

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	Methyl		Ethyl	
		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

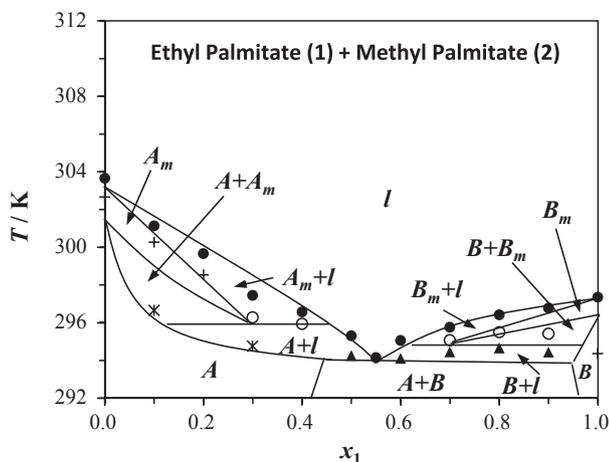


Fig. 1. Solid-liquid equilibrium diagram for the ethyl palmitate (1) + methyl palmitate (2) system. Symbols: (▲) = eutectic transition; (+) solid-solid transitions; (●) melting temperature; (○) metatectic transition; (*) initial melting observed in microscopy. Letters: A = Solid solution phase rich in methyl palmitate; A_m = solid phase formed during the melting temperature after the metatectic transition; B = Solid solution phase rich in ethyl palmitate; B_m = solid phase formed during the melting temperature after the metatectic transition; Full lines sketches the interpretation of the phase diagram.

carbon atoms, no simple eutectic profile is observed but these systems present instead complex phase diagrams with peritectic, and metatectic reactions, and also the formation of solid solutions in some concentration regions. These reactions were also previously observed for binary mixtures of saturated methyl fatty ester [7], but not for mixtures of ethyl fatty ester systems [6].

Based on the DSC thermograms, and the previous knowledge of the phase diagrams for system of saturated methyl fatty esters [7], and saturated ethyl fatty esters [6,12], Fig. 1 presents an interpretation of

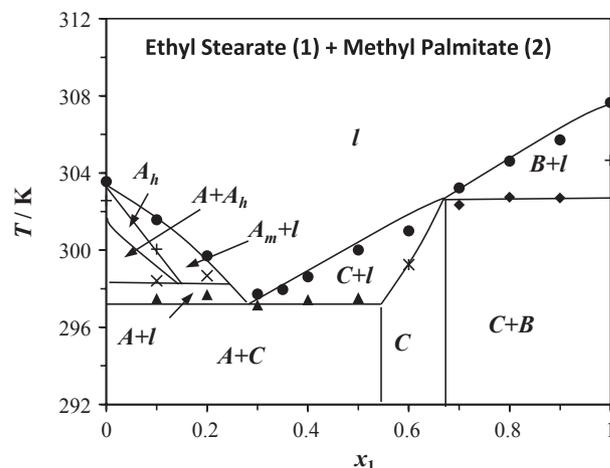


Fig. 3. Solid-liquid equilibrium diagram for the ethyl stearate (1) + methyl palmitate (2) system. Symbols: (▲) = eutectic transition; (x) metatectic transitions; (+) solid-solid transition; (●) final melting temperature; (◆) peritectic transition; (*) initial melting observed in microscopy. Letters: A = Methyl palmitate; A_m = solid phase formed during the melting temperature after the metatectic transition; B = Ethyl palmitate; C = Solid solution phase rich in Peritectic compound; Full lines sketch the interpretation of the phase diagram.

the solid-liquid equilibrium phase diagram for this system. All lines of the diagram were drawn taking into account the experimental observations, and the Gibbs phase rule. A eutectic transition was observed at the lowest temperature, with a eutectic point close to $x_1 = 0.55$. A solid solution probably occurs at the left hand side of the diagram since no eutectic transition is observed up to $x_1 = 0.50$. A solid solution could also appear close to pure ethyl palmitate, at the right hand side of the diagram. These proposals are further supported by the Tammann plots

