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The effects of an additive on the release of potassium in biomass combustion

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A R T I C L E I N F O

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A B S T R A C T

This study focuses on the effects of an aluminosilicate additive on the fate of potassium during biomass combustion. Such additives have shown some success in mitigating slagging and fouling problems in boilers and furnaces, and the mobility of potassium in combustion systems is one of the key factors dictating ash behaviour. To investigate this, a flame emission spectroscopy technique was used to evaluate the differences in the gas-phase potassium release profiles during the combustion of 5 mm diameter pellets of different biomass suspended in a methane-air flame. The biomass pellets were evaluated with various mixes of an aluminosilicate based additive (5, 15 and 25 wt%). Potassium emission detection, coupled with high speed video of the combustion process, indicated that potassium evolves over the three stages of volatile combustion (a sharp peak in the emission profile), char combustion (a broader peak) and "ash cooking" (a very broad peak over an extended period, long after the end of combustion). In the absence of additive, the three biomass studied (softwood, wheat straw, olive residue) behaved quite differently in terms of potassium release profiles. When the results are normalized for the amount of potassium in the fuel, it is clear that a large fraction of potassium enters the gas phase during the volatile and char combustion of the softwood. Olive residue, releases a lower fraction of potassium during the volatile and char combustion stages, indicating that more potassium is fixed in the ash. In contrast, wheat straw shows a release of potassium during combustion, and then, after a period of "ash cooking", a substantial gradual release with continued exposure to hot combustion gases. The difference in the emission profiles can be interpreted in terms of the K:Cl ratios and the K:(Si + Al) ratios: high chlorine and/or low (Si + Al) facilitates the release of KCl or KOH to the gas phase, while high (Si + Al) helps to fix K in the solid phase. The addition of the aluminosilicate additive shows a clear reduction in the potassium released from all the biomass pellets, particularly during the char-oxidation and "ash cooking" stages, and the level of additive required is related to the amount of K in the biomass. The potassium emission experiments were complemented by laboratory-scale preparation of ash at different temperatures, and detection of residual potassium in the ash using Atomic Absorption Spectroscopy (AAS). These results validated the findings and quantified the higher fractions of potassium retained within the ash when additives are used. For the wood ash 70–100% of K is retained in the ash in the presence of additive; for the wheat straw, this figure is 60–80% and for the olive pellets it is 70–100%.

1. Introduction

The combustion of biomass fuels for power generation results in the formation of major flue gas constituents and the partitioning of inorganic components, such as K, Na, Ca, P, Fe, S, N and Cl. These are present in raw biomass and can either be released into the vapour phase during combustion, or are retained in the solid phase as ash.

Potassium is an essential nutrient for plant growth and is present in higher quantities in most solid biomass fuels than in fossil fuels. Amounts of potassium present in biomass can vary substantially depending on the biomass type, for example the types of biomass used by this study: wood pellets, wheat straw and olive cake are typically composed of 0.1 wt%, 1 wt% and 3 wt% potassium, respectively [1]. Insight into the behaviour of potassium during the combustion of biomass fuels can be gained from an understanding of how potassium is associated within raw biomass. Small amounts (< 10%) of potassium in biomass fuels are bound to the organic structures within biomass such as hemicellulose, usually via hydroxyl or carboxyl groups or other oxygen containing groups [2,3]. These organic structures decompose during the low temperatures of volatile combustion (200–500 °C) [4–7] resulting in the potential release of potassium into the gas phase. The release is likely to occur in the form of potassium ions (K^+) in the gas

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which combines to form KCl (g) if the biomass K:Cl ratio is low, or as KOH (g) for higher K:Cl ratios [8]. The remaining potassium plays a key role in char formation [9–11] and some is released during the char combustion stage at temperatures above 600 °C [5,6,11–13], which can be described by an evaporation model [11–13].

Potassium is highly mobile in living biomass and is mostly present as free K^+ ions in solution within the xylem cells. However, during drying these ions precipitate as inorganic potassium salts (e.g. KCl, KNO_3) which make up more than 90% of the total potassium in raw biomass [14]. Since these species are soluble, the majority of potassium in biomass is extractable by water washing [15]. This, together with possible remobilization during plant senescence, accounts for the variability of potassium within different biomass. KNO_3 is known to dissociate at temperatures above 400 °C, whereas KCl is found to almost completely evaporate at temperatures between 780 and 950 °C [16]. Under the high temperatures of combustion, much of the inorganic and organic forms of potassium found in raw biomass are volatilised which can result in undesirable deposition and corrosion effects as they condense out on boiler surfaces, or result in ash deposition after rejoining with solid phase ash particles [17].

Work by Van Lith et al. suggested that any potassium that is not vaporised during the volatile combustion stage is most likely held in the solid phase as K_2CO_3 and KCl. The carbonates decompose in the higher temperatures of char combustion (> 850 °C), which may result in the formation of potassium in the gas phase, which again can react with OH or Cl to form KOH or KCl respectively [18]. Any potassium that remains in the solid phase after complete combustion will have typically reacted with other inorganic elements present in the ash to form minerals such as K_2CaSiO_4 and $KAlSi_3O_8$ [19]. Indeed, silicates have been shown to help “fix” the potassium in the ash as potassium silicates [5].

Additives are often used in power generation plant to abate the harmful effects from the formation of potassium species by various mechanisms; chemical adsorption, physical adsorption, increasing ash melting temperatures or preventing ash sintering [20]. This study will examine the effects of using a chemical adsorption additive (coal fly ash) on the release of potassium from different biomass. Coal fly ash is an aluminosilicate-based additive ($Al_xSi_yO_z$) which, owing to its abundant availability from conventional power plant, is a promising additive for power generation uses. It is reported that aluminosilicates react with the potassium chloride to create potassium-aluminum silicate (mineral) and hydrogen chloride which is governed by chemical kinetics and mass transfer constraints [21]. Many studies [22–24] have proven that coal ash additives high in Al or Si are effective at capturing potassium during biomass combustion, with the side-effect of increasing chlorine release. However there is some evidence of important impacts on the flue gas composition from the use of additives, namely increased SO_2 levels, reduced CO and increased ash deposition, but less KCl and K_2SO_4 present [23] and a less sintered deposit.

While the mechanism of action for aluminosilicate additives is known, the efficacy when used with different biomass types (and with varying contents of potassium and other inorganics) has been less studied. In addition, limited research has been published around the quantities of additives required to see the desired effects. However, some studies have found evidence of threshold ratios of additive to biomass ash, whereby further increasing the quantity of additive above this threshold value has been found to show no improvements in potassium capture [23,25]. This study will investigate (i) how the use of aluminosilicate additives affects the release of potassium for different biomass types, and (ii) varying levels of additive, in order to investigate the effects on potassium held in the solid ash phase. Two approaches are employed: Firstly, a novel in-situ flame technique developed by Mason et al. [26] is used to measure K-release profiles, complemented by high speed video interrogation of the combustion process; Secondly, complementary, more conventional laboratory studies, involving metal analysis of ash residues after ashing at different temperatures, are used to quantify the potassium partitioning. The combination of these methods will enable further investigation of the effects that additives have on the release of potassium at various combustion temperatures. Three different types of biomass are studied, wood pellets, wheat straw and olive cake. Each of these has very different contents of potassium and other inorganics, in order to gain insight into how the inorganic composition impacts on potassium release.

