



B20 to B100 Blends as Heating Fuels

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and
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**Brookhaven National Laboratory
Sustainable Energy Technologies Department
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Table of Contents

Introduction.....	1-1
1. Pump Seal Material Evaluation	1-3
Experimental	1-6
Hardness.....	1-7
Volume Swell.....	1-7
Tensile Strength	1-8
Compression Set	1-9
Results.....	1-9
Discussion	1-14
Conclusions.....	1-14
References.....	1-15
2. Evaluation of Oil Burner Pumps Under Operating Conditions	2-1
In-Lab Cycling Tests.....	2-1
Evaluation of Pumps from the Field	2-3
Conclusions.....	2-8
3. Exposure of “Yellow Metals” at Low Temperature	3-1
Experimental	3-Error! Bookmark not defined.
Results.....	3-3
Discussion	3-3
Conclusions.....	3-4
4. Exposure of Yellow Metals at High Temperature	4-1
Experimental	4-1
Results.....	4-1
Discussion	4-5
Conclusion	4-5
5. Combustion and Flame Sensor Response	5-1
Experimental	5-1
Results.....	5-3
Conclusion	5-10

6. Review of Field Experience with Biodiesel Blends	6-1
7. Conclusions.....	6-1
Appendix I – Summary Reports Prepared on Selected Topics for Submission to ASTM in Support of Evaluation of Changes to the ASTM D396 Standard.	A-1

List of Tables

Table 3-1 Test Matrix in Long-Term, Room Temperature Metal Exposure Test	3-1
Table 4-1 Preliminary Results of First High Temperature Metals Test (175 °F)	4-1
Table 4-2 Results of High Temperature Yellow Metal Studies.....	4-4
Table 6-1 Response to Survey Question on Biodiesel-Related Service Problems	6-2
Table 6-3 Results of Analysis of Biodiesel Blend Samples from Nassau County, Long Island .	6-3
Table 6-4 Results of Analysis of Biodiesel Blend Samples from Eastern, Pa.....	6-4

List of Figures

Figure 1-1 Typical oil burner fuel pump shaft seal.....	1-4
Figure 1-2. Type M Durometer used for hardness measurements of the nitrile samples before and after exposure to fuels.	1-7
Figure 1-3 Tensile testing to failure of nitrile samples performed with a TiraTest 26005 uniaxial load frame with pneumatic grips (left); Nitrile dogbone specimen after testing to failure	1-8
Figure 1-4 Compression set of nitrile samples induced with chrome-plated pressure plates per ASTM D395 to 20% strain (left and center). Specimen thickness change was measured after 22 hours at 125°F in a laboratory furnace (right).	1-9
Figure 1-5 Impact of biodiesel content on measured tensile strength	1-10
Figure 1-6 Impact of biodiesel content on measured hardness.....	1-10
Figure 1-7 Impact of biodiesel content on measured compression set	1-11
Figure 1-8 Impact of biodiesel content on measured volume swell	1-11
Figure 1-9 Impact of elevated acid number on tensile strength. B-100.....	1-12
Figure 1-10 Impact of elevated acid number on hardness	1-12
Figure 1-11 Impact of elevated acid number on compression set.	1-13
Figure 1-12 Impact of elevated acid number on swell.....	1-13
Figure 2-1 Pumps under test at Penn State University	2-2
Figure 2-2 Photo of pump with a carbon face seal after 11 months of testing with biodiesel.....	2-3
Figure 2-3 Partially disassembled pump. Field operation - 3 years, B20.	2-4
Figure 2-4 Photo of a new oil pump shaft seal.	2-5
Figure 2-5 Sketch of oil pump shaft seal.	2-5
Figure 2-6 Image of the sealing edge of a new oil burner shaft seal.	2-6
Figure 2-7 Image of the sealing edges of a shaft seal from a pump after 3 years of field operation on B20.....	2-7
Figure 2-8 Image of the sealing edge of a shaft seal from a pump after six months of field operation on B100.....	2-7
Figure 2-9 Image of the sealing edge of a shaft seal from one of the pumps in the Penn State long term test. This pump operated with a B0 blend.	2-8
Figure 3-1 Photo of long term, low temperature metal exposure test.....	3-2
Figure 3-2 Acid numbers of the test fuels after the six month period	3-3
Figure 4-1 High temperature metals exposure test, B-100. Appearance of the B-100 sample with a brass nozzle (left) and stainless steel nozzle (right) after 1 week at 175 F.....	4-2
Figure 4-2 Photos of fuel samples after 5 weeks of storage at 170 °F with either brass or stainless steel nozzles. (Control samples not shown).	4-3
Figure 4-3 Samples of ULS, without biodiesel. Impact of elevated acid number and a nozzle. .	4-4
Figure 6-1 Photos of fuel samples taken from Eastern Pennsylvania sites.....	6-5

Introduction

Biodiesel is mono-alkyl esters of long chain fatty acids derived from naturally occurring oils or fats which conform to ASTM D6751 specifications. Biodiesel refers to the pure fuel before blending with traditional distillate type petroleum-based fuels such as diesel fuel or home heating oil (petrodiesel). Biodiesel blends are denoted as, "BXX" with "XX" representing the percentage of biodiesel by volume contained in the blend (i.e.: B20 is 20% biodiesel, 80% petrodiesel).

Biodiesel offers a near-term opportunity to displace petroleum-based heating oil with a low carbon, renewable fuel. Biodiesel can be made from a variety of domestically produced oils and fats such as commonly available vegetable oils or animal fats as well as other oils such as used frying oils, reclaimed distillers corn oil from ethanol plants, algal oils, etc. In the US, about half the biodiesel is made from soybean oil, with the remainder about evenly split between canola oil, animal fats, used cooking oils, and distillers corn oil.

ASTM specification for pure biodiesel (B100) intended for blending with petrodiesel, ASTM D6751, was formally approved in 2001. This specification was based primarily on lab and field testing and data from 1993-2001 with B20 blends in the on-road diesel market in the US made with biodiesel that met the physical and chemical properties and values found in ASTM D6751. During that time, the EPA mandated sulfur level of on-road diesel was 500 ppm maximum, while off road diesel was 5000 ppm maximum. In 2006, the EPA mandated sulfur level for on-road diesel was changed to 15 ppm maximum (referred to as Ultra Low Sulfur Diesel (ULSD), and diesel vehicles underwent a tremendous change to reduce diesel tailpipe emissions. Diesel engines incorporated exhaust gas recirculation and high-pressure common rail (HPCR) fuel injection systems to better control engine-out emissions. The reduced sulfur levels of ULSD allowed the implementation of exhaust aftertreatment catalyst systems such as diesel oxidation catalysts (DOC), diesel particulate filters (DPF), and Selective Catalytic Reduction technology (SCR).

The original D6751 B100 specification was modified during the 2001-2008 timeframe to accommodate the new ultra-low sulfur diesel and additional controls needed for modern diesel engines and aftertreatment systems. Specifications were added for stability and metals for HPCR fuel systems and exhaust aftertreatment catalysts, and additional controls on minor components were implemented in 2008 after the introduction of ULSD.

In 2008, after the modifications and improvements to the D6751 B100 standard and a significant amount of lab testing and positive field experience, ASTM International successfully balloted changes to both the D975 on/off road diesel specification as well as the ASTM D396 home heating oil specification to allow blends up to 5% by volume as fungible components of the No. 1 and the No. 2 grades of D975 and D396. In the case of both D975 and D396, the same parameters and test methods and the same limits apply to finished fuels regardless of the biodiesel blend value up to 5% biodiesel, with the added requirement that the B100 must meet D6751 prior to blending. For the D396 heating oil standard, major oil burner manufacturers, Underwriters Laboratory (UL), and

Brookhaven National Laboratory (BNL) contributed to the technical work which supported the argument for this change. This technical work included materials compatibility, validation that B5 fuel blends could meet all of the burner performance criteria normally applied for burner listing, and other basic storage and use tests.

By 2008 a significant amount of positive field experience was also available with B20 blends in conventional diesel engines and ASTM also successfully balloted standards for finished B6-B20 blends for on/off road diesel engines. Since both No. 1 and No. 2 fuels are used in the same engines and are often blended together in cold weather, the B6-B20 standard simply combined the two into one grade and using the same test methods and limits as are found in either the No. 1 or No. 2 grades. For B6-B20 additional parameters for the finished biodiesel blends were also added for acid value and oxidation stability reserve to help ensure adequate protection against degradation over time, and the 90% distillation temperature (T-90) was allowed to be 5 °C higher due to the high flash point nature of biodiesel. With the same methods and limits and limits as conventional diesel, and additional controls for biodiesel blends, the National Biodiesel Board reports that B6-B20 blends have been used in existing diesel engines successful for many years even though these engines may not have been originally designed with B20 in mind.

Very little experience or market demand existed for blends higher than B5 in the home heating oil market in 2008, however. In comparison to modern high-pressure common rail diesel engines equipped with DOC/DPF/SCR aftertreatment, fuel oil-based home heating systems are much simpler and can accept a wider range of fuels than are needed for modern diesel engines. This allowed the heating oil research community to build on that learned from the on-road market and focus B6-B20 technical activities for heating oil on those differences specific to heating oil type systems. Based on interest from fuel oil dealers to find novel ways to compete against what is perceived to be cleaner burning natural gas, the National Oilheat Research Alliance teamed with the National Biodiesel Board, industry and university technical experts, and Brookhaven National Laboratory to fill in the technical gaps identified for B6-B20 in home heating oil applications. The work conducted between 2008 and 2015, largely summarized in this report, included efforts with B20 and with higher blends up to B100 in some cases. These efforts culminated in the successful balloting of a B6-B20 grade into the ASTM D396 fuel oil standard in 2015. Since much of the home heating oil in the market today is simply on/off road diesel fuel that has been redesignated, the B6-B20 home heating oil grade mirrors that of B6-B20 being used for on/off road diesel, i.e. combining the No. 1 and No. 2 grades using the same test methods and limits while adding oxidation stability reserve and acid value and allowing a slightly T-90.

Currently, biodiesel/heating oil blends at levels up to B5 are commonly used in heating systems in the Northeast. This is a fully accepted fuel in existing equipment and fueling infrastructure and is being embraced by much of the market as a means to reduce the carbon footprint of home heating oil while providing other environmental, economic, and performance benefits. With the research and testing completed on B20 that has resulted in the B6-B20 grade in the ASTM D396 standard,

several retail fuel oil marketers have been successfully selling B20 blends to their existing heating oil customer base for over 10 years, while some early adopters are using blends over B20.

As biodiesel production increases through plant capacity growth, improved crop yields, increased waste resource use, and novel crops including algae, there is a potential to also increasingly displace petroleum with this renewable fuel. The work done in this research explored specific aspects of the use of biodiesel at blend levels of 20% and over.

The specific technical aspects evaluated over several projects included:

1. Compatibility of conventional fuel pump shaft seals with higher blend levels.
2. Evaluation of pumps under field operating conditions
3. Impact of exposure of “yellow metals” at low and high temperature on biodiesel blends.
4. Combustion characteristics of biodiesel blends and flame sensor response.
5. Documentation of field experience with biodiesel blends including higher blend levels.

Work done and results of studies for each of these aspects are described in the following sections. As part of the work on this project, BNL spearheaded a series of review documents for submission to ASTM for their consideration in updates to the D396 standard on heating oil. These reviews were important for this process and include important background information on combustion performance and other areas. This package of review documents is included as Appendix I to this report.

1. Pump Seal Material Evaluation

Oil burners commonly used in homes and smaller commercial applications are fixed firing rate, with pressure atomized burner nozzles. Fuel pressure delivered to the nozzle is typically 100 – 150 psi. The fuel pump in these systems are gear-type positive displacement pumps which include the following features:

- An integral pressure regulator with adjustable discharge pressure.
- Some type of flow control which only allows flow to the nozzle when the pump is running and quickly turns the flow on and off during cycling operation.
- An inlet strainer.
- High suction lift to rapidly clear air out of an empty suction line.

In oil burner pumps there are several different seals used. In consultation with the pump manufacturers and other industry stakeholders, the pump shaft seals were identified at the start of this project at the area of most concern. A leaking shaft seal has potential to allow oil to drip onto the floor of the home, an undesirable outcome.

The most common pump types used in North America include lip-type shaft seals with a specific nitrile material. Less common, but still important are carbon-face type shaft seals. In this section of this report, work done on the basis interaction between the nitrile used in most pump shaft seals and biodiesel blends is presented. The evaluation of pumps under operating conditions with lip seals and carbon-face seals is discussed in the next section.

The work that is the subject of this section has been focused on the impact that biodiesel blend use can have on the nitrile seal material used in the market-dominant fuel pump shaft seal. This is a nitrile lip seal and, while the focus is on this specific seal, nitrile generally is used in other legacy heating system seal applications including other pump, filter, and valve components. The focus on this specific seal was a decision made in consultation with pump manufacturers. A leak in the shaft seal could potentially lead to fuel spillage inside of the building space.

Figure 1 provides a photo and sketch of the lip seal used in the burner pump installed in a strong majority of building heating applications in the U.S. It is a common double-lip type seal with a metal casing. The seal is pressed into to pump body during manufacture and is not practically field-replaceable.

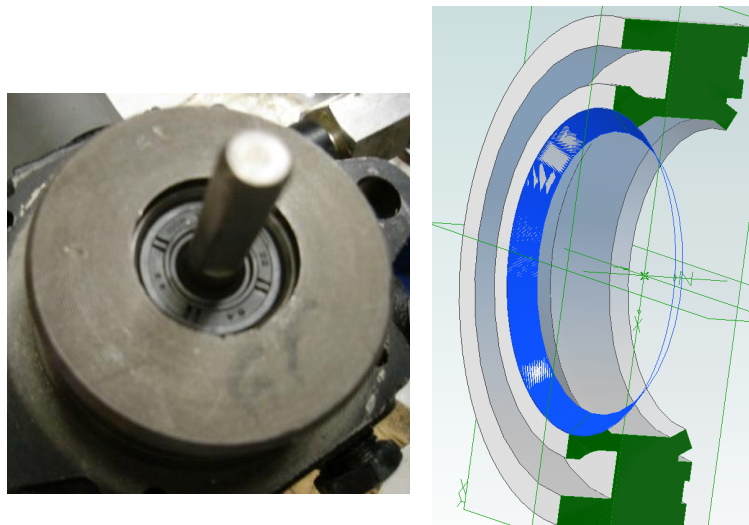


Figure 1-1 Typical oil burner fuel pump shaft seal

In legacy heating systems, the dominant seal material is nitrile-acrylonitrile butadiene rubber or NBR; an unsaturated copolymer constructed of acrylonitrile and butadiene monomers. The presence of the acrylonitrile monomer imparts permeation resistance characteristics to a wide

variety of solvents and chemicals, while the butadiene component in the polymer contributes toward the flexibility.

Like any given polymer, the mechanical properties of nitrile vary depending on its constituents. Differences in composition may be based on the acrylonitrile content used in synthesis (commercial nitrile rubber can vary from 25% to 50%), reinforcement fillers, plasticizers, antioxidants, processing aids, and cross-linking agents [2, 3].

In the process of obtaining a listing approval for a burner for application in this market, testing is typically done, guided by Standard UL 296 [4] which effectively incorporates material compatibility tests for elastomeric materials, UL 157 [5]. This test involves an immersion period of 70 hours at 23 ± 2 °C (73 ± 3.6 °F). Suitable elastomers are required to retain more than 60% of their unconditioned tensile strength and elongation and volume swell must fall within the range of -1 to +25%.

Generally, nitrile materials have good resistance to petroleum products and are commonly used with heating oil applications. The chemical resistance, however, of nitrile to biodiesel fuel or biodiesel/heating oil blends was not as well established. There are nitrile materials offered commercially which are at least nominally compatible with biodiesel blends to the B-100 level [6].

In a study published in 1997 [7, 8] Southwest Research Institute reported on their evaluation of a range of different elastomer types exposed to biodiesel/petroleum blends. Fuels included in this study included JP-8, B-100, low-sulfur diesel fuel, “reference” diesel fuel and blends at the B-20 and B-30 level. Samples were immersed at 51.7 °C (125 °F) for 0, 22, 70, for 694 hours. Tests reported in the study by Southwest Research Institute showed a notable effect of the biodiesel blend on the nitrile materials. This included volume swell in the 20% range and a reduction in tensile strength as high as 38%. These tests were done prior to the implementation of oxidation reserve specifications and the lowering of the acid value specification for B100, and at higher temperature and for much longer times than required by UL 157. Even so, the magnitude of property change reported is within the acceptable range under UL 157, although marginally.

In a more recent study [9] Southwest Research Institute and the National Renewable Energy Laboratory, evaluated the compatibility of several elastomers including three different types of nitrile in B20 blends and ethanol-diesel blends. The nitrile materials included a general purpose NBR, and high aceto-nitrile content rubber, and a peroxide-cured nitrile rubber. These materials were selected as being typical of materials used in automotive applications. Samples were immersed at 40 °C (104 °F) for 500 hours.

Tests reported in the earlier study by Southwest Research Institute for elastomers common to diesel engines showed some effect of the biodiesel blend on the nitrile materials. This included volume swell in the 20% range and a reduction in tensile strength as high as 38%. The later study reported on by SwRI and NREL showed no significant effect of the biodiesel blends on the NBR

materials studied, leading to the conclusion “all of these elastomers appear to be fully compatible with 20% biodiesel blends”.

In another, potentially relevant study done by Underwriters Laboratories [10] the compatibility of B5 blends with elastomers typically used in oil burner applications was studied in compliance with the UL157 standard. Two specific nitrile materials were included. This study showed no significant effect of the biodiesel blend on the materials tested.

The goal of the work done in this project was to extend the prior NBR elastomer studies on biodiesel compatibility to the entire range from B0 to B100 and to focus specifically on the NBR material used in legacy pump shaft seals in oil burner pumps. This specific component was selected cooperatively with equipment manufacturers as potentially the most vulnerable part of existing systems. A key question for this study was the “limit value” i.e. the maximum amount of biodiesel that could be used in a legacy system at least based on this one specific metric.

The experimental work reported in this section was done by Dr. Chad Korach and Richard Anger at the State University of New York at Stony Brook under contract to BNL, as part of this project.

Experimental

In this study the impact of biodiesel at a wide range of blend levels was evaluated for the nitrile material commonly used on legacy oil burner pumps in the U.S. Sheets of the nitrile material were obtained with assistance from the Suntec Corporation. The specific material is grade A795 NBR from the NOK corporation [11]. Samples of this material were cut into standard dog bone shapes as well as circles and rectangular shapes. Immersion with different biodiesel / No. 2 oil blends was done for 670 hours at 51.7 °C (125 °F).

After immersion, all samples were removed from the oil, cleaned, and then subjected to non-destructive hardness and swell measurement tests prior to the destructive tensile or compression set tests. The cleaning process consisted of a ~3 second acetone dip to remove residual oil, and blotting with laboratory tissues to dry. All samples, both discs and dog bone specimens, were used to measure the volume swell and hardness; dog bone samples only were used to measure tensile strength; and the disc samples only were used to measure the compression set of the materials.

The biodiesel fuel used in this effort was a commercial sample, received from Hero BX, Erie Pa. The No. 2 fuel oil used was also a commercial sample, obtained locally.

When biodiesel degrades during extended storage, one possible eventual outcome is the formation of organic acids. The current ASTM standard which defines biodiesel as a blend stock, provides a limit of TAN, or total acid number of 0.5 maximum, down from initial industry specifications of 1.2 and the first ASTM D6751 specification of 0.8. To evaluate the potential impact which severely degraded fuel might have on the target elastomer, some tests were done in

which biodiesel samples with high acid numbers were used. These high acid numbers were achieved by adding decanoic acid to the fuel samples to achieve TAN levels far higher than the allowed limit. All of these elevated acid number tests were done using just biodiesel (B100). Decanoic acid was selected for use in this study because it is highly soluble in biodiesel and fuel oil and it was the organic acid used to produce biodiesel at the limit of acidity in the UL study of B5 blends [10].

