U.S. Department of Energy (DOE)
Bioenergy Technologies Office (BETO)
2017 Project Peer Review

Bio-Oil Deployment in the Home Heating Market

March 6, 2017
Demonstration and Market Transformation
Session Area Review

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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 equipment 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.

Executive Summary

1) Project Team

- BNL Sustainable Energy Technologies Department – long history of work on stationary combustion applications and collaboration with oil heating industry. Including technical support for conversion to ULS heating oil and adoption of biodiesel fuels in this market sector.
- National Oilheat Research Alliance (NORA) – key industry organization providing support to this project on end use industry outreach.

Executive Summary Cont.

2) Original Objectives of this AOP Project

- Review status of near-commercial upgraded bio-oils
- Draft fuel specification
- Outreach to heating industry organizations including supply chain
- Obtain samples and prepare fuel blends
- Longer term combustion tests in typical equipment

Assessment – All of these objectives were met. However, the project team found limited availability of candidate biofuels and limited interest by biofuel producers in this market.

Executive Summary Cont.

3) High-level project description:

- This project has involved laboratory benchtop and pilot scale evaluation of the potential use of upgraded bio-oils in home heating equipment.
- Fuels for this project were solicited from near-commercial fuel producers.
- The key goal of the project as planned is to evaluate the technical potential to displace petroleum in the market sector with a small level of residual oxygenates in the fuel.
- The project started in FY 13 and the final report was submitted in FY 16.
- The main project success factors were a completion of the evaluation of the basic technical feasibility of using bio-oil in this sector and an evaluation of technical areas of concern particularly with the presence of some residual oxygenates.

Executive Summary Cont.

4) High-level review of the Project Team's accomplishments since the last Peer review (or since project start for new projects):

- Completion of longer term combustion tests
- Completion of longer term pump circulation tests
- Publication of a paper in Energy and Fuels
- Project final report including assessment of technical feasibility and technical areas that may affect the degree of upgrading required.

5) High-level review of the future plans for the project:

- Project is complete.

Quad Chart Overview

Timeline

- Project start date- Oct. 2013
- Original project end date – sept. 2015
  - Revised project end date – July 2016 (delays in obtaining fuel samples)
- Percent complete -100

Budget ($,000)

	Total Costs FY 12 – FY 14	FY 15 Costs	FY 16 Costs	Total Planned Funding (FY 17-Project End Date
DOE Funded	$226	$296	$ 53	$575
Project Cost Share (Comp.)*	$0	$0	$0	$0

- 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. Some of these have provided fuel samples and technical input

Key Milestones

Milestone	Original Planned Completion Date	Actual Completion Date
Obtain Upgraded Bio-Oil Samples	Dec-14	Mar-15
Combustion Tests	Feb-15	Sep-15
Complete Materials Testing	Mar-15	Sep-15
Obtain Larger Samples	Mar-15	Mar-15
Longer term Performance Tests	Mar-15	May-16
Project Report	Sep-15	Jul-16

The milestones for this project were significantly delayed and are not presented in the requested standard format. The key reason for this is the difficulties which were encountered in getting commercial organizations to commit to supplying samples and the time associated with completing agreements needed for the supply of these samples. For these reasons the sample obtained came in over a much longer time period and the associated materials, storage, and combustion tests were spread over nearly all of the project time. The milestone start and end dates were not as clearly defined as was planned.

Detailed Project Scope Change Table

Scope Changes	Date	Logic / Reasoning	Approval / Rejection Date
- Scope Change 1	July, 2015	Because of the difficulties in obtaining near-commercial fuel samples, a decision, in consultation with the DOE manager, was made to add the work on synthetic blends.	Approved October, 2015

1 - 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.

1 - Project Overview

- This was an AOP project and there were no changes in project team throughout the course of the project.
- It was planned to obtain a range of near commercial fuel samples and evaluate their techical potential for use in the home heating market.
- The biofuel industry response was less than hoped-for although sufficient fuel quantities were obtained for longer term combustion testing.
- In response to the limited fuel availability, the scope of bench-scale testing was increased and some studies of synthetic bio-oils were completed.

2 – 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

2 – 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 in close collaboration with BNL have included:

- 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 included focused meetings with industry leaders, preparation of briefing materials – brochures, web info, and trade journal articles, presentations at key industry conferences
- NORA provided feedback on key concerns and logistical barriers

2 – Approach (Technical)

- Broad outreach to obtain test fuels
- 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
- Industry outreach to obtain feedback on potential use of this fuel and technical factors which will influence acceptance.
- 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.

