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Bio-Oil Deployment in the Home Heating Market

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Abstract

Distillate fuel oil is used in many stationary heating applications, predominantly in the Northeastern part of the United States. Total estimated non-transportation distillate use in 2014 was estimated to be 10.9 billion gallons. This study has focused on potentially displacing part of this petroleum use with biofuel derived from woody biomass. The fuel production route considered is pyrolysis which creates a liquid fuel high in oxygen, organic acids, and water. While this fuel can be used in stationary applications without significant further processing, to do so would require significant upgrades in current heating equipment. Alternatively this raw pyrolysis oil can be upgraded through catalytic hydrogenation to produce a bio-oil with near-negligible oxygen, water, and acidity.

The focus of this work has been exploration of such upgraded fuels. The quality of upgraded fuels is affected by process conditions and there is a cost /quality tradeoff. Partially upgraded fuels may be the economical compromise – containing residual oxygenates while still providing good performance in use. The goal of this work has been such; partially upgraded fuels which are fully miscible with petroleum, can be blended at a minimum of 20% and these blends used in the field without required upgrading of equipment.

Four different near-commercial biofuels were studied ranging from minimally upgraded and not miscible with petroleum to high quality, partially upgraded fuels, and fully upgraded fuels from a commercial developer. Combustion testing was done firing in both a quartz cylinder combustion chamber and a typical residential heating boiler. The non-miscible fuel was fired without blending and required fuel heating and higher than normal pump pressure. Overall, the combustion quality of the tested fuels was seen as acceptable.

Tests were also done to determine the compatibility of the test fuels with nitrile elastomers, which are commonly used in the target applications. Measured swell in both the minimally upgraded fuels and upgraded fuels with high residual oxygen content were found to be unacceptable. Storage stability was also found to be unacceptable except in the fuels which have been fully upgraded.

To further explore the impact of the level of oxygenates left in a partially upgraded fuel, synthetic bio-oil blend studies were done in which specific oxygenates were added into petroleum heating oil to study effects on elastomer swell and storage stability. The oxygenate studies – ketones and phenols – were shown to increase elastomer swell. Results from storage stability tests indicated the addition of phenols increased the production of filterable insoluble under higher temperature storage conditions.

It is recommended that one route to inclusion of such upgraded bio-oils into the fuel market could involve modification of the current standards for heating oil to include a storage stability specification. This would provide a performance based metric to ensure acceptable bio-oils are used. Overall the study indicates strong potential for this fuel in this market.

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Table of Contents

<i>Bio-Oil Deployment in the Home Heating Market</i>	1
Abstract	ii
Acknowledgements	iii
Introduction	1
End-Use Equipment	2
Logistics and the Fuel Distribution System	4
Codes and Standards	6
Sources of Upgraded Bio-Oil	7
“Synthetic” Upgraded Bio-Oil	8
Experimental	9
Test Fuels	9
Combustion Studies	9
Elastomer swell test	10
Storage stability at 80 °C	10
Test Results	10
Avello Biofuel	10
Fuel from Utah State University	12
PNNL Upgraded Bio-oil	14
Total acid number of the blends fuels that were stored in the refrigerator	18
Thermal Stability Test (ASTM D6468)	18
Long Term Storage Stability Test (ASTM D4625)	19
Effect of yellow metals on storage stability of fuels	21
Influence of antioxidant-butylated hydroxytoluene (BHT) on storage stability of fuels	22
Chemical composition analysis of the aged oils and the insolubles formed by PyGC/MS & FTIR	23
Effect of blend fuels on elastomer swell	25
Combustion of blend fuels	25
Kior Upgraded Bio-oil	28
Synthetic Biofuel Blends	37
Industry Outreach	45
Discussion	47
Conclusions	48
References	49

Introduction

Distillate fuel includes diesel; kerosene; and No. 1, No. 2, and No. 4 heating oil. These fuels are used in many applications in the U.S. including on-highway transportation, off-highway, residential, commercial, industrial, farm, power generation, marine, military, and other uses [1]. Table 1, below lists the end use of distillate fuel oil by sector for 2014.

Table 1: Distillate Fuel End Use by Sector in 2014 [1]

End-Use Sector	Volume (millions of gallons)
Residential	3,803
Commercial	2,544
Industrial	2,418
Oil Company	2,105
Farm	3,209
Electric Power	717
Railroad	3,670
Vessel Bunkering	1,593
On-Highway	38,533
Military	221
Off-Highway	2,014
Total	60,828

This project explores the potential to displace petroleum distillate fuel with biofuel derived from pyrolysis in the non-transportation applications. From the data presented in Table 1, the transportation sector, by far, uses the greatest volume of distillate fuel. However, the stationary applications are technically less challenging than transportation diesel engines and are seen as a potentially attractive market entry point for such biofuels. The total of the non-transportation distillate fuel use in Table 1 is 10,870 (million gallons). Assuming an average price of \$2.25/gallon, this represents a cost to the U.S. economy of 24.5 billion dollars annually.

While the work of this study potentially impacts all stationary applications which use distillate fuels, the technical work has been focused on residential heating. Some six million homes in the U.S. currently use oil for home heating and 88% of the home heating oil usage is in the Northeast [2, 3].

For this work the biofuel considered is pyrolysis oil, upgraded to different degrees. The ideal objective is a biofuel which can be blended with petroleum oil easily and displace 20% (initial target) of the petroleum fraction. This fuel would be used in existing equipment and across the existing supply infrastructure without the requirement for changes. The feedstock for upgrading is fuel produced by fast pyrolysis of lignocellulosic biomass. The raw fuel produced by this process has a high water and acid content. Because of its polar nature it is not miscible with petroleum products. Considerable work has been focused on the direct combustion of this raw bio-oil in boilers, diesel engines, and gas turbines and there are some commercial applications at present [4]. This type of raw bio-oil is not the subject of this study. Rather, bio-oils which have been upgraded to remove water and oxygen and reduce acidity, leading to a fully petroleum

miscible fuel have been considered. Review papers covering the state of the art in fast pyrolysis and downstream upgrading are available [5, 6, 7, 8].

The most commonly explored approach for upgrading is catalytic hydrogenation and the residual oxygen content of the upgraded fuel is often used as a metric of the degree of upgrading. While upgrading to a near perfect fuel with residual oxygen less than 1% is possible, it may not be the economic option. The cost / residual oxygen tradeoff has been explored [9]. Thus an upgraded pyrolysis oil could be expected to have residual oxygenates at levels higher than found in petroleum fuels.

The work in this project, presented in this report includes the following elements:

- Review of sources of upgraded pyrolysis oil;
- Fuel sample property evaluation;
- Miscibility testing;
- Basic combustion testing in representative equipment;
- Elastomer compatibility testing;
- Storage stability testing;
- Outreach to the heating oil industry to communicate this opportunity and to obtain input on their concerns and requirements;
- Consideration of fuel specifications and requirements.

End-Use Equipment

The technical focus of this work is on typical residential and light commercial oil-fired heating equipment. General descriptions of the equipment and configurations used in this target sector can be found in the ASHRAE Handbook [10] and the Oilheat Technical Manual published by the National Oilheat Research Alliance (NORA) [11].

In this application, fuel is typically delivered to the site by truck and fuel marketers either have a contract with the customer for automatic delivery or deliveries are based on customer requests (“will-call”). Automatic deliveries are based on heat demand estimated from degree days and historical fuel use patterns at the site. Typically three to five deliveries are made annually and fuel tank levels at delivery are one-third to a half full. Run-outs do occur but are not common. During the non-heating season, demand is either zero (heating only application) or very low (domestic hot water).

Most fuel tanks are steel although polyethylene tanks with galvanized steel outer enclosures are growing in popularity [12]. Fuel tanks found in the field may be installed outside underground or above ground or inside. Inside tanks are becoming the most common case for new or upgraded installations.

Fuel lines running from the tank to the burner unit are commonly copper. Fuel is filtered between the tank and burner. A variety of filter types are in use. The most common is a wool felt material with a nominal filtration rating of 10 μm .

During very cold weather, fuel line blockage due to wax formation in the outside fuel lines can be a concern. Solutions to this include electric heating as needed and kerosene blending to lower the fuel’s cloud point.

Burners are very commonly pressure-atomized using common swirl atomizers. In residential and smaller commercial applications single firing rate burners are used with input modulation achieved with cycling. Burners commonly cycle from 6,000 to 12,000 times annually. Atomizing nozzles can be either brass or stainless steel. In larger commercial applications two-stage or fully modulating firing can be used.

With fixed firing rate burners, fuel pressure at the atomizer ranges 100 to 150 psi. Nozzles are rated for flow at 100 psi and that has been the most common pressure historically. There is a trend toward the higher pressure level, motivated by improved combustion performance.

Fuel pumps are positive displacement type with integrated pressure regulators. The regulators are piston plunger bypass types. Relief flow from the regulator is directed either back to the pump suction (“one-pipe” system) or back to the storage tank (“two-pipe” system). Several different seals are used within the pump including for the pump shaft seal and the pressure regulator piston face seal. For the pump shaft seal a nitrile lip seal is most common although carbon face seals are found in some pumps available on the market.

Figure 1, below, provides a simplified illustration of a residential oil-fired heating system with the fuel storage inside the structure.

Figure 1 Simple illustration of an oil-fired home heating system.

The heating appliance in homes can be either a warm air furnace or a boiler (hydronic hot water heating system). Boiler systems are most commonly found in the Northeast. Domestic hot water

(DHW) can be produced by a separate, oil-fired water heater or, in the case of a hot water heating system, the DHW can be produced also by the heating boiler.

Logistics and the Fuel Distribution System

In the Northeast, distillate heating oil can be produced by refineries within the region, delivered by pipeline, or brought in by barge. Figure 2 shows an overview of the supply chain for the region.

Figure 2 Illustration of Northeast heating oil supply chain.

