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RELEASE OF GAS PHASE POTASSIUM DURING COMBUSTION OF BIOMASS - EXPERIMENTAL AND MODELLING OBSERVATIONS

FREIGABE DER GASPHASE KALIUM BEI DER VERBRENNUNG VON BIOMASSE - EXPERIMENTELLE BEOBACHTUNGEN UND MODELLIERUNG

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Abstract

Pulverized fuel furnaces fired with biomass or co-fired with coal and biomass commonly operate at temperatures above 1600K. Such temperatures affect the partitioning of inorganic components through phase transformations. In most biomass fuels, potassium is a significant component present as inorganic species or bound to organic molecules. At temperatures approaching 1600K KOH and KCl become volatilized and are released to the gas phase. These gases condense out in cooler parts of the furnace 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 influencing fouling and slagging in the furnace. In order to model these processes and predict the likely fate of potassium during the combustion process, it is necessary to understand the release mechanisms and patterns of release. The patterns of potassium release from particles of biomass burning in a gas flame can be observed using a flame emission spectroscopy technique. This is implemented using a solid-state photo-detector and optical band-pass filter to measure the intensity of the spectral emission of potassium at 766nm wavelength. The experimental results are used to inform a model of single particle combustion which incorporates a model of gas-phase potassium release. The modelled potassium release mechanisms can be used to predict the partitioning between gas-phase and solid phase ash in different parts of the furnace.

Introduction

Potassium is an essential nutrient for plants and trees and is present in significant amounts in most solid biomass fuels. As with the wide ranging variability of many aspects of biomass fuels, potassium content is no exception. Solid biomass fuels which have typically been used in large scale power plant include coniferous woods such as pine, hardwoods such as eucalyptus, agricultural residues such as straws and olive waste, and energy crops such as miscanthus and short rotation coppiced willow. An indication of the range of typical potassium content in such fuels can be illustrated using data extracted from the published online datab*ase Phyllis2* [1]. From this database, the values for selected materials, such as would be typically burned in large-scale power generation plant, are presented in Figure 1. It can be seen from this study that woody biomass has potassium present in quantities in the region of 1-6 g/kg or 0.1-0.6% weight (dry basis). Herbaceous energy crops and straws tend to have higher quantities. There is also wider variation in these materials especially in the case of straw which is likely affected by different cultivation conditions and treatments. Olive residue is very high in potassium (up to 3% weight) as are other materials derived from seeds and fruits owing to the natural nutrient concentration in these parts of plants. Coals generally have lower quantities of potassium content than most biomass and have significantly lower potassium in proportion to other major inorganic components (Figure 1).

In the raw fuels, 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 [2] [3].

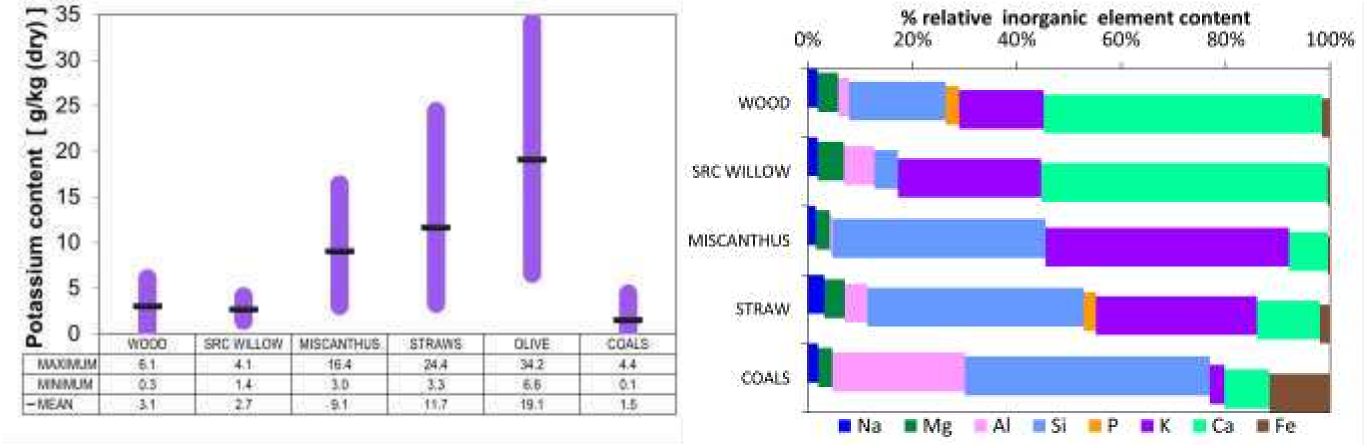

Figure 1 –potassium content of a selection of solid biomass fuels and coals: (a) absolute potassium content; (b) relative content of major inorganic components (data source: [1])

