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Observations on the release of gas-phase potassium during the combustion of single particles of biomass

Patrick E. Mason [*], Leilani I. Darvell, Jenny M. Jones, Alan Williams

School of Chemical and Process Engineering (SCaPE), University of Leeds, Leeds LS2 9JT, UK

HIGHLIGHTS

- A method for observing patterns of K-release from combusting particles of biomass.
- Patterns of gas-phase potassium release presented for 13 different biomass fuels.
- Relationship between potassium content and rate of release demonstrated.
- Differences in K-release behavior for wood and herbaceous fuels identified.
- A means of determining proportion of K-release at end of burn-out proposed.

ARTICLE INFO

ABSTRACT

One of the more significant characteristics of solid biomass fuels as compared to coal is the quantity of potassium that they contain. Potassium content influences ash deposition and corrosion mechanisms in furnaces, the effects of which may differ depending on phase transformations of potassium species in the gas phase and condensed phase. The fate of potassium from the fuel during the combustion process is therefore an important concern. To investigate this, an experimental method is presented in which the release patterns from single particles of various biomass fuels are measured by use of flame emission spectroscopy implemented using a custom-built photo-detector device. Single particles of fuel are combusted in a methane flame with a gas temperature of ∼1800 K. The observed potassium release patterns for thirteen solid biomass materials are presented. The data are analyzed to examine the relationships between: the level of potassium in the fuel particle; the fraction of potassium released at each stage of combustion and the peak rate of release of potassium to gas-phase during combustion. Correlations between these quantities are identified with key trends, patterns and differences highlighted. The analyses provide useful information for the development and validation of modelling of potassium release during combustion of biomass.

1. Introduction

Many large scale power plants use pulverized fuel furnaces with combustion temperatures above 1600 K. Such temperatures affect the partitioning of inorganic components through phase transformations. In biomass fuel in particular, potassium, which may be present as various species in solid fuel, is released to the gas phase during combustion at such elevated temperatures. Subsequently, as combustion gases are cooled at furnace surfaces, potassium chloride and hydroxide condense out and lead to increased corrosive deposits and adhesion of ash. Gas-phase potassium can also lead to the formation of sulfate aerosols and re-combine with other

solid-phase ash components affecting ash melting behavior and therefore influencing fouling and slagging in the furnace [1]. In some applications, the level of residual potassium in the char is significant. Since char reactivity is catalyzed by potassium content, it is possible that unburned char with high potassium content could continue to burn or re-ignite after leaving the furnace and where ash is accumulated. The ability to determine the degree to which potassium is released from the char during combustion is therefore useful. In order to model this and predict the likely fate of potassium during the combustion process, it is necessary to understand the release mechanisms and patterns of release.

Woody biomass has potassium present in quantities in the region of 0.1% weight (dry basis) while herbaceous energy crops and straws tend to have higher levels from 0.2% to 1% or more. Seed and fruit residues such as olive can have levels at 3% or even

* Corresponding author.
    E-mail address: pmpem@leeds.ac.uk (P.E. Mason).

higher [2]. In raw plant-based biomass, potassium can be present as inorganic salts (e.g. KCl), organic compounds (e.g. R–COO⁻K⁺) and minerals (e.g. K_2O_3Si). The salts and organic-bound potassium can be leached from the material since it is almost all in a water soluble form. Consequently, the majority of the potassium content can be removed from woody biomass fuels by water washing [3,4].

As a particle of fuel combusts, the potassium within it is either released into the gas phase or retained in the condensed-phase ash particle. Potassium released into the gas phase at temperatures above 1000 K is generally as $KCl_{(g)}$, $KOH_{(g)}$ or $K_{(g)}$ since these species remain stable in the gas phase at such temperatures [5]. The proportions of these species is dependent on the availability of chlorine and moisture in the material [6]. The vaporized potassium species subsequently condense either directly on furnace surfaces where they can cause direct corrosion reactions, or they are recombined with other components into the solid ash which can deposit on heat exchange surfaces and cause fouling. The phase transformations and chemical reactions which take place in the combustion environment are functions of the temperatures of the gases and solids and the presence of other compounds present in the ash. Analysis of some of these aspects of gas-phase potassium partitioning in biomass combustion have been presented in recent years [7–13].

Measurement of potassium release from biomass at different combustion temperatures [8,9] has shown relatively low levels of release to the gas phase below 1000 K. The vapor pressure of KCl and KOH rises rapidly above 1000 K with KOH reaching standard pressure boiling point at 1600 K and KCl at 1693 K [14,15]. A study of previously published data [8,13,16,17] on potassium measured in ash at differing combustion temperatures is presented in Fig. 1. This illustrates that below temperatures of around 1000 K, there is very little significant loss of potassium in the ash residue compared to the initial fuel content. With increasing temperatures, the proportion of potassium left in the ash is reduced as more potassium is evaporated. The inference is that full combustion of particles of these biomass fuels at elevated temperatures (>1600 K) is expected to result in the majority of the potassium entering the gas phase. The fraction of potassium retained in the char and ash respectively depends on the degree of burn-out and heating of the ash particle which in turn depends on the combustion characteristics of the material and the residence time in the furnace.

