

Interaction Between Biodiesel and Pre-existing Heating Oil Tank Sediment

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Abstract

It has been reported that biodiesel fuels, when mixed with middle distillate petroleum fuels such as diesel or No. 2 heating oil, have a solvency effect, which can clean pre-existing tank deposits and lead to increased maintenance for downstream components such as filters, at least initially. The purpose of the work described in this report was to quantify this solvency effect as it may impact preexisting sediments on the bottom of heating oil storage tanks. This is relevant to the displacement of petroleum fuels in heating boilers through biodiesel blends and blends with 5% biodiesel are targeted. Several different measures were used. In initial testing, dried sediment samples were dispersed in 100% biodiesel and then filtered to provide a bulk measure of the fraction dissolved. In a second series of tests a laser system was used to measure the particle size distribution of sediment dispersed in No. 2 oil and biodiesel. This was complimented with high resolution photos of the dispersed particles. Finally, the FTIR spectra of biodiesel and biodiesel in which sediment was dispersed and then allowed to settle were compared to quantify chemical changes which may occur in the biodiesel from the sediment exposure. All of these tests failed to show any level of solvency.

In an additional series of tests, the settling rate of sediment in heating oil, a 5% biodiesel in heating oil blend, and 100% biodiesel were compared. Results clearly showed a much slower settling rate in the 100% biodiesel. Consideration of simple Stokes Law settling and the results above leads to the conclusion that the slower settling rate is due to higher viscosity and density of the biodiesel. Settling rates in the 5% blend were essentially the same as for the No. 2 oil.

Introduction

Biodiesel fuel consists of methyl esters derived from virgin or used vegetable oil. This fuel, produced to ASTM D 6751 specifications is currently available on the U.S. market for blending with diesel fuel or heating oil and the later application is the specific focus of this work. Interest in the heating oil application is increasing rapidly and currently many retail heating oil marketers are offering customers blends ranging from 2% (“B-2”) to 20% (“B-20”) [1].

In all fuel oil storage systems degradation of fuels occur over time due to oxidation and biological activity and this can lead to the formation of sediments which can cause operational problems [2,3]. This is of particular concern in building heating applications where fuels are often stored for much longer periods that in vehicles.

It has been reported that biodiesel can act as a solvent against pre-existing sediment deposits [4], leading to increased rates of filter replacements when first used and cleaning of fuel systems. For building heating applications the impact that biodiesel can have on service requirements is an important consideration that could impact reliability and acceptance. The main objective of this study is a quantitative evaluation of this solvency effect and the potential impact of biodiesel use on pre-existing sediment in heating systems.

The basic approach has been laboratory studies with some limited, complimentary field studies. In the laboratory tests were performed of the dissolution of representative sediments in heating oil, heating oil/biodiesel blends and pure biodiesel. Measurements were also made of the size distribution of redispersed sediments in these same fuels and settling rates. Details of the methods used are provided in the next section.

Experimental

Tank sediment samples were obtained from heating system service organizations which collected relatively large samples from tank removal / replacement operations. The samples collected were combined and vacuum filtered to a uniform consistency level which was essentially a dry cake. It is recognized that these dried sediment samples which were used in all laboratory tests contained some residual, adsorbed oil and consideration was given to use of solvents to remove this oil residue. This was not done, however, to ensure that the sediments were as close to those found in actual storage systems as possible.

For initial tests, weighed amounts of the “dried” sediment deposits were blended with clean fuel samples using a simple mixer until the sediments were fully dispersed. In initial tests of solvency, these samples of dispersed sediment in fuel were filtered to determine the fraction of the added sediment that could be recovered. The difference could be considered as a rough indicator of the amount of sediment which has gone into true solution. The filtration procedure used was the same as that used to generate the dry cake samples from the collected tank bottoms.

Evaluations were also done of the relative settling rate of resuspended sediment in different fuels. For this a blend of sediment and fuel was prepared in a 200 ml beaker and mixed until fully dispersed. The blended sample was then stored, unagitated for a specific amount of time. After this time the top 50% of the sample volume was removed and the solids content in this part of the sample was measured by a centrifuge, following the procedures in ASTM D2709. In this test the sediment is measured volumetrically, in the bottom of a tapered centrifuge tube.

