



Saturated monoglyceride effects on low-temperature performance of biodiesel blends[☆]



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ABSTRACT

The effect of saturated monoglyceride (SMG) content of four B100s on the cloud point (CP) of blends with four diesel fuels was examined. Detecting CP with a more sensitive light-scattering method allowed observation of an early (higher temperature) CP in blends containing approximately 0.01 wt.% to 0.03 wt.% SMG. Blend samples with SMG content in this range may be particularly prone to unexpected filter clogging above the measured CP. Results for a 140 blend sample matrix revealed that SMG content had a larger effect on CP than other blend properties. An increase of 0.01 wt.% SMG in a biodiesel blend increased CP by as much as 4 °C. At a constant SMG level, increasing biodiesel content lowered CP, as did increasing the diesel fuel aromatic content, by improving the solubility of SMG. This implies that lowering the SMG content of a B100 allows preparation of higher biodiesel content blends having the same or lower CP. Increasing the unsaturated monoglyceride-to-SMG ratio by blending in monoolein lowered CP, presumably because monoolein inhibits nucleation of SMG. In most blends with SMG content above 0.01 wt.%, polymorphic phase transformation of crystallized SMG (converting from the metastable α -form to the less soluble, stable β -form) was observed.

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1. Introduction

Problems with the low-temperature operability performance of biodiesel in blends with petroleum diesel are infrequent, but continue to limit the use of biodiesel in winter months. A troubling aspect of this problem is that in some cases precipitates above the blend cloud point (CP) have been detected and have led to plugging of fuel filters and subsequent vehicle stalling, as well as plugging of fuel dispenser filters [1]. CP is considered a conservative indicator of the low-temperature performance of a fuel [2]. The Coordinating Research Council found that for B100 fuels with a high cold soak filtration time, low-temperature operability issues were observed at and above the CP for B20 blends [3]. Implementation of a cold soak filtration time limit in the B100 standard (ASTM D6751) led to a reduction in the frequency of low-temperature operability issues. However, these issues still occur, and in many cases are attributed to the precipitation of saturated monoglycerides (SMG), an impurity in B100.

Van Gerpen and coworkers [4] found that SMG were a main component of a “creamy paste-like” material that was found on a plugged fuel filter from a vehicle operating on B20. It was also noted that diglycerides, especially saturated diglycerides, were also present on the plugged fuel filters. Selvidge and coworkers also found that a blend with 2.5 vol.% soy-derived B100 containing above about 0.07 wt.% SMG could block dispenser filters as temperatures dropped to -18 °C [5]. Poirier and coworkers concluded that SMG could be the cause of filter plugging during heavy-duty vehicle testing at low temperature [6], while Brewer showed that SMG were responsible for storage tank deposits and dispenser filter clogging [7].

Recently, we investigated the effect of SMG and other impurities on precipitate formation at cold temperatures in B100s [8,9]. The studies included measurement of CP (cooling the sample) and final melting temperature (FMT), measured by heating the sample. B100 samples were spiked with SMG, water, and steryl glucosides (SG) at various levels. The main component that affects both the CP and FMT was SMG. Water and SG did not show a significant effect in any of the B100. The polymorphic phase behavior [10] of SMG can explain their impact on the FMT measurements. In some samples, FMT was much higher than CP, indicating that the SMG were undergoing a solvent-mediated polymorphic phase transition [8,9]. The increase in CP and FMT was observed above a concentration level of about 0.2 wt.% to 0.3 wt.% SMG. The rate at which the samples were heated during the test also had an effect on the measured FMT. For some samples, polymorphic behavior of the SMG was only revealed at relatively slow

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(0.1 °C/min) heating rates for laboratory bench tests. Notably, a heating rate of 0.1 °C/min or 6 °C/h may be considered fast for the diurnal heating and cooling cycles experienced by a parked vehicle or in an aboveground storage tank. Investigating the polymorphic phases of SMG in B100 by differential scanning calorimetry revealed that a meta-stable α -gel is initially formed upon cooling the sample [9,11]. This metastable phase then converts to the most stable β phase, which is much less soluble and has a higher melting temperature. Measurement of the solubility of the stable β phase versus the meta-stable α phase in B100 shows that they may differ by as much as an order of magnitude at 5 °C. Polymorphs are also known to occur for hydrocarbon waxes that precipitate from diesel fuel [12]. However, the difference in solubility for the various forms is relatively small.

Because biodiesel is typically blended with petroleum-derived diesel fuel, it is important to understand the low-temperature phase behavior in these blends. To this end, we measured CP and FMT when blending spiked and unspiked B100 into various diesel fuels to create various levels of SMG in the finished blends. The B100 were blended into the diesel fuel at three different blend levels; B5, B10, and B20. Four diesel fuels with a wide range of aromatic content and CP were employed.

2. Materials and methods

2.1. Fuels

Diesel fuels used for blending included a Tier 2 certification diesel (Fuel A), a high-aromatic (37%) diesel (Fuel B), a local (Colorado) No. 2 diesel (Fuel C), and a low CP No. 1 diesel from Minnesota (Fuel D). Additionally, we prepared some blends with a Canadian fuel designated CP43 (Fuel E), and a second low-CP No. 1 diesel (Fuel F). All petroleum diesel fuels were ultra-low sulfur diesel meeting the requirements of ASTM D975 for their respective grades.

