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Thermodynamic modeling of the condensable fraction of a gaseous effluent from lignocellulosic biomass torrefaction

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A B S T R A C T

The condensable fraction of the gaseous effluent from the torrefaction process of wood is a complex mixture of more than one hundred oxygenated species (alcohols, acids, aldehydes, ketones, furans, phenolic, *g*aiacols and sugars) diluted in water where some of them are likely to react. This effluent is currently burnt to provide energy but it could be valorized as bio-sourced chemicals. To recover target products like acetic acid, glycolaldehyde, furfural and eugenol a first step of thermodynamic modeling of this complex mixture is required to be able to propose different strategies of separation-purification. This was done here by coupling the UNIQUAC model with chemical equilibria involved in the reactive mixture. Binary interaction parameters were identified using vapor–liquid equilibria data from the literature. The predicted results are in good agreement with the experimental data of systems containing water, methanol, formaldehyde, acetic acid, formic acid, propionic acid, furfural and furfuryl alcohol, main components of the considered mixture and their associated reaction products.

Keywords:
Reactive phase equilibria
Modeling
Torrefaction
Volatile matter
UNIQUAC

1. Introduction

Sustainable resources and processes are nowadays increasingly studied to propose alternatives to the use of fossil raw materials. Lignocellulosic biomass, as wood for example, is a renewable resource but its moisture content is high and it is not an easily grindable material [1]. Furthermore, its energy density is lower than coal. These issues could be overcome thanks to the torrefaction process.

Torrefaction is a thermal process carried out at temperatures below 300 °C, under inert atmosphere, at atmospheric pressure, and with residence times for the solid biomass ranging from few minutes to several hours [2,3]. Torrefied wood is a solid product constituted by more than 70% of the initial mass with properties close to those of coal. The 30% remaining part is a gaseous effluent [2,3], composed of about one third of non condensable gases - carbon monoxide and carbon dioxide - and two thirds of condensable species.

Currently, torrefied wood is the main product of interest and is usually transformed into energetic gases by the gasification process [4–6] or directly used as coal for combustion [7,8]. Conversely, gaseous by-products are considered at present time as a waste [9] and in the best case are burned to provide energy to the process [6]. Yet, the recovery and valorization of the condensable fraction as bio-sourced chemicals is worth considering.

An experimental study of the torrefaction of four various biomass types showed that there were significant differences in gaseous product composition depending on the nature of the biomass [10]. Condensable species composition exhibit more than one hundred oxygenated components (partially identified and quantified) and significantly differs depending on the biomass type.

Any preliminary study to assess new routes, as for instance non energetic valorization of such gaseous effluent, requires knowledge of thermodynamics of these complex mixtures. Indeed, some thermodynamic models already exist for part of this mixture. In the general biorefinery field, some experimental and modeling studies of vapor–liquid equilibria have been published [11,12]. More specifically, thermodynamics of formaldehyde (one of the major components of this gaseous effluent), and its mixtures with water, were developed using an approach coupling physical and chemical

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equilibria [13,14].

This work is indeed an extension of our previously published model [13] with the aim at representing now the vapor–liquid thermodynamic behavior of the whole torrefaction condensable fraction using a combined physical and chemical model. In this paper, a strategy for modeling the vapor–liquid equilibria for a mixture of 22 representative components is proposed, including possible chemical reactions.

The paper is organized as follows. In Section 1 the characteristics of condensates from lignocellulosic biomass torrefaction are briefly introduced. In Section 2, the strategy to develop the thermodynamic model is exposed and the choice of UNIQUAC to calculate activity coefficients is justified. Section 3 presents the method to estimate the unknown UNIQUAC binary interaction parameters. In Section 4 the results are reported and discussed. Indeed, such a thermodynamic modeling is the pre-requisite to propose and assess (on energetic and economic criteria) different separation schemes to produce bio-sourced chemicals from the gaseous effluent of the torrefaction process. These future studies (not in the scope of this work), based on this modeling, will be able to provide the quantitative data to decide the viability of such a valorization strategy.

2. Characterization of condensates from lignocellulosic biomass torrefaction

Few descriptions of the volatile matter after torrefaction are available in the literature. Table 1 gives a short inventory of the species identified in torrefaction effluents. Non condensable gases are mainly carbon monoxide and carbon dioxide. A focus on the condensable part of the volatile matter shows that condensates are a multicomponent mixture, chemically and thermally unstable, containing oxygenated species diluted in water. The oxygenated species belong to different chemical classes: water, alcohols, acids, aldehydes, ketones, furans, phenolics, gaïacols.

The main component is water accounting for 60%mol to 80%mol. Minor components are diluted in water which makes their separation a hard task. Moreover, minor components are present in proportions varying with the processed biomass [2].

As it is impossible to consider all the components present in condensates for modeling, a representative mixture was established for condensates. The analysis of the experimental data collected in the frame of INVERTO project enabled us to select an acceptable number of 22 components including: water (*W*), methanol (*ME*), formaldehyde (*FA*), methylene glycol (*MG*), hemiformal (*HF*), 6 poly(oxyethylene) glycols from a degree 2 to a degree 7 (*MG*₂–*MG*₇), 6 poly(oxyethylene) hemiformals from a degree 2 to a degree 7 (*HF*₂–*HF*₇), acetic acid (*A*₁), formic acid (*A*₂), propionic acid (*A*₃), furfural (*Fu*) and furfuryl alcohol (*FuAl*). All these compounds are present in significant amounts (a few g/L in the condensed aqueous phase).

A previous study was dedicated to the modeling of aqueous solutions of formaldehyde and methanol [13] and the same approach is used here to be extended to the modeling of the representative mixture of the torrefaction condensates.

3. Thermodynamic model

The complexity of the condensate mixture makes its purification a difficult task and this complexity has to be handled first by a suitable thermodynamic description. An important point to emphasize is the presence of reactive components in the mixture: carboxylic acids associate in the vapor phase and formaldehyde polymerizes with water and methanol to produce hemiformal, methylene glycol, poly(oxyethylene) hemiformals and poly(oxyethylene) glycols. So, vapor–liquid equilibria must be coupled with those chemical equilibria for a suitable description of condensates thermodynamic behavior.

Table 1
Inventory of species identified in torrefaction effluents listed in the literature.

Chemical class	CAS number	Component	[1]	[15]	[16]	[17]	[2]	[10]	Our mixture
Alcohol	67-56-1	Methanol	✓			✓	✓		✓
Aldehydes and Ketones	116-09-6	Hydroxyacetone (acetol)	✓	✓		✓		✓	✓
	75-07-0	Acetaldehyde						✓	
	141-46-8	Hydroxyacetaldehyde (glycolaldehyde)		✓				✓	✓
Acids	50-00-0	Formaldehyde		✓			✓	✓	✓
	64-19-7	Acetic acid	✓	✓		✓	✓	✓	✓
	64-18-6	Formic acid	✓	✓		✓	✓	✓	✓
	79-09-4	Propionic acid		✓				✓	✓
	50-21-5	Lactic acid	✓			✓			
Furans	98-01-1	Furfural	✓			✓	✓	✓	✓
	98-00-0	2-furanmethanol						✓	✓
Phenolics and Gaïacols	108-95-2	Phenol	✓		✓				
	90-05-1	2-methoxyphenol (gaïacol)			✓				
	106-44-5	4-methylphenol (p-cresol)			✓				
	93-51-6	2-methoxy-4-methylphenol (4-methylgaïacol)			✓				
	2785-89-9	4-ethyl-2-methoxyphenol (4-ethylgaïacol)			✓				
	91-10-1	2,6-dimethoxyphenol (syringol)			✓				
	97-53-0	2-methoxy-4-prop-2-enylphenol (eugenol)			✓				
	121-33-5	4-hydroxy-3-methoxybenzaldehyde (vanillin)			✓				
			2-methoxy-4-(1E)-prop-1-en-1-ylphenol			✓			
	121-34-6	4-hydroxy-3-methoxybenzoic acid (vanillic acid)			✓				
	6443-69-2	1,2,3-trimethoxy-5-methylbenzene			✓				
			2,6-dimethoxy-4-prop-2-enylphenol			✓			
			1,4-hydroxy-3,5-dimethoxyphenylethanone			✓			
	2478-38-8	7,9-dihydroxy-3-methoxy-1-methyl-6H-dibenzo(b,d)pyran-6-one			✓				
Water	7732-18-5	Water	✓	✓		✓	✓	✓	✓
Incondensables	124-38-9	Carbon dioxide	✓	✓		✓	✓	✓	
	630-08-0	Carbon monoxide	✓	✓		✓	✓	✓	

3.1. Description of the thermodynamic behavior of the reactive mixture

As mentioned above, when modeling thermodynamics of such systems, the main difficulty is to account for the coupling of chemical and physical equilibria of these reactive molecules. A review of thermodynamics for reactive mixtures has been given by Maurer [14] where it is suggested to uncouple the physical and the chemical phenomena in the model so as to differentiate the effects of weak intermolecular interactions of the physical equilibria from the strong intermolecular interactions involved in the chemical reactions. This modeling approach has also the advantage of avoiding spreading the uncertainty on the chemical equilibrium constant into the physical equilibrium parameters.

