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Solubility Measurement for the Reaction Systems in Pre-Esterification of High Acid Value *Jatropha curcas* L. Oil[†]

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Crude *Jatropha curcas* L. oil (Oil) normally contains some free fatty acids (FFAs), and it must be pre-esterified with methanol before it is used as the feedstock of the transesterification operation in biodiesel production. The mutual solubility of the pre-esterification reaction mixture was measured over the reaction temperature range from (303.1 to 333.1) K. The phase diagrams included the ternary diagrams of FFA + oil + methanol, FFA + methanol + water, *Jatropha curcas* L. oil methyl ester (FAME) + methanol + water, and FAME + methanol + oil. The data show that the mutual solubility increases with temperature. High FFA content can increase the mutual solubility of methanol and oil. The products, namely, water and FAME, change the distribution of oil and methanol.

Introduction

As a feed stock of biodiesel, *Jatropha curcas* L. oil has received much attention.[1−3] Many countries are planning to plant such oil trees to provide the raw material for their biodiesel production. In the production of biodiesel, the most common method is the alkali-catalyzed transesterification process, which refers to a reaction between methanol and vegetable oils or animal fats. To provide the basic data in the transesterification, we measured the mutual solubility of methanol + oil + *Jatropha curcas* L. oil methyl ester (FAME), methanol + glycerol + oil, and methanol + glycerol + FAME in our previous work.[3] The data included important systems in the transesterification process.

However, the crude *Jatropha curcas* L. oil often contains some amount of free fatty acid (FFA) which varies from 2 % to 7.5 %. The content of FFA depends on the planting area of *Jatropha curcas* L. trees and the storage of the oil. The crude oil can not be directly used as the feedstock of the transesterification reaction because the FFAs could react with alkali catalyst to produce soaps that make the separation difficult in a latter washing process with water. One method to reduce FFA content is pre-esterification, which is the esterification between methanol and FFAs in the presence of an acid catalyst. Sulfuric acid is usually the most effective catalyst, although many new solid acid catalysts have been reported for the process.[4−6]

In the pre-esterification, the system consists of FFAs, methanol, triglycerides, and acid catalyst. The physicochemical properties and mutual solubility of those components are very important to the whole production of biodiesel. In the pre-esterification reaction, methanol and FFAs are miscible, but methanol and triglycerides are partially miscible. In addition, the formation of water and FAME may also change the distribution of reaction components in different phases. It not only affects the reaction rate but also affects the final separation of water and methanol in the products.

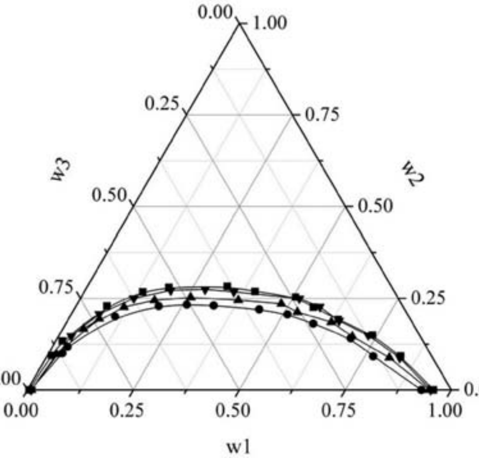

Figure 1. Phase diagram of oil (1) + oleic acid (2) + methanol (3): ■, 303.1 K; ▼, 313.1 K; ▲, 323.1 K; ●, 333.1 K.

In this work, the solubility of multicomponent systems, including FFAs, methanol, water, FAME, and *Jatropha curcas* L. oil, in the pre-esterification process was measured. The acid catalyst was not concerned because of its low content in the mixture. The phase diagram was divided into four main ternary−component systems according to the process of pre-esterification. The phase diagrams of the FAME + oil + methanol system have been described in our earlier work,[3] and here the other three phase diagrams of the systems (oil + oleic acid + methanol, FAME + methanol + water, oleic acid + methanol + water) were measured.

