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Cold Flow Testing of Biodiesel Blends with Additives

Final Report

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Executive Summary

There are several advantages associated with using biodiesel blends in shipboard diesel-powered systems: reduced overall emissions, reduced engine wear through increased lubricity, and reduced consumption of petroleum. However, biodiesel has higher Cloud Point (CP), Pour Point (PP), and Cold Filter Plugging Point (CFPP) than diesel oil. The increase in these cold flow properties is related to the gelling of biodiesel at higher temperatures than diesel fuel oil. The use of biodiesel blends, thus, pose potential operational problems in ship systems exposed to the cold external environments present in the Great Lakes region.

CP, PP, and CFPP quantify cold weather operating limits for a fuel and are determined via standard test procedures defined by ASTM International. The CP is the highest temperature at which wax crystals first appear in a fuel sample and is the highest of the three cold flow properties. The PP is the lowest of the three cold flow properties and indicates the temperature at which a fuel gels. CFPP testing simulates a cold start of an engine and defines the lowest temperature at which fuel can be moved through a fuel filter of defined pore size. The primary means of lowering the cold flow properties of a fuel and improving cold weather operability of diesel ship systems is through the use of cold flow additives.

This project was undertaken to identify the effect that a select number of cold flow additives have on the CP, PP, and CFPP of biodiesel blends. No. 2 low sulfur diesel and soybean biodiesel (soy methyl ester) were used to produce the six blends employed; No. 2 diesel, B5, B10, B20, B50, and B100. Four commercially available cold flow additives were tested; AMSOIL Diesel Cold Flow Improver, FPPF Deluxe Total Power, Howe's Diesel Treat, and Power Service Diesel Fuel Supplement + Cetane Boost. The CP, PP, and CFPP of the blends both with and without additives were measured using a Tanaka MPC-102L CP/PP tester and a Tanaka AFP-102 CFPP tester. The amount of additive (loading) was also varied from the manufacturer's recommended amount (100% loading) to twice the recommended amount (200% loading). Each CP, PP, and CFPP measurement for a given blend and additive loading combination was conducted 3 times to ensure repeatability of the results.

The results for fuel blends without additives indicated the following:

- A simple volume average mixing rule was employed to estimate the CP of intermediate blends (B5, B10, B20, and B50) to within 1°C.
- A linear correlation of CFPP with CP was observed, in agreement with the literature.
- As the biodiesel content in the blend increases, the CP, PP, and CFPP increases, and the difference between the CP, PP, and CFPP decreases.

The difference between the CP, PP, and CFPP obtained at a given additive loading and those obtained without the use of an additive was used to define the additive effectiveness. An effective additive will cause a large reduction in the cold flow properties. Data obtained for 100 and 200% additive loading revealed the following general trends:

- The additives had no noticeable effect on CP at either loading, in agreement with the literature.
- At 100% loading, all four additives were effective in decreasing the PP, particularly for B50 blends and lower (B50, B20, B10, B5, and No. 2 diesel).

- One of the additives (AMSOIL) produced a significant reduction in CFPP for B20 and lower blends, and another two additives (FPPF and Power Service) caused a significant reduction in CFPP for B10 blends and lower.
- Increasing the additive loading from 100% to 200%:
  - Tended to decrease PP at higher biodiesel percent blends.
  - Had very little effect on the PP of B100.
- No general trend could be established for the effect of increased additive loading on CFPP with some additive/blend combinations showing a slight increase in CFPP and some showing a slight decrease in CFPP.
- None of the additives were effective in reducing the CFPP of B50 and B100.

The present study investigated four of the many commercially available cold flow additives, each of which contain proprietary chemical compounds. The four additives employed were specifically designed for diesel fuel. This is most likely the reason that the additives were unable to significantly decrease the PP of B100, and the CFPP of B50 and B100. The experimental results indicate that none of the additives should be used with high biodiesel content blends (B50 and B100). Future studies will include additives designed specifically for use with biodiesel to determine if significant reductions in the cold flow properties of B50 and B100 can be achieved. The low sulfur No. 2 diesel employed in the current study will be replaced by ultra low sulfur diesel (ULSD) in future tests to reflect the coming transition to ULSD for marine fuel supplies.

1. Introduction

Legislative and industrial efforts point to the use of biodiesel blends up to 20% (B20) for both on-road and off-road applications in the near future. Ship systems that utilize biodiesel blends instead of no. 2 diesel are more susceptible to fuel gelling when exposed to cold weather environments due to the increase in cold flow properties associated with the use of biodiesel. The cold flow properties are quantified using standard Cloud Point (CP) [1], Pour Point (PP) [2], and Cold Filter Plugging Point (CFPP) [3] tests. These tests establish limits for the use of fuels under cold weather conditions. The cloud point is defined as the temperature at which the smallest observable cluster of wax crystals first appears, the pour point is the lowest temperature at which movement of a test specimen is observed, and the cold filter plugging point is an estimation of the lowest temperature at which a fuel will give trouble-free flow in certain fuel systems. There are two primary means of improving the cold flow properties of biodiesel blends; (1) the addition of cold flow additives or "improvers", and (2) winterization of the biodiesel component prior to blend preparation. Several investigators have studied one or more of the cold flow properties of biodiesel and biodiesel blends based on different types of vegetable oils (for example, see [4-16]).

Dunn and Bagby conducted low-temperature flow test (LTFT), CFPP, and CP tests on biodiesel blends derived from vegetable oils [4,5]. Their results indicated an almost linear dependence of CFPP and LTFT on CP. The presence of cold flow additives in the blends resulted in very little change in the correlation between CFPP and CP however, the correlation between LTFT and CP was noticeably different. Despite the observed effect of additives on their results, they concluded that CFPP and LTFT were statistically similar. Dunn et al. [6] also investigated the effect of 12 cold flow additives on CP, PP, LTFT, and CFPP. Their results showed that the additives significantly improved the PP, but did not greatly affect the CP.