Fig. 1 illustrates the outline of this model. Note that in our approach the system is considered at chemical and physical equilibrium and therefore no chemical or physical kinetic data are considered.

Thus, the reactive vapor–liquid equilibrium model includes:

- physical phase equilibria described using a $\gamma - \phi$ approach to account for this multicomponent system with a large range of molar masses and volatilities. The physical interactions between all species are taken into account through activity coefficients calculation in the liquid phase and through an equation of state for the gas phase.
- 2 chemical reaction equilibria for the formation of methylene glycol and hemiformal:
 - formation of methylene glycol: $FA + W \rightleftharpoons MG$
 - formation of hemiformal: $FA + ME \rightleftharpoons HF$
- 12 chemical reaction equilibria between the poly(oxy-methylene) glycols, poly(oxymethylene) hemiformals:
 - formation of poly(oxymethylene) glycols: $MG_{n-1} + MG \rightleftharpoons MG_n + W$

- formation of poly(oxymethylene) hemiformals: $HF_{n-1} + HF \rightleftharpoons HF_n + ME$
- 3 direct dimerization and 3 crossed dimerization chemical equilibria of acetic acid, formic acid and propionic acid are assumed to occur in the vapor phase:
 - direct dimerization of a carboxylic acid A_i : $2A_i \rightleftharpoons A_{i2}$
 - crossed dimerization of A_i and A_j : $A_i + A_j \rightleftharpoons A_iA_j$

where A_i and A_j correspond to one of the following carboxylic acid: acetic acid, formic acid, propionic acid. A total of 20 reactions are accounted for in the description of the behavior of the reactive mixture.

Note that once the vapor–liquid equilibrium equations and the chemical reaction equilibrium equations in one phase are satisfied, the chemical-reaction equilibrium equations in the other phase are automatically satisfied.

3.2. Vapor-liquid equilibrium model

As the model will not be used under pressure, the gas phase was considered as a perfect gas where gas phase associations of carboxylic acids; and methylene glycol and hemiformal formations are included.

To calculate the activity coefficients of the liquid phase, three models based on the local composition were considered: UNiversal Functional Activity Coefficient Original (UNIFAC Original). Non Random Two Liquids (NRTL) and UNiversal QUAsi Chemical (UNIQUAC). Table 2 synthesises a comparison of these thermodynamic models. The advantage of the UNIFAC Original model lies in its predictive capability and is interesting when experimental data are lacking. Meanwhile, its range of temperature applicability is relatively poor [18]. Pressure and temperature ranges of UNIQUAC applicability are greater than UNIFAC Original. Semi-empirical models like NRTL or UNIQUAC are more accurate for the binaries

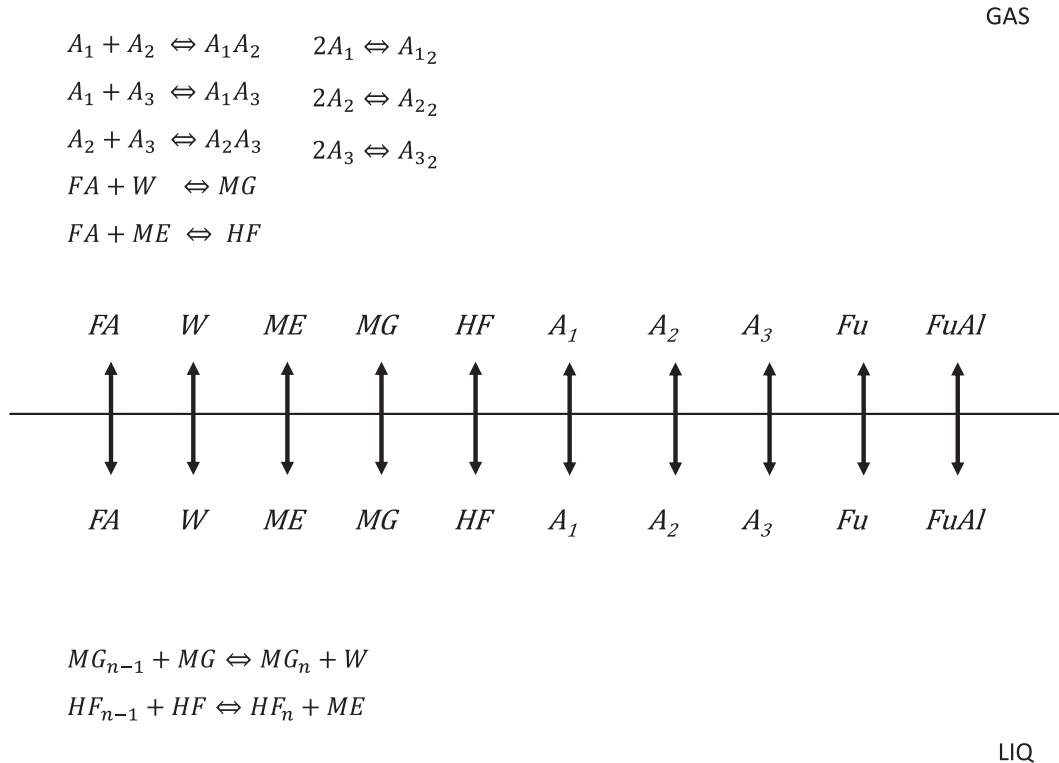


Fig. 1. Scheme of the reactive vapor–liquid equilibrium for the representative mixture.

Table 2

Comparison of thermodynamics models based on the local composition concept.

Thermodynamic model	Advantages	Drawbacks
UNIFAC Original	No experimental data required (predictive model) Multicomponent vapor–liquid equilibria	Not recommended for process design Not able to differentiate isomers Poor range of temperature applicability
NRTL	Multicomponent vapor–liquid and liquid–liquid equilibria Widely used for flowsheeting and process design Experimental data taken into account in the model	Large number of binary interaction parameters to identify Molecule shape and size difference effects not taken into account
UNIQUAC	Multicomponent vapor–liquid and liquid–liquid equilibria Widely used for flowsheeting and process design Experimental data taken into account in the model Molecule shape and size difference effects taken into account directly in the model	Large number of binary interaction parameters to identify

for which experimental data are available. Compared to NRTL, UNIQUAC takes into account the molecule shape and size difference effects and is then more suitable for the studied asymmetric mixture containing both small molecules (methanol, formaldehyde, formic acid ...) and larger ones (furfural, poly(oxyethylene) glycols ...).

Therefore, the UNIQUAC model was selected to describe the non-ideality of the liquid phase. UNIQUAC equations [19] are given by:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (1)$$

$$\ln \gamma_i^C = \ln \frac{\phi_i}{x_i} + \frac{Z}{2} \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_{j=1}^{n_c} x_j l_j \quad (2)$$

$$\ln \gamma_i^R = q_i \left(1 - \ln \sum_{j=1}^{n_c} \theta_j \tau_{ji} - \sum_{j=1}^{n_c} \frac{\theta_i \tau_{ij}}{\sum_{k=1}^{n_c} \theta_k \tau_{kj}} \right) \quad (3)$$

$$\phi_i = \frac{x_i r_i}{\sum_{i=1}^{n_c} x_i r_i} \quad \text{and} \quad \theta_i = \frac{x_i q_i}{\sum_{i=1}^{n_c} x_i q_i} \quad (4)$$

$$l_i = \frac{Z}{2} (r_i - q_i) - (r_i - 1) \quad (5)$$

$$\tau_{ij} = \exp \left(-\frac{A_{ij}}{RT} \right) \quad \text{and} \quad \tau_{ji} = \exp \left(-\frac{A_{ji}}{RT} \right) \quad (6)$$

$$A_{ij} = A_{ij}^0 + A_{ij}^T (T - T_{ref}) \quad \text{and} \quad A_{ji} = A_{ji}^0 + A_{ji}^T (T - T_{ref}) \quad (7)$$

The UNIQUAC binary interaction parameters (see equation (7)) were identified for the different binaries of the condensate representative system using either experimental vapor–liquid data from literature when available or numerical data generated by UNIFAC Original [20,21]. The determination of UNIQUAC binary interaction parameters is detailed in the following part.

4. Determination of UNIQUAC binary interaction parameters

UNIQUAC binary interaction parameters must be estimated for systems including water, methanol, formaldehyde, methylene glycol, hemiformal, poly(oxyethylene) glycols (*MG* – *MG*₇), poly(oxyethylene) hemiformals (*HF* – *HF*₇), acetic acid, formic acid, propionic acid, furfural, furfuryl alcohol. The binary interaction parameters of the formaldehyde – water – methanol reactive system were formerly identified [13]. Some binaries (like water – methanol, water – acetic acid ...) have been widely studied in the

literature. Nevertheless, as the reported binary interaction parameters may have been estimated with other values of the pure component properties than those used in this study, they were identified again in this work using experimental data recommended by the DECHEMA.

