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Liquid-Liquid Equilibria of Water + Solutes (Acetic Acid/Acetol/Furfural/Guaiacol/Methanol/Phenol/Propanal) + Solvents (Isopropyl acetate/Toluene) Ternary Systems for Pyrolysis Oil Fractionation

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Abstract

Solvent extraction of valuable compounds from pyrolysis oil is a promising way for biorefineries optimization, and the design of such operations requires accurate thermodynamic models based on experimental data. Liquid-liquid equilibria (LLE) were investigated at atmospheric pressure and 298.15, 303.15 and 313.15K between pyrolysis oil compounds in aqueous phase and organic solvents. New liquid-liquid equilibrium data were measured involving seven typical pyrolysis oil organic compounds (acetic acid, acetol, furfural, guaiacol, methanol, phenol and propanal), water and two potential extraction solvents (Toluene and Isopropyl acetate). These new datasets together with literature LLE data have been correlated with UNIQUAC and NRTL models. Both compositions and solutes partition coefficients have been successfully correlated with those models.

Keywords: pyrolysis oil; liquid-liquid equilibrium; solvents extraction; biorefinery

1 Introduction

The use of renewable and low environmental impact raw materials for energy and chemicals production is one of the major 21st century's concerns. Bio-refineries are particularly adapted to this requirement since their aim is to produce multiple products including bio-sourced fuels and industrial chemicals [1]. Biomass can be converted into various chemicals via thermochemical treatments such as gasification, fast pyrolysis and liquefaction. Fast pyrolysis of lignocellulosic biomass leads to solid char, bio-oil and non-condensable gas with different yields depending on the type of biomass treated and on the operating conditions of the pyrolysis process [2]. Pyrolysis oil, which is the main product of

this process, contains hundreds of oxygenated compounds such as acids, ketones, aldehydes, alcohols, furanic and phenolic compounds [3]–[6]. Extraction of organic compounds from pyrolysis oil aqueous fraction is a promising way for the optimization of second generation bio-refineries, as it allows producing valuable chemicals, while the organic fraction can be used to produce bio-fuels [7], [8]. Concerning the process, liquid-liquid extraction is one of the most suitable operations for pyrolysis oil aqueous phase fractionation. By addition of a solvent in the pyrolysis oil aqueous phase, the organic compounds distribute in certain proportion in the water-rich phase and in the solvent-rich phase. The possibility of recovering the target chemicals depends on the selectivity of the solvent. The choice of the solvent is then one key aspect in the design of the liquid-liquid extraction operation. Many solvents have been investigated based on the methodology developed by Gani et al. [9]. The following criteria have been used: price, toxicity, physico-chemical properties (such as viscosity, interfacial tension, boiling temperature...) and efficiency (selectivity, partition coefficients, solvent loss). The price, toxicity and physico-chemical data were retrieved from literature and the efficiency criteria were predicted with the modified UNIFAC (Dortmund) model [10]. The solvents selected were Toluene and Isopropyl acetate. Toluene is used to extract aldehydes, ketones, phenolic and furanic compounds from aqueous phase. Isopropyl acetate is used to extract the other components from aqueous phase (acids, alcohols, cetoalcohols, and glycols).

The process conception and design of separation operations requires accurate thermodynamic models. In the case of liquid-liquid extraction, the model will give information about the Liquid-Liquid Equilibrium (LLE) between the solutes, the solvents and water (diluent) and will calculate the partition coefficient and the selectivity of the solutes between aqueous and organic phase.

The aim of this work is to provide an accurate thermodynamic model for the representation of liquid-liquid equilibria between water, pyrolysis oil organic compounds and extraction solvents. The solutes considered are acetol, acetic acid, furfural, guaiacol, methanol, phenol and propanal, which are representative molecules of the different chemical families composing the pyrolysis oil aqueous phase. Some experimental LLE datasets have already been measured in this way and were available in the literature. This article also provides new sets of LLE data. Table 1 presents the LLE systems data measured in this work and the ones already available in the literature. All these LLE data were used for the modeling.

Table 1: Systems considered for the modeling of LLE

N°	Systems	Temperature (K)	Source
1	Water + Furfural	273 - 363	[9]
2	Water + Guaiacol	298 - 323	[10]
3	Water + Phenol	273 - 340	[11]
4	Water + Propanal	288 - 313	[12]
5	Water + Isopropyl acetate	282 - 348	[13]
6	Water + Toluene	273 - 363	[14]
7	Water + Isopropyl acetate + Acetic acid	298	[15]
8	Water + Isopropyl acetate + Acetol	298, 323	this work
9	Water + Isopropyl acetate + Furfural	298, 323	this work
10	Water + Isopropyl acetate + Guaiacol	298, 323	this work
11	Water + Isopropyl acetate + Methanol	298, 323	this work
12	Water + Isopropyl acetate + Phenol	298, 323	[16], this work
13	Water + Isopropyl acetate + Propanal	298, 313	this work
14	Water + Toluene + Acetic acid	298, 313	[17]
15	Water + Toluene + Acetol	298, 323	this work
16	Water + Toluene + Furfural	303	[18]
17	Water + Toluene + Methanol	298	[19]
18	Water + Toluene + Phenol	293, 303, 313	[20]
19	Water + Toluene + Propanal	298, 313	this work

2 Experimental

2.1 Materials

Table 2 presents the chemicals used in this work. Components purity was assessed by gas chromatography and by measuring the refraction index of pure components, and comparing it with the reference values. No further purification was done after this analysis showed no significant impurities. Water was purified by a Millipore system with a 0.22 μ m membrane.

