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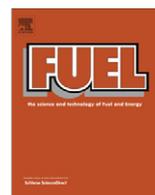
Thermodynamic equilibrium calculations of the volatilization and condensation of inorganics during wood gasification

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HIGHLIGHTS

▶ Steam gasification of wood was studied by a dual approach (thermodynamic, measurement).
▶ Speciation of 26 elements was calculated versus temperature, pressure and reactor technology.
▶ Speciation of the main gas is calculated to be N_2, H_2S, KOH and KCl with trace of HCl.
▶ Cooling calculations predicted K_2CO_3 followed by KCl as the main condensate compounds.
▶ Some agreements with tests exist for N, S, Cl, Al, Ca, Mg, Mn but no conclusion for K, Na, P.

ARTICLE INFO

ABSTRACT

In Europe biomass is a widely available resource and it would be worthwhile to develop advanced, high-efficiency integrated processes. Advanced processes involve using gasification to produce a clean syngas for fuel synthesis, powering motors, turbines and even Solid Oxide Fuel Cells (SOFCs). In comparison to H_2 or natural gas feedstock, one of the challenges is that the syngas is dirty and must be cleaned to remove particles, organic and inorganic minor species, in line with different specifications depending on the various uses.

Predictive calculations are valuable when designing the most suitable cleaning process. The present work outlines a dual approach developed at CEA, based on theoretical assessment and experimental validation, focusing in particular on inorganic species. The biomass is wood, which has a very low inorganic-species content. This content has been measured to serve as input data for thermodynamic equilibrium calculations performed with FactSage software. Our two main goals are to evaluate the release of inorganic species in the syngas, depending on the gasification process, and then to assess the condensation behaviour (temperature and speciation) of the condensable gases, which are responsible for corrosion of refractory lining and metallic structures of the reactors, and fouling of pipes, among others. We have investigated several reactor technologies such as fluidized bed or entrained flow reactor under allothermal or autothermal conditions. We have also calculated the total pressure effect and condensation behaviour when gas is cooled. These calculations are compared with experimental results in the literature and obtained from facilities developed at CEA.

Agreements with calculations were obtained for elemental mass balance measurements of N, S, Cl classified as volatile and Al, Ca, Mg and Mn as condensed. Speciation of gas is calculated to be N_2, H_2S, KOH and KCl with trace of HCl in agreement with explicit measurements for H_2S but not for N_2 (kinetics) and no quantitative conclusions for KOH, KCl and HCl. Cooling calculations predicted K_2CO_3 followed by KCl as the main condensate compounds without experimental comparison available.

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1. Introduction

In Europe it is very important to develop renewable energies in order to decrease greenhouse gas emissions and to increase energy independence. Biomass, widely present in the form of forest and agriculture crops, could be gasified in advanced plants, to produce heat and electricity, or to synthesize biofuels (methanol, DME, Fischer–Tropsch diesels,) or high value molecules.

One main issue is the behaviour of the mineral part of biomass during the high temperature processes, linked to the need to clean synthesis gas, or syngas: in addition to the main gaseous species

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(CO, H_2, CH_4, etc.), some minor ones obtained from minerals become volatile, carrying chlorine, sulphur, alkali and other harmful elements either in the gas phase or in form of condensable species. They may damage or foul pipes and deactivate catalysts. This issue becomes increasingly important for entrant feedstock with a higher inorganic-species content, ranging from wood (generally less than 1 wt% ashes in the dry matter) to waste, or even sludge (up to 50 wt%), through straw (about 10 wt%).

This work focuses on the fate of inorganics during biomass gasification. Biomass contains a very large spectrum of inorganic elements (alkali metals, earth alkali metals, metalloids, transition metals, halogen, etc.) and in very different quantities depending on biomass (wood, agricultural residue, short rotation forestry, sludge or waste). It is important to determine the distribution of these inorganics among gas or condensed phases and their chemical form as they may have a powerful effect on the process, causing corrosion, agglomeration, hot-gas cleaning and catalyst poisoning. The inorganics may also be a source of environmental concerns (air pollution or slag recovery).

The inorganics can be measured experimentally by high temperature in situ experiments, but this is expensive, difficult and time-consuming, given the large variety of biomass feedstock with widely differing input compositions.

The relationship between inorganic input and the composition of the gasification streams (gas, condensed species) can be determined by thermodynamic equilibrium calculations. The thermodynamic calculations give an upper limit of the reaction rate. The higher the temperature and residence time, the more likely it is that thermodynamic equilibrium has been reached. Typically, gasification processes occur at high temperatures (>750 °C to 1500 °C). Such processes allow residence times close to one or a few seconds. Thermodynamic equilibrium can now be calculated using robust off-the-shelf software (FactSage, Gemini2, etc.) [1,2] taking into account several dozen elements and several hundred associated compounds.

This approach has already been used for coal gasification [3–11]. Frandsen et al. [3] published thermodynamic calculations with a stoechiometric compound database of a sub-bituminous coal in combustion and gasification conditions for 18 trace elements (As, B, Be, Cd, Co, Cr, Ga, Ge, Hg, Ni, P, Pb, Sb, Se, Sn, Ti, V and Zn). Helble et al. [4] related experimental results for trace elements during gasification of an Illinois N°6 coal sample in a laboratory-scale drop tube working at 1500 °C to simulate an entrained flow reactor at atmospheric pressure. Eight trace elements were considered (Sb, As, Cr, Pb, Hg, Ni, Se, Zn + Cl, S and N) in the thermodynamic calculations with a simplified stoechiometric compound database. In both publications the calculations did not take account of the main coal inorganics (Al, Ca, Si, K, Na, Mg, Mn); trace elements were taken into account one by one (e.g. CHONS + trace + Cl) excluding possible interaction between elements. Thompson and Argent [8–10] and Argent and Thompson [11] are the only publications describing the equilibrium distribution of major, minor and trace elements (27 elements in all) in coal gasification (Pittsburgh no. 8 and Eggborough). Several solution databases were used in addition to a stoechiometric compounds database in order to represent all inorganics for the condensed phase. Furthermore Thompson and Argent [9,10] is the only author in which condensation of the gas phase from the high to the low temperature part of the reactor is modeled assuming that no equilibrium between gas and solid is reached.

To our knowledge, the existing publications on biomass gasification concern the release of some elements (N, Cl, S, alkali) [12–18]. Mojtahedi et al. [12] and Kilpinen et al. [13] performed thermodynamic calculations of peat gasification with, respectively, a CHONS + NaKCl and CHONS compound database to study Na and

K release, and nitrogen release. Zevenhoven-Onderwater et al. [14] and Ohman et al. [15] carried out thermodynamic calculations for several biomasses under gasification and combustion conditions (Salix, forest residue, Miscanthus) with a solution database containing the major elements CHONS + NaKCl AlCaSiPMgMn (+Fe for [15]) to study ash melting and ash/bed material interactions. Wei et al. [16], Kuramochi et al. [17] and Turn [18] performed thermodynamic calculations with a compound database CHONS + NaKCl AlCaSiPMgMn (+18 traces elements for [17]) of several biomasses (Wood, Danish Straw, sewage sludge) in pyrolysis, gasification and combustion to study the behaviour of Cl, K and Na release. However, Kuramoschi et al. [17] takes into account all the elements but does not present any results concerning trace release.

In conclusion, a thermodynamic approach describing the release behaviour of all inorganic elements including trace and major elements for biomass gasification has apparently not been carried out before. It is presented in this work for woody biomass. Furthermore, cooling and condensation calculations from 1300 °C to room temperature are also presented. Part of these results has already been presented in companion publications for wood [19] and for sludge gasification [20]. In this paper, calculations were carried out taking into account various gasification technologies: Fluidized Bed reactor (FB) and Entrained Flow Reactor (EFR). Autothermal gasification, where part of the initial biomass is burned to supply energy, and allothermal gasification [21], where external energy such as electricity (or methane and H_2) is brought in the reactor, are also considered in the calculations. The temperature is varied from 500 to 1500 °C, and total pressure from one to 80 bar in order to take into account usual working temperature and total pressure values for FB (750–900 °C) and EFR (1200–1500 °C). These calculations were compared with experimental results from the literature and from facilities developed at CEA.

