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Solubility of Multicomponent Systems in the Biodiesel Production by Transesterification of *Jatropha curcas* L. Oil with Methanol

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Biodiesel is manufactured by transesterification of animal fat or vegetable oil. The reactants (oil and methanol) and the products (fatty acid methyl ester and glycerol) are partially mutual soluble in the reaction process. Inter-solubility of the reaction components is essential data for the production design and process operation. In this work, the *Jatropha curcas* L. oil (oil) has been transesterified to give *Jatropha curcas* L. oil methyl ester (FAME). The inter-solubility of FAME + methanol + glycerol, oil + FAME + methanol, oil + glycerol + methanol, and oil + FAME + glycerol in the range from 298.15 K to 333.15 K has been conducted. Methanol is completely soluble in both FAME and glycerol but is not soluble in oil. With an increase in the mass fraction of FAME, the solubility of methanol in the oil + FAME phase increases. The transesterification reaction is carried out in the methanol phase, and as a result, the reaction shows an induction period. When FAME content increases to 70 %, the oil + methanol + FAME mixture becomes a homogeneous phase. Glycerol has a low solubility in both oil and FAME and, hence, is easily separated from the final product of biodiesel. The solubility is temperature insensible.

Introduction

As fossil fuel reserves rapidly decline, renewable alternative fuels are more and more attractive.[1−3] Use of biodiesel is growing quickly because of its excellent fuel properties.[4] Diesel engines can be directly fueled with biodiesel without any mechanical change.[5−8] Because biodiesel is renewable, biodegradable, and environmentally benign, [4,9−11] engines fueled with biodiesel reduce the emission of toxic gases, such as SO_2, CO, and hydrocarbons.[4,9]

Biodiesel consists of mono-alkyl esters of long-chain fatty acid manufactured by transesterification of vegetable oil or animal fat with methanol or ethanol. The transesterification reaction in traditional production of biodiesel is catalyzed by acid/base catalyst. Triglyceride (TG) in oil or fat reacts with methanol to produce biodiesel and fatty acid methyl ester and release glycerol:[4]

$$\text{TG} + 3\ \text{methanol} \xleftrightarrow{\text{catalyst}} 3\ \text{fatty acid methyl ester} + \text{glycerol}$$

KOH, NaOH, etc. are usually the most effective catalysts.[12] Even though many new catalysts (such as solid base/acids,[13−15] enzymes,[16−19] organic bases,[20] and metal oxides[21]) have been reported to be effective for the transesterification reaction, most of the biodiesel plants at present operate with caustic bases.[22]

The physical properties and inter-solubility of the components are very important for the biodiesel production. Researchers have studied certain physical properties of other oils.[23,24] In the reaction of transesterification, reactants, methanol, and oil are partially miscible.[25] Alkali catalyst exists in the methanol phase. Comparing the reaction rates of methanol with butyl alcohol, Boocock et al.[22] suggested that the transesterication reaction takes place in the methanol phase. So, the reaction rate greatly depends on the solubility of oil in methanol. On the other hand, the formation of glycerol and FAME may change the distribution of reaction components in different phases. The final products also exist in two separate phases, thus glycerol can be separated from FAME by settling. The solubility of glycerol in the product FAME directly influences the following purification of biodiesel. Unreacted methanol distributes in both FAME and glycerol phases. The inter-solubility is also essential data for the methanol recovery.

The *Jatropha curcas* L. tree is a popular perennial plant in the area of southwest China. Its planting area is quickly enlarging under the promotion of the Planting Plan along the Yangzi River, and its oil is used to produce biodiesel. Concerning the reaction mixture, reactants (oil and methanol) and products (FAME and glycerol) often coexist. We were not concerned with the influence of intermediates, monoglyceride (MG) and diglyceride (DG), because of their short life spans or with the catalyst and impurities because of their low contents in the mixture. We also considered the FAME or oil as a single component, even though they are mixtures of fatty acid esters with different chains. The solubility data presented in this paper is a global property of the *Jatropha curcas* L. oil. The results are applicable. In this research, solubility of multicomponent systems, containing the above four components, in the biodiesel production from *Jatropha curcas* L. oil was measured. The phase diagram was divided into four ternary-component systems according to the permutation and combination laws. The phase diagrams of four ternary systems (FAME + glycerol + methanol, oil + FAME + methanol, oil + glycerol + methanol, and FAME + glycerol + oil systems) were drawn on the basis of the solubility data.

