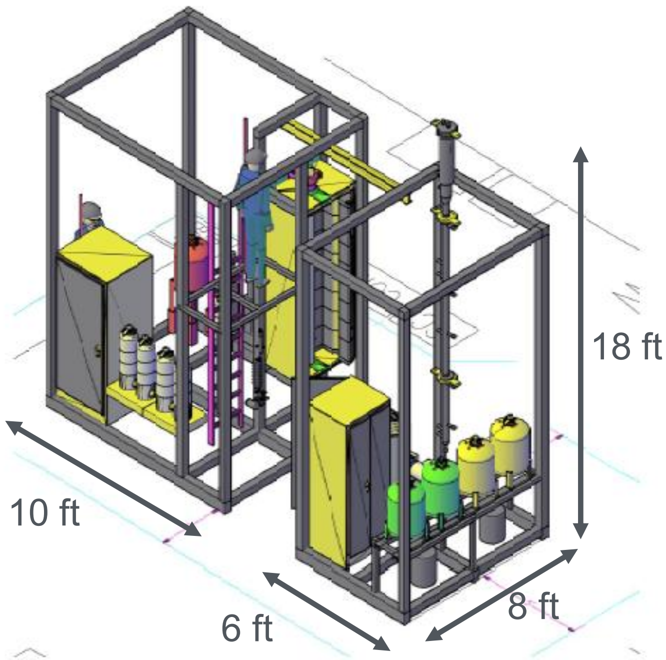
EB hydrocarbon products

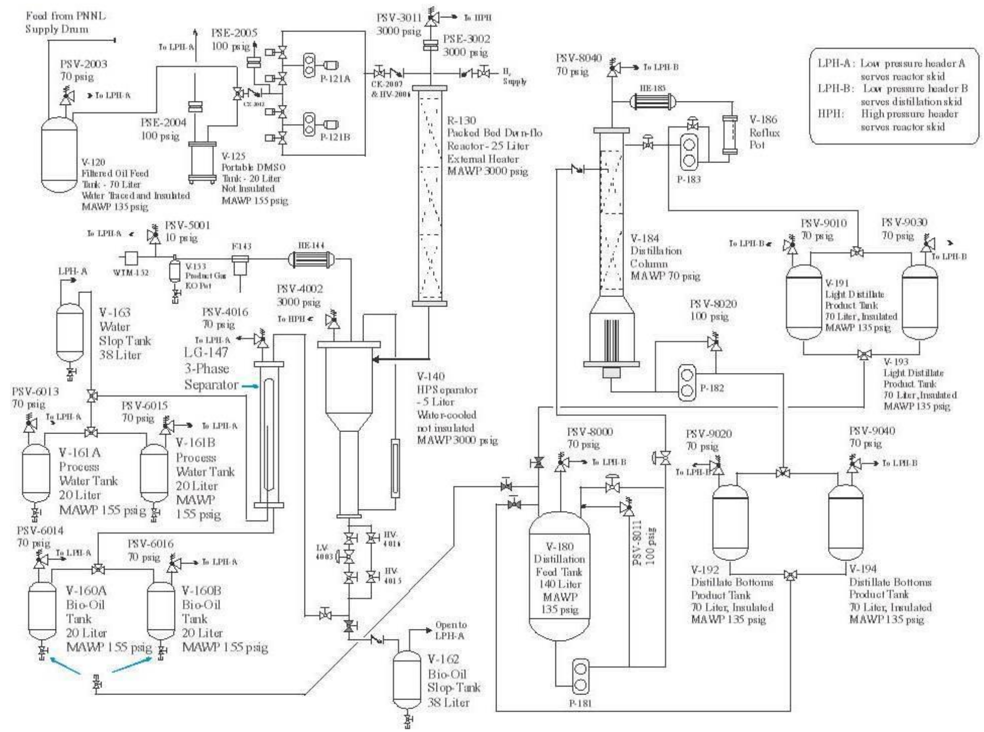
Accomplishments:

- Completed design, construction, installation, and shakedown
- Initial testing underway in separate R&D project
- Longest test to date: 48hr

2. Technical Progress: Large Hydrotreater and Separations Equipment

Goal: Construct bio-oil upgrader/distillation unit to produce fuel cuts at scale relevant to industry testing and acceptance





Hydrotreater: 60 L/day, 400 °C, 135 atm, 20L catalyst bed, l/l/g separations
Distillation: 20 L/hr, 25 – 350 °C, 1-2 atm, variable reflux, onboard recycle
Enclosure: Class 1, Div. 2, heavy mist fire suppression, integrated auto shut down for facility and gas detection

