

2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review

Stabilization of Bio-Oil Fractions for Insertion into Petroleum Refineries

May 20, 2013

Bio-Oil Technology Area Review

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Goal/Objective Statement

- The goal of this project is to develop pyrolysis intermediates suitable as feedstocks for upgrading in a petroleum refinery. Specific objectives include:
 - Production of four upgrading fractions of bio-oil
 - Stabilization of the soluble carbohydrate fraction (sugars and furans) through aldol condensation, ketonization, oxidation, hydrogenation;
 - Stabilization of the clean phenolic oligomers fraction through hydroprocessing;
 - Stabilization of the middle fraction through alkylation and hydrodeoxygenation;
 - Stabilization of the light ends through ketonization and hydrogenation reactions;
 - Estimation of capital and operating costs for the production of refinery feedstocks via stabilization of pyrolysis intermediates.

Goal/Objective Statement

- Response to DE-FOA-0000686: Accelerate development of thermochemical liquefaction technologies to produce a bio-oil that can be utilized within a petroleum refinery
- This project addresses the U.S. DOE Office of Biomass Program's mission to develop advanced renewable fuels from lignocellulosic biomass.

Project Quad Chart Overview

Timeline

- Project start date: Jan. 1, 2013
- Project end date: Dec. 31, 2013
- Percent complete: 30%

Barrier Addressed

- Tt-E: Pyrolysis of Biomass and Bio-oil Stabilization



Budget

- Total project funding: \$937,500
- Funding rec. in FY 2013: \$937,500
- No ARRA Funding
- One year project at \$937,500

Partners & Roles

- Iowa State University (ISU): Production and characterization of bio-oil fractions; TEA of stabilization system.
- PNNL: Stabilization of clean phenolic oligomer fraction.
- University of Oklahoma (OU): Stabilization of soluble carbohydrate, light oxygenate, and middle fractions. Determine suitable refinery insertion points for stabilized fractions.

Project Overview

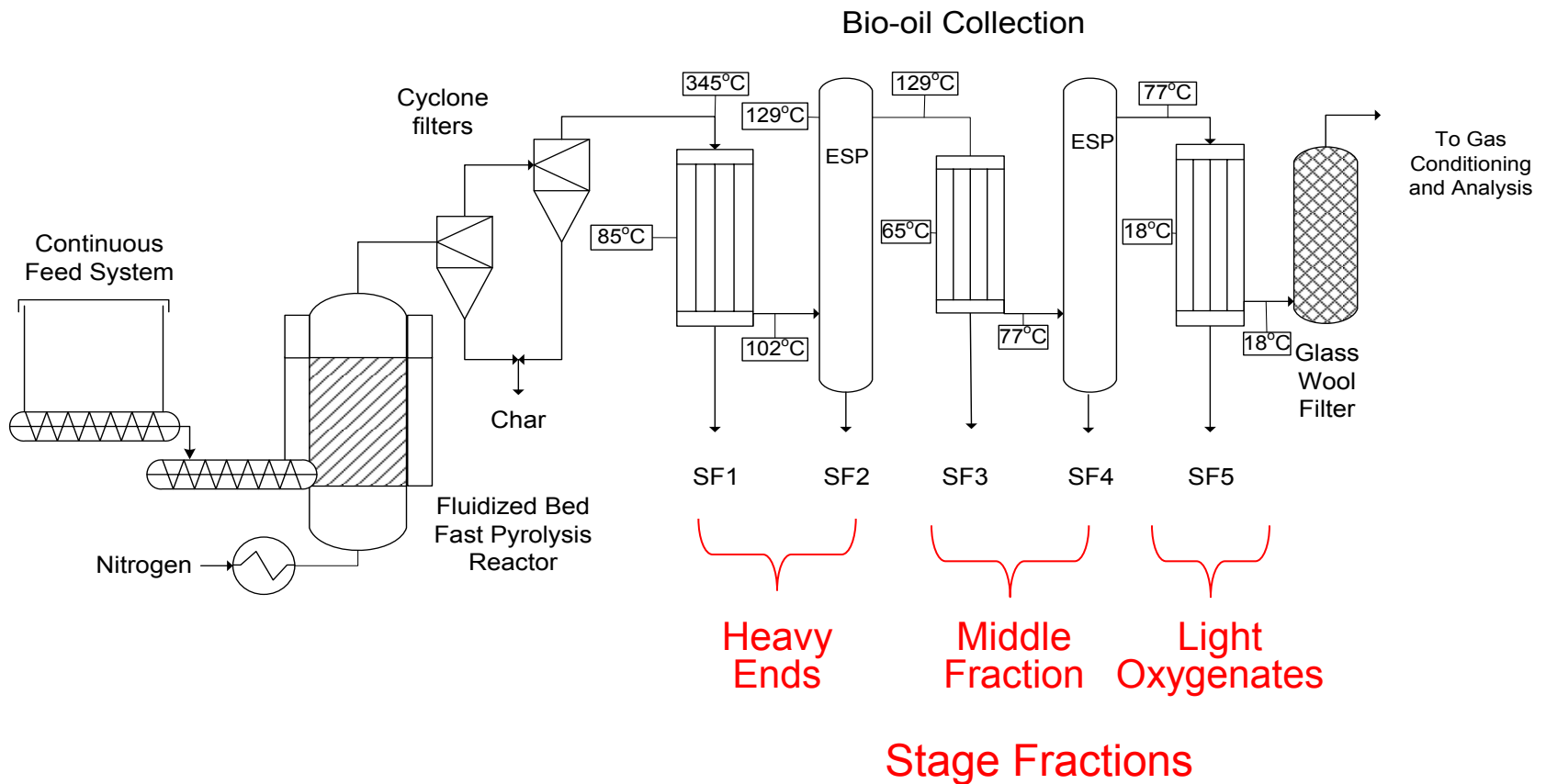
- Shortcomings of Bio-oil
 - High acidity
 - High moisture
 - High oxygen
 - Poor thermal stability
- Barriers to upgrading bio-oil
 - Many kinds of molecules must be upgraded
 - Many molecules are much smaller than desired fuel range molecules
 - High viscosity, low volatility of lignin-derived compounds
- Strategy for overcoming these barriers:
 - Recover bio-oil as distinctive stage fractions
 - Prepare upgrading fractions from the stage fractions
 - Stabilize upgrading fractions through catalytic processing that is customized to the physical and chemical properties of each fraction



