

Prediction of Cloud Points of Biodiesel†

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The predictive UNIQUAC model, previously applied with success to the description of wax formation in fossil fuels, is extended here to the modeling of the precipitation of saturated and unsaturated fatty acid methyl/ethyl esters. Correlations for the thermophysical properties of the fatty acid esters are proposed, and the model is evaluated against experimental data of binary mixtures. Despite the lack of accurate data for the cloud points of biodiesel, the results obtained here allow for an adequate evaluation of the model proposed, showing that it can produce good predictions of the cloud points of mixtures of fatty acid esters.

1. Introduction

Given the high price of crude oils and the worldwide concern for CO₂ emissions, support for the production and use of biofuels is increasing.

Because of its environmental benefits, resulting from a decrease in CO₂ emissions, its origin from renewable resources, and the increase in crude oil costs, biodiesel is becoming increasingly attractive. It is expected that in Europe by 2010 transport diesel will incorporate 10% of biodiesel. However, the high cost is still the main limitation to widespread commercialization because the final price of biodiesel depends upon 60–70% of the cost of the fats and oils used on their production. The use of cheap and nonedible oils can help minimize this problem, but the formulation of biodiesel must conform to a number of standards that must be met.

The most commonly used method for biodiesel production is the transesterification of vegetable oils and fats.¹ It consists of a number of alkali-catalyzed reactions, where the triglycerides are converted into fatty acid esters by the reaction with an alcohol (methanol/ethanol), producing glycerol as a secondary product.

The biodiesel properties are dependent upon the raw material used in its production. Chemically, it is much less complex than conventional diesels. This biofuel consists of a blend of liquid, nontoxic, biodegradable fatty acid esters, yellow-colored and immiscible with water. Their cold flow performance depends upon both the oil and alcohol used in the transesterification. Biodiesel from cheap vegetable oils, such as palm oil, with a large concentration of saturated fatty acid esters, although less

vulnerable to oxidation and displaying better combustion properties, has a worst performance at low temperatures, because of its tendency to crystallize.^{2,3}

There are several specifications for the biodiesel performance under low-temperature conditions. The most important are the cloud point (CP; EN 23015 and ASTM D-2500), the pour point (PP; ASTM D-97 and ASTM D-5949), the cold filter plugging point (CFPP; EN 116, IP-309, and ASTM D-6371), and the low-temperature filterability test (LTFT; ASTM D-4539).⁴

The CP is defined as the temperature at which crystallization of the heavier fatty acid esters starts as the fluid is cooled. As the solid phase develops in the liquid bulk, the solution becomes cloudy. With a further decrease in the temperature, the crystal particles grow rapidly and agglomerate, reducing the capacity of the liquid to flow through porous media by plugging the filters, and eventually gel the fluid, preventing it from flowing altogether. In comparison, a biodiesel has higher CPs than a conventional diesel. The CP is essentially determined by the amount of saturated esters and does not depend upon the composition of the unsaturated esters.^{2,3} Saturated fatty compounds have higher melting points than unsaturated fatty compounds and crystallize at higher temperatures.^{2,3} Thus, biodiesel derived from oils or fats with considerable amounts of saturated fatty compounds will display high CPs. The presence of solid crystals in the biodiesel affects its viscosity, volatility, flowability, and filterability.

Most biodiesel properties can be predicted from the knowledge of their compositions, which are easily determined by gas chromatography. In this study, the CPs are predicted for fluids with known compositions. Although the CP is the only cold flow property that can be defined thermodynamically and thus be the object of a thermodynamic-based model, as previously

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shown for conventional diesel,⁵ the PP, CFPP, and LTFT can be related to the CP and be predicted from its value. It has also been shown by Dunn and Bagby that for biofuel formulations both CFPP and LTFT are linear functions of the CP.³ A thermodynamic model able to predict the CP of a biodiesel from its composition can be used to evaluate the cold flow behavior of these biofuels and used for their formulation.

This work is structured as follows: After a description of the experimental technique used to measure the CPs of a number of binary mixtures, the predictive CP model proposed here is presented. This model is based on a γ - φ approach, where the liquid phase is described by a cubic equation of state (EoS) and the solid phase is described by the predictive UNIQUAC model.⁶⁻⁹ The model requires the knowledge of the thermo-physical properties of fatty acid esters usually present on these biofuels. For this purpose, literature data of thermophysical properties of saturated and unsaturated fatty acid esters were collected and correlations for these properties were developed.

