



Full Length Article

Determination of cloud point in binary and ternary mixtures containing biodiesel and diesel constituents. Part I – Ethyl palmitate, ethyl stearate and *n*-hexadecane



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HIGHLIGHTS

- The cloud point of synthetic diesel–biodiesel blends was studied using DSC.
- Saturated esters were used to represent the biodiesel and *n*-hexadecane to diesel.
- All of the systems present a eutectic point.
- No difference was found in the cloud point of *n*-hexadecane rich mixtures.
- The influence of the ester composition on the cloud point is clearly demonstrated.

ARTICLE INFO

Article history:

Received 24 December 2015

Received in revised form 26 March 2016

Accepted 11 April 2016

Available online 20 April 2016

Keywords:

Solid–liquid equilibrium

DSC

Synthetic system

Phase diagrams

Eutectic point

ABSTRACT

Diesel fuel is being substituted by biodiesel in many countries. But, this gradual addition of biodiesel to diesel is causing problems such as the formation of sludge in storage tanks, poor engine performance, transportation difficulties and others. There is strong concern about the use of biodiesel–diesel blends at low temperatures. This study evaluated the cloud point of mixtures containing biodiesel and diesel constituents by preparing solid–liquid equilibrium (SLE) curves obtained by differential scanning calorimetry (DSC). T–x phase diagrams were prepared of solid–liquid equilibrium of binary and ternary systems involving the use of the main saturated esters found in biodiesel; ethyl palmitate (P), ethyl stearate (S) and the representative alkane of diesel, *n*-hexadecane (H). The diagrams of pseudo-binary systems were also determined, as an alternative way to represent the same data. These phase diagrams studied present eutectic points at 0.2 M fraction of ethyl esters. The experimental results showed no statistically significant difference in cloud point if the mixture has a mass of *n*-hexadecane equal or greater than 80% according to a *T*-test. In general, for lower amounts of *n*-hexadecane, the presence of ethyl palmitate resulted in lower cloud points than when ethyl stearate was used. This work clearly contributed to a better understanding of the behavior of cloud point in biodiesel–diesel blends.

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1. Introduction

Although biodiesel has advantages in comparison to petroleum diesel, there is great concern about the thermal behavior of biodiesel–diesel blends at low temperatures. While diesel has a cloud

point of around 257 K, biodiesel's cloud point is around 273 K [1]. Knowing the thermal behavior of this mixture can prevent problems such as fuel system clogging and poor engine performance.

The formation of crystals in biodiesel is related to the presence of saturated esters that have a higher melting point than unsaturated esters, which favors the formation of crystals at low temperatures [2–5]. The formation of the first crystals promotes the nucleation of new crystals and accelerates their agglomeration and consequent precipitation [6,7]. Although the crystallization phenomena is quite complex, and is strongly influenced by kinetic

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factors related to nucleation, the determination of the solid–liquid equilibrium is fundamental to avoid the conditions that favor the formation of crystals in biodiesel–diesel blends.

Solid–liquid equilibrium (SLE) has a fundamental importance in the crystallization process. The classical method for measuring SLE involves producing a saturated solution and analyzing the solution's concentration by an analytical method such as spectroscopy or gas or liquid chromatography. Normally this procedure is tedious and subjected to errors [8]. Differential scanning calorimetry (DSC) has been widely used for the determination of SLE curves because it is a rapid and precise technique [9,10].

Biodiesel, most often produced with methanol or ethanol, is a mixture of fatty acid methyl or ethyl esters. There are advantages and disadvantages to the use of either methanol or ethanol. Methanol is less expensive to process than ethanol, but it is a non-renewable petroleum derivative, while ethanol can be obtained from biomass, and is thus a renewable energy source. Part I of this study used fatty acid ethyl esters (FAEE).

Biodiesel's composition in fatty acid esters is related to the vegetal oils or animal fats used as the raw material. Considering only saturated esters, which are mainly responsible for crystallization, palmitate and stearate esters are the most abundant in biodiesel produced from fleshing oil and chicken fat [11], palm and soybean oils [12,13], tallow [12] and poultry fat [4]. In the two main biodiesel sources used in Brazil, soybean oil and bovine fat [14], palmitate and stearate represent over 90% (m/m) of the saturated esters [2,15–17].