Project Overview

Recovery of Bio-Oil as Stage Fractions (ISU)

System processes 1/4 tpd biomass to produce over 1/2 bpd bio-oil



Project Overview

Composition of Stage Fractions

- Heavy ends (SF 1 + SF 2) – viscous, non-volatile fraction mostly consisting of sugars and phenolic oligomers.
- Middle fractions (SF 3 + SF 4) – moderate viscosity, volatile fraction consisting mostly of phenolic monomers and furans.
- Light oxygenates (SF 5) – aqueous phase containing carbohydrate-derived C2 and C3 compounds, mostly acetic acid.

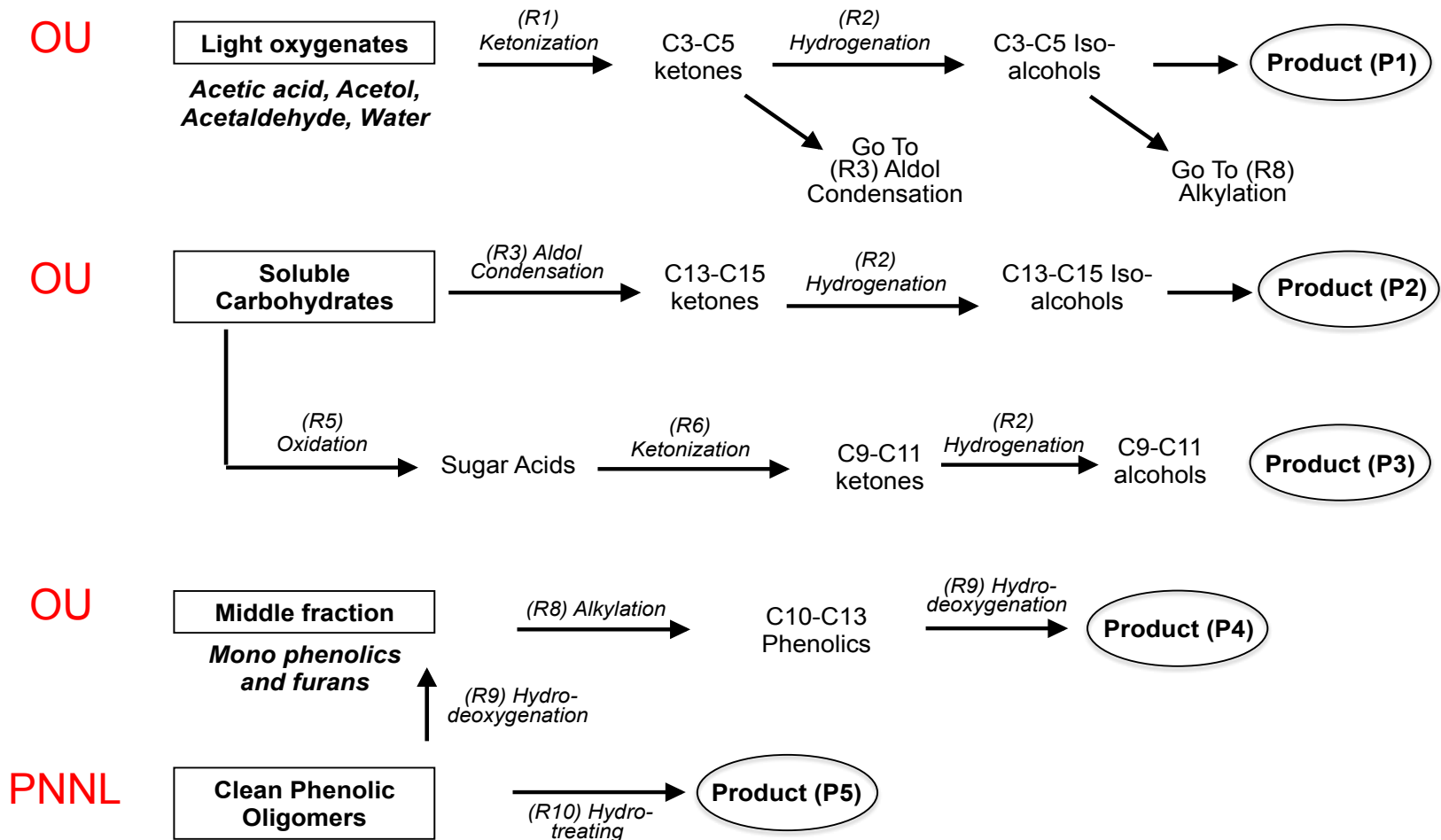
Project Overview

Preparation of upgrading fractions from bio-oil stage fractions (ISU)

Upgrading fraction	Preparation from stage fractions	Composition
Soluble carbohydrate	Solution obtained from combining and washing SF 1 and SF 2	Primarily levoglucosan, xylose, mannose, and smaller amounts of aldehydes and ketones
Light oxygenates	Untreated SF 5	Concentrated solution of acetic acid and smaller amounts of other carboxylic acids and aldehydes
Middle fraction	Obtained by combining SF 3 and SF 4	Mostly phenolic monomers and furans
Clean Phenolic Oligomers	Raffinate obtained from combining and washing SF 1 and SF 2	Water-insoluble phenolic oligomers derived from lignin