Direct measurements were made of the size distribution of sediment redispersed in different fuel samples using a Lasentec Model FBRM D600 optical probe. This system uses a laser probe to directly measure the size distribution (chord length) of dispersed particles of sediment in the test fuel. Focused light from a diode laser is used to illuminate the particles in the liquid and the reflection is measured for the chord length determination. The laser is protected by a quartz window, which is kept clean by the motion of the agitated liquid sample. A second instrument used was a Lasentec Model PVM camera which captures images of the dispersed particles with a resolution to 5 microns. The purpose of these measurements was to evaluate the effects that biodiesel may have on the dispersion of sediments. Smaller dispersed particles with biodiesel fuels could be responsible for longer settling times following a fill and increased passage of particulates through filters.

As another measure of the dissolution of sludge material into biodiesel FTIR analysis was done on both virgin biodiesel and the same biodiesel in which sediment was dispersed and then removed by filtration.

Results

In the initial tests of solvency, as discussed above, 2.0 grams of vacuum-filtered sediment was dispersed in both normal heating oil and B-100. The samples were allowed to settle for 12 hours, remixed, allowed to settle for another 16 hours, remixed again and then refiltered. In the case of the normal heating oil, 1.60 grams of sediment was recovered on the filter and in the case of B-100, 1.62 grams of sediment was recovered. For both samples the filtrate was then centrifuged and the amount of sediment recovered was found to be roughly consistent with the difference between the original 2.0 grams and the roughly 1.6 grams collected on the second filter. The conclusion from this simple test is that a significant part of the sediment is not being dissolved into the B-100.

Initial tests which were done on the resuspension and resettling of sediment in both No. 2 oil and B-100 were qualitative with simple observation of the appearance. Figure 1 provides photos of these two cases at different times during the test and this clearly shows a slower setting rate for the resuspended sediment in the B-100 case.

No. 2 oil

B-100



Just
before
mixing



Just after
mixing



3 hrs after
mixing



16 hrs
after

Figure 1 Photos of initial settling rate comparison

In the next series of tests the settling rate was evaluated more quantitatively by centrifuging the top half of the sample after specific time periods. Results are shown in Figure 2. The metric used here is the ml of sediment in the bottom of the standard centrifuge tube. These results again show a much slower settling rate with the B-100 fuel but the B-5 and No. 2 heating oil behavior is similar.

