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Liquid–liquid equilibrium in the systems FAMEs + vegetable oil + methyl alcohol and FAMEs + glycerol + methyl alcohol

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ABSTRACT

In the present work the liquid–liquid equilibrium (LLE) data were obtained for systems relevant for biodiesel production process. The ternary systems of FAMEs + vegetable oil + methyl alcohol and FAMEs + glycerol + methyl alcohol were investigated at the three temperatures of 293, 313 and 333 K and atmospheric pressure. The experimental LLE data have been correlated using NRTL model and binary interaction parameters of systems components have been calculated. Using F-test the reliability of the experimental data and the adequacy of NRTL activity coefficient models with obtained binary interaction parameters have been confirmed.

1. Introduction

Nowadays, biodiesel (fatty acid methyl esters, FAMEs) is considered as one of the most promising alternatives for the petrodiesel fuel due to its renewability and environmental friendliness [1–4]. Moreover, FAMEs can be an attractive raw material for obtaining a wide range of demanded products such as surfactants [5], plasticizers [6], PVC stabilizers [7], lubricants [8] and etc.

Biodiesel is produced via the transesterification reaction of fats and oils (usually soybean, rapeseed, palm, algae and wastecooking oils) with an excess of methyl alcohol in the presence of alkali metal hydroxides or alkoxides as catalysts [9–12].

The mutual solubility of vegetable oil and methyl alcohol is negligible at the temperatures 60–65 °C corresponding to the conventional transesterification process. Thus, the transesterification rate is in great dependence of process hydrodynamic regime.

On the other hand, FAMEs and glycerol, obtained in the transesterification reaction, are poorly miscible also, resulting in the formation of two immiscible liquid phases during the separation of these products. The bottom (dense) phase is rich in glycerol and the head phase (with lower density) contains the FAMEs. The unreacted methyl alcohol is distributed between two phases. In this way, the phase equilibrium knowledge for systems of raw materials and products is necessary for the transesterification process optimization and design of the equipment.

In the literature, the phase equilibrium data of ternary systems with glycerol, methyl alcohol and fatty acids esters [13–15] or real biodiesel [16–22] are presented in sufficient detail. Bell et al. [15] studied the liquid–liquid equilibrium for systems of methyl ester + glycerin + water at 333.15 K. Rostami et al. [23,24] measured equilibrium in ternary systems of glycerol + methyl alcohol + biodiesels obtained from either canola, sunflower, palm and soybean oils within a temperature range of 297.2–333.2 K. At the same time, there is practically no information for the systems contained vegetable oil [25,26].

This work is focused on the studying of the liquid–liquid equilibrium (LLE) of the ternary systems containing FAMEs + vegetable oil + methyl alcohol and FAMEs + glycerol + methyl alcohol. Binodal curves and tie-lines were determined at 293, 313 and 333 K. The results were correlated with the NRTL activity coefficient model and the adequacy of the models with obtained binary interaction parameters has been confirmed.

2. Materials and methods

2.1. Materials

The rapeseed oil (State standard of the Russian Federation GOST 31759-2012) and the soybean oil (State standard of the Russian Federation GOST 31760-2012) were used without further purification (free fatty acids content is less than 0.2 wt%, water content is less than 500 mg/kg). The fatty acids composition of using oils (Table 1) was determined in accordance with GOST 30418-96.

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Table 1
The fatty acid composition of the vegetable oil.

Fatty acid	Content (wt%)	
	Rapeseed oil	Soybean oil
Capric acid (10:0)	0.6	–
Lauric acid (12:0)	–	0.1
Myristic acid (14:0)	0.1	0.3
Palmitic acid (16:0)	5.1	10.9
Stearic acid (18:0)	2.1	3.2
Arachidic acid (20:0)	0.2	0.1
Behenic acid (22:0)	0.2	–
Palmitoleic acid (16:1)	–	0.3
Oleic acid (18:1)	57.9	24.0
Gadoleic acid (20:1)	1.0	–
Erucic acid (22:1)	0.2	–
Linoleic acid (18:2)	24.7	54.5
Linolenic acid (18:3)	7.9	6.6

Methyl alcohol (a purity ≥ 99.5 wt%), glycerol (a purity ≥ 99.7 wt % and a water content of 0.02 wt%) were obtained from Chemreagents (Nizhny Novgorod, Russia) and were used without any treatment. Glycerol tristearate (a purity ≥ 99.0 wt%) were purchased from Sigma-Aldrich.

Stabilized tetrahydrofuran (EKOS-1, Moscow, Russia) was distilled with sodium hydroxide to remove peroxide compounds before using.

