Research paper

The impact of aluminosilicate-based additives upon the sintering and melting behaviour of biomass ash

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ABSTRACT

The composition of ash arising from biomass combustion can cause significant slagging and fouling issues in pulverised-fuel boilers, particularly if high concentrations of alkalis are present. Al–Si additives have shown promise in improving the ash deposition characteristics of troublesome biomass, converting volatile potassium to potassium aluminosilicates. This article presents results of lab-scale testing for two high-potassium biomass ashes, olive-cake (OCA) and white-wood (WWA), combined with two promising additives, coal pulverised fuel ash (PFA) and kaolin powder, at 5% mass fraction. Ash fusion testing results show that the use of these additives consistently increases flow temperatures. For WWA, kaolin was observed to reduce deformation temperatures and increase flow temperatures to far above combustion temperatures. Sinter strength testing showed that additive use significantly improves the deposition properties of OCA, preventing the precipitation of KCl and formation of deposits that are highly undesirable for removal via sootblower. Sintering was eliminated at all temperatures measured with the use of kaolin. Both additives had negative effects upon the sintering of WWA, indicating that Al–Si additive use should be restricted to high K, high Cl biomass. High temperature viscometry of OCA, combined with thermodynamic modelling, showed that viscosities at combustion temperatures were far below ideal values due high Mg concentration and silicate formation. Kaolin at 5% mass fraction was predicted to significantly improve this behaviour, with aluminosilicate formation producing favourable viscosities. Results indicate that kaolin addition to high K, high Cl biomass such as OCA shows promise in making the ash compositions viable for pulverised-fuel combustion.

1. Introduction

Biomass is increasingly being used to replace coal in many commercial and industrial applications such as power generation. Compared to coal, biomass often contains high levels of organically-bound inorganic species that are crucial to the growth and metabolism of the biomass source, such as K, Ca, P, Fe, S and Cl. Many of these species are released in the vapour phase during combustion, later condensing and producing solid ash. Alkali and alkaline earth metals are particularly troublesome: they may react with silica in the ash, producing eutectics that have initial melting temperatures far below typical combustion temperatures, such as potassium silicate (600–980 °C) and potassium-sodium silicate (540–1170 °C) systems [1].

Such low temperature systems will result in molten or sticky ash particles that agglomerate, impact or condense upon heat transfer surfaces, reducing the efficiency of the boiler. Volatilised alkali metals from biomass with high Cl content can produce hydroxides and carbonates that, in turn, react with HCl in the flue gas to form alkali chlorides [2].

While alkali chlorides have low melting temperatures of ~800 °C and are significant fluxes in certain systems [3], the most significant impact of chlorides in combustion applications is the corrosive tendency of chlorine. Metal chlorides can react with SOx in the flue gas, producing Cl and HCl local to the boiler heat-exchange surfaces, forming additional chlorides [2]. Where chlorides contact exposed steel, $FeCl_2$ may form, resulting in chlorine regeneration through a process termed active oxidation [4], which significantly accelerates

corrosion.

Studies have been published on the use of additives to fuel [5–8] as a method of altering the composition of ash produced during combustion. Additives improve the behaviour and rate of deposition by reducing the concentration of problematic species in the ash and increasing the melting temperature of the ash systems that form [9]. Aluminosilicate (Al–Si) additives have shown a strong ability to convert vapour and liquid phase KCl and $KSiO_3$ to higher melting temperature potassium aluminium silicates [10], binding the potassium within the ash. This subsequently significantly reduces the presence of KOH and KCl within the flue gas, in turn preventing the production of alkali chlorides through interactions with HCl and subsequent corrosion via active oxidation. These reactions typically occur in and around the combustion zone, reducing the formation of fine particles and water-soluble alkali metal salts [10]. The prevention of alkali metal volatilisation early in combustion prevents the regenerative process for gaseous chlorine from occurring.

One issue that arises with the use of additives in pulverised fuel combustion is the increased cost associated with obtaining the additives. Additives that have been shown as effective in literature, such as kaolin or limestone, are often not readily available to power stations and must be sourced externally. As a result, there is strong interest within industry of the potential of coal pulverised fuel ash (PFA) as an additive, as PFA is readily available to many converted power stations with minimal cost. Although coal ash compositions can vary significantly depending upon the type of coal, some coal ash compositions can contain significant concentrations of SiO_2 and Al_2O_3, and may have potential as aluminosilicate-based additives.

The purpose of this study was to determine the effect of a high Al–Si coal PFA in improving the ash sintering and melting properties of biomass fuels of interest to large scale biomass generation. Kaolinite has been shown to be an effective additive in previous studies [7,10,11], and is used in this study to provide a benchmark additive against the coal PFA. Samples were subject to experiments across a range of temperatures in order to provide a clear picture of ash melting behaviour and the impact of additives upon ash melting behaviour at both fouling/melting and slagging/flow temperatures.

2. Material and methods

2.1. Ash characterisation

The coal PFA investigated as a potential additive within this study was sourced from a large-scale pulverised fuel power plant (UK) using coal from La Loma coal mine (Colombia). This particular PFA was selected due to its high aluminium and silicon content, giving it a similar oxide composition to other previously tested Al–Si-based additives within literature. The ash of two solid biomass fuels were derived from: industrial fuel pellet produced from European olive residues – here referred to as olive cake ash (OCA) and; ISO 17225–2:2014 grade I2 industrial fuel pellet – here referred to as 'white wood' pellet ash (WWA). These were both provided by UK power stations. The biomass species and cultivars cannot be specified and provenance and chain of custody information cannot be provided beyond the previous descriptions. The authors believe that this work exemplifies the behaviour of ash with additives. However, it is recognised that variability of such materials may hinder exact reproduction of the work presented.

A second additive, kaolin powder (KAO), supplied by Sibelco (Devon, UK) was selected for comparison purposes. The composition of the samples in this study are shown in Table 1.

