Fuel properties and precipitate formation at low temperature in soy-, cottonseed-, and poultry fat-based biodiesel blends

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**ABSTRACT**

The formation of precipitates in biodiesel blends may have serious implications for diesel engine fuel delivery systems. Precipitates were observed in Soybean oil (SBO-), cottonseed oil (CSO-), and poultry fat (PF-) based biodiesel blends after storage at 4 °C. CSO- and PF-based biodiesel had a lower mass of precipitates observed than the SBO-based. Moreover, different rates of precipitate formation were observed for the B20 versus the B100. These suggested that the formation of precipitate during cold temperature storage was dependent on the feedstock and blend concentration. The solvency effects of biodiesel blends were more pronounced at low temperature than at room temperature leading to a higher amount of precipitates formed. Fourier transform infrared (FTIR) spectra, and gas chromatography-flame ionization detector (GC-FID) chromatograms indicated that steryl glucosides are the major cause of precipitate formation in SBO-based biodiesel; while for PF-based biodiesel, the precipitates are due to mono-glycerides. However, the precipitates from CSO-based biodiesel are due to both steryl glucosides and mono-glycerides.

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1. Introduction

Biodiesel is a renewable and environmentally friendly alternative fuel, which is comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats [1]. Biodiesel and its blends with petroleum-based diesel fuel can be used in diesel engines without any significant modification to the engine [2–4]. The advantages of biodiesel over petroleum diesel are improved lubricity, a higher flash point, lower toxicity, and biodegradability [5–7]. Also, since biodiesel is oxygenated, combustion is more complete and produces fewer harmful emissions and pollutants [8,9]. However, the use of biodiesel is limited by its poor low temperature flow characteristics [10]. Cold-flow properties of diesel fuel are usually characterized by the following three temperature measures: cloud point (CP) at which crystallization begins, cold filter plugging point (CFPP) at which fuel starts to plug a fuel filter, and pour point (PP) at which fuel no longer pours. The cloud point of biodiesel fuels is generally higher than that of petrodiesel fuel, and biodiesel has a 15–40 °C higher pour point than that of diesel fuel [11]. Thus, biodiesel begins to gel at crystallization temperatures, and it can clog filters or eventually become so thick that it cannot be pumped from the fuel tank to the engine [6].

Previous studies concerning the cold properties of biodiesel [2,10–12] have determined that the length of the hydrocarbon chains and the presence of unsaturation greatly affect low temperature flow properties [11]. Biodiesel from vegetable oils such as soybean oil (SBO) has better fluidity in cold climates than that from animal fat because SBO-biodiesel had more unsaturated components [10]. However, the effects of biodiesel on cold-flow fuel properties when blended with ultra-low sulfur diesel (ULSD) have not been fully elucidated. Some reported that the dilution effect of the biodiesel in B20 is sufficient such that most problems encountered are minor [13]. A survey of United States state transportation agencies found that nine states reported no fuel filtering problems in cold weather, and eight states identified fuel filtering problems while using blended fuel with petroleum diesel [14]. It is therefore critical to ascertain the conditions under which these precipitates may form for different sources of biodiesel, both neat and when blended with ULSD.

Many studies have reported precipitate formation when fuels were exposed to high temperatures in the presence of oxygen [15–19]. The amount of precipitates may be related to fuel filter plugging and engine deposit formation [15–18]. Samples were usually evaluated in terms of the total insolubles formation (filterable + adherent), which is measured according to ASTM D2274 [20] or ASTM D4625 [21]. Some reported that total insolubles were less than 0.5 mg/100 ml measured according to ASTM D2274 [22], others reported high levels of 2.5–72 mg/100 mL [15,23,24]. There are a number of possible reasons for the great differences that
exists in total insoluble levels within these studies: the presence of natural antioxidants, sample storage conditions prior to testing, and variability in the test procedure. Stavinoha and Howell [15] found that temperature above 80 °C could mask the “effects” of antioxidant, and then increased the total insolubles. Westbrook [23] reported the best discrimination between fuels comes at higher temperatures and longer test times. Kinast [24] reported biodiesel from multiple feedstocks formed different amounts of total insolubles. However, there was no general agreement about the nature of precipitates. Some studies concluded that ULSD is a poor solvent, as compared to neat biodiesel, thus precipitates was formed [19], while other study found the biodiesel fuel was acting as an oxidant to cause the petroleum fuel to produce a higher level of precipitate [25].