2. Technical Progress: Large Hydrotreater and Separations Equipment

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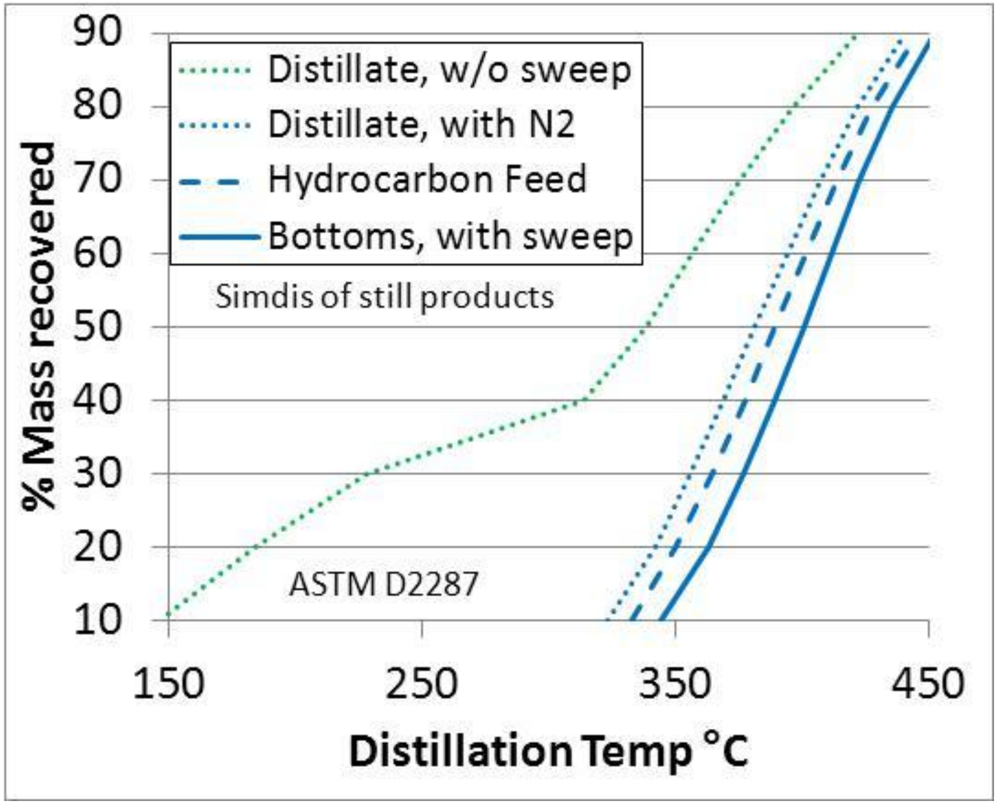
Accomplishments:

- Design based on bench scale hydrotreater and ebullated bed
- Construction and acceptance testing complete
- System delivered and enclosure complete

2. Technical Progress: Large Hydrotreater and Separations Equipment



Accomplishments:

- Model compound testing in reactor and distillation system during acceptance testing
- Completed process hazard analysis with operators, SMEs, and stakeholders
- Finishing tie-in and preparing SOP prior to shakedown testing

2. Technical Progress: Hydrotreating Physically Stabilized Pyrolysis Oil (New)

FY2013 New Project WBS 3.2.2.32 P.I.: Doug Elliott at PNNL in collaboration with Mark Davis at NREL

Goal: Production of a more stable oil that improves upgrading and catalyst lifetime

- Hot vapor filtered (HVF) bio-oil production at NREL
- Process evaluation of catalytic hydrotreatment of HVF bio-oil at PNNL
- Improve catalyst lifetime by removal of bio-oil contaminants
- Improve bio-oil stability by removal of bio-oil contaminants
- Initial hydrotreating tests expected to be completed by end of FY13
- Process optimization and large scale testing envisioned for FY14

This collaboration between NREL and PNNL leverages existing expertise to assess the impact of filtration, both hot-gas and liquid-phase filtration at NREL on the hydrotreating process to produce liquid transportation fuels at PNNL

3 - Relevance

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MYPP Barriers addressed
- Tt-E. Pyrolysis of Biomass and Bio-Oil Stabilization
- Tt-G. Fuel Synthesis and Upgrading
- Tt-K. Themochemical process integration

Applications of the Expected Outputs
- External use of methods for stabilization and upgrading of bio-oil
- External use of analysis tools for evaluation of bio-oil intermediates
- Industrial technical evaluation of individual bio-fuel distillate cuts

Relevance to MYPP Milestones (Bio-Oil conversion)
- Produce data to demonstrate prior year cost goals and technical targets
- FY14Q4: data to establish out-year cost and technical targets
- FY15Q4: data to validate bench scale, process via liquefaction
- Performance Goal: MYPP Conversion cost of $1.83/GGE via bio-oil pathway (FY17)

MYPP Tasks supported:
- R 3.6.3.2.1 - Develop Fast Pyrolysis Technology
- R 3.6.3.2.2 - Develop bio-oil upgrading and conditioning processes

4 - Critical Success Factors

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Critical Success Factors

- Proven process for bio-oil HDO to fungible liquid fuels
- Large scale demonstration of catalysis for upgraded fuel products from bio-oil
- Market understanding and acceptance of functional qualities of bio-oil-derived fuels

Key Challenges

- Bio-oil is chemically different than existing refinery feeds
- Catalytic processing of bio-oil is the largest challenge
- Must understand quality and characterization of bio-derived fuels and how they fit into the existing refinery infrastructure

Successes in this project will:

- Inform the market on the characteristics of refinery compatible biomass fuels through analysis and samples at industrially relevant quantities
- Meet technical targets to enable modeled conversion cost targets for pyrolysis derived fuels