2. Input data and thermodynamical calculation methodology

Thermodynamic equilibrium calculations were performed with FactSage software. The two main objectives were to evaluate, in an initial step, the release of inorganic species in the syngas depending on the gasification process (§3.1), and secondly the condensation behaviour (temperature and speciation) of the condensable species (§3.2).

2.1. Input data

The elementary composition of a typical wood biomass (spruce and pine sawdust including bark) is shown in Table 1 for one kilogram of dry matter sorted in alphabetical order.

Wood is a rather clean biomass containing a very low dry ash content (0.5 wt%). There are 26 inorganics reported in this table which are found naturally in the matrix of wood at different concentrations levels (no detritus picked up). Five of them are the main elements with a concentration exceeding 150 ppm: nitrogen (900 ppm), potassium and calcium (560 ppm), sulphur (200 ppm) and silicon (170 ppm). Chlorine (74 ppm) is among the 10 elements exceeding 10 ppm (Al, Ba, Fe, Mg, Mn, Na, P, Sb, Ti). Of the 11 elements present at concentrations less than 10 ppm six (As, Cd, Cr, Hg, Pb and Se) have less than one ppm.

The working conditions chosen as initial data for the calculations are:

- Entrance biomass: 1 kg ~7 mol. assuming biomass chemical formulae is $C_6H_9O_4$ with molar mass 145 g [22].
- Reactor pressure: 1–10 and 80 bar.
- Reactor temperature: from 500 to 1500 °C.

Table 1
Typical elementary composition of 1 kg of dry wood biomass (coloured cases are major elements).

Element	Mass concentration on dry matter	Input molar amount taken for calculation (1000 g)
C	50.7%	42.25
H	6.47%	64.70
O	42.57%	26.61
Ag	5 ppm	4.6×10^{-5}
Al	26.6 ppm	9.86×10^{-4}
As	1 ppm	1.33×10^{-5}
B	2.6 ppm	2.4×10^{-4}
Ba	14 ppm	1.02×10^{-4}
Ca	570 ppm	0.0142
Cd	0.1 ppm	1×10^{-6}
Cl	73.7 ppm	0.00208
Cr	0.5 ppm	9×10^{-6}
Cu	1.3 ppm	2×10^{-5}
F	3 ppm	1.58×10^{-4}
Fe	36.6 ppm	6.55×10^{-4}
Hg	0.01 ppm	5×10^{-8}
K	560 ppm	0.0143
Mg	120 ppm	0.00494
Mn	88.3 ppm	0.00163
N	900 ppm	0.064
Na	42.3 ppm	0.0018
P	50 ppm	0.00161
Pb	1 ppm	4.83×10^{-6}
S	200 ppm	0.00625
Sb	26 ppm	2.14×10^{-4}
Se	1 ppm	1.27×10^{-5}
Si	170 ppm	0.00605
Ti	25.3 ppm	5.28×10^{-4}
Zn	8.1 ppm	1.24×10^{-4}

Allothermal and autothermal reactions were considered for both reactor technologies (FB and EFR). For the inputs to the equilibrium calculations we needed to know the gasification atmosphere (H_2O/O_2 amounts), which differs slightly with each reactor technology [21]. The aim is to analyse the effect of the syngas composition, associated with various gasification technologies, on the release of inorganic species.

- An allothermal reaction is an ideal reaction where the necessary energy is introduced from the outside. This ideal reaction is expressed as:

$$C_6H_9O_4 + 2H_2O = 6CO + 6.5H_2 \quad \text{ideal biomass gasification} \quad (1a)$$
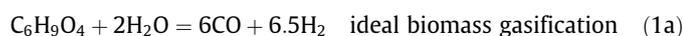
For FB technology, it is well known that this reaction is not at equilibrium because of kinetic limitations due to the lower temperature in comparison to EFR technology [23,24]. Excess steam is thus added for FB to encourage the reaction. It was decided to add almost six moles H_2O instead of two which would have been sufficient, as seen in reaction (Eq. (1a)) (Table 2).

- Input gas content was calculated for autothermal conditions by adding oxygen, to obtain energy from partial combustion of the biomass. The new equations are written as:

$$C_6H_9O_4 + 6.25O_2 = 6CO_2$$
$$+ 4.5H_2O \quad \text{combustion for a part of biomass} \quad (1b)$$

$$C_6H_9O_4 + 2H_2O = 6CO$$
$$+ 6.5H_2 \quad \text{gasification of the rest of biomass} \quad (1c)$$
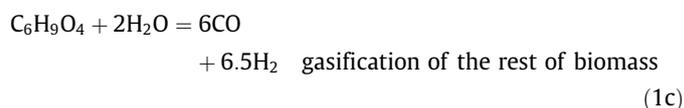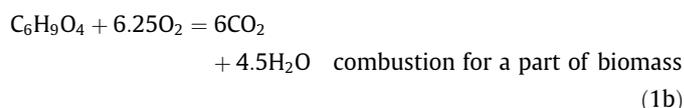
The amount of oxygen is adjusted to obtain zero enthalpy for the entire reaction at 900 °C for FB and 1300 °C for EFR, including exothermal combustion of part of the biomass (reaction [Eq. (1b)]). In the EFR case, no additional steam was necessary as combustion produced enough water, and the oxygen was sufficient to fully convert the biomass into syngas. For FB technology, excess steam was retained.

Table 2 shows the initial composition of reactants and experimental conditions for the various technologies.

2.2. Calculations methodology

Calculations were performed with FactSage V 5.4.1 and the associated databases ELEM (elements), FACT 53 (gases and condensed phase), FTsteel, FTmisc, FToxid, FTsalt (condensed phase). Solution databases were not used in the calculations presented in this paper because of the too numerous elements (29) of the system which leads to exceed the size of the software for compounds. Effect of taking into account melts in the calculations would lead to decrease the partial pressure of some elements in the gas phase by dissolution in the liquid one. As this paper deals only with vapour pressure behaviour, it has been decided to neglect the melt formation and results calculated without melts will give the maximum possible volatility. This maximum volatility is a first set of information that can help prediction of potential processes damages (corrosion, agglomeration or catalyst poisoning) that may occur and environmental concern. No data seems to be available in literature for biomass in a so large range of investigation.

Calculations taking into account melt formation with solution database were already published for biomass fluidised bed at 750–900 °C [14,15] with a reduced number of about 10–15 elements, but they did only discuss about the melting behaviour and not about volatility one (quantity and speciation).

Vapour pressure relative error predicted while using solutions databases are estimated by Thompson and Argent [9] to be around 35%, which is better than the relative error associated with prediction from compounds database (estimated to be between 30% and 100%). In the case of coal, calculations with solution databases [9] were found to be roughly in agreement with compound

Table 2
Working feature for each reactor technology.

	FB		EFR	
	Alloth.	Autoth.	Alloth.	Autoth.
Working temperature (°C)	900	900	1300	1300
Working pressure (bar)	1–10	1–10	1–80	1–80
Steam/dry Biomass (mol/mol)	5.86 or 0.75 g/g	5.86 or 0.75 g/g	2 or 0.28 g/g	0
O_2/dry Biomass (mol/mol)	0	2.65	0	2.6
Chemical reactions involved	$C_6H_9O_4 + 5.86 H_2O$	$C_6H_9O_4 + 5.86 H_2O + 2.65 O_2$ ($\Delta H = 0$ kJ/mol to 900 °C)	$C_6H_9O_4 + 2 H_2O$	$C_6H_9O_4 + 2.6 O_2$ ($\Delta H = 0$ kJ/mol to 1300 °C)
Input gas added to 1 kg dry biomass (in mol)	41 H_2O	41 H_2O + 18.6 O_2	16 H_2O	18.5 O_2

database calculations done by Helble et al. [4] and Frandsen et al. [3] without solutions so without melts.

Even without taking into account melt in the calculations, it was necessary to reduce the number of species involved from more than 2000 to less than 1500 (software limitation). Some compounds non occurring in the considered reactions were taken off for the calculations:

- Gas, liquids and solids C_nH_m with $n > 3$.
- Gas, liquids and solids whose specific heat law description in the database is valid below 700 K (427 °C). Indeed, the temperature range of validity of the specific heat indicates the temperature existence of the specie. In many cases, it is a mathematical breakdown and the same specie is described with a higher temperature range. Cooling calculations results below that temperature will have to be interpreted with care as some condensed phase may have been eliminated from the database or Cp evolution is extrapolated from higher temperature.

