Characterization of Ash Melting of Reed and Wheat Straw Blend

Siim Link,* Patrik Yrjas, Daniel Lindberg, and Andres Trikel

1. INTRODUCTION

The increased worldwide energy demand has decreased fossil fuel reserves, and concerns with climate change have paved the way for renewable energy resources.1,2 Biomass fuel is an abundant and readily accessible alternative energy; it is receiving increasing attention because of its renewability and carbon-neutral nature.3 Biomass combustion units were originally designed for wood firing.4,5 However, during recent decades, more attention has been paid to multifuel firing boilers.6 A number of low-grade biomass fuels have been considered as potential fuels.7 Biomass ashes contain a variety of inorganic elements that form complex compounds in gaseous, liquid, and solid phases during thermal conversion.8 Agglomeration is one of the key issues in terms of co-firing of biomass in the fluidized bed boiler.9 The prediction of ash-related problems requires detailed knowledge of the fuel being fired.10

When fuels are blended, the properties of the formed ash cannot be predicted according to the properties of the ash of a single fuel, i.e., the behavior of inorganic and some organic constituents is not necessarily linear with blends. In addition, ashes originating from mixtures of several parent fuels have shown a complex melting behavior depending on the mineral composition. Therefore, knowing the impact of a certain blend on the properties of the final ash enables us to avoid fuel combinations with unwanted properties or even to design an ash material for a certain application.11–15 A number of studies have focused on the behavior of ash melting of biomass-to-biomass or biomass-to-coal blends.14–17

Wheat straw wastes are an herbaceous agricultural residue composed of leaves, bran, and straw, which are usually incinerated or landfilled.3 Common reed (Phragmites australis) is widely distributed worldwide,18 where its availability and usage for energetic purposes have become attractive.19–22 Reed and wheat straw are both complex fuels for thermochemical conversion due to their chemical composition. Nevertheless, these fuels are available worldwide and have been used for energetic purposes. Reed and wheat straw differ by their mineral composition. Due to high silicon content, reed ash is considered as ash with a high melting temperature. Conversely, wheat straw ash has low melting temperature influenced by potassium and chlorine.23–27

Numerous methods and techniques are available to study the ash melting behavior—ash melting tests, determination of the chemical and mineralogical composition, morphology analyses, and prediction of the ash melting behavior by modeling.28–39 However, no detailed stepwise studies of the biomass ash melting process combined with various laboratory methods have been reported.

The fireside ash deposit accumulation in boilers is the main concern of the plant operators, and the temperature at which the particle changes from nonsticky to sticky is critically

Received: October 11, 2021
Accepted: December 27, 2021
Published: January 6, 2022

https://doi.org/10.1021/acsomega.1c05087
ACSOmega 2022, 7, 2137−2146
important in boiler design and operation. It has been found that fly ashes could be sticky, containing at least 15% of melt, i.e., liquid fraction. However, regarding the stickiness of the ash particle, the percentage of the molten phase of ash allows only a coarse estimation. Modeling programs such as FactSage allow for estimating the ash chemistry and molten fraction according to the given composition and the Gibbs free energy minimization principle. The modeling results, however, do not necessarily represent real life scenarios, though their aim is to evaluate the nature of the whole process.

According to our previous work, the blend of reed and wheat straw showed the most complex ash melting behavior among the studied blends, and blending with certain amounts could result in eutectics. The behavior of the blend of reed and wheat straw differs a great deal from that of the parent fuels; it needs detailed analysis regarding its suitability as a boiler fuel.

In this study, the ash melting behavior and chemistry of the reed and wheat straw blend were investigated in detail with different methods and an alternative approach. As is different from previous studies, we applied a new approach and explored the ash melting mechanism using stepwise thermal treatment. Variations in mineralogical properties were determined by the ash melting mechanism using stepwise thermal treatment. The obtained data will provide valuable information on the usage of this blend, e.g., in boilers and gasifiers.

2. RESULTS AND DISCUSSION

2.1. Characterization of Materials. Table 1 shows that the ash content is higher for WSP (4.5% dry basis) compared to reed (3.8% dry basis). WSP contains more S and Cl as well.

Table 2 gives the composition and the loss of ignition (LOI) of the parent fuel ashes as suggested by the XRF analyses.

| Table 1. Proximate Analysis, Ultimate Analysis, and Cross-Calorific Value of the Parent Fuels |
|------------------|------------------|------------------|------------------|------------------|------------------|
| fuel            | moisture (wt %)  | ash (wt %)       | volatile matter (wt %) | fixed carbon (wt %) | ultimate analysis, dry basis (wt %) | gross calorific value(MJ/kg) |
| WSP             | 8.2             | 4.5              | 77.3              | 18.2              | 46.6  | 6.2 | 0.4 | 41.9 | 0.1 | 0.3 | 18.8 |
| R               | 6.3             | 3.8              | 80.9              | 15.3              | 47.5  | 6.2 | 0.2 | 42.2 | 18.9 |

2.2. Standard Ash Melting Tests. The results of the ash melting test of 50R/50WSP according to the standard method of CEN/TS 15370 are presented in Figures 1 and 2.

The curves of a series of heat treatment tests are shown in Figure 2. The heat treatment procedure of the standard method of CEN/TS 15370 was applied for HSM tests using different end temperatures. We can observe a similar path of heat treatment curves for all the HSM tests, which gives evidence of a relatively good repeatability of the process.