Rapeseed and soybean FAMEs were obtained according to the methodology proposed at [27]. The rapeseed oil and soybean oil were converted into methyl esters by transesterification with methyl alcohol by using calcium glyceroxide as catalyst. The catalyst amount was of 1 wt% (based on oil weight), with a methanol-to-oil molar ratio of 9:1. The reaction was carried out at 333 K for 160 min. After that the reaction mass was separate and the FAMEs rich head phase was neutralized with phosphoric acid, filtered and washed with excess of distilled water. Finally, the biodiesel was distilled at pressure of 4 mmHg. The obtained FAMEs were tested according to ASTM D 6751 and EN 14213 (Table 2). The FAMEs fatty acids composition was determined with using gas chromatographic technique and was corresponded to the raw rapeseed oil (Table 1).

2.2. Apparatus and procedure

2.2.1. Binodal curves

The binodal curves for the ternary systems were determined by the cloud-point method using the titration procedure under isothermal conditions as described by Silva et al. [28]. The experiments were carried out in the glass cell equipped with a water jacket and two sampling ports, as described elsewhere [28,29]. The cell temperature was regulated by a thermostatic bath with an uncertainty of ± 0.1 K. For the mixing of components LLE apparatus equipped with a magnetic stirrer.

A two-component mixture with known concentrations was weight on an analytical balance with a precision of 0.0001 g, placed into the LLE cell and thermostated to the set temperature under continuously stirring (900 rpm). The third component was titrated inside the cell using a 5 mL syringe until the cloud point was obtained visually (turbid solution). The quantity of added third component was recorded and the resulting mixture composition was calculated to obtain a point on the binodal curve. This procedure was repeated by changing the mixture composition. Each experimental point was replicated at least twice and the complete binodal curve was obtained using averaged points.

Table 3
Binodal curves data of the ternary systems composed of rapeseed FAMEs (1), methyl alcohol (2) and glycerol (3).[a]

Weight percent, wt%								
T = 293 K			T = 313 K			T = 333 K		
1	2	3	1	2	3	1	2	3
0.40	30.05	69.55	89.17	10.17	0.66	0.51	29.87	69.62
0.49	39.76	59.75	77.51	20.98	1.51	0.60	39.82	59.58
0.68	49.59	49.73	68.16	29.71	2.13	1.39	49.23	49.38
1.38	59.03	39.60	57.80	39.12	3.08	3.17	58.09	38.74
3.19	68.29	28.52	47.94	47.94	4.12	6.40	65.39	28.21
6.06	75.17	18.77	36.44	57.96	5.60	16.38	66.95	16.67
8.61	77.43	13.96	27.79	65.11	7.11	16.60	66.40	17.00
18.84	75.75	5.40	9.43	72.41	18.17	26.18	62.09	11.73
29.37	67.82	2.80	4.38	66.90	28.72	36.10	54.65	9.25
37.82	60.18	1.99	2.22	58.68	39.10	46.65	46.64	6.71
49.49	49.10	1.42	0.96	49.67	49.37	57.46	37.61	4.94
59.27	39.57	1.17	0.67	39.57	59.77	78.45	19.64	1.91
69.41	29.96	0.63	0.44	29.96	69.61	89.11	9.94	0.94
77.81	21.34	0.85	0.48	19.86	79.66	66.62	28.70	4.69
88.52	10.74	0.74	17.82	71.37	10.80			

[a] Experimental standard error 1.8%.

2.2.2. Tie lines determination

The tie-lines of LLE were obtained using the same equipment described in the previous section.

The ternary mixtures corresponding to the immiscibility region delimited by the obtained binodal curves were prepared directly inside the LLE cell by weighing known quantities of each component on an analytical balance with a precision of 0.0001 g. The mixtures were thermostated to the set temperature under vigorously stirring (900 rpm) for 3 h and left to settle for at least 10 h at the specified temperature. After this rest period, a two transparent phases were observed (FAMEs/oil-enriched phase and glycerol-enriched phase) with clearly interface. Samples of each phase were collected for analysis.

The compositions of the phase samples were determined using GPC on a Chromos LC-310 liquid chromatograph equipped with a HPLC pump, column system for GPC, column thermostat, refractive index detector and hardware and software module. For the analysis, a system with two serially connected Phenomenex Phenogel 00H-0441-K0 (300 × 7.8 mm) columns filled with styrene divinylbenzene copolymer

Table 2
The properties of the rapeseed FAMEs.

Properties	Test method	Measured value	Limits according to EN 14213	Limits according to ASTM D 6751	Units
Viscosity at 40 °C	ASTM D 445	3.67	3.5–5.0	1.9 ÷ 6.0	mm^2/s
Acid value	EN 1414	0.1	0.5	0.5	mg KOH/g
Calcium & Magnesium, combined	EN 14538	4.8	–	5.0	ppm (μg/g)
Free Glycerin	ASTM D 6584	0.01	0.02	0.02	mol%
Methanol content	EN 14110	0.005	0.2	0.2	mol%
Water content	EN ISO 12937	170	500	0.05*	mg/kg
Ester content	EN 14103	99.8	96.5 min	–	mol%
Pour point	ISO 3016	−2	0	–	°C
Density at 15 °C	EN ISO 3675, EN ISO 12185	876	860 ÷ 900	–	kg/m^3

* vol%.