3. Results and discussion

Results concerning calculations of the inorganic volatility are presented in §3.1. and those concerning condensation during cool-down in §3.2. These calculations were compared with experimental results from the literature and from facilities developed at CEA in Section 3.3.

3.1. Calculations of the inorganic volatility

Volatilization calculations were carried out to determine the equilibrium state between initial biomass composition (Table 1) and gasification atmosphere for each reactor technology (Table 2) between 500 and 1500 °C, the full temperature range for the considered reactors. Results are presented as calculated at one bar total pressure, in terms of the elemental release fraction (§3.1.1), speciation of the gaseous phase (§3.1.2) and speciation of the condensed phase (§3.1.3). The total pressure effect is analyzed in Section 3.1.4.

3.1.1. Elemental release fraction

The elemental release fraction (the mass or mole of element "i" in the gas phase divided by its initial quantity in biomass) is a simple and easy way to determine the proportion of each element transferred to the gas phase. It thus can be compared with measurements when the elemental composition of the gas is known. The results calculated for the autothermal EFR case (Table 2) are presented in Fig. 1. It is noteworthy that roughly the same results are obtained for allothermal and autothermal FB cases versus temperature due to very similar reducing conditions, as shown by the oxygen partial pressure (Table 3).

Fig. 1 thus shows the calculation results for the allothermal and autothermal FB case, as well as the autothermal EFR case. The working temperature ranges for the FB and EFR cases are shown in this figure.

Regardless of which reactor technology is used – i.e. whatever the temperature range – 15 elements behave in the same way:

- Ten elements (N, S, Cl, Zn, Hg, Cd, Pb, Se, F, Sb) were completely volatilized. Table 4 presents the speciation of these elements calculated at 900 °C for FB technology. Four (Zn, Hg, Cd, Pb) were in their elemental form and the others were mainly in hydride or oxihydride form.
- Five elements (Ca, Si, Al, P, Ti) remained completely in a condensed phase, in the form of oxides. Their speciation is presented in Table 4 at 900 °C and one bar.
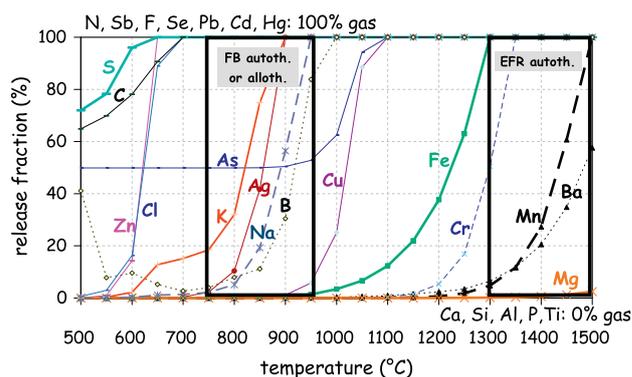

Fig. 1. Release fraction in the gaseous phase versus temperature calculated at 1 bar for EFR autothermal and for FB allothermal and autothermal wood gasification.

Table 3
Oxygen partial pressure calculated at 1000 °C and 1 bar total pressure for each reactor technology.

	FB		EFR	
	Alloth.	Autoth.	Alloth.	Autoth.
$p(O_2)$ (in bar at 1000 °C)	3×10^{-16}	10^{-15}	10^{-19}	8×10^{-16}

As the EFR reactor operates at a higher temperature than its FB counterparts, it was to be expected that more elements would be volatilized in the EFR process (see Fig. 1).

In the FB case six more elements were in a condensed phase: Cu, Fe, Cr, Mn, Ba and Mg. It should be noted that Cu was the only element for which the condensed phase was not an oxide (Cu_3As). Finally, at the FB working temperature, five elements were semi-volatile: As, K, Ag, Na and B.

There are some differences for the allothermal EFR technology represented in Fig. 2 in the 800–1200 temperature range. Sulphur is semi-volatile (50% release fraction) due to the condensation of CaS and MnS species. This effect does not occur in the allothermal and autothermal FB temperature range (Fig. 1). These differences are explained by the more reducing conditions of the EFR allothermal initial mass balance as shown by the oxygen partial pressure calculated at 1000 °C and one bar total pressure (Table 3).

In conclusion, allothermal and autothermal FB inorganic release behaviour is similar, contrary to the allothermal and autothermal EFR processes. Of the five main wood-biomass inorganics, two (N and S) are completely volatile and two others (Ca and Si) are completely non-volatile whatever the reactor technology. The last one, potassium, is semi-volatile for FB and 100% volatile for EFR due to the higher EFR working temperature.

3.1.2. Speciation of the gaseous phase versus temperature

The major (H_2, CO, CO_2, H_2O) and inorganic gaseous species are discussed separately.

3.1.2.1. Major gaseous species. The volume fraction of the major gaseous species calculated at one bar is reported for each reactor technology at working temperature in Table 5.

Allothermal EFR calculations show that if equilibrium is reached at 1300 °C in the reactor, stoichiometric conversion of biomass into CO and H_2 is almost reached depending on the reaction [Eq. (1a)]. However in this case, external energy is needed. It should be noted that at 1300 °C all the H_2O is consumed. In this case the H_2/CO ratio slightly exceeds unity which is favourable for further synthesis, as is the case with the Fischer Tropsch (FT) process, which needs a ratio value of two.

Table 4
Speciation of the elements sorted in alphabetic order for wood gasification calculated at 1 bar for autothermal FB technology at 900 °C (the 2–3 main gaseous species are cited for each element).

| Elements	Autothermal fluidized bed 900 °C	
	Gaseous species	Condensed species
Ag	Ag	
Al		$Ca_3MgAl_4O_{10}$, $BaOAl_2O_3$
As	$AsSb$, AsH_3	Cu_3As
B	KBO_2, H_3BO_3	$Ca_3B_2O_6$
Ba	$Ba(OH)_2$	$BaOAl_2O_3$
Ca	$Ca(OH)_2$	$Ca_3MgSi_2O_8$, $Ca_5HO_{13}P_3$, Ca_2SiO_4, $Ca_2Fe_2O_5$, $Ca_3Ti_2O_7$, $Ca_3MgAl_4O_{10}$, $Ca_3B_2O_6$
Cd	Cd	
Cl	KCl, HCl, K_2Cl_2, $NaCl$	
Cr		$MgO(Cr_2O_3)$
Cu	Cu	Cu_3As
F	HF, KF	
Fe	$Fe(OH)_2$, Fe	$Ca_2Fe_2O_5$
Hg	Hg	
K	KOH, KCl, K	
Mg		$Ca_3MgSi_2O_8$, MgO, $Ca_3MgAl_4O_{10}$, $MgO(Cr_2O_3)$
Mn		MnO
N	N_2, NH_3	
Na	$NaOH$, Na, $NaCl$	Na_4TiO_4
P		$Ca_5HO_{13}P_3$
Pb	Pb, PbS, $PbSe$	
S	H_2S, HS, COS	
Sb	Sb_2, Sb	
Se	H_2Se, $PbSe$	
Si		$Ca_3MgSi_2O_8$, Ca_2SiO_4
Ti		$Ca_3Ti_2O_7$, Na_4TiO_4
Zn	Zn	

Fig. 2. Release fraction versus temperature calculated at 1 bar for allothermal gasification in EFR technology for wood.

Autothermal EFR calculations show that CO_2 and H_2O are present in the equilibrium gas at 1300 °C because some of the biomass has been burned (combustion reaction equation [Eq. (1b)]) to provide energy. No steam was added initially as a gasification agent. In this case the H_2/CO ratio was less than unity and required complementary H_2 for further synthesis as FT.

The same results for the autothermal FB calculations were observed as for EFR, i.e. CO_2 and H_2O occurrence. More H_2O is calculated for FB because excess steam was fed into the FB reactor to counterbalance the lack of equilibrium at the FB working temper-

ature (900 °C). Indeed, the stoichiometric conversion of biomass was obtained for a Steam-to-dry-Biomass ratio (S/B) of 2 mol/mol and calculations for FB were performed with $S/B = 5.86$ (Table 2). We also calculated that no CH_4 (<1000 ppm vol.) was present above roughly 750 °C, which disagrees with the FB literature because of well known kinetic limitations [23,24].