De Greyt et al. [26] investigated the nature of “haze” materials in soy and palm biodiesel, and identified that there are “persistent” and “soft” haze. In another study, Pfalzgraf et al. [27] identified steryl glucosides (Fig. 1) [28] in biodiesel and examined their effects on filterability. Nevertheless, there are very few reported studies on the effect of biodiesel and its blend with ULSD on the amount of precipitates was also investigated.

2.2. Fuel property

2.2.1. Composition

The fatty acid methyl ester (FAME) composition of each biodiesel was determined using a PerkinElmer Clarus 500 GC–MS with a split automatic injector, and a Rtx-WAX (Restek, Bellefonte, PA) column (length: 60 m; ID: 0.25 mm, coating: 0.25 µm). The column was held at 120 °C for 1 min and then ramped to 240 °C at 20 °C/min, and it was then held at 240 °C for 13 min. The transfer line between GC and MS was kept at 240 °C. Helium (99.9999%, Cryogenic Gases, Detroit, MI) was used as the carrier gas with a flow rate of 1.5 mL/min. Total Ion Count (TIC) was used for the quantification of each component.

2.2.2. Kinematic viscosity and acid number

The viscosity of each biodiesel at 40 °C was determined following ASTM D445 using a Rheotek AKV8000 automated kinematic viscometer (Poulten Selfe & Lee Ltd., Essex, England). Total acid number of biodiesel in this study was determined according to ASTM D664 using a Brinkman/Metrohm 809 Titrando (Westbury, NY). The acid number is the quantity of base, expressed as milligrams of potassium hydroxide per gram of sample, required to titrate a sample to a specified end point.

2.2.3. Cloud point, pour point, and cloud filter plugging point

The CP, PP, and CFPP measurements were done as per ASTM standards, D2500-05 for CP [30], D97-96a for PP [31], and D6371-05 for CPFP [32]. A Lawler model DR-34H automated cold properties analyzer (Lawler Manufacturing Corporation, Edison, NJ) was used to measure the cold-flow properties.

2.2.4. Free glycerin and total glycerin

Total glycerin is the sum of free and mono-, di-, and tri-glyceride. Free glycerin and total glycerin were determined according to ASTM D6584 [33] with a PerkinElmer Clarus 500 GC equipped with a flame ionization detector (GC-FID). A PE-5HT column (15 m in length, with a 0.32 mm internal diameter, and a 0.1 µm film thickness) was used. The column was held at 50 °C for 1 min and then ramped to 180 °C at 15 °C/min, 230 °C at 7 °C/min, and 380 °C at 30 °C/min, respectively. Finally, it was held at 380 °C for 10 min. Hydrogen (99.9999%, Cryogenic Gases, Detroit, MI) was used as the carrier gas with a flow rate of 3 mL/min.

2.3. Time to filter and precipitate mass

The CP, PP, and CFPP measurements were done as per ASTM standards, D2500-05 for CP [30], D97-96a for PP [31], and D6371-05 for CPFP [32]. A Lawler model DR-34H automated cold properties analyzer (Lawler Manufacturing Corporation, Edison, NJ) was used to measure the cold-flow properties.

