ASH FORMATION DURING PILOT-SCALE TRIALS OF PRESSURISED ENTRAINED-FLOW GASIFICATION OF WOODY BIOMASS

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ABSTRACT

Deposits, ash samples and residues from pressurised entrained-flow gasification (PEFG) of stem wood, bark and rejected pulpwood have been characterised with SEM-EDS during trials in an O\textsubscript{2}-blown pilot-scale reactor. Global thermochemical equilibrium calculations based on the conditions inside the hot reactor were carried out to investigate the phase distribution of potassium as both a function of temperature and Si reactivity. Substantial deposit formations on the reactor probe were only evident in the trials with the woody fuels containing a higher ash content; i.e., experiments with pulpwood and bark. Of these, the deposits formed during gasification of the pulpwood fuel, likely to have been relatively highly contaminated, showed more hard and sintered material. The deposits/slag formed contained typical sand particles (e.g. quartz and feldspars) embedded in a silicate rich melt. The melt in the slag is dominated by silicon 40-55 mol\%, aluminium \textasciitilde 15 mol\% and calcium 10-20 mol\%, with a further \textasciitilde 10 mol\% consisting of alkali metals sodium and potassium. The preliminary results suggest that fuel contaminants (e.g., quartz and feldspars) may play a significant role in the slag formation process in entrained flow gasification of woody biomass fuels and that a significant share of the potassium is leaving the hot reactor as gaseous alkali species.

\textbf{Keywords:} ash formation, pressurised entrained-flow gasification, woody biomass slag
1 INTRODUCTION

Forest-based biomass has the potential to become a significant renewable energy resource for the production of power and biofuels via gasification [1]. The successful industrial production of high quality syngas via pressurised entrained-flow gasification (PEFG) of coal has motivated interest to apply this process to woody biomass fuels [2, 3]. Important attributes of coal that render its suitability for PEFG are the high ash contents and well-characterised ash behaviours. The high and evenly distributed temperatures in coal-fired PEFG reactors facilitate the formation of ash slag that flows steadily down the side of the reactor to insulate and protect ceramic linings or cooling screens against harsh operating conditions. However, significant differences in quantity, composition and behaviour exist between coal ashes and woody biomass ashes. This implies that knowledge regarding ash transformation processes is a significant aspect in adapting woody biomass fuels for PEFG. Ash contents in woody biomass are generally lower in quantity while the mode-of-occurrence of ash forming elements exhibit higher reactivity and volatility compared to coal. Experiments in bench-scale PEFG reactors and thermodynamic equilibrium modelling have shown that wood ashes are not prone to significant slag formation [4]. Empirical viscosity models developed for coal slags are also not applicable to the small amounts of woody biomass ash melts that are formed, which can contain high levels of alkali and alkaline metals. The composition of slags and other deposits within the reactor need detailed characterisation for appropriate extraction measures, as well as to assess possible chemical interactions with the reactor containment material. Moreover, potential problems due to ash forming processes are not restricted to inside the reactor. Crude syngas can carry ash particles that cause undesirable effects downstream; e.g., corrosion of heat recovery systems; contamination of syngas cleaning sorbents; poisoning of biofuel production catalysts [5, 6]. There is also a need to evaluate the suitability of the ash for recirculation back to the environment, since much of the essential nutrients are contained in forest residues. Therefore, essential knowledge regarding ash transformations during PEFG of woody biomass is necessary to formulate countermeasures against problems throughout the overall syngas production process. This paper focuses upon the slag formed in a pilot-scale PEFG reactor firing woody biomass. We present some preliminary results regarding the composition of ash slag and residues that were sampled. Of particular interest is the fractionation of potassium due to its role in the slag formation process [7], and this is discussed based on the current preliminary findings. Further analysis results will lead to elucidation of some of the ash transformation reactions involving the major ash-forming elements.