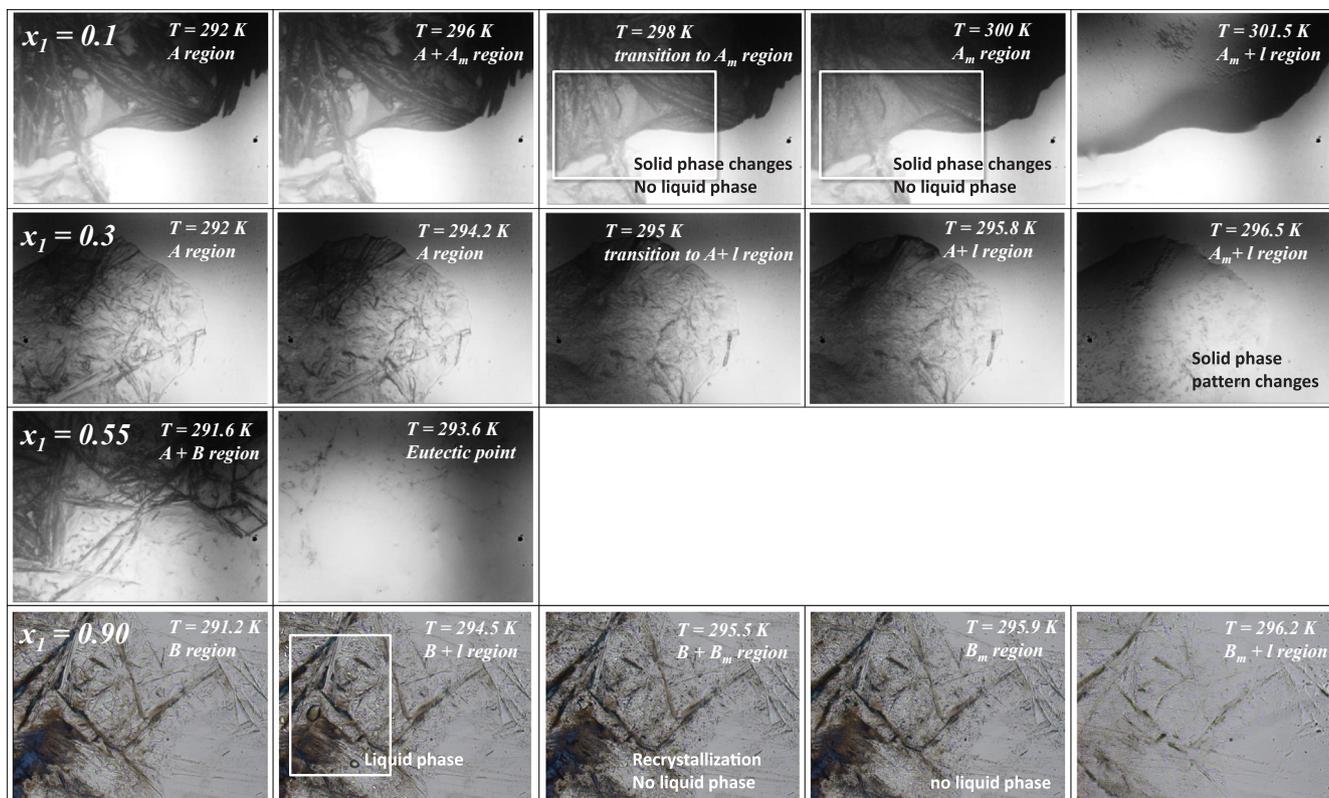


Fig. 2. Optical microscopies of the ethyl palmitate (1) + methyl palmitate (2) system.

presented in Fig. S4 (in SM). They sketch the behavior of the enthalpy of the invariant transitions as a function of the concentration. It is expected that if the transition observed is an invariant transition, the enthalpy should present a linear dependency of the concentration of the system. For the supposed eutectic transition, the Tammann plots showed the characteristic triangular shape in which the maximum enthalpy occurs at the eutectic concentration. In this case, the enthalpy of the eutectic transition was close to zero at a concentration close to pure ethyl palmitate and at a concentration close to $x_1 = 0.4$ supporting the hypothesis that solid solutions were formed in both regions as proposed.

Moreover, at both sides of the diagram, the two possible hypotheses for the interpretation of the events observed above the eutectic transition would be a peritectic or a metatectic transition. In fact, according to the Tammann plot, linear profiles were observed for these invariant transitions. Since the melting profile of both sides of the diagram obeys a typical eutectic profile, probably no peritectic transition occurs and the metatectic transition could be considered in this case. This assumption could be confirmed by optical microscopy as discussed below.

