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Cloud point and crystallization in fatty acid ethyl ester biodiesel mixtures with and without additives

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ABSTRACT

Biodiesels, composed of saturated fatty acid alkyl esters (FAAE), have relatively high cloud points (CP), which limit their commercial application. However, fatty acid ethyl esters (FAEE) have potentially advantageous properties, including those related to cold flow, compared to their methyl analogs. This work systematically evaluates FAEE cloud point and crystallization data to aid in the development of FAEE biodiesel blends with practical cold flow properties. Neat FAEE CP increases with alkyl-chain length and decreases with greater degree of unsaturation. Mixtures of saturated/saturated FAEE show partial cocrystallization, which impact the mixture's CP. The effects of cold-flow improving additives dimethyl azelate (DMAz) and triacetin on fatty acid methyl esters (FAME) and FAEE are also analyzed. Additives lowered the overall CP, however the degree of depression for each additive varied indicating different crystallization mechanisms. Thermodynamic ideal solution modeling predicts binary FAEE CP with and without additives within 2% of experimental values.

1. Introduction

Biodiesel is a promising alternative to fossil-derived liquid fuels [1]. Some advantages of biodiesel include its renewability, biodegradability, lubricity, and low emission of sulfurous and aromatic species [2,3]. Other favorable fuel properties include its high flash point, complete miscibility with petrodiesel at all blend levels, and ability to directly replace petrodiesel in diesel engines [2–5]. Other uses include home heating oil, lubricants, and numerous other applications [6,7].

Biodiesel is synthesized via the transesterification of triglycerides sourced from biofeedstocks to produce fatty acid alkyl esters (FAAE) [3]. Typically, this reaction uses methanol as the reagent, yielding fatty acid methyl esters (FAME) [8]. Methanol is favored due to its low production cost [9]; however, it is toxic and commonly derived from natural gas, meaning that it is nonrenewable [10]. An alternative to FAME are fatty acid ethyl esters (FAEE), produced via transesterification with ethanol (ethanolysis). In the United States, bioethanol is most commonly derived from corn, [11] meaning that FAEE biodiesel can be completely produced from renewable feedstocks. FAEE biodiesel also has enhanced heat content and cetane number, and emits less carbon monoxide than FAME biodiesel [12]. However, FAEE production may demand increased feedstock costs as well as energy and separations requirements compared to FAME [13]. These processing challenges may be improved with technology and feedstock advancements [14,15] as well as further characterization of these relatively under-studied esters to aid in the development of better fuel properties.

Despite its advantages, biodiesel may have higher NO_x emissions, lower oxidative stability, and poorer cold-flow properties (operability at low temperatures) [16] compared to petrodiesel. The use of FAEE instead of FAME has been shown to reduce NO_x emissions [16] and can potentially improve cold-flow behavior.

Solidification of biodiesel typically occurs between 263 and 298 K, in comparison to 246 to 258 K for petrodiesel [7,17,18]. These higher phase transition temperatures can lead to poor cold weather performance; as such the use of biodiesel is commonly limited to petrodiesel blends, typically at 20 wt% biodiesel (B20) or less [1,19].

Cloud point (CP) is often considered the most important and difficult cold-flow metric to improve [6,7,20]. It is defined as the temperature at which solid wax crystals at least 0.5 μm in diameter are formed [21], causing the solution to appear opaque and "cloudy." As such, the CP is the temperature at which engine problems begin to occur due to formation of solids within the biodiesel fuel. Although no numerical standards exist for biodiesel CP, ASTM D6751 specifies that it must be reported [22]. Several approaches can be taken to improve biodiesel CP: utilizing/manipulating biofeedstocks with advantageous lipid profiles, blending with petrodiesel, modifying the FAAE transesterification product via fractionation or winterization, or adding cold-flow improving chemical additives [20,23,24]. The appropriate selection of lipid profiles and additives for FAEE based biodiesel requires a general understanding of the role of FAEE composition and

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interactions. However, most cold-flow research, especially the studies assessing pure FAAE properties, has focused on FAME biodiesel. Some studies [25–28] have analyzed the eutectic/metatectic behavior in binary and ternary FAEE mixtures using melting point, yet there is a lack of extensive CP data in literature for both pure FAEE and FAEE blended with chemical additives.

Biofuel additives may be chosen based on their physicochemical properties and their ability to be renewably-derived. Two potential additives, triacetin and dimethyl azelate, show particular promise in these metrics. Triacetin, which can be produced via interesterification of triglycerides with alkyl acetates [29,30] or through esterification of glycerol [31], has been shown to improve the CP of FAME biodiesel blends [4]. Dimethyl azelate can be derived from glycerol; it has a low CP, is miscible with biodiesel, and has been shown to be a pour point depressant for sunflower oil biodiesel [32].

In this work, a systematic analysis of the CP and crystallization behavior of neat and binary FAEE mixtures was conducted to deepen the understanding of FAEE biodiesel cold-flow properties and aid in the development of biodiesel blends with favorable cold-flow properties. The effects and mechanisms of triacetin and dimethyl azelate as additives were also evaluated for both pure FAEE and FAEE mixtures. Furthermore, the results were compared against a thermodynamic model using solid-liquid equilibrium (SLE) with assumptions based on ideal solution theory to allow for the prediction of CPs of multi-component FAEE and FAME blends.

