

Liquid-liquid equilibria of biodiesel + glycerol and biodiesel + water binary systems

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ABSTRACT

The liquid-liquid equilibria (LLE) of the biodiesel + glycerol and biodiesel + water binary systems are experimentally measured at atmospheric pressure and in the temperature range from 310.35 K to 338.15 K, conditions relevant to the industrial process, solving the experimental challenges related to their direct measurement. The LLE data of these binary systems are pivotal for designing the biodiesel purification processes and determine the chemical equilibrium constant of the transesterification reaction of vegetable oil into biodiesel. However, unlike to the present study, this information is typically indirectly extrapolated from models regressed on ternary systems, undermining the reliability of the results. The experimental data were compared against the calculations provided by the UNIQUAC and UNIFAC models, with the binary interactions parameters (BIPs) of the UNIQUAC model validated on the experimental data. To ensure a thermodynamically consistent representation of the phase behaviour and smooth the experimental scattering of trace components, the BIPs are regressed by means of an algorithm that considers the experimental uncertainty. The results are compared with LLE data for biodiesel + glycerol and biodiesel + water from ternary systems measured by other laboratories.

1. Introduction

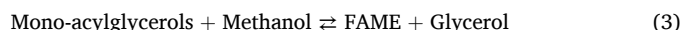
Biodiesel is one of the candidate renewable fuels to displace fossil fuels in the hard-to-decarbonise transportation sector and its demand is driven by the current use in blends with regular petroleum diesel [1].

The production process typically starts with the transesterification reaction of tri-acylglycerols in the oil to obtain biodiesel among the products [2,3]. Biodiesel is a mixture of fatty acid esters, commonly methyl-esters (FAMES) or ethyl-esters (FAEEs), obtained by letting the vegetable, animal or waste oil react with a primary alcohol in presence of a homogeneous alkali catalyst at atmospheric pressure and mild temperature (ambient temperature to 333.15 K) [4].

The wide range of fatty acids composing the biodiesel directly depends on those present in the original oil, adding a layer of complexity to the interpretation of the phase equilibria since they show as overall result from the complex mixture of fatty acid esters.

This study used Methanol (MeOH) as alcohol, therefore the

transesterification reaction scheme is as follow [5]:



Reaction (1) shows as a heterogeneous liquid-liquid system because of the practical immiscibility between the tri-acylglycerols-rich phase (oil-rich phase) and the MeOH. Reaction (3) is a second heterogeneous liquid-liquid system because of the low miscibility between FAMES and glycerol.

To the best of our knowledge, limited experimental liquid-liquid equilibrium (LLE) data are available for the FAMES + glycerol binary system due to the experimental challenges in the accurate identification of traces of FAMES in the glycerol-rich phase and glycerol in the FAMES-rich phase over an extended range of temperatures. Currently, the LLE of the practically-immiscible FAMES + glycerol binary system is assessed

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Nomenclature	
<i>Latin symbols</i>	
a_{ij}, a_{ji}	binary interaction parameters of the UNIQUAC model [K];
a_{mn}, a_{nm}	group interaction parameters of the UNIFAC model [K];
l	parameter of UNIQUAC model;
m	mass;
q	surface area structural parameter of UNIQUAC model;
Q_k	surface area structural parameter of the group k of the UNIFAC model;
r	volume structural parameter of UNIQUAC model;
T	temperature [K];
u	uncertainty;
$v_k^{(i)}$	number of group k present in the i th component;
w_i	mass fraction of i th component;
x_i	mole fraction of i th component;
X_m	mole fraction of group m in the mixture;
$X_m^{(i)}$	mole fraction of group m in the i th component;
z	parameter of UNIQUAC model;
<i>Greek symbols</i>	
γ_i	activity coefficient of i th component;
Γ_k	residual contribution to the activity coefficient of the UNIFAC model of group k in the mixture;
$\Gamma_k^{(i)}$	residual contribution to the activity coefficient of the UNIFAC model of group k in a reference solution containing only the component i ;
θ_i	area fraction of the i th component;
Θ_m	surface area fraction of group m ;
τ_{ij}, τ_{ji}	dimensionless binary interaction parameters of UNIQUAC model;
ϕ_i	segment (or volume) fraction of the i th component;
Ψ_{mn}, Ψ_{nm}	dimensionless group interaction parameters of the UNIFAC model;
<i>Acronyms</i>	
BIP	binary interaction parameter
CTP	common tangent plane;
HPLC	high performance liquid chromatograph
LLE	liquid-liquid equilibrium;
RID	RID10A differential refractometer
UV	UV-vis detector
<i>Subscripts/superscripts</i>	
calc	calculated;
comb	combinatorial;
exp	experimental;
res	residual;

Table 1

List of chemicals used in the experimentation.

Chemicals	CAS number	Purity	Supplier
Methanol, Chromasolv® Plus for HPLC	67-56-1	≥ 99.9 wt%	Sigma-Aldrich
Glycerol, ACS reagent	56-81-5	≥ 99.5 wt%	Sigma-Aldrich
Water, HPLC-gradient grade PAI	7732-18-5	≥ 99.9 wt%	Panreac
Tetrahydrofuran, UV-IR-HPLC-GPC PAI	109-99-9	≥ 99.9 wt%	Panreac
KOH, reagent grade	1310-58-3	≥ 90 wt%	Sigma-Aldrich
Methanolic HCl	–	3N	Supelco
Sunflower Oil	–	Commercial edible oil grade	–
Biodiesel	–	≥ 95 wt%	Laboratory

from models regressed on measurements of ternary systems, where a third solvent is introduced to increase the mutual miscibility of the individual components [6–9].

Downstream the reactor, after splitting the FAMES-rich phase from the glycerol-rich phase, the FAMES-rich phase is water-washed at atmospheric pressure and mild temperature (40–50 °C) to lower the residual glycerol content below the limits specified by the EN 14,214 of free glycerol content in biodiesel (<0.02 wt%). Also in this case, there is a lack of binary experimental LLE data for FAMES + water, which undermines all assessments on their separation. As in the case of glycerol, studies use to add a third component to the binary mixture to increase the mutual solubility and improve the detection of the components, carrying uncertainty on the reliability of the equilibrium extrapolated from the ternary system rather than directly measured [6,7,10,11].

The quasi-immiscibility of the FAMES + glycerol and FAMES + water binary systems results in LLE binary data with low accuracy. This in turn strongly affects the design of the separation and reaction steps, along with undermining the compliance of the biodiesel produced with the strict purity requirements from standards.

