



A new UNIFAC parameterization for the prediction of liquid-liquid equilibrium of biodiesel systems



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ABSTRACT

The environmental adversities and the global concern about the conservation of non-renewable natural resources have stimulated a search for environmentally friendly energy sources. In this context, biodiesel has emerged as an important alternative to replace fossil fuels, due to its renewability, non-toxicity and biodegradability. Modeling, simulation and design of unit operations involved in the production of edible oils and biodiesel require knowledge of phase equilibrium. Several versions of the UNIFAC model are frequently used for process design when experimental determination of phase equilibrium data is difficult or time-consuming. In this work, the original UNIFAC model parameters are first checked for their predictive capability and then modified in terms of new readjusted binary interaction parameters. It was noted that the UNIFAC model without any changes in its parameters results in inadequate predictions. Thus, in order to obtain a good predictive tool, a comprehensive liquid-liquid equilibrium data bank of systems present in biodiesel production was organized and new UNIFAC interaction parameters were adjusted. At first, the molecules were divided into UNIFAC traditional structural groups. However, this first approach resulted in poor prediction, probably as a consequence of the strongly polar hydroxyl groups bonded to the consecutive carbon atoms of glycerol and acylglycerol molecules. Thus, a new group ('OHgly') was introduced and two matrices of parameters were adjusted. In general, satisfactory predictions were obtained and a significant improvement in the performance of this group contribution model has been achieved.

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1. Introduction

Increasing search for alternatives to petroleum-based fuels has led to the development of fuels from various sources, including renewable feedstocks such as fats and oils. Several types of fuels can be derived from these triacylglycerol-containing feedstocks. One of them is biodiesel, which is defined as the mono-alkyl esters of vegetable oils or animal fats [1]. Considering its well-known environmental and economic benefits, biodiesel is expected to be a good alternative to petroleum-based fuels. It can be used to address the limitations associated with fossil fuels, as the continued rise in

crude oil prices, scarce fossil energy resources and environmental concerns [2].

So far, biodiesel has mainly been produced by transesterification of triacylglycerols (TAGs) and/or esterification of free fatty acids (FFAs) using homogeneous basic or acid catalysts [3,4]. The transesterification reaction is a three-stage reaction, which produces two intermediate products (diacylglycerols and monoacylglycerols). Stoichiometrically, the reaction requires a molar ratio alcohol:oil of 3:1, but excess alcohol (methanol being the most commonly used alcohol) is usually added to shift the reaction towards the products [4,5]. In Brazil, however, the use of ethanol is advantageous because of its large scale production, apart from allowing obtaining biodiesel through a totally renewable process. On the other hand, one disadvantage related to the use of ethanol is that the phase separation can be more difficult when compared with methanol [6]. In this sense, a better understanding and prediction of phase equilibrium of the biodiesel related systems are

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required for the proper design, operation and optimization of the reactor and separation units [4].

Modeling of the reaction and separation processes required to produce higher purity biodiesel involves determining the liquid–liquid equilibrium and thus, a reliable thermodynamic model is essential [7]. However, because of the size of the molecules and the strong molecular interactions involved in the transesterification, the thermodynamic modeling is particularly challenging [8].

Considering that the biodiesel production process basically involves fatty acid esters, alcohol and glycerol, and that the various kinds of esters have many physical-chemical similarities among them, such systems are generally treated as a pseudoternary one, consisting of an equivalent alkyl ester of fatty acid + alcohol + glycerol. Based on this assumption, equilibrium data for a wide variety of alkyl esters may be correlated using models such as UNIQUAC (Universal Quasi Chemical) and NRTL (Non-random, two liquid) with very good results [7,9–12]. An alternative to the usually applied activity coefficient models to predict systems with polar compounds with strong associative interactions found at the biodiesel production and purification processes is the use of association equations of state. Among these associating equations are the statistical associating fluid theory (SAFT) [13] and the Cubic-Plus-Association (CPA) equations of state [14]. Recently, both equations have been used to describe these systems [15–20], presenting encouraging results, although their predictive character is still limited to simpler fatty compounds.

Nevertheless, this approach does not take into account the different behaviors of triacylglycerols, fatty acids and specific esters and does not permit reliable prediction of equilibrium data for different types of biodiesel/oil systems (different compositions in terms of esters/triacylglycerols) with the parameters adjusted using those models. Furthermore, the number of components involved is usually large and the experimental information is scarce, so that it is particularly interesting to use a group contribution method.