Risk Registry Table

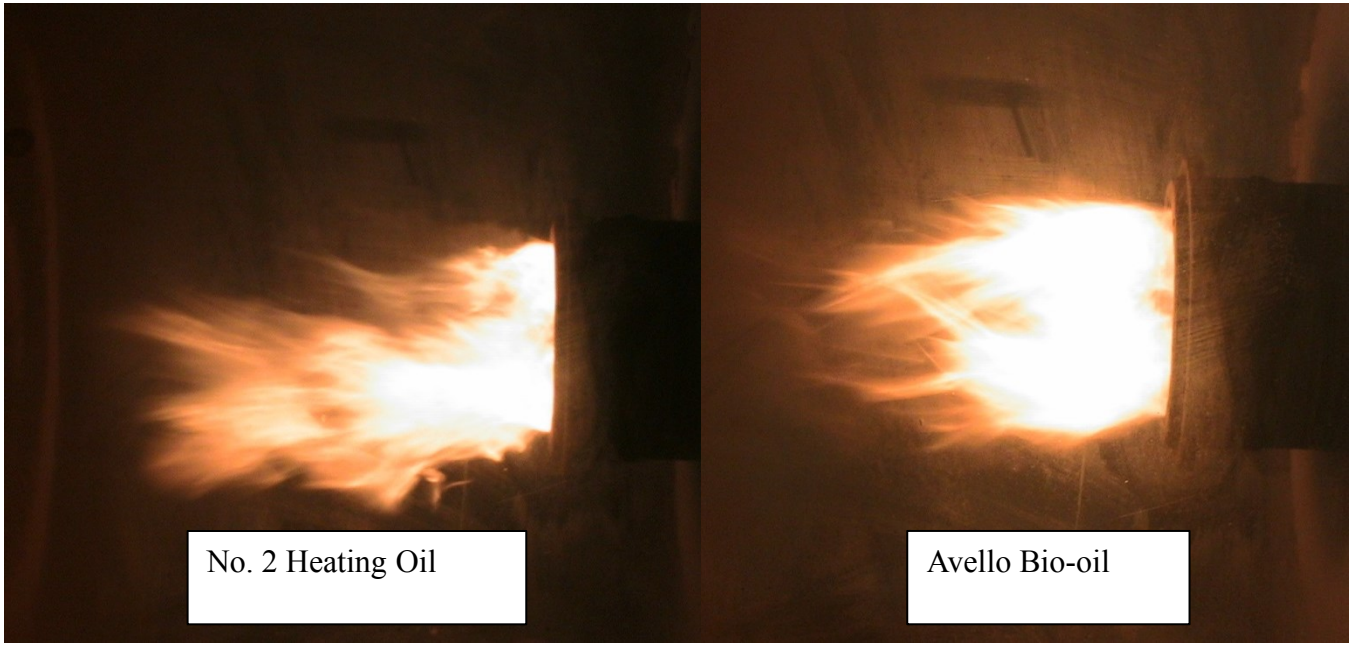
	Risk Identified			Mitigation Strategy		Current Status
Risk ID	**Process Step**	**Risk Description**	**Severity (High/ Med/Low)**	**Mitigation Response**	**Planned Action Date**	**Active/ Closed**
Fuel Transport and Handling						
1		Separation	Med	Fuel specification needed		
2		Tank Corrosion	Med	Fuel specs and studies needed		
3		Elastomer Compatibility	Med	Fuel specs and studies needed		
4						
Storage and Use at the Home Site						
1		Oxidative Degradation	High	Fuels need to be fully defined and a storage stability specification needed.		
2		Elastomer Compatibility – potential for in-home fuel leakage	Med	Material compatibility needs to be fully understood		
3						
4						

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 and included in studies, 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);
- Other fuel samples obtained from Avello Bioenergy, Inc.; Utah State University; and Pacific Northwest National Laboratory.

Technical Accomplishments/ Progress/Results (cont'd)

- Example – evaluation of a fractionated pyrolysis oil (Avello Bioenergy)
  - Not chemically upgraded and not miscible with No. 2 oil.
  - Combustion tests done on pure bio-oil



For acceptable combustion, fuel was atomized at elevated pressure and temperature. Cold ignition was done on petroleum No. 2. Combustion acceptable but equipment changes needed.