Measurement and quantification of the partitioning of potassium between solid and gas phases during combustion requires a means of detecting gas-phase K and a means of determining the quantity of K remaining in the solid phase.
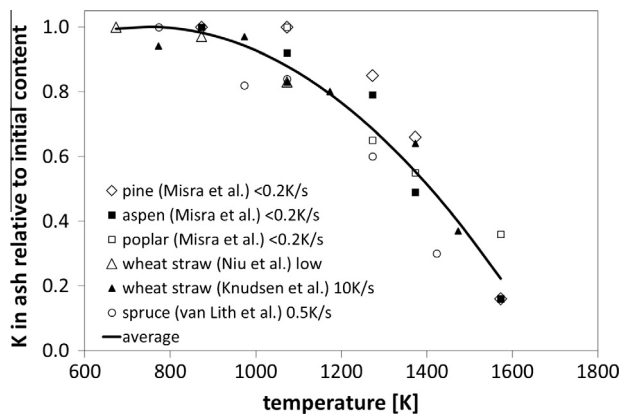
Gas-phase detection of potassium in combustion processes is possible by various forms of spectroscopy, details of which are covered in the review by Monkhouse concerning spectroscopic detection of metal species in industrial process [18]. Some of these methods have been employed in laboratory investigations on potassium release in biomass combustion. Molecular beam mass spectrometry (MBMS) has been used by Dayton et al. [19] to determine mass fractions of the principal potassium species present in the flame during switchgrass combustion. This showed KCl and KOH as significant species in the gas phase with K_3PO_4, K_2SO_4 and KCl being significant condensed phase species. Collinear photo-fragmentation atomic absorption spectroscopy (CPFAAS) has also been shown by Sorvajarvi et al. [5] to be an effective method for detecting and discriminating potassium species (K, KOH and KCl) in flue gases. Laser induced breakdown spectroscopy (LIBS) is a method used by Hsu et al. [20] and more recently by Zhang et al. [21] and Fatehi et al. [22] to investigate the temporal release of potassium from combusting wood. The former of these studies showed a means of quantifying the concentration of potassium in the combustion gases by calibrating with a seeded flame. The results from Zhang et al. and Fatehi et al. both include a quantification of the potassium release rate and measurement of particle temperature.

Sophisticated and costly laboratory apparatus is required for the techniques as described above. However, studies on the patterns of potassium release during biomass combustion are also possible using basic emission spectroscopy techniques. An aspect of the work presented here is to demonstrate that use of simpler techniques for the detection of potassium release in combustion can be effective. The method presented allows expeditious data capture and therefore multiple experiments on a large range of fuels are practical in a short time frame.

2. Experimental method

2.1. Biomass fuel samples and characterization

A range of solid biomass such as would typically be used as fuel in large scale power generation pulverized fuel furnaces were selected for study and sourced from various power plant operators and suppliers. Characterization of the samples using standard methods (EN 14774, EN 14775, EN 14918, EN 15104, EN 15148) was undertaken to determine moisture, volatile content, ash content and calorific value together with elemental analysis to determine CHN content. The fuels and their characteristics are listed in Table 1. While the bulk fuels were supplied in various forms, it was possible to extract single particles with similar mass: 1.1 mg ± 0.1 mg (dry basis). For consistency, particles were trimmed to be approximately cuboid with aspect ratios of between 2 and 3. This corresponds to particles with dimensions approximately $1 \times 1 \times 2$ mm for woody materials and $1 \times 1 \times 3$ for the herbaceous materials. Olive residue and black pellet (steam-exploded wood pellet) were fractured into quasi-spherical particles of about 1 mm diameter.

2.2. Measurement of potassium in solid phase

The potassium content was determined for duplicate samples of each biomass material using nitric acid digestion and quantitative determination by AAS in accordance with standard EN 15290:2011. The water-soluble fraction of potassium and chlorine was also determined in accordance with standard EN 15105:2011. The results are presented in Table 1. It is notable that for all materials, the fraction of potassium extracted as soluble in water is more that 90% and in some cases up to 100%. This is consistent

Fig. 1. Compilation of published data [8,13,16,17] showing relationship between combustion temperature and potassium retained in ash (heating rates shown on legend).

Table 1
Biomass fuel characteristics.