5. Future Work

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- Extending long-lifetime catalyst demonstration
- ^{13}C NMR, ATR-IR to optimize hydrotreater intermediates (intra-bed catalysts and conditions)
- Characterize feedstock blending impact on pyrolysis and upgrading yields, performance and fuel quality
- Pyrolysis Scale Transfer Function: correlate conditions and performance of bench and micro scale pyrolysis
- Assess pretreatments: HVF, etc.
- Large scale demonstration and production of industrially relevant samples of distilled diesel, gasoline, and jet

5. Future Work

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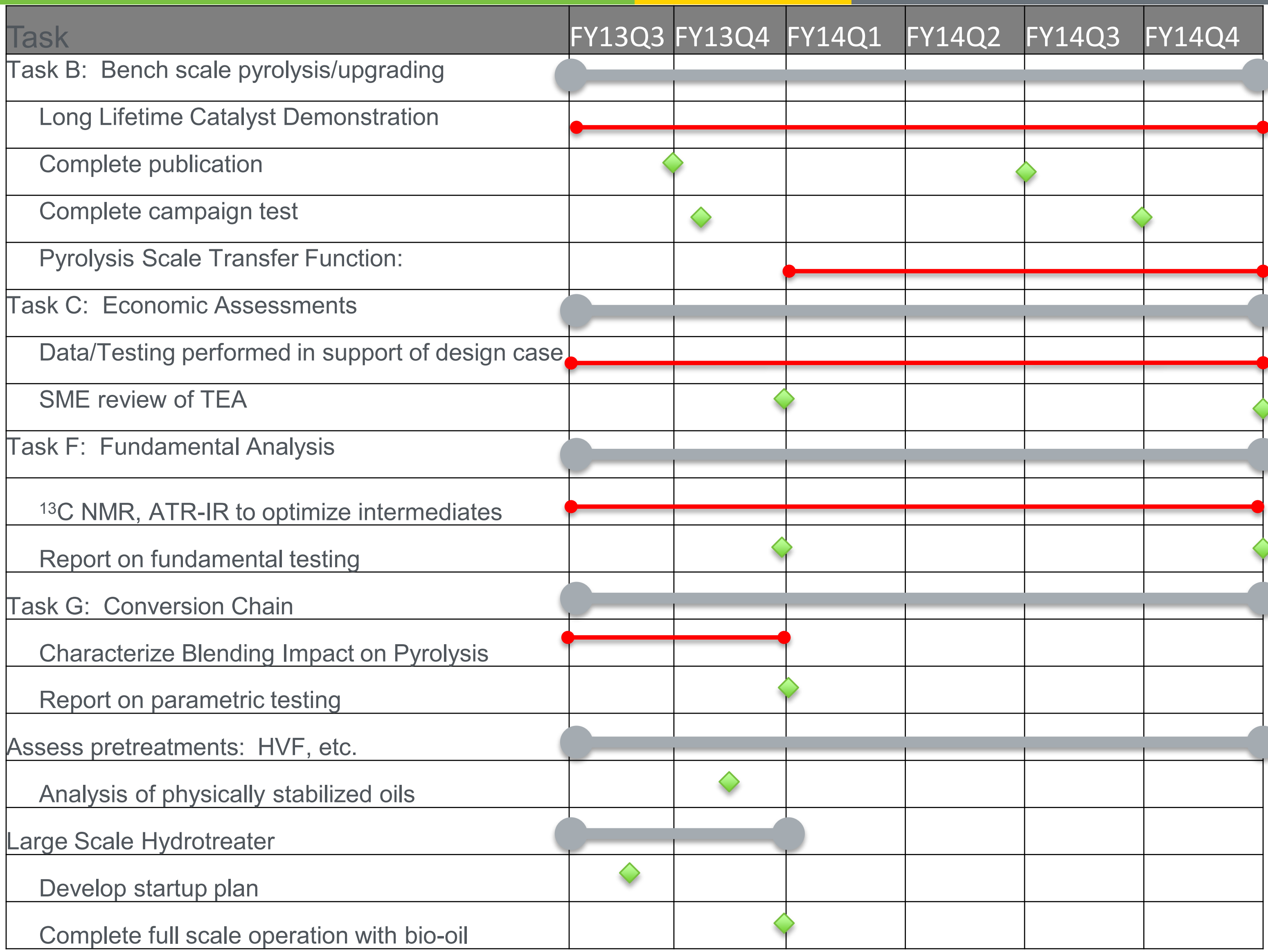

Summary

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Relevance: Driving pyrolysis/upgrading technology towards MYPP goals and targets. Barriers addressed: Tt-E, *Tt-G, Tt-K*

Approach: Evaluating many aspects of the pathway to fuels

Accomplishments: Hitting targets, driving the state of technology, new catalyst lifetime achievements

Future work: Aimed at answering current questions and overcoming existing barriers

Success factors: Proven process for pyrolysis bio-fuel to demonstrate biomass fuel quality and meet MYPP technical targets

Challenges: Catalyst lifetime, market acceptance, and quality of fuel

Status:

- 2011: 338hr on stream (plug/replace 10% catalyst)
- 2013: 700+ hr on stream (no plugging, no replacement needed)

Additional Slides

Responses to Previous Reviewers' Comments

Most of the comments in the last review were Strengths

Weaknesses identified in previous review:

1. I would have liked to see more discussion about energy balances and minimizing losses in going to a usable fuel.
2. Good to see torrefaction included, but do we understand overall energy balance implications? Good to see catalytic pyrolysis, but it is important to understand if this is a "game changer" or if we are exchanging one set of problems for another.
3. it would be good for this program to focus more on commercialization issues as the projects works towards completion.