The heating oil supply infrastructure for the Northeast is diverse, including pipeline transport from the U.S. Gulf Coast through the Colonial Pipeline, regional distribution through the Buckeye pipeline, marine transportation from the Gulf Coast and foreign sources, regional barge transfer, distribution by other regional pipelines, and extensive truck distribution [13]. In just New York State there are 43 terminals which handle heating oil and this includes primary and secondary terminals. The secondary terminals are smaller and are typically associated with marketers distributing fuel only to their customers.

Figure 3 provides another image of the pipeline and terminal structure in the Northeast (all products).

Figure 3 Illustration of petroleum pipelines and storage terminals in the Northeast [14]

Prior to 2012, the sulfur content of No. 2 home heating oil was typically 2000 ppm and in some regions of the U.S. significantly higher sulfur content was found. During combustion, most of the sulfur in the heating oil is oxidized to sulfur dioxide (SO_2) and emitted into the atmosphere. This SO_2 contributes to acid rain concerns. A very small fraction ($\sim 1\%$) of the sulfur is oxidized to sulfur trioxide (SO_3) in the combustion chamber and this converts to sulfuric acid (H_2SO_4) in the cooler, downstream heat exchanger sections of the boiler. About half of this sulfuric acid condenses on boilers surfaces leading to corrosion of heat exchanger surfaces and the formation of a corrosion product scale, primarily iron sulfate. The iron sulfate scale leads to reduced heat transfer, lower boiler and furnace efficiency, increased maintenance costs, and, in severe cases, to heat exchanger blockage and flue gas spillage.

The fraction of the sulfuric acid which passes through the heat exchanger is emitted from the stack and becomes fine particulate matter ($\text{PM}_{2.5}$; 2.5 microns and smaller). Most of the $\text{PM}_{2.5}$ emitted from oil-fired heating systems with conventional sulfur levels is this sulfuric acid aerosol. The heating oil industry has supported a transition to lower sulfur levels to reduce fine particulate emissions, reduce service costs, and enable the introduction of higher efficiency and more compact heating equipment. In July 2012, a new regulation became effective in New York State requiring that all heating oil be at 15 ppm sulfur. This represented a 99% reduction in heating oil sulfur. Other States are transitioning to low sulfur heating oil at different schedules [15]. Any biofuel to be considered for use in the heating oil sector in the Northeast will need to be compatible with this very strong shift to an ultralow sulfur future.

Over the past 15 years the heating oil industry has been exploring the use of biodiesel blended into heating oil and currently some heating oil marketers are distributing blends as high as 20% biodiesel by volume. The properties of heating oil are formally defined in the ASTM D396 standard [16]. In 2009 a change to this standard was approved which allows up to 5% biodiesel which meets the ASTM D6751 [17] standard to be blended into home heating oil. Blended in this way the fuel still meets all of the requirements of D396. One very important result of this is equipment which has been listed against UL standards for safety in the past are now approved for

use with 5% biodiesel blends. Again the implication of this for the biofuels under consideration in this project is that the fuel needs to be compatible with heating oil that may contain up to 5% biodiesel.

Codes and Standards

The composition and properties of heating oil used in the subject applications is defined in the ASTM D396 standard [16] and other standards referenced therein. Table 1 of this standard defines the properties of heating oil in different grades (e.g. No. 2, 4, 6). Properties specified which may be most important for the goals of this project include flash point, distillation temperature range, viscosity, copper strip corrosion, and density. Over the past roughly 7 years the ASTM D02 committee, under which this standard falls, has been making changes to the standard to more clearly address the role of biofuels in this market.

The ASTM D396 standard is under the ASTM Committee Petroleum Products and Lubricants and the biofuels that are the subject of this work are clearly not petroleum products. However, several recent changes to language within the standard are important for this point. The following specific sections are most relevant.

“The grades of fuel oil specified herein shall be hydrocarbon oils, except as provided in 4.3, free from inorganic acid and free from excessive amounts of solid or fibrous foreign matter. The inclusion of additives to enhance performance properties, if required, is allowed.”

Note- Section 4.3 referred to in this paragraph addresses biodiesel and this is discussed separately below.

Hydrocarbon oil is defined as: “a homogeneous mixture with elemental composition primarily of carbon and hydrogen that may also contain sulfur, oxygen, or nitrogen from residual impurities and contaminants associated with the fuel’s raw materials and manufacturing processes and excluding added oxygenated materials.”

In discussion it is also stated: “The hydrocarbon oil may be manufactured from a variety of raw materials, for example, petroleum (crude oil), oil sands, natural gas, coal, and biomass.”

The implication of the current language for upgraded bio-oils is, if the level of oxygen left in the fuel from upgrading can be considered as a residual impurity and the fuel meets all of the properties in Table 1 of the standard, a separate standard for upgraded pyrolysis oil is not required. Specific limits of allowable oxygen and other impurities are not provided in the current standard.

Oil burners are tested for safety against UL standard 296 [18]. This prescribes the fuels for which the burner is approved for use. If a new fuel were defined and a building owner/operator was interested in using this new fuel a burner which has specifically been tested and approved for use with this fuel should be used. Existing burners cannot practically be re-listed for use with a new fuel; a listed replacement burner would have to be installed. Considering the large number of sites using oil as a heating fuel, the requirement for a burner change would be a significant market barrier.

Considering for example the case of a fuel marketer servicing 3000 homes; if interested in delivering a new fuel the marketer could arrange for changing all customer’s burners to a new

one which is approved for the new fuel. This would represent a significant investment cost. If the marketer were to arrange for some of the homes to be changed to new burners then this could lead to the situation where different fuels were delivered to different homes. This would present a significant logistical problem requiring separated storage, separate trucks for each fuel, and a more complex and less efficient truck delivery routing.

The case of biodiesel can be considered as an example of how a new fuel could penetrate the heating oil market. In 2008, the definition of No. 2 heating oil in ASTM D396 was changed to allow up to 5% biodiesel, clearly an oxygenated fuel. This allowed use of biodiesel up to this blend level without impact to the safety approval status for burners in the field. Following this change biodiesel became a widely used fuel at the 5% blend level. In 2015, ASTM again changed D396 with biodiesel blends from 6 to 20% being defined. It is important to note, however, that this was done as a new fuel within Table 1 of the standard. Safety approvals in place for existing burners do not extend to these new fuel blends. While many marketers are already providing B20 blends to homes, the formal approval for the use of these fuels in these burners is not in place. New burners, listed for use with the new fuels, are not yet available on the market.

ASTM Standard D7544 defines properties of biofuels derived from pyrolysis and could be considered relevant to this work [19, 4]. This standard defines two grades – Grade G and Grade D. These are essentially raw bio-oil fuels not miscible with petroleum products and not fully compatible with the existing infrastructure and the goals of this project. Both grades may contain up to 30% water. For Grade G, the specification states: *“not intended for use in residential heaters, small commercial boilers, engines or marine applications.”* For Grade D the specification is similar *“not intended for use in residential heaters, engines, or marine applications not modified to handle these types of fuels.”*

Sources of Upgraded Bio-Oil

A key focus of this project is to evaluate the potential use of upgraded pyrolysis oil fuels which may be near-commercial in status. During the course of this project several potential sources of biofuel samples were identified and an outreach effort executed. To support this, a short brochure on the goals of this project was prepared and distributed. Not all of these sources were in a position or willing to provide test samples for the objectives of this project. In the section a discussion of sources identified and considered for study are reviewed. Several sources provide recent updates on the status of commercial activities and demonstration projects [5, 20, 21] and essentially all of the key organizations were approached for participation in this project. Samples of bio-oil, as discussed below, at different stages of upgrading were obtained for evaluation.

Some of the fuels included in this study were really just minimally upgraded and not miscible with petroleum-based fuels. In this sense these fuels do not meet the project objectives. They were included, however, to provide a basis for comparison with the strongly upgraded fuels.

Avello – Avello Bioenergy, Inc. is developing a unique process for the production of fractionated pyrolysis oil products including furnace fuels [22, 23]. This is not an upgraded, deoxygenated product but was explored early in our studies to provide some baseline information.

Utah – Research work at Utah State University involves catalytic fast pyrolysis to produce improved bio-oils [24]. A sample of one fuel produced from pinyon-juniper biomass using a HZSM-5 zeolite catalyst was received and evaluated during this project.

Kior – Kior has developed a patented process for the conversion of biomass into a range of upgraded fuel products [25]. Elements of the process include integrated pyrolysis and catalytic upgrading, and separation, regeneration, and recycling of the catalyst. Commercial implementation of this process was started but is not moving forward at the present time. The company, however, made available to this project, large samples of different upgraded products that provided the opportunity to evaluate the potential use of these in home heating systems [26].

The biomass-derived fuels were produced from solid biomass using a three-step process. Depolymerization is the first conversion step and has the goal of breaking down the lignocellulose into lower molecular weight fragments. Because high temperature favors depolymerization both thermodynamically and kinetically, this step is carried out by a Biomass Fluidized Catalytic Cracking process (BFCC). KiOR uses a combined thermal and catalytic process to affect depolymerization and produce intermediate bio-oils containing a complex mixture of hydrocarbons and oxygen-containing organic compounds, with an elemental oxygen content of <30% (by mass). Hydroprocessing is the next step to remove oxygen from the intermediate bio-oil. The bio-oil is processed through a hydrotreating unit in the presence of hydrogen at high pressure, to remove the organic oxygen and transforming the oxygenated compounds to hydrocarbons. During this process a concurrent saturation of aromatic compounds can take place, to some extent, depending on process severity. Fractionation is the final process to produce the upgraded products. A distillation column is used to separate naphtha and distillate cuts overhead and a fuel oil bottoms. The last fractionation processing step also insures that any heavy materials, impurities or solids will be removed and will not contaminate the distillate product.

