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Washington State Ferry Biodiesel Project (Task II C)

Revised Laboratory Research Report

Submitted by

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Summary

The purpose of this lab test is to provide technical support for the 2008 biodiesel fuel test. In current lab tests, the effects of biodiesel quality were studied, including minor compounds, water content, and temperature, on precipitate formation, which could lead to fuel filter clogging. The insoluble particles (precipitates) in B20 are formed under certain conditions. Laboratory tests showed that clogging precipitates can be formed in the presence of water. Incubation at warm temperatures, such as 38^{o}C, favored the precipitates formation. However, the composition of the precipitate is not currently clear and requires further research. It was also attempted to simulate the centrifugal fuel purifier on the WSF by running B20 and a combination of B20 and water through a centrifuge. This was an attempt to replicate the "butterscotch pudding type material" observed in the 2004 test. However, the tests have not resulted in the production of any butterscotch pudding type material such as that noted during the 2004 test. No difference was found between biodiesel produced from soy or canola. Varying water content, flow rate, temperature, etc., also did not show any emulsions like those observed in 2004. A thin milky emulsion inside the centrifuge was observed under some conditions but it was not stable and it broke down as soon as it was to be collected.

It must be pointed out that the lab results in this report are based on the information and knowledge the project team currently has. As the research progresses, new lab tests may be proposed to reflect and build on what has been learned.

Laboratory Research on Identifications of the Causes of Clogging

1. Biodiesel suppliers for the B20 blend

This test started with biodiesel from three different suppliers. Considering that soybean and canola are the two dominant feedstocks, this test focused on them. The soybean biodiesel was obtained from Renewable Energy Group (REG, or as previously named, West Central Soy) which also supplied the biodiesel for the 2004 ferry fuel test. The canola biodiesel was obtained from Imperium Renewables (IR) in Washington State. The samples from both biodiesel suppliers met current ASTM D6751-07a specifications. Another soybean biodiesel was obtained from the University of Georgia. This soy sample had high contents of diglycerides and triglycerides (data shown in Table 2 below). Therefore, this soybean biodiesel sample was not used in further tests.

1.1 Experimental procedures

Blending the two biodiesel samples separately with #2 ultra low sulfur diesel (ULSD) from local Busch Distributors was done in the lab to produce B20 with total volume of 3.5 liters. Water was not added to the B20 samples. After mixing, the B20 samples were settled under two temperatures, that is, either room temperature (about 25 ^{o}C) or 38 ^{o}C which could be achieved in the Ferry system. These samples were aged overnight to ensure temperature equilibrium. Then the samples were filtered by passing them through Whatman glass microfibre filter (934-AH with pore size of 1.5 μm) under vacuum.

1.2 Results and discussion

Observations were made in terms of precipitates and filtration. Figure 1 shows the pictures of soy B20 and B100. Both samples are clear solution, and they can easily pass through the filter, suggesting no clogging problem.

Figure 1 (a) Soy B20 Soy without water

Figure 1 (b) Soy B100 without water

The canola samples have also shown the clear solution obtained above, with the same indication of no significant precipitates formed.

2. Effect of minor compound content in the B20 blend and temperature

Recently, the Archer Daniels Midland (ADM) reported that minor components, such as monoglycerides (MG), sterol glucosides (SG), soaps, and water, affected the cloud point (CP) and filterability of the biodiesel after a cold soak treatment (Biorenewable Resources No. 4 in September 2007). MG and soaps or water in combination with MG had significant impact on CP. SG did not have a negative effect on CP. However, the filter test response was particularly sensitive to SG and soaps. The effect of MG concentration was much less dramatic. Water negatively affected the filterability of the tested fuel. Interactions between water and other components were suggested but not conclusive. The mechanism of these interactions needs further investigation.

In our lab tests, B20 was used rather than B100 as reported by ADM since the ferry used B20 in the 2004 test. The effects of the minor compounds on the filter performance were studied using the two biodiesel samples containing different levels of the minor compounds. In addition, during the operation process in the ferry, the biodiesel blends might absorb water from air, and water also enters the fuel through condensation, causing an increase of water content in the fuel. The water in the B20 blend may exacerbate the formation of precipitates, causing filter clogging. Temperature could also affect the precipitate formation. The effects of water and temperature on precipitate formation were investigated in this test.