The OCA was produced in the lab directly from the 'as received' biomass fuel while the WWA was produced in an external lab. All ash was produced according to BS EN ISO 18122:2015 at 550 °C. PFA and KAO were analysed as received. Moisture and carbon analyses were determined using BS EN ISO 18134:2019 and BS EN ISO 18122:2015. The ash compositions were determined through ICP analysis.

Table 1

Ash composition mass fraction of samples (MOx mass fractions in ash given on dry basis).

Ash Component (%)	Coal PFA	Kaolin	Olive Cake	White Wood
Ash mass fraction (dry fuel)	–	–	9.87	1.20
Moisture in ash (a.r.)	0.48	12.3	0.52	0.26
Carbon in ash (d.b.)	2.79	11.6	1.54	1.43
SiO_2	58.2	48.3	11.2	27.1
Al_2O_3	20.8	36.4	1.2	4.6
Fe_2O_3	9.3	0.9	0.9	2.3
TiO_2	0.9	0.06	0.1	0.3
CaO	2.9	0.04	10.3	24.8
MgO	1.4	0.4	3.0	4.7
Na_2O	2.3	0.06	0.6	1.5
K_2O	1.7	2.6	32.3	9.2
Mn_3O_4	0.1	–	0.1	1.5
P_2O_5	0.2	–	5.0	2.0
SO_3	0.9	–	2.4	1.6
Ash Preparation	As Received	As Received	Lab @ 550 °C	Lab @ 550 °C

The OCA and WWA samples were chosen for study due to their high potassium concentrations which is a subject of interest in this study. Olive cake also contains significantly greater chlorine (0.24% mass fraction of as received fuel) when compared to the white wood pellets (< 0.01% mass fraction of as received fuel) which is also of interest. Sample preparation showed behaviour consistent with the presence of KCl in the form of sylvine, as indicated by XRD and SEM-XRF analysis.

A fixed blend rate of 5% mass fraction of additive to biomass fuel was chosen for study since this is commensurate with additive rates in commercial operations. Since the WWA was supplied already as ash, to maintain consistency OCA samples were also converted to ash before being mixed. It was not possible to subject KAO to the same method of preparation, since kaolin dehydrates at temperatures similar to those used for ashing, producing amorphous metakaolinite. Instead, the KAO was dried at 120 °C for 24 h before mixing, to remove residual moisture. The ashes were blended at the ratios shown in Table 2, placed into containers and shaken vigorously to produce a homogenous sample. The calculation used to determine the ash content mass fraction required to simulate a biomass-additive blend is as follows:

$$\frac{\% \, dry \, fuel * dry \, fuel \, ash \, content}{(\% \, dry \, fuel * dry \, fuel \, ash \, content) + \% \, additive}$$

Afterwards, the mixtures were heated to 650 °C, to produce an ash that was representative of expected biomass-additive compositions.

Particle size distributions of each sample were determined using a Malvern 2000E Mastersizer laser diffraction granulometer. The diameter of the particles is known to have an effect upon the rate of sintering of a sample: smaller particles tend to sinter at lower temperatures due to the higher free energy resulting from greater surface curvature [12]. The average distribution from 10 experiments was used: these distributions are shown in Fig. 1. KAO displayed a significantly greater proportion of < 1 μm particles compared to the other samples. OCA and WWA showed distributions that are similar to PFA, indicating that they are representative of an ash from a large-scale boiler.

Table 2

Sample ash to additive concentration at a blend rate of 5% mass fraction to dry fuel.

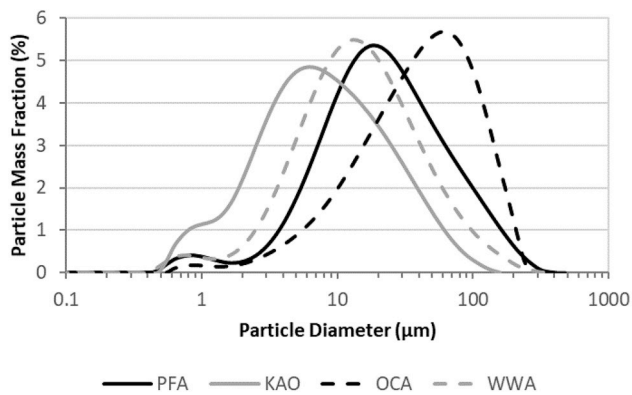|	
OCA	0.65
Adtv.	0.35
WWA	0.19
Adtv.	0.81

Fig. 1. Particle size distribution of samples.

2.2. Ash fusion testing

Ash Fusion Testing was conducted according to ASTM D1857. The samples were prepared using a water with 10% dextrin solution as a binder, as per the standard method. The solution was added in drops, to minimise leaching and to prevent the mixture from becoming too fluid. The samples were formed into cylindrical shapes in a mould and then air-dried overnight. These samples were then heated at a rate of 5 K/min inside a Carbolite digital ash fusion furnace equipped with a greyscale camera to capture images at 5 K intervals. Tests were performed under oxidising conditions. In an extension to the standard ash fusion test procedure, which literature has shown to be limited and prone to error [13], the height of the pellets was recorded for every image taken throughout testing rather than at specific points in the changing sample morphology, as suggested by Pang et al. [13].

2.3. Sinter strength testing

The sinter strength is defined as the compressive force required to propagate a fracture through the geometry of a pre-melted pellet. This gives an indication of the strength of an ash deposit at the sintering temperature used to prepare the pellet. Sinter strength compression testing is typically based upon the methodology devised by Barnhart [14]. The aim of sinter strength testing is not to simulate deposit removal via sootblowing, where sintered deposits are removed when the peak impact pressure (PIP) of the sootblower is greater than the compressive strength of the deposit. This occurs during boiler operation at high operating temperatures and it is difficult to recreate in a laboratory setting. Rather, the aim is to quantify the extent of sintering present at a given temperature, which is typically due to the presence of liquid phase within the deposit which accelerates the sintering process. The effects of sintering remain apparent after cooling to room temperature, and so it was possible to use room-temperature characterisation and mechanical testing as indicative of the effects of sintering on deposit strength. It should also be noted that other methods of deposit shedding exist (for instance fast-growing deposits can shed naturally under gravity, where both deposit bond strength with the substrate and shear strength are of importance), and as such compressive strength alone is not sufficient to fully quantify deposit durability.