This study bridges the gaps in the LLE binary data outlined above and in their corresponding thermodynamic modelling. By exploiting ad-hoc liquid chromatography methods and equipment, the biodiesel + glycerol and biodiesel + water LLE is measured at ambient pressure in a range of temperature from 310.35 K to 338.15 K. The UNIQUAC model is regressed on the data, considering their experimental uncertainty and checking the thermodynamic consistency of the interaction parameters. The study includes a comparison between the correlative UNIQUAC model and the predictive UNIFAC, to quantify the applicability of the two approaches.

2. Materials and methods

2.1. Reagents and materials

Table 1 summarises the type of chemicals used in this work. They included the Sigma-Aldrich (Milan, Italy) methanol Chromasolv Plus for High Performance Liquid Chromatography (HPLC) 99.9 %, water HPLC gradient grade PAI, and Panreac tetrahydrofuran (THF) HPLC gradient grade PAI.

Commercial edible-grade sunflower oil, methanol 99.8 % (Fluka), and Sigma-Aldrich dry potassium hydroxide (KOH) reagent grade 90 % were purchased for transesterification. Biodiesel was produced and purified from a commercial edible-grade sunflower oil, with an acid value of 0.09 mg of KOH g⁻¹ oil [12] and a peroxide value lower than 0.02 meq of peroxide kg⁻¹ of oil [13]. The oil was agitated and transesterified in a three-neck flask for two days with methanol, 1:10 molar ratio oil:MeOH, and with 0.5 wt% KOH in respect to methanol, at room temperature. The biodiesel-rich phase was separated from the glycerol phase produced, and then re-transesterified for a second time at the same conditions to convert the residual tri-acylglycerols, di-acylglycerols and mono-acylglycerols in biodiesel and glycerol. After transesterification, the biodiesel-rich phase was separated from the produced glycerol and unreacted MeOH. The residual catalyst, in biodiesel phase, was neutralized with methanolic HCl and washed three times with pure water; to eliminate the residual glycerol, MeOH and eventual soaps. After separation of water phase, the biodiesel was then dried. HPLC analysis by the method in [14] shown that it is composed of 48 wt%

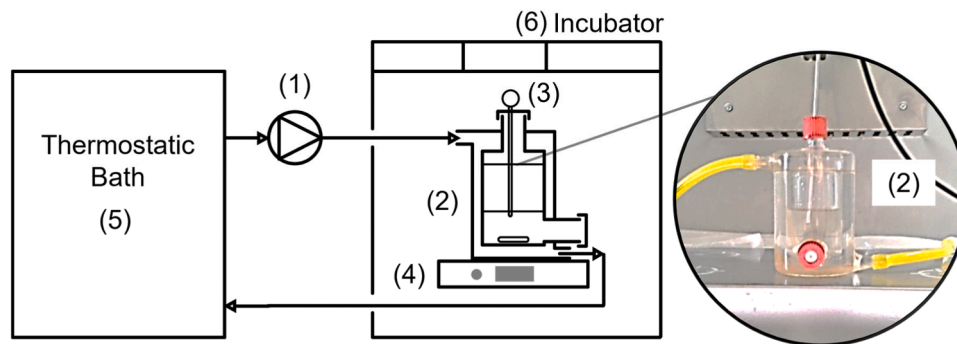


Fig. 1. Experimental LLE apparatus; (1) Heidolph Peristaltic pump model pumpdrive 5101; (2) Jacketed LLE glass cell, 63 ml internal volume with two septa on top and bottom for collection of samples from each phase; (3) Pt100 temperature sensor passing through the top septum; (4) Velp Scientific S.r.l. magnetic agitator model multistirrer 6; (5) Tamson Holland TMV40 thermostatic bath; (6) MPM Incubator.

Table 2

Details of the samples prepared and of the analytical techniques used.

	Biodiesel + water	Biodiesel + glycerol
<i>Upper Phase</i>		
Sample features	1:2 w/w in THF	1:3 w/w in THF
Analytical equipment	HPLC – UV + RID	HPLC – UV + RID
Method	[14,15]	[14,15]
Target analyte	FAMES	Glycerol
Secondary analytes (traces)	Glycerol, TG, DG, MG	FAMES, TG, DG, MG,
<i>Bottom Phase</i>		
Sample features	1:5 w/w in THF	1:5 w/w in water
Analytical equipment	Karl-Fisher Coulometer	HPLC – UV + RID
Method	–	[14,15]
Target Analyte	Water	FAMES
Secondary analytes (traces)	–	TG, DG, MG, glycerol

Note: the UV and RID detectors are in series.

methyl oleate and 52 wt% methyl linoleate.

2.2. Apparatus and experimental procedure

The experimental LLE apparatus in Fig. 1 allows to set the temperature from ambient up to 333.15 K. A jacketed glass equilibrium cell with a volume of 63 cm³ is maintained at a set temperature by means of a water loop and an external thermostatic bath (Tamson Holland TMV40, ±0.1 K) controlled by a Vertex analogue thermometer. A magnetic stirrer ensures the agitation of the mixture (Velp Scientific S.r.l.), while the temperature of the mixture is measured by a Pt100 (±0.1 K) in contact with the stirred fluid.

The mixture is introduced in equilibrium cell and stirred vigorously for at least six hours to guarantee complete mixing and temperature stabilization. After six hours, the stirrer is stopped and left for six hours for complete phase separation.

A sample of each phase is then withdrawn by using two different 50 mm³ micro-syringes (Hamilton 1705 RNR, ±0.5 mm³), kept at the same temperature of the experiment and diluted in specific solvents before their analysis. The entire process was repeated three times for each temperature. Only the average value and the uncertainty range are presented.

2.3. Sample preparation and analytical methods

In order to deal with the specific analytical technique, the sampled amounts were mixed with solvents to obtain homogeneous and transparent phases, as detailed in Table 2. The solvents were transferred with a single channel mechanical pipette, with a working volume of 10 - 100 mm³ (±1.3 mm³).

A Gibertini analytical balance, model E42S-B (±0.1 µg) was used for weighing throughout the experimental chain from sunflower oil to the

preparation of the samples. In most of the cases, the analytical methods used to analyse the samples relied on the use of high performance liquid chromatography (HPLC), according to methods specifically developed to deal with the complexity of the samples and published elsewhere [14, 15]. HPLC allows the analysis of complex mixtures without the need for derivatization, thus enabling the sample to remain liquid simplifying the overall procedure and reducing the uncertainty of sample preparations.

