Liquid + Liquid Equilibria of the Ternary System Water + Glycerol + 1-Butanol System: Experimental Data and Modeling

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ABSTRACT: *In this study, solubility and tie-line data of ternary system water + glycerol + 1-butanol were determined at 293.2, 298.2, and 303.2 K and atmospheric pressure. This thermodynamic system is relevant for the production and purification of biofuels. Phase equilibrium data have been determined by the cloud-point titration method and the tie-lines were obtained by correlating the refractive index of the binodal curves as a function of mixture composition. All measured LLE data were modeled by UNIQUAC and NRTL activity coefficient equations obtaining a satisfactory accuracy with modeling errors lower than 0.4%. Binary interaction parameters of tested thermodynamic models were estimated to predict the value of tie lines using a hybrid bio-inspired swarm intelligence optimization algorithm, that is, MAKHA without and with closure equation. This hybrid method was reliable to solve the global optimization problem for the binary interaction parameter identification of this ternary system. The results of this paper provide useful information for the design and modeling of industrial units for glycerol recovery, which is a relevant industrial feedstock.*

KEYWORDS: *Liquid-liquid equilibria; Glycerol; MAKHA; Closure equation; Hybrid algorithm.*

INTRODUCTION

Glycerol is a versatile compound that has a variety of industrial applications due to its physicochemical properties. In the food and beverages industry, this chemical serves as a humectant and it can be used as a sweetener in drinks or solvent for food coloring, is an important moistening agent for baked goods, and can be also added to freezing and confectioners to avoid sugar crystallization and to liquors as a congealing agent. It is a food additive with the designated E number E422 [1-3]. Additionally, the glycerol is also a feedstock in pharmaceuticals and
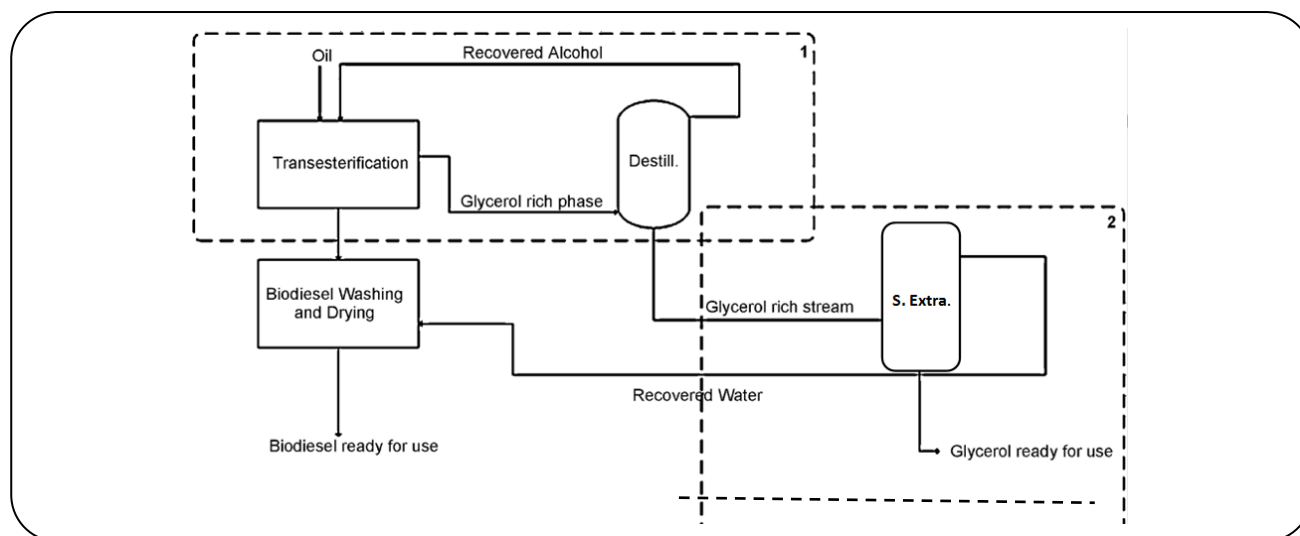
Fig. 1: Biodiesel production simplified flowsheet.

cosmetics. It very well may be found in toothpaste, healthy skin items, shaving cream, and mouthwash. As an improving specialist, it is some of the time added to pharmaceuticals and is additionally used as a tablet-covering operator. Glycerol also finds different applications as a levigating agent for drugs and it has been used to reduce the particle size of drug powders [2, 5]. Recently, the study of thermodynamic properties of glycerol-based systems has increased due to its presence during the production and purification of biofuels [6,7]. In addition, fats and oils are valuable sources for different industrial processes due mainly to their content of carboxylic acids which are combined with glycerol in the form of esters (see Fig. 1(1)). Glycerol remains as a solution in water when the acids are set free from these compounds and its recovery can be performed using solvent extraction, coagulating, or evaporating the water (see Fig.1(2)). The accurate knowledge of the LLE of water + glycerol + 1-butanol mixture is thus essential for the design of the separation process of the glycerol recovery section [8].

Solvent extraction is an ecologically friendly method for glycerol recovery that requires less energy and products lower contamination than other separation techniques. Be that as it may, the determination of the extraction specialist is the principal issue for this separation method [9]. The performance of the glycerol extraction process depends on the thermodynamic properties of the systems to be analyzed. For example, the extraction of glycerol from aqueous solutions resulting

from the biodiesel production process is industrially important [10] and its operating conditions may vary substantially with respect to other multi-component mixtures that also contain glycerol. Hence, the data and size to define the phase equilibrium performance of systems composed of glycerol are significant for a suitable process enterprise and action for both food technology and purification services involved in biofuel production among other industrial applications [11]. Until now, a few investigations on ternary LLE data involving water + glycerol + solvent. *Chen, H et al.* [12] studied the use of inorganic salts to measure the LLE data of water + glycerol + 2-butanol. The introduction of dissolved salts promoted an increase in glycerol selectivity. However, more experimental data are required to design cost-effective extractions processes for glycerol recovery.

