Full Length Article

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

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ABSTRACT

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

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.