2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review

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

CA-02 Pyrolysis and Upgrading Collaboration with Canada

May 21, 2013 Kristiina Iisa, Alan Zacher

Technology Area Review: Bio-oil Technology

Organizations: NREL, PNNL

Goal/Objective Statement

- Objective: Combine US and Canadian expertise to advance pyrolysis of residue woody feedstocks for biofuels and biopower applications
  - Production and upgrading of bio-oil to meet requirements for use in transportation and stationary power applications
- Relevance to EERE and BETO
  - Generate data to enable use of low-value residue woody biomass to meet biofuels targets
  - Meet national commitments to the US-Canada Clean Energy Dialogue

Project Quad Chart Overview

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Timeline

- Start: September 2009
- End: September 2017
- Percent complete: 45%

Barriers

- Barriers addressed
  - Tt-E. Liquefaction of Biomass and Bio-Oil Stabilization
  - Tt-G. Fuel Synthesis and Upgrading
  - Ft-A. Feedstock Availability and Cost

Budget

Total project funding

DOE (NREL/PNNL): $1,100k

Natural Resources Canada: $1,100k

Funding in FY 2011:	-
Funding in FY 2012:	$100k (DOE)
Funding for FY 2013:	$100k (DOE)
Project funding so far:	$600k (DOE) over 3.5 years

Average annual funding: DOE $100k

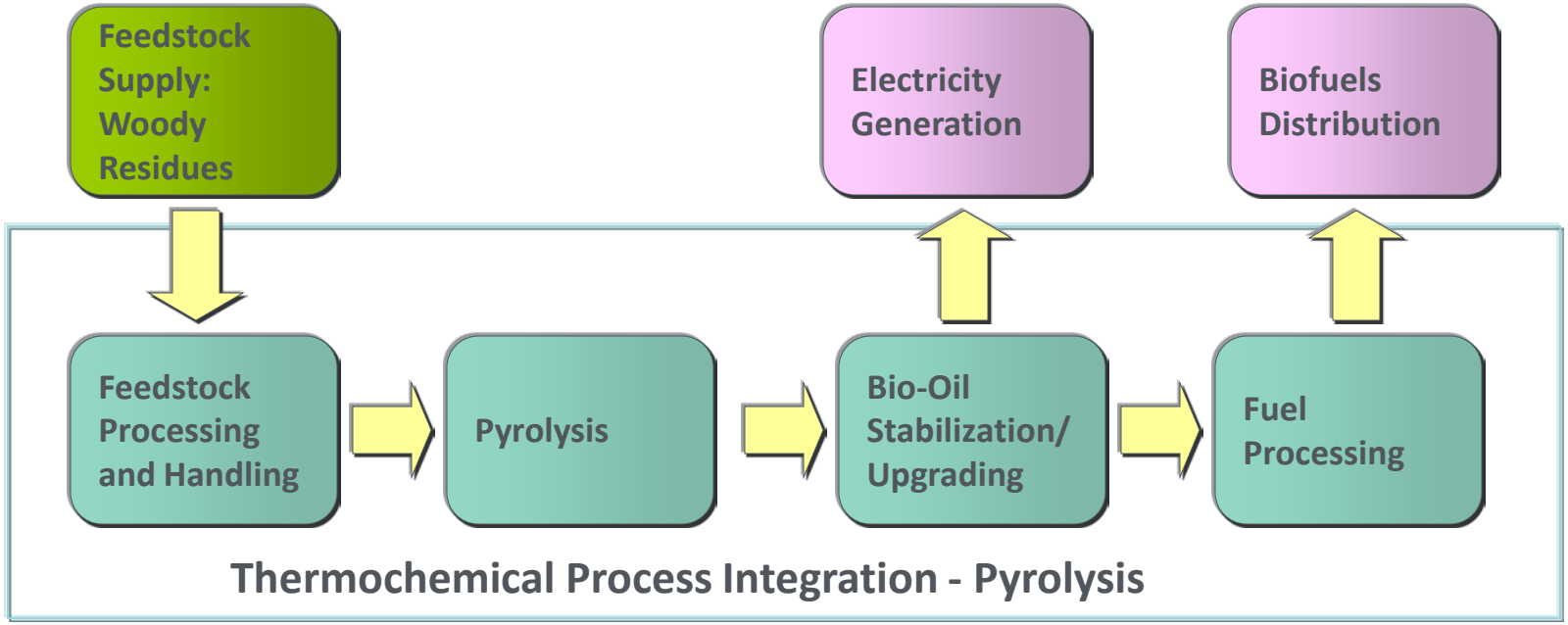
Partners & Roles

- NREL and PNNL
- National Resources Canada/CanmetENERGY

- Each country funds own activities

Project Overview

- Fast pyrolysis of low-quality woody residues: hog fuels and pine-beetle killed trees
- Determination of impact on oil yield and quality
- Comparisons between pyrolysis technologies and scales
- Upgrading of bio-oil for biofuels and biopower applications



