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Study of liquid-liquid equilibrium of hydrolyzed palm oil containing triacylglycerol with water and ethanol by NRTL and UNIFAC thermodynamic models

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Abstract

In this work, the liquid-liquid equilibrium (LLE) data for systems containing palm oil or palm oil fractions, short-chain alcohols (ethanol), and water (5% mass fraction in aqueous alcohols), were experimentally determined at temperature 298.15K under atmospheric pressure. Two thermodynamic models (NRTL model and UNIFAC model) were used to correlate the experimental liquid-liquid equilibrium data. The obtained interaction parameters were used to describe the liquid-liquid equilibrium of real systems.

Keywords: Liquid-liquid, equilibrium, hydrolyzed, triacylglycerol, NRTL, UNIFAC

Introduction

Biodiesel, as a new fuel for diesel engines, has aroused increasing attention in recent years. It has many merits, such as renewable, biodegradable and non-toxic. Moreover, biodiesel produces less carbon dioxide or sulfur [1, 2] and it can be used directly in most diesel engines without extensive engine modification. Biodiesel which is defined as fatty acid alkyl esters is commonly produced by transesterification of triacylglycerols from vegetable oils and animal fats with short-chain alcohols in the presence of catalysts [3-5]. Alcohols that are generally used in the transesterification reaction are methanol, ethanol, propanol, butanol and amyl alcohol. In the perspective of economy and environment, methanol and ethanol have more advantages than other short chain alcohols [6]. As for the lipid materials to produce biodiesel, different countries might have different choices, depending on the climate and soil conditions. For example, soybean oil is used in the United States and Brazil as source of biodiesel while rapeseed oil is mainly used in many European countries and palm oil is mainly used in Asian countries [7]. In most cases, the transesterification reactions are conducted at temperatures from (293.15 to 333.15) K [8-11]. The reactants (vegetable oils and alcohols) are generally partially miscible. The mutual solubility between the vegetable oils and alcohols can significantly affect the reaction process [12–15]. In addition, the inclusion of water in the mixed system might greatly influence the reaction rate during the production of biodiesel. Furthermore, the liquid-liquid equilibrium (LLE) data that can adequately describe these multiphase systems are of great importance in theoretical studies as well as in the design and optimization of chemical processes. Therefore, knowledge on the liquid-liquid equilibrium of systems containing vegetable oils + anhydrous alcohols or aqueous alcohols is important for the better design of manufacturing processes of biodiesels. Follegatti-Romero *et al*. have measured binary systems composed of palm olein + anhydrous ethanol at (298.15-333.15) K and palm oil + anhydrous ethanol at (298.15–333.15) K [16]. However, no systematic study about the phase behavior of palm oil and its fractions in alcohols and water systems can be found. In this work, the liquid-liquid equilibrium (LLE) data for systems containing palm oil or palm oil fractions, short-chain alcohols (ethanol), and water (5% mass fraction in aqueous alcohols), were experimentally determined at temperature 298.15K under atmospheric pressure. Two thermodynamic models (NRTL model [17] and UNIFAC model) [18] were used to correlate the experimental liquid-liquid equilibrium data. The obtained interaction parameters were used to describe the liquid-liquid equilibrium of real systems.

Experimental

Liquid-Liquid Equilibria Measurements

Palm oil with different iodine values was kindly supplied by Merck.