3.1.2.2. Inorganic gaseous species. Fig. 4 shows the results of the main inorganic gaseous species as calculated at one bar for autothermal FB. As it should be possible to measure inorganic species above roughly 1 ppm vol. using conventional methods (micro-GC, FTIR, mass spectrometry, impinger), then the scale of Fig. 3 starts at this value. Minor (<1 ppm vol.) species are reported in Fig. 4. These species should be more difficult to measure explicitly. Only a few differences exist for the alternative reactor technologies (initial mass balance see §2.1), so the differences in the results are only discussed in the text.

The main inorganic species are N_2, KOH and H_2S in the 100 ppm vol. range in the temperature range of an FB reactor (700–900 °C). Notice that there is almost 10 times less KCl than KOH in the working temperature range of both FB ad EFR reactor technologies. This is because there is less Cl than K in wood (K/Cl molar ratio ∼7). These species belong to the five main inorganic elements of wood.

For the temperature range of the autothermal EFR reactor (>1300 °C), metallic K gaseous species appear in the 100 ppm vol. range. N_2 and H_2S are not sensitive to the temperature unlike KCl and KOH (Fig. 3) at low temperatures.

Table 5
Speciation of the major gaseous species calculated at 1 bar at working temperature for wood gasification (900 °C FB and 1300 °C EFR).

| Reactor technology		H_2 (vol.%)	CO (vol.%)	H_2O (vol.%)	CO_2 (vol.%)	CH_4 (vol.%)	H_2/CO
FB (900 °C)	Alloth.	49	29	15	7	<0.01	1.7
	Autoth.	28	18	35	18	<0.01	1.6
EFR (1300 °C)	Alloth.	53	47	<0.01	<0.01	<0.01	1.1
	Autoth.	30	46	17	11	<0.01	0.7
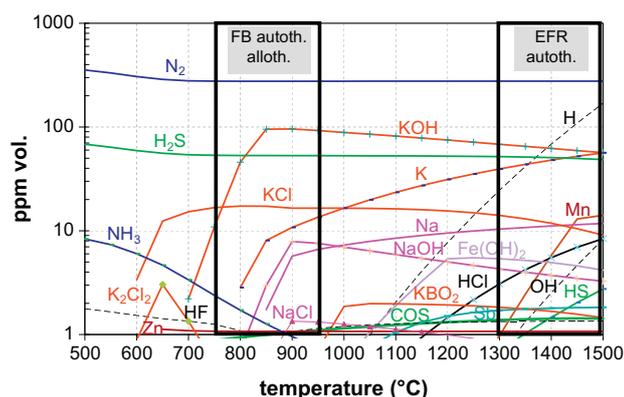
Fig. 3. Speciation of main inorganic gaseous species (>1 ppm vol.) calculated at 1 bar for FB autothermal and allothermal wood gasification (700–900 °C) and autothermal EFR (>1300 °C).

The KCl volume fraction increases with the temperature because of its saturation vapour pressure. Above 650 °C all condensed KCl is vaporized (no condensed KCl left in Fig. 5), after which the related volume concentration remains constant as the temperature increases.

The KOH volume fraction increases with the temperature because of the reaction involving K-carbonates (Fig. 5). Above 850 °C K-carbonates phases are not stable any longer, after which the KOH volume concentration remains constant as the temperature increases.

(a) Elemental species

(b) Hydrides, oxides, … species

Fig. 4. Speciation of minor (<1 ppm vol.) inorganic gaseous species calculated at 1 bar for autothermal and allothermal wood gasification in FB (700–900 °C) and autothermal EFR (>1300 °C) (a) Elemental species and (b) Hydrides, oxides, … species.
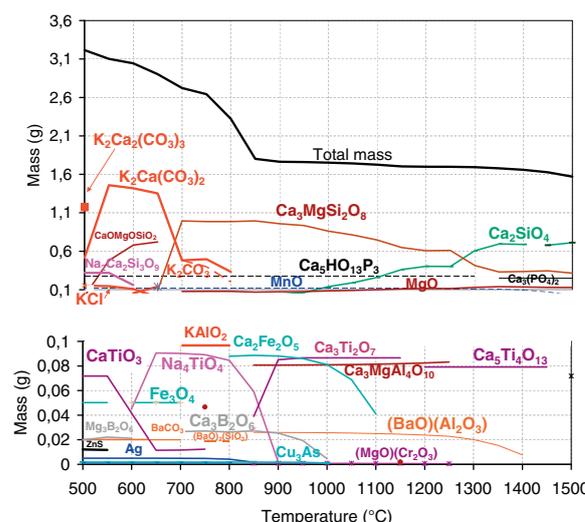

Fig. 5. Speciation of the condensed phase calculated at 1 bar for autothermal FB (in g).

In the 1–10 ppm vol. range, NH_3, Na, NaOH, NaCl, HF, COS and Zn are present in the FB.

Again for the EFR reactor temperature range (>1300 °C) more species appear such as $Fe(OH)_2$, HCl, Mn and Sb.

Minor inorganic species, below the ppm vol. level, are shown in Fig. 4a (elemental) and Fig. 4b (hydrides and oxides).

The concentration of all inorganic gaseous species is summarized for each reactor technology at one bar and working temperature in Table 6.

The only specific difference is that the composition for the EFR allothermal reactor shows the presence of inorganics in metallic forms (K, Mn, Mg) in larger quantities than for the other two, indicating more powerful gasification reducing conditions. This is confirmed by the oxygen partial pressure that is calculated to be lower for allothermal EFR (Table 3).

Table 6
Speciation of the inorganic gaseous species calculated at 1 bar for wood gasification at working temperature (900 °C FB and 1300 °C EFR).

ppm vol.	Auto. and Allo FB 900 °C	Auto. EFR 1300 °C	Allo. EFR 1300 °C
Ag	0.4	0.6	0.5
As	0	0.04	0.04
COS	1	5	2
Cu	0	0.3	0.2
Fe	0	0.7	0.7
H_2S	52	78	66
HCl	0.08	2.5	2
HCN	0	0.01	2
HF	1	2	2
K	6	69	132
KBO_2	0.5	3	2.5
KCl	16	24	21
KCN	0.2	0	0.2
KOH	100	95	2
Mg	0	0.0009	1
Mn	0	3	18
N_2	276	428	351
Na	4	17	19
NaCl	1.6	1.3	0.7
NaCN	0	0	0.03
NaOH	10	6	0.07
NH_3	1	0.1	0.4
Sb	0.2	3	3
Zn	1	2	1

3.1.3. Speciation of the condensed phase versus temperature

The mass values of the condensed phases as calculated at one bar for autothermal FB technology are reported in Fig. 5 versus temperature. Calcium is present in almost all condensed phases which is not surprising as it is, with potassium, the main inorganic in wood after nitrogen (Table 1). Potassium is present in the condensed phase until 900 °C in the form of K-carbonates (K_2CO_3), K-Ca-carbonates ($K_2Ca_2(CO_3)_3$, $K_2Ca(CO_3)_2$) or K-aluminate ($KAlO_2$), in contrast to sodium which is present as Na-Ca-silicates ($Na_2Ca_2Si_3O_9$) or Na-titanate (Na_4TiO_4). The only condensed chlorine species is KCl, which disappears above 700 °C. The same results are observed for the three compositions of the various reactor technologies except for the allothermal EFR composition where CaS and MnS appear in the 800–1200 °C temperature range.

3.1.4. Total pressure effect

The total pressure effect from one to 80 bar is presented for the autothermal FB mass balance only, as the same trends are observed for the other mass balances.

As expected from a thermodynamic point of view, increasing the total pressure favours condensation (or delays volatilization) of most inorganic elements as illustrated in Fig. 6 for Cl, K, Cu and Mn. Iron and barium releases are not affected by total pressure (not shown in Fig. 6).

Two of the 10 elements (N, S, Cl, Zn, Hg, Cd, Pb, Se, F, Sb) which were totally gaseous, become semi-volatile when the total pressure is increased at the FB working temperature (Zn and Cl, in addition to As, K, Ag, Na and B) which means that larger amounts will remain in the bed of the fluidized bed reactor.

For the EFR working temperature, Mn, Cr, P and Mg become less volatile when the total pressure is increased.