1 - Approach

Technical Approach

- Common woody residue feedstocks provided to all partners
- Screening of feedstocks and pyrolysis conditions at milligram scale
  - Vapor analysis by molecular beam mass spectrometry (MBMS)
- Production of oil and upgrading at bench scale
  - 1 kg/h and 10 kg/h fluidized bed pyrolyzers
  - Continuous trickle bed hydrotreater
  - Evaluation for biofuels and biopower applications
- Production and testing of larger quantities of residue pyrolysis oil (future)

Management approach

- Milestones/reports
- Periodic communication and materials and data exchange to ensure international collaboration
- Annual workshops
  - 2012 at PNNL
  - 2013 at NREL

2 - Technical Accomplishments

- 2009-2011 we tested six woody biomasses of common interest
  - Reference (interior), coastal, and salt laden hog fuel
  - Mountain pine-beetle killed pine
  - Reference pine and birch
- Pyrolysis at mg scale (Py-MBMS) and in fluidized bed reactor

- 2011-2013
  - Continued analysis of data
  - Pretreatment to remove salt
  - Upgrading of oil

Reference Hog Fuel
MPBK Wood

Coastal H.F.
Pine

Salt Laden H.F.
Birch

Pyrolysis: Micro-Scale Results

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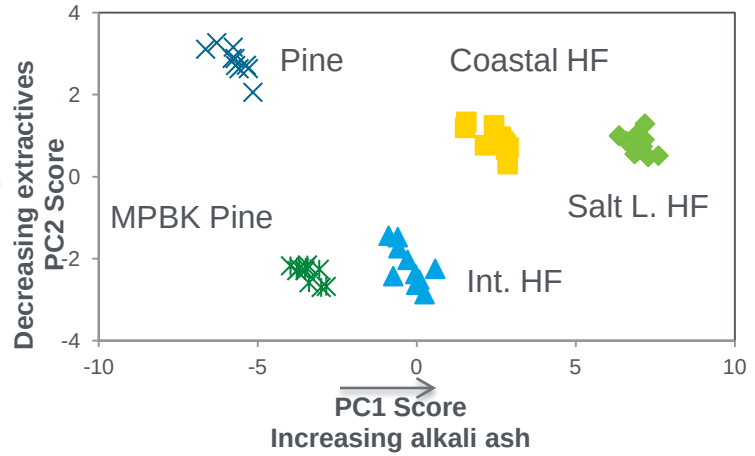
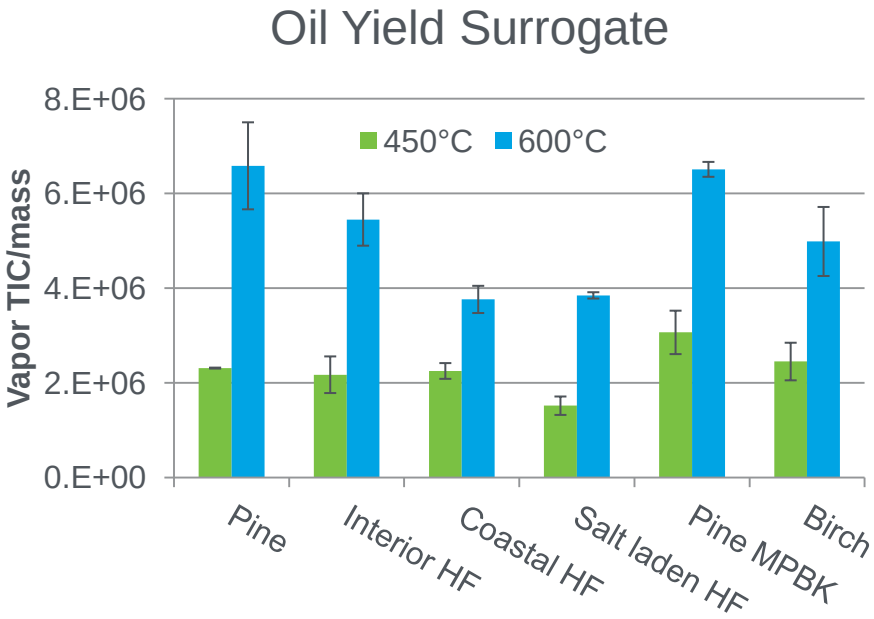
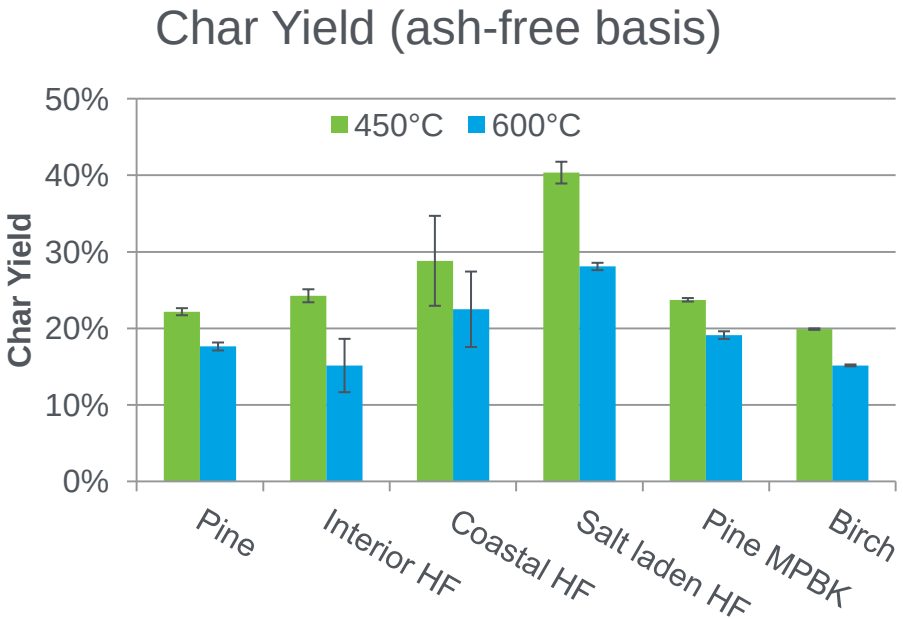
- Pyrolysis-MBMS
  - Char yield
  - Vapor analysis
  - Multivariate analysis