The iodine value is 58.2 for refined palm oil. The TAG compositions of palm oil or palm oil fractions were determined according to the AOCS Official Method Ce 5c-93 (AOCS 2009) 160 by using an Agilent HPLC instrument (Agilent HPLC Series 1200, Degasser Model G1322A, Quaternary Pump Model G1311A, RI Detector Model G1362A) by Millipore Corporation. The triacylglycerol was separated on a Merck Lichrosphere 100RP-18Column (250 mm 4.6 mm, particle size 5mm) (Darmstadt, Germany). Methanol and ethanol are analytical grade reagents (the mass fraction purities of them are higher than 0.995). They were obtained from Merck and were used without any further purification. The liquid-liquid equilibrium data for the model systems which contain refined palm oil + ethanol and refined oil + ethanol + water were measured at temperature 298.5K. The mutual solubility data were determined using equilibrium glass cells (30 mL) which have been described by Silva *et al.* [19]. Palm oil/palm oil fractions and solvents (anhydrous alcohols and aqueous alcohols which contain 5 mass % water) at oil/ solvent mass ratio of 1:1 were weighed by an electronic analytical balance (Mettler Toledo ML204, Switzerland) with an uncertainty of 0.0001 g. Then they were added directly into the equilibrium glass cells whose temperature was controlled by a thermostatic bath (Julabo CF41, Germany) with temperature uncertainty of 0.01 K. The mixture was kept at constant temperature under agitation by a magnetic stirrer (HONOUR EMS-9A, China) for about 3 h to make sure that the system reached liquid-liquid equilibrium. Then the agitation was stopped, and the solution was kept static for more than 12 h to allow the formation of two separate transparent liquid phases which have a well-defined interface. Finally, samples were taken separately from the upper and bottom phases by syringes that contain previously weighed masses of hexane to guarantee an immediate dilution of the samples and to avoid their separation into two liquid phases at ambient temperature. The total masses of the samples were weighted. Then the samples were evaporated in a vacuum oven (TAISITE, model DZ-2BC, China) at T = 298.15 K for about 20 h until a constant mass was achieved. Then the masses of the leftovers were weighed again. The total solvent mass (anhydrous alcohol, water, and hexane) could be determined by the mass differences of the two weighing since fatty components could be regarded as non-volatile under this condition. The water contents were determined by the Karl Fischer titration following the AOCS method Ca 23–55 [20] using a KF Titranor (METTLER TOLEDO, V20, Switzerland). The alcohols contents were determined by the difference. The type A standard uncertainty of the equilibrium data are in the range of from 0.0005 to 0.0065 for the fatty components, from 0.0001 to 0.0035 for alcohol and from 0.0003 to 0.0045 for water, respectively. These results indicate that the data presented in this work are reliable.

Theoretical

NRTL and UNIQAC Models

To evaluate the reliability and accuracy of the experimental equilibrium data, the procedure developed by Marcilla *et al.* [21] was used to evaluate the experimental data. According to this approach, with i representing each component of the system, material balances of component i can be written by

$$m^{OC}w_i^{OC} = m^{AP}w_i^{AP} + m^{OP}w_i^{OP} \tag{1}$$

Where m^{OC} is the mass amount of the overall composition (initial mixture); m^{AP} and m^{OP} are the masses of alcohol and oil phases, respectively; $w^{OC}{}_i$ is the mass fraction of component i in the initial mixture; $w^{AP}{}_i$ and $w^{OP}{}_i$ are the mass fractions of component i in the alcoholic and oil phases, respectively. By calculation, the values for m^{AP} and m^{0P} can be determined. Then by comparing the sum of them with the actual value of total mass used in the experiments (m^{OC}), a relative deviation for the mixture can be obtained and expressed as

$$\delta = \frac{|(m^{AP} + m^{OP}) - m^{OC}|}{m^{OC}} \tag{2}$$

NRTL thermodynamic model

The NRTL (nonrandom, two-liquid) model which was developed by Renon and Prausnitz [22] is applicable to partially miscible systems [23-25]. This equation was originally formulated in molar fraction. Because of the large difference in molar masses between vegetable oils, alcohols and water, mass fractions were also used as unity of concentration in previous investigations [26]. Thus, on the basis of mass fractions, the NRTL model for multicomponent mixtures can be expressed as follows:

$$\ln\gamma_i^w = \left(\frac{\sum_j^K(\tau_{ji}G_{ji}w_j/\overline{M}_j)}{\sum_j^K(G_{ji}w_j/\overline{M}_j)} + \sum_{j=1}^{K}\left[\frac{w_jG_{ij}}{\overline{M}_j\sum_{k=1}^K(G_{kj}w_k/\overline{M}_k)}\left(\tau_{ij} - \frac{\sum_{k=1}^K(\tau_{kj}G_{kj}w_k/\overline{M}_k)}{\sum_{k=1}^K(G_{kj}w_k/\overline{M}_k)}\right)\right]\right)/\overline{M}_i(\sum_{j=1}^{K} w_j/\overline{M}_j)) \tag{3}$$

Where

$$\tau_{ij} = \frac{(g_{ij} - g_{jj})}{RT} \qquad \tau_{ji} = \frac{(g_{ji}) - g_{ii}}{RT}$$

$$\frac{(g_{ij} - g_{jj})}{R} = A_{0,ij} + A_{1,ij}T \qquad \frac{(g_{ji} - g_{ii})}{R} = A_{0,ji} + A_{1,ji}T$$

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \quad G_{ji} = \exp(-\alpha_{ji}\tau_{ji}) \quad \alpha_{ij} = \alpha_{ji}$$

where $\gamma^w{}_i$ represents the corresponding activity coefficient of component i expressed on the mass fraction; M_j and w_j represent the average molar mass and the mass fraction of the pseudocomponents j, respectively; T represents the absolute temperature; $A_{0,ij}$, $A_{0,ji}$, $A_{1,ij}$, and $A_{1,ji}$ represent the temperature-dependent characteristic molecular energy parameters of the interactions between components i and j; G_{ij} is a Boltzmann-type expression for the local composition energy interactions between components i and j. α_{ij} is the non-randomness parameter of the mixture. The value of α_{ij} generally varies from 0.2 to 0.47 [22]. In this work, α_{ij} = 0.3 was used for the correlation of liquid–liquid equilibrium data. Thus, in this work, there are four adjustable parameters for each pair of substances [27-28]. These parameters can be estimated with experimental data by using the procedure below. For the parameter estimation, it can be assumed that different triacylglycerols in palm oil behave in a similar way in the investigated model systems [29]. Thus, palm oil was assumed to be composed of a single triacylglycerol with an average molar mass. Finally, on the basis of this hypothesis, the model systems of palm oil or palm oil fractions + alcohols can be treated as pseudobinary systems and the model systems of palm oil or palm oil fractions + alcohols + water can be treated as pseudo-ternary systems. The interaction parameters estimation was based on the minimization of the objective function of the composition using the modified simplex method developed by Stragevitch and d'Avila [30].

$$OF(w) = \sum_{m=1}^{D}\sum_{n=1}^{N}\sum_{i=1}^{K-1}\left[\left(\frac{w_{i,n,m}^{AP,exp} - w_{i,n,m}^{AP,calc}}{\sigma_{w_{i,n,m}^{AP}}}\right)^2 + \left(\frac{w_{i,n,m}^{OP,exp} - w_{i,n,m}^{OP,calc}}{\sigma_{w_{i,n,m}^{OP}}}\right)^2\right] \qquad (4)$$

where D represents the total number of data groups; N is the total number of tie lines of the corresponding system, and K is the total number of compounds or pseudo-compounds in the group of data m; w represents the mass fraction; $\sigma_{wAP\ i;n;m}$ and $\sigma_{wOP\ i;n;m}$ are the standard deviations observed in the compositions of the two liquid phases. The average deviations (Δw) between experimental and calculated compositions for each system was calculated according to Eq. (5):

$$\Delta w = \sqrt{\frac{\sum_{n}^{N}\sum_{i}^{K}\left[\left(w_{i,n}^{AP,exp} - w_{i,n}^{AP,calc}\right)^2 + \left(w_{i,n}^{OP,exp} - w_{i,n}^{OP,calc}\right)^2\right]}{2NK}} \qquad (5)$$