Table 2: Chemical samples used for experimental work

Chemicals	CAS number	Supplier	Purity (area %)	Analysis method ^a	Refractive index	
					Measured ^b at 20°C and 101.25 kPa	Supplier
Acetol	116-09-6	Fisher Scientific	> 95.0%	GC	1.4262	-
Furfural	98-01-1	Sigma Aldrich	> 99.0%	GC	1.5264	1.5261
Guaiacol	90-05-1	Fisher Scientific	> 99.0%	GC	1.5441	1.5429
Methanol	67-56-1	Sigma Aldrich	> 99.99%	GC	1.3293	1.3292
Phenol	108-95-2	Sigma Aldrich	> 99.5%	GC	1.5405 ^c	1.5408 ^c
Propanal	123-38-6	Fisher Scientific	> 99.0%	GC	1.3644	1.3646
Toluene	108-88-3	Sigma Aldrich	> 99.9%	GC	1.4969	1.4967
Isopropyl acetate	108-21-4	VWR	> 99.0%	GC	1.3779	1.3773

^aGC: gas chromatography. ^bMeasured with an Anton Paar Abbemat 300 Refractometer (standard uncertainty: refractive index $u(nD) = 10^{-4}$ pressure (GE Druck DPI 142 Barometric Indicator) $u(p) = 0.029$ kPa, and temperature $u(T) = 0.03$ °C). ^cMeasured at $T = 41$ °C

2.2 Experimental apparatus

Experimental work was carried out at CTP laboratory. The apparatus and experimental procedure for the LLE measurements were identical to the ones presented in a previous publication of Auger et al. [21] and were based on the “static analytical method”. The LLE glass cell, with a volume of 100mL, was enclosed with a stainless steel end-cap, and was equipped with three sampling points for the liquid phase I, the liquid phase II and the vapor phase (which was not used). The sampling points were equipped with air-tight septa to prevent any loss of material. The temperature was measured using a Pt100 Ω platinum probe ($u(T) = 0.05 K$).

All measurements were done at atmospheric pressure. The chemicals were introduced in the cell in adequate amount so that the interface between the liquid phases was above the heavy liquid phase sampling point and under the light liquid phase sampling point. The cell was introduced in a water bath and the temperature set to the desired value and the magnetic stirrer switched on. The two phase mixture was stirred for at least 1 hour and then the stirrer was switched off and the mixture was allowed to reach equilibrium during at least 2 hours. Approximately 0.5mL of each phase was sampled and their compositions were measured by gas chromatography. All samples were injected into the Gas Chromatograph (temperature of injector is equal to 200°C, flow of carrier gas (helium) equal to 20mL per minute). FID temperature was set to 200°C and TCD temperature was set to 180°C. All columns used were 2 meters length and with a diameter of 2mm. Table 3 presents the columns names and the temperature profiles for the systems studied.

Table 3: Chromatograph conditions for the compositions measurements within the different systems

Systems	Column name	Temperature profile				
		Initial temperature (K)	Level time (min)	Increasing rate (°C/min)	Final temperature (K)	Level time (min)
8, 9, 10, 12	Chromosorb100	90	2	5	110	2
11, 13	20%OV210	120	2	20	180	5
15	30%RTX1	85	6	-	-	-
19	20%OV210	60	2	5	80	-

The GC detectors (TCD and FID) were calibrated by injecting known quantities of each chemical using GC liquid syringes. Uncertainties methods and calculations are provided in appendix.

Othmer and Tobias correlation for tie-lines [22] was used to assess the smoothed trend of the data measured.

3 Models

3.1 Thermodynamic models

The activity coefficients were calculated using NRTL [23] and UNIQUAC [24] Excess Gibbs Energy models.

For NRTL model, $G_{ji} = \exp(-\alpha_{ji}\tau_{ji})$ and $\tau_{ij} = a_{ij} + \frac{b_{ij}}{T}$, where α_{ji} is the non-randomness parameters, and a_{ij} and b_{ij} are respectively the temperature dependent and temperature independent binary interaction parameters. The use of NRTL requires three sets of parameters a_{ij} , b_{ij} and α_{ij} . For the studied systems α_{ij} was set equal to α_{ji} .

For UNIQUAC model, $\tau_{ij} = \exp\left(a_{ij} + \frac{b_{ij}}{T}\right)$, where a_{ij} and b_{ij} are respectively the temperature dependent and temperature independent binary interaction parameters. The use of UNIQUAC requires two sets of parameters a_{ij} and b_{ij} . The use of UNIQUAC model requires two sets of parameters a_{ij} , b_{ij} , and r_i and q_i parameters that are listed in Table 4.