Project Overview

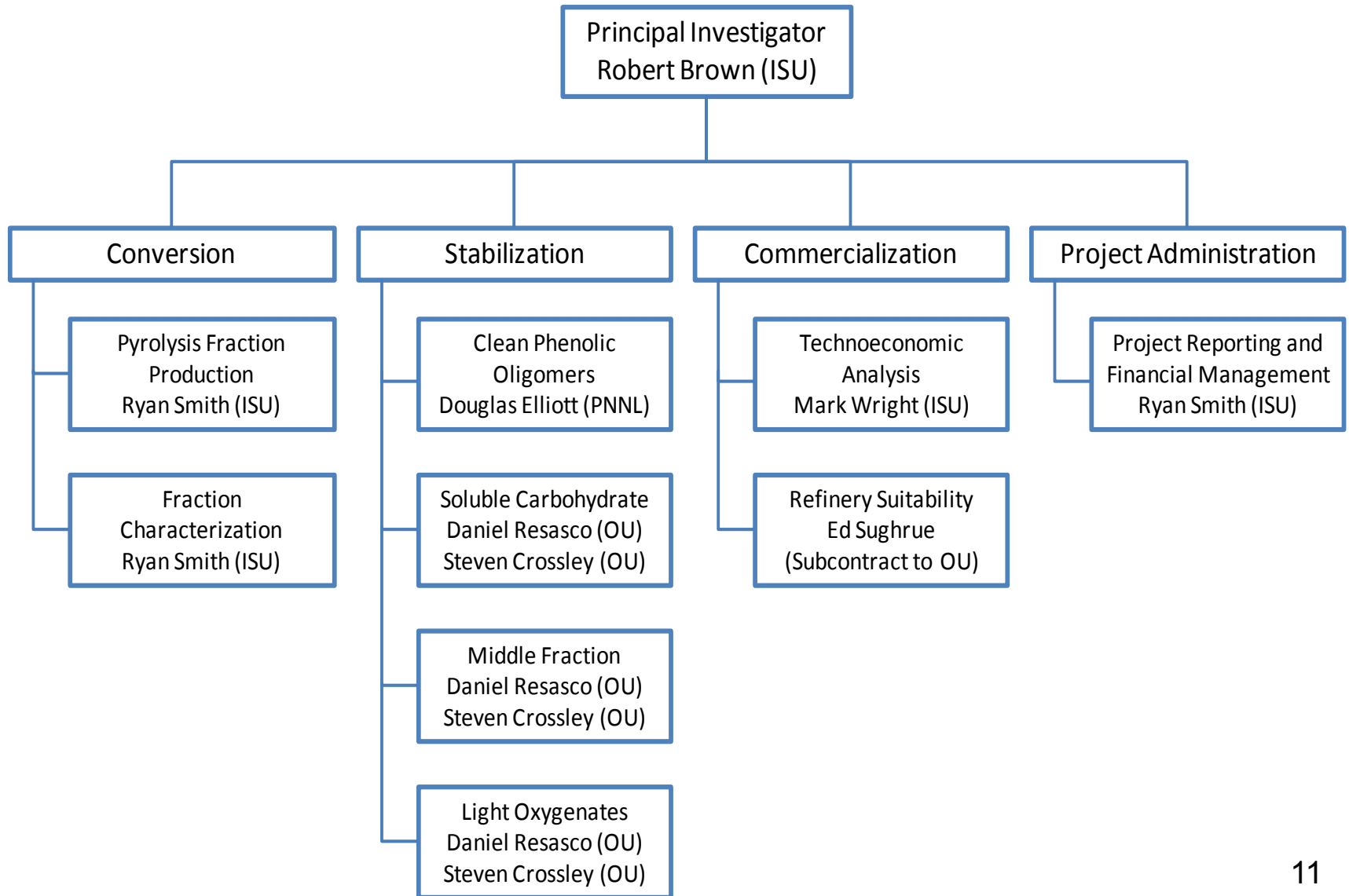
Stabilization of upgrading fractions



1 - Approach

- Produce upgrading fractions using pilot-scale pyrolyzer and bio-oil recovery system (1/2 tpd biomass; 1/2 bpd bio-oil)
- Stabilize upgrading fractions in bench-scale reactor systems
 - CPO upgrading: continuous, trickle bed hydroprocessing system at PNNL
 - Other fractions: semi-batch Parr reactors at OU
- Evaluate feasibility of inserting stabilized upgrading fractions in a refinery with assistance of petroleum industry consultant
- Perform TEA of bio-oil production and stabilization

1 – Approach (cont.)



2 - Accomplishments/ Progress/Results

Task 1.0 Production and analysis of bio-oil fractions (ISU)

Planned Activities

- Prepare first batch of bio-oil fractions
- Prepare second batch of bio-oil fractions
- Determine physical properties of first batch of bio-oil fractions
- Determine chemical properties of first batch of bio-oil fractions
- Determine physical properties of second batch of bio-oil fractions