2. Experimental method

2.1. Biomass fuel and ash characterisation and sample preparation

Three types of biomass were selected for use in these experiments: North American white wood pellets; UK wheat straw; and European olive cake. These are representative of some of the different types of biomass used in large scale power generation. The additive used in this work is a pulverised coal fly ash from a UK power station. The fuels were characterized using a Carbolite AAF 1100 furnace and Carbolite moisture oven in accordance with the European Standard methods for the determination of moisture, ash, volatile (EN 18134–1, EN 18122, EN 18123) with fixed carbon content calculated by mass difference. CHNS content was determined using an EA1112 elemental analyzer in accordance with EN 16948. The results of the fuel and additive analysis are presented in Tables 1 and 2. Wheat straw and olive cake are both high in ash and chlorine content relative to the wood pellets. Table 2 reveals the high K and Ca content present in the ash of the three biomass types, and the high Al and Si content of the additive. Wheat straw is particularly high in silica and olive cake is very high in potassium (35 wt% K_2O in the ash). Note that a 5% mix of additive and raw biomass has ash ratios (on a mass basis) of 1:1, 1:0.16: and 1:1.6 for wheat straw, wood pellets and olive cake, respectively for ash produced at 550 °C.

The raw fuels were supplied in a variety of forms. In order to make consistent, suitably-sized single pellets for use on the combustion test rig described in Section 2.2, the biomass materials (20–60 mg) were pressed into 5 mm diameter pellets using a SPECAC hand press and die. To ensure good homogeneity, the samples were first ground to a fine powder (< 100 µm particle size), using a liquid-nitrogen cooled freezer mill prior to the blending of additive. After pressing, a fine hole (0.8 mm diameter) was drilled into the centre of each biomass pellet in order to enable the insertion of a needle (0.5 mm diameter) for securement of the pellet during experiments.

Ashes for atomic adsorption spectrometry (AAS) analysis of metals, and for the experiments described in Section 2.3. were produced using a large sample size (10–100 g) in a muffle furnace and a large inert stainless-steel tray in accordance with EN 18122. Carbon in ash weight percentages of the biomass ashes and additive blends generated were determined using an EA1112 elemental analyzer in accordance with EN 16948.

Ashes were digested in accordance with EN 16967 and metals were

Table 1
Fuel composition data.

Content	Basis	Units	Wheat straw	Wood pellets	Olive cake	Additive
Moisture	a.r.	wt%	10.4	7.3	6.8	0.4
Volatiles	a.r.	wt%	78.6	83.3	73.9	2.3
Ash	a.r.	wt%	5.1	0.8	8.1	96.9
Fixed carbon*	a.r.	wt%	5.9	8.5	11.3	0.4
Elemental						
C	daf	wt%	48.5	52.8	55.2	84.4
H	daf	wt%	7.3	6.7	6.9	3.1
N	daf	wt%	0.5	0.2	3.1	< 0.1
S	daf	wt%	0.05	0.02	0.14	9.7
Cl	daf	wt%	0.08	< 0.01	0.28	0.32

* By difference.

Table 2
Chemical analysis of major elements present in biomass ashes and additive used.

Parameter	Wheat straw (wt%)	Wood pellets (wt%)	Olive cake (wt%)	Additive (wt%)
SiO_2	66.2	16.6	11.2	58.2
Al_2O_3	0.2	2.5	1.2	20.8
Fe_2O_3	0.3	2.1	0.9	9.3
CaO	9.2	29.3	10.3	2.9
MgO	1.7	5.9	3.0	1.4
Na_2O	0.2	2.2	0.6	2.3
K_2O	11.0	10.0	34.8	1.7
MnO	0.1	2.1	< 0.1	< 0.1

measured via AAS (Varian AA240FS). Digested samples were analysed in duplicate and a coal ash reference material was used to validate and normalise the data gathered from this ash analysis technique, which was found to measure potassium with an accuracy of 0.18%.

2.2. Measurement of potassium release into the gas phase

Single particle combustion (SPC) experiments allow the opportunity to closely analyse the combustion of the small (5 mm diameter) biomass particles described in Section 2.1. The SPC apparatus used by this study is detailed further in previous articles [1] and enabled the study of K-release under relatively high heating rates (~85 degrees/s) and temperatures. The rig uses a stainless-steel needle to suspend a particle above a methane burner which is used to ignite the particle. Based on the principles of atomic emission spectroscopy (and assuming a steady temperature of the flame ~1600 K) a photodetector with an optical band-pass filter is used to measure the relative intensity of the strong electronic spectral emissions around 766 nm. This wavelength is characteristic of potassium and the detector signal then indicates the relative concentration of potassium atoms in an excited state present in the flame above the particle.

The effects of an additive on the potassium release were investigated by adding a measured weight percentage of the additive to the biomass pellets. Each sample biomass type and quantity of additive was repeated three times. A high-speed video camera (FujiFilm Finepix HS10 camera) was used to insure a consistent integrity of the biomass pellets was maintained and to interrogate the combustion events further. A high-speed thermal imaging camera (FLIR A655sc) was used to measure particle surface temperatures concurrent with K-release for the olive cake experiments.

2.3. Detection of potassium in solid phase

Experiments were also undertaken at lower heating rates by producing ashes of the blended biomass with additive. The method of ash generation (Section 2.1) utilised three stainless steel trays (approximately 300 mm length × 150 mm width) to spread the milled raw biomass over a large surface area prior to combustion in a Carbolite AAF 1100 furnace at 550 °C for 5 h. This method helped to minimize carbon in ash. Samples were weighed before and after ashing. Carbon analysis of the ashes from this procedure showed the carbon contents to be low – between 1 and 9 wt% for the raw biomass. The presence of additive was found to decrease the carbon-in-ash, over and above that expected by dilution.

The additive was mixed with the biomass in varying amounts (5 wt%, 10 wt% and 15 wt%) on an as received basis. Pulverised coal fly ash from a UK power station was used as the additive for these experiments. The ashes prepared at 550 °C were then heated in platinum crucibles at three different temperatures, namely 850 °C, 1000 °C and 1150 °C, for 1 h. The primary method used for analysis of the inorganics in the generated ash samples was atomic absorption spectroscopy (AAS) as described in Section 2.1.

2.4. Processing of recorded data

2.4.1. In situ flame measurements of potassium release

The single particle combustion rig used by this study uses two photodetectors to measure the radiative wavelength (766 nm) emissions associated with potassium release. An average of the three runs on each sample was taken and smoothed over 12 data points to remove noise from the recorded signal. The general procedure starts with a short (< 2 s) ignition delay, followed by the visible onset of a volatile flame and disappearance of this flame. Further information on the experimental set-up and identification of the combustion phases is detailed in previous work [26].

