B20 to B100 Blends as Heating Fuels

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The following is an excerpt from *B20 to B100 Blends as Heating Fuels*, released November 2018

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 ±1/2 hours at 23 ± 2 ºC (73.4 ± 3.6 ºF). 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 ºF) 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 ºF) 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 compatibly 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

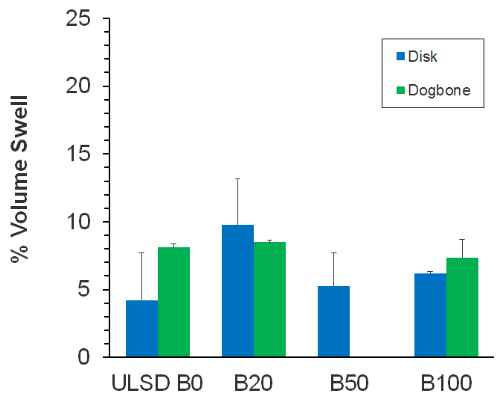

Figure 1. Example results, tests at BNL. Impact of biodiesel content in blend on NBR material volume swell.

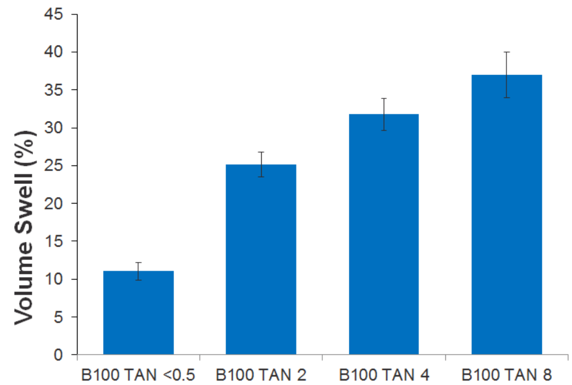

Figure 2. Example results, tests at BNL. Impact of acid number on NBR material volume swell in B-100.

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.

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).

<u>**Part 2: Impact of Biodiesel Blends on Durability of Oil Burner Pumps**</u>

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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.

Figure 1 Photo of pump test stands

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.

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.

<u>Key Results</u> – 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.

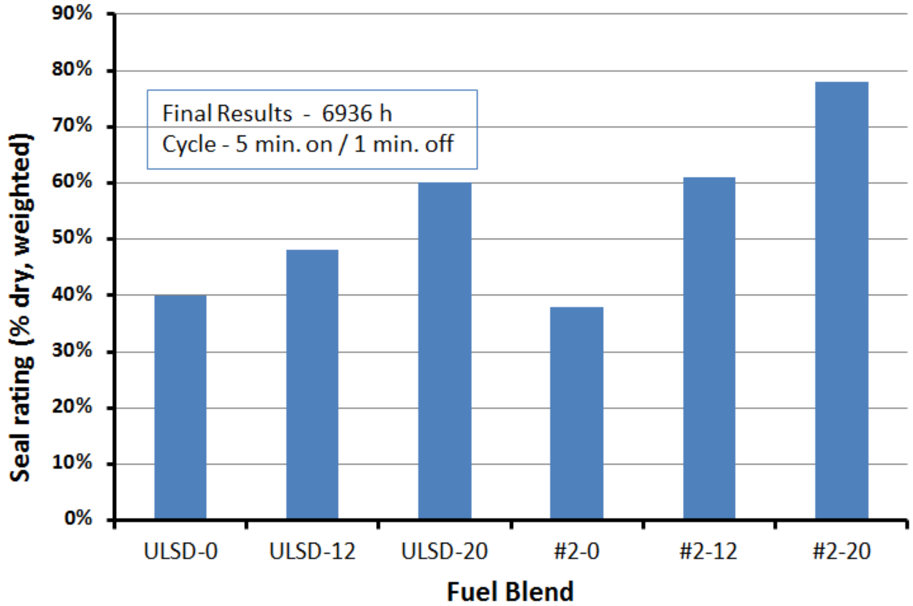

Figure 2 Overall results of pump stand testing. These results illustrate better performance (higher seal rating) as biodiesel content in blend increases.