UNIFAC thermodynamic model In NRTL model, the equilibrium data were correlated for palm oil and they are represented in terms of mass fractions of pseudocomponents. However, this approach does not take into account the differing partition behavior of specific TAGs. Thus, to obtain a more meaningful predictive tool, it is necessary to consider the true characteristics of these mixtures. The UNIFAC thermodynamic model which was developed by Fredenslund *et al.* [31] and then modified by many other researchers [32-35] was widely used to predict the vapor–liquid and liquid–liquid equilibrium of multicomponent mixtures. In this work, the original UNIFAC model was used since different versions of UNIFAC model seem to provide almost the same predictive results for fatty systems [36-39]. According to UNIFAC model, the activity coefficient of component i in a multicomponent mixture can be expressed as:

$$\ln\gamma_i = \ln\gamma_i^C + \ln\gamma_i^R \qquad (6)$$

Where superscripts C and R denote combinatorial part and residual part of the activity coefficient, respectively. The combinatorial part can be given by:

$$\ln r_i^C = \ln\left(\frac{\phi_i}{x_i}\right) + \frac{z}{2}q_i\ln\frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i}\sum_j x_j l_j \qquad (7)$$

Where,

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j}\ \phi_i = \frac{r_i x_i}{\sum_j r_j x_j}$$

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1)$$

Where z is the lattice coordination number and was assumed to be equal to 10. Pure-component parameters r_i and q_i are measures of molecular van der Waals volumes and molecular surface areas respectively, which can be calculated as the sum of the group volume and area parameters R_k and Q_k:

$$r_i = \sum_k v_k^{(i)} R_k q_i = \sum_k v_k^{(i)} Q_k \qquad (8)$$

Where $v_k^{(i)}$, always an integer, denotes the number of times that groups k appears in molecule i; group volume and surface area parameters R_k and Q_k are obtained from Hansen's parameters [32] because they are very effective for LLE. Moreover, a new group division ($CH_{5/3}$) which was proposed by Hirata *et al.* [39] in liquid–liquid equilibrium of fatty systems has also been used in order to simplify the description of the triacylglycerols. The values of volume (R_k) and surface area (Q_k) were obtained by linear interpolation of the corresponding values for groups CH, CH2, CH3 and CH4.
The residual part of the activity coefficient is given by:

$$\ln\gamma_i^R = \sum_k^G v_k^{(i)}\left(\ln\Gamma_k - \ln\Gamma_k^{(i)}\right) \qquad (9)$$

Where Γ_k is the group residual activity coefficient and $\Gamma_k^{(i)}$ is the residual activity coefficient of group k in a reference solution containing only molecules of type i

$$\ln\Gamma_k = M_k Q_k\left[1 - \ln\left(\sum_m \Theta_m \Psi_{mk}\right) - \sum_m\left(\frac{\Theta_m \Psi_{km}}{\sum_m}\Theta_m \Psi_{mk}\right)\right] \qquad (10)$$

Where Θ_m is the area fraction of group m; Ψ_m is the group interaction parameter. They can be calculated by the following equations:

$$\Theta_m = \frac{Q_m X_m}{\sum_G^n Q_n X_n} \quad \Psi_{mn} = \exp\left(-\frac{U_{mn} - U_{nn}}{RT}\right) = \exp\left(-\frac{a_{mn}}{T}\right) \qquad (11)$$

Where X_m is the mole fraction of group m in the mixture; U_{mn} is a measure of the energy of interaction between Groups m and n. The group interaction parameters α_{mn} used in this study are obtained from the literature[40]except the group $CH_{5/3}$ which was acquired by further appropriate deduction. The average deviations between the experimental and calculated equilibrium compositions by the UNIFAC model were also calculated according to eq. (5).

