



Improving the cold flow behavior of methyl biodiesel by blending it with ethyl esters



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ABSTRACT

Blending biodiesels is a well-established approach for the lowering of cloud and pour points. The use of ethylic biodiesel, with better cold weather properties due to the lower melting points of ethylic esters, could be another interesting alternative, promoting the utilization of more saturated oils and fats. To study that possibility this work evaluated the melting behavior of 3 mixtures of esters composed of ethyl palmitate, ethyl stearate or ethyl oleate with methyl palmitate. These esters are based on some of the most abundant fatty acids present on soybean and palm oils, two of the most expressive vegetable oils sources for biodiesel production. The solid-liquid phase diagrams in the entire concentration range of these 3 systems were evaluated with all phase transitions reported. The systems composed of saturated ethyl/methyl esters showed a very complex behavior, with the formation of solid solutions (organic alloys), peritectic reactions, and metatectic transitions. The *liquidus* lines of these systems were compared with the equivalent mixtures based on methyl esters alone showing that lower melting temperatures were achieved. Therefore blends between ethyl esters and methyl esters are suggested to improve the low temperature behavior of biodiesels.

1. Introduction

The high cost of fossil fuels and their global environmental impact are stimulating the use of liquid biofuels worldwide. Biodiesel is produced from renewable resources, and thus can considerably decrease the net CO₂ emission and also of other pollutants, in particular particulates and sulfur, moreover it is biodegradable and non-toxic. It is a mixture of fatty esters produced by transesterification of fat or oils with short chain alcohols in the presence of a catalyst [1,2]. The composition of fatty esters of the biodiesel is defined by the triacylglycerols profile of the vegetable oils and the alcohol used in the reaction. For example, the ester profile of soybean oil biodiesel, the second most produced vegetable oil in the world, is rich in unsaturated methyl linoleate but contains 15–20% of saturated methyl palmitate and stearate, while palm oil biodiesel, the most produced vegetable oil in the world, can have up to 50% of saturated esters on its composition [1]. This characterization is of utmost relevance since the carbon chain length and unsaturation largely defines the physicochemical properties of the mixture of fatty esters produced, and the profile of saturated esters has a huge impact upon the cold flow properties of biodiesels.

For the biodiesel synthesis, methanol is the most widely used alcohol and soybean oil the principal feedstock in most countries. The advantages of methanol and soybean oil are their wide availability and low cost. However, the use of ethanol instead of methanol could be an economically viable option in ethanol producing countries such as Brazil, enhance the renewable behavior of the biodiesel, and improve some properties such as higher stability toward oxidation, better lubricity and lower iodine value [3].

Another interesting advantage of using ethylic biodiesel is its lower cloud and pour points, which improves the performance of the fuel in cold weather [4]. The cold flow properties are of utmost importance taking account the design of engines, pumps or filters. The major factor influencing the cold flow behavior of biodiesel is the high melting point of the saturated fatty esters. Table 1 shows the melting properties of saturated even and consecutive methyl and ethyl esters obtained from literature where it is possible to observe the lower melting temperature of ethyl esters. Higher melting point esters such as methyl stearate and methyl palmitate increase the fuel tendency to crystallize at lower temperatures, precipitate and settle at the bottom of storage tanks during cold weather, and clog diesel filters causing problems in vehicles

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Table 1
Melting temperatures and enthalpies of methyl and ethyl esters.

Ester	Properties	Methylic		Ethylic	
		Value	Ref.	Value	Ref.
Caprate	T_{fus}/K	260.33	[8]	254.10	[6]
	$\Delta_{fus}H/kJ mol^{-1}$	35.917	[8]	30.23	[6]
Laurate	T_{fus}/K	278.18	[8]	272.31	[6]
	$\Delta_{fus}H/kJ mol^{-1}$	43.147	[8]	38.07	[6]
Myristate	T_{fus}/K	292.14	[8]	286.98	[6]
	$\Delta_{fus}H/kJ mol^{-1}$	52.008	[8]	45.91	[6]
Palmitate	T_{fus}/K	302.59	[9]	297.92	[6]
	$\Delta_{fus}H/kJ mol^{-1}$	56.85	[9]	53.75	[6]
Stearate	T_{fus}/K	311.45	[9]	307.63	[6]
	$\Delta_{fus}H/kJ mol^{-1}$	64.84	[9]	61.60	[6]
Oleate	T_{fus}/K	253.15	[10]	254.61	[6]
	$\Delta_{fus}H/kJ mol^{-1}$	Not available		25.39	[6]

operation. This is an important limiting factor for production of biodiesel from palm oil, and other oils and fats rich in saturated compounds.

In order to improve the cold flow properties of biodiesel many techniques are used, but blending is one of the most simple and significant [5]. Some works concerning the phase equilibria of mixtures of ethyl esters [6] or methyl esters [7] show a significant decrease in their melting temperatures when compared with the pure esters. However, mixtures of ethyl esters and methyl esters could be an interesting alternative, combining the low cost of methanol with the sustainability and improved cold flow properties of ethanolic esters.

This work was aimed at investigating the melting behavior of three mixtures of esters composed of ethyl palmitate, ethyl stearate or ethyl oleate with methyl palmitate. This group of esters was chosen considering: i) the fatty acid profile of soybean and palm oil, the most expressive vegetable oils sources, ii) the high melting temperatures for palmitate and stearate esters; iii) the evaluation of the effect of carbon chain size and unsaturation in the melting temperature depression. The complete solid-liquid phase diagrams of these systems were measured, and a discussion on its impact on the biodiesel crystallization problems is presented.