Experimental Section

Materials. The *Jatropha curcas* L. oil was obtained by pressing the seeds of the *Jatropha curcas* L. tree collected from the Panzhihua area, Sichuan Province, Southwest of China. Oil was purified, and FAME was obtained as described in the literature.[3] The composition of fatty acid in the oil is listed in Table 1. Oleic acid which has a purity ≥ 97 % was chosen as FFA added in crude *Jatropha curcas* L. oil. The purity of methanol is ≥ 99.5 %. In addition, distilled water was used to obtain mixtures with different water content. To prevent the influence of impurities, such as gums and dust, on the measure-

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Table 1. Fatty Acid Composition of *Jatropha curcas* L. Oil

fatty acid	C 14:0[a]	C 16:0	C 16:1	C 18:0	C 18:1	C 18:2	C 20:0	C 26:0
mass fraction (%)	0.13	18.97	1.18	5.60	35.28	38.36	0.13	0.37

[a] In C, *x*:*y*, x = number of carbons and y = number of double bonds.

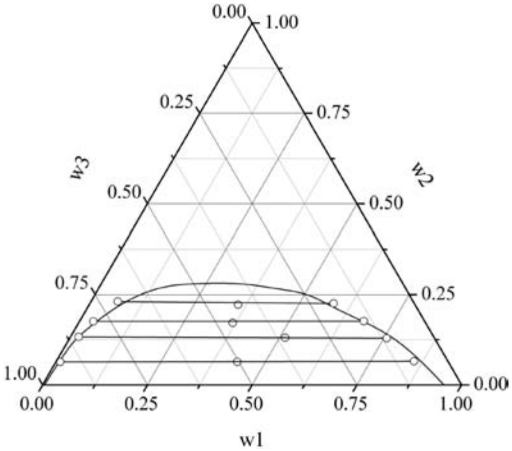

Figure 2. Tie line of the system oil (1) + oleic acid (2) + methanol (3) at 303.1 K.

Table 2. Comparison of Solubility of Benzene (1) in Ethanol (2) + Water (3)

		measured data			literature[7]		
T/K	NO	w_1	w_2	w_3	w_1	w_2	w_3
298.1	1	0.1157	0.5099	0.3744	0.1261	0.5039	0.3700
298.1	2	0.2744	0.5012	0.2244	0.2746	0.5011	0.2243
298.1	3	0.5938	0.3253	0.0809	0.5941	0.3251	0.0808

ment of mutual solubility, we used refined *Jatropha curcas* L. oil mixing with oleic acid to simulate high FFA content crude *Jatropha curcas* L. oil.

Apparatus and Procedures. (a) Phase Diagram of Oil + Oleic acid + Methanol. The phase boundary was determined by turbidimetric analysis using the titration method under isothermal conditions. A long neck flask was immersed in a water bath with a magnetic stirrer. The temperature was controlled with a thermostatic bath in which the fluctuation of temperature was within ± 0.1 K.

Methanol was added with a buret to the mixture of oil and oleic acid while stirring with a magnetic stirrer. The point when the mixture transferred from transparent to turbid was considered to be the saturation point of methanol in oleic acid + oil. Methanol was added dropwise into the mixture with different initial mass fractions of oil and oleic acid. The mass was obtained by determining the mass changes of the long neck flask with an analytical balance (precision was 0.0001 g).

(b) Tie Lines of the Oil + Oleic Acid + Methanol System. A mixture of oil + oleic acid + methanol with known composition (in mass) from the heterogeneous zone of the diagram at a given temperature was prepared. The mixture was stirred vigorously with a magnetic stirrer for at least 2 h and then settled at the same temperature for 4 h. Finally, the mixture separated into two phases with a clear interface.

