



Full Length Article

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



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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.

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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.

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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

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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. K₂O₃Si). 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.

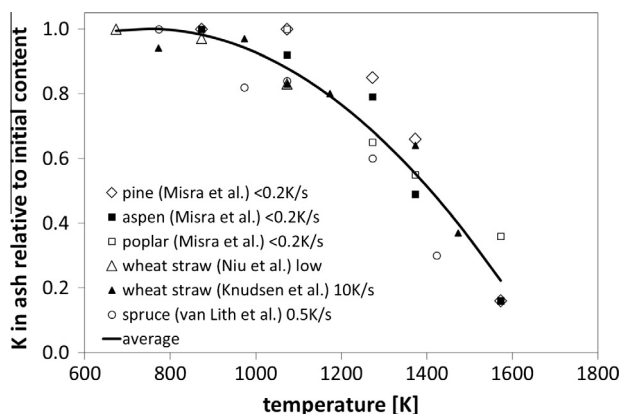


Fig. 1. Compilation of published data [8,13,16,17] showing relationship between combustion temperature and potassium retained in ash (heating rates shown on legend).

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 K₃PO₄, K₂SO₄ 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 × 1 × 2 mm for woody materials and 1 × 1 × 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 than 90% and in some cases up to 100%. This is consistent

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