2.4.2. Analysis of ashed biomass and additive blends

Data acquired from the atomic absorption spectrometer for the measurement of potassium retained in the ash was recorded in parts per million. This is used to calculate an inferred potassium oxide (K_2O) weight percentage. An average of the duplicates was taken prior to accounting for the ash dilution effects of the additive. The combination of the additive with the biomass prior to ash generation will result a dilution effect on the biomass ash generated due to the high ash content (96% on an as received basis) of the additive. Data processing is further complicated by the change in ash yield with temperature. This is shown in Fig. 1. In line with previous thermogravimetric analysis (TGA), higher quantities of additive were found to result in lower levels of mass loss during combustion [27].

Thus, the ash contents of the additive and of the biomass samples were measured separately at elevated temperatures in order to calculate the equivalent mass of the biomass ash in accordance with Eq. (1). This was used to calculate the ratios of biomass ash to additive for the experiments with the biomass-additive blends; it assumes that the ash content of the biomass and additive is unchanged when mixed together before ashing.

$$(Biomass\ blend\ ash\ mass)_T = (Biomass\ ash\ mass)_T + (Additive\ ash\ mass)_T \qquad (1)$$

3. Results

3.1. Gas phase potassium release profiles of biomass fuels with additive

The potassium release (K-release) profiles for the three biomass fuels, each with varying amounts of additive are shown in Fig. 2. The combustion phases were clearly identified from the visual inspection of the high-speed video camera. Photodetector recordings were made for a period of 8 min and 20 s (500 s) in order to examine the potassium release behaviour of the remaining ash particle during the continued high temperatures after char burn-out – denoted “ash cooking”. In the case of biomass combustion for power generation, different combustion technologies have different residence times and fate of ash particles. Therefore, the length of time that particles are exposed to high temperatures can vary.

Examination of the K-release profile for the wood pellet, Fig. 2(a), shows a small rapid release during volatile combustion, followed by a slow increase in the potassium release rate until a peak that marks the end of char combustion. The K-release then slowly decreases during the “ash cooking” stage. This profile is very similar to the characteristic profiles for woody biomass found in previous work using this method [1]. Addition of the additive has a profound effect: While the potassium release during the volatile combustion stage shows a small reduction, the rate of potassium evolving during the char combustion stage reduces very significantly, and is, in fact, reduced almost to zero, at high additive loadings. Similarly, there is no K-release during “ash cooking” except for a small fraction with the 5% additive.

The K-release profiles for the wheat straw pellets are shown in Fig. 2(b). The profile of the raw fuel is very different to that observed for the white wood; there is a rapid release of K during volatile

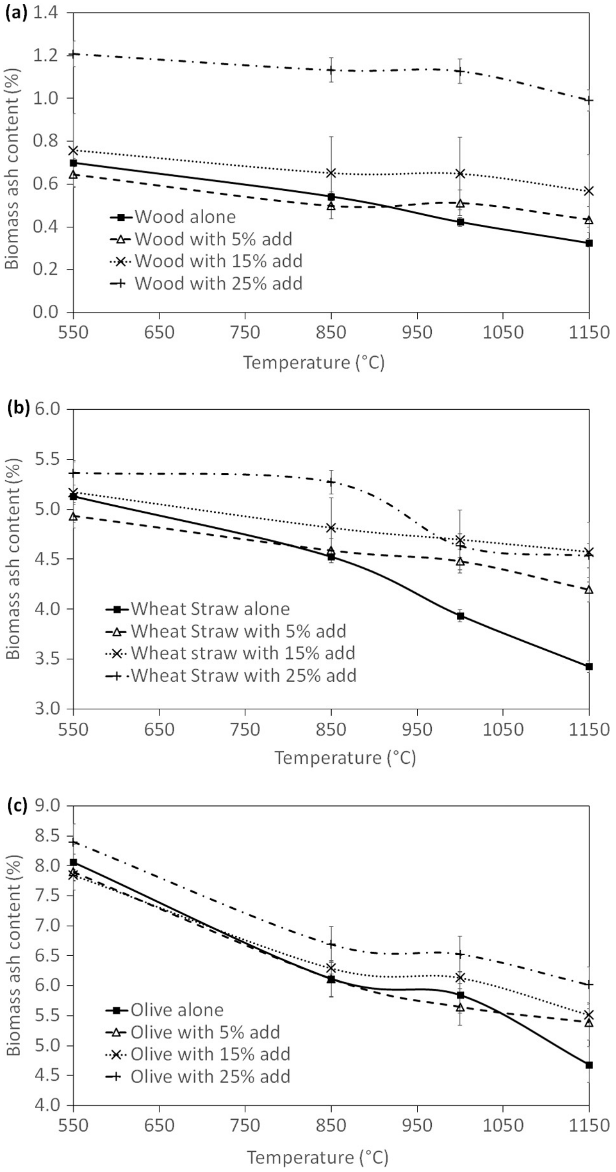

Fig. 1. The variation of ash content with temperature for (a) wood (b) wheat straw and (c) olive cake.

combustion, but the profile during char combustion is quite different, and K-release increases slowly until peaking near the end of char combustion. The wheat straw pellets have a notably longer release of potassium after char burn-out which is seen to increase to a later peak during an "ash cooking" phase of the experiments. The "ash cooking" stage sees some disintegration of the ash residue, but not complete, and thus evolution of K during this stage indicates transformation of minerals under high temperature conditions with concomitant evaporation of potassium salts; the profile also suggests that there are significant quantities of potassium in ash after the char burnout. Interestingly, this part of the profile is almost completely absent when additive is mixed with the wheat straw, and there is a slight reduction in the peak in potassium release during the volatile combustion stage. Thus, the higher amounts of additive can be seen to prevent potassium release after char burn-out and maintain this low release rate during the "ash cooking" stage which could be very important within a biomass boiler. Ash deposits that are more stable will release less potassium even if they are held at high temperatures.

Olive cake, has the highest potassium content of all three fuels, and shows the largest K-release profile of the raw biomass as presented in Fig. 2(c). The profile shows overlapping peaks for K-release from volatile combustion and char combustion, but the profile is dominated by K-release during char combustion. Increasing amounts of the additive dramatically decrease the potassium release rate, particularly during this char combustion stage. After the peak in potassium release rate associated with combustion, a characteristic slow decrease in release rate is seen during the "ash cooking" phase. Interestingly, K-release from the pellets with additive during this stage seems to plateau at lower signal intensity for the 15 and 25% additive blends. This implies that the additive is fixing potassium in the ash, which is then released only very slowly at high temperature, compared to behaviour of the raw fuel ash.