Table 4: r_i and q_i parameters of considered components for UNIQUAC model

Chemical	r_i^*	q_i^*
Acetol	2.874	2.612
Acetic acid	2.202	2.072
Furfural	3.172	2.500
Guaiacol	4.531	3.512
Methanol	1.431	1.432
Phenol	3.552	2.680
Propanal	2.574	2.336
Water	0.920	1.400
Toluene	3.923	2.968
Isopropyl acetate	4.152	3.652

*Values from Simulis™ software

3.2 Data regression

The α_{ij} parameters of NRTL equation were set to the recommended values by Renon and Prausnitz [23], depending on the type of components (non-polar, polar and self associative, or polar and non-self associative). When the correlation between the data calculated with the NRTL model and the experimental data was not satisfactory the α_{ij} parameters was regressed.

In order to regress the binary interaction parameters for both models, different objective functions were used depending of the available data. For the pairs of components with partial miscibility the binary interaction parameters were regressed on the binary systems LLE data, and for the pairs of miscible components the binary interaction parameters were regressed on the ternary systems LLE data.

Binary systems:

For both models binary interaction parameters between two components with partial miscibility, as it is the case in systems 1 to 6 (see Table 1), were regressed on the binary systems LLE. For these pairs of components both a_{ij} and b_{ij} parameters of each activity coefficient model were regressed as the data available for the corresponding binary systems cover a large range of temperature. The objective function used for the regression of these parameters was the following equation (Eq. 5).

$$OF_1 = \sum_{k=1}^{NP} \sum_i^2 \left(\frac{x_{k,i,calc}^{org} - x_{k,i,exp}^{org}}{\sigma_{k,i,exp}} \right)^2 \quad (\text{Eq. 5})$$

Where $x_{k,i,calc}$ is the mole fraction calculated of component i for the k^{th} experimental value; $x_{k,i,exp}$ is the mole fraction measured of component i for the k^{th} experimental value; NP is the number of points in the data sets; and $\sigma_{k,i,exp}$ is the uncertainty on the mole fraction measured of component i for the k^{th} experimental value.

Ternary systems:

The binary interaction parameters of components that are miscible were regressed on ternary systems LLE data sets. For these systems, only temperature independent parameters (b_{ij}) were regressed as the data sets are available at one, two, or three temperatures only (see Table 1). It is to be noted that the binary interaction parameters of water-methanol, water-acetic acid and water-acetol systems are involved in two ternary systems, corresponding to the two solvents considered. Thus, these parameters were regressed using both systems datasets at the same time in order to obtain consistent values for the parameters. The objective function (Eq. 6) takes into account the partition coefficient K_i in the calculations of the parameters as it is a key value for the liquid-liquid extraction simulation and conception.

$$OF_2 = \sum_{k=1}^{NP} \sum_{i=1}^{NC} \left[\left(\frac{x_{k,i,calc}^{org} - x_{k,i,exp}^{org}}{\sigma_{k,i,exp}} \right)^2 + \left(\frac{x_{k,i,calc}^{aq} - x_{k,i,exp}^{aq}}{\sigma_{k,i,exp}} \right)^2 + \left(\frac{K_{k,solute,calc} - K_{k,solute,exp}}{\sigma_{K_{solute},k,exp}} \right)^2 \right] \quad (\text{Eq. 6})$$

Where $x_{k,i,calc}$ is the mole fraction calculated of component i for the k^{th} experimental value; $x_{k,i,exp}$ is the mole fraction measured of component i for the k^{th} experimental value; NP is the number of points in the data sets; NC is the number of components in the dataset; aq refers to the aqueous phase; org refers to the organic phase; $K_{k,solute,calc}$ is the partition coefficient of the solute between organic and aqueous phases, detailed in equation (Eq. 7); $\sigma_{k,i,exp}$ is the uncertainty on the mole fraction measured of component i for the k^{th} experimental value; $\sigma_{K_{solute},k,exp}$ is the uncertainty on the partition coefficient obtained with experimental data.

$$K_i = \frac{x_i^{org}}{x_i^{aq}} \quad (\text{Eq. 7})$$

Commercial software Simulis™ from PROSIM, France, was used to correlate the experimental data with the UNIQUAC and NRTL models.

4 Results and Discussion

In the supplementary work, Tables 1 to 8 present the results with the uncertainties obtained for the ternary systems LLE.

The empirical tie-line Othmer-Tobias correlation (Eq. 8, [22]) was used in order to check the smoothed trend of the experimental LLE data.

$$\ln\left(\frac{1-x_1^I}{x_1^I}\right) = a + b \ln\left(\frac{1-x_3^{II}}{x_3^{II}}\right) \quad (\text{Eq. 8})$$

Where x_1^I is the mole fraction of water in the aqueous phase, x_3^{II} is the mole fraction of solvent in the organic phase, a and b are adjusted on experimental data. Two examples are presented in Figures 1 and

2 for the water-acetol-toluene and water-guaiacol-isopropyl acetate systems respectively. All the charts are available in supplementary work (Figures 1 to 8). We can observe that all charts have a smoothed trend and most of the determination coefficients are close to 1. The only datasets that have low determination coefficients are the ones of the water-guaiacol-isopropyl acetate system. If we take into account the accuracies of the Othmer-Tobias's approach of testing reliability of LLE data, we can see that the datasets reliability is satisfactory (Figure 2).

