Full Length Article

Phase equilibrium data and modeling of ethylic biodiesel, with application to a non-edible vegetable oil

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ABSTRACT

Contributing to extending the knowledge for the design and operation of biodiesel production processes, isobaric PTxy vapor-liquid equilibria data of ethanol + ethyl hexanoate, 1-pentanol + ethyl hexanoate and 1-pentanol + ethyl octanoate at two different pressures are reported for the first time. Consistency tests were applied to attest the quality of the collected data, for these especially complex measurements. Besides that, vapor pressures of the pure ethyl esters have also been measured. For modeling purposes, the Lyngby and Dortmund UNIFAC variants were used to predict the VLE phase diagrams. Generally, the predictions are of very good quality, being the UNIFAC-Do (Dortmund) better, as the deviations in temperature and vapor compositions are always lower to 1.0 K and 0.020, respectively. Checking for the viability for extrapolations in pressure, CPA EoS was also applied to the modeling of the experimental data with very good results. Finally, aiming at examining the model capabilities to describe multicomponent systems, VLE measurements involving two alcohols and the fatty acid ethyl ester mixture obtained from non-edible vegetable oil have been carried out showing the good performance of the predictive models.

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1. Introduction

The ever increasing worldwide concern for environmental protection and for the conservation of non-renewable natural resources have led to the development of fatty acid esters as diesel substitutes, known as biodiesel [1]. For a rational design and operation of biodiesel production processes, it is essential to have quantitative and reliable information about the vapor-liquid equilibrium (VLE) and liquid-liquid equilibrium of mixtures containing alcohols, fatty acid esters or glycerol. However, experimental data for many of theses systems is still missing [2]. In 2014 the extended review by Coniglio et al. [2] highlighted the great lack of data, while in the work by Cunico et al. [3], from the same year, a comprehensive application of thermodynamic consistency tests for VLE over systems containing the main classes of compounds present in the biodiesel production, showed that only 3% of the data sets had quality factors higher than 0.5 (maximum is 1.0) [3].

These works [2,3] strongly suggested the need of more precise and consistent measurements that can be used to test and develop models for the design and operation of the biodiesel production processes. Among those, conventional excess Gibbs energy models such as Wilson, NRTL, and UNIQUAC equations, group-contribution approaches of the UNIFAC family, but also equations of state (EoS) like CPA, Peng-Robinson, SAFT have been applied [2,4,5], but further developments are still needed. In particular, due to the real competition of edible oils for human nutrition, non-edible vegetable oils (NEVO) are becoming one of the leading raw materials for biodiesel production, for which fundamental and application studies are extremely necessary. The oil based on *Balanites aegyptiaca* (BA) [6,7] is well characterized, containing mostly the fatty acids C16 and C18, with a well-known impact on fuel properties. Moreover, the BA oil quality parameters are quite similar to those of soy oil, which is one of the most used for biodiesel production. In addition, ethyl esters of BA oil showed cleaner combustion than petrodiesel [8]. This suggests that BA can be an attractive alternative for sustainable biodiesel production.

Therefore, the aim of this work is to deliver a large body of consistent and complete experimental VLE data for compounds, and mixtures, of relevance in the biofuel industry. Besides that,

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group-contribution approaches and Cubic-Plus-Association (CPA) equation of state (EoS) are evaluated for their predictive capabilities, not only in binary mixtures, but perhaps more importantly over a multicomponent mixture containing alcohols and ethyl esters synthesized from BA oil.

2. Material and methods

2.1. Chemicals

The list of chemicals used in this work is given in Table 1 along with supplier and purity. These chemicals were used as received without any further purification.

2.2. Production of BAEEs

Balanites aegyptiaca oil was obtained by extraction, i.e. simultaneous cold pressing and filtration of the seed kernels collected from trees growing in arid and semi-arid regions of Burkina Faso [6,7]. The BA ethyl esters (BAEEs) were synthesized via alkali catalysis (KOH), under a two-stage procedure based on intermediate addition of glycerol. Alkali catalysis was operated at 35 °C, with an ethanol to oil molar ratio equal to 8:1, a catalyst concentration of 1 wt% based on the initial mass of oil, and a reaction time of 50 min, while the addition of glycerol marking the start of the second step was carried out after 30 min of reaction. The ester content of the BAEEs yielded 97% on weigh basis. The resulting ethyl esters are later purified by the dry-washing method conducted in batch mode, using 4 wt% of rice husk ash, which were mixed and stirred continuously for 20 min and heated at 35 °C. A vacuum distillation (180–200 °C; 10 mbar) was finally carried out in order to insure a high grade level of the BAEE mixture used afterwards for VLE study. The BAEE final composition and details of the analytical method [9] used to obtain it are presented in Supplementary Material, SM1 and SM2, respectively.

