Phase equilibria description of biodiesels with water and alcohols for the optimal design of the production and purification process

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HIGHLIGHTS

- The soft-SAFT EoS was applied to assist the design of biodiesel purification units.
- Phase behavior of ester + water/alcohol mixtures were described, in broad T/P ranges.
- Ester–water/alcohol solvation explicitly considered through a new association scheme.
- Only one binary parameter ξ is used for all ester–water/alcohol mixtures.
- Water solubility in biodiesels is predicted from the ester–water binary systems.

ARTICLE INFO

ABSTRACT

The water solubility in fatty acid esters and biodiesels and the vapor–liquid equilibria (VLE) of fatty acid ester + methanol/ethanol systems, formed at biodiesel production and purification industrial units, were modeled in this work to complete the development and application of the soft-SAFT equation of state (EoS) to the design and optimization of biodiesel production plants.

The soft-SAFT EoS is able to accurately describe the water solubility and the VLE of methanol and ethanol with a large number of binary systems, composed of a variety of esters, in wide ranges of temperature, including near/supercritical conditions, with the use of just one binary interaction parameter. This parameter is chain length dependent for the water systems, while it is constant for the methanol and the ethanol binary mixtures.

An entirely predictive scheme is proposed for the soft-SAFT EoS water solubility in biodiesels description, being only necessary to know the biodiesel fatty acid esters composition to determine the required molecular and binary interaction parameters. A new association scheme to explicitly consider the solvation phenomenon between esters and water/alcohols is also proposed.

The results obtained in this work with soft-SAFT are clearly superior, regarding qualitative and quantitative agreement with the experimental data and predictive ability of the model, to those obtained with other similar modeling approaches, namely with the Cubic-plus-Association equation of state (CPA EoS) and other SAFT-type EoSs, as discussed throughout the work.

The soft-SAFT EoS is shown here as a valuable tool to assist the design of biodiesel purification units, specifically for applications in the biodiesel washing, drying and alcohol removal, in order to obtain the biodiesel with the quality specifications required by the international standards.

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1. Introduction

The development of reliable thermodynamic models able to properly predict the phase equilibria of associating and non-associating pure compounds and their mixtures, in wide ranges of temperature, pressure and composition, is essential for the proper design, optimization and operation of production facilities. For the biodiesel production industry, this thermodynamic characterization is important in order to produce the biodiesel in accordance with the quality standards established by the American Society of Testing and Materials (ASTM) D6751 [1] in North America, by the EN 14214 [2] in Europe, and by the RANP 07/08 [3] in Brazil.

Two of these imposed biodiesel quality standards are the alcohol and the water contents. Water and alcohol are introduced during the biodiesel production. Biodiesel, a blend of alkyl

monoesters of fatty acids, is produced through a transesterification of vegetable oils with short-chain alcohols. The basic catalyzed reaction takes place in a multiphase reactor where oil reacts with an alcohol, usually in presence of a catalyst, to form fatty acid esters and glycerol. At the outlet of the reactor, two liquid phases co-exist: one of them rich in glycerol and the other in fatty acid methyl esters (FAMEs). The unreacted alcohol is distributed between these two liquid phases. The methyl ester stream leaving the transesterification reactor is then washed with acidified water to neutralize the catalyst and to convert any existing soaps to free fatty acids [4].

Higher contents of these compounds alter the biofuel properties and cause engine problems. An excess of alcohol will originate a decrease of the biodiesel densities, viscosities and flash points, and the use of the biodiesel with high amounts of alcohol on its composition will result on the deterioration of the natural rubber seals and on the corrosion of Al and Zn pieces of the engine [5,6].

Unlike diesel fuels, biodiesel is hydrophilic causing problems in the storage and use of biodiesels. Water is introduced during the biodiesel production, as explained above, and is also typically present in the distribution and storage, being even used in tanks as cleaner and ballast. However, water decreases the oxidation stability of the biodiesel, and oxidation products will be formed during long storage periods [7,8]. The presence of water in biodiesel will also cause biological growth during storage, namely yeast, fungi, and bacteria. The resulting biodiesel with a high content of water will, in the long term, originate the engine corrosion and block the injection system due to the formation of sludges and slimes [6].

The control of the amount of alcohol and water present in the biodiesel, to meet the quality standards imposed by the different norms, is carried out in the biodiesel production facility in purification units. After being washed with water, the fatty acid esters are dried to produce biodiesel with an acceptable water content [9]. Evaporations and/or distillation units are also used to remove excess alcohol from the fatty acid ester stream coming out of the transesterification reactor [9,10].