Subsequently, the model is evaluated by comparing its predictions with the experimental CPs for a number of binary systems either measured on this work or obtained from the literature. Conclusions on the ability of the model to describe the CPs of the studied systems are drawn.

2. Experimental Section

The fatty acid esters used were obtained from Sigma Aldrich with purities of 99% and were used with no further purification. The mixtures were prepared by weight on an analytical balance, and the weighed quantities of the components, placed in a glass tube, were heated under stirring in a nitrogen atmosphere to a temperature 10 K above the higher melting point of the pure components. Thermograms of these mixtures were obtained using a MDSC 2920, TA Instruments calorimeter. The calorimeter was equipped with a refrigerated cooling system, allowing for the operation between 258 and 423 K. Samples (2–5 mg) of each mixture were weighed in a microanalytical balance (Perkin-Elmer AD6) with $\pm 0.2 \times 10^{-5}$ mg precision and sealed in aluminum pans. To erase previous thermal histories, each sample was heated to 15 K above the highest melting temperature of the pure components and kept at this temperature for 20 min. The samples were then cooled to 25 K below the lowest melting point of the components and equilibrated for 30 min. After this pretreatment, the thermogram of each sample was then collected in a heating run, at a heating rate of 1.67×10^{-2} K s⁻¹. The CP was taken as the melting temperature of the mixture.

The accuracy of the experimental data was evaluated on the basis of repeated runs performed for the calibration substances and some of the investigated mixtures. Calibrations of the calorimeter with standards were performed in quintuplicate, with absolute average deviations (AADs) ranging from 0.03 to 0.06 K for all of the standards. Duplicates of the differential scanning calorimetry (DSC) thermal curves for some selected fatty acid mixtures were used to extract the melting temperatures, with AADs ranging from 0.03 to

0.2 K. On the basis of these experimental runs, the uncertainty of the equilibrium data can be estimated as no higher than 0.2 K.

3. Modeling

The phase equilibrium of fatty acid esters is described here using an approach previously proposed by us for alkane mixtures⁶⁻¹⁹ and also applied to fatty acids with success.²⁰

Equilibrium conditions are obtained from the equality of fugacity of each component in the liquid and solid phase

$$f_i^L(T, P, x_i^L) = f_i^S(T, P, x_i^S) \quad (1)$$

The liquid phase fugacity can be written as

$$f_i^L(T, P, x_i^L) = P x_i^L \varphi_i^L \quad (2)$$

where the fugacity coefficient φ_i^L is calculated using the Soave-Redlich-Kwong EoS,²² with the LCVM mixing rules.^{23,24} The volumetric properties calculated by the cubic EoS are corrected using the volume translation proposed by Peneloux et al.²⁵

The solid-phase fugacity at a pressure P is obtained by the equation

$$\ln f_i^S(P) = \ln f_i^S(P_0) + \frac{1}{RT} \int_{P_0}^P \bar{V}_i^S dP \quad (3)$$

where the fugacity of the component i in the solid phase at pressure P_0 is calculated from its fugacity in the subcooled liquid state at the same temperature T

$$f_i^S(P_0) = x_i^S \gamma_i^S(P_0) f_i^{\theta,L}(P_0) \exp \left[-\frac{\Delta_{\text{fus}} H_i}{RT} \left(1 - \frac{T}{T_{\text{fus},i}} \right) \right] \quad (4)$$

where γ_i^S represents the activity coefficient of the compound i in the solid phase and $T_{\text{fus},i}$ and $\Delta_{\text{fus}} H_i$ are, respectively, the fusion temperature and enthalpy of fusion of the pure compound i . Because all of the systems studied here were at atmospheric pressure, the Poynting correction term in eq 3 can be neglected and eq 3 can be written as

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$$f_i^S(T, P, x_i^S) = x_i^S \gamma_i^S(T, P_0, x_i^S) f_i^{\theta, L}(T, P_0) \exp \left[-\frac{\Delta_{\text{fus}} H_i}{RT} \left(1 - \frac{T}{T_{\text{fus}, i}} \right) \right] \quad (5)$$

