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Impact of Some Common Impurities on Biodiesel Cloud Point

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***Abstract*.** Commercial biodiesel is allowed to contain some impurities, such as free and bound glycerin, residual alcohol, soap and moisture within a limit specified in ASTM D6751. Compared to conventional diesel fuel, biodiesel has an unfavorable cold flow property. Cold flow properties of biodiesel depend both on fatty acid profile and, amount and types of impurities. This study reports the impact of biodiesel impurities on its cloud point. Commonly used biodiesel (methyl and ethyl esters of canola and soybean) and their blends were considered for viscosity, soap content, free and total glycerin, moisture content, and alcohol content test. The tests indicated that the blend level has the major impact on CP of the biodiesel. The presence of higher level of total glycerol in soy esters significantly increased CP (R^2 ~ 0.93), but no strong relation was observed for canola esters. The combined effect of total glycerol and moisture level improved the regression coefficients for all feedstock, but 95% confidence interval for moisture showed that the impact of moisture was negligible. The completeness of the transesterification reaction is essential to keep the total glycerol level low and to lower CP of the biodiesel. The impact of other impurities under study did not have significant effect on the biodiesel CP.

Keywords. Biodiesel, Impurities, Cloud point, Total glycerol, Moisture.

Introduction

Biodiesel is a cleaner, renewable and biodegradable alternative fuel. Biodiesel comprises of mono-alkyl esters of long chain fatty acids, primarily from 16 to 22 carbon chain lengths, derived from vegetable oils, animal fats and waste fats and oils (Van Gerpen et al., 2004). Biodiesel is produced when oil or fat is chemically reacted with an alcohol in the presence of catalyst such as sodium or potassium hydroxide. Soybean and canola are the best feedstock for Midwest biodiesel facilities (Conley, 2006). A comparison of the most common sources of oil and fat in the United States indicated that the cold flow properties of B100 soybean and canola biodiesel were substantially better than those of grease, lard or tallow.

The batch process is the simplest method of making biodiesel, in which ester and crude glycerol are produced by the transesterification reaction. In proportion, 100 lbs of oil is reacted with 10 lbs of short chained alcohol in the presence of a catalyst to produce 100 lbs of biodiesel and 10 lbs of glycerol. The crude glycerol, which is heavier than the esters, will collect to the bottom after several hours of settling. Excess alcohol and residual catalyst were water washed from the esters and dried as required. The finished biodiesel must be analyzed prior to use as a commercial fuel using sophisticated analytical equipment to ensure it meets biodiesel standard, ASTM D6751 specifications. Complete reaction, removal of glycerin, removal of catalyst, removal of alcohol and absence of free fatty acids are the most important aspects of biodiesel production to ensure trouble free operation in diesel engines (NBB, 2007a).

The low temperature operability of biodiesel is commonly characterized by the cloud point and pour point (Chiu et al., 2004). ASTM (2003a) defines cloud point (CP) as the temperature of a liquid specimen when the smallest observable cluster of wax crystals first appears upon cooling under prescribed fuel. Pour point (PP) is defined as the lowest temperature at which movement of the test specimen is observed under prescribed condition of test (ASTM, 2003b). Since the cloud and pour points of biodiesel are higher than diesel fuel, vehicles running on biodiesel may experience more fuel systems plugging problems than petroleum diesel fuel products (Copeland, et al., 2006). In most of the United States, especially in the months of December through March, the environment temperature can drop low enough to freeze biodiesel fuel (Tayal, 2006).

Blending biodiesel with diesel fuel improves the cold flow properties of the biodiesel blend. The resulting blend will have better cold flow properties than the 100% biodiesel. B5, B20 and B100 are the most commonly used biodiesel blends. Biodiesel blend is a blend of biodiesel fuel meeting ASTM D 6751 with petroleum-based diesel fuel, designated BXX, where XX represents the volume percentage of biodiesel fuel in the blend (NBB, 2007b).

