EFFECTIVENESS OF COLD FLOW ADDITIVES ON VARIOUS BIODIESELS, DIESEL, AND THEIR BLENDS

D. S. Shrestha, J. Van Gerpen, J. Thompson

ABSTRACT. One of the major reasons hindering the use of biodiesel is its filter plugging temperature, which is higher than that of No. 2 diesel. Cloud point (CP) and pour point (PP) temperatures have been shown to be well correlated with filter plugging point, which primarily determines the operability of a diesel engine in cold weather. Many biodiesel cold flow additives are available in the market that claim to reduce pour point. In this study, neat and blended biodiesel fuels from different feedstocks were tested for change in CP and PP with various cold flow additives at 100%, 200%, and 300% of the specified loading (application) rate. The additives in general worked better for ethyl esters than for methyl esters. Average reductions in CP and PP for neat mustard methyl esters were 0.3 °C and 7.2 °C, respectively, compared to 3 °C and 19.4 °C for mustard ethyl ester at the recommended loading rate. In general, mustard biodiesel responded to additives better than soybean or used vegetable oil biodiesel for reducing PP. The effect of additives on CP of diesel fuel was not statistically significant, but PP was reduced to ≤ -36 °C with all additives at recommended loading. This result is expected as additives are mainly targeted to inhibit the crystal growth not necessarily the onset of crystallization. The additives were found to be more effective in diesel than in biodiesel for reducing PP, and hence the higher the percentage of diesel in a blend, the better the effectiveness was. Most additives reduced the PP of B20 and lower blends to ≤ -36 °C at 100% loading, and all additives did that at 200% loading. No added benefit was observed at more than 200% loading.

Keywords. Biodiesel blend, Biofuel, Cloud point, Fuel additives, Pour point.

With rapidly increasing petroleum prices, biodiesel is becoming more popular throughout the world. In the northern part of the U.S. and other cold regions of the world, one of the major concerns among biodiesel users is its unfavorable cold flow temperature. Handling and blending 100% biodiesel (B100) in cold weather can be difficult. This limits the use of biodiesel during the winter season. Petroleum No. 2 diesel in general has lower cloud point (CP) and pour point (PP) temperatures (Peterson et al., 1997). ASTM (2003a) defines CP for petroleum products and biodiesel fuels as the temperature of a liquid specimen at which the smallest observable cluster of wax crystals first appears upon cooling under prescribed conditions. ASTM (2003b) defines PP as the lowest temperature at which movement of the test specimen is observed under prescribed test conditions. Cold flow properties of biodiesel depend on many factors, including oil feedstock and type of alcohol used. Peterson et al. (1997) compared ethyl and methyl esters of four biodiesel feedstocks on the basis of fuel characteristics and short-term engine performance tests. They reported 16°C CP for tallow biodiesel, compared to -12°C for No. 2 diesel.

Low-temperature engine operability is usually measured with a low-temperature flow test (LTFT) in the U.S. and by cold filter plugging point (CFPP) in Europe. The ASTM standard for biodiesel quality (ASTM D6751) does not specify the CP required for sale in a particular region, but it requires that producers disclose the CP of B100 biodiesel. CP and PP have been routinely used to characterize the cold flow operability of diesel fuels. Chiu et al. (2004) showed LTFT as a nonlinear function of CP and PP. The nonlinear coefficient showed that, for the same CP and PP, the LTFT was lower for fuel with a lower percentage of biodiesel. Dunn and Bagby (1995) showed that both LTFT and CFPP of formulations containing at least 10% by volume of methyl esters are linear functions of CP.

When a heterogeneous mixture of liquid is cooled from liquid state to near cloud point, the fraction that has the highest freezing point starts to crystallize and form cloud nuclei. An individual crystal is too small to see with the naked eye. As the temperature continues to decrease, crystalline growth and agglomeration continue until the crystals become large enough to be visible as a form of cloud, known as cloud point (Chandler et al., 1992). In pure biodiesel, the saturate fraction crystallizes first and forms the cloud seed. Once the cloud seed is present, it is easy for other molecules to agglomerate because the molecules go to a lower state of free energy by doing so (Bierce, 1973). The higher the fraction of saturates, the higher the cloud point will be. Therefore, any fraction in the biodiesel matrix, including impurities such as monoglycerides, that crystallizes at high temperature can serve as cloud seed, making the overall cloud point higher.