The objective of the presented work was to determine experimental data of liquid-liquid equilibria of the ternary system water + glycerol + 1-butanol, which is of attention for the making of biodiesel. Especially, phase equilibrium data were obtained at 293.2, 298.2, and 303.2K. Distribution coefficients and separation factors were determined to analyze the feasibility of 1-butanol as a solvent for the separation of the mixture of water + glycerol in tested operating situations. The experimental tie-line data were assessed by the Othmer–Tobias [13] and the Hand [14] correlation equations. Experimental tie-line data were modeled with the NRTL (Non-Random Two Liquid) [15,16] and the UNIQUAC (UNI versal Quasi Chemical) models [16,17]. Binary interaction parameters

Table 1. Refractive index(n_D), Supplier and Mass Fraction Purity of compounds used in this work[a].

Compound	Refractive index, n_D						Purity[b]	Supplier
	Experimental			Literature				
	293K	298K	303K	293K	298K	303K		
Water	1.3333	1.3323	1.3320	1.3333[20]	1.3325[20]	1.3319[20]	-	-
Glycerol	1.4732	1.4728	1.4708	1.4746[21]	1.4730[21]	1.4710[22]	≥ 0.99	Merck
1-butanol	1.3994	1.3972	1.3951	1.3993[20]	1.3974[21]	1.3954[22]	≥ 0.99	Merck

a) Standard uncertainties u are: u(T) = ±0.1 K; u(nD) = ± 0.0007. b)Purity stated by the manufacturer.

of these thermodynamic models were obtained using the hybrid optimization algorithm MAKHA [18,19] with and without the use of conclusion conditions and the determined syntheses were contrasted and the test ones. In summary, the results of this paper provide useful information for the design and modeling of industrial units for glycerol recovery. The rest of this paper has been planned as follows. Parts 2 and 3 present the experimental procedure for determining phase equilibrium data and the approach used for phase equilibrium data processing and parameter determination of thermodynamic models, respectively. Analysis and discussion of results are presented in part 4, while part 5 reviews the conclusions.

EXPERIMENTAL SECTION
Materials

The organic reagents glycerol and 1-butanol were provided by Merck. The purity of these synthetic substances was estimated by the Abbe refractometer and found to run from 99.2 to 99.8%. The source, purity grade, and refractive index of the pure components are summarized in Table 1. There is a good agreement with the literature data [20-22].

The refractive indexes of the components were measured with an Abbe refractometer (AR4 Kruss, Germany). The standard uncertainty in refractive index measurements was 0.0007.

Apparatus and procedure for liquid-liquid equilibrium measurements

The binodal curve and tie-lines data were determined using the cloud point method [23, 24] at T= (293.15, 298.15, and 303.15K). The measurements were made in a glass equilibrium thermostated cell equipped with a magnetic stirrer. The cell temperature was measured with a mercury-in-glass thermometer with an estimated uncertainty of ± 0.1 K. A homogeneous and transparent

mixture of glycerol + water with known composition was prepared in a glass equilibrium cell at a constant temperature. The mixture was made by mass using a Sartorius analytical balance (Model Nahita YP402N, accurate to ±0.0001 g). Then, 1-butanol was progressively added to the mixture using a micro-burette. The cloud point was determined by observing the transition from a homogeneous to a heterogeneous mixture as indicated by the mixture turbidity. This approach was used for obtaining the water-rich side of the curves. On the other hand, the experimental data for the solvent-rich side of the curves were determined by titrating the homogeneous mixture of glycerol + 1-butanol with water until obtaining the mixture was turbidity. Composition determinations were accurate to ± 0.0015 mass fraction using this procedure.

The tie-line data for experimental results were determined by using a glass cell with a volume of 200 cm³and equipped with a thermostatically controlled water jacket. A variety of mixtures within the heterogeneous gap was prepared for the ternary mixture glycerol + 1-butanol + water at tested temperatures. The cell was loaded up with every one of these blends and vivaciously mixed for 3 h. After the stirrer was killed, the substances were quickly brought into the partition pipe. After the stirrer was turned off, the contents were immediately introduced into the separation funnel. After complete separation of the phases, a suitable amount of each layer was removed for analysis. Samples of both phases were collected and the tie-line values were calculated by measuring the refractive index. Proper calibration curves were used for these quantifications. This experimental procedure was conducted at 293.15, 298.15 and 303.15 K. Figure 2 shows the relationships between the mass fraction of water and glycerol in both phases and the refractive index of samples, typically at 298.15 K. For other temperatures, similar trends were appropriate (see the Supporting Information, i.e. Fig. S.1 and S.2).
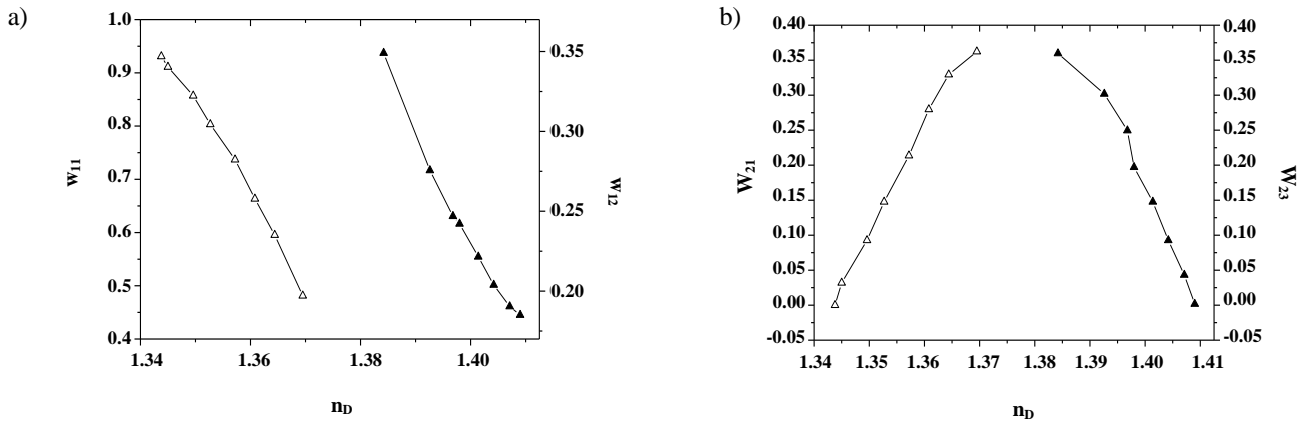
a)