The fate of potassium in combustion

A particle of biomass fuel entering a furnace will heat up and devolatilize very rapidly. The flux of volatiles out of the particle may carry with it some potassium including that which is bound to organic components and that which is entrained in the flow of volatile gases. KCl and KOH start to volatilize at temperatures above 1000K with KOH reaching standard pressure boiling point at 1600K and KCl at

1693K [4, 5]. Since devolatilisation proceeds at temperatures below 1000K, there is little entrainment of gas-phase KCl and KOH at this stage of combustion. Following complete devolatilisation of the biomass fuel particle, combustion is predominantly char oxidation and the temperature of the particle can reach 1400-1600K or more. At these temperatures, gas-phase KCl and KOH are vapourised within the particle and diffuse out in the gas-phase through the char structure, eventually being released at the surface.

Experimental work by Westberg et al. [6] showed that where sufficient water vapor is present in the fuel KOH is released and is stable in the gas-phase. Where sufficient chlorine is present, potassium is also released as KCl. Once in the gas phase, these potassium species interact with the other components in the gas including other chlorides and sulfates. By thermodynamic modelling, Blomberg [7] has shown that the ratio between potassium and chlorine and their concentration effects the proportions of KCl versus KOH in the gas phase. The presence of sulfur in the fuel leads to SO_2 in the gas phase and the formation of K_2SO_4 which produces condensed phase aerosols. The process of gas phase sulfation of KCl in biomass combustion has been shown in experimental investigations and modelling by Li et al. [8] and Hindiyarti et al. [9]. At high temperatures, potassium pyrosulfate ($K_2S_2O_7$) can also form. The resulting condensed phase sulfates lead to direct deposition on furnace surfaces or agglomeration with other solid phase ash components. As combustion gases move to lower temperature parts of the furnace, KCl and KOH will also condense directly on surfaces and on ash particles[10, 11].

Potassium not released to gas phase and remaining in the fuel particle can be retained in the solid as, for example, carbonates in the char while some potassium is also retained as metal atoms intercalated between graphitic carbon layers [12]. As char combustion progresses, more potassium is released to gas phase as carbonates decompose and as graphitic carbon oxidizes unlocking intercalated atoms. As complete combustion is reached, potassium retained in the solid phase eventually has the opportunity to react with other solid phase inorganic components producing various forms of ash. The presence of other elements such as silicon, aluminium, calcium, and iron in the fuel also affects the fate of the potassium and lead to the formation of minerals such as $K_2Fe_2O_4$, $KAlSiO_4$ and K_2CaSiO_4 [12, 13]. Upon deposition, further transformations in the ash can occur with different thermal and oxidizing environments to form feldspars ($KAlSi_3O_8$), feldspathoids ($KAlSi_2O_6$) and micas ($KAl_2(AlSi_3O_{10})(F,OH)_2$) and many other mineral forms [14]. Potassium in the solid phase ash affects ash melting behavior and increases its tendency to adhere to heat exchange surfaces leading to a higher propensity for fouling.

In high temperature environments, potassium from the transformation and decomposition of ash minerals can continue to be released to gas phase. A simplified diagram of the routes of potassium to ash formation and deposition and the phase partitioning of potassium during the combustion process is shown in Figure 2.

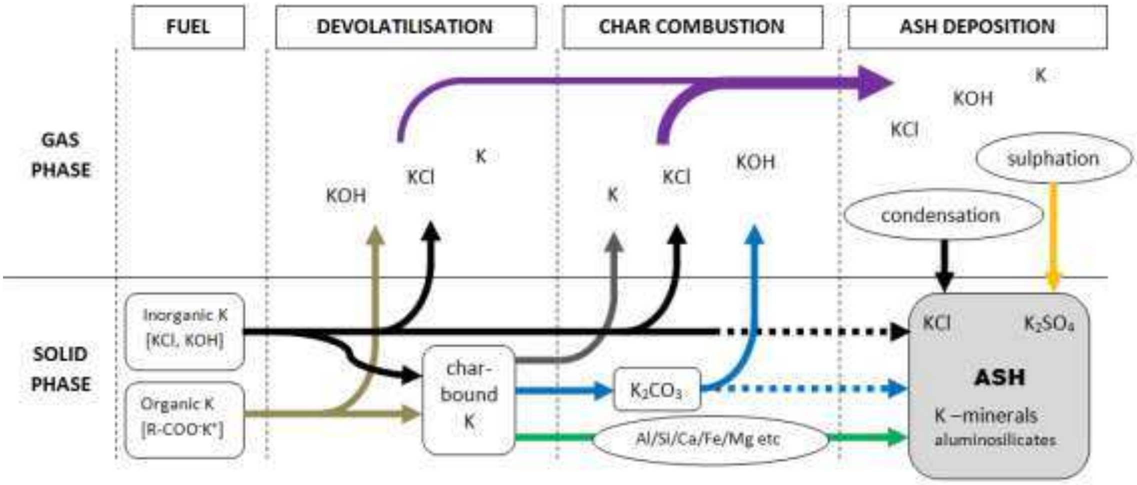

Figure 2 – Potassium phase and species transformations during combustion through to ash deposition