- Determine chemical properties of second batch of bio-oil fractions

2 - Accomplishments/ Progress/Results

Task 1.0 Production and analysis of bio-oil fractions (ISU)

Actual Accomplishments

- Oak-derived bio-oil fractions produced and analyzed

Yield and Composition of Stage Fractions (From the Pyrolysis of Red Oak at 500°C)

	Heavy Ends		Middle Fractions		Light Oxygenates
	SF1	SF2	SF3	SF4	SF5
Yield (% of total bio-oil)	20	31	6.8	2.2	40
Moisture (%)	2.9	3.6	9	15	55
MAN (mg KOH/g)	36	25	73	94	118
Total Sugar (% wb)	17.2	17.9	12.8	12.1	4
Water Insolubles (% wb)	43	45	3.1	7.1	1.1
Solids (% wb)	2.4	2.3	1.3	1.2	1.1
C (wt% db)	59.6	62.6	53.4	51.3	43.1
H (wt% db)	6.2	6.3	6.7	6.7	6.5
N (wt% db)	0.05	-	-	-	-
O (wt% db)	34.1	31.1	39.9	42	50.4

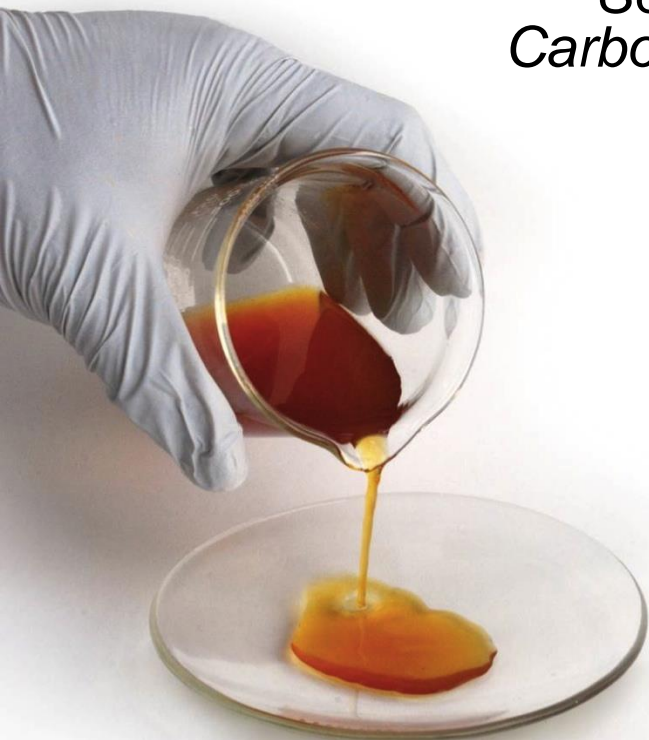
2 - Accomplishments/ Progress/Results

Task 1.0 Production and analysis of bio-oil fractions (ISU)

Actual Accomplishments

- Oak-derived bio-oil fractions converted to upgrading fractions and shipped to UO and PNNL