Pyrolysis: Fluidized Bed Results

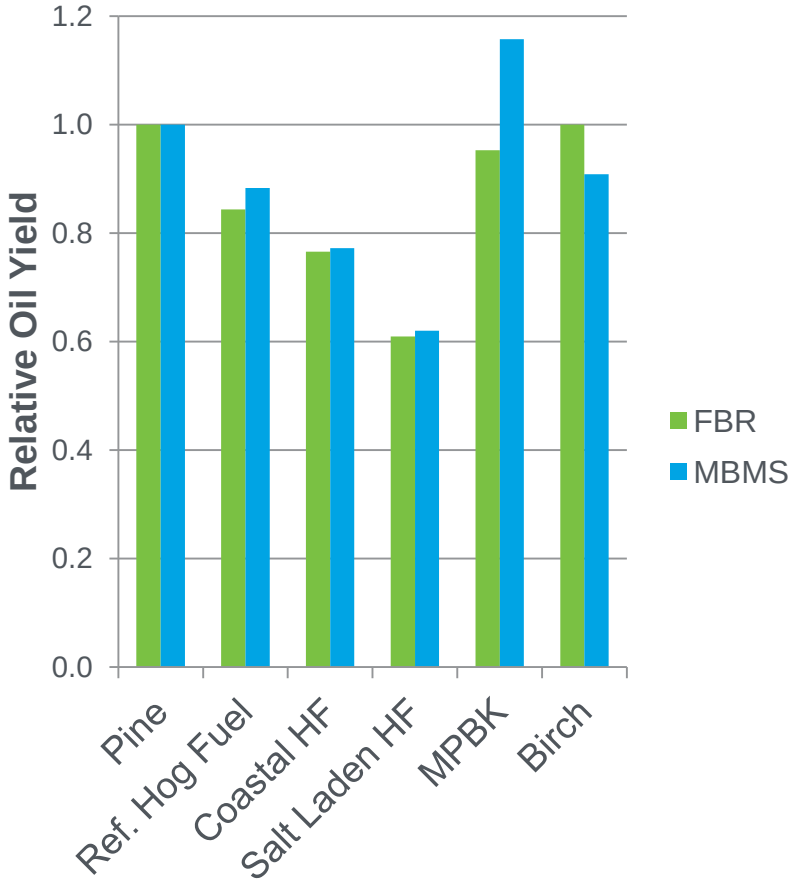
- **Lower quality feedstocks result in**
  - **Lower oil yields**
  - **Increased char yield (also on ash-free basis)**
  - **Higher CO_2:CO**

Feed		Mass % Yields			Dry Oil Analysis					
Type	Ash%	oil	char	gas	C	H	O	H_2O	TAN	CO_2:CO
Pine	3.9	64	14	19	56	6.7	33	14	68	1.4
Reference Hog Fuel	5.0	54	25	21	58	7.0	30	13	75	2.0
Coastal Hog Fuel	13	49	36	18	59	6.9	34	12	67	2.1
Salt Laden Hog Fuel	10	39	33	21	59	6.7	30	23	63	3.0
Beetle Killed Pine	1.1	61	17	18	57	7.0	35	8.2	68	1.5
White Birch	3.2	64	13	n/a	59	7.0	31	14	n/a	n/a

