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# Thermodynamic equilibrium approach to predict the inorganic interactions of ash from biomass and their mixtures: a critical assessment<sup>1</sup>

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## Abstract

Process simulation approaches based on thermodynamics calculations can provide good capabilities to predict the ash behavior of biomasses and their mixtures. In the present work, a critical assessment of such simulations was performed in the field of biomass ashes, and experimentally checked to be at equilibrium. Two commercial thermodynamic databases, FToxid and GTOX, were used together with the FactSage Gibbs energy minimization software. For the first time in literature, a comparison was performed between the calculated phase equilibria using the recent market versions of the two databases. The predicted results were then compared to those measured on various ash samples of straws and barks along with their ash mixtures, highlighting the lingering need for improvements for the recent versions of these commercial databases.

The phase diagram approach showed excellent capabilities in predicting the physical state of the ash (solid, liquid, or solid-liquid mixture) using both databases. Global simulations using the FToxid database showed better prediction capabilities for single biomass ash than those using the GTOX database. Unfortunately, predictions using the former were significantly limited in the case of ash mixture samples, whereas using the latter were a total failure. Nevertheless, both databases showed correct volatilization prediction capabilities but failed to forecast the solidus and liquidus characteristic temperatures. Further work is still needed to enhance the prediction capabilities of this tool.

**Keywords:** Biomass ash, biomass ash mixtures, thermodynamic equilibrium, global thermodynamic simulation, ash behavior prediction, phase diagram CaO-K<sub>2</sub>O-SiO<sub>2</sub>.

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# 1 1. Introduction

2 A decade ago, Morey et al. [1] were the first to investigate the phase relations in the ternary  
3 CaO-K<sub>2</sub>O-SiO<sub>2</sub> system. Compositions in this ternary are used in the glass production industry,  
4 such as bottles, containers, etc. [2]. This system is also relevant for advanced ceramic  
5 applications, such as in biocompatible ceramic material production for biomedical applications  
6 [3]. Most importantly, around 90 wt.% of biomass ash is formed of silicon, potassium, and  
7 calcium [4]. Hence, a thorough knowledge of the phase equilibria in the CaO-K<sub>2</sub>O-SiO<sub>2</sub> ternary  
8 system can help better understand and predict the complicated chemical interaction of the  
9 inorganic elements in the biomass ash in real-life processes during combustion and gasification.

10 High alkali-silicate biomasses, such as agricultural residues, often result in ashes with low  
11 melting points [5]. This can cause corrosion and sintering in a furnace or lead to a reaction with  
12 the bed materials in the fluidized bed and cause agglomeration [6–8]. Therefore, mixing  
13 agricultural residues with biomasses with high melting points, such as oak bark, can alter the  
14 chemical and physical properties of the ashes in the mixture, hindering the ash-related  
15 problematics [5,9–11].

16 Advanced multicomponent/multiphase thermodynamic modeling can be an important tool in  
17 predicting ash-related processes in biomass combustion. Thermodynamic modeling can predict  
18 the ash deposition, corrosion, bed agglomeration of fluidized beds, and ash interaction and  
19 compositions. However, consistent and accurate thermodynamic data are needed for all the ash  
20 phases that may form in furnace and boiler conditions [12]. This prediction tool can be more  
21 efficient than the costly and time-consuming random mixing approach. In addition, it helps to  
22 control the operational problems related to ash, hence inducing economic savings. The FactSage  
23 software package and its thermodynamic databases are widely used to perform phase diagram  
24 calculations and process-related simulations based on proper thermodynamic equilibrium  
25 constraints. The thermodynamic databases FToxid [13] and GTOX [14] in their most recent  
26 versions are most relevant for use in simulations of ash formation during biomass combustion.  
27 In general, authors in the literature tend to use the FACT database package without a detailed  
28 explanation for their choice.

29 Recent literature works investigated the capabilities of such an approach to predict the  
30 combustion ash behavior of biomasses and their blends. For instance, Wiinikka et al. [15]  
31 investigated the influence of fuel ash composition on high-temperature aerosols formation  
32 during fixed-bed combustion of woody biomass (two wood pellets and one bark pellet) in a

33 laboratory reactor compared to theoretically chemical equilibrium model calculations  
34 (FactSage 5.2 with FACT and SGTE databases). In parallel, Elled et al. [16] investigated the  
35 composition of agglomerated materials. They aimed to highlight the reasons for sintering and  
36 agglomeration during the thermochemical conversion of bark and its blend with straw. They  
37 compared their experimental results in a 12 MW circulating fluidized bed reactor (using quartz  
38 sand as bed material) against thermodynamic equilibrium modeling using FactSage 6.2  
39 equipped with FTSalt, FToxid, and Fact53 databases.

40 In addition, Rizvi et al. [17] compared the predicted slagging results by ash fusion tests on soft-  
41 wood, peanut shell, sunflower husk, and miscanthus with those simulated by FactSage 6.3  
42 equipped with FToxid and FactPS databases using all the elements and at varying temperatures  
43 between 700°C and 1500°C. Reinmoller et al. [18] also used FactSage 6.3 equipped with  
44 FToxid, FatcPS, FTSalt, and FTmisc databases in air on 23 different biomasses (including wood,  
45 bark, and straw) to investigate the slag and the mineral phase composition compared to  
46 experimental data (ash fusion test). More recently, Magdziarz et al. [19] used the same approach  
47 on three wood and one straw samples. Dizaji et al. [20] tried to study wheat straw's combustion  
48 ash transformation reactions using an experimental ash test (ash annealing) compared with  
49 calculated results from simulations done with FactSage 8.0 equipped with FToxid, FTSalt, and  
50 FactPS databases at various temperatures. Link et al. [21] also used the same simulation  
51 approach (but with FactSage 7.3) compared with the standard ash melting test to assess the  
52 melting behavior and ash phase transformation in wood, reed, and their blends. In addition,  
53 Fakourian et al. [22] tried to model the ash deposit growth rates and the melting fraction and  
54 temperature for a wide range of solid fuels (including woody biomass) in a 100 kW combustor  
55 using a simulation approach using FactSage 7.3.

56 All these authors reported the limited success of this tool in predicting the real ash behavior of  
57 biomass and their mixtures compared with the experimental findings. For instance, the  
58 predicted amounts of the crystalline compounds were always different from those measured  
59 [17–19]. The predicted melting temperatures also differed from those measured [18,19,21],  
60 which was the same case for the slagging proportion [20]. Though the aerosol predicted values  
61 showed a preliminary match against the measured P-XRD results, some experimental values  
62 were not initially at equilibrium due to temperature or residence time limitations, which further  
63 biased the prediction [15].

64 In his recent review, Lindberg et al. [12] summarized the leading cause of all these limitations  
65 as the lack of comprehensive databases containing the thermodynamic data of ash compounds

66 and phases formed during combustion. Elled et al. [16] reported that this same problem led to  
67 a biased predicted value for the agglomeration temperature (deviated liquidus temperature  
68 compared to experimental results). Elled et al. [16] further elaborated that the thermodynamic  
69 equilibrium assumes a complete reaction of the ash, which might not be the real life case [16].  
70 Hence, deviations between the thermodynamic equilibrium behavior and the real one always  
71 remained.

72 On the other hand, the phase relationships in the ternary phase diagram CaO-K<sub>2</sub>O-SiO<sub>2</sub> consist  
73 of a more simplified prediction approach. In general, the authors in the literature normalize the  
74 CaO, K<sub>2</sub>O, and SiO<sub>2</sub> mole or weight percentages from the measured elemental compositions on  
75 each biomass or blend. Then, they position the feedstock on the calculated ternary phase  
76 diagram CaO-K<sub>2</sub>O-SiO<sub>2</sub> to get some qualitative information on its ash behavior. For instance,  
77 Ohman et al. [7] used this diagram to qualitatively predict the presence of slag in wheat straw,  
78 wood, peat, cane trash, wood residues, reed canary grass, bark, and RDF in a fluidized  
79 combustion bed. Similarly, Rebling et al. [6] used phase equilibria information of this ternary  
80 diagram to predict the slag formation of wood, peat, and their mixtures in three separate grate-  
81 fired combustion boilers of different sizes, 0.2 MWth, 2MWth, and 4 MWth, respectively. In  
82 addition, Defoort et al. [9] used this phase diagram information to predict the ash state (solid,  
83 liquid, or solid-liquid) of oak bark, wheat straw, and their mixtures in two different laboratory-  
84 scale combustion tests using biomass pellets and ash chips. Zhu et al. [23] also tried to verify  
85 the deformation temperatures of more than 15 biomasses (including wood and straw). They  
86 compared the experimental results on a laboratory scale against the thermodynamic equilibrium  
87 information of this ternary phase diagram (using their normalized oxides percentages) after  
88 adding Al<sub>2</sub>O<sub>3</sub> as a fourth oxide to the system.

89 All these authors reported the success of this tool in predicting the state of the total ash after  
90 combustion. However, some crystalline phases appeared experimentally but were absent in the  
91 thermodynamic database, such as K<sub>2</sub>Ca<sub>6</sub>Si<sub>4</sub>O<sub>15</sub> and K<sub>2</sub>Ca<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> [9]. Others were predicted but  
92 were never found experimentally, such as K<sub>2</sub>CaSiO<sub>4</sub> [9]. In addition, the calculated liquidus  
93 line was shifted compared with the experimental results [6,7,23]. Consequently, they all  
94 concluded that the thermodynamic database needs to be revised to calculate the equilibria in  
95 the entire composition and temperature space. Recent thermodynamic improvements were  
96 made to the FACT database package (especially FToxid) in 2017 [24], but they still need to be  
97 assessed against experimental data.

98 This work aims to assess the capabilities of using the most recent versions of these  
99 thermodynamic databases to predict the interactions between the inorganic elements (i.e., phase  
100 relationships) in the ash of biomass and their mixtures. First, for the first time in the literature,  
101 a comparison was performed between the calculated phase equilibria obtained with the two  
102 databases (FToxid vs. GTOX) regarding predicted crystalline phase compositions and  
103 volatilization behavior. Two prediction approaches were used as done previously [9,25]: a  
104 simplified one using phase diagram calculations and a more sophisticated one called global  
105 simulation. Both approaches were then compared to experimental results on multiple ash  
106 samples already checked to be at equilibrium (from single biomass and mixtures) [26]. This  
107 aimed to evaluate the thermodynamic approach prediction capabilities using the most recent  
108 databases and suggest improvements.

## 109 2. Materials and methods

### 110 2.1. Feedstock

111 Oak bark, wheat straw, and two mixtures were received in the form of compressed pellets  
112 (1.5cm (L) x 0.5cm (D)). Three different barks and three different wheat straw sources were  
113 used:

- 114 □ Two oak barks (BC and BF) sawmill residues from the southwest of France and a  
115 hardwood bark (BI) residue from Italian logs preparation in the wood industry.
- 116 □ Two wheat straws (WC and WF) from the southwest French agriculture industry and a  
117 wheat straw (WI) residue from the Italian one.

118 The BCWC mixture was prepared by Defoort et al. [9], and the BFWF blend was received as a  
119 pellet in the work of Valin et al. [27]. The other mixtures were formed manually. Single biomass  
120 pellets were ground in a Fisher Bioblock Scientific Retsch grinder below 1 mm. After drying  
121 the biomass powder at 105°C for 24h, bark-straw mixtures of 5 g each were put in a plastic  
122 bottle and mixed in a “turbula” mixer (Willy A. Bschofen AG Maschinenfabrik CH-4005  
123 Basel/Schweiz mixer), with various bark weight fractions ( $\alpha$ ) (Table 2). The bark weight  
124 fraction ( $\alpha$ ) of each biomass mixture (Table 2) was varied to cover a considerable part of the  
125 CaO-K<sub>2</sub>O-SiO<sub>2</sub> phase diagram.