b)

Fig. 2: Dependency of the solute mass fraction on the refractive index of cloudy solutions at 298.15K, (a) for water, and (b) for glycerol.
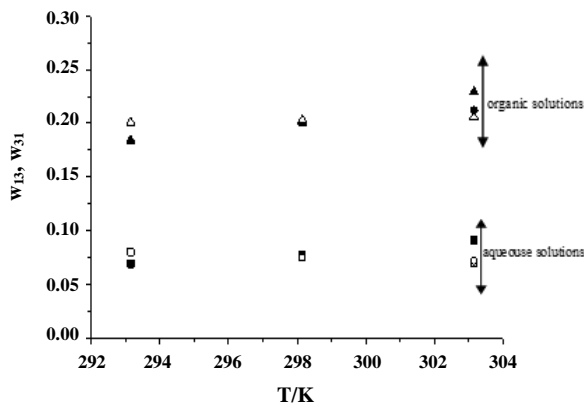

Fig. 3: Comparison of the mass fractions of 1-butanol in water solution (w_{31}) and water in 1-butanol solution (w_{13}); with the corresponding literature data[26, 27] ($\triangle$, $\square$ and, $\bullet$, $\bigcirc$, respectively).

In order to determine the solubilities of water and 1-butanol, a synthetic method has been applied. In this regard, the cloud-point technique was used as described in previous works [25]. Figure 3 shows a comparison between observed LLE data in this paper with those reported in the literature [26] without the glycerol. In general, the difference between these LLE data values is due to different dominant conditions (e.g., analysis method, purity of chemical reagents and ambient pressure).

THEORETICAL SECTION
Data consistency of phase equilibrium data

Othmer-Tobias and Hand equations [13,14] were applied to assess the thermodynamic reliability of tie-line experimental data of the tested ternary system. These models are defined as

$$\ln\left(\frac{1 - w_{33}}{w_{33}}\right) = A + B \ln\left(\frac{1 - w_{11}}{w_{11}}\right) \tag{1}$$

$$\ln\left(\frac{w_{21}}{w_{11}}\right) = A' + B' \ln\left(\frac{w_{23}}{w_{33}}\right) \tag{2}$$

Where w_{11}, w_{21} are mass fractions of water and glycerol in the aqueous phase; w_{23} and w_{33} are mass fractions of glycerol and 1-butanol in the organic phase. A linear regression of these models was performed where the adjustment indicates the grade of reliability of experimental data.

Calculation of distribution coefficients and separations factors

Data from experimental phase equilibria were used to calculate the distribution coefficients (D) and separation factors (S) for the ternary system glycerol + 1-butanol + water. These thermodynamic parameters were calculated by the following equation [28]:

$$D_i = \frac{w_{i3}}{w_{i1}} \tag{3}$$

Where, w_{i1} and w_{i3} are the mass fractions of the ith component in the aqueous phase and organic rich phase, respectively.

$$S = \frac{D_2}{D_1} \tag{4}$$

Where D_1 and D_2 are the distribution coefficients of water and glycerol, respectively.

Phase equilibrium data modeling

NRTL and UNIQUAC activity coefficient models were applied to the correlation of the experimental liquid-liquid equilibrium data. The activity coefficient of component i obtained from the UNIQUAC model can be expressed as follows

$$\ln \gamma_i = \ln \frac{\varphi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\varphi_i} + l_i - \frac{\varphi_i}{x_i} \sum_{j=1}^{n} x_j l_j + \tag{5}$$

$$q_i \left[1 - \ln \left(\sum_{j=1}^{n} \theta_j \tau_{ji} \right) - \sum_{j=1}^{n} \frac{\theta_j \tau_{ij}}{\sum_{k=1}^{n} \theta_k \tau_{kj}} \right]$$

where

$$\theta_i = \frac{q_i x_i}{q_T}, \quad q_T = \sum_{k=1}^{n} q_k x_k, \quad \varphi_i = \frac{r_i x_i}{r_T}, \quad r_T = \sum_{k=1}^{n} r_k x_k \tag{6}$$

$$l_i = \frac{z}{2} (r_k - q_k) + 1 - r_k \tag{7}$$

$$\tau_{ij} = exp \left(-\frac{A_{ij}}{T} \right) \tag{8}$$

Note that the coordination number was defined as z=10, while the values of r and q used for phase equilibrium calculations are listed in Table 2. On the other hand, the activity coefficient of component i using the NRTL model is presented as:

$$\ln \gamma_i = \frac{\sum_{j=1}^{n} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{n} G_{ki} x_k} + \sum_{j=1}^{n} \frac{x_j G_{ij}}{\sum_{k=1}^{n} G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_{i=1}^{n} x_i \tau_{ij} G_{ij}}{\sum_{k=1}^{n} G_{kj} x_k} \right) \tag{9}$$