The analyses were conducted with a Shimadzu VP series High Performance Liquid Chromatograph (HPLC) equipped with two LC-10ADVP solvent delivery units, one SPD-10AVVP UV–vis detector (UV) set at 210 nm, one RID10A differential refractometer (RID), one manual Rheodyne 7725(i) sample injector (20 mm³ injection volume, ±0.2 mm³), one CTO-10ASVP Peltier oven, one SCL-10AVP system controller including the LC-Solution 2.1 software for remote management. A Teknokroma (Barcelona, Spain) Mediterranea sea18 analytical column with internal diameter 4.6 mm, length 25 cm, and particle size 5 µm, was used in all HPLC analyses. The uncertainty, of analytes determination using HPLC, are of ±1.718 µg for biodiesel and ±2.38 µg for glycerol. One 831 Karl-Fisher Coulometer (Metrohm, ±0.1 µg) was used in all cases where water is the target analyte.

3. UNIQUAC and UNIFAC models

The LLE measurements of the studied binary systems are compared with the behaviours provided by UNIQUAC model [16] and the UNIFAC model [17]. The UNIQUAC model is characterized by the following expressions for the activity coefficient of the *i* th component (γ_i):

$$\ln \gamma_i = \ln \gamma_i^{\text{comb}} + \ln \gamma_i^{\text{res}} \quad (4)$$

$$\ln \gamma_i^{\text{comb}} = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j \quad (5)$$

$$\ln \gamma_i^{\text{res}} = q_i \left[1 - \ln \left(\sum_j \theta_j \tau_{ji} \right) - \sum_j \frac{\theta_j \tau_{ij}}{\sum_k \theta_k \tau_{kj}} \right] \quad (6)$$

where γ_i^{comb} is the activity coefficient's combinatorial part, γ_i^{res} is the activity coefficient's residual part, $\phi_i = x_i r_i / \sum x_j r_j$ is the segment (or volume) fraction, x_i is the mole fraction, r_i is the volume structural parameter, z is the average coordination number (usually $z = 10$), $\theta_i = x_i q_i / \sum x_j q_j$ is the area fraction, q_i is the surface area structural parameter, $l_i = (r_i - q_i) z / 2 - (r_i - 1)$, $\tau_{ij} = \exp(-a_{ij} / T)$ and $\tau_{ji} = \exp(-a_{ji} / T)$ are the dimensionless binary interaction parameters (BIPs), and a_{ij} and a_{ji} are the BIPs in K.

Constant and temperature-dependent BIPs were regressed from the experimental data of the binary systems presented in this study. In particular, the following linear temperature-dependent correlations for the parameters were used: $a_{ij} = \alpha_{ij}^A + \alpha_{ij}^B T$ and $a_{ji} = \alpha_{ji}^A + \alpha_{ji}^B T$. The

Table 3

UNIQUAC structural parameters (r_i and q_i).

	r_i	q_i
Methyl-ester of oleic acid	13.1304	10.790
Methyl-ester of linolenic acid	13.3625	11.003
Glycerol	4.7957	4.908
Water	0.9200	1.400

Note: the biodiesel is composed of 48 wt% methyl oleate and 52 wt% methyl linoleate.

Table 4

Calculated combined standard uncertainty of masses.

Measurement	Combined standard uncertainty [μ g]
Biodiesel in water phase	1.8
Water in biodiesel phase	0.51
Biodiesel in glycerol phase	1.84
Glycerol in biodiesel phase	2.44
Biodiesel in biodiesel phase	1.79
Glycerol in glycerol phase	2.48
Water in water phase	0.56

values of the UNIQUAC parameters and correlation coefficients were determined by using the algorithm in [18,19] and ensure a thermodynamically consistent representation of the LLE. As clearly explained by Marcilla and his co-workers [20–23], the need of a robust algorithm to derive the model parameters is related to the fact that local composition models, such as the NRTL and UNIQUAC, can provide inaccurate and unrealistic phase behaviour descriptions due to unreliable parameters. For this reason, different algorithms to regress the model parameters including necessary and sufficient conditions for the stability of the phases, such as the minimization of the Gibbs free energy or the Common Tangent Plane (CTP) condition in addition to the isoactivity conditions [24,25], were developed and usually tested with the NRTL model [26–28]. Instead, the algorithm used in this study [18,19] was validated by determining the UNIQUAC parameters. It presents two nested iteration loops that allow to minimize the deviation between the experimental and calculated values and, at the same time, ensure the CTP criterion by taking into account the uncertainty of the composition. A software containing the algorithm to estimate single temperature UNIQUAC parameters from LLE data of binary systems is freely available in [19].

The structural parameters r and q of glycerol and water reported in Table 3 were used in the calculations. Instead, considering that it is not a trivial task to accurately determine r and q of the biodiesel phase since its high number of components, this phase was treated as a pseudo-component with structural parameters regressed through the above-mentioned algorithm [18,19]. In the regression, r and q values were constrained between that of methyl-ester of oleic acid and methyl-ester of linolenic acid (reported in Table 3) since they are the main components of the biodiesel phase.

The UNIFAC model allows to predict γ_i by combining a combinatorial part and a residual part as expressed by Eq. (4). While the combinatorial part of the UNIQUAC model (Eq. (5)) is directly used in the UNIFAC, the residual part has the following form:

$$\ln \gamma_i^{\text{res}} = \sum_k v_k^{(i)} [\ln \Gamma_k - \ln \Gamma_k^{(i)}] \quad (7)$$

where $v_k^{(i)}$ is the number of group k present in the i th component, Γ_k is the residual contribution to the activity coefficient of group k in the mixture, and $\Gamma_k^{(i)}$ is the residual contribution to the activity coefficient of group k in a reference solution containing only the component i . The expression of $\ln \Gamma_k$ is as follows:

Table 5
Mass fractions (w_i), mole fractions (x_i) and temperatures (T) for LLE measurements of biodiesel (1) + glycerol (2) binary system.