Technical Accomplishments/ Progress/Results (cont'd)

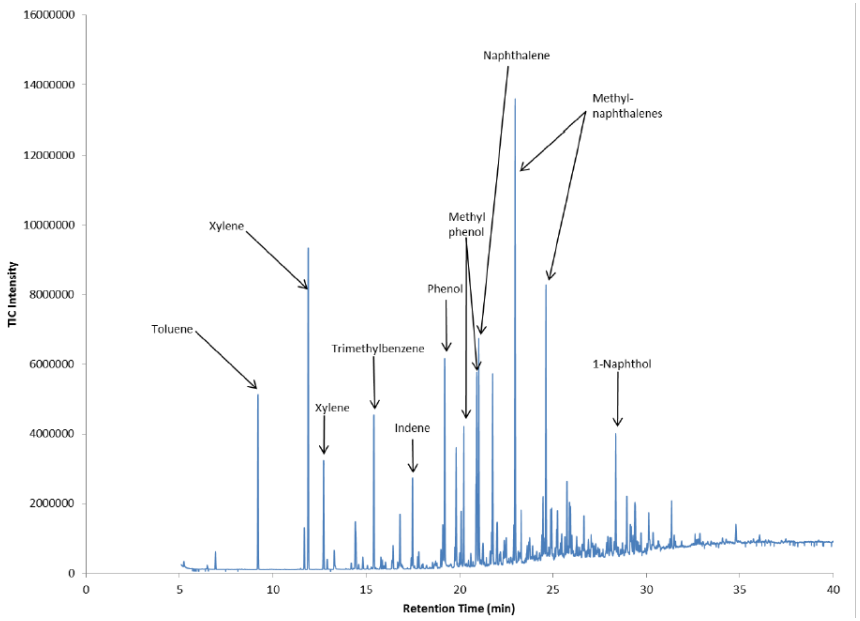
Example -partially upgraded fuels from PNNL. Composition of the neat fuels – tests were done on 20% blends of these fuels with No. 2 oil.

	HT209-MOx	HT209-HOx
Water by Karl Fischer (wt%)	1.05	1.23
Acid Number (mg KOH/g)	46.82	49.54
Carbon (wt%)	79.04	78.75
Hydrogen (wt%)	11.32	9.68
Nitrogen (wt%)	0.08	0.13
Oxygen (wt%)	9.47	11.33
Sulfur (wt%)	<0.1	<0.1
Viscosity (cSt)	3.07	17.74
Density (g/mL)	0.892	0.962

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



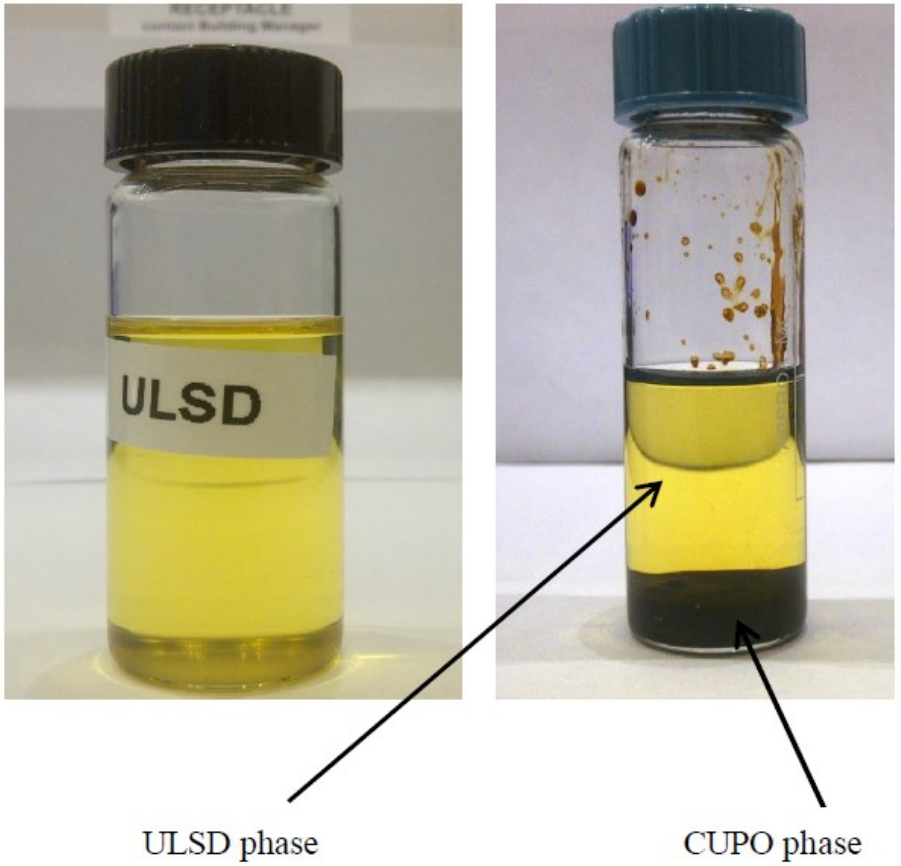
Fuel mainly aromatic hydrocarbons and phenolics. Substituted benzenes (xylene, toluene, alkylbenzenes), napthalenes, indene, and indane accounted for 62% (area) of the total.