2 MATERIALS AND METHODS

2.1 Fuels

Three woody biomass fuels were used for the experiments: pine stem wood (Wood); soft wood bark (Bark) and; rejected pulpwod from pine and spruce that consisted of both stem wood and bark (Pulpwood). Table 1 shows the composition of the fuels after milling; i.e., in the same form as that fed into the reactor. The Si, Al and Na levels in the bark and pulpwood are significantly higher than that of pure woody biomass, which suggests the inclusion of typical sand-based contaminants; e.g., quartz and feldspars.
Table 1. Fuels: major ash-forming elements (top) and partial ultimate analysis (bottom)

<table>
<thead>
<tr>
<th>mg/kg dry fuel</th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Cl</th>
<th>K</th>
<th>Ca</th>
<th>Mn</th>
<th>Fe</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood</td>
<td>19.7</td>
<td>204.4</td>
<td>41.0</td>
<td>140.5</td>
<td>45.8</td>
<td>55.1</td>
<td>79.0</td>
<td>390.6</td>
<td>771.9</td>
<td>109.6</td>
<td>61.2</td>
<td>11.1</td>
</tr>
<tr>
<td>Bark</td>
<td>431.4</td>
<td>790.0</td>
<td>1106.1</td>
<td>4807.6</td>
<td>460.4</td>
<td>330.0</td>
<td>119.0</td>
<td>2033.9</td>
<td>8719.2</td>
<td>537.9</td>
<td>709.6</td>
<td>96.8</td>
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<tr>
<td>Pulpwood</td>
<td>600.5</td>
<td>678.4</td>
<td>1412.3</td>
<td>6027.6</td>
<td>408.7</td>
<td>257.5</td>
<td>128.0</td>
<td>1880.3</td>
<td>6089.2</td>
<td>402.7</td>
<td>694.9</td>
<td>121.0</td>
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<table>
<thead>
<tr>
<th>% dry fuel</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>O</th>
<th>Ash at 550°C</th>
<th>H2O (% fuel)</th>
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<tbody>
<tr>
<td>Wood</td>
<td>50.9</td>
<td>6.3</td>
<td>0.1</td>
<td>42.4</td>
<td>0.4</td>
<td>4.6</td>
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<tr>
<td>Bark</td>
<td>52.2</td>
<td>5.6</td>
<td>0.41</td>
<td>37.5</td>
<td>4.3</td>
<td>7.6</td>
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<tr>
<td>Pulpwood</td>
<td>52.6</td>
<td>6.4</td>
<td>0.38</td>
<td>38.3</td>
<td>3.8</td>
<td>3.8</td>
</tr>
</tbody>
</table>

2.2 Experimental facility, operating conditions and procedures

Ash deposits/slags and particle samples were taken from PEFG trials of each fuel in a pilot-scale reactor (ETC Piteå, Sweden). The reactor consists of a cylindrical pressure vessel lined internally with mullite-based refractory bricks (Figure 1). Milled fuel carried with N2 was fed from a single top-fired central burner with O2 as the oxidant. One trial was fired with wood using CO2 as the fuel carrier. The reactor was maintained at approximately 2 bar(a) with a fuel input of 40 kg/h (~200 kWth) for each trial. The overall O2 concentration was approximately 70% and the O2 rate supplied for each trial corresponded to a stoichiometric O2-to-fuel ratio (λ) of 0.45. The gasification process was solely driven by the heat of oxidative reactions inside the reactor. Crude syngases were quenched with water sprays before passing through a bubbling quench. Each trial was 5-6 hours in duration, with an additional 4-day long trial firing wood.

Figure 1. Simplified schematic of PEBG reactor with ash/residue sampling locations: 1. Slag/deposit probe; 2. Quench bottom residue; 3. Sedimentation tank residue; 4. Particle sampling with LPI; 5. Outflowing quench effluent
Ash or residual materials were collected for chemical characterisation for inorganic elemental composition at five locations (Figure 1). A non-cooled probe with a 6 cm x 6 cm horizontal platform tip was inserted from the side of the reactor (1). It was cast from the same refractory as the reactor lining and was inserted with only the tip protruding into the reactor. The horizontal platform was set perpendicular to the reactor wall, such that both gas flow ash deposits and flowing slags upon the wall could be collected. The probe was installed before each trial and retrieved afterwards. Samples of residues accumulated in the quench base (2) and sedimentation tank (3) were also collected. Because the latter contained material that was both floating and non-floating material, the tank was stirred vigorously prior to sampling to ensure that both fractions were collected. During steady operation, entrained particulate matter in the crude syngas were sampled with a LPI (4), while outflowing quench effluents (5) were also sampled (2 per trial). The effluent was filtered through 0.45 μm Whatman filter papers before analysis. The crude syngas composition was recorded via a μGC analyser. Thermocouples were placed inside the reactor at top, middle and bottom (same level as the probe) locations, with their measurement tips flush with the wall.