Three-hundred mL of fuel in 500 mL media bottles with fluoropolymer resin-lined caps were stored in a refrigerator at a predetermined temperature for 24 h. After the cold soak was completed, the sample was removed and allowed to come to room temperature without external heating before filtering to obtain the time to filter (TTF) and the precipitate mass. The precipitate mass was measured using the filtration apparatus according to ASTM 2274 [20] and ASTM D4625 [21]. Each set of test filters consists of one test membrane filter and one control membrane filter. Briefly, the initial mass of a pair of membrane filters (GF/F Whatman, 0.7 µm) was weighed and recorded before being placed on the filter support, and then the filter funnel was clamped to the support. Three-hundred mL of the fuel was poured into the funnel and filtered into a clean 500-mL glass suction flask, maintained at 68 kPa by a KNF Laboprt filtration pump (KNF Neu- berger Inc., Trenton, NJ). The time to filter (TTF) was recorded. Subsequently, the inside of the sample container, funnel, and the joint between the funnel and filter base were rinsed thoroughly with isooctane (Sigma–Aldrich Inc., St. Louis, MO), and then the funnel was separated from the filter base. The membrane filter was washed by directing a gentle stream of isooctane from the edge.

Fig. 1. Chemical structure of (a) steryl glucoside and (b) acylated steryl glucoside (Taken from reference [28]).
to the center, and a vacuum maintained after the final washing for 10–15 s to remove excess isooctane from the membrane filter. The test and control membrane filters were removed from the filter base and placed in a clean, covered petri dish, followed by drying at 80 °C for 30 min, cooling at room temperature for 30 min, and weighing.

2.4. Characterization

2.4.1. Isolation of the precipitates

After the cold soak was completed, the sample was allowed to come to room temperature without external heating. Most of the fuel was then removed carefully to obtain concentrated precipitates in biodiesel. To prepare the pure precipitates, the concentrated precipitates were centrifuged at 3800 rpm for 10 min at 4 °C and then the upper layer of liquid was removed. The precipitates were then washed using 15 mL heptane (Sigma–Aldrich Inc., St. Louis, MO) to remove the residual biodiesel. However, the precipitates from PF-based biodiesel were not washed by heptane.

2.4.2. Images

Optical images of the concentrated precipitates in biodiesel were taken using an Olympus BX51 microscope (Optical Analysis Corp., Nashua, NH).

2.4.3. FTIR

Standard free steryl glucoside (Matreya LLC, Pleasant Gap, PA) and precipitate samples were dissolved with chloroform and methanol (Sigma–Aldrich Inc., St. Louis, MO) at a volume ratio of 2:1. FTIR spectra of the samples were obtained with a Digilab Scimitar FTS 2000 series FT-IR spectrometer, with 4 cm⁻¹ resolution. The spectrum of chloroform and methanol solvent (2:1) was used as a background.

2.4.4. GC-FID

Stigmastanol (>95%), cholesteryl stearate (96%), and pyridine (>99%) were purchased from Sigma–Aldrich Inc. (St. Louis, MO). Standard solutions of steryl glucoside, stigmastanol, and cholesteryl stearate (1 mg/mL) were prepared by mixing appropriate amount of standards with pyridine, respectively. A standard mixture solution was then obtained by mixing equal amounts of three standard solutions. 2 mg/mL of precipitate solutions were prepared with pyridine. 200 μL of precipitate solution or 200 μL standard mixture solution was then mixed with 50 μL of internal standard (8 mg/mL of tricaprin in pyridine, Supelco, Bellefonte, PA), and 100 μL of N-Methyl-N-trimethylsilyl trifluoroacetamide (MSTFA, Sigma–Aldrich Inc., St. Louis, MO) in a 8 mL vial, and allowed to set for 30 min at room temperature. After that, 4 mL of heptane was added to the vial. 1 μL of the mixture was then injected and analyzed with a PerkinElmer Clarus 500 GC-FID. Details have been described above.

