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

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ABSTRACT

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, gaïacols 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.

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(oxymethylene) glycols from a degree 2 to a degree 7 (MG_2–MG_7), 6 poly(oxymethylene) 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(oxymethylene) hemiformals and poly(oxymethylene) 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)		✓				✓	✓
	50-00-0	Formaldehyde		✓			✓	✓	✓
Acids	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-methylgaïcol)			✓				
	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	✓	✓		✓	✓	✓	