Pacific Northwest National Laboratory (PNNL) – PNNL prepared upgraded bio-oil specifically for consideration for the home heating market. The raw bio-oil was produced using a fast pyrolysis process. This fuel was then upgraded using a catalytic hydrogenation process. The upgrading process involved a continuous-flow reactor system with a dual temperature stage fixed bed reactor configuration. The goal of this work was to produce an upgraded fuel that was fully miscible with middle distillate heating oil but still contained residual oxygenates and so represented an economical “compromise” fuel.

“Synthetic” Upgraded Bio-Oil

In this project a second approach was taken toward evaluating the impact of bio-oils which are upgraded but which may still contain oxygenated compounds in the heating oil sector. This involved blending targeted oxygenates into petroleum fuels at different levels to evaluate key performance measures including stability and elastomer swell. This approach provided greater flexibility in blend composition and provided information on potential areas of deployment concern, leading to guidance on fuel requirements and specifications for this application. In part this approach was launched because of the limited current market availability of partially upgraded bio-oils within a residual oxygen range being considered as potentially economical.

Experimental

Test Fuels

As discussed in the prior section, fuel from different sources, representing different upgrade levels were received for testing as candidate heating application fuels. Some of the fuels received were not significantly upgraded and represent cases only for comparison. In all cases the fuel suppliers provided at least some analysis of property data and these results, as available, are provided in this report.

All as-received samples were evaluated for apparent separation, presence of bottom sediment and adherent gums. Samples were evaluated for basic miscibility with No. 2 heating oil as appropriate. Some of the samples as received were already blended with No. 2 heating oil.

Combustion Studies

Two separate combustion experiments were conducted for received fuels as appropriate. The first combustion test was performed using a transparent quartz combustion chamber equipped with a Carlin EZ-1HP oil burner (Carlin Combustion Technology, Inc., North Haven, CT, USA). The installed burner is a conventional, pressure-atomized oil burner with a commonly-used swirl nozzle, primary control, and solenoid oil shutoff valve.

The control system for this burner uses a cadmium sulfide photo-resistor sensor (“Cad Cell”) as part of the safety system. The function of this sensor and the associated control is to stop fuel flow in the event of a no-flame condition to prevent flooding of the chamber. Flame is proven when a resistance of this sensor is fewer than 3500 ohms. One of the parameters monitored during the tests was the resistance of this sensor to evaluate the potential for control response concerns. Beyond the control operation, the resistance of this sensor provides some additional information on the flame. A flame with less emissivity would produce less light and a higher sensor resistance. Flames with poor stability lead to high and fluctuating resistance signals.

The quartz chamber combustion test was done to provide a basic visual evaluation of flame stability, size, and shape relative to the baseline heating oil. The second test was carried out in a typical residential heating boiler. One of these was a Dunkirk boiler, Model 3EW1.00Z, with an input of 140 MBH (140,000 Btu/hr) and heating capacity of 119 MBH (Dunkirk Boilers, Utica, NY USA). It is a 3-section, cast iron boiler with a tankless coil installed for domestic hot water. Some testing was also done in a Thermodynamics LM 75 residential boiler. This is a steel boiler with a horizontal, cylindrical, refractory lined combustion chamber. Both of these residential boilers are very representative of Northeast, oil-fired heating systems. The same Carlin EZ-1HP oil burner used in the quartz chamber studies was used in the Dunkirk boiler.

For typical fuel testing, the burner is adjusted to an excess air level which provides a “smoke number” of zero but is just above the excess air level at which air flow is too low and smoke number increases. Burners are typically adjusted in this way to provide the highest efficiency possible consistent with clean combustion. Following a careful tuning procedure to achieve this condition the burner would be operating at roughly 15% excess air, which is rather low for this type of equipment operating in the field. This could be considered an “ideal” tune situation. A Testo 350-XL flue gas analyzer was used to monitor O₂, CO, and NO_x. The analyzer was calibrated prior to its use. Other performance metrics including smoke number and Cad Cell value were also evaluated. Smoke number measurements were made following ASTM D2156-

09. In each combustion experiment, a dual fuel feeding train equipped with a standard 10 µm, felt fuel oil filter was employed to allow seamless switching between the unblended heating oil and the fuel being tested during boiler operation. Such a system permitted a direct comparison between the combustion performances of the fuels. For all the tests, the combustion system was first started and warmed on heating oil and, after establishing baseline data, the fuel supply was switched to the test fuel.

Elastomer swell test

For some of the tested fuels, the volume swell of hard nitrile slabs used in the lip seal on the most common pump in the U.S was evaluated. The test material was obtained from the pump manufacturer (Suntec Industries). In general, nitrile materials differ greatly depending on composition and use of additives and so it is important to use the actual material for the swell tests. Specimen of approximate dimensions: 12.5 by 25 by 2.0 mm were made and used for the tests. The swell tests were conducted following similar protocols described in ASTM D471 and UL 179. Each specimen was immersed with the use of a thin Kanthal wire fitted to a stopper in a total volume of 25 mL of the test liquid. The swell was determined by measuring the length (*l*), width (*w*), and thickness (*t*) of the specimen before and after the specified exposure period. The change in volume was then computed as follows:

$$\Delta V\% = \frac{(L \times W \times T) - (l \times w \times t)}{l \times w \times t} \times 100$$

Where,

l, *w*, and *t* are the length, width, and thickness of the specimen before the immersion and exposure.

L, *W*, and *T* are the length, width, and thickness of the specimen after the immersion and exposure.

Storage stability at 80 °C

The storage stability of the fuel blends was performed at 80 °C for a week. This accelerated storage stability test has been shown to have good correlation with ASTM D4625 and the amount of total insolubles formed in each method is comparable. Three pre-filtered (0.8 µm) 50 mL of each fuel sample were prepared and stored at 80 °C for a week in uncapped 25 X 200 mm heavy wall glass test tubes. After aging, the samples were cooled and filtered through a pre-weighed, oven dried 47-mm nylon filter (nominal pore size 0.8 µm) under vacuum. Iso-octane was used to rinse the filter, funnel, and the test tubes to remove trace fuel. The test tubes were oven dried afterwards and weighed prior to washing out the adherent insolubles with trisolvant (equal volume mixture of methanol, acetone, and toluene). After washing, the test tubes were oven dried and weighed again. Oven drying of filter papers and test tubes were done at 90 °C for 30 minutes. The total yield of insolubles in mg/100 mL was determined gravimetrically.

Test Results

Avello Biofuel

The fractionated bio-oil fuel sample received from Avello had a nominal water content of 7% and a heating value of 96,000 Btu/gal. This heating value is significantly lower than that of

conventional heating oil (approx. 139,000 Btu/gal) but higher than would be expected for a non-fractionated bio-oil. This fuel was not found to be miscible with petroleum heating oil but combustion testing was done with the unblended sample. These tests were done only in the quartz combustion chamber at BNL. For these tests the burner was configured in a custom manner. Fuel atomization pressure was increased from the conventional 100 psig to 300 psig. Fuel temperature was increased from the conventional ambient to 240 °F. These steps were taken in consideration of the higher viscosity of this fuel. The heating was done using a special high surface area heating cartridge provided for this purpose by Carlin Combustion Technologies as part of a new burner development effort. This heating system has since been commercialized by Carlin in a new variable firing rate burner product although it is not now used commercially at temperatures as high as was tested in this project.

For these tests the burner was setup with a dual fuel inlet and the quartz combustion chamber was pre-warmed with conventional No. 2 heating oil. The bio-fuel was partially heated prior to the start of the test and the fuel lines were wrapped with electrical heating tape, although it is not clear this was necessary. The bio-oil fuel container was approximately two liters in capacity. An in-line, 90 µm, sintered metal strainer was used in the bio-oil line.

Figure 4, below, provides a comparison of the flame appearance of a conventional No. 2 heating oil flame and the flame realized with this bio-oil sample in the quartz combustion chamber. The conventional No. 2 heating oil was burned at 100 psig and without fuel heating.

Figure 4 Comparison of the flame of No. 2 oil vs Avello bio-oil fired in a quartz cylinder combustion chamber

This test shows that this fractionated bio-oil can be burned in a residential oil burner at typical firing rates, at least under the specific conditions tested. To implement this in the field some significant burner modifications would be required to achieve the temperature and pressure conditions.

Fuel from Utah State University

As discussed above, the fuel received from Utah State University (USU) was produced by catalytic (HZSM-5 zeolite) fast pyrolysis and the feedstock for this fuel was pinyon-juniper. The catalytic pyrolysis was conducted in a 2 kg/h fluidized bed pyrolysis unit. A catalyst to feed ratio of 1(w/w %) was used. The reactor was maintained at an average temperature of 475 °C. The vapors/aerosols were condensed with the aid of tube-in-shell heat exchangers, a venturi scrubber, and a wet electrostatic precipitator maintained a 30 kV. The non-condensable gases were further cleaned with coalescing filters before entering a syngas compressor for recycling into the pyrolysis unit. No upgrading beyond the basic fuel production was done. Table 2, below provides physicochemical property data, provided by USU. This fuel has been labeled CUPO (catalytic upgraded pyrolysis oil).

Table 2: Properties of Bio-oil Received from Utah State University

Property	Catalytic upgraded pyrolysis oil (CUPO)
<i>Elemental, wt.% (dry basis)</i>	
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
<i>Physical properties</i>	
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

*oxygen by difference

Compositional analysis by gas chromatography and mass spectrometry (GC/MS) was performed on the as-received CUPO. A concentration of about 60 mg/mL of CUPO in methanol was prepared and analyzed on an Agilent 7890A gas chromatograph and 5975C mass spectrometer detector. A 60 m x 0.25 mm DB-1701 capillary column of 0.25 µm film thickness was used for the separation of products. The GC inlet was set to 275 °C and a split ratio of 75:1 was used. The column followed a temperature program of 40 °C for 1 min, 6 °C/min to 130 °C, 10 °C/min to 275 °C held for 20 min. Column flow was controlled to maintain a constant linear velocity of 1 mL/min. The ion source and the interface of the mass spectrometer detector were held at 230 °C and 250 °C respectively. Electron ionization of the compounds was performed at 69.9 eV and the ions were separated by their mass-to-charge (m/z) ratios in the range of 28 to 350. Results are provided in Figure 5, below.

