An ASAE Meeting Presentation

Paper Number: 056121

Cold flow properties of biodiesel and effect of commercial additives

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Written for presentation at the
2005 ASAE Annual International Meeting
Sponsored by ASAE
Tampa Convention Center
Tampa, Florida
17 - 20 July 2005

Abstract. *One of the major reasons hindering widespread use of biodiesel is its higher filter plugging temperature than regular diesel fuel. Cloud point (CP) and pour point (PP) temperature are shown to be well correlated with filter plugging point which primarily determines the operability of a diesel engine. Many biodiesel fuel additives are available in the market claiming to reduce cloud point and pour point. Biodiesel from different feedstocks at different blend levels were tested for cloud and pour point with various fuel additives readily available in the market at 100, 200 and 300% of the specified loading rate. Although reduction in both CP and pour points were significant, the magnitudes of reduction were not equal. Average reduction in cloud point temperature was 2.3°C whereas average reduction in pour point was 14.1°C. It was observes that mustard ethyl ester (MEE) responded best for fuel additives followed by mustard methyl ester (MME) for both cloud and pour point. B20 blend level responded the least for reduction in cloud point temperature but response for pour point reduction was found to be the highest. It was concluded that right choice of fuel additive depends both on feedstock and biodiesel blend level. In general higher percentage loading of fuel additive lower the cloud and pour point more up to 200% of loading of specified concentration but the effect was not significant after 200%. Therefore fuel additive loading of more than 200% of specified level was not recommended.*

Keywords. Biofuel, Fuel additives, Biodiesel blend, pour point, CP.

Introduction

Biodiesel is a proven bioenergy that can be used in place of petroleum diesel fuel without any engine modification. Biodiesel has many environmental benefits over petroleum diesel and is a renewable fuel. Peterson and Hustrulid (1998) estimated that CO_2, a green house gas, can be reduced up to 113-136 billion kg per year due to use of biodiesel. In general, biodiesel reduces particulate matter and carbon monoxide up to 50%, hydrocarbon up to 70% but, NOx emission usually increased up to 10% for B100 i.e. 100% biodiesel (IEA (2004)).

With rapidly increasing petroleum oil price, biodiesel is becoming more popular throughout the world. In the USA and other cold regions of the world, one of the most concerned properties among biodiesel users it its unfavorable cold weather flow properties. Handling and blending 100% biodiesel (B100) in cold weather can be difficult. This limits the use of biodiesel during the winter season. Biodiesel in general has higher cloud point (CP) and pour point (PP) which is correlated with cold filter plugging point. Fuel filter plugging is one of the most frequently experienced troubles in colder weather operation.

Cold flow properties of biodiesel depends on many factors including impurities, oil feedstock, type of alcohol used, and amount of bound glycerin in biodiesel . 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 a 25°C difference in PPs among the biodiesel fuels. Van Gerpen et al. (1997) found that the presence of unsaponifiable matter in the oil up to 2% did not significantly changed cloud and PP. Usually vegetable oil contains less than 2% of unsaponifiable matter. However, CP increased with increasing amount of the saturated monoglycerides (MG) and diglycerides (DG). Presence of MG and DG up to 1% did not change the PP temperature.

CP and PP have been routinely used to characterize the cold flow operability of diesel fuels (Chiu et al., 2004). ASTM biodiesel specification does not specify the required values for CP but it requires the producers to specify the temperatures in specification. The standard however, does not require stating the PP temperature. In actual operation of a diesel engine it is the cold filter plugging point (CFPP) (or low temperature filterability (LTFT) in Europe) that is more important to successful operation. Chiu et al. (2004) showed LTFT as a non linear function of CP and PP. The non linear coefficient showed that for the same CP and PP, the LTFT was lower for fuel with 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 function of CP.

Different fuel additives for diesel and biodiesel to improve the cold flow properties are available in market. Generally, additives are developed to distort the wax crystal shape and to some extent alter their size to inhibit their growth and thereby reducing PP temperatures. Many additives contain proprietary components, and copolymers of ethylene and vinyl acetate or other olefin-ester copolymers (Chiu et al., 2004). Fuel additives available in the market for pure biodiesel and biodiesel-diesel blends are supposed to reduce the gelling temperature of fuel and make it operable at low temperature. The problem is more prominent for higher blend level of biodiesel.