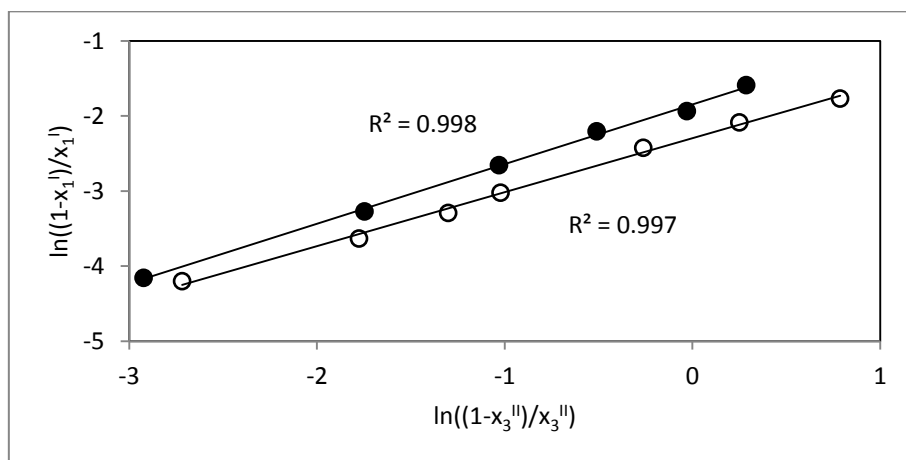


Figure 1: Data treatment of the ternary system water (1) - acetol (2) - toluene (3) using the Othmer-Tobias correlation (o): 298.15 K, and (●): 323.15 K

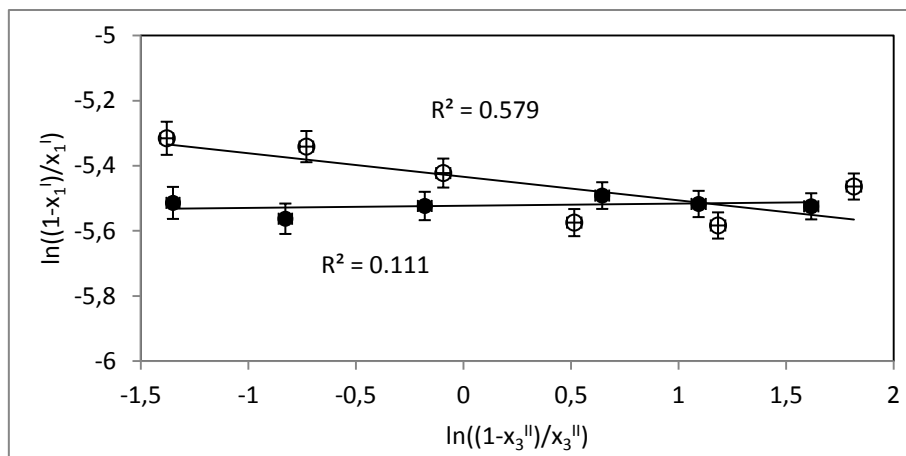


Figure 2: Data treatment of the ternary system water (1) - guaiacol (2) - isopropyl acetate (3) using the Othmer-Tobias correlation (o): 298.15 K, and (•): 323.15 K

A density inversion phenomenon is observed for systems containing furfural, guaiacol or phenol. These solutes have higher densities than water, while the solvents used in this work have lower densities than water. The organic phase, mostly containing solvent and solute, has lower density than the aqueous phase when its composition is rich in solvent, and higher density than the aqueous phase when its composition is rich in solute. When organic phase density is equal to aqueous phase density, an emulsion is obtained but decantation is impossible as gravity plays insufficient role as the driving force for phase separation. This phenomenon has not been deeply investigated because it has no impact on the liquid-liquid extraction process of the pyrolysis oil since the solutes concentrations are too low for causing the described phenomenon. However, it has an impact on the measurements. When organic phase and aqueous phase densities are similar, decantation phenomenon is much slower and may be incomplete when sampling. The density inversion phenomenon can be investigated by analyzing the density variations of each phase in order to find the compositions in which the density of the two phases is the same.

For the purpose of this work, the thermodynamic models should represent properly the molar compositions and the partition coefficients of solutes, and especially for low solute concentrations. All the calculated LLE values and the ternary diagrams are presented in supplementary work (Tables 9 to 27 and Figures 9 to 39). As examples, the LLE ternary diagrams for water-acetol-isopropyl acetate and water-methanol-isopropyl acetate are presented in Figures 3 and 4.