Different cases were considered for the binary interaction parameters estimation (see Table 3):

1. case 1: non-reactive binary systems
2. case 2: binary systems involving formaldehyde species and other components except carboxylic acids
3. case 3: binary systems involving carboxylic acids

Component abbreviations are defined in the nomenclature. The reactive vapor–liquid equilibrium of the water-methanol-formaldehyde system was already modeled [13] so the reference of the publication is given for these binaries.

For case 1 and case 2, the same physical phase equilibrium equations were used, given by:

$$y_i P = x_i \gamma_i(T, x) P_i^S(T) \quad (8)$$

The coefficients a_i of the equations to calculate the vapor pressure of pure component i with respect to temperature were taken from the DIPPR Database [22] available through the Simulis Thermodynamics package (ProSim):

$$\ln P_i^S(T) = a_{1,S} + \frac{a_{2,S}}{T} + a_{3,S} \ln T + a_{4,S} T^{a_{5,S}}$$

When available in the literature experimental vapor–liquid data were used for the identification of the UNIQUAC binary interaction parameters. When no data were available, vapor–liquid numerical data at constant vapor ratio and temperature (or pressure) were generated using the UNIFAC Original model [21,20]. As mentioned above, it was chosen to uncouple the physical and chemical phenomena for systems involving formaldehyde species to avoid to spread the uncertainty of the chemical equilibrium constants into the parameters of the physical equilibrium. Because of the presence of the chemical reactions, no uncoupled vapor–liquid experimental data were available in the literature. So, vapor–liquid data were generated using the UNIFAC Original model for case 2. Note that binary interaction parameters of systems labeled 2 in Table 3 have to be ascertained as soon as experimental data become available.

Finally, for case 3 (binaries involving carboxylic acids), conventional physical phase equilibrium equations, with an association term to account for chemical equilibria, were used for the identification. Nevertheless, when dealing with the dimerization equilibria of carboxylic acids, it was found more convenient not to uncouple physical and chemical equilibria. Indeed, for these specific compounds, the uncoupled approach has been developed for long [23] and was already implemented in the Prosim Plus software. In this case, it is proposed to use a correction term in equation

Table 3

Matrix of the modeling assumptions for each binary of the mixture.

	A_1	A_2	A_3	W	ME	FA	MG	$MG_2 - MG_7$	HF	$HF_2 - HF_7$	Fu	$FuAl$
A_1	—	—	—	—	—	—	—	—	—	—	—	—
A_2	3	—	—	—	—	—	—	—	—	—	—	—
A_3	3	3	—	—	—	—	—	—	—	—	—	—
W	3	3	3	—	—	—	—	—	—	—	—	—
ME	3	3	3	1	—	—	—	—	—	—	—	—
FA	3	3	3	[13]	[13]	—	—	—	—	—	—	—
MG	3	3	3	[13]	[13]	[13]	—	—	—	—	—	—
$MG_2 - MG_7$	3	3	3	[13]	[13]	[13]	[13]	—	—	—	—	—
HF	3	3	3	[13]	[13]	[13]	[13]	[13]	—	—	—	—
$HF_2 - HF_7$	3	3	3	[13]	[13]	[13]	[13]	[13]	[13]	—	—	—
Fu	3	3	3	1	1	2	2	2	2	2	—	—
$FuAl$	3	3	3	1	1	2	2	2	2	2	1	—

1 non-reactive binary systems.

2 binary systems involving formaldehyde species and other components except carboxylic acids.

3 binary systems involving carboxylic acids.

[13] formaldehyde – methanol – water reactive system formerly identified.

(8), $\phi_i^{V,S}$, which accounts for the presence of the dimerization equilibria:

$$y_i \frac{\phi_i^V(T, P, y)}{\phi_i^{V,S}(T, P_i^S(T))} P = x_i \gamma_i(T, x) P_i^S(T) \quad (9)$$

At equilibrium, components present in the vapor phase follow the perfect gas law so $\phi_i^V(T, P, y) = 1$. The correction terms, also termed vapor fugacity coefficients of pure constituent i at saturation pressure, are calculated as follows: $\phi_i^{V,S} = \frac{-1 + \sqrt{1 + 4K(T)P_i^S(T)}}{2K(T)P_i^S(T)}$.

Note that $\phi_i^{V,S}(T, P_i^S(T)) = 1$ for all other components.

Chemical reaction equilibrium constants are obtained as follows:

- Direct dimerization of carboxylic acid A: $\log K_{A_2} = \alpha_A + \frac{\beta_A}{T}$
- Direct dimerization of carboxylic acid B: $\log K_{B_2} = \alpha_B + \frac{\beta_B}{T}$
- Crossed dimerization of carboxylic acid A and carboxylic acid B: $K_{AB} = \sqrt{K_A K_B}$ and $\log K_{AB} = \alpha_{AB} + \frac{\beta_{AB}}{T}$

For direct dimerization, parameters α_A , α_B , β_A , β_B are taken

from the DECHEMA literature [24]:

Component	\hat{a}	\hat{a}
Acetic acid	-10.421	3166
Formic acid	-10.743	3083
Propionic acid	-10.843	3316

When available, experimental data were used for the identification and simulated data were generated using UNIFAC Original when not available.

Table 4 summarizes the different cases considered for the identification of the UNIQUAC binary interaction parameters.

In the case of systems with formaldehyde species (with or without carboxylic acids), some preliminary calculations showed that it was not useful to differentiate between the binary interaction parameters of the poly(oxymethylene) glycols (MG_n) and poly(oxymethylene) hemiformals (HF_n) from degree 2 to 7 with other components. This indeed assumes that the interaction in the second term of the residual part of the activity coefficient for these

Table 4

Assumptions for the identification of UNIQUAC binary interaction parameters.

Case n#	Binaries	\bar{a} calculation	ϕ calculation	Chemical equilibrium constants
1: Non-reactive binaries	Methanol – water, furfural – furfuryl alcohol, furfural – water, furfural – methanol, furfuryl alcohol – water, furfuryl alcohol – methanol	UNIQUAC	Mixture of perfect gases	—
2: Binaries involving formaldehyde species and components which are not carboxylic acids	Furfural – {formaldehyde, MG, HF, MG_n , HF_n }, furfuryl alcohol – {formaldehyde, MG, HF, MG_n , HF_n }	UNIQUAC	Mixture of perfect gases	Not taken into account in the identification
3: Binaries involving carboxylic acids	Acetic acid – formic acid, acetic acid – propionic acid, acetic acid – furfural, acetic acid – furfuryl alcohol, acetic acid – methanol, acetic acid – water, acetic acid – {formaldehyde, MG, HF, MG_n , HF_n }, formic acid – propionic acid, formic acid – furfural, formic acid – furfuryl alcohol, formic acid – methanol, formic acid – water, propionic acid – furfural, formic acid – {formaldehyde, MG, HF, MG_n , HF_n }, propionic acid – furfuryl alcohol, propionic acid – methanol, propionic acid – water, propionic acid – {formaldehyde, MG, HF, MG_n , HF_n }	UNIQUAC	Mixture of perfect gases + Association term	Not necessary because chemical equilibrium constants are already taken into account in the association term

Table 5

Binary interaction parameters estimated from literature data.

Component 1	Component 2	A_{ij}^0	A_{ji}^0	A_{ij}^T	A_{ji}^T	References of data used for the identification
Acetic acid	Formic acid	-174	-173	-0.36	1.50	[25–27]
Acetic acid	Furfural	379	-482	-0.02	0.79	[28]
Acetic acid	Methanol	130	1189	0.91	-4.52	[29,30]
Acetic acid	Propionic acid	-46	52	-0.05	0.16	[31–33,25,26]
Acetic acid	Water	46	306	-1.00	0.60	[35,36,34]
Formic acid	Furfural	1904	-316	-6.00	3.90	[37]
Formic acid	Propionic acid	-828	1539	1.83	-3.00	[25,26,32]
Formic acid	Water	-205	-205	-0.17	0.20	[36]
Furfural	Furfuryl alcohol	533	-570	0.05	0.67	[38]
Furfural	Methanol	751	1106	-0.93	-3.36	[39]
Furfural	Water	475	691	-1.70	0.12	[25,41]
Furfuryl alcohol	Water	118	82	-1.37	2.05	[42,43]
Propionic acid	Methanol	1156	-101	-0.38	-1.33	[44]
Propionic acid	Water	157	211	-1.09	1.50	[36]
Methanol	Water	156	-369	0.91	0.20	[45,46]

compounds is equal to that of the poly(oxymethylene) hemiformal and poly(oxymethylene) glycol of degree 2 for all the poly(oxymethylene) hemiformals (HF_n) and poly(oxymethylene) glycol (MG_n). Finally, with this simplification, 46 sets of parameters have to be identified.

