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Liquid–liquid and vapor–liquid equilibrium data for biodiesel reaction–separation systems

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HIGHLIGHTS

- ▶ We measured phase equilibrium data for the system involving biodiesel, methanol, ethanol, glycerol and soybean oil.
- ▶ VLE and LLE data were measured for binary and ternary systems.
- ▶ The boiling point temperatures were obtained using Othmer-type ebulliometer.

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ABSTRACT

This work reports experimental vapor–liquid and liquid–liquid equilibrium data for binary and ternary systems comprised of various mixtures of biodiesel (from soybean oil), methanol, ethanol, glycerol and soybean oil. The binodal curves for biodiesel + methanol + glycerol, biodiesel + ethanol + glycerol, biodiesel + methanol + soybean oil and biodiesel + ethanol + soybean oil systems were obtained at two different temperatures by titration. An Othmer-type ebulliometer was used for vapor–liquid equilibrium measurements at pressures ranging from 14.0 kPa to 92.0 kPa. Binodals curves (LLE) indicated that the temperature range used in this study has no effect on the immiscibility region for the biodiesel + methanol + soybean oil system. By contrast, for the biodiesel + ethanol + soybean oil system, the immiscibility region was larger at the lower temperature. For the vapor–liquid equilibrium data, the results showed that the addition of glycerol to the biodiesel + ethanol binary system does not significantly affect the boiling temperature of the system while with the addition of methanol to the biodiesel + soybean oil system the boiling temperatures of the ternary mixture are reduced. These results can be used to enhance the reaction conversion and the purification processes associated with biodiesel production.

1. Introduction

Due to environmental problems and economic issues related to the use of fossil fuels, intensive research has been carried out in the past decade with the main objective of developing renewable and economically sustainable alternative energy sources. Derivatives of vegetable oils and animal fats, known as biodiesel, obtained through chemical transformation processes constitute an interesting alternative to fossil fuels, in so far as their use contributes to reducing emissions of the main gases related to global warming and the dependence of certain countries on diesel [1,2].

Biodiesel can be produced through the transesterification of vegetable oils and animal fats or the esterification of free fatty acids by means of acid, alkaline or enzymatic catalysis, in homogeneous or heterogeneous media [3–5]. An analysis of the Brazilian Program for Production and Use of Biodiesel (PNPB) shows that soybean oil is the main raw material used for this purpose, accounting for 77.90% of the national production, compared with 3.50% for cottonseed oil, 16.15% for beef tallow and only 2.45% of other fatty materials [6].

Due to factors related to process simplification, biodiesel is commonly produced by homogenous catalysis using methanol and NaOH as catalyst. Purification is carried out in a sequence of unit operations which include removal of the free glycerol, excess alcohol and residual catalyst. The purification process includes several techniques, for instance, washing with distilled water and acid,

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washing through a solid adsorbent, extraction with organic solvent like ether or hexane, and water and/or physical separation using membranes [7]. When ethanol is used instead of methanol, purification constitutes an important step in obtaining a product with market specifications [8,9]. Regardless of the process employed, knowledge of the phase diagram for the multicomponent system is essential to designing an adequate, suitable and reliable process for biodiesel production. Thus, obtaining the phase diagrams of the reaction medium represents a fundamental step for the optimization of the purification process. Liquid–liquid and vapor–liquid equilibrium (LLE and VLE, respectively) involving alkyl esters, methanol, ethanol and glycerol systems have been published in the literature in recent years [10–12]. However, pure alkyl esters were used in most of these studies and they did not take into account the fact that biodiesel, in general, is a mixture of 5–10 or more alkyl-esters. Only few studies available in the literature are related to the use of complete biodiesel samples (such as those obtained from soybean oil by transesterification) [13,14].

In this context, the main objective of this work was to enhance the experimental databank by providing information on the VLE and LLE related to binary and ternary systems that could be involved in biodiesel production and purification processes. These systems include biodiesel + ethanol, biodiesel + methanol, biodiesel + ethanol + glycerol, biodiesel + methanol + glycerol, biodiesel + methanol + soybean oil and biodiesel + ethanol + soybean oil.

2. Materials and methods

2.1. Chemicals

Methanol (0.998 mass fraction purity) and ethanol (0.998 mass fraction purity) were supplied by Synth (São Paulo/SP/Brazil), and glycerol ($\geqslant$0.995 mass fraction) by Sigma–Aldrich (São Paulo, SP, Brazil). Soybean oil (Liza, Cargill Agrícola S/A, Mairinque, SP) was purchased in a local store. All chemicals were used without further treatment.