Experimental Section

Materials. The *Jatropha curcas* L. oil was prepared by grinding the seeds of the *Jatropha curcas* L. tree from the Panzhihua area, Sichuan Province, southwest China, and the oil was purified by filtering solid impurity. After being processed with NaOH and active earth, the composition of fatty acid and

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Table 1. Composition and Properties of Purified Panzhihua *Jatropha curcas* L. Oil

w_{H_2O}	<0.1 %	
acid value/mg of KOH/g of oil	<1	
saponification value/mg of KOH/g of oil	184.9	
composition of fatty acid of *Jatropha curcas* L. oil (mass fraction)	C14:0	0.37 %
	C16:0	13.34 %
	C16:1	0.99 %
	C18:0	4.91 %
	C18:1	32.03 %
	C18:2	45.05 %
	C18:3	0.23 %
	C20:0	0.16 %
	C20:2	2.92 %

properties of *Jatropha curcas* L. oil are listed in Table 1.

The moisture, the acid value, and the saponification value were determined following the methods described in the National Standard of PRC GB/T 5528-1995, GB 9104.3-88, and GB9104.2-88, respectively. The composition of fatty acid was analyzed by an Agilent GLC6890 after methylation. FAME was prepared in the laboratory by transesterification of the oil with methanol. Analytical reagents of glycerol and methanol were from Chengdu Chemical Reagent Co., Ltd. (China).

Apparatus and Procedure. (a) Preparation of FAME. The FAME was prepared by transesterifying *Jatropha curcas* L. oil with methanol using potassium hydroxide (KOH) as the catalyst. And the dosage of KOH was 1.3 wt % of the oil. The oil and methanol with a mole ratio of 1:6 reacted at 337.15 K for 30 min. The product obtained was settled in a separating funnel to separate glycerol. The upper ester layer was collected and washed with deionized water several times until the FAME was free of methanol and catalyst. Finally, the ester was dried with anhydrous magnesium sulfate. The total content of FAME in the final products was 99.2 % in mass fraction, obtained by gas chromatography analysis. It corresponded to the full conversion of the oil shown in Table 1.

(b) Phase Diagram of FAME + Methanol + Glycerol. The phase boundary was determined by turbidimetric analysis using the titration method under isothermal conditions. The three-necked flask was immersed in a constant-temperature water bath equipped with a temperature controller that was capable of maintaining the temperature within a fluctuation of ± 0.2 K. Measurement procedure includes the following:

(i) Titrating FAME with a microburet into mixtures of glycerol and methanol while stirring with a mechanical agitator. The point, when the mixture changed from transparent to turbid, was considered to be the saturation point of FAME in glycerol + methanol solution. With the volume of FAME used, the amount of FAME solved in the glycerol + methanol solution was calculated. The solubility of FAME was measured in different initial compositions of the glycerol + methanol solution. The density of FAME is 0.88 $g\cdot cm^{-3}$ obtained by a pycnometer.

(ii) Titrating glycerol into mixtures of FAME + methanol as in procedure (i). The solubility of glycerol in the FAME + methanol solutions with different compositions was obtained.

(iii) To check the data around the meeting point of above two branches of solubility curve, methanol was titrated into a FAME + glycerol mixture of given mass ratio to observe the point where the turbid mixture became clear.