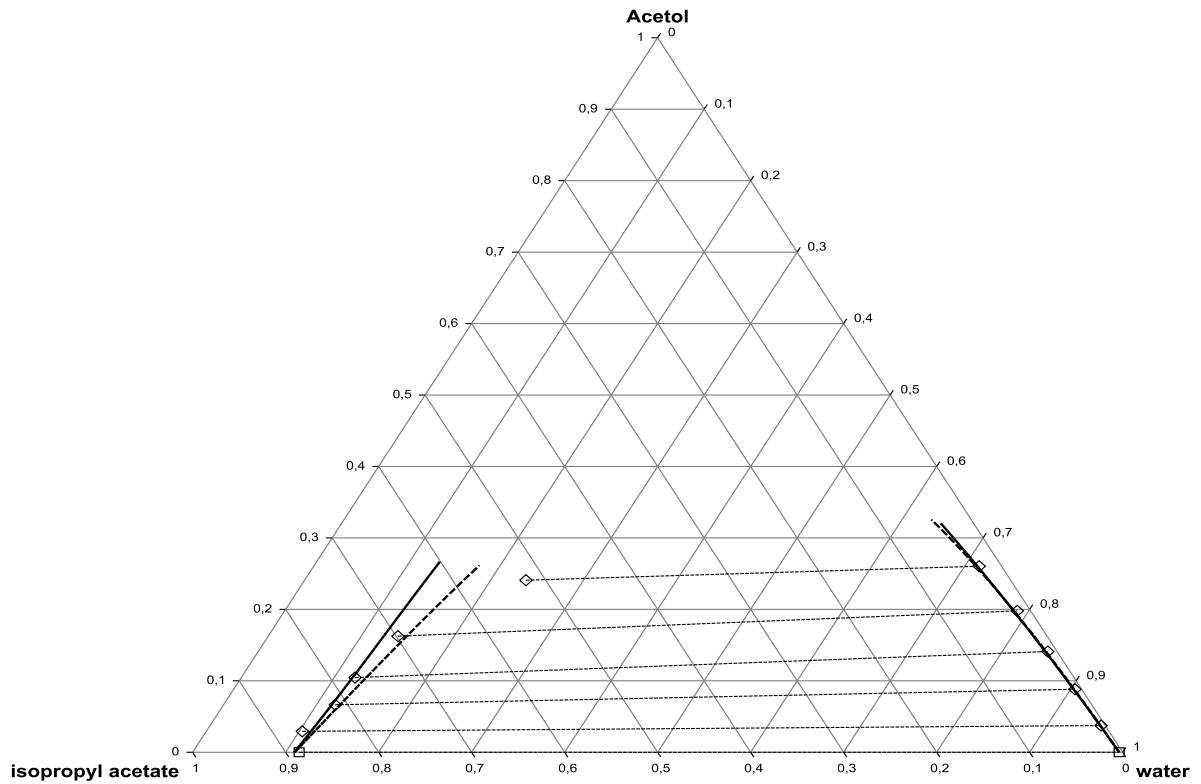


Figure 3: Ternary diagram for water - acetol - isopropyl acetate system LLE at 323.15K and atmospheric pressure, (□): experimental data [13], (◊): experimental data [this work], (—): UNIQAC model, (- - -): NRTL model