3. Results and discussion

3.1. Composition and physical properties of SBO-, CSO-, and PF-based biodiesel

The FAME compositions for the biodiesel produced from different feedstocks are shown in Table 1. For SBO-based biodiesel, methyl linoleate (C18:2) is the predominant FAME (48.7%); methyl oleate (C18:1) is the next most abundant FAME (25.3%), followed by methyl palmitate (C16:0, 14.1%). CSO-based biodiesel also was predominantly methyl linoleate (53%), but with methyl palmitate having the second greatest abundance (24.7%), followed by methyl oleate (18.5%). The FAME composition of PF-based biodiesel differed greatly from the vegetable oil-based biodiesel, where methyl oleate (36.6%) was the predominant FAME, followed by methyl linoleate (27%), and methyl palmitate (21.8%). For SBO-based biodiesel, total saturated FAME (19.2%) was lower than the values of CSO (28.2%) and PF (30.9%). These results are in good agreement with other reports [13,24].

The viscosity, acid number, free and total glycerin, CP, PP, and CFPP of biodiesel produced from SBO, CSO, PF, and ULSD are presented in Table 2. All were found to be within ASTM D6751-06e1 specifications. The kinematic viscosity is a basic fuel specification for injectors used in diesel engines. The viscosity of PF-based biodiesel was slightly higher than that of SBO-based biodiesel, with CSO-based biodiesel viscosity slightly lower. These findings agreed with those of Wyatt et al. [9] that viscosities for animal fat-derived biodiesel were higher than those for soy-based biodiesel. Demirbas [34] also reported that the viscosities for CSO-based biodiesel were lower than SBO-based biodiesel.

The acid number is an indicator of the quality of the product as well as an indicator for the stability of the fuel because the acid value may increase with time as the fuel degrades due to contact with air or water [19,35]. The acid number of PF-based biodiesel was slightly higher than CSO- and SBO-based biodiesel.

Biodiesel fuel produced from PF had a higher CP, PP, and CFPP than the SBO-based biodiesel, but was similar to CSO-based biodiesel. These results are in agreement with those reported for soy biodiesel [9,10]. Van Gerpen et al. [35] reported that saturated methyl esters are the first to precipitate and that the amount of methyl palmitate (C16:0) and methyl stearate (C18:0) are the determining factors for the CP. Soriano et al. reported that CP and PP increased linearly with increasing chain length, and increased with the degree of saturation [10,11]. They also found that these properties were affected by the intermolecular forces of attraction, which became greater with increasing chain length. The presence of double bonds disrupts the attractive forces operating between molecules along the hydrocarbon chain, causing these physical properties to decrease [10]. This is in agreement with our findings: the more saturated for PF- and CSO-based biodiesel, the higher the CP and PP, as compared with SBO-based biodiesel. However, Immahara et al. [36] found the CP of biodiesel could be determined only by the amount of saturated fatty acid methyl esters regardless of composition of unsaturated esters. Gomez et al. [37] and Wyatt et al. [9] reported that the CFPP values increased with the percentage of saturation. This is consistent with our finding that PF- and CSO-based biodiesel had higher a CFPP than SBO-based biodiesel.

Free glycerin results from incomplete separation of the ester and glycerol products after the transesterification reaction. Free glycerin can cause fuel separation and materials compatibility problems. Glycerides have much higher boiling points than biodiesel or conventional diesel fuel, and can lead to carbon deposits in the engine and durability problems [18,35]. The free and total glycerin measured here for SBO-, CSO-, and PF-based biodiesel were all within the ASTM specification.
3.2. Physical appearance and optical images

Fig. 2 shows the physical appearance of ULSD, SBO-based biodiesel and its blends with ULSD stored at 4 °C after 24 h and then returned to room temperature. Precipitates were observed in B5, B10, B20, and B50. Similarly, precipitates were observed in B5, B10, B20, B50, B70, and B100 after storage at −15 °C, and return to room temperature. On the other hand, no precipitate was observed on the control samples maintained at room temperature. A few studies have reported residuals in the filter and fuel system during cold weather and have characterized the filter plugging materials as a “snowflake-like” material[14]. Fig. 3 shows the optical image of the precipitates at 5× and 20× magnification. The typical micrographs showed irregularly shaped agglomerates (a size of 269 μm) embedded with cloud-like materials (Fig. 3).