The quantity of FFAs in each phase was determined by means of titration analysis according to the National Standard of PRC GB/T-5530-1995. To measure the amount of methanol, the solution was heated in a drier at 343.1 K to completely evaporate methanol, and the methanol content in the solution was calculated with the mass loss during the drying process. The oil content in the solution was further obtained by mass balance. The tie lines were obtained by connecting the composition points of two phases in the phase diagram.

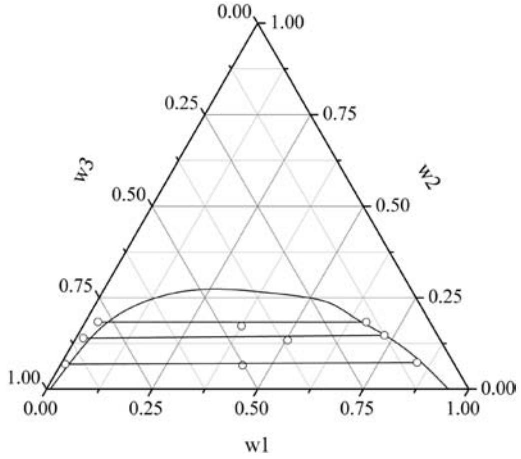

Figure 3. Tie line of the system oil (1) + oleic acid (2) + methanol (3) at 313.1 K.

(c) Phase Diagrams of the FAME + Methanol + Water and Oleic Acid + Methanol + Water Systems. Measurement procedures were the same as those for the phase diagram of oil + oleic acid + methanol.

Uncertainties. To determine the uncertainty of the experiments and the error of personal operation, we measured the solubility of benzene in ethanol + water by turbidimetric analysis described above. The data were compared with those published in the literature,[7] as shown in Table 2 (w_1, w_2, and w_3 are the mass fraction of benzene (1), ethanol (2), and water (3) in the system, respectively).

Measurements were performed in triplicate. After calculation, the maximal relative standard deviations were 0.22 % for benzene, 0.08 % for ethanol, and 0.08 % for water. Compared to the literature,[7] the maximal relative errors were −8.25 % for benzene, 1.19 % for ethanol, and 1.18 % for water. It showed that the experimental procedure used was acceptable.

Results and Discussion

Phase Diagram of the Oil + Oleic Acid + Methanol System. From Figure 1, oil + oleic acid and methanol + oleic acid are two completely miscible systems between (303.1 and 333.1) K. However, oil + methanol is partially miscible. The solubility of methanol in oil is slightly greater than that of oil in methanol.

As shown in Figure 1, both methanol and oil can be dissolved in the FFA, and the mixture is completely miscible and can form a homogeneous phase in the range of high FFA content. The solubility in the ternary mixture is enhanced with an increase of temperature from (303.1 to 333.1) K. The homogeneous region is enlarged at higher temperature, which may promote the pre-esterification reaction.

Tie Lines of the Oil + Oleic Acid + Methanol System. For the ternary mixture in a heterogeneous area, two liquid phases exist. Figures 2 to 5 illustrate the composition analysis data in both the oil-rich phase and methanol-rich phase with different initial mixture compositions. The oleic acid content can be calculated from the solubility phase diagram. Table 3 shows the tie line data for the system. By comparing the analysis data

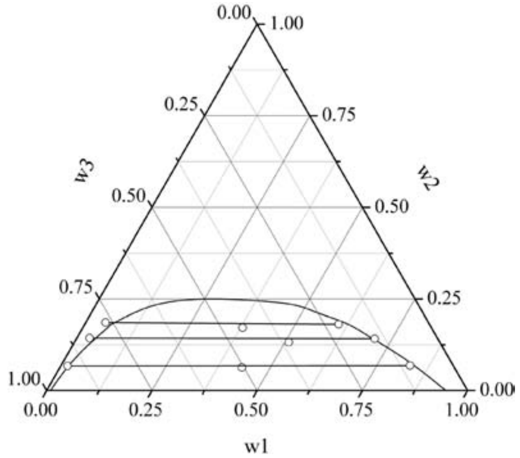

Figure 4. Tie line of the system oil (1) + oleic acid (2) + methanol (3) at 323.1 K.