Chiu et al. conducted LTFT, CP, and PP tests to investigate the impact of four cold flow improvers on B80, B90, and B100 soybean-based biodiesel blends [8]. They observed that the additives had little effect on the cloud point but two of the additives had a significant effect on the pour point of the blends tested. The results from the LTFT test, which is similar to the CFPP test, showed a significant decrease (improvement) in the LTFT with the addition of the additive Bio Flow-875.

Conley and Tao reviewed the results of CP, PP, and CFPP tests of pure biodiesel (B100) conducted by other investigators [9]. Biodiesel created from soy, canola, lard, and edible tallow was considered. They concluded that soy and canola based biodiesel provided the best performance of the types of B100 reviewed.

Joshi and Pegg measured the CP and PP of B80, B60, B40 and B20 blends made with No. 2 diesel and biodiesel derived from ethyl esters of fish oil [10]. They developed empirical equations for predicting the cloud and pour point for a given blend that were in good agreement with experiments.

Shrestha et al. measured the effect of four additives on the CP and PP of No. 2 diesel, and B5, B20, and B100 biodiesel blends [14]. Four types of biodiesel were used in the experiments; soy methyl ester (SME), mustard ethyl ester (MEE), mustard methyl ester (MME), and used vegetable oil methyl ester (UVME). The additives tested had no effect on the CP and a significant effect on PP, particularly for blends of 20% (B20) biodiesel content and lower. They observed that the additives generally worked better with ethyl esters than methyl esters and that a higher percentage of diesel in the blend resulted in better additive effectiveness.

Winterization of biodiesel consists of removing the saturated methyl esters by inducing crystallization with cooling and then separating the high melting temperature components by filtration. The liquid biodiesel that remains has improved cold flow properties and can be used neat, or in the preparation of a blend. The winterization process tends to result in low yields, on the order of 25% [6, 15]. Thus, instead of winterization, the usual method employed to improve cold flow properties is through the use of additives. As cited above, there are some results in the literature for the cold flow properties of biodiesel. However, the results are limited. In addition, there is very little data available in the literature covering the effect of cold flow additives.

The current study addresses the effect of common cold flow additives on the CP, PP, and CFPP of biodiesel blends created using soybean-based biodiesel, which is supplied in the Great Lakes region. Measurements of the CP, PP, and CFPP were performed with and without additives. The amount of additive used was also varied. The specific goals of the project included determining which cold flow properties were affected by the use of additives, and if further improvements in cold flow properties are obtained by adding more than the manufacturer's recommended amount of additive.

1.1 Project Description

Standard testing equipment was purchased and used to measure the CP, PP, and CFPP of No. 2 diesel and biodiesel blends with and without additives in accordance with the applicable ASTM standards. The purchase of the equipment was partially funded through GLMRI with matching funds provided by the Swenson College of Science and Engineering at the University of Minnesota Duluth.

Four cold flow additives were selected and tested in six different fuel blends; No. 2 diesel, B5, B10, B20, B50, and B100. Initial measurements of the CP, PP, and CFPP of the fuel blends without any additives were taken to establish baseline values for the properties. CP, PP, and CFPP were also measured when the amount of additive recommended by the manufacturer was added to each blend (100% loading) and when twice the recommended amount was added (200% loading). The difference between the CP, PP, and CFPP obtained at a given additive loading and those obtained without the use of an additive was used to define the additive effectiveness. Each CP, PP, and CFPP test, which consists of a given fuel mixed with a given amount of a specific additive, was repeated 3 times to ensure the repeatability of the results.

Portions of the results presented in this report were incorporated in a presentation given at the GLMRI University Affiliates Meeting held in Duluth, MN on September 24th and 25th, 2009.

2. Experimental Procedures

2.1 Materials

Soybean biodiesel (soy methyl ester) and No. 2 low sulfur diesel were obtained from Murphy Oil Corporation's Superior, WI refinery. The following four cold flow additives were selected for testing; FPPF Deluxe Total Power, Power Service Diesel Fuel Supplement + Cetane Boost, AMSOIL Diesel Cold Flow Improver, and Howe's Diesel Treat.

2.2 Equipment and Methods

Cloud point (CP), pour point (PP), and cold filter plugging point (CFPP) tests are used to define the low-temperature operating limits for diesel fuel. In order to minimize the potential effect of human error on the experimental data, automated fuel testing equipment was used to perform the tests. The CP and PP were measured using a Tanaka MPC-102L CP/PP tester (Figure 1c) which determines both the cloud point (in accordance with ASTM D2500) and the pour point (in accordance with ASTM D6749) at 1°C intervals in a single automated test. The manufacturer states that the MPC-102L has a typical repeatability of ±1°C, a reproducibility of ±2°C, and is capable of measuring PP down to -40°C when supplied with tap water, and -60°C when supplied by a refrigerated bath. The unit was operated using tap water in the lab and the observed minimum PP during testing was -52°C. The CFPP was measured using the Tanaka AFP-102 CFPP tester (Figure 1a), which performs the test in accordance with ASTM D6371, connected to a Neslab RTE-7 D1 refrigerated bath (Figure 1b). The AFP-102 is capable of measuring CFPP down to -60°C and the RTE-7 has a temperature range of -25°C to 150°C.

The variables in the tests include the fuel blend, the additive, and the additive loading. There were six fuel blends used; No. 2 diesel, B5, B10, B20, B50, and B100. The four additives discussed in the Materials section were use with three different additive loading levels; no additive, 100% loading, and 200% loading, where 100% loading is defined as the amount of additive recommended for use by the manufacturer, and 200% loading is twice the recommended amount. The recommended amounts for each additive are shown in Table 1.

