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## On the relevance of thermodynamics to predict the behaviour of inorganics during CO<sub>2</sub> gasification of willow wood

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### Abstract

This work is a contribution to the understanding of the behavior of inorganic elements during the gasification process of biomass, with the help of a robust thermodynamic equilibrium calculation methodology. A specific procedure combined with a thorough investigation of available thermochemical databases was developed in order to calculate the behaviour of 23 inorganic elements during CO<sub>2</sub> gasification. In parallel, the gasification of willow wood was performed in a laboratory fixed bed reactor, providing the chemical composition of solid residue and major gases. The specificity of the methodology consists in (i) considering an open system to simulate a gas flow in the system (ii) determining the amount of gasification agent added at each calculation step based on experimental measurements of CO<sub>2</sub> and CO concentration profiles. One of the main conclusions is that the thermodynamic approach is a relevant and powerful tool since most of the inorganics behavior is correctly reproduced.

**Keywords:** biomass, CO<sub>2</sub> gasification, inorganic elements, thermodynamics.

### 1. Introduction

Wastes such as contaminated biomass are widely available resources, which could be gasified to produce syngas, biofuels and electricity and thus help to cope with fossil fuel depletion and reduction of greenhouse gases emissions. However, contaminated biomass is hardly used in such processes due to its potentially high content in heavy metals (HM). As exemplified by the case of phytoextraction plants used to extract contaminants from polluted soils, HM accumulate inside the roots, stems and leaves of these plants (Gupta and Sinha, 2007). Recent works have shown that some HM can have a significant influence on the gasification reaction. Furthermore, after the thermochemical process of biomass gasification with H<sub>2</sub>O, CO<sub>2</sub> or O<sub>2</sub>, HM as well as other inorganics are found in the ash, gas and tar products, which make them difficult to use, and may increase risks to human health and the environment (Nzihou and Stanmore, 2013).

The aim of this work is to understand the behavior of HM and other inorganics during the gasification process of biomass, with a robust thermodynamic equilibrium calculation methodology. Thousands of compounds exist in the multicomponent system composed of contaminated biomass. As evidenced by recent works (Froment et al., 2013, Kottinen et al, 2013, Kaknics et al., 2015, Ma et al., 2015), thermodynamic calculations in such

systems face several challenges: database limitations (Lindberg et al., 2013), software capacities, large deviation from equilibrium. Several modeling options and databases sets are considered here, using the Gibbs energy minimization method. The calculations are compared to experimental data obtained through CO<sub>2</sub> gasification of willow wood in a laboratory scale fixed bed reactor. A careful characterization of gaseous and solid products was carried out, taking into account 23 elements in addition to major ones (C, H, O, N).

## 2. Experimental procedures

### 2.1. Wood samples

The willow wood pellets, obtained from ‘pépinières-Naudet’ company (France), were dried, crushed and sieved to a range of particle size of 0.5 - 1 mm. The C, H, O and N chemical content of wood was determined by an elemental analyser CHNO. The amount of inorganic elements was measured by inductively coupled plasma optical spectroscopy (ICP-OES) analyses, after a specific mineralization procedure (described in Said et al., 2017). The halogens content (F, Cl) was determined by ionic chromatography, according to the norm NF-M-03-009. The wood average composition, based on four samples analysed three times each, is provided in Table 1. Apart from a few elements (F, Cl, Cd, Mg), the uncertainty for the inorganics content is below 20 %.

### 2.2. Pyro-gasification device

The pyro-gasification reactions were carried out in a fixed-bed reactor, with 5 g of wood. The reactor was composed of a quartz tube, in which the wood samples were held by a sintered quartz disk. The wood samples were pyrolysed under N<sub>2</sub> flow (6 L/h) up to 450 °C. After 1 hour at 450 °C, a mixed atmosphere (5.4 L/h of CO<sub>2</sub> and 0.6 L/h of N<sub>2</sub>) was flushed in the reactor, and the furnace was heated from 450 to 950 °C. The sample was then maintained for one hour at 950 °C, before cooling.

### 2.3. Product characterizations

The gases produced were collected in successive 0.5 L sampling bags, and analysed by gas chromatograph equipped with two analytical columns. This protocol provided the quantitative amount of major gases N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, CO, CH<sub>4</sub>, CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>. The solid residues were collected, weighted and their elemental composition was determined by CHON and ICP-OES analyses.