Figure 5 GCMS analysis of primary components of bio-oil from USU

The GC/MS analysis showed that the CUPO consisted mainly of aromatic hydrocarbons and phenolics. Substituted benzenes (xylene, toluene, alkylbenzenes), naphthalenes, indene, and indane accounted for 62 % (area) of the total ion chromatogram. Phenols constituted the largest fraction of oxygenates found in the CUPO at approximately 23%. The remaining fraction was made up of aromatic oxygenates such as benzofurans, naphthalenols, and indenols. A small amount of levoglucosan (1.4%) was also found in the oil.

The miscibility of this fuel in petroleum heating oil was evaluated by preparing mixtures with ultra-low sulfur diesel fuel (ULSD). This type of fuel is now the standard heating used in New York State. The fuel was found to clearly separate (Figure 6) and the insoluble part was found to be dominated by levoglucosan and phenols. For this test the blend was 10% CUPO. Agitation of the two phases resulted in coating of the vial with CUPO.

The miscibility of the CUPO with heating oil was further investigated with a commercial biodiesel (B100). Contrary to the observations made with ultra-low sulfur heating oil (ULSD), it was found that the CUPO was partially soluble in B100 after agitating the two phases. The insoluble fraction was dissolved in methanol and analyzed by GC/MS. The results from the GC/MS indicate that most of the substituted benzenes in CUPO were soluble in B100. However, levoglucosan and phenols were found to be relatively less soluble. Importantly, some constituents of B100 were found to be present in the insoluble fraction that was analyzed. Specifically, methyl esters of fatty acids such as linoleic acid, 9-Octadecenoic acid, and hexadecanoic acid were identified. Overall, the study suggests that B100 could be used to some extent as a co-solvent to blend partially upgraded pyrolysis oil in diesel fuels. This is particularly relevant in the Northeast, where, heating oil commonly contains biodiesel as part of the commercial blend.

Figure 6 Image of separation of CUPO in ultralow sulfur diesel (heating oil).

PNNL Upgraded Bio-oil

Table 3, below, provides the basic composition of the two upgraded bio-oils produced by PNNL. As discussed above the goal of the effort at PNNL was the preparation of a partially upgraded fuel that might perform well in the home heating market in a blend with petroleum heating oil but still be economical. The two fuels were labeled MOX for moderate oxygen content and HOX for high oxygen content.

Table 3: Composition of Partially Upgraded Bio-Oil Produced by PNNL (data from PNNL)

	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

Blends of 20% partially upgraded bio-oil in No. 2 heating oil were further prepared by PNNL and sent to BNL for testing along with a sample of the home heating oil (HHO) used in preparation of the blends. The analysis of these blends is provided in Table 4, below.

Table 4: Composition of Partially Upgraded Bio-Oil Produced by PNNL Blended with No. 2 Heating Oil at 20% (data from PNNL)

	HHO-MOx	HHO—HOx
Water by Karl Fischer (wt%)	0.03	0.08
Acid Number (mg KOH/g)	8.31	8.55
Carbon (wt%)	85.14	85.17
Hydrogen (wt%)	12.68	12.36
Nitrogen (wt%)	<0.05	<0.05
Oxygen (wt%)	2.15	2.29
Sulfur (wt%)	<0.1	<0.1
Viscosity (cSt)	2.68	3.21
Density (g/mL)	0.838	0.849

Figure 7 provides an analysis of the functional groups of the raw pyrolysis oil, the two upgraded pyrolysis oils, and the home heating oil (data provided by PNNL).

Chemical Shift range (ppm)	Carbon assignment	Feed	MOx	HOx	HHO #2
0 – 53	 Short, long, and branched aliphatics	14.22	72.16	66.19	88.48
53 – 62	 Ethers, methoxy groups	3.25		1.01	
62 – 95	 Alcohols, carbohydrate sugars	27.46	0.33	3.31	
95 – 142	 Aromatic, olefins	22.54	18.17	19.04	11.01
142 - 170	 phenolic	15.3	3.43	4.04	0.51
170 – 190	 Carboxylics, ethers, lactones	8.56	1.96	2.98	
190 – 220	 Ketones, aldehydes	8.68	3.95	3.42	

Figure 7 Functional group analysis of the raw pyrolysis oil, two upgraded bio-oils and feed home heating oil used for blends using ^{13}C NMR (data from PNNL)

The blend samples received at BNL were kept in refrigerated storage for periodic analysis. Filterable insolubles and gums were apparent on the walls and bottom of the storage container of R-HHO-HOX sample after two months of storage at 5 °C (See Figure 8). Significantly less filterable insolubles were present in the R-HHO-MOX sample. In contrast, the neat HHO fuel which was stored at room temperature (approx. 23 °C) did not show any sign of instability.

Evaluation of the stability of the fuels by visual inspection indicated that the R-HHO-HOX blend is relatively unstable.

Figure 8 Inspection of the fuel storage containers after two months of storage.

A sample of the gum sediment at the bottom of the R-HHO-HOX container was analyzed by GC/MS and the total acid number (TAN) was also determined. The GC/MS chromatogram of the gum is shown in Figure 9. The results revealed that the gum was made up of mostly oxygenated compounds. The predominant species were phenols (phenol and alkylated phenols), carboxylic acids (acetic acid and propanoic acid), and ketones (2-pentanone, 2-hexanone, and cyclopentanones). Aromatics such as alkylbenzenes, naphthalenes, and indene were also present in the gum. The acid number of the gum was found to be 35.4 mg KOH/g. The separation of these oxygenates out of the blend fuel matrix is a sign that the minimally upgraded bio-oil (HOX) was not fully miscible with HHO. The results suggest that the usage of HOX as a blend component would be problematic from a fuel quality standpoint. Hence, it needs further upgrading.

Figure 9 GCMS pyrogram of the gum sediment in the R-HHO-HOX

Total acid number of the blends fuels that were stored in the refrigerator

For the R-HHO-HOX sample, the acidity appears to remain about the same from April 7 2014 to August 12 2014. By contrast, the TAN of the R-HHO-MOX sample showed an increase after the initial storage time but it then decreased after wards. It is unsure why the measured TAN of R-HHO-MOX increased. These results may be seen in Figure 10, below. The most apparent observed change in the refrigerated fuels was in the accumulation and deposition of insolubles and gums on the walls and bottom of the container.

Figure 10 TAN of blend fuels over time during storage under refrigerated conditions

Thermal Stability Test (ASTM D6468)

The results from the ASTM D6468 test shown in Table 5 provide a snapshot of the tendency of the selected fuels to form insolubles during storage and more importantly for the fuels to produce deposits in nozzle area of burners when exposed of high temperatures within a short time. The reflectance ratings of the filter papers after the stability test were 93.9%, 13.6%, and 0% for neat HHO, R-HHO-MOX, and R-HHO-HOX respectively. From the results, it can be seen that the neat HHO fuel had acceptable filter paper ratings (> 80%) while the filter paper ratings for the blended fuels were unacceptable. The R-HHO-HOX sample degraded extensively and formed high levels of filterable insolubles/sediments. As a result, the filter paper had zero reflectance reading and the measured amount of total insolubles formed by the R-HHO-HOX after exposure to 150 °C for 180 mins was 493.3 mg/100 mL. In comparison, R-HHO-MOX and neat HHO fuels produced total insolubles of 19.0 mg/100 mL and 2.5 mg/100mL respectively. Clearly, it can be seen that the blended fuels; particularly, R-HHO-HOX, has very poor resistance to thermal degradation.

Table 5: Thermal Stability Test (ASTM D6468) Results

Fuel Stability Parameter	Test Fuel Samples		
	HHO	R-HHO-MOX	R-HHO-HOX
Filter pad rating before test, % Reflectance	95.1	76.1	68.97
Filter pad rating after D6468 test, % Reflectance	93.85	13.5	-
*Initial Total Insolubles, mg/100 mL	1.13	6.80	11.07
D6468 Total Insolubles, mg/100 mL	2.47	19.0	493.3

*Filterable insolubles obtained in the pre-filtration of the fuels before testing.

Long Term Storage Stability Test (ASTM D4625)

The long term storage stability test (ASTM D4625) is the most widely used method for predicting fuel oxidation and other degradative reactions that result in sediment formation. It has good correlation with actual fuel stability at ambient conditions. Also, it was reported that the amount of insoluble material formed in a week at 43 °C is comparable to the amount formed in a month at ambient temperature (18-24 °C). In this study, a modified ASTM D4625 was used. The method requires sample size of 400 mL, but because of the lack of large volumes of the blended fuels; two 150 mL of each HHO-MOX and HHO-HOX were used instead. The samples were stored in vented borosilicate glass bottles at 43 °C for 12 weeks. About 30 mL aliquots were sampled out at 4, 6, 8, 10, and 12 weeks to monitor formation of filterable insolubles and TAN. The filtration set-up is the same used in the ASTM D6468 method described above. The filtrates were analyzed for iso-octane insolubles, TAN (D974), kinematic viscosity (D445), and chemical composition (by FT-IR and GC/MS).

The amount of filterable insolubles formed in the diesel fuel blends evaluated by the modified D6425 method (150 mL, 12 weeks storage period at 43 °C) are shown in Figure 11. This result does not show the adherent insolubles formed. The measurements were made with aliquots taken from the storage bottles at the various time intervals; the first analysis was conducted at 4 weeks. As already observed in ASTM D6468, the R-HHO-HOX sample formed very high amount of filterable insolubles (> 400 mg/100 mL by the 12th week). The R-HHO-MOX sample on the other hand, formed relatively lower filterable insolubles (< 30 mg/100 mL by the 12th week). Both measured values are beyond the levels commonly considered acceptable, 2.5 mg/100 mL. Thus, suggesting that the upgraded bio-oils, particularly the HOX sample may be an unacceptable fuel blending component for No. 2 fuel used in home heating applications.

