DOE Bioenergy Technologies Office (BETO) 2015 Project Peer Review

Bio-Oil Deployment in the Home Heating Market

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Goal Statement

- Goal- Evaluate the feasibility of using near-commercial, upgraded bio-oils in the heating market. Focus is on state of current fuel availability, technical aspects of end use, supply and distribution constraints, and barriers to manufacturer and end user acceptance.
- Heating oil and diesel transportation both use the same fuel – renewable fuel use in both areas has a similar national impact;
- Heating applications are technically simpler, providing a logical entry point for biofuels, enabling more rapid growth in fuel use and scale up;
- Experience with end use equipment, supply and distribution, manufacturer and code acceptance in the heating oil market will facilitate the acceptance process in the transportation market.

Quad Chart Overview

Timeline

- Project start date – Oct. 2013
- Project end date – Sept. 2015
- Percent complete – 40%

Budget ($,000)

	Total Costs FY 10 – FY 12	FY 13 Costs	FY 14 Costs	Total Planned Funding (FY 15-Project End Date
DOE Funded	$0	$0	$226	$349
Project Cost Share (Comp.)*	$0	$0	$0	$0

*If there are multiple cost-share partners, separate rows should be used.

- Barriers addressed
  - Dm-A, Distribution Infrastructure
  - Mm-A, Industry and Consumer Acceptance
  - Dt-B Codes, Standards and Approval for Use
  - Tt-E, Pyrolysis of Biomass and Stabilization
  - Im-D, Lack of Industry Standards
- Partners
  - The National Oilheat Research Alliance (NORA) is a subcontractor to BNL. NORA's role is to provide outreach to industry to ensure that industry concerns and constraints are addressed. $25K, 4% of the total project budget
- Project involves outreach to near-commercial upgraded biofuel producers

Project Overview

- The heating oil market represents an opportunity for the early commercial use of bio-oil.
- Market size is 7.2 billion gallons annually, mostly in the Northeast.
- End use equipment is technically simpler than diesel engines.
- Storage conditions, including temperature, relatively predictable.
- Relative to diesel engines, however, storage times are considerably longer – typical 1 year stability required.
- Well established supply and distribution chain.
- Work in this project seeks to evaluate the technical feasibility of deploying in this market sector upgraded bio-oils which are in a near-commercial status.
- Project seeks to draft specifications for technical requirements of an upgraded bio-oil suitable for use in this market.

Approach (Technical)

- For candidate fuels complete basic analysis plus evaluation of factors which affect suitability for end use in this market including:
  - miscibility
  - storage stability
  - compatibility with legacy elastomers
  - combustion performance
- Evaluate the impact of compounds common in partially upgraded bio-oils to identify most significant contributors to performance concerns in this application;
- Develop “synthetic” bio-oil blends by mixing selected compounds back into neat No. 2 heating oil;
- Prepare recommendations for a specification for a bio-oil fuel blend stock for this application;
- Long term operational testing planned, based on fuel availability.

Approach (Management)

- Outreach to potential near-commercial sources of upgraded bio-oil;
- Challenge – availability of bio-oils that meet technical requirements;
- Challenge – interest of fuel producers in this market;
- Challenge - path for component manufacturer acceptance of this new fuel in legacy and new equipment;
- Challenge – acceptance of this new fuel by supply chain and fuel retailers/service organizations

Approach (Management cont.)

- The National Oilheat Research Alliance (NORA) is the national association responsible for the research, educational needs, and consumer education of the industry

NORA tasks will include:

- Works with every level of the industry with petroleum wholesalers, retailers, manufacturers, and researchers serving on its Board
- NORA supported a technical team in the qualification of biodiesel blends, now in widespread use
- In this project, tasks will include focused meetings with industry leaders, preparation of briefing materials – brochures, web info, and trade journal articles, presentations at key industry conferences
- NORA will provide feedback on key concerns and logistical barriers

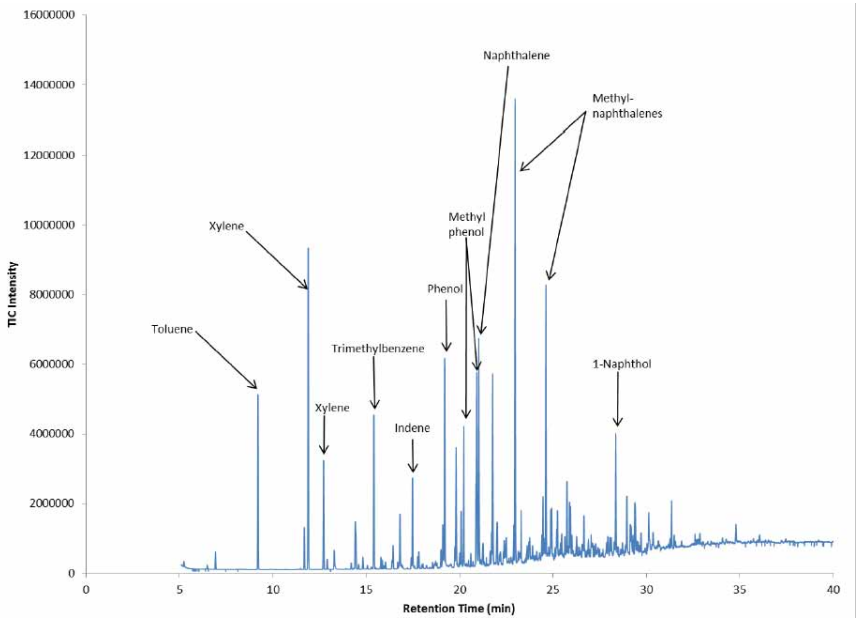
Technical Accomplishments/ Progress/Results

- Outreach to all significant fuel developers as planned;
- Reluctance to supply fuel samples based on proprietary concerns, commitments to other projects;
- Some upgraded samples received, not technically suitable;
- Some focus shift toward production of synthetic bio-oils and evaluation of specific compounds on key performance factors;
- Kior, following significant effort on agreement terms, provided significant samples needed in two fuel grades (details of results following slides)

Technical Accomplishments/ Progress/Results (cont'd)

- Example – evaluation of an upgraded pyrolysis oil from USU (Utah)
  - Produced from catalytic fast pyrolysis of pinyon-juniper biomass using HZSM-5 zeolite.