The most common impurities in biodiesel, either because of incomplete reaction or through fuel degradation, are free glycerol and monoglycerides. The melting point of monoglycerides is the highest, followed by saturates (methyl palmitate, methyl stearate, and methyl arachidate), followed by free glycerol, and finally unsaturates (table 1). Biodiesel...
though biodiesel fractions such as methyl stearate have a high melting point, they do not crystallize at their melting point temperature. This is because a higher melting point fraction behaves as solutes that are dissolved in lower-melting methyl esters (DeMan, 2000). Crystals are formed only when the solution is saturated with solutes.

Different techniques have been used to lower the cloud point and pour point of biodiesel for cold weather operation. Winterization is the process of removing saturated methyl esters by introducing crystallization by cooling and then separating the high melting components by filtration. Lee et al. (1996) found that the CP of a common soybean biodiesel could be reduced to -7.1°C through winterization. Davis et al. (2007) used soybean methyl ester fractionation by urea and methanol to produce a modified biodiesel with CP as low as -45°C. In either case, a significant amount of the high-CP biodiesel fraction is removed. Lee et al. (1996) concluded that winterization is not an efficient way of removing saturated methyl esters because of the low yield (26%) of separated liquid fraction to produce a CP of -7.1°C from neat soybean biodiesel. In many cases, it is not practical to store the high-CP fraction for summer use or to transport it to a warmer climate region. The use of a branched-chain alcohol is an alternative way to reduce CP. Isopropyl and 2-butyl esters of normal soybean oil crystallized 7°C to 11°C and 12°C to 14°C lower, respectively, than the corresponding methyl esters (Lee et al., 1995). However, use of isopropyl alcohol is more expensive, and the reaction is harder to complete.

Different fuel additives to improve the cold flow properties for diesel and biodiesel are commercially available. Dunn et al. (1996) studied the effect of 12 cold flow additives for petroleum diesel on cold flow behavior of biodiesel. They concluded that the additives significantly improved the PP of diesel/biodiesel blends but did not affect the CP greatly. On the contrary, Chiu et al. (2004) found that two out of four fuel additives significantly affected the PP of soybean biodiesel. Many additives contain some proprietary components, copolymers of ethylene, vinyl acetate, or other olefin-ester copolymers. Because of these proprietary compounds, the impact on cold flow of different types of biodiesel such as canola, mustard, and used vegetable oil needs to be determined experimentally.

It was reported that engine operators who use biodiesel add more than the recommended amount of cold flow depressant, assuming that the cold flow improvers have a linear effect. The effects on cold flow properties of adding more than the recommended amount (loading) are not well documented. One of the objectives of this research was to evaluate the loading effect on additive effectiveness.

The main objective of this research was to evaluate commonly available cold flow improver additives specified for biodiesel. This research evaluates the effect on CP and PP of biodiesel from different feedstocks, at various blend levels, and at various loading rates.

### Experimental Setup

Four variables (feedstock, fuel additive, loading rate, and biodiesel blend level) were identified as important variables affecting the cold flow properties of biodiesel and biodiesel blends with diesel. Soybean methyl ester (SME), mustard ethyl ester (MEE), mustard methyl ester (MME), and used vegetable oil methyl ester (UVME) from a local restaurant were selected as biodiesel types. Even though ethyl esters are not commercially used, MEE was included to study the difference between methyl and ethyl esters. The feedstocks were prepared at the Department of Biological and Agricultural Engineering at the University of Idaho. Four commercially available biodiesel additives were selected for this study: Flozol 503 (Labrizol Corp., Wickliffe, Ohio), BioFlow 875 (Octel Sterron, Newark, Del.), MCC P205 (Midcontinental Chemical, Overland Park, Kans.), and Arctic Express 0.25% (Power Service, Weatherford, Tex.). The biodiesel blend levels were selected at 5% (B5) and 20% (B20), as these are the most commonly used blend levels. The amount of additive (loading) was varied at four levels: no additive, 100% of specified level, 200% of specified level, and 300% of specified level. The difference in CP or PP of each sample with and without a fuel additive was considered as the effect of that additive.