Experimental observations of gas-phase potassium release

To investigate the pattern of gas-phase potassium released during combustion of single particles of biomass, an experimental study was undertaken. Singles particles of a range of biomass fuels in the size range 0.5-4mm maximum length were suspended above a methane burner using apparatus described in previous studies [15]. The particles were exposed to a flame with a temperature of 1600K. The surface temperature of the particles was measured using a thermal imaging camera assuming a surface emissivity of 0.85. The relative concentration of gas-phase potassium in the region of the flame above the combusting particle was observed by a flame emission spectroscopy technique using a photodetector with an optical band-pass filter [16].

Examples of the recorded gas-phase potassium release from three samples of I2 industrial standard wood pellets is shown in Figure 3. Key features of the potassium release profile are observed: (i) an initial minor peak in K release rate associated with devolatilisation; (ii) continued increase in the rate of release as the combustion of the char particle proceeds; (iii) a peak in K release rate towards the end of char combustion (burn-out); (iv) rapid decrease in K-release rate after burn-out to a low (but non-zero) level. Similar profiles have been observed using other techniques including laser induced breakdown spectroscopy (LIBS) [17, 18]. While the form of these profiles is similar for most biomass fuels, differences in the shape of the profile are apparent for different types of fuels and the proportion of potassium released in each stage of combustion can vary. In some low-ash fuels (such wood pellets), the majority of potassium can be volatilised during burn-out and little remains in the solid-phase ash. In other cases, such as wheat straw, the majority of potassium can be retained in the ash [16]. Being able to predict the composition of ash deposits and corrosive chlorides in different parts of the furnace and formation of sulphate aerosols in the flue gases is important for design, operation and control of combustion plant. These experimental observations are useful in informing predictive models of the behavior of potassium in this context.

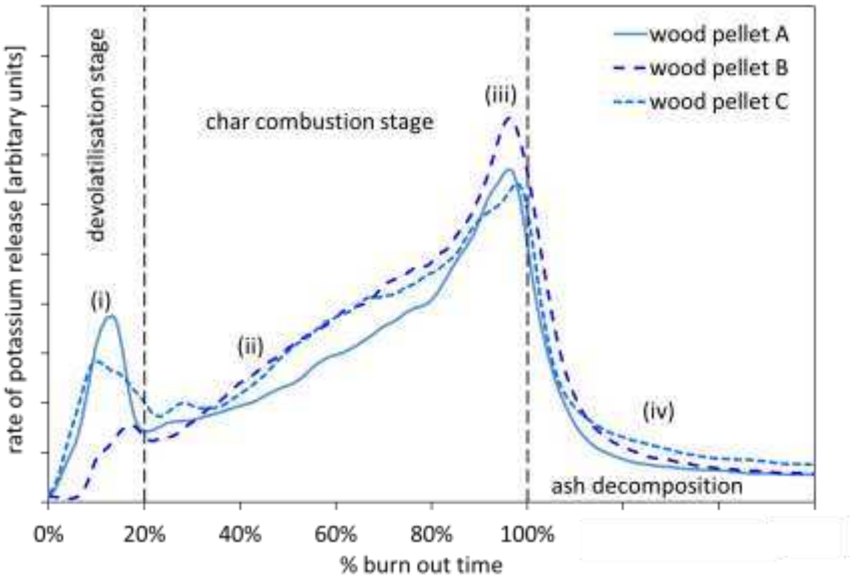

Figure 3 – Example of potassium release profiles for 3 different wood pellets

Modelling gas-phase potassium release

Modelling of the gas-phase release of potassium during the combustion process is an important part of the understanding of inorganic phase transformations and their potential influence on ash deposition and particulate emissions. In developing such modelling it is necessary to construct an adequate model of the applicable combustion process first. This requires sub-models to account for devolatilisation and char oxidation kinetics and incorporating mass transfer (diffusion of volatiles to surface, and oxygen from the surface) and heat transfer (radiative and convective to surface, conductive internally). As mentioned in the previous section, the supposed mechanism for the potassium release model is the volatilisation of (mainly) KCl and KOH. This is highly temperature dependent, so the combustion model needs to accurately determine heat transfer to the surface and internal to the fuel particle, accounting for the energy balances associated with the combustion reactions. The particle model consists of a number of concentric spherical layers for which the temperature, reaction kinetics and gas-phase concentrations are calculated on a discrete time step basis. Heat transfer and gas-phase diffusion inside the particle are determined from the temperature and concentration differences between adjacent layers. A full description of the mathematical basis of this model is included in previous work [19].