Property	Catalytic upgraded pyrolysis oil (CUPO)
Elemental, wt.% (dry basis)	
C	80.24
H	6.92
O*	12.29
N	0.55
S	BDL
H/C molar ratio	1.03
O/C molar ratio	0.11
Physical properties	
pH	4.51
Density (g/cm^3)	1.06
Gravity, °API	2.0
Kinematic Viscosity (at 40 °C, cSt)	15.3
Dynamic Viscosity (at 40 °C, cP)	16.2



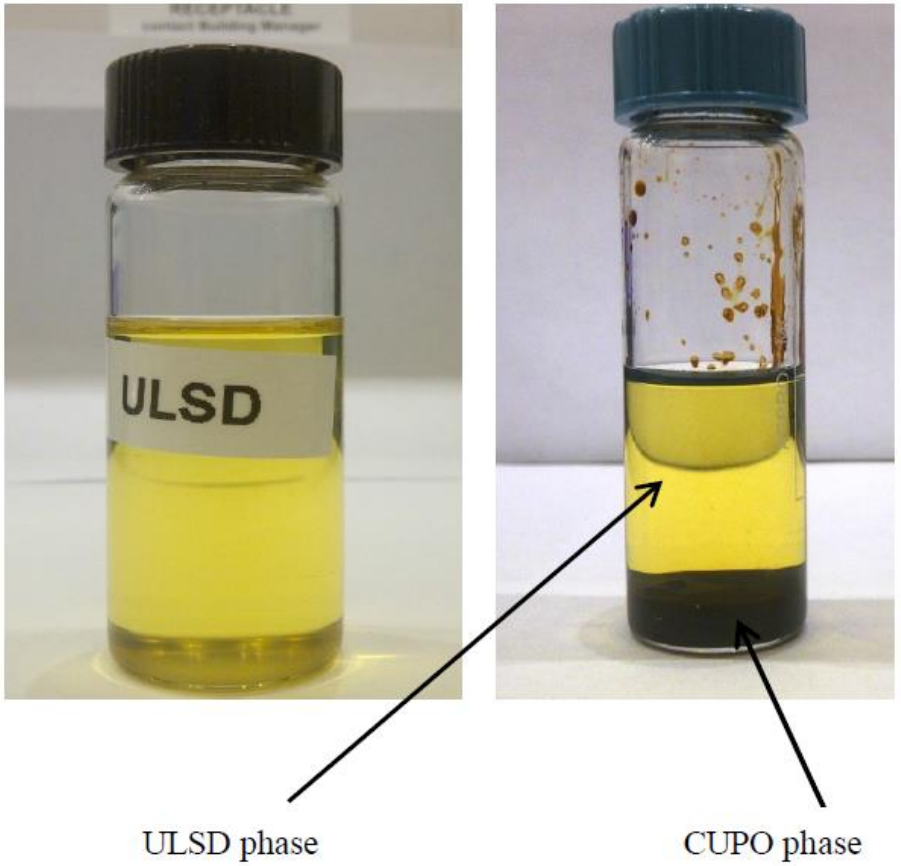
Fuel mainly aromatic hydrocarbons and phenolics. Substituted benzenes (xylene, toluene, alkylbenzenes), napthalenes, indene, and indane accounted for 62% (area) of the total.

Technical Accomplishments/ Progress/Results (cont'd)

- Example – evaluation of an upgraded pyrolysis oil from Utah State University

Fuel was found to be insoluble in No. 2 oil. Partial solubility in biodiesel, suggesting a potential route to a co-solvent. Insoluble part dominated by levoglucosan and phenols.

Note - biodiesel at levels of 5% (or in some cases greater) are now very common in heating oil. This is simply part of the current fuel mix.



Technical Accomplishments/ Progress/Results (cont'd)

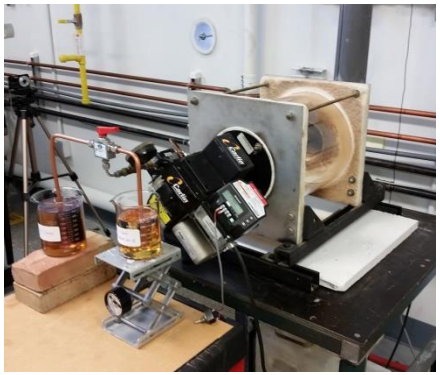
- Kior fuel – two fuel samples submitted for testing under this program. Produced via Biomass Fluidized Catalytic Cracking (BFCC) Process, followed by hydroprocessing and fractionation. "Kior Distillate" and "Kior Gas Oil". Miscibility of the distillate grade excellent. Miscibility of the Gas Oil at 20% good, higher blend levels not evaluated.