(c) Tie Lines of the FAME + Methanol + Glycerol System. Mixing FAME, methanol, and glycerol under 2 h intensive agitation obtained the two-phase equilibrium systems of different ratios in the heterogeneous zone, and then the mixture was kept in an isothermal water bath for 12 h. The ternary mixture was separated into two phases. The upper phase was enriched FAME, and the lower layer was enriched glycerol. The content of glycerol was determined following the method described in the National Standard of PRC GB/T 13216.6-91, in which the glycerol is oxidized into formic acid by $NaIO_4$ and then titrated by NaOH to obtain the content of glycerol. The methanol and FAME contents were measured by gas chromatography using a gas chromatogram (Fuli 9790, China) equipped with a split/splitless injection system and a flame-ionization detector. The column was a 10 m × 0.53 × 10^{-3} m × 0.15 × 10^{-6} m Dexil-300 capillary column (Frontier, Japan) with splitless injection. H_2 gas was used as the carrier gas in a flow rate of 7 $cm^3\cdot min^{-1}$. The injector and the detector temperatures were 653.15 K. The column was heated linearly from 323.15 K to 503.15 K at a rate of 8 $K\cdot min^{-1}$ and then held at this temperature for 2 min, then heated further to 653.15 K at a rate of 25 $K\cdot min^{-1}$. Finally, the column temperature was kept at 653.15 K for 5 min. Methyl salicylate was used as the internal standard. After obtaining the composition of the glycerol-rich phase and the FAME-rich phase, the tie lines were obtained by plotting the data in the phase diagram and connecting the two points with beeline.

Table 2. Measured and Reported Solubility of Benzene (1) in Ethanol (2) + Water (3)

T/K	w_2	w_3	w_1 this work	w_1 lit[26]
298.15	0.5039	0.3700	0.1248	0.1261
298.15	0.5011	0.2243	0.2721	0.2746
288.15	0.5162	0.3791	0.1025	0.1047
288.15	0.5293	0.2369	0.2200	0.2338

(d) Phase Diagram of Oil + FAME + Methanol, Oil + Glycerol + Methanol, and FAME + Glycerol + Oil Systems. Measurement procedures were the same as those for the phase diagram of FAME + methanol + glycerol. The density of the oil (*Jatropha curcas* L. oil) was 0.90 $g\cdot cm^{-3}$.

Results and Discussion

To check the accuracy of the experimental procedure, the solubility of benzene in ethanol + water was determined by the turbidimetric analysis method described above, and the results were compared with those obtained from literature, 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).

Phase Diagram of FAME + Methanol + Glycerol System. As shown in Figures 1 and 2, FAME and methanol and glycerol and methanol, are completely mutually soluble, but glycerol and FAME are partially soluble in each other. The solubility of FAME in the glycerol phase is slightly greater than that of glycerol in the FAME phase. Comparing the RME (rapeseed oil methyl ester) and methanol system, the solubility of FAME of *Jatropha curcas* L. oil in methanol is much higher. The mass fraction solubility of methanol in pure RME is only 17.3 % at 293.15 K.[27] The difference may be due to different fatty acid chains. The fatty acids contained in rapeseed oil have longer chains and less unsaturated bonds, which corresponds to smaller polarity. So, it is reasonable that the solubility of methanol in REM is lower than in FAME of *Jatropha curcas* L. oil.

From Figures 1 and 2, the solubility in the ternary mixture changes insignificantly with temperature in the range from 298.15 K to 333.15 K. The reaction conversion is usually very high with catalysts such as NaOH and KOH. The final product can be considered to be a ternary mixture of FAME, glycerol, and methanol. The solubility indicates that the separation of