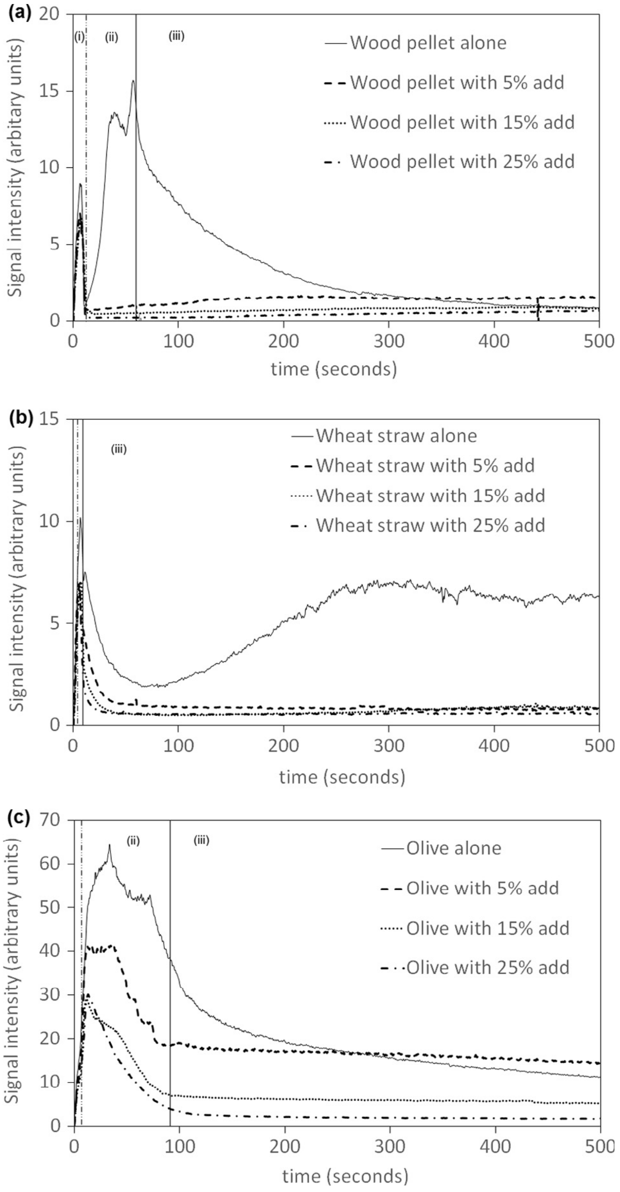

Fig. 2. Potassium release profiles for biomass pellets with 0/5/15/25 wt% additive for (a) 31 ± 6 mg of wood (b) 35 ± 7 mg of wheat straw and (c) 35 ± 7 mg of olive cake. Profiles are averages of a minimum of three test runs. Labels refer to (i): Volatile combustion; (ii): Char combustion; (iii): 'Ash cooking'.

Fig. 3 illustrates the normalised release signal intensity per molar quantity of potassium in the biomass pellets. This analysis of the results reveals a similar maximum in intensity/per mol K for wheat straw and olive (Fig. 3(b) and (c)). However, perhaps surprisingly, Fig. 3(a) shows a much higher maximum intensity/mol K for the wood pellets, nearly ten times larger than the other biomass. Thus indicating that although

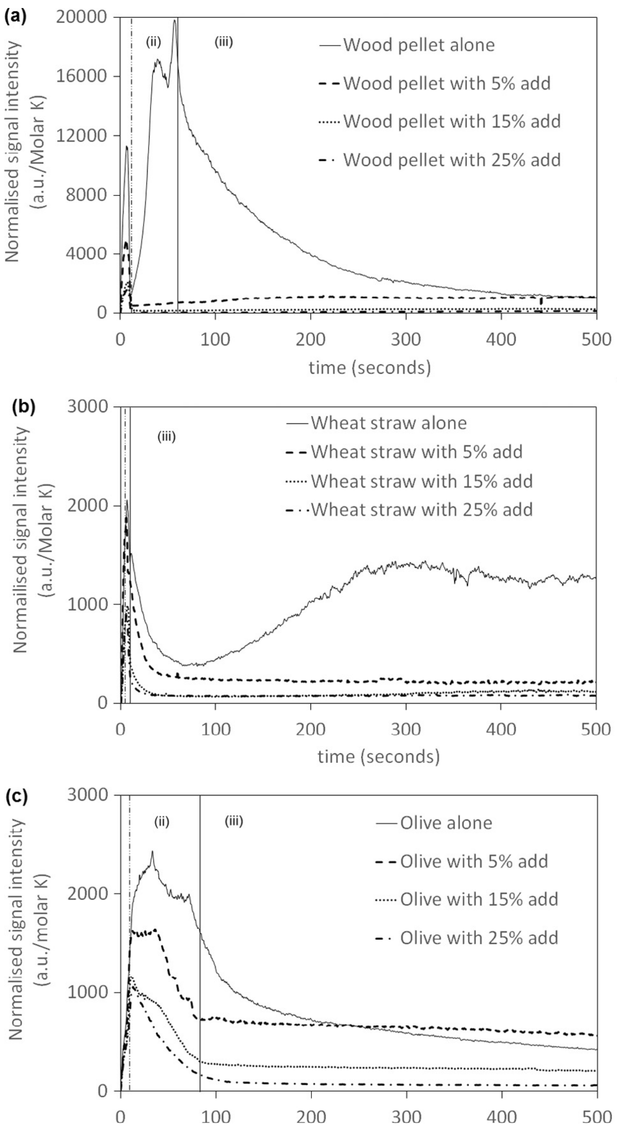

Fig. 3. Potassium release per molar K in the biomass pellets with 0/5/15/25 wt% additive for (a) 31 ± 6 mg of wood (b) 35 ± 7 mg of wheat straw and (c) 35 ± 7 mg of olive cake. Profiles are averages of a minimum of three tests runs. Labels refer to (i): Volatile combustion; (ii): Char combustion; (iii): 'Ash cooking'.

the wood contains the smallest quantities of potassium in the raw biomass, it is highly mobile under the high heating rates of this experiment. The wood pellets contain the lowest chlorine content of the three fuels studied, and so it can be assumed that the majority of K released during combustion is mainly from the evaporation of KOH. In contrast, both wheat straw and olive residue have an excess of chlorine compared to potassium, so it can be assumed that much of K released in combustion is mainly from the evaporation of KCl. Crystalline KOH melts at a much lower temperature than KCl (405 °C compared to 769 °C), meaning KOH is more mobile under combustion conditions. While the boiling points are more similar (1326 °C compared to 1406 °C for KOH and KCl respectively) there is approximately a threefold difference in vapour pressure at the particle temperature (based on data from [28,29]) and thus the evaporation rate of KOH will be greater than that of KCl. Since evaporation will be competing with reactions that help fix K in the ash (e.g. formation of potassium silicates), this may begin to explain the high mobility of K into vapour phase in the case of the wood pellets. With the addition of the mitigant it is clear that the ash-fixing reactions with potassium begin to dominate, and far less evaporation of potassium occurs during combustion.