A completely randomized design was used in this experiment. Biodiesel was made in batches, and each batch was used to prepare different blend levels. The biodiesel was prepared in the laboratory as needed, and one batch of biodiesel was used to prepare several blend samples; hence, it was assumed that the variability coming from making biodiesel (batch effect) was randomized. Each batch was tested and verified to meet the ASTM D6751 biodiesel quality standard. Additive type, percent loading, and percent biodiesel blend were randomly selected for a given batch of biodiesel; hence, their effect on the final results was also considered randomized.

Four feedstock types and four levels of blending made a total of 13 combinations of neat diesel, neat biodiesel, and their blends (because B0 does not have feedstock type). Four additives and four levels of loading (again note that with no additive, additive type does not matter) made a total of 13 combinations for additive-loading effect. The combination of feedstock and additive-loading with three replications each calls for a total of 507 observations in a balanced design. However, in this experiment, more than one batch of a feedstock was prepared, causing some additional measurement of neat biodiesel, for a total of 539 observations. This fact was taken into account using an unbalanced ANOVA model.

### Table 1. Melting point of common biodiesel constituents and impurities (sources: O’Connor, 1960; Mittelbach and Remschmidt, 2005)

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Melting Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl palmitate (methyl hexadecanoate)</td>
<td>30.5</td>
</tr>
<tr>
<td>Methyl stearate (methyl octadecanoate)</td>
<td>39.1</td>
</tr>
<tr>
<td>Methyl oleate (methyl cis-9-octadecanoate)</td>
<td>-20</td>
</tr>
<tr>
<td>Methyl linoleate (methyl cis, cis-9,12-octadecadienoate)</td>
<td>-35</td>
</tr>
<tr>
<td>Methyl arachidate (methyl cicosanoate)</td>
<td>54.5</td>
</tr>
<tr>
<td>Glycerol</td>
<td>18</td>
</tr>
<tr>
<td>1-Mono-palmitin</td>
<td>74</td>
</tr>
<tr>
<td>1-Mono-stearin</td>
<td>79</td>
</tr>
<tr>
<td>1-Mono-olein</td>
<td>32</td>
</tr>
</tbody>
</table>

[a] Constituents of biodiesel.
[b] Common biodiesel impurities.
Table 2. Average CP and PP (°C) of neat biodiesel and diesel used in this study.

<table>
<thead>
<tr>
<th></th>
<th>SME</th>
<th></th>
<th>MEE</th>
<th></th>
<th>MME</th>
<th></th>
<th>UVME</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B5</td>
<td>B20</td>
<td>B100</td>
<td>B5</td>
<td>B20</td>
<td>B100</td>
<td>B5</td>
</tr>
<tr>
<td>CP</td>
<td>-16</td>
<td>-13</td>
<td>1</td>
<td>-14</td>
<td>-12</td>
<td>2</td>
<td>-14</td>
</tr>
<tr>
<td>PP</td>
<td>-20</td>
<td>-15</td>
<td>0</td>
<td>-18</td>
<td>-16</td>
<td>-5</td>
<td>-18</td>
</tr>
</tbody>
</table>

**CLOUD POINT AND POUR POINT MEASUREMENT**

The method specified in ASTM standard D 2500-02 was used to test the CP of all blends of biodiesel fuel. In this method, the specimen is cooled at specified rate and examined periodically. The temperature at which a cloud is first observed at the bottom of the test jar is recorded to the nearest 1 °C as the CP. Ethanol was used as the cooling medium. The ASTM standard reports that the test method has repeatability of ±2 °C and reproducibility of ±4 °C with 95% confidence interval. Repeatability is defined as the difference between successive results obtained by the same operator using the same apparatus under constant operating conditions on identical test material. Reproducibility is defined as the difference between two single and independent test results obtained by different operators working in different laboratories on identical test material.

The PP was determined according to the method specified in ASTM standard D 97-02. In this method, after preliminary heating, the sample is cooled at a specified rate and examined at intervals of 3 °C for flow characteristics. The lowest temperature at which movement of the specimen is observed is recorded as the PP. The ASTM standard reports that the method has repeatability of 2.52 °C and reproducibility of 6.59 °C with 95% confidence interval. For this experiment, when the PP was below -36 °C, it took a long time to get the temperature any lower; hence, we stopped the PP measurement at -36 °C and recorded the PP as ≤ -36 °C.