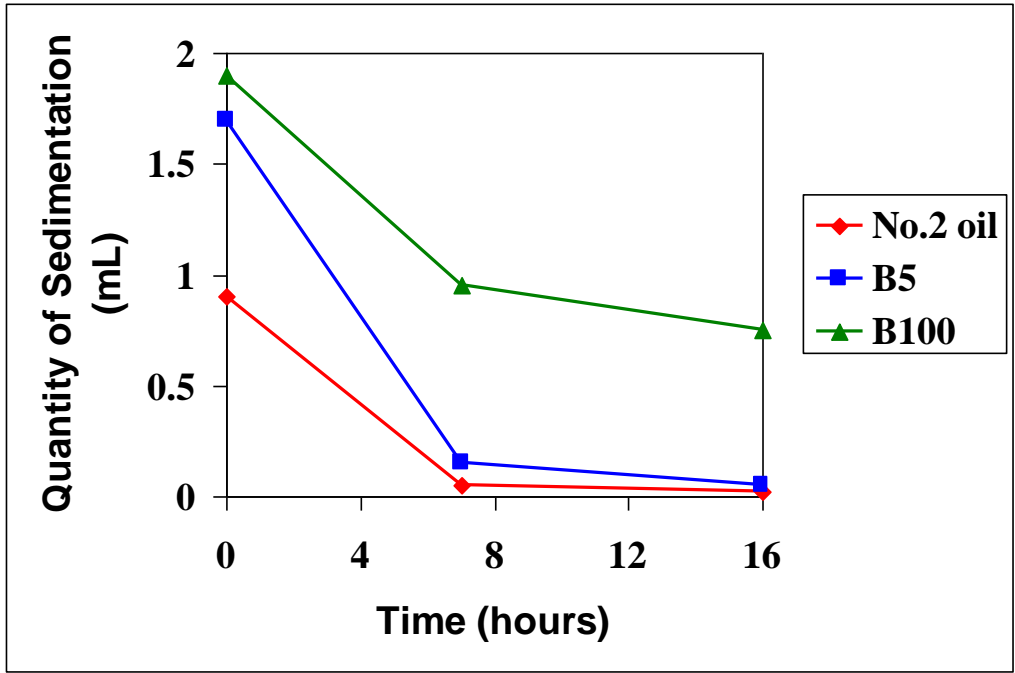
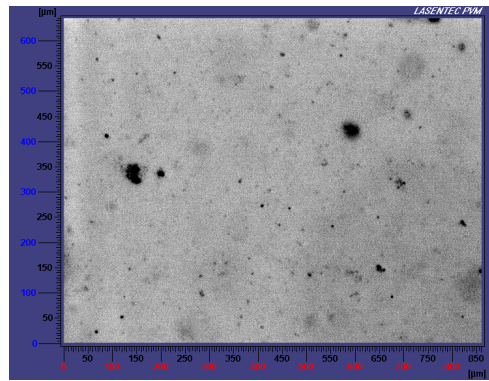
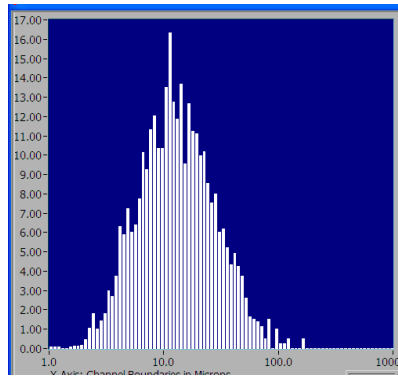


Figure 2. Results of settling rate tests in which the top portion of the settling sample was taken off and sediment content determined by centrifuge. Note that each data point represent a completely different test, i.e. after the top part of the sample is removed for analysis the test with that sample is ended.

Figure 3 shows the results of measurements made of the particle sizes of dispersed sediment in both heating oil and B-100 along with captured images. These show a mean size (based on number count) on the order of 10 microns and that there is no significant difference between the two fuels.

No. 2 oil



B100

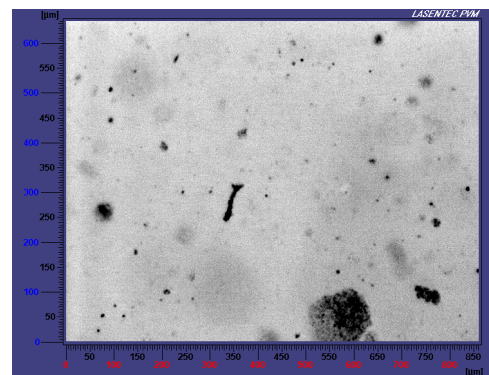
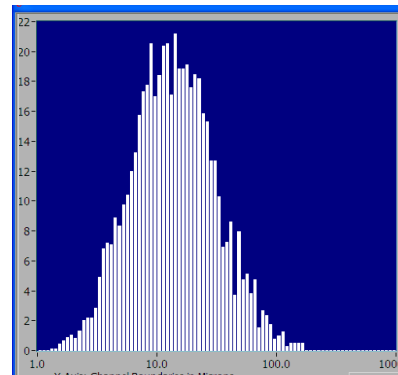


Figure 3 Results of measurements of the size distribution of resuspended sediment particles in No. 2 oil and B-100. Left side shows measured particle size distribution and right side shows particle images taken directly in agitated dispersion. For the chart on the left side the scale is in microns i.e. – the mode of the distributions are about 15 microns. The abscissa is the particle count for a specific sampling time.

As discussed in the Experimental section, the purpose of the FTIR tests was to determine if components of the sediment are dissolving in the Biodiesel to a significant degree. Figure 4 provides the results of the FTIR spectra measurements for both virgin B-100 and B-100 in which sediment has been added, agitated for an extended time period and then allowed to settle. Comparison shows that the results are essentially the same, indicating no detectable solubility for the sediment and this is consistent with the measurements reported above.