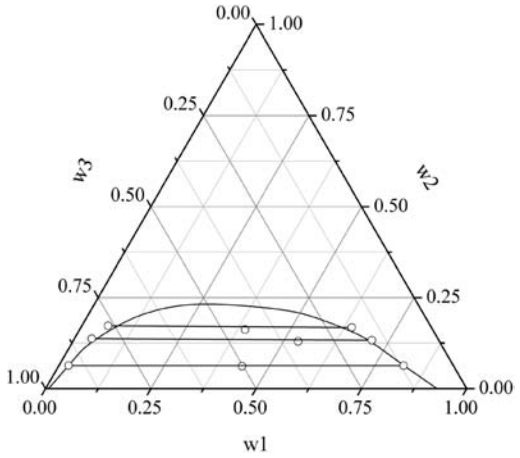

Figure 5. Tie line of the system oil (1) + oleic acid (2) + methanol (3) at 333.1 K.

with the solubility data obtained by the turbidimetric technique, as shown in Figure 2 to Figure 5, the crunodes of tie lines are in good agreement with the solubility curves. It also indicates that the turbidimetric technique is reliable. In addition, from Table 3, the distribution coefficient of oleic acid between the oil-rich phase and the methanol-rich phase is about 1.

Figure 6 shows the comparison between our result and the literature.[8] It can be found that the solubility in the system of *Jatropha curcas* L. oil + oleic acid + methanol is similar to the system of canola oil + oleic acid + methanol. It seems that the type of vegetable oil here has little effect on the solubility.

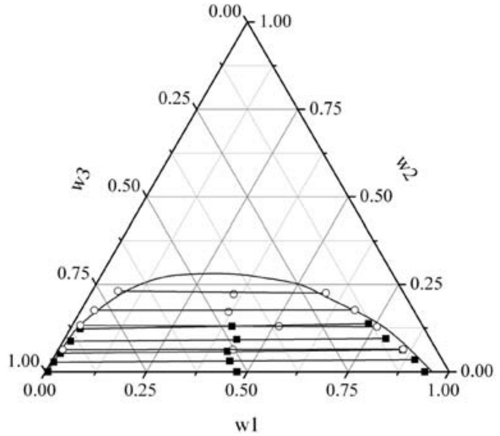

Figure 6. Tie line of oil (1) + oleic acid (2) + methanol (3) at 303.1 K. ○, *Jatropha curcas* L. oil; ■, carnola oil.[8]

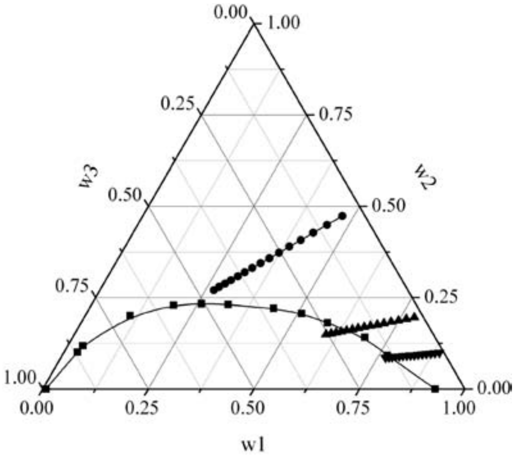

Figure 7. ■, Phase diagram of oil (1) + oleic acid (2) + methanol (3) at 333.1 K;▼, the mole ratio of methanol to oleic acid is from 1 to 15, and the mass fraction of oleic acid in raw material oil is 10 %; ▲, the mole ratio of methanol to oleic acid is from 1 to 15, and the mass fraction of oleic acid in raw material oil is 20 %; ●, the mole ratio of methanol to oleic acid is from 1 to 15 and the mass fraction of oleic acid in raw material oil is 50 %.