**RESULTS AND DISCUSSION**

The difference in CP or PP of each sample with and without a fuel additive was considered as the effect of that additive. Observed mean CP for all B100 samples without additives was between 0 °C and 5 °C (table 2). This accords with the CP values reported by Peterson et al. (2000) and Briggs and Pearson (2005). The range of PP was much larger than that of CP. Among the selected biodiesel samples, the PP of mustard methyl ester was found to be the lowest, with an average of -15 °C (table 2).

**EFFECT OF ADDITIVES ON CLOUD POINT**

Four-way ANOVA was carried out to determine the significance of each of the four variables. All four factors (feedstock, blend level, additive type, and loading) had a significant effect on reducing CP temperature. Further analysis with the Bonferroni method of multiple comparisons (Johnson and Wichern, 2002) showed that the collective effect of fuel additives on MEE was highest, with an average reduction in CP of 3 °C (fig. 1) at 100% loading. The vertical line in figure 1 indicates 95% confidence interval. Only MEE showed a significant decrease in CP when loading increased from 100% to 200%. A decrease in CP among methyl esters (SME, MME, and UVME) was not statistically significant. Since MEE and MME were prepared from the same oil source, the result indicated that fuel additives were more effective in reducing CP of ethyl ester than methyl ester. At 100% loading, the 95% confidence interval line of SME and MME includes a 0 °C decrease in CP, indicating that the effect of additives at 100% loading on SME and MME is not statistically significant.

When the effect was separated for additive type, MCC P205 and Arctic Express had a higher CP depressant effect on MEE at 100% loading (table 3). For methyl esters, there was no significant advantage of one additive over another. Since the additives inhibit the growth of crystals and not necessarily their first appearance, they usually have minimal impact on CP. The crystallized nucleus is submicron in size and invisible to the naked eye. As the crystals continue to grow and reach of diameter of 0.5 μm in sufficient quantity, they become visible and are defined as cloud point. Some cold flow improvers co-crystallize with biodiesel molecules to change the crystal lattice in such a way that crystal adhesion is reduced (Chandler et al., 1992), hence reducing the cloud point. For methyl stearate, x-ray diffraction studies revealed long spacing that was nearly twice that of ethyl ester (Gunstone, 1967). The methyl ester molecule possesses sufficient polarity in the carboxylic group at one end to attach itself with another methyl ester molecule (fig. 2). In the case of ethyl ester, the carboxylic group is too far inside molecular structure to have a strong polar attraction to form a head-to-head joint. Instead, ethyl stearate has non-polar chains in the head group that are sufficiently large to shield the forces between polar pairs of head groups. Hence, this group forms a weaker bond between crystal layers, and the molecules are arranged head-to-tail fashion (Dunn, 2005; Larson and Quinn, 1994; Gunstone, 1967). This allows additive molecules an easier access to the carboxyl head group.

This may be the reason that the additives worked better for ethyl esters. For an additive to lower CP, it has to attach itself and co-crystallize with the biodiesel molecules, forming more numerous but smaller crystals (the same quantity of crystals divided by a larger number of growth sites). The cold flow additive then absorbs onto growing crystal surface, preventing plate-type growth patterns (Chandler et al., 1992). Since it is easier for an additive to attach itself to the
The reason that additives are more effective in MME than in SME or UVME may be explained by their fatty acid profile. MME typically has about 5% saturates (methyl palmitate and methyl stearate combined) compared to 15% saturates in SME and UVME. The saturated methyl esters have much higher melting points than unsaturated methyl ester (table 1). Therefore, the saturated fractions of the methyl ester are the fractions that form the crystal nuclei, which act as cloud seeds. As discussed earlier, cold flow additives absorb onto the growing crystal surface, preventing plate-type growth patterns. Since there are smaller number of saturates in mustard methyl ester to begin with, the biodiesel-additive co-crystals are farther apart and have less probability of coming together to adhere for crystal growth. In addition, only a fraction of the additive is needed to combine with the saturate fraction in MME compared to SME or UVME. As the temperature continues to drop, there is more unused additive available to co-crystallize with the crystallizing biodiesel molecule. There may be adequate additive molecules to co-crystallize in the case of MME, but not for SME or UVME at 100% loading. This also explains why a higher amount of additive was more effective in SME and UVME than in MME (fig. 3).