Results and Discussion

TAG compositions of palm oil and palm oil fractions are given in table 1. With the help of these data average molecular mass of the palm oil was calculated [41] which was 821.7 g.mol^{-1}. For the pseudobinary (ethanol as solvent) and pseudoternary (aqueous ethanol containing 5 masses% of water as solvent) model systems, the overall experimental compositions and the phase compositions in the alcoholic and the oil phases at temperature 298.15K are presented in table 2 and 3 respectively.
From the experimental result, the overall mass balance deviations calculated by eq. (2) were lower than 0.55%. This indicates good reproducibility of the experimental data. The

experimental mutual solubility data for which are composed of refined palm oil and anhydrous/ aqueous ethanol are shown in fig. 1.

It can be concluded that the inclusion of water in the solvent extends the phase splitting region and decreases the mutual solubility between oil and alcohol, which will consequently impact the reaction process in biodiesel production. NRTL model was used to correlate the experimental data and table 4 presents the corresponding temperature-dependent parameters of the systems under investigation. The average deviations between experimental and calculated compositions in both phases (Eq. (11)) which are listed in Table 5 are lower than 0.85%. The correlated equilibrium data by NRTL equation are also given in fig. 1.

It can be found that the differences between the calculated data and experimental data are very small. These results indicate that the NRTL model can accurately describe the liquid–liquid equilibrium (LLE) for these investigated systems. For each alcoholic system (oil + ethanol), the critical solution temperature was determined using flash calculations[42] with the same parameters presented in table 4. The results indicate that the mutual solubility of oils and anhydrous ethanol increases steadily until the critical temperature is reached. As shown in fig. 1, for systems which are composed of oil and anhydrous ethanol, the critical temperature which is represented by the symbol X are 337.1 K for refined palm oil. Moreover, to obtain a predictive model which considers the true characteristics of these specific TAGs, the UNIFAC thermodynamic model was also used to predict the experimental liquid–liquid equilibrium of the investigated systems. Model parameters obtained from literatures[43-44] were used in the prediction of the LLE of the investigated ternary systems (table 6).

Despite the improvement in the practicality by introducing a new group division (CH5/ 3), the UNIFAC model showed higher deviation than the NRTL model for all the investigated systems (table 5). It means that the chosen binary parameters for UNIFIAC model might not be ideal for predicting the LLE of the investigated systems. The results presented demonstrate that the estimated parameters of the NRTL model can be used to predict liquid-liquid equilibrium of the investigated systems satisfactorily.

Table 1: Triacylglycerol composition of palm oil and palm oil fractions

Main TAG	**Mg mol^{-1}**	**Refined Palm Oil**	
		100x^{a}	**100w^{b}**
LLL	639.1	1.216	0.951
LnLL	719.3	0.3896	0.3428
LnLnL	799.4	0.2827	0.2764
MLP	723.2	1.037	0.9178
OLL	721.3	0.8898	0.7851
OLO	803.5	2.239	2.2
OOO	885.6	4.307	4.666
PLL	695.3	3.744	3.184
PLLn	775.4	0.6295	0.5971
PLO	777.4	11.62	11.05
PLP	751.4	12.16	11.17
POO	859.6	23.67	24.89
POP	833.5	27.72	28.26
POS	861.6	5.341	5.628
SOO	887.6	3.198	3.472
SOS	887.6	0.224	0.2432
PPS	835.6	1.309	1.338
PPP	807.5	0.1174	0.12

Table 2: Experimental liquid-liquid equilibrium data for Binary System of Anhydrous Ethanol + Refined Palm Oil at T = 298.15K

Oil	**Overall Composition**		**Alcoholic Phase**		**Oil Phase**	
	100w^{b}_{o}	**100w_a**	**100w^{a}_{o}**	**100w_a**	**100w_o**	**100w_a**
Ethanol + Refined Palm Oil	50	50	7.23	92.77	85.5	14.5

*b w_o is oils mass fraction, w_a is alcohol mass fraction.