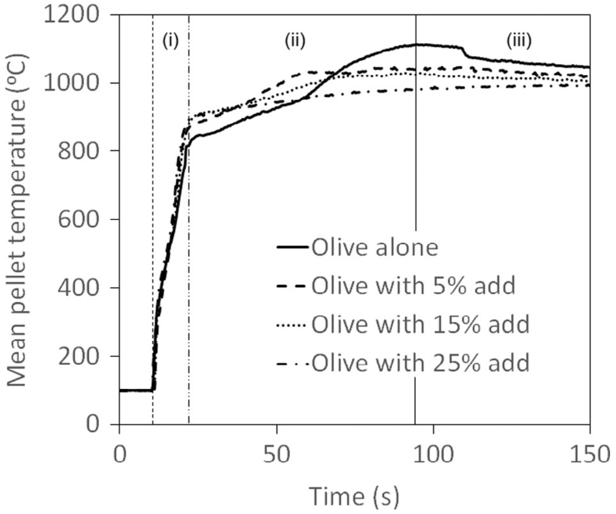

Fig. 4. Mean surface temperature of olive pellets derived from thermal imaging analysis for (i) devolatilisation (ii) char combustion and (iii) "ash cooking".

3.2. Particle surface temperature measurements

Thermal imaging analysis of the olive cake pellets during the experiments revealed a sharp rise in pellet temperature during devolatilisation up to approximately 850–900 °C as is illustrated in Fig. 4. The char combustion stage is identified by the exothermic reaction causing the temperature to rise further (particularly evident in the results for olive cake alone). The equilibrium temperature of approximately 1000 °C among the pellets (which decreases slightly with additive addition) continues into the "ash cooking" phase. While thermal imaging was only used for the olive pellet experiments, these results, coupled with previous work [26] indicate that the samples heat rapidly during volatile combustion and reach a final temperature of approximately 1100 °C during the char combustion stage i.e. temperatures are similar to the highest temperatures applied in the complementary study detailed in the next Section.

3.3. Residual potassium retained in the solid phase of biomass fuels with additive

Biomass samples with additive were combusted to ash under different conditions as described in Section 2.1. The results of AAS analysis on the residual potassium retained in the ash of the wood, wheat straw and olive cake as a function of ashing temperature are shown in Fig. 5(a)–(c) respectively. In general, the amount of potassium (given as wt% K_2O) retained in the raw biomass ashes formed between 550–1150 °C remains quite constant, although there appears to be some difference at the highest temperature studied. These amounts are ~10 ± 1% for wood, ~12 ± 0.1% for the straw and 36 ± 2.5% for olive. The slight variation in potassium percentages measured for the 550 °C ashes across the biomass types is possibly due to the small amounts (< 10%) of organically associated potassium lost at low temperatures (< 500 °C) [4–7] combined with the slight inhomogeneity in potassium concentrations throughout the fuels. If we assume there is no interaction between the ashes at 550 °C then, for all fuels, an indication of the errors in the method of analysis is approximately ± 2% of potassium oxide content.

At any given temperature, when additive is present, the fraction of potassium retained in the ash is always higher than in the raw biomass cases. However, trends are quite complex and it does not always follow that higher additive equates to higher fixation of potassium in the ash. For example, the optimum concentration of additive for fixing potassium in white wood pellet ash (and possibly wheat straw) appears to be 5 wt%, while 15 or 25% is better for the olive pellet. This can be

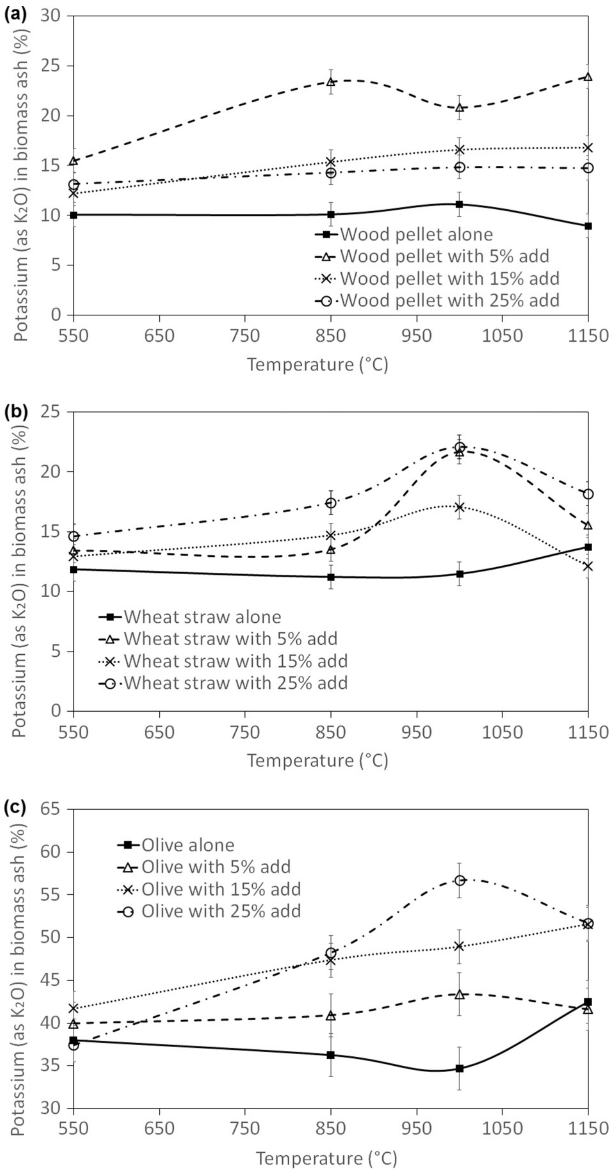

Fig. 5. Residual potassium oxide (K_2O) in biomass ash with additive at increasing temperatures for (a) wood (b) wheat straw and (c) olive cake.

related to the K:(Si + Al) ratios of the raw biomass fuels and the formation of potassium aluminosilicates (K_2O-SiO_2-Al_2O_3) which help fix potassium in the ash [20]. For example, wood pellets have an atomic K:(Si + Al) in the order of 1:1 whereas olive cake has a notably high potassium content (K:(Si + Al) = 3:1) and wheat straw has a low potassium content relative to combined aluminum and silica (K:(Si + Al) = 1:3). Thus, it is sensible that higher levels of additive are needed to fix potassium in olive ash. In some cases, the fraction of K fixed in the ash peaks at 1000 °C and this is particularly evident for the wheat straw and olive cake ashes. If we consider the top-most temperature studied (1150 °C), then the best retention of potassium in the ash is of the order of 20% for white wood and wheat straw (i.e. double that seen without additive), and 50% for the olive cake.

