EERE Biomass Program

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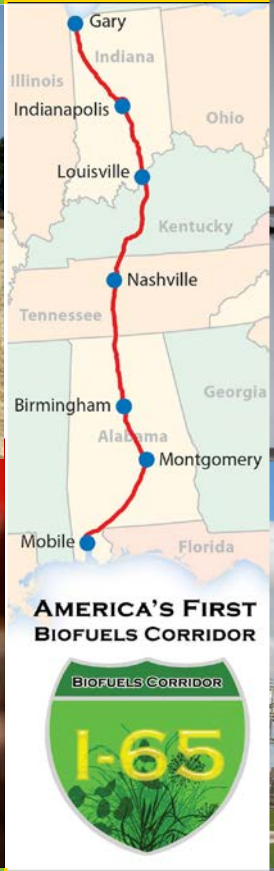

U.S. – Canada, U.S. and Finland Pyrolysis Collaborations

Webinar on International Collaboration

December 5, 2012

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Replacing the Whole Barrel

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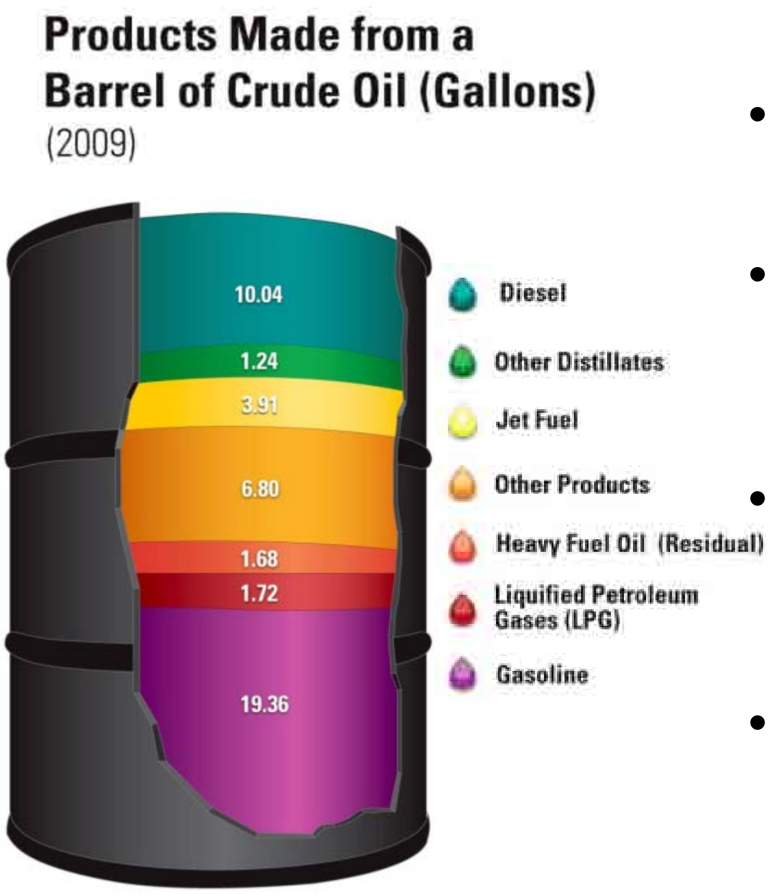
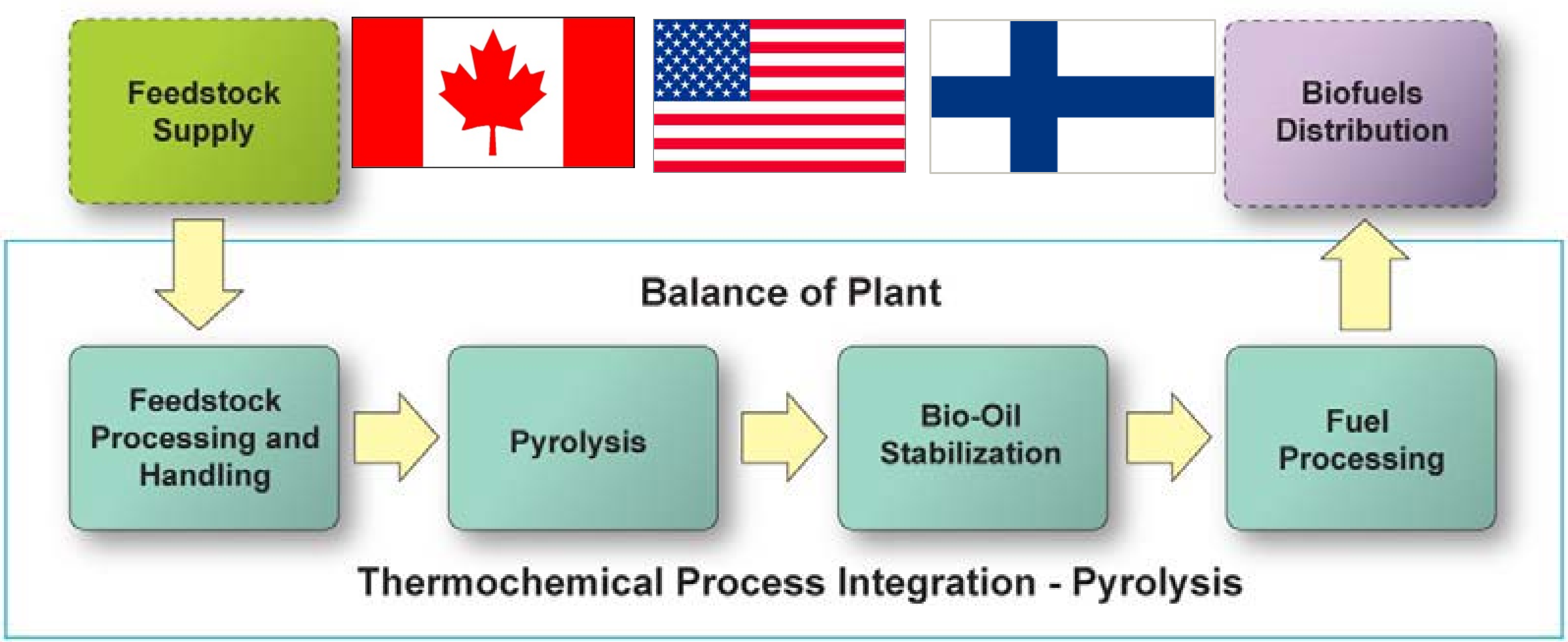


