

Phase Equilibrium and Emulsion Stability on Ethyl Biodiesel Production

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Liquid-liquid equilibrium data was measured for ethyl soybean oil biodiesel + glycerol + ethanol ternary system at 300.15 K and compared with data obtained from literature. Thermodynamic model UNIQUAC was used to correlate experimental data at 300.15, 323.15 and 343.15 K. Results show that the model was capable to correlate experimental liquid-liquid equilibrium behavior for the system studied. Two systems were considered in order to investigate emulsion stability. The first one is composed by all the transesterification reaction products before and after glycerol enriched phase separation. It can be observed that remove glycerol enriched phase after the reaction avoid the formation of stable emulsion in the presence of water. The second system contains only purified biodiesel with 5, 10 and 20 % (v/v) of water. The emulsions stability decrease with an increase on water content.

1. Introduction

The use of biodiesel in diesel is a reality in many countries nowadays. In Brasil all diesel should contain five percent of biodiesel, mixture called B5. Although biodiesel is produced from vegetable oils or animal fats, only using ethanol in the transesterification reaction leads to a product entirely made from renewable resources. However, difficulties in the production of ethyl biodiesel are cited in the literature (Zhou *et al.*, 2003), principally those related to separation and purification processes.

Liquid-liquid equilibrium is involved during biodiesel production. The raw material of transesterification reaction, alcohol and triglycerides, are partially soluble. After reaction, the main products formed, glycerol and biodiesel have a poor mutual solubility. The system composed by biodiesel, glycerol and alcohol (in excess to guarantee high conversions) represents the major components of the system after transesterification, and because of this, it have been investigated (Negi *et al.*, 2006; Liu *et al.*, 2008; França *et al.*, 2009).

Besides phase equilibrium, it is important to investigate the stability of possible emulsions formed during the separation step provided by water washing of biodiesel.

This can cause significant loss of the product. In alkaline catalyzed transesterification small quantities of soap can be formed and act as emulsifier in a biodiesel-water emulsion increasing its stability.

The main objectives of this work are estimate UNIQUAC parameters for the ternary system composed by ethyl soybean oil biodiesel (FAEE), glycerol and ethanol at temperatures from 300.15 to 343.15 K, and verify the stability of emulsions formed by the basic catalyzed transesterification reaction products and water.

2. Experimental Section

2.1 Materials

Ethanol and glycerol used in the experiments were obtained from Vetec Química with purity of 99.5 %. Distillated water was used for emulsion measurements. The refined soybean oil was supplied by Liza. Biodiesel was prepared in the laboratory via basic catalyst transesterification of vegetable oil with ethanol at room temperature and atmospheric pressure. The glycerol enriched phase produced was removed by decantation and biodiesel enriched phase was washed several times with water. After washed the biodiesel was heated up to 379.15 K to remove any remaining water and alcohol. The final water content was 0.07 % determined by Karl Fisher analysis.

2.2 Liquid-liquid measurements

For liquid-liquid equilibrium measurements the same procedure of a previous work (França *et al.*, 2009) was used. Binodal curves were determined by the cloud point using the titration method under isothermal conditions, with density measurements. Mixtures with different concentrations of biodiesel and glycerol were prepared and stirred while homogeneous mixtures of glycerol + alcohol (glycerol-enriched phase) or biodiesel + alcohol (biodiesel-enriched phase) were titrated with a buret. The point when the mixture changed from turbid to transparent was considered to be a binodal curve point. All experiments were replicate three times.

Tie-line data were measured by mixing biodiesel, glycerol and ethanol with different global compositions. The mixtures remained under intensively agitation during 30 min. After that, they were kept at rest until two clean liquid phases were observed. The mass fraction of FAEE, glycerol, and ethanol in the samples of the two phases was determined from the density calibration equations for each component.

2.3 Emulsion preparation and characterization

The first system considered for emulsion study was composed by all products formed with a transesterification reaction conducted with 1:9 oil:alcohol molar ratio, NaOH as catalyst at room temperature and atmospheric pressure. After 1 h of reaction, while keeping stirred the reaction medium, a sample was collected and mixture with 40% (v/v) of water. The rest of the products were put on a separator funnel for 24 h. The glycerol enriched phase can be removed and the biodiesel enriched phase was mixture with 40% (v/v) of water.

In order to evaluate effect of water on biodiesel-water emulsion three samples were prepared with water concentrations of 5, 10 and 20% (v/v). In this case, the biodiesel used was produced and refined (as described on materials section).

All emulsions were homogenized using an Ultra Turrax T25 homogenizer during 4 min, at the speed of 13500 rpm. The stability emulsions were monitored using the optical scanning instrument Turbiscan Lab Expert. This instrument measured the transmission and back scattering intensity of light from an emulsion as a function time and height.