In Figure 2, the ash melting path of the selected sample material could be divided into four regions: 1 - unaffected by heat treatment; 2 - sintering stage, densified mass by the end; 3 - expanding stage, porous medium; 4 - flowing liquidous mass by the end. The $T_{sp}$ ("sintering point," and in our case, $T_{sp} = 688 \, ^\circ C$) in region 2 indicates the temperature where the swelling behavior changed to height decrease. $T_{exp}$ ("expansion point," and in our case, $T_{exp} = 780 \, ^\circ C$) shows the temperature where due to melting, the height decrease of the sample body turns to height increase. $T_{emp}$ ("excessive melting point," and in our case, $T_{emp} = 933 \, ^\circ C$) expresses the temperature where the excessive melting starts. The expansion in region 3 could be attributed to several effects such as the thermal expansion of ash particles and primary pores trapping air in the ash particle as well as the evolution of gases during the decomposition of ash components. Region 4 shows the last step of the ash melting process; the fluctuations (seen as...
Figure 3. Images of the ash samples. (a1) Initial ash sample at 550 °C, SEM picture at 30x magnification; (a2) Initial ash sample at 550 °C, SEM picture at 1000x magnification; (a3) Initial ash sample at 550 °C, SEM picture at 1000x magnification; (b1) Ash sample at 600 °C, regular photo at 1x magnification; (b2) Ash sample at 600 °C, regular photo at 30x magnification; (b3) Ash sample at 600 °C, SEM picture at 1000x magnification; (c1) Ash sample at 700 °C, regular photo at 1x magnification; (c2) Ash sample at 700 °C, SEM picture at 30x magnification; (c3) Ash sample at 700 °C, SEM picture at 1000x magnification; (d1) Ash sample at 800 °C, regular photo at 1x magnification; (d2) Ash sample at 800 °C, SEM picture at 30x magnification; (d3) Ash sample at 800 °C, SEM picture at 1000x magnification; (e1) Ash sample at 900 °C, regular photo at 1x magnification; (e2) Ash sample at 900 °C, SEM picture at 30x magnification; (e3) Ash sample at 900 °C, SEM picture at 1000x magnification; (f1) Ash sample at 1000 °C, regular photo at 1x magnification; (f2) Ash sample at 1000 °C, SEM picture at 30x magnification; (f3) Ash sample at 1000 °C, SEM picture at 1000x magnification; (g1) Ash sample at 1050 °C, regular photo at 1x magnification; (g2) Ash sample at 1050 °C, SEM picture at 30x magnification; (g3) Ash sample at 1050 °C, SEM picture at 1000x magnification; (h1) Ash sample at 1099 °C, regular photo at 1x magnification; (h2) Ash sample at 1099 °C, SEM picture at 30x magnification; (h3) Ash sample at 1099 °C, SEM picture at 1000x magnification.

2.3. Results of SEM/EDX Analysis. The SEM images and the EDX results of the initial ash sample and the ash samples after heat treatment with HSM are shown in Figure 3 and Tables 3 and 4.

According to their ash composition, Saidur et al. have divided biomass fuels into three categories:

(1) Ca- and K-rich, Si-lean ashes (generally woody biomass)

(2) Si-rich, Ca- and K-lean ashes (generally herbaceous or agricultural biomass)

(3) Ca-, K-, and P-rich ashes (sunflower and rapeseed)

The composition of 50R/50WSP ash (see also Table 3, initial) does not match well with the classification above; in our case, it is Si-, K-, and Ca-rich ash. The ash composition of the biomass blend could result in a new category of ash material. Therefore, general trends of the ash melting behavior of a certain type of single biomass are not valid for biomass blends.

The initial ash sample (see also Figure 3a1) exhibits particles with irregular shapes. The three main elements detected were Si, Ca, and K (see also Table 3). The ash particle in Figure 3a2 noise or oscillations in the plot) in height are the result of bubbling.

Table 3. Chemical Composition of the Initial Ash and Ash Samples after Heat Treatment up to 1000 °C Obtained by EDX Analysis

| area | initial (Figure 3a1) | 600 °C (Figure 3b2) | 700 °C (Figure 3c2) | 800 °C (Figure 3d2) | 900 °C (Figure 3e2) | 1000 °C (Figure 3f2) |
|------|----------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| SiO2 | 59                   | 50                  | 42                  | 18                  | 25                  | 14                  |
| K2O  | 17                   | 20                  | 25                  | 39                  | 34                  | 38                  |
| Na2O | 1.4                  | 1.1                 | 1.2                 | 0.9                 | 1.4                 | 1.7                 |
| CaO  | 11                   | 14                  | 12                  | 4.9                 | 5.7                 | 4.8                 |
| MgO  | 2.7                  | 3.3                 | 2.9                 | 0.8                 | 1.25                | 0.8                 |
| SO3  | 3.7                  | 4.3                 | 4.3                 | 3.5                 | 32                  | 40                  |
| CI   | 3.4                  | 4.1                 | 1.8                 | 0.4                 |                     |                     |
| P2O5 | 2.0                  | 2.8                 | 2.6                 | 0.8                 | 0.9                 | 0.6                 |