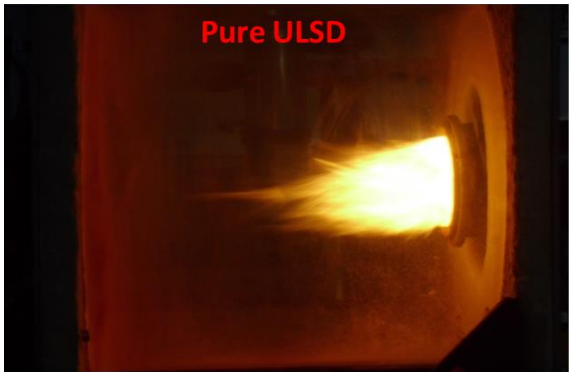
Physical Properties	ASTM Test Method	D396 Limits	Standard No.2 Fuels*		Test Fuels	
			No.2 S500	No.2 S5000	KiOR Distillate	KiOR Gas Oil
Flash point, C	D39	min	38	38	60	53.89
Water & Sediment, % vol.	D2709	max	0.05	0.05	0.0001	0.09
Distillation	D86					
90%		min	282	282	326.3	-
90%		max	338	338		-
Kinematic viscosity at 40 °C, mm^2/s	D445	min	1.9	1.9	2.9	834
		max	4.1	4.1		
Ramsbottom carbon residue on 10% distillation residue % mass	D524	max	0.35	0.35	0.11	-
Sulfur, ppm	D7039	max	500	5000	7.3	5.6
Copper strip at 50 °C	D130	max	No. 3	No. 3	No.1a	
Density at 15 °C, kg/m^3	D1298	max	876	876	903	958
Pour Point °C	D97	max	-6	-6	<-40	-6
Cloud Point, °C	D2500	ND	ND	ND	<-60	-
Acid Number, mg KOH/g	D664	ND	ND	ND	<0.02	-

*ASTM standard No.2 grade fuels, ND= Not defined in D396

Technical Accomplishments/ Progress/Results (cont'd)

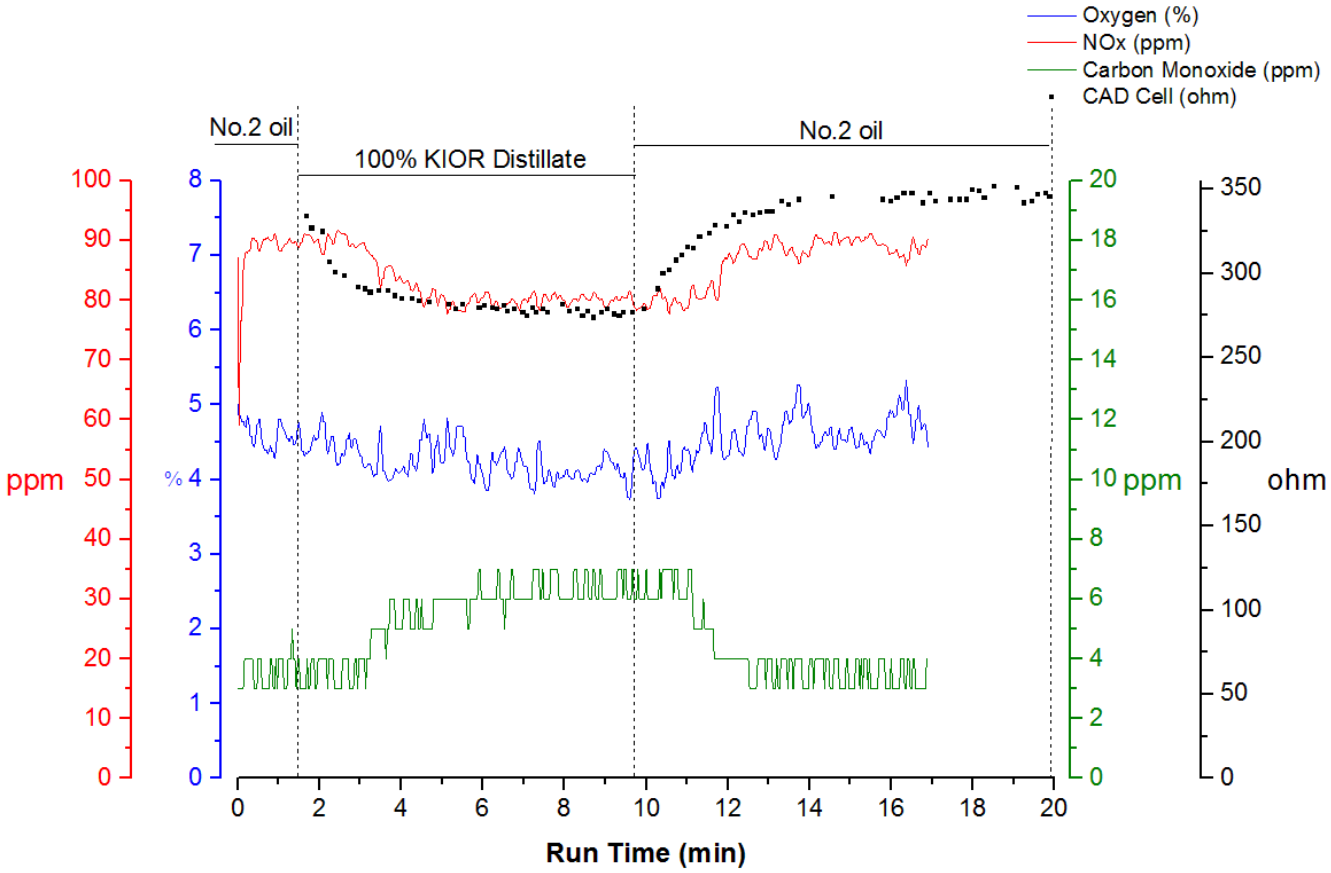
- *Combustion Testing – Quartz Combustion Chamber – full size residential burner. Allows flame visualization.*





Technical Accomplishments/ Progress/Results (Cont)

- *Typical residential boiler / burner combination*



To conserve fuel samples, testing was done switching back-and-forth

Technical Accomplishments/ Progress/Results (cont'd)