Content	Basis	Units	Wood pellet A	Wood pellet B	Wood pellet C	Pine	Eucalyptus	Willow A	Willow B	Wheat straw A	Wheat straw B	Rape straw	Miscanthus A	Olive residue	Black pellet
Moisture	a.r.	wt%	8.9	5.5	6.9	8.3	8.1	8.3	3.1	10.8	8.1	14.3	7.4	5.9	7.2
Ash	dry	wt%	0.3	1	1.2	2	0.9	5.4	2	7.5	6.3	6.3	4.9	7.6	4.2
Volatile	daf	wt%	85	83.9	84.8	82.5	83.3	82.5	83.6	79.3	81.8	82.1	81.6	80.1	79.4
Fixed carbon	daf	wt%	15	16.1	15.2	17.5	16.7	17.5	16.4	20.7	18.2	17.9	18.4	19.9	20.6
GCV	dry	MJ kg^{-1}	19.5	20	20.3	18.6	19.4	18.9	19.8	18.2	18.1	18.4	18.8	20.1	20
Elemental															
C	daf	wt%	49.2	50.7	50.8	47.4	49.2	49.5	50.8	48.6	48.8	48.7	48.5	52.8	52.7
H	daf	wt%	6	6	6.1	5.3	5.6	5.8	6	6	6.1	5.9	6	6.5	5.8
O	daf	wt%	44.7	43.2	43.1	45.9	45.1	44.1	42.7	44.8	44.5	44.2	44.9	39.1	41.2
N	daf	wt%	<0.1	0.1	<0.1	1.3	0.1	0.5	0.4	0.6	6.1	1.1	0.6	1.6	0.2
K	daf	wt%	0.04	0.08	0.04	0.12	0.10	0.24	0.21	1.27	0.82	0.45	0.75	2.92	0.2
Water soluble K	daf	wt%	0.04	0.08	0.04	0.10	0.10	0.22	0.17	1.10	0.68	0.39	0.72	2.61	0.2

with the findings reported in a recent review by Gudka et al. [23]. The chlorine content measured in all fuels was close to the measurement limit or nil. In relation to the potassium content, it is inferred that where KCl is present it is not necessarily the dominant species in the solid phase.

2.3. Detection of potassium in gas-phase

The combustion behavior of biomass fuels can be examined by studying the combustion of individual single particles exposed to a methane flame. This is done using a support rig to hold the particle on a needle in the center of the flame which has a temperature of ~1800 K and an oxygen concentration of ~10.7% by volume. The flame temperature is within the range expected in a pulverized fuel biomass furnace. The support rig is fitted with a retractable, water-cooled sleeve to shield the particle from the flame such that it can be exposed at a clearly defined moment. Full details of this experimental method is described in previous work [24] in which the demarcation between different stages of combustion (ignition delay, volatile flame combustion and char combustion) was established by use of high speed video recording. In the current investigation, the same method is used and it is complemented by a photo-detector for indicating the relative potassium content in the flame above the combusting particle.

The intensity of the spectral emission of potassium is determined by the proportion of atoms in the excited state which is a function of temperature. In this experiment, the flame temperature above the combusting particle is assumed to be at a steady temperature for the duration of the observation. The intensity of spectral emission is therefore taken to be proportional to the concentration of volatilized potassium in the flame. Flame temperatures of 1600–1800 K are sufficient to excite the gas phase potassium for obtaining a strong spectral emission – the experimental technique is not suitable for lower temperature combustion environments. At high concentrations of potassium and in flames with deep cross-section, self-absorption may introduce a nonlinearity to the relationship between concentration and observed emission intensity [25]. However, in these single particle combustion experiments, the concentration of potassium in the flame is low and the observed surface of the flame is large with respect to the cross-section. Any non-linearity is therefore assumed to be small, if not negligible, and no adjustment to account for self-absorption has been applied.

A monochromator or an optical band-pass filter can be used to select a signature wavelength from the emitted radiation, the intensity of which can be observed with a photo-detection device. Potassium has a strong spectral emission line at 766 nm. In this experiment, a traditional-coated (Edmund Optics Techspec®) band-pass interference filter with center wavelength of 766 nm and a bandwidth of 10 nm was used. It is important to note that, in addition to the potassium emission, there is also a continuous black-body radiation spectrum emitted from any solid phase component of the flame (i.e. soot). To account for this it is necessary to measure the intensity of radiation from the flame at a wavelength window close to, but avoiding, 766 nm. For this purpose, a second photo-detection device was operated in parallel using a similar type of bandpass interference filter with center wavelength of 750 nm and a bandwidth of 10 nm.

Similar experiments [26] have used photomultiplier electron tubes for photo-detection. In the current experiment, a low cost solid state photo-detector was custom designed and built (Converter Technologies Ltd.). The photo-detector device used is a photo-diode (Vishay BPW34) with a relative sensitivity of over 0.8 (of maximum) at 766 nm wavelength. A precision amplifier was designed to control the photodiode as a current source and convert it to a 0–5 V output signal linearly proportional to the

intensity of incident radiation. The electronics were mounted in a light-sealed enclosure with an aperture for an optical filter and a lens to focus the incoming light onto the photodiode. The output voltage signal was sampled at 1 kHz using National Instruments USB-6000 interface and LabView data acquisition software. The photodetector device measurement precision is estimated <1%.

The measurement technique does not discriminate potassium species so it is not possible to determine the relative quantities of gas phase KCl and KOH. Both species are volatile in the temperature range of the flame (1800 K). Differences in release rates between the two species are not expected to be distinguishable. The measurement and analysis then refers to gas-phase potassium release without qualification of the speciation.

2.4. Reference samples

A set of samples of willow impregnated with known quantities of potassium is also included in the sample range. This allows comparison of the other materials against a reference. The differing potassium content in the reference material can also be used to examine the relationship between potassium concentration, release rate and total potassium release. The materials were demineralized by washing and subsequently impregnated with known quantities of potassium. Impregnation was by addition of potassium acetate solution to batches of particles and subsequent drying. Potassium was added to obtain samples with 0.1%, 0.25%, 0.5%, 0.75%, 1.5% by weight. Since the samples were initially washed, it is assumed that the chloride content is negligible for these. Details of the sample preparation technique used in other investigations are described by Saddawi et al. [27]. For consistency with the other samples, particles of 1.1 mg ± 0.1 were prepared in the same manner to that described in Section 2.1.