Test pieces were formed from 1.0 g (± 0.1 g) of sample material pressed into cylindrical pellets using a 10 mm die and a SPECAC hydraulic press. Unlike in ash fusion testing, dextrin was not used in the pellet-making process for sinter strength testing. A compression pressure of 1.73 MPa was selected as literature shows that this best simulates typical boiler deposits [15]. The pressure was applied gradually in order to produce a uniform pellet and avoid the need for additional pressure. In the case of friable pellets, deionized water was added in concentrations of approximately 10% mass fraction to produce pellets strong enough to handle. Triplicate test pieces were produced for each

sample material.

Once pelletised, the samples were placed on ceramic tiles, inserted in a muffle furnace and heated at a rate of 5 K/min. The slow heating rate was required to avoid thermal shock and structural damage within the pellet. Target temperatures of 800, 850, 900 and 950 °C were used, with a dwell time of 3 h. These temperatures are considerably lower than the combustion zone temperatures of typical PF boilers (1100–1300 °C). However, across the convective heat transfer sections of such boilers, the gas temperatures typically range from 1100 °C at the inlet to < 500 °C at the outlet. At the end of the dwell time, the furnace was switched off and the pellets were allowed to cool slowly via convection, again to avoid thermal shock. Some tendency for the pellets to adhere to the ceramic tiles used during sintering was observed, most noticeably OCA samples. To minimise any resulting thermal stresses during cooling, pellets were furnace cooled to produce a relatively low cooling rate. Pellets with visible failures after sintering were disregarded.

The compression strength of the pellets was measured using a H10KS Tinius Olsen tensile strength machine with a modified compression cage, using a moving load speed of 5 mm/min. The pellets were left on the ceramic tiles during testing, since removal of adhered pellets could potentially compromise pellet strength. Compression strength in MPa was recorded for every 1 μm displacement producing a compression profile for each pellet from which the peak pressure was taken. After peak strength was reached, measurements were programmed to stop recording at 50% of the peak compression strength. Experiments were repeated in triplicate, with average values and errors reported.

2.4. Viscosity testing

As noted within the introduction, the presence of alkali compounds and salts within the fuel can produce ash with melting temperatures far below those encountered within the combustion zone of the boiler, often resulting in a running slag. At temperatures of 1093 °C and above, the viscosity of the slag is the primary physical property [16], affecting both the flow behaviour of the slag and the nature of the resulting deposit. As a slag deposit cools, solid crystalline phases begin to form within the deposit at a temperature known as the critical viscosity (T_{cv}): this T_{cv} is dependent upon the composition of the slag. At temperatures above T_{cv} the slag behaves as a Newtonian fluid, where the measured viscosity is independent of the shear rate [17]. In order to determine the viscosity of ashes within this temperature region, high temperature viscometry is required.

Biomass ashes require pre-treatment before being subjected to viscosity experiments due to the high concentration of alkali metals, chlorine and sulphur present. This is necessary partly because viscosity measurements are only useful if ash compositions are representative of compositions found in biomass slags. Temperatures in areas where slags are formed are high enough to volatilize many alkali species and stimulate silicate melting. Another reason for pre-treatment is to remove alkali metals and alkali chlorides which can cause damage to the instrument's platinum crucibles and sensor materials.

Since a platinum crucible was also used for sample fusing, heating the samples to remove alkali salts was not possible as alkali salts such as potassium chloride will aggressively react with platinum. There is also a risk of residual or condensed alkali salts being retained in the sample which is considered too great for high-temperature viscometry. Instead, washing samples of ash produced at standard biomass ashing temperatures of 550 °C is required to remove many of the salts before chemical reactions can occur. However, since Al–Si additives react primarily with KCl and $KSiO_3$, this would remove these troublesome species during washing, resulting in non-representative ash compositions. To account for this, the ashes were reheated to 800 °C in a separate furnace for 3 h to stimulate chloride precipitation and initiate melting, before being subjected to repeated washes in a beaker at a

ratio of 30 g ash to 300 ml deionized water. The beaker was placed onto a hot-plate stirrer at 125 °C for 1 h, with a stirrer bar set to 10 Hz (600 rpm) to agitate the sample. The sample was removed and allowed to both cool and settle within the beaker before filtering using qualitative filter paper with an 11 μm pore size. Part of the remaining wash water was then filtered using a syringe filter with pore size 0.45 μm. The wash-water was then analysed by ion chromatography for the determination of removed potassium and chlorine. This was repeated five times for both samples. Finally, any residual carbon within the ash was removed by decarburising the ash at 700 °C for 16 h.

Viscosity measurements were conducted using a Bahr VIS 403HF high temperature rotational viscometer. The washed samples were fused at temperatures of 1450 °C in a platinum-gold crucible, to increase the density of the ash. 24 g of fused sample was then placed into the viscometer cup, which was situated inside a furnace capable of temperatures up to 1500 °C. The sample was gradually heated up to a target temperature at which the sample was observed to become molten. This peak temperature was held for 10 min to allow the sample to heat fully and reach equilibrium. The viscosity was then measured by recording the shear stress and shear rate of a bob immersed in the molten ash rotating at 5 Hz (300 rpm), as the temperature was cooled at a controlled rate of 10 K/min. The samples were gradually cooled towards T_{cv}, where slag behaviour transitions from Newtonian to non-Newtonian behaviour and the shear stress becomes dependent on the shear rate [16]. This transition is observed as a sharp increase in the apparent viscosity of the sample due to the formation of crystalline phases, at which point the experiment must be halted to prevent damage to the equipment.

3. Results

3.1. Ash fusion test

The AFT height profiles for both OCA and WWA are shown in Fig. 2. For the OCA, it is observed that a severe initial deformation starts at approximately 900 °C. For the WWA, it is observed that deformation starts at 1100 °C. Both samples showed onset of severe melting at 1300 °C, indicating that *critical viscosity* was reached, and a flowing slag would be present at this temperature.