3.3. Time to filter

Fig. 4 shows the “time to filter” (TTF) at room temperature for 300 mL of SBO-based biodiesel and its blends with ULSD stored at 23 °C, 4 °C, and −15 °C for 24 h as a function of the concentration of biodiesel. Data shown is the average of three determinations for each sample. For samples stored at 23 °C, the TTF remained relatively constant (~2–3 min) throughout different blend levels. There is only a slight increase in TTF with concentration of biodiesel. For samples stored at 4 °C, TTF for B10, B20, and B50 increased significantly compared with the control (room temperature sample). Interestingly, for samples stored at −15 °C, a significant increase in TTF was observed for B50, B70, and B100. It should be noted that −15 °C is below the cloud point or even the pour point for the B50, B70 and B100. These different times to filter suggested that low temperature storage has an effect on cold-flow operability of the fuel. However, different TTF were obtained for the 4 °C and −15 °C samples. This may be attributed to the effect of temperature, especially below or above cloud point, on particle size formed at different biodiesel concentration.

Table 2

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<thead>
<tr>
<th>Physical properties of SBO-, CSO-, and PF-based biodiesel</th>
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<td><strong>ASTM method</strong></td>
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<tr>
<td>Viscosity, 40 °C (mm²/s)</td>
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<td>Acid number (mg KOH/g)</td>
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<td>Free glycerin (mass%)</td>
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<td>Cloud point (°C)</td>
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<td>Pour point (°C)</td>
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<td>Cold filter plugging point (°C)</td>
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* Specification as given in Ref. [1].

3.4. Effect of storage temperature on precipitate formation

In order to quantify the effect of temperature on precipitate formation, the mass of precipitates was determined for various blend levels. Fig. 5 shows the mass of precipitates (average over three determinations) of SBO-based biodiesel and its blend stored at 23 °C, 4 °C, and −15 °C for 24 h as a function of blend level. The “calculated” line was defined by the precipitate content of the two pure components, ULSD and B100. It represents the amount of precipitate which would result from the corresponding contribution of B100 and ULSD, assuming there was no effect of bio/petrodiesel interaction. The “measured” line was based on experimental data obtained in this study. For samples stored at 23 °C, the amount of precipitates measured increased slightly as the biodiesel blend level increased, however, there is very small difference in the “measured” and “calculated” values (Fig. 5a). This suggests that no significant mass of “new” precipitate was formed as a result of blending when the fuel was stored at room temperature. For samples stored at 4 °C, the mass of precipitates increased
significantly for B10, B20, B50, and B70, as compared to the calculated amount (Fig. 5b). The deviation between the measured and calculated values increased as the percentage of biodiesel increased until a maximum was reached at around 70%. It is interesting to note that the amount of precipitates in B70 is higher than that of B50, while the TTF for B70 was less than B50 (Fig. 4). This may be attributed to the smaller and more uniform precipitates formed from B70, thus maintaining the fluid flow properties through the filter. For the samples stored at −15 °C, the mass of precipitates increased as the percentage of biodiesel increased, however, there was no significant difference between the “measured” and “calculated” value (Fig. 5c). This strongly suggests the “above the cloud point precipitate” is very different in nature as compared to the normal wax-crystal like precipitate formed below cloud point.

3.5. Effect of storage time on precipitate formation

Fig. 6a shows the mass of precipitates formed from SBO-based B100 at 4 °C as a function of storage time. There was no significant change in the first 8 h. An appreciable amount was first observed after 24 h and increased further after 3 days and 1 week. The amount observed after 2 weeks was essentially the same as after 1 week storage. Fig. 6b shows the mass of precipitates formed from B20 at 4 °C as a function of storage time. In contrast to B100, B20 blends show a significant increase within the first 24 h and eventually level off. These data suggest that there are two different mechanisms for the precipitate formation from B20 and B100. In the B20 case, the relatively fast appearance of precipitate can be attributed to the solvency effect [23]. On the other hand, it takes a much high concentration of “insoluble” before it precipitates out from B100 (a very good solvent).