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)

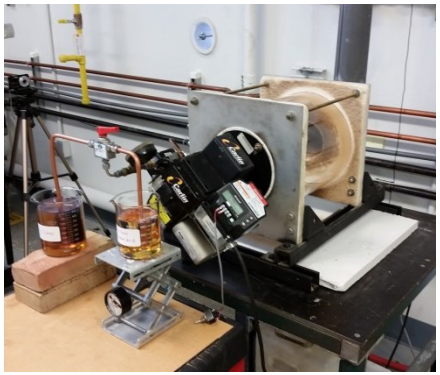
- Kior fuel – two fuel samples submitted for testing under this program. Produced via Biomass Fluidized Catalytic Cracking (BFCC) Process, followed by hydroprocessing and fractionation. "Kior Distillate" and "Kior Gas Oil". Miscibility of the distillate grade excellent. Miscibility of the Gas Oil at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

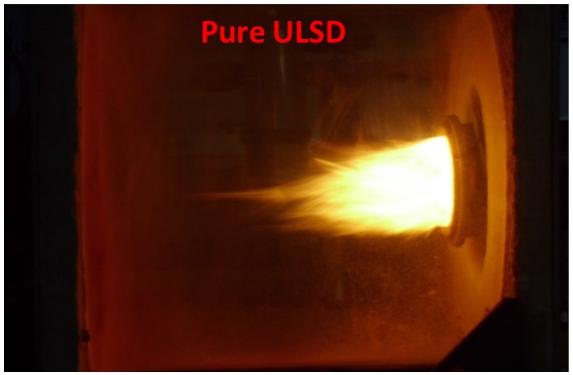
Physical Properties	ASTM Test Method	D396 Limits	Standard No.2 Fuels*		Test Fuels	
			No.2 S500	No.2 S5000	KiOR Distillate	KiOR Gas Oil
Flash point, C	D39	min	38	38	60	53.89
Water & Sediment, % vol.	D2709	max	0.05	0.05	0.0001	0.09
Distillation	D86					
90%		min	282	282	326.3	-
90%		max	338	338		-
Kinematic 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)

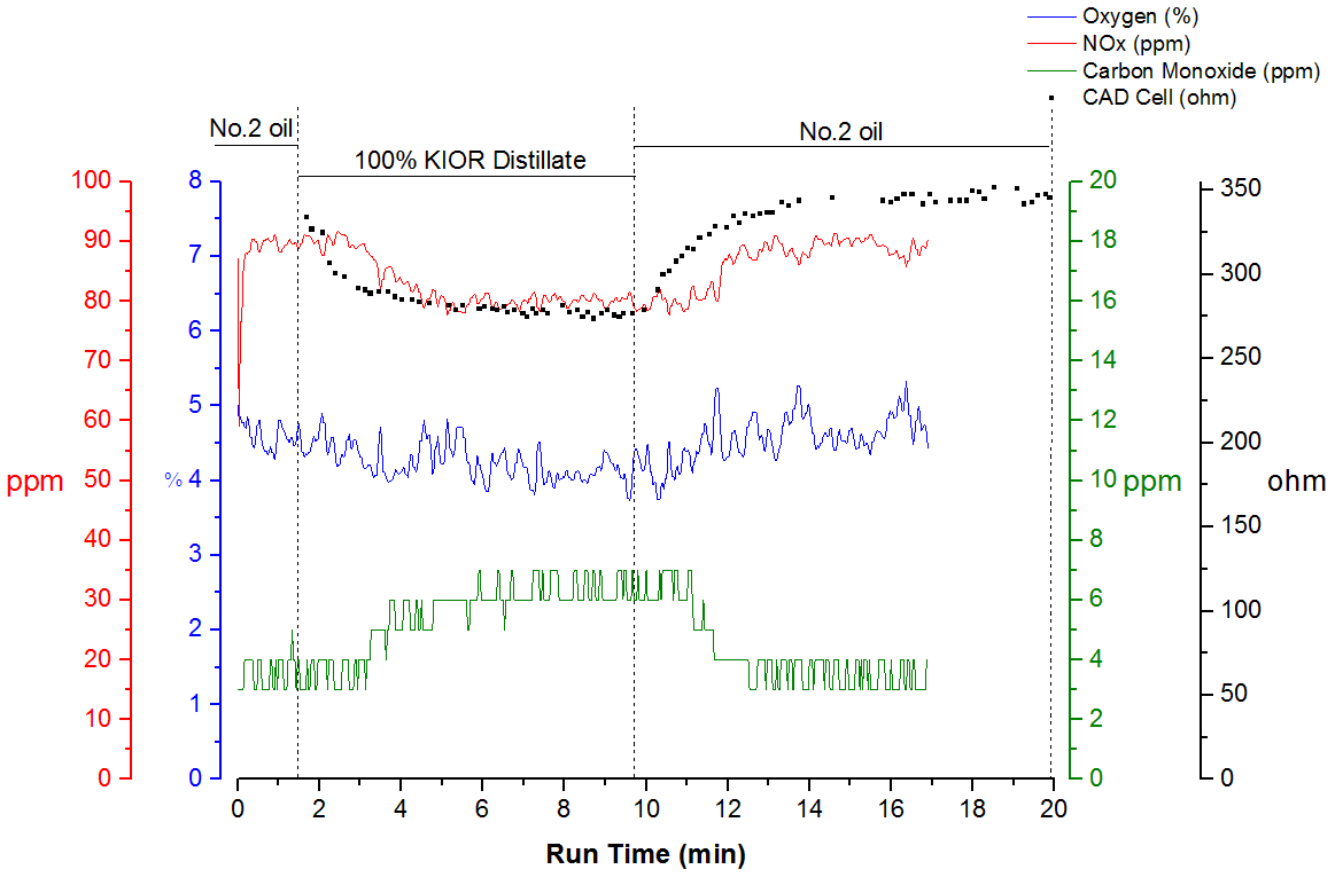
- *Combustion Testing – Quartz Combustion Chamber – full size residential burner. Allows flame visualization.*