2.3. VLE apparatus and measurements

The VLE experiments were performed by using an all-glass dynamic recirculating ebulliometer, model EEA 3000 manufactured by Pignat Company (France), represented in Fig. S1 of SM3 [10]. This device is equipped with a Cottrell circulation pump that promotes a vigorously mixing of liquid and vapor phases. The adiabaticity of the equilibrium chamber (1) is attained by vacuum with a silver wall having an outlet temperature (TI/02) from the vapor-liquid outlet of the Cottrell pump. The vapor phase is condensed (3) and sent by gravity into the buffer cell (6) equipped with a magnetic stirrer, while the liquid phase is fed directly by gravity in the same buffer cell. The two mixed phases are then recycled to the boiler (2). The samples are taken from the two sampling outlets by collecting them in a test tube fitted on the return

Table 1
Source and purity of compounds used in this study.

Chemical name	CAS	Source	Purity/mol %
Ethanol	64-17-5	Sigma Aldrich	≥99.8
1-Butanol	71-36-3	Fluka	≥99.5
1-Pentanol	71-41-0	Sigma Aldrich	≥99
1-Octanol	111-87-5	Sigma Aldrich	≥99
1-Decanol	112-30-1	Fluka	≥99.5
1-Dodecanol	112-53-8	Sigma Aldrich	≥98
Ethyl hexanoate	123-66-0	Sigma Aldrich	≥99
Ethyl octanoate	106-32-1	Sigma Aldrich	≥99
Ethyl oleate	111-62-6	Sigma Aldrich	≥98
Methyl heptadecanoate	1731-92-6	Fluka	≥99
Potassium hydroxide	1710-58-3	Fluka	≥85

circuits of condensed vapor and liquid phases, upstream of the buffer cell. The vacuum circuit (4) consists of two solenoid valve pressure control systems (EV1 and EV2). A dry ice trap (7) is also available at the top of the equipment to protect the pressure sensor (PIC/01) from contact with the fluids being studied, but is also needed for precise measurements under atmospheric pressure. The uncertainty of the temperature sensor is ±0.01 K, while pressure sensor presents an uncertainty of ±0.013 kPa (±0.1 mmHg).

Initially, the sensors accuracy was analyzed calibrating the temperature sensor in the ebulliometer using a reference thermometer, and measuring the vapor pressure at different temperatures for ethanol selected as reference compound (green species with well-known properties in a large temperature range). After, the vapor pressures of some pure ethyl esters to be studied in binary and multicomponent mixtures are determined using the dynamic ebulliometer. The measurement of vapor pressure serves two guiding purposes: to check the calibration of the equipment and to extend considerably the available vapor pressure data for the studied compounds.

For the isobaric VLE measurements the more volatile compound is initially introduced into the boiler (2) via the funnel (5). A portion of the liquid is evaporated in the boiler by means of an electrical resistance of 500 W, and the system let to equilibrate. The equilibrium state, commonly reached in 0.5 to 1 h of recirculating, is identified when steady temperature is observed for the selected set-point pressure, leading then to assume that composition of both the liquid and vapor phases is also constant. Then, the equilibrium temperature is noted down and samples are collected simultaneously from the liquid and vapor phases for quantification. The less volatile component (esters) are after introduced through funnel (5) in amounts equivalent to the quantity removed from the ebulliometer in the form of vapor and liquid samples. This procedure is continued until the samples in both the liquid and vapor phases finally result in pure ester, signifying the end of the equilibrium diagram. This is perceptible as the temperature of the ebulliometer reaches a constant value, and the addition of more esters has an insignificant effect on the equilibrium temperature and the composition of both phases. For each binary system two different set-point pressures are studied.

2.4. Analytical method

All collected samples were analyzed in an Agilent Technology gas chromatograph coupled with a flame ionization detector (GC-FID). Details of the equipment, operating conditions and calibration are given in SM2. The temperature programs selected for the GC-column and the internal standard (IS) selected for calibration were adapted to the analyzed mixture. For all investigated systems, two ISs were used to determine the collected sample composition (one for the alcohol(s) and the other one for the ester(s)). Preliminary GC-FID calibration was carried out with standard solutions of well-known composition in the two ISs and components of the studied system, prepared over the full range of composition. Calibration performance was then checked by preparing supplementary standard solutions with intermediary compositions in the system components. This last stage allowed for estimating the composition uncertainty ranging from ±0.001 for the binary systems to ±0.004 for the mixtures involving BAEEs.

3. Results and discussion

3.1. Pure component vapor pressure

After the calibration procedure, the equipment was tested to measure the vapor pressure of ethanol. The experimental values