Fuel 180 (2016) 332–342

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Liquid–liquid equilibrium data for systems important in biodiesel production, involving vegetable oils + ethyl esters + monoacylglycerols and diacylglycerols + anhydrous ethanol, at 303.15 and 318.15 K

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HIGHLIGHTS

- The systems studied in this work are related to ethylic biodiesel production.
- LLE data studied involved refined oils + ethyl esters + commercial partial acylglycerols + anhydrous ethanol.
- The distribution of ethyl esters and partial acylglycerols in the LLE phases was evaluated.
- The experimental data were well modeled using NRTL model and were better modeled using UNIFAC-HIR than UNIFAC-LLE.

ARTICLE INFO

Article history:
Received 13 January 2016
Received in revised form 6 April 2016
Accepted 11 April 2016

Keywords:
Liquid–liquid equilibrium
Ethyl esters
Partial acylglycerols
Ethanol
NRTL
UNIFAC

ABSTRACT

In biodiesel production from vegetable oils, mono- and diacylglycerols are intermediate compounds of transesterification reaction of triacylglycerols with short chain alcohols, and may contaminate the final product, when the fatty ester conversion is not complete. Thus, this study aims to determine the liquid–liquid equilibrium data of systems important to biodiesel production, containing triacylglycerols (TAG) of refined oils (soybean, cottonseed and rice bran) + commercial mixture of fatty acid ethyl esters (linoleate and oleate) + diacylglycerols (DAG) + monoacylglycerols (MAG) of commercial mixture of partial acylglycerols + anhydrous ethanol at (303.15 and 318.15 K). The High Performance Size Exclusion Chromatography (HPSEC) method was used for quantification of all components: TAG, DAG, MAG, fatty acid ethyl esters and ethanol in both phases in equilibrium. The preference of fatty acid ethyl esters and DAG for the oil phase is consistent with the reported data in literature. The mass fraction of MAG was greater in the solvent phase. The average deviation between experimental and calculated compositions, using NRTL model, was less than 0.60%. Using the original version of UNIFAC model with two different set of parameters, the deviations varied within the range of (4.25–11.45)%.

1. Introduction

Biodiesel is an energy fuel source comprised of mono-alkyl esters of long-chain fatty acids, used alternatively to the fossil diesel, which can be produced from renewable biological sources, as vegetable oils and animal fats. In the case of ethyl esters, biodiesel can be considered completely bio because ethanol is commonly derived from renewable resources such as corn and sugarcane [1]. The use of ethanol from sugarcane is promising in Brazil, due to the large ethanol production and availability in this country [2].

The most important raw material sources used for biodiesel production in Brazil are: soybean seeds (83.26%), followed by bovine fat (12.34%) and cottonseeds (2.17%) [3]. Mono- (MAG) and diacylglycerols (DAG) are natural components in various fats and oils, at levels up to 10% (w/w). While soybean oil contains 1% DAG, cottonseed and rice bran oils contain up to 9.5% and 7.6%, respectively, and approximately 0.2% MAG [4].

Some research groups have published experimental results of liquid–liquid equilibrium of biodiesel production from transesterefication using vegetable oils, including soybean oil [5,6]; canola oil [7,8]; sunflower oil [3,9]; and palm oil [10]. Some non-edible and under exploited vegetable oils have also been used in biodiesel production, such as Brazil nut oil [11], macauba pulp oil, crambe oil, and fodder radish oil [12].

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http://dx.doi.org/10.1016/j.fuel.2016.04.056
0016-2361/© 2016 Published by Elsevier Ltd.

The transesterification reaction typically follows three steps, in which alkyl esters, glycerol and other compounds are obtained by a chemical reaction between oil and alcohol. The reaction system is essentially biphasic at the beginning (oil/alcohol) and the end (esters/glycerol) of biodiesel production. Thus, the unconverted triacylglycerols, diacylglycerols, monoacylglycerols, glycerol, water, and other undesirable components may remain in the final product, leading to severe engine damages and loss of power [2,13].

Although the transesterification reaction is well known, there is a lack of knowledge of the phase composition during the reaction process of ethylic biodiesel, which can be solved by the measurement and modeling of phase equilibrium, including the steps of oil extraction, deacidification, transesterification reaction, and purification of biodiesel. These measurements should be carried out to properly optimize the operating conditions for economical and efficient ethylic biodiesel purification and alcohol recuperation processes [9].

Liquid–liquid equilibrium systems involving alkyl esters, ethanol and glycerol, which correspond to the end of the transesterification reaction, have been extensively published in the literature in recent years [7,10,12,14]. However, little information is found in literature about the initial stage of ethylic biodiesel production and the behavior of partial acylglycerols and ethyl esters in this kind of system (transesterification of vegetable oils and ethanol). Furthermore, considering the mono-, diacylglycerol and ethyl ester distribution in ethanolic and oil phases, a methodology to elucidate the phase composition and to study each component individually is needed.