2.3 Chemical characterisation of slag, ash and water samples

Slag/deposits from the reactor probe tips and distinct/separable melt fragments found in the quench residue were mounted in epoxy and polished to characterise their cross-sections by spot and area SEM-EDS analyses. The probe tips from 5-hour trials of stem pine wood had insufficient thicknesses of deposits for cross-sectional examination; hence, their surfaces were analysed instead. Residues from the quench and sedimentation tank were analysed for inorganic elemental compositions with ICP-AES/-SFMS. Cl was not quantified for the bulk residues taken from the quench and sedimentation tank because it was assumed that Cl is in highly soluble form both in the fuel and as products after fuel conversion [8]. One quench sample that was analysed showed a Cl level below the detection limit of 0.1 wt% dry matter. The filtered water samples were analysed with ICP-AES/-SFMS/-QMS, and ion chromatography. The composition of the inlet water to the water sprays was subtracted from the trial samples in order to account for the substances originating from the water supply.

2.4 Thermodynamic equilibrium calculations

The global thermodynamic equilibrium phase compositions for each fuel at conditions inside the reactor were obtained with the Equilib module of FactSage 6.1 (Gibbs energy minimisation) [9, 10]. Relevant thermodynamic databases containing pure stoichiometric phases as well as solid/liquid salt/oxide solutions were included in the calculations (Table 2). Emphasis was placed upon observing the relationship between K and Si as they have an important role in slag formation from combustion studies [7, 11]. In a first set of calculations, the phase distribution of K with each respective fuel composition (Table 1) was observed as a function of temperature (800-2000°C) at conditions inside the reactor (2 bar, λ=0.45). The results from these calculations shall indicate the possible stable phases of K inside the reactor, allowing for variation in temperature. In a second set of calculations, the distribution of K in slag phase was observed as a function of Si (Si varied from zero to a level > fuel Si) to reveal the phase distribution of K in relation to
the amount of reactive Si. This was carried out because a significant share of the Si in the wood fuels seems to be found in contaminants; e.g., quartz and feldspars, which have less reactivity than Si inherent to the fuel [12, 13]. The pressure and composition of other elements were unchanged from the first calculation set; the temperature range was 1000–1500°C (100°C increments) based on near-wall measurements in the reactor, which could be close to the slag temperature. Furthermore, previous results in suspension-fired biomass experiments have shown that reactions involving condensed phases are kinetically-limited compared to reactions between gaseous ash compounds [14]. Because gas-solid reactions may dominate over solid-solid reactions during suspension firing of particles, it was worthwhile to observe the differences in fractionation of K in the scenario where Si reactions with K—a readily volatilised element with relatively high contents in woody biomass—is dominant over Si reactions with less volatile elements and those that are low in content. Hence, a third set of calculations was carried out, with identical conditions to the second set except for the omission of the elements Mg, Al, Si, P, Ca, Mn, Fe and Zn.

Table 2. Databases used in calculations (in order of precedence for common compounds)

<table>
<thead>
<tr>
<th>Database</th>
<th>Full name</th>
</tr>
</thead>
<tbody>
<tr>
<td>FToxid</td>
<td>SLAGA (oxide melt: Na₂O, MgO, Al₂O₃, SiO₂, K₂O, CaO, MnO, FeO, Fe₂O₃, ZnO, &lt; 10% S)</td>
</tr>
<tr>
<td>FTpulp</td>
<td>MELTA (Na⁺, K⁺ // CO₃²⁻, Cl⁻, OH⁻, S²⁻, SO₄²⁻ salt melt)</td>
</tr>
<tr>
<td></td>
<td>HEXA (Na⁺, K⁺ // CO₃²⁻, S²⁻, SO₄²⁻ solid solution)</td>
</tr>
<tr>
<td></td>
<td>ACI (Na⁺, K⁺ // Cl⁻, OH⁻ solid solution)</td>
</tr>
<tr>
<td>FTsalt</td>
<td>LCSO (K⁺, Ca²⁺ // CO₃²⁻, SO₄²⁻ melt)</td>
</tr>
<tr>
<td></td>
<td>SCSCO (K⁺, Ca²⁺ // CO₃²⁻, SO₄²⁻ solid solution)</td>
</tr>
<tr>
<td>FACT53</td>
<td>Pure stoichiometric gas, liquid, solid phases</td>
</tr>
</tbody>
</table>