3. Results and Discussions

3.1 Liquid-liquid equilibrium behavior and correlation

The results obtained for binodal curve to the system FAEE + glycerol + ethanol at 300.15 K are represented in Figure 1a. It can be observed that the solubility of biodiesel in glycerol enriched phase is poor. This behavior indicates small losses of biodiesel in glycerol enriched phase through separation step of decantation. Tie-line measurements shown in Figure 1b indicate that, for high alcohol concentrations, experimental data have lower deviation compared with results provided by Liu *et al.* (2008).

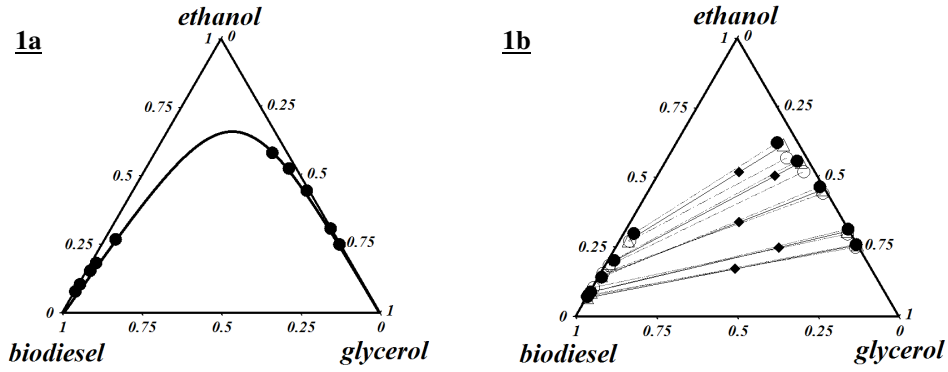


Figure 1. Phase diagram of soybean oil biodiesel + glycerol + ethanol at 300.15 K. a – Binodal curve; b – (♦) global composition, (●) experimental tie-lines, (○) Liu *et al.*, (2008), (△) UNIQUAC.

The UNIQUAC model was used to correlate experimental data. Besides the results represented in Figure 1, liquid-liquid equilibrium data for same ternary system at 323.15 and 343.15 K (Liu *et al.*, 2008) were also considered on parameters estimation. It was used an algorithm proposed by Prauznits *et al.* (1980) and adapted to Simplex method, through the objective function described by Equation 1.

$$F = \sum_k^D \sum_j^M \sum_i^{N-1} \left\{ (x_{ijk}^{I,exp} - x_{ijk}^{I,calc})^2 + (x_{ijk}^{II,exp} - x_{ijk}^{II,calc})^2 \right\} \quad (1)$$

where D is the number of data sets; N and M are the number of components and tie lines in each data set; w is the mole fraction; superscripts I and II refer to the two liquid phases in equilibrium; and superscripts exp and $calc$ refer to the experimental and calculated values of the liquid phase concentrations.

Table 1 presents molecular volume, r , surface area, q , calculated from UNIFAC LLE (Magnussen *et al.*, 1981) and binary interaction parameters, A_{ij} , estimated with experimental data of FAEE, glycerol, and ethanol at 300, 323 and 343 K. The average absolute deviations ($AAD = (1/N) \cdot \sum_i |x_i^{exp} - x_i^{calc}|$) were calculated and are also shown in Table 1.

Table 1: Parameters estimated and deviations of thermodynamic model.

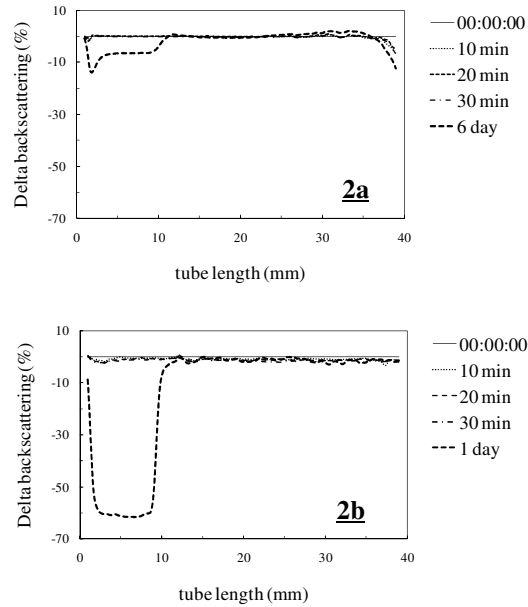
compound	structural param.		pair	interaction param.		AAD		
	r	q	i-j	A _{ij} [K]	A _{ji} [K]	biodiesel phase	glycerol phase	
biodiesel	(1)	13.767	11.312	1-2	6051.859	6505.122	0.085	0.002
glycerol	(2)	4.796	4.908	1-3	5184.652	9710.674	0.004	0.017
ethanol	(3)	2.105	1.972	2-3	-107.014	4781.085	0.083	0.019

A comparison between the experimental and calculated composition of each component of two phases at equilibrium was made with the parameters estimated and showed satisfactory correlation. The global AAD for UNIQUAC model was 3.5 %.