Shrestha et al. (2006) investigated the effect of commonly available biodiesel additives on the improvement of the cold flow operability. They tested CP and PP of biodiesel from different feedstock at different blend levels using various fuel additives. They found that the addition of fuel additive significantly reduced both CP and PP temperatures. However, the average reduction of PP was higher (14.1°C) than that of CP (2.2°C). They found a linear relation between biodiesel blend level and CP temperature. A non linear relation between biodiesel blend level and PP temperature was observed. Hall et al. (1995) found the similar trend for CP of the biodiesel. They reported that data points were scattered about the straight line drawn from 0% to 100% blend data.

Biodiesel cold flow properties depends on many factors including impurities, oil feedstock, alcohol types, amount of free and bound glycerin, moisture content, amount of fatty acid esters, etc. The cold flow properties of biodiesel depend on the feedstock and the alkyl esters from which it is made. This is due to the difference in the degree of unsaturation of the fatty acids of the oil. Vegetable oils consist of numerous fatty acids, for instance, palmitic, stearic, oleic, linoleic and linolenic (Hofman et al., 2006).

Peterson et al. (1997) conducted the cold flow tests on biodiesel prepared using four different feedstock. They found a difference of 25°C among the methyl and ethyl esters of the biodiesel fuels.

Van Gerpen et al. (1996) and Van Gerpen et al. (1997) investigated on the possible contaminants of the biodiesel production. They considered water, free and bound glycerin, alcohol, free fatty acids, soaps, catalyst, unsaponifiable matter and the products of oxidants as the contaminants. They studied the effect of unsaponifiable matter and bound glycerin on the crystallization properties of biodiesel and its blend with no. 1 diesel fuel. They found that the presence of unsaponifiable matter up to 2% had no significant effect on CP and PP. However, high levels of bound glycerin can cause crystallization and increased viscosity. MGs and DGs (particularly saturated MGs and DGs) result in crystallization problem of fuels because they have high melting points and polar characteristics. The partially reacted glycerides, particularly the saturated MGs, have very low solubility in methyl esters and require high temperatures to keep them from crystallizing. The CP of the samples increased with increasing amounts of the saturated MGs or DGs, and even the sample with 0.5% saturated MG (Table 1) had a CP significantly higher than that of the control. DGs were observed to have lower crystallization temperature and seemed to inhibit the crystal formation by MGs.

Table 1. CP of neat methyl esters with various amounts of pure monoglyceride or diglyceride

% MG or DG in esters	1 - monopalmitin	1 - monostearin	dipalmitin
1.0	22	26	21
0.5	10	22	11
0.3	1	9	1
0.1	-3	-1	-4
0.0 (control)	-6	-6	-6

Source: Van Gerpen et al. (1996)

Conley (2006) reported that the high levels of MG plugs engine filter during cold weather. MGs result due to incomplete reaction of fats or oils in making biodiesel. MGs are only partially soluble in biodiesel and as biodiesel gets cold, MGs drop out of solution resulting in a slimy gum that quickly clogs paper filters. Pfalzgraf et al. (2007) identified sterol glycosides (SG) as one source of the filter clogging particulates. SG, which occurs naturally in vegetable oils mainly as soluble fatty acid esters, crystallizes and agglomerates over time that may prevent many of the cold flow methods determining the impact of SG for filter plugging.

McCormik (2006) mentioned the potential impurities in biodiesel to be methanol, free and bound glycerin and catalyst. He further reported that free glycerin and unconverted or partly converted fat (bound glycerin) result in very poor cold flow properties.

The objective of this research is to investigate the impact of some common impurities on biodiesel cloud point. This study is focused on the investigation of effect of water, soap, free glycerol, total glycerol, and alcohol on the crystallization temperature of the biodiesel and also quantifying the effect of the bound glycerol by sensitivity analysis. However, this study does not include the effect of the impurities on the pour point of the biodiesel because the previous investigation has showed that PP can be significantly reduced by adding the fuel additives compared to that of CP.

Methodology

Nine variables: type of feedstock (soybean and canola), type of alkyl esters (methyl and ethyl), blend levels (B5, B20 and B100), moisture content, alcohol content, free glycerin, total glycerin, viscosity, and soap content were investigated for their effect on CP of the biodiesel. Feedstock, alkyl, and blend level were categorized as control variables. The rest of the variables were measured in the laboratory.