T/K^a	Biodiesel-rich phase			Glycerol-rich phase			Biodiesel-rich phase			Glycerol-rich phase		
	w_1	$u(w_1)^b$	w_2	$u(w_1)^b$	w_2	$u(w_2)^b$	x_1	$u(x_1)^b$	x_2	$u(x_1)^b$	x_2	$u(x_2)^b$
338.35	0.9935	8.62E-04	0.0065	8.62E-04	1.46E-03	6.11E-04	0.9985	6.11E-04	0.9985	6.11E-04	0.9985	6.11E-04
330.95	0.9988	6.81E-04	0.0012	6.81E-04	1.58E-03	7.54E-04	0.9984	7.54E-04	0.9984	7.54E-04	0.9984	7.54E-04
327.65	0.9971	6.29E-04	0.0029	6.29E-04	2.01E-04	5.63E-04	0.9998	5.63E-04	0.9998	5.63E-04	0.9998	5.63E-04
322.25	0.9980	5.70E-04	0.0020	5.70E-04	2.45E-03	2.58E-04	0.9976	2.58E-04	0.9976	2.58E-04	0.9976	2.58E-04
320.15	0.9905	5.19E-04	0.0095	5.19E-04	4.24E-04	5.24E-04	0.9996	5.24E-04	0.9996	5.24E-04	0.9996	5.24E-04
318.75	0.9962	5.21E-04	0.0038	5.21E-04	4.40E-05	5.31E-04	1.0000	5.31E-04	1.0000	5.31E-04	1.0000	5.31E-04
316.75	0.9933	5.68E-04	0.0067	5.68E-04	5.50E-04	6.05E-04	0.9995	6.05E-04	0.9995	6.05E-04	0.9995	6.05E-04
313.75	0.9973	4.77E-04	0.0027	4.77E-04	1.97E-04	5.58E-04	0.9998	5.58E-04	0.9998	5.58E-04	0.9998	5.58E-04
310.35	0.9947	5.67E-04	0.0054	5.67E-04	1.93E-03	5.23E-04	0.9981	5.23E-04	0.9981	5.23E-04	0.9981	5.23E-04

^a Temperature uncertainty is ± 0.1 K.

^b Propagated combined standard uncertainty.

Table 6
Mass fractions (w_i), mole fractions (x_i) and temperatures (T) for LLE measurements of biodiesel (1) + water (2) binary system.

T/K ^a	Biodiesel-rich phase				Water-rich phase				Biodiesel-rich phase				Water-rich phase			
	w_1		w_2		w_1		w_2		x_1		x_2		x_1		x_2	
	$u(w_1)$ ^b	$u(w_2)$ ^b	$u(w_1)$ ^b	$u(w_2)$ ^b	$u(w_1)$ ^b	$u(w_2)$ ^b	$u(w_1)$ ^b	$u(w_2)$ ^b	$u(x_1)$ ^b	$u(x_2)$ ^b	$u(x_1)$ ^b	$u(x_2)$ ^b	$u(x_1)$ ^b	$u(x_2)$ ^b	$u(x_1)$ ^b	$u(x_2)$ ^b
338.35	0.9929	6.73E-05	0.0071	6.73E-05	2.39E-04	5.80E-04	0.9976	5.80E-04	0.8952	9.50E-04	0.1048	9.50E-04	1.50E-05	1.96E-06	0.99985	1.96E-06
330.95	0.9925	2.87E-05	0.0075	2.87E-05	9.40E-05	4.23E-04	0.99991	4.23E-04	0.8897	3.94E-04	0.1103	3.94E-04	6.00E-06	1.43E-06	0.999994	1.43E-06
327.65	0.9928	3.02E-05	0.0072	3.02E-05	2.11E-04	1.95E-04	0.99979	1.95E-04	0.8938	4.27E-04	0.1062	4.27E-04	1.30E-05	6.57E-07	0.999987	6.57E-07
322.25	0.9944	2.03E-05	0.0056	2.03E-05	1.77E-03	2.03E-04	0.99823	2.03E-04	0.9163	2.88E-04	0.0837	2.88E-04	1.09E-04	6.87E-07	0.999891	6.87E-07
320.15	0.9951	4.90E-05	0.0049	4.90E-05	2.40E-05	2.53E-04	0.99998	2.53E-04	0.9257	7.15E-04	0.0743	7.15E-04	1.00E-06	8.53E-07	0.999999	8.53E-07
318.75	0.9950	9.15E-05	0.0050	9.15E-05	6.50E-05	2.68E-04	0.99994	2.68E-04	0.9245	1.27E-03	0.0755	1.27E-03	4.00E-06	9.06E-07	0.999996	9.06E-07
316.75	0.9940	2.79E-06	0.0060	2.79E-06	N.A.	N.A.	N.A.	N.A.	0.9098	3.70E-05	0.0902	3.70E-05	N.A.	N.A.	N.A.	N.A.
313.75	0.9949	6.68E-05	0.0051	6.68E-05	2.59E-04	2.75E-04	0.99974	2.75E-04	0.9234	8.80E-04	0.0766	8.80E-04	1.60E-05	9.29E-07	0.99984	9.29E-07
310.35	0.9961	1.08E-05	0.0039	1.08E-05	1.67E-03	2.55E-04	0.99833	2.55E-04	0.9403	1.44E-04	0.0597	1.44E-04	0.000103	8.62E-07	0.999897	8.62E-07

^a Temperature uncertainty is ± 0.1 K.

^b Propagated combined standard uncertainty.

Table 7

UNIQUAC parameters for biodiesel (1) + water (2) binary system and deviations between the experimental and calculated data.

T/K	Constant UNIQUAC parameters ^a		Temperature-dependent UNIQUAC parameters ^b	
	Biodiesel-rich phase ^c	Water-rich phase	Biodiesel-rich phase ^d	Water-rich phase
	$ x_{1,\text{exp}} - x_{1,\text{calc}} $	$ x_{1,\text{exp}} - x_{1,\text{calc}} $	$ x_{1,\text{exp}} - x_{1,\text{calc}} $	$ x_{1,\text{exp}} - x_{1,\text{calc}} $
338.35	0.00601	0.00007	0.02019	0.00010
330.95	0.01853	0.00009	0.00550	0.00010
327.65	0.01749	0.00008	0.00961	0.00010
322.25	0.00003	0.00001	0.00006	0.00000
320.15	0.00749	0.00010	0.00502	0.00011
318.75	0.00505	0.00009	0.00068	0.00010
313.75	0.00043	0.00008	0.01010	0.00009
310.35	0.01347	0.00000	0.00071	0.00000

^a $a_{12} = 911.60$ K and $a_{21} = -91.075$ K.

^b $a_{12}(T) = 1962.55 - 3.23725 \cdot T$ and $a_{21}(T) = -83.13 - 0.0229617 \cdot T$.

^c $r = 13.136$ and $q = 10.797$.

^d $r = 13.259$ and $q = 10.983$.

Table 8

UNIQUAC parameters for biodiesel (1) + glycerol (2) binary system and deviations between the experimental and calculated data.