It is shown in Fig. 8a for the major gaseous species, that below 1000 °C the hydrogen and CO volume fraction decrease as the total pressure increases. On the contrary, the steam and CO_2 volume fraction increase with total pressure. The same behaviour is observed for CH_4. This is explained by the fact that the reaction is sensitive to the total pressure (Le Chatelier's principle), such as methanation reactions (Eqs. (2a) and (2b)).

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad (2a)$$

$$2CO + 2H_2 \rightarrow CH_4 + CO_2 \qquad (2b)$$

These calculations show that for the SNG (Synthetic Natural Gas) application, increasing the total pressure in the FB working temperature range (750–950 °C) favours CH_4. However these methanation reactions are known to be very slow without a catalyst [25]. Hence FB technologies operate at pressures exceeding 1 bar for technological reasons (smaller reactor size, SNG synthesis requiring high pressure) rather than thermodynamic reasons [25].
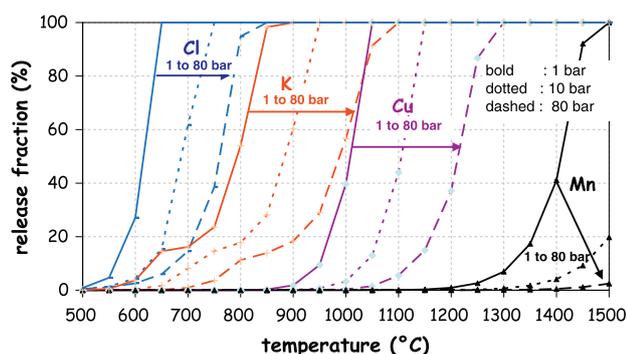
Concerning the main inorganic gaseous species, they are affected by the total pressure as shown in Fig. 7b for NH_3, KOH or KCl.

For NH_3, it is explained by the fact that the main reaction (Eq. (3)) involving NH_3 is sensitive to total pressure (Le Chatelier's principle).

$$2NH_3 \rightarrow N_2 + 3H_2 \qquad (3)$$

For KCl it is explained by condensation which is favoured when the total pressure increases. The saturation vapour pressure is therefore decreased in the FB working temperature range (750–950 °C). Less condensation consequently occurs in the exhaust gas but more potassium remains in the condensed phase in the reactor, perhaps even as a liquid favouring bed agglomeration.

For temperatures exceeding 1100 °C, the major gaseous species (H_2, CO, CO_2 and H_2O) are not affected by an increase in the total pressure as shown in Fig. 7a. This is because the only reaction which occurs is the Water Gas Shift (Eq. (4)] which is not sensitive to total pressure (Le Chatelier principle).

$$CO_2 + H_2 \rightarrow H_2O + CO \qquad (4)$$

The same behaviour for major species was calculated for the EFR autothermal case (Table 2). Only a few total pressure effects are observed for the main inorganic gaseous species above 1100 °C (Fig. 7b). Condensation is favoured when the total pressure is increased for some minor inorganic species as Mn for example (Fig. 6). The saturation vapour pressure was thus decreased in the EFR working temperature range (1300–1500 °C). The consequences are that less species are present in the exhaust gas due to high pressure. EFR technologies usually operate at higher

(a) Major species

(b) Main inorganic species
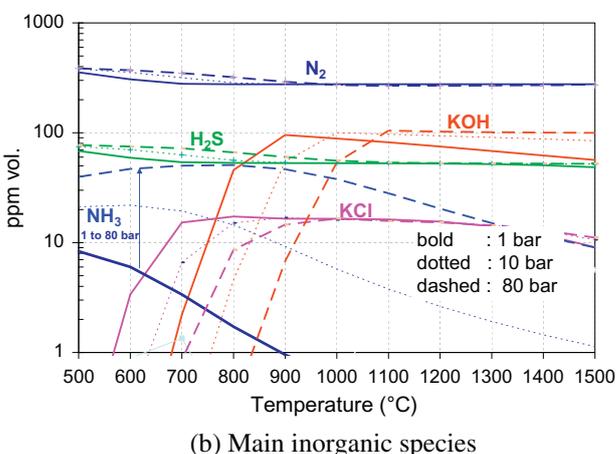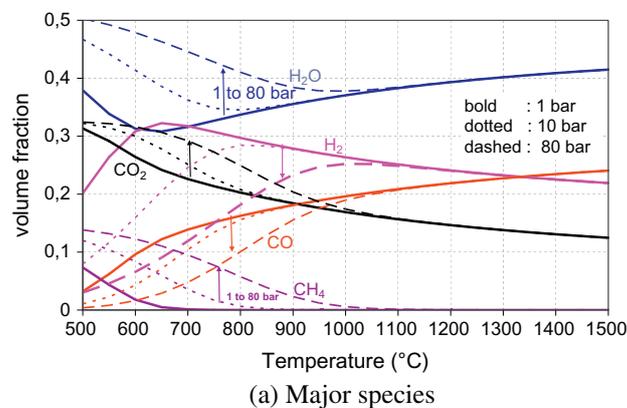
Fig. 7. Temperature and total pressure effects on the main gaseous species calculated for autothermal FB. (a) Major species and (b) main inorganic species.

Fig. 6. Temperature and total pressure effects for Cl, K, Cu and Mn release fraction calculated for autothermal FB.
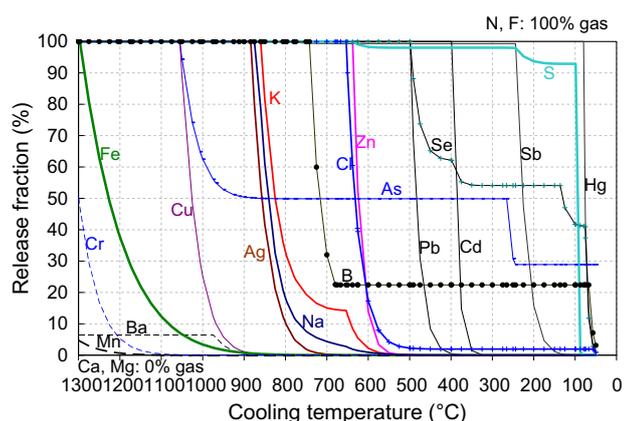
(a) Fraction of element staying in gaseous phase during cooling
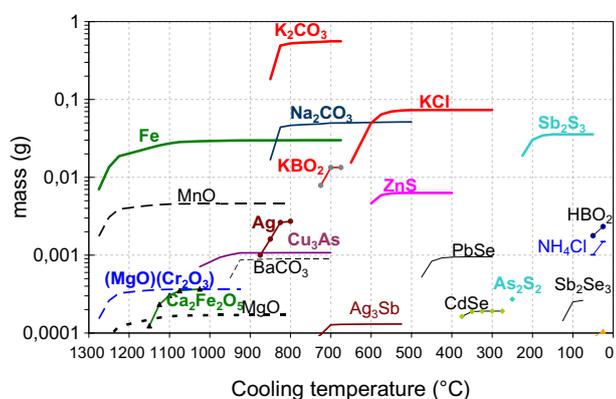
(b) Speciation of condensed phase during cooling

Fig. 8. Cooling calculations from 1300 to 20 °C for wood gasification at 1 bar (autothermal EFR). (a) Fraction of element staying in gaseous phase during cooling and (b) speciation of condensed phase during cooling.

temperatures than their FB counterpart for thermodynamic reasons, because equilibrium is more likely to be reached. Like FB technology, EFR operates at higher than atmospheric pressure mainly for technological reasons (smaller reactor size, FT synthesis needing high pressures).

3.2. Calculations of inorganic condensation

Thermodynamic equilibrium assumes that reactions are reversible when temperature is either increasing or decreasing. Due to the temperature gradient encountered by the gas leaving the reactor, the condensation reactions are not likely to be reversible when temperature is decreasing. Then, condensation (or cooling) calculations were performed using the Gulliver Scheil cooling model. This model is currently used to predict the solid/liquid alloys composition during solidification in metallurgy. It assumes a non-equilibrium solidification path by calculating stepwise a succession of equilibrium states and for each step assumes a complete mixing of solute in the liquid phase (here replaced by the gas phase) and no diffusion in the solid one. Calculations are starting with a representative composition of the gaseous phase at high temperature (1300 °C for EFR for example), this latter being decreased stepwise: if one condensed phase appears, the amount of corresponding elements is removed from subsequent calculations. The initial composition of each step was started with a 100% gaseous phase. The results of these calculations yield:

- The condensation temperature for each species, taken as the temperature level at which the species first appears as a solid or liquid.
- The composition of the solid deposited stepwise, considering that no solid diffusion occurred.