3. Results

3.1. Form of recorded data

The data obtained from the photo-detectors was processed to subtract the 750 nm signal from the 766 nm signal and to remove noise from flame flicker (by smoothing the signal over 10 data points). An example of the output and derived signal is presented in Fig. 2. The various stages of combustion are identified in the profile based on the visual examination of the combusting particle as described in previous studies [24]. The labelling describes the dominant process at each stage. The end of char combustion is a useful reference point. There is a short ignition delay from the initial withdrawal of the water-cooled sleeve to the signal(s) initial
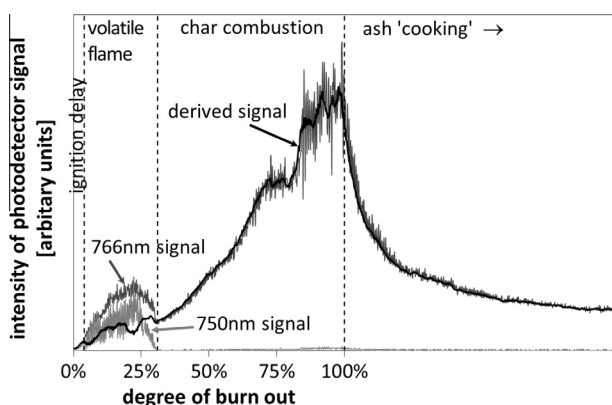
rise. Following this, the volatile flame produces a distinct signature from both the 766 nm and 750 nm detectors. At the end of the volatile flame, the 750 nm signal falls to zero (since thereafter there is no black-body radiation from soot). The derived signal in this period shows a low level of potassium release compared with the subsequent period. Nevertheless, there is an increased release rate noticeable above the underlying trend which may be attributed to entrainment of potassium in the volatilized gases. This is more accentuated in some fuels while virtually absent in others. The char combustion stage is characterized by an approximately steady increase in the release rate which appears to peak just before the char burn-out is complete. Thereafter, the remaining material being heated in the methane flame is a melted ash particle. The potassium release profile at this stage is, in most cases, an exponential decay as any remaining potassium available for volatilization is released. The shape of this part of the profile is influenced by the proportion of ash content. Since there is noise in the recorded signals and variations from one particle to the next, in order to produce a more representative "typical" profile for each material the data from multiple experiments should be taken and a mean average derived. In all cases, data from between 3 and 6 samples was obtained. This approach is used for the materials presented in the following sections. The mean difference between the measured data and the averaged signal varied for different materials ranging up to ±8% owing to variability in the samples – only the averaged signal is shown in Figs. 3–6.

3.2. Profiles of potassium release from reference samples

A series of experiments were performed using the reference materials with five different levels of potassium content (0.1%, 0.25%, 0.5%, 0.75% and 1.5% by dry weight). Although not fully quantitative, the data from the reference can provide a baseline for comparison with the fuels being examined. To determine a typical release profile for each concentration level, the data from at least 3 particles was obtained and a mean average of the measured signal was derived. The results of this are presented in Fig. 3. The data was analyzed to determine the magnitude of total observed potassium release (area under each profile curve), peak release rate (maximum point on each profile curve) and duration of the combustion (burn-out time). The correlation between potassium content and the potassium released to gas phase is clear enough from a superficial examination. This is examined in more detail in the following analysis discussion and the correlation is used to normalize the photo-detector signal to an estimated release rate. The peak release rate and potassium content also have an apparent
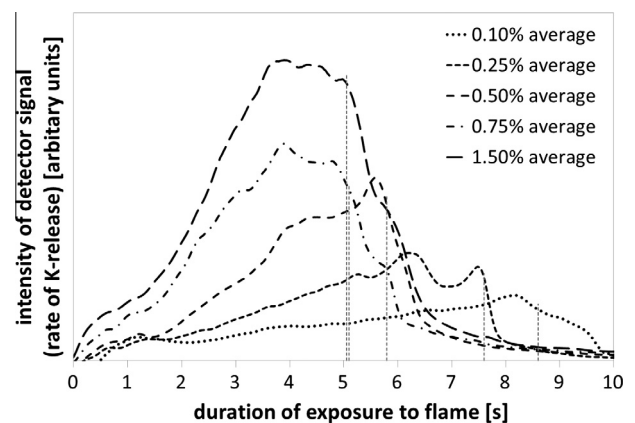
Fig. 2. Example output from photo-detectors from the combustion of a willow particle indicating dominant processes at different stages.