Fig. 2 shows micrographs for this system at various concentrations as function of temperature. At $x_1 = 0.10$, the SLE diagram proposed implies that a solid solution is formed at a temperature below 295 K. When system is heated, no liquid phase (L) is observed up to a temperature close to 301.5 K. Moreover, during the heating, the solid phase crystals changed aspect. When the system at $x_1 = 0.30$ is heated, a similar series of events was observed. A liquid phase is observed only above 295 K, i.e. above the metatectic reactions, and the crystalline structure of the system was also modified. This new solid phase that is observed to appear upon heating was indicated in the phase diagram as A_m . At $x_1 = 0.55$, i.e. close to the eutectic point, the system melts in a very narrow temperature range, as would be expected from the phase diagram proposed. Moreover, at this point, the solid phase clearly presented a different crystalline habit. In fact, at the right hand side, a solid solution B appears as proposed by the Tammann plot. Therefore between $x_1 = 0.50$ and 0.90, approximately the solid solution A crystallizes independently of the solid solution B. At $x_1 = 0.90$, the system started to melt at a temperature close to the supposed eutectic event. However during the heating, similarly to what occurred to system at the left hand side, the crystalline habit of the solid phase was modified, probably also due to a metatectic reaction.

Metatectic transitions are uncommon events for organic systems. They are invariant transitions that occur during the melting of the system, i.e. in the biphasic region (solid + liquid system), in which the system recrystallizes, imposing a drastic modification in the melting profile of system, and consequently, in other physical properties of the system. On the other hand, solid solution are often found in lipidic mixtures, especially when the compounds present the same or similar crystalline structures, such as mixtures of fatty acids, triacylglycerols and fatty alcohols, with consecutive carbon numbers [15]. For fatty systems this phenomenon frequently occurs in regions of high concentration of one of the compounds, but also throughout the concentration range [16], which is the case of mixtures of TAGs with great structural similarity.

Some other thermal events were also observed in the biphasic region and marked with the symbol (+). They did not present any temperature-invariant behavior. Pure esters naturally show polymorphic transitions before their melting temperature. Therefore, these events could be attributed to structural modifications of the solid phase of the mixture during heating, i.e. solid-solid transitions.

3.2. System ethyl stearate + methyl palmitate

For the ethyl stearate (1) + methyl palmitate (2) system, three main thermal transitions were also observed in the DSC thermograms (Fig. S2, SM), in addition to the final melting temperature. Similarly to what occurred in the previous system, a simple eutectic profile could not be

assumed and some invariant transitions were also observed. Fig. 3 presents the interpretation for the solid-liquid phase equilibrium in this case. The theoretical lines were established taking into account the experimental data, the Tammann plots (Fig. S5, SM) and the Gibbs phase rule. The system presents one eutectic transition with a eutectic point close to $x_1 = 0.30$. This event is observed in the DSC only up to $x_1 = 0.55$. In this system, at the right hand side of the diagram, an invariant transition occurs from $0.66 < x < 1.0$. In this case, the melting points (liquidus line) show the characteristic shape of a peritectic event. Peritectic transitions have been largely discussed in literature, for organic mixtures [17], including lipidic systems [18,19]. They comprise the occurrence of an intermediate, also called as peritectic, compound, during the crystallization, in which compounds are in a “stoichiometric” ratio, similar to a chemical reaction. In this case, the peritectic compound is formed at a ratio close to 0.66 M fraction of ethyl stearate. Moreover, since no eutectic, or invariant event was observed from $0.5 < x < 0.66$ the proposal is that in this region a solid solution is formed. In fact, according to the Tammann plot (Fig. S5), the enthalpy of the eutectic transition was close to zero at a concentration close to pure methyl palmitate and at a concentration close to $x_1 = 0.5$. This means that, if no eutectic transition is observed above this concentration, a solid solution also probably occurs. Also, according to the Tammann plot (Fig. S5, SM), no solid solution is formed close to pure compounds. At the left hand side of the diagram the interpretation of the data is the same proposed to the previous system, i.e. a metatectic event. All these assumptions were also confirmed by optical microscopy.