It was reported that the engine operators who use biodiesel add more than recommended amount of cold flow depressant assuming that the cold flow improvers have a linear effect. The effect of adding more than recommended amount on cold flow properties are not well documented. There may be a limited advantage from doing so.

The objective of this research is to evaluate commonly available biodiesel additives that the users can buy in the United States to improve cold flow operability in biodiesel from different feedstocks.

Experimental Setup

Experiment has been divided into two steps. The first step was intended to reduce the number of feedstocks and fuel additive in the study by identifying the most important ones. To identify the important feedstocks, biodiesel with similar characteristics in terms of their cold flow properties were grouped and a representative feedstock was chosen for further study. For the fuel additives, the ones which showed effectiveness in initial testing were considered to be the most effective and were considered for further test.

Initial screening:

Commonly used Biodiesel were considered for study. The biodiesel type considered were canola methyl ester (CME), mustard ethyl ester (MEE), mustard methyl ester (MME), used peanut oil methyl ester (PME), Soybean methyl ester (SME) and used vegetable oil methyl ester (VME). The data indicated that CME and MME had similar cold flow properties. Even though both MME and MEE were coming from mustard their CP and PP both were significantly different. Therefore CME was screened out and MME was included in the final study. SME, VME and PME had similar cold flow properties but since SME is the primary source of biodiesel in USA we have selected SME and PME both to be included in the study. Therefore the biodiesel feed stocks considered for further studies were MEE, MME, PME and SME.

Commercially available biodiesel additives (Wintrox , UK), Flozol 503 (The Lubrizol Corporation, Wickliffe, OH), Bioflow 875 (Octel Sterron, Newark, DE), MCC P205 (Midcontinental chemical, Overland Park, KS), K100-D (Kinetic laboratories, Youngstown NY), Arctic express 0.25% (Power service, Weatherford, TX), and Flow Master (Primrose oil Co, Dallas, TX). In the initial study we have observed that Bioflow 875 (Bioflow), Flozol 503 (Flozol), MCC P205 (MCC) and Arctic express from power service (PS) were more effective than others in B100. Based on their effectiveness Bioflow, Flozol, MCC and PS were selected for this study.

Experimental design

Four variables: type of feedstock, type of additive, percentage of biodiesel in a blend and amount of fuel additive were identified as important variables affecting cold flow properties of the biodiesel diesel mixture. A completely randomized design was used in this experiment. Biodiesel were made in batched and each batch of biodiesel was used to prepare different blend levels of biodiesel. The biodiesel were prepared in the laboratory as needed and one batch of biodiesel was used to prepare variable numbers of samples, hence it was assumed that the variability coming from making biodiesel (batch effect) was randomized. Percent loading and percent biodiesel blend were randomly selected for a given batch of biodiesel and hence their effect on final result was also considered randomized. Biodiesel getting different fuel additive and loading treatments were also completely randomized.

The biodiesel blend levels were selected at 5% (B5), 20% (B20) and 100% (B100) as these are the most commonly used blend levels. The amount of additive was varied at four levels: no additive, 100% of specified level, 200% of specified level and 300% of specified level. Most of the additive had 1:1000 specified loading levels.

Cloud point and pour point measurement

ASTM (2003a) defines CP for petroleum products and biodiesel fuels as the temperature of a liquid specimen when the smallest observable cluster of wax crystals first appears upon cooling under prescribed conditions. ASTM D 2500-02 specification 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 cooling medium. It is reported in the specification that 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 of a petroleum product is defined as the lowest temperature at which movement of the test specimen is observed under prescribed condition of test (ASTM, 2003b). Same definition was used for biodiesel. The PP was determined according to ASTM D 97-02 specification. In this method after preliminary heating, the sample is cooled at a specified rate and examined at interval of 3°C for flow characteristics. The lowest temperature at which movement of the specimen is observed is recorded as the PP. It is reported in the specification that the method has repeatability of ±2.52°C and reproducibility of 6.59°C with 95% confidence interval.

Result and discussions

Total of 444 samples were tested for CP and PP determination. Observed mean of CP for all B100 biodiesel under study were between 0° and 5° C with 95% confidence interval. This data accords with CP reported in earlier literatures by Peterson et al. (2000) and Briggs and Pearson (2005). Among the selected biodiesel, the PP of mustard methyl ester was found to be the lowest with average temperature of -15°C. Total of four batches of biodiesel were tested with each feedstock.