Fig. 3. Comparative potassium release profiles (average of at least 3 samples) for 1.1 mg willow particles impregnated with potassium at 0.1%, 0.25%, 0.5%, 0.75% and 1.5%. Vertical lines indicate estimated burn-out time.
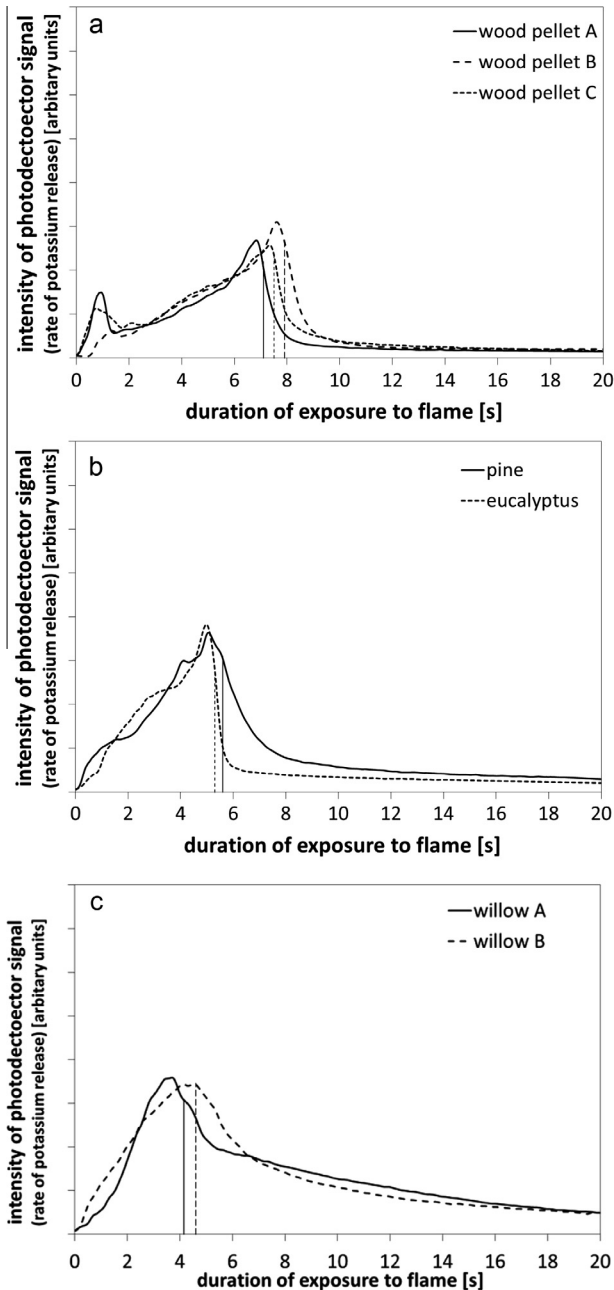
Fig. 4. Potassium release profiles for 1.1 mg single particles of various woody materials: (a) wood pellets; (b) pine and eucalyptus; (c) willow.

Fig. 5. Potassium release profiles for 1.1 mg single particles of various herbaceous materials: (a) wheat straw; (b) rape straw and miscanthus.

positive correlation and it is noted that the burn-out time is extended for samples with lower potassium content. Similar relationships should be expected for the fuel samples and these aspects are examined later in the analysis.

3.3. Profiles of potassium release from biomass fuel samples

3.3.1. Woody biomass materials

The woody biomass materials (wood pellets, pine, eucalyptus and willow) all have potassium content measured to be less than 0.4% by weight. The potassium release profiles for all the woody materials are shown in Fig. 4a–c in which some notable similarities and differences are observable. In most cases, the volatile combustion stage is discernible by a minor peak or shoulder in the potassium release rate. The general shapes of the release patterns are
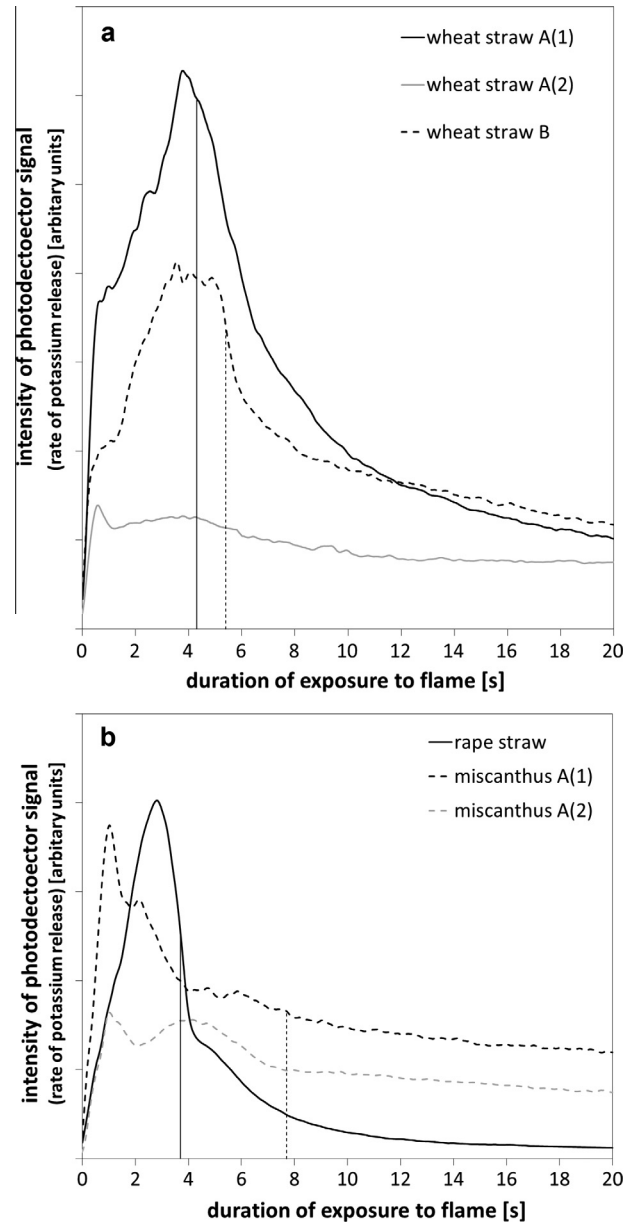
similar. For similar materials (especially for the wood pellets) there is a strong resemblance in the release curves with a steady increase in release rate during char combustion up to a peak which is coincident with the ending of char burn-out. The materials with lowest potassium content and lower ash content show a more rapid decrease in release rate after char burn-out (just after the peak of the curve). This implies that the potassium content in these materials is "exhausted" during the char combustion process.