126 Afterward, each biomass pellet and the ground mixtures were ashed at 550°C for 2h in natural  
127 air with the same procedure as detailed in Atallah et al. [26]. This step at 550°C removed all  
128 organic oxygen and hydrogen (along with organic nitrogen and part of chlorine) while  
129 preserving the majority of the other elements. Then 0.5 g of ash from each mixture and single

130 biomasses were compressed as ash chips with the same procedure described in Atallah et al.  
 131 [26] to favor the contact between the inorganic ash particles.

132 Note that the bark weight fraction in the ash bark-straw mixture ( $\beta$ ) can be calculated using the  
 133 bark weight fraction in the biomass bark-straw mixture ( $\alpha$ ), taking into account the ash yield of  
 134 every single biomass (noted  $A_1$  for bark and  $A_2$  for straw) and is:

$$135 \quad \beta = \alpha A_1 / (\alpha A_1 + (1 - \alpha) A_2) \quad (1)$$

136 For instance, a BCWC biomass mixture of 50% biomass bark weight percentage corresponds  
 137 to an ash mixture of 59% ash bark weight percentage in the mixture.

138 The elemental composition of each single biomass ash (Table 1) and ash mixture (Table 2) was  
 139 measured by an Elementar Vario EL cube CHN analyzer along with an inductively coupled  
 140 plasma atomic emission spectroscopy (ICP–AES) for Si, Ca, K, P, Al, Mg, Fe, Na, and Mn. C  
 141 (std =  $\pm 1\%$ ), H (std =  $\pm 2\%$ ), and N (std =  $\pm 15\%$ ) contents were measured according to the NF  
 142 EN 15104 norm. Ca, K, P, Al, Mg, Fe, Na, and Mn amounts were measured according to the  
 143 NF EN ISO 16967 norm (std =  $\pm 5\%$ ). The amounts of S and Cl were evaluated in an ion  
 144 chromatography after combusting the samples in a bomb calorimeter, according to the EN  
 145 15289 norm (std =  $\pm 15\%$ ). Si contents were measured by an internal ICP method (std =  $\pm 5\%$ ).  
 146 The weight percentage of the oxides of interest (CaO, K<sub>2</sub>O, and SiO<sub>2</sub>) in every biomass and  
 147 mixture was calculated based on Ca, K, and Si contents measured by the ICP-AES. The values  
 148 are reported in Tables 1 and 2.

149 *Table 1: Biomass ash elemental composition on a dry basis along with their SiO<sub>2</sub>, CaO, and K<sub>2</sub>O weight percentages.*

<i>All elements in wt.% ash</i>	<b>WC</b>	<b>WF</b>	<b>WI</b>	<b>BC</b>	<b>BF</b>	<b>BI</b>
<b>C</b>	4.360	1.200	0.900	4.860	6.100	6.400
<b>O</b>	45.140	44.705	41.933	52.003	51.993	46.233
<b>S</b>	0.940	1.404	1.755	0.378	0.088	0.377
<b>Cl</b>	0.141	0.329	0.113	0.007	0.005	0.008
<b>Si</b>	17.095	25.351	18.520	5.699	10.351	8.693
<b>Ca</b>	5.045	4.036	6.924	30.462	25.271	25.101
<b>K</b>	24.667	20.192	25.066	3.108	2.402	7.837
<b>P</b>	1.160	1.215	1.673	0.380	0.229	0.862
<b>Al</b>	0.076	0.107	0.612	0.874	1.414	1.100
<b>Mg</b>	0.795	1.098	1.364	0.860	0.534	1.887
<b>Fe</b>	0.141	0.127	0.563	0.412	1.034	0.907
<b>Na</b>	0.355	0.165	0.460	0.138	0.237	0.556
<b>Mn</b>	0.084	0.070	0.117	0.820	0.342	0.040

<b>Ash 550°C (wt.%)</b>	5.8	8.47	3.98	8.4	11.68	8.3
<i>SiO<sub>2</sub></i>	49.9%	64.4%	49.9%	20.8%	36.7%	29.5%
<i>CaO</i>	9.6%	6.7%	12.2%	72.8%	58.5%	55.6%
<i>K<sub>2</sub>O</i>	40.5%	28.9%	37.9%	6.4%	4.8%	14.9%

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Table 2: Biomass ash mixtures elemental composition on a dry basis along with their *SiO<sub>2</sub>*, *CaO*, and *K<sub>2</sub>O* weight percentages.

All elements in wt.% ash	BCWC	BCWI	BCWF	BIWC	BIWI	BFWC	BFWI	BFWF
<b>α</b>	0.500	0.314	0.559	0.616	0.550	0.352	0.242	0.500
<b>β</b>	0.590	0.490	0.557	0.697	0.718	0.522	0.484	0.580
<b>C</b>	6.30	5.20	5.50	5.00	4.60	4.40	4.00	4.90
<b>O</b>	45.75	46.24	48.75	47.95	46.79	48.62	50.34	47.19
<b>S</b>	0.79	0.76	0.64	0.56	0.65	0.80	Not measured	0.56
<b>Cl</b>	0.56	0.36	0.45	0.34	0.26	0.61	Not measured	0.29
<b>Si</b>	11.62	11.10	13.40	14.30	13.40	13.50	14.00	16.00
<b>Ca</b>	20.95	20.49	18.83	13.47	15.90	14.69	15.37	17.37
<b>K</b>	11.00	12.27	9.38	13.15	12.44	14.21	12.34	10.18
<b>P</b>	0.55	0.73	0.46	0.83	1.04	0.66	0.75	0.52
<b>Al</b>	0.82	0.75	0.80	1.59	1.69	0.85	1.05	1.16
<b>Mg</b>	0.71	1.04	0.72	1.44	1.66	0.68	0.95	0.76
<b>Fe</b>	0.45	0.59	0.67	0.78	0.89	0.53	0.73	0.70
<b>Na</b>	0.26	0.22	0.16	0.54	0.61	0.27	0.25	0.16
<b>Mn</b>	0.26	0.25	0.23	0.06	0.07	0.19	0.22	0.21
<b>Ash 550°C (wt.%)</b>	7.10	5.37	8.43	7.34	6.36	7.87	5.84	10.08
<i>SiO<sub>2</sub></i>	36.9%	35.4%	43.3%	46.9%	43.5%	43.4%	45.2%	48.4%
<i>CaO</i>	43.4%	42.6%	39.7%	28.8%	33.7%	30.9%	32.4%	34.3%
<i>K<sub>2</sub>O</i>	19.6%	22.0%	17.0%	24.2%	22.7%	25.7%	22.4%	17.3%

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## 2.2. Experimental procedure

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The compressed ash chips were annealed with the same procedure as in the “ash test” of Atallah et al. [26]. A 95-5 wt.% Pt-Au crucible was used in each experiment. This material was selected to avoid any interaction between the sample and the crucible. It was shown by Atallah et al. [26] that equilibrium for the bark-straw BCWC mixture was experimentally reached at 850°C in 24h, 1000°C in 6h, and 1200°C in 6h [26]. Consequently, all the experiments using the other mixtures were conducted at 1000°C and 6h in air. These laboratory conditions favor chemical reactions and should lead to a final phase assemblage close to thermodynamic equilibrium (high proximity of ash grains).



### 2.3. P-XRD analysis

A Bruker D8 Advance Powder X-Ray diffraction (P-XRD) equipped with Cu K $\alpha$  (40 kV and 30 mA) radiation was used to analyze the crystallographic composition and the amorphous contents in each sample. Samples were manually ground in an agate mortar, placed in an amorphous silica sample holder, and then flattened with glass to obtain a well-defined surface. Diffractograms were obtained over a 2 $\theta$  interval between 15° and 70°. The identification and semi-quantification of the crystalline phases were first performed using the Bruker EVA software and its I/Cor module. Afterward, 10 wt.% of TiO<sub>2</sub> Anatase (99.99 wt.%, Sigma-Aldrich) was added as an internal standard to quantify the amorphous phase (assumed to be a solidified liquid silica-rich phase). Then, full XRD quantification was conducted by applying Rietveld refinement to each sample using the Panalytical Instruments Highscore plus software. The ICDD 2020 crystallography database was used in the software mentioned above. The detailed procedure can be found in the work of Atallah et al. [15].

### 2.4. Total and elemental weight loss analysis

#### 2.4.1. Total weight loss analysis

The total weight loss was measured from the ash test experiments described in section 2.2 using a mass balance ( $\pm 0.001$  g) between the beginning of each experiment and its end. In parallel, a SETARAM Setsys 16/18 EO simultaneous thermogravimetric analysis-differential thermal analysis (TGA-DTA-MS) was used to evaluate the dynamic weight loss and differential heat flow as a function of temperature. A piece of compressed ash chip (1.3 cm diameter compressed at a pressure of 10 bar) of BCWC mixture was used as the sample. It was put in a 3 mm diameter x 8 mm height Pt crucible ( $\sim 70$  mg) under air flow rate (50 mL/min). The TGA program was composed of a 10K/min ramp until 1350°C followed by a 30 min plateau and a slow cooling (10°C/min), and a 1h plateau and fast cooling (33°C/min). The detailed results and analysis methods are presented in Appendix D.

#### 2.4.2. Elemental weight loss (or elemental volatilization)

The elemental weight loss ( $L_i$ ) was calculated using the proportionality rule from the ICP-AES results in Table 2 as follows:

$$L_i = \left( 1 - \frac{(1-m_t) \times m_{fin,i}}{m_{in,i}} \right) \times 100 \quad (2)$$

Where  $m_{in,i}$  denotes the weight of each element (i) measured by the ICP-AES in the BCWC mixture at 550°C (Table 2), and  $m_{fin,i}$  denotes the one measured after annealing at 1000°C or 1200°C.

195 2.5. Phase diagram calculation and global simulation  
196 All thermodynamic equilibrium calculations and simulations were performed assuming that all  
197 elements and phases are homogeneously distributed and available for reaction.

198 2.5.1. Phase diagram approach  
199 Calculations of the ternary phase diagram  $K_2O$ - $CaO$ - $SiO_2$  (Figure 1) were conducted using the  
200 “phase diagram” module of FactSage (version 8.1, June 2021) at three different temperatures  
201 (850°C, 1000°C, 1200°C) with GTOX (2018) and FToxid 8.1 (2021) databases. GTOX and  
202 FToxid are among the widely used thermodynamic databases in the market that contain  
203 thermodynamic data for oxides and their solutions. GTOX modeling was based on the work of  
204 Hack et al. [14], while FToxid modeling was based on the work of Kim et al. [24,28].

205 2.5.2. Global simulation approach  
206 Global simulations of predicted amounts of crystalline phases, liquid slag, and volatilization  
207 behavior were conducted to assess further the database quality. The main difference between  
208 the global simulation and the phase diagram approach is that the latter uses only Ca, Si, and K  
209 oxides without gas. At the same time, the former considers the concentration of the other  
210 elements and the gaseous atmosphere (air). The FactSage software was also used to conduct the  
211 simulations using its “Equilib” module. Two sets of databases were applied for database  
212 comparison:

- 213 □ Set 1: GTOX (version 2018) for oxides (compounds & solutions) combined with FactPS  
214 (June 2021) for the gas species and additional inorganic solid phases.
- 215 □ Set 2: FToxid 8.1 (June 2021) for oxides (compounds & solutions) combined with  
216 FactPS (June 2021) for the gas species and additional inorganic solid phases and FTSalt  
217 (June 2021) for salt melts and solutions.