Several studies have investigated the solid–liquid equilibrium behavior of biodiesel composed of saturated and unsaturated esters using DSC [18–25]. In these studies, the temperatures of the solid–liquid transitions identified by DSC showed an excellent correlation of cloud point with the official standard (ASTM-D2500). The thermal behavior of biodiesel has been well explored in recent years [2,18–28], but there are few studies in the literature regarding biodiesel–diesel blends [4,29–31].

This study aims to contribute to evaluating the cloud point of the solid–liquid transitions of saturated constituents found in biodiesel in the mixture with the alkane representative of the diesel (*n*-hexadecane) used as a standard in cetane testing. To conduct this analysis, solid–liquid phase diagrams involving binary and ternary mixtures were obtained by differential scanning calorimetry (DSC).

2. Materials and methods

2.1. Materials

The standard used for the calibration of the DSC was indium (>99.9%) certified by Perkin Elmer (São Paulo, Brazil). The saturated esters found in the biodiesel and the representative alkane of diesel used to prepare the samples were of high purity, and no further purification was conducted. They were ethyl palmitate (>99%),

ethyl stearate (>99%) and *n*-hexadecane (>99%), purchased from Sigma Aldrich (St Louis, USA). The high purity nitrogen (>99.99%) used in the calorimeter was supplied by White Martins (Santa Catarina, Brazil).

2.2. Sample and microsample preparation

The samples used in this work were prepared on an analytical balance (AUX320 Shimadzu) with an accuracy of ± 0.2 mg to obtain the molar fraction. After weighing mixtures were placed in a glass tube and heated to 10 K above the highest melting point of the components and simultaneously stirred. After this preparation, the sample was refrigerated at 263 K until use in the DSC analysis.

After melting the sample, DSC analyses were performed by placing an aliquot (microsample) in hermetic aluminum pans with 50×10^{-5} L capacity. The masses of the aliquots were weighed in a Perkin-Elmer AD6 microanalytical balance with an accuracy of $\pm 0.2 \times 10^{-5}$ mg to obtain samples around 2–3 mg. The standard uncertainty in the molar fraction for all components was estimated to be less than 0.0026. Table 1 shows all the solid–liquid equilibrium systems obtained in this study.

2.3. Determination of solid–liquid equilibrium by DSC

The experimental data for solid–liquid equilibrium were obtained using a DSC 8500 Perkin Elmer. The method used to erase previous thermal histories was similar to that used in other studies [18–20]. Starting at 298 K, each sample weighed on a microanalytical balance and placed on a hermetic aluminum pan was submitted to a heating run of 5.0 K min^{-1} until reaching a temperature 15 K above the components' highest melting point. After 10 minutes at this temperature, the samples were cooled at a rate of 2.0 K min^{-1} to 25 K below the components' lowest melting point and allowed to remain at this temperature for 10 min. Each sample was then analyzed in a heating run, at a heating rate of 1.0 K min^{-1} until reaching a temperature 15 K above the highest melting point, returning to its initial condition. Nitrogen was fed at a rate of 20 mL min^{-1} .

Preliminary experiments determined the peak temperatures to be used to represent the temperature of the event. This procedure is justified in previous studies using DSC which found that peak temperature is better for representing melting temperature than onset temperature [22,32,33]. The average of the absolute deviations (AAD) between the average of the melting temperature measurements in triplicate for the pure components studied and literature was calculated using Eq. (1). The average of the measurements in triplicate were also used to estimate the experimental standard deviations (SD) in Eq. (2).

$$\text{AAD} = \frac{1}{n} \sum_{i=1}^n |T_{lit} - T'| \quad (1)$$

Table 1
Solid–liquid equilibrium according to component.

SLE	System	System according to component
SLE 1 (binary)	P + H S + H P + S	Ethyl palmitate + <i>n</i> -hexadecane Ethyl stearate + <i>n</i> -hexadecane Ethyl palmitate + ethyl stearate
SLE 2 (pseudo-binary)	P20S80 + H P40S60 + H P60S40 + H P80S20 + H	(Ethyl palmitate 20% + ethyl stearate 80%) + <i>n</i> -hexadecane (Ethyl palmitate 40% + ethyl stearate 60%) + <i>n</i> -hexadecane (Ethyl palmitate 60% + ethyl stearate 40%) + <i>n</i> -hexadecane (Ethyl palmitate 80% + ethyl stearate 20%) + <i>n</i> -hexadecane
SLE 3 ^a (ternary)	P + S + H	Ethyl palmitate + ethyl stearate + <i>n</i> -hexadecane

^a SLE 3 has not been prepared. It was determined by binary and pseudo-binary mixtures prepared.

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