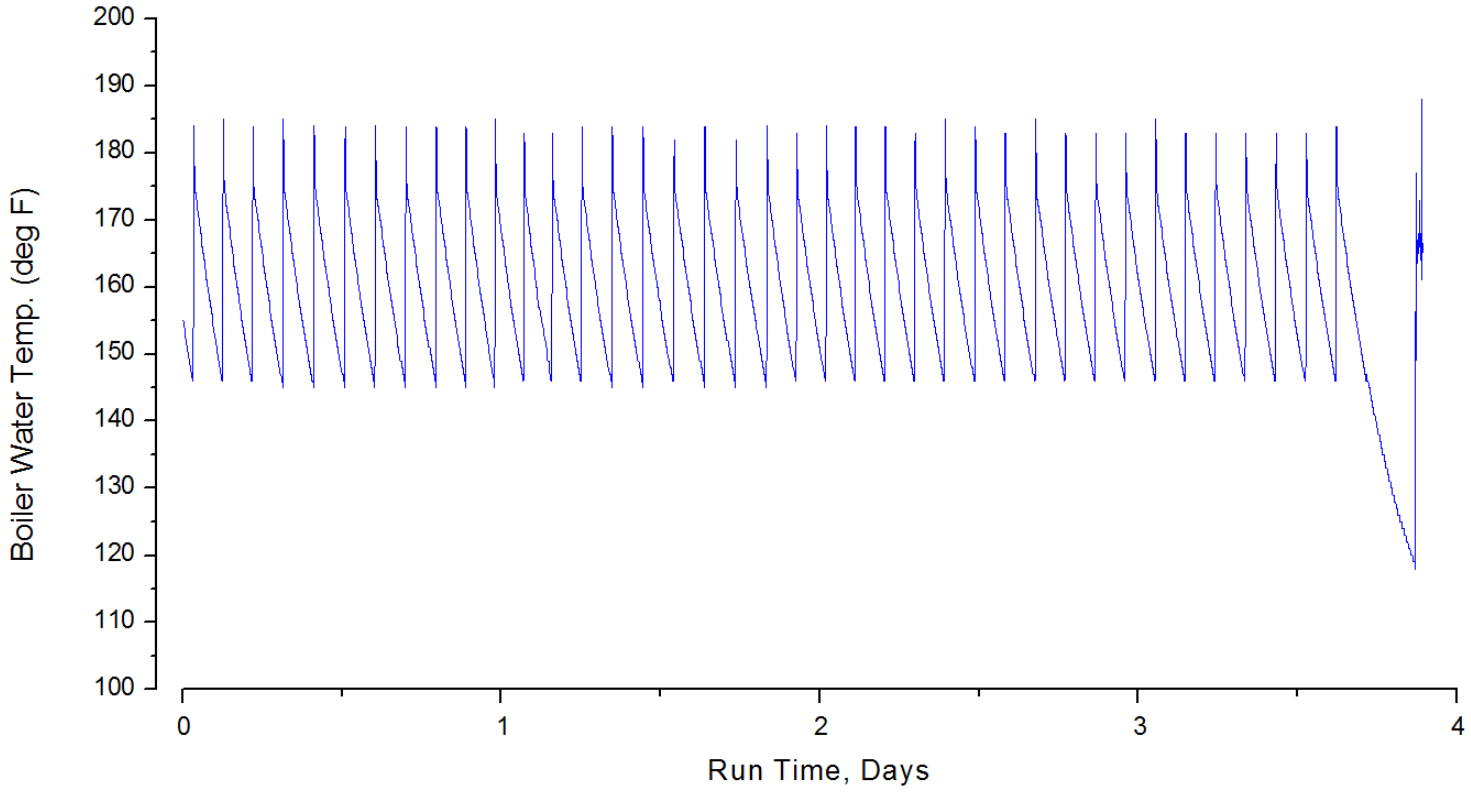
Steady State Emission Testing / Kior Fuels

Parameter	Summary of Combustion Results			
	ULSD	100% KiOR Distillate	50% KiOR Distillate	20% KiOR gas oil
Oxygen, %	4.57	4.20	4.37	4.51
NOx, ppm	89.37	80.17	84.26	101.26
CO, ppm[1]	4	6	5	4
Smoke Number	-	-	-	-
Cad cell Resistance, ohms	340	280	300	400

1 all CO levels are considered negligible

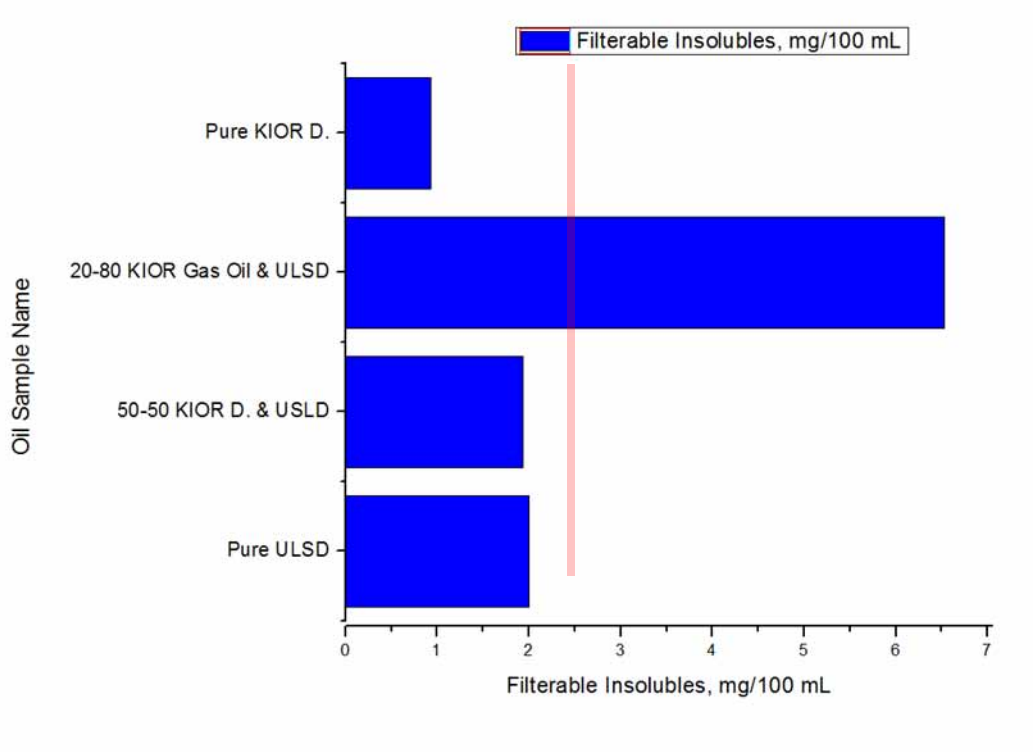
Technical Accomplishments/ Progress/Results (cont'd)

Burner Cycling Tests – using 100% of the Kior distillate the system was set to automatically cycle with unattended operation. A slow cycling pattern – 5 minutes on / 2 hours off was selected to evaluate ability of burner to light reliably under relatively cold chamber conditions. Perfect performance / 4 days.