Hardness

Samples were tested per the ASTM D2240 Durometer Hardness test. A Type M durometer (Checkline RX-1600-M attached to a Checkline OS-3 test frame, Figure 1) was used which lowers a hardened steel pin into contact with the sample, measuring deformation and determining Durometer (M) rating on a scale of 0 to 100. The instrument was calibrated using Type M standard materials prior to each set of samples tested. For each specimen 10 durometer measurements were made and then averaged for a group of specimens. Measurements were made at the center of the dog bone sample base, and the disc sample centers. Durometer hardness is reported as a function of conditioning protocol.



Figure 1-2. Type M Durometer used for hardness measurements of the nitrile samples before and after exposure to fuels.

Volume Swell

Samples were measured for volume swell per ASTM 471 Fluid Aging test. All specimens, dogbone and discs, were weighed both in air and while submerged in water, using a specimen sling, before and after oil immersion. Specimens were dipped in acetone and blotted with lint free lab paper prior to measurements to remove residual surface water or oil. Archimedes principle is used to calculate the percent change in volume from the mass values, as the body's density (and volume) are related to the buoyancy forces acting on the samples while submerged in water. The % volume change (ΔV) is computed by the equation:

$$\Delta V = \frac{(M_3 - M_4) - (M_1 - M_2)}{(M_1 - M_2)}$$

Where, M_1 is the initial mass of the sample in air, M_2 is the initial mass of the sample in water, M_3 is the mass of the sample in air after oil immersion, and M_4 is the mass of the sample in water after oil immersion.

Tensile Strength

Tensile strength of the nitrile was tested per ASTM D412 Tension test. Sample geometry of the nitrile samples were die-cuts (ASTM D638 Type V) from a ~2 mm nitrile slab using a hardened steel die in the shape of dog bone specimens with initial gauge cross-section width of 3.175 mm and thickness of ~2 mm. Samples were tested using a screw-driven uniaxial load frame (TiraTest 26005, Figure 2) fitted with pneumatic-actuated grips and a 0.5 kN load cell. After the cleaning process, samples were immediately gripped in an un-stressed position and load was applied using a crosshead rate of 500 mm/min as per ASTM D412. A computer-controlled data acquisition system was used to control the experiment and to record the load and displacement data simultaneously at a 50 Hz sampling rate. Testing was completed after sample rupture which resulted in an immediate loss of load. Tensile strength (S_t) is computed from the force at failure and the nominal cross-section prior to loading by the equation:

$$S_t = \frac{F_f}{A_o}$$

Where, F_f is the applied on the specimen at failure, and A_o is the initial cross-sectional area, computed by the width and thickness of the gauge region for each specimen.

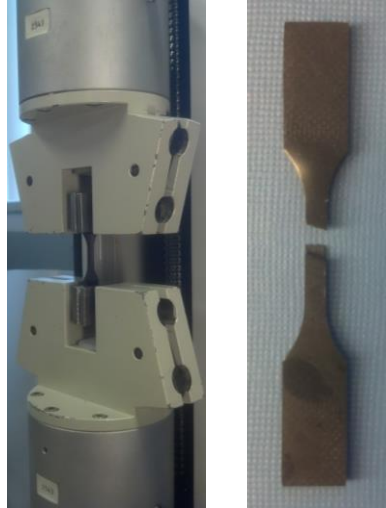


Figure 1-3 Tensile testing to failure of nitrile samples performed with a TiraTest 26005 uniaxial load frame with pneumatic grips (left); Nitrile dogbone specimen after testing to failure (right).

Compression Set

Samples were tested for resistance to permanent compressive deformation per ASTM D395 Method B, Rubber Property Compression Set Under Constant Deflection in Air. Nitrile disc specimens were compressed ~20% (varying by individual specimen's post-exposure thickness) in a polished steel, chrome plated compression rig (Figure 1-4) separated by calibrated, hardened steel spacer shims. Bolts were used to apply the compressive load to the platens. Once the samples were engaged in the compression rig the entire rig was placed in a 51.7°C (125°F) furnace (Blue M) for 22 hours. Sample thickness was measured before and after compression set testing to compute changes in relaxed height and to determine the percent of plastic deformation to original compressive deformation (Compression Set) C_B by:

$$C_B = \frac{(t_o - t_i)}{(t_o - t_n)} \cdot 100$$

Where t_o is the original sample thickness after the oil immersion conditions, but prior to compression set testing, t_i is the final sample thickness after the compression set conditions, and t_n is the spacer thickness.

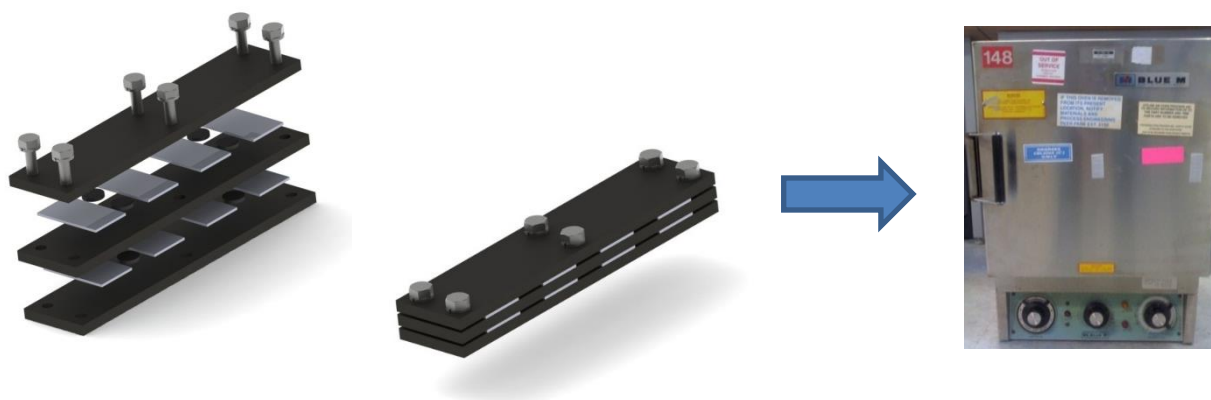


Figure 1-4 Compression set of nitrile samples induced with chrome-plated pressure plates per ASTM D395 to 20% strain (left and center). Specimen thickness change was measured after 22 hours at 125°F in a laboratory furnace (right).

Results

Figure 1-5 to 1-8 present the results of testing done with different biodiesel blend levels. Figure 1-5 shows the tensile strength results. Averages of three area measurements were used for each specimen. Results of tensile strength are reported as a function of the oil immersion protocol and do not illustrate a clear trend with biodiesel level. In all cases the elastomer easily retained greater than 60% of the unexposed tensile strength.

Figure 1-6 shows the results for the hardness measurements. There is a slight trend toward greater hardness retention with increasing biodiesel level in the blend but these results also show no concern about biodiesel interaction. Figure 1-7 shows results for compression set but again the impact is very small. Figure 1-8 shows the volume swell. There is no clear trend with increasing biodiesel content and all values are clearly less than the nominally allowed 25% under UL 157.

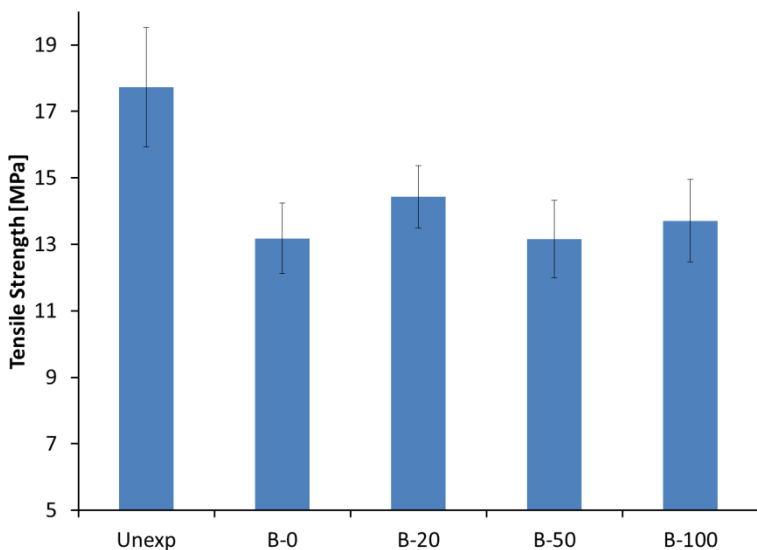


Figure 1-5 Impact of biodiesel content on measured tensile strength

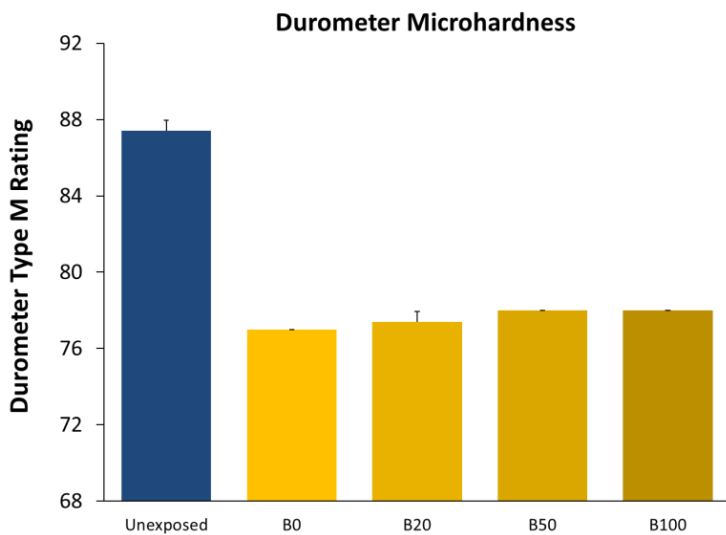


Figure 1-6 Impact of biodiesel content on measured hardness

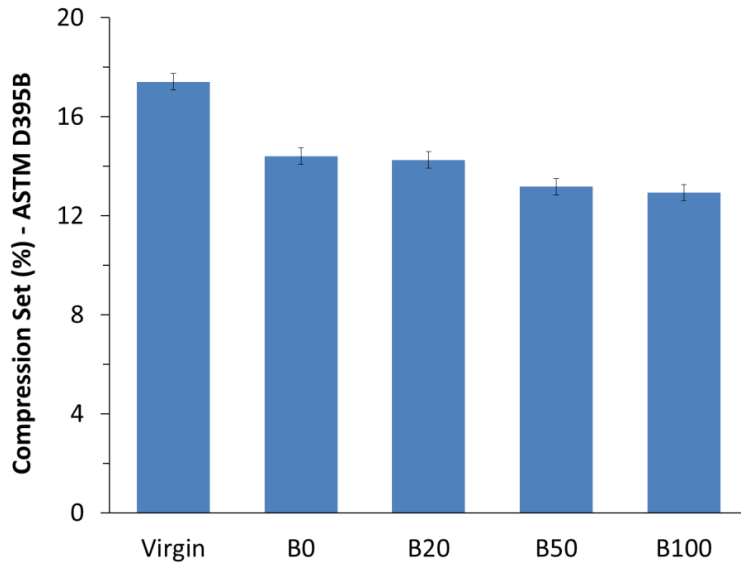


Figure 1-7 Impact of biodiesel content on measured compression set

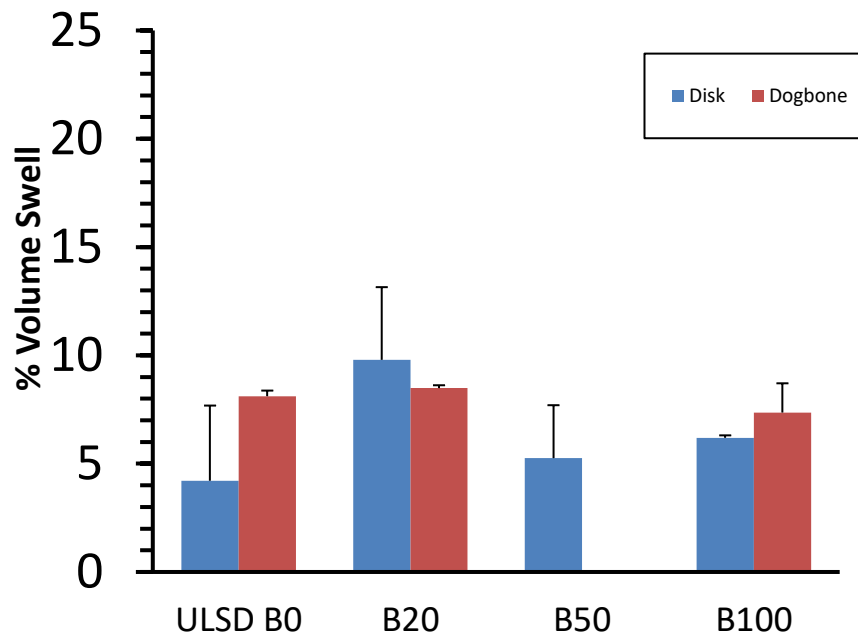


Figure 1-8 Impact of biodiesel content on measured volume swell

Figures 1-9 through 1-12 present the results of the studies with B-100 with elevated acid number. Figure 1-9 shows the impact of elevated acid number on tensile strength. Using the criterion in UL 157, a tensile strength of less than 10.5 MPa would be under the 60% of the unexposed sample tensile strength. Samples exposed in biodiesel with a TAN of 2 or greater would not be considered an acceptable outcome.

As shown in Figure 1-10, the impact of acid number on hardness is not very significant and a trend is not apparent. Figure 1-11 shows a clear increase in compression set with increasing acid number. UL 157 does not set a limit on either of these parameters, however.

Figure 1-12, volume swell shows a strong increase in this parameter with acid number. At an acid number of 2 the limit of 25% swell in UL 157 has been reached.

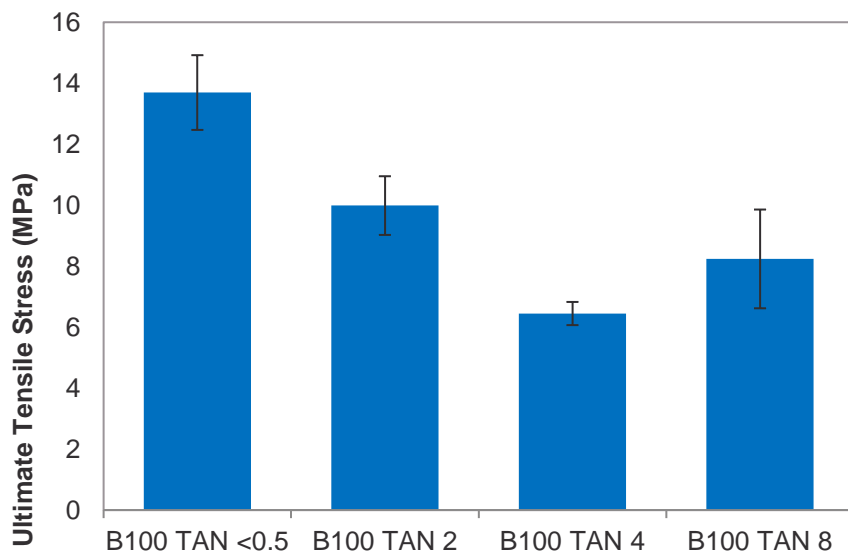


Figure 1-9 Impact of elevated acid number on tensile strength. B-100.

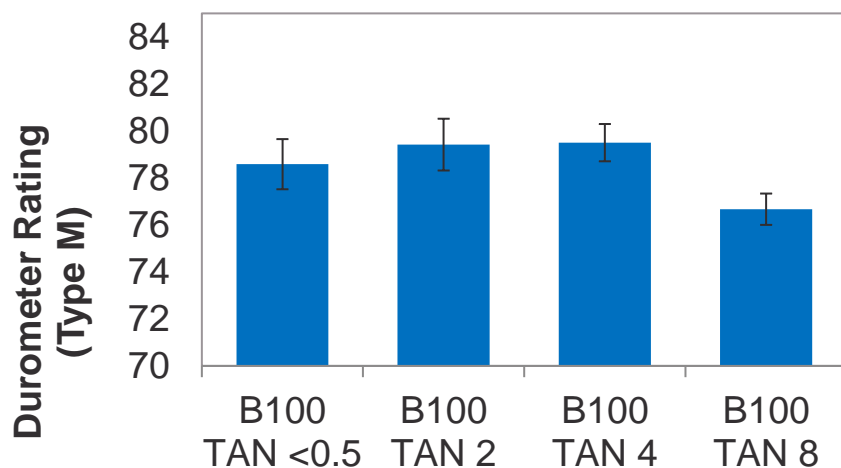


Figure 1-10 Impact of elevated acid number on hardness

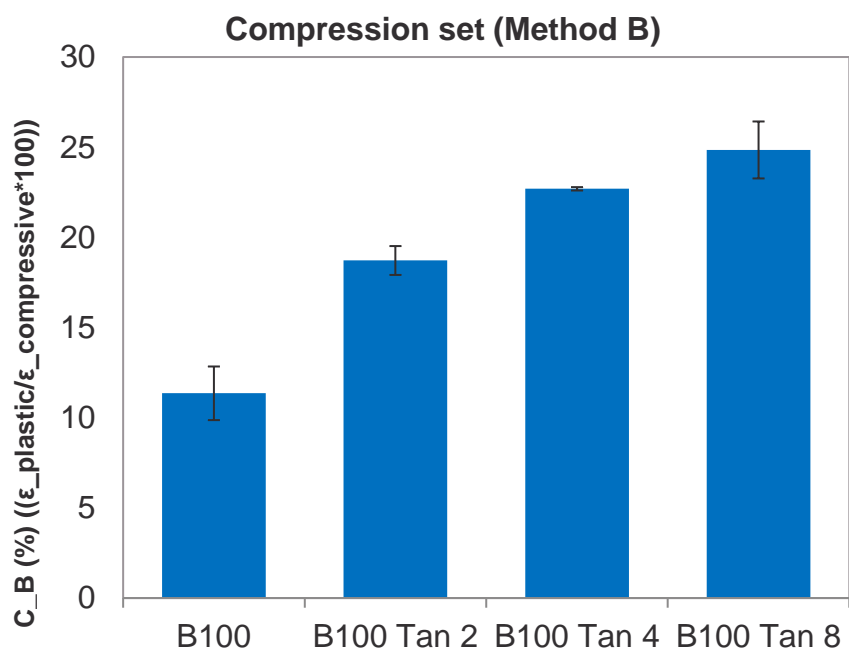


Figure 1-11 Impact of elevated acid number on compression set.

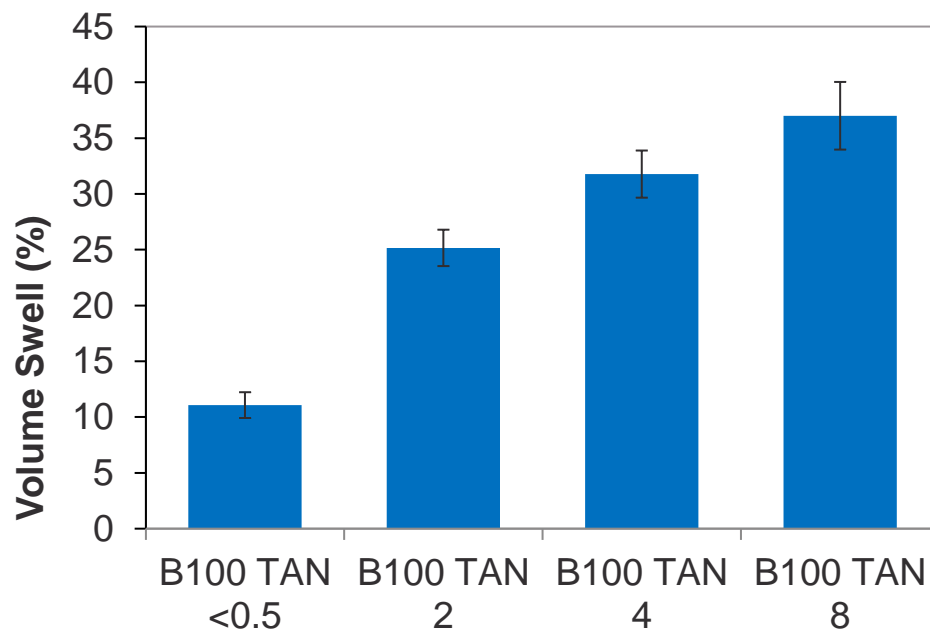


Figure 1-12 Impact of elevated acid number on swell

Discussion

Conventional elastomer impact testing under the UL 157 procedure is by soaking the fuel for a total of 70 hours at room temperature (~73°F). For this testing, much higher temperatures (125°F) and much longer soak times (670 hours) were used. For biodiesel/heating oil blends meeting current ASTM standards the results presented above show no significant changes in the properties measured with biodiesel blend levels to 100% for the specific elastomer evaluated relative to the base fuel oil. This elastomer, which is used in current and legacy oil burner pump shaft seals, was selected as a critically important seal component representative of elastomers generally used in oil-fired heating systems. The results with biodiesel/heating oil blends meeting today's ASTM standards, do not provide a cause for concern about biodiesel use in these systems.