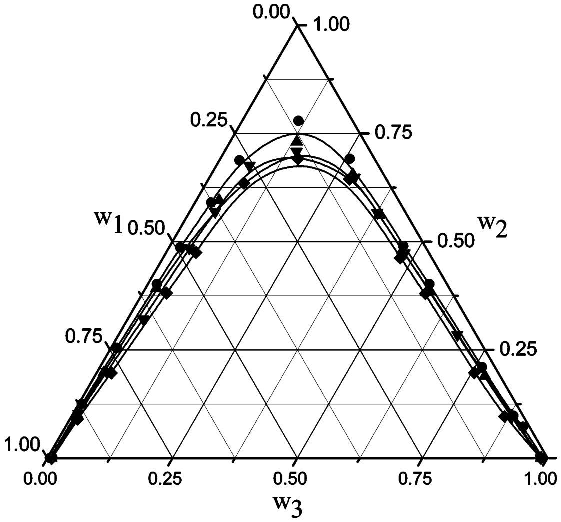

Figure 1. Phase diagram of FAME (1) + methanol (2) + glycerol (3): ●, 298.15 K; ▲, 308.15 K; ▼, 318.15 K; ■, 328.15 K.

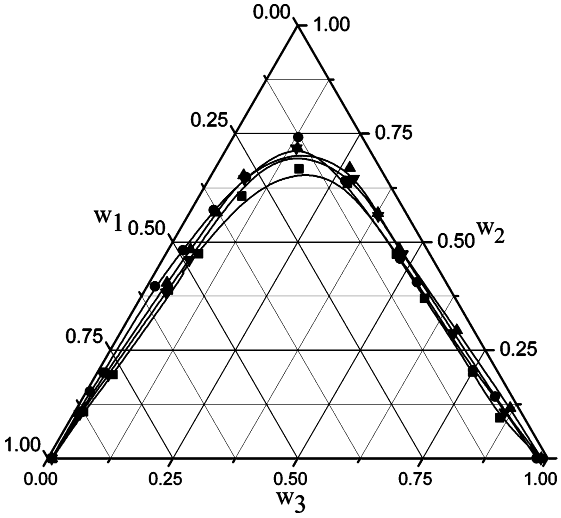

Figure 2. Phase diagram of FAME (1) + methanol (2) + glycerol (3): ●, 303.15 K; ▲, 313.15 K; ▼, 323.15 K; ■, 333.15 K.

glycerol can be conducted in situ at reaction conditions, which is beneficial for simplifying the process and reducing the cost.

Tie Lines of FAME + Methanol + Glycerol System. For the ternary mixture in a heterogeneous area, two liquid phases exist. Figures 3 to 6 show the composition analysis data in both the FAME phase and the glycerol phase for mixtures with different initial compositions. The amounts of methanol and glycerol remaining in the FAME phase can be precisely calculated from the solubility phase diagram.

By comparing the analysis data with the solubility data obtained by turbidimetric technique, as shown in Figures 3 to 6, the crunodes of tie lines are in good agreement with the solubility curves. It indicates that the turbidimetric technique is reliable. The relative data are compared in Table 3.

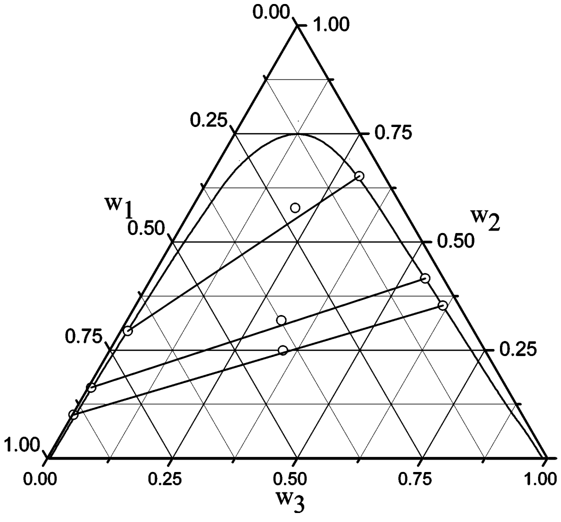

Figure 3. Tie line of the system FAME (1) + methanol (2) + glycerol (3) at 298.15 K.