218 The SGTE pure substance database is usually recommended with GTOX [29], but the authors  
219 did not have access to it. Hence, it was replaced by FactPS in dataset 1. The thermodynamic  
220 data of FTSalt are compatible with FToxid but not with GTOX. Hence, FTSalt was used with  
221 the former rather than with the latter.

222 The comparison of the predicted results using the global simulations between the two sets of  
223 databases was conducted using the elemental analysis of only BC and WC ashes in Table 1  
224 since the analyses were similar to the other biomass ashes. Since the global simulation for the  
225 database comparison was conducted on ash samples, bark weight fraction in the ash bark-straw  
226 mixture ( $\beta$ ) was used. In the simulations, the bark weight fraction in the ash samples ( $\beta$ ) was

227 varied between 0 and 1 in air. A simulation temperature of 1000°C was set, at which equilibrium  
228 was experimentally reached in previous work using the same raw materials [26].

229 Afterward, the elemental analysis of each ash sample from single biomasses and mixtures in  
230 Tables 1 and 2 was used to simulate the experimental ash test. 0.5 g of compressed ash chips  
231 were applied in this laboratory test. Hence, the simulation inputs from Table 2 were converted  
232 to per 0.5 g ash. The partial pressure of oxygen was kept constant by setting its activity at 0.21  
233 during the simulation since the experimental reactions were conducted in a 0.7 L vertical  
234 laboratory furnace opened to air. The weight of nitrogen inside the reactor was calculated using  
235 the ideal gas equation at 1 atm and 1000°C. It was found to be 0.147 g/h. Since the experiments  
236 were conducted for 6h, the added nitrogen weight to the feedstock in the inputs of the  
237 simulations was 0.882 g.

### 238 3. Results and discussion

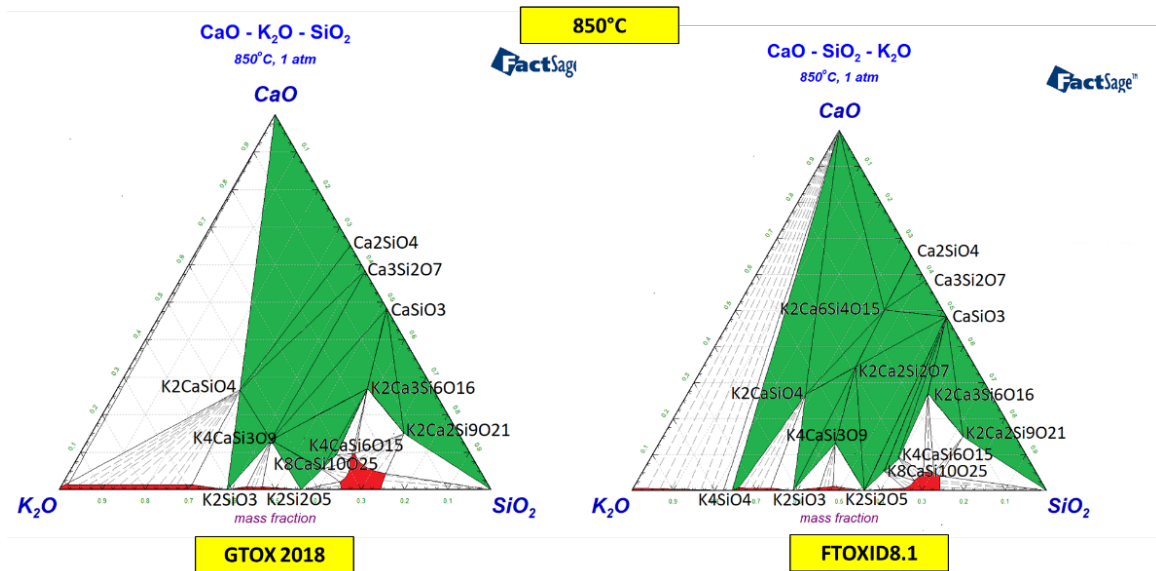
239 3.1. Predicted results comparison between the thermodynamic databases  
240 In this section, calculated results using the GTOX and FToxid thermodynamic databases were  
241 compared against each other in terms of the phase diagram approach (section 3.1.1.) and the  
242 global simulation approach (section 3.1.2.).

#### 243 3.1.1. Phase diagram approach

244 The CaO-K<sub>2</sub>O-SiO<sub>2</sub> ternary phase diagram may have the capability to predict the state of the  
245 biomass ash and their ash mixtures, i.e., if they are in the solid, the liquid, or the solid-liquid  
246 phases. In Figure 1, the calculated isothermal sections of the ternary phase diagrams CaO-K<sub>2</sub>O-  
247 SiO<sub>2</sub> at 850°C, 1000°C, and 1200°C using GTOX and FToxid were shown. The green sections  
248 referred to the pure solid region, while those in red color referred to the liquid region [30]. The  
249 white sections denoted the solid-liquid mixed regions [30].

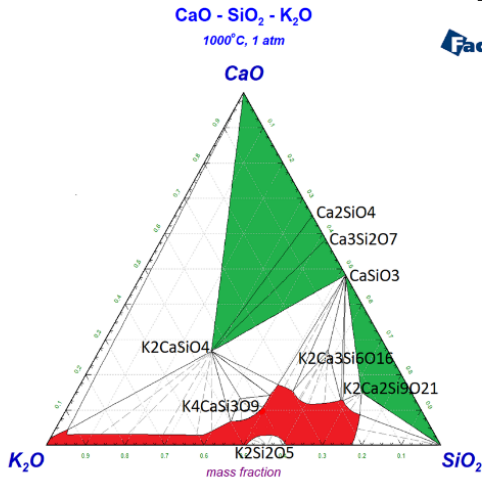
250 In terms of binary sub-systems, the two thermodynamic databases contained the same binary  
251 phases, besides K<sub>4</sub>SiO<sub>4</sub>, which was added in FToxid based on Kim et al. [28]. FToxid included  
252 two ternary phases in the ternary system, K<sub>2</sub>Ca<sub>6</sub>Si<sub>4</sub>O<sub>15</sub> and K<sub>2</sub>Ca<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> (called O15 and O7,  
253 respectively), which are absent in GTOX. However, the thermodynamic data of these two  
254 ternary phases were never measured and were only based on estimations [24]. Other ternary  
255 compounds, such as K<sub>4</sub>CaSi<sub>3</sub>O<sub>9</sub>, K<sub>2</sub>Ca<sub>3</sub>Si<sub>6</sub>O<sub>16</sub>, and K<sub>2</sub>Ca<sub>2</sub>Si<sub>9</sub>O<sub>21</sub>, were calculated at equilibrium  
256 using the GTOX database at 850°C and 1000°C but were not at equilibrium at 1000°C using  
257 FToxid. Most importantly, the positions of the various tie lines (equilibrium lines), solidus, and  
258 liquidus lines differed between the two databases.

259 To better understand the differences between the two databases, the standard enthalpy and  
 260 entropy of formation of the ternary compounds in terms of the pure simple oxides CaO, K<sub>2</sub>O  
 261 and SiO<sub>2</sub>-quartz in each database were calculated at 25°C (298K). They are shown in Table 3.  
 262 This table included values for only the phases found in the calculated ternary phase diagrams  
 263 CaO-K<sub>2</sub>O-SiO<sub>2</sub> at 850°C, 1000°C, and 1200°C. The values in this table highlight the first factor  
 264 leading to the different ternary diagrams calculated using each database, as shown in Figure 1.  
 265 From the data in Table 3, although the values of the binary compounds were similar, those of  
 266 the ternary compounds were different. This difference highly affected the tie line and the  
 267 equilibria between the compounds. Another factor was the addition of O15 and O7, which  
 268 changed the whole equilibrium, especially in the central section of the diagram. One last factor  
 269 may be the different models used to describe the thermodynamic properties of the liquid phase  
 270 (the associate model in GTOX vs. the quasichemical model in FTOXID) applied in each database.

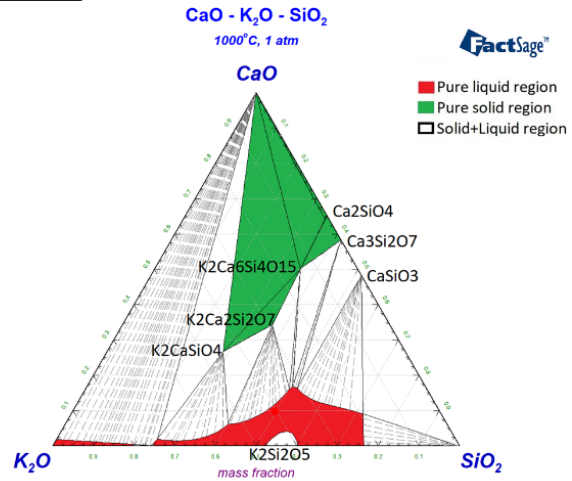


271

1000°C



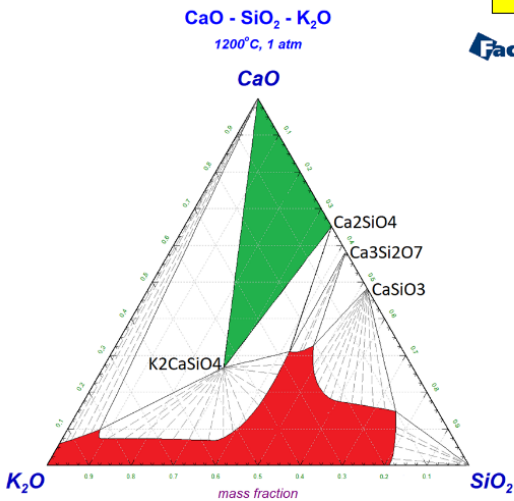
GTOX 2018



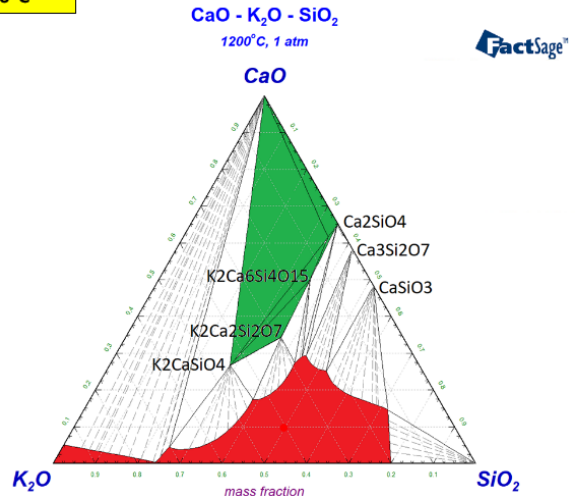
FTOXID8.1

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1200°C



GTOX 2018



FTOXID8.1

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274

Figure 1: Calculated ternary phase diagrams CaO-K<sub>2</sub>O-SiO<sub>2</sub> at 850°C, 1000°C, and 1200°C using GTOX and FToxid.

275

276

Table 3: Comparison between GTOX and FTOXID in terms of the enthalpy and entropy of formations at 298K of binary and ternary compounds.

