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Determination of the Fuel Filter Plugging Potential of Palm Oil Biodiesel by an Alternative Method

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Investigating the suitability of turbidimetry as an alternative method to determine the precipitate content and fuel filter plugging potential of biodiesel was the primary objective of this study. First, different levels of precipitate isolated from turbid palm oil biodiesel (POB) were added to distilled POB, and turbidity of the resulting blends at 25 °C was measured. Turbidity had high repeatability (average standard deviation < 0.07 FNU), evidencing the suitability of turbidimetry. In addition, a simple first-order model capable of explaining more than 99 % of the turbidity variability with the level of precipitate was obtained by lineal regression analysis. Blends of turbid and non-turbid POB were then prepared, and turbidity of the resulting blends at 25 °C were measured. The blends were also analyzed in accordance with the ASTM D7501 and D7321 Standard Test Methods. Thus, a simple first-order model capable of explaining more than 98 % of the turbidity variability with the precipitate content was obtained by lineal regression analysis. More important, it was found that turbid POB possessing turbidity lower than 5.3 FNU would meet the ASTM D6751 limit for CSFT. Finally, the effect of temperature effect on turbidity was also examined at 25, 35, and 45 °C, but it was not statistically significant.

1. Introduction

Currently, precipitate formation above the cloud point temperature is one of the main problems that biodiesel producers are facing (Plata et al., 2012). Precipitate is caused by the presence of compounds with high melting temperatures and low solubility in biodiesel such as saturated monoglycerides and free steryl glucosides (Tang et al., 2008). These compounds may precipitate over time during biodiesel storage, even at room temperature (Plata et al., 2012). Since precipitate has caused plugging of fuel filters in engine fuel delivery systems and formed deposits on engine injectors, the American Society for Testing and Materials (ASTM) developed a cold soak filtration test in an effort to address the fuel filter plugging potential of biodiesel. This test, denominated as the ASTM D7501 Standard Test Method, was intended to determine if biodiesel is sufficiently free of precipitate capable of plugging fuel filters. ASTM D6751 Standard Specification requires that biodiesel have a cold soak filtration time (CSFT) below 360 s.

An additional test intended to determine the precipitate content of biodiesel by filtration is the ASTM D7321 Standard Test Method. However, this is a laborious, time-consuming standard (Dunn, 2009), and measurement of precipitate content by filtration has been reported to be susceptible to errors due to contamination and loss of material (Raphael and Rohani, 1996). An alternative, non-gravimetric method for determining the precipitate content of biodiesel, and consequently the fuel filter potential, will be helpful in dealing all these issues.

Palm oil is a perennial crop, unlike soybean and rapeseed. Moreover, palm plantations have the highest oil yield in terms of oil production per ha. These characteristics have made palm oil ideal for biodiesel production in tropical locations (Mekhilef et al. 2011). Currently, there are seven palm oil biodiesel (POB) plants in Colombia with an annual capacity of 550,000 t, making Colombia one of the leaders of biodiesel production in Latin America (Janssen and Rutz, 2011). These plants are the centerpiece of the Colombian Biofuel National