The height profiles for samples of OCA with additives included (for 5% blending ratio) are shown in Fig. 3a. It is observed that the additives increase the temperature of initial deformation, with an increase of ~120 °C observed with PFA and ~220 °C with KAO. Flow temperatures also increased substantially with KAO addition (~200 °C) compared to PFA which increased the onset of severe melting by approximately 30 °C. These results indicate that the use of both additives has a useful effect upon OCA melting behaviour during combustion, with KAO being most effective.

Additive use with WWA had mixed results regarding the effects on the AFT. The AFT profiles for WWA with both PFA and KAO are shown
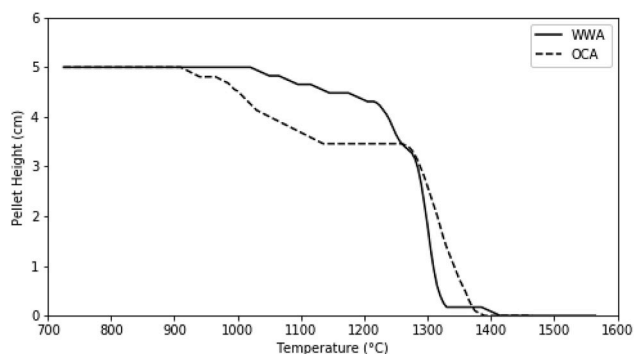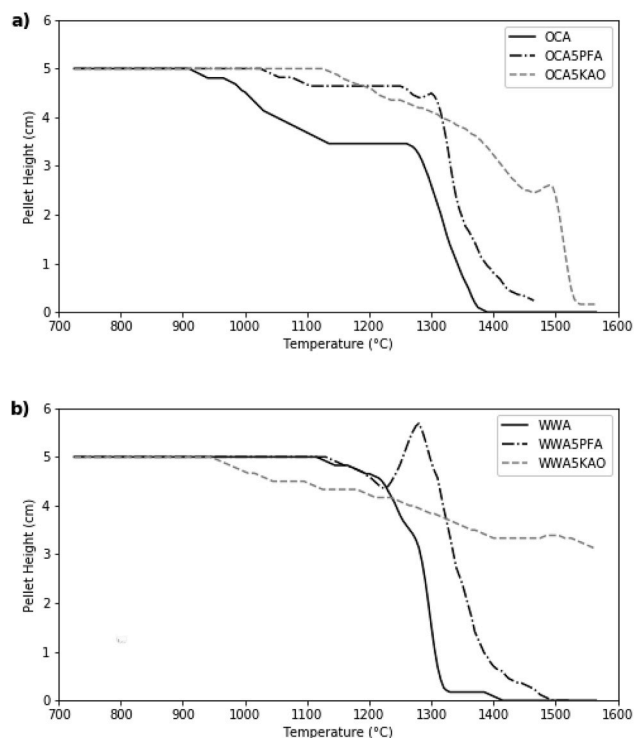

Fig. 3. Comparison of a) OCA AFT height profile with height profile of 5% PFA (OCA5PFA) and 5% KAO (OCA5KAO) addition and b) WWA AFT height profile with height profile of 5% PFA (WWA5PFA) and 5% KAO (WWA5KAO) addition.

in Fig. 3b. The use of 5% PFA had no effect on initial deformation temperatures, while the addition of 5% KAO reduced IDT by over 200 °C. The additives had a greater impact on flow temperatures when used with WWA compared to OCA, with 5% PFA increasing WWA flow temperatures by approximately 100 °C. 5% KAO increased flow temperatures to above the limit of the AFT furnace (greater than 1585 °C): hence, no flow was observed. Ash fusion temperatures are summarised in Table 3.

3.2. – sinter strength testing

Average peak compression strengths for OCA and OCA-additive blends are shown in Fig. 4a. A compression strength of 5 MPa has been defined in the literature as the strength corresponding to a boiler deposit that would be difficult to remove by means of soot-blowing [15]; this value is highlighted on the sinter strength graphs. However, it should be noted that reported values for this vary widely in the literature: the original Barnhart experiment used a much greater limit of 34.8 MPa [18]. However, the Barnhart experiment was conducted on coal ashes produced at high temperatures, thereby removing volatile compounds that could potentially induce sintering within the sample. The Gibb study was conducted upon coal ashed at 550 °C, and therefore accounts for sintering behaviour caused by volatilisation: this is more important for biomass samples, given the increased volatile alkali

Fig. 2. Comparison of OCA and WWA AFT height profiles.

Table 3
Ash fusion testing temperatures for ST, HT and FT, in °C, with errors.

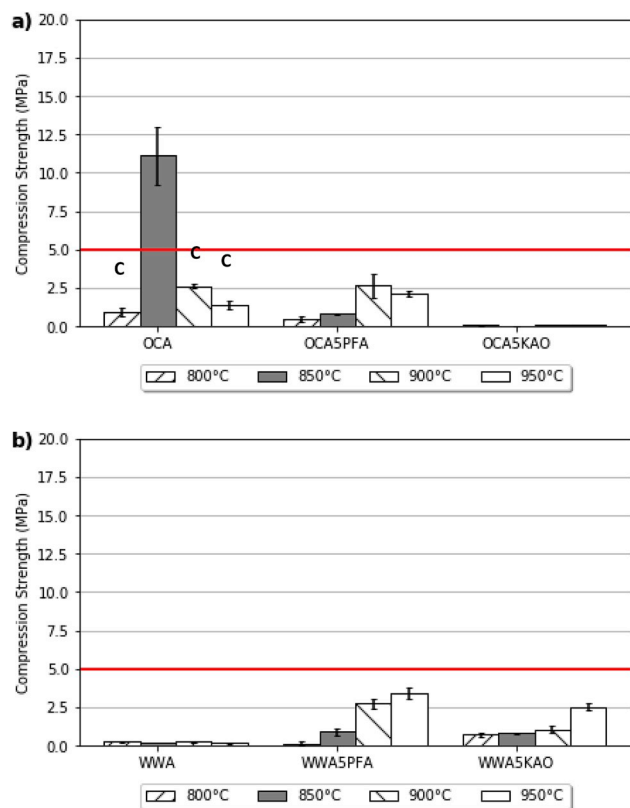| AFT (°C)	IDT		HT		FT	
OCA	935	± 10	1290	± 5	1325	± 5
OCA5%PFA	1027.5	± 5	1325	± 5	1360	± 5
OCA5%KAO	1135	± 10	1445	± 5	1500	± 5
WWA	1075	± 40	1275	± 5	1290	± 5
WWA5%PFA	1130	± 5	1320	± 5	1375	± 5
WWA5%KAO	927.5	± 25	–		–	