Technical Accomplishments/ Progress/Results (cont'd)

Accelerated storage stability test – 80 C / 1week

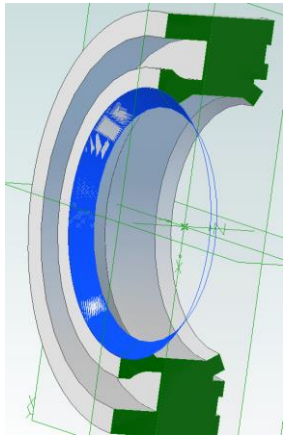


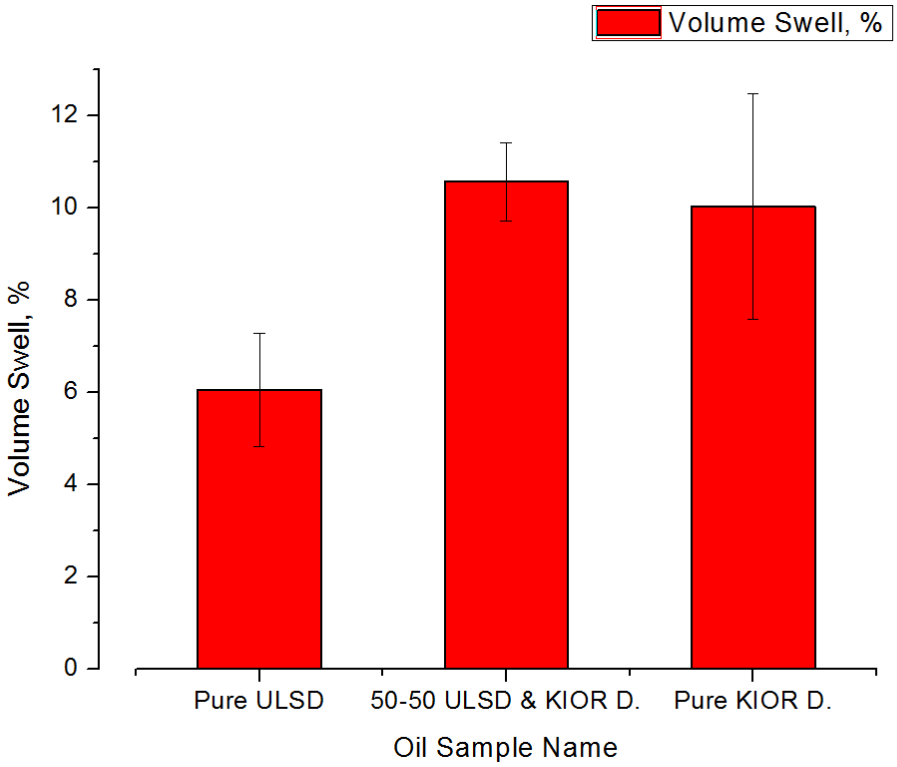
The "diesel" grade blends showed good stability. The "gas-oil" blend yielded higher filterable insolubles than is considered acceptable (2.5 mg/100 ml)

Technical Accomplishments/ Progress/Results (cont'd)

Elastomer compatibility – using nitrile slabs of standard pump shaft seal material.

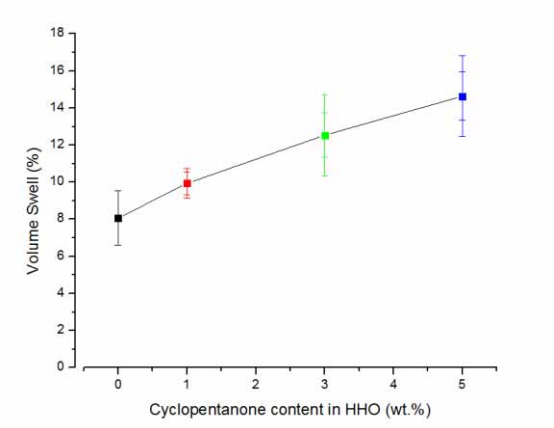
Swell testing done at 43 C for 1 month. A 25% swell is considered acceptable.



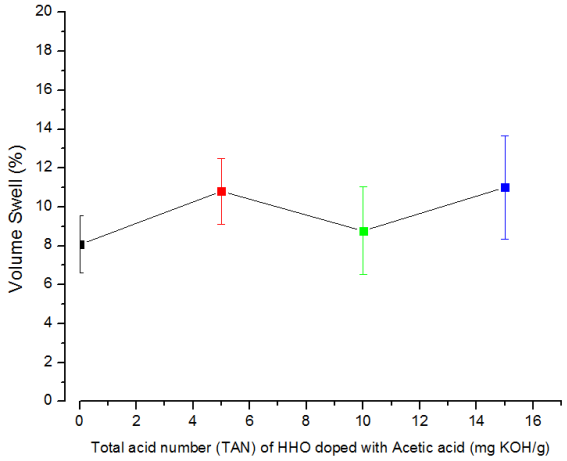


Technical Accomplishments/ Progress/Results (cont'd)