4. Analysis and discussion

4.1. Flame studies

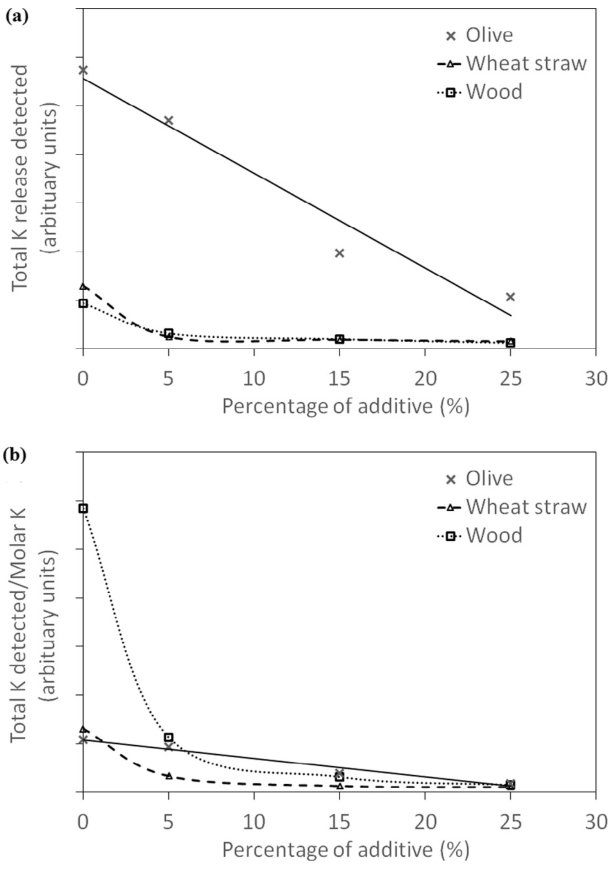

Fig. 6. Relationship between the percentage of additive and (a) the total K release (b) total K release per mole of K.

This work has identified how the aluminosilicate additive affects the potassium release profiles of three different biomass types. As shown in Fig. 6(a), using increasing proportions of additive in biomass combustion results in an overall decrease in the quantities of potassium released to the gas phase across the three fuels tested in this study. The additive shows a linear reduction in the fraction of potassium released for the highest potassium content fuel, olive cake, whereas the fuels with lower potassium content are found to show little impact from larger proportions of additive. This indicates that there is a threshold quantity of potassium that may be captured by a quantity of additive. Fig. 6(b) shows how the normalised release signal (per molar quantities of K) is affected by the additive for each of the biomass. The results for olive show a rather linear effect of the additive on this normalised signal whereas wheat straw and wood pellets show large reductions from raw biomass signals, likely due to the smaller quantities of potassium in those fuels.

Fig. 7(a)–(c) provides a semi-quantitative comparison for the release of K during volatile combustion, char combustion and “ash cooking” for each of the three biomass studied. These relative release totals are obtained by integrating the area under the rate release profiles in each of the three stages and for each of the biomass fuels. Fig. 7(a) shows that the K-release during volatile combustion is less sensitive to the addition of the additive. K-release in this region may be more related to physical effects, mainly entrainment in rapidly evolving volatiles. The impact of the additive is more apparent in Fig. 7(b) and (c) which illustrate the reduction in K-release rates with increasing additive present during the char combustion and “ash cooking” stages. Wood pellets were found to show a dramatic reduction in potassium release during the char combustion phase (Fig. 7(b)), whereas this reduction is more prominent in the “ash cooking” phase of combustion for wheat straw (Fig. 7(c)). This could be an important effect for the combustion of biomass in a boiler since ash deposits on furnace surfaces will be more stable with the use of an additive and may prevent the release or

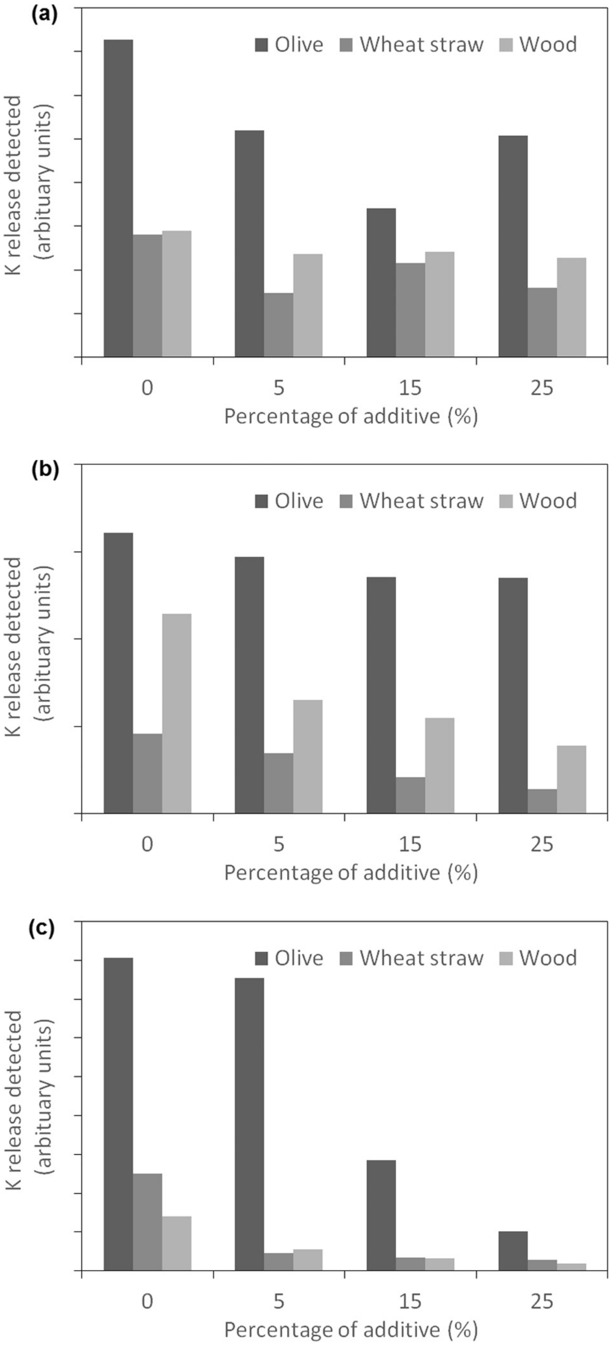

Fig. 7. Quantities of K released during (a) volatile combustion (b) char combustion (plotted on a logarithmic scale) and (c) the 'ash-cooking' stages.

evaporation of vapour phase potassium at high temperatures.

The potassium release profiles demonstrate potassium is released over the volatile and char combustion stages as reported previously [1]. Where the chlorine content is relatively high (relative to potassium content) the potassium is largely released in the form of KCl due to its high volatility at temperatures between 700 °C and 800 °C [5,6,17]. For low chlorine fuels, KOH becomes the main species evaporated during combustion. However, potassium release is also seen as the ash is "cooked" by the high temperature gases from the methane-air flame. The type of fuel, and therefore, ash composition, does have an impact on the level of potassium release over these three stages. The high chlorine content of wheat straw and olive (provided in Table 1) promotes K release during combustion, but there is no obvious relationship between the observed level of emission and Cl content. However, the release of potassium during the "ash cooking" for the raw wheat straw compared to the olive and wood pellets may be explained by the high Si and low Al content of this fuel. For example, K-oxides are known to associate with Si species (e.g. K_2OSiO_2) and begin to melt at temperatures of approximately 1000 °C [5,17,20], which could then lead to K-release in the "ash cooking" stage. In contrast, the slightly higher Al contents of olive and wood pellets may result in the formation of potassium feldspars with higher melting points [24]. This could explain the mitigating effects of the additive to wheat straw in the "ash cooking" phase, as the additional Al provided by the additive would lead to the formation of K feldspars rather than K-silicates.