The calculations were performed at decreasing-temperature steps of 25 °C from 1300 °C. The "Sheil cooling gas phase" tool in the FactSage software was used for these calculations.

We investigated the FB and EFR reactor technologies and the effect of total pressure. As no important differences were observed between these calculations, the results are given only for the autothermal EFR reactor at one bar from 1300 °C. Speciation of the elements when condensed, and the condensation temperature calculated under these conditions, are shown in Table 7, which also shows speciation of the gas remaining at 100 °C.

As the starting composition of these calculations is a gaseous phase, it is obvious that elements that are not present in the gas phase at the considered temperature do not appear in Table 7. This applies to Si, P, Ti and Al which are not volatilized at all at 1300 °C: silicate, phosphate, titanate and aluminate species are consequently not found in the condensed phases in the cooling calculations. These species, already present at lower temperatures, will remain, or will be entrained as particulates downstream from the reactors.

For EFR, as Ca and Mg are only slightly volatilized, they play little part in the condensation (less than 1 mg in Fig. 8b), in the form of $MgCr_2O_3$, MgO, $Ca_2Fe_2O_5$. For FB cooling from 900 °C, fewer elements play a limited part in condensation (Cr, Mn, Mg, Ba, Fe).

The results below 427 °C should be treated with care as kinetic limitations are more probable and the database has been simplified (see §2–2). Below 100 °C, the elements N, F, S, Se, As, B, Cl and Hg remain in the gaseous phase to some extent. Table 7 presents the speciation of these elements calculated at 100 °C. N_2 and H_2S are the species present in the largest quantity (>100 ppm vol.), followed by HF, H_3BO_3, HCl, NH_3, H_2Se and AsF_3 in terms of ppm vol. The gaseous species Hg, COS and $Sb(OH)_2$ are rated by ppb vol.

Some of them are soluble in water as (HF, H_3BO_3, HCl, NH_3) and may be trapped if water washing is applied after gasification.

It is convenient to use the elemental fraction remaining in the gas-phase parameter. Fig. 8a presents the cooling results calculated for autothermal EFR from the gaseous phase at 1300 °C and cooled to room temperature. The results of speciation of the condensed phase are quantitatively presented by mass as "output accumulation" in Fig. 8b. There are only a few differences in relation to the other reactor technologies, so only specific results are discussed in the text.

These calculations show that largest deposit is K_2CO_3 followed by KCl, Na_2CO_3 and Fe with one order of magnitude lower. The condensation temperature (Fig. 8b and Table 7) of these species are below their melting points (respectively 901 °C, 771 °C, 858 °C, 1538 °C) which means that they are in solid form. Even if melt is taken into account between the three salts K_2CO_3, KCl and Na_2CO_3 the analysis of their binary phase diagram [1] indicates that the melt would not have been present or in a really few amount. The most corrosive species is KCl and a particular attention must be paid to this species if condensation occurs after gasification. However if water scrubbing is done after gasification, these species will be dissolved in water.

Some other practical information is given by these results. For example to measure potassium it is necessary to sample gas at a reactor location heated at 850 °C in order to prevent condensation in the pipes before the analyser.

3.3. Comparison with experimental data

In order to improve confidence, these calculations were compared with measurements obtained for wood gasification from

Table 7
Condensation temperature for each condensed species calculated at 1 bar for the autothermal EFR reactor.

Elements	Condensed species	Condensation[a] Temperature (°C)	Gaseous species at 100 °C
Ag	Ag	875	
	Ag_3Sb	775	
As	Cu_3As	1050	$AsF_3 \sim 0.1$ ppm vol.
	As_2S_2	250	
B	$Ca_3B_2O_6$	925	$H_3BO_3 \sim 1$ ppm vol.
	KBO_2	725	
	HBO_2,	75	
Ba	$BaCO_3$	950	
Cr	$(MgO)(Cr_2O_3)$	1275	
	$(Na_2O)(Cr_2O_3)$	875	
Ca	CaO	1200	
	$Ca_2Fe_2O_5$	1150	
	$Ca_3B_2O_6$	925	
Cd	CdSe	375	
Cl	KCl	650	$HCl \sim 1$ ppm vol.
	NaCl	475	
	NH_4Cl	50	
Cu	Cu_3As	1050	
F			$HF \sim 3$ ppm vol.
Fe	Fe	1275	
	$Ca_2Fe_2O_5$	1150	
	$FeCr_2O_4$	900	
	FeO	650	
	Fe_3O_4	625	
Hg	HgSe	75	$Hg \sim 10^{-3}$ ppm vol.
K	K_2CO_3	850	
	KBO_2	725	
	KCl	650	
Mg	MgO	1275	
	$(MgO)(Cr_2O_3)$	1275	
Mn	MnO	1275	
N	NH_4Cl	50	$N_2 \sim 666$ ppm vol. $NH_3 \sim 0.6$ ppm vol.
Na	$(Na_2O)(Cr_2O_3)$	875	
	Na_2CO_3	850	
	NaCl	475	
Pb	PbSe	475	
S	ZnS	625	$H_2S \sim 100$ ppm vol. $COS \sim 10^{-3}$ ppm vol.
	As_2S_2	250	
	$H_2SO_4(H_2O)_6$	75	
Sb	Ag_3Sb	775	$Sb(OH)_2 \sim 10^{-3}$ ppm vol.
	Sb_2S_3	225	
Se	PbSe	475	$H_2Se \sim 0.1$ ppm vol.
	CdSe	375	
	Sb_2Se_3	150	
	HgSe	75	
Zn	ZnS	625	

[a] The exact condensation temperature is between the listed temperature and 25° higher.

FB data in the literature and experiments carried out on our allothermal FB facility. The setup is described in [25]. It was impossible to make such comparisons for inorganic measurements of EFR biomass gasification, as no experimental data could be found in the literature. The only experimental results deal with coal gasification in EFR and will not be reported here as the inorganic content of coal is very different from biomass (high N and S and very low Cl).

Experimental difficulties are encountered obtaining reliable inorganic measurements:

– Sampling condensable species by trapping media is difficult to perform because the sample point must be located in high temperature zones to make sure trapping is totally efficient [12].
– Bed agglomeration prevents carrying out a bed mass balance (bed cannot be separated from ash).
– Bed material attrition and entrainment disturb the mass balances.
– Corrosion of the stainless tube of the various pipes adds or traps elements or species.

Cui et al. [26] made specific blank experiments (no biomass in reactor) in an allothermal steam gasification FB and concluded that "more than 50% of Fe, K, Cr, Cu, Mn and Ni come from the gasifier system, i.e. reactor materials, lubricants and residual from the last test"!

Comparison concerns the speciation of the inorganics released in the gas phase (§3.3.1) and elemental analysis (§3.3.2).

3.3.1. Speciation of the inorganics released in the gas phase
Only a few inorganic gaseous species are reported in the literature as being measured explicitly:

– Most of the results concern NH_3, H_2S, HCN and COS [13,25,27–29], using adequate measurement methods (micro-GC-TCD, FTIR, impinger).
– Alkali gaseous species are difficult to sample and to quantify explicitly because they are condensable and the sample point must be located in high temperature zones [12], Hydrogen chloride measurements are usually done by trapping it in water and analyzing the Cl⁻ anion: the difficulty is that other species such

as alkalis contribute to the Cl measurement (KCl soluble in water). Dayton et al. [30] and Porbatzki et al. [31] are the only authors able to identify them explicitly in the gaseous phase using molecular beam mass spectrometry.

3.3.1.1. NH₃. and H₂S. Table 8 summarizes our results for NH_3 and H_2S measurements during steam gasification of wood under FB allothermal conditions for several tests in the 800–900 °C temperature range, with 1 to 7 bar total pressure [25]. The results of calculations simulating the same conditions (Table 2) are also reported in Table 8.

For H_2S an agreement with the thermodynamic equilibrium calculations is observed. This agreement has already been observed in the literature for various types of biomass [28,17]. No visible effect is measured for H_2S when varying temperature and total pressure as calculated (Figs. 3 and 7b).