The biodiesel (fatty acid methyl esters-FAMEs) was obtained using soybean oil by alkali-catalyzed transesterification with an oil to methanol molar ratio of (1:12), 0.5% of NaOH (mass basis) for the formation of alkoxide and 500 rpm at 65 °C. The reaction time was 1 h. The methanol was removed by evaporation and the ester phase was washed twice with hot water at 50 °C and then dried. The esters were then purified using a solid adsorbent (Perlimax®) with agitation for 30 min at 65 °C. The material was then filtered to remove solids and the biodiesel (esters) was dried using anhydrous sodium sulfate.

After purification, the biodiesel by gas chromatography (GC) using the ASTM D 15342 standard method. The GC analysis showed an ester content of 96.6 wt% while contaminants were partially characterized as free glycerol (0.153 wt%), triacylglycerols (0.018 wt%), monoacylglycerols (0.402 wt%), methanol (0.500 wt%) and water (0.0012 wt%). After characterization, the methyl esters were transferred to an amber flask, flushed with N_2 and stored in the dark for no longer than 60 days until use in the phase equilibrium experiments. Table 1 presents the results from the characterization of biodiesel produced in this work.

The soybean oil used for biodiesel production was analyzed by AOCS Method Ce 1e-91 and the fatty acid composition was linoleic 53 wt%, oleic 23 wt%, palmitic 11 wt%, stearic 4 wt%, linolenic 8 wt% and other minor fatty acids 1 wt% [15,16].

2.2. LLE apparatus and procedures – binodal curves

Binodal curves were determined considering the cloud point obtained using the titration method under isothermal conditions. The experiments were performed in a liquid–liquid equilibrium jacketed-cell with temperature controlled by an ultrathermostatic bath. For the temperature monitoring inside the cell, a thermocouple with an uncertainty of around 0.5 K was used. The solution inside the cell was kept continuously mixed using a magnetic stirrer to allow complete homogenization of the system. Fig. 1 shows the experimental scheme used in this work. The binodal curves were obtained from the mass fraction (w) and presented in triangular diagrams.

The binodal or equilibrium curves for the ternary systems, at constant temperature, were determined by the titration of the two-component mixture (known concentrations) with a third component until clouding of the solution. This is also known as the turbidity point technique. Initially, known quantities of two miscible components were weighed on an analytical balance with a precision of 0.0001 g (Marte, model AM220) and added directly inside the equilibrium cell following the procedure used by Silva et al. [17], Stragevitch and D'Ávila [18] and Ardila et al. [19]. The two-component mixture is kept in a closed jacketed bottle to prevent evaporation. The device is connected to a water circulating bath to allow rigorous temperature control during the experiments. Titration is then started by adding the third component through an orifice at the top of the equilibrium cell and the solution is continuously mixed by a magnetic stirrer until the visual appearance of a turbid mixture. The added volume is then recorded and the resulting mixture composition can be computed to obtain a point on the binodal curve. This procedure is repeated by changing the solution composition until the obtainment of a complete binodal curve.

2.3. VLE apparatus and procedures

The vapor–liquid equilibrium data were measured using an Othmer-type ebulliometer as shown in Fig. 2, and presented in the previous work [20]. The proposed all-glass ebulliometer is a

Table 1
Characterization analysis of biodiesel synthesized in this work.

Analysis	Value	Unit	Method
Ester content	96.60	wt%	ABNT NBR 15342/EN 14103
Acidity index	0.45	mg KOH g^{-1}	ABNT NBR 14448/ASTM D 664/EN 14104
Glycerol total	0.153	wt%	ABNT NBR 15344/ASTM D 6584/EN 14105
Free glycerol	0.001	wt%	ABNT NBR 15341/ASTM D 6584/EN 14105, EN 14106
Monoacylglycerol	0.402	wt%	ABNT NBR 15342, ABNT NBR 15344/ASTM D 6584/EN 14105
Diacylglycerol	0.308	wt%	ABNT NBR 15342, ABNT NBR 15344/ASTM D 6584/EN 14105
Triacylglycerol	0.018	wt%	ABNT NBR 15342, ABNT NBR 15344/ASTM D 6584/EN 14105
Methanol	0.50	wt%	ABNT NBR 15343/EN 14110
Specific mass at 20 °C	0.877	kg m^{-3}	ABNT NBR 7148, ABNT NBR 14065/ASTM D 1298, ASTM D 4052/EN ISO 3675, EN ISO 12185
Water content	1198	mg kg^{-1}	ASTM D 6304/EN ISO 12937
Soap content	66.30	Sodium oleate %	AOCS Official Method Cc 17–95
Molecular weight	292.2	g $gmol^{-1}$	National Biodiesel Board