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Program, which was designed to develop the agricultural sector, generate permanent jobs, improve the air quality and replace illicit crops.
Turbidimetry is one of the techniques commonly used to monitor crystallization from solutions (Herri et al., 1999). Using this technique, nucleation and crystal growth, aggregation, and break-up (Crawley et al., 1996) can be directly detected and followed (Lavilla et al., 2009), and the presence of crystals at trace levels (mg L^{-1}) can be detected with high sensitivity (Crawley et al., 1997). Turbidimetry is based on the measurement of the attenuation of an incident light beam passing through a non-absorbent liquid medium where particles in suspension are present (Rabesiaka et al., 2011). The light beam is subjected to scatter and adsorption by the particles, and intensity of the light beam is attenuated. Detectors set around the liquid measure the amount of light transmitted and scattered as an indication of turbidity, which depends on the wavelength of the light beam and the angle at which the detector is set (Pavanelli and Bigi, 2005). Formazin Nephelometric Unit (FNU), one of the most used measurement unit for turbidity, measures turbidity using a near infrared light source and a detector set at 90° from the light beam. Formazin is a stable synthetic material with uniform particle size used as standard for calibration (Morais et al., 2006).
Turbidimetry has also been successfully used to determine the amount of suspended particles of liquid mediums, especially water samples (Pavanelli and Bigi, 2005). The repeatability of turbidity readings, the simplicity of the technique, and the minimal exposure to measurements errors makes turbidimetry suitable for other potential applications (Pavanelli and Bigi, 2005) including the measurement of biodiesel precipitate content. Therefore, the primary objective of this study was to investigate the suitability of turbidimetry as an alternative method to determine the precipitate content of POB. Related objectives were to obtain a model capable of predicting turbidity as a function of the precipitate content with high precision, and to relate filterability of POB to turbidity. Since biodiesel is subjected to different temperatures during the cold soak filtration test, a subsidiary objective was to investigate the effect of temperature on turbidity at different precipitate contents.

2. Materials and methods

2.1 Materials

Turbid POB and precipitate collected after filtration of biodiesel between storage tanks through a polishing bag were supplied by Ecodiesel Colombia S.A. (Barrancabermeja, Colombia). The POB was obtained dynamically from a sampling loop in a distribution line in the processing facility. One portion of the POB was filtered through a 0.7 µm glass microfiber filter (Whatman GF/F, 47 mm diameter, Piscataway, NJ) under 86 kPa of vacuum and was denominated as non-turbid POB; the other portion was not filtered. The precipitate was purified in accordance with Plata et al. (2015) and was denominated as Hz1. Distilled POB was produced using vacuum distillation (180-200 °C, 86 kPa below atmospheric pressure, 180 min). All solvents were Carlo Erba Reagents (Milan, Italy) ACS reagent grade. Silica gel 60 (0.063-0.200 mm) was obtained from Merck KGaA (Darmstadt, Germany).
The experimental set-up (Figure 1) comprised a glass cylinder reactor cell of 80 mm diameter and 140 mm height, surrounded by a cooling jacket through which water/ethylene glycol (50/50 *V/V*) was circulated from a LAUDA-Brinkmann LCK 4907 refrigerated circulator, a HANNA Instruments HI 7609829-4 turbidimetric sensor coupled to a HANNA Instruments HI9829 Multiparameter Meter, and a 3-blade propeller coupled to an IKA RW 20.n mechanical stirrer and located at 25 mm above the bottom of the reactor cell.