3 RESULTS

3.1 Syngas composition and temperature measurements

During steady operation of the PEFG reactor, the composition of the syngases were approximately 20 wt% H₂, 40 wt% CO, 15 wt% CO₂ and 2 wt% C1/C2 on a dry gas basis (similar compositions were obtained for both CO₂ and N₂ carrier). Temperatures in the reactor near the refractory wall were between 1050-1250°C, with temperatures highest at the top and around 100°C cooler at the bottom. Water sprays at the outlet of the reactor fed the bubbling quench, which cooled the product gases to below 70°C upon leaving the reactor. There were some interruptions during the trials, mainly due to fuel feeding issues. After each trial, N₂ was purged through the reactor until it was cool enough to retrieve the deposit probe.

3.2 Thermochemical equilibrium calculations

The results of the first set of calculations (phase distribution of K as a function of temperature) show that for all fuels above 1000°C, the global equilibrium fractionation of K is either in a silicate-rich slag (K₂O(SLAGA#1,2)) or gas phase (K(g), KCl(g), KOH(g)). The stability of K in the melt drops decreases as the temperature rises above 800°C, 1200°C
and 1400°C for wood, bark and pulpwood, respectively. In terms of solid phases, K can be stable as carbonates (K$_2$CO$_3$, K$_x$Ca$_y$(CO$_3$)$_z$) up to 900°C for wood, and ~10 mol% as KAlSi$_2$O$_6$ (leucite) up to 1000°C for pulpwood. The composition of bark does not show any stable solid phases of K in the temperature range (700-2000°C). The results of the second set of calculations (phase distribution of K as a function of Si reactivity) are plotted as Figure 2 to Figure 4 for wood, bark and pulpwood, respectively. Each shows the distribution of at least 99.5 mol% of K in each fuel. The top axes indicates the fraction of reactive Si (i.e., Si amount input into calculation) in relation to the total Si content in each fuel. The bottom axes show the non-dimensionalised ratio Si/(Si + 2K), which is essentially the fraction of reactive Si in relation to K and was chosen for convenience in presenting the results and comparing between the fuels.

Figure 2. Wood: K distribution at 1200°C/2 bar as a function of Si reactivity

Figure 3. Bark: K distribution at 1200°C/2 bar as a function of Si reactivity
The results show that reactivity of Si is the dominating factor in the fractionation of K into condensed (molten) phases. The fuels only show sustained increasing stability of K in slag phase as the level of Si increases such that Si/(Si+2K) $\geq 0.3$-$0.4$. The fractions of fuel Si required for K stabilisation in the melt shows that wood is not prone to such behaviour, whereas partial reactivity will produce a K-containing melt for bark and pulpwood. The propensity to induce K into the melt for a particular fraction of Si reactivity is highest for the latter. The stability of gaseous K species also increases with temperature, such that fractionation of K into the melt decreases for all fuels, though trends remain similar to the figures presented for 1200°C; i.e., increase of K in slag as Si increases, with pulpwood having the highest proportion of K in the melt for a given fraction of reactive Si. Conversely, the fraction of K in slag increases as temperature is lowered.

The results from the third set of calculations (phase distribution of K as a function of Si reactivity in the absence of Al, Si, P, S, Cl, Ca, Mn, Fe, Zn) show that the proportion of K in the slag increases almost linearly with Si/(Si+2K) until the ratio of reactive Si : total fuel Si is at unity. At unity, all fuel Si is considered reactive and in this scenario where Si is predominantly limited to interaction with K (and Na), the thermodynamically stable fractions at 1200°C of K in the slag phase for wood, bark and pulpwood are 0.31, 0.95 and 0.95, respectively. It is expected that in practice, Si shall react with solid species; e.g., Ca, to an extent, especially if both Ca and Si originate from the fuel. Hence, the true composition prevailing in the reactor could be represented by a scenario between the second and third sets of calculations; i.e., partial inclusion of the remaining elements in addition to K.