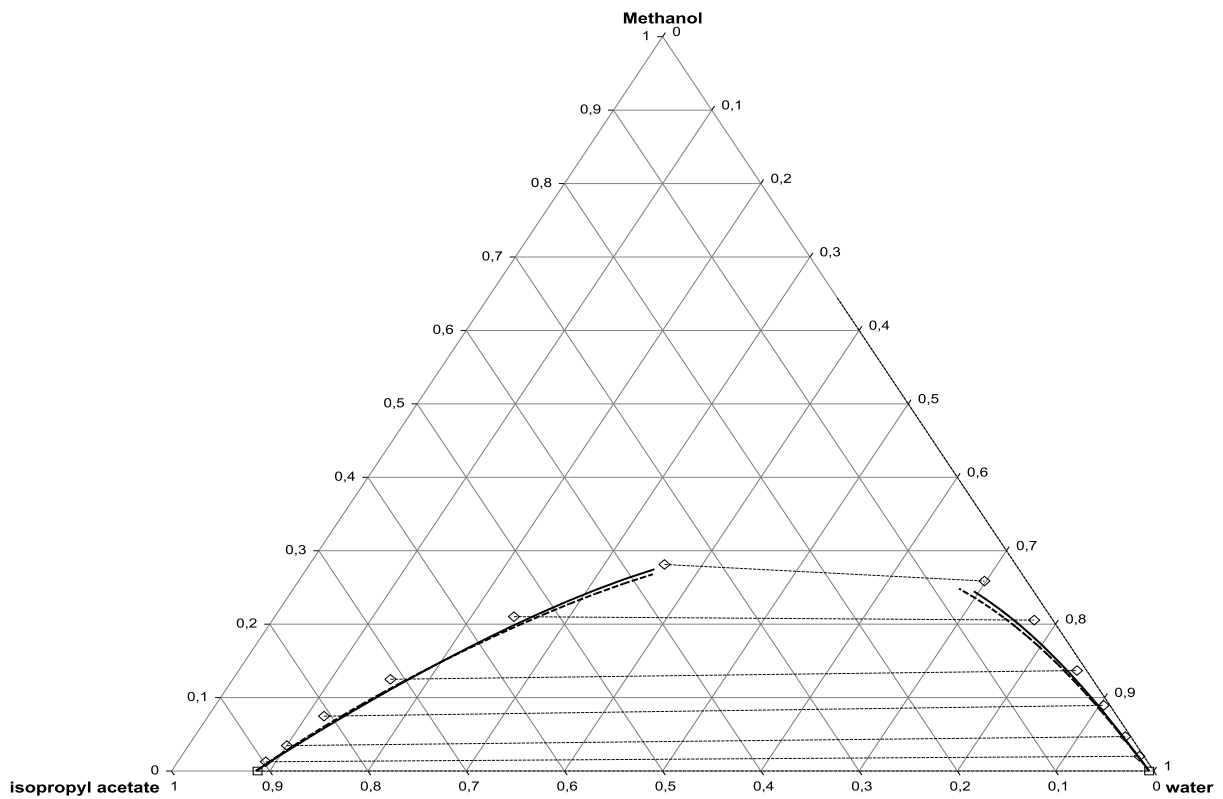


Figure 4: Ternary diagram for water - methanol - isopropyl acetate system LLE at 298.15K and atmospheric pressure, (□): experimental data [13], (◊): experimental data [this work], (—): UNIQAC model, (- - -): NRTL model

All the NRTL model α_{ij} parameters were fixed at the recommended values except for the isopropyl acetate-phenol binary because it allowed a significant improvement of the representation of the water-phenol-isopropyl acetate ternary system LLE experimental data. Figure 5 is the LLE ternary diagram for water-phenol-isopropyl acetate system at 323.15K with the experimental data and the calculated values with NRTL model with the recommended α_{ij} parameter (0.47) and with NRTL model with the regressed α_{ij} parameter (-0.093).

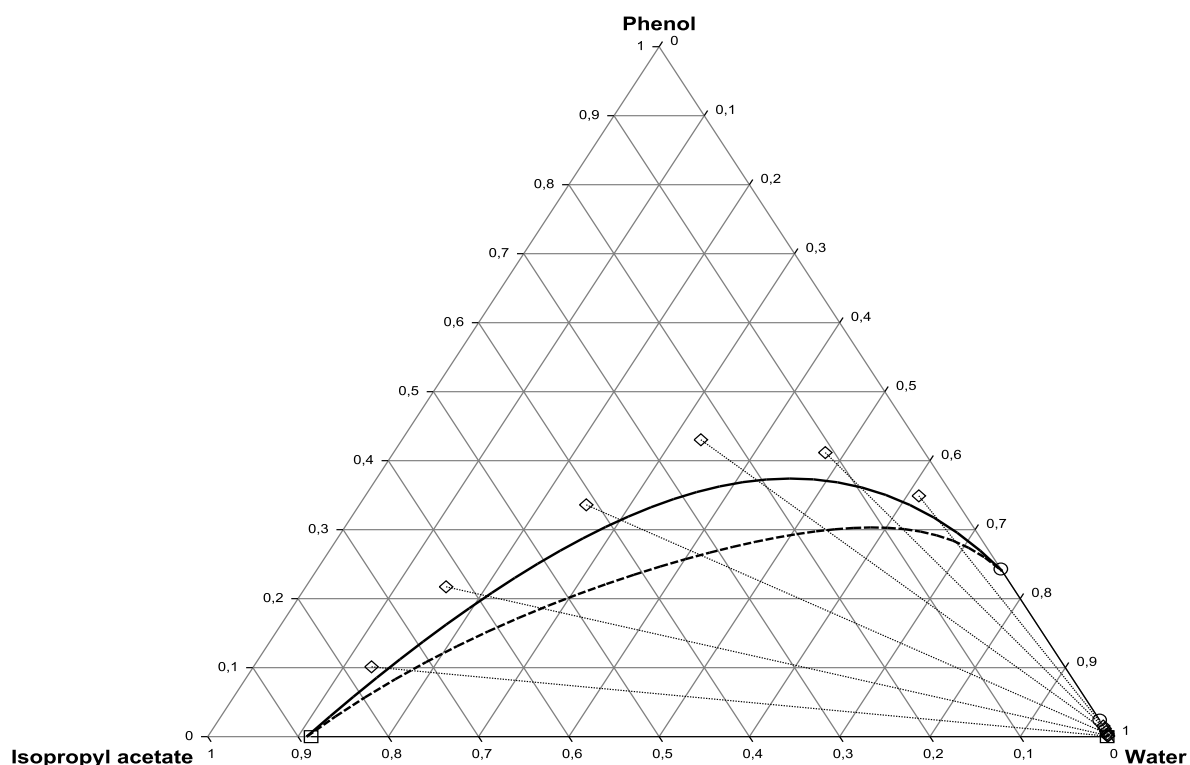


Figure 5: Ternary diagram for water - phenol - isopropyl acetate system LLE at 323.15K and atmospheric pressure. (\square): experimental data [13]. (\circ): experimental data [11]. (\diamond): experimental data [this work]. (---): NRTL model with recommended parameter [23], (—):NRTL model with regressed parameter.