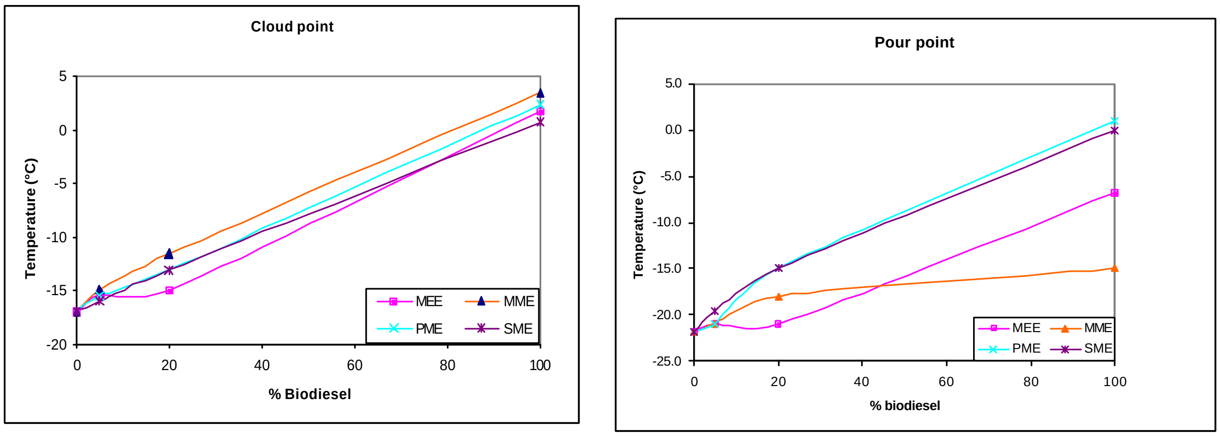
Table 1. Average cloud and pour point temperature of four feed stocks under study. Figures under parenthesis shows standard error.

	MEE	MME	PME	SME	#2 Diesel
Cloud	1.8 (0.3)	3.5 (0.3)	2.3 (0.3)	0.8 (0.3)	-17.0 (0.0)
Pour	-6.8 (0.8)	-15.0 (0.0)	1.0 (1.0)	0.0 (0.0)	-21.8 (0.8)

The PP of MME was close to the rapeseed methyl ester (RME) reported by Peterson et al. (1997). PP of mustard ethyl ester was higher than the temperature reported by Thompson et al. (1998), Peterson et al. (1997) and Peterson et al. (2000). However the PP recorded for RME varied from -10°C to -15°C in different literatures. This may be coming from difference between fatty acid profiles of two oils. Mustard oil has higher percentage of Oleic and Linoleic acid whereas Rapeseed has higher percentage of Erucic acid.

When biodiesel was added to diesel, CP increased with increasing amount of biodiesel (fig 1). The relation was near linear except for MEE. The CP temperature at B5 was not significantly different from B20. However the data points indicated only the average of different batches of biodiesel. In order to test for adequacy of linear model, orthogonal contrast was generated in SAS statistical program (SAS Institute, Cary, NC) and measured for linear, quadratic and cubic polynomial effect (Kuehl, 1999). The analysis showed that the linear equation adequately characterized the relationship between biodiesel blend level and CP. The coefficient of determination (R^2) for all feedstocks were found to be greater than 0.99. From which it was conclude that the biodiesel blend level without an additive has a linear relation between blend level and CP temperature.

The relationship between PP temperature and biodiesel blend level appeared to be non linear relation (fig 1b). Quadratic and cubic effects were significant which shows that the relationship was non linear. It was noticed that for MEE, PP remained constant almost at the level of diesel fuel up to B20. For SME, PP increased significantly with increasing biodiesel blend level under study.



(a) (b)

Figure 1. Cloud point and pour point of various blend levels of biodiesel. The relationship was found linear for cloud point but it was non linear for pour point.

