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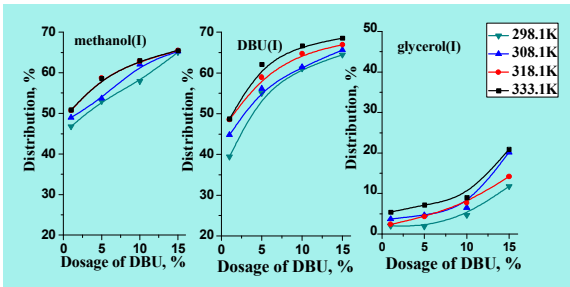
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A table of contents entry:



One sentence highlight:  
Increasing the dosage of DBU and/or temperature enhances the distribution and solubility of methanol, DBU and glycerol in biodiesel-rich phase.

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## ARTICLE TYPE

Inter-solubility of Product Systems in Biodiesel Production from *Jatropha Curcas*

## L. oil with Switchable Solvent DBU/methanol

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Switchable solvent 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU)/methanol can be used in transesterification with oil to produce biodiesel (fatty acid methyl ester). The reactants (methanol, oil and catalyst DBU) and the products (fatty acid methyl ester and glycerol) are partially soluble in the production process. Phase equilibrium of the product components is essential data for biodiesel separation and process operation. In this work, the effects of catalyst dosage and temperature were studied on the phase equilibrium of the product systems. The phase composition of the product systems and the distribution of components were measured. The results showed the distribution of methanol, DBU and glycerol in biodiesel-rich phase increases with the increase of DBU dosage from 1wt% of oil to 15wt% of oil and temperature from 298.1K±0.1K to 333.1K±0.1K, and decreases accordingly in glycerol-rich phase. The distribution of biodiesel in both phases varies little. Increasing the dosage of DBU and/or temperature enhances the distribution and solubility of methanol, DBU and glycerol in biodiesel-rich phase. This phenomenon was explained by estimating and analyzing Van der Waals forces and hydrogen bonds.

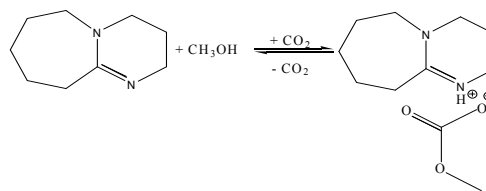
## 1 Introduction

With the increasing price and decreasing reserves of fossil fuels, renewable alternative fuels are being rapidly developed. One environmentally friendly alternative fuel, biodiesel, is attracting extensive attention worldwide.<sup>1</sup> Biodiesel is the mono-alkyl ester of long chain fatty acids prepared by transesterification from triglycerides with short chain alcohols (methanol, ethanol, etc.). The feedstocks are renewable vegetable oils, animal fats or recycled cooking oils.<sup>2</sup>

The typical commercial production process of biodiesel is transesterification catalyzed by homogeneous base (e.g. KOH). However, these catalytic systems suffer from some drawbacks. First, biodiesel has stringent purity requirements, such as water content < 0.1% and acid value < 1.0 mg-KOH/g-oil.<sup>3,4</sup> Second, the immiscibility of oil with methanol and the catalyst enrichment in the methanol phase lead to low transesterification rate.<sup>5</sup> Also, the product of fatty acid methyl ester (FAME) contains various amounts of waste catalyst, methanol and byproduct glycerol, which need to be removed, often with a water wash resulting in a large amount of contaminated wastewater. In this process, homogeneous catalyst cannot be recycled and large energy consumption is necessary to dry the product.<sup>6</sup> Therefore, improving efficiency, decreasing waste and reducing energy consumption are serious tasks. In addition to traditional method of base catalysis, supercritical method, solid catalysis and enzyme catalyzed reaction systems are also widely studied.<sup>7-9</sup>