For water-acetol-isopropyl acetate system (Figure 3, supplementary work, Table 16, Figure 17) the compositions calculated by the models showed a significant deviation from the experimental data when approaching the liquid-liquid critical point. For acetol lower concentration, the models were accurate. NRTL model was slightly more accurate than UNIQUAC model for this system. For water-guaiacol-isopropyl acetate and water-furfural-isopropyl acetate systems (supplementary work, Tables 17 and 18, Figures 18, 19, 20 and 21), an accurate representation of the data with NRTL model was obtained, but UNIQUAC model was unable to represent accurately the experimental LLE data for these systems. For water-furfural-toluene system (supplementary work, Table 24, Figure 32), an accurate representation of the data with UNIQUAC model was obtained, and NRTL model showed significant deviation for high furfural concentrations. For ternary systems containing phenol

(supplementary work, Table 20, Figures 25 and 26), a significant deviation between calculated and experimental data was obtained for both models.

The average absolute deviation (AAD, Eq.9) for all the systems is presented in Tables 5 and 6, and the parity charts of partition coefficients of solutes (experimental vs. calculated) are presented in supplementary work (Figures 40 to 63).

$$AAD = \sum_{i=1}^N \frac{|x_{i,calc} - x_{i,exp}|}{N} \quad (\text{Eq. 9})$$

Table 5: Average Absolute Deviations (AAD) for the compositions calculated with UNIQUAC and NRTL models with respect to the experimental data for binary systems

Systems*	UNIQUAC				NRTL			
	Organic phase		Aqueous phase		Organic phase		Aqueous phase	
	water	solute	water	solute	water	solute	water	solute
1	0.0055	0.0055	0.00094	0.00094	0.0090	0.0091	0.0013	0.0013
2	0.0024	0.0024	0.00010	0.00010	0.0038	0.0038	0.000031	0.000031
3	0.0112	0.0145	0.0059	0.0050	0.0078	0.0097	0.0052	0.0038
4	0.0139	0.0129	0.0096	0.0089	0.0071	0.0071	0.0078	0.0078
5	0.0034	0.0026	0.00011	0.00011	0.0024	0.0028	0.00014	0.00015
6	0.00029	0.00030	0.000023	0.000024	0.00026	0.00026	0.000023	0.000022
AAD	0.0061	0.0064	0.0028	0.0025	0.0051	0.0055	0.0024	0.0022

*The system numbers refers to the ones in Table 1

Table 6: Average Absolute Deviations (AAD) for the compositions calculated with UNIQUAC and NRTL models with respect to the experimental data for ternary systems

Systems*	UNIQUAC						NRTL					
	Organic phase			Aqueous phase			Organic phase			Aqueous phase		
	water	solute	solvent	water	solute	solvent	water	solute	solvent	water	solute	solvent
7	0.026	0.0091	0.017	0.00093	0.0031	0.0034	0.022	0.0042	0.017	0.0045	0.0020	0.0038
8	0.019	0.0083	0.026	0.0069	0.0061	0.0028	0.018	0.0061	0.021	0.0067	0.0050	0.0026
9	0.031	0.015	0.016	0.00059	0.00037	0.00050	0.024	0.013	0.011	0.00087	0.00095	0.00045
10	0.053	0.029	0.024	0.00027	0.00012	0.00020	0.025	0.014	0.011	0.00029	0.00016	0.00030
11	0.019	0.0028	0.020	0.0061	0.0019	0.0065	0.018	0.0038	0.021	0.013	0.0046	0.012
12	0.075	0.040	0.036	0.0018	0.0016	0.00022	0.035	0.017	0.019	0.0014	0.0012	0.00023
13	0.018	0.0086	0.0096	0.0046	0.0044	0.00056	0.015	0.0064	0.0084	0.0054	0.0052	0.00059
14	0.0034	0.0023	0.0028	0.0020	0.0021	0.00040	0.0018	0.0033	0.0047	0.0026	0.0027	0.00042
15	0.0015	0.0077	0.0076	0.0064	0.0031	0.0034	0.0016	0.0090	0.0098	0.0074	0.0017	0.0071
16	0.016	0.0060	0.010	0.0013	0.0013	0.00012	0.050	0.027	0.023	0.00093	0.00080	0.00014
17	0.0039	0.0057	0.0074	0.0020	0.0038	0.0027	0.0046	0.0078	0.0044	0.0066	0.0059	0.0027
18	0.033	0.019	0.014	0.039	0.0021	0.00012	0.059	0.027	0.032	0.0014	0.0014	0.00011
19	0.017	0.0081	0.0095	0.0027	0.0027	0.00011	0.017	0.0078	0.0092	0.0030	0.0031	0.00011
AAD	0.024	0.012	0.015	0.0057	0.0025	0.0016	0.022	0.011	0.015	0.0042	0.0027	0.0023

*The system numbers refers to the ones in Table 1

The AAD on the molar compositions is 0.0089 with the UNIQUAC model and 0.0082 with the NRTL model. We can observe that both models represented the data with a good agreement and that the NRTL model was slightly better for the systems considered. These two activity coefficient models calculate data with a significant deviation with experimental data. Practically, thermodynamic models with parameter adjusted on experimental data should represent the LLE for the considered systems more accurately. This deviation should be contextualized in the frame of extraction process simulations. The use of this model with the regressed parameters still represents an improvement, and it allows estimating the compositions and partition coefficients with an error of less than 20%.