3.2 Emulsion stability

During biodiesel production via alkaline catalyst the soap formation may occur through triglyceride hydrolyses (Rinaldi *et al.*, 2007). To avoid this unexpected byproduct it is recommended a medium reaction free from water, which is very difficult. When the ethanol is used, the reaction products may not form two liquid phases, turning the first separation process by decantation impossible and requiring water washing. When water is introduced the formation of soap may begin, leading to a stable emulsion formation. This behavior is completely different when two phases occurs and glycerol enriched phase is removed by decantation before the first washing step. Results of reference backscattering profile obtained for this two system can be observed in Figure 2a and 2b. Emulsion stability as a function of time, determined by light scattering technique show that all transesterification products formed a stable emulsion with water (Figure 2a). Only a slight clarification on the bottom of the sample occurs even after six days. For biodiesel enriched phase only the emulsion with water shows some clarification on the bottom after one day. This behavior may be explained by the fact that most of the catalyst remaining in the glycerol enriched phase after reaction (Zhou and Boocock, 2006), and increase the possibility of soap formation when all products are mixing with water. If the soap acts as an emulsifier, the emulsion tends to be more stable.

Figure 2. Reference back scattering as function of time and tube length for emulsions consisted by transesterification products and 40% (v/v) of water. a – All products; b – Biodiesel enriched phase.



The stability study showed that water-in-biodiesel (w/b) emulsions were destabilized by coalescence and sedimentation processes, as it can be observed in the reference backscattering percentage (%BS) profiles on Figure 3(a-c). For system with 5 % of water content (Figure 3a) droplets coalescence are poor, and the behavior of %BS suggests an increasing in particle size and sedimentation.

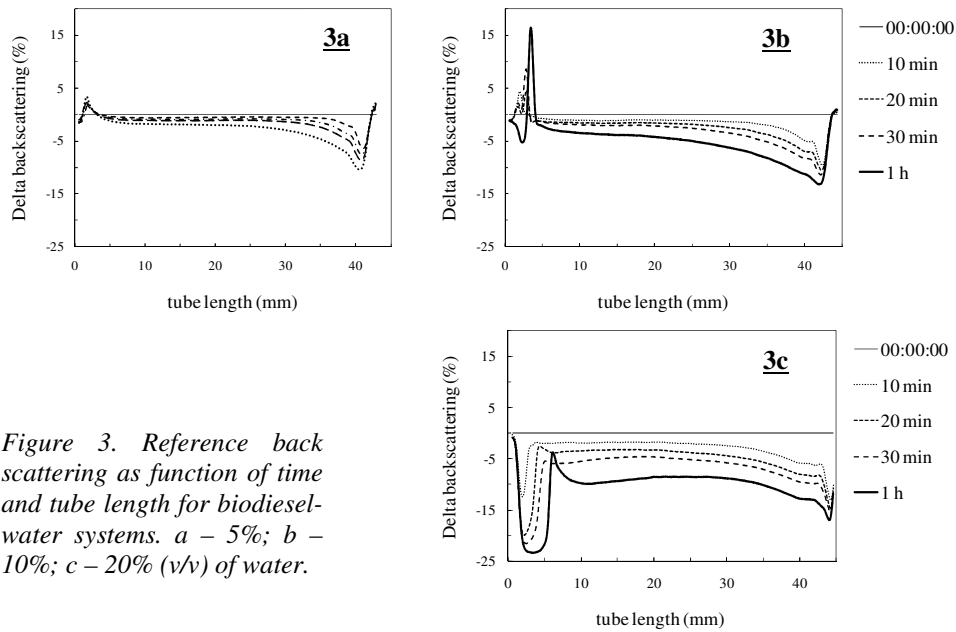


Figure 3. Reference back scattering as function of time and tube length for biodiesel-water systems. a – 5%; b – 10%; c – 20% (v/v) of water.

A similar behavior is observed for emulsion with 10% of water content. However, with bigger droplets and more accentuated sedimentation. It was also observed a beginning of clarification after 1 h at the bottom (0-5 mm of the tube length).

A different behavior can be observed for emulsion with 20% of water compared to those with 5 and 10%. First, the %BS at the medium and top of the sample indicates greater increase on droplets size. These results award a smaller stability than the other systems. Besides, at the bottom of the sample %BS decrease indicating a clarification caused by droplet coalescence.

4. Conclusions

The biodiesel solubility on glycerol enriched phase increases with alcohol content. So, when high alcohol:oil molar ratio is used in transesterification it is possible that two liquid phases after reaction are not formed and the separation step become complicated. When water is used as solvent for liquid-liquid extraction technique stabilized emulsions can be formed and leading to product losses. The emulsions stability tends to decrease with increase on water content.

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