Recently switchable solvents are attracting much interest in extraction and separation due to their reversible switchable properties under mild conditions.<sup>10</sup> Switchable solvents with alkaline (e.g. amidine, guanidine) can be used for transesterification reaction to produce biodiesel.<sup>11,12</sup> 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU) is a typical switchable solvent proposed by Jessop et al.<sup>13</sup> DBU is an amidine with strong alkalinity,<sup>11</sup> which can catalyze transesterification. It can

promote the dissolution between oils and methanol, resulting in high reaction efficiency. At the end of the reaction, it can react quantitatively with water,<sup>14</sup> methanol or glycerol by absorbing CO<sub>2</sub> to form ionic compounds. Scheme1 shows the reaction between DBU and methanol with CO<sub>2</sub> as a trigger. The ionic compounds dissolve into glycerol-rich phase, thus DBU can be separated from the product FAME. Water and byproduct glycerol can also be removed from the main product. Exposing the ionic liquid layer to nitrogen or heating to desorb CO<sub>2</sub>, DBU switches back to non-polar form.<sup>15</sup> Therefore, DBU can realize the recovery and reuse. The new process is very promising because it may reduce requirements for raw materials, decrease separation energy and improve product purity. Cao et al.<sup>12</sup> reported that the transesterification efficiency of soybean oil is 95.2% under 70°C, the molar ratio of DBU to CH<sub>3</sub>OH 1:18, and 20min reaction time. The FAMES can be separated easily with high purity and clean glycerol can be obtained by extraction separation of DBU. The recycled DBU has high purity and can be reused in the next experiments directly. Xue et al.<sup>16</sup> reported that the highest biodiesel yield catalyzed by DBU could reach 97.9% under ethanol-oil ratio 12:1, DBU-oil molar ratio 2:1, reaction temperature 70°C, reaction time 2h. In the above two work, the content of DBU is 34.6% and 56.8% of oil mass, respectively.



Scheme1 Reversible chemical absorption of CO<sub>2</sub> by methanol and DBU

*Jatropha Curcas* L. oil is one suitable feedstock to produce biodiesel. *Jatropha Curcas* L. trees can grow in arid and semiarid wastelands. It has a high seed yield and high oil content.<sup>17</sup> The

non-edible oil from the seeds can be used in many areas, especially to produce biodiesel. Biodiesel prepared from *Jatropha Curcas* L. oil has excellent characteristics meeting the American and European Biodiesel Quality Standards. We explored the new process to produce biodiesel catalyzed by DBU using *Jatropha Curcas* L. oil as feedstock. The preliminary results indicated that the new process is feasible. The conversion of oil can reach >94% when the content of DBU is 10% of oil mass under 333.1K, 6:1 molar ratio of CH<sub>3</sub>OH to oil and 60min. And it is not so sensitive to water and free fatty acid as KOH. After reaction, biodiesel-rich phase and glycerol-rich phase are formed.

To make the new process into a commercial one, much fundamental work needs to be done. For example, to separate DBU from biodiesel phase, the compositions of the biodiesel-rich phase and the glycerol-rich phase need to be investigated. Measuring the relative solubility of the different components in the product streams in the presence of DBU at different temperatures can provide the basic data and theoretical basis for the process design. In this work, we focus on measuring the component profiles of the product streams in biodiesel production. Biodiesel from *Jatropha Curcas* L. oil, methanol, glycerol and DBU were mixed together at different ratios. After settling, two phases were formed, biodiesel-rich phase and glycerol-rich phase. If the dosage is too low in this process, the catalytic effect may be poorer than traditional base catalysis. If the dosage is too high, it will not be conducive to the subsequent separation and recovery of DBU. As a result, the dosage of DBU was from 1wt% to 15wt% of oil. The temperature was from 298.1K±0.1K to 333.1K±0.1K. The distribution of components in each phase and the effects of DBU dosage and temperature on relative solubility were studied.

2 Experimental

2.1 Materials

The acid value of refined biodiesel is < 0.6mg-KOH/g, measured by the National Standard of PRC GB/T 5530-2005. The characterization of biodiesel was analyzed by gas chromatography (GC) according to ASTM D6584, shown in Fig.1. And its fatty acid composition fatty acid composition is listed in Table1. Monoglycerides and diglyceries were not detected.

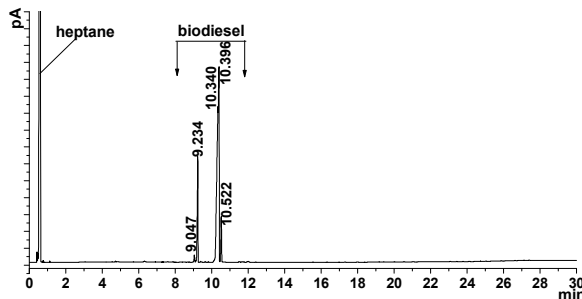


Fig.1 The gas chromatography of *Jatropha Curcas* L. biodiesel

Table1 Fatty acid composition of *Jatropha Curcas* L. biodiesel

Fatty acid*	C16:1	C16:0	C18:2	C18:1	C18:0
mass fraction	1.00%	15.30%	43.79%	33.33%	6.58%

\* In C<sub>x</sub>:y, x is number of carbons and y is number of double bonds.