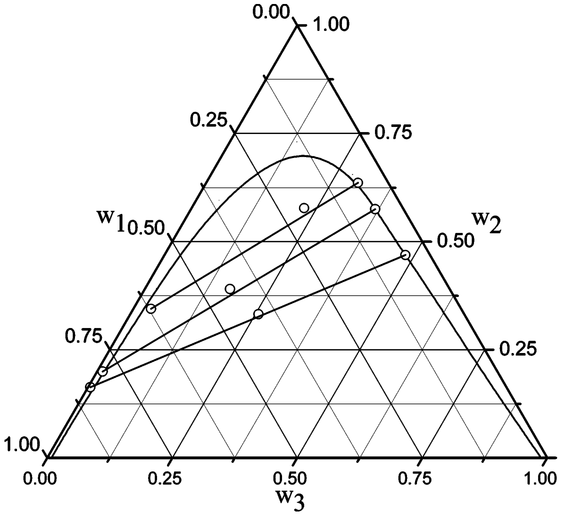

Figure 4. Tie line of the system FAME (1) + methanol (2) + glycerol (3) at 308.15 K.

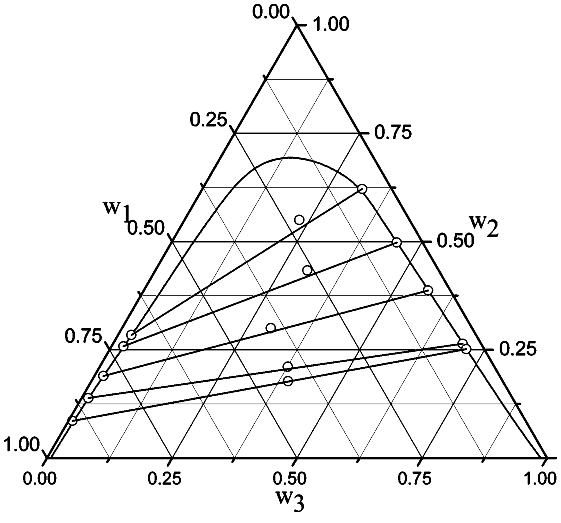

Figure 5. Tie line of the system FAME (1) + methanol (2) + glycerol (3) at 318.15 K.

According to the phase rule, the freedom number is 3 when a ternary system is in equilibrium with two phases. In definite temperature and pressure, only one component can independently change its concentration. Other concentration parameters vary following the phase equilibrium. Although FAME is the mixture of esters with various fatty acids in the system of FAME + methanol + glycerol, it is feasible to regard approximately the system consisting of ternary components. Therefore, the phase rule is applicable. Suppose the mass fraction of methanol in glycerol phase is w_2^{I}, and the mass fraction of glycerol is w_3^{I}. The relationship between w_2^{I} and w_3^{I} at different temper-

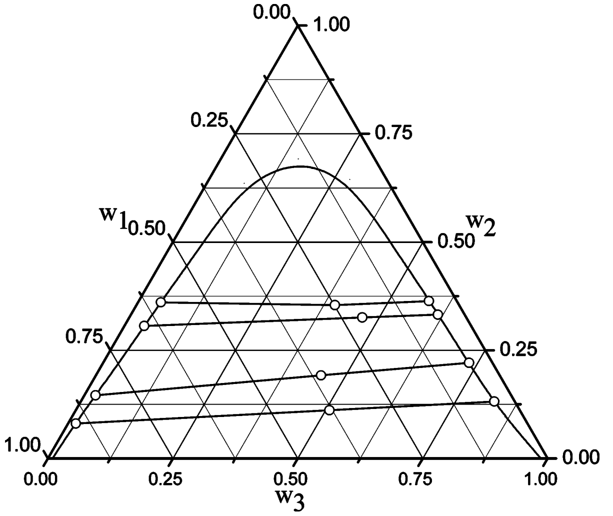

Figure 6. Tie line of the system FAME (1) + methanol (2) + glycerol (3) at 328.15 K.