Fig. 4 shows micrographs for this system. At $x_1 = 0.10$, the SLE diagram of this system proposed that the pure solid phase A (methyl palmitate) and the solid solution C (solid solution rich in the peritectic compound) crystallized independently below the eutectic temperature. Above the eutectic point, a region composed of A + liquid phase appears. However, as the system was heated, the melting is interrupted and, as a new solid phase A_m recrystallized, through the metatectic transition, a liquid phase started to appear only above 300.5 K, approximately. It is important to note that when a dark field lens is used, no liquid phase is observed in the sample. This supports the interpretation of the metatectic event proposed in this region. At $x_1 = 0.50$ the system starts to melt at the eutectic temperature, as expected. However, at $x_1 = 0.60$ the melting started above the eutectic temperature. Since a clearly different crystalline structure was observed, a solid solution might explain these observations. Similarly, at $x_1 = 0.90$ the system melted only above 303 K, approximately. This means that up to this temperature only a solid phase is present. Moreover the solid phase in this region is clearly different from region C and region A + C, as expected for this region comprising the solid solution C and pure solid phase B (ethyl stearate).

3.3. System ethyl oleate + methyl palmitate

In the third system, ethyl oleate + methyl palmitate only two thermal events were observed in the DSC thermograms (Fig. S3, SM). This is a more common profile for binary mixtures: the event at a lower temperature could be attributed to the eutectic transition and the higher temperature, to the melting of the sample. This is what in literature is known as simple eutectic mixture. In the Tammann plot of this system (Fig. S6), the enthalpy of the eutectic transition was close to zero at a concentration close to pure methyl palmitate, showing that the two compounds crystallized independently in the solid phase. In this case there are 4 regions: 1 liquid phase region, 1 solid phase region formed by the two compounds crystallized independently, and 2 biphasic regions of liquid plus pure solid ethyl oleate, or pure solid methyl palmitate. Also, the fact that the eutectic point is located very close to the pure compound, this system can be called a “monotectic system”. In fact, the region at the right hand side of the diagram, i.e. the biphasic region with a solid phase composed of pure ethyl oleate is small enough