Effect of fuel additive

When fuel additives were loaded to the fuel, both CP and PP decreased at various magnitudes. Difference in mean temperature of each combination of treatment with and without fuel additive is considered as the effect of fuel additive. A contrast between the CP temperature without fuel additive and with fuel additive showed that the CP temperature has reduced by average of 2.2 °C with 95% confidence interval of 2.1°C to 2.3 °C. Standard errors for contrasts were adjusted to take account of variable numbers of replications for with fuel additive and without fuel additive (Kuehl, 1999). Similarly PP depression from using additive was on average 14.1°C with 95% confidence of interval between 13.6°C and 14.7°C.

Four-way ANOVA was fitted with main and interactive effect with model:

$$\Delta t = a_1\, FS + a_2\, BD + a_3\, AD + a_4\, LD + a_5 FS \times BD + a_6 FS \times AD + a_7 FS \times LD + a_8 BD \times AD \\ + a_9 BD \times LD + a_{10} AD \times LD + e \qquad (1)$$

Where Δt is the decrease in temperature, *FS* is feedstock, *BD* is percent biodiesel, *AD* is additive type, *LD* is percent of recommended loading and *e* is random error. This model was used to analyze the effect on both CP and PP.

Effect on cloud point

All four factors played a significant role in reducing CP temperature. Interaction effects were significant except for additive and loading. To identify the group means that were different, group means and their confidence interval were plotted for different variables (fig 2). Bonferroni method of multiple comparisons (Johnson and Wichern, 2002) showed that the collective effect of fuel additive on MEE was highest with average reduction in CP of -3.2°C. This temperature was significantly lower than the temperature effect on other biodiesel feedstocks. MME also showed significantly decrease in CP temperature than SME and PME. Although SME had the lowest decrease in CP temperature of -1.4°C it was not significantly higher than PME (fig 2a).

Percentage of biodiesel had significant effect response to fuel additive at 95% confidence interval ($F_{2,314} = 6.5$; $P>F = 0.0017$) . The decrease in CP was not linear with %biodiesel in the mixture. B20 showed significantly lower effect on CP reduction than B5 or B100. The difference between B5 and B100 was not significant (fig 2b).