With the elevated acid number, using the decanoic acid, there is, however, a very clear interaction between the fuel and the elastomer when acid numbers are well in excess of the current limits in ASTM D6751 and this has important implications for two reasons. First, if a biodiesel fuel is produced with high acid number or if a biodiesel fuel degrades during extended storage to yield such an extremely high acid number, there could be concerns about elastomer behavior. Such high acid numbers are unlikely to occur in practice. Second, many of the prior studies which have been done on elastomer – biodiesel (i.e. methyl esters of oils and fats) interaction were prior to the implementation of oxidative reserve limits and lower acid value limits for biodiesel. In some of these studies the TAN of the fuel used is not reported. This approach could lead to inaccurate conclusions from previous studies about elastomer suitability with biodiesel meeting today's ASTM standards.

Conclusions

This work has focused specifically on the nitrile elastomer used in the shaft lip seal on the home heating burner pump used in most oil-heated homes in North America. With biodiesel that is not degraded, i.e. has an acid number which meets the current specification for biodiesel blend stock for both acid value and oxidative reserve which serve to minimize the likelihood for acid formation during use, no significant impact of the biodiesel on the elastomer was observed at blend levels to B100. This is based on time periods and temperatures which could be considered conservative relative to those used in practice for material qualification.

When the acid number of the biodiesel blend was elevated through the addition of decanoic acid, significant impact on the elastomer was observed. While today's ASTM specification have been designed to prevent such degradation, severely degraded biodiesel with acid numbers above 2 could lead to accelerated degradation of seal materials.

References

1. *Standard Specification for Fuel Oils D396-15a*. 2015, American Society for Testing and Materials.
2. Chakraborty, S., et al., *Application of FTIR in characterization of acrylonitrile-butadiene rubber (nitrile rubber)*. Polymer Testing, 2007. **26**(1): p. 38-41.
3. Yasin, T., et al., *Effect of concentration of polyfunctional monomers on physical properties of acrylonitrile-butadiene rubber under electron-beam irradiation*. Radiation Physics and Chemistry, 2005. **73**(3): p. 155-158.
4. *UL 296 Standard for Safety - Oil Burners Tenth Edition*. 2013, Underwriters Laboratories.
5. *UL 157 Standard for Safety - Gaskets and Seals - Second Edition*. 1996, Underwriters Laboratories.
6. Company, W.A.R. *Bio-Diesel Nitrile (Buna-N)*. Available from: <http://www.warco.com/sheet-rubber/nitrile/bio-diesel-nitrile>.
7. Bessee, G.B. and J. Fey, *Compatibility of Elastomers and Metals in Biodiesel Fuel Blends SAE Paper 971690*. 1997, Society of Automotive Engineers.
8. Frame, E., G. Bessee, and H. Marbach, *Biodiesel Fuel Technology for Military Application*. 1997, Southwest Research Institute.
9. Frame, E. and M. R., *Elastomer Compatibility Testing of Renewable Diesel Fuels*. 2005.
10. *Report on the Interchangeability of B5 Biodiesel within Residual Oil-Burner Appliances Intended for Use with No. 2 Fuel Oil*. Underwriters Laboratories.
11. *Oil Seal*. April 6, 2015]; Available from: www.nok.com/sg/oillseal.aspx#oilseal.

2. Evaluation of Oil Burner Pumps Under Operating Conditions

The work reported in Section 1 of this report addresses the basic interaction between burner pump elastomers and biodiesel blends. As an alternative method of exploring the question of the use of commonly available oil burner pumps cycling tests of actual pumps with and without biodiesel blends were also explored. This section provides a description of these cycling tests.

In-Lab Cycling Tests

In a separate project, over the 2010-2013 timeframe, the operational reliability of the most common oil burner pump type, representing over 80% of the U.S. market, was evaluated in a series of tests at Penn State University. This involved rack of pumps operating under controlled cycling conditions of 5 minutes on, 1 minute off. The fuel in these tests was recirculated from 5-gallon containers. The base fuels for these tests included both “conventional” high sulfur heating oil (~ 1500 ppm) and ultralow sulfur (ULS) heating oil (15 ppm). Biodiesel blend levels ranged from B0 to B20. The key focus in this work was on pump shaft lip seal leakage and a detailed metric to quantify observed leakage was developed by the pump manufacturer for use in these tests. Figure 2-1 provides a photo of the pump setup. In the final round of these tests, 42 pumps were run and blend levels used included B0, B12, and B20. Seven pumps were run at each blend level and total run time for each pump was 7,000 hours. Quality of all fuels was monitored throughout the project to insure the fuel had not degraded significantly during the test due to the stressing of the fuel in the test. Acid number was considered the primary criterion for this. High acid numbers were not observed, and thus the test considered acceptable from that standpoint.



Figure 2-1 Pumps under test at Penn State University

Under the test conditions, all pumps were found to leak very slightly. In an analysis of the results using success criteria provided by the manufacturer, it was found that the pumps with biodiesel had lower leak rates over the course of the test than did the pumps without biodiesel.

While the pump study above covered most of those in the market, the majority of the remaining pumps in the market have carbon face seals vs. lip shaft seals. It was also desired to confirm performance with these carbon face seal pumps. Under a separate project, additional testing of carbon face seal pumps was also completed at BNL. For these tests, the pump racks from the Penn State test were moved to BNL. The pumps used in the tests at BNL were from two different manufacturers which both use carbon-face type shaft seals.

This test included a total of 42 pumps and the run period was 11 months. With a 5 minute on/1 minute off period over 8,030 hours this yields 80,000 on/off cycles. The biodiesel level was B0, B12, and B20. There were 7 pumps at each biodiesel level and the base fuel for all tests was ultralow sulfur heating oil (15 ppm). In contrast to the tests at Penn State with the lip seal pumps (similar time period and cycling pattern) no leaks were observed in the tests with these pumps with either B0 or the biodiesel blends. Figure 2-2, shows for example the shaft seal area, post-test for one of the pumps tested at BNL with carbon face seals.



Figure 2-2 Photo of pump with a carbon face seal after 11 months of testing with biodiesel.

In this testing, and the same fuel was recirculated for the entire test but the fuel was allowed to recirculate for the entire test and only checked at the completion of the test period. For all fuel samples measurements were made of the acid number (TAN) following completion of the tests. For some of the biodiesel blends in this test the TAN was found to be quite high at the completion of the test—on the order of 12. This indicated the test was quite severe to the point of depleting the fuels oxidation reserve which allowed fuel oxidation and acid formation. The TAN of the pumps run with the base fuel was the lowest, in all cases under 1. The fuel was not changed during the 11-month test, representing a significant stress. It was noted that even with the fuels which did degrade during this severe test—to the point of elevated high acid values which could potentially cause leakage with NBR lip seals—the carbon face seals did not experience leakage.

Evaluation of Pumps from the Field

In another approach to evaluating the impact of biodiesel, fuel pumps were collected from service companies which had been using biodiesel blends. Two sources participated in this. The first is a Long Island fuel marketer which has been marketing B20 blends to thousands of homes for at least 5 years. The second is a New York City-based company which has been marketing B100 to mostly commercial buildings since roughly 2010. In this study the received pumps were disassembled when received and inspected with a focus on the condition of the lip shaft seal. None of the received pumps had carbon-face seals.

Figure 2-3 illustrates, for example, a partially disassembled pump which had operated in the field for 3 years with B20. This pump was removed from service for this project and, as with all of the field pumps evaluated in this study it was operating well at the time of removal.

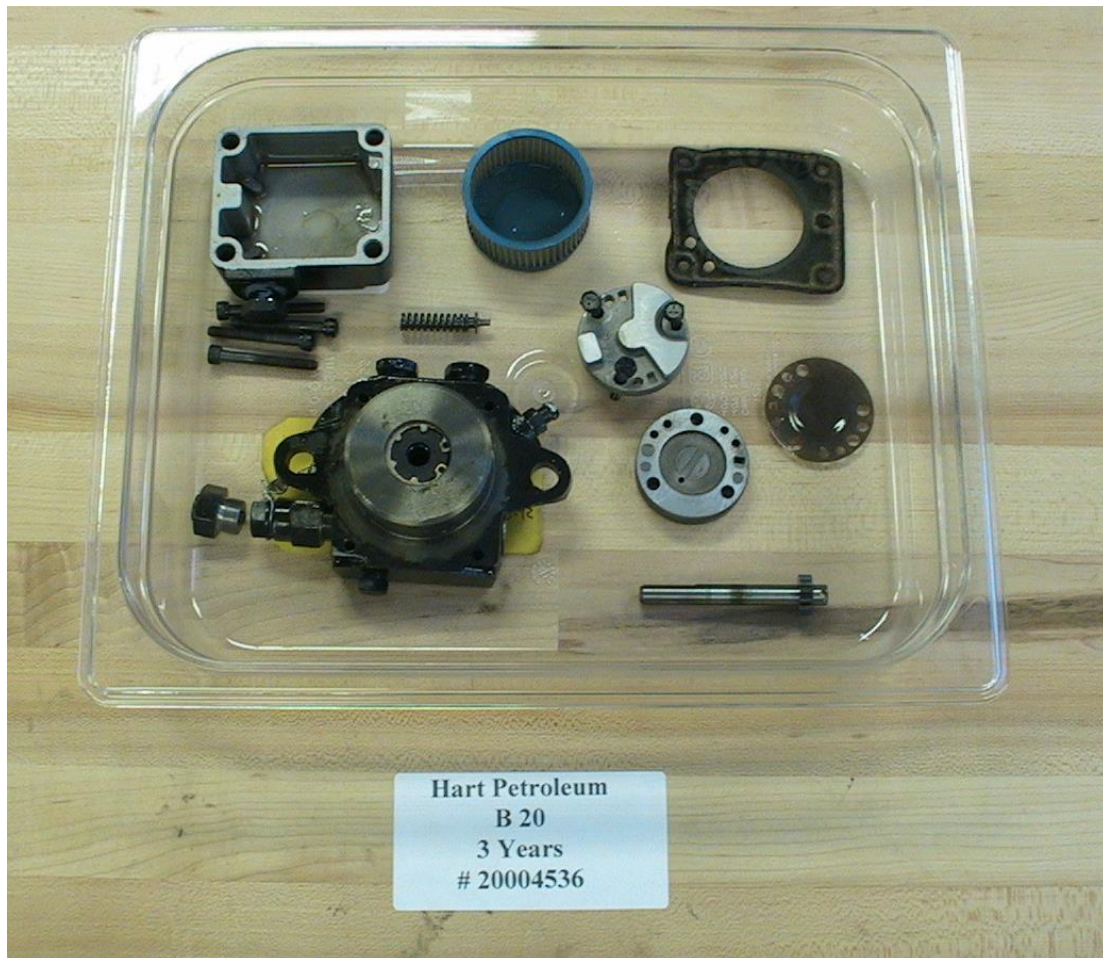


Figure 2-3 Partially disassembled pump. Field operation - 3 years, B20.

As with the lab long term run studies, the focus of this inspection has been on the lip-style shaft seal. Figure 2-4 provides a photo of this seal. Figure 2-5 is a sketch of the seal and Figure 2-6 shows a low magnification microscope image of the sealing edge of a new seal.



Figure 2-4 Photo of a new oil pump shaft seal.

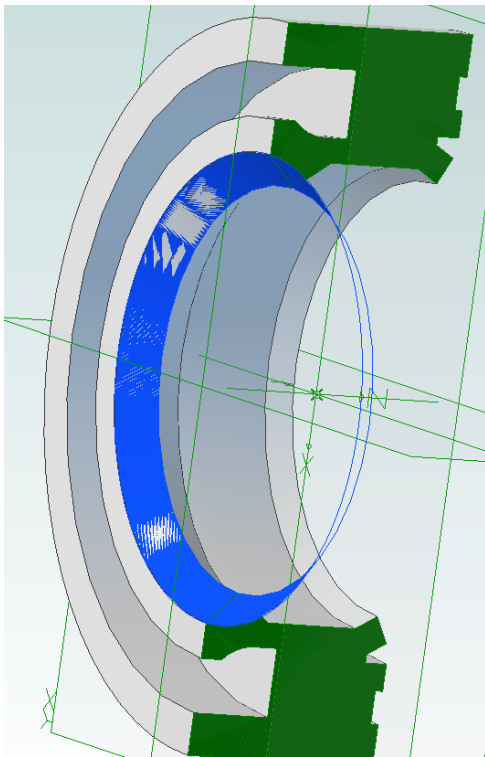


Figure 2-5 Sketch of oil pump shaft seal.

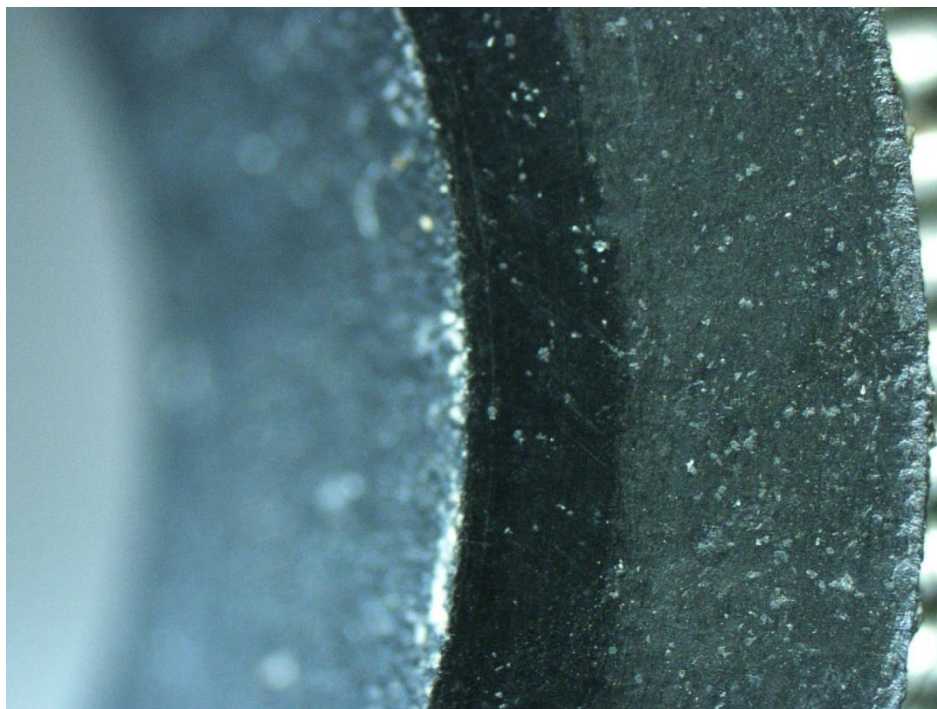


Figure 2-6 Image of the sealing edge of a new oil burner shaft seal.

This seal, as is common with lip seals, has two lips. The inner one is the sealing surface and the outer one acts as a dust barrier. The blue surface on the drawing in Figure 2-5 is the inner face of the sealing lip. This faces the interior of the pump and is well “flushed” by the pumped oil.

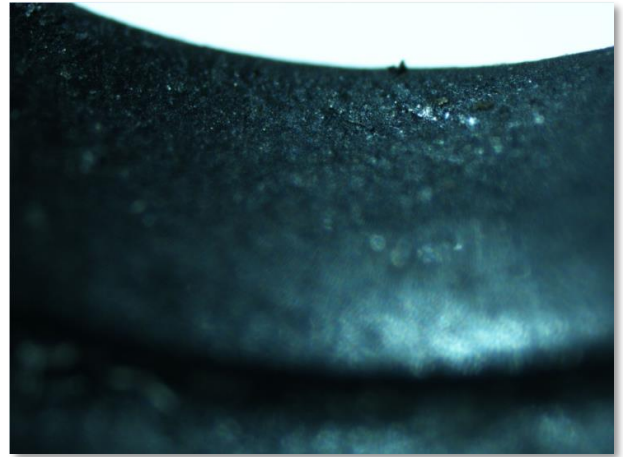
Figure 2-7 shows the inner and outer faces of the sealing lip of the pump seal which had been using B20 in the field for 3 years. This study showed no significant damage relative to a new seal.

Figure 2-8 shows the edge of a seal from a pump which had been using B100 for 6 months in the field. Again, there is no significant sign of damage to the sealing edge.

Figure 2-9 shows the edge of a seal from one of the pumps used in the tests at Penn State University using the baseline B0. In this case there is clear indications of damage to the pump seal and this is likely the reason why some shaft leakage was observed during the Penn State tests. This result shows that the fast-cycling during the in-lab testing provides more stress on the shaft seal than normal operation in the field. From the Penn State tests, no significant difference could be noted in the appearance of the shaft seals based on fuel used.



Inner face



Outer face

Figure 2-7 Image of the sealing edges of a shaft seal from a pump after 3 years of field operation on B20.

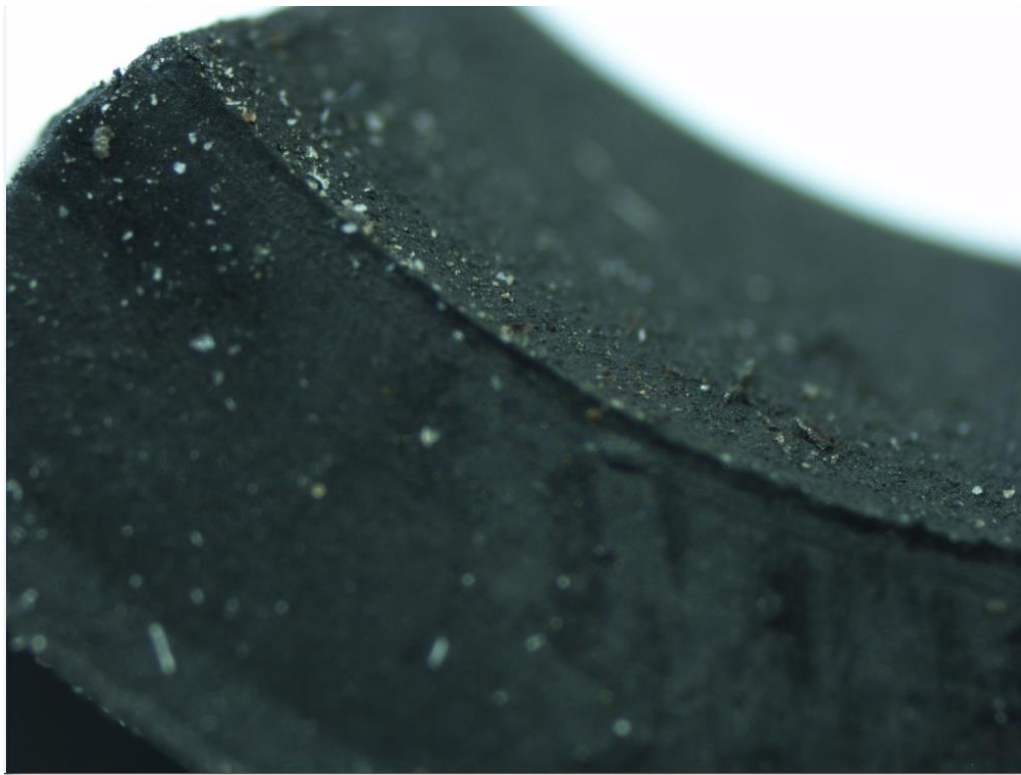


Figure 2-8 Image of the sealing edge of a shaft seal from a pump after six months of field operation on B100.