Table 4. Chemical Composition of Ash Samples after Heat Treatment at 1050 °C (Figure 3g2) and Flow Temperature (Figure 3h2) Obtained by EDX Analysis

|                | 1050 °C (1) | 1050 °C (2) | 1050 °C (3) | FT (1) | FT (2) | FT (3) |
|----------------|-------------|-------------|-------------|--------|--------|--------|
| SiO2           | 5           | 39          | 0.3         | 3.8    | 48     | 2.6    |
| K2O            | 46          | 25          | 46          | 43     | 21     | 45     |
| Na2O           | 1.0         | 1.4         | 2.2         | 1.3    | 1.7    | 2.4    |
| CaO            | 13          |             |             | 3.8    |        | 12     |
| MgO            | 2.3         |             |             |        | 2.6    |        |
| SO3            | 47          | 17          | 51          | 47     | 10     | 49     |
| CI             |             |             |             |        |        |        |
| P2O5           | 0.8         | 2.7         |             | 1.4    | 2.9    | 0.5    |

https://doi.org/10.1021/acsomega.1c05087
ACS Omega 2022, 7, 2137−2146
has porous structure, and the composition is SiO2 (56%), K2O (16%), CaO (12%), Cl (5%), SO3 (4%), P2O5 (3%), MgO (3%), and Na2O (2%), which supports the composition of the total sample as shown in Table 3 marked as “initial.” White particles in Figure 3b contain mainly K2O, Cl, and SiO2. The gray outer layer contains mainly SiO2 (90–92%) and less K2O (5%), Na2O (1%), and Cl (1%). Both reed and wheat straw stem particles have circular plate-like shapes with white particles on the surface. However, based on the surface morphology (SEM images), the particle shown in Figure 3a3 could be attributed to reed.47,48 On this particle, the circular “plates” contain 99% of SiO2 and 1% of K2O, and the gray outer layer contains SiO2 (92%) and less K2O (4%) and CaO (2%). At 600 °C, the surface of the ash sample (Figure 3b1,b2) has holes, and the inorganic particles are neither softened nor stuck together (see also Figure 3b3). By increasing the end temperature, the surface of the sample body became more even. At 700 °C (see Figure 3c1–c3), the first transition from rough surface toward smooth surface is observed, and from the temperature of 800 °C, a glassy surface appears (see Figure
As can be seen, the number of pores visible on the surface decreased with the increase in temperature. The molten and glassy surface has filled the pores. This could also explain the expansion of the sample body, while the evolved gases have limited pass-through from the inside of the sample body to the outside. At 900 °C (see also Figure 3e1−e3), the sample body is curved and has a scabrous surface, which is most probably caused by bubbling and penetration of evolved gases. After the excessive melting point (933 °C), it started to collapse and build glassy material (as seen in Figure 3f1−h3). The melted material (Figure 3g2 and h2) divided into three zones differing by composition (see also Table 4). The middle zone (marked as number 1 in Figure 3g2 and h2) contains mainly K and S, revealing molten K2SO₄. The next zone around the middle area (marked as number 2 in Figure 3g2 and h2) contains Si, K, Ca, Mg, S, and P. The outer zone (marked as number 3 in Figure 3g2 and h2) again contains mainly K and S. As can be seen, the content of Na increases from the middle to the outside (see also Figures 3g2,h2 and Table 4). The reason is that compounds containing Na and K were the first that started to melt, and the melted fraction has flown away from the center of the sample body.

In general, the chemical composition of the surface changes along with the temperature increase (see also Tables 3 and 4). With higher temperatures, the Si and Ca contents of the surface are decreasing, and the contents of K and S are increasing. This reveals that a K and S compound (e.g., K₂SO₄) covers the surface.

2.4. Results of XRD Analysis. XRD analysis was performed for the initial ash material gathered after the standard ashing procedure (CEN/TS 14775:2004) at 550 °C and the ashes with end temperatures of 800, 1000 and 1100 °C. The XRD analysis enabled us to detect crystalline species...
at 550 and 800 °C (as seen in Figure 4) but basically not at 1000 and 1099 °C.

K₂SO₄ was detected also by XRD, which confirms the existence of the K and S detected by SEM as K₂SO₄. Du et al. have also found K₂SO₄ in wheat straw ash at the final heat treatment temperatures of 815 and 1000 °C, and the other two main crystalline compounds were SiO₂ and KAlSiO₄. At the lower heat treatment temperature of 600 °C, they have detected CaCO₃, KCl, SiO₂, CaMg(CO₃)₂, and K₂SO₄. Our results showed brianiite, dmitryivanovite, nepheline, and KCl as crystalline compounds present in the initial ash material. At higher temperatures, the two main compounds were KCl and K₂SO₄.

K and Si are the two main elements in the ash. According to Ma et al.,33 only part of the K species in the biomass ash is present in the crystalline phase. Other types of K species may be present as amorphous phases, such as potassium silicates. The ash does not contain all the chemical compounds in the crystalline phase. According to Uibu et al.,39 the estimated amorphous phase content of oil shale ashes could be up to 21–40%. In the studied ash material, the ash started to turn glassy and therefore amorphous from 800 °C.