### 3.3 Chemical characterisation of slag, ash and quench water samples

The analysis results of each of the following fuels are presented in the order that they were trialled in the PEFG reactor. This is important to note, as ash residues remaining on the walls of the reactor from a previous fuel may influence the ash formation behaviour...
of subsequent fuels. In addition, fuels can leave or accrue residual matter during passage through milling equipment and fuel supply lines. For all trials, the residues collected from the quench consisted mainly of black granulous material. Separable fragments of melt in the quench were found from the pulpwood and 4-day stem wood trials. Residues from the sedimentation tank consisted of two fractions: a floating foamy and paste-like black residue, and a granulous black material that settled to the bottom of the tank. The SEM-EDS analyses all detected high levels of O, but was not quantifiable reliably. The following inorganic compositions should therefore be interpreted as oxides.

### 3.3.1 WOOD TRIAL

The amount of ash collected by the reactor probe was not significant enough for examination of its cross-section. Hence, SEM-EDS analysis was carried out upon the surface instead. The dominant feature of the surface was the coverage by branched crystal structures (right bottom diagonal portion, Figure 5). Si, Al and alkaline metals dominate the inorganic elemental composition of these areas, with a near absence of K (Figure 6). However, melt structures rich in K were found (top centre, Figure 5). These melt particles appear to be relatively inhomogeneous as shown by the variations of K and Ca. Upon closer examination, the portion richer in K appears more uniformly consolidated, while crystal formations are present for the portions richer in Ca. These melted particles were very rare compared to the crystal structures. Clustered structures (near-centre, Figure 5) exhibiting varying degrees of melting were more abundant than the K-rich melts. Their compositions are high in Ca and P (Figure 6).

![Figure 5. Wood: BSE image of probe surface deposits (a) Al-Si-Ca-O rich (crystallized) melt (b) Si-Al-K-O rich (melt) particle (c) Ca-P-Si-Al-O rich (melted) structure.](image)

The quench residue sample (4.7% wt ash) shows a high level of Fe which may be due to contamination from the sample storage container. Nonetheless, enrichment of Al, Si and Na in the sample compared to the fuel is evident, as is the reduction in Mg, K and Ca. The sedimentation residue (5.2% wt ash) has an inorganic distribution that is more...
similar to the original fuel, though Si and Al are enriched while Ca and Mg are diminished.

![Graph](image)

Figure 6. Wood: Inorganic elemental composition of probe deposits and ash residues (normalized on a C- and O-free basis) in comparison with fuel

### 3.3.2 BARK TRIAL

Deposits with loosely sintered ash with high porosity was collected upon the reactor probe (Figure 7). Particles with compositions resembling sand contaminants; e.g., quartz or K-rich feldspars, were found embedded within a aluminosilicate melt that had two distinct compositions: one rich in Ca and the other slightly richer in K. The latter is also significantly richer in Si than the former, though Al levels are approximately the same. These melts are indicated by the lighter and darker regions, respectively, in Figure 7.

![Image](image)

Figure 7. Bark: BSE image of probe deposit (polished cross-section) (a) Si-Ca-Al-O rich melt (b) Si-K-Ca-Al-O rich melt (c) Si-Al-K-O rich (feldspar) particles
The inorganic composition of residues sampled from the quench (36% wt ash) are similar to that of the fuel (Figure 8), though there is a slight enrichment of Si while a reduction in K. In comparison to the other trials, the composition of the residue collected from the sedimentation tank (28% wt ash) does not show close resemblance to the fuel, with Ca enrichment in approximately the same amount as Si reduction, with K diminishing also.

Figure 8. Bark: Inorganic elemental composition of probe deposits and ash residues (normalized on a C- and O-free basis) in comparison with fuel

3.3.3 PULPWOOD TRIAL

The slag collected on the probe of the pulpwood trial also consisted of typical sand contaminants embedded in a aluminosilicate-rich melt (Figure 9).

Figure 9. Pulpwood: BSE image of probe slag (polished cross-section) (a) Si-Al-Ca-O rich melt (b) Si-O rich (quartz) particles (c) Si-Al-K-O rich (feldspars) particles

Compared to the deposits sampled during the bark trial, these were harder and more sintered. The melt component is mainly Al and Si (Figure 10), with high levels of
alkaline (~15 mol%) and alkali (~10 mol%) metals. The remainder is around 5 mol% transition metals Mn and Fe, and 1% P. Preliminary constituent mappings of the SEM-EDS images show possible quartz particles distributed throughout the melt. Larger particles rich in Al, Si, alkali and alkaline metals—likely to be alkali-dominated feldspars—are also present in a similar manner. In the quench, a small quantity of distinguishable and separable green slag droplets resided with the bulk of black granulous residue. Their composition (Figure 10) is similar to the slag melt obtained from the probe, but the Si content is less dominant whilst Ca content is higher. These droplets were relatively scarce and it is expected that they had flowed down as slag from the reactor. The black granulous quench residue (77% ash) is enriched in Si and, to a lesser degree, Al, when compared to the composition of the fuel. In the sedimentation tank, residues (45% ash) had inorganic compositions to that of the original pulpwood fuel.