The activity coefficients γ_i^S of the solid phase were described by means of the new predictive UNIQUAC model recently proposed by us.^{8,9} The UNIQUAC model can be written as

$$\frac{g^E}{RT} = \sum_{i=1}^n x_i \ln \left(\frac{\Phi_i}{x_i} \right) + \frac{Z}{2} \sum_{i=1}^n q_i x_i \ln \frac{\theta_i}{\Phi_i} - \sum_{i=1}^n x_i q_i \ln \left[\sum_{j=1}^n \theta_j \exp \left(-\frac{\lambda_{ij} - \lambda_{ii}}{q_i RT} \right) \right] \quad (6)$$

with

$$\theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \quad \text{and} \quad \Phi_i = \frac{x_i r_i}{\sum_j x_j r_j} \quad (7)$$

The predictive local composition concept^{26–30} allows for the estimation of the interaction energies, λ_{ij} , used by this model without fitting to experimental data. The pair interaction energies between two identical molecules are estimated from the enthalpy of sublimation of an orthorhombic crystal of the pure component

$$\lambda_{ii} = -\frac{2}{Z} (\Delta_{\text{sub}} H_i - RT) \quad (8)$$

where Z is the coordination number. A value of the coordination number of 10 will be used for the new version of predictive UNIQUAC^{8,9,31,32} used here, in both eqs 6 and 8. The enthalpies of sublimation, $\Delta_{\text{sub}} H = \Delta_{\text{vap}} H + \Delta_{\text{fus}} H$, are calculated at the melting temperature of the pure component.

The pair interaction energy between two nonidentical molecules is given by

$$\lambda_{ij} = \lambda_{ji} = \lambda_{ij} (1 - \alpha_{ij}) \quad (9)$$

where j is the compound with the shorter alkyl chain of the pair ij . In this work, the interaction parameter α_{ij} was used with a value of 0.03. As discussed previously for fatty acids,²¹ it may be of importance for the description of the solid solution formation but has little impact on the liquidus line.

The solid–liquid equilibrium model adopted here is a predictive model that uses, in the calculation of the phase behavior, only pure component properties. Correlations for the thermophysical properties of fatty acid esters, such as critical properties and acentric factors to use in the EoS, and the melting temperatures and enthalpies, required by eqs 4 and 5, and the enthalpies of vaporization used for the estimation of the interaction energies in eq 9 are proposed in the following section.

4. Pure Component Thermophysical Properties

The ability to describe the thermophysical properties of the pure fatty acid esters is essential to an adequate description of the CPs of biodiesel using the model described above. Literature

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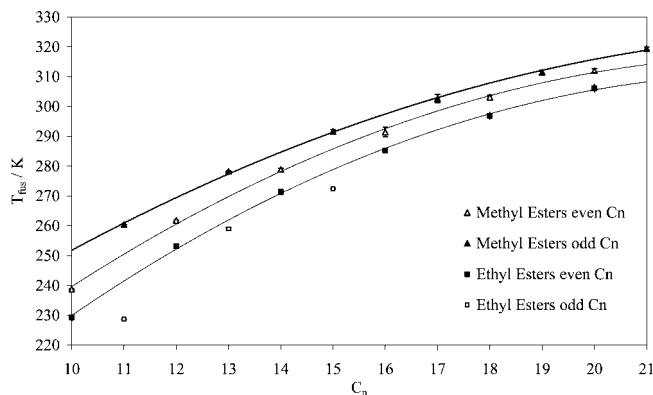


Figure 1. Melting temperatures of fatty acid methyl and ethyl esters.

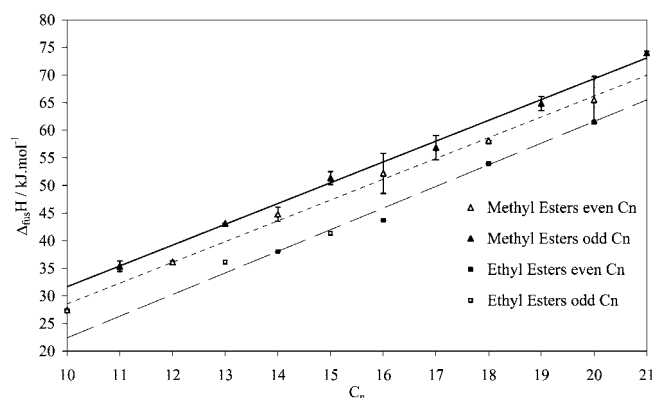


Figure 2. Melting enthalpies of fatty acid methyl and ethyl esters.

data of thermophysical properties of saturated and unsaturated fatty acid methyl/ethyl esters, from C_{10} to C_{21} , were collected, and correlations were developed for melting temperatures and enthalpies and enthalpies of vaporization. For the critical properties, no experimental data were available and correlations were selected among the available correlations for critical temperatures and pressures and acentric factors.