The UNIQUAC binary interaction parameters were identified by minimizing the relative errors (see equations (10)–(19)) between experimental data when available, or simulated data generated using UNIFAC Original when not available, and UNIQUAC vapor–liquid equilibrium calculations:

$$\min_{\tau_{ij}^0, \tau_{ij}^T, \tau_{ji}^0, \tau_{ji}^T} F_{obj} \quad (10)$$

$$F_{obj} = \frac{F_{obj,bubble} + F_{obj,dew}}{n_{bubble} + n_{dew}} \quad (11)$$

where for (T,x,y) diagrams:

$$F_{obj,bubble} = \sum_{l=1}^{n_{bubble}} \frac{(|y_{1,exp}^{bubble} - y_{1,calc}^{bubble}|)_l}{(\bar{y}_1^{bubble})_l} + \frac{(|y_{2,exp}^{bubble} - y_{2,calc}^{bubble}|)_l}{(\bar{y}_2^{bubble})_l} + \frac{(|p_{exp}^{bubble} - p_{calc}^{bubble}|)_l}{(\bar{p}^{bubble})_l} \quad (12)$$

Table 6

Binary interaction parameters estimated from UNIFAC.

Component 1	Component 2	A_{ij}^0	A_{ji}^0	A_{ij}^T	A_{ji}^T
Formaldehyde	Acetic acid	396	-613	-0.95	1.10
Formaldehyde	Formic acid	290	-499	0.89	0.10
Formaldehyde	Furfural	102	-107	-0.60	0.20
Formaldehyde	Furfuryl alcohol	51	89	-0.14	-0.79
Formaldehyde	Propionic acid	372	-572	-1.00	1.10
Methylene Glycol (MG)	Acetic acid	-29	375	-1.29	2.00
Methylene glycol (MG)	Formic acid	-78	74	0.14	-0.90
Methylene glycol (MG)	Furfural	-218	836	-1.44	1.50
Methylene glycol (MG)	Furfuryl alcohol	-545	359	-0.24	-0.47
Methylene glycol (MG)	Propionic acid	-100	615	-0.74	2.00
Poly(oxymethylene) glycols ($MG_{i, i \geq 2}$)	Acetic acid	-733	936	-0.01	-1.50
Poly(oxymethylene) glycols ($MG_{i, i \geq 2}$)	Formic acid	-474	-46	-0.38	-0.12
Poly(oxymethylene) glycols ($MG_{i, i \geq 2}$)	Furfural	470	-126	0.62	-1.50
Poly(oxymethylene) glycols ($MG_{i, i \geq 2}$)	Furfuryl alcohol	664	-195	0.34	-1.49
Poly(oxymethylene) glycols ($MG_{i, i \geq 2}$)	Propionic acid	30	-136	0.47	-0.83
Hemiformal (HF)	Acetic acid	16	-22	0.54	-1.03
Hemiformal (HF)	Formic acid	14	-29	-0.07	-0.73
Hemiformal (HF)	Furfural	91	-75	0.66	-1.50
Hemiformal (HF)	Furfuryl alcohol	103	-85	0.97	-1.50
Hemiformal (HF)	Propionic acid	470	-309	-0.24	-0.24
Poly(oxymethylene) hemiformals ($HF_{i, i \geq 2}$)	Acetic acid	-355	32	-0.20	-0.27
Poly(oxymethylene) hemiformals ($HF_{i, i \geq 2}$)	Formic acid	-468	-13	-0.21	-0.22
Poly(oxymethylene) hemiformals ($HF_{i, i \geq 2}$)	Furfural	290	-116	0.37	-1.48
Poly(oxymethylene) hemiformals ($HF_{i, i \geq 2}$)	Furfuryl alcohol	1207	-454	-1.11	-0.87
Poly(oxymethylene) hemiformals ($HF_{i, i \geq 2}$)	Propionic acid	-54	51	-0.15	-0.59
Acetic acid	Furfuryl alcohol	435	-374	0.13	-0.12
Formic acid	Furfuryl alcohol	107	-175	1.00	-0.30
Formic acid	Methanol	-402	675	0.00	0.00
Furfural	Propionic acid	-414	883	-0.04	-0.34
Furfuryl alcohol	Methanol	440	-388	-0.46	0.54
Furfuryl alcohol	Propionic acid	435	-374	0.13	-0.12

$$F_{Obj,dew} = \sum_{l=1}^{n_{dew}} \frac{(|x_{1,exp}^{dew} - x_{1,calc}^{dew}|)_l}{(\bar{x}_1^{dew})_l} + \frac{(|x_{2,exp}^{dew} - x_{2,calc}^{dew}|)_l}{(\bar{x}_2^{dew})_l} + \frac{(|p_{exp}^{dew} - p_{calc}^{dew}|)_l}{(\bar{P}^{dew})_l} \quad (13)$$

and for (P,x,y) diagrams:

$$F_{Obj,bubble} = \sum_{l=1}^{n_{bubble}} \frac{(|y_{1,exp}^{bubble} - y_{1,calc}^{bubble}|)_l}{(\bar{y}_1^{bubble})_l} + \frac{(|y_{2,exp}^{bubble} - y_{2,calc}^{bubble}|)_l}{(\bar{y}_2^{bubble})_l} + \frac{(|T_{exp}^{bubble} - T_{calc}^{bubble}|)_l}{(\bar{T}^{bubble})_l} \quad (14)$$

$$F_{Obj,dew} = \sum_{l=1}^{n_{dew}} \frac{(|x_{1,exp}^{dew} - x_{1,calc}^{dew}|)_l}{(\bar{x}_1^{dew})_l} + \frac{(|x_{2,exp}^{dew} - x_{2,calc}^{dew}|)_l}{(\bar{x}_2^{dew})_l} + \frac{(|T_{exp}^{dew} - T_{calc}^{dew}|)_l}{(\bar{T}^{dew})_l} \quad (15)$$

with

$$(\bar{y}_k^{index})_l = \frac{y_{k,exp}^{index} + y_{k,calc}^{index}}{2} \quad \text{with } k \in [1; 2] \text{ and index} \\ = \text{bubble or dew} \quad (16)$$

$$(\bar{x}_k^{index})_l = \frac{x_{k,exp}^{index} + x_{k,calc}^{index}}{2} \quad \text{with } k \in [1; 2] \text{ and index} \\ = \text{bubble or dew} \quad (17)$$

$$(\bar{P}^{index})_l = \frac{p_{exp}^{index} + p_{calc}^{index}}{2} \quad \text{with index = bubble or dew} \quad (18)$$

$$(\bar{T}^{index})_l = \frac{T_{exp}^{index} + T_{calc}^{index}}{2} \quad \text{with index = bubble or dew} \quad (19)$$

The identification was performed using the Excel solver which

Table 7
Average deviation of the gas-phase composition and average deviation of the pressure or temperature for binary vapor–liquid and chemical equilibria plotted in Figs. 2 and 3.

Compound 1	Compound 2	Type of diagram	$\Delta\bar{T}$ or $\Delta\bar{P}$ (%)	$\Delta\bar{y}_1$ (%)	References
Formic acid	Acetic acid	T = 70° C	2.38	2.08	[25]
Formic acid	Acetic acid	T = 30° C	4.37	3.52	[26]
Formic acid	Acetic acid	P = 1013 mbar	0.21	3.05	[27]
Acetic acid	Furfural	P = 493 mbar	0.77	1.22	[28]
Acetic acid	Furfural	P = 890 mbar	0.39	0.95	[28]
Acetic acid	Methanol	P = 1013 mbar	3.24	4.86	[30]
Acetic acid	Methanol	P = 941 mbar	1.00	4.23	[29]
Acetic acid	Propionic acid	T = 70° C	2.03	0.51	[25]
Acetic acid	Propionic acid	T = 40° C	1.00	0.87	[33]
Acetic acid	Propionic acid	T = 30° C	8.07	10.39	[26]
Acetic acid	Propionic acid	P = 1000 mbar	0.04	2.59	[32]
Acetic acid	Propionic acid	P = 1013 mbar	3.51	1.69	[31]
Water	Acetic acid	P = 1013 mbar	0.22	1.07	[34]
Water	Acetic acid	P = 167 mbar	0.61	0.50	[35]
Water	Acetic acid	P = 333 mbar	0.11	0.41	[35]
Water	Acetic acid	P = 93 mbar	0.78	8.88	[36]
Formic acid	Furfural	P = 1013 mbar	0.57	8.10	[37]
Formic acid	Propionic acid	T = 70° C	2.09	1.68	[25]
Formic acid	Propionic acid	T = 30° C	2.76	6.98	[26]
Formic acid	Propionic acid	P = 1000 mbar	0.34	3.92	[32]
Formic acid	Propionic acid	P = 1013 mbar	0.33	–	[31]
Water	Formic acid	P = 1013 mbar	0.12	1.01	[36]
Water	Formic acid	P = 266 mbar	0.25	3.48	[36]
Water	Formic acid	P = 93 mbar	0.66	3.67	[36]
Furfural	Furfuryl alcohol	P = 33 mbar	0.54	8.73	[38]
Methanol	Furfural	P = 400 mbar	–	11.76	[39]
Water	Furfural	P = 1013 mbar	1.00	2.34	[40]
Water	Furfural	P = 946 mbar	1.12	1.02	[41]
Water	Furfuryl alcohol	P = 40 mbar	7.39	0.75	[43]
Water	Furfuryl alcohol	P = 73 mbar	3.08	0.82	[42]
Propionic acid	Methanol	T = 25° C	1.53	–	[44]
Propionic acid	Methanol	T = 27° C	1.67	–	[44]
Propionic acid	Methanol	T = 35° C	1.63	–	[44]
Propionic acid	Methanol	T = 45° C	1.20	–	[44]
Propionic acid	Water	P = 1013 mbar	0.83	1.98	[36]
Propionic acid	Water	P = 266 mbar	0.68	1.41	[36]
Propionic acid	Water	P = 93 mbar	0.73	1.29	[36]
Water	Methanol	P = 1013 mbar	0.18	1.90	[45]
Water	Methanol	P = 666 mbar	0.43	3.58	[46]
Water	Methanol	P = 466 mbar	0.84	5.46	[46]
Water	Methanol	P = 266 mbar	0.57	6.37	[46]