The purity of DBU (Shanghai Beihe Chemicals Co., Ltd., China) is 99%. Its moisture is less than 0.1% tested by the National Standard of PRC GB/T 5528-1995. Other chemical reagents (Chengdu Kelong Chemical Reagent Factory, China) are all analytical reagents and used as received.

2.2 Preparation and separation of biodiesel-rich phase and glycerol-rich phase

The transesterification reaction can be expressed as follows:

triglycerides + 3 methanol  $\rightleftharpoons$  3 FAME (biodiesel) + glycerol  
Mixtures of biodiesel, glycerol, methanol and DBU were prepared assuming complete conversion of triglycerides to biodiesel. This assumption simplifies the experimental matrix by neglecting the very large number of mixtures containing various amounts of tri-, di-, and monoglyceride encountered during partial conversion of the reaction mixture, permitting a focus on the effects of DBU dosage and temperature. If the biodiesel production were carried out with an initial oil and methanol molar And excess methanol will be 3:1:3 at the end of the reaction. With 100.00g *Jatropha Curcas* L. oil as a base, the dosage of the catalyst DBU was 1wt%, 5wt%, 10wt% and 15wt% of oil. The mass ratio of mixture of biodiesel, methanol, glycerol and DBU was 10: 1: 1: (0.1, 0.5, 1.0, 1.5).

Biodiesel, methanol, glycerol and DBU were hermetically sealed in a conical flask (250mL), with 1minute intensive agitation. Then the conical flask was kept in a water bath for 4 h. The temperature of water was kept at 298.1K±0.1K, 308.1K±0.1K, 318.1K±0.1K and 333.1K±0.1K, respectively. The mixture separated rapidly into two phases with a clear interface, an upper biodiesel-rich phase and a lower glycerol-rich phase.

2.3 Analytical method

Two phases were obtained after separation. The amount of methanol in different phases was quantified by reduced pressure distillation. Each phase was separately distilled in a rotary evaporator at 320.1K±0.1K with 0.05MPa vacuum to remove methanol completely, and the methanol content was calculated by the mass loss after the distillation process.

After distillation, for biodiesel-rich phase, the quantity of DBU was determined by acid-base titration analysis.<sup>18</sup> The mass fraction of glycerol was measured by UV spectrophotometer.<sup>19</sup>

Biodiesel content was further obtained by mass balance.

For glycerol-rich phase, the measurement method of DBU was the same as above. The content of biodiesel was determined by extraction and distillation. Samples of the glycerol-rich phase were diluted with an equal volume of ethanol (95%) aqueous solution. Then biodiesel was extracted from the diluted sample with 20mL petroleum ether. Removal of petroleum ether by distillation left the easily measurable quantity of biodiesel. Glycerol content was further obtained by mass balance.

All the experiments were repeated at least two times. The average values were used as the final results.

3 Results and discussion

3.1 Composition of biodiesel-rich phase and glycerol-rich phase

**Table 2 Mass fraction of components in biodiesel-rich phase (I) and glycerol-rich phase (II) at different DBU dosages and temperatures: Methanol (1) +DBU (2) +Glycerol (3) +Biodiesel (4)**