Figure 2-9 Image of the sealing edge of a shaft seal from one of the pumps in the Penn State long term test. This pump operated with a B0 blend.

Conclusions

Overall, from the work described in this section, there was no strong correlation between biodiesel blend level and pump shaft seal degradation or failure impact between B0 and biodiesel blends up to B20. One important observation was that the pump seals in the lab test showed degradation and impacts for both B0 and biodiesel blends that were not observed with the pumps exposed to B0 or biodiesel blends in the field for years evaluated in this study. This again is most likely due to the fast-cycling testing which places more stress on the shaft seal than normal operation in the field.

3. Exposure of “Yellow Metals” at Low Temperature

There is considerable prior published research that demonstrates that exposure to copper can accelerate the oxidative degradation of fuels including No. 2 fuel oil and biodiesel, which can result in the formation of sludge and sediment. The ASTM D975 standard for on/off road diesel states, “Copper and copper-containing alloys should be avoided. Copper can promote fuel degradation and can produce mercaptide gels. Zinc coatings can react with water or organic acids in the fuel to form gels that rapidly plug filters.” It goes on further to state, “The formation of degradation products can be catalyzed by dissolved metals, especially copper salts. When dissolved copper is present it can be deactivated with metal deactivator additives.” In general, copper is not recommended for either distillate fuel oils or for biodiesel due to these factors.

In oil-fired home heating systems, however, copper fuel lines are commonly used due to their lower cost and ease of manipulation and installation. Most installations in the United States are “one-pipe” systems where fuel flows from a steel tank, through copper lines, through a fuel filter, to the burner’s pump. Between the pump and the nozzle, copper lines are again commonly used. Fuel nozzles are either brass or stainless steel and could provide the opportunity for fuel to be exposed to yellow metals (i.e. those containing copper) at higher temperatures. This is addressed in the next, high temperature, section.

Some installations are “two-pipe” systems. In this case, the pump pressure regulator bypass flow returns to the fuel tank through a second copper line.

Experimental

When the burner is in regular operation, the residence time of the fuel in the copper line is short. The most significant opportunity for long exposure times is during the summer shut-down of an oil-fired appliance which is used for heat only, such as a warm air furnace. Combination appliances which also provide domestic hot water would run in the summer as well. In this project, a study was done of the impact of such a long-term storage in copper tube. A set of tubes, each 10 inches in length, was assembled in a holder with a vertical orientation. Table 3-1 details the metals used in the exposure test. Each tube was filled and this system idle at ~ 21 °C (70 °F) for six months. Figure 3-1, below, provides an image of the tube arrangement for the six-

month period. Two of these assemblies were used in the test. For each of these the following test matrix was used:

Table 3-1 Test Matrix in Long-Term, Room Temperature Metal Exposure Test

	B0	B20	B100
Stainless Steel	X	X	X
Old Copper	X	X	X
New Copper	X	X	X

In one of the two test assemblies conventional No. 2 fuel oil with approximately 1500 ppm sulfur was used. In the other ultralow sulfur diesel (ULS) with sulfur below 15 ppm was used as the base fuel.

The old copper was a fuel line which had been in service for around 30 years. Over such a long time, it could be expected that the inner surface of the copper tube might become passivated which could reduce the interaction between the metal and the bulk fuel.

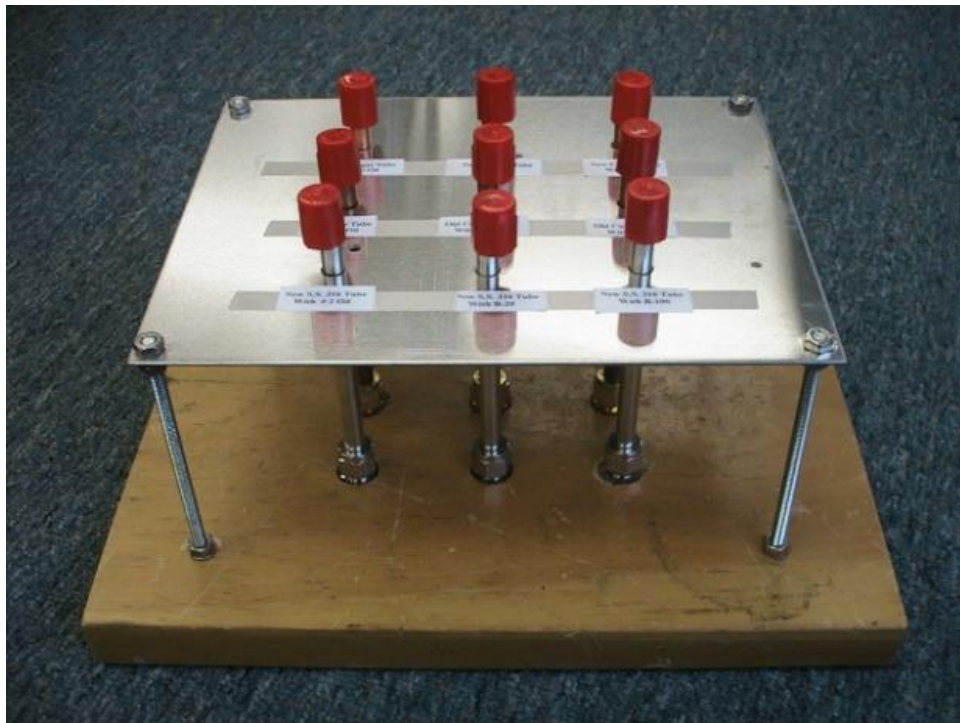


Figure 3-1 Photo of long term, low temperature metal exposure test.

Results

Figure 3-2, provides the measured acid numbers after the completion of the six-month period for the conventional, 1500 ppm No. 2 fuel oil. Results with the ultra-low sulfur diesel samples were similar.

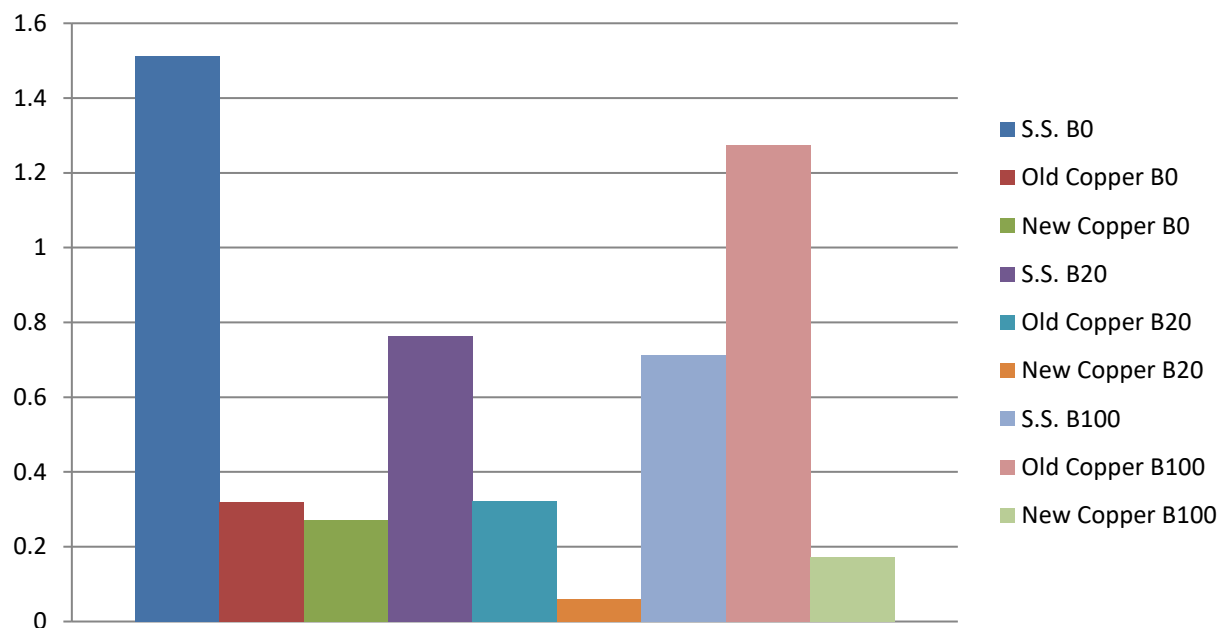


Figure 3-2 Acid numbers of the test fuels after the six-month period

The starting acid number for the fuel were approximately 0.4. Overall, this shows results for the biodiesel blends were comparable or lower to that of B0 soaked in stainless steel, and that samples soaked in copper did not lead to increased acid number versus stainless steel. For the stainless-steel samples, for the B0 and B20 fuels did have higher acid number at the end of the test than the copper samples, although all were below the acid value of 2 which was shown in bench testing to have potential effects on elastomer properties. For B100 the stainless-steel results were mixed between the stainless steel and new and old copper.

Discussion

One possible explanation for these results is that acids, produced during the long-term storage complex with the copper and are effectively neutralized. It should also be noted that these containers were sealed limiting the diffusion of oxygen to the fuel. This is similar to the situation that would exist in the fuel lines during a long summer shutdown. Overall, however, these results do not indicate a strong concern with copper in this case or differences for the biodiesel blends outside those generally observed with B0. We postulate the controls in the most recent, updated version of the B100 ASTM standard D6751 for acid number and oxidation reserve contributed

significantly to these results, as there are no current controls in conventional fuel oil for acid number or stability.

Some of the copper tubes were cut open for inspection of the internal surface. Figure 3-3, below, provides a comparison of the appearance of the “new” copper tubes after the exposure period. All of the tubes examined illustrated no damage, interaction with the fuel, or fuel degradation deposits. Both samples show some particulate deposits simply from the cutting operation. This result is consistent with the ASTM copper strip corrosion test which all these fuels are required to pass.



Heating oil



B-20 blend

Figure 3-3 Photos of internal surfaces of "new" copper tube after the six month exposure period.

Conclusions

These tests were conducted at low temperatures, simulating summer shutdown of a heat-only boiler or furnace. The test results showed no obvious impact on the copper tubing used as a reactor vessel in this test. The results also showed that the end-of-test acid number for the samples exposed to copper was not higher than for the samples stored in stainless steel. In two of the three samples the acid number for the copper stored samples was significantly lower than for the samples stored in stainless steel tubes.

4. Exposure of Yellow Metals at High Temperature

In typical heating oil systems in North America, in addition to copper fuel lines the other major source of metallic components with yellow metals are brass nozzles which are used to create a spray for combustion in the fire box of the boiler. These nozzles are typically replaced once per year, or when the unit is serviced. The fuel flowing through the nozzle has relatively little contact time with the nozzle, but fuel that stays inside the nozzle between firings can become hotter than fuel in the copper lines leading up to the nozzle. It was desired to determine whether there were any impacts of biodiesel vs. No. 2 oil with brass nozzles, as well as to determine any differences between brass and stainless-steel nozzles.

Experimental

To understand how yellow metals are affected at high temperature, several test setups were started which included biodiesel blends, open top glass beakers, and either stainless steel or brass nozzle assemblies. The concept here is to simulate the high temperatures which can occur in a nozzle following burner shut down, particularly in a hot combustion chamber environment. Such an environment would involve a thick refractory chamber liner and an absence of a post purge following burner shut down. These test setups were stored in an oven at 80 °C (175 °F).

Results

The first analysis of the basic appearance and acid numbers was done after one week. Table 4-1, below provides information on the acid number for the different test cases.

Table 4-1. Preliminary Results of First High Temperature Metals Test (175 F)

Fuel	Nozzle Material	Acid Number after one week
B0	None – control, not stored at high temperature.	0.23
B0	Brass	0.49
B0	Stainless	0.33
B20	Brass	0.61
B20	Stainless	0.46
B100	Brass	0.28
B100	Stainless	0.58

The results in Table 4-1 suggest that for B0 and B20 the brass nozzle had more impact on acid number under these conditions than stainless steel although all impacts are relatively small. In the case of B100, the stainless material had more impact, although this impact was also relatively small. Considering the long exposure time in this test at this high temperature, the differences in acid number are relatively small and similar for all fuels.

One interesting note is that the samples with the brass were darker in color than the samples with the stainless-steel nozzles, even though there was not clear increase in acid number with the brass nozzles relative to the stainless-steel nozzles. This is illustrated in Figure 4-1, below.



Figure 4-1 High temperature metals exposure test, B-100. Appearance of the B-100 sample with a brass nozzle (left) and stainless-steel nozzle (right) after 1 week at 175 F.

This test was returned to the oven for an additional month and acid numbers were again measured. Again, these acid number measurements indicated no significant difference. This is a rather extreme test set to simulate the impacts that copper might have in a burner nozzle. Here the fuel could be exposed to high temperatures but only for minutes, not the weeks used in this test.

Figure 4-2 provides a visual comparison of the fuels after approximately 5 weeks of exposure. As we noted above, the samples with the brass nozzle are a bit darker than the samples with the stainless-steel nozzles indicating the possibility of the fuel complexing with copper, with the B100 sample being more noticeable. As also noted above this color difference did not translate to an acid number difference.

A comparative FTIR study was done of these fuels after the 5 weeks of exposure. No notable differences in the absorption spectra were observed.

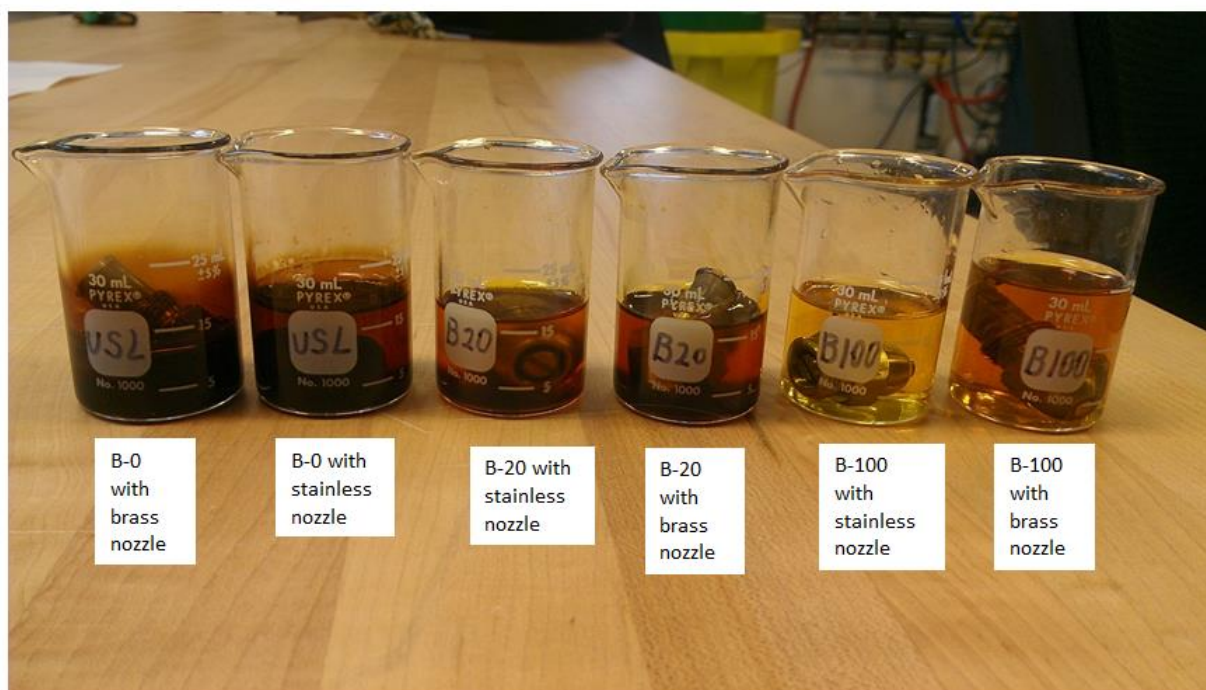


Figure 4-2 Photos of fuel samples after 5 weeks of storage at 170 °F with either brass or stainless-steel nozzles. (Control samples not shown).

Following this study, another round of testing was conducted using this high temperature exposure approach. In this next round we are also including fuels which have an elevated acid number, based on decanoic acid addition to the fuels. The purpose of this next round is to explore possible effects of the elevated acid number. The acid number in these tests was adjusted to a value of 10 which can be compared with the acceptable limit value for fresh B20 blends of 0.3 maximum.

An interesting observation on these tests is illustrated in Figure 4-3, below with B0. This photo is only for fuel samples which were prepared and then stored over a weekend at room temperature. The base fuel in this case is only ULS, no biodiesel was present. One fuel sample without a nozzle contained no decanoic acid and another, also without a nozzle contained decanoic acid adjusted to an acid value of 10. Both of these fuel samples remained “yellow” and clean. A fuel sample without decanoic acid but with a nozzle turned slightly dark. A sample with decanoic acid and a nozzle turned a clear shade of green, a clear indication of a small amount of copper compound in solution.

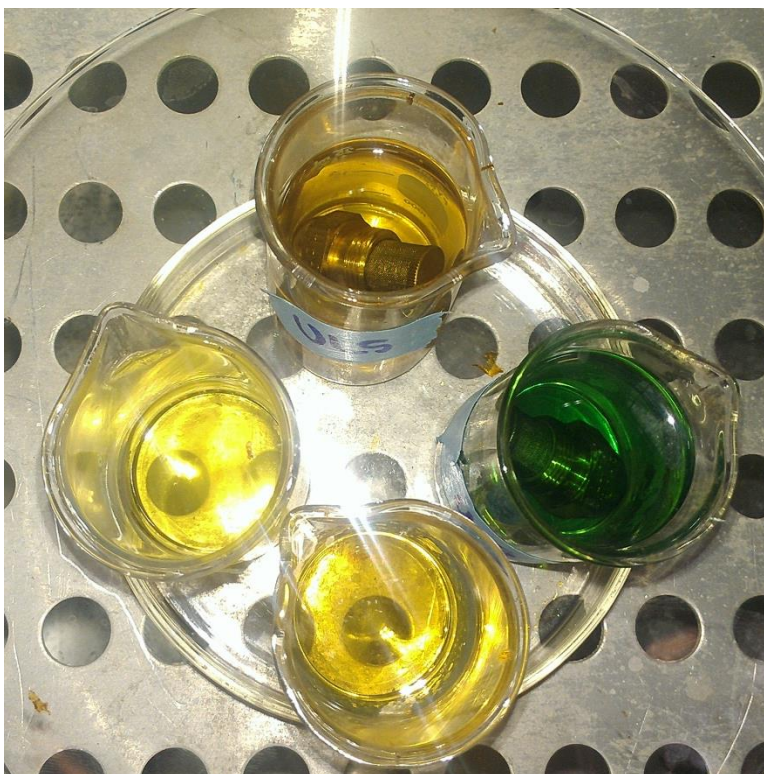


Figure 4-3 Samples of ULS (B0). Impact of extremely elevated acid number and a nozzle over one weekend at room temperature.

The results of several elevated acid number tests on the increase in acid number are summarized in Table 4-2, below.

Table 4-2 Results of High Temperature Yellow Metal Studies (All values are TAN – Total Acid Number)

	ULS Heating Oil	B 20 Blend	B 100	High Acid ULS	High Acid B-20
Pre- Exposure	1.43	1.22	1.23	10.9	11.1
Post-Exposure Without Nozzle	4.94	20.8	5.43	18.1	22.3
Post-Exposure With Nozzle	2.83	2.05	0.72	14.6	9.37

These results show that the acid numbers increase with exposure and considering the severe temperature and duration this would be expected. What is particularly interesting to us is that the presence of the nozzle in the sample container actually decreases the acid number. Again, one possible explanation for this is that the yellow metal is complexing with the organic acid, effectively neutralizing it.

After all tests the nozzles were examined for signs of corrosive attack. No obvious attack was found.