2.5. Thermodynamic Modeling. According to FactSage, the initial composition of the ash blend at 550 °C consists mainly of K₂MgSi₅O₁₂, CaSiO₃, SiO₂, KCl, K₂SO₄, Na₂CaSi₅O₁₆, and Ca₃P₂O₈ as well as less amounts of KAlSi₃O₈ and Na₂SO₄ as seen in Figure 5. At 660 °C, the first melting takes place, and KCl and K₂SO₄ (see also Figure 6) as well as NaCl and Na₂SO₄ tend to melt. While the content of liquid mass fraction in the two latter compounds is relatively low (<1%), they are not shown in Figure 6. Arvelakis et al. have found that the mixture of 50% KCl and 50% K₂SO₄ starts to melt at 688 °C, i.e., the mixture of compounds starts melting earlier than one separate compound. The two main liquid compounds were KCl and K₂SO₄ and the liquid mass of KCl/K₂SO₄ comprises 12.5% of the total initial mass of the ash blend sample together with NaCl and Na₂SO₄; the liquid mass fraction is 13.8%. This reveals that the studied blend ash could already be sticky at 680 °C.30 Our modeling reveals that the temperature range of 660–680 °C could be considered as the starting point of melting.

In the temperature range of 680–780 °C, no additional liquid mass fraction was added, although in the eutectic melting of KCl and K₂SO₄, liquid fraction increased with increasing temperature. According to calculations with FactSage, in that temperature range, solid K₂Ca₂Si₃O₉ was composited as an intermediate solid compound, but at 800 °C, K₂Ca₂Si₃O₉ and Na₂CaP₂O₇ were totally decomposed. Also, the solid fraction of K₂MgSi₅O₁₂ showed a moderate decrease at 800 °C, but the content of CaSiO₃, Ca₃P₂O₈, and SiO₂ had increased moderately. Additionally, the molten fraction of SiO₂ and K₂O was detected. The temperature of 800 °C could be considered as the start of the intensive stage of melting, which ends at 980 °C. In this range, an intensive melting of the ash material was observed, i.e., by the end of this temperature range, almost 65% of ash was melted. At the temperature of 860 °C, the content of solid K₂MgSi₅O₁₂ started to decline and reached zero at 980 °C. The SEM pictures indicate that the glassy material was formed from 800 °C and above. The glass transition of K₂O–MgO–SiO₂ compounds could start from ~900 °C. At this temperature, a small amount of solid CaMgSi₅O₁₂ was composited as an intermediate product, which started to decompose and melt immediately after it was built. Three Ca-containing compounds, Ca₃P₂O₇, CaSiO₃, and CaMgSi₅O₁₀, were the only solid fractions left at this temperature. In terms of liquid fractions, the contents of K₂O, SiO₂, CaO, and MgO were increased. Among the liquid compounds, the molten SiO₂ is the main mass fraction, which constitutes 37.5 wt % of the total initial amount of the ash blend. Consequently, this region is a temperature region where the decomposition and extensive melting of such main solid compounds as K₂MgSi₅O₁₂ and SiO₂ occur.

At the temperature of 980 °C, the final stage of melting starts and then ends at 1220 °C. From the temperature of 980 °C forward, the content of solid CaSiO₃ tends to decrease and reaches zero at 1220 °C. The solid fraction of Ca₃P₂O₇ is the only solid material that remains until the end of the process, i.e., up to 1500 °C. Rizvi et al.55 have presented ash melting thermodynamic modeling by FactSage for miscanthus, peanut, sunflower, and pine wood ashes, and for all related ashes, Ca₃P₂O₇ was solid up to 1500 °C as well. Similarly to our results, they showed liquid SiO₂, K₂O, Na₂O, and CaO above 700 °C.

2.6. FactSage Modeling Compared to Other Methods. The height curve of HSM, the mass loss curve of TGA, the DTA curve, and the melt fraction curve obtained by simulation using FactSage are shown in Figure 7.

![Figure 7. HSM, STA, and melt fraction curves.](https://doi.org/10.1021/acsomega.1c05807)
indicate any clear endothermic peak in this temperature range. Consequently, as indicated by modeling, this region could be described as a temperature region where the decomposition and extensive melting of such main solid compounds as $K_2MgSi_5O_{12}$ and $SiO_2$ occur. This extensive melting of Si and K compounds, evaporation of liquids, and the trapped gases in the molten mass resulted in the swelling (increase in height) of the HSM sample body. The start of this melting stage fits well with the $T_{exp}$ or “expansion point” in Figure 2. In general, the extensive melting started at 800 °C and continued up to 980 °C, when the content of the molten phase was 65% from the initial mass of the ash. The molten fraction reached the critical content where the swelling turned to collapsing of the sample body as indicated by the HSM test. According to the FactSage modeling, the critical content of the molten phase is 25% from the initial sample mass in our case.

As an alternative to Pang et al., we staged the melting process (shown in Figure 8) for the studied blend as follows:

![Figure 8. Proposed staging of the ash melting process.](image-url)

Region 1 – unaffected by heat treatment; region 2 – the first stage of melting and $T_{mp}$ is a “starting point” of melting; region 3 – intensive melting stage, $T_{exp}$ is an “extensive melting point,” and $T_s$ is a “critical point” where the sample body starts to diminish; region 4 – flowing liquid mass by the end. Of course, such a behavior is not valid for all biomasses or their blends; it is rather exceptional.