Figure 11 Filterable insolubles measured for R-HHO-MOX and R-HHO-HOX samples in the modified ASTM D4625 test

Weekly monitoring of the acid value after 1 month of storage at 43 °C showed that the TAN overall did not change significantly. Results can be seen below in Figure 12. Even though the first measurement taken at week 5 showed a drop in TAN, the subsequent weekly tracking at 6, 7, 8, 9, 10, and 12 weeks showed that the total acid numbers for each blend were comparable. The lower TAN value measured on the 5th week may be due to operator error. The lack of correlation between the trends of TAN and the filterable insolubles suggests that the degradation of the blends is not accompanied with acid formation. On the other hand, the increase in the formation of insolubles suggests that higher molecular weight compounds could have been formed due to polymerization reactions. One of the simple ways to confirm this notion is to measure the viscosity of the oils. In our study, the filtrates of the aged oils were measured for kinematic viscosity. The results in Figure 13 generally show that there was a slight increase in the viscosity of the oils over time. Most likely, the viscosity of the aged oils itself would have given a much better result but it was impossible to measure their viscosities with the Cannon Fenske Viscometer due to clogging of the viscometer with particulates.

Figure 12 TAN of R-HHO-MOX and R-HHO-HOX samples during the stability test by ASTM D4625

Figure 13 Kinematic viscosities of the blend fuels during the storage stability test by ASTM D4625

The results from the study also showed that iso-octane precipitates and the filterable insolubles formed by the fuel blends had a strong correlation with R^2 of 0.93. From the data, it can be inferred that a blended diesel fuel with upgraded bio-oil must at most yield less than 120 mg/100 mL of iso-octane insolubles to form less than 2.5 mg/100 mL of D4625 filterable insolubles.

Effect of yellow metals on storage stability of fuels

Figure 14 shows the impact of the exposure of brass nozzles to the oils stored at 80 °C for a week. Clearly, the presence of the yellow metal reacted with the fuels and catalyzed the formation of insolubles. In all the oils, the measured amount of insolubles increased to unacceptable levels. Visually, it can be seen in Figure 15 that more deposits formed on the nozzle placed in the R-HHO-HOX fuel which has been shown to be relatively unstable.

Figure 14 Effect of brass nozzle on the formation of insoluble during fuel storage at 80 °C

Figure 15 State of the brass nozzles after the storage stability test at 80 °C

Influence of antioxidant-butylated hydroxytoluene (BHT) on storage stability of fuels

The addition of antioxidants to diesel fuels has been report to be useful in stabilizing the oils during storage. The BHT additive is one of those antioxidants that have been shown to stabilize diesel fuels. However, in this study, the addition of BHT to the blend fuels at a concentration level of 1000 ppm was found to ineffective. The formation of insolubles in both R-HHO-MOX and R-HHO-HOX fuel samples increased (Figure 16). A possible explanation for this observation could be that the presence of phenols in the blend fuels inhibited the stabilizing effect of BHT and possible reacted with the additive to form insolubles.

Figure 16 Effect of BHT additive on the formation of insolubles during fuel storage at 80 °C

Chemical composition analysis of the aged oils and the insolubles formed by PyGC/MS & FTIR

The Pyrolysis gas chromatography mass spectrometry (Py/GC/MS) of the insoluble sediment formed in the R-HHO-HOX sample during the ASTM D6468 test in Figure 17 revealed that oxygenated species such as cyclopentanone, alkylated phenols, and levoglucosan are unstable and participated in the formation of the insolubles. Also, PyGC/MS analysis (not shown) confirmed that the iso-octane precipitates constituted primarily of phenolics (phenol, methylphenol, dimethylphenol, alkylphenols), ketones (cyclopentanone, cyclohexanone), acids (acetic, propanoic, butanoic), and aromatic hydrocarbons (alkylbenzene, naphthalenes, indenenes).

The Fourier transform infrared spectroscopy (FTIR) spectra in Figure 18 show the chemical change in the aged R-HHO-HOX sample by comparing the chemical composition before the test, after the test, as well as the composition of its respective collected filterable insolubles. The analysis of the oil filtrate indicates that the intensity of the absorbance of the C-H stretch decreased. This suggests that aliphatic hydrocarbons were consumed in the reactions leading to the formation of insolubles. The O-H stretch at 3400 cm^{-1} , C-O stretch absorption bands between 1300 and 1000 cm^{-1} , and the C=C stretches (ring mode band) around 1600 cm^{-1} of the IR spectrum of the insolubles formed reveal the participation of phenolics, aromatics, and carbonyl compounds in their formation. This confirms the Py/GCMS results. Additionally, the FTIR analysis indicated that the compositions of the insolubles formed by both blended diesel fuels (MOX and HOX) were identical as well as those of the D4625 filterable insolubles and the iso-octane precipitates.

Overall, the chemical composition analysis shows that poplar compounds present in the blend fuels are principally responsible for the formation of filterable insolubles during the storage. This implies that the lower amount of filterable insolubles formed in the R-HHO-MOX sample is due to lower concentration of the poplar compounds. Hence, phenols, ketones, and acids in the blend fuels would have to be reduced significantly to improve the stability of the blended fuels.

Figure 17 Py/GC/MS of the insoluble sediment formed in the R-HHO-HOX sample during the ASTM D6468 test

Figure 18 FTIR spectra of D4625 filterable insolubles and iso-octane precipitates from the R-HHO-HOX diesel fuel sample

Effect of blend fuels on elastomer swell

Table 6 shows the results of swell tests done for a one month period using the physical size change method. Table 7 presents the results of swell tests done for two weeks using the volume displacement method. The criterion for acceptance is a swell less than 25% in a 72 hour exposure. Based on this the pump seal nitrile material may pass. However, the magnitude of swell is considerably higher than we have observed in the past with No. 2 fuel oil, which typically has a swell level in the 5% or less range. These results raise concerns about the long term durability of legacy seal materials with these specific bio-oils.

Table 6: Swell Test Results – Physical Size Change Method (Volume Percent Swell)

Days Exposure	Generic Nitrile		Pump Seal Nitrile Material	
	R-HHO-HOX	R-HHO-MOX	R-HHO-HOX	R-HHO-MOX
0	0	0	0	0
10	70.4	34.8	27.6	22.6
30	96.6	47.9	40.0	31.6

Table 7: Swell Test Results – Volume Displacement Method (Volume Percent Swell)

Days Exposure	Generic Nitrile		Pump Seal Nitrile Material	
	R-HHO-HOX	R-HHO-MOX	R-HHO-HOX	R-HHO-MOX
0	0	0	0	0
3	50	50	17	25
15	90	70	33	33

Combustion of blend fuels

For the first series of tests, the burner was operated in a transparent quartz combustion chamber. The flame appearance with both No. 2 fuel oil (HHO) and HHO-HOX blend was compared. Both photos and a video were taken. Figure 19 shows the two flames. While operating on the bio-oil blend the flame was very stable, showed excellent retention to the burner head, and its appearance was the same as when operating on No. 2 oil. No concerns with fuel filter blockage were noted in any of these combustion tests. In looking at the photos some small differences might be noted but these are really due to the normal fluctuations in flame appearance.

Figure 19 Appearance of flames of No. 2 oil and 20 % HHO HOX Blend in the quartz combustion chamber.

The video also shows no significant difference. Tests were done only with the HOX fuel because this was considered the more challenging fuel and there was a need to conserve the very small fuel sample provided. By starting with normal No. 2 heating oil a combustion test using only 250 ml of the test fuel blend was achieved.

Following the tests in the quartz combustion chamber, tests were also done with the same burner firing in a typical residential boiler. Figure 20 shows a time plot for the most important of the collected data.

Figure 20 Illustration of the transition between No 2 oil, the bio-oil blend, and back again to No. 2 oil during combustion testing.

Table 8, below, provides an average of the measured gas composition and the “cad cell” resistance for the different fuels.

Table 8: Summary of Emissions Data

Parameter	Units	No. 2 Oil	R-HHO-HOX Blend	R-HHO-MOX Blend
Oxygen	%	3.19	3.31	3.21
NOx	ppm	90.1	114.7	104.5
CO	ppm	neg. ¹	neg. ¹	neg. ¹
Smoke Number	-	0	0	0
Cad Cell Resistance	ohms	324	340	339

1. CO is at levels considered negligible for all tests.

The cad cell is (a cadmium sulfide photoconductor) normally used for flame proving in the safety controls. Some biofuels previously tested have shown very high cad cell resistances, due

to oxygen content, leading to false indications of a flame out and burner shut down. High resistance values can also be an indicator of poor flame retention or stability. A low cad cell resistance would be consistent with a flame which has a high carbon particle concentration and likely higher particulate emissions. A high resistance is due to less light “hitting” the sensor.

These results show that the oxygen is slightly higher with the bio-oil blends and this would be expected based on the fuel oxygen content. There is an increase in NO_x with the bio-oil and this is quite significant in the case of the HOX blend. Smoke number and CO are close to zero for all cases. With the bio-oil blends there is a very small increase in cad cell resistance. This is certainly too small to be of any practical consequence for burner operation. Overall these results are very positive and indicate that basic combustion performance is not likely to be a concern with these fuel blends. The increase in NO_x is, of course, not desirable. However, this market sector is not subject to any NO_x emission regulations in states where heating oil is used.

Kior Upgraded Bio-oil

Two fuel samples termed “cellulosic distillate” and “gas oil” were supplied by KiOR Inc. (Pasadena, TX, USA) for testing. Locally obtained, ultralow sulfur heating oil (ULSD) was again used in preparing fuel blends.