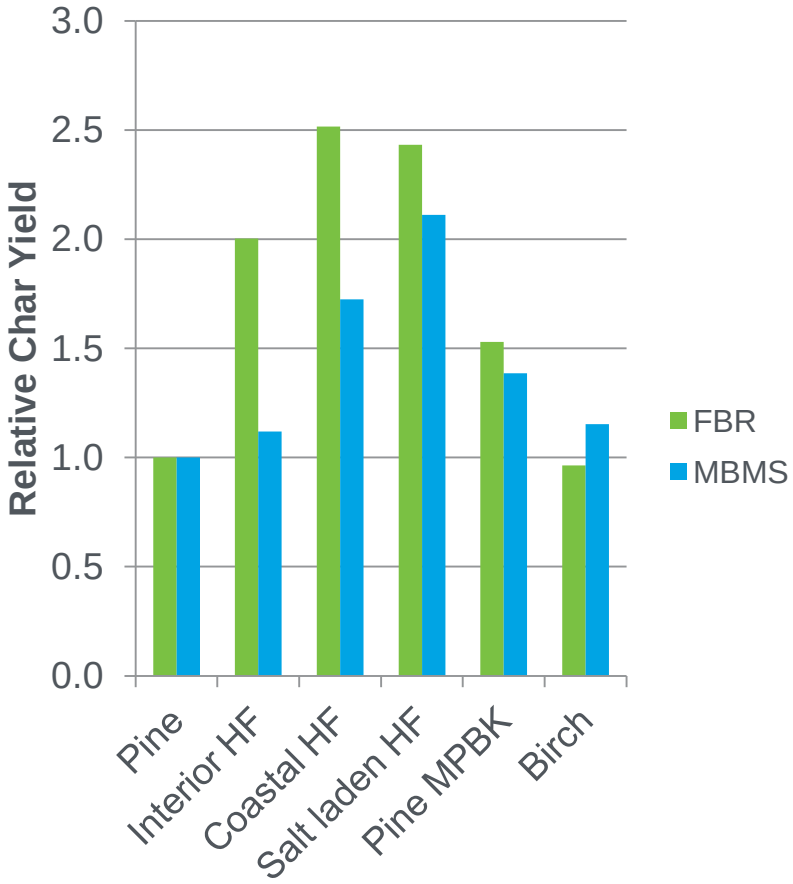
Bubbling fluidized bed pyrolysis, 480°C, ~1 kg/hr, 0.8s vapor res.time, under nitrogen

Similar Results in mg Scale and Fluidized Bed Reactor

Relative Oil Yield

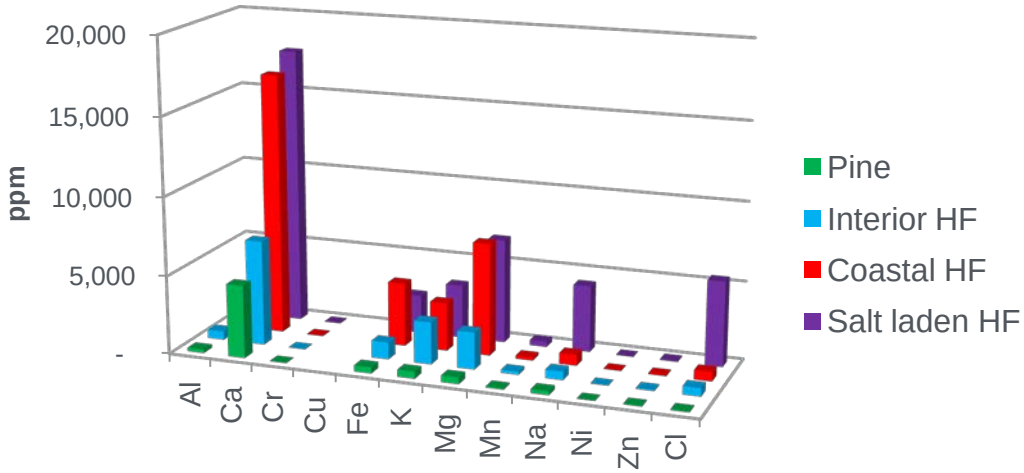


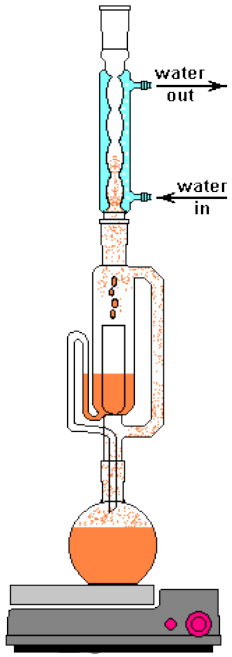
Relative Char Yield



Reducing Salt Content to Improve Oil Yield

- Ash-forming compounds reduced oil yields
- Highest impact in logs transported in ocean (salt laden hog fuel)
- Water washing was tested as a means of reducing salt contents