3.3.2. Herbaceous biomass materials

The herbaceous biomass materials (wheat straw, rape straw and miscanthus) all have potassium content measured to be more than 0.4% but less than 1.3% by weight. The potassium release profiles for all the herbaceous materials are shown together in Fig. 5a and b. The plot is on the same scale as Fig. 4 and it is immediately clear that the quantity of potassium release from these materials is greater than any of the woody materials. From the moment of first exposure to the flame, the rate of potassium release increases
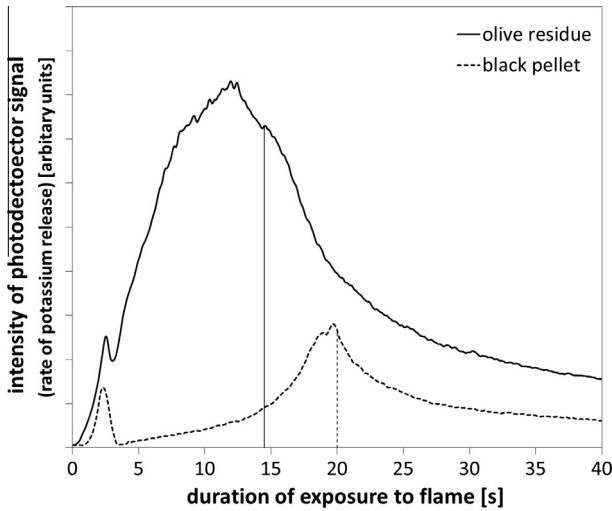
Fig. 6. Potassium release profiles for 1.1 mg single particles of olive residue and black pellet.

figure is to a different scale to Figs. 4 and 5 to allow the extended combustion time for the materials to be fitted. The vertical-axis is to the same scale. The general shapes of the profiles are consistent with the patterns observed for the other materials in that there is a distinct peak of release during the volatile combustion stage, the subsequent release rate shows an increase to a peak at burn-out and is followed by a long decaying tail of release from the ash. Both materials took much longer for devolatilisation and full burn-out compared to the other materials. This is related to the density, heat transfer properties and kinetics of the materials.

4. Analysis and discussion

The release profiles all appear to comply with a general form with the peak of potassium release occurring near or at the point at which there is effective char burn-out (indicated on the figures by the vertical lines) followed by a rapid decay in release rate. These patterns are consistent with the observations made by recent similar studies including Fatehi et al. [22] and Zhang et al. [21] both of which studied combustion of larger sized (>20 mg) particles of a single wood type in gas flame burners. In both these studies softwoods are used, the published profiles resembling that of pine in this study (Fig. 4b).

The previous discussions of the form and features of the recorded potassium release profiles note a number of apparent correlations. These are worthy of further analysis to determine the quality of the relationships. An important feature to verify in this experiment is the relationship between the total quantity of potassium contained in the sample and the cumulative total of that which is detected. While the photo detection measurement does not provide an absolute measure of potassium release, there

much more rapidly than for the woody materials. The rate is so steep that the volatile combustion stage which is discernible in the woody biomass is not easily distinguishable. It is notable that all these materials show a more extended release of potassium after char burn-out than woody materials. This implies a significantly larger quantity of potassium remaining in the ash after the char combustion stage. Two distinct combustion profiles were observed for wheat straw A and miscanthus A: denoted by suffix A (1) and A(2). There did not appear to be an intermediate mode of potassium release for the particles observed. The profiles with lower release rates – wheat straw A(2) and miscanthus A(2) – reach a certain release rate and then level off to become coincident with the release rate of the ash from those particles with higher release rates. This implies an uneven distribution of potassium and possibly different K-species in the straw even though all particles were prepared from similar part of the stem of the respective plants.