Fig. 4. Comparison of peak compressive strengths for a) OCA and OCA with 5% PFA (OCA5PFA) and 5% KAO (OCA5KAO) addition; and b) WWA and WWA with 5% PFA (WWA5PFA) and 5% KAO (WWA5KAO) addition. The red horizontal line represents the 5 MPa sootblowing limit. Pellets displaying compressive behaviour, and therefore giving unreliable peak strengths, are denoted by "C".

concentrations typically observed within the ash when compared to coal ashes. As this is the standard ashing temperature for biomass, the Gibb value has been chosen.

OCA showed a marked increase in sinter strength at dwell temperatures of 850 °C, well above the 5 MPa soot-blowing limit. Above this dwell temperature, the measured sinter strengths were observed to decrease with increasing temperature. This is in contrast with expectations in that sinter strength should increase with temperature, as higher fractions of liquid phase within the sample would lead to further sintering and increased compressive strength.

OCA samples showed different behaviour to the other samples investigated in this study. Pellets were observed to shrink significantly at temperatures of 850 °C and above due to the release of potassium chloride, resulting in a green hue. This release of KCl also resulted in abnormal compression behaviour. Rather than a clean fracture, as observed in sintered pellets (Fig. 5a), or powdery behaviour in non-sintered pellets (Fig. 5b), OCA samples at 850 °C and above failed to fracture. Instead, the pellets would compress and densify, resulting in further increases in sinter strength beyond the initial pellet break as shown in Fig. 5c. As a result, sinter strengths for pellets displaying this compressive behaviour are unreliable.

A significant consequence of this behaviour is that deposits of this type are likely to pose major difficulties for sootblower removal. Such deposits show plastic behaviour and measure little compression force, making them difficult to remove: rather than breaking the deposit, soot-blowing could instead densify and worsen the deposit [18].

The use of additives with OCA eliminated this plastic-like behaviour. Instead, the compression test produced clean fractures in the sample pellets – a more favourable behaviour for sootblower removal.

In addition, compression strengths were significantly reduced for samples produced at 850 °C for both PFA and KAO addition. This indicates that the use of the additives should improve deposition behaviour at such temperatures. 5% KAO eliminated all signs of sintering within the OCA pellets, whereas sintering was observed at 900 °C and above with 5% PFA addition. Both samples produced sinter strengths below the recommended 5 MPa limit for sootblower removal when used with OCA.

Compressive strength testing of WWA showed no indications of sintering at temperatures up to 950 °C (Fig. 4b). In contrast to the behaviour of additives with OCA, additives with WWA consistently resulted in increased sinter strengths compared to the case with no additive. The addition of 5% PFA resulted in lower sinter strengths at 800 °C when compared to 5% KAO, although sinter strengths increased for PFA use above 900 °C. Compressive strengths for all WWA samples and temperatures tested remained below safe limits, indicating that resulting deposits would be efficiently removed via soot-blowing. Compression strengths are summarised in Table 4.

3.3. Viscosity testing

Based upon AFT and sinter strength results, it was determined that KAO shows the most promise in improving the properties of OCA to acceptable levels. Therefore, OCA and OCA with 5% KAO addition was chosen for further study. XRF analysis of the washed samples (Table 5) showed that OCA5KAO had significantly greater potassium concentration than the washed OCA. This suggests that the KAO had effectively bound potassium during the 800 °C heat treatment prior to washing (please refer to section 2.4). As expected, the Al_2O_3 concentration was much higher at five times the level of OCA. OCA contained much higher proportion of CaO, MgO and P_2O_5, which are known to create fluxing effects in silicate melts.

A consequence of this difference in composition was that, at fusing temperatures of 1450 °C, the OCA5KAO sample failed to produce a flowing melt upon removal from the furnace. This made measurements in the viscometer impossible for the sample. Although potassium is a well-known fluxing component in silicate melts, the presence of Al_2O_3 produces potassium aluminosilicates with melting temperatures of up to 1500 °C. In contrast, OCA produced a low viscosity flowing melt at 1400 °C, enabling viscosity measurements.

Critical viscosity due to the onset of crystallisation was reached with OCA at approximately 1245 °C, as indicated by the change in gradient in Fig. 6. The test was stopped at 1225 °C due to significant solid phase presence, which disrupted flow as indicated by the increased noise present in the measurement. Bryers [19] uses a viscosity of 25 Pa s (T_{25}) as a slagging index. T_{25} at 1245 °C and below is considered to cause high slagging in dry bottom boilers: OCA reaches this value at approximately 1240 °C, indicating that significant slagging issues would be present.

As measurements were not possible for the OCA5KAO sample, the sample compositions from Table 5 were input to the FactSage software (v7.2) to predict the viscosity-temperature relationship. FactSage has a single-phase liquid slag model which directly relates the viscosity to the structure of the melt, and where the structure, in turn, is calculated from the thermodynamic description of the melt using the Modified Quasichemical Model [20]. There are two FToxid viscosity databases available for this purpose [21]. The database for melts is valid for liquid and supercooled slags of low viscosity (where ln [viscosity (Pa.s)] < 15), and hence was used for this calculation where measured viscosities are well below this value. As the model is strictly a single-phase predictive model, the model cannot predict the onset of T_{cv} and subsequent change in viscosity due to crystallisation. Therefore, predictions were conducted at temperatures > 1300 °C: above T_{cv} of the OCA sample.