For NH_3 strong disagreement with thermodynamic equilibrium calculations is observed as already mentioned in the literature for various types of biomass. Kilpinen et al. [13] performed thermodynamic calculations covering broad variations in conditions (temperature, pressure, O_2 content) and compared the results with NH_3 measurements of peat gasified in an air-fluidized bed (no H_2O added except peat humidity). He found that in all cases no more than 10–100 ppm vol. NH_3 could be calculated at atmospheric pressure which is far below the measured values of 1000–5000 ppm vol.. He concluded that this was most likely due to incomplete NH_3 dissociation (reaction [Eq. (3)]) as NH_3 is the most likely natural form of N leaving the biomass.

$$2NH_3 \rightarrow N_2 + 3H_2 \qquad (3)$$

To confirm this assumption, a new thermodynamic calculation was performed, preventing the reaction (Eq. (3)) from occurring by removing the N_2 gaseous species from the database. By doing this, the NH_3 produced from the biomass was forced to remain in the gaseous phase as NH_3. Only a few minor gaseous species, such as HCN or KCN, which amount is less than ppm vol. level, are involved in the chemical reaction with N_2. They are only slightly modified by this new equilibrium calculation.

The result of this new calculation shows a NH_3 value of 725 ppm vol. (dry gas without neutral gas) in better agreement with the measurement in Table 8, suggesting that the NH_3 decomposition reaction (Eq. (3)) does not occur, probably limited by kinetic effects. HCN was measured but the results are too close to the detection limit. Some N_2 may be coming from the reaction (Eq. (3)) but it could not be measured because N_2 is the dilution gas in our FB experiments. Zhou et al. [27] performed gasification experiments with a biomass very rich in nitrogen (leucaena: 2.5%N), without N_2 as a dilution gas: he explicitly measured N_2 and NH_3 in the same order of magnitude, indicating that the reaction (Eq. (3)) is not at equilibrium.

3.3.1.2. HCN and COS. HCN and COS were explicitly observed and measured by FTIR as traces in ppm vol. levels in FB gasification of miscanthus and wood by de Jong [29] in agreement with calculations for COS (Fig. 3) but not for HCN (Fig. 4b).

Table 8
Comparison between equilibrium calculations and measurements in our FB for wood gasification for NH_3 and H_2S [25].

Volume concentration (dry gas without neutral gas)	Measurements [25] 800 °C from 2 to 10 bar	Thermodynamic Calculations 800 °C from 2 to 10 bar
NH_3	550–650 ppm vol.	1–20 ppm vol.
H_2S	20–50 ppm vol.	50–70 ppm vol.

3.3.1.3. HCl and alkali. HCl and alkali gaseous species have not been evidenced explicitly in our facility but data are available in the literature. Portbatzki et al. [31] observed HCl and KCl for miscanthus and straw and KOH for wood, during oxygen gasification in two facilities: a lab scale FB and batch experiments in a tube furnace at 800, 900 and 1000 °C. No quantification could be done.

In conclusion, in the FB temperature and pressure range, the main inorganic species which are calculated to be in the gaseous phase where explicitly observed experimentally (H_2S, COS, NH_3, HCN, KCl, KOH, HCl) giving good confidence in thermodynamic calculations. However for some of them, such as NH_3 and HCN, considerable non-equilibrium effects were observed. Due to experimental difficulties some species as KOH/KCl/HCl were not really quantified.

In the EFR temperature range, no experimental data for biomass gasification is available to give confidence to these calculations.

3.3.2. Elemental analysis

The elemental analysis method is an implicit measurement as the exact chemical form (speciation) of the inorganic is not known. It is possible to obtain the elemental fraction of gas released (element measured in the gas phase over element injected from the feedstock) and the elemental fraction of the condensed phase (element measured in the condensed phase collected in the reactor over element injected from the feedstock). The sum of both quantities should be 100%.

Researchers have measured the elemental fraction released in gas in various ways:

- Some of them [12,32–34,26] and the present work, measured the elemental fraction released in the gas directly from elemental analysis of a sampled gas stream. Gas analysis can be explicit, i.e. by speciation of the element (NH_3, H_2S, etc. by μGC, FTIR, etc.), as presented in the previous paragraph or it can be implicit by elemental analysis of liquid solutions from impingers after gas sampling.
- Another researcher [35] measured the elemental fraction released in the gas indirectly from elemental analysis of solids remaining in the reactor (left in bed or trapped in filters) and assuming that the gas released corresponded to the result of a subtraction from 100%.

No closure mass balance can be done in the second case. In the first one, if the solids remaining in the gasifier (residue in bed or filter candle) are analyzed then a mass balance closure is possible.

In the present work we carried out steam gasification of wood in our FB facility under allothermal conditions for several tests in the 800–900 °C temperature range and 1–7 bar total pressure [25]. Elemental measurements were taken of residues left in the bed, of the deposit collected in the filter candle, and on the basis gas analysis (impinger or micro-GC). Results are presented in Fig. 9 for 10 elements: Al, Ca, Cl, K, Mg, Mn, N, Na, P and S. The quantities of 12 other elements were too small (<50 ppm) in the feedstock wood (Table 1) to yield reliable results. The elements (Cr, Fe, Ni and Si) were also measured but the results are not shown as they were polluted by bed material (Si from SiC) or by stainless steel from the biomass screw feeder (Cr, Fe, Ni). The influence of the temperature and total pressure on these elemental-fraction measurements was investigated, without any significant effect observed regarding their uncertainties.

The experimental results presented in Fig. 9 indicate that Cl, N and S are mostly released in the gas phase. Closure of the total nitrogen and sulphur mass balance is incomplete, with only 35–50% of all the nitrogen and sulphur being found in the gas, in the form of NH_3 or H_2S respectively. About 10–20% is found in the residue left in the bed of the gasifier. On the contrary, the chlorine
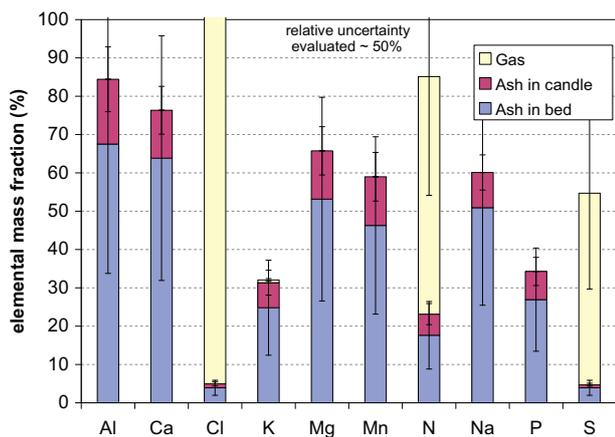
Fig. 9. Elemental mass balance of wood gasification in FB at CEA Grenoble in several test (800–900 °C and 1–7 bar) [25].

total mass balance is higher than 100%. However, these elemental-fraction measurements have a high relative error, estimated to be 50%. Indeed, this error must make allowance for the uncertainty of many measurements (low Cl, N or S input in wood, NH_3 or H_2S measurement in gas, the Cl^- anion measurement in water, mass of collected residues after test, mass of gasified biomass, total volume of gas gasified during the test). According to the results of the thermodynamic calculations (Fig. 1), these three elements are entirely in the gas phase in the FB temperature and pressure range. Therefore, allowing for experimental uncertainties, we may consider that we have achieved agreement with the experiments for the elemental release fraction in the gaseous phase even if NH_3 is not the calculated nitrogen species released in the gaseous phase.

Turn [33] measured chlorine and found that it was completely absent from the bed with some found in the filter candle and the major part in the gas. The amount of chlorine in the gas phase was higher than the total alkali content in the gas phase suggesting that chlorine species other than alkali were present (e.g. HCl). This agrees with our measurements (Fig. 9).

Fig. 9 shows that Al, Ca, Mg and Mn elements are mainly measured in the condensed phase in the bed or as particulates entrained in the stream and stopped by the filter candle. These elements are not present in the gas extracted from the main stream and sampled with impingers. The total mass balance is quite high (>50%) for these elements. Closure of these mass balances is considered to have been achieved, taking into account all uncertainties. According to the results of the thermodynamic calculations (Fig. 1), these elements are entirely in the condensed phase in the FB temperature and pressure range, in agreement with the measurements (no temperature or total pressure effect observed experimentally). These experimental results do not agree with Jiang [35] who found that Ca and Mg were partially released (12–16%) in the gas phase during char gasification with steam of maize stalk, rice husk and cotton stalk in a quartz fixed-bed reactor at 900 °C. This discrepancy comes from the indirect method used by these authors to measure elemental gas releases. Indeed, elemental analysis of solids remaining in the reactor was carried out and the amount of gas released was obtained by assuming subtraction from 100%.