Melting points of saturated fatty acid methyl ($T_{\text{fus methyl esters}}$) and ethyl ($T_{\text{fus ethyl esters}}$) esters were compiled from the literature,³³ and the correlations proposed are given by eqs 10 and 11 for the methyl esters with an odd and even total carbon number (C_n) in the molecule and in eq 12 for the ethyl esters with an even total carbon number (C_n) in the molecule

$$T_{\text{fus methyl esters}} (\text{K}) = -0.3033C_n^2 + 15.50C_n + 127.1 \quad \text{for odd } C_n \quad (10)$$

$$T_{\text{fus methyl esters}} (\text{K}) = -0.4114C_n^2 + 19.52C_n + 85.54 \quad \text{for even } C_n \quad (11)$$

$$T_{\text{fus ethyl esters}} (\text{K}) = -0.4450C_n^2 + 20.90C_n + 65.34 \quad \text{for even } C_n \quad (12)$$

where C_n is the total number of carbons in the molecule. A comparison between the correlations and the experimental data is reported in Figure 1.

Given the very different structure of the solid phase of the ethyl and methyl esters,³⁴ it is not possible to produce a single

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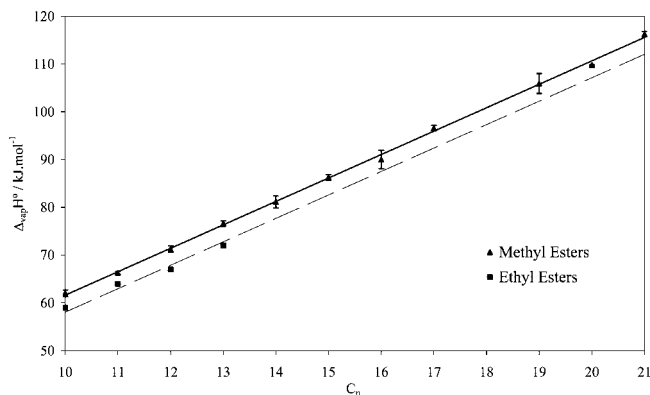


Figure 3. Standard vaporization enthalpy temperatures of fatty acid methyl and ethyl esters.

correlation that is able to describe the melting temperatures of both families simultaneously. This difference in solid-phase structures leads to a curious situation for which the melting points of the methyl esters are larger than those of ethyl esters of similar size.

Melting enthalpies of saturated fatty acid methyl ($\Delta_{\text{fus}}H_{\text{methyl esters}}$) and ethyl ($\Delta_{\text{fus}}H_{\text{ethyl esters}}$) esters were compiled from the literature,³³ and the correlations obtained are presented in eqs 13 and 14 for the methyl esters with an odd and even total carbon number (C_n) in the molecule and in eq 15 for the ethyl esters with an even total carbon number (C_n) in the molecule

$$\Delta_{\text{fus}}H_{\text{methyl esters}} (\text{kJ mol}^{-1}) = 3.828C_n - 7.427 \quad \text{for odd } C_n \quad (13)$$

$$\Delta_{\text{fus}}H_{\text{methyl esters}} (\text{kJ mol}^{-1}) = 3.932C_n - 10.98 \quad \text{for even } C_n \quad (14)$$

$$\Delta_{\text{fus}}H_{\text{ethyl esters}} (\text{kJ mol}^{-1}) = 3.919C_n - 16.80 \quad \text{for even } C_n \quad (15)$$

where C_n is the total number of carbons in the molecule. A comparison between the correlations and the experimental data is reported in Figure 2.

Again, for the reasons discussed above, it was not possible to develop a single correlation for both families, and $\Delta_{\text{fus}}H_{\text{methyl esters}}$ is also larger than $\Delta_{\text{fus}}H_{\text{ethyl esters}}$.