Discussion

The FTIR results from all the fuels exposed to metals at a high temperature (170 °F) for 5 weeks indicated no significant chemical structure changes. There exists a color change as well for the case with a fuel with an extremely elevated acid number. Specifically, the results from Figure 4-3 demonstrate the impact that high levels of organic acid has on interactions with the yellow metal. As a further observation, the nozzles exposed to the highly elevated acid number solution showed a dull surface appearance after exposure compared to the nominal acid number fuels. These results are the same for all fuels, with or without biodiesel indicating that there may not be a significant difference in the copper interaction between petroleum No. 2 oil and biodiesel.

Conclusion

In the tests reported in this section, B0 and biodiesel blends were exposed to brass and stainless steel nozzles at high temperature (170 °F) for much longer than they would experience in the field to determine any significant adverse impacts with the use of brass nozzles versus stainless steel. The acid number of the samples in brass was not found to be significantly elevated relative to the stainless-steel tubing. The color change when brass is present for all fuels observed was noticeable, sometime with a characteristic green color, indicating the likely interaction of copper with all fuels to a certain extent. The results from this high temperature exposure for longer periods of time than would be experienced in the field do not indicate significant adverse impacts with biodiesel or biodiesel blends with brass nozzles compared to that of B0, leading to the conclusion the presence of brass nozzles is unlikely to impact burner operation with B20 to a greater extent than B0.

5. Combustion Performance and Flame Sensor Response

Successful use of a fuel in home heating applications requires demonstration of acceptable combustion performance and satisfactory operation of the other combustion related components contained in a home heating oil system, particularly the flame sensor. Combustion of No. 2 heating oil in a home heating oil system is very different than combustion of No. 2 diesel fuel in a high-pressure compression ignition diesel engine, although heating oil and diesel fuel have very similar properties and are in many cases interchangeable.

In today's diesel engines, the fuel typically passes through an on-board fuel filter with nominal pore size between 2 and 30 microns into a high-pressure common rail pump and is atomized through a multi-hole injector into a closed cylinder. The tolerances of the high-pressure fuel pump and injectors are very tight, as fuel injection pressures commonly exceed 20,000 psi.

In a home heating oil system, fuel passes through a strainer and gear pump into a retention head style burner with a swirl pressure nozzle. The fuel filter, upstream of the pump and strainer is commonly rated for 10 microns. The burner atomizes fuel at 100-150 psi into an open chamber fire box. Fuel is lit by an igniter located close to the burner nozzle which provides a spark similar to that of a spark plug in an engine, which initiates open flame combustion of the fuel oil. The hot gases then flow through the convective section of the boiler or furnace, transferring heat to the boiler water or air, and then exit through the flue. Home heating oil systems are much less complicated and operate at higher tolerances and much lower pressures than today's high-performance diesel engines.

In comparison to the closed cylinder system in a diesel engine, heating oil systems are open flame systems and excess air (or excess flue gas oxygen, O_2) is always used to ensure essentially complete combustion. The amount of excess flue gas oxygen to insure good combustion, generally between 3% and 6% excess O_2 or 15% and 40% excess air to minimize smoke and ensure very low levels of carbon monoxide, is generally set by the installation technician when the burner is installed versus being controlled by an electronic control module found on diesel engines. The combustion performance and excess O_2 level is normally re-checked on services calls or when the nozzles are replaced, typically once every one or two years.

In a home heating oil system, the key aspects of acceptable combustion include providing reliable ignition under field conditions, a flame which is stable and does not pulse substantially, low potential for formation of carbon deposits on burner head and nozzle tip, and low levels of exhaust smoke and CO. Since properly operating home heating oil systems burn the fuel completely in excess air and emissions are low, emissions are not regulated like those of gasoline or diesel engines although sulfur dioxide emission are indirectly regulated through the fuel sulfur level. Due to this clean combustion, heating oil emission are typically not measured or monitored, with the exception of smoke and CO which are used in the field to ensure the heating oil system is properly tuned to avoid the practical issues of particulate buildup on boiler tubes and any appreciable amount of carbon monoxide in the home.

Each home heating system is also equipped with a sensor that detects if a viable flame has been established and is being maintained as fuel is being sprayed into the fire box. Most flame sensors in home heating systems are relatively low-cost cadmium sulfide photoconductors (commonly called a 'cad cell') which respond largely to visible light from incandescence in the combustion flame zone. This visible light is translated by the cad cell into a resistance value that can be used to stop the fuel flow in the event a flame is not established during ignition or is suddenly extinguished during normal operation.

Another option for flame sensing is photodiode-based systems. These have faster time response and can be used with a matched circuit to respond to the alternating part of the flame brightness signal. This provides better discrimination between the flickering light of a flame and the steady light from combustion chamber refractory. These sensors are commonly used in residential oil burners in Europe with highly recirculating burners which have less visible light. These sensors are also used in larger (commercial) boilers.

The goal of the work done in this area was to evaluate the proper atomization and combustion performance of biodiesel blends in conventional home heating oil burner systems and to determine any impacts of the presence of biodiesel on flame sensor operation and effectiveness. Prior studies have shown that biodiesel flames emit less light overall than petroleum-based flames and this is largely a function of particulate concentration in the flame zone. This impact was also studied during this project.

Experimental

As discussed in the introduction section, a general review of the combustion performance is included in Appendix I. Generally, biodiesel blends have combustion performance similar or better than that of petroleum-based No. 2 oil. Biodiesel has sulfur levels typically under 10 ppm and so sulfur dioxide emissions are reduced compared to home heating oils with higher sulfur values. Although NO_x emissions are not regulated and are not normally monitored or measured for home heating oil applications, in many tests in boilers and furnaces flue gas NO_x levels were found to be reduced with biodiesel but some results were reported to be similar to those with No.2 fuel oil. Smoke and CO emissions are typically as low or lower than with petroleum No. 2 heating oil.

During this project, additional experimental data was obtained specifically on the impact on combustion, excess air values, and flame sensor sensitivity to changing biodiesel content in delivered fuels. As an oxygenated and ultra-low sulfur fuel, biodiesel typically requires less combustion air and burns with less particulates than conventional No. 2 fuel oil. A conventional cast iron home heating boiler and a common retention head oil burner and cadmium sulfide flame sensor were used in these tests. While there are some small technical differences from manufacturer to manufacturer, this system is a good example of the vast majority of systems in the home heating oil market in the US. A fresh sample of B100 meeting ASTM D6751 was provided by a major biodiesel producer for these tests.

The fuel system was arranged with split suction so that the test fuel could be changed without shutting down the burner. Test fuels were located on lab balance for direct measurement of the mass flow rate. During these tests, the burners safety control was bypassed to enable direct measurement of the cadmium sulfide photoconductor resistance. With the common burner control used in these tests, a resistance level under 1600 ohms in steady state is associated with proper performance.

The testing was done in two phases. In the first, the burner excess air value was tuned as is normally done for a home heating oil system (i.e. low CO and smoke number) and set at approximately 4.75% excess oxygen (27% excess air) based on operating in steady state with B0. After this, the biodiesel blend level was changed and combustion performance measurements were made keeping the air flow control damper position fixed. This would simulate a home set up and running on conventional No. 2 oil switching to the higher blends without making any adjustment in the flame sensor operation or excess air setting.

In the second phase, the burner operated on just B100. The burner's air shutter setting was then changed to evaluate the impact on the flame sensor resistance as a function of flue gas O₂ measured in the exhaust.

Results

Figure 5-1 shows the impact of biodiesel blend level of fuel mass flow and shows an increase with increasing biodiesel content. It is well known that these nozzles have higher mass flow with higher fuel viscosity and this is likely the cause of this small increase.

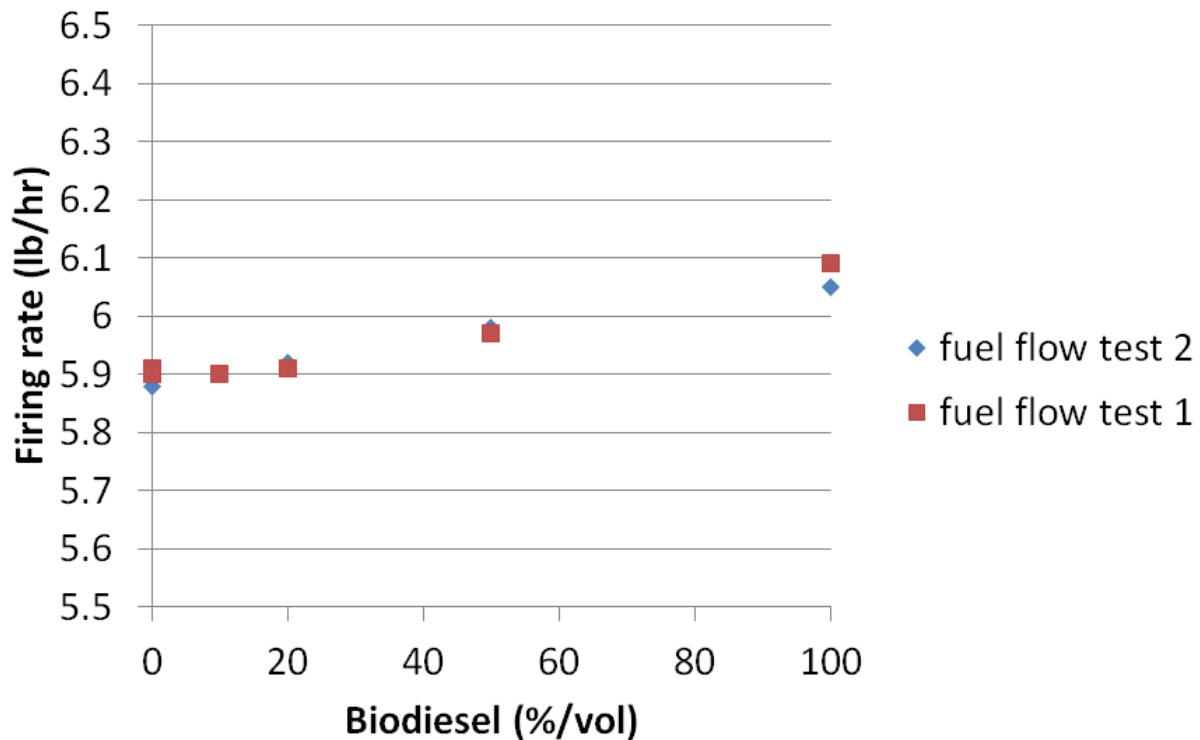


Figure 5-1 Fuel mass flow vs. biodiesel content.

In Figure 5-2 this fuel mass flow has been converted to a volume flow, based on density. In Figure 5-3 this is further converted to input rate (Btu/hr.) based on typical heating value of No. 2 petroleum heating oil and the heating oil reported by the fuel supplier for the test fuel. Figure 5-4 shows the measured flue gas oxygen content. In Figure 5-5 this flue gas oxygen content has been converted to excess air based on typical ultimate analyses for petroleum No. 2 oil and biodiesel. This is then calculated from the measured flue gas oxygen. It should be noted that in all these tests the flue gas CO and smoke number were negligible and so these would not affect the excess air calculation.

Figure 5-6 shows the resistance of the cadmium sulfide photoconductor flame sensor as a function of biodiesel content. At biodiesel levels above ~ 50% without changing the air setting this burner would have a cad cell resistance too high for reliable operation with the specific burner primary control evaluated.

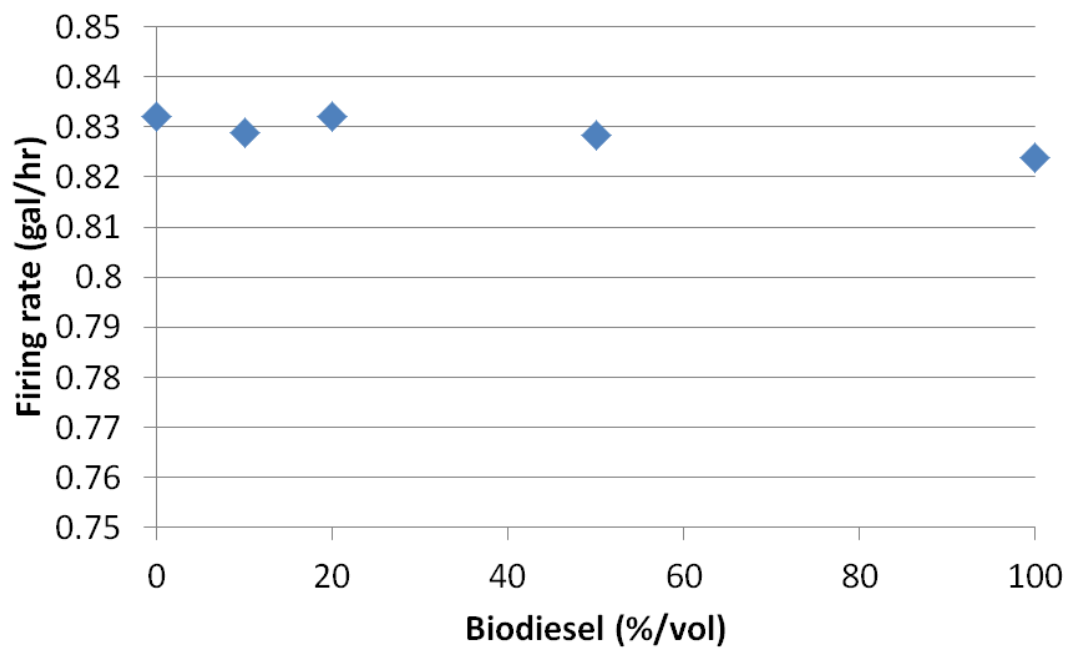


Figure 5-2 Fuel volume flow vs biodiesel content

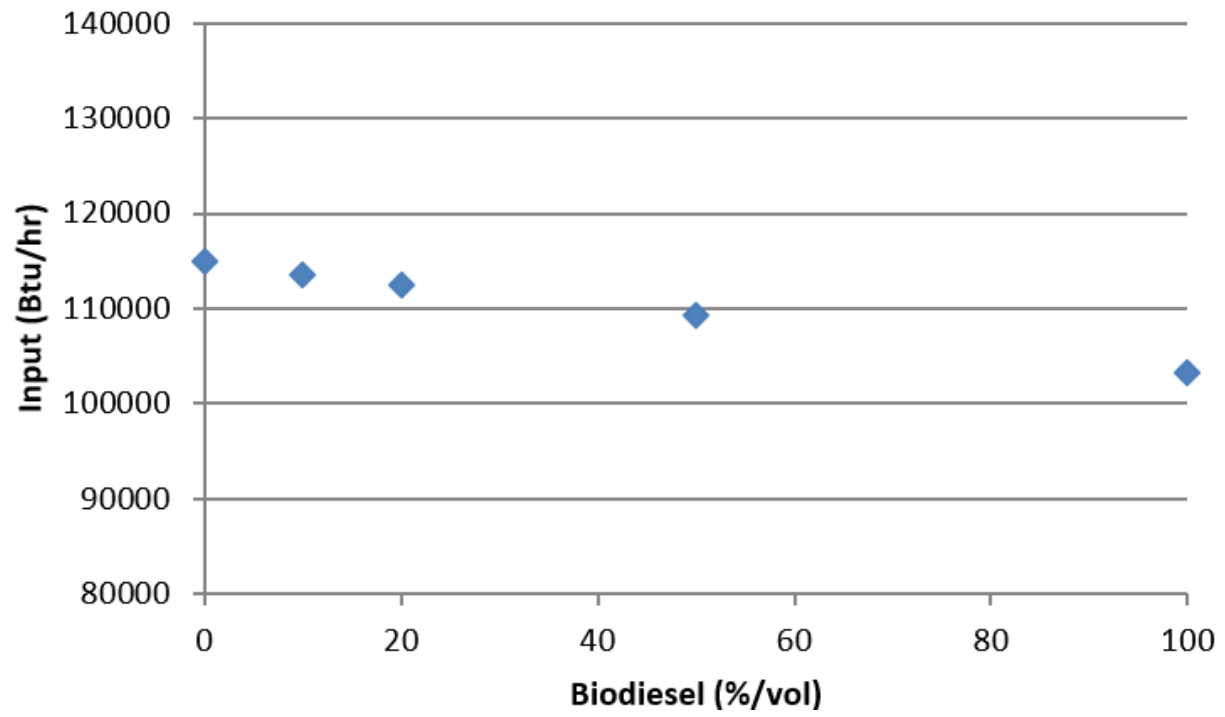


Figure 5-3 Fuel energy input rate vs biodiesel content.