Items	I. Biodiesel-rich phase				II. Glycerol-rich phase			
	1%	5%	10%	15%	1%	5%	10%	15%
$T=298.1\text{K}\pm 0.1\text{K}$								
$100\omega_1$	4.13	4.56	4.07	5.67	31.81	24.60	20.55	18.88
$100\omega_2$	0.39	2.57	5.51	8.16	3.91	13.33	22.74	29.89
$100\omega_3$	0.20	0.18	0.42	1.00	63.25	60.48	55.65	49.82
$100\omega_4$	95.28	92.69	90.00	85.17	1.03	1.59	1.06	1.41
$T=308.1\text{K}\pm 0.1\text{K}$								
$100\omega_1$	4.49	4.66	5.01	5.43	31.62	26.18	19.34	16.74
$100\omega_2$	0.43	2.63	5.55	8.48	3.51	12.98	23.48	30.20
$100\omega_3$	0.37	0.45	0.57	1.88	63.86	58.46	55.30	51.07
$100\omega_4$	94.71	92.26	88.87	84.21	1.01	2.38	1.88	1.99
$T=318.1\text{K}\pm 0.1\text{K}$								
$100\omega_1$	4.58	5.47	5.03	5.14	30.34	22.32	19.34	19.08
$100\omega_2$	0.46	2.70	5.77	8.56	3.39	12.31	21.10	30.05
$100\omega_3$	0.23	0.44	0.73	1.16	65.85	64.61	58.68	49.81
$100\omega_4$	94.73	91.39	88.47	85.14	0.42	0.76	0.88	1.06
$T=333.1\text{K}\pm 0.1\text{K}$								
$100\omega_1$	4.63	5.05	5.10	5.03	31.34	26.77	22.96	19.50
$100\omega_2$	0.49	2.89	5.93	8.77	3.61	11.96	20.48	28.39
$100\omega_3$	0.53	0.69	0.80	1.90	64.85	60.74	55.77	50.67
$100\omega_4$	94.35	91.37	88.17	84.30	0.20	0.53	0.79	1.44

**Table 3 Distribution of biodiesel in biodiesel-rich phase (I) and glycerol-rich phase (II) at different DBU dosages and temperatures**

Temperature	I				II			
	1%	5%	10%	15%	1%	5%	10%	15%
$298.1\text{K}\pm 0.1\text{K}$	99.83	99.73	99.82	99.75	0.17	0.27	0.18	0.25
$308.1\text{K}\pm 0.1\text{K}$	99.84	99.59	99.69	99.65	0.16	0.41	0.31	0.35
$318.1\text{K}\pm 0.1\text{K}$	99.94	99.87	99.85	99.83	0.06	0.13	0.15	0.17
$333.1\text{K}\pm 0.1\text{K}$	99.97	99.91	99.87	99.76	0.03	0.09	0.13	0.24

The composition of biodiesel-rich phase and glycerol-rich phase were tested at different DBU dosages and temperatures. The results are shown in Table 2.

From Table 2, one can observe that the mass fraction of components in each phase varies with different DBU dosages, while they vary little with different temperatures. The fraction of biodiesel in the biodiesel-rich phase decreases from 95.28% at 1%DBU and 298.1K to 84.30% at 15%DBU and 333.1K. The fraction of glycerol in the glycerol-rich phase decreases from 65.85% at 1%DBU and 318.1K to 49.81% at 15%DBU and 318.1K. The mass fractions of DBU both in biodiesel-rich phase and glycerol-rich phase all increase with increase of DBU dosage, ranging from 0.39% to 8.77% in the biodiesel-rich phase and from 3.39% to 30.20% in the glycerol-rich phase. The content of methanol in biodiesel-rich phase varies little and remains within a range of 4.07% to 5.67%. However, methanol content in the glycerol-rich phase decreases significantly with an increase of DBU, falling from 31.81% to 18.88% at 298.1K. The content of glycerol in biodiesel-rich phase increases with increase of DBU dosage and temperature, ranging from 0.18% to 1.90%. Therefore, increase of the dosage of DBU promotes the inter-solubility of FAME and glycerol. As a result, the purities of biodiesel-rich phase and glycerol-rich phase decrease.

### 3.2 Effects of catalyst DBU and temperature on distribution of constituents

In biodiesel-rich phase and glycerol-rich phase, biodiesel, glycerol, methanol and DBU are included. The distribution of the components between the two phases is determined by their relative solubility. The distribution of each constituent in two phases is defined as:

$$D_i(\text{I}) = \frac{\omega_i(\text{I}) \times m(\text{I})}{\omega_i(\text{I}) \times m(\text{I}) + \omega_i(\text{II}) \times m(\text{II})}$$