Table 3. Tie Line Data for Oil (1) + Oleic Acid (2) + Methanol (3) at Different Temperatures

global composition			oil-rich phase			methanol-rich phase			distribution coefficient of oleic acid
$100\, w_1$	$100\, w_2$	$100\, w_3$	$100\, w_1^{I}$	$100\, w_2^{I}$	$100\, w_3^{I}$	$100\, w_1^{II}$	$100\, w_2^{II}$	$100\, w_3^{II}$	(w_2^{I}/w_2^{II})
					$T = 303.1$ K				
35.57	22.23	42.20	58.23	22.54	19.23	6.40	23.12	70.48	0.98
36.82	17.15	46.03	67.86	17.66	14.48	3.30	17.60	79.10	1.00
51.40	13.03	35.57	75.73	12.88	11.39	2.02	13.24	84.74	0.97
43.30	6.32	50.39	85.40	6.53	8.07	1.07	6.32	92.61	1.03
					$T = 313.1$ K				
37.55	17.31	45.14	66.56	18.34	15.10	2.98	18.45	78.58	0.99
50.45	13.37	36.18	72.70	14.72	12.58	1.74	14.00	84.26	1.05
43.20	6.51	50.29	84.17	7.30	8.53	1.08	6.80	92.12	1.07
					$T = 323.1$ K				
37.97	17.15	44.87	60.30	18.13	21.57	4.71	18.62	76.68	0.97
50.93	13.20	35.87	70.85	14.18	14.97	3.02	14.32	82.66	0.99
43.28	6.26	50.46	82.96	6.79	10.25	1.63	6.68	91.69	1.02
					$T = 333.1$ K				
39.30	16.19	44.51	64.35	16.77	18.88	6.24	17.25	76.51	0.97
53.51	12.95	33.54	70.87	13.26	15.87	4.15	13.69	82.16	0.97
43.59	6.14	50.27	81.88	6.33	11.79	2.32	6.35	91.33	1.00

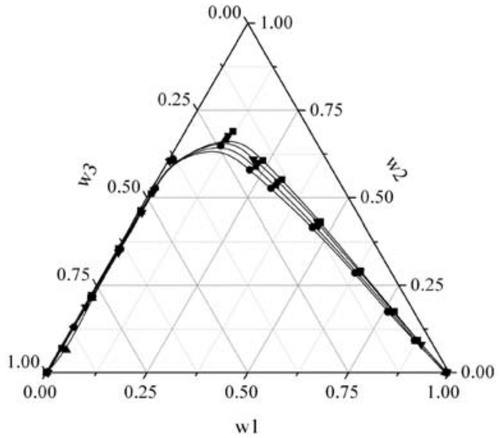

Figure 8. Phase diagram of oleic acid (1) + methanol (2) + water (3): ■, 303.1 K; ▼, 313.1 K; ▲, 323.1 K; ●, 333.1 K.

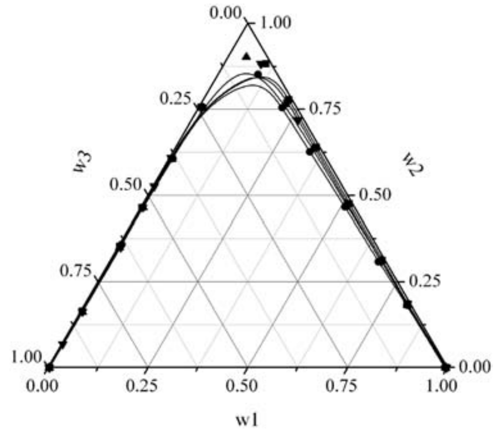

Figure 9. Phase diagram of FAME (1) + methanol (2) + water (3): ■, 303.1 K; ▼, 313.1 K; ▲, 323.1 K; ●, 333.1 K.