**Table 1.** Elementary composition of dry willow.

Element	mol/kg	Element	mol/kg	Element	mol/kg
H	59.70 ± 3.1E-01	P	1.2E-02 ± 1.4E-03	Cu	4.4E-04 ± 7.4E-05
C	41.23 ± 1.3E-01	Mg	7.9E-03 ± 2.0E-03	Sn	3.3E-04 ± 1.7E-05
O	27.67 ± 1.1E-01	Na	6.0E-03 ± 9.3E-04	Mn	2.7E-04 ± 3.9E-05
N	5.1E-01 ± 5.0E-02	Al	3.0E-03 ± 4.3E-04	Pb	2.2E-04 ± 2.7E-05
Ca	1.0E-01 ± 1.9E-03	Cl	2.4E-03 ± 1.2E-03	Sb	1.8E-04 ± 6.3E-06
F	7.2E-02 ± 3.4E-02	Fe	1.4E-03 ± 2.7E-04	Cd	1.6E-04 ± 1.1E-04
K	2.0E-02 ± 1.4E-03	Zn	7.6E-04 ± 1.5E-04	Cr	1.4E-04 ± 2.0E-05
S	1.8E-02 ± 2.7E-03	B	4.5E-04 ± 9.0E-05	Co	6.9E-05 ± 6.3E-06
Si	1.2E-02 ± 2.6E-03	Ni	4.4E-04 ± 4.0E-05	Ba	3.5E-05 ± 5.7E-06

### **3. Thermodynamics: calculations methodology**

#### *3.1. Software and thermochemical database*

Equilibrium calculations were performed with the FactSage 7.0 commercial software (Bale et al., 2016). The calculation is based on the Gibbs energy minimization method, taking into account Gibbs energy functions of compounds and solutions existing in the multi component system composed by the 27 elements reported in Table 1.

A selection of the databases available within the FactSage package was made, using a combination of SGPS (for gas only), FACT PS, FToxid and FTsalt databases. Even if Konttinen et al. (2013) or Kaknics et al. (2015) used larger database sources, the review of Linberg et al. (2013) gives support to this selection.

As thousands of compounds and phases exist in the multicomponent system consisting of willow wood, a preliminary selection of the compounds which might form in gasification conditions was required: software limitations, computing and post processing times impose to take into account a maximum of 3,000 compounds. The selection procedure, based on the systematic calculation of predominance diagrams for gaseous compounds, has been described previously (Said et al., 2015). In the specific system of the wood described in Table 1, about 600 gaseous compounds were removed from the SGPS+FactPS databases. Hydrocarbons C<sub>n</sub>H<sub>m</sub> with n>3 (~ 400 compounds) were also removed, since they are not stable at high temperature. In such thermodynamic approach, the behavior of tar is indeed not possible to evaluate since it is governed by kinetic factors. As for the solutions phases, two liquid solutions phases were considered: (i) SALTF, which describes liquid salts solutions (Na, K/F, Cl, CO<sub>3</sub>) with low melting points, and represents fly ashes (ii) SLAGA, which describes liquid silicates solutions (Si, K, Ca // O, S) with high melting points, and represents bottom ashes. As pointed out by Ma et al. (2015) and Kaknics et al. (2015), in the reducing atmosphere conditions of the gasification, most of the sulfur form a stable H<sub>2</sub>S gaseous compound, which leads to the absence of any liquid sulfate solution. To sum up, the final data selection includes 373 gaseous, 247 liquid and 1115 solid species, as well as 2 liquid solution phases.

#### *3.2. Calculation procedure*

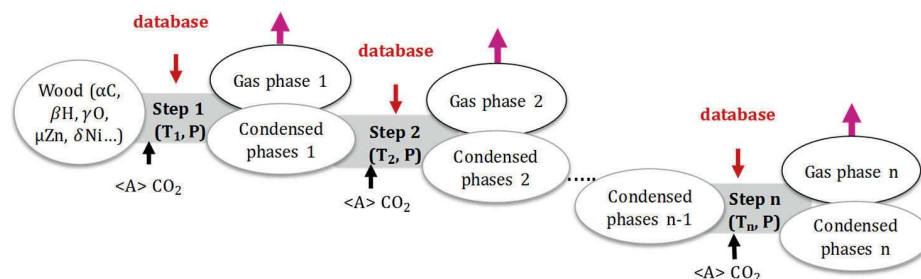
The conditions fixed for the calculations are the initial quantity of wood (1 kg), the pressure (1 bar), the temperature (every 10 °C from 350 to 1000 °C) and the nature of the gasification agent (CO<sub>2</sub>). The total amount of CO<sub>2</sub> added in the system was fixed at 82.5 mol/kg of wood, according to a preliminary calculation detailed in section 4.1.