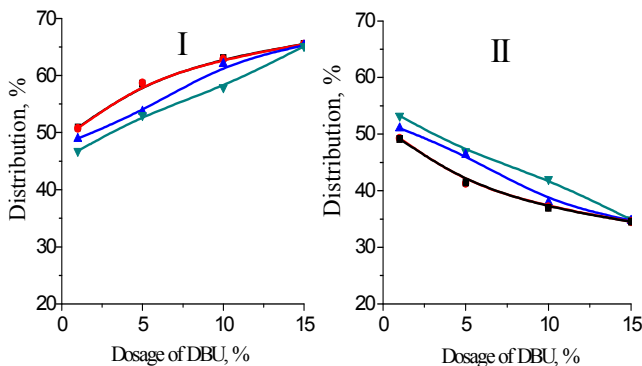
$$D_i(\text{II}) = 1 - D_i(\text{I})$$

Where  $\omega_i$ : mass fraction of constituents in biodiesel-rich phase(I) or glycerol-rich phase(II),  $i=1$ , methanol;  $i=2$ , DBU;  $i=3$ , glycerol;  $i=4$ , biodiesel.  $m$ : the mass of biodiesel-rich phase(I) or glycerol-rich phase(II).

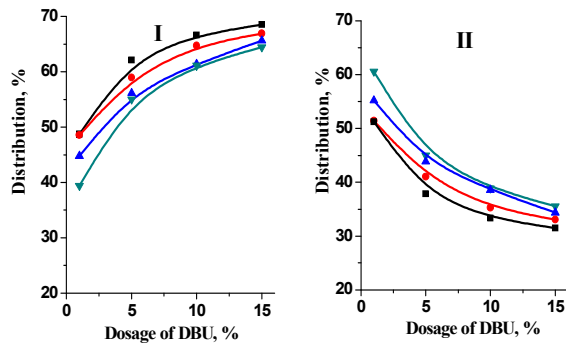
With the increase of DBU dosage (1wt%, 5wt%, 10wt% and 15wt% of oil) and temperature (298.1K $\pm$ 0.1K, 308.1K $\pm$ 0.1K, 318.1K $\pm$ 0.1K and 333.1K $\pm$ 0.1K), the distribution of methanol, DBU, glycerol and biodiesel varies. The results are shown in Fig.2, Fig.3, Fig.4 and Table 3.

From Fig.2, one can observe that the distribution of methanol increases gradually in biodiesel-rich phase with the increase of DBU wt% of oil and temperature, which is from 46.78% to 65.49%. The increase of DBU dosage and temperature enhances the solubility of methanol in biodiesel-rich phase to make more methanol distribute in it. More than 50% of methanol dissolves in biodiesel-rich phase except that the DBU dosage is 1wt% of oil at





**Fig.2** Distribution of methanol in biodiesel-rich phase (I) and glycerol-rich phase (II) at different DBU dosages and temperatures: ▼, 298.1K±0.1K; ▲, 308.1K±0.1K; ●, 318.1K±0.1K; ■, 333.1K±0.1K.

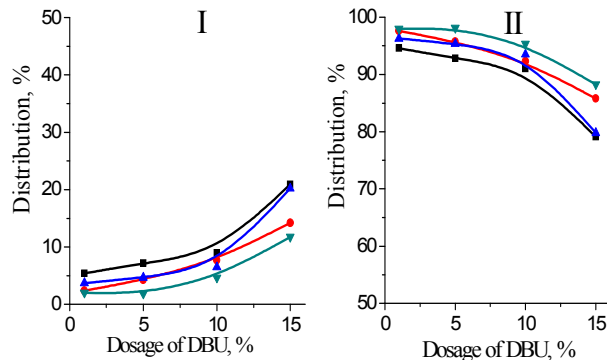


**Fig.3** Distribution of DBU in biodiesel-rich phase (I) and glycerol-rich phase (II) at different DBU dosages and temperatures: ▼, 298.1K±0.1K; ▲, 308.1K±0.1K; ●, 318.1K±0.1K; ■, 333.1K±0.1K.

298.1K±0.1K and 308.1K±0.1K. About 65% of methanol dissolves in biodiesel-rich phase when the catalyst dosage is 15wt% of oil. On the contrary, the distribution of methanol decreases correspondingly in glycerol-rich phase.

From Fig.3, the distribution of DBU increases gradually in biodiesel-rich phase with the increase of DBU wt% of oil and temperature, which is 39.43% to 68.53%, and decreases correspondingly in glycerol-rich phase. The increase of DBU dosage and temperature also enhances the solubility of DBU in biodiesel-rich phase to make more DBU distribute in it. More than half of DBU distributes in biodiesel-rich phase except that the catalyst DBU is 1wt% of oil. More than 65% of DBU distributes in biodiesel-rich phase when the catalyst amount reaches 15wt% of oil.