Table 9 shows the properties of the pure KiOR distillate and gas oil (KGO) fuels in comparison to the specification of No.2 heating oil as defined in ASTM D396. KiOR designates the distillate fuel as “Hydroprocessed Depolymerized Cellulosic Distillate” (HDCD) and this terminology is used throughout this section of the report. From the viewpoint of the measured properties, it can be seen that the HDCD fuel in particular is extremely suitable for home heating as it meets most of the D396 requirements for No.2 fuel. The main limitation of the HDCD fuel is its density. The maximum density specified for No.2 is 876 kg/m³. Based on that, the HDCD fuel can be blended up to 50% and still meet ASTM D396 specification for heating oil. Additionally, the lower sulfur content and superior cold flow property (Cloud Point lower than -50 °C) of the HDCD fuel make it very attractive. For instance, in New York State, No.2 heating oil is mandated to have a sulfur content of no more than 15 ppm; thus, HDCD fuel can be considered as ultra-low sulfur heating oil. Furthermore, the cold flow property of HDCD reduces the chances of having cold weather related issues such as filter clogging when used during cold winter seasons. Typically, outdoor standalone heating oil storage tanks are susceptible to cold winter temperatures and as a consequence the oil within the tank could form wax crystals which can reduce the mobility of fuel, clog filters, and eventually prevent the fuel from reaching the furnace. With these issues in mind, the HDCD fuel may be advantageous relative to other potential alternative fuels.

The gas oil fuel (termed KGO) fuel, on the other hand, does not meet a number of the D396 specification requirements. The most obvious ones include viscosity and density. As shown in Table 9, the KGO had a density of 958 kg/m³ and a viscosity of 834 mm²/s; both values are higher than the maximum allowed specification in D396. Also, it narrowly meets the pour point specification. The sulfur content (5.6 ppm) appears to be the main advantageous property of KGO that could enable it use as fuel oil in applications where Nos. 4, 5, and 6 grades are utilized. Considering the properties of the as-received fuel, the KGO could be considered for industrial heating where residual fuel oil (fuel oil No.6) is primarily used.

Table 9: Properties of Test Fuels

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	129
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	<-60	-6
Cloud Point, °C	D2500	ND	ND	ND	<-50	-
Acid Number, mg KOH/g	D664	ND	ND	ND	<0.02	-

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

Combustion Test in Transparent Quartz Chamber

The steady-state flame characteristic, specifically, flame luminosity and shape obtained from the combustion of the test fuel blends and the 100% ULSD in the transparent quartz chamber are shown in Figure 21. As mentioned earlier, the combustion operating conditions were established with the pure ULSD and the same conditions were used for the three test fuels. Visually, it was found that the luminosity of the 50% HDCD blend and the 100% HDCD fuels were both comparable to that of the pure ULSD fuel. By contrast, the flame luminosity for the 20% KGO blend fuel appeared different and made the quartz chamber slightly transparent. In general, all the test fuel flames were stable with excellent retention to the burner head. It was difficult to identify differences in the shape/structure of the flames of the 50% HDCD blend and the 100% HDCD with that of the pure ULSD. However, the 20% KGO flame appeared to be relatively thinner and longer than all the test fuels. In summary, the results of the test in the quartz chamber indicated that both the 100% HDCD and 50% HDCD blend fuels have similar combustion characteristics to the pure ULSD fuel.

Figure 21 Appearance of flames of ULSD, 100% HDCD, 50% HDCD blend, and 20% KGO blend in the quartz transparent combustion chamber.

Combustion Test in a Residential boiler

The combustion of the fuel blends were successfully completed in the Dunkirk 3EW residential boiler. Overall, the results indicated that the test fuels performed satisfactorily. Figures 22, 23, and 24 show the trends for the Cad Cell resistance and the concentrations of NO_x , CO, and O_2 in the flue gas for each fuel blend. From Figure 22, it can be seen that switching from ULSD to 50% HDCD fuel blend resulted in a gradual decrease in NO_x , O_2 , and the Cad Cell resistance with an increase in the concentration of CO emission. Likewise, the transition from ULSD fuel to 100% HDCD as shown in Figure 23 indicated a higher increase in CO emission and a decrease in both NO_x and Cad Cell resistance. On the other hand, the change from ULSD to 20% KGO fuel blend caused an increase in NO_x emission and Cad Cell resistance without an obvious effect on CO emission (Figure 24). Considering CO, it should be noted that all of the CO levels measured are extremely low and can be considered near-negligible and any differences within the accuracy of the instrument. For residential home oil burners a CO level under 25 ppm is considered clearly acceptable.

Figure 22 Showing the effect of switching from ULSD to 50% HDCD fuel blend on NOx, O2, CO, and Cad Cell resistance

Figure 23 Showing the effect of switching from ULSD to 100% HDCD fuel blend on NOx, O2, CO, and Cad Cell resistance

Figure 24 Showing the effect of switching from ULSD to 20% KGO blend fuel on NO_x, O₂, CO, and Cad Cell resistance

The steady state emission values and the Cad Cell resistance are shown in Table 10. The emission levels are comparable to previous studies on oil-fired boilers [26]. For ULSD, the average NO_x and CO concentrations were 89.3 ppm and 3.6 ppm respectively. In the case of the 50% HDCD blend, the average NO_x was 84.3 ppm and CO was 4.8 ppm. For the combustion of 100% HDCD fuel, the steady state NO_x was 80.2 ppm and CO was 6.1 ppm. The combustion of the 20% KGO produced NO_x of 101.3 ppm and CO of 3.9 ppm. This means the change from ULSD to the 50% HDCD resulted in a 5.7% decrease in NO_x emission. Also, the pure KiOR distillate produced 11.4% less NO_x when compared to the ULSD. The lower amount of NO_x produced from the KiOR distillate fuel could be because it contained less amount of fuel-bound nitrogen. Likewise, the higher amount of NO_x formation from the combustion of 20% KGO may be attributed to higher fuel-bound nitrogen content in KGO. Also, it should be pointed out that thermal NO_x from atmospheric nitrogen could play a role since it is influenced by the combustion temperature [26]. Thus, fuels that lead to higher temperatures in the burner area could promote NO_x formation via thermal mechanism. In general, NO_x emission is an issue of concern in the combustion of fuels but it is not currently regulated for small residential burners in states where heating oil is used [26]. Studies suggest that techniques such as exhaust gas recirculation and retarded injection timing could be used to achieve lower NO_x emissions if needed [26].

Table 10: Steady State Emission Concentrations and Cad Cell Resistance Values

Parameter	Summary of Combustion Results							
	ULSD	100% Distillate	KiOR	50% Distillate	KiOR	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	3.59	6.09		4.77		3.91		
Smoke Number	-	-		-		-		
Cad Cell Resistance, ohms	342	279		301		399		

The result from the combustion studies of the pure KiOR distillate under cyclic condition at a slow rate of two hour per cycle over a period of four days is provided in Figure 25. The graph shows the boiler water temperature over the period of cyclic testing. The test was conducted to simulate actual operation of home-heating boilers where heat is demanded intermittently. The result clearly shows that the burner was able to operate in an on-and-off mode continuously on the pure KiOR distillate for the entire cyclic operation without any failure. Overall, the results from all the combustion results are very positive and indicate that basic combustion performance is not likely to be a concern with these test fuel blends. However, higher blends of KGO could result in higher NOx emissions.

Figure 25 Boiler water temperatures showing the cyclic operation with the KiOR distillate for approximately 4 days.

Elastomer compatibility and stability tests

Figure 26 shows the results from the elastomer compatibility test based on the change in volume of the rectangular specimens after immersion in the fuels for a month at 43 °C. The volume swells of the nitrile slabs determined by dimensional-change method were 6.05%, 10.56%, and 10.03% for ULSD, 50% HDCD, and pure HDCD, respectively. The 20% KGO blend was not included in this study. The results showed that both the KiOR distillate and its blend caused the nitrile material to swell about 4.0% more than the ULSD. According to UL 179, the criterion for acceptance is a volume swell less than 25% in a 72 hour exposure. Therefore, the pump seal nitrile material could be considered compatible with the KiOR distillate and its fuel blends based on the fact that the testing condition used in this study was more aggressive (for a month).

Figure 26 Fuel blend effect on the volume swell of nitrile slabs

Fuel stability is another important property to evaluate when considering the use of new fuels for heating applications. Technically, the fuel could change during handling, storage, and usage [26]. Studies have shown that diesel fuels and other alternative fuels like biodiesel could undergo degradation reactions (e.g., oxidation, acid-base, condensation, and polymerization) when stored over extended period of time [26]. For heating applications, the degradation by-products in a form of filterable insolubles could cause operability problems in storage tanks and burner fuel delivery systems.

Figure 27 shows the results from the stability test at 80 °C for a week. In this study, the formation of filterable insolubles in mg/100 mL was used as a metric in evaluating the stability of the test fuels. Also, it is worthwhile to point out that the accelerated storage stability test at 80 °C for a week has been shown to have a good correlation with ASTM long term test method

D4625. The results showed that the amount of filterable insolubles formed in the pure HD CD, 50% HD CD, 20% KGO, and ULSD were 0.93, 1.93, 6.53, and 2.0 mg/100 mL respectively.

Figure 27 Fuel stability of the various fuel blends tested

According to ASTM D2274 and ASTM D5304 methods, the formation of filterable insoluble sediments up to 2.5 mg/100 mL in distillate fuels are considered as acceptable levels^{14,15}. This means that all the test fuels were stable with the exception of the 20% blend of KGO which formed relatively high amount of insolubles. It is also worth pointing out that about 13.1 mg/100mL of insolubles was filtered out of the 20% KGO blend during the pre-filtration step prior to the stability test. These results suggest that the 20% KGO fuel blend may have stability issues. Excessive filterable insolubles carried by the fuel during oil burner operations could potentially cause blockage of the inlet filter, pump inlet strainer, the nozzle body sintered metal, and eventually the nozzle orifice. Hence, it is important that the fuel being in heating systems are stable.