**EFFECT OF ADDITIVES ON POUR POINT**

Four-way ANOVA showed the main effect of PP due to feedstock was significant (P>F = 0.0001). Analysis with the Bonferroni method of multiple comparisons showed that the collective effect of fuel additives on MEE was significantly higher, with average reduction in PP of 19.4°C (fig. 3) at 100% loading. Since the same oil feedstock was used for making MME and MEE, the result confirmed that the fuel additives were significantly more effective in reducing the PP of ethyl ester than methyl ester. The effectiveness of additives on MEE was also significantly better than on SME or UVME up to 200% loading. The effects on SME and UVME were not statistically significant, and the 95% confidence interval line actually crossed the 0 decrease line in both cases, thus rejecting the hypothesis that the mean effect is not equal to 0.

The reason that additives are more effective in MME than in SME or UVME may be explained by their fatty acid

![Figure 2. Molecular structures of methyl and ethyl stearates: (a) methyl stearate possesses sufficient polarity in the carboxylic head group to form a bilayer structure with head groups next to each other; (b) ethyl stearate has non-polar chains in the head group that are sufficiently large to shield the forces between polar pairs of head groups (sources: Dunn, 2005; Larson and Quinn, 1994; Gunstone, 1967).](image)

![Figure 3. Mean additive effect on PP for B100 at different loadings. Middle point indicates mean, and vertical line indicates 95% confidence interval of the mean.](image)
greater effect with additives than neat biodiesel. For mustard biodiesel (both MME and MEE), all of the additives had PP below -36°C (table 4) for up to B20. For B5, all additives on all feedstocks had PP ≤ -36°C. For B20, Arctic Express lagged behind for SME and UVME, and BioFlow 875 lagged for UVME. For B100, Arctic Express performed better on UVME, and Flozol 503 underperformed for MEE.

**Effect of Loading**

With higher loading, the PP values of all B5 and B20 blends were ≤ -36°C. The difference between 200% and 300% loading could not be detected since B0, B5, and B20 all reached a PP of ≤ -36°C at 200% loading. For B100, the effect was different for different feedstock-additive combinations (table 5). The difference in PP between 100% and 200% loading was highest for MEE (from -15°C to -28°C at 200%) treated with Flozol 503. Except for this particular case, there was no significant benefit of using higher loading for either MEE or MME. For SME and UVME, other additives except Flozol 503 had some advantage when higher loading was used.

**CONCLUSION**

Four commercially available cold flow additives were evaluated for their effectiveness in reducing the PP and CP of biodiesel from different feedstocks. It was found that both CP and PP of neat biodiesel were reduced by fuel additives. The additives were significantly more effective in ethyl ester than in methyl ester. The average reduction of CP in B100 methyl ester was 0.6°C, compared to 3°C reduction in ethyl ester. The difference was statistically significant. The reason that additives worked better for ethyl ester than for methyl ester could be because of the strong bonding between the carboxylic groups of methyl ester molecules compared to ethyl ester molecules. The additive could easily co-crystallize with ethyl ester molecules and slow crystal growth. Decrease in CP among methyl esters (SME, MME, and UVME) was not statistically significant.

The collective effect of fuel additives in reducing PP was significantly higher for MEE, with an average reduction of 19.4°C. The effectiveness of additives on MME was also significantly better than on SME or UVME up to 200% loading. This effect was attributed to the higher fraction of saturates in SME and UVME compared to MME. In general, the additives worked better in reducing PP for mustard biodiesel because of its low saturate content. The difference in additive effect on SME and UVME was not statistically significant.

All of the additives reduced the PP of B5 to ≤ -36°C. In general, the additives worked better for diesel fuel, and hence the lower the percentage of biodiesel in a blend, the better the additives worked in reducing PP. For B20, Arctic Express lagged behind for SME and UVME, and BioFlow 875 lagged for UVME. For B100, Arctic Express performed better on UVME, and Flozol 503 underperformed for MEE. When twice the amount of recommended loading was used, all additives reduced the PP to ≤ -36°C for B20.

**REFERENCES**