One test is required for a given blend without an additive and there are four additives at two loadings (100% and 200%), resulting in 9 combinations for the additive/loading effect on each blend. There are 6 blends and therefore 54 combinations to be tested. Finally, each test was performed 3 times to ensure repeatability of the results, for a total of 162 tests for each of the three cold flow properties CP, PP, and CFPP. The results for all of the tests, along with the computed averages for CP, PP, and CFPP, are shown in Appendix C.

2.3 Blend Preparation and Additive Loading

Fuel blends were prepared in 300 mL batches using graduated cylinders of 250 mL ± 1.4 mL and 50 mL ± 0.4 mL. Because of the uncertainties associated with the volume measurements, the intermediate biodiesel blends B5, B10, B20, and B50 are not exact. For example, the B10 blend has an uncertainty of B10±0.14. The blend uncertainties, and an example of their calculation, are shown in Appendix A (Table 8).

Samples for testing additives at different loadings were created by mixing the appropriate volume of additive for the given loading (100% or 200%) with a 300 mL sample of the desired blend. A 100-1000 μL adjustable pipette with an accuracy of ± 6 μL was used to measure the additive. The pipette was adjustable in 5 μL increments and thus the precise volume required for the ratio of additive/fuel suggested by the manufacturer could not be added to the 300 mL sample. Table 9 in Appendix B shows the manufacturer's recommended volume to add to 300 mL of fuel along with the actual volumes added to the test samples for 100% and 200% loading. The uncertainties in the additive volume ratio, defined as the ratio of the volume of additive to the sample volume (300 mL), and an example of their calculation, are also shown in Appendix B (Table 10 and Table 11).

(a) **(b)** **(c)**

Figure 1: Testing Equipment - (a) Tanaka AFP-102 CFPP Tester, (b) Neslab RTE-7 D1 Refrigerated Bath, and (c) Tanaka MPC-102L CP/PP Tester

Additive	**Recommended Amount***	**Volume Ratio (additive/fuel)**
FPPF	1 quart/250 gal.	0.001
Power Service	8 oz./25 gal.	0.0025
AMSOIL	2 oz./5 gal.	0.003125
Howe's	1 oz./5 gal.	0.0015625

Table 1: Cold Flow Additives used in Testing. *Recommended Amount = 100% Loading

3. Results and Discussion

The results obtained from the CP, PP, and CFPP tests are shown in Appendix C. All of the blends (No. 2 diesel, B5, B10, B20, B50, and B100) were tested without additives to obtain baseline results. The difference in CP, PP, and CFPP of each sample with and without a given additive was used to define the effect of that additive.

3.1 Results without Additives

Figure 2 shows the average CP, PP, and CFPP as a function percent biodiesel in the blend when no additives were used. Each test was run three times to obtain the average value. Cloud point, which is the temperature at which wax crystals first form, is the highest of the cold flow properties. The average cloud point of a blend (CP_{Blend}) varies approximately linearly with the biodiesel content and can be described using the mixing rule [16]

$$CP_{Blend} = VF_{B100}CP_{B100} + VF_{D2}CP_{D2}$$

where VF_{B100}, CP_{B100}, VF_{D2}, and CP_{D2} are the volume fraction (VF) and cloud point of B100 and No. 2 diesel (D2), respectively. When no additives are used, this linear mixing rule predicts the average CP of intermediate blends in the current study to within 1°C. It should be noted here that the results of Dunn et al. [6] appear to indicate that the linear mixing rule is inappropriate if No. 1 diesel is used in the blend.

The PP corresponds to the lowest temperature at which movement of a test sample is observed and is the lowest of the cold flow properties. The value for CFPP is between the values for PP and CP. The current data follow this trend for blends of B20 and lower; however, PP is higher than CFPP for B50 and B100 (see Figure 2). Two factors may have contributed to the PP being higher than CFPP at high percentage biodiesel blends (B50 and B100); (1) The difference between the highest and lowest cold flow properties is small when biodiesel content is high, and (2) CP and PP are measured using one device, and CFPP is measured with a separate device, with both devices having a repeatability of ±1°C and a reproducibility of ±2°C. Given these contributing factors, a PP that is greater than CFPP by approximately 2°C is not unexpected. The data for CFPP and PP shown in Figure 2 also suggest a nonlinear variation of these properties with biodiesel content and thus the simple mixing rule employed for CP would be inappropriate for use with CFPP and PP.

Cloud point has been shown to correlate well with CFPP in the literature. Dunn and co-workers [4, 6] used a linear correlation to model the CFPP as a function of CP in their experiments with varying blends of soybean-based biodiesel (soy methyl esters). Figure 3 shows the current data for average CFPP versus the average CP when no additives were employed. A linear regression of the raw data is also displayed. The regression analysis yielded $R^2 = 0.9646$ and the following equation for CFPP in degrees Celsius:

$$CFPP = 0.8537 \times CP - 4.72$$

where CP is the cloud point in degrees Celsius. The slope and intercept shown in the above equation are similar to those obtained by Dunn and co-workers [4, 6]. A visual comparison of the average data in Figure 3 with the fitted line, as well as the high value for R^2 obtained, indicate that a linear model for CFPP as a function of CP is appropriate for the current data.