Table 3. Comparison between Phase Boundary Data with Tie Lines Results of FAME (1) + Methanol (2) + Glycerol (3)

	solubility curve			tie line		
T/K	100 w_1	100 w_2	100 w_3	100 w_1	100 w_2	100 w_3
298.15	3.50	40.18	56.32	3.59	41.59	54.82
318.15	78.18	19.98	1.84	79.26	18.97	1.77
328.15	89.48	8.99	1.53	90.41	8.04	1.55

atures can be estimated by the following equations (SD stands for the standard deviation):

$$\text{at 298.15 K:}\quad w_3^{\mathrm{I}} = -1.0578\, w_2^{\mathrm{I}} + 0.9881,\ \mathrm{SD} = 2.76\cdot 10^{-3}$$

$$\text{at 308.15 K:}\quad w_3^{\mathrm{I}} = -1.0712\, w_2^{\mathrm{I}} + 0.9846,\ \mathrm{SD} = 1.05\cdot 10^{-3}$$

$$\text{at 318.15 K:}\quad w_3^{\mathrm{I}} = -1.0636\, w_2^{\mathrm{I}} + 0.9803,\ \mathrm{SD} = 7.04\cdot 10^{-4}$$

$$\text{at 328.15 K:}\quad w_3^{\mathrm{I}} = -1.0637\, w_2^{\mathrm{I}} + 0.9675,\ \mathrm{SD} = 2.27\cdot 10^{-3}$$

In the FAME phase, the mass fraction of FAME, w_1^{II}, can also be expressed as a function of the mass fraction of methanol, w_2^{II}:

$$\text{at 298.15 K:}\quad w_1^{\mathrm{II}} = -1.0603\, w_2^{\mathrm{II}} + 1.0039,\ \mathrm{SD} = 2.63\cdot 10^{-3}$$

$$\text{at 308.15 K:}\quad w_1^{\mathrm{II}} = -1.1674\, w_2^{\mathrm{II}} + 1.0226,\ \mathrm{SD} = 3.10\cdot 10^{-2}$$

$$\text{at 318.15 K:}\quad w_1^{\mathrm{II}} = -1.0924\, w_2^{\mathrm{II}} + 0.9998,\ \mathrm{SD} = 2.98\cdot 10^{-3}$$

$$\text{at 328.15 K:}\quad w_1^{\mathrm{II}} = -1.1086\, w_2^{\mathrm{II}} + 0.9932,\ \mathrm{SD} = 1.31\cdot 10^{-3}$$

Analysis data in both phases are listed in Table 4.

Phase Diagram of the Oil + FAME + Methanol System. As shown in Figures 7 and 8, oil and methanol are almost immiscible in the range from 298.15 K to 333.15 K. Oil and methanol have much different properties in their polarity. But both oil and methanol can be completely soluble in FAME. Increasing the amount of FAME, the solubility of oil in methanol gradually increased. At last, the ternary mixture becomes a homogeneous solution when the mass fraction of FAME increases to 70 %. The transesterification reaction takes place in the methanol phase; thus the reaction rate greatly depends on the solubility of oil in the methanol phase. The reaction kinetic curve often shows a S-pattern.[28,29] It is partially associated with the increasing solubility of oil in methanol with the formation of FAME.

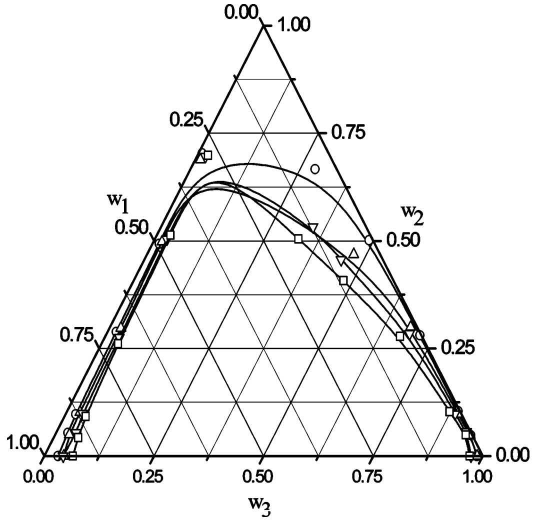

Figure 7. Phase diagram of FAME (1) + methanol (2) + glycerol (3): ○, 298.15 K; △, 308.15 K; ▽, 318.15 K; □, 328.15 K.