2.1 Experimental procedure

The experimental procedure was similar to that described in section 1.1. The differences were water addition and temperature control. Water in concentration of 0.1 % (v/v) was added into the soy and canola B20 samples since the B20 would be saturated at this level of water. After mixing, the B20 samples were settled in a 38 ^{o}C oven overnight. In the morning, the oven was turned off and the oven door was not opened, so that the temperature decreased slowly. It took several hours to cool down to room temperature. After that, the samples were filtered by passing through the Whatman filter under vacuum.

2.2 Results and discussion

The excess water can be observed in the bottom of the bottle, suggesting that the B20 was saturated with water in concentration of 0.1 % (v/v). Figure 2 shows the soy B20 samples. The soy B20 sample in the presence of water looks cloudy (Figure 2(b)) after incubating in 38^{o}C, as compared with the clear sample (Figure 2 (a)) without 38^{o}C incubation.

Figure 2 (a) Soy B20 without 38 ^{o}C incubation

Figure 2 (b) Soy B20 with 38 ^{o}C incubation

However, the canola B20 samples did not look much different. Figure 3 shows the canola B20 samples. Figure 3 (a) and Figure 3 (b) did not appear significantly different.

Figure 3 (a) Canola B20 without 38 ^{o}C incubation

Figure 3 (b) Canola B20 with 38 ^{o}C incubation

The clear soy B20 turned cloudy, suggesting some insoluble materials formation. In order to reflect this change, absorbance or scattering was measured at 700 nm using a spectrometer. The 700 nm was selected because both the soy and canola biodiesel and the diesel do not have any absorbance at this wavelength. Thus the original B20 did not have the absorbance at 700 nm. The change of absorbance or scattering could come from the insoluble suspended particles in the samples. Table 1 below shows the absorbance or scattering for the B20 samples. Only the soy Sample (TZ-B2-3#) studied here and shown in Figure 2 (b) had a significant change of the scattering of 0.198, suggesting that the light at 700 nm was scattering by the particles from the cloudy soy B20 sample. This scattering result indicated the particles formed only in the presence of water and incubation at 38 ^{o}C. This sample was also observed under a microscope and the particles can be found. However, particles could not be found from other clear samples under the microscope.

Table 1 Absorbance or scattering at 700 nm for the B20 samples.

B20 Sample ID	Biodiesel stock	Water (% v/v)	Incubation at 38 ^{o}C	Absorbance or Scattering
TZ-B2-9#	Soy	0	No	0
TZ-B2-1#	Soy	0	Yes	0
TZ-B2-10#	Soy	0.1	No	0
TZ-B2-3#	Soy	0.1	Yes	0.198
TZ-B3-1#	Canola	0.1	No	0
TZ-B3-3#	Canola	0.1	Yes	0

In order to determine whether these samples can cause filter clogging problems, filtration experiments were also conducted. All the canola B20 samples can pass through the 1.5 μm filter without any problems, suggesting the canola sample studied did not lead to the filter clogging. However, the cloudy soy B20 had significant filter clogging. This soy B20 could pass easily through the filter at the beginning, and gradually became difficult as more liquid passed through the filter. The filter was shown to have a significant clogging problem after passing through about 2.5 liters of the soy B20. Therefore the particles in this sample would result in filter clogging.

Identification of the particle composition from the filter was investigated. The insoluble precipitates from the filter paper appeared to dissolve in methylene chloride (CH_2Cl_2), but did not dissolve well in either methanol or chloroform ($CHCl_3$). The precipitates dissolved in methylene chloride were analyzed using GC at the University of Idaho, in comparison with B100 and diesel used. Figure 4 shows the GC results. Figure 4 (a) shows the precipitate results. These precipitate peaks appeared differently from those of the soy B100 (Figure 4 (b)) and the diesel (Figure 4 (d)). These results suggested that the precipitate composition is much different from either the soy biodiesel or the diesel.

However, the precipitate composition could not be determined from these Figures. Further research, such as analysis using FT-IR, and GC/MS, *etc*., is needed to identify the precipitate composition.