T/K	Constant UNIQUAC parameters ^a		Temperature-dependent UNIQUAC parameters ^b	
	Biodiesel-rich phase ^c	Glycerol-rich phase	Biodiesel-rich phase ^d	Glycerol-rich phase
	$ x_{1,\text{exp}} - x_{1,\text{calc}} $	$ x_{1,\text{exp}} - x_{1,\text{calc}} $	$ x_{1,\text{exp}} - x_{1,\text{calc}} $	$ x_{1,\text{exp}} - x_{1,\text{calc}} $
338.35	0.00001	0.00009	0.00739	0.00004
330.95	0.01518	0.00001	0.01561	0.00013
327.65	0.00898	0.00039	0.00718	0.00029
322.25	0.01040	0.00035	0.00591	0.00042
320.15	0.01325	0.00027	0.01855	0.00021
318.75	0.00403	0.00038	0.00175	0.00033
316.75	0.00549	0.00020	0.01184	0.00018
313.75	0.00639	0.00029	0.00064	0.00030
310.35	0.01528	0.00020	0.02290	0.00025

^a $a_{12} = 206.61$ K and $a_{21} = 59.983$ K.

^b $a_{12}(T) = 1750 - 4.71063 \cdot T$ and $a_{21}(T) = -850 + 2.80222 \cdot T$.

^c $r = 13.140$ and $q = 10.780$.

^d $r = 13.137$ and $q = 10.804$.

$$\ln \Gamma_k = Q_k \left[1 - \ln \left(\sum_m \Theta_m \Psi_{mk} \right) - \sum_m \frac{\Theta_m \Psi_{km}}{\sum_n \Theta_n \Psi_{nm}} \right] \quad (8)$$

where Q_k is the surface area structural parameter of the group k , $\Theta_m = X_m Q_m / \sum X_n Q_n$ is the surface area fraction of group m , X_m is the mole fraction of group m in the mixture, $\Psi_{mn} = \exp(-a_{mn}/T)$ and $\Psi_{nm} = \exp(-a_{nm}/T)$ are the dimensionless UNIFAC group interaction parameters, and a_{mn} and a_{nm} are the group interaction parameters in K. Eq. (8) is also used to calculate $\ln \Gamma_k^{(i)}$ but the mole fraction of group m in the i th component, $X_m^{(i)}$, is considered instead of X_m .

Given the complexity in accurately determine the functional groups of the biodiesel phase due to its high number of components, this phase was approximated as methyl-ester of oleic acid or methyl-ester of linolenic acid in the UNIFAC calculations. The set of UNIFAC group interaction parameters (a_{mn} and a_{nm}) proposed by Bessa et al. [29] were used. In fact, since these parameters were specifically developed from LLE measurements of systems involved in the biodiesel production, it was shown their higher accuracy in the LLE description of the systems containing biodiesel compared to other parameter sets [29,30].

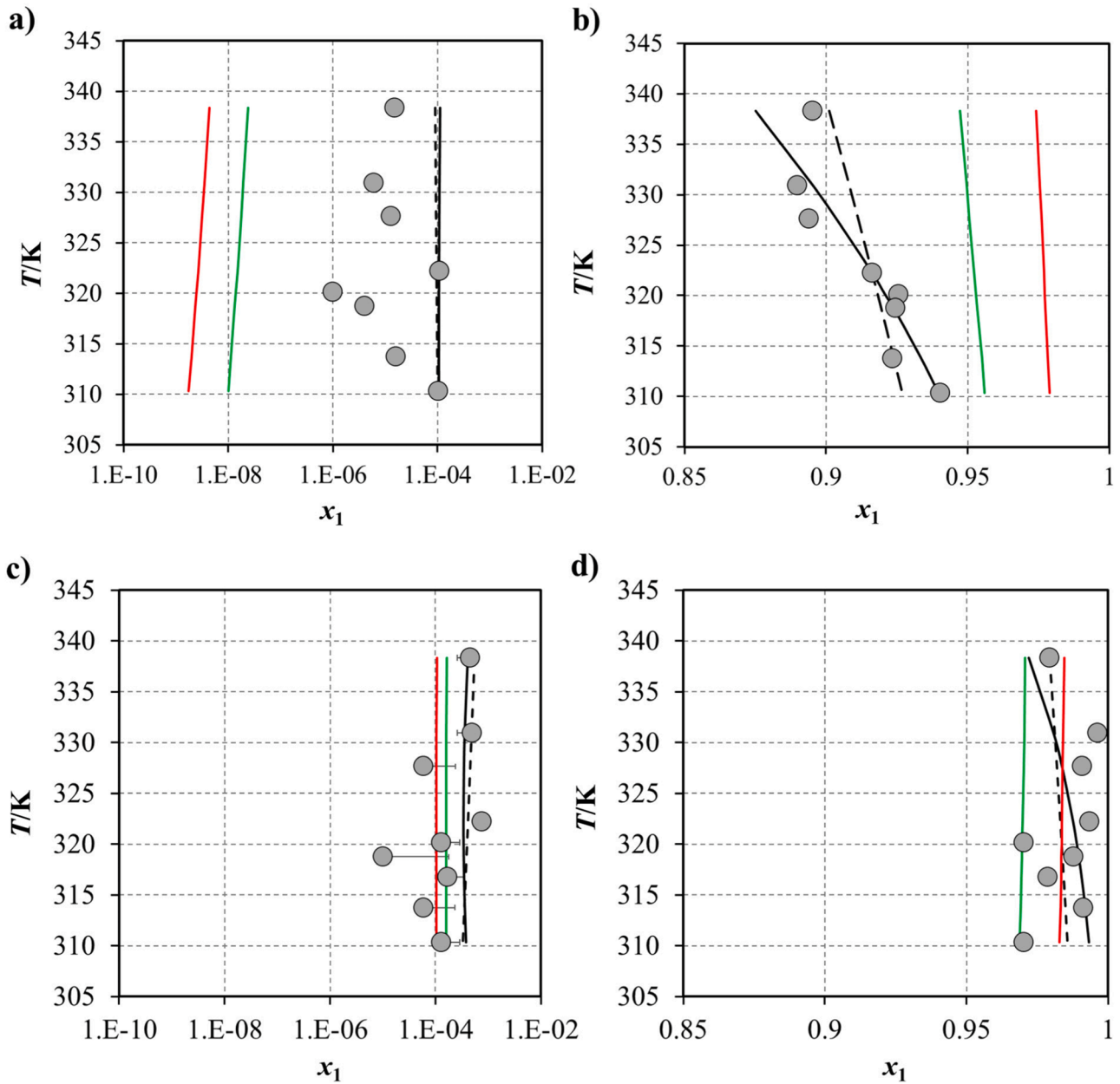


Fig. 2. LLE measurements (grey points) for biodiesel (1) + water (2) and biodiesel (1) + glycerol (2) binary systems together with the calculations provided by the UNQUAC model with constant and temperature-dependent parameters (dotted and solid lines, respectively) and the UNIFAC model by approximating the biodiesel phase as methyl-ester of oleic acid (red lines) and methyl-ester of linolenic acid (green lines): a) water-rich phase of biodiesel (1) + water (2); b) biodiesel-rich phase of biodiesel (1) + water (2); c) glycerol-rich phase of biodiesel (1) + glycerol (2); d) biodiesel-rich phase of biodiesel (1) + glycerol (2).