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)

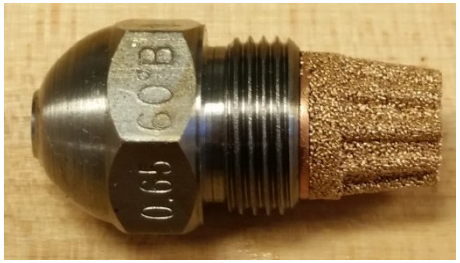
Steady State Emission Testing / Kior Fuels

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

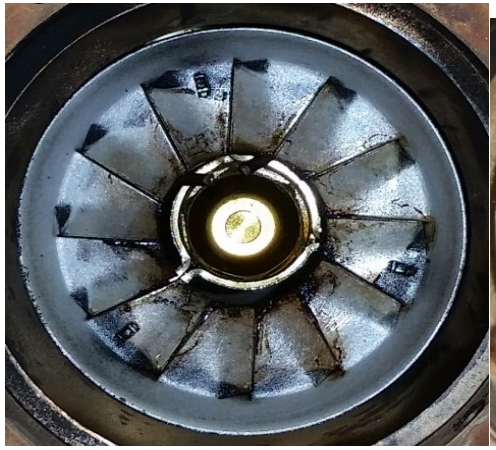
1 all CO levels are considered negligible

Technical Accomplishments/ Progress/Results (cont'd)

Kior fuel cycling test – 4000 hours at 5 min on / 55 minutes off.
20% blend, typical residential heating boiler.
No operational problems observed.
Post test inspection of burner head indicated no deposits or concerns.



Inspection of atomization nozzle and burner head after test showed no concern.



Before

After

Technical Accomplishments/ Progress/Results (cont'd)

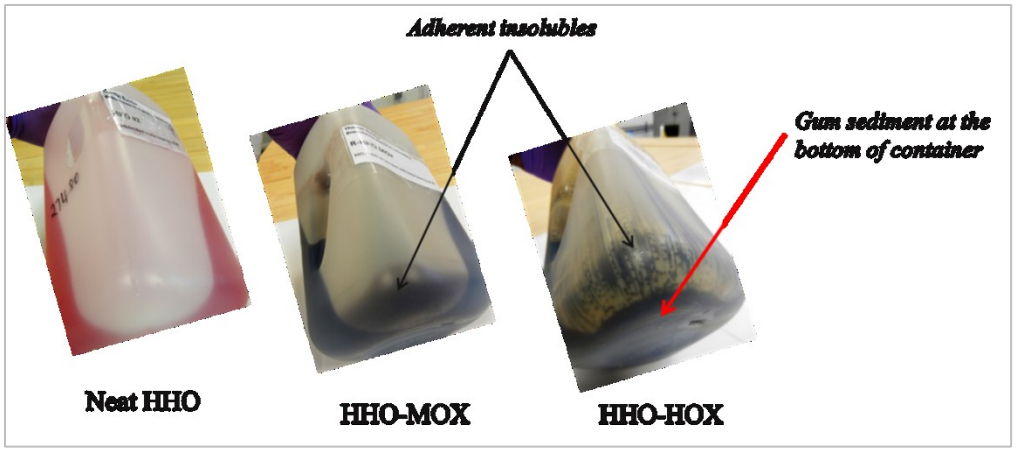
Storage stability testing

Thermal Stability (ASTM D6468)

Long Term Storage Stability (ASTM D4625)

Non upgraded fuels and the partially upgraded fuels from PNNL did not pass in general.