Responses:

1. Our focus will remain on the critical factors for making pyrolysis commercial. Energy balance and minimizing losses are key issues to address in the commercialization process. However, the energy balance can only be modeled from the laboratory data and is a part of the analysis effort, to which our data contributes. The results of that modeling were presented separately. Minimizing losses (maximizing yields) can be validated in the laboratory tests and we are ever vigilant in minding the balances, working toward a complete definition of the yields, and maximizing the yield of the liquid fuel product.
2. The further consideration of the value provided by torrefaction and catalytic pyrolysis will be key elements in the plan. We will continue to consider the implications of the work on scale-up issues.
3. Our project is a key foundational project for the Thermochemical Platform and we have made good progress since the last review. The results of this project provide much of the basis for the DOE solicitations for further development of fuels from pyrolysis and scale-up of the technology in the biorefinery platform (the UOP/Tesoro project).

Publications and Presentations

- Westover T, M Phanphanich, M Clark, S Rossberg, S Egan, C Wright, R Boardman, AH Zacher, and DM Santosa. 2012. "Impact of thermal pretreatment on the fast pyrolysis conversion of southern pine." PNNL-SA-91542, Pacific Northwest National Laboratory, Richland, WA.
- Bu Q, H Lei, AH Zacher, L Wang, S Ren, J Liang, Y wei, L Yupeng, J Tang, Q Zhang, and R Ruan. 2012. "A review of catalytic hydrodeoxygenation of lignin-derived phenols from biomass pyrolysis ." PNNL-SA-90300, Pacific Northwest National Laboratory, Richland, WA.
- Elliott DC, TR Hart, GG Neuenschwander, LJ Rotness, Jr, MV Olarte, AH Zacher, and Y Solantausta. 2012. "Catalytic Hydroprocessing of Fast Pyrolysis Bio-oil from Pine Sawdust." Energy and Fuels 26(6):3891-3896. doi:10.1021/ef3004587
- Olarte MV, AH Zacher, DC Elliott, DM Santosa, GG Neuenschwander, TR Hart, and LJ Rotness, Jr. 2011. "Bio-Oil Upgrading and Stabilization at PNNL." Presented by Mariefel V. Olarte (Invited Speaker) at Harvesting Clean Energy Conference 2011 , Boise on October 23, 2011. PNNL-SA-83598.
- Olarte MV, AH Zacher, DC Elliott, DM Santosa, GG Neuenschwander, TR Hart, and LJ Rotness, Jr. 2011. "Bio-Oil Upgrading and Stabilization at PNNL." Presented by Mariefel V. Olarte (Invited Speaker) at WSU Graduate Seminar, Richland, WA on October 28, 2011. PNNL-SA-83729.
- Zacher AH. 2011. "Catalysis of Pyrolysis Oil." Presented by Alan Zacher (Invited Speaker) at WSU Tricities Class ChE581, Richland, WA on October 12, 2011. PNNL-SA-83389.
- Elliott DC, GG Neuenschwander, TR Hart, LJ Rotness, Jr, and MV Olarte. 2011. "Bio-oil upgrading by catalytic hydroprocessing in a fixed-bed reactor." Presented by Douglas C. Elliott at TCBiomass 2011, Chicago, IL on September 27, 2011. PNNL-SA-82778.
- Zacher AH, DM Santosa, and DC Elliott. 2011. "Mild Catalytic Fast Pyrolysis of Biomass and Catalytic Hydrotreating to Liquid Transportation Fuels Plus Development of a Ebullated Bed Reactor." Presented by Alan Zacher at TCBiomass 2011 , Chicago, IL on September 30, 2011. PNNL-SA-82908.

Publications and Presentations

- Brown C, D Beckman, AH Zacher, and DC Elliott. 2011. "Development of an Ebullated Bed Reactor for Bio-oil Upgrading." Presented by David Beckman at TCBIOMASS2011, Chicago, IL on September 27, 2011. PNNL-SA-82977.
- Male JL, DC Elliott, AH Zacher, and DM Santosa. 2011. “Pyrolysis of Biomass” Presented by Jonathan Male (Invited Speaker) at EBI and JBEI Joint Workshop: Lignin - Characterization, Extraction & Adding Value, Emeryville, CA on July 19, 2011.
- Elliott DC. 2011. "“Process Routes for Biomass Pyrolysis to Produce Hydrocarbon Fuels—Comparisons and Recent Results”." Presented by Douglas C. Elliott (Invited Speaker) at 7th International Conference on Renewable Resources and Biorefineries, Brugge, Belgium on June 9, 2011.
- Zacher, A.H. and DC Elliott “Bio-Oil Upgrading and Stabilization” Presented by AH Zacher (invited speaker) to The Kansas State University Bioenergy Symposium, April 27, 2011.
- Elliott DC. 2011. "Process Development for Biomass Conversion to Fuels by Thermochemical Methods." Presented by Douglas C. Elliott (Invited Speaker) at visit to KTI, Karlsruhe, Germany on April 5, 2011.
- Elliott DC. 2011. "Process Routes for Biomass Pyrolysis to Produce Hydrocarbon Fuels – Comparisons and Recent Results." Presented by Douglas C. Elliott (Invited Speaker) at KiOR visit, Houston, TX on March 9, 2011.
- Elliott DC. 2011. "Hydrothermal Processing." Chapter 7 in Thermochemical Processing of Biomass:Conversion into Fuels, Chemicals and Power, ed. Robert C. Brown, pp. 200-231. Wiley-Blackwell, Oxford, United Kingdom.