4. Results and discussion

4.1. LLE measurements

For each sample analysed as described above, a combined standard uncertainty was calculated, according to JCGM 100:2008 [31] and reported in Table 4. The experimental results obtained for the binary systems biodiesel + glycerol and biodiesel + water are reported, respectively, in Table 5 and Table 6.

The combined standard uncertainty was then propagated to mass fraction and mole fraction using the following equations:

$$\begin{aligned}
 u(w_i) &= \sqrt{\left(\frac{\partial w_i}{\partial m_1} \times u(m_1)\right)^2 + \left(\frac{\partial w_i}{\partial m_2} \times u(m_2)\right)^2} \\
 &= \sqrt{\left\{\left[\frac{m_2}{(m_1 + m_2)^2}\right] \times u(m_1)\right\}^2 + \left\{-\left[\frac{m_1}{(m_1 + m_2)^2}\right] \times u(m_2)\right\}^2} \quad (9)
 \end{aligned}$$

$$\begin{aligned}
 u(x_i) &= \sqrt{\left(\frac{\partial x_i}{\partial n_1} \times u(n_1)\right)^2 + \left(\frac{\partial x_i}{\partial n_2} \times u(n_2)\right)^2} \\
 &= \sqrt{\left\{\left[\frac{n_2}{(n_1 + n_2)^2}\right] \times u(n_1)\right\}^2 + \left\{-\left[\frac{n_1}{(n_1 + n_2)^2}\right] \times u(n_2)\right\}^2} \quad (10)
 \end{aligned}$$

Table 9

Comparison between the constant binary interaction parameters a_{12} and a_{21} from published ternary systems including FAME and from the binary systems in this study.

FAME's original oil	a_{12}/K	a_{21}/K	Refs.
<i>System: Biodiesel (1) + water (2)</i>			
Palm – from ternary system data	1086.25	−87.936	[11]
Soybean – from ternary system data	1016.00	−67.765	[11]
Corn – from ternary system data	1277.00	−190.281	[6]
Soybean – from ternary system data	873.46	−129.977	[7]
Sunflower – from binary system data	911.65	−91.080	This study
<i>System: Biodiesel (1) + glycerol (2)</i>			
Corn – from ternary system data	871.85	143.060	[6]
Soybean – from ternary system data	273.81	−10.191	[7]
Soybean – from ternary system data	315.27	83.945	[8]
Jatropha – from ternary system data	302.33	0.570	[9]
Sunflower – from binary system data	206.63	59.986	This study

where $u(w_i)$ and $u(x_i)$ represent the propagated combined standard uncertainties calculated for mass fraction and mole fraction, while $u(m_1)$ and $u(m_2)$ are the combined standard uncertainty for the masses and $u(n_1)$ and $u(n_2)$ are the combined standard uncertainty for the moles. For biodiesel, glycerol and water mass measured with the analytical equipment described above, the uncertainty is equal to the limit of detection of the chromatographic methods as described in Santori et al. [14].

4.2. Calculated LLE behaviour

Constant and temperature-dependent UNIQUAC parameters for the biodiesel + water and biodiesel + glycerol binary systems determined with the algorithm described above are reported in Tables 7 and 8, together with the deviations between the experimental and calculated data. In detail, the constant UNIQUAC parameters are equal to $a_{12} = 911.60$ K and $a_{21} = -91.075$ K for biodiesel (1) + water (2) binary system and $a_{12} = 206.61$ K and $a_{21} = 59.983$ K for biodiesel (1) + glycerol (2) binary system. The temperature-dependent UNIQUAC parameters have the following expressions: $a_{12}(T) = 1962.55 - 3.23725 \cdot T$ and $a_{21}(T) = -83.13 - 0.0229617 \cdot T$ for biodiesel (1) + water (2) binary system and $a_{12}(T) = 1750 - 4.71063 \cdot T$ and $a_{21}(T) = -850 + 2.80222 \cdot T$ for biodiesel (1) + glycerol (2) binary system. A comparison between the LLE provided by the UNIQUAC model against the experimental data is in Fig. 2. The LLE behaviours obtained with the UNIFAC model by approximating the biodiesel phase as methyl-ester of oleic acid and methyl-ester of linolenic acid are also shown in Fig. 2.

Occasionally, the experimental data fall below the detection limits of the analytical techniques [14] or their order of magnitude is comparable to the uncertainty, proving the challenge of performing these specific binary measurements and justifying an experimental strategy based on ternary system experiments. However, biodiesel has strict standard requirements, specifying extremely low levels of water and glycerol, which cannot be reliably achieved without binary experimental data. The design of separation units with information extrapolated from ternary systems is inherently uncertain and requires a trial-and-error approach to avoid incurring in off-standard compositions.

As shown in Fig. 2, only when a suitable model (UNIQUAC in this study) is regressed with thermodynamic consistency, the scattering of the experimental data can be regularised over temperature and composition and provide reliable binary interaction parameters for robust prediction of the LLE in separation units.

Instead, the UNIFAC model gave a less accurate description of the phase behaviour for biodiesel + water binary system. It provided the following average deviations:

- $|x_{1,\text{exp}} - x_{1,\text{calc}}| = 0.06316$ for the biodiesel reach-phase and $|x_{1,\text{exp}} - x_{1,\text{calc}}| = 0.00003$ for the water reach-phase when the biodiesel phase is approximated as methyl-ester of oleic acid.

- $|x_{1,\text{exp}} - x_{1,\text{calc}}| = 0.03849$ for the biodiesel reach-phase and $|x_{1,\text{exp}} - x_{1,\text{calc}}| = 0.00003$ for the water reach-phase when the biodiesel phase is approximated as methyl-ester of linolenic acid.