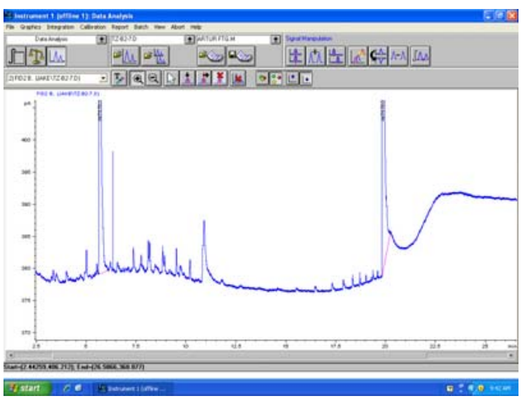


Figure 4 (a) Precipitates dissolved in CH_2Cl_2 from soy B20

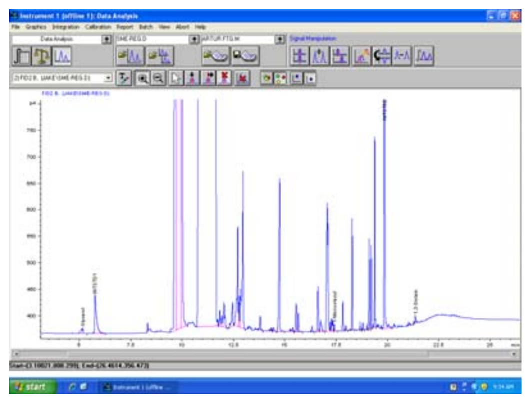


Figure 4 (b) Soy B100 used for B20

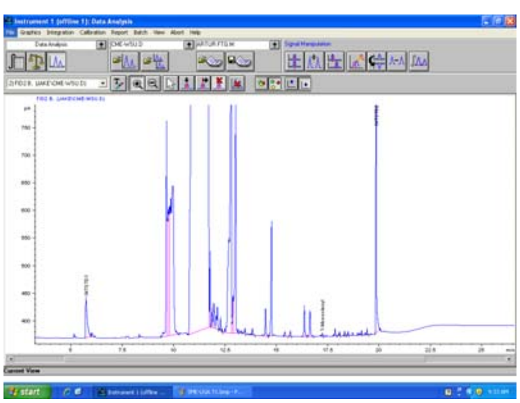


Figure 4 (c) Canola B100 from Imperium Renewable

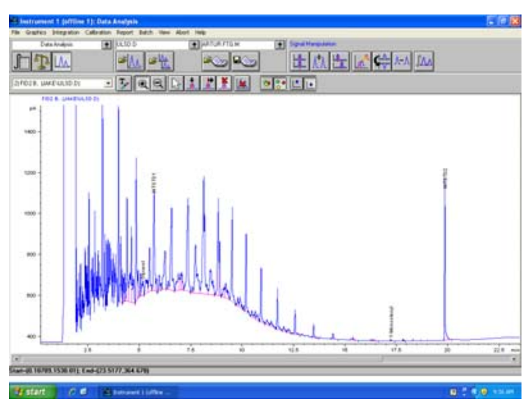


Figure 4 (d) ultra low sulfur diesel used for B20

However, some minor compounds were able to be determined by this GC analysis. Table 2 shows the results of the B100 samples. Comparing the soy B100 with the canola B100 sample, the canola sample has lower contents of these minor compounds (such as glycerin, monoglycerids, and diglycerides) than those of the soy sample. The results for contents of the minor compounds suggested that the canola biodiesel has better quality than the soy biodiesel. However, the sterol glucoside content has not obtained. Sterol glucoside cannot be determined by this common GC analysis as it is a heavier compound. As reported by ADM, the minor compounds combined with water may form precipitates which results in filter clogging. In the tests reported, water was added into the B20 samples. The soy sample tended to form the precipitates by the minor compounds with water under certain conditions. The canola sample was not able to form precipitates because of the low content of the minor compounds.

Table 2 Composition of some minor compounds in the B100 samples

Sample	Free glycerin (% w/w)	Total glycerin (% w/w)	Monoglycerids (% w/w)	Diglycerides (% w/w)	Triglycerides (% w/w)
CME–IR [1]	0.004	0.0205	0.0636	0	0
SME-REG [2]	0.01	0.1510	0.528	0.0284	0
SME-UGA [3]	0.00007	0.1824	0.5136	0.2538	0.1102

* 1: CME-IR was the canola B100 from Imperium Renewables;
2: SME-REG was the soy B100 from REG;
3: SME-UGA was the soy B100 from the University of Georgia.

It should be noted that it is not concluded that canola biodiesel can form the precipitates while soy biodiesel is not able to form the precipitates. Biodiesel origin may not be a dominant factor on the precipitate formation, although soy oil may contain higher sterol glucosides than canola oil. Contents of the minor compounds remaining in biodiesel are dependant on both feedstocks and the production process. Soy biodiesel may have very low content of sterol glucosides because the sterol glucosides are removed during production. Thus it may be focused on content of the minor compounds in biodiesel rather than the biodiesel origin.