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{R.T} = \frac{A_{ji}}{T} \tag{10}$$

$$G_{ji} = exp \left(-\alpha_{ji} \tau_{ji} \right) \tag{11}$$

Where $\alpha_{ji} = \alpha_{ji} = 0.3$. Ternary liquid-liquid equilibrium experimental data were applied to obtain the ideal binary interaction parameters between water, glycerol, and 1-butanol for NRTL and UNIQUAC equations.

Thermodynamics models were adjusted to experimental data by an iterative PC program dependent on the blend of the Newton-Raphson strategy and a hybrid swarm intelligence metaheuristic namely MAKHA [18, 19]. The objective

Table 2: The UNIQUAC structural parameters r and q [available within the HYSYS® database].

Component	r	q
water	0.9200	1.3997
glycerol	4.7957	4.9080
1-butanol	3.4542	3.0520

function for the binary parameter documentation of NRTL and UNIQUAC models was defined in terms of the experimental and calculated values of tie-lines for the ternary system glycerol + 1-butanol + water

$$min \, F = \sum_{k=1}^{M} \sum_{j=1}^{2} \sum_{i=1}^{c} fp_{ijk} (w_{ijk}^{cal} - w_{ijk}^{exp})^2 \tag{12}$$

Where M is the number of experimental tie-lines used in data fitting, w^{exp} and w^{cal} are the experimental and calculated mass fractions and the subscripts i, j, and k correspond to the component, phase, and tie-line, respectively; while fp_{ijk} is the weight factors associated with the experimental points that were used in data correlation.

Experimental data fitting was performed via the global minimization of Eq.(12) with unit weights fp_{ijkm}. The minimization of this objective function was done using the binary interaction parameters as decision (i.e., optimization) variables where MAKHA was the optimization tool. MAKHA [18,19] is a stochastic method that combines the intensification and diversification stages of the Monkey Algorithm (MA) and the Krill Herd Algorithm (KHA). This hybrid algorithm includes the following procedures: 1) the watch-hop process, 2) the searching action process, 3) the physical arbitrary dissemination process, 4) the hereditary transformation and hybrid procedure and 5) the somersault procedure.

For the sake of brevity, Fig. *S*.3 shows the pseudo-code of this optimization method where the details of its numerical implementation can be found in references [18,19].

Data processing of liquid-liquid equilibrium of the ternary system was performed using MAKHA with the algorithm parameters reported in [18,19]. For each set of the binary interaction parameters proposed by MAKHA, the Newton-Raphson method has used the determination of the tie-lines with the corresponding activity coefficient model. In particular, the flash formulation was solved with this local method where the experimental phase equilibrium compositions were used as initial guesses. Fig. 4 shows
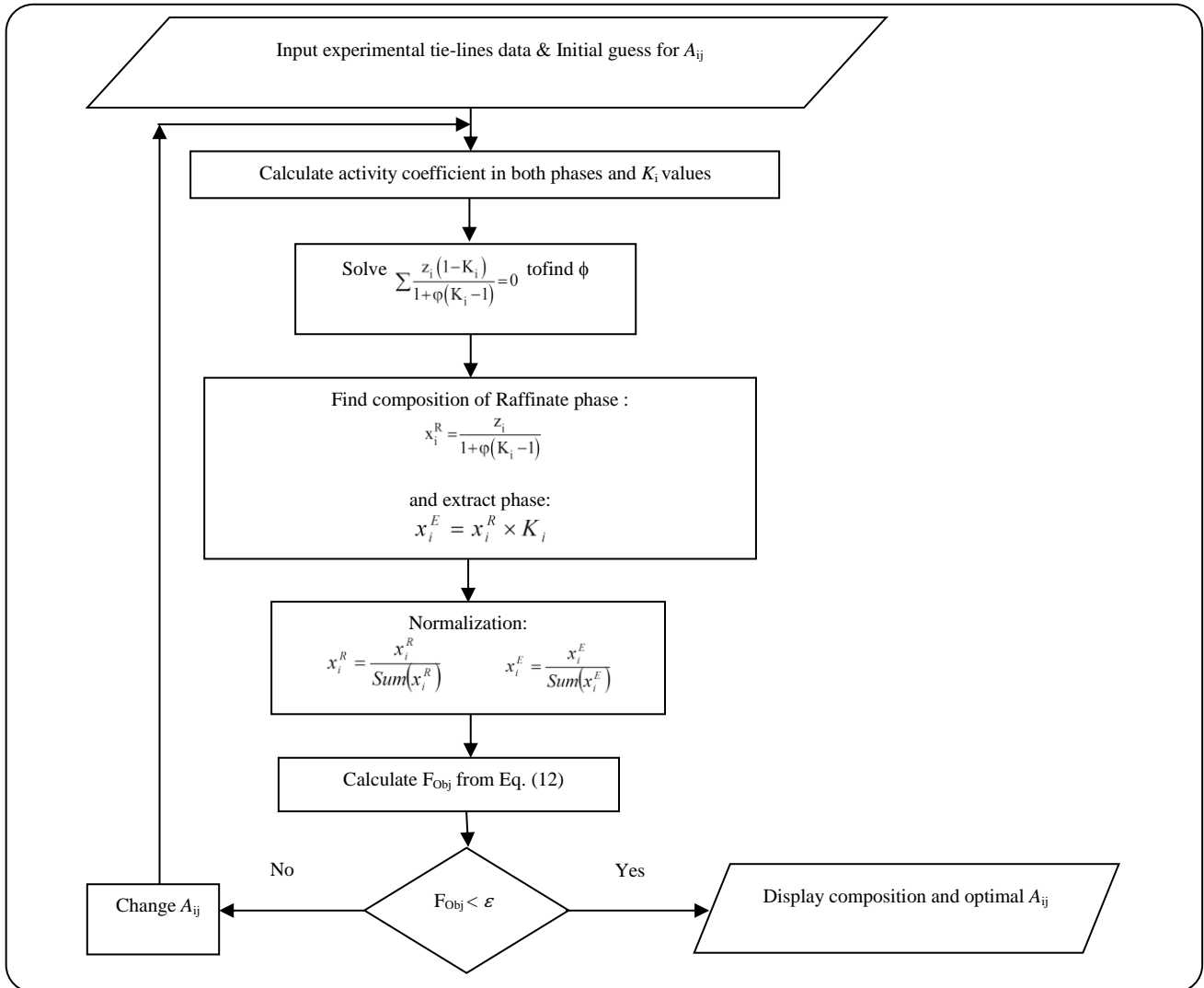
Input experimental tie-lines data & Initial guess for A_{ij}