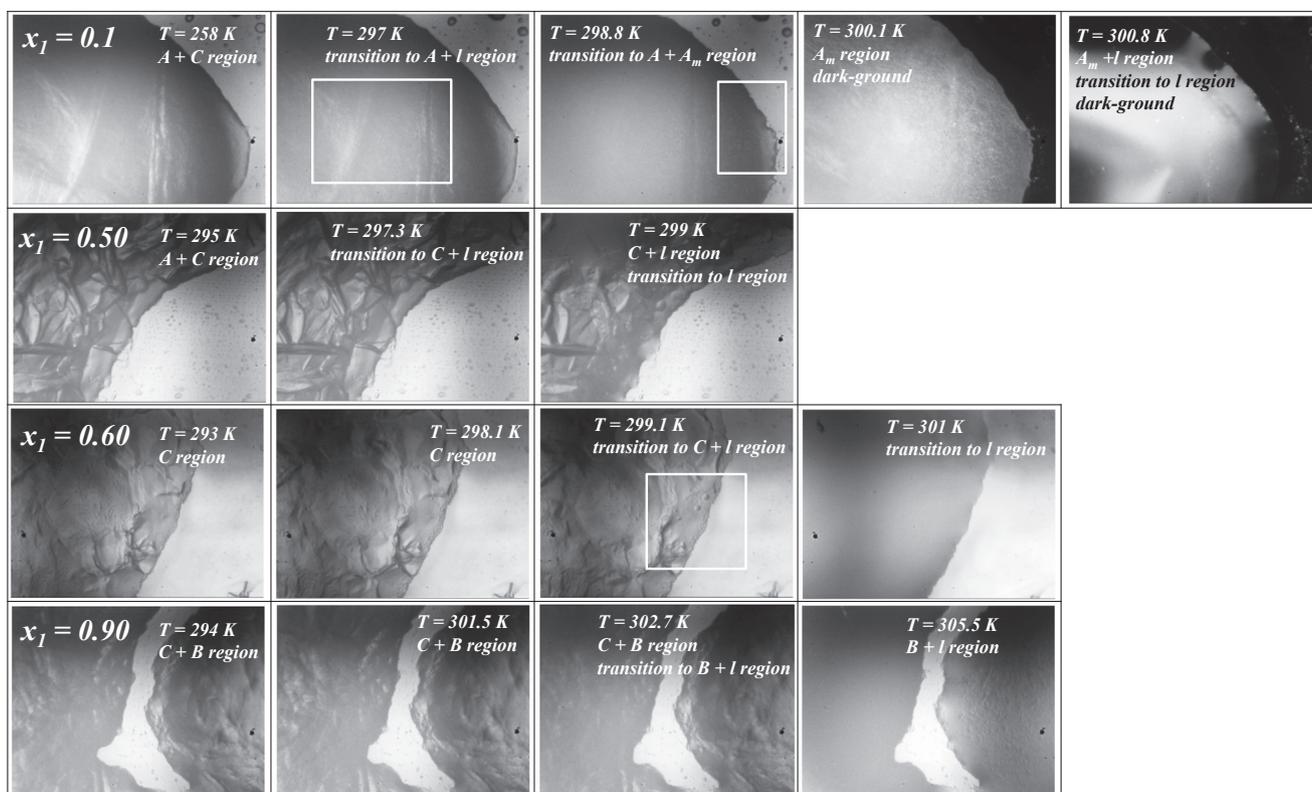


Fig. 4. Optical microscopies related to the ethyl stearate (1) + methyl palmitate (2) system.

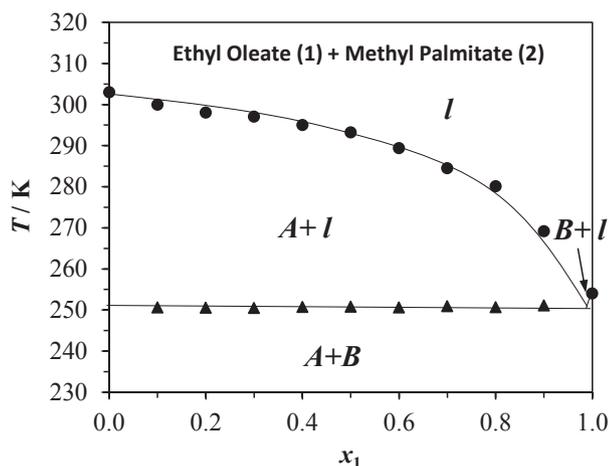


Fig. 5. Solid-liquid equilibrium diagram for the ethyl oleate (1) + methyl palmitate (2) system. Symbols: (\blacktriangle) = eutectic transition; (\bullet) final melting temperature; Letters: A = methyl palmitate, B = ethyl oleate; l = liquid phase; Full lines sketch the interpretation of the phase diagram.

to be neglected in this case. The phase diagram proposed is represented in Fig. 5.

3.4. Comparison between methyl/ethyl esters blends and ethyl/ethyl or methyl/methyl blends

Figs. 6 and 7 presents a comparison between the *liquidus* lines (melting temperatures) of the systems evaluated in this work (ethyl stearate + methyl palmitate, ethyl palmitate + methyl palmitate, and ethyl oleate + methyl palmitate), and those previously presented in literature composed of ethyl ester + ethyl ester or methyl ester + methyl ester, with the same compounds: methyl stearate + methyl

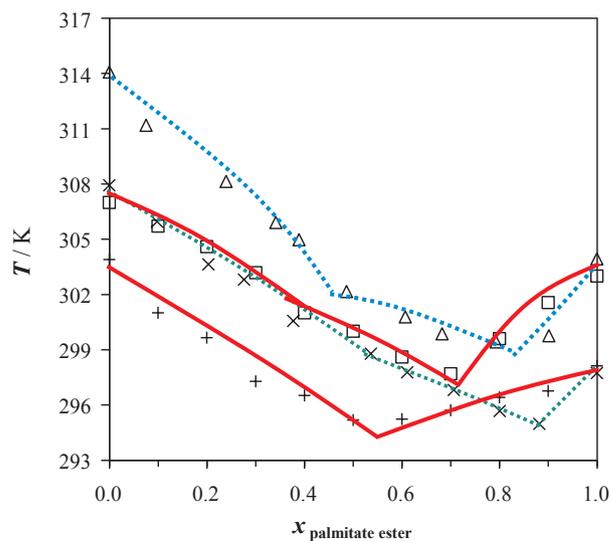


Fig. 6. *Liquidus* lines (melting temperatures) of the esters blends. Red continuous lines are for methyl/ethyl ester blends studied in this work: (\square) ethyl stearate + methyl palmitate, (+) ethyl palmitate + methyl palmitate. Blue dashed line is for methyl/methyl ester blend (literature): (Δ) methyl stearate + methyl palmitate [7]; Green dashed line is for ethyl/ethyl ester blend (literature): (\times) ethyl stearate + ethyl palmitate [6].