	FTOXID 8.1		GTOX 2018	
	ΔHf (kJ)	S° (J/mol.K)	ΔHf (kJ)	S° (J/mol.K)
<b>K2CaSiO4</b>	-297.71	196.49	-381.68	172.29
<b>K2Ca2Si2O7</b>	-430.92	268.55		
<b>K2Ca6Si4O15</b>	-740.16	490.49		
<b>K4CaSi3O9</b>	-654.81	380.00	-906.83	213.80
<b>K4CaSi6O15</b>	-686.71	564.00	-761.37	515.64
<b>K8CaSi10O25</b>	-1391.92	897.00	-1534.78	800.00
<b>K2Ca2Si9O21</b>	-537.02	558.30	-639.02	500.00
<b>K2Ca3Si6O16</b>	-569.03	512.50	-684.99	428.45
<b>Ca2SiO4</b>	-126.63	119.66	-140.28	120.57

<b>Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub></b>	-223.76	205.56	-225.60	210.89
<b>CaSiO<sub>3</sub></b>	-88.89	79.81	-88.43	81.99
<b>K<sub>4</sub>SiO<sub>4</sub></b>	-412.20	245.47		
<b>K<sub>2</sub>SiO<sub>3</sub></b>	-271.60	146.15	-287.96	146.15
<b>K<sub>2</sub>Si<sub>2</sub>O<sub>5</sub></b>	-320.80	190.58	-339.44	182.00

277 3.1.2. Global simulation approach  
 278 Figure 2 shows the variation of the predicted amounts of the crystalline solids (Figures 2.a and  
 279 2.c) and the volatilization behavior (Figure 2.b and 2.d) as a function of the changes of the bark  
 280 weight fraction in the BC-WC ash mixture at 1000°C. Figures 2.a and 2.b shows the predicted  
 281 results using the GTOX dataset 1. Figures 2.c and 2.d presented those predicted using the  
 282 FToxid dataset 2. The previous phase diagram approach used Ca, K, and Si oxides in the  
 283 prediction (atmosphere absent, so no volatilization prediction), while the global approach used  
 284 all the elements in the calculations, considering the air atmosphere.

285 Comparing the predicted solid and liquid phases using the GTOX dataset (Figure 2.a) and the  
 286 FToxid dataset (Figure 2.c), more liquid phase contents and higher Ca<sub>2</sub>SiO<sub>4</sub> and Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub>  
 287 contents were predicted using the GTOX dataset than the FToxid dataset. In addition, the  
 288 stability range of Ca<sub>2</sub>SiO<sub>4</sub> was wider in the calculated results using the GTOX dataset than the  
 289 those using the FToxid dataset. Most importantly, K<sub>2</sub>CaSiO<sub>4</sub> was not at equilibrium in the  
 290 simulation using FToxid, while K<sub>2</sub>Ca<sub>6</sub>Si<sub>4</sub>O<sub>15</sub> was absent from the GTOX database. Calculations  
 291 using the FToxid dataset predicted several minor phases with Mg and Al, while those using the  
 292 GTOX dataset failed to do that. CaSiO<sub>3</sub> and the potassium-based phases such as K<sub>3</sub>PO<sub>4</sub>,  
 293 KAlSiO<sub>4</sub>, and KAlO<sub>2</sub> found with FToxid calculations were also absent from those using GTOX.  
 294 In GTOX, a slag solution phase called LIOS is modeled. This solution dissolves oxides, metals,  
 295 sulfides, sulfates, and fluorides. Consequently, the K-bearing compounds must have dissolved  
 296 within this slag phase.

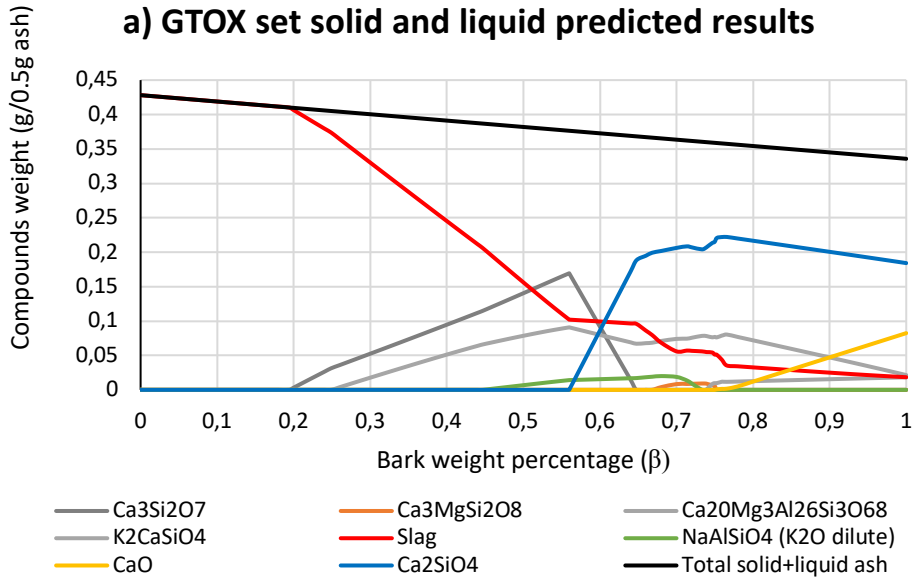
297 On the other hand, several potential liquid solution descriptions are available in the FToxid 8.1  
 298 database called Slag A or Slag B. According to the documentation file of the FToxid database,  
 299 slag A is a liquid solution of various oxides that can dissolve sulfur as sulfides. Therefore, it is  
 300 more used in literature than slag B [31–33]. In contrast, the FactSage description of Slag B says  
 301 that it is a liquid solution of various oxides that can dissolve sulfur as sulfates as a dilute solution  
 302 with a maximum concentration of 10 wt.%. Sulfates, especially in the form of K<sub>2</sub>SO<sub>4</sub>, rather  
 303 than sulfides, are generally found in the biomass ash. Hence, Slag B is usually chosen for  
 304 feedstock rich in sulfur due to its ability to handle both silicates and sulfates interactions with  
 305 various positively charged ions [34] and accommodate for SO<sub>3</sub> dissolution [35]. However,

306 according to the documentation file of the FToxid database, slag B was never optimized for the  
307 system CaO-K<sub>2</sub>O-SiO<sub>2</sub>. Consequently, Slag A was chosen in FToxid in all experimental  
308 simulations in this work rather than Slag B.

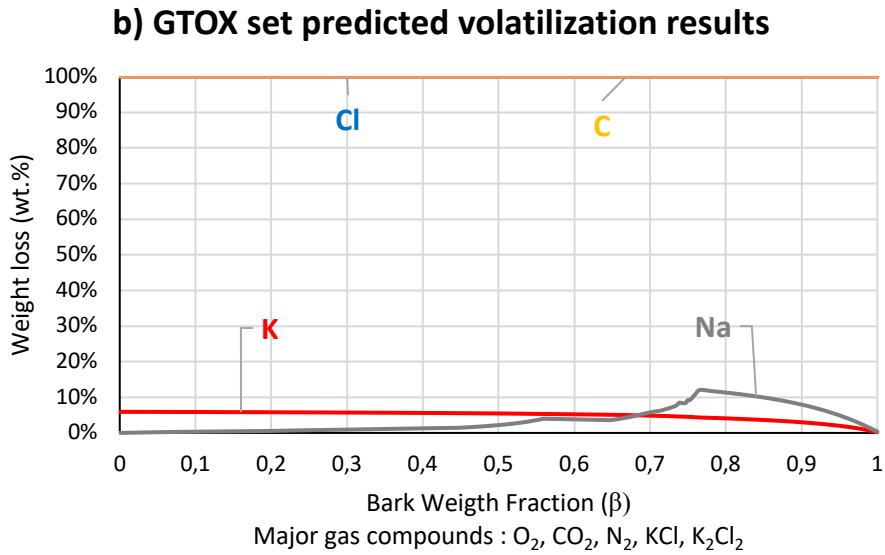
309 A detailed analysis of the effect of using Slag A vs. Slag B and adding FTSalt to the  
310 experimental simulations is presented in Appendices B and C. From Figure B in Appendix B,  
311 adding the FTSalt database to the experimental simulations in dataset 2 did not significantly  
312 affect the predicted condensed phases and volatilization. In addition, from the results in  
313 Appendix C, using slag B in the simulations rather than slag A destabilized several major K-  
314 rich phases found experimentally, such as KAlSiO<sub>4</sub>, K<sub>2</sub>Ca<sub>6</sub>Si<sub>4</sub>O<sub>15</sub>, and K<sub>2</sub>Ca<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>. This is  
315 because K was dissolved in slag B instead of reacting with alkaline earth-silicate compounds.  
316 Hence, simulations using this slag increased the liquid contents and the amounts of some  
317 alkaline earth-silicate binary phases, such as Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub> and Ca<sub>2</sub>SiO<sub>4</sub>.

318 The clear difference between the two databases can be highlighted by taking the 50-50 bark-  
319 straw ash mixture ( $\beta$ ) case (BCWC) in Figure 2, as an example. Using the GTOX dataset (Figure  
320 2.a), liquid, Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub>, Ca<sub>2</sub>SiO<sub>4</sub>, and K<sub>2</sub>CaSiO<sub>4</sub> were present in the mixture at equilibrium. On  
321 the contrary, using the FToxid dataset (Figure 2.c), less liquid and minor amounts of Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub>  
322 were present. In addition, the primary crystalline solid was K<sub>2</sub>Ca<sub>6</sub>Si<sub>4</sub>O<sub>15</sub> in the simulations using  
323 FToxid instead of the Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub> and K<sub>2</sub>CaSiO<sub>4</sub> in those using GTOX. Again, all these  
324 differences may be related to the different liquid phase models (the associate model in GTOX  
325 vs. the quasichemical model in FToxid) and their extrapolation into the ternary system as well  
326 as the different compounds and their thermodynamic data (Table 3) used in each database.

327 In terms of elemental volatilization, according to Figures 2.b and 2.d, both databases predicted  
328 full C and Cl volatilization in the form of CO<sub>2</sub>(g), KCl(g), and K<sub>2</sub>Cl<sub>2</sub>(g). Both databases showed  
329 minor differences of K and Na predicted volatilization. Besides, slightly higher Na  
330 volatilization was predicted using the GTOX dataset at  $\beta$  higher than 0.7 (bark rich region). The  
331 predicted volatilizations for the rest of the inorganic elements were negligible and were omitted  
332 from Figures 2.b and 2.d.