Water Washing: Results from Micro-Scale Screening

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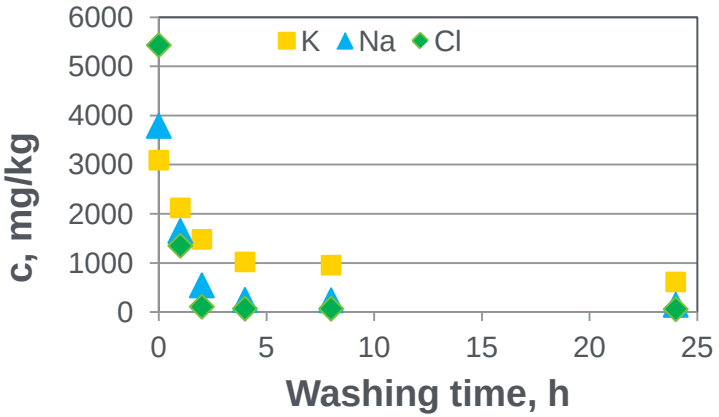
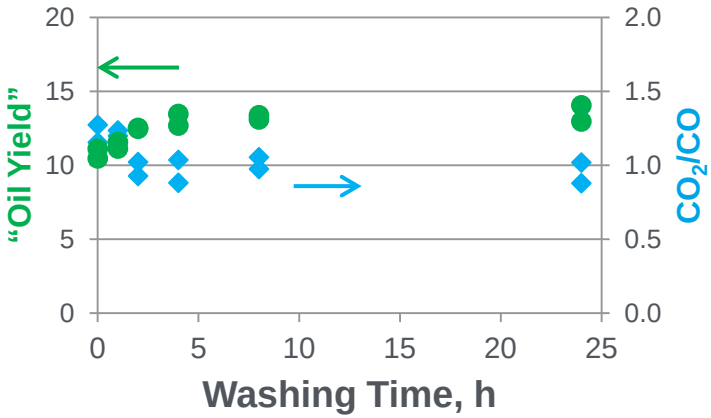
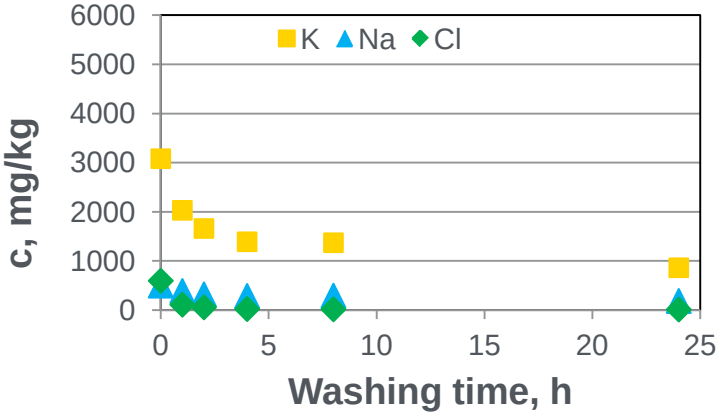
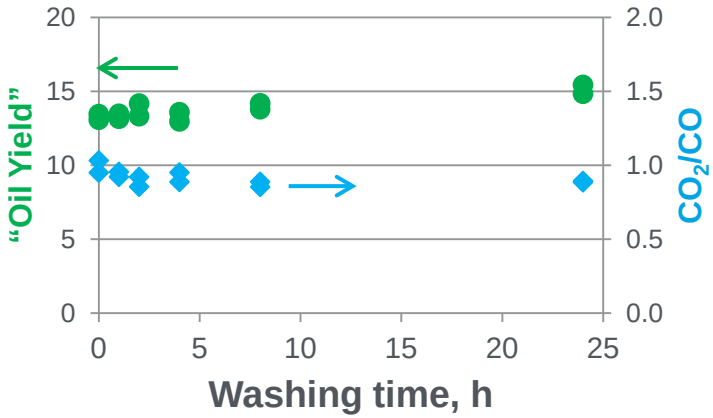
Salt Laden Hogfuel





Coastal Hogfuel





Water Washing cont'd

- Water washing for 4 h in micro scale sufficient to reduce Na and Cl and to increase surrogate oil yield, decrease char yield, and transform compositions to levels comparable to other hog fuels
- Tested further in bench scale in fluidized bed reactor for salt laden hog fuel

Feed	Dry Basis (wt%)						Moist. (wt%)
	C	H	N	O	S	ash	
Reference Hog Fuel	48.4	6.1	0.2	46.4	0.1	8.9	5.0
Coastal Hog Fuel	45.4	5.7	0.2	41.4	0.1	13.3	7.2
Salt Laden Hog Fuel	**47.0**	**5.9**	**0.2**	**39.3**	**0.1**	**10.2**	**10.6**
Washed SL Hog Fuel	**47.7**	**5.3**	**0.2**	**39.4**	**0.0**	**5.3**	**4.1**