2. Experimental

Methyl palmitate, ethyl palmitate, ethyl stearate and ethyl oleate were purchased from Sigma Aldrich (St. Louis) with purities greater than 99% confirmed by DSC using the analysis software from TA Instruments (New Castle). Three binary systems (ethyl palmitate + methyl palmitate, ethyl stearate + methyl palmitate, ethyl oleate + methyl palmitate) were prepared (Precisa Gravimetrics analytical Balance, Dietkon, precision of 2×10^{-4} g) with molar fractions ranging from 0.0 to 1.0 in steps of 0.1 (estimated uncertainty less than 1×10^{-3} M fraction). Samples (approximately 1.0 g) were prepared by heating under stirring and nitrogen atmosphere, until complete melting of the components.

The crystallization and melting profile of each sample (solid-solid and solid-liquid transitions) were determined by differential scanning calorimetry (DSC, MDSC 2920 calorimeter, TA Instruments, New Castle) using nitrogen for purge, and the standards indium (PerkinElmer, Waltham), naphthalene and cyclohexane (Merk, Whitehouse Station) for calibration (purity ≥ 0.99 mass fraction). Samples of 5 mg (approximately) were weighed in sealed aluminum pans (Microanalytical balance AD6, PerkinElmer, Waltham, precision = 2×10^{-6} g) following the approach described by Costa, Rolemberg, Boros, Krahenbuhl, de Oliveira and Meirelles [11]. The temperature program used was specially designed for the determination

of the solid-liquid equilibrium of fatty compounds taking into account the standardization of the crystalline structure of the material: 1) isothermal at 10 K higher than the melting temperatures of pure components for 15 min, 2) cooling ramp at $1 K min^{-1}$ up to 40 K below the melting temperature of the components; 3) isothermal for 30 min; and 4) heating ramp at $1 K min^{-1}$ up to 10 K above the melting points of the pure compounds. Solid-solid and solid-liquid transitions were determined through peak top temperatures, taking into account the existence of overlapped peaks which prevents the determination of onset temperature, that are also meaningless for eutectic mixtures since unlike for pure compounds the mixture is not expected to melt at a fixed temperature, except at the eutectic point. Moreover, the enthalpies of the transitions, used for the Tammann plots, were determined by the peak area using the TA Instruments (New Castle) software. The temperature uncertainties were evaluated as less than 0.5 K (highest standard deviation found in three repeated DSC runs for pure compounds and selected mixtures).

Optical Microscopy was used for analysis of the solid phases of the mixtures and solid-solid events observed in the DSC analysis. A BX51 Olympus optical microscope (Olympus, Tokyo) and a LTS120 Linkam temperature-controlled stage (Linkam Scientific Instruments, Tadworth) working at $243.15 K \leq T \leq 393 K$ were used for evaluation of 2 mg of samples in concave slides with coverslips. The sample was cooled until full crystallization (close to 243.15 K) kept at this low temperature for 10 min and heated at a controlled and low rate of $1 ^\circ C/min$ (similar to DSC) when images were taken sequentially.

3. Results and discussion

In previous works we have extensively studied the phase behavior of mixtures of methyl esters [7], and ethyl esters [6,12] but never mixtures of the two. To the best of our knowledge the only study attempting to describe a phase diagram of mixtures of fatty acid methyl and ethyl esters is by Lutton and Hugenberg [13] for the system ethyl stearate + methyl stearate, but only the liquidus lines, with poor definition and accuracy, is reported. To evaluate the advantages of using mixtures of ethyl and methyl esters for the depression of the melting points of these compounds the systems composed by the saturated esters ethyl palmitate + methyl palmitate and ethyl stearate + methyl palmitate and for the system composed for the unsaturated ester ethyl oleate + methyl palmitate were measured by DSC and the temperatures of the transitions identified are presented on Figs. 1–3. The DSC thermograms are shown in Figs. S1–S3 at Supplementary Material (SM) where the cooling process (exothermal events) are represented in dashed lines while the heating (endothermal events) are presented in full lines. In the Tables S1–S3 (at SM) detailed values for the transitions measured by DSC are also reported. Here the crystallization temperature $T_{crystallization}$ describes the first peak observed during the cooling, and melting temperature $T_{melting}$ describes the last peak observed during the heating. Other transitions were also observed during the heating process that could be related to eutectic, metatectic, peritectic transitions that occur during the melting of the system, as will be discussed.

3.1. System ethyl palmitate + methyl palmitate

For the system ethyl palmitate + methyl palmitate, in addition to final melting process, three other main thermal transitions were observed in the DSC thermograms (Fig. S1). This system clearly did not present a simple eutectic profile since no invariant transition was observed throughout the entire concentration range, as expected for a simple eutectic system. However, some transitions occurred at the same temperature and at different concentrations, and one might suppose that they could be associated to invariant transitions observed in other fatty systems. Costa, Sardo, Rolemberg, Coutinho, Meirelles, Ribeiro-Claro and Krahenbuhl [14] showed that in almost any binary system composed of fatty acids, i.e., monocarboxylic acids composed of 10–18

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