Table 3: Experimental liquid-liquid equilibrium data for Ternary System of Ethanol + Water + Refined Palm Oil at T = 298.15K

Oil	**Overall Composition**			**Alcoholic Phase**			**Oil Phase**		
	100w^{c}_{o}	**100w_a**	**100w_w**	**100w_o**	**100w_a**	**100w_w**	**100w_o**	**100w_a**	**100w_w**
Ethanol + water +Refined Palm Oil	50	47.5	2.5	1.32	93.86	4.82	92.78	6.8	0.42

*c w_o is oils mass fraction, w_a is alcohol mass fraction, w_w is water mass fraction.

Table 4: Temperature Dependent NRTL Parameters

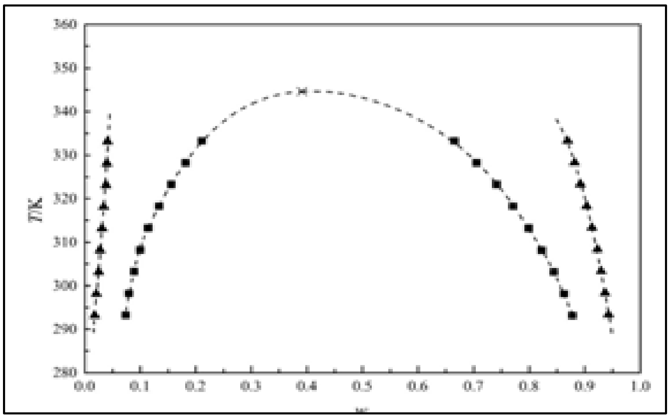
Pair ij	**$A_{0\,ij}$/K**	**$A_{0\,ji}$/K**	**$A_{1\,ij}$**	**$A_{1\,ji}$**
Refined palm oil(i) + anhydrous ethanol (j)	3196	-5115	-12.4	20.64
Refined palm oil(i) + water(j)	3798	-40.9	-9025	1.232

Table 5: Average deviations between experimental and calculated phase compositions of the investigated systems

Systems	**100Δw**	
	NRTL	**UNIFAC**
Refined palm oil + anhydrous ethanol	0.3583	2.659
Refined palm oil + water	0.8403	3.3

Table 6: UNIFAC structural molecular groups

Sub-groups	**Volume(R_k)**	**Surface area (Q_k)**
CH_3^{a}	0.9011	0.8480
CH_2^{a}	0.6744	0.5400
$CH_{5/3}^{b}$	0.5983	0.4520
OH^{a}	1.000	1.200
$CH{=}CH^{a}$	1.117	0.8670
CH_2COO^{a}	1.676	1.420
H_2O^{a}	0.9200	1.400



*a ref. 45 *b this work

Fig 1: Experimental and correlated Liquid-liquid equilibrium for the systems which are composed of palm oil and (■) anhydrous ethanol, and (Δ) aqueous ethanol; The abscissa axis represents the mass fraction of oil and the dashed lines are calculated values by using the NRTL model; X is the extrapolated critical solution temperature.

Conclusion

This work presented the liquid-liquid equilibrium (LLE) data for systems containing palm oil or palm oil fractions, short-chain alcohols (Ethanol,) and water (5% mass fraction in aqueous alcohols), were physiochemical and experimentally analyzed at temperature 25.15°C (298.15K) under atmospheric pressure. In this article, two thermodynamic models (NRTL model and UNIFAC model) were used to correlate the experimental liquid-liquid equilibrium separation. These parameters enabled the prediction of liquid-liquid equilibrium and the obtained interaction parameters were used to describe the liquid-liquid equilibrium of real systems.

The thermodynamically models enables the investigation and analysis of different scenarios and allow communication with packages. The results obtained in the present work might be valuable for process development, phase separation, and optimization related to DAG-enrichment oil processes.

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