Just as for previous elements, K, Na and P are only measured as residues left in the bed material and collected in the filter candle and are not measured in the gas (Fig. 9). The difference is that the K, Na and P total mass balances are really very low (<50%), except Na (60%). Mojtahedi et al. [12], Turn [33], Salo [32] and Liao [34] performed alkali elemental measurements during gasification, in the 800–850 °C temperature range and 1–10 bar total pressure

range, of several biomasses (peat, wood, alfafa, bagasse, banagrass, etc.). Total mass balance closure is given for Mojtahedi et al. [12] and Turn [33] and is close to 100%, i.e., much better than ours. The poor mass balance closure for K and Na in our work can be explained by a too low sampling temperature for gas leaving the reactor (300 °C) unlike [12,33,32] for whom temperature sampling is much higher (750–800 °C). Indeed, 300 °C is well below the condensation temperature calculated for K_2CO_3, Na_2CO_3, KCl, NaCl and KBO_2 (Fig. 8b and Table 7). We assume that we condensed alkali between the filter candle and gas sampling in our setup, which would explain our poor mass balance closure. Mojtahedi et al. [12] and Turn [18] compare the measurements of alkali in the gas phase (elemental analysis) with their own thermodynamic calculations and found that the alkali values measured are always lower than the calculated values. Furthermore, neither the total pressure nor the temperature effect was observed experimentally by these authors and by our experiments, contrary to the thermodynamic calculations in the FB (T, P) range.

However these authors did not try to establish the speciation of the gaseous potassium forms involved (KCl, KOH) or the speciation of the condensed form on the filter candle and cyclone (K, KCl, K_2CO_3). In these publications it is not clear whether the alkali collected in the filter candle or cyclone are condensed from the gas phase as aerosols or are transported from the bed as particulates. Turn [18] explained the low alkali content in the gaseous phase by assuming interaction between biomass ashes and bed material (alumino-silicate) using thermodynamic calculations to fit experimental results.

In conclusion, thermodynamic calculations cannot be validated experimentally for alkali elements K and Na because of the difficulty of correctly sampling condensable species and because of the lack of understanding of and detail on published results.

Unlike alkalis, phosphorus is involatile (Fig. 1), hence the discrepancy between observation and prediction cannot be associated with gas sampling. P should be found only in residues left in the bed or collected in the filter candle as for Al, Ca, Mg, Mn elements. One reason could be the P concentration (50 ppm), which is too low to provide reliable results.

In this publication no experimental results are given for elements in too low quantity (<50 ppm), such as heavy metals in the feedstock wood (Table 1) because no reliable results were obtained. Some data exists in the literature but they do not concern wood feedstock (bagasse, banagrass, Leucenea [33,26]) or our gasification conditions (air gasification circulating FB [34]). Hence comparison with our calculations is difficult.

In conclusion, in the FB temperature and pressure range, the main inorganic elements which are calculated and measured as being fully in the gaseous phase are N, S, Cl; the elements not in the gaseous phase are Ca, Mg, Mn, resulting in good confidence for the corresponding thermodynamic calculations. However for some other elements (K, Na and P) it is not possible to give clear conclusions concerning agreement with the calculations due to experimental difficulties sampling them or because of the limited amount, resulting in unreliable experimental results.

In the EFR temperature range, no experimental data for biomass gasification is available to corroborate the calculations.

4. Conclusions

Equilibrium calculations using a compound thermodynamic database (Factsage compound database) were carried out to simulate biomass gasification for several reactor technologies including Fluidized Bed (FB) and Entrained Flow Reactor (EFR). Total pressure and temperature effects were investigated as well as cooling calculation effects to determine condensation temperatures and species.

This work clarifies the behaviour of some inorganics including traces and major elements for wood, a relatively clean biomass (<0.5 wt% dry ash) for FB and EFR. This work also shows that thermodynamic equilibrium can be a useful tool for predicting the behaviour (volatility, condensation) of very complex chemical systems containing numerous chemical elements. Calculations are also a useful tool for designing experimental set-ups such as sampling for gas measurements (extraction temperature), or cleaning devices (candle filter temperature, material interactions, etc.).

Of the 26 elements measured in wood only nine have concentrations higher than 50 ppm (N, Ca, K, S, Si, Mg, Mn, Cl and P)

For all the reactor technologies:

- Three elements are completely released in the gas phase (N, S, Cl) as N_2, NH_3, H_2S, COS, KCl. HCl is calculated to appear only for EFR technology, i.e. at elevated temperatures.
- Five of them are entirely in the condensed phase (Ca, Si, P, Mg, Mn) in the form of oxides, except Mn and Mg which are semi-volatiles for the EFR technology, as Mn(g) and $Mg(OH)_2$(g).
- Potassium is the only major element to be semi-volatile for FB technology mainly in the gaseous form of KOH followed by KCl. Condensed phases are K-carbonates, K-Ca carbonates or KCl.

Only a few differences were found between reactor technologies for inorganics behaviour: more elements in the gas phase for EFR and more reducing conditions for allothermal EFR technology giving more elemental gaseous species. The main differences are for major organic gaseous species (CO, CO_2, H_2, H_2O), where the H_2/CO ratio is higher for autothermal FB (1.5) due to the water–gas shift reaction, and lower for autothermal EFR (0.7).

As expected from a thermodynamic point of view, increasing total pressure favours condensation and thus decreases the release fraction of condensable species such as KCl. Species involved in chemical reactions sensitive to pressure will be affected, such as CH_4 in the methanation reaction or ammonia in its thermal decomposition reaction.

Cooling calculations show that the major condensed phase is K_2CO_3 followed by KCl and Na_2CO_3. The condensation temperature is very high for alkaline species (850 °C). The first practical consequence is that to measure alkali correctly, gas must be sampled at high temperature. The second consequence is that for high temperature applications, potassium-carbonate deposits will be less corrosive than potassium chlorides.

We were able to cross-check some of the calculations in the FB temperature range against our measurements or the results in the literature. However, no EFR experimental data could be find. Comparison with FB experimental data from the literature is sometimes difficult because it refers to other forms of biomass than wood.

Obviously the results for inorganics in larger quantities are more reliable (N, S, Ca and Cl). Although it is well known that some reactions involving major organic gases, such as H_2, CO, CO_2 and CH_4, do not reach equilibrium in the FB temperature range [23,24], it has been found that, for some inorganics, an agreement with thermodynamic calculation is observed as with H_2S [17] but not for NH_3 [13] due to incomplete NH_3 dissociation. Calculation with the N_2 gaseous species removed from the database allows better agreement. HCN and COS are also explicitly observed [29] KOH, KCl and HCl are hardly observed explicitly experimentally in the gas phase for wood [31] and clear agreement with calculations is difficult to state: is KOH really the main K gaseous species for wood gasification in the FB temperature range?

In the elemental measurements a good agreement is found with the calculation for N, S, Cl, Al, Ca, Mg and Mn. No conclusion can be reached for K, Na and P.

To go further in the understanding of inorganic behaviours and check the limits of confidence in thermodynamic calculations, explicit measurement of gaseous species should be carried out in the future particularly for alkali and chloride species. Indeed, elemental analysis provides incomplete information, for example for N which is fully released as N_2 in the calculation but almost entirely released as NH_3 in the measurements. The consequences may be important as for example N_2 will not be oxidized to NO_x in a further combustion process, unlike NH_3. In the same way, it is important to determine whether potassium is mainly released as chloride (KCl) or hydroxide (KOH) because it will deposit differently (KCl or K_2CO_3) and corrosion problems will not be the same.

Another field of investigation could be to check experimentally by X ray diffraction the speciation of the condensed phase in equilibrium with gas. Also, thermodynamic calculations will be performed with a solution database particularly in the EFR temperature range where liquid is expected to be present in large amount.

This approach, coupling calculations and measurements, will be applied to other kind of biomass.

Acknowledgments

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