Fluidized Bed Tests with Water Washed Salt Laden Hog Fuel

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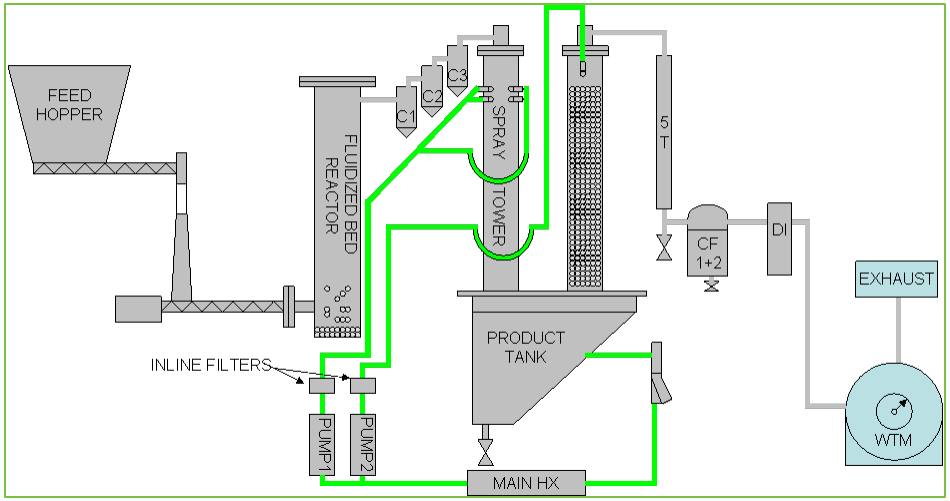
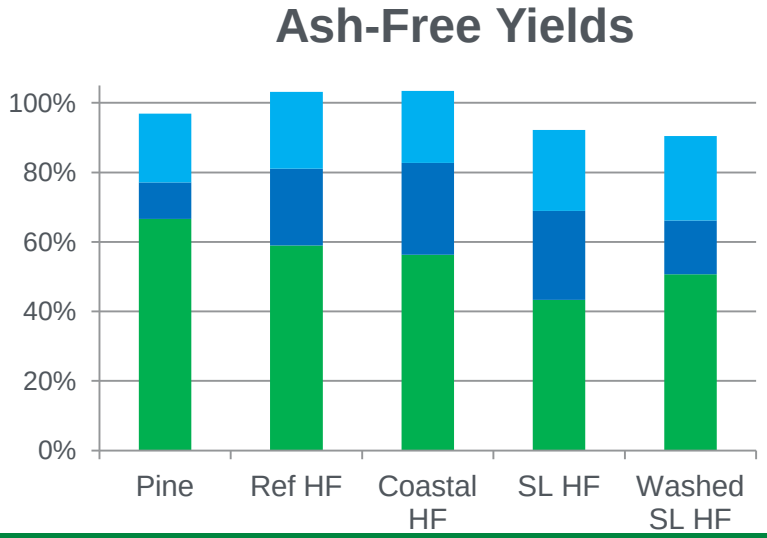
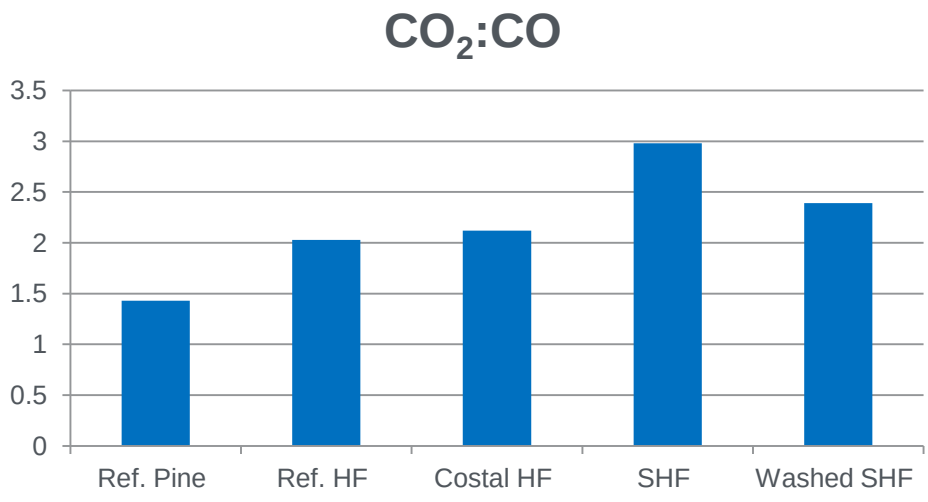
- Water washing reduced ash by 50% and Na and K by 50-80%
- Improved oil yield
- Decreased char yield
- Decreased CO_2:CO