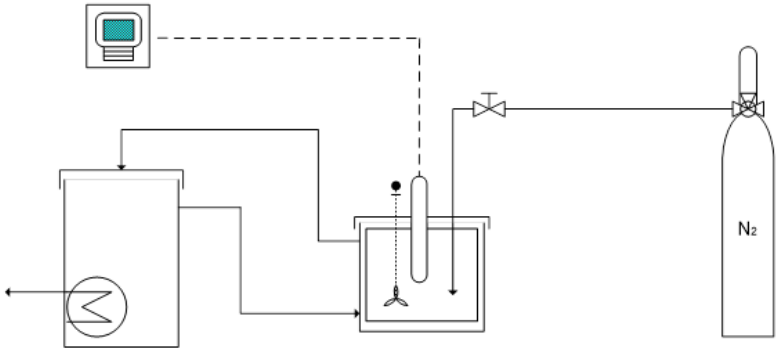

Figure 1: experimental set-up

2.2 Biodiesel analysis

Four different samples were prepared and analyzed in this study: non-spiked distilled POB, distilled POB spiked with different levels of Hz1 (10 to 170 mg L^{-1}), blends of turbid and non-turbid POB (0/100, 15/85, 30/70, 45/55, 60/40, 75/25, 100/0 *V/V*), and POB spiked with two levels of silica gel (45 and 100 mg L^{-1}). In general, 300 mL of each sample were placed in the reactor cell, and turbidity was measured every 15 s for 15 min by total immersion of the turbidimetric sensor in the sample at 25 °C. Stirring of the sample was held at 290 rpm during each experiment. Turbidity of the POB spiked with silica gel was also determined at 35 and 45 °C. Silica gel was chosen over Hz1 to eliminate the possibility that Hz1 was dissolved into the biodiesel at high temperatures. Each experiment was replicated two times.
The blends of turbid and non-turbid POB were also analysed in accordance with the ASTM D7501 and D7321 with minor modifications. The blends were filtered through a 0.7 µm glass microfiber filter (Whatman GF/F, 47 mm diameter, Piscataway, NJ) under 70 to 80 kPa of vacuum, and the time required for the blends to pass through the filter was recorded as the time to filter (TTF). The filtration proceeded until all biodiesel had passed through the filter, in contrast to the ASTM D7501 where filtration is stopped after 720 s. After filtration, the reactor cell was rinsed with *n*-heptane, and the rinses were poured into the funnel and filtered through the glass microfiber filter. Similarly, the funnel was rinsed, and the rinses were filtered. With the vacuum applied, the periphery of the glass microfiber filter was washed with *n*-heptane by directing a gentle stream from the edge to the center. The vacuum was maintained for 10 to 15 s to remove excess *n*-heptane from the glass microfiber filter. The glass microfiber filter was dried in an oven at 110 °C for 30 min and weighed. The precipitate content was calculated from the increase in the mass of the glass microfiber filter.

2.3 Statistical analysis

Data were analyzed by ANOVA followed by the least significant difference (LSD) test for multiple comparisons using Statgraphics Centurion software (free trial version, StatPoint Technologies, Inc., Warrenton, VA). A *p*-value of less than 0.05 was considered statistically significant.

3. Results and discussion

Investigating the suitability of turbidimetry as an alternative method to determine the precipitate content of POB was the primary objective of this study. As noted above, repeatability of turbidity readings is crucial to ensure the suitability of turbidimetry for a potential application. In this regard, turbidity of distilled POB spiked with Hz1 was repeatable, i.e., the average standard deviation was below 0.07 FNU. Moreover, the standard deviation did not increase markedly with the level of Hz1.
As depicted in Figure 2, turbidity of DPOB spiked with Hz1 increased linearly with the level of Hz1, indicating that turbidity variability with the level of Hz1 might be described by a first-order model. Using lineal regression analysis, the model given in Eq. (1) was obtained, where y denotes turbidity [FNU] and x denotes the level of Hz1 [mg L^{-1}]. The goodness of fit was evidenced by a high coefficient of determination (R^2=0.998), indicating that more than 99 % of the turbidity variability might be explained by the model.

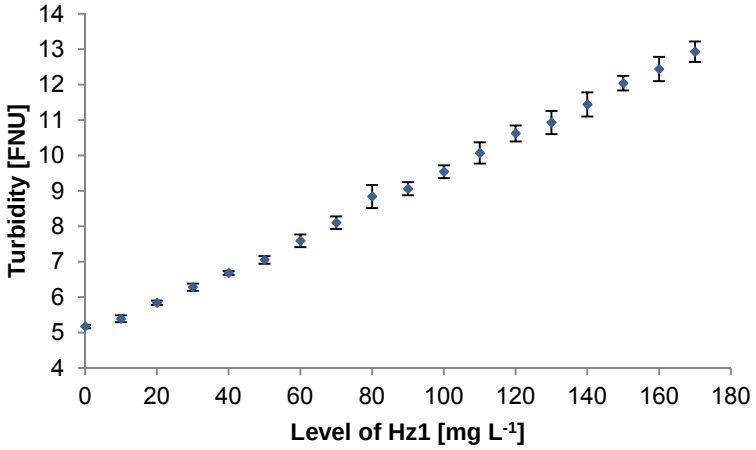

Figure 2: relationship between turbidity and the level of precipitate of distilled palm oil biodiesel (POB) spiked with precipitate (Hz1) isolated from turbid POB. Error bars show standard deviation of two replicates