The binary interaction parameters for both models are presented in Table 7.

Table 7: Binary interaction parameters for UNIQUAC and NRTL models

Component i	Component j	UNIQUAC				NRTL				
		a_{ij} (-)	a_{ji} (-)	b_{ij} (K)	b_{ji} (K)	a_{ij} (-)	a_{ji} (-)	b_{ij} (K)	b_{ji} (K)	α (-)
water	furfural	-1.782	3.109	425.6	-1111	3.471	-3.338	31.44	1264	0.3
water	guaiaicol	-3.988	5.600	1096	-1857	5.884	-5.185	-288.8	1807	0.3
water	isopropyl acetate	-1.828	1.774	450.7	-1015	7.790	-0.4584	-1015	669.9	0.3
water	phenol	-0.01308	1.062	-569.5	-55.63	1.228	-5.239	764.7	1662	0.47
water	propanal	-2.429	1.215	710.5	-710.0	7.604	1.696	-1674	-217.4	0.3
water	toluene	-1.102	1.766	29.73	-1373	7.119	-2.440	-96.85	1855	0.2
water	acetol	0	0	446.4	-1997	0	0	-304.7	388.3	0.3
water	acetic acid	0	0	-20.50	222.3	0	0	-409.4	904.7	0.3
water	methanol	0	0	497.3	-2023	0	0	-134.6	-674.4	-0.093
isopropyl acetate	propanal	0	0	17.72	-20.29	0	0	3844	-181.4	0.3
isopropyl acetate	furfural	0	0	-10.79	10.49	0	0	-99.63	205.7	0.47
isopropyl acetate	phenol	0	0	-547.8	384.6	0	0	825.0	-275.3	0.3
isopropyl acetate	guaiaicol	0	0	-4.119	45.83	0	0	616.4	-182.2	0.47
isopropyl acetate	acetol	0	0	91.54	-137.8	0	0	493.4	296.2	0.3
isopropyl acetate	acetic acid	0	0	283.8	-29.20	0	0	-79.78	14.74	0.3
isopropyl acetate	methanol	0	0	-445.5	164.4	0	0	614.0	-435.4	0.3
toluene	propanal	0	0	-23.70	3.452	0	0	-98.03	-276.3	0.3
toluene	furfural	0	0	-1290	272.1	0	0	-166.1	498.9	0.3
toluene	phenol	0	0	-291.1	91.56	0	0	-419.8	314.3	0.3
toluene	guaiaicol	0	0	-0.1296	-311.0	0	0	-445.1	265.4	0.3
toluene	acetol	0	0	-109.5	-74.79	0	0	393.2	439.9	0.47
toluene	acetic acid	0	0	28.90	-124.7	0	0	73.64	369.3	0.47
toluene	methanol	0	0	-508.9	43.68	0	0	399.3	384.4	0.47

5 Conclusion

In this study, new LLE data were measured from 298.15 K to 323.15 K at atmospheric pressure for eight ternary mixtures with static analytical method. These mixtures represent typical systems involved in biorefinery processes. They were combined with other LLE data available in the literature

and were represented accurately with NRTL and UNIQUAC activity coefficient models. The modeling of these systems is valuable for the simulation of liquid-liquid extraction process of oxygenated compounds from pyrolysis oil aqueous phase using two solvents. According to the literature and the measured data, toluene is considered to be a good candidate as extraction solvent for phenol, furfural and propanal. However, toluene is a toxic a petroleum based solvent and alternative solvents should be investigated. Similarly, Isopropyl acetate is considered to be a good candidate as extraction solvent for all the solutes considered.

Appendix

The uncertainties on the molar compositions have been calculated based on the error of measurements on the FID and TCD. The calibration of the detectors was done by injecting known values of products. Linear correlations between the chromatogram peaks areas and the molar quantities of injected products was done. The relative error $\left(\frac{\Delta n_i}{n_i}\right)$ of the correlations is less than 6.0%. The distribution of the values of the molar quantities has been considered rectangular. Thus, the uncertainty on the molar quantities is $u(n_i) = \frac{\Delta n_i}{\sqrt{3}}$.

The calculation of the uncertainties on the molar composition was calculated as follow:

$$\frac{u(x_i)}{x_i} = \sqrt{(1 - x_i)^2 \cdot \left(\frac{u(n_i)}{n_i}\right)^2 + \sum_{j \neq i} \left[x_j^2 \cdot \left(\frac{u(n_j)}{n_j}\right)^2 \right]}$$

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