Table 4. Tie Line Data for FAME (1) + Methanol (2) + Glycerol (3) at Different Temperatures

glycerol-rich phase			FAME-rich phase			
100 w_1^{I}	100 w_2^{I}	100 w_3^{I}	100 w_1^{II}	100 w_2^{II}	100 w_3^{II}	distribution coefficient of methanol ($w_2^{\mathrm{II}}/w_2^{\mathrm{I}}$)
			T = 298.15 K			
4.96	65. 22	29.82	69.20	29.42	1.38	0.45
3.59	41.59	54.82	83.06	16.34	0.60	0.39
3.23	35.28	61.49	89.73	10.05	0.22	0.28
			T = 308.15 K			
6.07	63.58	30.35	62.01	34.48	3.51	0.54
5.63	57.51	36.86	78.92	19.99	1.09	0.35
4.88	46.92	48.20	83.20	16.33	0.47	0.35
			T = 318.15 K			
5.92	62.16	31.92	68.90	28.45	2.65	0.46
5.14	49.79	45.07	71.80	25.80	2.40	0.52
4.43	38.72	56.85	79.26	18.97	1.77	0.49
3.65	26.42	69.93	84.84	13.86	1.30	0.52
3.57	25.18	71.25	90.61	8.58	0.81	0.34
			T = 328.15 K			
5.57	36.36	58.07	59.34	36.06	4.60	0.99
5.36	33.20	61.44	65.41	30.59	4.00	0.92
4.66	22.07	73.27	83.16	14.58	2.26	0.66
4.09	13.13	82.78	90.41	8.04	1.55	0.61

Phase Diagram of Oil + Glycerol + Methanol and Oil + FAME + Glycerol. The product glycerol is hardly soluble in FAME or oil. The *Jatropha curcas* L. oil in the oil + glycerol + methanol ternary mixture exists in a separate phase (see Table 5). In the initial period of reaction, most of the product glycerol goes into the methanol phase, and the product FAME goes in the oil phase. As the reaction proceeds, the amounts of glycerol and FAME increase. More methanol gets into the oil + FAME phase, and the glycerol/methanol ratio increases in the methanol + glycerol phase. In the final period of reaction, the system divides into the FAME phase and the glycerol phase. The oil dissolves in the FAME phase, and the methanol distributes in both FAME and glycerol phases.

Table 6 shows the phase diagram of the oil + FAME + glycerol ternary system. The system exists in two phases, the glycerol phase and the oil + FAME phase. Glycerol is almost

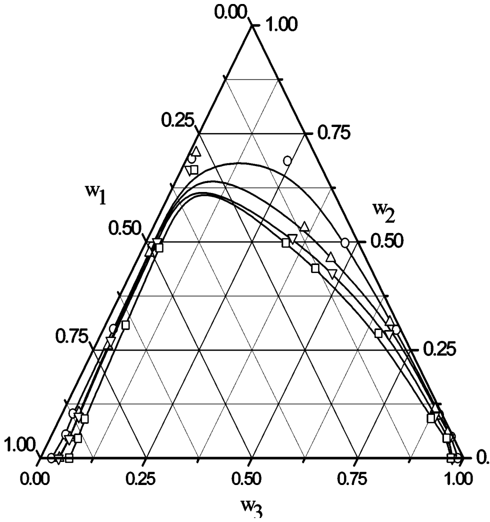

Figure 8. Phase diagram of FAME (1) + methanol (2) + glycerol (3): ○, 303.15 K; △, 313.15 K; ▽, 323.15 K; □, 333.15 K.