Predictions were first compared to OCA results, to ensure that the model gives reasonable figures. Fig. 7 shows that FactSage prediction of OCA viscosity provides a good match with experimental results.
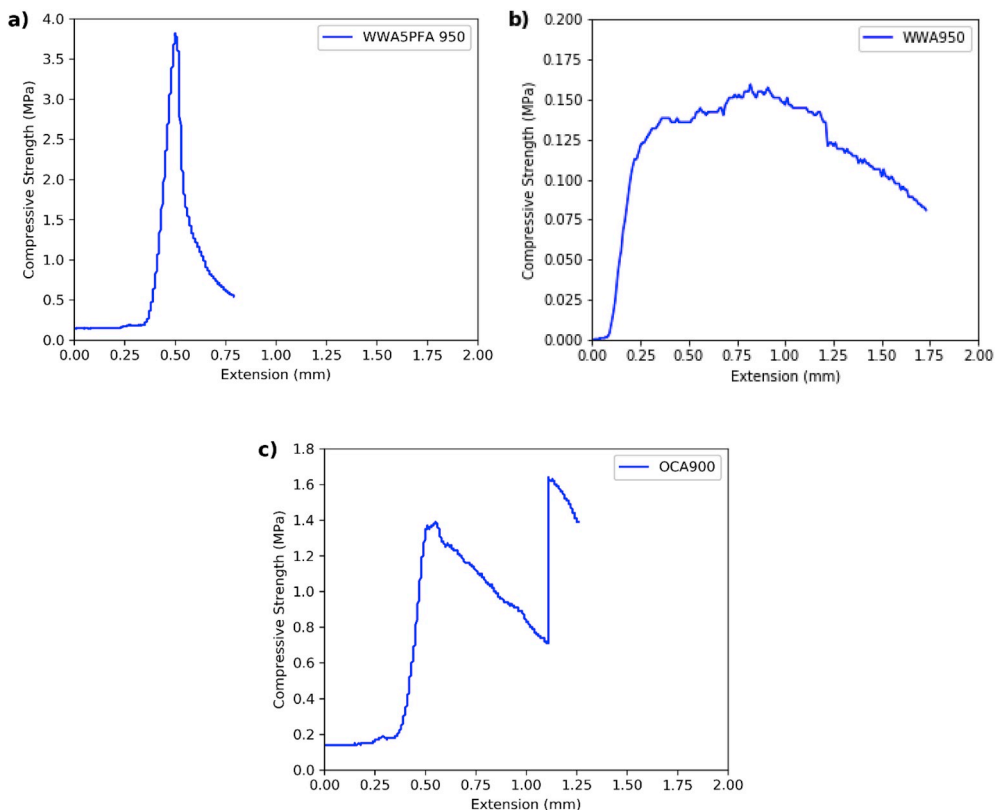
Fig. 5. Comparison of compression profiles for a) WWA with 5% PFA addition sintered at 950 °C, b) WWA sintered at 950 °C, and c) OCA sintered at 900 °C.

Table 4
Peak compression strengths for biomass and biomass-additive compositions, with compressive behaviour of samples included.

Samples	Temperature (°C)							
	800°C (MPa)		850°C (MPa)		900°C (MPa)		950°C (MPa)	
WWA	0.25	Powder	0.19	Powder	0.24	Powder	0.15	Powder
WWA 5% PFA	0.14	Powder	0.88	Sintered	2.73	Sintered	3.44	Sintered
WWA 5% KAO	0.70	Sintered	0.79	Sintered	1.06	Sintered	2.53	Sintered
OCA	0.93	Compress	11.09	Sintered	2.60	Compress	1.37	Sintered
OCA 5% PFA	0.47	Sintered	0.81	Sintered	2.65	Compress	2.09	Sintered
OCA 5% KAO	0.06	Powder	0.05	Powder	0.06	Powder	0.08	Powder

Table 5
XRF Analysis of washed ash samples used in viscosity studies, showing MOx mass fraction (%) in Ash.

Ash Component (%)	OCA5KAO	OCA
SiO_2	34.8	30.5
Al_2O_3	21.0	4.18
Fe_2O_3	3.34	3.02
CaO	10.2	30.8
MgO	5.29	14.2
K_2O	18.0	2.86
Na_2O	0.490	0.690
TiO_2	0.400	0.220
P_2O_5	5.300	14.2
Cr_2O_3	0.044	0.060

FactSage predictions for OCA5KAO viscosities indicated that viscosities would be increased substantially when compared to OCA, with T_{25} occurring at approximately 1600 °C. This indicates that optimal slagging conditions may be achieved with the use of KAO as an additive for OCA and similar compositions, assuming that T_{cv} has been reached by combustion temperatures.
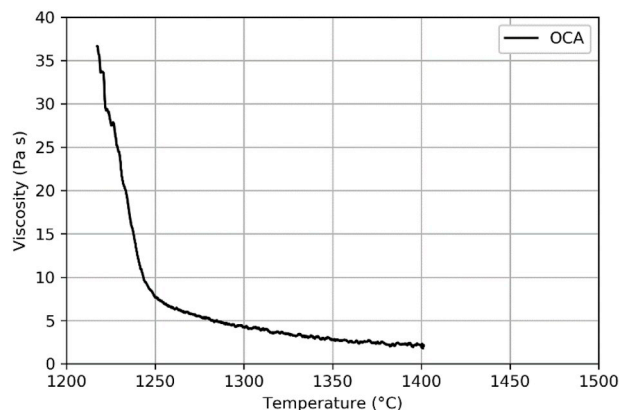

Fig. 6. Viscosity measurements for washed OCA.