After extensive melting, the liquid mass fraction increases quite linearly in the temperature range of 980 and 1200 °C and achieves its maximum value of 70%, counting from the initial mass of the ash sample.

The EDX results of the ash samples after thermal treatment at 1050 °C and flow temperature (see Figures 3g2,h2 and Table 4) show that the K and S are the main components at the edge and on the top of the sample body. According to FactSage results, the K and S are in the form of molten compounds. The results reveal that the Si, Mg, Ca, and P containing solid and melted fractions are surrounded by melted potassium compounds, which are more available on the top and on the edges of the sample body.

From 1240 °C onward, the melting process is stabilized, i.e., solid, liquid, and gaseous masses remain unchanged.

3. CONCLUSIONS

Our focus has been on the melting behavior of the ash of the biomass blend of 50% reed and 50% wheat straw pellet as a potential fuel for boiler houses. For this purpose, we used a number of laboratory methods such as simultaneous thermal analysis, heating microscopy, scanning electron microscopy with energy dispersive X-ray (SEM/EDX) analysis, and X-ray powder diffraction (XRD). FactSage software was used for thermodynamic modeling of the ash melting process.

Our results showed that the ash started to melt at 660–680 °C with the melting of $KCl$, $NaCl$, $K_2SO_4$, and $Na_2SO_4$. The content of the liquid mass fraction was 13.8%, revealing that the studied ash blend could already be sticky at 680 °C. The results demonstrated that after the first melting, the liquid $K_2SO_4$ covers the surface. The melted $K_2SO_4$ could cover the single particle in the thermal units and could cause stickiness of the ash particle.

Intensive melting started at 800 and at 980 °C; the content of the molten phase was 65% from the initial mass of the ash. During the intensive melting, the studied ash material started to swell, and when the liquid mass fraction was 25% (950 °C) from the initial mass, the ash material started to dwindle. Rapid melting between 950 and 980 °C was caused by the melting of $SiO_2$ and $K_2MgSi_5O_{12}$, and the material became glassy and amorphous. $K_2MgSi_5O_{12}$ was decomposed to oxides according to FactSage modeling. After 980 °C, the remaining 5% of the ash material was melted, and the process ended with a flowing material.

The FactSage modeling is a helpful tool for interpreting the results of the ash melting behavior and supplements well the results obtained by other methods used in this study, especially regarding the stickiness of the ash material. The alternative distribution of the melting stages for the studied ash blend was proposed.

4. EXPERIMENTAL SECTION

4.1. Parent Materials and Characterization. In our study, reed (R) and wheat straw pellets (WSP) were used as parent fuels. WSP originates from North Lithuania and R from the west-coast areas of Estonia. The parent fuels were prepared and characterized by standard analysis (according to the standard methods of CEN/TS 14774-1:2004, CEN/TS 14775:2004, and CEN/TS 15148:2005), elemental analysis (according to the standard methods of EN 15104:2011 and EN 15289:2011) by a Vario EL CHNOS elemental analyzer, and gross calorific value (according to the standard method of EN 14918) by an IKA C 5000 calorimetric bomb.

4.2. Ashing, Characterization, and Blending of Ashes. The ashing procedure was carried out according to the standard method of CEN/TS 14775:2004: (a) from room temperature to 250 °C with a heating rate of 4.5 °C/min, (b) 60 min at 250 °C, (c) heating to 550 °C with a heating rate of 10 °C/min, (d) 120 min at 550 °C, and (e) cooling down to room temperature.

The X-ray fluorescence (XRF) technique was applied to determine the elemental composition of the ashes of the parent fuels using a Rigaku ZSX Primus II WDXRF device with a rhodium anode (4 kW) and a 30 μm tube.

The ash blend of R and WSP was prepared as follows: (a) the fuels were ashed separately and (b) after ashing of a single fuel, the ashes were blended according to the proportions of the parent fuels of 50% of R and 50% of WSP (50R/50WSP), i.e., it was not 50% reed ash and 50% wheat straw ash but the relevant ash amounts that a single parent fuel contains, which depicts the ash blend left after the thermal treatment of the parent fuel blend mixed by ratios of 50/50.
4.3. Ash Melting Behavior. Ash fusion characteristics were determined according to the standard method of CE/N
TS 15370-1:2006 using a Misura 3 HSM ODHT 1600-5008
(HSM, hot stage microscope). Shrinkage temperature (ST),
deformation temperature (DT), hemispherical temperature
(HT), and flow temperature (FT) were measured. In addition
to the standard ash melting test, a number of end temperatures
were chosen (600, 700, 800, 900, 1000, and 1050 °C), and the
ash material was heated up to the desired end temperature.
The aim of various end temperatures is to collect ash material
for further analysis and investigate the chemical composition
stepwise along the thermal treatment process as described in
Section 2.4. The tests were performed under the atmosphere
of air.

A TA Instruments SDT Q600 device was used for
simultaneous thermal analysis (STA) of the ash blend, i.e.,
thermagravimetric analysis (TGA) coupled with differential
thermal analysis (DTA). The sample was heated from room
temperature up to the final temperature with a heating rate of
10 °C/min, and an alumina crucible was used. Synthetic air (a
mixture of 21 mL/min O2 and 79 mL/min N2) was used as
carrier gas.