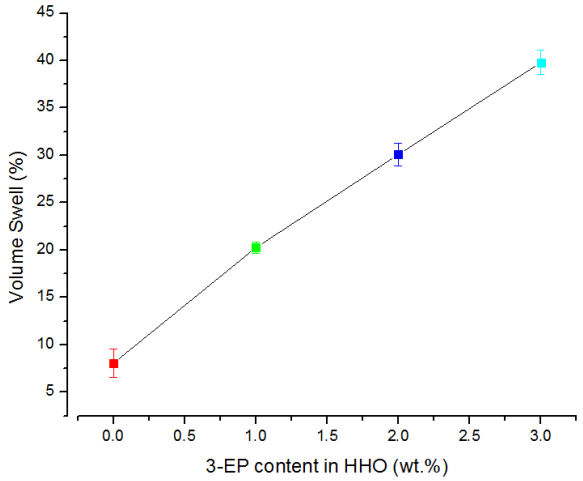
Elastomer swell – impact of specific target compounds. Done to understand which bio-oil compounds may be most problematic to support standard setting. No. 2 oil, doped with low levels of select compounds.



Cyclopentanone



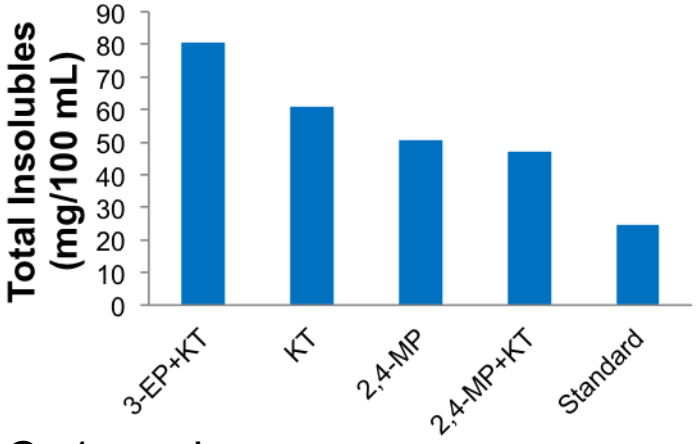
Acetic Acid



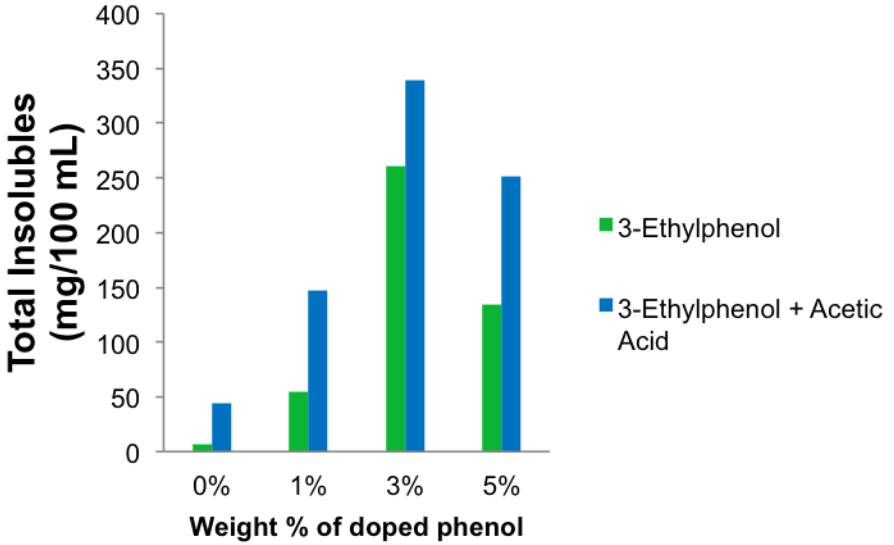
3-ethylphenol

Technical Accomplishments/ Progress/Results (cont'd)

Stability – impact of specific target compounds. Done to understand which bio-oil compounds may be most problematic to support standard setting. No. 2 oil, doped with low levels of select compounds.



80 C, 1 week



Result - Ketones, phenols, acetic acid promote reduced stability and can cause a fuel to have unacceptable stability at 1% levels.

Technical Accomplishments/ Progress/Results (Cont)

- *Standards and Approvals*
  - *Burners and other fuel handling components in this market sector are approved for use against UL standards*
  - *"Listing" defines the fuels for which components are approved*
  - *Heating fuels are defined in ASTM D396.*
  - *ASTM D7544 – Standard for Pyrolysis Liquid Biofuel not applicable*
  - *Two options:*
    - *Define a new bio-oil specification (inside or outside of D396)*
    - *Fuel product is so low in oxygen content it is considered a hydrocarbon and so is equivalent to No. 2 oil*
  - *If a new fuel is defined, component manufacturers will develop and list new products*
  - *Manufacturers reluctant to approve existing products for a new fuel – they assume risk and listing costs without the benefit of new product sales.*

Technical Accomplishments/ Progress/Results (Cont)

- *Hydrocarbon (from D975)*
  - *"Hydrocarbon oil – homogeneous mixture or solution with elementary composition primarily of carbon and hydrogen and also containing sulfur, oxygen or nitrogen from residual impurities and contaminants and excluding oxygenated materials.*
- *A fuel like the Kior distillate could qualify as a No. 2 heating oil under ASTM D396, no additional specifications required.*
- *If upgraded to a lesser degree, and containing more than a "contamination level" of oxygen, a new specification will be required.*
- *In addition to the parameters listed in Table 1 of ASTM D396 the following are tentatively proposed:*
  - *Stability – ASTM D6468, thermal 180 minutes, 150 C, 80% reflectance?*
  - *Acid number – 0.5 mg KOH/g*
  - *Data on long term storage stability, ASTM D4625 needed as well as comparison with accelerated tests.*

Relevance

- *Heating oil as a target market is specifically discussed in the BETO Multi-Year Program Plan.*