The lack of literature data for the fatty acid ethyl esters, in particular for those with an odd total carbon number (C_n) in the molecule, does not allow for the development of correlations for its melting points and enthalpies. The same situation was observed for unsaturated esters.

Vaporization enthalpies of saturated fatty acid methyl ($\Delta_{\text{fus}}H_{\text{methyl esters}}$) and ethyl ($\Delta_{\text{fus}}H_{\text{ethyl esters}}$) esters do not show any parity effect as expected for liquid-phase thermophysical properties. Data for this property were compiled from the literature,^{33,42,43} and the correlations obtained are presented in eq 16 for the methyl esters and eq 17 for the ethyl esters

$$\Delta_{\text{fus}}H_{\text{methyl esters}} (\text{kJ mol}^{-1}) = 4.904C_n - 12.56 \quad (16)$$

$$\Delta_{\text{fus}}H_{\text{ethyl esters}} (\text{kJ mol}^{-1}) = 4.90C_n - 9.0 \quad (17)$$

where C_n is the total number of carbons in the molecule. A comparison between the correlations and the experimental data is reported in Figure 3.

For the critical properties, critical temperature (T_c), critical pressure (P_c), and acentric factor (ω), no experimental data for these compounds were available in the literature; thus, it was not possible to develop correlations for these values. To identify

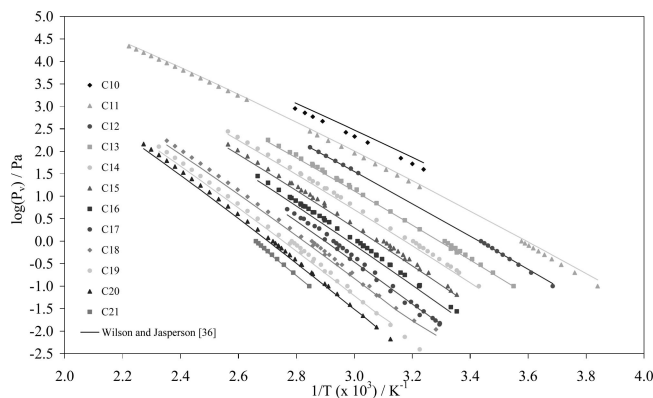


Figure 4. Experimental and predicted vapor pressures for methyl esters using SRK EoS and the critical properties estimated using the Wilson and Jaspersion³⁶ method.

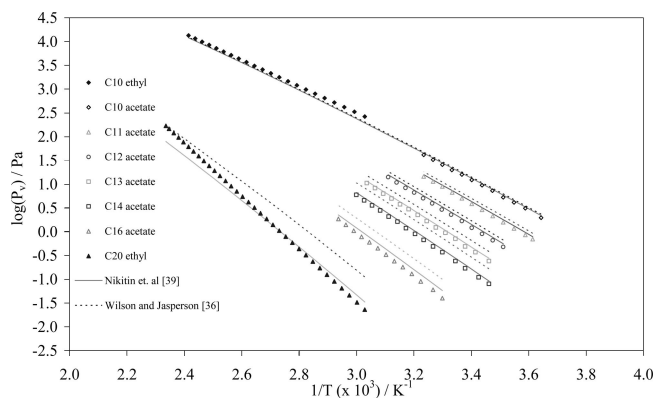


Figure 5. Experimental and predicted vapor pressures for ethyl esters and alkyl acetates using SRK EoS and the critical properties estimated using the Wilson and Jaspersion³⁶ and Nikitin et al.³⁹ methods.

the best correlations for these properties among the correlations for critical properties available, the data for vapor pressures for the fatty acid esters were used along with the cubic EoS used by the model. The best set of correlations for the critical properties was chosen as that which would provide the best description of the vapor pressure of these compounds using the SRK EoS. The models of Wilson and Jaspersion,^{35,36} Marrero and Pardillo,^{35,37} Joback and Reid,^{35,38} and Nikitin et al.³⁹ were evaluated for the critical temperatures and pressures, while for the acentric factor, the model of Han and Peng⁴⁰ was the only one evaluated.