provides a multidimensional constrained non-linear method of minimization (non-linear GRG method), coupled with the Simulis Thermodynamics add-in for estimation of thermodynamic properties.

5. Results and discussions

5.1. UNIQUAC binary interaction parameters estimation

The UNIQUAC binary interaction parameters estimated in this work are reported in Tables 4 and 5. For all data points used in this work, the mean relative error was calculated as $F_{obj} = 5.60\%$ with

$n_{exp} = 671$. This relatively low value indicates a good estimation of the UNIQUAC binary interaction parameters as can be seen from the graphical comparisons of experimental data and calculated data presented in the Section 4.2.

Table 5 reports the values of the estimated UNIQUAC binary interaction parameters for which literature vapor–liquid data were available. Table 6 reports the binary interaction parameters of binaries for which no experimental data were available in literature. Excluding systems with formaldehyde species, few binaries are concerned. Nonetheless, interactions between formaldehyde species and other components like carboxylic acids were not studied in the literature.

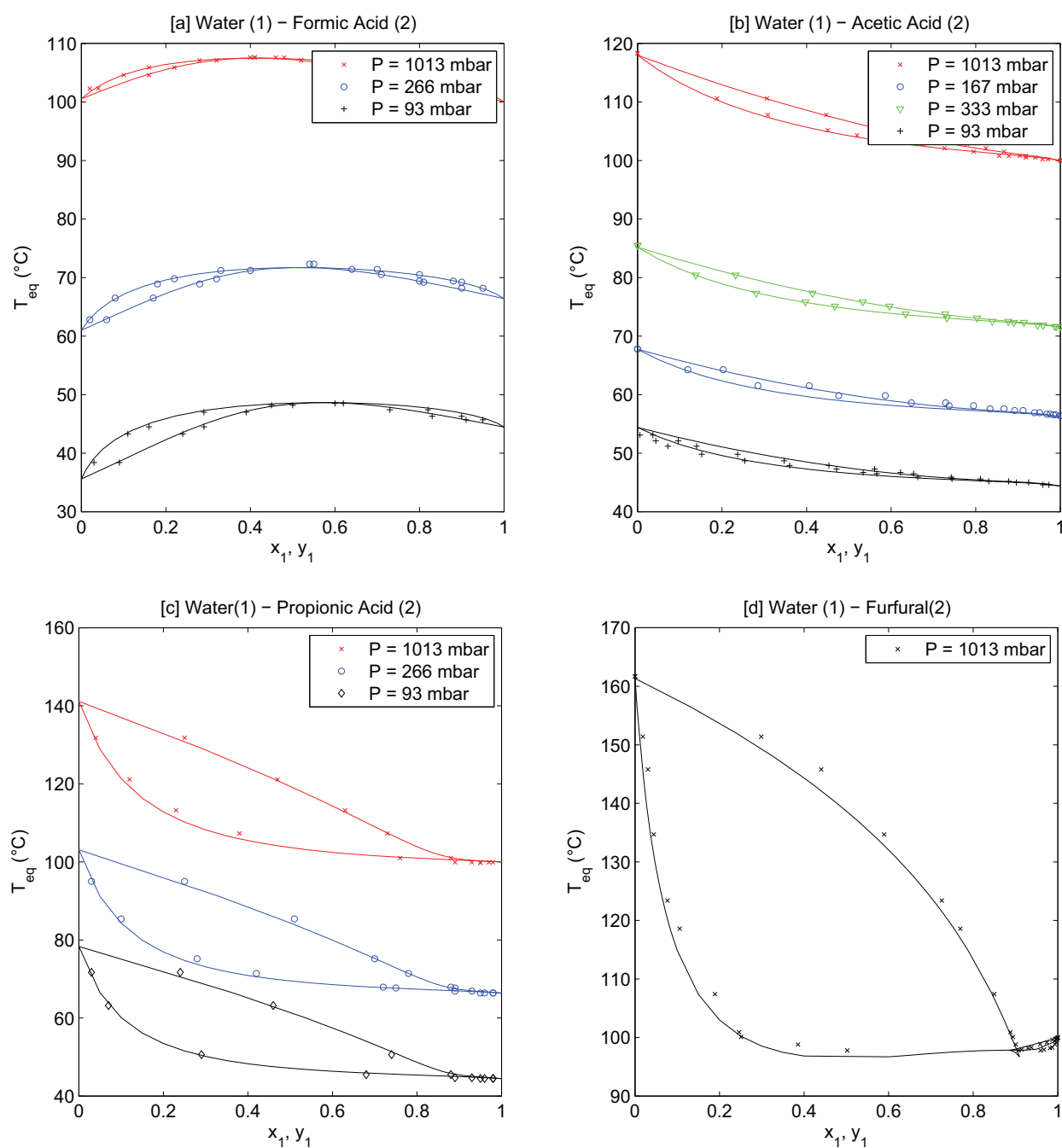


Fig. 2. Prediction of azeotropic systems vapor–liquid and chemical equilibria at different pressures and temperatures. (×) experimental data from the literature. Solid line: predicted phase diagram with UNIQUAC model coupled to chemical equilibria.

5.2. Comparison of the UNIQUAC model with binary vapor–liquid data used for the identification

This section presents the comparison of each set of experimental data used for the identification with the calculated data obtained with the estimated UNIQUAC binary interaction parameters. References of the experimental data are indicated in Table 7.

For each binary system, the average deviation of the vapor composition and the average deviation of the pressure - in the case of (T,x,y) diagrams - or the average deviation for the temperature - in the case of (P,x,y) diagrams - between experimental data and our work were calculated as:

$$\overline{\Delta y_1} = \frac{1}{n_{exp}} \sum_{l=1}^{n_{exp}} \frac{(|y_{1,exp} - y_{1,calc}|)_l}{\bar{y}_{1,l}} \quad (20)$$

$$\overline{\Delta P} = \frac{1}{n_{exp}} \sum_{l=1}^{n_{exp}} \frac{(|P_{exp} - P_{calc}|)_l}{\bar{P}_l} \quad (21)$$

$$\overline{\Delta T} = \frac{1}{n_{exp}} \sum_{l=1}^{n_{exp}} \frac{(|T_{exp} - T_{calc}|)_l}{\bar{T}_l} \quad (22)$$