The experimental design was a strip-split plot design, with blend levels as whole plots or strip, feedstock as split plots, alkyl esters as split plots and alcohol level as strip plots with two replications for each. The biodiesel batches were prepared in the laboratory as needed and each biodiesel batch was used to prepare different blend levels of biodiesel.

Most commonly used biodiesel (methyl and ethyl esters of soybean and canola) were considered for study. Three different batches of soybean methyl ester (SME), soybean ethyl ester (SEE), canola methyl ester (CME) and canola ethyl ester (CEE) were prepared to keep different levels of moisture, free glycerol and total glycerol in the samples. The biodiesel batches prepared under this study can be categorized into three groups: (A) Control biodiesel batch; (B) Wet biodiesel batch; and (C) Incomplete biodiesel batch. The control biodiesel batch (Batch A) was prepared following the general biodiesel making procedure as described in the introduction section. In the wet biodiesel batch (Batch B), all the process was carried out normally except it was not dried completely at the end leaving the higher amount of water in it. In the incomplete biodiesel batch (Batch C), the reaction was carried out only for 10 minutes, such that it had higher amount of Mono-, Di- and Tri-glycerides. Summer diesel no. 2 was used to prepare 5% (B5) and 20% (B20) blends for each batch.

The specification tests were conducted for each batch and blend levels of biodiesel. The moisture content in the biodiesel was determined using Karl Fischer coulometer. Viscosity measurement was made using viscometer. Free and bound glycerin was determined by Gas chromatography. The soap content was determined using titration. Alcohol content was measured by difference in weight before and after drying alcohol from the sample.

The cold flow tests were run for all the batches and blends of biodiesel samples prepared. CP was determined to the nearest 1°C according to ASTM D2500 specification. Ethanol was used as a cooling medium. It is reported in the specification that the ASTM D2500 has repeatability of ± 2°C and reproducibility of ± 4°C with 95% confidence interval (ASTM, 2003). 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 and 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.

Result and discussions

CP temperatures were determined for total of 116 biodiesel samples. With different types of biodiesel batches and their blends, CP varied at various magnitudes. The mean CP of B100 biodiesel fuel for control batch (batch A) under study were found to be 0, -1, -2 and -1°C for SME, SEE, CME and CEE respectively. These CP values were close to the values reported by Peterson et al. (1997) and Knothe et al. (2004).

The specification test showed that the maximum range of the moisture content in the wet biodiesel was 2727 ppm, which was nine times higher than that of the control batch. The maximum values of free and total glycerin in the incompletely reacted batch (batch C) were found to be 0.26% and 0.95% respectively, which were higher than the values specified by ASTM (2007). Maximum viscosity of 7.41 cst was observed for the batch C.

The correlation matrix indicated the blend level to be the first major factor affecting CP with an R-squared value of 0.91769 and p-value less than 0.0001. The lower blend levels (B5 and B20) had most of it characteristics obtained from the summer diesel used to make it.

The alcohol level in the biodiesel sample showed no significant effect on CP. Likewise, soap showed no effect on CP of the biodiesel. A plot of residual error versus soap didn't give any particular pattern.

Effect of free and total glycerol on CP

The levels of free glycerol and total glycerol in the biodiesel blends (B5 and B20) were adjusted according to the amount of the biodiesel present in the mixture. Free and total glycerol levels present in B100 were factored by 5% and 20% to calculate their amount present in B5 and B20 respectively. The regression analysis showed weak relationship ($R^2 = 0.7872$ for SME, 0.6315 for SEE, 0.6993 for CME, and 0.5520 for CEE) between free glycerol and CP of the biodiesel samples under study. But, a strong relationship was observed between total glycerol and cloud point for soybean biodiesel (fig 1), however no strong relationship was observed for canola biodiesel.