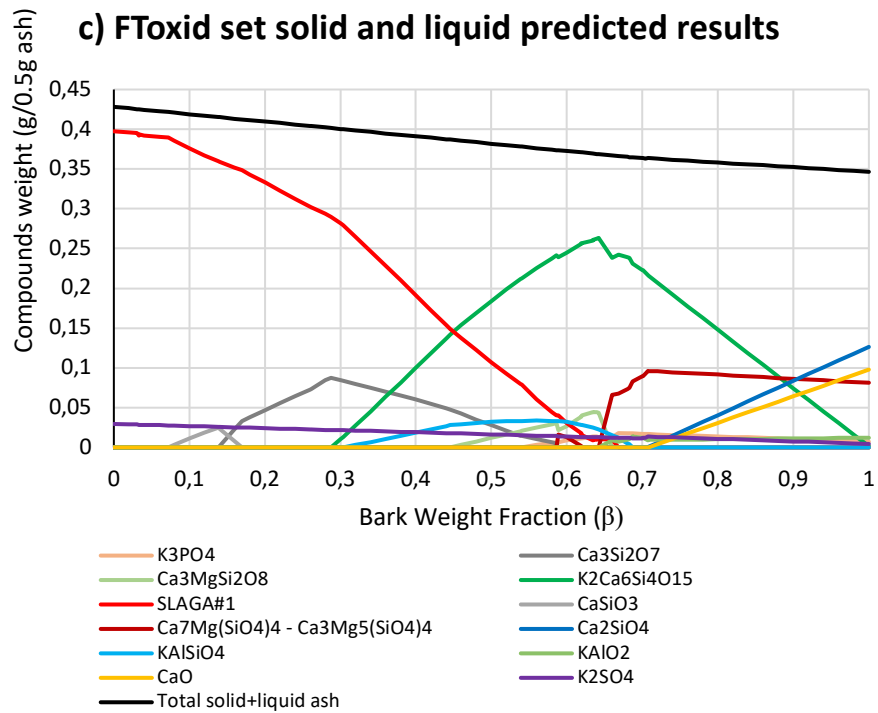


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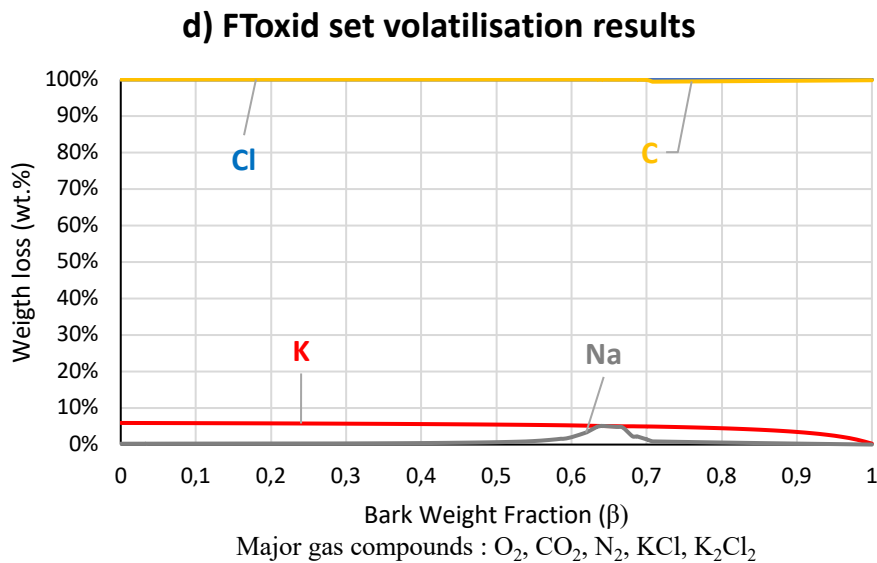


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337  
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Figure 2: Global simulation at various BC weight fraction in WC-BC ash mixture calculated at 1000°C using GTOX (a,b) and FToxid (c,d) database sets.

339

3.2. Comparison between the phase diagram approach and the global simulation

340

approach

341

To compare the prediction capabilities between the phase diagram and the global simulation

342

approaches, calculations were conducted using the same inorganic elements Ca, K, and Si.

343

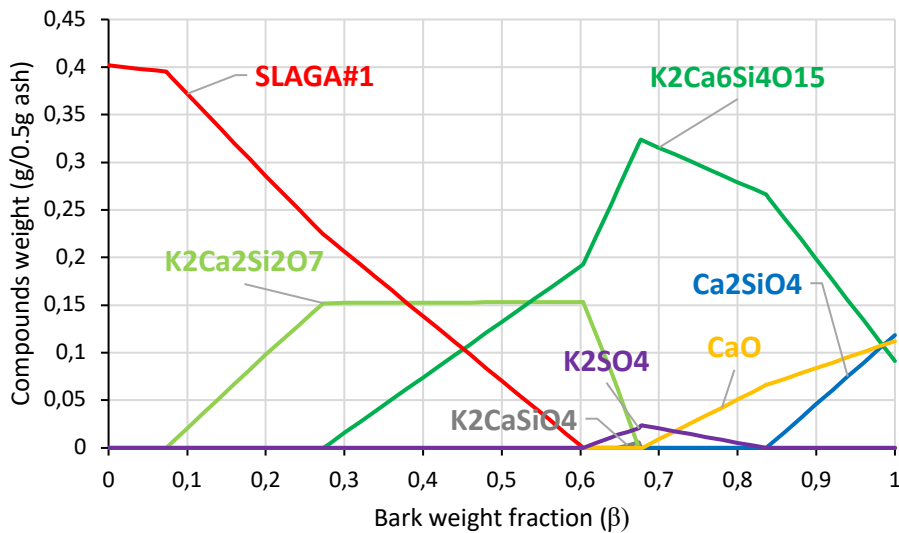
Hence, the global simulation in this section was done using C, H, N, and O along with Ca, K,

344

and Si elements. The FTOXID dataset 2 (with FactPS and FTSalt) was used at 1000°C (Figure

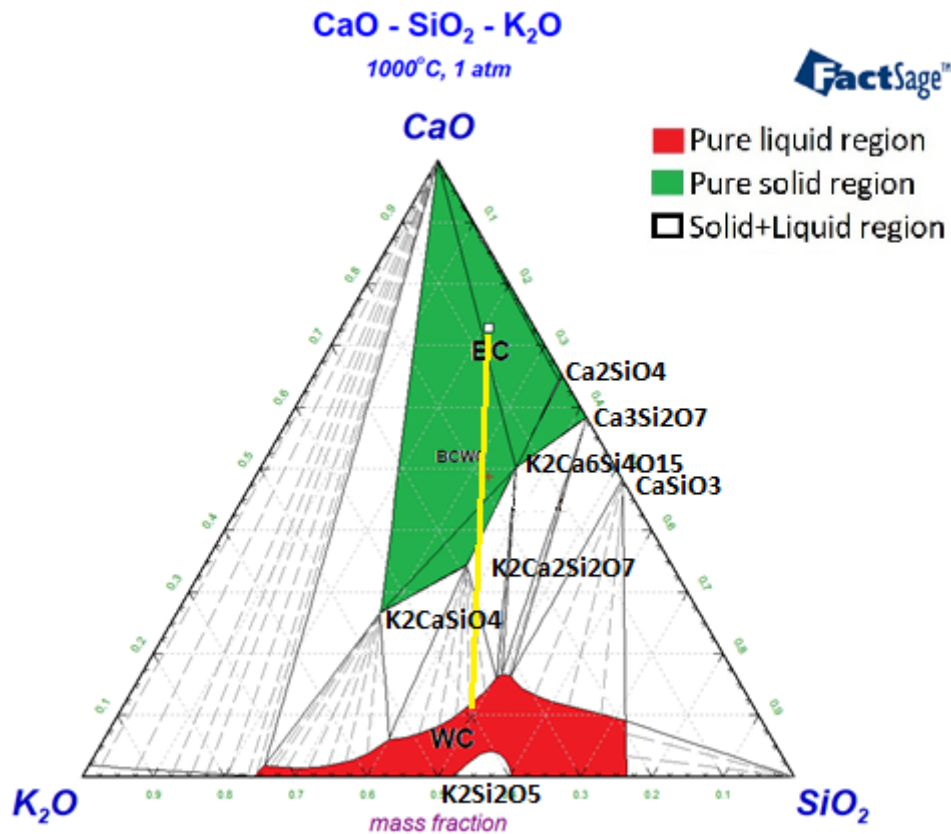
345 3). The elemental compositions of BC and WC from Table 1 were used as input data. The other  
346 barks and straws exhibited similar behavior, along with their mixtures.

347 No inorganic volatilization was found with the global simulation approach. The condensed  
348 predicted phases (Figure 3) agreed with the phase diagram calculation (Figure 4). To illustrate  
349 this, in Figure 4, the ash of pure bark (BC) started in a three-phase region (CaO-Ca<sub>2</sub>SiO<sub>4</sub>-  
350 K<sub>2</sub>Ca<sub>6</sub>Si<sub>4</sub>O<sub>15</sub>) and then moved into another three-phase region as the bark weight fraction  
351 decreased in the mixture until  $\beta=0.85$  (CaO-K<sub>2</sub>Ca<sub>6</sub>Si<sub>4</sub>O<sub>15</sub>-K<sub>2</sub>CaSiO<sub>4</sub>). Beyond this  
352 composition, as the ash bark contents  $\beta$  further decreased, reaching 0.65, K<sub>2</sub>Ca<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>  
353 appeared and replaced CaO in the three-phase region. Liquid appeared at  $\beta=0.6$ , where the  
354 mixture stayed in a K<sub>2</sub>Ca<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>-K<sub>2</sub>Ca<sub>6</sub>Si<sub>4</sub>O<sub>15</sub>-liquid three-phase region until  $\beta=0.28$ . For  
355  $0.05 < \beta < 0.28$ , the mixture was in the K<sub>2</sub>Ca<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>-liquid two-phase region, after which it  
356 reached the pure liquid region for pure straw WC. The pathway mentioned above from the  
357 global simulation was precisely according to the proposed phase diagram pathway drawn as  
358 the yellow line in Figure 4. In conclusion, the two approaches exhibited the same behavior  
359 when the same elements were used. This was mainly due to the absence of K-volatilization in  
360 the global simulation approach.



361

362 *Figure 3: Global simulation at 1000°C using FToxid as database and CaO, SiO<sub>2</sub>, and K<sub>2</sub>O as inorganic oxides between WC*  
363 *and BC ashes.*



364

365

Figure 4: Ternary phase diagram CaO-K<sub>2</sub>O-SiO<sub>2</sub> using FTToxid 8.1 at 1000°C.

366

However, some differences were observed when comparing the global simulation results in Figure 2.c (using all elements) against those in Figure 3 (using only 3 oxides). K<sub>2</sub>Ca<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> was present among the phases predicted by the simulations in Figure 3 (using only 3 oxides), while it was absent from the predicted results using all elements (Figure 2.c) at the expense of more liquid. In parallel, Ca, Si, and especially K volatilization in the three elements simulation were negligible. In contrast, a moderate K volatilization (as KCl, K<sub>2</sub>Cl<sub>2</sub>) in the case of the full element global simulation (Figure 2.d) was found in the range of 8 wt.% as β varied. Hence, it was clear that another inorganic element (i.e. S, Cl, Na, Mg, P, Fe, or Mn) was increasing K volatility and destabilizing K<sub>2</sub>Ca<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>.

375

To further investigate this effect, simulations were repeated, adding one element X (X denoted Mn, Na, Fe, Al, S, Mg, Cl, and P) to the combination C, H, O, N, Ca, K, and Si. FTToxid oxide solution Slag A was always used. The detailed results are shown in Appendix A. From Figure A.1 in Appendix A, the addition of each new element X led to the addition of crystalline solids and solutions linked to it, like KAlSiO<sub>4</sub> and KAlO<sub>2</sub> in the case of Al (i.e., for the CHNOCaKSiAl system), Ca<sub>3</sub>Fe<sub>2</sub>Si<sub>3</sub>O<sub>12</sub> in the case of Fe (CHNOCaKSiFe), and more. Nevertheless, this single addition kept K<sub>2</sub>Ca<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> stable and K volatility negligible. As a result,

381

382 more elements were added to the initial combinations, and simulations were repeated to analyze  
383 further the combination of elements that destabilized  $K_2Ca_2Si_2O_7$  and increased K volatility.