3. Incomplete tank cleaning

It is very difficult to simulate ferry tank cleaning conditions. While it was planned to do a pilot ferry dock-side test of this hypothesis during November 2007, the test was cancelled due to the ferry being unavailable. So, this hypothesis will be evaluated in the 2008 fuel test.

4. Biodiesel oxidation stability

Oxidation stability is one of the most important properties of biodiesel. As this project progresses, more information is obtained on biodiesel application and the WSF systems, including operating conditions. It is believed that biodiesel oxidation may not have significantly contributed to the filter clogging in the 2004 test. Dr. Steve Howell, a reviewer of the 2008 work plan, has supported our statement of oxidation stability. A simple test was also performed to confirm oxidation stability. A B20 sample was exposed to air for more than a week. This sample remained in a clear solution without any significant change. The sample also can easily pass through the filter, suggesting that the oxidation may not be a cause for the filter clogging problem.

5. Centrifuge tests with B20 with CME and SME (University of Idaho)

Test Set-up:

ULSD and off-road diesel from Busch Distributors was blended with CME from Imperium and SME from REG to a B20 blend, and water was added at varying percentages in a 10 gallon vessel. A mixer paddle driven by a Dayton gear motor rotating at 100 rpm was mounted in order to keep the water mixed. A Cole-Parmer Easy Load II peristaltic pump with #6401-24 tubing was used to feed the centrifuge at varying rates from 500 to 1500 ml/min. The inlet tubing to the pump was positioned near the bottom of the vessel. The centrifuge was an Alpha Laval model WSB 103B-74-60 using 55 disks, running at a bowl speed of 8600 rpm. Two sets of disks were used. Disk set 1 had the flow holes in the middle of the skirt while disk set 2 had the holes near the bottom of the skirt. Both light and heavy phase outlets were directed back into the vessel for recirculation. During cold temperature trials, the 10 gallon vessel was placed outside and an additional peristaltic pump was employed to transfer the output from the centrifuge back to the cold environment. Initial tests were 4 hours in duration and subsequent tests were terminated at 2 hours.


Testing protocol:

B20 – no water – no prime

Vary Flow Rate – 500, 1000, 1500

Temperature – Ambient, 10 C and 60 C

Water – 1, 2, 3 and 5%

Catalysts – 0.1% (16 grams per 5 gal of fuel) iron oxide, salt, soap, dye (used in off-road diesel)

High Temp trial: 500 ml/min, 2% H2O, 60 C – used barrel heater w/ temp control.

Teats with CME:

The first test with CME B20 with 1% water and at a flow rate of 1000 ml/min at 24°C produced a little sludge in the solids basket but was never repeated. The sludge is believed to be formed by residue from the centrifuge, lines and mixing vessel that were dissolved and subsequently spun out.

Subsequent testing with CME B20 at water contents of 2 and 3 % water and flow rates of 500, 1000 and 1500 ml/min at 24°C consistently produced whitish flakes of fuel/water emulsion in the bowl and between the disks. This flakey emulsion was weak and tended to break up upon disassembly. Light phase output was always clear and bright using disk set 1.

Tests with SME:

SME B20 tests were conducted in the same manner starting with 1% water, then 2 and 3% with flow rates of 500, 1000 and 1500 ml/min at 24°C. The same results was experienced as with disk set 1. At 3% water the KF moisture of the light phase output was 105 ppm @ 500 ml/min, 110 ppm @ 1000 ml/min, and 113 ppm @ 1500 ml/min at the 3% water loading.

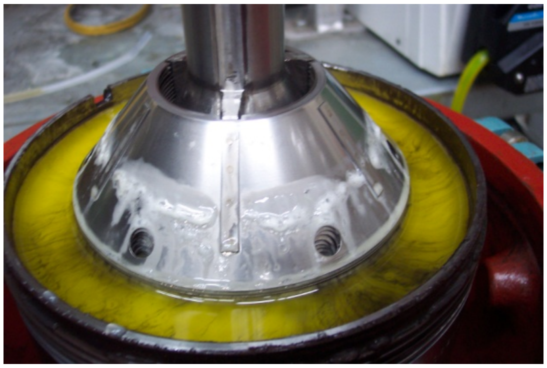
Disk set 2

The light phase output was cloudy at 1500 ml/min, not at 500 and 1000 ml/min flow rates. A similar flaky emulsion was found as before on disassembly. With this set of disks, the fuel must travel farther into the water interface before exiting.