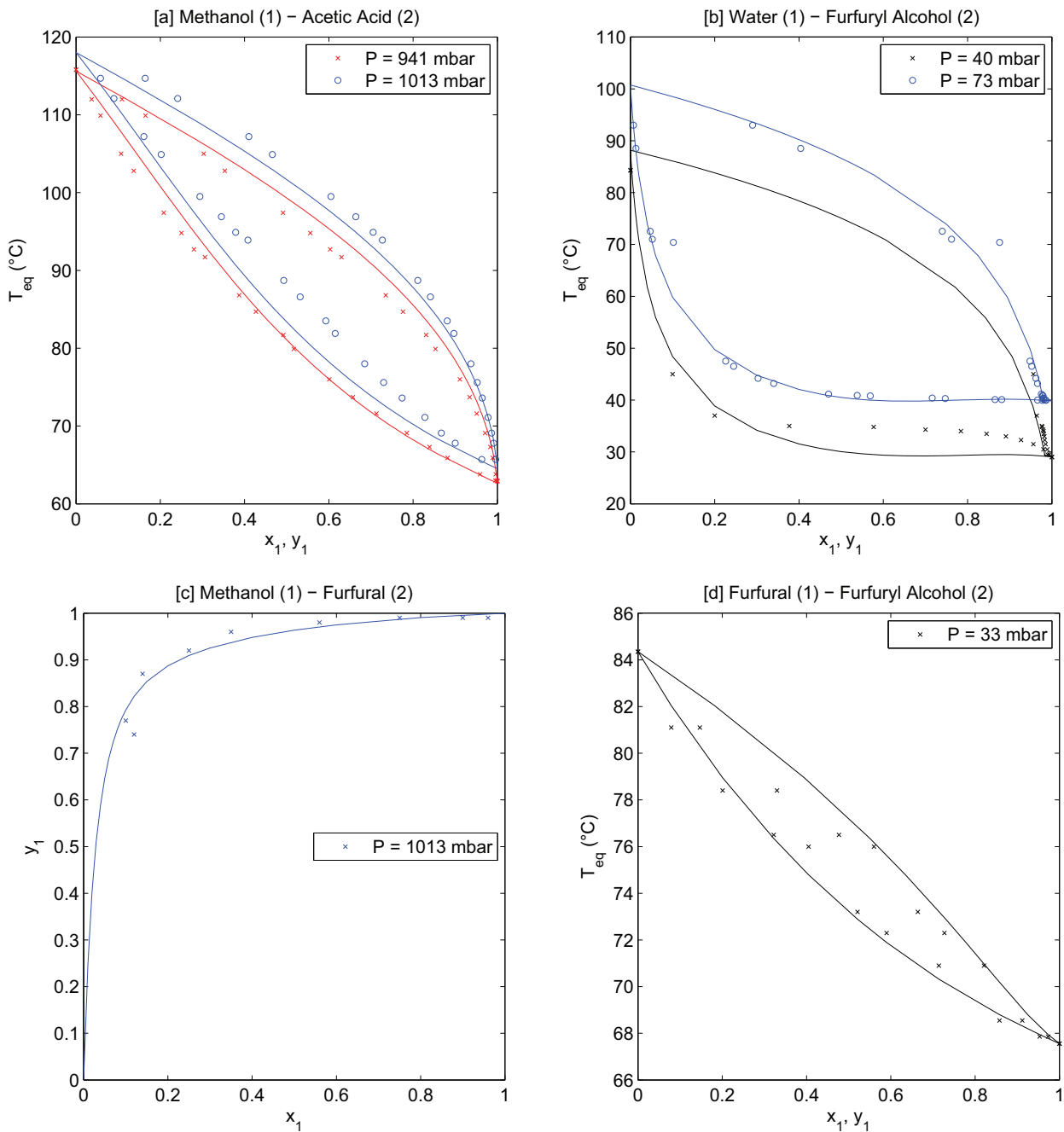


Fig. 3. Prediction of binary systems vapor–liquid and chemical equilibria at different pressures and temperatures. (×) experimental data from the literature. Solid line: predicted phase diagram with UNIQUAC model coupled to chemical equilibria.

with:

$$\bar{y}_{1,i} = \frac{(y_{1,exp} + y_{1,calc})_i}{2} \quad (23)$$

$$\bar{P}_i = \frac{(P_{exp} + P_{calc})_i}{2} \quad (24)$$

$$\bar{T}_i = \frac{(T_{exp} + T_{calc})_i}{2} \quad (25)$$

Table 7 presents the average deviation for the gas-phase composition and the average deviation for the equilibrium pressure (or temperature) between experimental data from the literature and the model, for all binary systems plotted in Figs. 2 and 3. Pressure and temperature deviations are between 0.04% and 8.07%, and gas-phase composition deviations between 0.41% and 11.76%. These values indicate that the UNIQUAC model developed in this work provides a fairly good description of the different binary systems, for large pressure and composition ranges. Note that all deviation values are very similar, which means that the quality of the prediction is similar for all binary

systems.

Fig. 2 shows the isobaric diagram of the following binary systems: (a) water - formic acid; (b) water - acetic acid; (c) water - propionic acid; (d) water - furfural. Good agreement was obtained between experimental data and the prediction of the azeotropic point at different pressures for all systems.

Fig. 3 presents the isobaric diagram of the following binary systems: (a) methanol - acetic acid; (b) water - furfuryl alcohol; (c) methanol - furfural; (d) furfural - furfuryl alcohol. Note that some inconsistent experimental points explain the larger deviation observed between the model and the experimental data.

Globally, all the figures and table confirm that estimated binary interaction coefficients give a good representation of all binaries. Every experimental data used for the identification are indeed adequately represented by the model.

5.3. Validation of the model from comparison with ternary vapor–liquid reactive equilibria

The complete reactive vapor–liquid model was used to validate the use of the binary interaction parameters for a ternary system. The model includes equations for the vapor–liquid equilibrium

Table 8

Chemical reaction equilibrium constants: $\ln K = a_1 + a_2/T$.

Reaction	Phase	Heat of reaction (kJ/mol)	a_1	a_2	References
$W + FA \rightleftharpoons MG$	Vapor	-43.51	-16.984	5233.2	[50]
$2MG \rightleftharpoons MG_2 + W$	Liquid	-0.234	$4.98 \cdot 10^{-3}$	869.5	[51,20]
$MG + MG_2 \rightleftharpoons MG_3 + W$					
$MG + MG_3 \rightleftharpoons MG_4 + W$					
$MG + MG_4 \rightleftharpoons MG_5 + W$	Liquid	-0.234	$1.908 \cdot 10^{-2}$	544.5	[51,20]
$MG + MG_5 \rightleftharpoons MG_6 + W$					
$MG + MG_6 \rightleftharpoons MG_7 + W$					
$ME + FA \rightleftharpoons HF$	Vapor	-53.73	-14.755	5969.4	[49]
$2HF \rightleftharpoons HF_2 + ME$					
$HF + HF_2 \rightleftharpoons HF_3 + ME$					
$HF + HF_3 \rightleftharpoons HF_4 + ME$	Liquid	-7.00	-0.4966	-491.3	[49]
$HF + HF_4 \rightleftharpoons HF_5 + ME$					
$HF + HF_5 \rightleftharpoons HF_6 + ME$					
$HF + HF_6 \rightleftharpoons HF_7 + ME$					

Table 9

Average deviation of the gas-phase composition and average deviation of the temperature for ternary vapor–liquid and chemical equilibria illustrated in Tables 10–13

Compound 1	Compound 2	Compound 3	P (mbar)	$\overline{\Delta T}$ (%)	$\overline{\Delta y_1}$ (%)	$\overline{\Delta y_2}$ (%)	References
Water	Acetic acid	Propionic acid	1013	0.53	4.29	6.05	[53]
Water	Formic acid	Acetic acid	67	1.44	2.74	4.61	[54]
Water	Formic acid	Acetic acid	1013	0.22	2.63	4.51	[55]
Methanol	Water	Acetic acid	1013	1.03	4.19	5.19	[52]
Water	Methanol	Furfural	1007	–	9.38	9.14	[56]
Water	Methanol	Furfural	400	–	7.47	9.59	[56]

Table 10

Prediction of vapor–liquid reactive equilibria of water (1) – acetic acid (2) – propionic acid (3) ternary system [53].

P (mbar)	x_1	x_2	$T_{eq,exp}$ (°C)	$T_{eq,calc}$ (°C)	ΔT (%)	$y_{1,exp}$	$y_{1,calc}$	Δy_1 (%)	$y_{2,exp}$	$y_{2,calc}$	Δy_2 (%)
1013	0.20	0.16	114.0	112.7	1.18	0.505	0.557	9.72	0.141	0.125	11.94
1013	0.63	0.07	102.3	102.4	0.08	0.825	0.821	0.46	0.038	0.041	6.54
1013	0.80	0.04	100.4	101.1	0.65	0.876	0.881	0.58	0.024	0.024	1.05
1013	0.20	0.32	113.0	112.3	0.63	0.438	0.490	11.28	0.282	0.257	9.35
1013	0.20	0.48	112.2	111.7	0.44	0.391	0.431	9.70	0.420	0.392	6.92
1013	0.60	0.24	102.7	103.0	0.26	0.762	0.764	0.32	0.151	0.149	1.06
1013	0.80	0.12	100.5	101.3	0.77	0.872	0.868	0.45	0.074	0.078	5.40
1013	0.2	0.64	111.3	110.9	0.33	0.358	0.378	5.48	0.537	0.529	1.50
1013	0.40	0.48	106.4	105.9	0.50	0.567	0.594	4.71	0.353	0.339	3.91
1013	0.71	0.23	101.8	102.0	0.21	0.817	0.811	0.73	0.143	0.152	6.27
1013	0.80	0.16	101.1	101.4	0.28	0.867	0.862	0.52	0.102	0.109	6.59

Table 11
Prediction of vapor–liquid reactive equilibria of methanol (1) – water (2) – acetic acid (3) ternary system [52].