384 In conclusion, this phase was found to be stable in the presence of the various combinations of  
385 CHNOCaKSi with Al, S, Fe, Mn, and Na (Figure A.2). However, the elements that were found  
386 to destabilize  $K_2Ca_2Si_2O_7$  were P, Cl, and Mg: P (Figure A.3) due to its competition with K and  
387 Ca on the silicate matrix, Cl (Figure A.4) due to its reaction with K to produce  $KCl(g)$  in the  
388 gaseous phase, and Mg (Figure A.5) by its substitution reaction with Ca. As a result, the  
389 simulations validated that several minor inorganic elements can affect the predicted ash  
390 behavior.

391 3.3. Assessing the prediction capabilities with respect to experimental data  
392 In this section, the predicted solid and liquid phases along with volatilization were compared  
393 to experimental data obtained at thermodynamic equilibrium [26] using the ash of single  
394 biomasses and their ash mixtures presented in Tables 1 and 2. The experimental data were  
395 recorded at 1000°C for six biomasses and eight ash mixtures. In addition, three temperatures  
396 (850°C, 1000°C, and 1200°C) were studied for the mixture BCWC (called MP2b in the work  
397 of Atallah et al. [26] and Defoort et al.[9]).

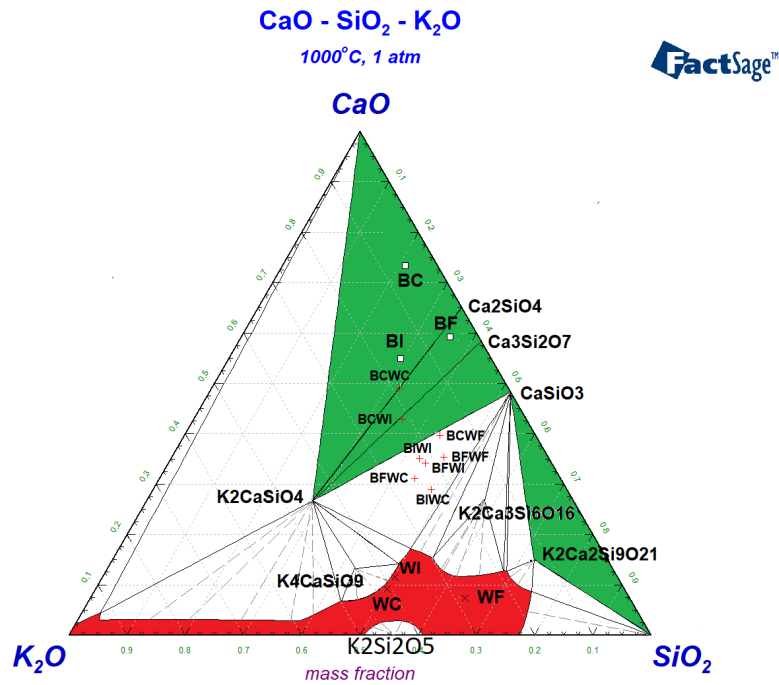
398 To assess the prediction capabilities of the phase diagram approach, the single biomasses  
399 ashes were positioned in the CaO-K<sub>2</sub>O-SiO<sub>2</sub> phase diagram calculated at 1000°C in Figure 5,  
400 based on their CaO, SiO<sub>2</sub>, and K<sub>2</sub>O weight percentages shown in Tables 1 and 2. For  
401 simplicity, results only at 1000°C were shown in Figure 5 using each database. Similar  
402 outcomes were seen at 850°C and 1200°C.

403 3.3.1. Single biomass ash case

404 Figure 6 shows the measured P-XRD results for each straw and bark ash compared to those  
405 predicted by the global simulation approach using each database set at 1000°C.

406 In Figure 5, the three straws were located in the pure liquid region. Accordingly, the P-XRD  
407 results in Figure 6 showed that all the measured wheat straw samples at 1000°C were in the  
408 liquid phase with minor  $K_2SO_4$  concentration (< 10 wt.%). The amorphous contents was  
409 proportional to the alkali-silicate oxide contents and inversely proportional to the one of  
410 alkaline earth metal oxide [6,36]. Hence, the measured amorphous contents in the straw ash  
411 samples in Figure 6 could be ranked similarly to their K<sub>2</sub>O weight percentages (Table 1), in the  
412 following increasing order: WF < WI < WC. In terms of predictions, simulations using the  
413 GTX dataset failed to predict the presence of  $K_2SO_4$  in the three straws, showing instead a

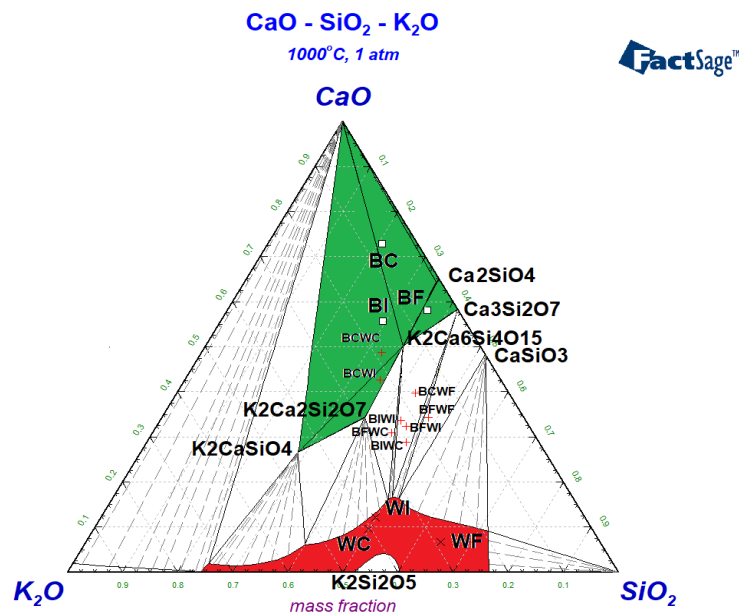
414 total solubility of K and S in the liquid phase LIOS. In contrast, calculations using FToxid set  
 415 successfully predicted the straw behavior with a minor quantitative difference with the P-XRD  
 416 measured values (<5% absolute error).



417

418

**GTOX**



419

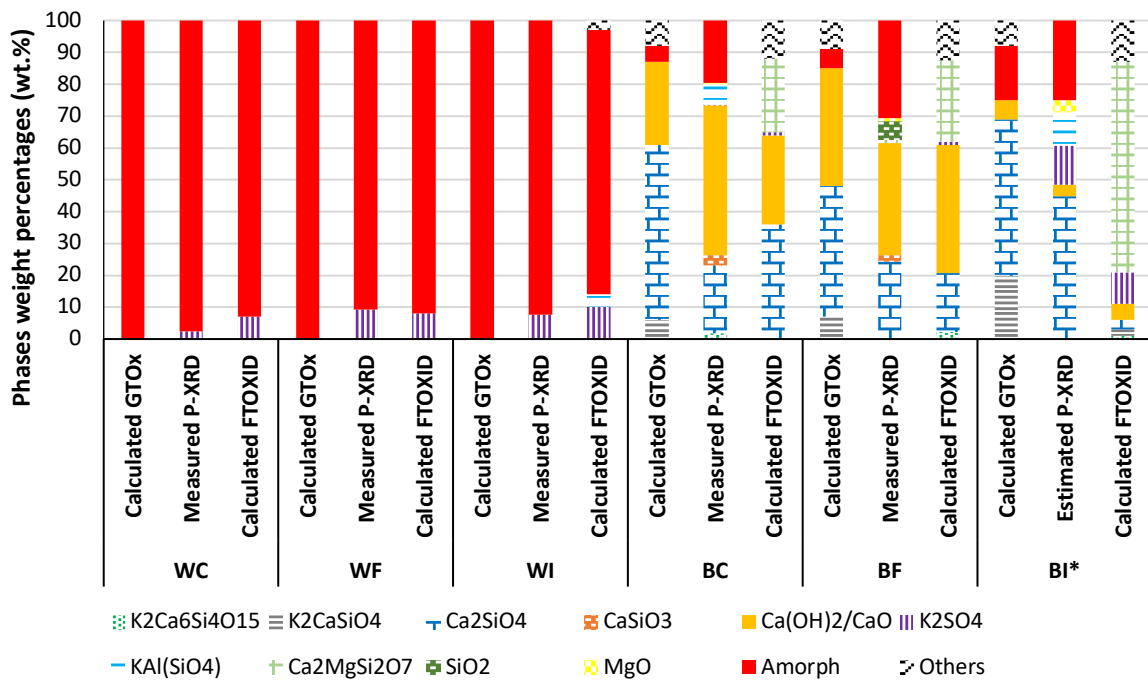
**FToxid**

420 *Figure 5: Position of the various single biomasses and their mixtures in the phase diagram calculated at*  
 421 *1000°C using GTOX and FToxid*

422 On the other hand, the three barks were located in the pure solid region in Figure 5. Accordingly,  
 423 from Figure 6, all the measured oak bark samples showed low amorphous contents (<30 wt.%).

424 It should be noted that the measured amorphous contents contain molten ash mixed with tiny  
 425 crystals of  $\mu\text{m}$  in size. Hence, the effective measured liquid contents had to be less than 30  
 426 wt.%. As a result, the phase diagram approach provided a good ash state prediction for single  
 427 barks cases.

428 According to Table 1, BF was mostly rich in Si among the three bark samples. Hence, it  
 429 presented the highest amorphous contents among the three barks. BC and BF presented close  
 430 weight percentages of CaO,  $\text{K}_2\text{O}$ , and  $\text{SiO}_2$  (Table 1). This explains the close concentration of  
 431 each phase found in their ashes (Figure 6). BI was the richest in Si, K, Na, P, Fe, and Mg and  
 432 the poorest in Ca. It contained three times the K contents in BC and BF at the expense of less  
 433 Ca (Table 1). Therefore, the measured  $\text{CaO}/(\text{CaOH})_2$  concentration in this sample was the  
 434 lowest at the expense of the abundance of  $\text{K}_2\text{SO}_4$  and  $\text{KAlSiO}_4$  concentrations.  $\text{Ca}_2\text{SiO}_4$  was  
 435 present in all the measured samples, while the predicted  $\text{K}_2\text{CaSiO}_4$  was experimentally absent.  
 436 This is not surprising as  $\text{Ca}_2\text{SiO}_4$  is the most stable compound in the CaO-SiO<sub>2</sub> binary system.