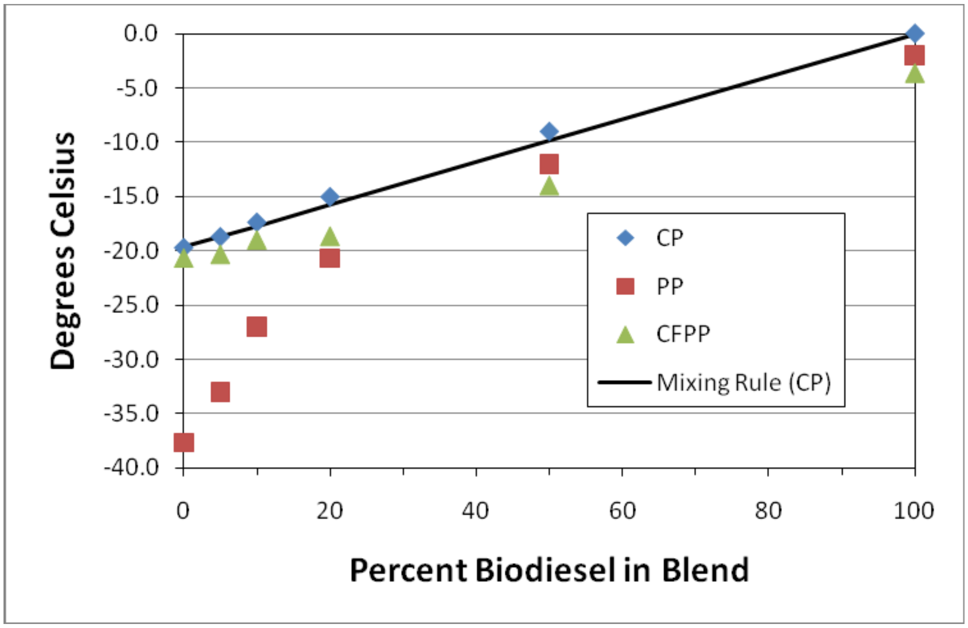

Figure 2: Average Cloud Point, Pour Point, and Cold Filter Plugging Point vs. percent biodiesel in blend. Blends contain no additive.

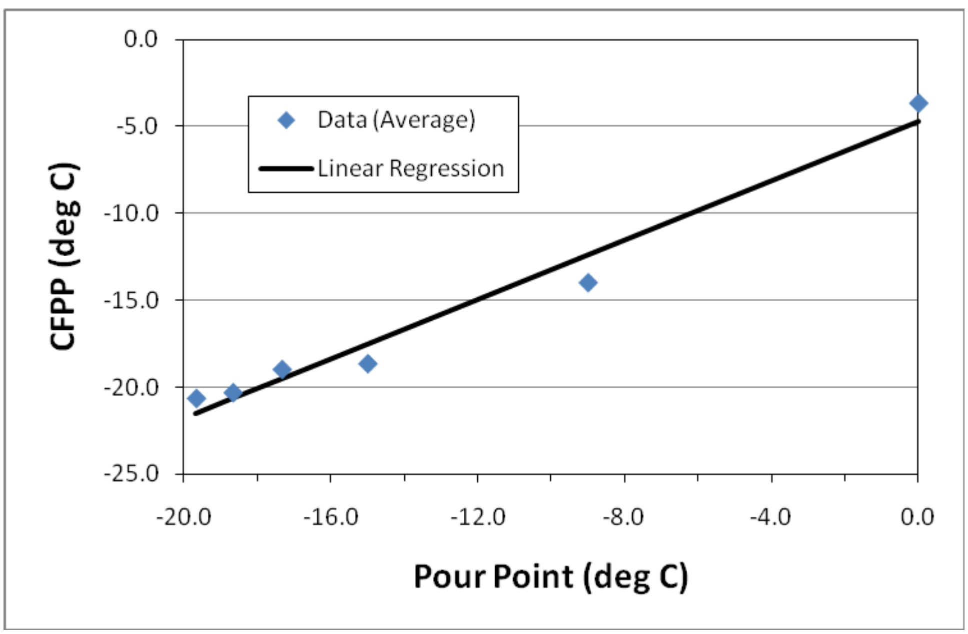

Figure 3: Average CFPP vs. PP

3.2 Effect of Additives

The effect of the four additives tested on the average CP, PP, and CFPP of No.2 diesel and various blends are discussed below and detailed in Appendix C. Each property was tested for each additive at 100 and 200% loading. The tables below present the reduction – defined as the difference between the property value without the additive and with the additive – in the various property values obtained during these tests. Positive values are desired, but were not obtained in many cases.

3.2.1 Cloud Point

Table 2 and Table 3 show the reduction in cloud point associated with each additive at 100 and 200% loading, respectively. The reduction in CP is defined as the difference between the CP without the additive and with the additive. A positive value is desired. Both tables show that all of the additives have very little, if any, effect on the CP. At lower percentage biodiesel blends, the additives appear to actually increase the CP (negative reduction) however, the increases are small. In addition, there is no statistical difference between the results at 100% loading and 200% loading. The lack of any significant additive effects on CP is in agreement with results available in the literature [6, 8, 14]. In general, cold flow additives are designed to inhibit the agglomeration and growth of wax crystals, not the initial formation of crystals. Since the CP measures the temperature at which wax crystals first appear, the observed lack of any additive effect on CP is expected.

Additive	**Reduction in Cloud Point (°C)**					
	#2	**B5**	**B10**	**B20**	**B50**	**B100**
AMSOIL	-0.7	-2.3	-1.0	-2.7	-2.0	1.0
FPPF	-1.7	-0.7	-0.3	-1.3	1.0	1.0
Howe's	-3.3	-3.3	-3.3	0.0	0.0	1.0
Power Service	-3.0	-3.7	-3.3	0.0	1.0	0.0

Table 2: Reduction in Average Cloud Point for 100% Additive Loading.