- U.S. spends more than $1,197M each day on crude oil imports*
- Cellulosic ethanol displaces light duty gasoline fraction only
- Only about 40% of a barrel of crude oil is used to produce light duty petroleum gasoline
- Reducing dependence on oil requires replacing diesel, jet, heavy distillates, and a range of other chemicals and products
- Greater focus needed on RDD&D for a range of technologies to displace the entire barrel of petroleum crude

Source: Energy Information Administration, "Oil: Crude Oil and Petroleum Products Explained" and AEO2009, Updated February 2010, Reference Case.
*American Petroleum Institute.

Goal Statement

- GOAL: Combine US and Canadian expertise to understand how pyrolysis of various forest residues can be used for biofuels and biopower applications
- GOAL: Using US and Finnish expertise accelerate the commercialization and deployment of pyrolysis bio-oil production and upgrading routes



U.S. - Canada Project Overview

- Collaboration of US (PNNL/NREL) and Canada (CanmetENERGY) to evaluate bio-oil production and use from forest residues using different fast pyrolysis technologies

- Supports US/Canada "Clean Energy Dialogue"
- Objectives
  - Fast pyrolysis of low quality hog fuels and pine-beetle killed trees and determination of impact on oil quality
  - Compare fluidized bed and auger pyrolysis technologies on identical feeds to compare bio-oil product quality
  - Evaluate pyrolysis oil vapor quality by small scale analysis
  - Understand upgrading requirements for bio-oil from low quality forest residues to improve existing models from "pure" wood research
  - "The future portion of this project will be to test the bio-oil on turbine and diesel engines to determine its ability and usefulness for these applications"