![Figure 10. Pulpwood: Inorganic elemental composition of probe deposits and ash residues (normalized on a C- and O-free basis) in comparison with fuel](image)

3.3.4 WOOD (4-DAY TRIAL)

The 4-day trial with the wood fuel was conducted after the pulpwood trial. Unlike the previous 5-hour wood trial, the entire probe tip was covered with deposits approximately 3 mm thick when it was retrieved. The slag appears to contain sand particles embedded in a Ca-rich silicate (crystallised) melt and particles (Figure 11). Particles were also observed for slag fragments found inside the quench (Figure 12), which were separable from the bulk black granulous residue. However, the melt regions do not exhibit crystallisation, unlike the melt found on the probe. The compositions of the probe and quench melts and embedded particles (Figure 13) are similar to the green droplet melts and embedded particles from the quench after the pulpwood trial, though Ca and Si levels are enriched and diminished, respectively. Al, Si, and Ca dominate the melt, with P, alkali and transition metals constituting the remainder at about 1, 10 and 4 mol%, respectively. The particles in the slag differ in both appearance and composition from those found in the slag of the pulpwood reactor probe. No sample from the quench was collected from this trial. Sedimentation tank residues (2.6% ash) had inorganic compositions very similar to the original milled stem wood fuel, though Si and Al, to a lesser extent, are enriched.
Figure 11. Wood (4-day trial): BSE image of quench melt (polished cross-section) (a) Si-Ca-Al-O rich (crystallized) melt (b) Si-Al-K-O rich (feldspar) particles

Figure 12. Wood (4-day trial): BSE image of quench melt (polished cross-section) (a) Si-Ca-Al-O rich melt (b) Si-Al-K-O rich (feldspar) particles
Figure 13. Wood (4-day trial): Inorganic elemental composition of probe deposits and ash residues (normalized on a C- and O-free basis) in comparison with fuel

3.3.5 WOOD WITH CO$_2$ CARRIER

The trial involving CO$_2$ as the fuel carrier produced only minor differences in the samples between those from the trial with N$_2$ carrier. Like the 5-hour wood trial with N$_2$, very little slag or deposits were collected on the probe. Because of this, SEM-EDS analysis was also performed upon the surface of the probe tip rather than the cross-section. Branched crystals, resembling to those in Figure 5, were also the dominant feature upon the surface. Their compositions are comparable with those observed on the probe with N$_2$ as carrier for wood; though in this case, the alkaline levels are approximately 10% lower, while Al and Si levels are both roughly 10% higher (Figure 15). Evidence of melt structures (Figure 14) consisting mainly of Ca and P were also found, similar to the clustered Ca-P melts found on the N$_2$ carrier probe.

Figure 14. Wood (CO$_2$ carrier): BSE image of probe deposit (a) Ca-Mg-P-O rich (melt) cluster
Small spheres (diameter 5 µm or less) indicative of a molten state were dispersed across the probe surface, which can also be seen on the N\textsubscript{2} carrier probe. Due to their size, it was not possible to attain an accurate composition; however, they appear to be rich in Al, Si and alkaline, as well as the transition metals Ti, Mn and Fe (~10 mol%). The black residue found in the quench (5.5% ash) also show similarities to the one sampled from the trial with N\textsubscript{2} carrier. Na and Si are enriched while Ca and K levels are diminished compared to the original fuel. However, the sedimentation tank residue (3.1% ash) does not show similarities with the fuel, unlike the sample taken from the N\textsubscript{2} carrier trial. Instead, there is an enrichment of Ca and Si, while K and Mg are diminished.