Long Term Combustion Trials

During this project long term cyclic combustion tests were done with the KiOR distillate fuel to identify areas of concern. This kind of long term testing is very important for industry acceptance of this and any new fuel. The testing was done using the Dunkirk 3EW cast iron residential boiler and a conventional residential retention head burner without modifications. A 20% fuel blend was used. The burner operated with a cycling pattern of 5 minutes on followed by 55 minutes off under control of the lab data acquisition control computer. The boiler remained hot throughout the duration of the test and the computer essentially controlled the opening and closing of the cooling water (load) valve. This cycling pattern is untypically slow for residential operation but was chosen for several reasons. First, the most challenging period of burner

operation is typically cold start where poor ignition can lead to burner head carbon deposits. Second, this cycling pattern gave the greatest potential for long term testing based on the amount of upgraded pyrolysis oil fuel available. For some aspects of the test including exposure of elastomer materials to the fuel the total test duration is the most important and actual firing time is secondary. The total test duration was 4000 hours and the burner cycled 4000 times during this period.

During the test program flue gas oxygen, CO, smoke number, flue gas temperature, and control flame signal were measured regularly and no significant changes in any of these parameters were observed. No operational problems or failures with the burner system were observed during the test period.

Figure 28, below, provides a comparison of the appearance of the retention head at the start and end of the test. This head includes stamped slots through which the flow rate and swirl of the combustion air is controlled. During burner testing manufacturers are very concerned about coke deposit accumulation on this head which can distort the flame pattern, reduce the burner air flow, and reduce the amount of light incident on the safety control. A comparison of the head at the start and end of the test shows no carbon accumulation above what is normal for No. 2 heating oil. From similar photos taken throughout the test period it is important to note that the coke deposits which did form, formed early and did not increase in extent during the period. This is a very important point used by burner manufacturers to evaluate the success of a head or fuel.

Figure 28 Photos of the burner retention head before (left) and after (right) the 4000 hour test run. The photos show a very slight carbon accumulation on the outer edges of the metal parts of the retention head (right – circled).

Figure 29, below, provides a photo of the atomizing nozzle assembly at the end of the test. This assembly includes a sintered bronze strainer on the right side which is clearly free from deposits. This is important and shows that no insoluble or solid particulates are present in the fuel or formed from the high burner head temperatures.

Figure 29 Post-test photo of the nozzle assembly

Figure 30 provides an example profile for the transient emissions during a five minute firing cycle. As shown in this Figure there is a peak in the CO emissions at both the start and end of the firing cycle. This behavior is typical for No. 2 oil and the magnitude of these peaks has not changed during the 4,000 hour test period.

Figure 30 Trends in flue gas composition during one firing cycle – end of test period

Synthetic Biofuel Blends

As discussed in the prior section, these studies were undertaken to enable a more flexible analysis of operational concerns which may occur with partially upgraded biofuels that will have residual levels of oxygenates higher than those found in petroleum-derived fuels. This work was done in several phases with different oxygenates and concentrations.

The work focused on specific phenols and ketones added to standard No. 2 heating oil and their impacts on elastomers and stability. These two performance aspects are seen as the areas of greatest concern relative to residual oxygenates. Combustion performance is seen as an area of little concern. The specific components added have been selected based on published reports as well as analyses completed of the upgraded bio-oil received from PNNL. For the initial round of tests BNL “doped” standard home heating oil (HHO) with the following: 2,4 Dimethylphenol (“MP”), 3-Ethylphenol (“EP”), and Cyclopentanone (“KT”).

In storage stability tests, standard HHO doped with phenols and ketones were aged at 80 °C for one week of storage time. The accelerated storage stability test at 80 °C for a week has been shown to have good correlation with ASTM D4625 test. The amount of total insolubles formed in each method was found to be comparable. Hence, the key metric of stability used was the mass of insoluble (degradation gums) formed. Figure 31 shows the preliminary results of one series of tests in which different polar compounds added at a dose level of 3 wt.%. These results show that both the ketone and the phenols decrease the stability and that, perhaps, the ketone evaluated in this test is more significant than the phenol.

Figure 31 Impact of the addition of different oxygenates on the stability of home heating oil.

Based on the results of stability of the doped diesel fuels at 80 °C for a week, it is obvious that oxygenates such as phenols and ketones increases the rate of formation of insoluble significantly. Extensive studies with focus on phenols (Figure 32) clearly showed that higher amount of insoluble sediments are formed in the phenol doped oils than in the neat diesel oil. It can be seen that the addition of phenols at 1, 3, 5 wt. % levels did not have a linear effect on the formation of insolubles; rather, it had a parabolic effect with maximum formation occurring at 3 wt.% level. The amount of insolubles in the 3 wt.% doped oils were: 261 mg/100 mL for the 3-ethylphenol (3EP) doped oil and 208 mg/100 mL for the 2, 4-dimethylphenol (24DMP) doped oil. It is worth noting that 6mg/100 mL of insolubles were formed in the diesel fuel oil without a phenol dopant. The results suggest that 3EP is more reactive than 24DMP. This also means that 3EP has a larger tendency to polymerize; and this can be attributed to the existence of unsubstituted positions ortho to the phenol hydroxyl in 3EP. Hence, it can be inferred that oils with cresols would degrade much more than oils with xylenols. It should be noted that the acceptable limits for both ASTM D 5304 and D 2274 is 2.5 mg/100 mL

Figure 32: Effect of phenols on the formation of filterable insolubles

Furthermore, the role of organic acids on fuel stability was also evaluated. In this test, acetic acid (HAc) was added to the doped fuels (oils with 1, 3, and 5 wt. % of 3EP) to model a TAN of 10. The result in Figure 33 indicates that HAc has a strong effect on the formation of insolubles. Even with the neat HHO, the amount of insolubles increased from 7.1 mg/ 100 mL to 43.8 mg/ 100 mL. Clearly, the presence of acids decreased the fuel stability of the oils.

Figure 33: The impact of acetic acid on the formation of filterable insolubles

Quantification of the filtrates by GC/MS showed that some of the phenols were indeed consumed during the accelerated storage studies. FTIR analysis of the filtrates revealed that the intensity of the absorbance of the C-H stretch decreased. This suggests that aliphatic hydrocarbons were also consumed in the reactions leading to the formation of insoluble sediments. It is also important to

point out that the presence of biodiesel in the test samples as evidenced by the ester carbonyl peak (around 1745 cm^{-1}) played a role in the formation of the insolubles. Preliminary studies on ketone doped oils suggest that ketones are much more detrimental than phenols.

In general, these results show that the presence of residual phenols, ketones, and acids, even at low levels, in upgraded bio-oil can significantly decrease the fuel stability of a blend in home heating oil. Further, it is not just the oxygenates that are oxidizing and forming gums but also the aliphatic components in the base oil. These results can help guide the assembly of a synthetic bio-oil and also provide limits on phenol, ketone, and acid content in a home heating oil blend feedstock. It may be necessary to have a fuel specification for an upgraded bio-oil feedstock which is acceptable and to also provide specific limits on oxygenates such as phenols and ketones.

Lastly, TAN evaluation of the doped oils revealed the effect of phenols on acidity. Phenols have been speculated to also contribute to the acidity of fuels, particularly when it comes to pyrolysis oils and upgraded bio-oils. The result in Figure 34 confirms this notion. Hence reducing the phenolic content in upgraded bio-oils will not only increase its fuel stability, but in addition decrease the acidity of the oil.

Figure 34: The effect of phenols on TAN

For the elastomer compatibility tests, nitrile slabs were used, provide by Suntec, Inc. This is the dominant oil burner pump manufacturer in the North American market and this material is used in pump shaft seals.

A summary of the volume swell test results is provided in Table 11. Figures 35, 36, and 37 further illustrate the effect of phenol, ketone, and acid on the swelling of the nitrile material used in the study. Clearly, 3-EP showed the most effect and had the highest degree of swelling. The effect of cyclopentanone up to 5 wt% seems moderate. In contrast, the elevated acidity of the oils appears not to cause excessive volume swell. It is worth noting that the volume expansion of the oils doped with 3-EP at 2 wt% and 3 wt% all exceeded the 25% standard limit. Hence, the

phenolic content of heating oil blends containing pyrolysis oil-derived fuels would have to be lower than 1 wt% to avoid unnecessary swelling of seal materials.

Table 11: Swell Test Results – Dimensional Change Method

Sample/Specimen	Change in Volume, % (Mean Values)	Std
Pure # Diesel (Blank)	8.07	1.47
<i>Effect of Phenol</i>		
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
<i>Effect of Ketone</i>		
Diesel with 1wt% CP	9.94	0.79
Diesel with 3wt% CP	12.53	2.18
Diesel with 5wt% CP	14.64	2.17
<i>Effect of Acid</i>		
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

Figure 35 Effect of phenol on the swelling of nitrile material in oils exposed to 43 °C for a month.

Figure 36 Effect of ketone on the swelling of nitrile material in oils exposed to 43 °C for a month

Figure 37 Effect of acidity on the swelling of nitrile material in oils exposed to 43 °C for a month

A second round of storage stability testing was done with a longer time and milder conditions. This followed ASTM D4625. Storage was at 43 °C for 12 weeks. During this test the focus was on heating oil specifically with the addition of 2% 2,4 dimethylphenol and 4-methylanisole. Samples were extracted at different times during this period for GC/MS analysis of compositional changes. Figure 38 shows the outcome of this test in terms of the formation of filterable insoluble. Considering the error bars associated with these results it cannot be concluded that the addition of these specific phenols increased the production of insolubles (and reduced stability).