Cold trials:

1. Temp 10°C SME B20, 5% water, Disk set 2

A similar but more pronounced emulsion was found upon disassembly, possibly due to the colder temperature. After a short period of time the emulsion dissolved and appeared to be about 90% to 95 % water with the remainder being fuel. Light phase was very cloudy at 1500 and 1000 ml/min and slightly cloudy at 500 ml/min, however, they all cleared up on heating.



2. Temp 8°C, SME B20, 3% water, Disk set 1

A light emulsion was found on the disks at the phase interface; this was much less than was noticed in the previous trial. It is believed that the holes in disk set 2 are positioned more optimally for this type of separation. Light phase was clear from all three flow rates after slight warming.

SME B20 without water and without priming the centrifuge:

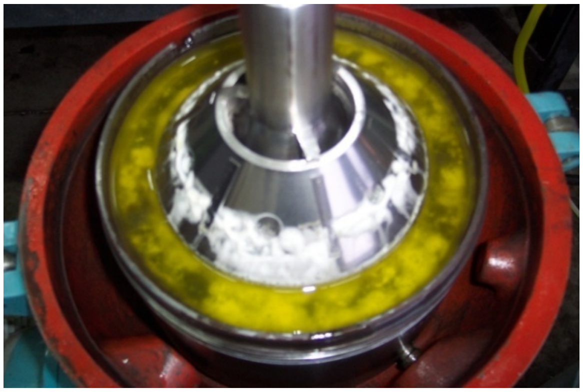
This was done at ambient temperature and at 1000 ml/min flow rate. The fuel exited the heavy phase outlet. Diesel fumes were very heavy in the room after an hour of running. Upon disassembly, the fuel was clear and the disk stack and bowl were very clean.

Elevated temperature run:

SME B20 with 2% water and centrifuge primed, disk set 1. Fuel temperature was 60°C, flow rate was 500 ml/min. Light phase output was clear. Fuel in the bowl was clear and there was a slight hint of whitish emulsion on the disks.

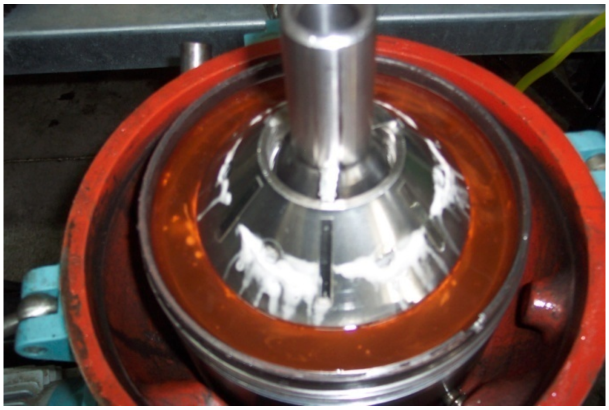
Catalyst trials:

1. SME B20, 5% water, disk set 1, ambient temperature, 1000 ml/min flow rate and 0.1% salt. A fair amount of white emulsion was noted floating in the bowl and between the disks in the area of the phase interface. Light phase output was clear.



2. Same as previous test with 0.1% soap added with the salt. Similar outcome, however, surprisingly there seemed to be a little less emulsion than the previous test.

3. SME B20, off-road diesel, 2% water, disk set 1, ambient temp, 1000 ml/min. Similar result as before with a white emulsion ring on the disks.



4. SME B20, off-road diesel, 3% water, disk set 1, ambient temp, 1000 ml/min, 0.1% salt and 0.1% iron oxide. This combination, although the emulsion on the disks was not significant, did create a semi-gelatinous sludge in the bowl. This was an emulsion of mostly water that broke down after a period of time.

A series of tests with soy and canola B20 blends with ULSD and off-road diesel were run with several contaminants such as water, salt, soap and iron oxide, alone and in combination. The water content was varied from 2 to 5%, the flow rate was varied from 500 to 1500 ml/min, and several different temperatures were used as well. The salt, soap and ferric oxide were added at 0.1% by weight. Under most conditions we saw a milky unstable emulsion on the centrifuge disks around the area of the phase interface. This emulsion was about 95% water and broke down over a short period of time after the disk stack was pulled out. A test with iron oxide and salt produced a pudding-like product in the bowl. It is not clear at this point how similar it was to what was found in the 2004 ferry trials. It was able to be collected with a spoon but broke down over a short period of time.