2. Materials and methods

All FAAE blends were prepared and analyzed via differential scanning calorimetry (DSC, TA Instruments DSC 2920), using the procedure reported previously [4]. The DSC was calibrated with deionized water; six calibration trials yielded a melting onset temperature of 272.8 K, with a standard deviation of 0.2 K.

The FAME and FAEE studied were chosen for the prevalence of their corresponding triglycerides in common biofeedstocks [9,20,24,33]. Methyl palmitate (methyl-C16:0, > 99%), methyl stearate (methyl-C18:0 ~99%), and methyl oleate (methyl-C18:1, > 99%) were sourced from Sigma-Aldrich. Methyl myristate (methyl-C14:0, > 99%) and methyl linoleate (methyl-C18:2, > 99%) as well as all ethyl esters –ethyl myristate (C14:0, > 99%), ethyl palmitate (C16:0, > 99%), ethyl stearate (C18:0, > 99%), ethyl oleate (C18:1, > 99%), and ethyl linoleate (C18:2, > 99%) – were sourced from Nu-Check Prep. All binary FAAE mixtures studied were composed of 50:50 mass ratios. Ternary mixtures were comprised of 50:50 FAAE ratios and additives dimethyl azelate (> 98.5%, Sigma-Aldrich) and triacetin (99%, Sigma-Aldrich), at 15 wt% of the total mixture. Additional experimentation was performed to examine the effects of predictive modeling using soybean oil derived biodiesel, SoyGold® (provided by Ag Processing Inc).

In this work, the cloud point is defined as the location on the DSC thermogram where the heat flow initially decreases due to phase transition. For cocrystallizing mixtures or samples containing polymorphic species with multiple freezing peaks, the cloud point is defined as the onset of the first (highest temperature) peak. Melting point is defined as the peak melting temperature, corresponding to the point of greatest endothermic heat consumption during heating; many other works have used this definition [25,26,34–38]. Enthalpy of fusion data corresponds to the heat released during crystallization of FAAE samples.

Experimental duplicates were conducted for all mixtures analyzed. Random analytical duplicates showed an average CP standard deviation of 0.2 K, and an average melting point standard deviation of 0.2 K.

3. Theory and calculations

3.1. Thermodynamic cloud point model

A thermodynamic model based on solid-liquid equilibrium was used for modeling of the phase transitions based on the work of Imahara et al. [39].

$$ln\left(\frac{f_i^L}{f_i^S}\right) = ln\left(\frac{\gamma_i^L x_i}{\gamma_i^S z_i}\right) = \frac{\Delta H_{fus,i}}{RT_{m,i}}\left(\frac{T_{CP,i}}{T}-1\right) - \frac{\Delta C_i}{R}\left(\frac{T_{CP,i}}{T}-1\right) + \frac{\Delta C_i}{R}\ln\left(\frac{T_{CP,i}}{T}\right) \quad (1)$$

where:

f_i^L and f_i^S are the liquid and solid phase fugacities of species i, respectively
γ_i^L and γ_i^S are the liquid and solid phase activity coefficients of species i, respectively
x_i and z_i are the liquid and solid phase mole fractions of species i, respectively
$\Delta H_{fus,i}$ is the molar enthalpy of fusion for species i (J mol^{-1})
R is the gas constant (8.314 J mol^{-1} K^{-1})
$T_{CP,i}$ is the cloud point of pure species i (K)
T is the cloud point of species i in solution (K)
ΔC_i is the difference of heat capacity of species i in the solid and liquid phases (J mol^{-1} K^{-1}).

Since all FAAE mixture components analyzed are structurally similar, as in real biodiesel blends, ideal solution behavior and activity coefficients of unity are assumed. This implies that:

1. All interactions between species in solution are identical
2. The change in heat capacity for species i between the liquid and solid phase is negligible ($\Delta C_i = 0$)
3. The first solid crystal at the mixture's cloud point is composed of one pure species, i, ($z_i = 1$)
4. The fugacity of species i is equal to its liquid phase mole fraction (since $\gamma_i^L = 1$).

These assumptions greatly simplify the SLE equation, allowing the mixture's CP to be solved for explicitly by Eq. (2):

$$CP = \frac{T_{CP,i}}{1-\frac{RT_{CP,i}}{\Delta H_{fus,i}}\ln(x_i)} \quad (2)$$

All species-dependent physicochemical parameters in Eq. (2) were determined experimentally in this research, and were consistent with literature ranges (see Supplementary Information).

4. Results and discussion

4.1. Pure FAEE cloud point, melting point, and enthalpy of fusion

To supplement the limited data on neat FAEE cold-flow properties available in literature, data on FAEE cloud point, melting point, enthalpy of fusion, and qualitative co-crystallization behavior was collected for pure and binary FAEE blends. For the sake of comparison, cloud point data for both pure FAEE and FAME are presented in Table 1.

The FAEE CPs in Table 1 are all statistically (p = 0.000) lower than the FAME CPs with the same fatty acid moiety. This conclusion is consistent with the literature consensus that FAEE inherently show slightly favorable cold-flow properties in comparison to FAME for both neat compounds [25,26,34–38] and biodiesel mixtures [24,40,41]. It has been proposed that the additional –CH_2 unit on the carbonyl end of FAEE molecules decreases the amphiphilic nature of the molecule as a whole, causing lower cloud and melting points [41]. Furthermore, the