437  
 438 *Figure 6: Measured (P-XRD) phases within the ash of the various biomasses versus those predicted by the global simulation*  
 439 *using GTOX and FToxid database sets after annealing for 6h at 1000°C. The error for the measured P-XRD results was in*  
 440 *the range of 2 wt.%.*

441 *\*The crystalline/amorphous compositions of BI were estimated based on the amorphous percentage of BC and BF and BI measured XRD*  
 442 *compositions without TiO<sub>2</sub>.*

443 In terms of predictions, calculations using both databases failed to predict the existence of the  
 444 minor phases in all bark samples, such as  $\text{CaSiO}_3$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{KAlSiO}_4$ ,  $\text{SiO}_2$ , and  $\text{MgO}$ .  
 445  $\text{Ca}_2\text{MgSi}_2\text{O}_7$ , always predicted by the calculations using the FToxid dataset, was never found

446 experimentally. In contrast, the simulations using the FToxid dataset failed to predict the  
447 amorphous contents that were found experimentally, and in the prediction using the GTOX  
448 dataset. Nevertheless, an amorphous concentration difference remained between the measured  
449 and the predicted values using the GTOX dataset. Both databases showed good prediction  
450 capabilities for  $\text{Ca}_2\text{SiO}_4$  and  $\text{CaO}/\text{CaCO}_3$  crystalline phases. However, the relative quantitative  
451 prediction error for these two compounds always ranged between 5% and 50%. Here again, the  
452 presence of  $\text{K}_2\text{CaSiO}_4$  in GTOX always hindered good predictions. In conclusion, despite its  
453 success in the case of single straws, the global simulation approach showed some limitations in  
454 the case of barks. The ash elemental interactions were more complex in the case of barks than  
455 straws, which might have limited the predictions in the case of barks. For instance, the major  
456 ash interactions in the case of straws were confined between K and Si, while Ca was present in  
457 addition to the first two elements in the case of barks (Table 1).

### 458 3.3.2. Biomass ash mixtures

459 Figure 7 shows the measured P-XRD results for each straw-bark ash mixture compared to those  
460 predicted by the global simulation approach using each database set at  $1000^\circ\text{C}$ . Figure 8 shows  
461 the measured experimental P-XRD results for the BCWC ash mixture at various temperatures  
462 compared to those predicted by each database.

463 According to Figure 5, all mixtures were positioned in the solid-liquid region, besides BCWC  
464 and BCWI. The latter was on the border of the solid and solid-liquid region. BCWC was deep  
465 in the solid region. Accordingly, from Figure 7, the measured P-XRD concentrations showed  
466 crystalline phase mixtures with significant amorphous contents, ranging between 40 wt.% and  
467 60 wt.%. The lowest amorphous contents were seen in the BCWC mixture. As a result, the  
468 phase diagram approach using both databases showed good prediction capabilities for the ash  
469 state in the case of the blends.

470 According to Figures 7 and 8, global simulations using the GTOX dataset failed to predict  
471  $\text{K}_2\text{Ca}_6\text{Si}_4\text{O}_{15}$  and  $\text{K}_2\text{Ca}_2\text{Si}_2\text{O}_7$ , the major ternary phases found experimentally. Unfortunately,  
472 they were absent from this database (Table 3). Besides, calculations using the GTOX dataset  
473 consistently predicted  $\text{K}_2\text{CaSiO}_4$  and ranked it as one of the major phases. However, this phase  
474 was never found experimentally neither in any mixtures nor in BCWC at various reaction  
475 temperatures. This experimental finding was in agreement with the work of Arroyabe et al.  
476 [37].

477 On the other hand, in Figure 7, equilibrium results obtained with the FToxid dataset presented  
478 good prediction capabilities for the major ternary phases in the mixtures located in the solid  
479 section (green section in Figure 1) or close to it, as BCWC, BFWC, and BCWI. However, the  
480 usage of the FToxid dataset failed to offer good predictions in the other mixtures, especially  
481 those in the solid-liquid sections (i.e., in the middle section of the diagram). Similarly, in Figure  
482 8, calculation results obtained with FToxid provided better predictions for the measured major  
483 phases, especially at 1000°C (equilibrium temperature for  $\text{K}_2\text{Ca}_6\text{Si}_4\text{O}_{15}$  and  $\text{K}_2\text{Ca}_2\text{Si}_2\text{O}_7$  [26]),  
484 than those using the GTOX dataset.

485 Simulations using the two databases predicted the presence of the liquid phase coherently with  
486 the measurements. However, discrepancies remained between the measured concentrations and  
487 those predicted using both databases in the different mixtures (Figure 7) and at different  
488 temperatures (Figure 8).

489 It should be noted that from the results in Figure 7, simulations using the GTOX dataset were  
490 able to better predict the presence of  $\text{Ca}_2\text{SiO}_4$  than using the FToxid dataset for the mixtures in  
491 the solid section (green section in Figure 5) or close to it (BCWC, BFWC, and BCWI).  
492 However, further improvements are still needed for a better quantitative prediction. For the case  
493 of BCWC at different temperatures, the use of both databases failed to predict the presence of  
494  $\text{Ca}_2\text{SiO}_4$  at 850°C but provided good qualitative and quantitative predictions at 1200°C.  
495 Nevertheless, only using the GTOX dataset predicted this phase at 1000°C. The different  
496 thermodynamic data applied in each database for this crystalline phase (Table 3) could be the  
497 main reason behind this behavior.

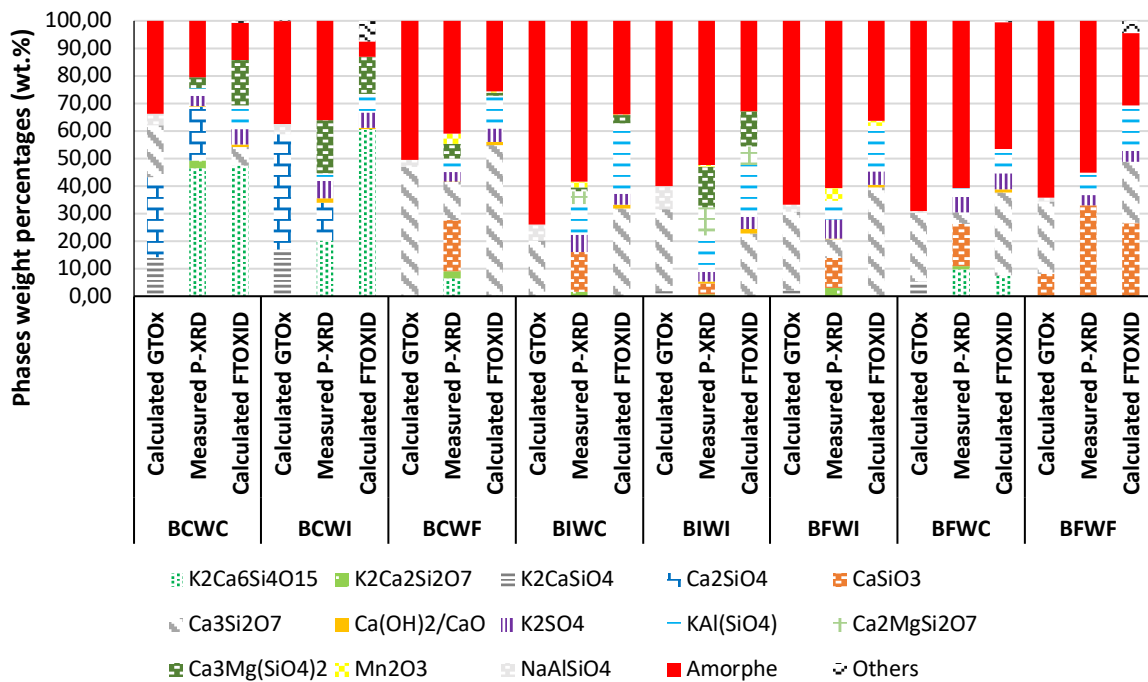
498  $\text{Ca}_3\text{Si}_2\text{O}_7$  was predicted using the two databases but was rarely found experimentally in the  
499 various mixtures (Figure 7) and at different temperatures (Figure 8). Its absence could be due  
500 to its slow kinetic formation [38]. However, its predicted appearance in the mixtures was always  
501 conjugated with the experimental  $\text{CaSiO}_3$  appearance (Figure 7). The latter was never predicted  
502 by any database.

503 In terms of minor compounds, simulations using the GTOX dataset could not predict the K-rich  
504 compounds (with aluminum and sulfur) found experimentally, according to Figures 7 and 8,  
505 such as  $\text{KAlSiO}_4$  and  $\text{K}_2\text{SO}_4$ . Instead, they were predicted to dissolve in the LIOS slag solution  
506 in the GTOX database modeling. Though simulations using the FToxid dataset were able to  
507 predict the presence of these experimental phases, it needed further improvement in terms of  
508 predicted concentrations. Furthermore, the only minor compound,  $\text{NaAlSiO}_4$ , predicted in



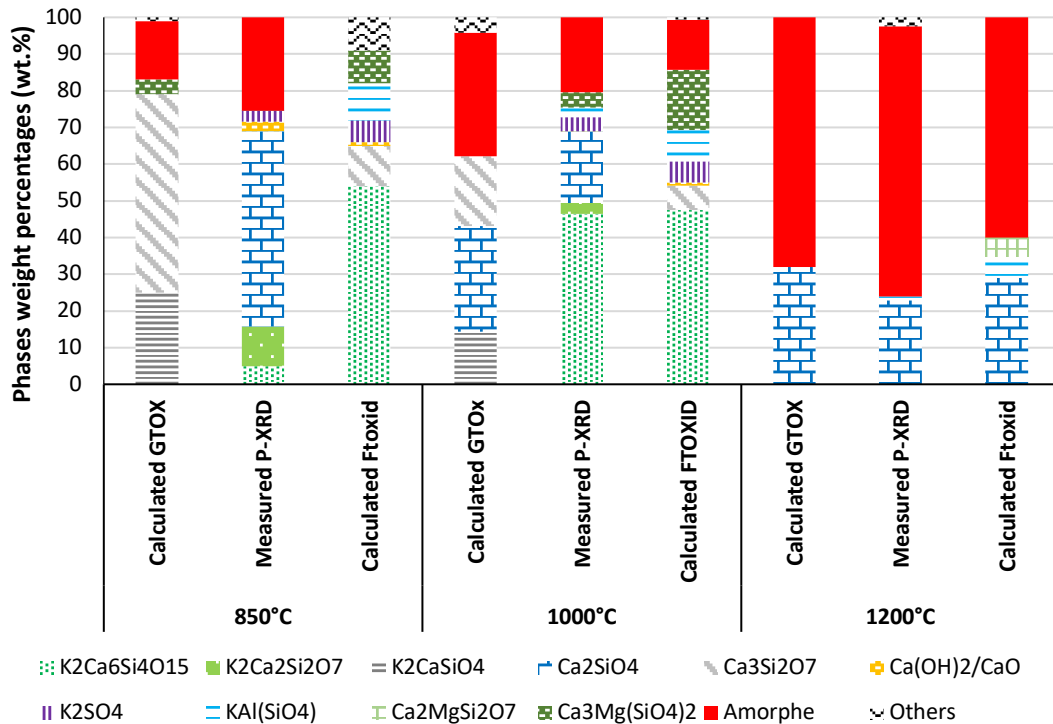
509 certain mixtures using GTOX calculations, was never found experimentally. Hence, using the  
 510 GTOX dataset for the simulations showed clear limitations for predicting the minor phases.  
 511 Calculations using the FToxid dataset behaved better but still needed further improvements.

512 The disagreement between the measured and predicted major crystalline phases along with the  
 513 liquid contents can be due to the estimated thermodynamic data of  $K_2Ca_6Si_4O_{15}$  and  $K_2Ca_2Si_2O_7$   
 514 in FToxid. It can also result from the thermodynamic extrapolation of the liquid phase from the  
 515 binaries. Once the missing / estimated properties are measured and added to the database, and  
 516 if this system is remodeled after excluding  $K_2CaSiO_4$ , the tie lines and phase equilibria may  
 517 change. This update can induce significant modifications to the predicted results, especially for  
 518 the samples in the central section of the ternary diagram. This remodeling may also increase  
 519 the quantitative prediction capabilities of the thermodynamic approach/database. In conclusion,  
 520 simulations using the FToxid database showed clear advantages over those using GTOX, but  
 521 both databases need further improvements.