Calculate activity coefficient in both phases and K_i values

Solve $\sum \dfrac{z_i(1-K_i)}{1+\varphi(K_i-1)}=0$ to find ϕ

Find composition of Raffinate phase :
$$x_i^R = \frac{z_i}{1+\varphi(K_i-1)}$$

and extract phase:
$$x_i^E = x_i^R \times K_i$$

Normalization:
$$x_i^R = \frac{x_i^R}{Sum(x_i^R)} \qquad x_i^E = \frac{x_i^E}{Sum(x_i^E)}$$

Calculate F_{Obj} from Eq. (12)

No — Change A_{ij}

$F_{Obj} < \varepsilon$

Yes — Display composition and optimal A_{ij}

Fig. 4: Flowchart of the approach used for parameter identification of tested thermodynamic models.

flowchart of the approach used in the parameter identification of tested thermodynamic models. Additionally, the performance of MAKHA has been checked presence and absence of the application of closure equations [11]. These equations describe a linear relationship among the binary interaction parameters of limited composition models for multicomponent mixtures and may be defined as follows for ternary systems:

$$A_{12} - A_{21} + A_{23} - A_{32} + A_{31} - A_{13} = 0 \tag{13}$$

Equation (13) demonstrates that lone five out of binary interaction parameters are free and, therefore, the minimization of Eq.(12) can be performed by choosing a lot of five choice factors A_{ij} and utilizing Eq.(13) for deciding the staying one.

The Root-Mean-square Deviation (RMSD) has been employed to determine the interest among the experimental and calculated values with both NRTL and UNIQUAC models after identifying the best binary interaction parameters. RMSD value was defined as [29,30]

$$RMSD = \left(\frac{F_{Obj}}{\pi \times N_c \times N_p} \right)^{0.5} \tag{14}$$

Where, π, N_C, and N_p are the number of phases, components, and tie-lines, respectively. The values of RMSD of both NRTL and UNIQUAC were compared and analyzed.

Table 3: Experimental data of binodal curve in mass fraction for the system water
(1)+ glycerol(2)+ 1-butanol(3)at 293.15, 298.15 and 303.15 K and 1 atm [a].

T, K	w_1	w_2	w_3	n_D
293.15	0.9308	0.0000	0.0692	1.3438
	0.9111	0.0319	0.0570	1.3450
	0.8569	0.0926	0.0505	1.3496
	0.8033	0.1477	0.0490	1.3527
	0.7369	0.2137	0.0494	1.3572
	0.6634	0.2797	0.0569	1.3608
	0.5954	0.3295	0.0751	1.3644
	0.4813	0.3623	0.1564	1.3695
	0.3491	0.3597	0.2912	1.3842
	0.2756	0.3019	0.4225	1.3926
	0.2469	0.2495	0.5036	1.3968
	0.2421	0.1971	0.5608	1.3980
	0.2215	0.1477	0.6308	1.4014
	0.2039	0.0926	0.7035	1.4042
	0.1904	0.0432	0.7664	1.4071
	0.1850	0.0017	0.8133	1.4090
	0.1842	0.0000	0.8158	1.4092
298.15	0.9220	0.0000	0.0780	1.3408
	0.8338	0.0910	0.0752	1.3439
	0.7445	0.1797	0.0758	1.3483
	0.6587	0.2522	0.0891	1.3517
	0.5269	0.3224	0.1507	1.3568
	0.3970	0.3171	0.2859	1.3771
	0.3120	0.2937	0.3943	1.3839
	0.2820	0.2550	0.4630	1.3871
	0.2402	0.1406	0.6192	1.3908
	0.1993	0.0290	0.7717	1.3961
	0.2010	0.0000	0.7990	1.3971
303.15	0.9088	0.0000	0.0912	1.3403
	0.8846	0.0183	0.0971	1.3409
	0.8423	0.0651	0.0926	1.3428
	0.7960	0.1145	0.0895	1.3440
	0.7424	0.1643	0.0933	1.3465
	0.6756	0.2220	0.1024	1.3495
	0.5934	0.2715	0.1351	1.3520
	0.3215	0.2578	0.4207	1.3783
	0.3000	0.2054	0.4946	1.3806
	0.2777	0.1450	0.5773	1.3831
	0.2620	0.0953	0.6427	1.3850
	0.2528	0.0568	0.6904	1.3864
	0.2398	0.0157	0.7445	1.3880
	0.2375	0.0000	0.7625	1.3885

[a] Standard uncertainties u are: u(T) = ±0.1 K; u(w) = ±0.0015, u(n_D) = ± 0.0007.