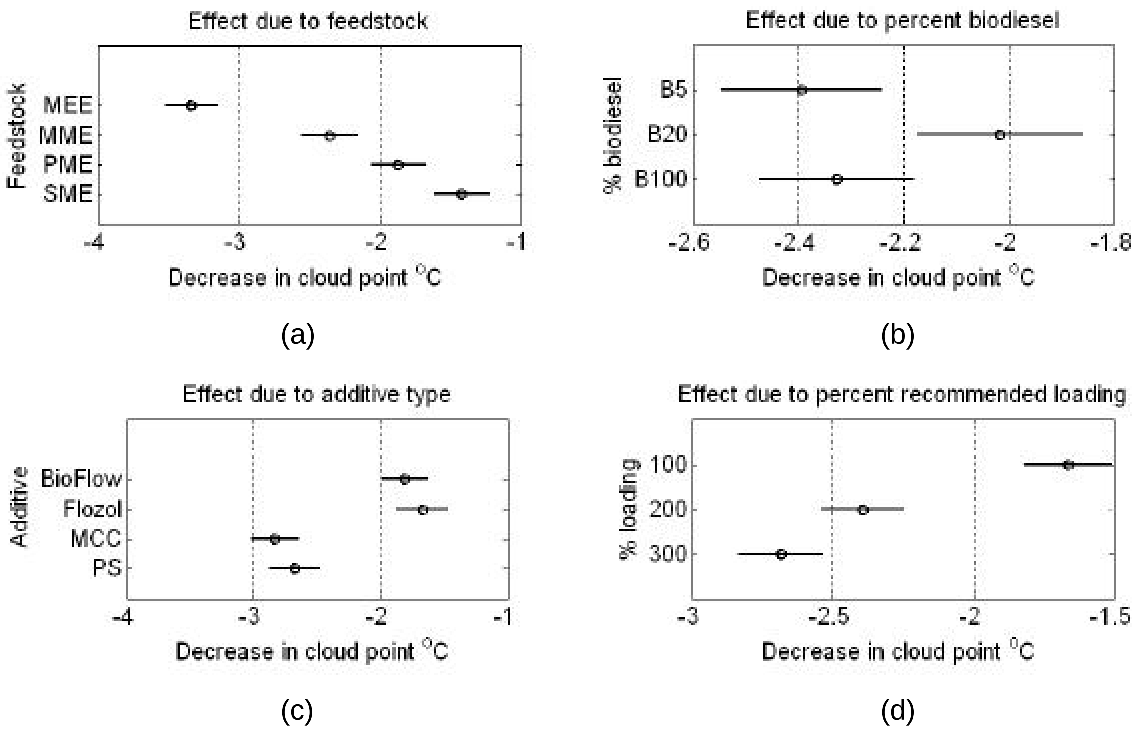


Figure 2. Effect of four different variables in decreasing CP temperature on effectiveness of fuel additive; a) effect due to feedstock, b) effect due to percent biodiesel c) effect due to additive type d) Effect due to loading. Middle circle indicates mean, horizontal bar indicates 95% confidence interval of the mean.

Effect of type of fuel additive on lowering CP temperature could be divided into two groups. Cloud point depression due to Bioflow or Flozol was significantly lower effect than due to MCC or PS (fig 2c). The difference between actual means of Bioflow and Flozol were not statistically significant neither were between MCC and PS. When 200% of specified fuel additive was used, the CP was significantly lower than using 100% loading. However, the mean difference between 200% and 300% loading was not significant.

Two factors interaction showed that the interaction effect between feedstock and additive type was highly significant ($F_{9,314} = 8.32$, $P>F = 0.0001$). This indicates that effect of fuel additive is different for different feedstocks i.e. some additives are better for one feedstock than others. The interaction between feedstock and percent biodiesel was also significant ($F_{6,314} = 25.46$, $P>F = 0.0001$). This indicates the effect of a fuel additive is not only different for different feedstocks but also some fuel additives works better for a specific blend of biodiesel. For instance, at specified additive loading, MCC and PS were comparatively more effective for B100 MEE, while MCC was the most effective for B20 SME which is the most common biodiesel and blend level in the US (Table 2).

Table 2: CP depression at 100% of recommended loading for biodiesel from various feedstocks and blend level

Additive	MEE			MME			SME			PME		
	5	20	100	5	20	100	5	20	100	5	20	100
Bioflow	-2.0	0.0	-2.3	-1.5	-1.5	-1.3	-1.5	-1.0	-0.6	-1.0	-2.0	-1.7
Flozol	-0.5	-1.5	-0.1	-1.0	-1.5	-0.5	-1.0	-1.0	-1.3	-0.5	-1.0	-1.8
MCC	-3.0	-2.5	-6.3	-2.5	-2.0	-0.5	-1.7	-1.8	-1.3	-1.5	-1.5	-2.1
PS	-3.5	-3.0	-6.4	-2.0	-2.5	-1.0	-0.3	0.0	-0.8	-2.5	-1.0	-2.3

Collective effect of fuel additives for all loadings and feedstocks showed that Bioflow is most effective in B5 and Flozol is most effective in B100. Even though MCC and PS are least effective in B20, they are significantly better than Bioflow or Flozol (fig 3a).

The interaction between feedstock and percent biodiesel indicates that some biodiesel performs better at higher blend level than others. For instance for MEE, B100 responded most to fuel additive but for SME, B5 responded better (fig 3c).