palmitate [7], ethyl stearate + ethyl palmitate [6], and ethyl oleate + ethyl palmitate [12]. The system presented by Lutton and Hugenberg [13], i.e. ethyl stearate + methyl stearate was not included in this analysis due to the fact that authors did not provided their experimental temperatures values. Another system methyl palmitate + methyl oleate presented by [20] were not included for the same reason. However, according the Figures presented by the authors, melting temperatures of these system were always higher than those for

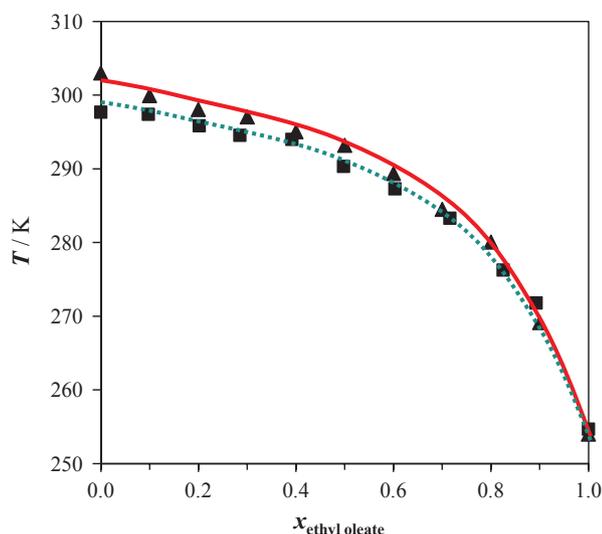


Fig. 7. Liquidus lines (melting temperatures) of the esters blends. Red continuous lines are for methyl/ethyl ester blends studied in this work: (\blacktriangle) ethyl oleate + methyl palmitate. Green dashed line is for ethyl/ethyl ester blend (literature): (\blacksquare) ethyl oleate + ethyl palmitate [12]

the systems here evaluated, being the minimum melting temperature for the system ethyl stearate + methyl stearate close to 305 K, and close to 260 K for the system methyl palmitate + methyl oleate.

When the liquidus line of the ethyl stearate + methyl palmitate (this work) is compared with the same methyl/methyl pair, a similar minimum temperature was observed. However, throughout the concentration range, lower melting temperatures were obtained for the ethyl/methyl pair (this work). When the same ethyl/methyl pair is compared with the ethyl/ethyl pair, it was observed that the ethyl/ethyl pair presented a minimum melting temperature slightly lower than the ethyl/methyl pair. In fact, this behavior was expected since ethyl esters present lower melting temperatures than methyl esters. However, for most of the concentration range (up to $x = 0.7$, methyl palmitate molar fraction), similar melting temperatures were observed. When the pair methyl/ethyl palmitate is compared with all other systems, it was observed that it presented the lowest minimum melting temperature. This is very interesting, and means that an ethyl/methyl palmitate ester blend can present a lower melting temperature than the pure ethyl or methyl palmitate ester, suggesting that a blend, for example of a methyl/ethyl palm oil biodiesel, rich in palmitate is highly favorable for decreasing its cold flow properties. The mixture methyl palmitate + ethyl oleate presented a similar behavior to that observed for ethyl palmitate + ethyl oleate. This is also in line with the results obtained for the saturated esters blends suggesting that blends of ethyl and methyl biodiesel in the adequate proportions could have a low temperature performance analogous to that of ethylic biodiesels and better than the methylic currently used.

4. Conclusion

The SLE diagrams here described for 3 ethyl/methyl esters systems showed in two cases a very complex melting behavior. The phase equilibrium for ethyl palmitate + methyl palmitate mixtures showed up to 12 phase equilibrium regions, with the formation of solid

solutions and with the appearance of a metatectic transition, as previously reported for lipidic compounds. The SLE diagram for the ethyl stearate + methyl palmitate system showed up to 9 phase equilibrium regions, with metatectic transitions, formation of solid solutions, but also formation of a peritectic compound. The system composed of ethyl oleate + methyl palmitate presented a simple eutectic profile, commonly observed for binary organic systems. In general the melting temperatures of the systems here presented were lower than melting temperatures of the analogous systems composed of methyl esters (Fig. 6). Therefore, considering the results presented in this work, ethyl biodiesel could be used in blends with methyl biodiesels as a strategy for improving the cold flow properties of biodiesels based on oils with a high content of saturated esters. This strategy allies the technical advantage of methyl biodiesel with the sustainable and economical appeal of using ethanol.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.fuel.2018.03.154>.

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