- *Relative to transportation, the heating oil market is technically simpler, yet contains many of the same barriers. It provides an important entry point for biofuels.*

- *Penetration into the heating oil market will increase the near-term market size for emerging bio-oil producers, yield considerable experience in the supply and distribution areas that are relevant to transportation, and create a pathway for fuel specification and acceptance.*

- *Through NORA, there is a direct market engagement mechanism for all parts of the heating oil industry.*

Future Work

- *Continue to seek additional samples/quantities of suitable upgraded fuel*
- *Pump run tests with upgraded fuel on hand*
- *Complete long term burner cycling test with available fuel. Based on available supply will plan for low cycle rate.*
- *Publication on work with commercial fuel to date (in review)*
- *Additional work needed to define limits in a bio-oil fuel specification for this market. e.g. evaluation of impacts of different phenols*
- *NORA Market outreach – presentations, workshops, live-fire demonstrations planned*

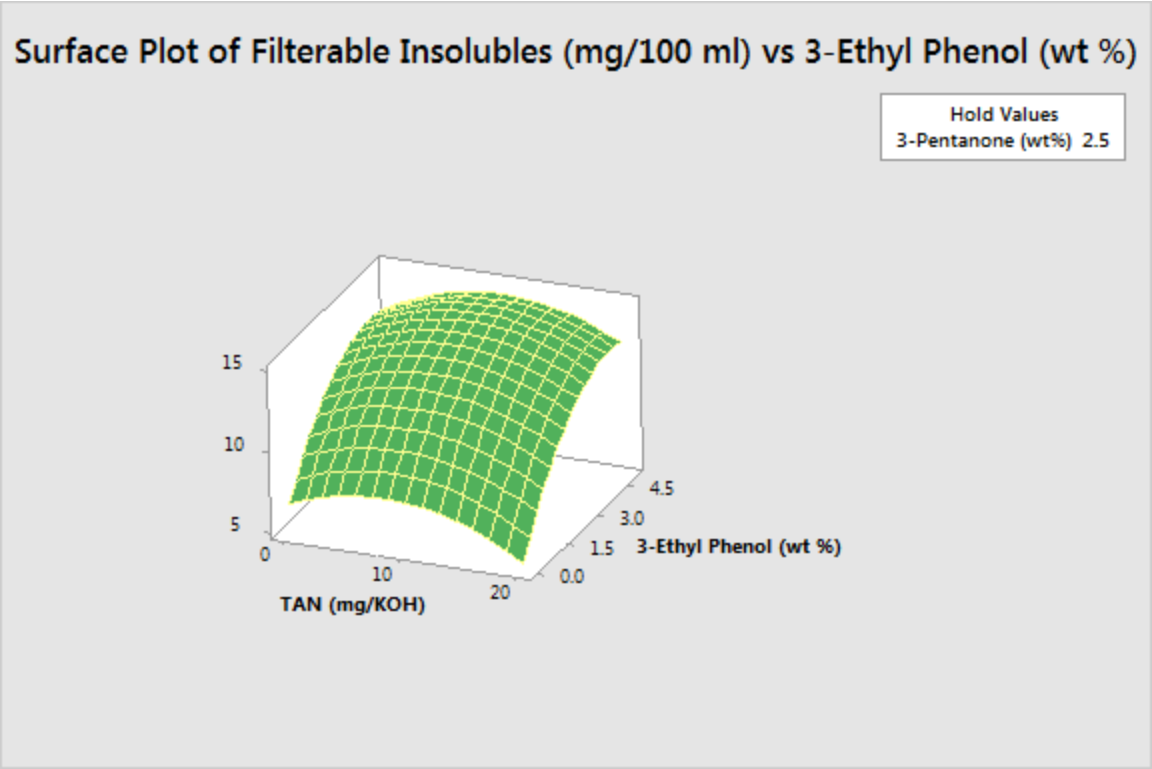
Summary

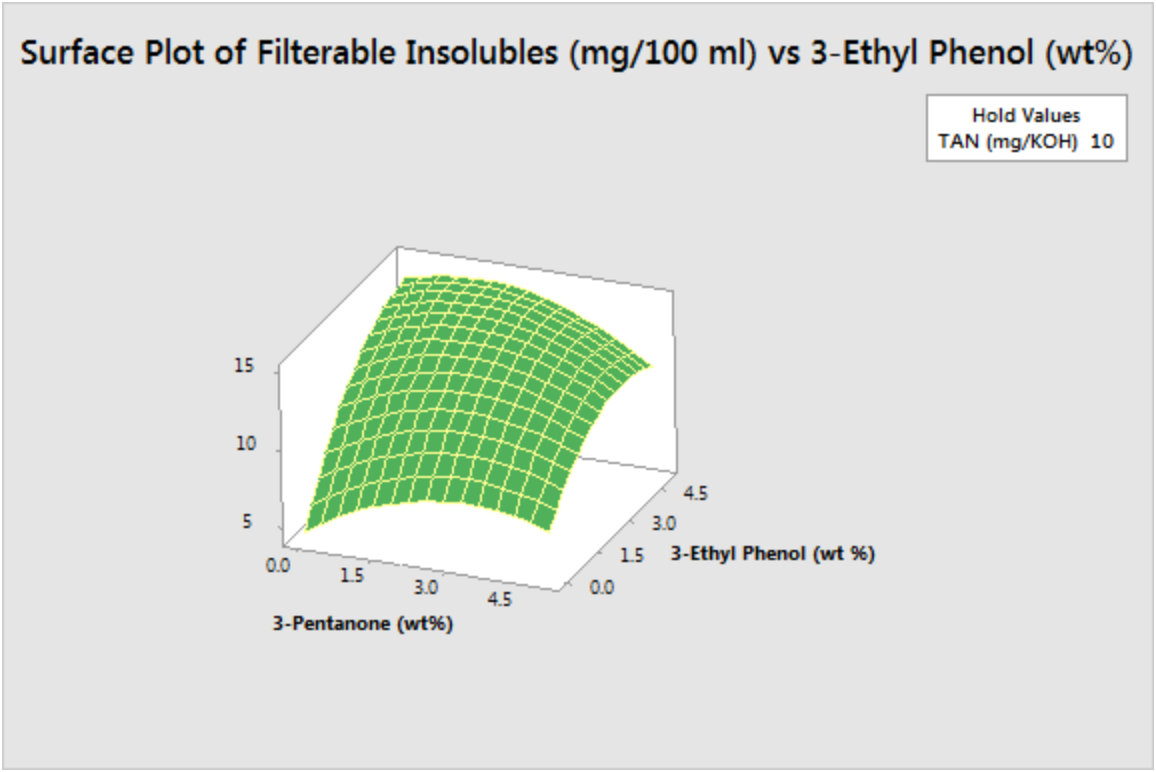
1. Overview
    1. Feasibility of near-commercial upgraded bio-oils in the heating oil market
    2. Industry outreach effort
    3. Standards development
2. Approach
    1. Seeking near-commercial fuel candidates
    2. Exploring impacts of specific classes of compounds
    3. Storage, elastomer, combustion testing
    4. Long-term operation planned
3. Technical Accomplishments
    1. One near-commercial fuel demonstrated as technically feasible
    2. Impacts of ketones, phenols, acids evaluated
    3. Industry outreach – manufacturer concerns
4. Relevance
    1. Heating oil is an attractive entry pathway for bio-oil
    2. Many of the supply and end use issues addressed in this market sector will be relevant for acceptance in the transportation market
5. Future Work
    1. Continue to seek new sources
    2. Long term boiler operating tests
    3. Industry outreach
    4. Improve basis of specification definition