Project Accomplishments

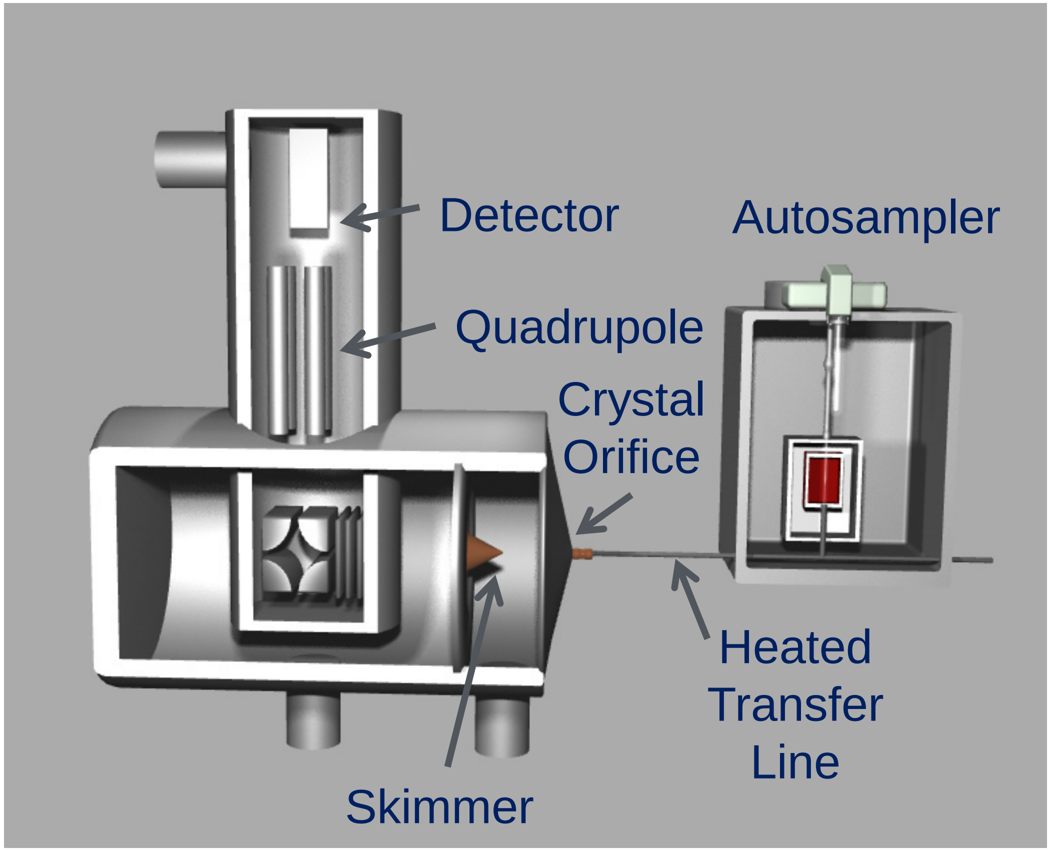
- Identical feeds received at all research labs
  - CanmetENERGY supplied significant amounts of target feeds
- Testing in bench-scale reactor configurations
  - Fluid bed testing complete
  - Auger pyrolysis met with additional challenges – refocus on ablative pyrolysis
- Microscale multivariate pyrolysis vapors analysis
- Evaluation of bio-oil quality (at two scales):
  - Bio-oils derived from mountain pine and mountain pine beetle killed
  - Interesting changes in bio-oils due to bark and chlorides
- Upgrading of bio-oils liquid transportation fuels from mountain pine beetle killed (MPBK) trees and hog fuel

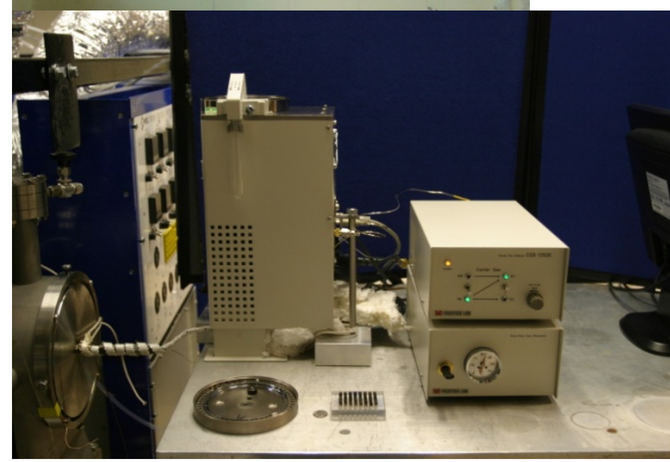
Pending

- Publish collaboration results in reviewed journal articles

Micro-scale Oil Quality Evaluation: Micro-Pyrolyzer with MBMS

Micro-pyrolyzer with molecular-beam mass spectrometer (MBMS)