These results prove that the model shows a bias in the prediction of the LLE for biodiesel + water binary system. On the other hand, the LLE values provided the UNIFAC model for biodiesel + glycerol are more aligned with the measurements. The following average deviations were provided by the UNIFAC model:

- $|x_{1,\text{exp}} - x_{1,\text{calc}}| = 0.00854$ for the biodiesel reach-phase and $|x_{1,\text{exp}} - x_{1,\text{calc}}| = 0.00019$ for the glycerol reach-phase when the biodiesel phase is approximated as methyl-ester of oleic acid.
- $|x_{1,\text{exp}} - x_{1,\text{calc}}| = 0.01452$ for the biodiesel reach-phase and $|x_{1,\text{exp}} - x_{1,\text{calc}}| = 0.00018$ for the water reach-phase when the biodiesel phase is approximated as methyl-ester of linolenic acid.

However, it is evident in Fig. 2 that, unlike the UNIQUAC model, the UNIFAC model is not able to accurately describe the temperature dependency of the predicted equilibrium compositions. Moreover, the type of FAME considered in the UNIFAC calculation resulted in a significant change of the predicted mole fractions of the biodiesel-rich phase for both the measured systems. This difference is not neglectable in the design of separation units to produce biodiesel with the strict purity requirements from standards.

A comparison between the binary interaction parameters for the UNIQUAC model presented in this study and those regressed from published ternary systems is reported in Table 9. All parameters for the two binary systems generally align on the same order of magnitude but show differences in their specific values. The variations in the BIPs can be due to the differences in the analytical techniques used for the measurements, regression procedures, and types of original oil used in biodiesel production. However, it is not a trivial task to determine their relative effect on the values of the parameters. It is worth noting a higher discrepancy between the BIPs presented by Rostami et al. [6] and the others. In particular, the BIPs of Rostami et al. [6] could not provide a thermodynamically consistent description of the phase behaviour of the binary systems since they do not verify the CTP condition.

Despite the above-mentioned differences, the comparison is a confirmation that both the experimental and regression process of the UNIQUAC model used in this study lead to reasonable outcomes. However, a small change in the parameters can result in large changes of the calculated compositions (ill-conditioned problem) [32,33], requiring reliable binary interaction parameters, as those rigorously estimated in this study from accurate measurements.

5. Conclusions

The equilibrium of biodiesel + glycerol and biodiesel + water binary systems are pivotal information for designing separation units in the biodiesel industry. However, these binary systems are typically extrapolated from ternary systems. This study ventured in the experimental investigation through liquid-liquid equilibrium measurements of the biodiesel + glycerol and biodiesel + water binary systems by tackling their experimental and theoretical challenges. The study capitalised on a liquid chromatography method previously developed, applicable to the complex mixtures in LLE systems in the biodiesel industry. Because of the extremely low miscibility of the binary systems, a validated and thermodynamic consistent regression algorithm that considers experimental uncertainties was applied, to reduce the data uncertainty.

With accurately regressed constant or temperature-dependent parameters, the UNIQUAC (original) model follows accurately the LLE of biodiesel + glycerol and biodiesel + water. The UNIFAC predictive model can produce results close to the UNIQUAC model and aligned with most of the experimental data for the FAMES + glycerol system. The same model shows a bias when used to predict the LLE of the FAMES

+ water system.

CRediT authorship contribution statement

Sebastiano Tomassetti: Writing – original draft, Visualization, Formal analysis, Data curation. **Giovanni Di Nicola:** Writing – review & editing, Supervision. **Fabio Polonara:** Supervision, Project administration. **Matteo Moglie:** Writing – original draft, Visualization, Validation, Methodology, Investigation. **Giulio Santori:** Writing – review & editing, Writing – original draft, Validation, Resources, Methodology, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