Publications and Presentations

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

- R. J. French, J. Stunkel, R. M. Baldwin, Mild Hydrotreating of Bio-Oil: Effect of Reaction Severity and Fate of Oxygenated Species, *Energy Fuels*, 2011, 25(7), 3266–3274.
- Christensen, E. D., Chupka, G., Luecke, J., Smurthwaite, T., Alleman, T. L., Iisa, K., Franz, J. A., Elliott, D. A., McCormick, R. L., Analysis of Oxygenated Compounds in Hydrotreated Biomass Fast Pyrolysis Oil Distillate Fractions, *Energy Fuels*, 25 (2011), 5462-5471.
- David, K., Ben, H., Muzzy, J., Feik, C., Iisa, K, Ragauskas, A., Chemical Characterization and Water Content Determination of Bio-Oils Obtained from Various Biomass Species Using ^{31}P NMR Spectroscopy, *Biofuels*, **3** (2012), 123-128.
- Czernik, S., Catalytic Pyrolysis of Biomass, in Advanced Biofuels and Bioproducts, Lee, J., Ed., Springer Science & Business Media, 2012.
- Czernik, S., Catalytic Pyrolysis of Biomass for the Production of Fuels, *Modern Energy Review* 2012 vol. 4, issue 2, 43-44.
- French, R., Oxygen Species from Partially Hydrogenated Biomass Pyrolysis Oils—Implications for Refineries, Keynote presentation at the 7th International Symposium on Hydrotreating/ Hydrocracking Technology held at the 242nd ACS National Meeting & Exposition, August 29, 2011, Denver, CO.
- Czernik, S., French, R., Catalytic Pyrolysis of Biomass, Oral presentation at TCBiomass2011 , Sept. 27-30, 2011, Chicago, IL.
- French, R., Stunkel, J., Baldwin, R., Mild Hydroprocessing of Biomass Pyrolysis Oil – Effect of Catalyst Type on Oxygenates and Refinery Use, Oral presentation at TCBiomass 2011, Sept. 27-30, 2011, Chicago, IL.
- Moens, L., Iisa, K., Study of Catalysts for Mild Hydrotreating of Phenolics Derived from Bio-Oil, Poster presentation at TCBiomass2011 , Sept. 27-30, 2011, Chicago, IL.

Publications and Presentations

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

- Stanton, A. R., Iisa, K., Czernik, S., Effect of Biomass Pretreatment on Liquid-Range Hydrocarbon Production during Catalytic Fast Pyrolysis of Pine, Presented at the ACS Spring National Meeting and Expo, San Diego, CA, March 25-29, 2012. Extended abstract in Preprints of Papers -- American Chemical Society, Division of Fuel Chemistry. Vol. 57(1), March 2012; Washington, DC: American Chemical Society (ACS) pp. 175-176.
- Iisa, K., Stanton, A. R., Czernik, S. (2012). Production of Hydrocarbon Fuels from Biomass by Catalytic Fast Pyrolysis, 2012 World Renewable Energy Forum. Denver, CO, May 13-17, 2012, 8 pp,
- French, R., Partial Hydrogenation of Biomass Pyrolysis Oils to Liquid Fuel Intermediates, 2012 World Renewable Energy Forum. Denver, CO, May 13-17, 2012.
- Czernik, S. French, R. (Invited presenttaton), Catalytic Pyrolysis of Biomass for Fuels Production, ACS Rocky Mountain Regional Meeting, Westminster, Co, October 17-20, 2012.
- Stanton, A., Iisa, K., Effect of Hydrogen on the Vapor-Phase Upgrading of Lignin Pyrolysis Product, ACS Rocky Mountain Regional Meeting, Westminster, Co, October 17-20, 2012.
- R. French, “Hydrogenation of Biomass Pyrolysis lignin to Fuel Intermediates,” Rocky Mountain Regional Meeting of the American Chemical Society, October 19, 2012, Westminster, CO.
- Moens, L. (Invited presentation) “Gen II Biomass Conversion – Lignocellulosic Bio-Oil,” Energy Workshop held at the National High-Magnetic Field Laboratory (Florida State University, Tallahassee, Florida) Nov. 7-8, 2012.
- French, R., “Refinery Feedstock From Partially Hydrogenated Biomass Pyrolysis Oil,” Spring meeting of the American Institute of Chemical Engineers (AICHE), April 28 - May2, 2013, San Antonio, TX.