*Soluble
Carbohydrates*



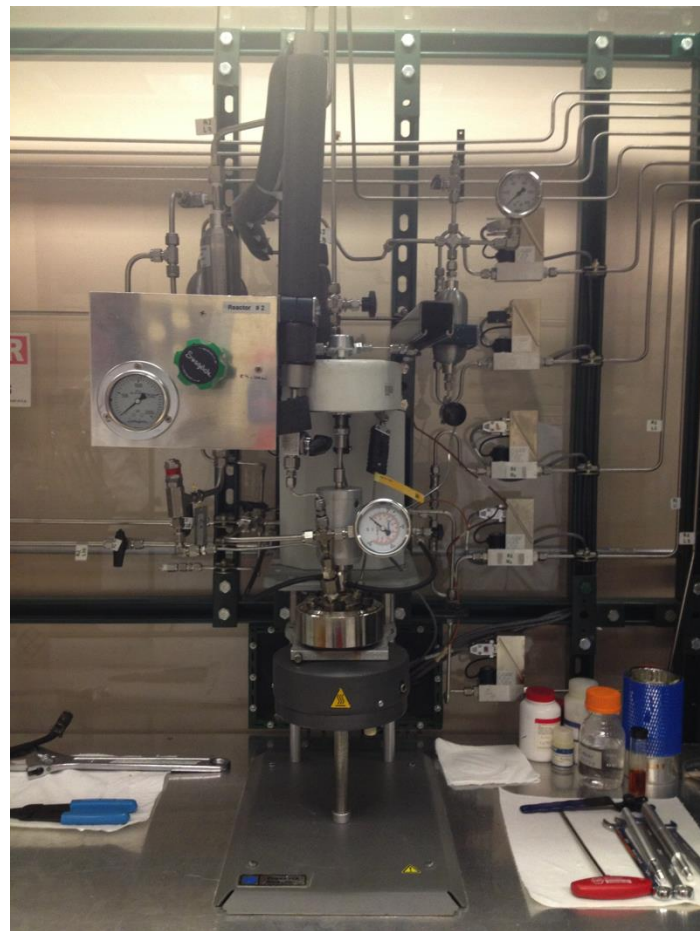
*Clean
Phenolic
Oligomers*



2 - Accomplishments/ Progress/Results

Task 2.0 Stabilization of light oxygenates

- **Planned Activities:**
 - Reception of samples from ISU
 - Analysis of samples in OU labs (GCFID, GCMS)
 - Vapor phase and liquid phase condensation followed by hydrogenation
 - Modification of existing reaction system to handle complex fraction SF5
 - Catalyst selection based on model compound mixtures (i.e. acetic acid, acetone, acetol)
 - Optimization of reaction conditions
 - Analysis of products
 - Obtaining reaction data



Task 2.0 Stabilization of light oxygenates (cont.)

Actual Accomplishments

2.1 Reception of oak-derived bio-oil fractions from ISU **Completed**

2.2. Analysis of samples in OU labs (GCFID, GCMS)

Major constituents

Acetone	3%	unknown	2%
Acetaldehyde	4%	unknown	1%
Acetol	6%	unknown	9%
Acetic acid	42%	Butanedione	12%
Pyruvic	10%	Methylenepentanal	10%

2.3. Reactions for upgrading of Fraction SF5

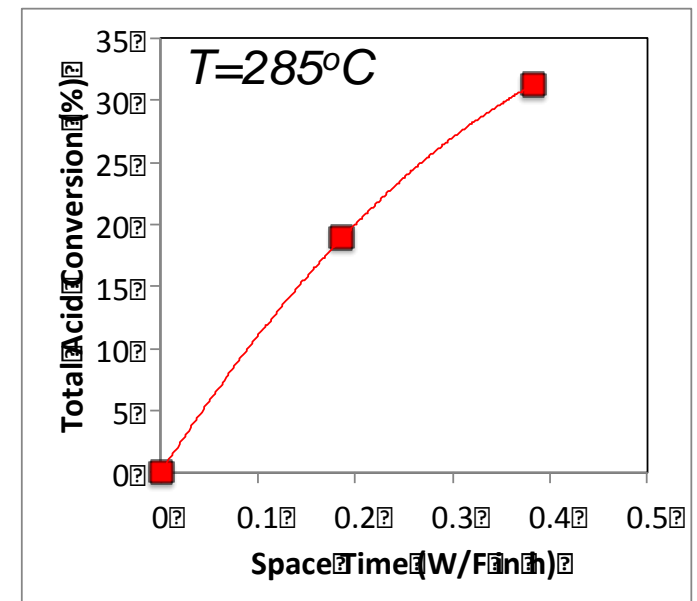
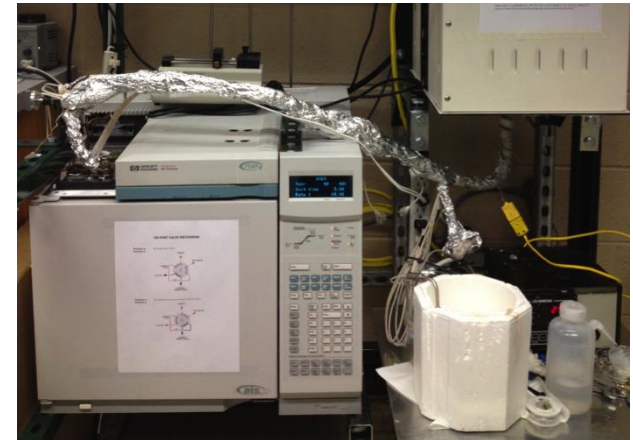
2.3.1. Vapor phase condensation