The regression model for total glycerol and CP of the biodiesel sample was fitted as:

$$CP = a_1 + a_2 \ln (TG) \quad \ldots\ldots\ldots \ (1)$$

Where, CP is the cloud point in °C, and TG is the total glycerol.

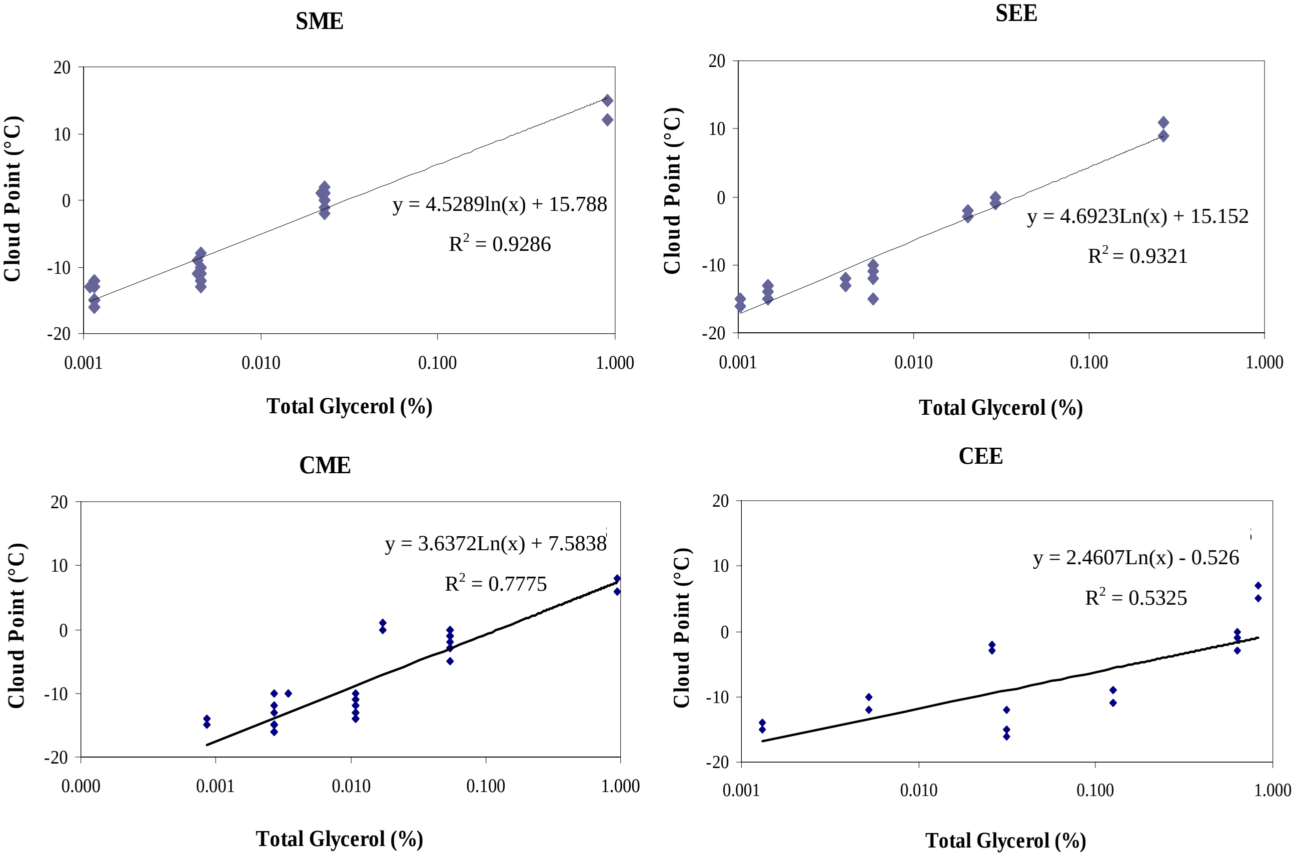

Figure 1. Effect of total glycerol on biodiesel cloud point.