Additive	**Reduction in Cloud Point (°C)**					
	#2	**B5**	**B10**	**B20**	**B50**	**B100**
AMSOIL	-2.0	-1.3	-2.0	-1.0	1.0	1.3
FPPF	-2.7	-3.0	-2.3	-3.0	-3.7	1.0
Howe's	-3.3	-3.0	-3.7	-4.3	0.7	1.0
Power Service	-2.7	-2.3	-2.3	-2.3	1.0	1.0

Table 3: Reduction in Average Cloud Point for 200% Additive Loading.

3.2.2 Pour Point

Table 4 and Table 5 show the reduction in pour point associated with each additive at 100 and 200% loading, respectively. The reduction in PP is defined as the difference between the PP without the additive and with the additive. A positive value is desired. The entries that are highlighted in yellow correspond to cases when the PP for the samples with the additive was <-52°C (the operating limit for the PP tester). The PP was set to -52°C (see data in Appendix C) to calculate the reduction in PP and thus the reduction in PP is greater than the value shown in the tables. Both tables show that all of the additives have a significant effect on PP, particularly for blends with less than 50% biodiesel. Comparing the results in Table 4 to those in Table 5, we observe a noticeable reduction in PP for B50 as loading is increased for 2 of the additives (FPPF and Power Service). The additive loading appears to have very little, if any, effect on B100. The biodiesel used in the present study is a soy methyl ester (SME). Shrestha et al. [14] used different additives than the present study in SME biodiesel (B100) and observed the same result; additive loading had very effect on PP. The additives used by Shrestha et al. [14] and the additives used in the current study were formulated for diesel fuel. A significant reduction in the PP of B100 might be achieved through the use of cold flow additives designed for biodiesel.

Additive	**Reduction in Pour Point (°C)**					
	#2	**B5**	**B10**	**B20**	**B50**	**B100**
AMSOIL	>14.3	>19.0	>25.0	>31.3	>40.0	10.0
FPPF	>14.3	>19.0	>25.0	>31.3	8.0	2.0
Howe's	>14.3	>19.0	18.0	10.3	4.0	3.0
Power Service	>14.3	>19.0	>25.0	>31.3	9.7	2.3

Table 4: Reduction in Average Pour Point for 100% Additive Loading.

Additive	**Reduction in Pour Point (°C)**					
	#2	**B5**	**B10**	**B20**	**B50**	**B100**
AMSOIL	>14.3	>19.0	>25.0	>31.3	29.0	11.0
FPPF	>14.3	>19.0	>25.0	>31.3	37.0	6.0
Howe's	>14.3	>19.0	21.7	20.3	6.0	3.0
Power Service	>14.3	>19.0	>25.0	>31.3	36.3	7.0

Table 5: Reduction in Average Pour Point for 200% Additive Loading.

3.2.3 Cold Filter Plugging Point

Table 6 and Table 7 show the reduction in CFPP associated with each additive at 100 and 200% loading, respectively. The reduction in CFPP is defined as the difference between the CFPP without the additive and with the additive. A positive value is desired. At 100% loading, one of the additives (AMSOIL) reduced the CFPP significantly for B20 and lower blends, and all of the additives reduced the CFPP for B5 and No. 2 diesel. Raising the additive loading from 100% (Table 6) to 200% (Table 7) either had little effect, or was detrimental, causing a rise in the CFPP for intermediate blends (compare AMSOIL in Table 6 and Table 7). There was some improvement with loading for some additive/blend combinations (for example the Power Service additive with B20), but there were no observable trends. None of the additives had a noticeable effect on the CFPP of B100 at either loading, and only one of the additives (AMSOIL) had a slight effect on the CFPP of B50 at 200% loading. As previously discussed in relation to the PP, the use of additives specifically designed for biodiesel might allow for a significant reduction in the CFPP of B50 and B100.

Additive	Reduction in Cold Filter Plugging Point (°C)					
	#2	**B5**	**B10**	**B20**	**B50**	**B100**
AMSOIL	13.0	13.7	12.3	13.3	0.0	-2.7
FPPF	14.7	14.7	14.3	5.0	-2.0	-1.7
Howe's	11.7	12.7	5.7	2.3	-2.0	-1.7
Power Service	11.3	13.7	10.0	6.3	-2.0	-2.3

Table 6: Reduction in Average Cold Filter Plugging Point for 100% Additive Loading.

Additive	Reduction in Cold Filter Plugging Point (°C)					
	#2	**B5**	**B10**	**B20**	**B50**	**B100**
AMSOIL	13.0	8.7	5.0	2.7	6.0	-2.7
FPPF	12.0	12.3	12.7	11.3	-2.0	-1.7
Howe's	12.0	10.3	10.0	2.3	-3.0	-2.7
Power Service	11.7	12.7	13.3	11.7	-1.0	-2.7

Table 7: Reduction in Average Cold Filter Plugging Point for 200% Additive Loading.

4. Conclusions and Recommendations

The effect of four cold flow additives on the cloud point (CP), pour point (PP), and cold filter plugging point (CFPP) of biodiesel blends was measured. The additives were tested at the recommended mixture levels (100% loading) and twice the recommended level (200% loading). Soybean biodiesel (soy methyl ester) and low sulfur No. 2 diesel were used in the preparation of the fuel blends which consisted of No. 2 diesel, B5, B10, B20, B50 and B100.

The results for fuel blends without the additives indicate that a simple volume average mixing rule can be employed to estimate the CP of intermediate blends (B5, B10, B20, and B50). A linear correlation of CFPP with CP was observed, in agreement with the literature. As the biodiesel content in the blend is increased, the difference between the CP, PP, and CFPP decreases. For the B50 and B100 tests, the average PP was slightly greater than the CFPP (< 2°C), which is physically unrealistic. However, this slight difference was reasonable when the accuracies of the separate PP and CFPP tests are taken into account.