RESULTS AND DISCUSSION
Experimental binodal curves and tie-lines

The equilibrium compositions on the binodal curve of the system water (1) + glycerol (2) + 1-butanol (3) at tested temperatures are reported in Table 3 where w_i signifies the mass fraction of the ith component is given in Table 3. The area of the two-phase region depends on the mutual solubilities of water and 1-butanol.
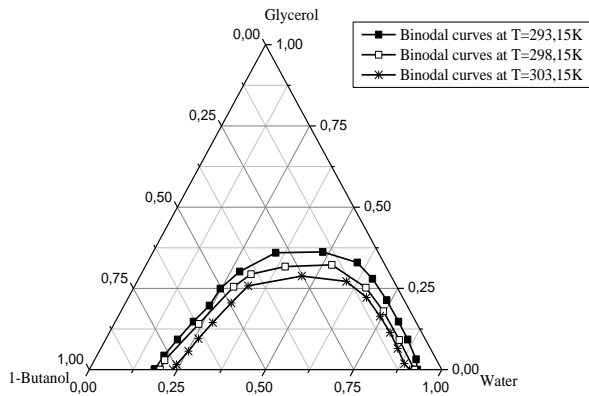
Fig. 5: Comparison of the binodal curves of the system water (1) + glycerol (2) + 1-butanol (3) at 293.15, 298.15, and 303.15 K and 1 atm.
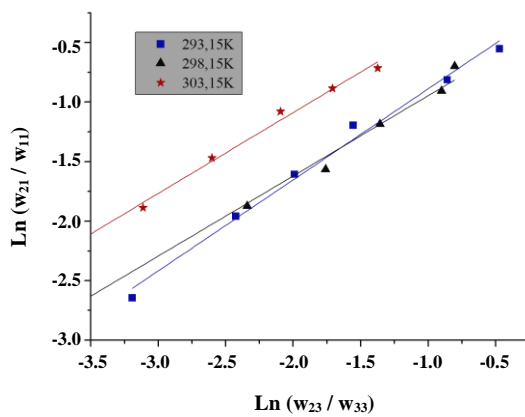

Fig. 6: Hand plot for experimental phase equilibrium data of the system water (1) + glycerol (2) + 1-butanol (3) at 293.15, 298.15, and 303.15 K and 1 atm.
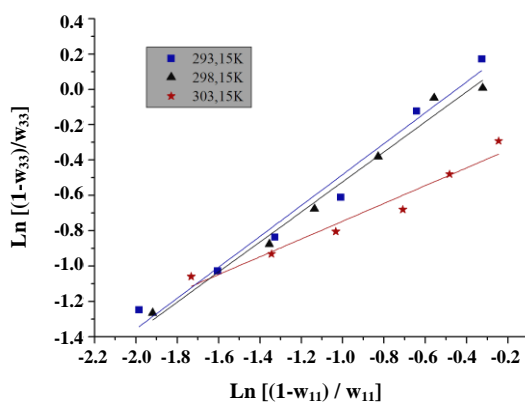

Fig. 7: Othmer-Tobias plot for experimental phase equilibrium data of the system water(1)+ glycerol(2)+ 1-butanol(3)at 293.15, 298.15, and 303.15 K and 1 atm.

The same solubility data were drawn in Fig. 5 to demonstrate the impact of temperature on the binary solubilities. As it can be seen, the temperature effect on the binodal curves and biphasic region of the ternary system is relatively evident at the temperatures studied.

On the other hand, Table 4 shows the experimental tie-line compositions at each temperature where w_{i1} and w_{i3} refer to component i in the water (1) rich-phase and 1-butanol (3) rich-phase, respectively.

The fitting parameters for the Othmer-Tobias and Hand equations and corresponding coefficients R^2 are listed in Table 5. The straight lines plotted by these two equations are also presented in Figs. 6 and 7. All coefficients (R^2) are close to 1, which indicates a high reliability of the LLE experimental tie-line data.

The distribution coefficients (D_2) and separation factors (S) for the ternary system are given in Table 4. The efficiency of the extraction of glycerol with 1-butanol has been analyzed using the calculated separation factor (S), which is an indication of the ability of 1-butanol to separate glycerol from water. Table 4 shows that separation factors were greater than one (S >1) at 293.15 and 298.15K. These results confirmed that the extraction of glycerol from water by 1-butanol is feasible at this temperature range.

As observed in Table 4, a noticeable temperature effect on the separation factor can be observed. As a result, for this ternary system, the separation factor increases in the order of temperature decreases. Therefore, it is better to perform the separation process at a lower temperature.

The obtained interaction parameters of the UNIQUAC and NRTL models for the ternary system glycerol+1-butanol+ water at each temperature are shown in Table 6. Calculated RMSD values for NRTL and UNIQUAC models are 0.37% and 0.44%, respectively. Data correlations showed that NRTL model can give a satisfactory fitting of experimental data. In particular, modeling errors of NRTL ranged from 0.37 to 0.82 %, while UNIQUAC model showed errors from 0.44 to 1 %. For illustration, the experimental and correlated LLE data for the ternary system at various temperatures have been reported in Figure 8. These figures show a high level of agreement between experimental and model-predicted tie-lines. However, the system studied shows type-1 behavior of the liquid-liquid equilibrium, where only one liquid pair (water + 1-butanol) is partially miscible [31].