One can see from Fig.4 that the distribution of glycerol increases with the increase of DBU wt% of oil and temperature, which is from 2.02% to 20.90%, and decreases correspondingly in glycerol-rich phase. The increase of DBU dosage and temperature also enhances the solubility of glycerol in biodiesel-rich phase to make more glycerol distribute in it. Less than 10% of glycerol is dissolved in biodiesel-rich phase when the catalyst DBU is 1wt%-10wt% of oil. When the catalyst dosage reaches 15wt% of oil, 11.76%-20.90% of glycerol distributes in biodiesel-rich



**Fig.4** Distribution of glycerol in biodiesel-rich phase (I) and glycerol-rich phase (II) at different DBU dosages and temperatures: ▼, 298.1K±0.1K; ▲, 308.1K±0.1K; ●, 318.1K±0.1K; ■, 333.1K±0.1K.

**Table 4** Distribution of constituents in FAME-rich phase (I) and glycerol-rich phase (II) for 1%DBU and 333.1K

Items	Process catalyzed by DBU		Process catalyzed by KOH*	
	I	II	I	II
Biodiesel	99.97%	0.03%	>99.9%	<0.1%
Glycerol	5.41%	94.59%	1.9%	98.1%
Methanol	50.87%	49.13%	33.0%	67.0%
catalyst	48.74%	51.26%	2.6%	97.4%

\*: The condition of process catalyzed by KOH in reference was: the methanol-to-oil molar ratio, 6:1; reaction temperature, 333.1K; reaction time, 1 h; and KOH as catalyst, 1.0 wt% in oil.

phase.

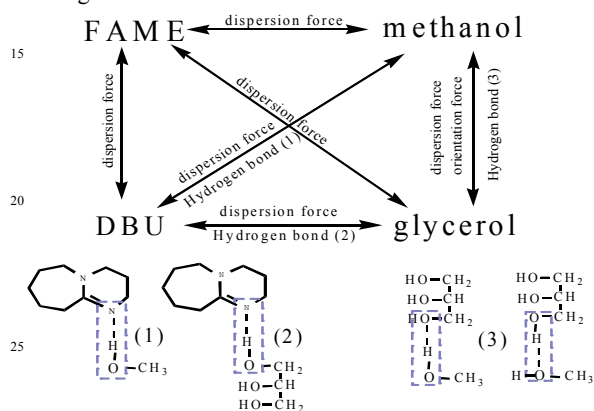
From Table 3, the distribution of biodiesel in biodiesel-rich phase and glycerol-rich phase varies slightly and maintains within >99.6% and <0.4%, respectively. It demonstrates that DBU dosage and temperature has almost no influence on the distribution of biodiesel. When the dosage of DBU was 1% and temperature was 333.1K, the distribution of constituents in product systems were compared with those catalyzed by KOH.<sup>6</sup> The results are presented in Table 4.

From Table 4, one can see the distribution of biodiesel is almost the same in the two processes. However, more glycerol, methanol and catalyst distribute into the biodiesel-rich phase in the DBU catalyzed process compared with the process catalyzed by KOH. Half of excess methanol distributes into the biodiesel-rich phase in process catalyzed by DBU, while only 33.0% of the methanol distributes into the biodiesel-rich phase in the KOH catalyzed process. Almost half of catalyst DBU is in biodiesel-rich phase, while less than 3.0% of KOH catalyst distributes into the biodiesel. At the same time, more than 5.0% of by-product glycerol distributes into the biodiesel when DBU is used as catalyst. It is clear that the presence of DBU improves the inter-solubility of biodiesel, methanol and glycerol. Methanol can be recovered by distillation. DBU in biodiesel-rich phase can react with glycerol or residual methanol by absorbing CO<sub>2</sub> to form ionic compounds to move into glycerol-rich phase. In this way,

the purification of biodiesel and recovery of catalyst can be achieved without water.

### 3.3 Inter-solubility analysis by Van der Waals force and hydrogen bond

The intermolecular interactions among methanol, DBU, glycerol and FAME promote their inter-solubility with different DBU dosages and temperatures. The intermolecular interactions are Van der Waals forces (including dispersion force, orientation force and induction force) and hydrogen bonds. In general, the induction force between molecules is very small,<sup>20</sup> so it is negligible in this system. The intermolecular interactions that present between FAME, methanol, glycerol and DBU are shown as Fig.5.