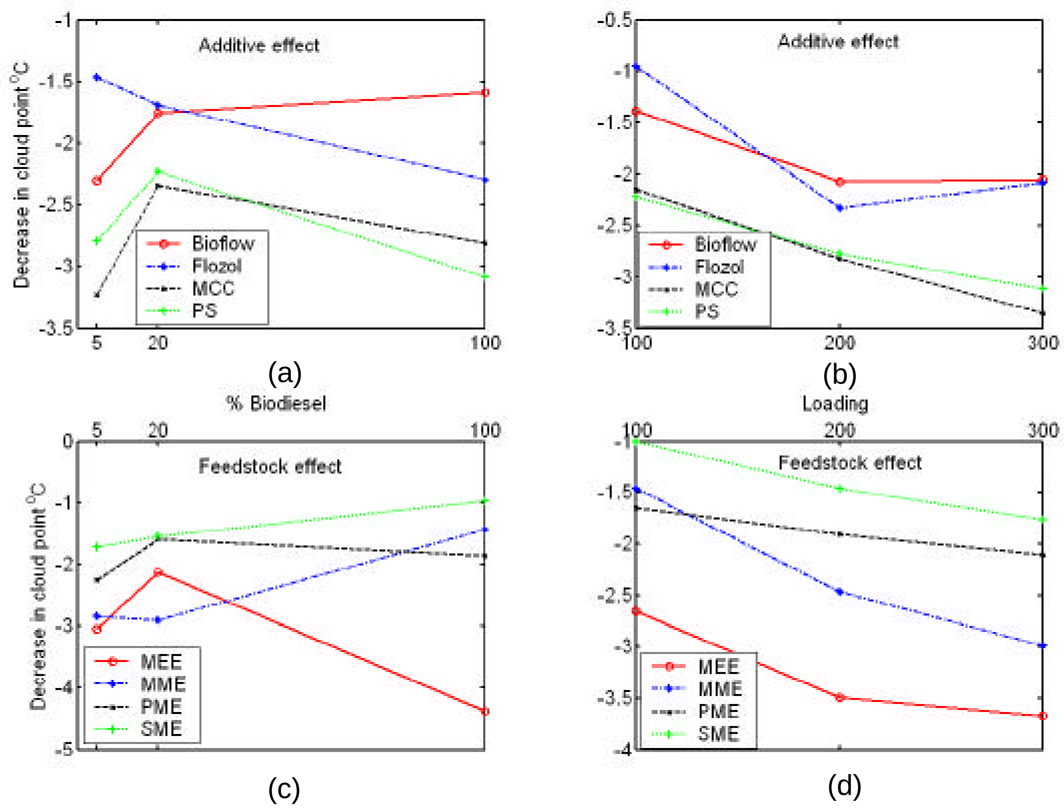


Figure 3. Interaction of Fuel additive, and feedstock versus percent biodiesel, and percent loading. Interaction between loading and additive was not statistically significant.

On average, the higher the concentration of fuel additive, the higher the effect was in reducing CP except for Flozol (fig 3b). The effect of overloading up to 200% was most effective for MEE and MME whereas it was marginally effective for SME and PME (fig 3d).

Effect on pour point

Similar analysis with ANOVA showed that the main effect of PP due to feedstock was significant ($F_{3,314} = 67.6$; $P>F = 0.0001$). Further analysis with Bonferroni multiple comparison showed that effect of fuel additives on MEE was significantly better than other feedstocks. Mean reduction in temperature on MEE was found to be -17.5°C. The difference in PP for MME was also significantly lower than PME and SME. The difference in mean temperature reduction between PME and SME were not statistically significant (fig 4a).

The effect of biodiesel blend level was also significant with B20 being most responsive to the fuel additive. This could be because all of the biodiesel additives were optimized to lower PP at B20 level. The additives had significantly lower impact on neat biodiesel with average reduction in temperature of -9°C (fig 4b).

The main effect of additive type showed that temperature reduction due to MCC was significantly lower than Flozol. Mean difference between Bioflow and PS with any other group mean were not significant (fig 4c).

Percent loading of fuel additive had similar effect as for CP. Reduction in temperature form 100% loading to 200% loading was significant. The added advantage on going from 200% loading to 300% loading was not significant (fig 4d).