$$y = 0.047x + 4.896 \quad (1)$$

To validate the model given in Eq. (1), the values predicted by the model for the precipitate content of turbid POB and the actual values were compared. As showed in Table 1, there was a slight difference between the predicted values and the actual values. A possible explanation for this was that the nature of Hz1 was different from that of the precipitate formed in the turbid POB. The nature of biodiesel precipitate may be quite heterogeneous depending on the location where the precipitate was originated (Moreau et al., 2008), the oil refining process, and the biodiesel production process (Tang et al., 2008). Therefore, to obtain a model capable of predicting the turbidity variability with the precipitate content of turbid POB, blends of turbid and non-turbid POB were prepared and analysed for turbidity and the precipitate content.

Table 1: Confirmatory experiments to validate the regression model for predicting the precipitate content of turbid palm oil biodiesel (POB)

Turbid POB	Actual precipitate content [mg L^{-1}]	Predicted precipitate content [mg L^{-1}]	Deviation [%]
Batch 1	157.7	136.2	13.5
Batch 2	104.3	93.7	10.1

As expected, turbidity of the blends increased with the precipitate content (Figure 3). Using lineal regression analysis, data on Figure 3 was fitted to the model given in Eq. (2), where y denotes turbidity [FNU] and x denotes the precipitate content [mg L^{-1}]. The goodness of fit was evidenced by a high coefficient of determination (R^2=0.984), indicating that more than 98 % of the turbidity variability might be explained by the model, and therefore the model might be used for prediction of the precipitate content of turbid POB with high precision. It is important to note, however, that the model was obtained for a particular batch. As noted above, the nature of biodiesel precipitate may vary depending on the oil refining process and the biodiesel production process, and therefore it may be necessary to adjust the model parameters for different batches.

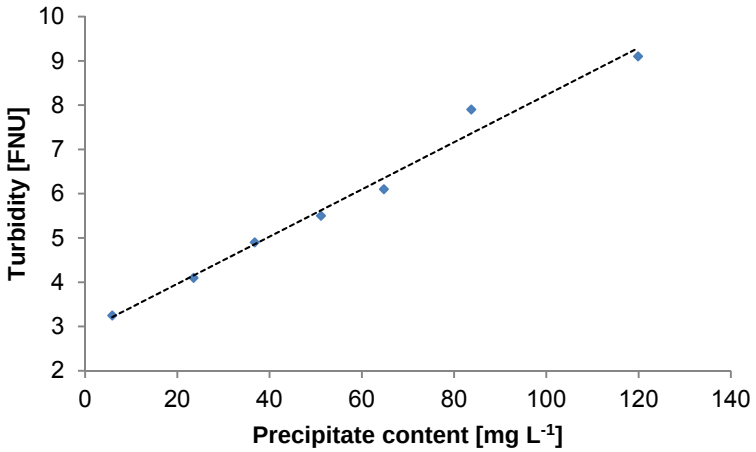

Figure 3: relationship between turbidity and the precipitate content of palm oil biodiesel

$$y = 0.053x + 2.898 \quad (2)$$

As depicted in Figure 4, TTF of the blends increased as turbidity rose from 3.3 to 4.9 FNU, but still met the ASTM limit for CSFT. The increase in TTF with turbidity was consistent with the increase in the precipitate content noted above. With a further increase in turbidity, TTF underwent a sharp rise to very high values (beyond the useful range of the ASTM D7501). A curve fitted through the data suggested that there is a turbidity threshold around 5.3 FNU above which TTF becomes unacceptable. A similar relationship between CSFT of canola biodiesel and the precipitate content was found by Lin et al. (2011). This finding suggested that turbid POB possessing turbidity lower than 5.3 FNU would meet the ASTM limit for CSFT.