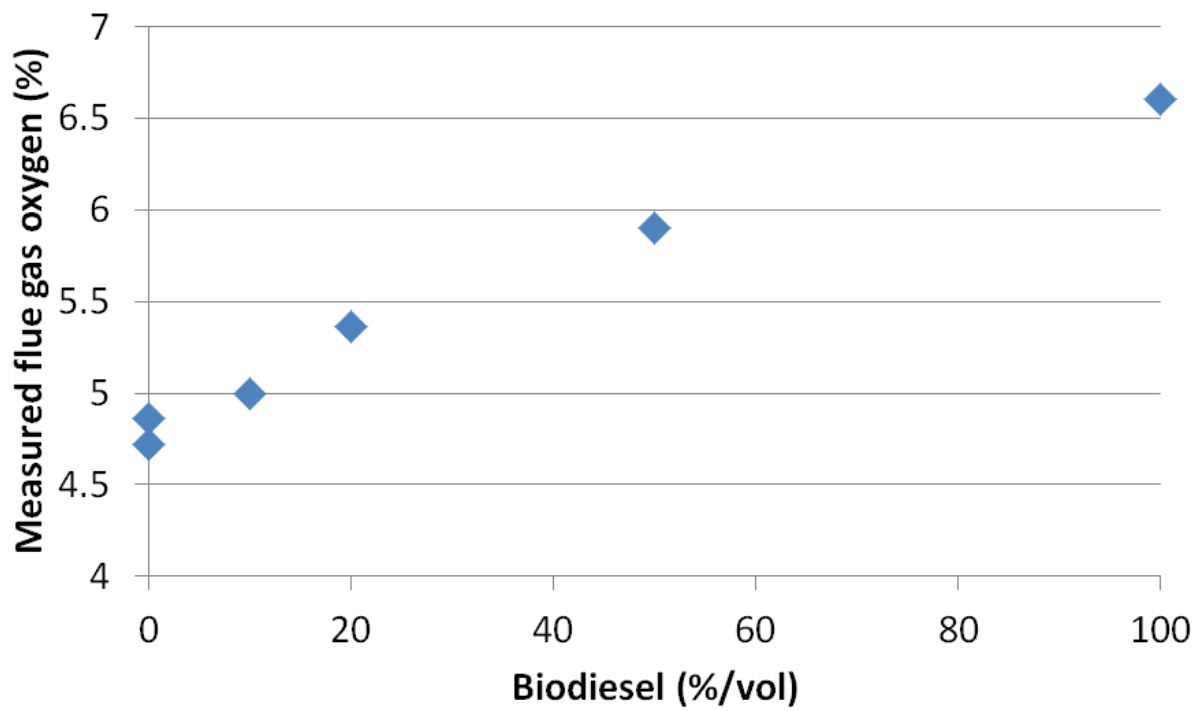


Figure 5-4 Flue gas oxygen vs biodiesel content

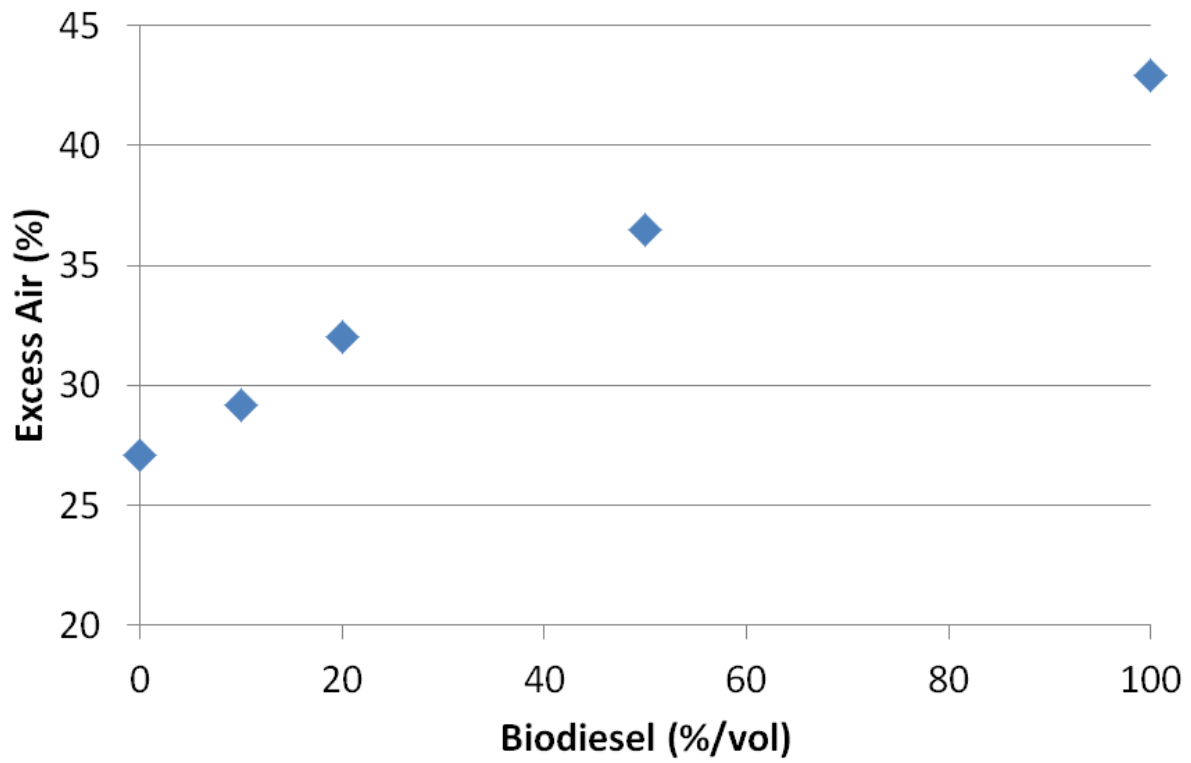


Figure 5-5 calculated excess air vs. biodiesel content

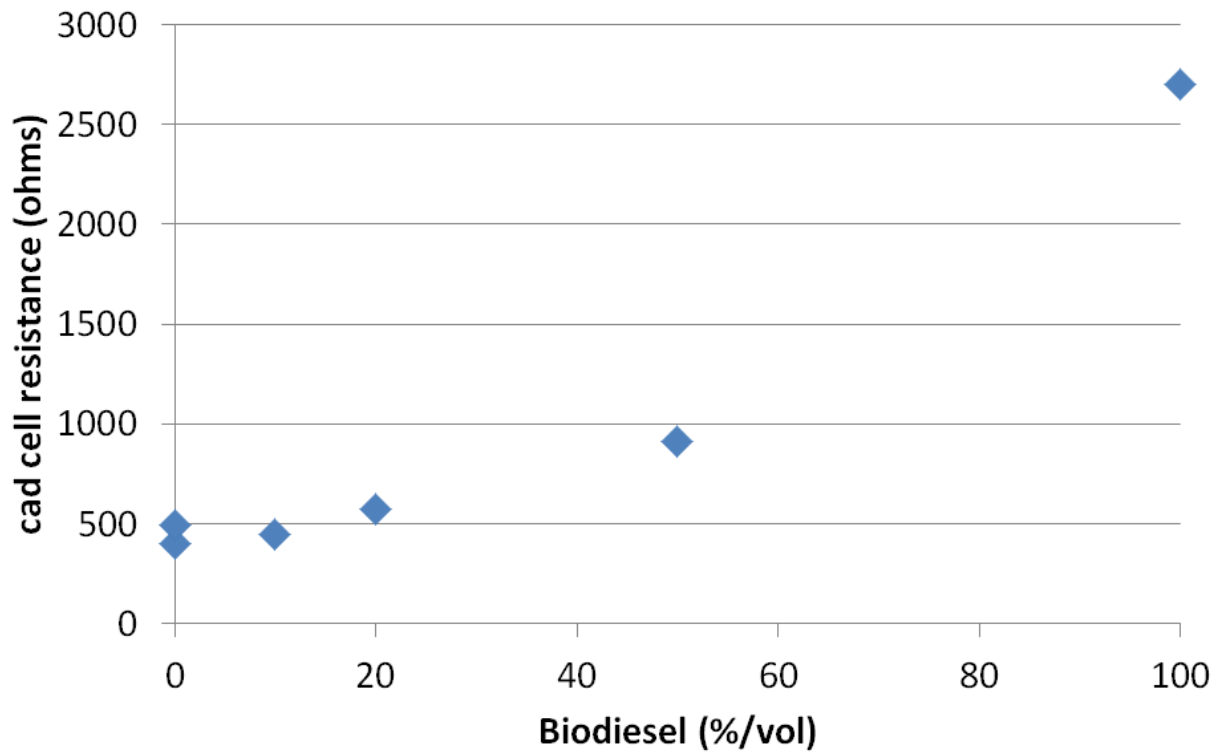


Figure 5-6 Cad cell flame sensor resistance vs biodiesel content

In the next phase of testing, at the B100 level the air shutter setting was adjusted. Results of this are shown in Figure 5-7 as a composite set of charts. This figure shows that the burner can be readjusted to a lower excess air point and this will bring the cad cell resistance down to a level acceptable for common operating controls without leading to an elevated level of CO or smoke.

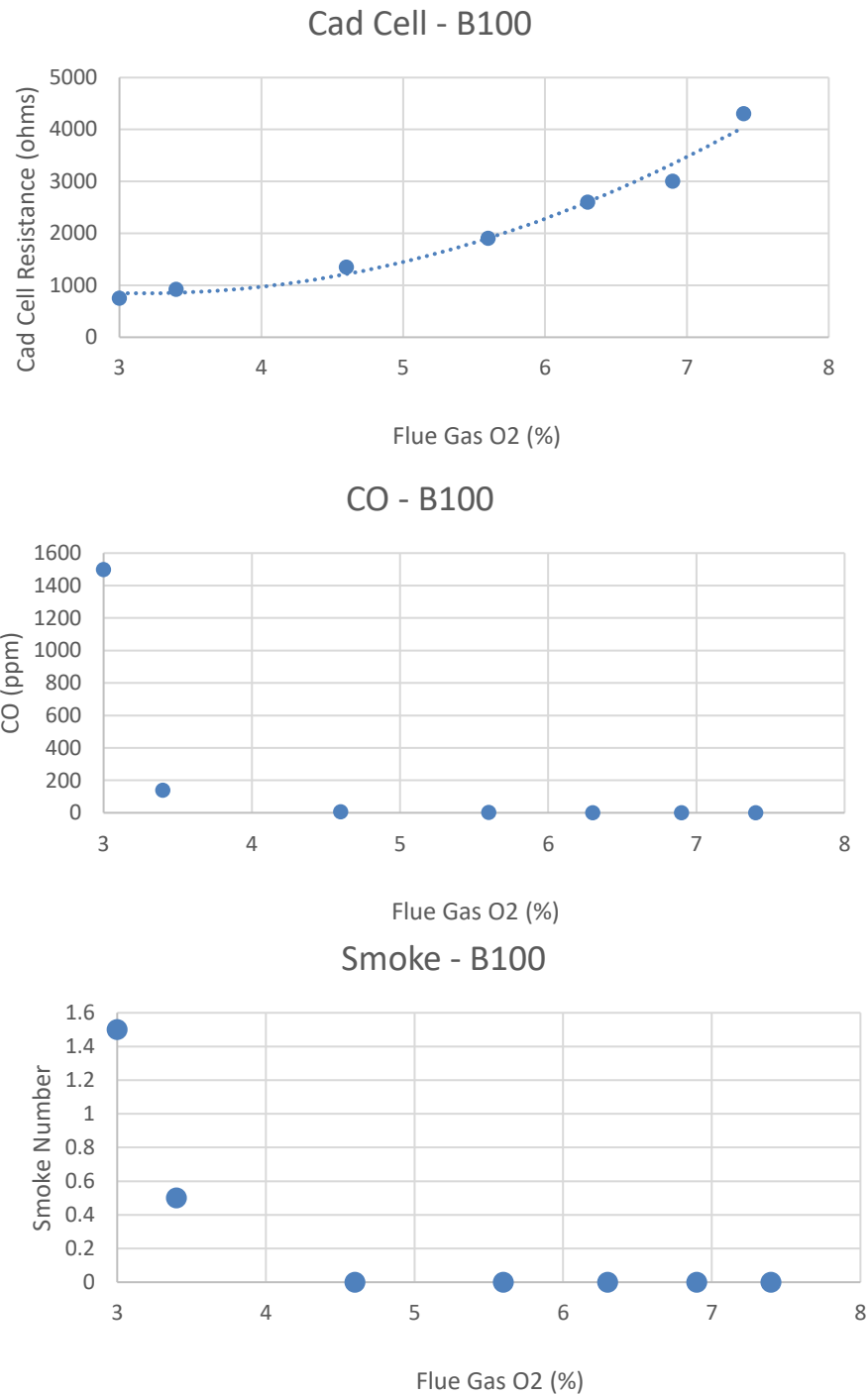


Figure 5-7 Testing at the B100 level. Cad cell resistance, flue gas CO, and smoke number vs flue gas O₂

Conclusion

The results in this section show that typical burners set up on No. 2 petroleum fuel oil can operate acceptably over the entire range of biodiesel blend levels without making changes in air/fuel ratio. However, as the blend level is increased, the operating excess air level will increase since biodiesel already contains some oxygen. The relatively small changes in B20 did

not affect flame sensor performance. As the blend level is increased above 50%, however, the increased excess air may affect the ability of some flame sensors to detect the presence of a flame, which could result in the premature shut down of a properly operating burner. Adjusting the air/fuel ratio to reduce the excess air with high biodiesel blends can bring the cad cell resistance down to a level acceptable for common flame sensors without leading to an elevated level of CO or smoke. If a unit has been adjusted to lower the air/fuel ration for high biodiesel blends, it will likely need to be readjusted if switching back to No. 2 oil to maintain adequate CO and smoke levels.

6. Review of Field Experience with Biodiesel Blends

Since about 2000 the use of biodiesel blends in the field has been steadily increasing. Initially this was laboratory research and focused field tests. This was followed by fuel marketers providing to their customer base biodiesel blends. The blend levels which have been and continue to be used by marketers vary. Many have been using low blend levels ~ B5. Others have been using B20 for all customers since ~ 2005. Still others have been distributing low blends to some customers and high blend levels to those who request it. This widespread use at different biodiesel blends represents an important experience base that can be used to identify technical concern areas.

Experimental

As part of our work to document field experience with higher biodiesel blends, we have planned and executed a survey of fuel oil marketers who have some involvement with bioheat blends. Our goals were to identify marketers who have significant experience with the use of higher blends and to evaluate clear technical limits which have been realized. The survey was arranged by the BNL Web Services Group, under a NoviSystems platform. The survey invitation was sent out for us by the National Oilheat Research Alliance (NORA) specifically to organizations which have registered to use the Bioheat[®] registered logo in order to capture biodiesel specific experience. A total of 85 responses were received. The survey was run in 2013 and the open period was only two weeks.

Of the respondents who reported they were using biodiesel blends, 32% reported they had used biodiesel for 3-5 years and 33% reported they had used this fuel for 6-9 years, indicating a strong historical experience.

Fifty eight percent of the respondents reported they delivered B5 blends and 13% reported they delivered B20 blends. Essentially all the respondents did not change any burner or system components when converting to biodiesel blends.

Table 6-1, below shows the response to a question about service problems related to use of biodiesel blends in the field. The results are very similar to earlier results from fuel surveys with No. 2 oil, indicating the biodiesel blends were performing similar to conventional No. 2 oil.

Table 6-1. Response to Survey Question on Biodiesel-Related Service Problems

Answer	Count	Percent answer
no unusual problems observed	40	55.56%
Fuel storage (sludge)	5	6.94%
Fuel filter blockage due to sludge	11	15.28%
Low temperature flow	4	5.56%
Corrosion	0	0.00%
Pump leakage	3	4.17%
Pump seizing or other pump problems	2	2.78%
Nozzle fouling	5	6.94%
Other	2	2.78%

Table 6-2 shows the results to a question about how many specific homes are at different blend levels. This shows the total number of reported homes across all respondents. It is very interesting to note that, at this time there were some 91,000 homes using B5. For blends between B10 and B40 the total number is 37,284. This shows that the use of biodiesel blends is quite well established and even higher-level blends are being used in a number of homes that is clearly past experimental use.

Table 6-2 Response to Survey Question on Number of Homes on Different Blend Levels.

Answer	Count	Percent answer
Up to B5	90711	68.25
b5-10	5328	4.01
b10-18	24521	18.45
b20	10330	7.77
b20-40	2397	1.80
b40-80	4	0.00
b80-100	380	0.29

As reported in Table 6-2 some 380 buildings were, at the time of the survey, using blend levels in the B80 to B100 range. From follow-up calls we are aware that some of these are on the west

coast but a large number are in New York City. It has been reported by fuel marketers that the number of B100 buildings in the city grew more recently to over 2000.

To supplement the field experience survey, samples of fuels were obtained for analysis from several fuel marketers who are using higher blend levels. The first of these is a marketer in Nassau County on Long Island marketing a nominal B20 blend. Fuel samples were taken from the bottom of tanks using a sampling equipment designed specifically for this purpose. Some of the analyses were done at BNL and some (Oxidative Reserve) were sent out to Southwest Research Institute. Table 6-3, below provides a summary of the test results. As shown, the oxidative reserve (Rancimat) test was done only for three of the ten samples.

Table 6-3 Result of Analysis of Biodiesel Blend Samples from Nassau County, Long Island.

Sample	Biodiesel Content	Water	Sediment	Acid No.	Oxidative Reserve (Rancimat)
	%	%	%	mg KOH/g	Hours
1	25.5	.05	.20	0.22	-
2	19.9	.25	1.15	0.21	0.5
3	20.3	0	0.30	0.20	-
4	20.3	0	1.50	0.21	-
5	6.4	.15	0.65	0.08	6.7
6	25.0	0	0.40	0.20	-
7	20.7	0	0.40	0.20	-
8	29.9	0	0.00	0.10	8.6
9	25.2	0	0.01	0.28	-
10	18.9	0	0.05	0.37	-

As shown in this table, the measured biodiesel content ranged from a low of 6.4% to a high of 29.9%. This range of variation, based on discussions with the marketer is simply due to delivery logistics. The marketer needs to take deliveries from a range of sources through the heating season. The acid number for all samples except for number 10 is below the limit of 0.3 in ASTM D396 for B20 blends and well below the acid number of 2 which was demonstrated to have potential issues with elastomers from earlier study. For the three samples tested for oxidative

reserve two, sample 5 and sample 8, were above the six-hour as-delivered minimum in D396 for blends up to B20. Sample 2 had an oxidative reserve of 0.2 hours indicating the oxidation reserve had been depleted, but the acid number was still quite low indicating the fuel had not changed to the point of being problematic.

Another sampling effort was undertaken in cooperation with a fuel marketer / service organization in Eastern Pennsylvania. This company was selected specifically because they market blends at levels greater than 20%. The actual blend used depends on market factors and logistical considerations.

Table 6-4 shows the list of samples and some observations provided by the dealer on tank age etc. Also shown is the biodiesel content, measured using an approximate FTIR method at BNL and Acid Number.

Table 6-4 Results of Analysis of Biodiesel Blend Samples from Eastern, Pa.

Sample	Biodiesel Content	Acid No.	Oxidative Reserve (Rancimat)
	%	Mg KOH/g	hrs
1	37.6	0.22	2.8
2	32.8	0.28	-
3	41.1	0.28	-
4	49.9	0.41	7.2
5	26.1	0.30	-
6	31.9	0.42	-
7	34.8	0.37	> 24
8	35.4	0.32	-
9	35.6	0.38	-

In this case the biodiesel content varied from a low of 26.1% to a maximum of 49.9%. The acid number specification for B100 as-produced is 0.5 mg KOH/g, so it is expected fresh blends with high biodiesel content will be between 0.5 and that of the base fuel oil. The base fuel oil acid number is normally low but it is not commonly measured as it is not part of the ASTM D396 specification for B5 and lower. The acid number values all fell below 0.5, far below the potentially problematic value in the range of 2. The as-produced oxidative reserve values for B100 is three hours minimum and for B6-B20 is six hours minimum. The oxidative reserve, measured for three of the samples was above six hours for two of the samples. For one of the samples the oxidative reserve was below six hours. This is an indicator the oxidation reserve had begun to be depleted but the acid number for that sample was low indicating the fuel had not begun to change significantly in-use.

Figure 6-1 shows the appearance of 4 of the samples taken. The two left samples show significant particulate content. The sample on the right has a clear water layer on the bottom.

This illustrates the conditions which are not uncommon in the field and that exist for conventional No. 2 oils with or without the presence of biodiesel.



Figure 6-1 Photos of fuel samples taken from Eastern Pennsylvania sites

Most of these tanks had their last deliveries in late winter/early spring so the fuels were in storage for most of the summer. After settling at BNL all samples were found to have solid deposits and/or water at the bottom and, again, this is to be expected with bottom samples. After settling all samples were found to be clear. None of the fuels in either the Long Island or the Pennsylvania study caused significant issues in use vs. that of conventional No. 2 oil according to the suppliers.

7. Conclusions

Based upon all of the studies completed during this project the following conclusions can be drawn:

1. For the specific nitrile material used in shaft seal in the most common oil burner pump on the market a clear limit on biodiesel blend level, above which the seal degradation becomes excessive, was not found. However, if the fuels become extremely acidic (i.e. over 2 mg KOH/g), the fuel can degrade these elastomers. None of the samples from the field had acid numbers over 0.5 mg KOH/g.
2. The long-term cycling pump tests done at Penn State University with the most common pump in the US home heating oil market showed that the leakage rate was lower with biodiesel blends than with No. 2 petroleum-based heating oil. All of these pumps have lip seals. In follow-on tests at BNL with pumps with carbon face seals, no leakage at all was observed with fuels with a range of biodiesel blend levels.
3. In copper exposure tests at room temperature in this study for six months, simulating summer shutdown, no impact of biodiesel on the copper tubing was found. A strong increase in acid number of fuel samples stored in copper tubes was not found. Further, old copper was not found to have less of an effect than new copper. Work on the copper impact is continuing.
4. At high temperatures, similarly, exposure to copper was not found to have a greater increase in acid number relative to exposure in stainless steel and no significant differences were found between biodiesel and its blends and conventional No. 2 fuel oil (B0).
5. In combustion tests it was found that due to the oxygen in the biodiesel increasing the biodiesel at a fixed burner air shutter setting increases the excess air and the cadmium sulfide photo conductor resistance (less sensor incident light intensity). At a high biodiesel content, the excess air can be tuned to achieve a proper sensor reading. If a burner is tuned at a high biodiesel level and then the fuel is changed to a B0 or very low biodiesel content fuel, it will likely need to be readjusted to maintain adequate CO and smoke levels.
6. Fuel samples of biodiesel blends from bottom samples of home tanks in the field have shown that biodiesel content can vary. Some of the field samples had depleted some of their oxidation reserve but none of the samples had elevated acid numbers indicating the fuel had not changed to the point of being problematic in the field.
7. Reported field experience with biodiesel blends has shown no clear technical issue compared to that of conventional No. 2 oil.

Overall, the results of this work have not identified a clear technical barrier which would limit the use of biodiesel in home heating systems. It should be emphasized that these results are only applicable to biodiesel which has been properly processed from its parent oil/fat into biodiesel and that meets the stringent ASTM D6751 specification for B100 prior to blending.

**Appendix I – Summary Reports Prepared on Selected Topics for
Submission to ASTM in Support of Evaluation of Changes to the ASTM
D396 Standard.**

Technical Summary

Combustion Performance of B-20 Biodiesel Blends in Residential Heating Appliances

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Brookhaven National Laboratory

April 2014

Introduction - Qualification of any fuel for use in the home heating market requires demonstration of acceptable combustion performance. Specific aspects of this include: reliable ignition under field conditions, flame stability, low air pollutant emissions, low potential for formation of coke on burner heads, and safe/reliable operation of the burner sensors and controls. Several important laboratory studies have been done on the combustion performance of biodiesel/heating oil blends in North America. Here, an overview of the key findings with an emphasis on blends at the B-20 level is presented.