4.4. Morphology and Inorganic Content of Ash Material.
The morphology of the ash material after heat
treatment in HSM was examined by scanning electron microscopy
(SEM); energy dispersive X-ray (EDX) spectroscopy was used to determine the inorganic matter on the
surface of the treated ash material. All SEM/EDX spectroscopy work was performed with a Leo 1530 Gemini at a voltage of 15
kV.

The mineralogy analysis was carried out by means of a Rigaku Ultima IV diffractometer using the X-ray powder
diffraction (XRD) method with Cu Kα1 radiation (λ = 1.5406 Å,
40 kV at 40 mA) and a silicon strip detector D/teX Ultra.

4.5. Thermodynamic Calculations. In our study, the
thermodynamic equilibrium was calculated to determine the
composition of the mineral matter and the molten fraction of the
selected ash sample. We used the FactSage 7.3 software
package and the following thermodynamic databases: FToxid-
SLAGA (P2O5 and P2O3S2 were excluded because the phosphorus content is moderate and the calculations were inaccurate), FTsalt-SALTF, FTsalt-B1 (NaCl and KCl were selected), FTsalt-oP28D, FTsalt-hP22 (Na2SO4, K2SO4, Na3CO3 and K2CO3 were selected), and FTsalt-hP14. The input for the calculations was the chemical composition of the fuel ashes shown in Table 2. The equilibrium calculation was made for the temperature range of 550–1500 °C with a step of 20 °C under pressure of 1 bar.

The gas atmosphere was not constrained in the calculations, and the data for the gas phase was taken from the FactPS database. The formation of the gas phase in the calculations was mainly due to the predicted decomposition of CO2 from carbonates. In all the calculations, the conditions were consistent with an either inert or oxidizing gas atmosphere. The effect of reducing or oxidizing atmospheres can lead to variations in the behavior of Fe- or S-containing species,52–54 but as the ash composition showed very low Fe contents and sulfur has been predicted as mainly composed of sulfates, the effect of the gas atmosphere is not considered in any further detail.

AUTHOR INFORMATION

Corresponding Author
Siim Link — Laboratory of Inorganic Materials, Department of Material and Environmental Technology, School of Engineering, Tallinn University of Technology, Tallinn 19086, Estonia; orcid.org/0000-0001-8090-332X; Email: siim.link@taltech.ee

Authors
Patrik Yrjas – Johan Gadolin Process Chemistry Centre, Laboratory of Molecular Science and Engineering, Åbo Akademi University, Turku 20500, Finland
Daniel Lindberg – Department of Chemical and Metallurgical Engineering, Aalto University, Aalto 00076, Finland
Andres Trikkel – Laboratory of Inorganic Materials, Department of Material and Environmental Technology, School of Engineering, Tallinn University of Technology, Tallinn 19086, Estonia

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c05087

ACKNOWLEDGMENTS

This work was supported by the European Regional Development Fund and the programme Mobilitas Pluss grant MPTT112, Estonian Ministry of Education and Research (IUT19-4), as well as the European Regional Development Fund through the project TK141 “Advanced materials and high-technology devices for energy recuperation systems.” Peter Backman, Linus Silvander, and Arvo Mere are acknowledged for their help on the characterization of materials and for valuable comments and discussions.