P (mbar)	x_1	x_2	$T_{eq,exp}$ (°C)	$T_{eq,calc}$ (°C)	ΔT (%)	$y_{1,exp}$	$y_{1,calc}$	Δy_1 (%)	$y_{2,exp}$	$y_{2,calc}$	Δy_2 (%)
1013	0.1148	0.6056	93.4	93.7	0.4	0.3442	0.3316	3.74	0.5361	0.5480	2.20
1013	0.0344	0.6787	99.6	99.3	0.3	0.1312	0.1203	8.66	0.7030	0.7077	0.67
1013	0.3555	0.5899	79.0	77.8	1.5	0.7039	0.7051	0.17	0.2682	0.2889	7.43
1013	0.3362	0.5591	80.6	79.7	1.1	0.7079	0.6801	4.01	0.2790	0.3051	8.93
1013	0.3795	0.5258	79.4	78.1	1.7	0.7237	0.7153	1.17	0.2608	0.2734	4.70
1013	0.1641	0.7961	85.3	85.2	0.1	0.5407	0.5142	5.03	0.4492	0.4771	6.01
1013	0.4069	0.5223	78.6	76.7	2.4	0.7530	0.7373	2.10	0.2394	0.2555	6.49
1013	0.0264	0.3894	104.6	103.9	0.7	0.0776	0.0731	5.96	0.5010	0.5223	4.16
1013	0.1268	0.5316	94.3	94.2	0.2	0.3741	0.3424	8.84	0.4867	0.5077	4.23
1013	0.0399	0.6684	98.9	98.9	0.0	0.1515	0.1367	10.24	0.6897	0.6923	0.38
1013	0.4386	0.4855	77.4	76.0	1.7	0.7765	0.7568	2.57	0.2157	0.2359	8.96
1013	0.4177	0.4968	78.5	76.8	2.2	0.7376	0.7427	0.69	0.2506	0.2484	0.88
1013	0.0467	0.6815	98.3	98.2	0.1	0.1786	0.1608	10.50	0.6782	0.6857	1.09
1013	0.3395	0.5184	81.4	80.5	1.1	0.6892	0.6763	1.90	0.2676	0.3014	11.89
1013	0.2225	0.5762	87.8	86.5	1.5	0.5558	0.5370	3.43	0.3869	0.4102	5.85
1013	0.3985	0.5217	78.7	77.2	2.0	0.7500	0.7306	2.62	0.2411	0.2608	7.85
1013	0.0702	0.5801	97.9	97.6	0.3	0.2190	0.2115	3.50	0.5949	0.6015	1.10
1013	0.0889	0.6060	95.7	95.8	0.1	0.2865	0.2667	7.16	0.5717	0.5854	2.37
1013	0.3583	0.5865	78.6	77.7	1.1	0.7309	0.7069	3.33	0.2634	0.2870	8.57

(see equation (26)) and the chemical reaction equilibrium (see equations (30)–(33)).

Values of the chemical reaction equilibrium constants were taken from the literature [24,47–49].

$$\begin{cases} \phi_i^{V,S}(T, P_i^S(T)) = \frac{-1 + \sqrt{1 + 4K(T)P_i^S(T)}}{2K(T)P_i^S(T)} & \text{for carboxylic acids} \\ \phi_i^{V,S}(T, P_i^S(T)) = 1 & \text{otherwise} \end{cases} \quad (28)$$

$$y_i P = x_i \gamma_i(T, x) P_i^S(T) \phi_i^{V,S}(T, P_i^S(T)) \quad (26)$$

$$\log K(T) = a_1 + \frac{a_2}{T} \quad (29)$$

$$\ln P_i^S(T) = a_1 + \frac{a_2}{T} + a_3 \ln T + a_4 T^{a_5} \quad (27)$$

$$K_{MG} = \frac{y_{MG}}{y_{FA} y_W} \cdot \frac{P_{ref}}{P} \quad (30)$$

Table 12
Prediction of vapor–liquid reactive equilibria of water (1) – formic acid (2) – acetic acid (3) ternary system [54,55].

P (mbar)	x_1	x_2	$T_{eq,exp}$ (°C)	$T_{eq,calc}$ (°C)	ΔT (%)	$y_{1,exp}$	$y_{1,calc}$	Δy_1 (%)	$y_{2,exp}$	$y_{2,calc}$	Δy_2 (%)
67	0.20	0.16	42.4	42.0	0.89	0.237	0.232	1.97	0.210	0.189	10.70
67	0.40	0.12	41.3	41.1	0.60	0.446	0.464	3.85	0.119	0.110	7.44
67	0.20	0.32	40.0	40.6	1.54	0.187	0.175	6.46	0.377	0.378	0.39
67	0.40	0.24	41.0	41.1	0.24	0.405	0.413	1.85	0.244	0.239	2.08
67	0.60	0.16	40.2	40.5	0.77	0.625	0.648	3.69	0.137	0.125	9.05
67	0.80	0.08	39.0	39.6	1.49	0.838	0.848	1.22	0.047	0.046	1.25
67	0.20	0.48	37.7	38.9	3.26	0.129	0.132	2.11	0.573	0.564	1.60
67	0.40	0.36	40.2	41.0	1.94	0.354	0.364	2.75	0.404	0.382	5.65
67	0.60	0.24	40.3	41.0	1.63	0.626	0.632	0.91	0.214	0.202	5.93
67	0.20	0.64	36.2	37.1	2.54	0.100	0.099	1.36	0.755	0.747	1.06
67	0.40	0.48	40.0	40.8	1.93	0.300	0.319	6.25	0.576	0.541	6.33
67	0.60	0.32	40.8	41.5	1.64	0.615	0.617	0.40	0.300	0.289	3.80
1013	0.20	0.16	109.2	109.3	0.13	0.250	0.273	8.79	0.160	0.171	6.68
1013	0.20	0.32	107.3	108.4	1.04	0.228	0.227	0.38	0.337	0.341	1.23
1013	0.20	0.64	106.0	106.4	0.41	0.150	0.164	8.82	0.713	0.681	4.53
1013	0.40	0.12	106.3	106.2	0.08	0.500	0.516	3.17	0.101	0.099	2.36
1013	0.40	0.24	106.7	106.6	0.09	0.454	0.480	5.54	0.217	0.209	3.69
1013	0.40	0.36	106.8	106.9	0.10	0.445	0.447	0.46	0.335	0.330	1.56
1013	0.40	0.48	107.1	107.2	0.08	0.393	0.418	6.23	0.482	0.461	4.41
1013	0.60	0.08	103.8	103.7	0.09	0.690	0.709	2.65	0.058	0.051	12.16
1013	0.60	0.16	104.4	104.3	0.08	0.690	0.698	1.14	0.114	0.109	4.08
1013	0.60	0.24	105.3	104.9	0.35	0.690	0.688	0.26	0.181	0.174	4.00
1013	0.60	0.32	105.3	105.6	0.29	0.690	0.681	1.37	0.229	0.245	6.71
1013	0.80	0.04	101.9	101.8	0.06	0.860	0.862	0.23	0.023	0.021	9.88
1013	0.80	0.08	102.0	102.2	0.20	0.866	0.867	0.08	0.044	0.043	2.64
1013	0.80	0.12	102.4	102.6	0.18	0.872	0.872	0.01	0.068	0.066	3.30
1013	0.80	0.16	102.7	103.0	0.30	0.876	0.879	0.30	0.089	0.089	0.39

$$K_{MG_n} = \frac{x_{MG_n} x_W}{x_{MG} x_{MG_{n-1}}} \cdot \frac{\gamma_{MG_n} \gamma_W}{\gamma_{MG} \gamma_{MG_{n-1}}} \quad \text{with } n \in [2; 7] \quad (31)$$

$$K_{HF} = \frac{y_{HF}}{y_{FA} y_{ME}} \cdot \frac{P_{ref}}{P} \quad (32)$$

$$K_{HF_n} = \frac{x_{HF_n} x_{ME}}{x_{HF_{n-1}} x_{HF}} \cdot \frac{\gamma_{HF_n} \gamma_{ME}}{\gamma_{HF_{n-1}} \gamma_{HF}} \quad \text{with } n \in [2; 7] \quad (33)$$

In this work, the chemical reaction constants (see Table 8) are expressed in the gas phase for the formation of methylene glycol (eq. (29)) and hemiformal (eq. (31)).

Binary vapor liquid data were used to regress the UNIQUAC binary interaction parameters and ternary vapor liquid data to

validate the model and to check the extensibility of the model to multicomponent mixtures. Experimental data were taken from the DECHEMA literature in the same ranges of pressure and temperature where the model has been identified.

The reactive vapor liquid equilibrium of the ternary water-methanol-formaldehyde mixture was already validated in a former publication [13]. No data were available to validate the model on other systems.

Tables 10–13 give the corresponding values and relative errors of all isobaric diagrams of the following systems: methanol - water - acetic acid; water - formic acid - acetic acid; water - acetic acid - propionic acid; methanol - water - furfural. Table 9 reports the average deviation of the equilibrium temperature and the average deviation of the gas-phase composition between experimental data from the literature ([52–56]) and our model, for ternary systems of

Table 13
Prediction of vapor–liquid reactive equilibria of methanol (1) – water (2) – furfural (3) ternary system [56].