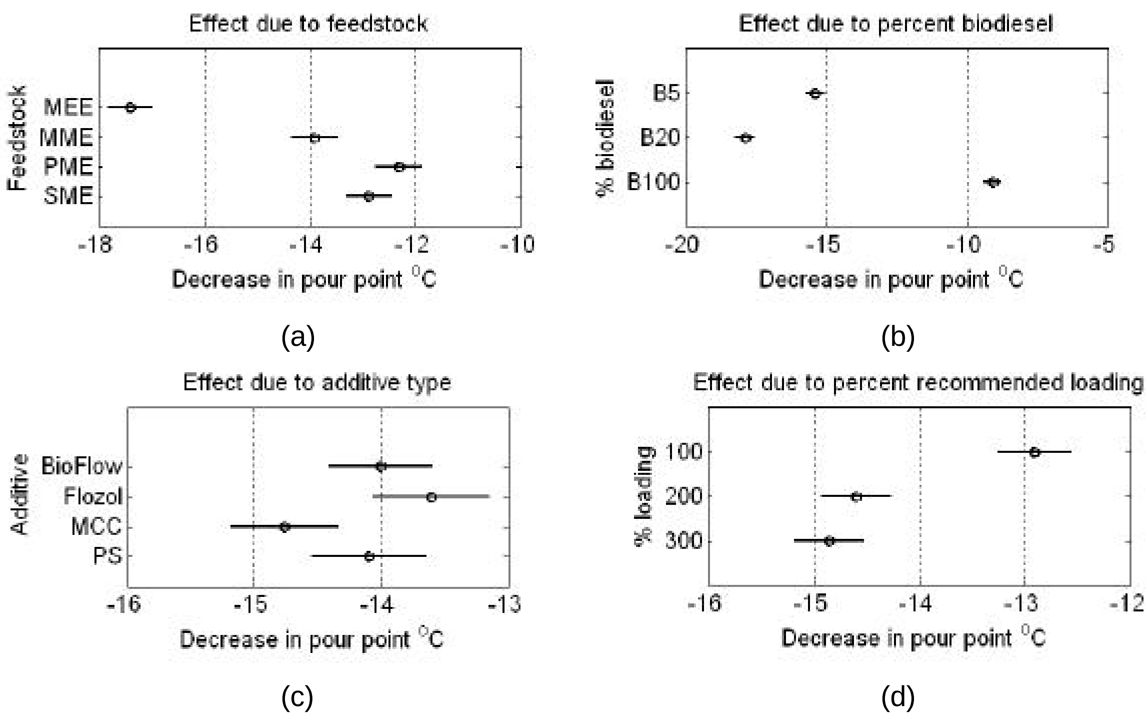


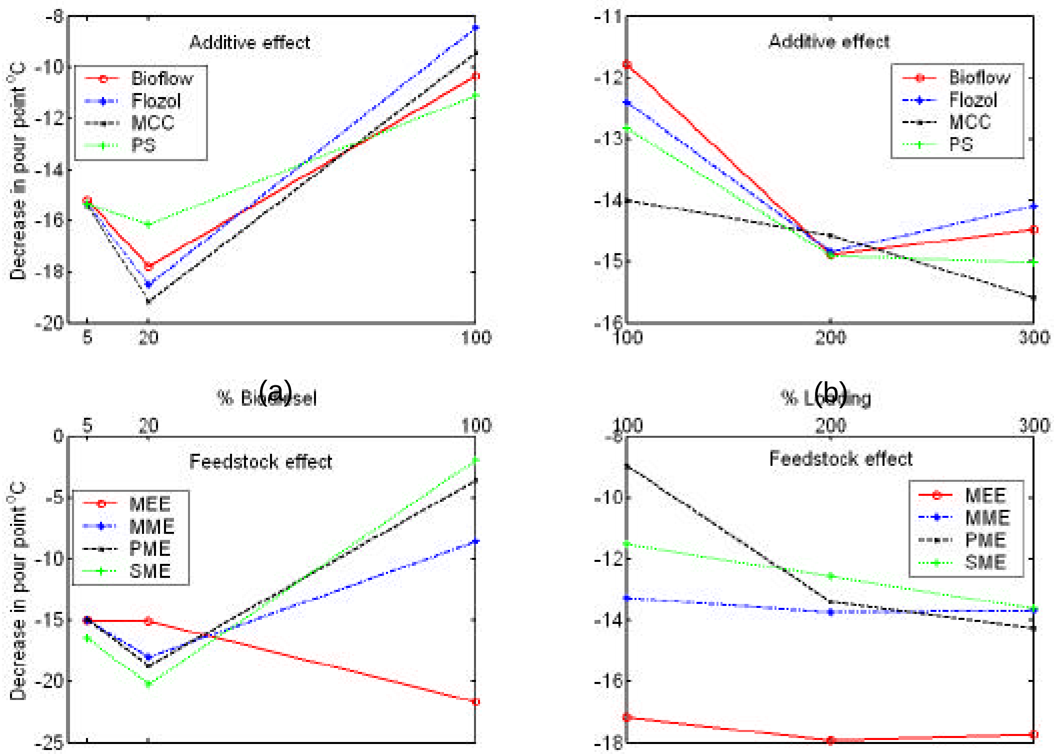
Figure 4. Effect of four different variables in decreasing PP temperature; a) effect due to feedstock, b) effect due to percent biodiesel c) effect due to additive type d) Effect due to loading. Middle circle indicates mean, horizontal bar indicates 95% confidence interval of the mean.