REFERENCES

(1) Huang, C.; Lai, C.; Wu, X.; Huang, Y.; He, J.; Huang, C.; Li, X.; Yong, Q. An integrated process to produce bio-ethanol and xylooligosaccharides rich in xylobiose and xylotriose from high ash content waste wheat straw. Bioresour. Technol. 2017, 241, 228–235.
(2) Tang, W.; Wu, X.; Huang, C.; Ling, Z.; Lai, C.; Yong, Q. Natural surfactant-aided dilute sulfuric acid pretreatment of waste wheat straw to enhance enzymatic hydrolysis efficiency. Bioresour. Technol. 2021, 324, 124651.
(3) Xu, Y.; Liu, X.; Qi, J.; Zhang, T.; Xu, J.; Wen, C.; Xu, M. Characterization of fine particulate matter generated in a large woody biomass-firing circulating fluid bed boiler. J. Energy Inst. 2021, 96, 11–18.
(4) The Different Uses of Wood Energy, Plane Énergies; http://www. plane-energies.com/en/medias/close/different-uses-wood-energy. (accessed 2021-06-30).
(5) Sturc, M. Analysis of the latest data on energy from renewable sources. Eurostat, Statistics in Focus, Renewable Energy; 2012, No. 44.
(6) Hupa, M. Interaction of fuels in co-firing in FBC. Fuel 2005, 84, 1312–1319.
(7) Hupa, M. Ash-Related Issues in Fluidized-Bed Combustion of Biomasses: Recent Research Highlights. Energy Fuels 2012, 26, 4–14.
(8) Monlań-Mędrala, A.; Magdzińska, A.; Gajek, M.; Nowińska, K.; Nowak, W. Alkali metals association in biomass and their impact on ash melting behaviour. Fuel 2020, 261, 116421.
(9) Morris, J. D.; Daood, S. S.; Chilton, S.; Nimmo, W. Mechanisms and mitigation of agglomeration during fluidized bed combustion of biomass: A review. Fuel 2018, 230, 452–473.
(10) Werkelin, J. Ash-forming elements and their chemical forms in woody biomass fuels. Academic dissertation. Åbo Akademi University: 2008.
(11) Reinhöller, M.; Klinger, M.; Schreiner, M.; Gutte, H. Relationship between ash fusion temperatures of ashes from hard coal, brown coal, and biomass and mineral phases under different atmospheres: A combined FactSage™ computational and network theoretical approach. Fuel 2015, 151, 118–123.
(12) Tillmän, D. A.; Duong, D. N. B.; Harding, N. S. Solid fuel blending. Principles, practices and problems; Elsevier Inc.: United States, 2012.
(13) Vanvuka, D.; Pitaroulis, M.; Alevizos, G.; Repouskou, E.; Pentari, D. Ash effects during combustion of lignite/biomass blends in fluidized bed. Renewable Energy 2009, 34, 2662–2671.
(14) Oladejo, J. M.; Adegbite, S.; Pang, C.; Liu, H.; Lester, E.; Wu, T. In-situ monitoring of the transformation of ash upon heating and the prediction of ash fusion behaviour of coal/biomass blends. Energy 2020, 199, 117330.
(15) Rodríguez, J. L.; Álvarez, X.; Valero, E.; Ortiz, L.; de la Torre-Rodriguez, N.; Acuña-Alonso, C. Design of solid biofuels blends to minimize the risk of sintering in biomass boilers. J. Energy Inst. 2020, 93, 2409–2414.
(16) Zeng, T.; Pollex, A.; Weller, N.; Lenz, V.; Nelles, M. Blended biomass pellets as fuel for small scale combustion appliances: Effect of blending on slag formation in the bottom ash and pre-evaluation options. Fuel 2018, 212, 108–116.
(17) Xu, J.; Wang, J.; Du, C.; Li, S.; Liu, X. Understanding fusibility characteristics and flow properties of the biomass and biomass-coal ash samples. Renewable Energy 2020, 147, 1352–1357.
(18) Wie, Q.; Cherif, M.; Zhang, G.; Almesrati, A.; Chen, J.; Wu, M.; Komba, N.; Hu, Y.; Regier, T.; Sham, T.-K.; Vidal, F.; Sun, S. Transforming reed waste into a highly active metal-free catalyst for oxygen reduction reaction. Nano Energy 2019, 62, 700–708.
(19) Gorip, T.; Haberl, A.; Rubel, O.; Ajder, V.; Kulchhtsky, L.; Smaliychuk, A.; Gorip, N. Potential for renewable use of biomass from reedbeds on the lower Prut, Danube and Dniester floodplains of Ukraine and Moldova. Mires Peat 2019, 25, No. 07.
(20) Kobbeng, J. F.; Theys, N.; Zerbe, S. The utilisation of reed (Phragmites australis): a review. Mires Peat 2013, 13, No. 01.
(21) Vaičekonytė, R.; Kiviat, E.; Nenga, F.; Ostfeld, A. An exploration of common reed (Phragmites australis) bioenergy potential in North America. Mires Peat 2013, 13, 12.
(22) Wichmann, S.; Kobbeng, J. F. Common reed for thatching—A first review of the European market. Ind. Crops Prod. 2015, 77, 1063–1073.
(23) Arvelakis, S.; Vourliotis, P.; Kakaras, E.; Koukias, E. G. Effect of leaching on the ash behavior of wheat straw and olive residue during Fluidized bed combustion. Biomass Bioenergy 2001, 20, 459–470.
(24) Kask, U.; Kask, L.; Link, S. Combustion characteristics of reed and its suitability as a boiler fuel. Mires Peat 2013, 13, No. 05.
(25) Link, S.; Kask, U.; Paist, A.; Siirde, A.; Arvelakis, S.; Hupa, M.; Yrjas, P.; Külaots, I. Reed as a gasification fuel: a comparison with woody fuels. Mires Peat 2013, 13, No. 04.
(26) Link, S.; Kask, U.; Krall, J.; Plank, H. Combustion tests of reed pellets. The 23rd European Biomass Conference and Exhibition; 2015, pp. 697–701.
(27) Link, S.; Yrjas, P.; Hupa, L. Impact of blending method on the melting characteristics of ashes of biomass blends. The 25th European Biomass Conference and Exhibition; 2017, pp. 547–551.