Figure 38 Twelve week storage stability study. Effect of selected phenols

Finally, another series of 1 week, 80 °C exposure tests was done using home heating oil (HHO), hexadecane (HD), and biodiesel (BD) as the base fuel with different phenols. The phenols included in this test included: 1- phenol at 0.25, 0.50, 0.75 and 1.0%, 2 vol% 2,4-dimethylphenol (DMP), and 2 vol% 4-methylanisole (MA). Results, in terms of filterable insoluble for the home heating oil are shown in Figure 39. Results for the hexadecane are shown in Figure 40 and for biodiesel in Figure 41. Results do not indicate a significant increase in filterable insolubles in HHO or HD with the exception of the 2% of either DMP or MA. It is unclear why there was such a large amount of insoluble particulates in the neat BD. The results from the BD blends showed a significant increase in filterable insolubles with the addition of 0.25% phenol and 2% of either DMP or MA.

Figure 39 Filterable insolubles - 1week / 80 °C study - home heating oil with added phenols

Figure 40 Filterable insolubles - 1 week / 80 C study - hexadecane with added phenols

Figure 41 Filterable insolubles - 1 week / 80 C study - biodiesel with added phenols

Industry Outreach

As part of this project, there has been an effort to engage key parts of the heating oil supply and distribution industry in the Northeast to obtain input on this initiative and constraints to widespread acceptance of this fuel. This effort included outreach through focus group meetings (webinar) organized by the National Oilheat Research Alliance (NORA) and involving key wholesale terminal and pipeline operators. In addition, BNL staff made presentations on this work at regional conferences including:

Annual Meeting of the Pennsylvania Petroleum Marketers Association (July 2015)

Annual Meeting of the Oil Heat Council of New Hampshire (Sept. 2015)

New England Fuel Institute Energy (NEFI) Expo (June 2015)

BNL also participated in the Technical Information Exchanger on Pyrolysis Oil Combustion Workshop (March 2015)

A survey instrument was used at the major NEFI Conference to solicit feedback on specific questions although the level of response was not as large as expected. In general, while the industry was interested and willing to provide feedback, the strength of the response was limited because of the very limited availability of fuel at the present time. Further, since the fuel which will be available to the industry is not yet really defined this exercise was seen as not one of near term relevance. Even with this situation the feedback that was received from the industry is important in helping to plan for future deployment activities and considerations.

In the outreach to industry the following general questions were put forward:

What technical concerns does the industry have about the use of a new fuel of this type?

What approvals would be needed for adoption of this new fuel?

What level of demonstration is needed?

What would motivate industry to accept such a new fuel?

Overall the feedback received indicates that the industry would be very willing to accept such a new fuel but reluctant to engage in an “experiment”. There are exceptions, of course, but for widespread commercial use the key feedback from the supply and distribution chain is that they expect all technical aspects will be fully resolved before deployment. It was clear from the discussions that industry looks to the R&D community to provide to them a fully ready fuel. Further guidance on the level of demonstration needed beyond that required for the R&D community to provide complete technical assurance was not provided by respondents.

In the service market segment, the most significant source of service cost is related to fuel degradation in storage leading to filter blockage, nozzle fouling and tank maintenance. A fuel that was not as good as petroleum fuels would clearly not be acceptable. A fuel that was better, relative to petroleum fuels could provide an important motivating factor.

For widespread commercial acceptance definition and approval of this fuel under an ASTM standard is seen as necessary. Also necessary is acceptance of this fuel by the burner and appliance manufacturers. These factors are needed for insurance and code compliance reasons. If

the product actually commercialized has oxygen levels that could be considered as trace residuals this may not be a concern.

The requirement for hardware changes needed for the use of this new fuel is seen as a significant market barrier. The situation is made unclear, however, by the dynamic situation in the marketplace relative to biodiesel use. New burner pumps and other components are being introduced to the markets which are “bio-compatible”. While this is focused on biodiesel and not the specific fuel that is the focus of this work, it may provide an opportunity for improved compatibility with the infrastructure broadly.

One area of concern raised is compatibility of this new fuel with pipeline transport. While it may be quite reasonable to begin deployment using local production and truck transport, for long term growth the pipeline question will need to be addressed. This has been a concern, for example, with biodiesel. With the use of pipelines for multiple products there is the potential for trailback of one product into another. The potential contamination of jet fuel with biodiesel from transported heating oil has been a major barrier in the transport of biodiesel blends by pipeline. A similar concern could exist with upgraded bio-oil, depending on the actual composition of the product going forward commercially.

During industry interactions some samples of upgraded fuels were physically presented to participants. For some of the fuels a significant concern was raised about odor. Since these fuels are to be used in a residential context a strong odor would clearly be unacceptable. The fuel retailers are concerned with the odor question even now with petroleum products and feel this is a factor which impacts their competitive position relative to other fuels. A new fuel which creates more of a concern in this area would be very difficult to achieve market acceptance.

Marketers on the wholesale and retail levels generally feel that the quality of the supply and source are important factors. Obtaining this new fuel from a regional supplier with a strong quality control program would be highly desirable. Obtaining this new fuel from an unknown source would raise concerns. There have been many incidents in the past where non-spec fuels have been moved through the market with unacceptable consequences. A recent example is unconverted vegetable oil. Retail marketers typically cannot afford to check fuel properties and compliance with standards and so, rely on upstream sources to ensure quality.

Relative to motivating factors for industry acceptance, the point that this is a renewable fuel is recognized as very important for the industry and consumers and is helpful. Fuel cost will, however, be the major factor.

Overall the results of this outreach effort indicate strong willingness to consider this new fuel but before taking any additional steps the fuel needs to be really defined. Once this is done burner and other key component manufacturers can get engaged in their own tests and evaluations leading to their potential acceptance. This could be followed by initial field deployment.

Discussion

Results of this study confirm the technical feasibility of using upgraded pyrolysis oil to displace petroleum in oil-fired home and commercial building heating systems that are commonly used in the Northeastern United States and Canada. A very wide range of bio-oils have been considered including those which have undergone minimal upgrading (not miscible with petroleum), those which have been partially upgraded (PNNL fuel – miscible) and those which are fully upgraded (Kior middle distillate fuel). Basic combustion tests across this range indicate good performance can be achieved with the systems commonly used in this application. With the minimally upgraded fuels the tests used higher than normal pump pressure and elevated fuel pressure. Otherwise the burner was not changed. With the partially and fully upgraded fuels good combustion performance was demonstrated without any changes to the burner hardware.

The goal of this project is evaluation of fuels that are fully miscible with No. 2 heating oil and which, when used in blends of nominally 20% will not require supply chain or end use hardware upgrades. The partially and fully upgraded fuels evaluated have strong potential to meet this but the key technical question remaining is how close to fully upgraded is necessary. The work performed here has shown that this is not likely to be a combustion performance question but rather an elastomer compatibility and long term storage stability question.

Tests with the partially upgraded fuel showed unacceptable performance from the elastomer and storage stability perspective while the fully upgrade fuel was clearly acceptable. This led to studies of synthetic bio-oils in which oxygenated components were added back into petroleum oil. Tests with cyclopentanone and several phenols showed that the addition of these oxygenates increased nitrile elastomer swell and these likely would have to be limited to less than 1% in commercial fuels. In studies of different oxygenates, mostly phenols, it was shown that under some conditions at least, there was an increase in the formation of filterable insoluble with increased oxygenates. The situation, however, is not very clear. The type of phenol and the metric used for stability can affect the outcome. Some phenols, for example, are used as additives for increasing the stability of biodiesel and biodiesel blends where stability is measured with oxidative reserve (“Rancimat”) test [9, 27]. It should be noted that the results found in this study for specific phenols and specific test conditions are similar to those reported by McCormick et.al. [9]. Hui-Peng et al. studied the impact of phenols on stability looking at both oxidative reserve and insoluble formation. They found an increase in induction time (improved stability) and an increase in insoluble formation (reduced stability). In the discussion they raise the idea that the insoluble formation is due to higher temperature phenol condensation reactions [28]. This leads to the situation where the impact of oxygenates on stability will depend on the measurement method. It is the opinion of the authors that an accelerated test based on insoluble formation would be preferable to an oxidative reserve test. Acceptance of upgraded pyrolysis oils into the home heating market may not require the definition of a new fuel but could, potentially, be achieved through the addition of a stability specification to the ASTM definition of heating oil. The ASTM D 396 standard does not, at the present time, include any stability limits for home heating oil. It is clear, from the industry interactions that an increase in fuel system insoluble formation associated with the introduction of upgraded pyrolysis oil would be a significant market barrier.

Conclusions

Work done during this project demonstrated the technical feasibility of displacing petroleum-based heating oil with upgraded pyrolysis oil to at least the 20% level. For the fuels tested combustion performance was found to be good in steady state and cyclic operation. Long term tests (4000 cycles, 4000 hours) with a fully upgraded bio-oil indicated no operational concerns.

Two bio-oils which could be considered minimally upgraded were not found to be miscible with No. 2, petroleum-based heating oil and so were not suitable candidates for the goals of this project. One partially upgraded fuel tested was found to be miscible and produced good combustion performance. This fuel, however, was not found to have acceptable performance relative to elastomer swell and storage stability. One fully upgraded fuel was tested extensively and found to be fully acceptable relative to combustion, elastomer swell, and storage stability.

To further explore the impacts that partial upgrading could have and support the development of a potential future specification for an economic upgraded bio-oil, studies of synthetic bio-oil blends were completed in which selected oxygenates were added back into petroleum-based No. 2 fuel oil. It was generally found that increasing oxygenates negatively impacted elastomer swell. Further, some oxygenates, particularly under higher temperature conditions, caused an increase in the formation of filterable insolubles in storage. This can be compared with oxidation reserve tests where phenols are used to increase stability. For stability, the limits on oxygenates concentration may best be set through a performance based test – i.e. storage stability as opposed to specific quantitative compositional limits. The current specifications for home heating oil do not have a stability limit.

In outreach to the distribution and marketing supply chain in the Northeast it was found that they are very willing to consider this new fuel as a blend stock. The industry expects that the fuel performance will be at least as good as petroleum fuels, that all standards are in place for the fuels, and that the equipment manufacturers have approved the fuel.

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