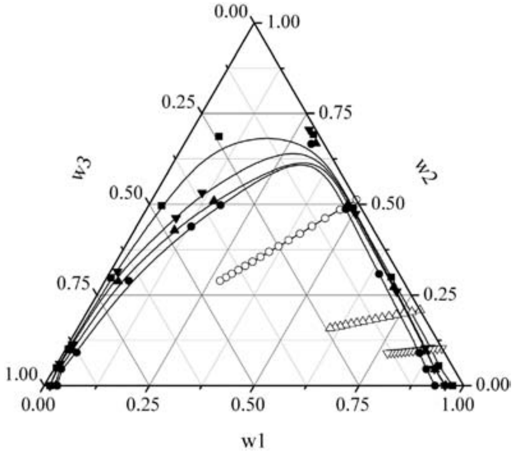

Figure 10. Phase diagram of oil (1) + FAME (2) + methanol (3):[3] ■, 303.1 K; ▼, 313.1 K; ▲, 323.1 K; ●, 333.1 K. ▽, the mole ratio between methanol and oleic acid is from 1 to 15, and the mass fraction of oleic acid in raw material oil is 10 %; △, the mole ratio between methanol and oleic acid is from 1 to 15, and the mass fraction of oleic acid in raw material oil is 20 %; ○, the mole ratio between methanol and oleic acid is from 1 to 15 and the mass fraction of oleic acid in raw material oil is 50 %.

Phase Diagram Analysis for the Pre-Esterification System with Different Contents of FFA and Methanol. In pre-esterification, the content of FFA varies with different raw material oils and accordingly the use of methanol varies with acid value. Figure 7 shows the components in pre-esterification with different content of FFA in oil and different methanol usage. It is clearly shown that the mutual solubility in the oil + oleic acid + methanol system is gradually improved at higher levels of oleic acid. If the content of oleic acid in crude oil reaches about 50 %, only a single phase exists in the reaction system at 333.1 K even though the molar ratio of methanol and oleic acid reaches 15.

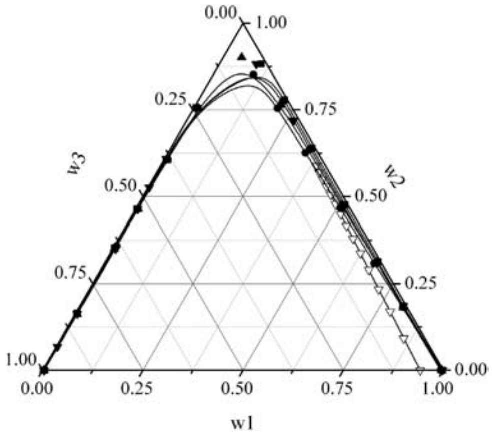

Figure 11. Phase diagram of FAME (1) + methanol (2) + water (3): ■, 303.1 K; ▼, 313.1 K; ▲, 323.1 K; ●, 333.1 K. ▽, the mole ratio of methanol to oleic acid is from 1 to 15.

Phase Diagrams of Oleic Acid + Methanol + Water and FAME + Methanol + Water. During the pre-esterification process, water and the unreacted oleic acid coexist in the reaction mixture. Figures 8 and 9 show the changes of solubility in the two systems between (303.1 and 333.1) K, respectively. In Figure 8, the homogeneous region of the oleic acid + methanol + water system is much smaller than that of the oil + oleic acid + methanol system (Figure 1). Especially when the mass fraction of water exceeds about 25 %, oleic acid is almost insoluble in the mixture of water + methanol. The intersolubility increases with temperature. In Figure 9, the homogeneous region is the smallest compared to the two systems mentioned before. It means that water and FAME are completely nonmiscible. The homogeneous range only appeared when the methanol mass fraction was > 87 %. From Figure 1, Figure 8, and Figure 9, it is concluded that the solubility in the process of pre-esterification becomes lower and lower with the formation of water and FAME. In the molecule of oleic acid, the long chain of alkyl R is a hydrophobic group, and $-COOH$ is a hydrophilic group. However, in the molecule of FAME, R and $-CH_3$ are both hydrophobic. According to the rule of similarity, oleic acid is more soluble than FAME in the mixture of water and methanol, which are both hydrophilic.

