Technical Summary

<u>Biodiesel/ Heating Oil Blends – Evaluation of Yellow Metals and Tank Sludge</u>
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.

<u>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.</u>

<u>Introduction</u> – 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.

<u>New Experimental Bench Test Data</u> – 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 5 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

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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).