Two main calculation procedures were explored. The first, which is rather standard (Froment 2013, Kaknics et al. 2015), consists in adding the whole amount of gasifying agent in the system, and calculate the equilibrium at increasing temperatures. This is referred later in the text as the *closed system* option.

The second procedure, whose principle is schematized in Figure 1, consists in adding a fixed amount <A> of gasification agent at each temperature step, and to remove the whole gas phase after each computation. This option, referred as the *open system* calculation, aims at obtaining a realistic description of the atmosphere in which are placed the inorganic elements, in order to provide an accurate description of their physical and chemical form with increasing temperature.

For each computation method, a thorough post processing was carried out, in order to determine the final composition of the system at 950 °C and compare it to the available experimental data. The solid residues were considered to be composed of all the solid phases stable at 950 °C, while, given the configuration of the experimental system, liquid

phases were considered to be trapped in the porous quartz holder and thus were not taken into account. Several calculations were carried out (open/closed systems, with or without SLAGA and SALTF solutions). A summary of the main results, confronted to the experimental data, is presented in the next section.



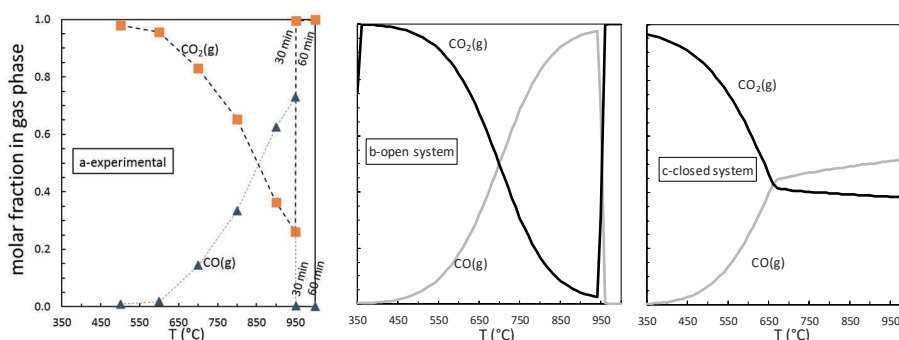
**Figure 1.** Principle of open system equilibrium calculations

## 4. Main results

### 4.1. Behavior of organic compounds

As illustrated in Figure 2-a, the gases produced during the runs were mostly composed of CO and CO<sub>2</sub>. Minor amounts of H<sub>2</sub> and CH<sub>4</sub> were also detected, but that will not be discussed here (see Said et al., 2017). After 30 minutes at 950 °C, the atmosphere is composed of pure CO<sub>2</sub>, indicating that there is no more C to be gasified. In *open system* calculations (Figure 2-b), the <A> value was adjusted so that the end of the gasification (i.e. no solid carbon in the system) occurred at 950 °C. With 66 temperature steps of 10 °C between 350 and 1000 °C, a good fit was obtained for <A> = 1.25 mol/kg wood. The <A> value is rather comparable to the experimental amount of CO<sub>2</sub> (1.78 mol/kg) flown through the reactor during the 2 min necessary to raise the temperature by 10 °C.

With this configuration, the calculated equimolarity between CO<sub>2</sub> and CO in the gas phase is around 700 °C, while it is measured at around 850 °C in the reactor. Even if this is a 150 °C discrepancy, the *open system* calculations provide a much more accurate description of the gaseous phase than the *closed system* (Figure 2-c), for which the CO/CO<sub>2</sub> behavior is very different from measurements at T > 700 °C.



**Figure 2.** Evolution of the gas phase composition during gasification of willow: comparison between measurements in fixed-bed reactor (a) and open (b) and closed (c) systems equilibrium calculations.