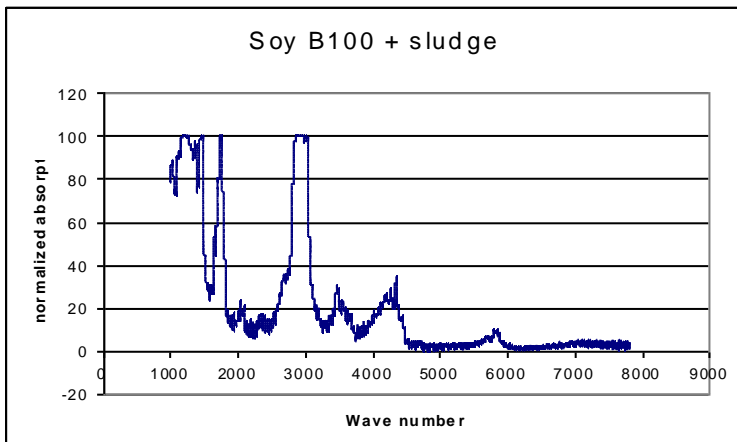
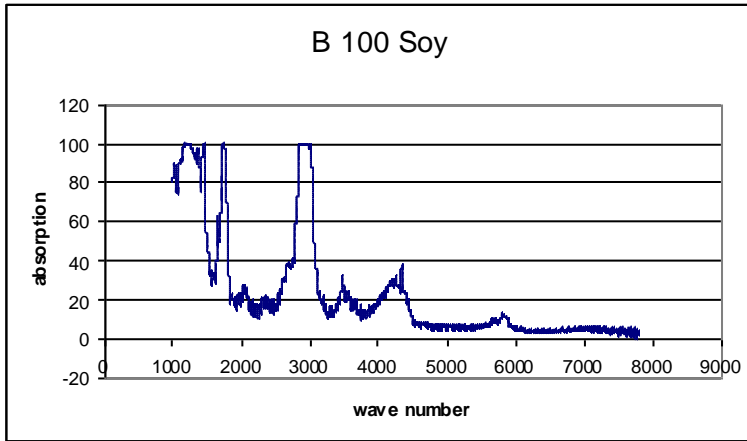


Figure 4. FTIR Spectra – comparison of virgin B-100 and B-100 in which sediment has been dispersed and then allowed to settle.

Discussion

Based on all of the results there is no indication that the sediment used in these tests shows any significant solubility in the biodiesel fuel. However, the results have clearly shown that the sediment settles slower in the B-100 fuel than in the No. 2 heating oil. For a particle, settling slowly in a fluid the terminal velocity is given by Stoke's law:

$$V_s = \frac{d^2 \cdot g \cdot (\rho_p - \rho_f)}{\mu_f}$$

where:

V_s = particle settling velocity (cm/sec)

d = particle diameter (cm)

$$g = 9.8 \text{ (cm/sec}^2\text{)}$$

$$\rho_p = \text{particle density (g/cm}^3\text{)}$$

$$\rho_f = \text{fuel density (g/cm}^3\text{)}$$

$$\mu_f = \text{fuel dynamic viscosity (poise)}$$

There are two physical properties of the biofuel that will lead to a lower settling rate: viscosity and density. The viscosity of biodiesel is roughly twice that of No. 2 oil leading directly to a settling rate of half. The effect of the density of the fuels depends directly upon the density of the particle which is not known. It seems mostly likely that the observed difference between the settling behavior in the No. 2 oil and the biodiesel is due to these fluid property differences. In the B-5 blends, where the fluid properties are essentially the same as for the No. 2 oil, the observed settling characteristics were also the same.

Conclusions

The results of these tests have not confirmed a significant solubility of sediment at the bottom of oil storage tanks in biodiesel fuel. The results however, have shown that resuspended sediment will settle slower in B-100 than in No. 2 oil. While this lower settling rate could be caused by breaking up of particles in the biodiesel fuel, this was not confirmed by particle size distribution measurements and it seems likely that the lower settling rate was simply due to increased viscosity and density of the biodiesel. This lower settling rate was not observed at lower blend ratios – i.e. B-5.

References

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