- Modification of existing reaction system to handle complex fraction SF5 **Completed**
- Catalyst selection based on model compound mixtures (i.e. acetic acid, acetone, acetol): Ru/TiO₂ P25 ; Ru/TiO₂ /carbon ; Ni/CeZrO₂ **Completed**
- Identification of reaction conditions and analysis (T= 250-300C, P=atmospheric, run in the absence of H₂ catalyst pretreatment = reduction in H₂ at 400C **Completed**

Task 2.0 Stabilization of light oxygenates (cont.)

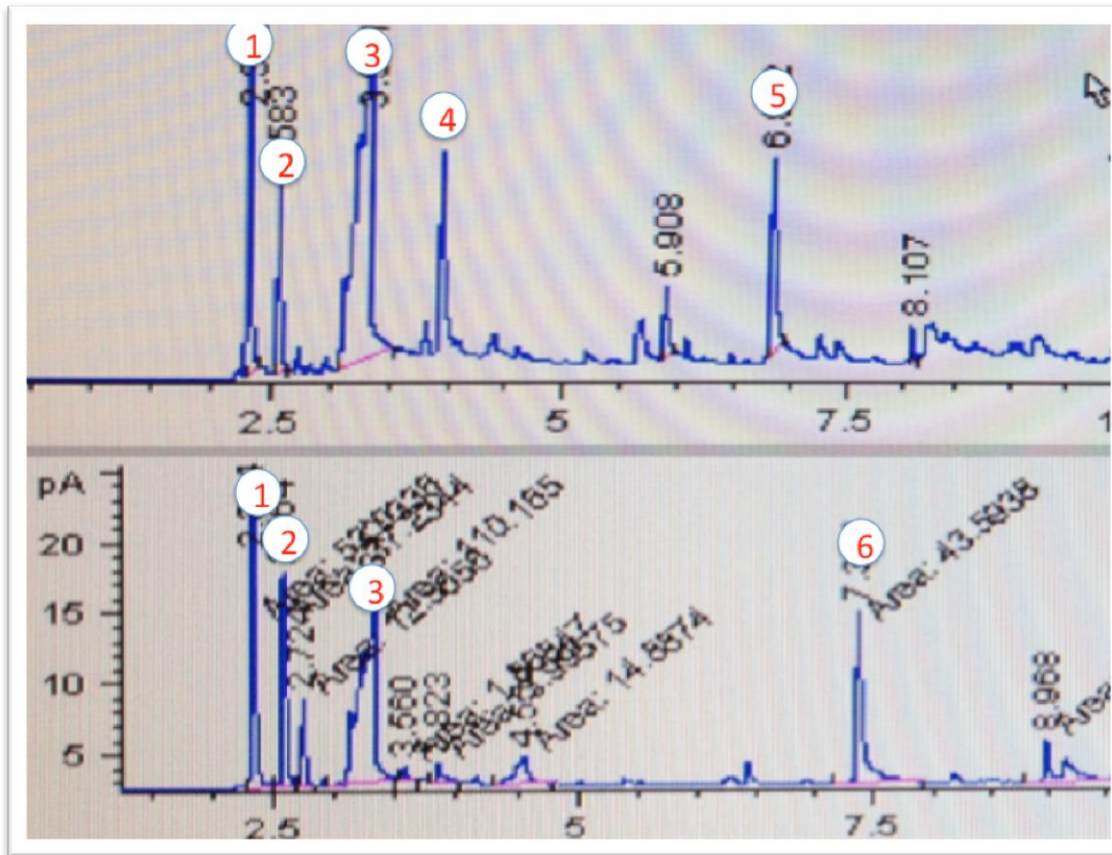
Example of ketonization reaction in the vapor phase

- Experimental Conditions
 - Temperature = 285°C
 - Pressure = 1 atm
 - Carrier gas flow (N₂) = 25 sccm
 - Catalyst 5 wt% Ru/TiO₂ (P25)
 - Catalyst pre-reduction (400°C in 50 sccm H₂)
 - Analysis Online GC-FID/GC-MS
- Results
 - Filtering through silica powder improved pumping performance
 - Significant conversion of acetic acid



Task 2.0 Stabilization of light oxygenates (cont.)