3.3.6 QUENCH WATER ANALYSIS

The estimated fraction of fuel input K that departed via the quench effluent outflow for the trials varied between 17-26% (Table 3). The uncertainties associated with each value is unclear because there are natural variations in the composition of the district water supplied to the quench sprays. However, two samples of the supply water collected on different days showed comparatively low levels of K: 0.636 mg/L and 0.756 mg/L. The lowest K concentration detected in the PEFG trial samples was 3.37 mg/L, while the average was 12.03 mg/L. The pH of the inlet water was 8.4 for both samples. The variations in the pH for samples taken at different times did not have large differences (< 0.6). Though temporal fluctuations are unknown, in general the gasification process appeared to acidify the water (Table 3).

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Wood (4-day trial)</th>
<th>Wood (CO\textsubscript{2} carrier)</th>
</tr>
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<tbody>
<tr>
<td>% of fuel input K</td>
<td>18</td>
<td>26</td>
</tr>
<tr>
<td>pH (1\textsuperscript{st}, 2\textsuperscript{nd} sample)</td>
<td>7.9, 8.1</td>
<td>7.9, 8.1</td>
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</table>
4 DISCUSSION

The three trials that yielded visible deposits/ slag on the reactor probe were bark, pulpwood and the 4-day trial of wood. Thermodynamic modelling shows that the composition of bark and pulpwood are prone to forming a silicate rich melt with K as a component, even if only a fraction of Si in the fuel is reactive (Figure 3 and Figure 4). The inclusion of K in the melt of these fuels is thermodynamically favourable even with the presence of e.g., Ca and Mg. For the 5-hour stem wood trials, very minute deposits were found, and K levels in these were very low (<0.5%), which is again in agreement with the global thermochemical equilibrium calculation results (Figure 2). The Ca-aluminosilicate rich crystallised melt observed on the reactor probes of the 5-hour trials with wood may have derived from slow cooling of a slag containing CaO and SiO₂, which is predicted by the results of the second set of thermochemical equilibrium calculations when Si is low. Other solid alkaline silicates (Ca₂SiO₄) are also stable phases as the reactivity of Si increases. Since the degree of contamination seems to be low for the wood fuel, Si and Ca (Mg) are most likely to have originated from the fuel; e.g., as inherent Si and Ca, making reactions between them more likely [8, 12]. Because of the low levels of K observed from these probe deposits, and from the results of the global thermochemical equilibrium calculations, it is unexpected that a slag containing approximately 5 mol% K in the melt was collected after the 4-day trial with stem wood. According to the thermochemical equilibrium calculation result shown in Figure 2, Si in the fuel would have to exhibit reactivity above which is possible to attain a high fraction of K in the melt. This suggests possibilities of: (1) alkali silicate formation on the surfaces of sand particles (i.e., fuel contaminants) via reaction with gaseous alkali species; (2) alkali silicate formation via reaction between gaseous alkali species and the aluminosilicate (mullite) refractory wall; or (3) recovery of remnant slag from the reactor wall due to the previous pulpwood trial, which incidentally was also the most likely to form slag and the first fuel observed to do so. The first possibility is difficult to disregard, since the fuels were not sampled continuously. Further to this, though the thermochemical equilibrium calculation results suggest that there would be a lack of K-containing slag, they were carried out in a global sense. This means that the entire reactor is assumed to have homogeneous conditions and composition. Even if conditions are homogeneous, the existence of fuel particles and small amounts of contaminant sand particles means that there could be localised regions enriched in particular elements. For example, if the Ca-aluminosilicate rich melt found on the reactor probe from the 5-hour trials of stem wood were to accumulate over time on the probe tip, this would create an area of localised enrichment of Si relative to the global scenario. This means that the fractionation of K in this localised region is represented by the Si-rich region to the right in Figure 2; i.e., a significant fraction of K in this localised region would be in melt phase. The second possibility leading to the slag found in the 4-day stem wood trial may be demonstrated by the melt spheres seen in Figure 14. Wu et al. [15] describes how mullite can react with Ca species to form low temperature melts in gasification conditions. A significant 2 mol% of Ti was detected in the spheres, which suggests that they may have originated from the refractory brick, since Ti is incorporated as a constituent in the refractory filler material. However, Ti was not detected in any of the slag melts, so this suggests that they did not originate from the refractory wall. The similarity in composition of the melt material in the slag collected from the probe and
quench of the pulpwood and 4-day wood trial suggest the third possibility could be likely. The 4-day wood trial was conducted after the pulpwood trial. This means that slag formed on the reactor wall during the pulpwood trial could have remained and solidified in the reactor afterwards. Upon commencing the stem wood trial, this remnant slag would flow and interact with the wood fuel. An indication of this is the increase of Ca by about 10% and a corresponding decrease in Si for the slag melt from the 4-day wood trial compared with the pulpwood trial (wood fuel is richer in Ca). However, a decrease in K is not observed, which would be expected given the depolymerising effect that increasing amounts of Ca might have upon wood ash melts [16, 17]. This, however, appears to be modelled by the slag database used for the calculations, as indicated by the low amounts of K in the slag when Si levels were also low. Formation of thermodynamically more stable solid Ca-silicates may also reduce the amount of Si participating in the slag phase, preventing the stabilisation of K in the slag. In general, the fraction of K retained in the slag is dependent upon operating conditions such as actual temperatures of particles, slag and gas, fuel feeding and flow regime, as well as interactions of other elements in the slag [18].