Figure 4 shows the vapor pressure description for saturated fatty acid methyl esters.^{41–43} In Figure 5, the vapor pressure modeling for saturated fatty acid ethyl esters is presented. The lack of literature data for the vapor pressure of fatty acid ethyl esters (solid symbols) is overcome by the use of vapor pressure

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data for alkyl acetates⁴⁴ (empty symbols). The study shows that the best model for the description of the critical temperatures and pressures of saturated and unsaturated methyl esters is the Wilson and Jasperson^{35,36} model. The limited amount of data for ethyl esters made the study less conclusive for these compounds. It seems however that the Nikitin et al.³⁹ correlation (solid line) provides a better description of the literature data than the Wilson and Jasperson correlation (dotted lines). For both families, the model by Han and Peng⁴⁰ for the acentric factor proved to be adequate.

5. Results and Discussion

Unfortunately, no reliable experimental data for CPs of biodiesel are available in the open literature. Data for binary mixtures of fatty acid esters is also very scarce, and most of the data previously available is of very poor quality. The deviations in the CPs of the mixtures can be estimated from the errors reported by the authors for the pure compound melting points and the scattering of the data. For this reason, the evaluation of the proposed model for CPs of biodiesel will be carried out here using data for five binary systems measured by us in this work and supplemented by the corrected data of Imahara et al.² and two systems by Dörfler and Pietschmann.⁴⁵ Unlike conventional fuels, for which the complexity of their composition does not allow for a simple mixture to be taken as representative of these fluid behaviors, a B100 biodiesel is a much simpler fluid, in that the limit may have no more than 2 or 3 different esters and, even in more complex situations, such as biodiesel produced from blends of oils, no more than 10 different esters are present in the mixture. The binaries presented here are thus representative of B100 biodiesel, and the modeling results can be safely extrapolated to real biodiesel. Nevertheless, more extensive studies of CPs of other binary mixtures, B100 and blends of B100 with conventional diesel, are currently under investigation for a more extensive evaluation of the proposed model.

5.1. Binary Mixtures of Fatty Acid Methyl Esters. The larger uncertainties on the thermophysical properties of the fatty acid esters are on the critical properties for which no experimental data were available, and the evaluation of the correlations was based on the vapor pressure of the compounds calculated by the EoS. The first study was thus the evaluation of the effect of the uncertainty of the critical properties on the model predictions at atmospheric pressure. Variations of ± 10 K on the critical temperature, ± 2 bar on the critical pressure, and ± 0.05 on the acentric factor were evaluated. As shown in Figure 6 for the system, methyl myristate–methyl palmitate, these variations produce negligible effects on the phase diagram predictions, with the lines of the different calculations being essentially identical. Figures 6 and 7 also allow for an evaluation of the quality and the agreement of the data and that reported by different authors. As can be observed, the scattering of the data is very large, with poor agreement between the different sources. Moreover, large deviations are observed even for the pure compound melting points. For the study presented here, only the data measured on this work and data for which the pure compound melting points were in good agreement with the literature were retained. Imahara et al.² recently presented a large number of CPs of binary systems of fatty acid methyl esters, for which a systematic deviation in the CPs is observed

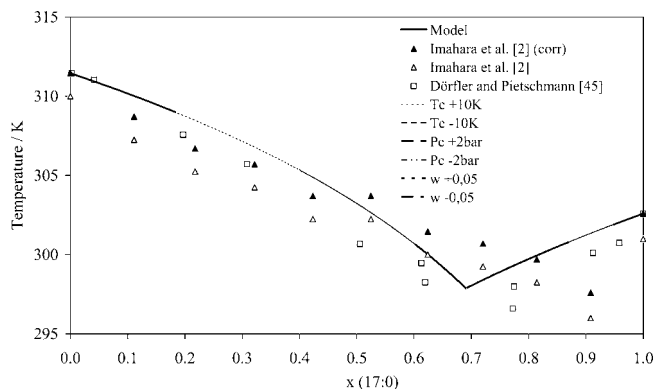


Figure 6. Study of the effect of the uncertainties on the critical properties on the model predictions for the CPs of the methyl palmitate plus methyl stearate ($C_{17:0}$ plus $C_{19:0}$) system.