Example of ketonization reaction in the vapor phase



1. Acetaldehyde no change
2. Acetone increases
3. Acetic acid decreases
4. Acetol decreases
5. Pyruvic acid decreases
6. Butanedione increases

2 - Accomplishments/ Progress/Results

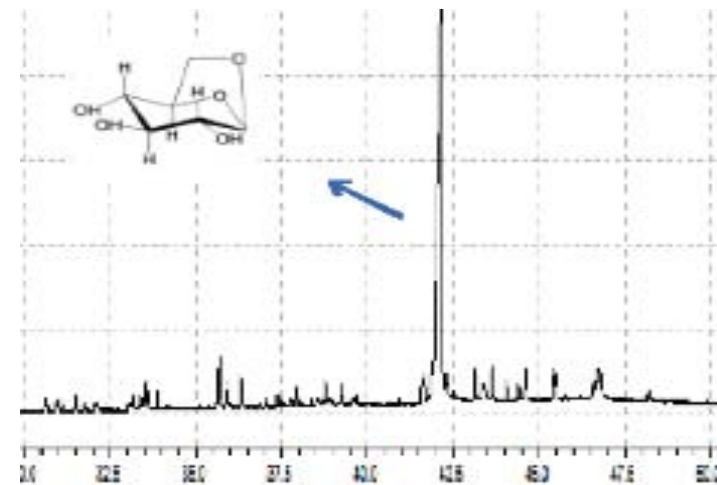
Task 3.0 Stabilization of Soluble Carbohydrates

Planned Activities:

- Reception of samples from ISU
- Analysis of samples in OU labs (GCFID, GCMS)
- Liquid phase oxidation followed by ketonization
 - Modification of existing reaction system to handle complex fraction SF5
 - Catalyst selection based on model compound mixtures (i.e. glucose, levoglucosan, glycol)
 - Optimization of reaction conditions
 - Analysis of products
 - Obtaining reaction data

Actual Accomplishments:

- Reception of samples from ISU
- Analysis of samples in OU labs (GCFID, GCMS, HPLC)
 - The GCMS analysis indicates that the most abundant compound in this fraction is *levoglucosan* (> 70 %)



Task 3.0 Stabilization of Soluble Carbohydrates (cont.)

Actual Accomplishments

A. Partial oxidation of soluble carbohydrates to acids followed by ketonization to enlarge the C-C chain

Experimental Conditions:

Ethylene glycol was chosen as model compound for partial oxidation reaction to prove the concept.

Reactor: Glass reactor

Reactant: Ethylene glycol

Oxidant: Hydrogen peroxide (50 %v)

Temperature: 70 C

Catalyst: 5Wt.% Pd/C

Pressure: Atmospheric pressure

Medium: Water

Reactant-to-oxidant mole ratio: (1:1)

Results:

Conversion: 10 %

Reaction time: 4 hrs

Major products: Oxalic acid and glycolic acid – positive result, proves the concept.

Task 3.0 Stabilization of Soluble Carbohydrates (cont.)

Actual Accomplishments

B. Hydrolysis of soluble carbohydrate fraction

Experimental Conditions

Reactor: Glass reactor

Reactant: levoglucosan-rich fraction SF1 and SF2 (Bio oil)

Medium: Water

Catalyst: Amberlyst – 15

Amount of catalyst: 200 mg

Temperature: 100 C

Pressure: Atmospheric pressure

Mole ratio: 1:50 (Reactant to Solvent)

Reaction time: 4 hrs

Results

- No significant hydrolysis product was observed with Amberlyst
- Conversion of levoglucosan to a mixture of sugars was obtained with Sulfuric acid (0.5 M) at 110 C and atmospheric pressure
- Sugar fragments identified by GCMS. Need HPLC (in repair) to properly identify types of sugars.

2 - Accomplishments/ Progress/Results

Task 4.0 Stabilization of Middle Fraction

Planned Activities:

- Receive feedstock from ISU
- Prepare and characterize hydrophobized zeolite catalysts
- Optimize analytical techniques and analyze feedstock
- Compare behavior of different hydrophobized zeolites
- Complete analysis, data processing and report writing

Actual Accomplishments:

- Task not scheduled to start until this quarter

2 - Accomplishments/ Progress/Results

Task 5.0 Stabilization of clean phenolic oligomer fraction

- Reception of wood and corn stover bio-oils from ISU (50% complete)
- Analysis of feedstock samples (20% complete)
- Hydrotreating CPO (awaiting receipt of corn-stover bio-oil)
 - Catalyst selection based on compound mixtures
 - Initial scoping tests
 - Optimization of reaction conditions
 - Analysis of products
 - Provide mass balance to ISU for process modeling



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

2 - Accomplishments/ Progress/Results

Task 6.0 Evaluation of suitability of stabilized fractions for insertion within a refinery

- P1 (C3-C5 alcohols) - if alcohols are monofunctional, could be used as direct gasoline blendstock or processed in alkylation unit to produce high octane gasoline. Fluid catalytic cracking would dehydrate alcohols to light olefins.
- P2 (C13-15 alcohols) - processed in a diesel hydrotreater should produce high cetane diesel. Monofunctional alcohols in this range could be used directly as diesel blendstocks in limited quantities.
- P3 (C9-C11 alcohols) - if predominantly monofunctional with linear carbon backbones, these could serve as diesel blendstock. Otherwise deoxygenation in a naphtha hydrotreater could produce high octane gasoline.
- P4 (Alkylated phenolic monomers/cycloalkanes) - If the degree of alkylation is significant, hydrotreating could produce diesel fuel. If less hydrogen consumption is desired, deoxygenation could produce gasoline.
- P5 (phenolic monomers/dimers/trimers) – robust upgrading equipment such as a gas oil hydrotreater or an FCC unit is required to convert these to fuels.