The primary B100 fuels used for this study were the same as those used in our previous investigation [9]. They consisted of a canola (B100 I) containing 6.7 wt.% saturated fatty acid methyl esters (FAME), soy-derived (B100 II) 15 wt.% saturated FAME, and two mixed feedstock B100s (B100 III and B100 IV) with 24 wt.% and 36 wt.% saturated FAME, respectively. They all met the requirements of ASTM D6751 as received. In addition, five B100 that were obtained as part of a nationwide B100 quality survey were also utilized. Details of their characterization are reported elsewhere [13].

The B100 were manipulated to have different levels of impurities prior to blending, including SMG, monoolein (MO), deionized water, and SG. For monoglyceride spiking, a custom monoglyceride mix of MO, monopalmitin, and monostearin was made for each feedstock. Because MO was added with the SMG to preserve the unsaturated:saturated monoglyceride ratio, the high spike level samples for B100 II and IV failed the ASTM D6751 limit for total glycerin, as did the spiked B100 I sample. Monoglycerides were obtained from NuChek Prep and were 99% pure or greater. SG was obtained from Matreya LLC. The

spiked B100 were heated and sonicated briefly until they were visually bright and clear prior to blending. Table 1 lists the B100 used to prepare biodiesel blends. Blends containing 5, 10, and 20 vol.% biodiesel were prepared by volume using a pipette resulting in 5 mL samples. This provided a total of 140 blend samples.

2.2. Fuel property tests

As received, B100 and diesel fuels were characterized using ASTM methods as noted earlier. FMT was measured using the Phase Technology 70X Analyzer. FMT is defined as the temperature at which the light scattering signal returns to baseline during warming because all of the crystals have re-dissolved into solution. The experiment is normally conducted at 1.5 °C/min heating rate; however, in some cases slower heating rates were used as noted.

The CP of diesel blends was measured using one or more CP methods, including D5771, D5773, and D7689. Comparison of the three instruments and methods used shows definite differences in their configurations, cooling rates, volumes utilized, and the manner in which they detect the formation of crystals. All three of the CP methods employed were automated and intended to produce results equivalent to the ASTM referee method, D2500, which is conducted manually with visual observation of crystal formation. D5771 bears the most physical resemblance to D2500. However, it functions by transmitting light towards the center of a bottom-mirrored test jar. An optical detector measures the intensity of the transmitted light in a 45-mL sample. Adequate levels of crystal formation reduce the intensity of the transmitted light, signaling that CP has been reached. This method uses a stepped cooling protocol rather than a constant (linear) cooling rate. D7689 also functions by measuring the loss of transmitted light. The light passes through a relatively thin cross-section of the 0.5-mL sample, parallel to the bottom of the container as the sample is cooled at a constant rate of 1.5 °C/min.

Method D5773 uses light scattering to detect the presence of crystals and employs the Phase Technology 70X Analyzer [14]. A 150 μ L sample is placed into a mirrored-bottom cup with a Peltier temperature control device. Light is then reflected off of the mirrored surface while the sample is cooled at 1.5 °C/min. When crystals are present, the light is scattered, registering a signal at the detector indicating the presence of solid particles. The detection method employed in D5773 is much more sensitive than the “loss of transmission” approach used in the other CP methods [15]. This method gives very close agreement with both the referee method, ASTM D2500 (relative bias of 0.03 °C), and the other methods employed here (D5771 and D7689).

D5771 and D5773 have been shown to be equivalent to D2500 (the referee CP method) for petroleum-derived fuels, while D7689 is equivalent if corrected for a small bias. Thus, they should in theory give equivalent results. However, relative rates of cooling (heat transfer) can dramatically affect the size, shape, and number of crystals formed at a given temperature. Both D5773 and D7689 have significantly larger surface-area-to-volume ratios compared to D5771. Additionally, while the cooling rates of D7689 and D5773 are well defined, the cooling rate in D5771 is not defined. D5771 has a significant area of air space between the cooling jacket and the sample. Heat transfer across this air space will not be as efficient as in D5773 and D7689 because of the close proximity of the sample to the cooling surface(s) in these methods.

3. Results

Table 2 lists the properties of the diesel fuels used for blending. Detailed B100 properties have been previously reported [9]; however, Table 3 contains information on the properties most relevant to this work. Tables containing all of the CP and FMT data for blends are included in the supplementary data.

Table 1
B100s used for preparation of biodiesel blends.

	B100s used to prepare diesel fuel blends
B100 I	As-received (0.053 wt.% SMG) Spiked to contain 0.1 wt.% SMG
B100 II	As-received (SMG below detection) Spiked to contain 0.05 wt.% SMG Spiked to contain 0.145 wt.% SMG (at total glycerin specification limit) Spiked to contain 0.23 wt.% SMG, 1000 ppm water, 40 ppm SG
B100 III	As-received (0.045 wt.% SMG) Spiked to contain 0.23 wt.% SMG (at total glycerin specification limit) Spiked to contain 0.32 wt.% SMG, 1000 ppm water, 40 ppm SG
B100 IV	As-received (0.152 wt.% SMG) Spiked to contain 0.33 wt.% SMG Spiked to contain 0.43 wt.% SMG, 1000 ppm water, 40 ppm SG

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