A direct comparison between experimental observation and model can be carried out by adopting the combustion conditions of the experiment (methane flame) and using proximate composition and reaction kinetics data obtained from laboratory analyses of the respective fuels. Figure 4 presents two such comparisons.

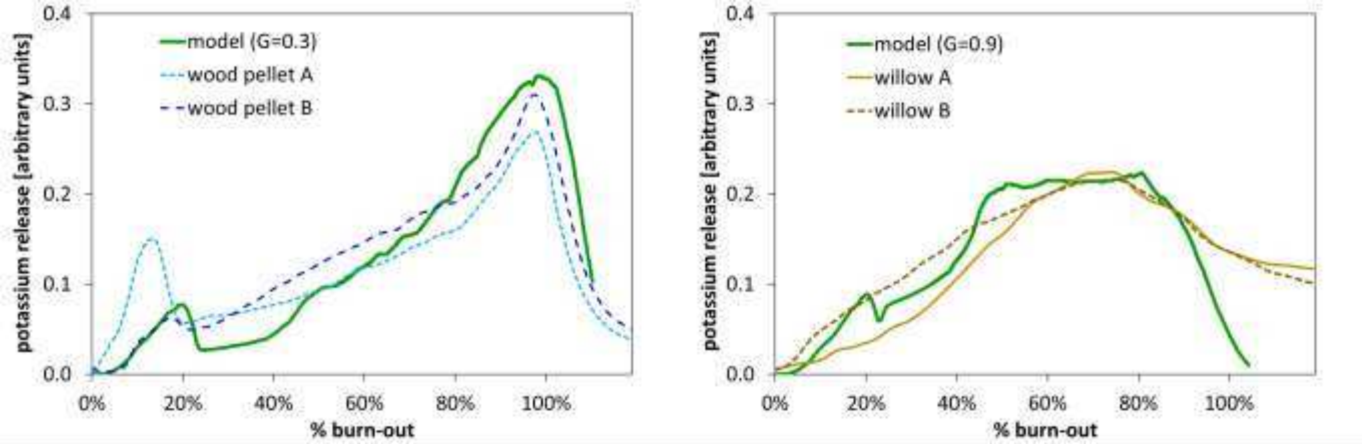

Figure 4 – model compared to observed potassium release profiles: (a) wood pellet; (b) willow

The main shape of the gas-phase potassium release profile produced by the model is influenced by the various physical characteristics of the combusting char particle. Principal amongst these is the temperature of each of the model layers which is partly a function of the heat transfer from the surrounding hot gas flame and partly a function of the internal heat generated from the enthalpies of the char oxidation reactions. It is the latter which contributes to the steady increase in temperature of the char particle which in turn produces an increase in the vapour pressure of KCl and KOH inside the particle as combustion progresses. The other factor that influences the shape of the profile is the rate of diffusion of the gas-phase potassium out of the particle. The effect is illustrated in the modelled outputs shown in Figure 4. The model of the wood pellet combustion (Figure 4(a)) adopts a low diffusivity of gas-phase potassium in the char. This is denoted by the model variable 'G' which derives the diffusivity of $KCl_{(g)}$ and $KOH_{(g)}$ relative to the calculated diffusivity of $O_{2\,(g)}$. The observed profiles of willow have a less pronounced peak in release rate and a model with a higher diffusivity is more representative. This analysis suggests a plausible explanation of the differences in the observed K-release profile between different fuel types.

Application of modelling

Having established a model of gas-phase potassium release from a single particle of combusting biomass, it is possible that this should be incorporated as a sub-model in full-plant CfD models such as those developed by Ma et al. [20] and Edge et al. [21]. The concentration of gas-phase potassium species in different parts of the furnace could then be simulated. Through combination of such a model with other sub-models for gas-phase partitioning of inorganic components, there should be a possibility of determining the relative propensities for corrosive deposits, fouling and particulate formation. Ultimately, these may be assessed in relation to the effects of changing key controllable variables such as particle size distribution and flame temperature. This would be a highly useful tool for optimizing operation with respect to mitigating against adverse ash behavior.

Summary

Observation of single particles of solid biomass fuels in a laboratory scale combustion experiment has produced valuable qualitative and quantitative data on the temporal patterns of release to gas-phase of potassium from the fuel. Mechanisms have been assumed for the release during devolatilisation by entrainment and during char oxidation by vaporization and subsequent diffusion of KCl and KOH. Incorporation of these mechanisms into a single particle combustion model have confirmed that these assumptions produce satisfactory simulation of the observed temporal release profiles. The model has the potential to be combined with higher level plant modelling to predict fouling and corrosion risks associated with combustion of solid biomass fuels.

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