Bio-oil Stabilization and Upgrading – Technical Challenges

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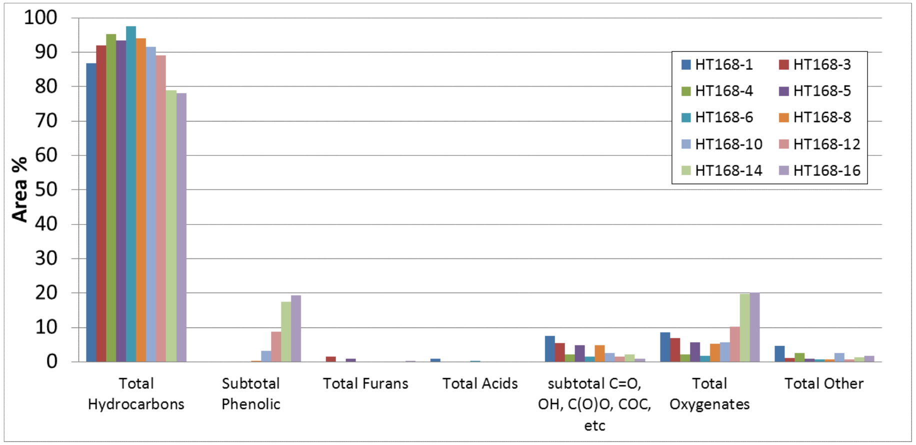
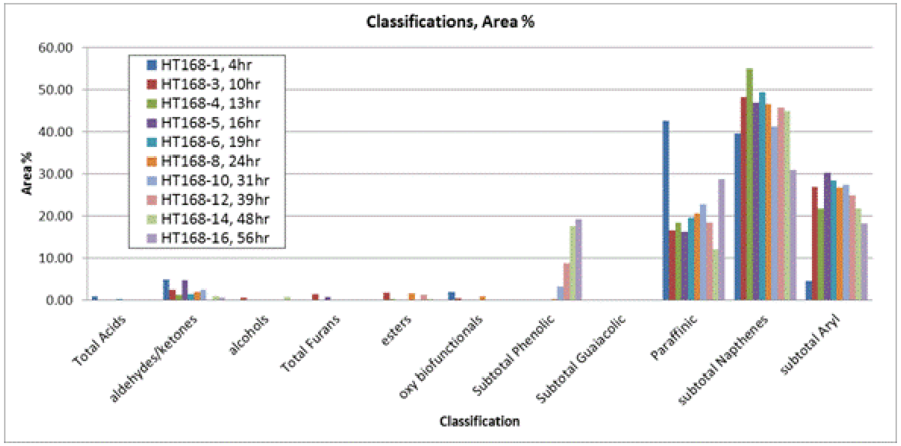
- Fast pyrolysis derived bio-oil has many undesirable properties, the main technical barrier is the removal of oxygen:
  - High O content: 35-40%
  - High water content: 15-30 wt%
  - High acidity; pH = 2.5, TAN > 100 mg KOH/g oil
  - Unstable (phase separation, reactions)
  - Low HHV: 16-19 MJ/kg
  - Distillation residue: up to 50 wt %
- Other direct liquefaction of biomass technologies provide different quality bio-oils in different yields

Energy & Fuels 18: 590-598 (2004)

2. Technical Progress:
Advanced Analytical: 2D GC x MS

Goal: Develop understanding of upgraded fuel product and catalyst functionality with time on stream





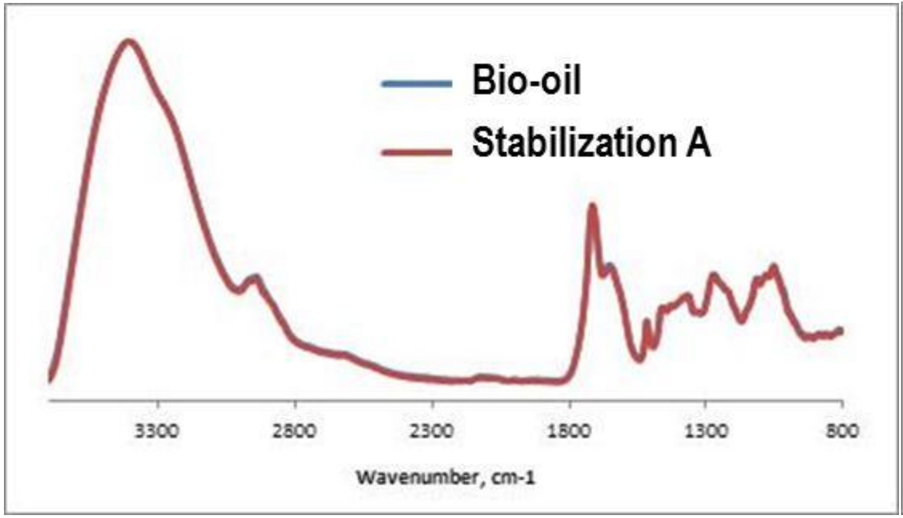
Accomplishments:

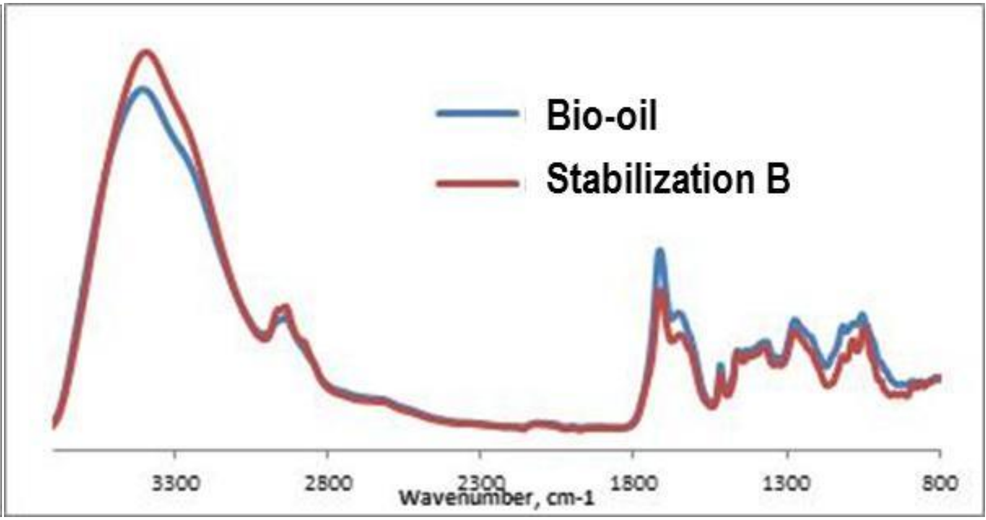
- Determined composition of upgraded fuel for design case modeling and industry interaction
- Insight into the changes in upgrading catalysts over extended use
- Identified residual oxygenates in upgraded fuels
  - Trended through change in catalyst activity over time

Characterization is a key linkage to industrial integration of pyrolysis derived fuels

2. Technical Progress
Advanced Analytical: ATR-IR, ^{13}C NMR

Goal: Develop tools to understand and predict success in bio-oil upgrading



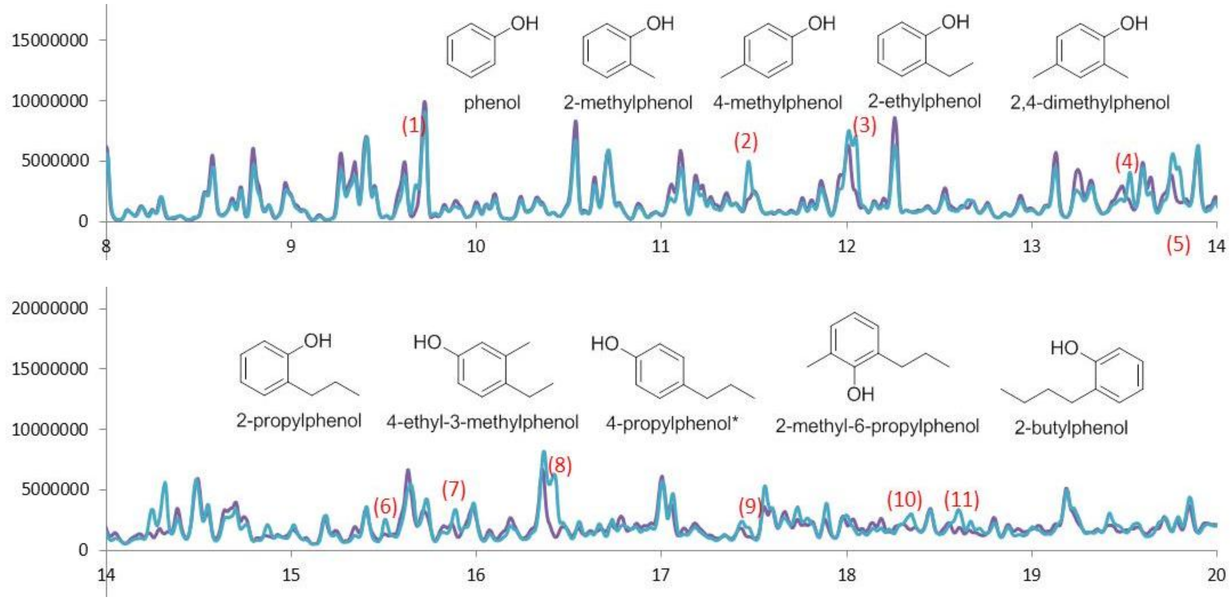


Accomplishments:
- Identified specific functional groups in bio-oil that correlate to empirically successful upgrading catalyst performance
- Developed an understanding of conditions required to successfully convert bio-oil from raw state through to finished fuel
- Developed operating strategy that enabled long catalyst lifetimes in upgrading tests

Oil characterization allows for understanding of reactive species and allows for optimization of bio-oil stabilization