4.2. Ashing experiments

The data in Fig. 5 and Fig. 1 was used to calculate the relative quantities of potassium in the biomass ash compared to the initial content, which is presented in Fig. 8(a–c). This figure helps identify trends in the fractions of potassium retained in the ash. Initial potassium contents for Fig. 8 were taken from the biomass with 25% additive blend at 550 °C for the truest representation of intial K content, since little potassium is expected to be released at temperatures $<$ 550 °C. For the raw fuels, there is evidence of potassium evolving when the ash is "cooked" at elevated temperatures and large decreases in K-content is seen for all fuels at the highest temperature studied (1150 °C). Note that this temperature is comparable to the top temperature experienced by the fuels in the flame studies, although residence times are much longer in the ashing experiments. From these ashing experiments the amount of potassium released can be quantified: Wood ash, evolves up to 80% of K at elevated temperature, wheat straw 50% and olive 40%. Note also, that the absolute K content is very different between these three biomass, as listed in Table 2.

It can be seen from Fig. 8 that very little or no potassium is released from all three types of biomass ash without additive between 850 °C and 1150 °C. This suggests, contrary to the wheat straw flame studies, that little potassium is released during the "ash cooking" phase of combustion. This may be explained by the low heating rate combustion of these experiments which results in a release of K during lower temperature "ash cooking", or the differences in the experimental configurations used by the two studies (i.e. there is a kinetic effect being observed in the flame studies). In the flame studies evaporation of melted ash components such as potassium silicates will be accelerated through the dynamic flow of hot gas around the heated particle. However Fig. 8 also demonstrates the fixation of K in ash by the additive and a change in the ease of evaporation of K at elevated temperature. For the wood ash 70–100% of K is retained in the ash in the presence of additive; for the wheat straw, this figure is 60–80% and for the olive pellets it is 70–100%.

5. Conclusions

The use of biomass as a solid fuel for power generation has known slagging and fouling problems associated with the high potassium content of some biomass types. This can result in undesired increases in operating costs and time off-line for power stations. Understanding the effects of additives on the fate of potassium during the combustion process is therefore of high importance for power plant operators.

Two potassium detection techniques have been employed in order to study this: the gas phase release of potassium from small biomass pellets suspended in a methane-air flame; and the residual potassium retained within the biomass ash when combusted in a furnace at different temperatures. Emission spectroscopy provided potassium release profiles for three types of biomass used in this study. During combustion, potassium is released over three stages of combustion: volatile combustion, char combustion and "ash cooking". The relative importance of each of these stages depends on the biomass type and the other inorganics present in the fuel. For wheat straw, there is a rapid

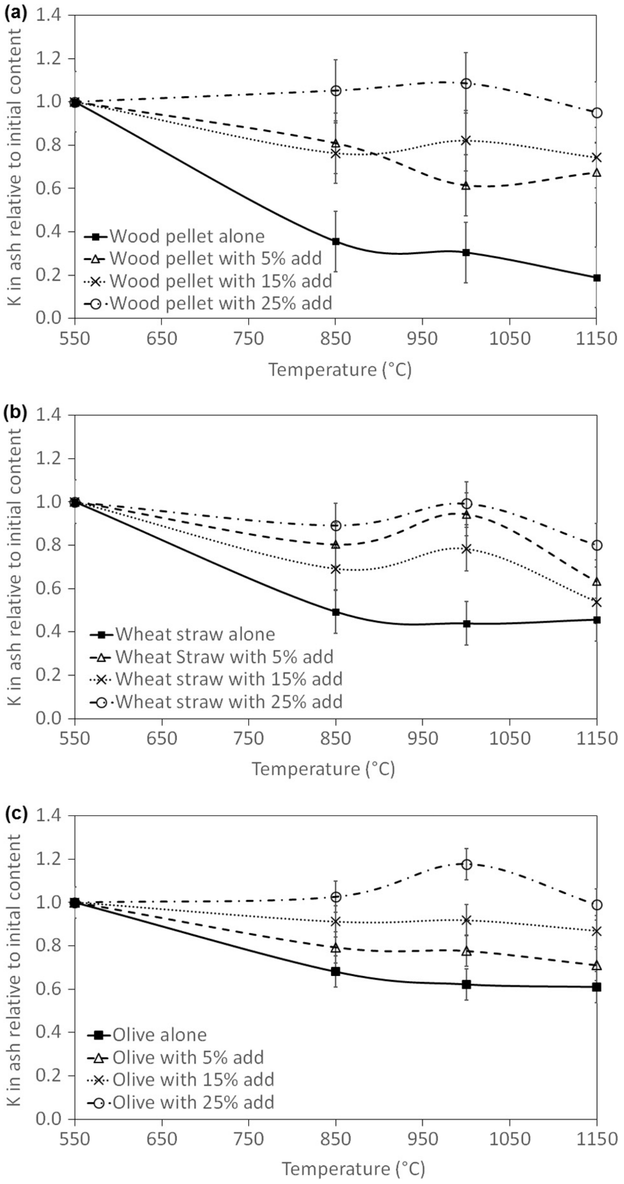

Fig. 8. Potassium in biomass ash relative to initial content for (a) wood (b) wheat straw and (c) olive cake.

release of K (probably as KCl) as the particle heats and burns, and then a slow release of K from the ash. This has important implications on the boiler slagging if ash deposits are kept at high temperatures, since the ash composition (and hence sintering properties) will change with time. Also revealed was the effectiveness of an aluminosilicate additive in biomass combustion for mitigating the release of potassium throughout the different stages of combustion, including the “ash cooking” phase in the case of wheat straw. The effects of different quantities (5, 15 and 25 wt%) of additive on the potassium release profiles show that optimization is necessary for each biomass; wood and wheat straw needed lower amounts of additive than olive residue, presumably because the potassium content of the olive cake was so much higher.

The softwood displayed a high potassium release rate when compared to the other biomass. This shows that the potassium in the wood is in a more mobile state. This could be due to a higher proportion of KOH in a low chlorine fuel. Differing diffusion rates within the particle structure will also affect mobility [30].

Ashes generated at temperatures ranging from 550 to 1150 °C were analysed by atomic absorption spectroscopy to identify the quantities of potassium lost at temperatures in this range and quantify the effects of additive. These were found to support the case for potassium being retained within the biomass ash from the use of the combustion additive tested, with wood pellets again seen to release a high proportion of K. In the absence of additive, the loss of K at the elevated temperature is 80% for wood pellets, 50% for wheat straw and 40% for olive. In the presence of additive, 70–100% of K is retained in the wood ash, 60–80% in the wheat straw ash, and 70–100% in the olive cake ash.