3.3.3. Olive residue and black pellet

The remaining materials, olive residue and "black pellet" (steam-exploded wood) are distinguished by having much higher density than the other materials examined. The potassium release profiles are presented in Fig. 6. Note that the horizontal-axis of this
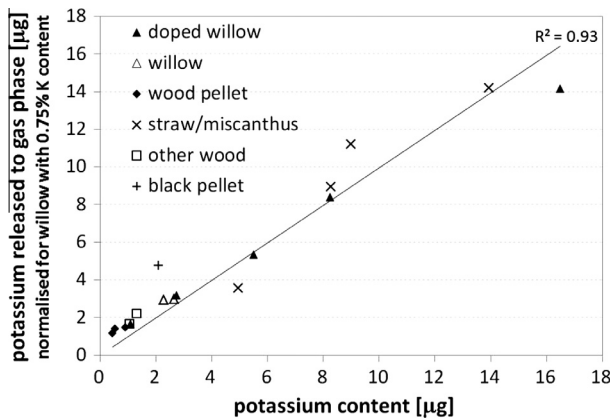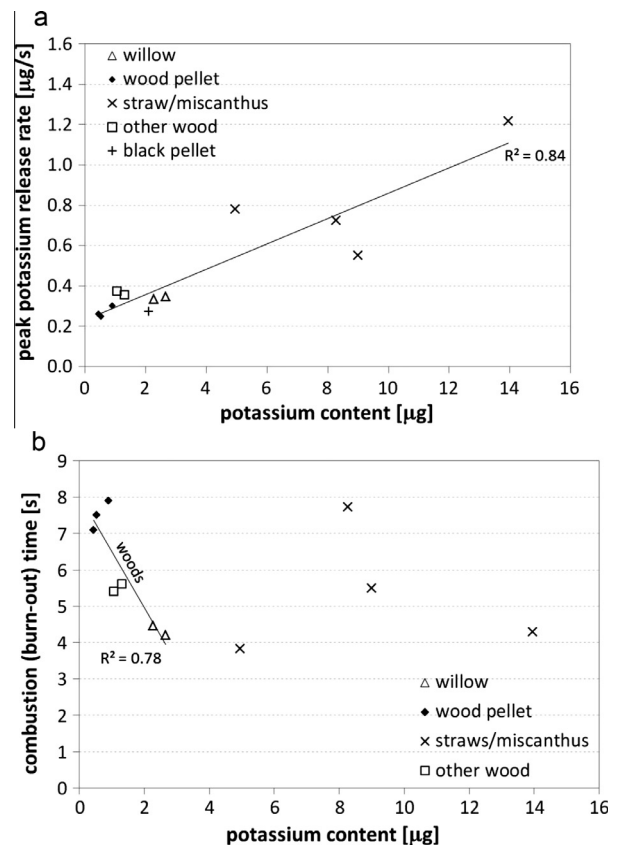

Fig. 7. Correlation between total measured release of potassium to gas phase and initial potassium content in the 1.1 mg particle [data normalized for values of K content and K release for the 0.75 wt% (mid-range) doped willow].

Fig. 8. Relationships between initial potassium content in the 1.1 mg particle and: (a) peak measured release rate of potassium to gas phase; (b) full burn-out time.

should be strong correlation between the area enclosed by the recorded profile (determined by simple integration of the data) and the total potassium content. This is shown to be the case in Fig. 7 where the potassium content of the sample is plotted against the inferred potassium released to gas phase – including the release from the ash as it is "cooked". The quantification of the area under the profile was subject to the error introduced by the variability between samples which ranged up to an 8% standard error for some materials. The linear regression function (forced to the origin) fitted to the data does indeed show a strong correlation (with a regression function R^2 value of 0.93). The experiments were run until the observed potassium release was negligible so it may be inferred that the full transformation of all potassium in the sample to gas phase is detected. Assuming this to be the case, the potassium release values (±8%) in Fig. 7 has been normalized to the datum of the willow reference material with 0.75 wt% potassium content (on the basis that this sample is mid-range). From this relationship, the intensity of the photo-detector signal can be translated to a potassium release rate (which is used in Fig. 8a). It should be noted that for the following analyses, the data for olive residue has been omitted in some cases for the purposes of clarity (since the potassium content an order of magnitude higher than the woody materials and so outside the scale of the plots).

It has been observed from Fig. 3 that, in the case of the reference materials, the peak potassium release rate is correlated to the potassium content of the sample. Fig. 8a shows the peak value of the release rate for each material plotted against initial potassium content of the particle. There is a clear trend identifiable (with a regression function R^2 value of 0.84) which indicates that the peak release rate is a function of the concentration of potassium in the particle. This would be consistent with the potassium release being governed by a diffusion mechanism and proportional to the concentration gradient of potassium at the surface of the particle.

Fig. 8(b) shows the duration of the volatile and char combustion stages (total burn-out time) for each material plotted against initial potassium content of the particle. While the herbaceous materials do not fit into a clear trend, there is a good correlation between burn-out time and potassium content for the woody materials. This is also evident in the relative burn-out times observed for the doped reference particles as shown in Fig. 3. The effect is consistent with the observed catalytic effect of potassium on the thermal decomposition and char reactivity as described in Jones et al. [26] and Saddawi et al. [27] and suggests some degree of kinetic reaction control in what is likely to be mainly diffusion controlled (zone II) char combustion.