The UNIFAC group contribution method [21] has proven to be a fast and in many cases a reliable tool for the prediction of liquid-phase activity coefficients. Extensive tables with revised and updated interaction parameters have been published [22–27]. However, the current methods and corresponding set of available parameters provide improperly description of the liquid-liquid equilibrium (LLE) of systems containing vegetable oils, partial acylglycerols, free fatty acids, alcohol and/or biodiesel [9–11,28–30].

For this reason, the purpose of this article is to present a UNIFAC parameter matrix especially suited for the prediction of LLE of biodiesel systems. The original UNIFAC model was first checked using two different sets of parameters available in the literature to assess their predictive capability and then improved in terms of new regressed binary interaction parameters. It was used an approach to readjust the interaction parameters for UNIFAC model based on experimental data for real multicomponent systems. A similar analysis has been previously performed by the research group for the adjustment of UNIFAC interaction parameters for systems present in the deacidification of vegetable oils, i.e., systems composed of (vegetable oil + fatty acids + ethanol + water) [31]. The database collected in that previous work has been updated and was also used in the present adjustment procedure. Thus, it was intended to obtain a matrix of parameters appropriate for the representation of fatty systems from the oil deacidification up to the biodiesel production.

With the correct representation of the phase equilibrium involved in the entire sequence of biodiesel production, the corresponding process can be investigated and optimized with confidence. A good-quality predictive tool contributes to an

improvement of industrial investment both in equipment design as in process optimization.

2. Thermodynamic modeling

In the context of the ever increasing importance of the liquid–liquid equilibrium in the processing of oils and fats, especially during the oil deacidification and biodiesel production, the readjustment of a new set of interaction parameters of interest for these types of systems is necessary to improve the predictive capacity of the UNIFAC method when applied to fatty systems. In the present work, the adjustment of new interaction parameters was based on experimental data for real fatty systems already available in the literature. In fact, experimental equilibrium data for systems containing pure fatty compounds are very rare and do not provide a data basis sufficiently comprehensive for readjusting parameters of existing groups.

In order to obtain a suitable predictive tool, it is required to work with an experimental liquid-liquid equilibrium database as comprehensive as possible. It has been collected, from the literature, 218 systems containing biodiesel/esters, partial acylglycerols (mono and diacylglycerol), alcohol (methanol or ethanol), glycerol and water, summing up a total of 1145 tie lines, at temperatures ranging from $T/K = 293.15$ to 393.15 . Table 1 shows a summary of the equilibrium systems used in the readjustment procedure. For each group of data, Table 1 gives the original oil, the number of systems, the number of tie lines, the temperature range and the corresponding reference. It should be considered that a larger set of liquid-liquid equilibrium data involving compounds of interest for this study is available in the literature, apart from the data shown in Table 1. However, all those data whose error in the sum of mass fractions at each phase was greater than or equal to 0.001 were not considered in the parameter readjustment procedure, since these data could incorporate errors in the deviations values not derived from the equilibrium calculations.

In addition, the data collected by Hirata et al. [31], which involve systems composed of (vegetable oil + fatty acids + ethanol + water), were updated and also considered, applying the same tolerance in the mass balance deviation adopted for biodiesel systems. For this type of systems, the final database comprises 105 systems summing up a total of 937 tie lines. Thus, it was intended to obtain a matrix of parameters that is appropriate for the representation of systems from the oil deacidification up to the biodiesel production.

The software used for adjusting the interaction parameters was developed in Fortran and was formulated in a previous work [31]. It is worth mentioning that the parameters obtained by Hirata et al. [31] presented a great improvement in the prediction of the systems studied by the authors. However, these parameters do not represent precisely systems containing biodiesel [10,11].

The modeling developed in this work is based on the original UNIFAC model [21]. The parameters adjustment is based on the minimization of the composition objective function, given by Eq. (1), using the simplex method [64].

$$S = \sum_{m=1}^D \sum_{n=1}^N \sum_{i=1}^{P-1} \left[(w_{inm}^{FI,exp} - w_{inm}^{FI,calc})^2 + (w_{inm}^{FII,exp} - w_{inm}^{FII,calc})^2 \right] \quad (1)$$

where D is the total number of data banks, N is the total number of tie lines, P is the total number of pseudocomponents in each data bank; i , n , and m stand for component, tie line and data group, respectively; FI and FII refer to phases I and II , respectively; exp and $calc$ stand for experimental and calculated mass fractions (w),

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