3 - Relevance

- Supports the goal of producing bio-oil with desirable qualities for making hydrocarbon transportation fuels in the gasoline, diesel, and jet range at less than \$3 per gallon
 - Stabilization research and technoeconomic analysis help demonstrate production of clean, low-cost bio-oil that can be integrated into a biorefinery to produce fuels
 - Testing with woody and ag residue biomass helps identify large, sustainable supplies of reasonable-cost high quality biomass
- Improves commercial prospects of biomass-based transportation fuels helping to meet EISA RFS goals

4 - Critical Success Factors

- Critical success factors
 - Technical: For maximum carbon efficiency, all fractions must be satisfactorily stabilized
 - Market: Must be able to identify refinery insertion points for all stabilized fractions
 - Business: Must identify petroleum company interested in developing stabilized fractions
- Challenges to be overcome
 - Robust catalysts for hydroprocessing clean phenolic oligomer (CPO) fraction
 - Conversion of light oxygenates (C2-C3) to less volatile molecules

5. Future Work

- Future work through project end date of Dec. 31, 2013
 - Further stability experiments
 - Refinery insertion assessment on each bio-oil fraction to start in Q4
 - Technoeconomic analysis of of bio-oil production and stabilization to start in Q4

	FY13			FY14
	Q2	Q3	Q4	Q1
Task 1.0 Production and analysis of bio-oil fractions				
Task 2.0 Stabilization of light oxygenate fraction				
Task 3.0 Stabilization of soluble carbohydrate fraction				
Task 4.0 Stabilization of middle fraction				
Task 5.0 Stabilization of clean phenolic oligomer fraction				
Task 6.0 Evaluation of suitability of stabilized fractions for refinery insertion				
Task 7.0 Technoeconomic analysis of refinery insertion of stabilized fractions				

Summary

- Relevance – success will result in stabilized bio-oil fractions that can be inserted into petroleum refineries;
- Approach – recover bio-oil as four distinct fractions followed by stabilization using upgrading processes customized to the physical and chemical properties of each fraction;
- Technical accomplishments – since project start date of January 1, 2013, we have produced oak-derived bio-oil fractions and upgrading fractions; and initiated upgrading experiments focused on carbohydrate-derived fractions;
- Future work – all other tasks will commence by next quarter.

Additional Slides

Responses to Previous Reviewers' Comments

- First year project

Publications and Presentations

- Elliott, D.C.; Hart, T.R.; Neuenschwander, G.G.; Rotness, L.J.; Olarte, M.V.; Zacher, A.H.; Solantausta, Y. 2012. “Catalytic Hydroprocessing of Fast Pyrolysis Bio-oil from Pine Sawdust.” *Energy & Fuel* **26**, 3891-3896. web published May 29, 2012.
- Elliott, D.C. “Transportation fuels from biomass via fast pyrolysis and hydroprocessing.” *WIREs Energy Environ.* 2013. doi: 10.1002/wene.74; web published February 25, 2013.
- Elliott, D.C.; Neuenschwander, G.G.; Hart, T.R. 2013. “Hydroprocessing Bio-oil and Products Separation for Coke Production.” *ACS Sustainable Chemistry & Engineering*. **1**, 389-392; web published March 11, 2013.
- D.C. Elliott “Fast Pyrolysis of Biomass to Bio-oil and Hydroprocessing to Liquid Fuels.” EBI Seminar, Energy Biosciences Institute, Berkeley, California, March 12, 2013.
- D. E. Resasco, “Catalytic Upgrading of Vapors and Liquids from Pyrolysis of Biomass” University of Houston, Houston, TX. Nov. 30 2012. Departmental Seminar
- D. E. Resasco, “Catalytic Upgrading of Vapors and Liquids from Pyrolysis of Biomass.” Invited speaker. Eastman Chemical Co., March 6 2013, Longview, TX
- D. E. Resasco, “Reaction Pathways for the Hydrodeoxygenation (HDO) of Biomass-derived Furfurals and Phenolic Compounds” Invited speaker. WE-Heraeus-Seminar “Energy-Related Catalysis Today and Tomorrow: From Fundamentals to Application” 24 – 27 March 2013 at the Physikzentrum 32 Bad Honnef (Germany)