**Fig.5** Intermolecular interactions that present between FAME, methanol, glycerol and DBU: (1) Hydrogen bond between DBU and methanol; (2) Hydrogen bond between DBU and glycerol; (3) Hydrogen bond between glycerol and methanol.

The dispersion force and orientation force are estimated

**Table 5** Molecular physical parameters of methanol, DBU, glycerol and FAME:  $V_m$ , molecular molar volume;  $R$ , molecular radius

Substance	Polarizability <sup>21</sup> , $10^{-24}\text{cm}^3$	Ionization Energy <sup>21,22</sup> , eV	Dipole moment <sup>21</sup> , D	$V_m$ , $\text{cm}^3/\text{mol}$	$R$ , nm
Methanol	3.25	10.85	1.70	40.56	0.25
Glycerol	8.31	10.11	2.56	73.09	0.31
DBU	~19.00	7.25	0	149.55	0.39
FAME	36.41	8.82	0	345.27	0.52

**Table 6** Values of Van der Waals force and hydrogen bond(“-”indicates negligible items)

Molecules	Van der Waals force ( $\text{kJ mol}^{-1}$ )			Hydrogen bond <sup>20</sup> , ( $\text{kJ mol}^{-1}$ )
	dispersion force	orientation force	induction force	
FAME and DBU	0.70	0	-	0
FAME and methanol	0.40	0	-	0
FAME and glycerol	0.63	0	-	0
FAME and FAME	0.67	0	-	0
DBU and DBU	0.84	0	-	0
DBU and methanol	0.57	0	-	15~50
glycerol and DBU	0.82	0	-	15~50
glycerol and methanol	0.66	In Table 7	-	50~100
glycerol and glycerol	0.89	In Table 7	-	>50

**Table 7** Values of orientation force

Molecules	Orientation force( $\text{kJ mol}^{-1}$ )			
	298.1K±0.1K	308.1K±0.1K	318.1K±0.1K	333.1K±0.1K
glycerol and methanol	0.60	0.58	0.56	0.54
glycerol and glycerol	0.74	0.71	0.69	0.66

according to reference<sup>20</sup> as follows:

$$\text{Dispersion force : } E_d = - \frac{3}{2} \frac{I_1 I_2}{I_1 + I_2} \frac{\alpha_1 \alpha_2}{r^6} \frac{1}{(4\pi\epsilon_0)^2}$$

$$\text{Orientation force : } E_o = - \frac{2}{3} \frac{\mu_1^2 \mu_2^2}{kTr^6} \frac{1}{(4\pi\epsilon_0)^2}$$

Where, the minus sign represents the energy reduction.  $I_1$  and  $I_2$  are ionization energies for components 1 and 2, J.  $\alpha_1$  and  $\alpha_2$  are polarizabilities,  $\text{C} \cdot \text{m}^2/\text{V}$ .  $\mu_1$  and  $\mu_2$  are dipole moments,  $\text{C} \cdot \text{m}$ .  $k$  is Boltzmann constant,  $k=1.38 \times 10^{-23} \text{J K}^{-1}$ .  $T$  is thermodynamic temperature, K.  $r$  is the distance between molecules, approximate to the sum of two molecular radii, m.  $\epsilon_0$  is vacuum permittivity,  $\epsilon_0 = 8.85 \times 10^{-12} \text{F/m}$ .

Table 5 shows the molecular physical parameters of methanol, DBU, glycerol and FAME.<sup>21,22</sup> The intermolecular interactions between methanol, DBU, glycerol and FAME molecules were analyzed and estimated. The results are listed in Table 6 and Table 7.

In Table 5, ionization energies are estimated by group contribution method.<sup>21,22</sup>  $V_m$  is estimated as:  $V_m = M/\rho$ . A molecule is regarded as a ball, so  $R$  is estimated as:  $V_m = 4\pi R^3/3$ .