The "fully" upgraded fuel from Kior was found full acceptable.

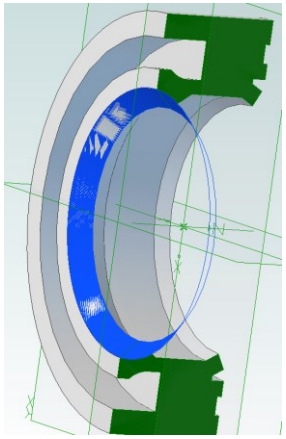


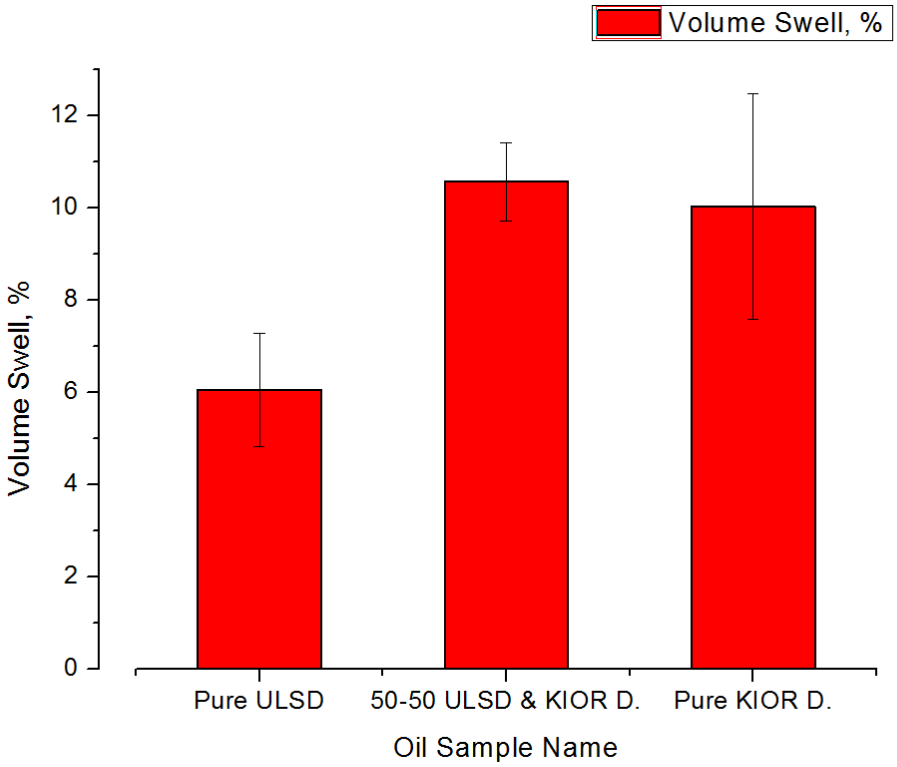
Partially upgraded fuel in storage

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.

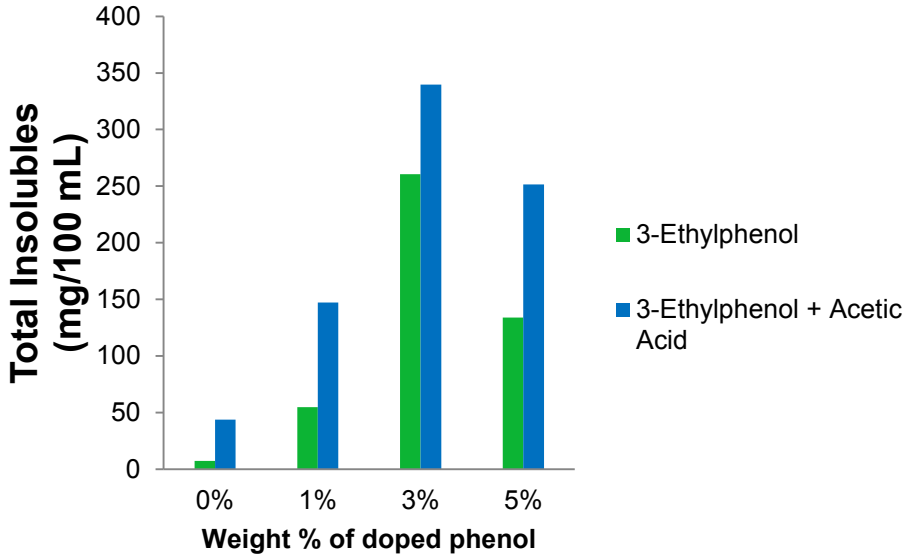




Partially upgraded fuels from PNNL produced excessive swell, fully upgraded fuels did not

Technical Accomplishments/ Progress/Results (cont'd)

Preparation of synthetic blends– adding oxygenates into home heating oil to help understand operational impacts and help inform standards development.