522

523 *Figure 7: Measured (P-XRD) phases within the ash of the various mixtures vs. those predicted by the global simulation using*  
 524 *GTOX and FToxid database sets after annealing for 6h at 1000°C. The error for the measured P-XRD results was in the*  
 525 *range of 2 wt.%.*



526

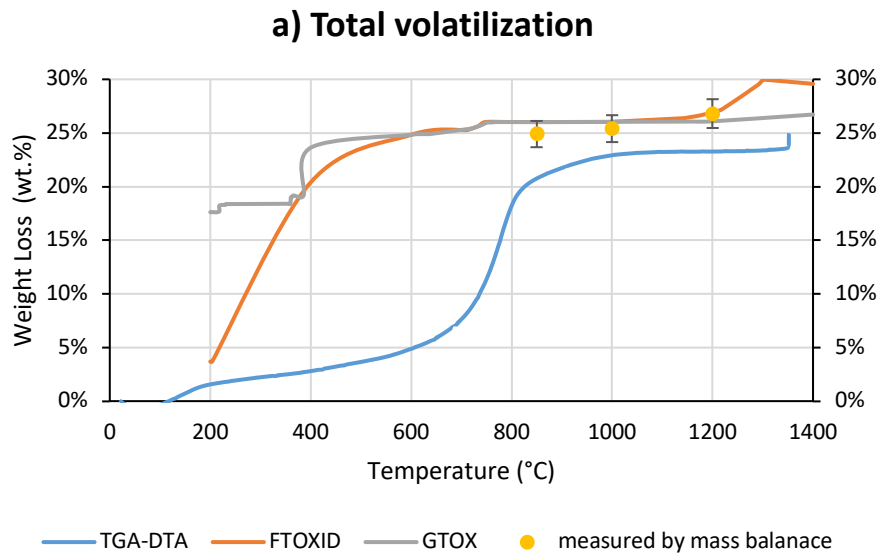
527 *Figure 8: Predicted phases by the global simulation approach using GTOX and FToxid database sets vs. those measured (P-*  
 528 *XRD) within the ash of the BCWC mixture after annealing for 24h at 850°C, 6h at 1000°C, and 6h at 1200°C. The error for*  
 529 *the measured P-XRD results was in the range of 2 wt.%.*

530 3.3.3. Total and elemental volatilization

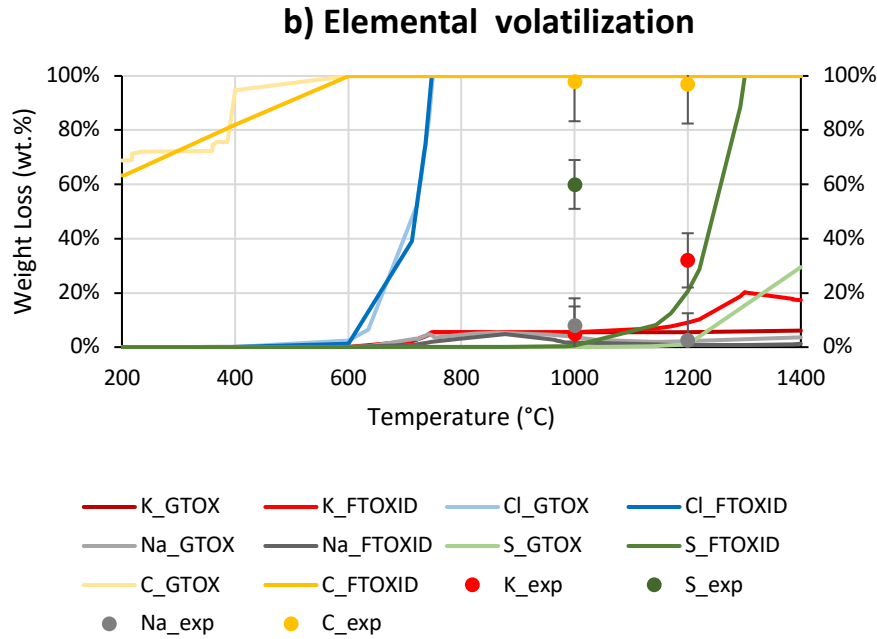
531 To further assess the capabilities of the thermodynamic tool to predict the annealing  
 532 experiments of ash, total and elemental volatilization (K, Na, and C) predicted by FToxid and  
 533 GTOX were compared to those measured experimentally in Figure 9 for the BCWC ash  
 534 mixture. It should be noted that the volatilization for the rest of the inorganic elements was  
 535 negligible (both in the measurements and the predictions).

536 As shown in Figure 9.a, the predicted total volatilization values from the two databases were  
 537 analogous. In addition, they were close to the dynamic total volatilization measured by the  
 538 TGA-DTA, especially at temperatures higher than 850°C. This temperature is considered the  
 539 minimum operating temperature of any combustion process in general [39,40]. However, the  
 540 total volatilization at temperatures lower than 850°C was different between the predicted and  
 541 the dynamically measured results. For instance, carbon volatilization was predicted to increase  
 542 below 850°C gradually. However, this volatilization happens faster in real-life processes. In  
 543 addition, the predicted total volatilization was also consistent with the three static total  
 544 volatilizations measured with the ash test (i.e., total experimental weight loss between the  
 545 beginning and the end of the experimental test).

546 In parallel, the percentage of error of the method used to calculate the elemental volatilization  
 547 from the measured ICP-AES values reached 15%. Hence, from Figure 9.b, it can also be  
 548 concluded that simulations using both databases were able to predict potassium, sodium, and  
 549 carbon volatilization efficiently. The total volatilization of carbon and the significant loss of K,  
 550 S, and Na into the gaseous phase, which were found experimentally, also agreed with the  
 551 literature. Bostrom et al. [36] ranked the stability of oxides in the following increasing order:  
 552  $K_2O < Na_2O < SO_2 < H_2O/P_2O_5 < CO_2 < CO < SiO_2 < MgO < CaO$ . Hence, at a high availability of  
 553 oxygen, such as in the combustion mode, carbon will be totally lost into the gaseous phase in  
 554 the form of  $CO_2(g)$  and  $CO(g)$  [41]. Alkali oxides ( $K_2O$  and  $Na_2O$ ) will primarily react with  
 555 water vapor and volatilize fast in the form of  $KOH(g)$  and  $NaOH(g)$  [10,36]. Sulfur has a lower  
 556 affinity to oxygen than to carbon and hydrogen [36]. Hence it will initially be released in the  
 557 form of  $H_2S$  to further oxidize in excess oxygen to form  $SO_2$  and later  $SO_3$  in the gaseous phase  
 558 [36,41]. Similarly, chlorine, which is considered an unstable oxide, will easily volatilize in the  
 559 form of  $KCl(g)$ ,  $Cl_2(g)$ , and  $HCl(g)$  vapor due to their low stability bonds with oxygen [42].



560



561

562

Figure 9: Predicted and measured total (a) and elemental (b) volatilization for the BCWC ash mixture.

563

#### 3.3.4. Characteristic temperatures

564

Table 4 shows the solidus and liquidus temperatures for the BCWC mixture as measured by TGA-DTA (Appendix D) and compared with those predicted. Calculations using the FTOXID and GTOX databases predicted a close liquidus temperature of around 1400°C while showing a 100°C difference in the solidus temperature. Though the liquidus temperature of the mixture was not able to be measured due to experimental limitations, the experimental solidus temperature was 1180°C, significantly higher than those predicted. This finding again highlighted the limitation of the current thermodynamic databases and the need for corrections. The work of Berjonneau et al. [43] confirmed the findings in this work. In one of the rare literature references that tried to compare the measured and predicted liquidus temperatures in the biomass ash, these authors annealed and then analyzed synthesized ash samples with close compositions to straw and miscanthus ashes, with and without K<sub>2</sub>O contents [43]. They conducted their prediction using the same approach in this work. Berjonneau et al. [43] found close measured and predicted liquidus temperatures for miscanthus ash samples synthesized without K<sub>2</sub>O. However, when K<sub>2</sub>O was added to the ash sample, the measured liquidus temperatures drastically decreased, and the deviations between the measured and the predicted values increased [43]. Similar to the current work, Berjonneau et al. [43] said that the lack of measured thermodynamic data for the K-compounds in the database highly affected the calculated liquidus temperatures.

581

Table 4: Solidus and liquidus measured by TGA-DTA and predicted by each database for the BCWC ash mixture.

	<b>Solidus</b>	<b>Liquidus</b>
<b>TGA-DTA</b>	1180°C	Undetected up until 1350°C
<b>FTOXID prediction</b>	878°C	1400°C
<b>GTOx prediction</b>	748°C	1436°C

#### 583 4. Conclusion

584 A critical assessment was carried out of two thermodynamic-based approaches to predict the  
 585 interactions between the inorganic elements in the ash of biomass and their mixtures. Rather  
 586 than picking one thermodynamic database package, a comparison between the calculated results  
 587 using two typical commercial databases (FToxid vs. GTOX) was conducted for the first time.  
 588 In addition, as part of ongoing work to provide an accurate thermodynamic database, the  
 589 simulated results using the most recent versions of two thermodynamic database sets were  
 590 compared against experimental values, highlighting the need for improvements. Several  
 591 conclusions can be drawn out from this assessment:

- 592  Critical differences could be seen between the results predicted by each database in the  
 593 phase diagram and the global simulation approaches. This was due to the adoption of  
 594 different solid compounds between the databases, especially after adding  $K_2Ca_2Si_2O_7$   
 595 and  $K_2Ca_6Si_4O_{15}$  in FToxid that were absent in GTOX. Considerable differences in the  
 596 modeled thermodynamic properties of the common ternary compounds were also  
 597 present. In addition, different liquid models were also used in both databases, which has  
 598 an impact on the extrapolation of the binary liquid into the ternary system.
- 599  The phase diagram and the global simulation approach predicted similar results when  
 600 the inputs were the same. However, the second approach performed better since it  
 601 accounted for the volatilization and the interactions between the minor elements.
- 602  The phase diagram approach showed excellent capabilities in predicting the ash (solid  
 603 or liquid) state using both databases.
- 604  Using the global simulation approach, simulations using the FToxid dataset offered  
 605 good qualitative and quantitative predictions for the single biomass ash. It also showed  
 606 decent qualitative prediction capabilities for the ash mixtures far from the central section  
 607 of the ternary diagram.
- 608  The global simulation prediction failed using both database sets in the case of the  
 609 mixtures located in the central section of the ternary diagram.
- 610  Both databases showed excellent volatilization prediction capabilities. Nevertheless,  
 611 they failed to forecast the characteristic temperatures for phase transitions.

612 Further corrections and improvements are still needed, especially in the central section of the  
613 diagram. Measuring the estimated thermodynamic properties of  $K_2Ca_2Si_2O_7$  and  $K_2Ca_6Si_4O_{15}$ ,  
614 and removing the  $K_2CaSiO_4$  compound from this system can significantly enhance the  
615 prediction capabilities. Afterward, the improved database can be used to reassess the  
616 capabilities of the two thermodynamic approaches to predict the ash behavior in biomass and  
617 their mixtures, not only in combustion mode but in gasification too. In addition, the improved  
618 database must be tested on mixtures of biomass where reactivity/interactions are lower than in  
619 the mixtures of ash of biomass that were used in this work.

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