6. Multiple factors for the clogging problems

The lab tests above have included multiple factors, such as minor compounds including water content, and temperature, and centrifuge process using B20.

It is planned to do more lab tests. These lab tests include evaluating minor components and growth of microbes. WSU will investigate the minor components for the filterability. Statistically designed experiments will be developed to study the influence of sterol glucosides (SG), soap, water and temperature on the filterability. B20 will be used for these tests rather than B100, which has been reported by ADM. Considering the operating conditions of the ferry, the lab tests will cover temperatures up to 120°F, up to 100% relative humidity. Compared with the tests conducted previously, the new tests will consider the combined impact of different factors.

UI may do some extra testing involving growth of microbes. To actually develop a sample of fuel that is contaminated would take some time, however, UI may be able to get a sample of algae or yeast from the microbiology department and mix it with some fuel and then see what happens when we centrifuge it out. It might produce a material that is similar to the butterscotch pudding seen in 2004.

These new lab tests will further narrow down the possible clogging causes for the 2004 tests. As described, some precipitates were obtained from the B20 under certain conditions. This result suggested that the minor components in the fuel might contribute to the precipitate formation. Further tests on this topic will provide more evidence to support this potential cause.

Conclusions and Recommendations

The precipitates from B20 could be formed in certain conditions, although the biodiesel studied met the current standard specification. Multiple factors, including biodiesel quality, minor compounds, and temperature affected the precipitate formation. Precipitates were obtained from the soy biodiesel blend B20 tested. The canola biodiesel blend B20 studied did not precipitate. The precipitates from soy were formed in the presence of water, and high temperature, such as 38 ^{o}C, favored precipitate formation. The precipitates obtained would lead to the filter clogging problems.

The centrifuge tests using B20, while varying water content, flow rate, temperature, etc., have not been able to result in any butterscotch pudding type material like that noted during the 2004 test. No difference was found between the two types of biodiesels. A thin milky emulsion inside the centrifuge was observed under some conditions but it was not stable and it broke down as soon as it was about to be collected. Since a thick stable emulsion was not produced over the course of these tests, it would have to be concluded that the exact conditions that caused problems for WSF were not replicated, although the sludge formed with the addition of iron oxide may point to deposits coming from the walls of the vessel deep tanks. It is not known at this time what exact conditions were responsible, be they contamination by sterols, algae, tank deposits or a combination of things, however, our recommendation would be to continue on as planned with the phase-in of biodiesel testing on the ferries themselves.

It was also recommended to do an additional test in the biodiesel specification for the 2008 fuel test based on the lab research results above. This test is described below.

Additional testing

(1) Sample preparation

One gallon of B20 sample will be made using the testing biodiesel of 0.2 gallon with #2 ultra low sulfur diesel of 0.8 gallon. Water in concentration of 0.1 % (v/v) will be added to the B20 sample as the B20 would be saturated at this level of water. After mixing, the B20 samples will be settled in a 38 ± 1 ^{o}C oven overnight. Then the oven will be turned off. The oven will not be opened until the sample reaches room temperature (about 25 ^{o}C). It is noted that the temperature is allowed to decrease slowly in order to incubate precipitate formation. It is better to cool down overnight to room temperature.

(2) Evaluation of the B20 sample

This B20 sample should pass two types of tests described below.

(a) Absorbance or scattering test

The B20 sample should look like a clear solution the same as the original B20 in the absence of water and without the 38 ^{o}C incubation. In addition, absorbance or scattering at 700 nm will be measured with water as a blank. The absorbance should be zero if no suspended particles are formed.

(b) Filtration test

The B20 sample will be filtered by passing through a Whatman glass microfibre filter (934-AH with pore size of 1.5 μm) under vacuum. This one-gallon B20 sample should pass through the 1.5 μm filter without any problems if no insoluble particles are suspended and present in the solution. However, if a cloudy sample is obtained, the cloudy B20 sample could lead to significant filter clogging.

In conclusion, the biodiesel used for the 2008 fuel test must meet current ASTM D 6751-07a standard specification and should pass the additional testing described above without any filter clogging problems.