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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.

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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.

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.