Introducing additives into the blends had no noticeable effect on CP at either loading which is in agreement with the literature. At 100% loading, all four additives were effective in decreasing the pour point, particularly for B50 blends and lower (B50, B20, B10, B5, and No. 2 diesel). One of the additives (AMSOIL) produced a significant reduction in CFPP for B20 and lower blends, and another two additives (FPPF and Power Service) caused a significant reduction in CFPP for B10 blends and lower.

Increasing the additive loading from 100% to 200% tended to decrease PP at higher biodiesel percent blends; three of the additives at 200% loading caused a significant decrease in PP for B50 blends and lower. An increase in additive loading had very little effect on the PP of B100. No general trend could be established for the effect of increased additive loading on CFPP with some additive/blend combinations showing a slight increase in CFPP and some showing a slight decrease in CFPP. None of the additives were effective in reducing the CFPP of B50 and B100.

The current work adds to the limited body of knowledge regarding the effects of additives on the cold flow properties of biodiesel blends however, significant work remains. The four additives used in the present study were formulated for diesel fuel and constitute a limited number of the available commercial products. More additives should be tested and tests using additives specifically designed for biodiesel should be conducted to see if larger reductions can be achieved in PP and CFPP for intermediate and high percentage biodiesel blends. In addition, ultra low sulfur diesel (ULSD) should be used in future testing since marine fuel will transition to ULSD in 2012.

References

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Appendix A

Sample Volume and Blend Uncertainties

Blend Uncertainty Example: B10

- **Total Sample Volume** of 300 mL: V_{total} = 300 mL
  - One full 250 mL graduated cylinder of #2 diesel: $V_1 = 250 \pm 1.4$ mL
  - 20 mL of #2 diesel in a 50 mL graduated cylinder: $V_2 = 20 \pm 0.4$ mL
  - 30 mL of B100 in a 50 mL graduated cylinder: $V_3 = V_{B100} = 30 \pm 0.4$ mL
- **Uncertainty in Total Sample Volume:** ΔV_{total}

$$V_{total} = V_1 + V_2 + V_3$$

$$\Delta V_{total} = \sqrt{\left(\frac{\partial V_{total}}{\partial V_1}\Delta V_1\right)^2 + \left(\frac{\partial V_{total}}{\partial V_2}\Delta V_2\right)^2 + \left(\frac{\partial V_{total}}{\partial V_3}\Delta V_3\right)^2}$$

$$= \sqrt{(\Delta V_1)^2 + (\Delta V_2)^2 + (\Delta V_3)^2}$$

$$= \sqrt{(1.4\,\text{mL})^2 + (0.4\,\text{mL})^2 + (0.4\,\text{mL})^2}$$

$$\boxed{\Delta V_{total} = \pm 1.5\,\text{mL} \qquad V_{total} = 300 \pm 1.5\,\text{mL}}$$

- **Biodiesel Volume Fraction:** BVF = V_{B100}/V_{total} = 30/300 = 0.1 (B10)
- **Uncertainty in Biodiesel Volume Fraction:** ΔBVF

$$\text{BVF} = \frac{V_{B100}}{V_{total}}$$

$$\Delta\text{BVF} = \sqrt{\left(\frac{\partial \text{BVF}}{\partial V_{total}}\Delta V_{total}\right)^2 + \left(\frac{\partial \text{BVF}}{\partial V_{B100}}\Delta V_{B100}\right)^2}$$

$$= \sqrt{\left(\frac{V_{B100}}{V_{total}^2}\Delta V_{total}\right)^2 + \left(\frac{1}{V_{total}}\Delta V_{B100}\right)^2}$$

$$= \sqrt{\left(\frac{30\,\text{mL}}{(300\,\text{mL})^2}1.5\,\text{mL}\right)^2 + \left(\frac{1}{300\,\text{mL}}0.4\,\text{mL}\right)^2}$$

$$\boxed{\Delta\text{BVF} = \pm 0.0014 \qquad \text{BVF} = 0.1 \pm 0.0014}$$

Blend	Total Volume (± Uncertainty)	B100 Volume Fraction (± Uncertainty)
B100	300 ± 1.5 mL	1.0
B50	300 ± 2.0 mL	0.5 ± 0.0057
B20	300 ± 1.5 mL	0.2 ± 0.0022
B10	300 ± 1.5 mL	0.1 ± 0.0014
B5	300 ± 1.5 mL	0.05 ± 0.0014
#2 Diesel	300 ± 1.5 mL	0.0

Table 8: Sample total volume and blend uncertainties.

Appendix B

Additive Loading Uncertainties

Additive Loading Uncertainty Example: B10 with AMSOIL at 100% Loading

- Additives were mixed with 300 mL samples of each blend.
- The volume of additive used for each loading was measured using a 100-1000 μL pipette with an accuracy of ± 6 μL. The pipette volume was adjustable in increments of 5 μL. Table 9 shows the volume of additive used for each of the loadings.

Additive	Recommended (100% Loading)		Actual Added (100% Loading)		Actual Added (200% Loading)	
	Volume (μL)	Volume Ratio	Volume (μL)	Volume Ratio	Volume (μL)	Volume Ratio
AMSOIL	937.5	0.003125	935	0.003117	1870	0.006233
FPPF	300.0	0.001	300	0.001	600	0.002
Power Service	750.0	0.0025	750	0.0025	1500	0.005
Howe's	468.8	0.0015625	465	0.00155	930	0.0031

Table 9: Volume of additive mixed with 300 mL sample for 100% and 200% loadings compared to recommended volume of additive for 100% loading.