FAME and DBU are non-polar molecules, however methanol and glycerol are weakly polar molecules. From Table 6 and Table 7, only small dispersion forces ( $0.40 \sim 0.70 \text{kJ mol}^{-1}$ ) exist between FAME and methanol, DBU, and glycerol molecules, as well as within the DBU-DBU pair. However, there are dispersion forces ( $0.57 \text{kJ mol}^{-1}$ ,  $0.82 \text{kJ mol}^{-1}$ ) and hydrogen bonds ( $15 \sim 50 \text{kJ mol}^{-1}$ ) between DBU and methanol or glycerol. There are dispersion forces ( $0.66 \text{kJ mol}^{-1}$ ,  $0.89 \text{kJ mol}^{-1}$ ), orientation forces ( $0.60 \sim 0.54 \text{kJ mol}^{-1}$ ,  $0.74 \sim 0.66 \text{kJ mol}^{-1}$ ) and hydrogen bonds ( $>50 \text{kJ mol}^{-1}$ ) between glycerol and methanol and between the glycerol-glycerol pair.

Due to the presence of hydrogen bonds between DBU or methanol and glycerol, 30%–50% of DBU or methanol distributed in glycerol-rich phase, despite only 1/10 of the mass of biodiesel-rich phase.

For DBU molecules, it is difficult to destroy Van der Waals force and stronger hydrogen bond between glycerol molecules ( $>51.54\text{kJmol}^{-1}$ ), but it is easier to break the intermolecular dispersion forces ( $0.67\text{kJmol}^{-1}$ ) between FAMES and form interactions due to dispersion force. So more DBU distributes in biodiesel-rich phase and the distribution of DBU increases gradually with the increase of dosage of DBU. At the same time, hydrogen bond between DBU and methanol molecules or DBU and glycerol molecules increases gradually with the increase of dosage of DBU. This promoted more methanol and glycerol to transfer into biodiesel-rich phase. Therefore the distributions of methanol, DBU and glycerol in biodiesel-rich phase all increased with the increase of DBU dosage.

When temperature varies and rises from  $298.1\text{K}\pm 0.1\text{K}$  to  $333.1\text{K}\pm 0.1\text{K}$ , orientation force and hydrogen bond changed. Orientation force and hydrogen bond will weaken with the increase of temperature. From Table 7, intermolecular orientation force in glycerol-rich phase decreases with the increase of temperature. As a result, the force balance among molecules is destroyed in biodiesel-rich phase and glycerol-rich phase. So the intermolecular interactions between (methanol, DBU or glycerol) and glycerol decreases, resulting in more distribution of methanol, DBU and glycerol in biodiesel-rich phase. Therefore the distribution of methanol, DBU and glycerol in biodiesel-rich phase increases with the increase of temperature.

The dispersion force is independent of temperature, so the intermolecular interactions between FAME molecules have almost no change with increasing temperature, and the distribution of biodiesel in both phases remains constant.

## 4 Conclusions

The relative solubility of product systems in biodiesel production from *Jatropha Curcas* L. oil with switchable solvent DBU/methanol is important for the separation and recovery operation. Phase equilibrium can provide the basic data and theoretical basis for the process design.

The results show that the mass fraction of components in each phase varies strongly with different DBU dosages, but varies weakly with different temperatures. With the increase of DBU dosage, the purities of biodiesel-rich phase and glycerol-rich phase decrease on the whole, which are 95.28% to 84.30% and 65.85% to 49.81%, respectively.

With the increase of DBU dosage and temperature, the distribution of methanol, DBU and glycerol in biodiesel-rich phase increase, which are 46.78% to 65.49%, 39.43% to 68.53% and 2.02% to 20.90%, respectively. The distribution of biodiesel in both phases varies slightly on the whole. It demonstrates that increase of DBU dosage and temperature can improve the distribution of methanol, DBU and glycerol in biodiesel-rich phase.

## Abbreviations

FAME - fatty acid methyl ester

DBU - 1,8-diazabicyclo-[5.4.0]-undec-7-ene

UV - ultraviolet spectrophotometer

*D*- distribution

I - biodiesel-rich phase

II - glycerol-rich phase

$E_d$  - dispersion force

$E_o$  - orientation force

*I*- ionization energy, J

$\alpha$  - polarizability,  $\text{C}\cdot\text{m}^2/\text{V}$

$\mu$  - dipole moment,  $\text{C}\cdot\text{m}$

*k* - Boltzmann constant,  $1.38\times 10^{-23}\text{J}\cdot\text{K}^{-1}$

*T*- thermodynamic temperature, K

*r*- the distance between molecules, approximate to the sum of two molecular radii, m

$\epsilon_0$  - vacuum permittivity,  $\epsilon_0=8.85\times 10^{-12}\text{F/m}$

$V_m$  - molecular molar volume

*R* - molecular radius

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