At the end of pre-esterification, oleic acid was completely converted to FAME, and the components in the final system included FAME, water, methanol, and oil. As shown in Figure 10 and Figure 11, the composition of the esterified mixture was illustrated with two ternary phase diagrams. From Figure 10, the mixture of oil + methanol + FAME changes from the homogeneous part to the heterogeneous part in the diagram with the increase of methanol usage. However, in the system of FAME + methanol + water (see Figure 11), the mixture changes from the heterogeneous region to the homogeneous region with the increase of methanol usage. In the actual reaction, the mixture was divided into two phases, a hydrophilic phase which contained most of methanol, water, and sulfuric acid and a hydrophobic phase which contained most of oil and FAME.

Conclusion

The *Jatropha curcas* L. oil often contains some FFAs, and it is required to be preprocessed by esterification before transesterification to obtain biodiesel. The mutual solubility of the pre-esterification system is important for the control of operation. The results showed that at the beginning the system contains methanol, oleic acid, and oil, and the mixture was divided into the methanol-rich phase and the oil-rich phase. FFAs are almost equally distributed in the two phases. The mutual solubility increased with temperature and also with the FFA amount. When the FFA mass fraction reached 50 % in crude oil, the mixture became completely miscible.

At the end stage of pre-esterification, the FFAs were converted into FAME. The reaction system contained oil, methanol, FAME, and water. Then the reaction mixture was divided into two different phases, a hydrophilic phase and a hydrophobic phase. Water and methanol were mainly distributed in the hydrophilic phase, and the FAME and oil were mainly distributed in the hydrophobic phase.

Supporting Information Available:

The data in Figure 1, Figure 8, and Figure 9 are shown. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Foidl, N.; Foidl, G.; Sanchez, M.; Mittelbach, M.; Hackel, S. *Jatropha curcas* L. as a source for the production of biofuel in Nicaragua. *Bioresour. Technol.* **1996**, *58*, 77–82.

(2) Berchmans, H. J.; Hirata, S. Biodiesel production from crude *Jatropha curcas* L. seed oil with a high content of free fatty acids. *Bioresour. Technol.* **2008**, *99*, 1716–1721.

(3) Zhou, H.; Lu, H.; Liang, B. Solubility of Multicomponent Systems in the Biodiesel Production by Transesterification of *Jatropha curcas* L. Oil with Methanol. *J. Chem. Eng. Data* **2006**, *51*, 1130–1135.

(4) Lotero, E.; Liu, Y.; Lopez, D. E.; Suwannakarn, K.; Bruce, D. A.; Goodwin, J. G. Synthesis of biodiesel via acid catalysis. *Ind. Eng. Chem. Res.* **2005**, *44*, 5353–5363.

(5) Serio, M. D.; Tesser, R.; Lu, P.; Santacesaria, E. Heterogeneous catalysts for biodiesel production. *Energy Fuels* **2008**, *22*, 207–217.

(6) Yang, Y.; Lu, H. F.; Liang, B. Influence of the calcination conditions of sulphated titania on the activity in the esterification of high acid value oil. *Chem. React. Eng. Technol.* **2007**, *23*, 13–18, In Chinese. .

(7) Guangzhao, M. *Practical solvents handbook*; Shanghai Technological Press: Shanghai, 1990.

(8) Batista, E.; Monnerat, S.; Kato, K.; Stragevitch, L.; Meirelles, A. J. A. Liquid−liquid equilibrium for systems of canola oil, oleic acid, and short-chain alcohols. *J. Chem. Eng. Data* **1999**, *44*, 1360–1364.

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