2. Technical Progress: Upgrading catalyst lifetime testing

Goal: Characterize subtle differences in upgraded fuels as the catalysts age

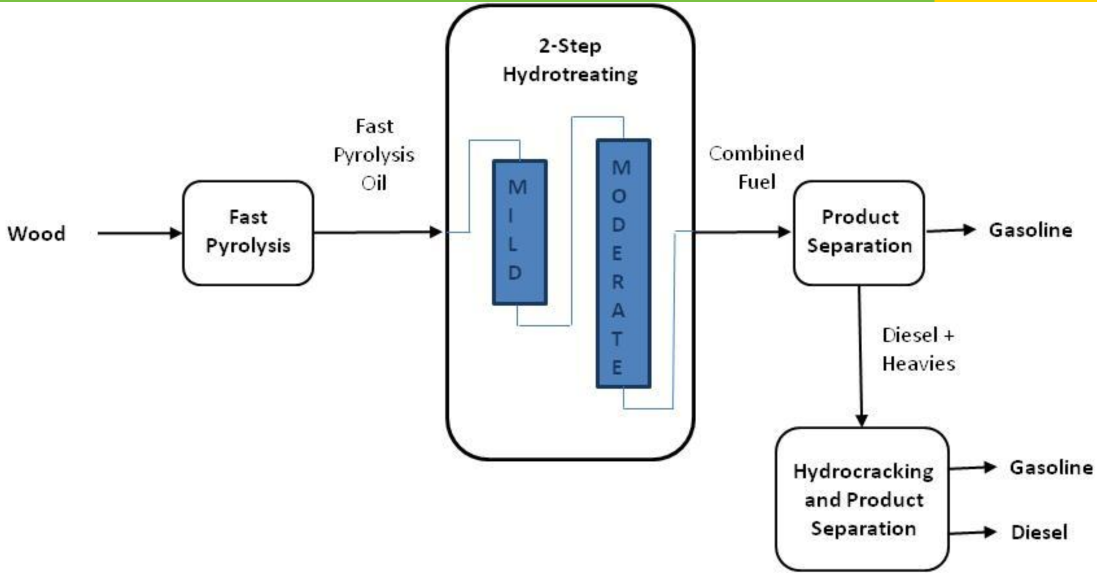


HOS	379	600
Density	0.84	0.87
wt% O	1.3%	2.5%

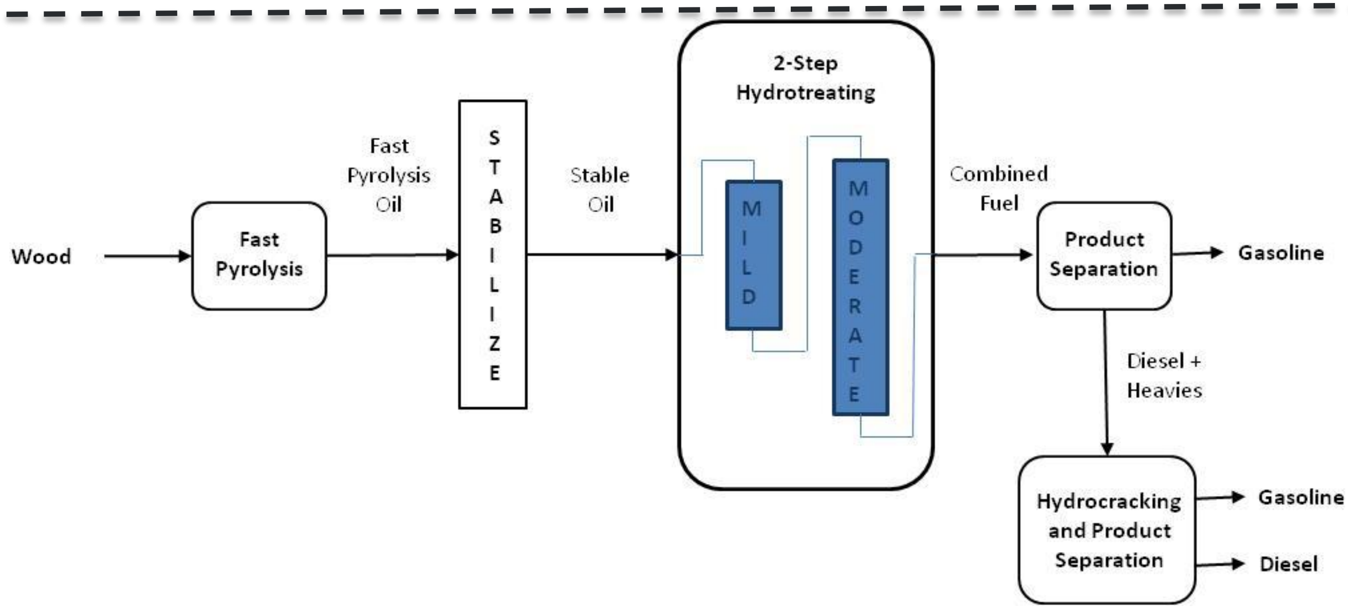
- Example GC/MS overlay of fuel product at 379hr and 600hr time on stream to detect changes in catalyst performance
- Increase in oxygen content due to alkyl substituted phenols

This provides speciation of the compounds potentially left in pyrolysis derived fuels as catalysts age.

Model Process Flow: 2011 To 2012



The 2011 SOT assumes 2-stage hydrotreating. R&D performed during 2011 and 2012 indicates that multiple stages result in better catalyst performance



The 2012 SOT assumes a stabilization-type stage prior to 2-stage hydrotreating

2. Technical Progres: Ebullated Bed Hydrotreater CapEx

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Goal: Construct novel bio-oil hydrotreater based on petroleum hydrotreater for processing similarly difficult petroleum oils

Approach

- Bench scale ebullated bed compatible with bio-oil
- Develop/demonstrate new elements needed specifically for challenges of bio-oil
- Generate data for scale up of existing hydrotreater concepts
- Continuous separation of liquid phases and gas
- Hydrogen recycle and byproduct gas purge
- Test unit operations needed to construct demonstration scale hydrotreater (any bed type)