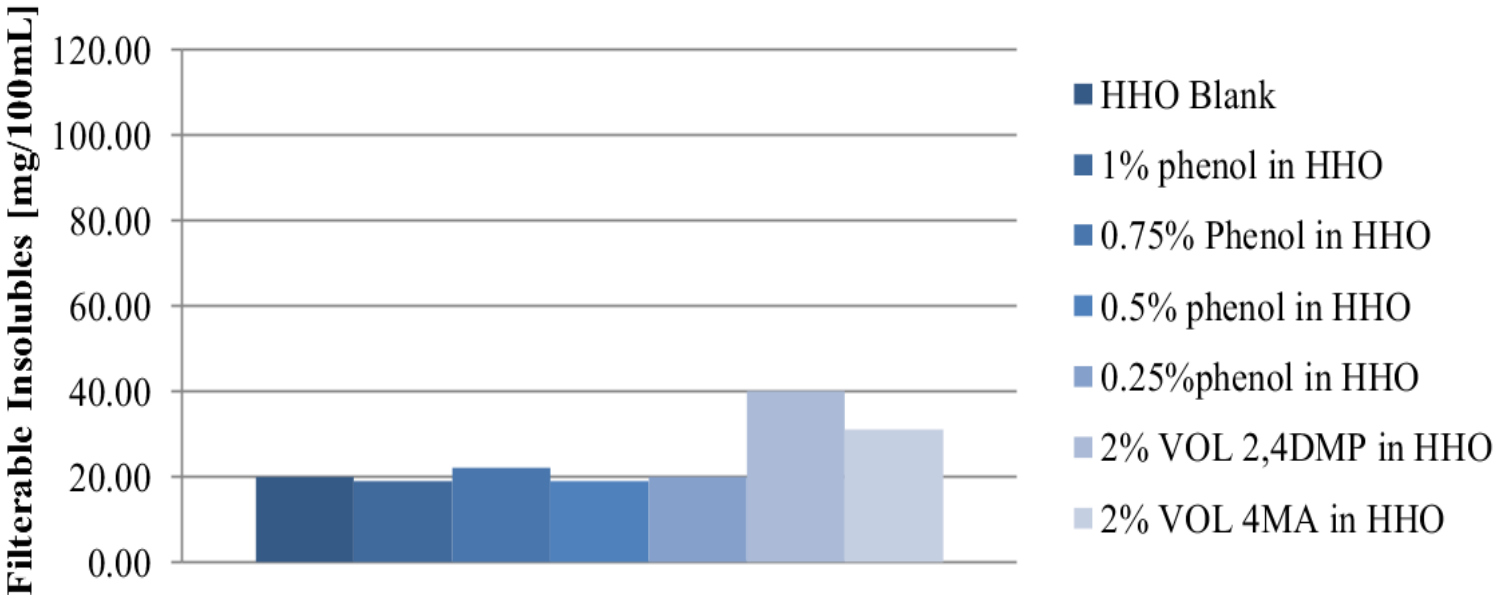


80 C, 1 week

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

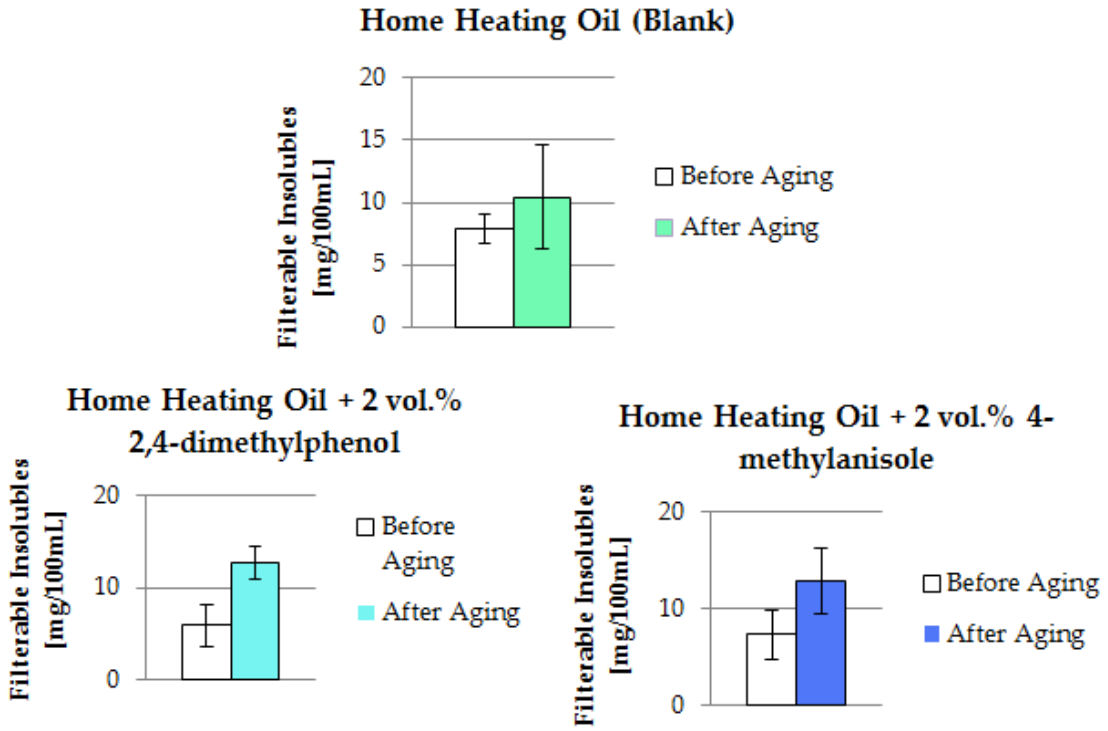
Technical Accomplishments/ Progress/Results (cont'd)