3.6. Effect of feedstock on precipitate formation

The mass of precipitate formed from CSO- and PF-based biodiesel stored at 23 °C, 4 °C, and −15 °C for 24 h as a function of the biodiesel concentration, compared with SBO-based biodiesel, are shown in Fig. 7. For samples stored at 23 °C, the SBO-based biodiesel blends (B2, B5, B10, B20, B50, and B70) exhibit slightly higher precipitate amounts than CSO-based biodiesel with the exception of B100, where CSO-based biodiesel shows a significantly higher amount of precipitate. There was a very low level of precipitate observed for PF-based biodiesel blends. For samples stored at 4 °C, SBO-based biodiesel blends have significantly higher amounts of filterable insoluble as compared to CSO- and PF-based biodiesel blends. The notable exception is the CSO-based B100 which had almost two times more precipitate than SBO-based biodiesel. In this case, 4 °C is below to the cloud point of CSO B100. Again, PF-based biodiesel has the least precipitate. When storage temperature decreased from 4 °C to −15 °C, the degree of precipitate formation remained relatively the same for SBO- and CSO-based biodiesel, however, a slight increase of precipitate level for poultry fat biodiesel/ULSD blend samples (B5, B10, B20, B50, and B70) was
observed. Nevertheless, the amount is significantly less than SBO-based biodiesel blends. In general, CSO- and PF-based biodiesel had lower precipitate levels than the SBO-based. The difference can be attributed to the different nature of the precipitates in the biodiesel.

3.7 Cold-flow properties

Fig. 8a, b, and c, shows the CP, PP, and CFPP of SBO-, CSO-, and PF-based biodiesel as a function of biodiesel concentration, respectively. In general, the CP, PP, and CFPP increased with biodiesel concentration. Moreover, CFPP is close to CP at low biodiesel concentrations, and as concentration increases, the CFPP approaches that of the PP.

For blend levels of 20% and higher, SBO-based biodiesel exhibits a lower CP, PP, and CFPP than PF- and CSO-based biodiesel blends. The CP, PP, and CFPP of B20 for the three types of biodiesel were around 20 °C lower than their corresponding values for B100. One interesting observation is that the CFPP for B20 of SBO-based biodiesel is almost the same as the CP; whereas for the CSO- and PF-based biodiesel, the CFPP was 4 °C and 2 °C lower than the CP, respectively. This may be attributed to the higher precipitate formation for B20 of SBO-based biodiesel than the other types of biodiesel at lower temperature. Thus, the difference between CP and CFPP can indicate relative extent of the precipitates formation above CP.

Previous work has shown that by blending biodiesel with diesel, their cold temperature properties can be improved to levels that
the following correlations were obtained: by empirical second-order polynomial equations [2]. In this study, than the PP. The CP and PP was correlated to the blend composition of the biodiesel fraction.

better than 0.99, suggesting that CP, and PP can be calculated as a function of total glycerides [14], dimers, trimers, tetramers of oxidative products [19]. In one survey report [14,18], it was suggested the precipitate was steryl glucoside. Others suggested the precipitate was formed at lower temperature in biodiesel. Fenwick [39] suggested that the precipitates are mainly due to steryl glucosides. It is noted that there are subtle differences in the spectra of precipitates of CSO-B100 (a doublet of OH peak was observed in Fig. 9c), and CSO-B50 (much sharper CH₂ absorption peaks and carboxyl absorption peak at 1750 cm⁻¹, Fig. 9d), as compared to SBO and steryl glucosides, which can be attributed to the fact that there was trace mono-glycerides or di-glycerides in precipitates of CSO-based biodiesel.