References

- [1] I.S.A. Manaf, N.H. Embong, S.N.M. Khazaai, M.H.A. Rahim, M.M. Yusoff, K.T. Lee, G.P. Maniam, A review for key challenges of the development of biodiesel industry, *Energy Convers. Manag.* 185 (2019) 508–517, <https://doi.org/10.1016/j.enconman.2019.02.019>.
- [2] G. Santori, G. Di Nicola, M. Moglie, F. Polonara, A review analyzing the industrial biodiesel production practice starting from vegetable oil refining, *Appl. Energy* 92 (2012) 109–132, <https://doi.org/10.1016/j.apenergy.2011.10.031>.
- [3] A. Demirbas, Comparison of transesterification methods for production of biodiesel from vegetable oils and fats, *Energy Convers. Manag.* 49 (2008) 125–130, <https://doi.org/10.1016/j.enconman.2007.05.002>.
- [4] D.Y.C. Leung, X. Wu, M.K.H. Leung, A review on biodiesel production using catalyzed transesterification, *Appl. Energy* 87 (2010) 1083–1095, <https://doi.org/10.1016/j.apenergy.2009.10.006>.
- [5] G. Vicente, M. Martínez, J. Aracil, A. Esteban, Kinetics of sunflower oil methanolysis, *Ind. Eng. Chem. Res.* 44 (2005) 5447–5454, <https://doi.org/10.1021/ie040208j>.
- [6] M. Rostami, S. Raeissi, M. Ranjbaran, M. Mahmoodi, M. Nowroozi, Experimental investigation and modeling of liquid-liquid equilibria in two systems of concern in biodiesel production, *Fluid Phase Equilib.* 353 (2013) 31–37, <https://doi.org/10.1016/j.fluid.2013.05.015>.
- [7] M.A. Mazutti, F.A.P. Voll, L. Cardozo-Filho, M.L. Corazza, M. Lanza, W.L. Priamo, J.V. Oliveira, Thermophysical properties of biodiesel and related systems: (Liquid + liquid) equilibrium data for soybean biodiesel, *J. Chem. Thermodyn.* 58 (2013) 83–94.
- [8] A. Casas, J.F. Rodríguez, G.L. Del Peso, R. Rodríguez, G. Vicente, A. Carrero, Liquid-liquid phase equilibria for soybean oil methanolysis: experimental, modeling, and data prediction, *Ind. Eng. Chem. Res.* 53 (2014) 3731–3736, <https://doi.org/10.1021/ie403927c>.
- [9] J.R.F. Silva, M.A. Mazutti, F.A.P. Voll, L. Cardozo-Filho, M.L. Corazza, M. Lanza, W.L. Priamo, J. Vladimir Oliveira, Thermophysical properties of biodiesel and related systems: (Liquid + liquid) equilibrium data for Jatropha curcas biodiesel, *J. Chem. Thermodyn.* 58 (2013) 467–475, <https://doi.org/10.1016/j.jct.2012.10.006>.
- [10] R.C. Basso, F.H. Miyake, A.J. De Almeida Meirelles, E.A.C. Batista, Liquid-liquid equilibrium data and thermodynamic modeling, at T/K = 298.2, in the washing step of ethyl biodiesel production from crambe, fodder radish and macauba pulp oils, *Fuel* 117 (2014) 590–597, <https://doi.org/10.1016/j.fuel.2013.09.020>.
- [11] M. Rostami, S. Raeissi, M. Mahmoudi, M. Nowroozi, Liquid-liquid phase equilibria of systems of palm and soya biodiesels: experimental and modeling, *Ind. Eng. Chem. Res.* 51 (2012) 8302–8307, <https://doi.org/10.1021/ie300093p>.
- [12] Official methods and Recommended practices of the American Oil Chemists' Society, AOCs Official method Cd 3d-63, (1999).
- [13] Official methods and Recommended practices of the American Oil Chemists' Society, AOCs Official method Cd 8b-90, (1999).
- [14] G. Santori, A. Arteconi, G. Di Nicola, M. Moglie, R. Stryjek, Quantitation of compounds in biodiesel mixtures with reversed-phase liquid chromatography, *Energy Fuels* 23 (2009) 3783–3789, <https://doi.org/10.1021/ef900140r>.
- [15] G. Di Nicola, M. Pacetti, F. Polonara, G. Santori, R. Stryjek, Development and optimization of a method for analyzing biodiesel mixtures with non-aqueous reversed phase liquid chromatography, *J. Chromatogr. A* 1190 (2008) 120–126, <https://doi.org/10.1016/j.chroma.2008.02.085>.
- [16] D.S. Abrams, J.M. Prausnitz, Statistical thermodynamics of liquid mixtures: a new expression for the excess gibbs energy of partly or completely miscible systems, *AIChE J.* 21 (1975) 116–128, <https://doi.org/10.1002/aic.690210115>.
- [17] A. Fredenslund, R.L. Jones, J.M. Prausnitz, Group-contribution estimation of activity coefficients in nonideal liquid mixtures, *AIChE J.* 21 (1975) 1086–1099, <https://doi.org/10.1002/aic.690210607>.
- [18] G. Santori, M. Franciolini, G. Di Nicola, F. Polonara, S. Brandani, R. Stryjek, An algorithm for the regression of the UNIQUAC interaction parameters in liquid-liquid equilibrium for single- and multi-temperature experimental data, *Fluid Phase Equilib.* 374 (2014) 79–85, <https://doi.org/10.1016/j.fluid.2014.04.014>.
- [19] S. Tomassetti, G. Di Nicola, G. Santori, Identification of UNIQUAC binary interaction parameters in liquid-liquid equilibrium, *Fluid Phase Equilib.* 510 (2020), <https://doi.org/10.1016/j.fluid.2020.112483>.
- [20] A. Marcilla, M. del M. Olaya, M.D. Serrano, Comments on liquid-liquid equilibrium data regression, *J. Chem. Eng. Data* 52 (2007) 2538–2541.
- [21] A. Marcilla, J.A. Reyes-Labarta, M.M. Olaya, Should we trust all the published LLE correlation parameters in phase equilibria? Necessity of their assessment prior to publication, *Fluid Phase Equilib.* 433 (2017) 243–252, <https://doi.org/10.1016/j.fluid.2016.11.009>.
- [22] A. Marcilla, M.M. Olaya, J.A. Reyes-Labarta, Ensuring that correlation parameters for liquid-liquid equilibrium produce the right results, *J. Chem. Eng. Data* 63 (2018) 1133–1134, <https://doi.org/10.1021/acs.jced.8b00260>.
- [23] J.A. Labarta, J.A. Caballero, A.F. Marcilla, Liquid-Liquid equilibrium data correlation: predicting a robust and consistent set of initial NRTL parameters. *Computer Aided Chemical Engineering*, Elsevier, 2023, pp. 3459–3464.
- [24] M.L. Michelsen, The isothermal flash problem. Part I. Stability, *Fluid Phase Equilib.* 9 (1982) 1–19.
- [25] L.E. Baker, A.C. Pierce, K.D. Luks, Gibbs energy analysis of phase equilibria, *Soc. Pet. Eng. J.* 22 (1982) 731–742.
- [26] L.D. Simoni, Y. Lin, J.F. Brennecke, M.A. Stadtherr, Reliable computation of binary parameters in activity coefficient models for liquid-liquid equilibrium, *Fluid Phase Equilib.* 255 (2007) 138–146, <https://doi.org/10.1016/j.fluid.2007.04.005>.
- [27] A. Mitsos, G.M. Bolas, P.I. Barton, Bilevel optimization formulation for parameter estimation in liquid-liquid phase equilibrium problems, *Chem. Eng. Sci.* 64 (2009) 548–559, <https://doi.org/10.1016/j.ces.2008.09.034>.
- [28] A. Marcilla, M.M. Olaya, M.D. Serrano, J.A. Reyes-Labarta, Aspects to be considered for the development of a correlation algorithm for condensed phase equilibrium data of ternary systems, *Ind. Eng. Chem. Res.* 49 (2010) 10100–10110, <https://doi.org/10.1021/ie1010383>.
- [29] L.C.B.A. Bessa, M.C. Ferreira, C.R.A. Abreu, E.A.C. Batista, A.J.A. Meirelles, A new UNIFAC parameterization for the prediction of liquid-liquid equilibrium of biodiesel systems, *Fluid Phase Equilib.* 425 (2016) 98–107, <https://doi.org/10.1016/j.fluid.2016.05.020>.
- [30] M.C. Ferreira, D. Gonçalves, L.C.B.A. Bessa, A.J.A. Meirelles, E.A.C. Batista, Performance of different UNIFAC parameter sets in describing experimental liquid-liquid equilibrium data of biodiesel systems, *J. Mol. Liq.* 383 (2023) 122022, <https://doi.org/10.1016/j.molliq.2023.122022>.
- [31] JCGM 101:2008, Evaluation of measurement data guide to the expression of uncertainty in measurement (2008). www.bipm.org.
- [32] W.B. Whiting, Effects of uncertainties in thermodynamic data and models on process calculations, *J. Chem. Eng. Data* 41 (1996) 935–941, <https://doi.org/10.1021/je9600764>.
- [33] W.B. Whiting, V.R. Vasquez, M.M. Meerschaert, Techniques for assessing the effects of uncertainties in thermodynamic models and data, *Fluid Phase Equilib.* 158–160 (1999) 627–641, [https://doi.org/10.1016/s0378-3812\(99\)00054-0](https://doi.org/10.1016/s0378-3812(99)00054-0).