The quartz and feldspar particles seen in the melt may play a crucial role in slag formation [7]. Gaseous K may interact with reactive silicate sites on the particles to create localised areas of sticky alkali-silicate melt. These areas may then spread and combine with other particles to form slag. Previous work have suggested that MgO and CaO particles formed during conversion of the wood particle can be dissolved into the formed alkali-silicate [11, 19]. The compositions of the melts formed in the work show that it is silicate-based, with significant levels of Ca and Mg. This has implications for the ultimate retention of K or Na in the silicate melt because of the competition for silicate network-modifier positions [17]. If the slag viscosity is high, the flow down the reactor would be slow allowing time for Na and K to re-release from the melt.

From the thermochemical equilibrium calculation results, the gaseous species of K are, or would become, highly water-soluble salts (KOH, KCl). The quench effluent can therefore carry significant amounts of K out of the system during the trials. Since the samples were filtered through 0.45 µm filter papers, the detected levels are due to either dissolved K+ ions or submicron insoluble minerals containing K; e.g., feldspars. If the latter is insignificant, then the values in Table 3 are an estimate of the fraction of gaseous K leaving the hot reactor. Some K-rich fine particles formed during cooling of the crude syngas can pass the bubbling quench; thus, the values are an underestimation. However, this implies that the remaining fractions of K were either retained within the slag, accumulated in the quench or sedimentation residues. In general, the fractionation of K depends upon the chemical thermodynamics and reaction kinetics in the reactor, which are dependent upon fuel composition, operating conditions and flow properties. Detailed pathways of the major ash-forming element may also be attained if modes-of-occurrence of fuel and ash residues are known, such as in the work by Jordan and Akay [20].

5 CONCLUSIONS

Substantial deposit formation on the slag probe were only evident in the trials with the woody fuels containing higher ash contents; i.e., the trials with bark and pulpwood. Both
these fuels appear to be contaminated with sand particles, especially in the latter. The deposits formed during gasification of pulpwood fuel showed harder and more sintered material. The deposits/slag contained typical sand particles (e.g. quartz and feldspars) embedded in a silicate-rich melt. The melt in the slag is dominated by Si 40-55 mol%, Al ~15 mol% and Ca 10-20 mol%. The remainder is approximately 10 mol% alkali. The preliminary results suggest that fuel contaminants (e.g., quartz and feldspars) may play a significant role in the slag formation process in PEG of woody biomass fuels and that a significant share of the potassium is leaving the reactor as gaseous alkali species.

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7 ABBREVIATIONS
BSE Backscattered electrons
CFA Chemical fractionation analysis
ETC Energy Technology Centre in Piteå, Sweden
ICP-AES inductively coupled plasma - atomic emission spectroscopy
ICP-SFMS inductively coupled plasma - sector field mass spectroscopy
ICP-QMS inductively coupled plasma - quadrupole mass spectroscopy
LPI low pressure impactor
PEFG pressurised entrained-flow gasification
SEM-EDS scanning electron microscope with energy dispersive spectroscopy
\( p \) pressure (bar)
\( T \) temperature (°C)
\( \lambda \) \( \text{O}_2 \)-to-fuel ratio (full stoichiometric oxidation of H and C with supply \( \text{O}_2 \))
\( \mu \text{GC} \) micro gas chromatograph

8 REFERENCES


tendencies of wood pellet ash during combustion in residential pellet burners,”