FTIR spectra of the precipitates formed by SBO-B100, SBO-B20, CSO-B100, and CSO-B50 fuel were compared with standard steryl glucoside, as shown in Fig. 9. The FTIR spectrum of standard steryl glucoside (Fig. 9e) reveals a broad OH absorption peak at 3366 cm⁻¹, CH₂ absorptions at 2945 and 2835 cm⁻¹; vibrations of CH₃ absorption at 1466 cm⁻¹ and absorptions at 1217 and 1028 cm⁻¹ attributable to C-O-C groups in the glucosides molecule [40,41]. The above peaks in the spectra of precipitates from SBO-B100, SBO-B20, CSO-B100, and CSO-B50 (Fig. 9a–d) coincide with the standard sterol glucosides. These suggest strongly that the precipitates are mainly due to steryl glucosides. It is noted that some of the peaks can be attributed to mono-palmitin, mono-olein, mono-sterin, free sterols, and steryl ester (Fig. 10b). This indicates that CSO-based biodiesel precipitates are more complex and consist of mono-glycerides, steryl glucosides, and possibly other minor

3.8. Nature of precipitate

There are few studies on the nature of the precipitates formed at lower temperature in biodiesel. Fenwick [39] suggested that the precipitate was steryl glucoside. Others suggested the precipitates were formed by dimers, trimers, and tetramers of oxidative products [19]. In one survey report [14,18], it was suggested the unusual residues and materials causing plugging at both the pump and the engine were glycerin. Thus, the nature of precipitate has not been fully elucidated. Factors such as the presence of steryl glucosides [26,27], mono-glycerides, di-glycerides, tri-glycerides of total glycerides [14], dimers, trimers, tetramers of oxidative products [19], and solvency effect when blended with ULSD are likely involved [23].

are comparable to petrodiesel [38]. Also, the CP is usually higher than the PP. The CP and PP was correlated to the blend composition by empirical second-order polynomial equations [2]. In this study, the following correlations were obtained:

For CP:

\[ T_{CP-SBO} = 247.33 + 42.362X - 13.768X^2 \quad R^2 = 0.998 \quad (1) \]
\[ T_{CP-CSO} = 247.24 + 64.098X - 32.156X^2 \quad R^2 = 0.992 \quad (2) \]
\[ T_{CP-PF} = 248.17 + 60.549X - 28.973X^2 \quad R^2 = 0.994 \quad (3) \]

For PP:

\[ T_{PP-SBO} = 237.16 + 55.133X - 22.442X^2 \quad R^2 = 0.995 \quad (4) \]
\[ T_{PP-CSO} = 236.59 + 83.649X - 44.462X^2 \quad R^2 = 0.997 \quad (5) \]
\[ T_{PP-PF} = 238.75 + 68.393X - 31.65X^2 \quad R^2 = 0.996 \quad (6) \]

where \( T \) is temperature (K), \( X \) is the volume fraction of biodiesel in the blend. The correlation coefficient, \( R^2 \), of these equations was all better than 0.99, suggesting that CP, and PP can be calculated as a function of the biodiesel fraction.

**Fig. 6.** The effect of storage time on the amount of precipitates from (a) B100 and (b) B20 SBO-based biodiesel blend with ULSD at 4 °C.
components. The GC-FID results were consistent with FTIR spectra analysis as described above.

Fig. 11 shows a typical GC chromatogram of standard glycerides, and precipitates from PF-based biodiesel stored at 4 °C for 24 h. Peaks of steryl glucosides are not found on precipitates of PF-based biodiesel (Fig. 11a), instead, peaks attributable to mono-palmitin, mono-olein, and mono-sterin are observed (based on the chromatogram of standard glycerides [Fig. 11b]) [33]. This indicates that the precipitates from PF-based biodiesel can be attributed to mono-glycerides, but not steryl glucosides.