4. Discussion

During experiments, OCA showed clear evidence of high concentrations of KCl developing within the sample during heating. KCl
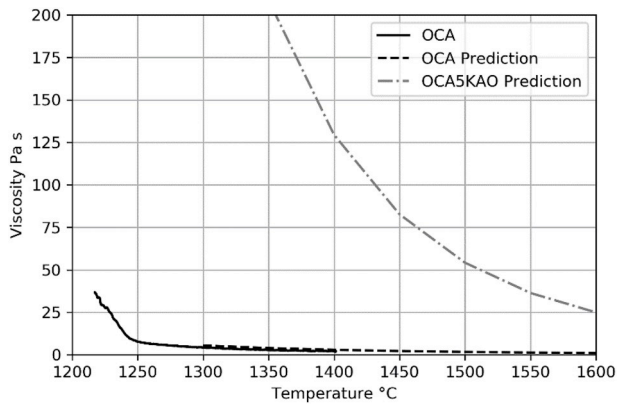
Fig. 7. Comparison of FactSage predictions for OCA and OCA5KAO with OCA viscosity measurements.

melting begins at temperatures as low as 770 °C [3], and was responsible for pellet shrinking and sintering during sinter strength testing and pellet deformation during ash fusion testing, both of which occur at similar temperatures as shown in Fig. 8a. The use of both additives prevented this deformation and sintering. XRF results of washed OCA samples (Table 5) showed that KAO use significantly increased potassium concentration at temperatures as low as 800 °C, indicating that the additives effectively converted KCl to silicates and aluminosilicates within OCA at these temperatures.

The washed OCA composition was analysed with MTData (Version 5.10), using the MTOX database from NPL v7.2. Phase equilibrium predictions (Fig. 9) indicate that a liquid phase mass fraction of greater than 30% begins to occur at temperatures of 1100 °C, coinciding with the formation of silicates such as olivine ($(Mg^{2+}, Fe^{2+})_2SiO_4$) and $\alpha CaSiO_2$. The onset of *critical viscosity* during experiments corresponds to an MTData mass fraction prediction of approximately 75% liquid
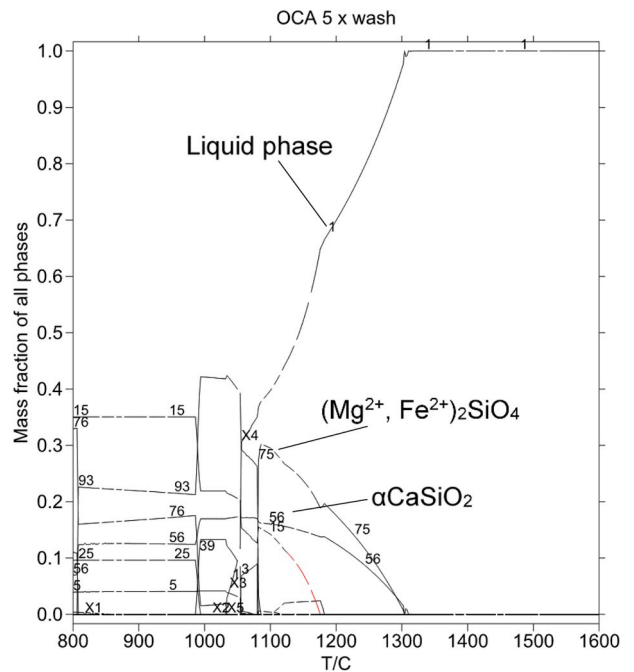

Fig. 9. MTData phase equilibrium predictions for washed OCA.

phase with 15% olivine and 10% $\alpha CaSiO_2$. It should be noted however that MTData corresponds to an equilibrium system, while viscosity testing inherently uses a dynamic system where the cooling rate has a direct effect upon crystallisation temperature.

KAO addition was observed to have a greater effect on sintering, pellet deformation and flow temperatures when compared to PFA. XRD analysis (Fig. 10) showed that the silicate compounds in PFA comprised mostly quartz (SiO_2) and mullite ($3Al_2O_3 \cdot 2SiO_2$ or $2Al_2O_3 \cdot SiO_2$). Mullite
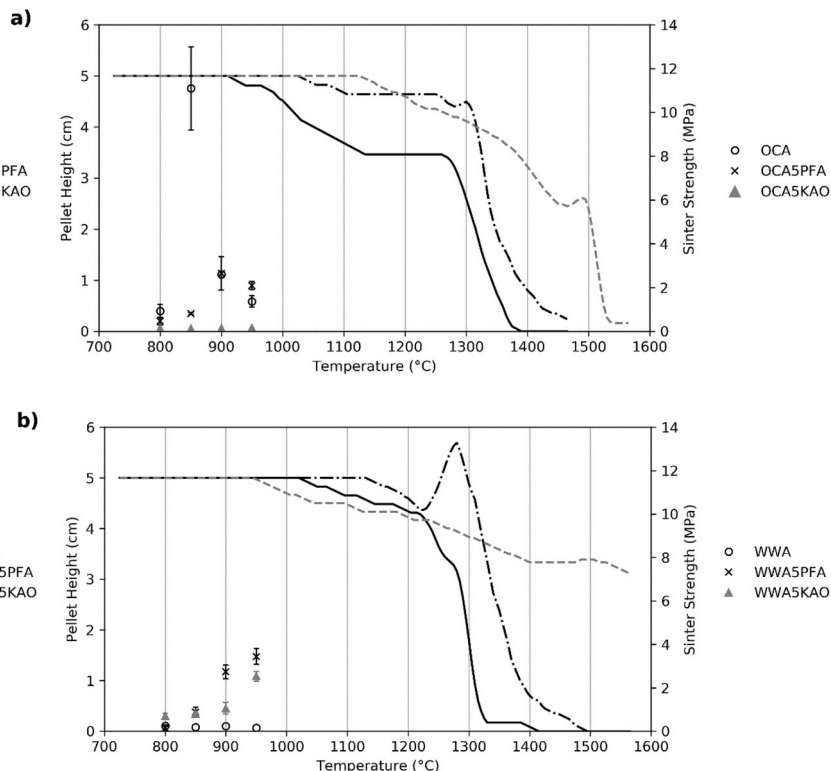