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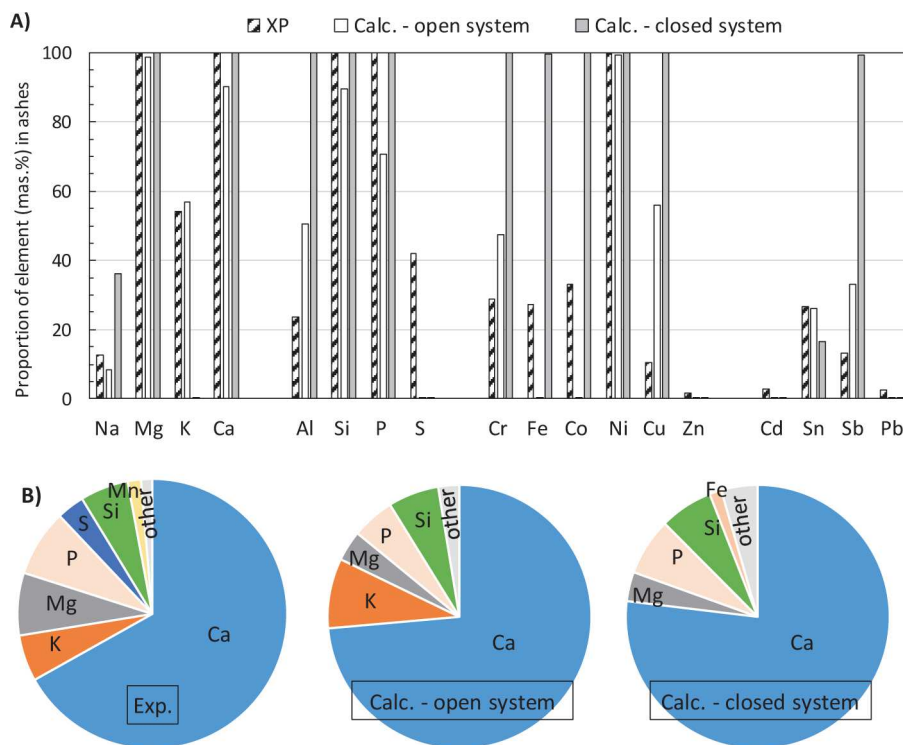
**4.2. Behavior of inorganics**

The mass ratio (in %) of inorganic elements left in the ashes relatively to the initial amount in the wood is presented in Figure 3-A for both experimental results ( $r_i^{meas}$ ) and thermodynamic calculations ( $r_i^{calc}$ ). The heavy metal (Cd, Sn, Sb, Pb) as well as alkaline (Na, Mg, K, Ca) element behavior is remarkably well reproduced by *open system* calculations. There is more discrepancy for some transitions metals (Fe, Co, Cu). Based on the criteria  $q$  calculated according to Equation (1), the *open system* methodology is about twice more accurate than the *closed system* option ( $q=3.8$  and  $8.8$ , respectively).

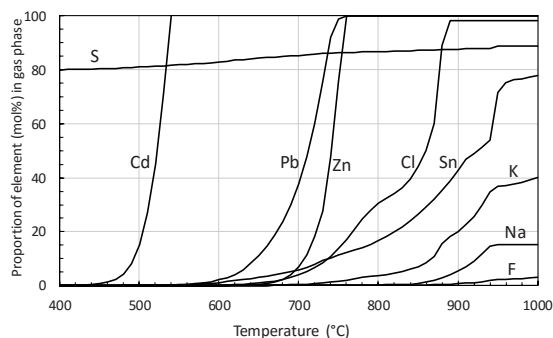
$$q = \frac{1}{23} \left( \sum_{i=1}^{23} (r_i^{calc} - r_i^{meas})^2 \right)^{1/2} \quad (1)$$

Considering the major components of the solid residues (Ca, K, Mg, P, Si), the mass fraction is also very well reproduced by *open system* calculations (Figure 3-B), with the noticeable exception of sulfur. Indeed, calculations indicate that sulfur volatilizes at low temperature as  $H_2S(g)$ , while a small proportion (about 10 %) is contained in a liquid phase. Our initial hypothesis to consider that all liquid phases were not recovered in the final residues might bring some error in the whole procedure.

Based on the rather good representation of the final ashes composition obtained with the *open system* methodology, the proportions of elements in gas phase versus temperature presented in Figure 4 should provide a qualitative picture of the behavior of volatile inorganic elements in the experimental reactor during the gasification reaction.



**Figure 3.** Experimental ashes composition compared to equilibrium calculations. A) Proportion of elements left in the ashes B) Repartition (in mass %) of the main elements in the ashes.



**Figure 4.** Calculated evolution of volatile inorganic elements (*open system*) versus temperature.

## 5. Conclusions

This paper proposes an original methodology for the estimation of the behaviour of biomass inorganic elements during gasification, which is fundamental to estimate the environmental impact of contaminated biomass valorisation processes. Combined with a thorough investigation of thermochemical databases, the calculation procedure is applied to CO<sub>2</sub> gasification of willow wood. The specificity of the methodology consists in (i) considering an open system to simulate a gas flow in the system (ii) determining the amount of gasification agent added at each calculation step with experimental measurements of CO<sub>2</sub> and CO concentration profiles, these data being easy to obtain for any reactor with standard chromatography techniques. The results are in good agreement with the solid residue composition obtained in an experimental fixed-bed reactor.

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