It is known that sterols exist as free sterols, steryl ester, steryl glucosides, and acylated steryl glucosides [42,43]. Steryl glucosides and acylated steryl glucosides have only rarely been reported in animal fats [44]. On the other hand, acylated steryl glucosides occur naturally in plant oils, mainly as soluble fatty acid esters. However, the acylated steryl glucosides are hydrolyzed during the transesterification process of the oil to produce biodiesel. This hydrolyzed, free form of steryl glucoside is much less soluble in the methyl esters. Thus, the steryl glucosides from SBO- and CSO-based biodiesel precipitate out at lower temperature, especially when blended with the ULSD (a poor solvent). Moreover, the precipitates agglomerate to a representative size of ~270 μm (Fig. 3), which are in the same range with Fenwick’s [39] finding on the size of steryl glucosides agglomerates. Therefore, the nature of “above cloud point precipitates” of SBO-based biodiesel is due to steryl glucosides. This agrees with the finding of De Greyt et al. [26], Pfalzgraf et al. [27], Ringwald [45] on the nature of “haze” or “filtered materials”.

Other evidence that “the above cloud point precipitates” are due to steryl glucoside is based on cold soak tests using distilled biodiesel. Distilled SBO-based biodiesel does not contain detectable amount of steryl glucoside, based on GC-FID chromatogram (data not shown). Thus, when distilled biodiesel was used to pre-
pare the B20 blended with ULSD, no precipitate was observed after cold soak at 4 and –15 °C for 24 h.

The ranges of steryl glucosides concentration were reported as 25–272 ppm and 8–22 ppm for SBO-based and CBO-based biodiesel, respectively [26,45]. These reported results correlate well with the trend observed here that SBO-based biodiesel has a much higher mass of precipitates than CSO-based, when cold soaked above cloud point (Fig. 7). It is interesting to note that the mass of precipitates formed in B50 SBO-based biodiesel at 4 °C were more than that of B100. This can be attributed to the solvency effect with ULSD. Steryl glucosides are highly polar [42] and may precipitate out when blended with non-polar diesel fuel.

In the oxidization and storage stability tests, some have concluded that polymeric species formed during storage of biodiesel in controlled conditions, were soluble in oxidized biodiesel (due to its high polarity) but became insoluble when oxidized biodiesel

Fig. 8. The cloud point, pour point, and cold filter plugging point of (a) SBO-, (b) CSO- and (c) PF-based biodiesel and their blend with ULSD fuel as function of biodiesel concentration.
was mixed with diesel fuel [19, 23]. In this study, samples of the filtered SBO-, CSO-, and PF-based biodiesel (i.e. with precipitates removed) were heated at 95 °C during an oxidation period in which 3 L/h O₂ is bubbled through for 16 h [20]. The increase in viscosity and acid number shows the formation of significant levels of oxidative products in these fuels [19] (data not shown). However, when these samples were stored at 4 °C and −15 °C for 24 h and then returned to room temperature, no precipitate is observed on these oxidized B100 biodiesel, or even on B20. This finding confirms the nature of “the above cloud point precipitate” formation is different from the oxidized insoluble observed from high temperature stability test of biodiesel.

Work is in progress to investigate the effectiveness of various approaches, such as: feedstock pretreatment, vacuum distillation,
filtration, and adsorption, to minimize the amount of precipitates formed in biodiesel.

4. Conclusion

1. The saturation and unsaturation composition influence the cold-flow properties: the more saturated the PF- and CSO-based biodiesel, the higher the CP and PP, as compared with SBO-based biodiesel. CFPP may indicate relative extent of the above cloud point precipitate formation.

2. Storage temperature, storage time, biodiesel blend level, and feedstock affect the mass of precipitate formed: more precipitates were formed in SBO-based biodiesel blends at 4 °C than that of both CSO- and PF-based biodiesel.

3. The rate of precipitate mass formation from B20 and B100 suggests a different precipitation mechanism, indicating that solvency of ULSD has a significant influence on precipitates formation.

4. Based on FTIR spectra and GC-FID chromatograms, precipitates from SBO-based biodiesel are due to steryl glucosides, while the precipitates from PF- and CSO-based biodiesel are due to both steryl glucosides and mono-glycerides. However, the precipitates from CSO-based biodiesel are due to mono-glycerides.

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References

[22] Stability of biodiesel used as a fuel for diesel engines and heating systems. Presented at BIOSTAB project results, Graz, Austria, July 3, 2003.