P (mbar)	x_1	x_2	$y_{1.exp}$	$y_{1.calc}$	Δy_1 (%)	$y_{2.exp}$	$y_{2.calc}$	Δy_2 (%)
1007	0.0023	0.9956	0.0168	0.0161	4.02	0.9714	0.9686	0.28
1007	0.0183	0.9654	0.1316	0.1019	25.4	0.8052	0.8296	2.99
1007	0.0237	0.8866	0.1057	0.0959	9.73	0.8156	0.8049	1.32
1007	0.0447	0.5827	0.1611	0.1334	18.7	0.7714	0.8073	4.55
1007	0.0300	0.9600	0.1633	0.1640	0.44	0.8003	0.7921	1.03
1007	0.1139	0.2025	0.5025	0.4192	18.0	0.4666	0.4998	6.86
1007	0.0431	0.9425	0.2265	0.2136	5.86	0.7231	0.7359	1.75
1007	0.1443	0.3721	0.4679	0.3959	16.6	0.4959	0.5550	11.2
1007	0.0809	0.8111	0.3014	0.2630	13.6	0.6511	0.6688	2.69
1007	0.0614	0.9284	0.3447	0.2859	18.6	0.6246	0.6805	8.57
1007	0.1836	0.3266	0.5688	0.4830	16.3	0.4056	0.4717	15.0
1007	0.1222	0.7963	0.4299	0.3703	14.8	0.5315	0.5741	7.71
1007	0.1597	0.6628	0.4386	0.4021	8.67	0.5248	0.5541	5.43
1007	0.2077	0.4922	0.5781	0.4752	19.5	0.3949	0.4885	21.1
1007	0.2307	0.4103	0.5932	0.5230	12.5	0.3862	0.4418	13.4
1007	0.1791	0.7164	0.5179	0.4587	12.1	0.4535	0.4991	9.57
1007	0.2416	0.5369	0.5891	0.5227	11.9	0.3891	0.4447	13.3
1007	0.3711	0.1649	0.7821	0.7816	0.06	0.2043	0.1884	8.12
1007	0.2082	0.7182	0.5752	0.5176	10.5	0.4013	0.4467	10.7
1007	0.3488	0.3721	0.7009	0.6631	5.55	0.2846	0.3116	9.05
1007	0.3010	0.5313	0.6597	0.5995	9.56	0.3232	0.3733	14.4
1007	0.4954	0.1467	0.8393	0.8526	1.58	0.1440	0.1264	12.9
1007	0.3500	0.5333	0.6779	0.6559	3.30	0.3081	0.3217	4.33
1007	0.5497	0.1566	0.8445	0.8649	2.38	0.1359	0.1174	14.5
1007	0.3283	0.6097	0.7079	0.6537	7.95	0.2766	0.3259	16.3
1007	0.3364	0.6131	0.6891	0.6664	3.36	0.2996	0.3155	5.17
1007	0.3645	0.5814	0.7145	0.6870	3.92	0.2734	0.2962	7.99
1007	0.3545	0.6304	0.7323	0.7035	4.02	0.2608	0.2888	10.2
1007	0.4902	0.4628	0.7656	0.7731	0.97	0.2295	0.2168	5.71
1007	0.9023	0.0902	0.9699	0.9601	1.01	0.0295	0.0389	27.5
400	0.0011	0.9983	0.0074	0.0085	14.0	0.9897	0.9859	0.39
400	0.0677	0.1470	0.4166	0.3887	6.92	0.5057	0.5082	0.49
400	0.0687	0.6107	0.1752	0.2206	22.9	0.7661	0.7293	4.93
400	0.1422	0.2299	0.5441	0.5216	4.22	0.4098	0.4275	4.22
400	0.0413	0.9548	0.2758	0.2353	15.8	0.7106	0.7432	4.48
400	0.0703	0.8125	0.2163	0.2501	14.4	0.7184	0.6772	5.91
400	0.1867	0.4647	0.4566	0.4884	6.72	0.5072	0.4776	6.02
400	0.2806	0.2329	0.6398	0.7092	10.2	0.3303	0.2617	23.1
400	0.1150	0.8743	0.4504	0.4462	0.94	0.5237	0.5269	0.61
400	0.1966	0.6213	0.4107	0.4935	18.3	0.5551	0.4698	16.6
400	0.1209	0.8732	0.4405	0.4683	6.13	0.5472	0.5158	5.91
400	0.1586	0.7753	0.4539	0.4705	3.60	0.5076	0.4814	5.31
400	0.2681	0.4990	0.5412	0.5947	9.42	0.4256	0.3774	12.0
400	0.3312	0.3927	0.6321	0.6797	7.25	0.3374	0.2969	12.7
400	0.1910	0.7606	0.5397	0.5341	1.05	0.4473	0.4277	4.49
400	0.1960	0.7521	0.5078	0.5386	5.88	0.4686	0.4235	10.1
400	0.3354	0.4969	0.5939	0.6675	11.6	0.3798	0.3088	20.6
400	0.2393	0.7539	0.6280	0.6375	1.51	0.3659	0.3541	3.28
400	0.3137	0.6056	0.6353	0.6577	3.46	0.3414	0.3175	7.25
400	0.3715	0.5872	0.7285	0.7203	1.13	0.2464	0.2636	6.76
400	0.5327	0.3226	0.7737	0.8219	6.04	0.2095	0.1636	24.6
400	0.4749	0.5098	0.7722	0.7951	2.92	0.2204	0.1992	10.1
400	0.6550	0.3149	0.8477	0.8744	3.10	0.1453	0.1200	19.1
400	0.7800	0.1907	0.9075	0.9243	1.83	0.0880	0.0713	20.9

Tables 10–13 Note that these data were not used for the estimation of the binary interaction parameters but only to validate the approach. Temperature deviations are between 0.22% and 1.44% and gas-phase composition deviations between 2.63% and 9.59%. This good agreement confirms that our model is able to represent the behavior of multicomponent systems.

As mentioned above, good agreement was obtained between experimental data set and estimated vapor–liquid equilibria with our model.

6. Conclusion

In this work a model to describe the thermodynamic behavior of a complex reactive mixture was developed. The model was applied to a representative mixture of the condensable fraction of the gaseous effluent from the wood torrefaction process. A model based on the local composition concept (UNIQUAC) was chosen and was coupled to chemical equilibria of this reactive mixture where 22 compounds and 14 chemical reactions are considered. With this uncoupling approach, effects of weak intermolecular interactions of the physical equilibria are differentiated from the strong intermolecular interactions involved in the chemical reactions. In the present case, chemical equilibrium constants were available in the literature and can then be considered as known. The hypothesis of similar interactions for poly(oxymethylene) glycols with other compounds and for poly(oxymethylene) hemiformals with other compounds allowed to limit to 46 the number of unknown vapor–liquid equilibrium binary interaction parameters. They were identified here from literature data for binary systems when available or from simulated data when not. This approach was validated by comparison with available experimental data for multicomponent systems.

This modeling was done with the purpose of designing separation-purification process for valorization of the gaseous effluent of the torrefaction process for bio-sourced chemicals. Nevertheless, we are confident that this approach, developed here for a specific application, can be generic to describe other complex thermodynamic systems including reactive components.

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Nomenclature

Mathematical symbols

$A_{i,j}, A_{j,i}$	UNIQUAC binary interaction parameters of the components i and j (cal/mol)
F_{obj}	objective function
K	chemical reaction equilibrium constant
n	degree of polymerization
n_C	number of components
n_{exp}	number of experimental data point
P	pressure of the system
P_i^S	equilibrium vapor pressure of pure component i
q_i	Van der Waals area parameter of the component i
r_i	Van der Waals volume parameter of the component i
T	temperature of the system (K)
T_{ref}	temperature at the reference state: $T_{ref} = 298.15$ K
T_{ref}	$T_{ref} = 298.15^\circ\text{C}$

x_i	liquid molar fraction of the component i
y_i	vapor molar fraction of the component i
Z	lattice coordination number set equal to 10

Components

A_i	carboxylic acid
A_{i2}	carboxylic acid dimer
FA	Formaldehyde
Fu	Furfural
$FuAl$	Furfuryl Alcohol
HF	hemiformal
HF_n	poly(oxymethylene) hemiformal
ME	methanol
MG	methylene glycol
MG_n	poly(oxymethylene) glycol
W	water

Greek symbols

γ_i	activity coefficient of the component i
ϕ_i	UNIQUAC volume fraction of the component i
$\phi_i^{V,S}$	vapor fugacity coefficient of pure constituent i at saturation pressure
ϕ_i^V	vapor fugacity coefficient of constituent i in the mixture
$\tau_{i,j}, \tau_{j,i}$	binary interaction characteristic energy parameters of the components i and j
θ_i	UNIQUAC area fraction of the component i

Subscripts

$calc$	calculated
exp	experimental
i, j, k	index of the components
l	index of the experimental points
ref	reference state

Superscripts

$bubble$	bubble point
C	combinatorial term
dew	dew point
R	residual term
S	saturation point

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