(28) Hansen, L. A.; Frandsen, F. J.; Dam-Johansen, K.; Sørensen, H. S. Quantification of fusion of ashes in solid fuel combustion. Thermochim. Acta 1999, 326, 105–117.
(29) Zevenhoven-Onderwater, M.; Backman, R.; Skrifvars, B.-J.; Hupa, M.; Lilienhåll, T.; Rosén, C.; Sjöström, K.; Engvall, K.; Hallgren, A. The ash chemistry in fluidised bed gasification of biomass fuels. Part II: Ash behaviour prediction versus bench scale agglomeration tests. Fuel 2001, 80, 1503–1512.
(30) Capablo, J.; Jensen, P. A.; Pedersen, K. H.; Hjuler, K.; Nikolaisen, L.; Backman, R.; Frandsen, F. Ash Properties of Alternative Biomass. Energy Fuels 2009, 23, 1965–1976.
(31) Vanvuka, D.; Kakaras, E. Ash properties and environmental impact of various biomass and coal fuels and their blends. Fuel Process. Technol. 2011, 92, 570–581.
(32) Mediavilla, I.; Fernández, M. J.; Barro, R.; Borjabad, E.; Bados, R.; Esteban, L. S. Effect of mechanical heating on the chemical composition and combustion behaviour of shrub Biomass. Energy 2020, 204, 117928.
(33) Ma, T.; Fan, C.; Hao, L.; Li, S.; Song, W.; Lin, W. Fusion characterization of biomass ash. Thermochim. Acta 2016, 638, 1–9.
(34) Magdziarz, A.; Wilk, M.; Gajek, M.; Nowak-Woźni, D.; Kopia, A.; Kalemba-Rec, I.; Kozinski, J. A. Properties of ash generated during sewage sludge combustion: A multifaceted analysis. Energy 2016, 113, 85–94.
(35) Rizvi, T.; Xing, P.; Pourkashanian, M.; Darvell, L. I.; Jones, J. M.; Nimmo, W. Prediction of biomass ash fusion behaviour by the use of detailed characterisation methods coupled with thermodynamic analysis. Fuel 2015, 141, 275–284.
(36) Xiong, Q.; Li, J.; Guo, S.; Li, G.; Zhao, J.; Fang, Y. Ash fusion characteristics during co-gasification of biomass and petroleum coke. Bioresour. Technol. 2018, 257, 1–6.
(37) Du, S.; Yang, H.; Qian, K.; Wang, X.; Chen, H. Fusion and transformation properties of the inorganic components in biomass ash. Fuel 2014, 117, 1281–1287.
(38) Fang, X.; Jia, L. Experimental study on ash fusion characteristics of biomass. Bioresour. Technol. 2012, 104, 769–774.
(39) Niu, Y.; Tan, H.; Wang, X.; Liu, Z.; Liu, H.; Liu, Y.; Xu, T. Study on fusion characteristics of biomass ash. Bioresour. Technol. 2010, 101, 9373–9381.
(40) Tran, H. N.; Mao, X.; Kuhn, D. C. S.; Backman, R.; Hupa, M. The sticky temperature of recovery boiler fireside deposits. Pulp Pap. Can. 2002, 103, 29–33.
(41) Skrifvars, B.-J.; Backman, R.; Hupa, M.; Sfris, G.; Åbyhammar, T.; Lyngfelt, A. Ash behaviour in a CFB boiler during combustion of coal, peat or wood. Fuel 1998, 77, 65–70.
(42) Eriksson, G.; Hack, K. ChemSage - A Computer Program for the Calculation of Complex Chemical Equilibria. Metall. Trans. B 1990, 21, 1013–1023.
(43) Miller, S. F.; Miller, B. G. The occurrence of inorganic elements in various biofuels and its effect on ash chemistry and behavior and use in combustion products. Fuel Process. Technol. 2007, 88, 1155–1164.
(44) Link, S.; Yrjas, P.; Hupa, L. Ash melting behaviour of wheat straw blends with wood and reed. Renewable Energy 2018, 124, 11–20.
(45) Pang, C. H.; Hewakandambay, B.; Wu, T.; Lester, E. An automated ash fusion test for characterisation of the behaviour of ashes from biomass and coal at elevated temperatures. Fuel 2013, 103, 454–466.
(46) Saidur, R.; Abdelaziz, E. A.; Demirbas, A.; Hossain, M. S.; Mekhilef, S. A review on biomass as a fuel for boilers. Renewable Sustainable Energy Rev. 2011, 15, 2262–2289.
(47) Link, S.; Arvelakis, S.; Paist, A.; Hupa, M.; Yrjas, P.; Külaots, I. Effect of leaching pretreatment on the char reactivity of pyrolyzed wheat straw. The 17th European Biomass Conference and Exhibition; 2009, pp. 1113–1121.
(48) Link, S. Reactivity of Woody and Herbaceous Biomass Chars; PhD Thesis. TUT Press: Tallinn, 2011.
(49) Uibu, M.; Tamm, K.; Viire, R.; Reinik, J.; Somelar, P.; Raado, L.-M.; Hain, T.; Kuusik, R.; Trikkal, A. The composition and properties of ash in the context of the modernisation of oil shale industry. Oil Shale 2021, 38, 155–176.
(50) Arvelakis, S.; Jensen, P. A.; Dam-Johansen, K. Simultaneous Thermal Analysis (STA) on Ash from High-Alkali Biomass. Energy Fuels 2004, 18, 1066–1076.
(51) Ma, X.; Ma, H.; Yuan, J.; Guo, R. Synthesis of K2O–MgO–SiO2 compounds as slow-release fertilisers from acidleached biotite residues. Ceram. Int. 2020, 46, 1403–1410.

(52) Wang, J.; Wie, B.; Li, X.; Yang, W.; Zhang, C.; Mian, I.; Tan, H.; Ma, F. Study on reduction characteristics of Fe species in coal ash under SNCR condition. Fuel 2020, 277, 118231.

(53) McLennan, A. R.; Bryant, G. W.; Stanmore, B. R.; Wall, T. F. Ash Formation Mechanisms during pf Combustion in Reducing Conditions. Energy Fuels 2000, 14, 150–159.

(54) Huffman, G. P.; Huggins, E.; Dunmyre, G. R. Investigation of the high-temperature behaviour of coal ash in reducing and oxidizing atmospheres. Fuel 1981, 60 (7), 585–597.