The two experimental techniques revealed some differing results in terms of suggested quantities of additive for combustion, related to the difference in time-temperature histories, however results agreed on the benefits of using additives for all types of biomass for the mitigation of potassium release to the vapour phase.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.fuel.2017.11.040.

References

[1] Mason PE, Darvell LI, Jones JM, Williams A. Observations on the release of gas-phase potassium during the combustion of single particles of biomass. Fuel 2016;182:110–7.

[2] Sjöström E. Wood chemistry: fundamentals and applications. Gulf Professional Publishing; 1993.

[3] Saddawi A, Jones JM, Williams A. Influence of alkali metals on the kinetics of the thermal decomposition of biomass. Fuel Process Technol 2012;104:189–97. http://dx.doi.org/10.1016/j.fuproc.2012.05.014.

[4] Yu C, Zhang W. Modeling potassium release in biomass pyrolysis. Prog Thermochem Biomass Convers 2001:1107–15.

[5] Jensen P, Frandsen F. Experimental investigation of the transformation and release to gas phase of potassium and chlorine during straw pyrolysis. Energy Ellipsis 2000;14:1280–5. http://dx.doi.org/10.1021/ef000104v.

[6] Olsson JG, Ja U, Pettersson JBC. Alkali metal emission during pyrolysis of biomass. Energy Fuels 1997;11:779–84. http://dx.doi.org/10.1021/ef960096b.

[7] Olsson JG, Pettersson JBC, Padban N, Bjerle I. Alkali metal emissions from filter ash and fluidized bed material from PFB gasification of biomass. Energy Fuels 1998;12:626–30.

[8] Akbar S, Schnell U, Scheffknecht G. Modelling potassium release and the effect of potassium chloride on deposition mechanisms for coal and biomass-fired boilers. Combust Theory Model 2010;14:315–29. http://dx.doi.org/10.1080/13647830.2010.483019.

[9] Antal MJ, Grønli M. The art, science, and technology of charcoal production. Ind Eng Chem Res 2003;42:1619–40. http://dx.doi.org/10.1021/ie0207919.

[10] Nowakowski DJ, Jones JM, Brydson RMD, Ross AB. Potassium catalysis in the pyrolysis behaviour of short rotation willow coppice. Fuel 2007;86:2389–402. http://dx.doi.org/10.1016/j.fuel.2007.01.026.

[11] Jones JM, Darvell LI, Bridgeman TG, Pourkashanian M, Williams A. An investigation of the thermal and catalytic behaviour of potassium in biomass combustion. Proc Combust Inst 2007;31:1955–63. http://dx.doi.org/10.1016/j.proci.2006.07.093.

[12] Mason PE, Jones JM, Darvell LI, Williams A. Gas phase potassium release from a single particle of biomass during high temperature combustion. Proc Combust Inst 2016:1–9.

[13] Yu C, Zhang W. Modeling potassium release in biomass pyrolysis. Prog Thermochem Biomass Convers 2008:1107–15. http://dx.doi.org/10.1002/9780470694954.ch89.

[14] Koppejan J, Van Loo S. The handbook of biomass combustion and co-firing. Routledge; 2012.

[15] Saddawi A, Jones JM, Williams A, Le Coeur C. Commodity fuels from biomass through pretreatment and torrefaction: effects of mineral content on torrefied fuel characteristics and quality. Energy Fuels 2012;26:6466–74. http://dx.doi.org/10.1021/ef2016649.

[16] Bridgwater AV, Boocock DG. Developments in thermochemical biomass conversion.

vol. 1. Springer Science & Business; 2013.

[17] Knudsen JN, Jensen PA, Dam-Johansen K. Transformation and release to the gas phase of Cl, K, and S during combustion of annual biomass. Energy Fuels 2004;18:1385–99. http://dx.doi.org/10.1021/ef049944q.

[18] van Lith SC, Jensen PA, Frandsen FJ, Glarborg P. Release to the gas phase of inorganic elements during wood combustion. Part 2: influence of fuel composition. Energy Fuels 2008;22:1598–609. http://dx.doi.org/10.1021/ef060613i.

[19] Vassilev SV, Baxter D, Vassileva CG. An overview of the behaviour of biomass during combustion: part II. Ash fusion and ash formation mechanisms of biomass types. Fuel 2014;117:152–83. http://dx.doi.org/10.1016/j.fuel.2013.09.024.

[20] Wang L, Hustad JE, Skreiberg Ø, Skjevrak G, Grønli M. A critical review on additives to reduce ash related operation problems in biomass combustion applications. Energy Proc 2012;20:20–9.

[21] Coda B, Aho M, Berger R, Hein KRG. Behavior of chlorine and enrichment of risky elements in bubbling fluidized bed combustion of biomass and waste assisted by additives. Energy Fuels 2001;15:680–90. http://dx.doi.org/10.1021/ef000213+.

[22] Steenari BM, Karlfeldt Fedje K. Addition of kaolin as potassium sorbent in the combustion of wood fuel - Effects on fly ash properties. Fuel 2010;89:2026–32. http://dx.doi.org/10.1016/j.fuel.2010.02.006.

[23] Wu H, Bashir MS, Jensen PA, Sander B, Glarborg P. Impact of coal fly ash addition on ash transformation and deposition in a full-scale wood suspension-firing boiler. Fuel 2013;113:632–43. http://dx.doi.org/10.1016/j.fuel.2013.06.018.

[24] Öhman M, Nordin A. The role of kaolin in prevention of bed agglomeration during fluidized bed combustion of biomass fuels. Energy Fuels 2000;14:618–24. http://dx.doi.org/10.1021/ef990198c.

[25] Damoe AJ, Wu H, Frandsen FJ, Glarborg P, Sander B. Combustion aerosols from full-scale suspension-firing of wood pellets. Impacts Fuel Qual Power Prod Environ 2012.

[26] Mason PE, Darvell LI, Jones JM, Pourkashanian M, Williams A. Single particle flame-combustion studies on solid biomass fuels. Fuel 2015;151:21–30. http://dx.doi.org/10.1016/j.fuel.2014.11.088.

[27] Höfer I, Kaltschmitt M. Assessment of additives avoiding the release of problematic species into the gas phase during biomass combustion—development of a fast screening method based on TGA. Biomass Convers Biorefinery 2016. http://dx.doi.org/10.1007/s13399-016-0229-3.

[28] Rodrigues PCR, Silva Fernandes FMS. Phase diagrams of alkali halides using two interaction models: a molecular dynamics and free energy study. J Chem Phys 2007;126:1–10. http://dx.doi.org/10.1063/1.2423030.

[29] Gurvich LV, Bergman GA, Gorokhov LN, Iorish VS, Leonidov VY, Yungman VS. Thermodynamic properties of alkali metal hydroxides. Part 2. Potassium, Rubidium and Cesium Hydroxides. J Phys Chem Ref Data 1997;26:1031–110. http://dx.doi.org/10.1063/1.555996.

[30] Mason PE, Darvell LI, Jones JM, Williams A. Release of gas phase potassium during combustion of biomass - experimental and modelling observations. VGB PowerTech J 2017;1.