Molecular Beam Mass Spectrometry samples hot pyrolysis vapors prior to condensation and freezes the composition

- To study impact of forest residue source on oil quality and yield
- Low energy: 22.5 eV vs. 70 eV leads to less fragmentation
- Rapid evaluation of impacts with small samples

Hogfuel Comparison Using Pure Component Loadings

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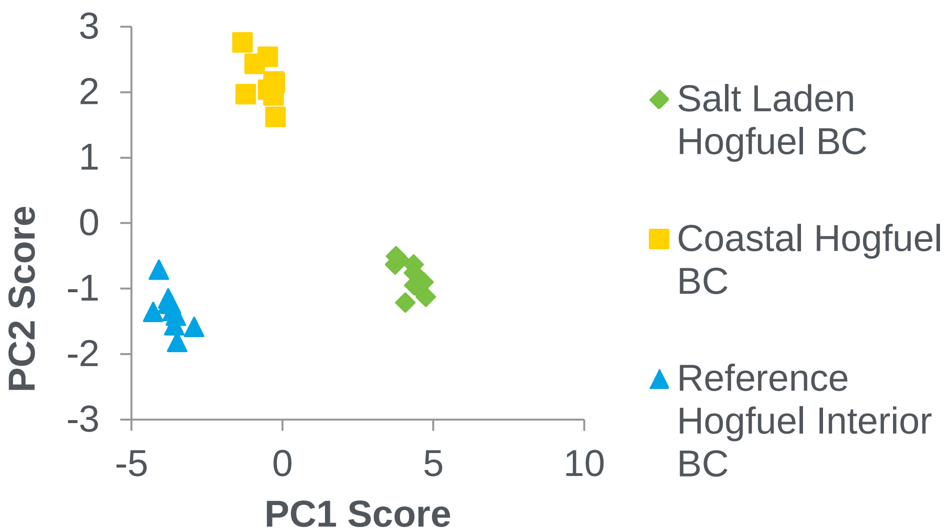
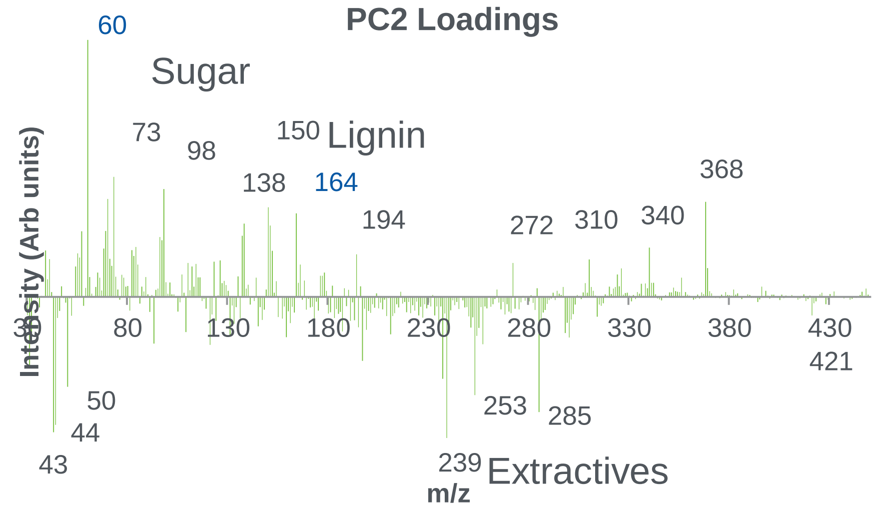
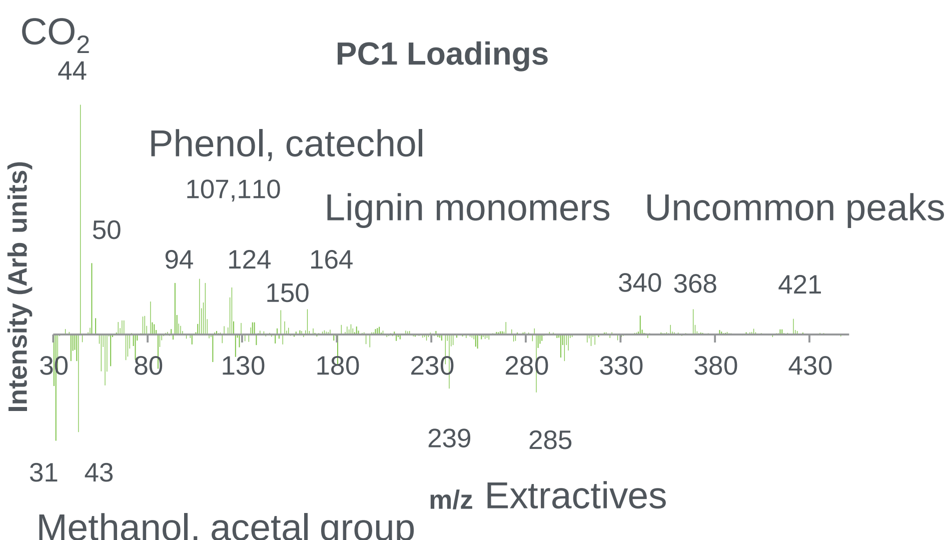