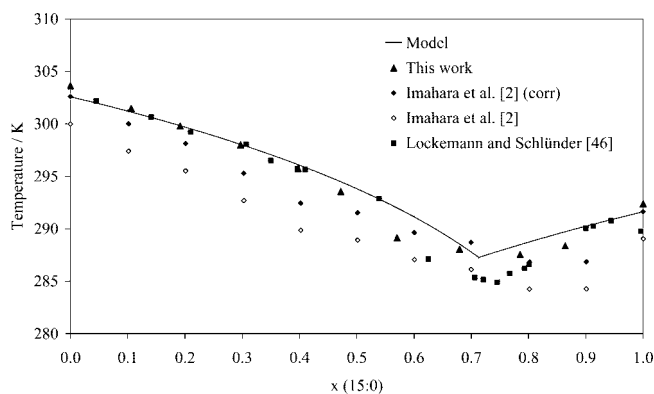


Figure 7. Experimental and predicted CPs of the methyl myristate plus methyl palmitate ($C_{15:0}$ plus $C_{17:0}$) system.

because of the analytical technique used. To overcome this deviation, Imahara et al.² CPs were translated here, so that the melting temperatures of the pure fatty acid esters are correctly described.

The cold flow properties of the biodiesel are determined by the saturated fatty acid esters because the melting points of the unsaturated esters are much lower, and these act essentially as solvents, in which the saturated esters are dissolved and from which they precipitate by effect of the temperature. Both CPs for mixtures of two saturated esters and mixtures of a saturated and an unsaturated ester are presented here. The CPs available seem to indicate that these systems form simple eutectic systems, but both the thermograms and modeling results indicate the presence of a much richer phase diagram below the saturation line. A complex phase diagram, not unlike what is observed for fatty acids, seems to exist for binary mixtures of fatty acid esters, but this is not relevant for the purpose of the present work and will be the object of a future work.

Figure 8 shows the modeling of the CPs for the system, methyl palmitate–methyl eicosanoate, presented by Dörfler and Pietschmann.⁴⁵ Figures 9 and 10 show various examples for the modeling of mixtures of a saturated and an unsaturated methyl ester using the corrected data by Imahara et al.² In Figure 9, two systems of saturated methyl esters with methyl oleate as the solvent are reported, while in Figure 10, results for two systems with methyl linoleate are presented. In all cases, a good description of the CPs of these systems is obtained. As discussed above and as suggested by Imahara et al.² and Dunn and Bagby,³ the results for the mixtures containing saturated and unsaturated fatty acid methyl esters show how the CPs are dominated by the saturated compound.

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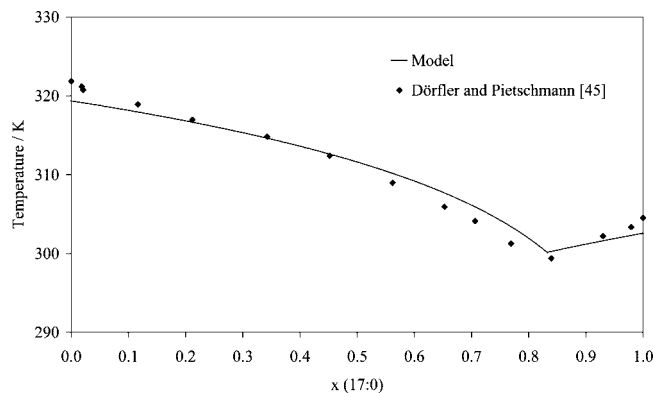


Figure 8. Experimental and predicted CPs of the methyl palmitate plus methyl eicosanoate (C_{17} plus C_{21}) system.

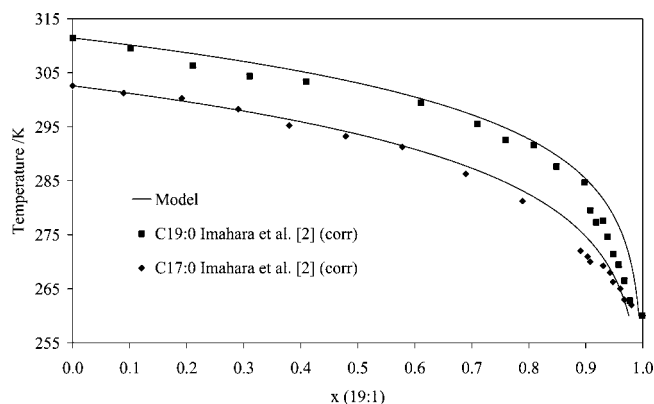


Figure 9. Experimental and predicted CPs of the methyl stearate plus methyl oleate ($C_{19:0}$ plus $C_{19:1}$) and methyl palmitate plus methyl oleate (C_{17} plus $C_{19:1}$) systems.