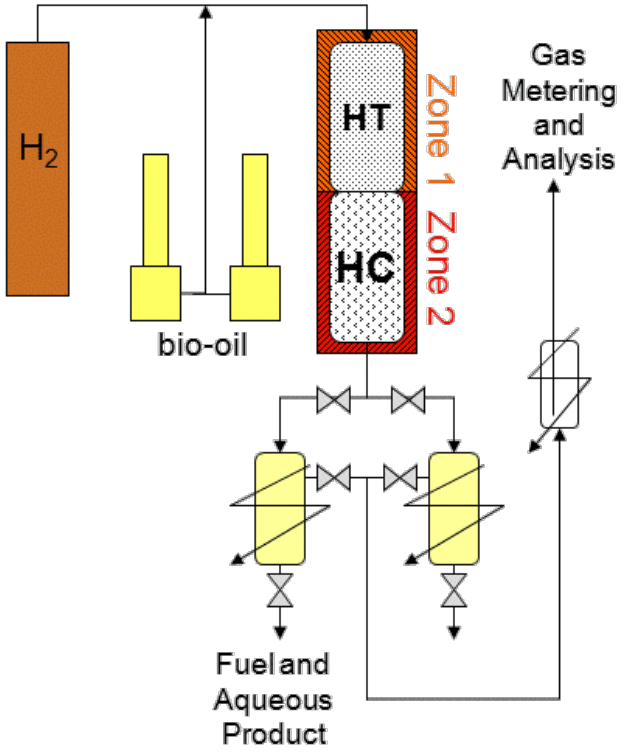




Upgrading of Woody Residue Pyrolysis Oils

Goal to evaluate feasibility of upgrading pyrolysis oil from woody residues

Tested with mountain pine-beetle killed wood (MPBK) and reference interior hog fuel



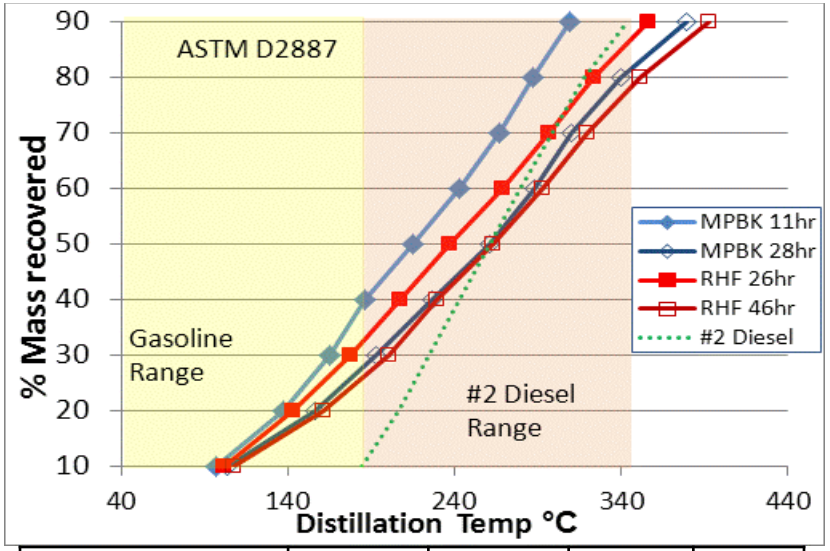
Upgrading Results

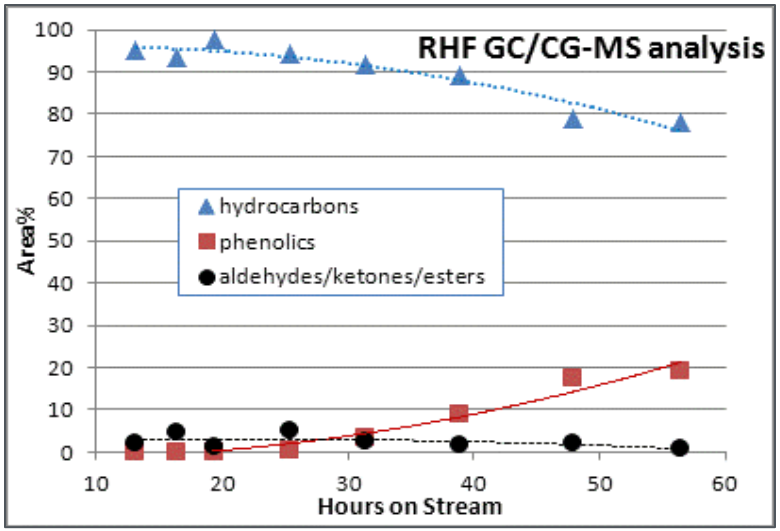
Upgraded bio-oils from hog fuel pyrolysis

Bio-oil	Temp. (°C)	Catalyst	Product Oil			Time-on-Stream (h)
			O	Density	TAN	
MPBK	171/404	CoMoS/C	0.3-1.7	0.83-0.94	<0.08	40 fouled
Hog Fuel	172/405	CoMoS/C	0.1-2.6	0.80-0.92	<0.09	>59 fouling

Upgrading Results cont'd

- Low-O oils in liquid transportation fuel range produced successfully
- Similar impacts to catalyst lifetime as with other non-stabilized bio-oils
- No additional challenges
- Overall mass yields of 25% for hog fuel to upgraded oil