- **Additive Volume Ratio:** AVR = V_{add}/V_{total} = 0.935/300 = 0.003117
  - 300 mL sample of B10: Vtotal = 300 ± 1.5 mL
  - AMSOIL additive volume using pipette: V_{add} = 935 ± 6 μL
- **Uncertainty in Additive Volume Ratio:** ΔAVR

$$\mathrm{AVR} = \frac{V_{add}}{V_{total}}$$

$$\Delta\mathrm{AVR} = \sqrt{\left(\frac{\partial \mathrm{AVR}}{\partial V_{total}}\Delta V_{total}\right)^2 + \left(\frac{\partial \mathrm{AVR}}{\partial V_{add}}\Delta V_{add}\right)^2}$$

$$= \sqrt{\left(\frac{V_{add}}{V_{total}^2}\Delta V_{total}\right)^2 + \left(\frac{1}{V_{total}}\Delta V_{add}\right)^2}$$

$$= \sqrt{\left(\frac{0.935\,\mathrm{mL}}{(300\,\mathrm{mL})^2}1.5\,\mathrm{mL}\right)^2 + \left(\frac{1}{300\,\mathrm{mL}}0.006\,\mathrm{mL}\right)^2}$$

$$\boxed{\Delta\mathrm{AVR} = \pm 2.54\mathrm{E}-05 \qquad \mathrm{AVR} = 0.003117 \pm 2.54\mathrm{E}-05}$$

Blend	Uncertainty in Additive Volume Ratio			
	AMSOIL	FPPF	Power Service	Howe's
B100	2.54E-05	2.06E-05	2.36E-05	2.14E-05
B50	2.88E-05	2.11E-05	2.60E-05	2.25E-05
B20	2.54E-05	2.06E-05	2.36E-05	2.14E-05
B10	2.54E-05	2.06E-05	2.36E-05	2.14E-05
B5	2.54E-05	2.06E-05	2.36E-05	2.14E-05
#2 Diesel	2.54E-05	2.06E-05	2.36E-05	2.14E-05

Table 10: Uncertainty in Additive Volume Ratio for 100% loading.

Blend	Uncertainty in Additive Volume Ratio			
	AMSOIL	FPPF	Power Service	Howe's
B100	2.98E-05	2.12E-05	2.67E-05	2.28E-05
B50	3.55E-05	2.21E-05	3.09E-05	2.48E-05
B20	2.98E-05	2.12E-05	2.67E-05	2.28E-05
B10	2.98E-05	2.12E-05	2.67E-05	2.28E-05
B5	2.98E-05	2.12E-05	2.67E-05	2.28E-05
#2 Diesel	2.98E-05	2.12E-05	2.67E-05	2.28E-05

Table 11: Uncertainty in Additive Volume Ratio for 200% loading.

Appendix C

Experimental Data for CP, PP, and CFPP

Note: The Pour Point values that are highlighted in yellow are set to -52°C which was the observed lower limit for the testing equipment. The actual Pour Point in these cases is < -52°C.

No Additives

Blend		Cloud Point (deg C)				Pour Point (deg C)				CFPP (deg C)			
		Test Number			Average	Test Number			Average	Test Number			Average
Name	% B100	1	2	3		1	2	3		1	2	3	
B100	100	0	0	0	0.0	-2	-2	-2	-2.0	-3	-4	-4	-3.7
B50	50	-9	-9	-9	-9.0	-12	-12	-12	-12.0	-14	-14	-14	-14.0
B20	20	-15	-15	-15	-15.0	-20	-21	-21	-20.7	-18	-19	-19	-18.7
B10	10	-18	-17	-17	-17.3	-27	-27	-27	-27.0	-19	-19	-19	-19.0
B5	5	-19	-18	-19	-18.7	-34	-33	-32	-33.0	-22	-19	-20	-20.3
#2 Diesel	0	-20	-20	-19	-19.7	-40	-37	-36	-37.7	-21	-21	-20	-20.7

AMSOIL - 100% Loading

Blend		Cloud Point (deg C)				Pour Point (deg C)				CFPP (deg C)			
		Test Number			Average	Test Number			Average	Test Number			Average
Name	% B100	1	2	3		1	2	3		1	2	3	
B100	100	-1	-1	-1	-1.0	-12	-12	-12	-12.0	-1	-1	-1	-1.0
B50	50	-10	-6	-5	-7.0	-52	-52	-52	-52.0	-14	-14	-14	-14.0
B20	20	-12	-12	-13	-12.3	-52	-52	-52	-52.0	-32	-33	-31	-32.0
B10	10	-19	-16	-14	-16.3	-52	-52	-52	-52.0	-30	-32	-32	-31.3
B5	5	-16	-17	-16	-16.3	-52	-52	-52	-52.0	-34	-34	-34	-34.0
#2 Diesel	0	-21	-18	-18	-19.0	-52	-52	-52	-52.0	-34	-34	-33	-33.7

FPPF - 100% Loading

Blend		Cloud Point (deg C)				Pour Point (deg C)				CFPP (deg C)			
		Test Number			Average	Test Number			Average	Test Number			Average
Name	% B100	1	2	3		1	2	3		1	2	3	
B100	100	-1	-1	-1	-1.0	-4	-4	-4	-4.0	-2	-2	-2	-2.0
B50	50	-10	-10	-10	-10.0	-20	-20	-20	-20.0	-12	-12	-12	-12.0
B20	20	-14	-14	-13	-13.7	-52	-52	-52	-52.0	-24	-24	-23	-23.7
B10	10	-17	-17	-17	-17.0	-52	-52	-52	-52.0	-34	-34	-32	-33.3
B5	5	-19	-19	-16	-18.0	-52	-52	-52	-52.0	-35	-35	-35	-35.0
#2 Diesel	0	-20	-17	-17	-18.0	-52	-52	-52	-52.0	-36	-35	-35	-35.3