Table 5. Composition of the Solubility Curves of Methanol (1) + Oil (2) + Glycerol (3) at Different Temperatures

100 w_1	100 w_2	100 w_3	100 w_1	100 w_2	100 w_3
	T = 298.15 K			T = 303.15 K	
4.91	0.32	94.77	5.82	0.42	93.76
11.15	0.31	88.54	12.82	0.41	86.77
30.98	0.35	68.67	31.00	0.40	68.6
54.41	0.45	45.14	48.17	0.54	51.29
70.58	0.37	29.05	69.28	0.50	30.22
88.95	0.35	10.70	88.05	0.40	11.55
94.94	0.21	4.85	94.51	0.42	5.07
	T = 308.15 K			T = 313.15 K	
5.11	0.43	94.46	6.16	0.42	93.42
11.38	0.63	87.99	12.08	0.62	87.30
30.68	0.62	68.70	29.23	0.84	69.93
49.94	0.75	49.31	49.82	0.83	49.35
68.28	0.61	31.11	69.53	0.83	29.64
88.97	0.42	10.61	89.13	0.63	10.24
93.59	0.42	5.99	94.01	0.64	5.35
	T = 318.15 K			T = 323.15 K	
4.47	0.63	94.90	3.99	0.85	95.16
10.29	0.63	89.08	12.66	1.00	86.34
30.35	0.83	68.82	30.38	1.07	68.55
49.65	1.01	49.34	49.59	1.24	49.17
68.77	0.82	30.41	72.74	1.08	26.18
88.64	0.85	10.51	87.41	0.84	11.75
94.25	0.64	5.11	92.90	0.83	6.27
	T = 328.15 K			T = 333.15 K	
6.69	1.23	92.08	6.37	1.84	91.79
10.11	1.23	88.66	11.23	1.81	86.96
29.37	1.46	69.17	29.35	2.01	68.64
48.84	1.63	49.53	48.92	2.39	48.69
68.29	1.45	30.26	67.19	2.04	30.77
85.51	1.43	13.06	88.06	1.87	10.07
93.70	1.25	5.05	92.55	1.65	5.80

completely unsoluble in the oil + FAME phase. This means that the byproduct glycerol can be easily separated from the biodiesel product.

Conclusions

The measurement of inter-solubility of *Jatropha curcas* L. oil, methanol, FAME, and glycerol shows that the solubility is temperature insensible in the temperature range of the transesterification reaction. The component distribution changes with the reaction process. The inter-solubility of the reaction system changes with the oil resources. It provides basic data for the biodiesel production from *Jatropha curcas* L. oil.

Table 6. Composition of the Solubility Curves of FAME (1) + Glycerol (2) + Oil (3) at Different Temperatures

100 w_1	100 w_2	100 w_3	100 w_1	100 w_2	100 w_3
	T = 298.15 K			T = 313.15 K	
50.75	0.53	48.72	0	0.34	99.66
58.97	1.30	39.73	20.12	0.21	79.67
68.56	0.74	30.7	39.06	0.41	60.53
31.14	1.95	66.91	58.97	2.08	38.95
21.23	0.30	78.47	78.61	1.26	20.13
80.21	0.31	19.48	99.18	0.82	0
	T = 323.15 K			T = 333.15 K	
0	0.35	99.65	0	0.27	99.73
10.66	0.14	89.20	19.89	0.41	79.70
50.35	1.71	47.94	40.65	0.21	59.14
68.42	1.48	30.10	58.46	2.22	39.32
89.30	0.63	10.07	78.14	0.62	21.24
99.25	0.75	0	99.08	0.92	0

Supporting Information Available:

Solubility and tie-line data. This material is available free of charge via the Internet at http://pubs.acs.org.

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