Synthetic blends – exploring effects of lower blend levels on insolubles formation at 80 °C / 1 week



Technical Accomplishments/ Progress/Results (cont'd)

Synthetic blends – exploring impact of phenols on storage stability 43 C / 12 weeks



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.

Sample/Specimen	Change in Volume, % (Mean Values)	Std
Pure # Diesel (Blank)	8.07	1.47
Effect of Phenol		
Diesel with 1wt% 3-EP	20.26	0.61
Diesel with 2wt% 3-EP	30.09	1.19
Diesel with 3wt% 3-EP	39.80	1.30
Effect of Ketone		
Diesel with 1wt% CP	9.94	0.79
Diesel with 3wt% CP	12.53	2.18
Diesel with 5wt% CP	14.64	2.17
Effect of Acid		
Diesel with TAN of 5	10.80	1.68
Diesel with TAN of 10	8.77	2.26
Diesel with TAN of 15	11.00	2.67

Technical Accomplishments/ Progress/Results (cont'd)

Industry Outreach

- Phone interviews with pipeline and terminal operators;
- Webinars;
- Presentations at oilheat industry conferences – and booth sample displays

Key Outcomes

- Industry very interested in adopting this new fuel but not will to do "tests" – we need to ensure it is ready.
- Local, reliable fuel producers attractive.
- Fuels need to meet ASTM standard and be accepted by primary equipment manufacturers (burners, pumps, components). This means "listed".
- Stability is critical – fuel quality is a very large issue now for this industry. A new fuel which adds more concerns would not be accepted.
- Fuel odors are not acceptable for home applications

Technical Accomplishments/ Progress/Results (Cont)

- *Standards and Approvals*
  - *For the home heating application a new standard or modification to ASTM D396 could be considered for partially oxygenated fuels.*
  - *A limit on oxygenates or phenols could be considered to enable consistent approval of materials such as elastomers.*
  - *A storage stability specification is recommended.*
  - *For a fully upgraded fuel, with oxygen at a trace level, fuels may be approved under current ASTM D396 standard.*

4 – Relevance

- *Renewable home heating oil as a target product 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.*

5 – Future Work

- *This project is now complete.*
- *Potential future projects could focus on:*
  - *Long term storage and performance evaluation of specific products with manufacturers of bio-oil ready to enter this market;*
  - *Testing of different long term storage stability metrics for the fuels to be used;*
  - *Technical support for standards modifications for this application.*

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. Example bio-fuels evaluated, one technically a commercial candidate
    2. Explored synthetic blends
    3. Storage, elastomer, combustion testing
    4. Long-term combustion testing with one fuel completed
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. Project is now completed
    2. Potential future projects should involve fuel producer

Additional Slides

Responses to Previous Reviewers' Comments

- The comments from the 2015 review were generally supportive and highlighted several needs to enable the barriers to this market to be overcome. This includes development of needed standards and more attention to this market by fuel producers. We fully agree with these comments. This work has demonstrated basic technical feasibility and also areas for attention such as storage stability and materials compatibility. Defining the fuel which really will be the target for this market in detail would greatly help focus the work. This improved definition is likely to be an iterative process between production cost and performance in stability and materials. Combustion performance in not seen as an area of concern.

Publications, Patents, Presentations, Awards, and Commercialization

Mante, O., Butcher, T., Wei, G., Trojanowski, R., and Sanchez, V. Evaluation of biomass-derived distillate fuel as renewable heating oil, Energy and Fuels, Vol. 29, No. 10, pp. 6536-6543, 2015.

Several presentations on this work were made at heating industry conferences and workshops to inform the industry about the work and the opportunity.