Table 4: Experimental tie-lines in mass fraction for the system water(1)+ glycerol(2)+ 1-butanol(3) under the Ambient Pressure and at 293.15, 298.15 and 303.15 K^a .

aqueous phase			organic phase			D_2	S
w_{11}	w_{21}	w_{31}	w_{13}	w_{23}	w_{33}		
293.15K							
0.8792	0.0624	0.0584	0.1911	0.0319	0.777	0.5112	2.3520
0.8327	0.1175	0.0498	0.1984	0.0651	0.7365	0.5540	2.3254
0.7906	0.1586	0.0508	0.2072	0.0953	0.6975	0.6009	2.2928
0.7328	0.2220	0.0452	0.2151	0.1367	0.6482	0.6158	2.0978
0.6553	0.2907	0.054	0.2450	0.2247	0.5303	0.7730	2.0674
0.5810	0.3348	0.0842	0.2575	0.2854	0.4571	0.8524	1.9234
298.15 K							
0.8720	0.0441	0.0839	0.2071	0.0129	0.7800	0.2925	1.2317
0.7949	0.1219	0.0832	0.2259	0.0681	0.7060	0.5587	1.9658
0.7571	0.1580	0.0849	0.2230	0.1140	0.6630	0.7215	2.4496
0.6960	0.2130	0.0910	0.2529	0.1531	0.5940	0.7188	1.9781
0.6359	0.2571	0.1070	0.2799	0.208	0.5121	0.8090	1.8380
0.5799	0.2880	0.1321	0.2790	0.2231	0.4979	0.7747	1.6101
303.15 K							
0.8497	0.0595	0.0908	0.2475	0.0100	0.7425	0.1681	0.5770
0.7932	0.1202	0.0866	0.2509	0.0319	0.7172	0.2654	0.8390
0.7374	0.1696	0.093	0.2579	0.0512	0.6909	0.3019	0.8632
0.6702	0.2276	0.1022	0.2545	0.0817	0.6638	0.3590	0.9453
0.6185	0.2552	0.1263	0.2704	0.1119	0.6177	0.4385	1.0030
0.5612	0.2744	0.1644	0.2825	0.1450	0.5725	0.5284	1.0497

^{a} Standard uncertainties u are: $u(T) = \pm0.1$ K; $u(w) = \pm0.001$.

Table 5: Results of liquid-liquid equilibrium data consistency using Othmer-Tobias and Hand equations for the ternary system water+ glycerol+1-butanol.

	Othmer-Tobias correlation			Hand correlation		
T, K	a	b	R^2	a'	b'	R^2
293.15	0.393	0.875	0.9705	-0.1236	0.7647	0.9881
298.15	0.327	0.850	0.9823	-0.2720	0.6734	0.9898
303.15	-0.240	0.503	0.9477	0.2728	0.6798	0.9949

Table 6: Results of binary interaction parameters of NRTL and UNIQUAC models
for the ternary systemwater (1) + glycerol (2) + 1-butanol (3).

Model	T, K	i-j	A_{ij}, cal/mol	A_{ji}, cal/mol	*RMSD*
NRTL	293.15	1-2	1145.58	-610.12	0.0037
		1-3	1187.06	941.48	
		2-3	-1025.47	484.65	
	298.15	1-2	1083.22	-859.61	0.0052
		1-3	1239.73	938.39	
		2-3	-1138.13	503.36	
	303.15	1-2	1125.64	-919.22	0.0082
		1-3	1292.07	973.29	
		2-3	-1203.95	522.13	
UNIQUAC	293.15	1-2	1394.38	-744.99	0.0044
		1-3	1087.08	-716.85	
		2-3	893.15	1228.59	
	298.15	1-2	1432.15	-601.93	0.0068
		1-3	1002.36	-682.06	
		2-3	843.28	1192.93	
	303.15	1-2	1326.85	-811.78	0.0098
		1-3	1138.27	-631.62	
		2-3	872.33	1241.08	

Moreover, the convergent process of MAKHA methods with and without closure equation on the parameter assessment of thermodynamic models problems can be given as follows (see Figure 8). Figure 9 shows the convergent history of MAKHA during the parameter estimation of NRTL and UNIQUAC models for the ternary system water-glycerol-1-butanol at 293.15K. It is clear that the MAKHA with closure equation causes has a better performance and converges within the tolerance much faster than the MAKHA without closure equation causes and with a fewer number of function evaluations during the whole optimization process. The value of the objective function after 800 iterations for NRTL was obtained to be 0.0005 with closure equation and 0.0031 without closure equation, respectively. These values were also obtained to be 0.0007 and 0.0035 for UNIQUAC model.