PC2: 15% of Variance



PC1: 66% of Variance

Salt modifies reaction pathways:

- CO_2 high in costal and salt laden hogfuel
- Extractives (bark) are lower in costal and salt laden hogfuel
- Uncommon peaks are high in costal and salt laden hogfuel
- Higher char yield and lower oil yield costal and salt laden hogfuel

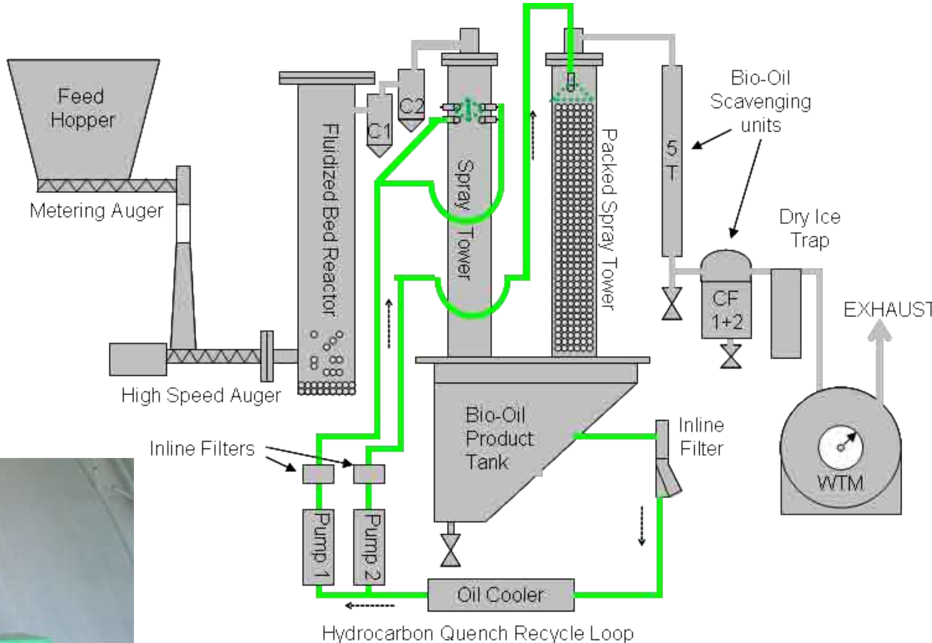
Technical Accomplishments: Bench-scale Testing of Forest Residues

Hog Fuel Feeds
- Reference Hog Fuel (interior British Columbia)
- Coastal Hog Fuel (British Columbia)
- Salt Laden Hog Fuel (British Columbia)

Forest Residue Feed
- Mountain Pine Beetle Killed Wood

Baseline Feeds
- Pine Sawdust (Thunder Bay, Ontario)
- White Birch (Northern Ontario)

CanmetENERGY Auger Pyrolysis System



US Bubbling Fluidized Bed Pyrolysis System

Hog Fuels are a mix of bark, sawdust, and planer shavings from a sawmill operation.