Key Results—The technical data all indicate that B20 and lower blends will perform as expected in the existing equipment base without modification. Higher blends also perform as expected, however as blend levels approaching 100 percent adjustments to the flame sensor system may be required due to the cleaner burning nature of biodiesel.

Laboratory Studies -Initial laboratory testing of biodiesel as a fuel was done by the R.W. Beckett Corporation in 1993. Using conventional burners this involved a simple comparison of B-100 and normal heating oil of the S5000 sulfur grade with nominal sulfur level of 1500 ppm. In a later study at Beckett [1] a comparison was done of the NO_x and SO₂ emissions of heating oil, B-20, and B-100.

Results of testing with a variety of space heating appliances were reported by Batey in 2003 [2]. This study directly compared performance of a conventional heating oil with a B-20 blend of soy-based biodiesel blended into 500 ppm sulfur oil. Equipment evaluated included a commercial steam boiler, an older residential hot water boiler, a compact residential hot water boiler, an older residential warm air furnace, and two additional typical residential hot water boilers. The work focused on steady state CO, smoke number, and NO_x emissions.

In another lab study, reported by Krishna et.al. in 2001 [3] both startup and steady state performance of biodiesel blends and conventional heating oil were studied using a conventional residential boiler. Blend levels to B-100 were included. In the transient part of this study CO emission profiles from cold start were compared. High startup CO emissions are an indicator of poor ignition performance, and were compared and found to be independent of biodiesel content. Cold start in this case was with the boiler at 55 F, much colder than typical in normal field operation.

Win Lee et al [4] conducted a set of careful measurements in a test facility in Ottawa, Canada using a cast iron, residential hot water boiler. Tests were run on the baseline fuel oil and on a B20 blend made from a commercial soy biodiesel. These studies included particulate emissions as well as gas-phase emissions.

Key Results A common result from all of the studies done is that the basic burner operation with biodiesel blends at B-20 (at least) is the same as with unblended heating oil. Observations are that startup behavior and flame stability are seamless. This general observation was specifically documented in the transient CO measurements made by Krishna et.al. [3]. Another observation is that smoke number and CO emissions in steady state are either the same or lower than with unblended heating oil.

Most of the studies showed that NO_x emissions are lower with B-20 although in some cases, at some excess air levels similar NO_x levels were reported.

Sulfur dioxide emissions are a function only of the sulfur content of the fuel. Relative to unblended heating oil, biodiesel can be considered nearly sulfur-free and so reductions in SO₂ were observed in proportion. Similarly, it has been shown that most of the fine particulate emissions from small oil burners are due to sulfates and these emissions are directly proportional to fuel sulfur content. Again, this leads to lower emissions with the biodiesel blends.

In tests at much higher blend levels, to B-100, it was shown that the amount of visible light produced by a biodiesel flame is lower than that of a flame from unblended heating oil. This is most likely due to the lower particulate emission and cleaner burning nature of biodiesel. The practical implication of this is that it could impact the ability of the flame sensor to detect a viable flame with higher concentrations

of biodiesel and shut off the burner unnecessarily. The flame sensor is part of the flame safety control system whose function is to determine if there is a viable flame when fuel is flowing through the burner nozzle. This helps ensure unburned fuel does not accumulate in the burner chamber. If high biodiesel blends are used, the flame sensing system may need to be modified to insure the unit does not shut off due to a cleaner, non-detectable flame with high concentrations of biodiesel. There have been no reports of this as a concern at the B-20 level.

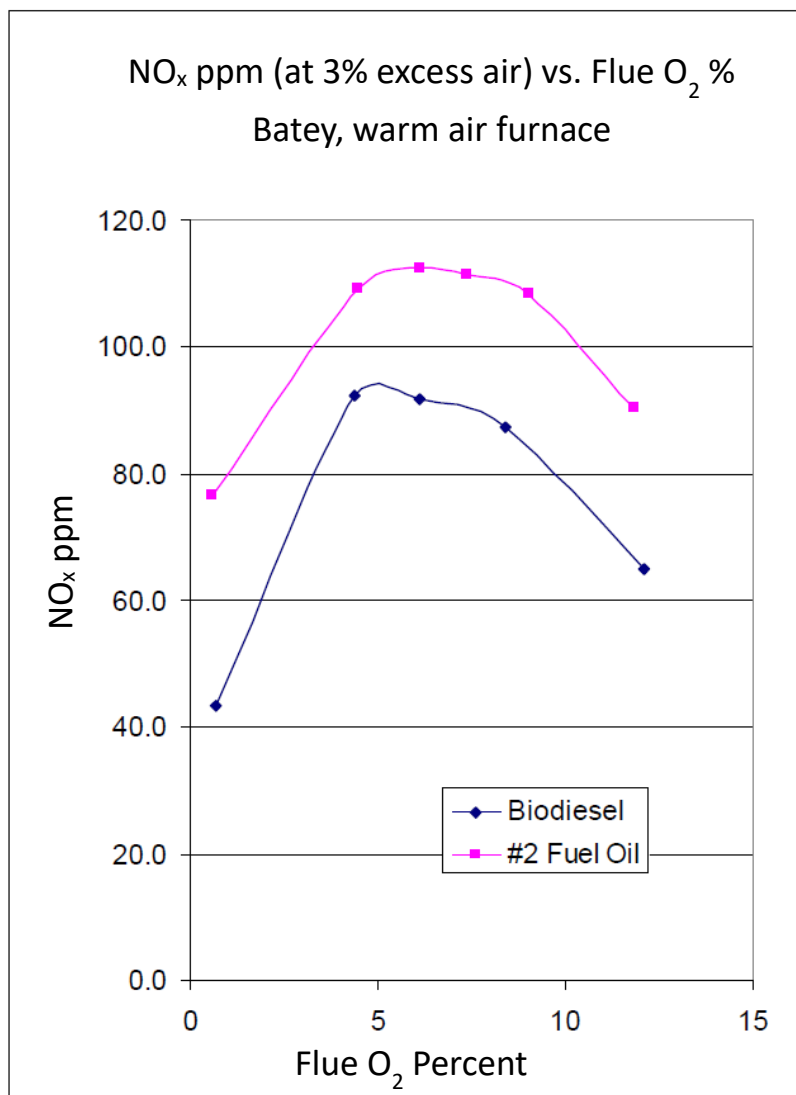


Figure 1 Example comparison of NO_x emissions, B-20 and unblended heating oil

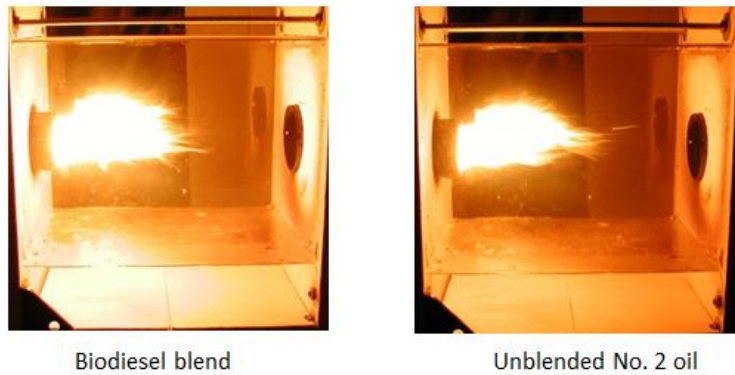


Figure 2 Comparison of the flame from a biodiesel blend and No. 2 oil.

References

1. Victor J. Turk, Factors affecting oil burner NO_x emissions, Paper No. 02-10, Proceedings of the 2002 National Oilheat Research Alliance Technology Conference, R. McDonald ed., Brookhaven National Laboratory Report BNL-52670 (2002).
2. John E. Batey, Combustion Testing of a Bio-diesel Fuel Oil Blend in Residential Oil Burning Equipment, Final Report to Massachusetts Oilheat Council and National Oilheat Research Alliance (2003).
3. C.R. Krishna, Yusuf Celebi, George Wei, Thomas Butcher, and Roger McDonald, Lab tests of biodiesel blends in residential heating equipment, Paper No. 01-14, Proceedings of the 2001 National Oilheat Research Alliance Technology Conference, R. McDonald ed., Brookhaven National Laboratory Report BNL-52670 (2001).
4. S. Win Lee, T. Herage, B. Young, Emission reduction potential from the combustion of soy methyl ester fuel blended with petroleum distillate fuel, Fuel 83 (2004) 1607–1613 (2004).

Technical Summary—Elastomer and Pump Durability of Biodiesel in Heating Oil Equipment

Key Result – Compatibility between biodiesel meeting ASTM 6751 and NBR (nitrile) elastomer seal materials historically used in oil burners is demonstrated to at least the B20 level.

Part 1: Compatibility of Heating Equipment Elastomer Seals and Biodiesel Blends

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April 2014

In this technical summary, a review of prior work done in the U.S. on the elastomer compatibility is provided, as well as specific compatibility of NBR seal materials common to heating oil system with biodiesel / heating oil blends is presented. The technical data from both short-term UL type testing (Part 1 below) and extended bench testing (Part 2 below) indicate current elastomers perform as expected in the existing unmodified equipment base when using B20 and lower biodiesel blends.

Introduction – For an alternative fuel to be used safely in home heating systems compatibility with the elastomeric seal materials in use is required. Seal changes, in the case of a non-compatible fuel are technically feasible but, with some 8 million home oil-fired systems, the requirement of a seal change would represent a significant market acceptance barrier.

In existing heating systems, the dominant seal material is nitrile (acrylonitrile butadiene rubber or NBR; an unsaturated copolymer constructed of acrylonitrile and butadiene monomers). The presence of the acrylonitrile monomer imparts permeation resistance characteristics to a wide variety of solvents and chemicals, while the butadiene component in the polymer contributes toward the flexibility [1].

Like any given polymer, the mechanical properties of NBR vary depending on its constituents. Differences in composition may be based on the acrylonitrile content used in synthesis (commercial nitrile rubber can vary from 25% to 50%), reinforcement fillers, plasticizers, antioxidants, processing aids, and cross-linking agents [2, 3].

In the process of obtaining a listing approval for a burner for application in this market testing is typically done guided by standard UL 296 which incorporates a material compatibility test for elastomeric materials, UL 157. This test involves an immersion period of $70 \pm 1/2$ hours at 23 ± 2 °C (73.4 ± 3.6 °F). Suitable elastomers are required to retain more than 60% of their unconditioned tensile strength and elongation and volume swell must fall within the range of -1 to + 25 %.

Previous Elastomer Compatibility Studies – In a study published in 1997 [4,5], Southwest Research Institute reported on their evaluation of a range of different elastomer types exposed to biodiesel / petroleum blends. Fuels included in this study included JP-8, B-100, low-sulfur diesel fuel, “reference” diesel fuel and blends at the B-20 and B-30 level. Samples were immersed at 51.7 °C (125 °F) for 0, 22, 70, and 694 hours.

In a more recent study [6], Southwest Research Institute and the National Renewable Energy Laboratory, evaluated the compatibility of several elastomers including 3 different types of nitrile in B-20 blends and ethanol-diesel blends. The nitrile materials included a general purpose

NBR, and high aceto-nitrile content rubber, and a peroxide-cured nitrile rubber. These materials were selected as being typical of materials used in automotive applications. Samples were immersed at 40 °C (104 °F) for 500 hours.

Tests reported in the early study by Southwest Research Institute [4,5] for elastomers common to diesel engines showed some effect of the biodiesel blend on the nitrile materials. This included volume swell in the 20% range and a reduction in tensile strength as high as 38%. These tests were done at much higher temperature and for much longer times than required by UL 157, but the magnitude of property change reported was still within the acceptable range under UL 157, although marginally. The later study reported on by Southwest Research and NREL [6] showed no significant effect of the biodiesel blends on the NBR materials studied, leading to the conclusion "...all of these elastomers appear to be fully compatible with 20% biodiesel blends".

In another, potentially relevant, study done by Underwriters Laboratories [8] the compatibility of B-5 blends with elastomers typically used in oil burner applications was studied in compliance with the UL157 standard. Two specific nitrile materials were included. The study conducted by UL [8] at the B-5 blend level also showed no significant effect of the biodiesel blend on the materials tested.

Elastomer Testing with NBR Used in Heating Oil Systems - As part of a new study [7] to evaluate the practical upper limit of biodiesel content in a blend with home heating oil, Brookhaven National Laboratory has completed compatibility tests with NBR at blend levels from 0 to B-100. In collaboration with the dominant manufacturer of pumps on legacy oil burners in the U.S., one specific NBR material commonly used in the heating oil industry was identified for evaluation. This is a high aceto-nitrile material used for the critical pump shaft lip seal. Slabs of this material were obtained from the manufacturer for use in these tests. Immersion was done for 670 hours at 51.7 °C (125 °F), conditions much harsher than that normally used to qualify seals per UL 157.

The studies at Brookhaven National Laboratory showed full compatibility between the NBR material used in common oil burner seals and biodiesel blends up to B-100. Figure 1 below, for example illustrates the effects on volume swell, which are described in more detail in the power point presentation attached, "Elastomers and Pump Durability of Biodiesel in Heating Oil Equipment, Brookhaven National Lab, April 2014". Results are similar for tensile strength, hardness, and compression set over the 670 hours regardless for petrodiesel and all biodiesel blends up to B100.

In an interesting part of the BNL study the effects of elevated acid number on NBR material properties was evaluated. It was shown that acid numbers well above the specification limits does lead to significant interaction with the NBR materials. In this test acid number was increased through the addition of decanoic acid and this effect is illustrated in Figure 2. It is postulated that elevated acid number caused by accelerated testing degradation contributed to observed effects of biodiesel on NBR materials in the earlier reported tests, especially since many of these earlier tests were completed prior to the addition of a stability specification for B100 and other changes to the B100 specifications which were implemented to secure the ASTM approval for biodiesel blends in 2008.

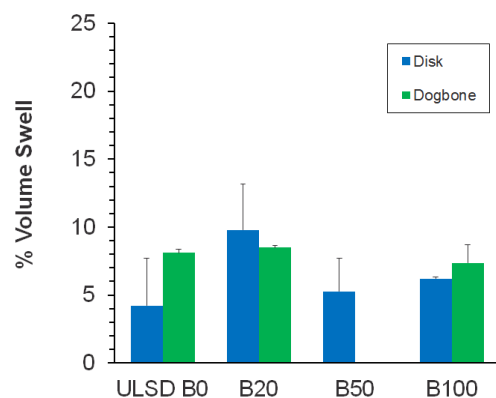


Figure 1. Example results, tests at BNL. Impact of biodiesel content in blend on NBR material volume swell.

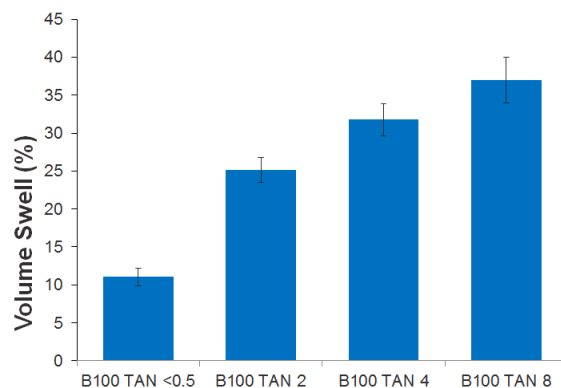


Figure 2. Example results, tests at BNL. Impact of acid number on NBR material volume swell in B-100.

References

1. Reichhold Chemicals, Inc., “What is Nitrile”, *Technicare Bulletin*.
2. S. Chakraborty, S. Bandyopadhyay, R. Ameta, R. Mukhopadhyay, A.S. Deuri., “Application of FTIR in characterization of acrylonitrile-butadiene rubber (nitrile rubber)”, *Polymer Testing*, **26** (2007) 38-41.
3. Tariq Yasin, Shamshad Ahmed, Munir Ahmed, Fumio Yoshii., “Effect of concentration of polyfunctional monomers on physical properties of acrylonitrile-butadiene rubber under electron-beam irradiation”, *Radiation Physics and Chemistry*, **73** (2005) 155-158.
4. Frame, E.A., G.B. Bessee, and H.W. Marbach, Jr., Biodiesel Fuel Technology for Military Application, Southwest Research Institute Interim Report TFLRF No. 317. Submitted to U.S. Army TARDEC (1997).
5. Bessee, Gary B., and J.P. Fey, Compatibility of elastomers and metals in biodiesel fuel blends, Society of Automotive Engineers paper 971690 (1997).
6. Frame, E., and R.L. McCormick, Elastomer Compatibility Testing of Renewable Diesel Fuels, National Renewable Energy Laboratory Report, NREL/TP-540-38834 (Nov. 2005).
7. Brookhaven National Laboratory and Stony Brook University, informal communication
8. Report on the Interchangeability of B5 Biodiesel within Residential Oil-Burner Appliances Intended for Use with No. 2 Fuel Oil, Underwriters Laboratories Report File: MP4132, Project 06CA55893 (May 2007).

Part 2: Impact of Biodiesel Blends on Durability of Oil Burner Pumps

Vic Turk – R. W. Beckett Corp.

and

Thomas Butcher- Brookhaven National Laboratory

April 2014

Introduction – A critical component in the fuel system of an oil-fired heating system is the burner pump. This unit performs the following functions:

1. Lifting the fuel from underground storage, clearing the fuel line air rapidly during initial operation;
2. Creating and regulating the required pressure for proper atomization, typically 100-150 psi.
3. Providing a “sharp” turn-on and turn-off of flow to the nozzle to prevent after-drip or injection of fuel under a low pressure, poor atomization condition.

The dominant manufacturer of the pumps in use in existing equipment in the field is Suntec Industries, with an estimated 90% market share for these installed units. This gear-pump includes a NBR lip-seal on the rotating input shaft. Potential leakage of this seal with biodiesel blends has been identified as a high priority area for evaluation in considering higher levels of biodiesel in heating oil.

Detailed bench level compatibility studies overviewed in Part 1 using elastomer slab samples provided by the pump manufacturer showed no impact of biodiesel blends up to B100 compared to conventional heating oil. To compliment these basic materials studies, a decision was made to undertake long term, cyclic durability tests with pumps. In the field, these burners and pumps cycle on/off 5,000 to 10,000 times annually, and it was desired to confirm the performance of the seals in actual pump operation.

The pump test was implemented at the Energy Institute of Penn State University with oversight by the industry Bioheat Technical Steering Committee. The pump manufacturer was very involved with the definition of the test setup and evaluation protocol. The methods were based on established methods used to evaluate candidate seal materials.

Pump Tests Conducted –The testing was planned to involve a 5-gallon fuel supply for each pump, setup in a continuous loop with a 5 minute on/ 1 minute off controlled cycling pattern. The piping was arranged without a fuel spray nozzle but the pump developed its full operating pressure each cycle. A photo of the setup is provided in Figure 1.

In the test program, a key performance measurement parameter was observed seal leakage rate. The project was started in 2010 but upon seeing some of the initial results it was discovered there was some confusion regarding the leakage rates measurements. The measurements were being done differently than that being used by the manufacturer. This was corrected, and all new pumps were installed and the test restarted.



Figure 1 Photo of pump test stands

The testing was done with two base fuels – a conventional No. 2 heating oil at 1500 ppm sulfur content and an ultralow sulfur heating oil at 15 ppm. Three different biodiesel blend levels were studied for each fuel – 0, 12, and 20%. The biodiesel was a commercial blended-feedstock fuel provided by Hero BX. This fuel met all requirements of ASTM D-6751-11. For each fuel blend a total of 7 pumps were run in this 7,000-hour test. Quality of all fuels was monitored throughout the project to insure the fuel had not degraded significantly during the test due to the stressing of the fuel in the test. Acid number was considered the primary criterion for this. High acid numbers were not observed, and thus the test considered acceptable from that standpoint.