Howe's - 100% Loading

Blend		Cloud Point (deg C)				Pour Point (deg C)				CFPP (deg C)			
		Test Number			Average	Test Number			Average	Test Number			Average
Name	% B100	1	2	3		1	2	3		1	2	3	
B100	100	-1	-1	-1	-1.0	-5	-5	-5	-5.0	-2	-2	-2	-2.0
B50	50	-9	-9	-9	-9.0	-16	-16	-16	-16.0	-12	-12	-12	-12.0
B20	20	-15	-15	-15	-15.0	-31	-31	-31	-31.0	-21	-21	-21	-21.0
B10	10	-14	-14	-14	-14.0	-45	-45	-45	-45.0	-24	-26	-24	-24.7
B5	5	-16	-15	-15	-15.3	-52	-52	-52	-52.0	-33	-33	-33	-33.0
#2 Diesel	0	-16	-17	-16	-16.3	-52	-52	-52	-52.0	-33	-32	-32	-32.3

Power Service - 100% Loading

Blend		Cloud Point (deg C)				Pour Point (deg C)				CFPP (deg C)			
		Test Number			Average	Test Number			Average	Test Number			Average
Name	% B100	1	2	3		1	2	3		1	2	3	
B100	100	-1	2	-1	0.0	-5	-4	-4	-4.3	-2	-1	-1	-1.3
B50	50	-10	-10	-10	-10.0	-21	-22	-22	-21.7	-12	-12	-12	-12.0
B20	20	-15	-15	-15	-15.0	-52	-52	-52	-52.0	-25	-25	-25	-25.0
B10	10	-14	-14	-14	-14.0	-52	-52	-52	-52.0	-29	-29	-29	-29.0
B5	5	-15	-15	-15	-15.0	-52	-52	-52	-52.0	-34	-34	-34	-34.0
#2 Diesel	0	-17	-17	-16	-16.7	-52	-52	-52	-52.0	-32	-32	-32	-32.0

AMSOIL - 200% Loading

Blend		Cloud Point (deg C)				Pour Point (deg C)				CFPP (deg C)			
		Test Number			Average	Test Number			Average	Test Number			Average
Name	% B100	1	2	3		1	2	3		1	2	3	
B100	100	-1	-2	-1	-1.3	-13	-13	-13	-13.0	-1	-1	-1	-1.0
B50	50	-10	-10	-10	-10.0	-42	-40	-41	-41.0	-20	-20	-20	-20.0
B20	20	-14	-14	-14	-14.0	-52	-52	-52	-52.0	-22	-21	-21	-21.3
B10	10	-15	-16	-15	-15.3	-52	-52	-52	-52.0	-24	-24	-24	-24.0
B5	5	-17	-18	-17	-17.3	-52	-52	-52	-52.0	-28	-30	-29	-29.0
#2 Diesel	0	-18	-17	-18	-17.7	-52	-52	-52	-52.0	-34	-33	-34	-33.7

FPPF - 200% Loading

Blend		Cloud Point (deg C)				Pour Point (deg C)				CFPP (deg C)			
		Test Number			Average	Test Number			Average	Test Number			Average
Name	% B100	1	2	3		1	2	3		1	2	3	
B100	100	-1	-1	-1	-1.0	-8	-8	-8	-8.0	-2	-2	-2	-2.0
B50	50	-6	-5	-5	-5.3	-49	-48	-50	-49.0	-12	-12	-12	-12.0
B20	20	-12	-12	-12	-12.0	-52	-52	-52	-52.0	-31	-29	-30	-30.0
B10	10	-15	-15	-15	-15.0	-52	-52	-52	-52.0	-31	-32	-32	-31.7
B5	5	-15	-16	-16	-15.7	-52	-52	-52	-52.0	-33	-33	-32	-32.7
#2 Diesel	0	-17	-17	-17	-17.0	-52	-52	-52	-52.0	-32	-33	-33	-32.7

Howe's - 200% Loading

Blend		Cloud Point (deg C)				Pour Point (deg C)				CFPP (deg C)			
		Test Number			Average	Test Number			Average	Test Number			Average
Name	% B100	1	2	3		1	2	3		1	2	3	
B100	100	-1	-1	-1	-1.0	-5	-5	-5	-5.0	-1	-1	-1	-1.0
B50	50	-9	-10	-10	-9.7	-18	-18	-18	-18.0	-11	-11	-11	-11.0
B20	20	-10	-11	-11	-10.7	-40	-42	-41	-41.0	-21	-21	-21	-21.0
B10	10	-14	-13	-14	-13.7	-48	-49	-49	-48.7	-29	-29	-29	-29.0
B5	5	-15	-16	-16	-15.7	-52	-52	-52	-52.0	-30	-31	-31	-30.7
#2 Diesel	0	-16	-17	-16	-16.3	-52	-52	-52	-52.0	-32	-33	-33	-32.7

Power Service - 200% Loading

Blend		Cloud Point (deg C)				Pour Point (deg C)				CFPP (deg C)			
		Test Number			Average	Test Number			Average	Test Number			Average
Name	% B100	1	2	3		1	2	3		1	2	3	
B100	100	-1	-1	-1	-1.0	-9	-9	-9	-9.0	-1	-1	-1	-1.0
B50	50	-10	-10	-10	-10.0	-47	-50	-48	-48.3	-13	-13	-13	-13.0
B20	20	-12	-13	-13	-12.7	-52	-52	-52	-52.0	-30	-31	-30	-30.3
B10	10	-15	-15	-15	-15.0	-52	-52	-52	-52.0	-33	-32	-32	-32.3
B5	5	-16	-16	-17	-16.3	-52	-52	-52	-52.0	-33	-33	-33	-33.0
#2 Diesel	0	-17	-17	-17	-17.0	-52	-52	-52	-52.0	-33	-33	-31	-32.3