Having established a means of relating the potassium content of the samples to the total detected potassium release, it is also possible to employ a similar method to estimate the relative quantity of potassium released at each stage of combustion. The devolatilisation and char combustion stages are clear in many of the
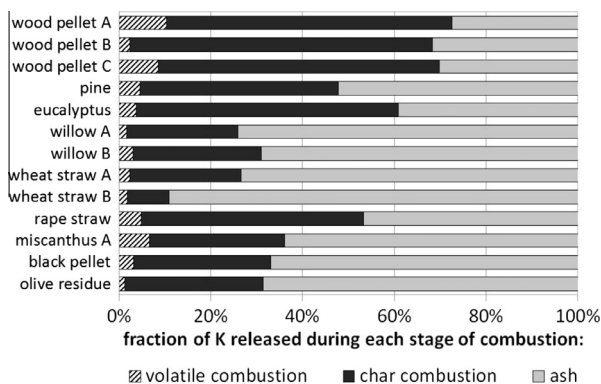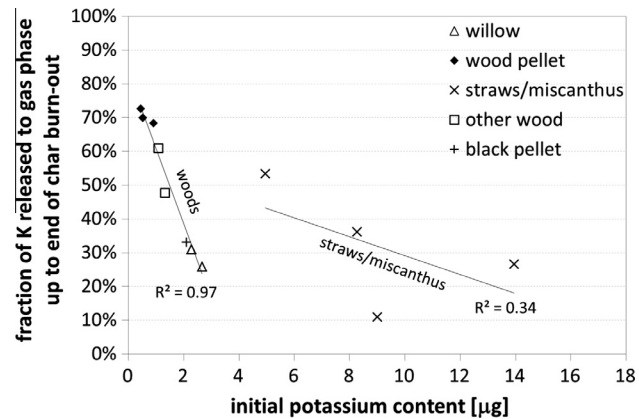

Fig. 10. Relationships between the proportions of potassium released to gas phase up to end of char burn-out and the initial potassium content of the 1.1 mg particle.

recorded profiles. Where the demarcation is not clear, the devolatilisation duration can be established using characteristics obtained from previous single particle experiments [24]. By integration of the respective areas of each stage as identified in the profiles, an estimate of the relative proportion of potassium released during devolatilisation and char combustion can be determined. The inferred fraction of potassium retained in the condensed-phase ash particle at the end of char burn-out is derived from the area under that part of the profile following the char combustion stage (subject to an evaluation error of ±5%). In the experiment this fraction of potassium is released by continued heating or "cooking" of the ash particle in the high temperature flame. The results of such an analysis are presented in Fig. 9. It is noted that the proportions of potassium release in each stage for pine in this figure are similar to those presented in other analyses performed in the study by Fatehi et al.

In the context of the situation inside a furnace, as opposed to the conditions of the experiment, the continuing exposure of the ash particle to high temperatures is dependent on the length of time exposed to the flame and whether it is entrained in the gas flow as fly-ash or drops out as bottom ash. The quantity of gas-phase potassium released in the furnace will then be a function of the particle size and its residence time.

An examination of the derived data in Fig. 7 leads to other relationships of interest. The fraction of potassium released during combustion plotted against the initial potassium content of the particle is presented in Fig. 10. While the overall data shows a weak correlation, there is a strong correlation shown for the woody materials. This shows a similar pattern to Fig. 8b and it is apparent that the fraction of potassium released during combustion is directly related to the burn-out time. An analysis of these parameters for the selected woody materials alone does indeed show a good correlation (with a regression function R^2 value of 0.83). The implication is that higher potassium content leads to faster burn-out (by catalytic effect) which in turn reduces the time during which potassium can be volatilized and diffuse away from the particle. Taken alongside the observations made on the data in Fig. 8b, it seems that the behavior of the herbaceous materials is distinct from the woody materials. This distinction between the two types of material is likely related to other ash components which affect the retention of potassium in the particle.

5. Conclusions

Solid biomass fuels contain significant amounts of potassium. In pulverized fuel fired large scale power generation plant, this is of concern since high potassium ash and high levels of gas phase

Fig. 9. Partitioning of potassium between combustion stages and ash.

potassium in the flue gases can lead to deposition and corrosion problems on heat exchange surfaces. Investigating patterns of potassium release to the gas phase is therefore important in the understanding of the potential ash deposition behavior of biomass. Typical ranges of potassium content for various types of biomass fuel have been presented along with those measured for a selection of fuels used in this study.

An emission spectroscopy detection method has been developed using an optical filter and photodiode detector. This has been shown to be an effective and expeditious means of observing the patterns of potassium release from a range of biomass fuels undergoing combustion at flame temperatures in the range 1600–1800 K – conditions similar to industrial pulverized fuel furnaces. The resulting potassium release profiles allow the fractions of potassium retained in ash and char relative to that released to gas phase to be estimated.

The potassium temporal release patterns for 13 different solid biomass fuel samples have been presented and allowed some general observations to be made as follows:

– The release of potassium during the devolatilisation stage of combustion is small compared with the subsequent release during char combustion for all materials examined.
– The peak rate of release of potassium during char combustion is correlated to the potassium content in the particle.
– The proportion of potassium released during combustion to that retained in the ash is correlated to the initial potassium content, although the latter relationship differs between wood and herbaceous materials.

These relationships and the data presented are useful for the development and verification of modelling for potassium release and partitioning during combustion.

Acknowledgments

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