The R^2 values and regression coefficients obtained from the regression model is shown in the table 2. Using the regression equation, an increase in CP by 0.189°C (32.340°F) and 0.196°C (32.353°F) for each 0.01% change in total glycerol was estimated for SME and SEE respectively. Likewise, the sensitivity analysis for canola biodiesel resulted in an increase of CP by 0.152°C (32.274°F) and 0.103°C (32.186°F) for each 0.01% change in total glycerol was estimated for CME and CEE respectively. The amount of total glycerol was assumed 0.24% in the equation (1) which is the specified level for total glycerol as mentioned in ASTM D6751.

Table 2. Regression analysis of CP and total glycerol.

Biodiesel	R^2 value	Co-efficient	
		a_1	a_2
SME	0.9286	15.788	4.5289
SEE	0.9321	15.152	4.6923
CME	0.7775	7.5838	3.6372
CEE	0.5325	-0.526	2.4607

Effect of moisture content and total glycerol on CP

The moisture content in canola esters was higher than that in the soy esters. Hence, it was necessary to investigate the effect of moisture content. The regression model for cloud point as a function of total glycerol and moisture content was fitted:

$$CP = a_1 + a_2 \ln (TG) + a_3 MC \text{ …. } (2)$$

Where, CP is the cloud point in °C, TG is the total glycerol and MC is the moisture content in ppm.

The result from this regression model is shown in the table 3. Except for SME, the coefficient of moisture level (a_3) for other biodiesel blends did not contain 0 in the 95% confidence interval, hence it can be concluded that the effect of moisture on CP was negligible. The sensitivity analysis of the regression model (2) was performed using ASTM D6751 specified level for total glycerol (0.24%) and assuming 0.01% and 0.05% change in total glycerol and moisture content respectively. With every 0.01% change in total glycerol and 0.05% change in moisture content, an increase of CP by 0.632°C (33.138°F), 0.366°C (32.659°F), 0.285°C (32.513°F) and -0.261°C (31.530°F) was estimated for SME, SEE, CME and CEE respectively.

Table 3. Regression analysis of CP, total glycerol and moisture content.

BD	R^2 value	Co-efficient			95% Confidence Interval					
		a_1	a_2	a_3	a_1		a_2		a_3	
					Lower	Upper	Lower	Upper	Lower	Upper
SME	0.9318	15.1684	4.4374	0.0013	12.7223	17.6144	3.9920	4.8828	-0.0008	0.0034
SEE	0.9465	8.7767	3.8185	0.0121	1.8619	15.6914	2.7841	4.8529	0.0002	0.0240
CME	0.8525	6.8480	3.5739	0.0030	4.2775	9.4185	3.0295	4.1184	0.0016	0.0045
CEE	0.7935	-6.2727	1.5842	0.0064	-10.0292	-2.5161	0.7042	2.4642	0.0035	0.0093

The predicted values of CP obtained using the regression equation (2) was plotted against the actual values of CP (fig 2). The figure depicted that the points are closer to the trend line in case of soybean biodiesel compared to that of canola biodiesel. The regression equation (2) was thus found fit to soybean biodiesel than canola biodiesel.

Further, the ANOVA analysis also showed that there is no significant effect of moisture content on CP of the biodiesel blends.