CONCLUSIONS

Experimental data of liquid-liquid equilibria of water+glycerol+1-butanol have shown that glycerol can be removed from water with 1-butanol as a solvent. However, the selectivity of this separation process decreases as the temperature increases indicating that it is better to perform the glycerol recovery at 293.15 and 298.15 K. Alternatively, NRTL model is better than UNIQUAC for modeling these phase equilibrium data. Overall, the experimental values reported in this study are relevant for the design, simulation, and optimization of glycerol recovery involved in different industrial applications
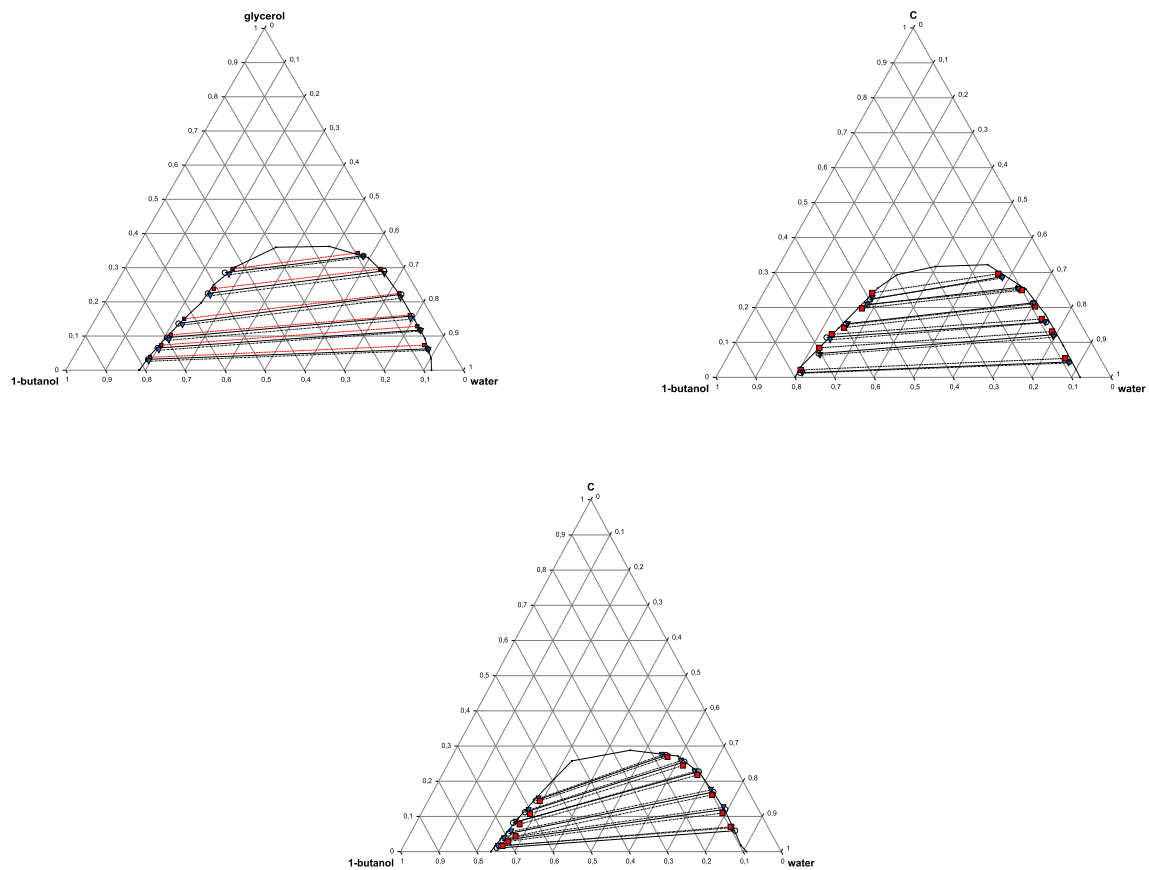
***Fig. 8: Ternary system of {water (1) +glycerol (2) 1-butanol (3)}, at: a) 293.15 K, b) 298.15K and c) 303.15K;
open dot and solid lines for experimental tie lines, blue triangle down solid and dashed lines for NRTL tie lines,
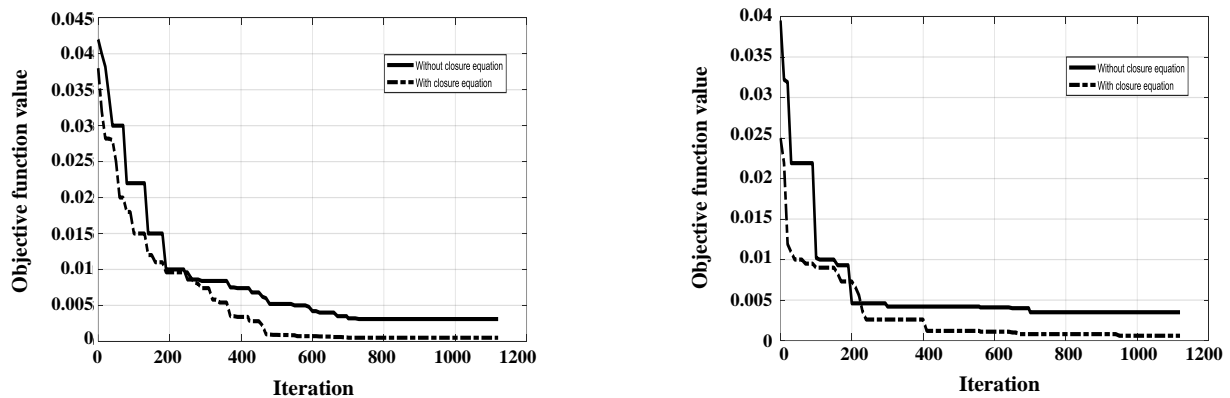red filled square and dashed lines for UNIQUAC tie lines.***

***Fig. 9: Convergence performance of MAKHA algorithm versus iteration for LLE parameter estimation in the system:
water+glicerol+1-butanol at 293.15 K, (a) NRTL, and (b) UNIQUAC.***

such as the biodiesel purification process. For future studies, the salting effect should be applied in this ternary system to increase the transfer of glycerol to the organic phase and also increase the separation factor.

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