Fig. 8. Comparison of AFT height profiles (lines, left scale) and sinter strength compression testing results (dots, right scale) for a) OCA, OCA 5% PFA (OCA5PFA) and OCA 5% KAO (OCA5KAO) compositions; and b) WWA, WWA 5% PFA (WWA5PFA) and WWA 5% KAO (WWA5KAO) compositions.
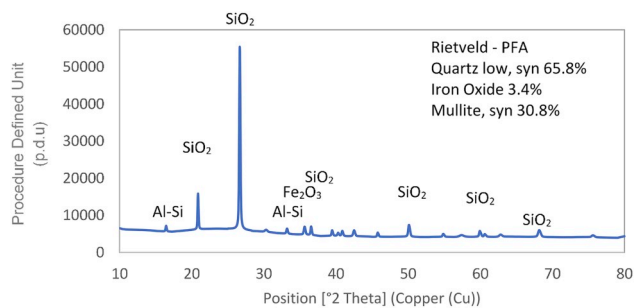
Fig. 10. XRD analysis of coal PFA additive, with selected peaks labelled.
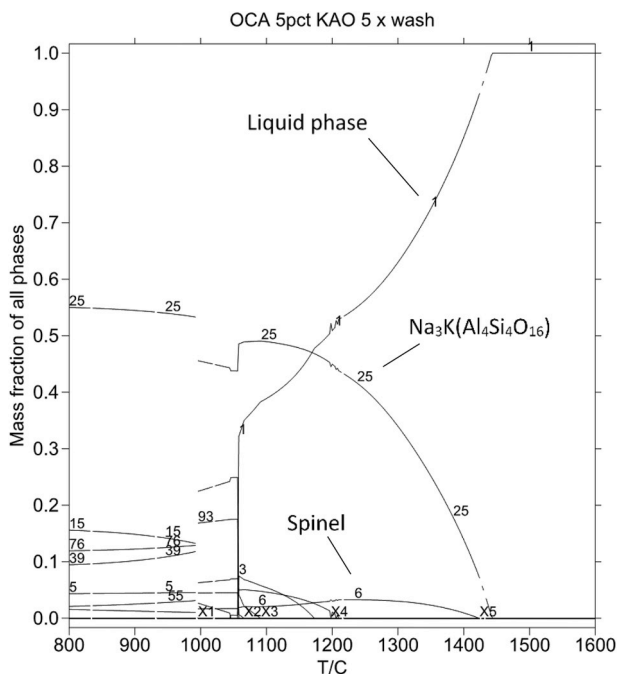

Fig. 11. MTData phase equilibrium predictions for washed OCA5KAO.

has been shown in literature to not react with KCl at temperatures up to 1300 °C [22]. As a result, much of the KCl released by the OCA sample reacted with the quartz coating the PFA particles, forming lower melting temperature potassium silicates rather than potassium aluminosilicates.

In contrast, KAO additive contains 70% kaolinite ($Al_2Si_2O_5(OH)_4$), which is known to favourably react with KCl to form potassium aluminosilicates. Kaolinite may convert to mullite at temperatures of above 1450 °C [23]; however, kaolinite has been shown to react with KCl at temperatures of 800 °C, converting kaolinite to potassium aluminosilicates before such phase changes can occur. This indicates that the mineral content of the additive is important in determining its effectiveness.

MTData results for the OCA5KAO composition (Fig. 11) corroborate this, indicating that a fully liquid phase would be expected at temperatures of 1450 °C and above. Nepheline ($Na_3K(Al_4Si_4O_{16})$) aluminosilicate formation rapidly occurs below this temperature, forming 20% solid phase at 1400 °C with a small mass fraction of aluminium spinel formation. T_{cv} of OCA5KAO would be expected to be at a similar temperature to this, based upon the mass fraction corresponding to T_{cv} of OCA and AFT height profiles.

However, additive use with WWA was shown to be less effective. Fig. 8b shows that, although 5% PFA addition increased deformation temperatures to above 1100 °C during ash fusion testing, sinter strength testing conversely showed that sintering was occurring at temperatures

as low as 900 °C. Deformation temperatures for WWA with 5% KAO addition corresponded well with the onset of sintering. The use of both additives instead resulted in increased sinter strengths at lower temperatures, indicating that fouling issues may be exacerbated with their use. Flow temperatures were increased with the use of additives: however, the use of KAO resulted in flow temperatures beyond the combustion temperatures of most biomass-fired boilers, which is undesirable. Such deposits will build quickly within the combustion zone due to higher viscosities and the presence of solid and crystalline phases, causing them to be prone to shedding events, potentially damaging refractory surfaces and nozzles. These results indicate that the effectiveness of Al–Si additives is dependent upon the potassium species formed during combustion, and that high potassium concentration alone is not a sufficient reason to use additives.

5. Conclusions

The effect of two aluminosilicate additives, coal PFA and kaolin powder, upon the melting behaviour of two high potassium biomass ashes, olive cake and white wood pellet, has been studied at a rate of 5% addition. Ash fusion testing indicated that the additives consistently increased the flow temperature of the ash compositions, with kaolin having a greater effect than the PFA. PFA increased deformation temperatures for both samples, but kaolin reduced deformation temperatures significantly when used with white wood.

Sinter strength testing showed that both additives significantly increased sintering of white wood ash at temperatures of 900 °C and above. Olive cake was observed to undergo severe sintering at 850 °C due to the sublimation of KCl, which would produce extremely difficult deposits for sootblower removal. Both additives significantly reduced sintering at this temperature, clearly inhibiting KCl release. Kaolin eliminated sintering in olive cake ash at all temperatures studied.

The strong performance of kaolin with olive cake ash prompted further studies of the effect of kaolin upon olive cake ash viscosity. Sample preparation confirmed that kaolin effectively binds potassium at temperatures of 800 °C, producing potassium concentrations of 5 times greater in the ash than without additive use. This was predicted to result in far greater viscosities at combustion temperatures, which would produce favourable slagging conditions. These results show that kaolin may be used to make troublesome biomass such as olive cake viable in biomass combustion. The performance of Al–Si additives was shown to be heavily dependent upon both the mineral composition of the aluminosilicates in the additives and the potassium species produced during combustion.

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