Fraction (BP range)	MPBK 11hr	MPBK 28hr	RHF 26hr	RHF 46hr
Gasoline IBP-184°C	39%	27%	33%	26%
Diesel 184-344°C	57%	55%	54%	52%
Heavies > 344°C	4%	18%	13%	22%
Jet A (overlap) 153-256°C	40%	29%	33%	30%
Oxygen%	0.3%	1.73%	0.68%	2.6%

3 - Relevance

- **Contributes to the overall Bio-Oils Pathways R&D goal**
  - ***'By 2017, achieve a conversion cost of $1.83 per gallon of total blendstock ($1.73 /GGE)($2011) via a bio-oil pathway'***
  - by evaluating the use of low-cost feedstocks
  - by leveraging international resources
- **Barriers addressed**
  - Tt-E. Liquefaction of Biomass and Bio-Oil Stabilization
  - Tt-G. Fuel Synthesis and Upgrading
  - Ft-A. Feedstock Availability and Cost
- **Applications of the expected outputs**
  - The data on pyrolysis and upgrading of low-quality woody feedstocks can facilitate adaptation of technology and assist in process design and development

4 - Critical Success Factors

- **Critical success factors**
  - Ability to demonstrate suitability of hog fuels for pyrolysis feedstocks
  - Availability of reactors
  - Effective sharing of information and materials
- **Top potential challenges**
  - Ash/contaminant impact on long-term performance and scaling up
  - Continued funding for international projects
  - Differences in US and Canadian national goals
- **Impacts upon success**
  - Data on pyrolysis and upgrading of low quality woody feeds will be available to assist industry with process design and application
  - Contributes to increase in availability of low-cost feedstock by expanding pyrolysis into low-quality feeds
  - Helps meet the goals of the US/Canada Clean Energy Dialogue

5. Future Work

- Evaluate impact of feedstock variability on oil yield and properties (micro scale)
- Produce, upgrade, and fractionate larger quantities of hog fuel oil
- Evaluate suitability of fractions for transportation fuels and stationary power applications
- Beyond September 2014: Produce upgraded oils in larger scale and test in stationary applications

Task	FY13 Q3	FY13Q4	FY14Q1	FY14Q2	FY14Q3	FY14Q4
Impact of feed variability on pyrolysis (microscale)						
Production of 10 L of hogfuel pyrolysis oil						
Upgrading of pyrolysis oil						
Oil fractionation						
Evaluation of fractions for end applications						

Summary

- International collaboration leveraging expertise in Canada and the US to evaluate pyrolysis of low-quality woody feedstocks for biofuels and biopower applications
  - Part of US-Canada Clean Energy Dialogue
- Experimental work at mg and bench scale
- Have successfully demonstrated the production of upgraded oils from low-value feedstocks
- Progress since 2011 evaluation
  - Upgrading of residue feedstocks
  - Evaluation of feedstock pretreatment (water washing)
- Future plans
  - Evaluate impact of feedstock variability on oil quality and yield
  - Assess suitability of upgraded fractions for end applications

Responses to Previous Reviewers' Comments

- *Are there enough residues and pine-beetle killed trees for them to be a significant feedstock compared to other biomass sources?*
- Low-cost residues and dead trees present an opportunity for initial adaptation of pyrolysis technology. Mill residue production is estimated at 7.4 million dry tons per year in the US[1] and at 21.1 million dry tonnes in Canada.[2] In the US, dead or dying trees in Wyoming and Colorado are estimated to be 5.1-6.7 million dry tons[3] and in Canada the pine beetle killed wood in British Columbia is estimated at over 200 million dry tonnes.[4]

1. US Billion-Ton Update, 2011
2. Estimated Production, Consumption and Surplus Mill Wood Residues in Canada – 2004, National Report, 2005.
3. Mountain Pine Beetle Area Long Term Stewardship Project Solicitation, US Forestry Service, 2010
4. Feedstock Availability and Power Costs Associated with Using BC's Beetle-Infested Pine, Final Report: November 3, 2005

Responses to Previous Reviewers' Comments cont'd

- *The researchers have not addressed several factors common to international collaborations such as alignment of goals and strategies and intellectual property.*
- The research seeks to address both countries' interests by evaluating common low-value woody feedstocks for both biofuels (US interest) and power applications (Canadian interest). The data generated in this project is pertinent to both applications.
- With respect to intellectual property, the technologies employed are already established and the focus is on assessing the application with these feedstocks. The project is not expected to generate new intellectual property.

Publications and Presentations

- Zacher, A., Iisa, K., Preto, F., Production of Transportation Fuel Range Oils via Pyrolysis and Upgrading of Woody Residues, Manuscript under preparation.

- Zacher, A., Iisa, K., Sykes, R., Preto, F., Pyrolysis and Upgrading of Woody Residues, Abstract submitted to 2013 TCBiomass, September 3-6, 2013.