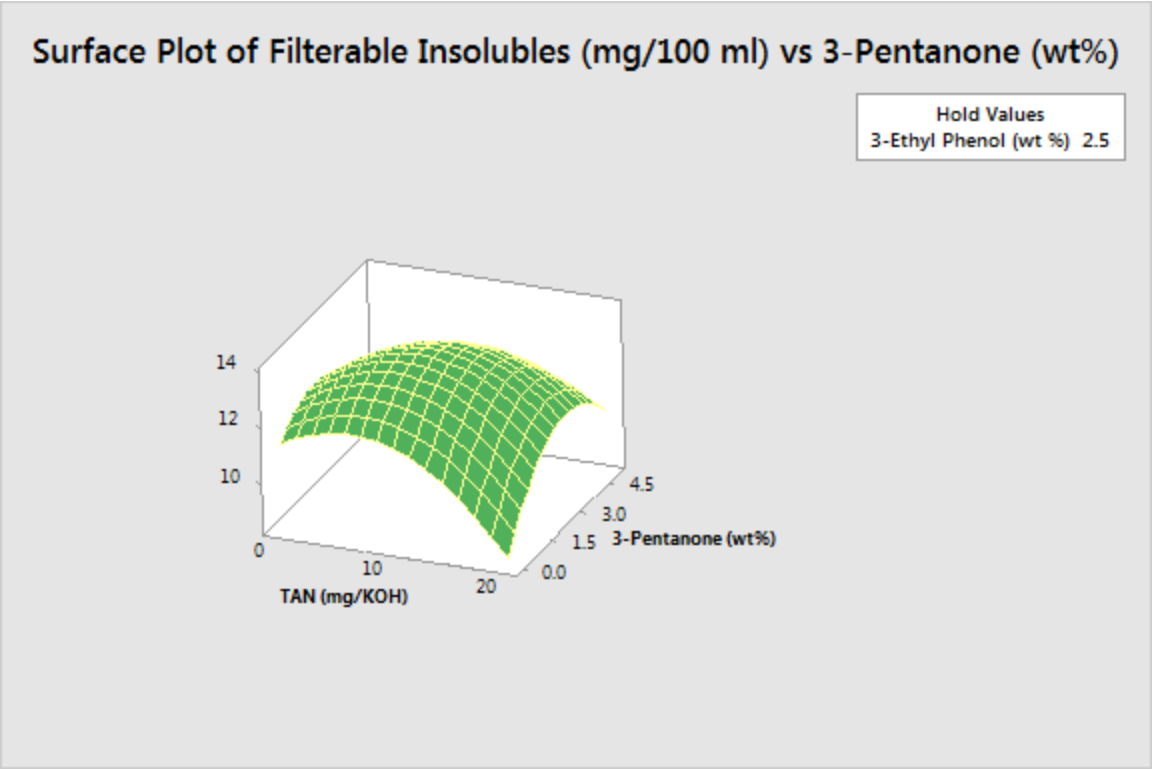
Additional Slides

Publications, Patents, Presentations, Awards, and Commercialization

- A draft paper on the work with the Kior fuel has been prepared and is currently in review.
- NORA presentations on this at industry spring meetings are planned.


Surface Plot of Filterable Insolubles (mg/100 ml) vs 3-Ethyl Phenol (wt %)
Hold Values
3-Pentanone (wt%) 2.5
15
10
5
0
10
20
TAN (mg/KOH)
0.0
1.5
3.0
4.5
3-Ethyl Phenol (wt %)


Surface Plot of Filterable Insolubles (mg/100 ml) vs 3-Ethyl Phenol (wt%)
Hold Values
TAN (mg/KOH) 10
15
10
5
0.0
1.5
3.0
4.5
3-Pentanone (wt%)
0.0
1.5
3.0
4.5
3-Ethyl Phenol (wt %)


Surface Plot of Filterable Insolubles (mg/100 ml) vs 3-Pentanone (wt%)
Hold Values
3-Ethyl Phenol (wt %) 2.5
14
12
10
0
10
20
TAN (mg/KOH)
0.0
1.5
3.0
4.5
3-Pentanone (wt%)