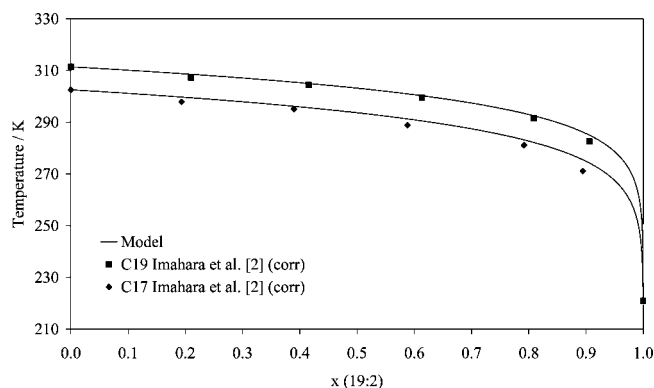


Figure 10. Experimental and predicted CPs of the methyl palmitate plus methyl linoleate ($C_{17:0}$ plus $C_{19:2}$) and methyl stearate plus methyl linoleate ($C_{19:0}$ plus $C_{19:2}$) systems.

The results presented here for fatty acid methyl ester mixtures show that, despite the evident limitations concerning the experimental data available, the model provides an excellent and robust prediction of the CPs of these simple biodiesel systems.

5.2. Fatty Acid Ethyl Esters. At present, just one country is producing (bio)ethanol-based biodiesel instead of methanol. The use of ethanol has several advantages. Despite being heavier and, thus, having a higher specific energy, a higher cetane index, and better lubricity, ethyl esters have lower melting points and,

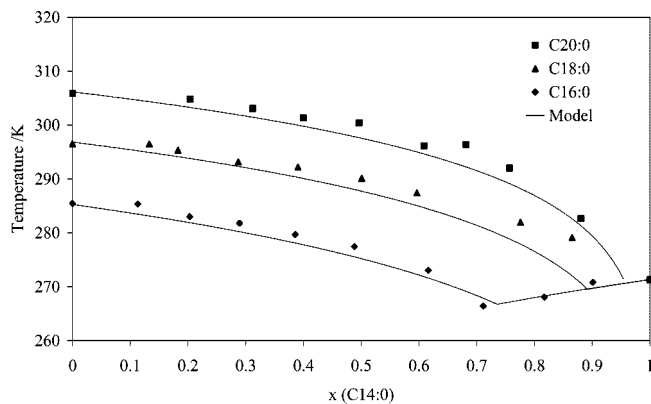


Figure 11. Experimental and predicted CPs of the ethyl laurate plus ethyl myristate ($C_{14:0}$ plus $C_{16:0}$), ethyl laurate plus ethyl palmitate ($C_{14:0}$ plus $C_{18:0}$), and ethyl laurate plus ethyl stearate ($C_{14:0}$ plus $C_{20:0}$) systems.

thus, better cold flow behavior than their methyl ester counterparts.⁴⁶ Moreover, with the increase availability of bioethanol, if this is used instead of methanol in the biodiesel production, a fully renewable fuel is obtained, unlike what happens nowadays. Because of their importance for the Brazilian biodiesel production, the CPs of fatty acid ethyl ester mixtures were investigated here. CPs for three binary mixtures of saturated fatty acid ethyl acids were determined by DSC, as described above. These systems were chosen because they are relevant to evaluate the cold flow behavior of biodiesel produced from palm oil. In Figure 11, a comparison between the experimental data and the model predictions is reported for the binary systems of ethyl laurate with ethyl myristate, palmitate, and stearate. As can be observed, a very good description of the experimental data is achieved, showing the ability of the model to predict the CPs of ethyl-ester-based biodiesel.

6. Conclusions

The cold flow properties of biodiesel are determined by their composition, in particular by their content in unsaturated fatty acids. Correlations for the thermophysical properties of the fatty acid methyl esters and ethyl esters were developed on the basis of the experimental data available.

A model, previously used for the prediction of CPs of conventional fuels, is extended here to the prediction of CPs of biodiesel. It is shown that the proposed model is able to provide an adequate description of the CPs of the binary mixtures of ethyl and methyl esters, for which data was available. It is expected that the model can predict the CPs of biodiesel based on both methyl and ethyl esters and, thus, be used in the production and formulation of these biofuels.

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