The development of modeling tools to accurately predict the water solubility in fatty acid esters and biodiesels and the VLE of fatty acid ester + alcohol systems is essential for the biodiesel production and purification processes, since they allow the choice of the best raw materials, as well as the correct design and optimization of the washing, drying and alcohol removal units and storage facilities, in order to obtain the biodiesel with the required quality. However, that is a quite difficult task since the association, solvation phenomena and sometimes the size asymmetry between the compounds, make these mixtures highly non-ideal [11–14].

A wide variety of theoretically based thermodynamic models have already been used for the description of the phase equilibria of these systems in the literature. Considering activity coefficient models, Rostami et al. [15,16] used the UNIQUAC method to successfully describe the water solubility in four biodiesels from palm, soya, corn and frying oil, with parameters regressed from the experimental data presented in the same work. Tu et al. [17] used the Margules, Wilson, NRTL and UNIQUAC models to satisfactorily describe the isobaric vapor–liquid equilibria data of the binary mixtures of methanol with methyl acetate and methyl acrylate. The same models plus the van Laar equation were used by Resa et al. [18,19] to correlate the isobaric vapor–liquid equilibria for methanol binary mixtures containing ethyl butyrate and ethyl propionate. Ortega et al. [20,21] chose the UNIFAC and the ASOG models to describe the isobaric vapor–liquid equilibria of methyl butanoate and propyl butanoate with ethanol binary systems. Using two versions of the UNIFAC model, Soto et al. [22] successfully described the isobaric vapor–liquid equilibrium data of the binary system composed of ethanol and ethyl methanoate.

Methods based on quantum mechanical (chemical) calculations have also been applied. Moderately successful results were found by Shah and Yadav [23] for the water solubility in fatty acid esters predictions with the COSMO-SAC model. Güzel and Xu [24] presented results for the prediction of the VLE of fatty acid ester + methanol/ethanol systems with the COSMO-RS model. Although the results for the ethanol systems are in agreement with the experimental data, improvements are still necessary for the description of the methanol systems.

Considering equations of state (EoSs) approaches, the high pressure vapor–liquid equilibria of methanol/ethanol + fatty acid methyl ester systems were described by Shimoyama et al. [25,26] using the Peng-Robinson (PR) EoS with different mixing rules. Results in agreement with the experimental data were obtained, nevertheless with the expense of using quite large and temperature dependent binary interaction parameters regressed from experimental data.

Equations of state that explicitly consider the effect of short-range association interactions are one of the most appropriate choices for modeling the water solubility in fatty acid esters and biodiesels and the VLE of fatty acid ester + alcohol systems. Ferreira et al. [27] used the group contribution with association equation of state (GCA-EoS) to describe ester + alcohol systems; however their study was focused only in small esters systems. The PR EoS with and without an association term was used by Arvelos et al. [28] for the description of the high pressure VLE data of the methanol/ethanol + fatty acid methyl ester systems, with the classical van der Waals mixing rules. Similar good results were obtained, but with the necessity of using temperature dependent binary interaction parameters in both approaches.

The first effort to apply an association EoS for a global and exhaustive description of fatty acid esters systems containing alcohols and water, in wide ranges of temperature and pressure, was performed by Oliveira et al. using the Cubic-Plus-Association equation of state (CPA EoS) [11–14,29]. Although in general quite good results were obtained, there is still room for improvements on the description of the water solubility in biodiesels as well as on the model predictive power for describing the VLE of ester + alcohol systems.

Improvements are expected when using more refined EoSs, such as EoSs based on statistical mechanics concepts. Among them, the Statistical Association Fluid Theory (SAFT) and its variants, which explicitly take into account the effects of molecular shape, dispersion forces and molecular association, represent an excellent choice to model those challenging systems.

Even though there is a growing interest in the description of the phase equilibria of systems of relevance for the biodiesel industry, few works have been devoted to the use of SAFT type EoSs for that purpose. Perdomo et al. [30] used the SAFT-VR equation for the description of the reactive equilibrium of the lauric acid esterification, involving the prediction of the phase equilibria of different multicomponent mixtures with acid lauric, methyl laurate, water and methanol. The same authors [31] have also used this model to describe the LLE of ternary systems composed of the fatty acid esters methyl palmitate, methyl linoleate and methyl oleate.

To our knowledge, the application of SAFT type equations to the description of water + fatty acid ester/biodiesel and methanol/ethanol + fatty acid ester systems, of key relevance for the biodiesel production and purification, has not been previously attempted. The closer contribution is the work of NguyenHuynh et al. [32], who used the polar-GC-SAFT EoS considering three different versions of SAFT, the SAFT-0, the SAFT-VR and the PC-SAFT, to describe the VLE of ester + 1-alkanol systems, but only small esters systems were considered.

In this contribution, we expand the work initiated in a previous publication [33], where a molecular model within the soft-SAFT