Interaction effect between feedstock and additive was significant ($F_{9,314}$= 8.32, P>F = 0.0001). This indicates that some additives work better for biodiesel from one feedstock than other. Interaction effect between feedstock and %biodiesel was also significant ($F_{6,314}$= 25.46, P>F = 0.0001). This indicates that right choice of fuel additive depends both on feedstock and percent loading. Table 3 shows that Flozol is not a good choice to use on neat biodiesel. Similarly for SME B20, except for PS, all three fuel additives had similar effect. Flozol and MCC worked significantly better for PME at B20 blend level.

Table 3: CP depression at 100% of recommended loading for biodiesel from various feedstocks and blend level

Additive	MEE			MME			SME			PME		
	5	20	100	5	20	100	5	20	100	5	20	100
Bioflow	-15.0	-15.0	-20.3	-15.0	-18.0	-8.3	-16.5	-21.0	0.0	-13.5	-7.5	-1.0
Flozol	-15.0	-15.5	-8.3	-15.0	-18.0	-6.0	-16.5	-21.0	0.0	-15.0	-21.0	-1.0
MCC	-15.0	-15.0	-24.8	-15.0	-18.0	-9.0	-16.5	-21.0	-1.5	-15.0	-21.0	-1.0
PS	-15.0	-15.0	-25.3	-15.0	-18.0	-9.0	-16.5	-10.5	0.0	-15.0	-1.5	-4.0

Interaction between percent biodiesel and additive was significant ($F_{6,314}$= 4.24, P>F = 0.0004). Overall effect of MCC was found to be lowest at B20 blend level but PS had the lowest mean effect for B100 (fig 5a). Interaction between percent biodiesel and feedstock was also found to be significant ($F_{6,314}$= 25.46, P>F = 0.00001). SME responded the best at B20 blend level but at B100 level, MEE was better (fig 5c).



(c) (d)

Figure 5. Interaction of Fuel additive, and feedstock versus percent biodiesel, and percent loading for reducing PP. Interaction between loading and additive was not statistically significant.

Interaction between additive and loading was not significant. This indicates similar trend of add fuel additives at various loading. Bioflow showed the greatest response to excess additive up to 200% loading. MCC showed the least response in the same region (fig 5b). Feedstock and loading was marginally significant ($F_{6,314}$= 2.22, P>F = 0.041). It was observed that except for PME going from 100% loading to higher percent of loading had only marginal advantage. In all cases, the use of fuel additive in excess of 200% of recommended loading is not recommended.

The reason for fuel additive being not significant may be due to the fact that the temperatures were recorded to minimum of -36°C only. Further data on actual PP is needed to confirm this conclusion. Interaction between percent biodiesel and different fuel additive indicates that fuel additives have different effectiveness for biodiesel compared to diesel fuel. It was observed that even though the absolute effect was maximum for B20, PS had the significantly lower PP reduction potential than other fuel additives where as the opposite was true for B100. All additives had similar effect on B5.

Conclusion

Four different biodiesel feedstock were evaluated for effectiveness of reducing PP and CP using commercially available biodiesel fuel additives. The blend level of biodiesel studies were 5%, 20% and 100% (v/v). Fuel additives were also applied at 100, 200 and 300% of the recommended loading. It was found that both CP and PP temperature were significantly reduced from addition of fuel additive; however average reduction of CP was only 2.2°C whereas average reduction of PP temperature was 14.1°C.

Biodiesel from different feedstocks reacted differently for added fuel additives. MEE responded the best for both cloud and PP followed by MME. Effect on PME and SME were not significantly different. MCC and PS reduced CP significantly lower than Bioflow or Flozol but for PP only the difference between MCC and Flozol was significant. The effect of a fuel additive was not only different for different feedstock but also some fuel additives worked better for a specific blend of biodiesel. Also it was concluded that right choice of fuel additive depends both on feedstock and percent loading.

In general higher percentage loading of fuel additive helped lower the CP and PP but the effect was insignificant after 200%. Therefore fuel additive loading of more than 200% of recommended level was not recommended.

Acknowledgements

This project was funded by biodiesel fuel education program sponsored by USDA, and the Department of Biological and Agricultural Engineering at University of Idaho.

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