There are few reports in literature on LLE systems showing the first step of transesterification considering the mono-, diacylglycerol and ethyl ester distribution in ethanolic and oil phases [8,9,15]. Dagostin et al. [5] studied systems containing soybean oil, ethylic biodiesel from soybean oil, ethanol, and water to understand the liquid–liquid equilibria related to biodiesel production as quaternary systems when water is present in ethanol. To improve the liquid–liquid equilibrium (LLE) database, the LLE data of the systems containing triacylglycerols, diacylglycerols, monoacylglycerols, fatty acids, esters, ethanol and glycerol must be determined.

Chromatographic techniques are commonly used to separate the acylglycerols, and the High Performance Size Exclusion Chromatography (HPSEC) stands out. The HPSEC technique is based on molar mass separation of compounds and well-applied in crude and refined oil quality evaluation, in quantification and separation of mono-, di-, and triacylglycerols and free fatty acids [16]. Arzamendi et al. [17] and Kittirattanapiboon and Krisnangkura [18] used the HPSEC technique to monitor the biodiesel production where the partial acylglycerols (DAG, MAG, and ethyl esters) were formed during the transesterification reaction.

Thus, the main objective of this study was to determine the LLE experimental data related to the systems involved in biodiesel production from vegetable oils and the purification processes, with emphasis on partial acylglycerols and ethyl esters. In this study, LLE data were investigated for the systems composed of refined oil (soybean, cottonseed and rice bran) + commercial mixture of fatty acid ethyl esters (linoleate and oleate) + commercial mixture of partial acylglycerols + anhydrous ethanol, at different temperatures (303.15 and 318.15 K) using High Performance Size Exclusion Chromatography (HPSEC) for quantification of the components in each phase. The LLE data set was used to adjust the NRTL model parameters and evaluate two different sets of UNIFAC parameters.

2. Materials and methods

2.1. Materials

Table 1 shows the solvents and the fatty compounds used in this study, with the respective suppliers and mass fraction purity. All chemicals were used without further purification.

2.2. Experimental methods

Refined oils, commercial mixture of partial acylglycerols, and commercial mixtures of fatty acid ethyl esters were analyzed by gas chromatography, according to the official method Ce 1–62 of the American Oil Chemists' Society (AOCS) [19] to determine the fatty acid composition. Prior to the chromatographic analysis, the refined oils and the commercial mixture of partial acylglycerols were transesterified to fatty acid methyl esters, according to Hartman and Lago [20]. The chromatographic analysis was carried out using a capillary gas chromatography system according to the experimental conditions reported by Lanza et al. [21].

The probable triacylglycerol compositions of the refined oils were determined from the fatty acid composition, using the algorithm suggested by Antoniosi Filho et al. [22], and groups with a total triacylglycerol composition lower than 0.5% were ignored. The probable mono- and diacylglycerol compositions were also determined from the triacylglycerol composition, performing all possible combinations.

The mass fraction of DAG was determined for the refined oils and the commercial mixture of partial acylglycerols from the composition of a fatty compound expressed in mono-, di-, and triacylglycerols, as reported by Shiozawa et al. [15]. The HPLC method described by Shiozawa et al. [15] was used to analyze the amounts of mono-, di- and triacylglycerols in the refined oils and commercial mixture of partial acylglycerols, and the amount of ethyl esters in the commercial ethyl esters.

The free fatty acid contents of the refined oils were determined according to the official method 2201 of the International Union of Pure and Applied Chemistry [23] with Titrando 808 automatic titrator (Metrohm, Switzerland).

2.3. Experimental procedures

For each LLE experiment, the commercial mixture of partial acylglycerols, commercial mixture of ethyl ester (linoleate or oleate), anhydrous ethanol, and refined oil were weighed on an analytical balance with precision of ± 0.0001 g (Precisa, model XT220A, Sweden) in glass tubes (10 mL) (Perkin Elmer). The tubes were sealed and vortexed for 20 min (Scientific Industries, model Vortex Genie 2, USA). The tubes were left at rest for a minimum of 36 h at constant temperature in a thermostatic bath (Cole Parmer, model 12101-55, Chicago, USA) accurate to ± 0.1 K. The liquid–liquid equilibrium was reached through the formation of two clear and transparent phases with a well-defined interface.

Equilibrium data for the systems containing refined soybean and cottonseed oils were measured at 303.15 K and 318.15 K using

Table 1
Reagents and fatty compounds used, its suppliers and mass fraction purity.

Component	Supplier	Mass fraction purity[a]
Ethanol	Merck (Germany)	>0.995
Acetic acid	Merck (Germany)	>0.998
Toluene	Sigma-Aldrich (USA)	>0.999
Commercial ethyl linoleate	Sigma-Aldrich (USA)	>0.650[b]
Commercial ethyl oleate	Sigma-Aldrich (USA)	>0.775[c]
Commercial mixture of partial acylglycerols	Danisco Brasil Ltd. (Brazil)	>0.900[d]
Refined soybean oil	Cargill (Brazil)	>0.999[e]
Refined cottonseed oil	Cargill (Brazil)	>0.999[e]
Refined rice bran oil	Cargill (Brazil)	>0.999[e]

[a] As reported by the supplier.
[b] Of ethyl linoleate.
[c] Of ethyl oleate.
[d] Of monoacylglycerols.
[e] Of fatty compounds.