Fuel pump shaft seal observed leakage was a key performance measure and this was monitored on a regular basis. The manufacturer provided a scale from 1 to 4 based on observed leakage. These are all very low leakage rates. For example, a No 2 leak is described as “wet seal with a slight accumulation in the seal cavity area”. A No 4 (highest) leak is actual fuel running down over the hub face. These leak rates likely would not be noticed in the field. A seal leak metric for the entire set of pumps was based on a weighted-percent-dry metric. The weighting penalizes a leak situation to a greater degree if it occurs early in the 7,000-hour test period.

Key Results – Figure 2 below provides a summary of the test results, which are described in more detail in the power point presentation attached, “Elastomers and Pump Durability of Biodiesel in Heating Oil Equipment, Brookhaven National Lab, April 2014”. In this figure the Seal Rating is used – a higher value indicates better performance. The most significant conclusions are:

- Seal performance improves with increasing biodiesel content
- Seal performance is equivalent at B0 for both 15 and 1500 ppm sulfur fuels
- Seal performance is better with 1500 ppm sulfur fuel than with the ULSD fuel at the same biodiesel level.

Two pumps “bound-up” in the 4600-5000-hour time frame. These were both at the B-12 blend level and both base fuels were involved. Other than this occurrence no operational problems were observed. Following these tests, the pumps were all shipped to Brookhaven National Laboratory for internal inspection. No unusual conditions or fuel related issues were noted from the inspection. Thusly, while both the seizures were with B12, it is not believed they were fuel-related.

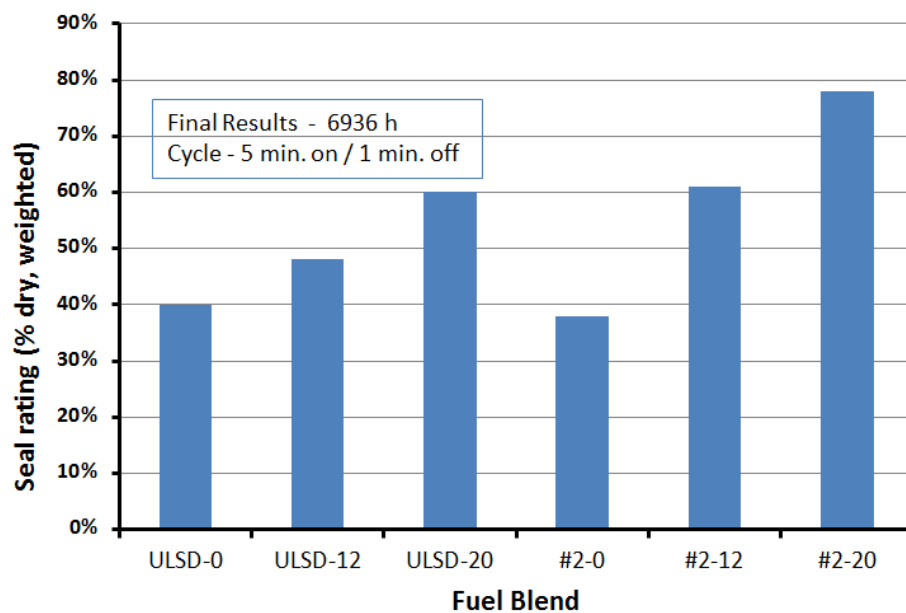


Figure 2 Overall results of pump stand testing. These results illustrate better performance (higher seal rating) as biodiesel content in blend increases.

Technical Summary

Biodiesel/ Heating Oil Blends – Evaluation of Yellow Metals and Tank Sludge

Brookhaven National Laboratory

April 2014

The industry group set up to identify the technical data needed to support higher levels of biodiesel than the current 5% allowed in D396 fuel oil in heating oil posed two additional areas of study in preparation for taking the data to ASTM. The two areas involved a more scientific evaluation of the impacts of higher biodiesel blends vs. fuel oil in yellow metals (i.e. copper, brass) common in fuel oil systems, and the potential for higher biodiesel blends to clean out tank bottom deposits or sludge common in fuel oil tanks. Brookhaven National Laboratory (BNL) conducted studies of biodiesel and biodiesel blends with fuel oils with biodiesel (B100) meeting the latest ASTM specifications which include parameters for acid number, stability, and lower levels of minor components. A power point file containing the information is attached “Biodiesel/Heating Oil Blends –Interaction with Yellow Metals and Tank Sludge, Brookhaven National Laboratories, April 2014” and the results are discussed below.

Key Results--The test results, which are corroborated with information from the field from fuel surveys conducted by BNL summarized elsewhere, indicate that B20 and lower blends meeting the proposed specifications—and made with B100 meeting the most recent D6751—will perform in a similar manner as conventional fuel oil in the existing unmodified equipment base regarding yellow metals and tank sludge.

Introduction – The industry technical steering committee raised two possible additional operational concerns relative to the use of biodiesel/heating oil blends at blend levels greater than B5. This includes 1) interactions between yellow metals (copper and brass) and 2) potential increased initial filter service due to “solubility” of pre-existing sludge deposits in the fuel.

In diesel engines systems, yellow metals are not recommended for use with either conventional diesel fuel or for biodiesel blends. In diesel engine systems, yellow metals can catalyze the oxidation of the fuel to create troublesome sediments that adversely affect fuel filtration equipment (i.e. 2-10-micron filters on today’s diesel engines) and tight tolerance diesel engine fuel injection equipment, especially today’s high-pressure common rail fuel injection systems. Previous studies have indicated this potential for diesel engine systems [1, 2, 3]. Based on this possibility, the National Biodiesel Board has traditionally not recommended copper containing materials be used with biodiesel or biodiesel blends. However, copper lines and brass burner nozzles are common in-home heating oil systems in the US, and the use of copper lines is actually required by local code in many cases regardless of the known issues with both conventional fuel oil and copper.

Fuel surveys from biodiesel use in the field over the last several years (summarized elsewhere) did not, however, indicate additional issues or concerns with biodiesel blends vs. conventional fuel oils. The industry steering committee wanted to see more science and bench testing of this phenomenon with equipment specific to the conventional installed heating oil base to further understand the specifics of the impacts of blends over B5 compared to conventional fuel oil that could corroborate or explain the relatively positive field experience.

In small heating system applications such as homes and commercial buildings, the fuel is not exposed to high temperatures for most of the system. Fuel storage, transfer to the pump,

recirculation back to the storage tank (if configured in this way) and delivery to the fuel nozzle are done at temperatures near ambient. During combustion, the fuel nozzle can be heated by radiation from the flame zone but is also directly cooled by combustion air passing over it and relatively cool fuel flowing through the nozzle. Temperatures approaching 100 °F can be reached [4]. After a burner cycles off and the air flow stops, the highest nozzle temperatures are observed for time periods on the order of minutes until the combustion chamber cools. When the burner restarts at the next call for heat the fuel in the nozzle flows out into the combustion chamber. Peak nozzle temperatures depend on the type of appliance fired into but can reach 175 °F. The filters or screens used in heating oil units are also typically much larger than those in diesel engines, approximately 90 or 100 microns for heating oil vs. 2-10 microns for engines. Both brass and stainless-steel nozzles are in use in small burners and these nozzles are typically replaced annually.

Oil storage tanks in small systems may be in service for time periods approaching 30-40 years. These systems are rarely cleaned and the gradual accumulation of products of the degradation of petroleum oil is common. In the diesel engine market, it has been reported that use of B20 blends can sometimes dissolve or clean-out this tank bottom material, resulting in initial engine fuel filter changes when first changing to a B20 blend. After the system is cleaned, then fuel filter changes revert to the normal frequency. This has not been widely reported with B20 in the heating oil market, and the industry steering committee was also interested in more science and bench testing regarding this phenomenon as part of the consideration for higher biodiesel blends.

New Experimental Bench Test Data – Both the practical impacts of yellow metal interaction in residential heating systems and the question of sludge dispersion were evaluated in tests done at BNL at the recommendation of the industry steering group. For the yellow metal interactions both low and high temperature was evaluated. In the low temperature tests copper tubing was used as the reaction vessel and both new and “old” copper were evaluated. The old copper was fuel system tubing removed from a heating system after approximately 30 years of service. Stainless steel tubing was used as a control. The tubing was stored in a vertical position, filled with different fuels at ambient temperature for 6 months. This time period was selected as typical of a summer shut-down period for a heating system.

For the higher temperature evaluation, fuel atomizers, both brass and stainless steel were exposed to both petroleum heating oil and B100 for periods up to 5 weeks at a nominal 175 °F storage temperature. In some of these tests the TAN of the samples was artificially elevated to explore the influence of a severely degraded fuel.

Biodiesel (B100) meeting the latest version of ASTM D6751 was used for blending and testing. This version includes parameters for acid number, stability, and control of minor components through the cold soak filtration tests that were implemented in 2008.

In the sludge/biodiesel solvency tests, samples of sludge from the bottom of a storage tank operating in the field for several decades was collected in cooperation with an oilheat service company. It is common that some sediment in existing tanks is disturbed when filling the tank, with the sediment settling back to the bottom of the tank after sufficient settling time. The solvency effect was studied using several metrics including fraction of sludge dissolved based on a filtration test, setting rate of dispersed sludge, size distribution of dispersed sludge, and FTIR analysis of base fuels following exposure to sludge. The size distribution measurements were made using a Lasentec Model FBRM D600 optical probe.

Key Results – Exposure tests of the new copper, old copper, and stainless-steel tubing samples in biodiesel blends for 6 months at room temperature showed no visible damage to the material and no changes in acid number. We attribute this result primarily to the ASTM B100 specifications which have put tighter controls on acid number, stability, and minor biodiesel components, as well as the lack of higher temperatures.

In the exposure tests at high temperature for 4 weeks, no damage to either stainless steel or brass nozzles was observed. Fuels in this test included B0, B20, and B100. For all test fuels, including the base fuel oil containing no biodiesel, the acid number was found to increase over the test period at these high temperatures. The acid number at the end of test was highest for the base fuel, but none of the fuels saw an acid number increase to levels that are expected to create issues with elastomers. It is interesting to note, however, that acid number increased to a greater degree in control sample containers which did not contain nozzles than in sample containers which did contain either brass or stainless-steel nozzles. Since the biodiesel blends in this high temperature test fared as well or better than the base fuel oil, this helps to explain the relatively positive results seen in the field survey. Again, we postulate the controls for acid number, stability and minor components at the B100 contributed significantly to these results, as there are no current controls in conventional fuel oil for acid number or stability.



Figure 1 Fuel nozzles exposed to B20 blends for 4 weeks at 175 F. Left - brass nozzle, Right - stainless steel nozzle.

In some of the high temperature nozzle tests, similar to the doping that was done for the elastomer testing, the fuel was modified at the start of the test to have an extreme acid number (TAN 10) by addition of decanoic acid. In this case, only with brass nozzles, the fuel after weeks of exposure was found to have the characteristic dark green color attributable to copper compounds. A similar result has been found in other studies with longer term, high temperature exposures where high acidity was generated due to fuel. This serves to confirm severely degraded fuel that is high in acid number does see adverse effects, but the current proposed specification for B20 and lower serve to prevent this phenomenon.

In the solvency tests, sludge from the bottom of a storage tank operating in the field for several decades was mixed with both conventional fuel oil and with B100, with B100 being considered a worst case, and analyzed by several means. The results found the sludge to be no more soluble in biodiesel than in conventional fuel oil, based on filtration mass tests. Measurements of the size distribution of dispersed sludge particles indicated no difference between B100 and B0 base fuel. Settling rate tests indicated a slower settling rate in B100 relative to B0, with the sediment moving eventually to the bottom of the container for both fuels. The slower observed setting rate in B100 can be accounted for based on viscosity and density differences, and with the proposed specification of viscosity for B20 and lower blends the same as that for conventional fuel oil this bench test serves to corroborate the field test results showing no significant difference with B20 and lower blends for this phenomenon in the existing installed base. It is also postulated that the relatively larger size of heating oil filters vs. diesel engine filters also plays an important role in this phenomenon in the field.

References

1. M.A. Fazal, A.S.M.A. Haseeb, and H.H. Masjuki, Comparative corrosive characteristics of petroleum diesel and palm biodiesel for automotive materials, *Fuel Processing Technology*, 91 (2010) 1308-1315.
2. S. Norouzi, F. Eslami, M. Wyszynski, and A. Tsolakis, Corrosion effects of RME in blends with ULSD on aluminum and copper, *Fuel Processing Technology* 104 (2012) 204-210.
3. D. Cursaru, G. Brănoia, I. Amadan, and F. Miculescu, Degradation of automotive materials upon exposure to sunflower biodiesel, *Industrial Crops and Products*, 54 (2014)149-158.
4. Butcher, T., F. McNeill, Y. Celebi, and J. Wegrzyn, Impact of Burner Design Features on Sooting in Residential Oil-fired Systems, Brookhaven National Laboratory Report, BNL 52102 (1986).

Technical Summary

Industry Survey on the Use of Biodiesel (Bioheat®) Blends

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April 2014

Introduction – Bioheat® is a trademark maintained by the National Oilheat Research Alliance (NORA). The term refers to the use of biodiesel / heating oil blends for stationary boiler and furnace applications. Fuel marketers obtain a license for the use of this trademark for the purpose of advertising their offering of these blends. The use of Bioheat® is now common and while most marketers have been offering blends at the B5 or lower level, there have been numerous informal reports of marketers using higher blends, even to B100. This large base of experience with B5 blends and blends at higher levels could provide an opportunity to learn and document the field experience with this relatively new fuel, and to understand any differences in the magnitude and type of operational problems which have occurred vs. those considered normal within the heating oil business. Thousands of homes using this fuel present a level of experience which is not possible to replicate in a laboratory environment.

Key Result: The results from the in-use fuel survey, which include over 13,000 buildings using at least B20, show that B20 and lower blends operate in the field in a similar manner as that of conventional heating oil. Thus, based on this survey B6-B20 blends will operate as expected in the field.

Bioheat® Use Survey – In 2013, an initiative was made to attempt to capture the experience that the fuel marketers involved with Bioheat® have had. The set of marketers chosen to invite to participate was the list of companies which had taken the Bioheat® trademark license from NORA. This group then represented companies which were clearly involved with or interested in Bioheat® use.

A survey to collect the data was developed by the Brookhaven National Laboratory (BNL) Information Technologies Division, based on a commercial on-line software tool – Novi Survey. A complex survey flow chart was developed to feed specific survey questions to specific groups. For example, groups which have not used Bioheat® were asked why and then the survey was complete. Groups which have used Bioheat® were asked detailed questions about their experience, system service requirements, and plans for the future. The survey focused on groups which have explored or regularly use Bioheat® blends at levels over 5% to capture their experiences and any areas of concern. Participants were invited by email and the survey was open for a two-week period in February, 2013. A total of 78 companies responded to the survey. Some of the questions refer to Bioheat® generally and, in this case, the fuel actually used could be anywhere from B5 to B100. Other questions were focused on the higher-level blends.

Findings – A detailed analysis of the survey responses is provided through the software, with more detail available in the power point slides attached, “Bioheat Use Survey, Dr. Tom Butcher, Brookhaven National Laboratory, April 2014”. Key findings can be summarized as follows:

- 81% of the respondents have used Bioheat®. Of the 19% who did not, the most common reason stated was lack of interest.
- Of those who have used Bioheat®, 93% are still using this fuel.
- 67% of those using Bioheat® have more than 3 years of experience with this fuel. 35% have more than 6 years of experience.
- For those using Bioheat® generally, 56% reported no unusual problems when using biodiesel blends. For the rest the results were distributed among the service requirements normally associated with no. 2 oil and were at a level consistent with that experienced with conventional heating oil [1]. This is illustrated in Figure 1, below.
- For those using blends over B20, 57% reported no unusual service requirements.
- For all respondents, a total of 90,711 buildings using Bioheat® blends at levels up to B5 were reported. A total of 37,632 buildings reported using Bioheat® at levels of 10% or greater, and 13,111 reported using B20 or greater. 380 buildings were reported to be at the B80 to B100 level. This is illustrated in Figure 2.

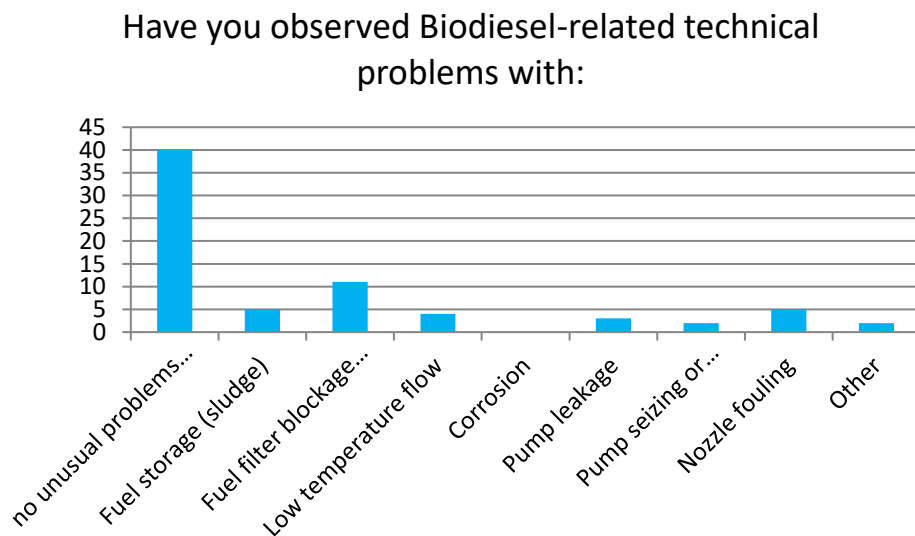


Figure 1 Survey results - reports of technical problems with all Bioheat® users.

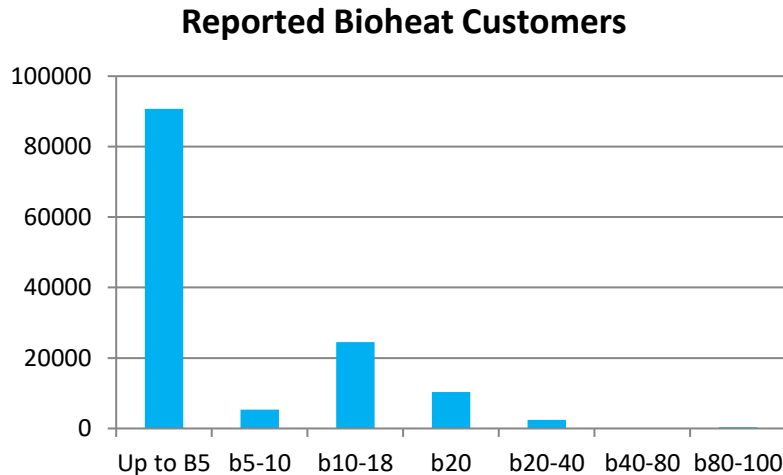


Figure 2 Survey results- number of buildings using Bioheat® at different levels

Regarding the service concerns illustrated in Figure 1: fuel quality, degradation in storage, related service requirements, and performance-enhancing additives have been high priority topics for the heating industry for many years, predating the use of biodiesel in heating oil blends. An industry survey in the early 1990's showed that fuel-related service requirements such as nozzle fouling, filter blocking, cold flow, and sludge formation in tanks dominated service requirements [2]. A broader survey in early 2000's including 65,000 service histories showed similar results [3]. One response to these concerns was the publication of an industry guide to fuel properties and problems in 2004 [4].

References

1. Personal discussion with Vic Turk, R.W. Beckett; April 2013
2. Coughlin, R.T., *Fuels, fuel quality, and storage*, in Proceedings of the 1990 Oil Heat Technology Conference and Workshop, R. McDonald and J. Andrews editors, Brookhaven National Laboratory Report BNL 52284, pp.123-136. Nov. 1990.
3. Litzke, W.L., and Hedden, R., *National Oilheat Research Alliance fuel performance research update*, in Proceedings of the 2003 National Oilheat Research Alliance Technology Symposium, R. McDonald editor, Brookhaven National Laboratory Report BNL 71337, pp.45-62. June 2003.
4. Litzke, W.L., A Guide to Fuel Performance – The NORA Fuel Quality Manual, published by the National Oilheat Research Alliance, August, 2004.