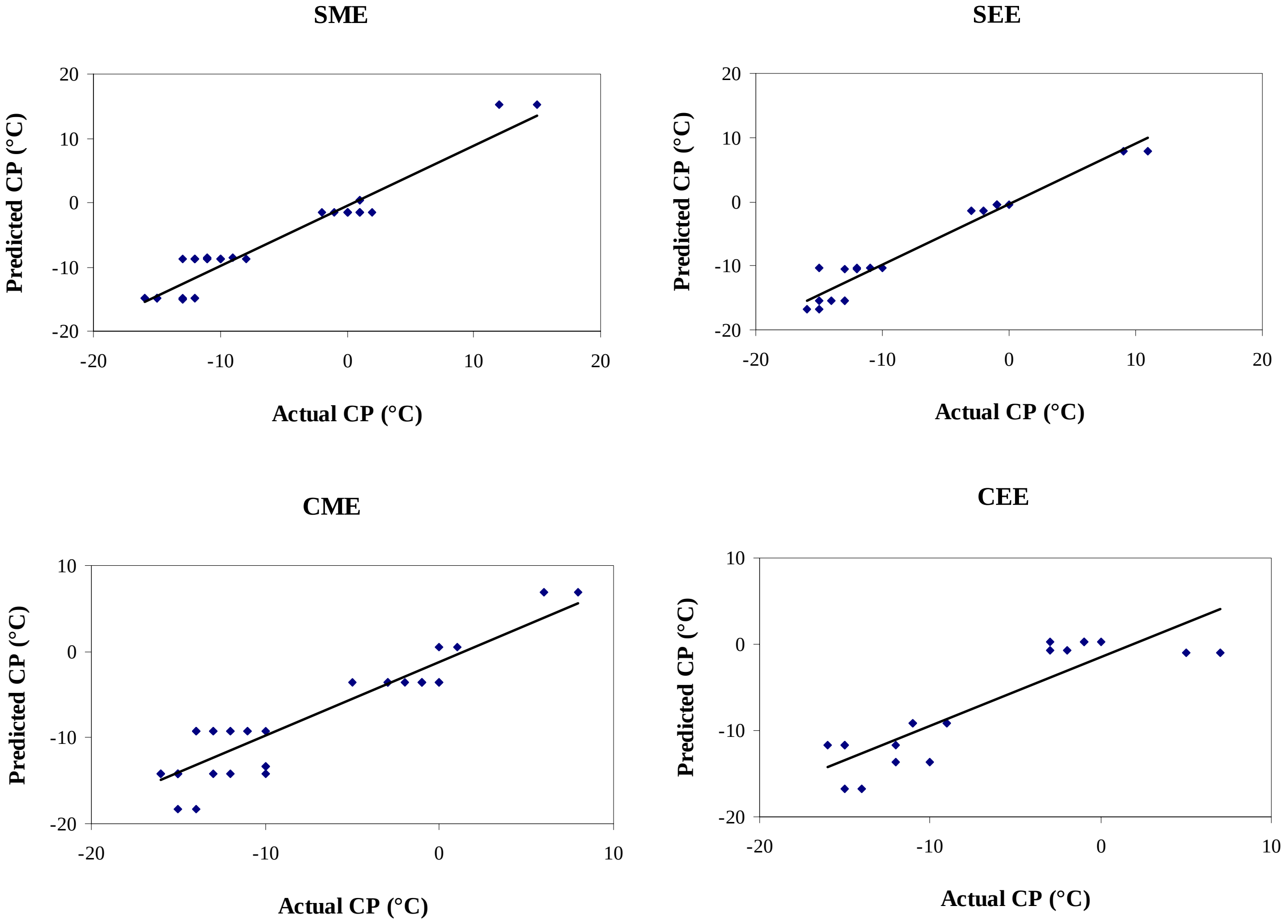

Figure 2. Actual CP versus predicted CP

Conclusion

Some common impurities were investigated for their effect on CP of the biodiesel. Soybean and canola were used as feedstock with blend levels of 5%, 20% and 100%. Nine parameters were studied. The average CP of B100 biodiesel for control batch was observed to be 0, -1, -2 and -1°C for SME, SEE, CME and CEE respectively

Biodiesel blend level showed the significant effects on CP. The presence of the higher amount of total glycerol in the biodiesel significantly increased CP of soy esters with R^2 values around 0.93, but a weak relationship was observed for CP of canola esters. A sensitivity analysis showed an increase in CP by 0.189°C and 0.196°C for each 0.01% change in total glycerol for SME and SEE respectively. The combined effect of total glycerol and moisture level increased the regression coefficients for all feedstock, but 95% confidence interval for moisture depicted that the impact of moisture was negligible. The presence of moisture did not affect the crystallization temperature as MGs and DGs only required a platform to gel. The completeness of the transesterification reaction is essential to keep the total glycerol level low and to lower CP of the biodiesel. The impact of other impurities under study did not have significant effect on the biodiesel CP.

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