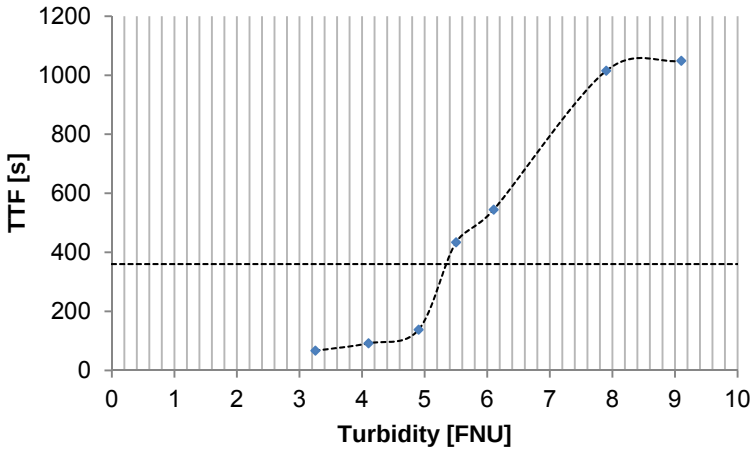

Figure 4: relationship between time to filter (TTF) and turbidity of palm oil biodiesel. The horizontal (dotted) line indicates the 360 s ASTM maximum limit for cold soak filtration time (CSFT)

After investigating the suitability of turbidimetry as an alternative method to determine the precipitate content of POB, the effect of temperature on turbidity at different precipitate contents was investigated. As showed in Table 2, turbidity of non-spiked distilled POB did not change with temperature. In contrast, turbidity of distilled POB spiked with silica gel slightly increased then decreased at 47 mg L^{-1}, and slightly decreased at 100 mg L^{-1}. The change in turbidity, however, was not statistically significant (*p*-value>0.05), regardless of the silica gel content. This indicated the suitability of turbidimetry for non-isothermic systems, and therefore to follow precipitate formation during the cold soak filtration test of biodiesel, regardless of biodiesel precipitate content.

Table 2: Turbidity of distilled palm oil biodiesel spiked with silica gel at different temperatures. Values having different letters are significantly different by the least significant difference multiple range test (p-value < 0.05)

Level of silica gel [mg L^{-1}]	Temperature [°C]					
	25		35		45	
	Turbidity [FNU]					
0	5.1	a	5.1	a	5.1	a
47	5.8	b	6.0	b	5.8	b
100	6.8	c	6.8	c	6.7	c

4. Conclusions

Suitability of turbidimetry as an alternative method to determine the precipitate content of POB was demonstrated. Turbidity of distilled POB spiked with different levels of precipitate was repeatable (average standard deviation < 0.07 FNU), and turbidity variability with the level of precipitate content was described by a simple first-order model with high coefficient of determination (R^2=0.998). No marked difference between the values predicted by the model for the precipitate content of turbid POB and the actual values was observed, confirming the suitability of turbidimetry. However, since the nature of the precipitate formed in the turbid POB was apparently different from the precipitate added to the distilled POB, the model parameters were adjusted for the turbid POB. Thus, a new simple first-order model with high coefficient of determination (R^2=0.984) was obtained using blends of turbid and non-turbid POB.

TTF of turbid POB increased with turbidity, but relationship between TTF and turbidity was not simple. Even so, a turbidity threshold around 5.3 FNU above which TTF becomes unacceptable was suggested by fitting a curve through the data. Thus, turbid POB possessing turbidity lower than 5.3 FNU would meet the ASTM limit for CSFT.

Turbidity of distilled POB spiked with silica gel did not significantly change with temperature between 25 and 45 °C. Thus, suitability of turbidimetry was further confirmed for non-isothermic systems, and therefore to follow precipitate formation during the cold soak filtration test of biodiesel.

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