Bench Scale Pyrolysis of Salted Hog Fuels, Normalized

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Feed		Reported Yield			Ash-free Basis		
Type	Ash	oil	char	gas	oil	char	gas
Pine (reference)	3.9	64	14	19	67	11	20
Reference Hog Fuel	5.0	54	25	21	56	22	22
Coastal Hog Fuel	13	48	35	17	54	26	20
Salt Laden Hog Fuel	10	39	33	21	43	27	23

Non condensable gas analysis			
Feed	%CO_2	%CO	CO_2/CO
Pine (reference)	0.86	0.60	1.43
Reference Hog Fuel	1.5	0.73	2.05
Coastal Hog Fuel	1.4	0.66	2.12
Salt Laden Hog Fuel	1.7	0.57	2.98

- Ash affects biomass-to-oil yield
- Some ash types affect the chemistry (CO_2/CO ratio)

Reference Hog Fuel Upgrading

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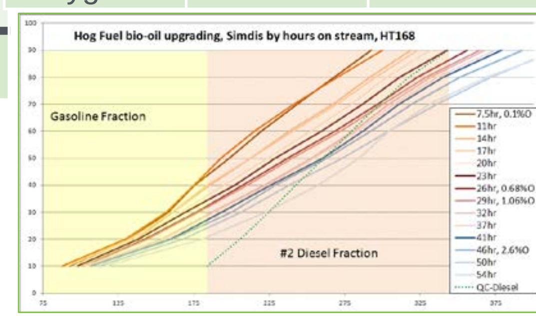
Sample Window ID	168-A	168-B	168-C	168-D
Average Hours on Stream	11	30	33	51
Product H/C, dry basis (ratio)	1.73	1.58	1.55	1.48
Product Oxygen, dry basis (wt%)	0.09%	0.70%	1.04%	2.36%
Product Oil Density (g/ml)	0.8	0.86	0.86	0.9
Product Oil Yield (g/g dry feed)	0.38	0.46	0.48	0.47
H_2 Consumed (g/g feed)	0.042	0.045	0.042	0.036
Product Oil C Yield	57.3%	70.5%	72.8%	71.0%
Aqueous C Yield	0.2%	0.7%	0.8%	0.8%
Gas (C1-C4) C Yield	20.8%	17.3%	19.5%	18.7%
Oil Gas (C5-C7) Yield	1.6%	1.4%	1.3%	1.3%
Carbon balance	79.9%	90.0%	94.3%	91.8%

Fraction (BP range)	RHF 26hr	RHF 46hr
Gasoline IBP-184°C	33%	26%
Diesel 184-344°C	54%	52%
Heavies > 344°C	13%	22%
Jet A (overlap) 153-256°C	33%	30%
Oxygen%	0.68%	2.6%



Bio-oil	Temp. 2-stage (°C)	Catalyst	Product Oil			TOS (h)
			O	Density	TAN	
Hog Fuel, Ref. F168	172-405	CoMoS/C	0.1-2.6	0.80-0.92	<0.09	>59 fouling

Summary

- Low quality wood feeds for pyrolysis/upgrading may be important to achieve national biofuels targets
- Low quality feeds can be upgraded to gasoline, diesel and jet range fuels
  - Processing of low quality residues has been successful
- Feed contaminants impact the yields
  - Hog fuel contaminants change product oil compound suite
  - The presence of salts in coastal and salt-laden hog fuels caused profound changes in reaction pathways (verified at two scales)
- Only minor differences between pine and MPBK
  - Some differences based on high extractives content (bark) (verified at two scales)

- International collaboration is effectively leveraging the expertise of both countries to help meet the EERE Biomass Program's goals

Production and Upgrading of Infrastructure Compatible Bio-oil

Collaboration of PNNL and VTT

This collaboration utilizes the expertise at VTT in fast pyrolysis and the expertise at PNNL in bio-oil hydrotreating

- Purpose
  - Accelerate commercialization and deployment of pyrolysis bio-oil production and upgrading routes.
  - Scope
  - Task A Bench-scale Experimental Evaluations – to allow optimization
    - A.1 Low-temperature hydrotreating to stabilize bio-oil
    - *A.2 High-temperature hydrotreating for hydrocarbon fuel production*
  - Task B. Economic Assessments of Pyrolysis and Upgrading
    - *B.1 Comparative TEA of fast pyrolysis and hydrothermal liquefaction*
    - B.2 TEA of low-temperature hydrotreating
  - Task C. Life Cycle Analysis
- Leading to Scale-up operations in new hydrotreater for fuel production
  - Low-severity and high-severity hydrotreating envisioned
  - Fuel product samples produced for testing