



Role of potassium in deposit formation during wood pellets combustion



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ABSTRACT

Biomass boiler issues regarding slagging, fouling and corrosion are related to alkali species present in fuels. These alkali species are released as gaseous alkali chlorides, hydroxides and/or sulfates during combustion. Alkali chlorides/sulfates later condense on cold boiler surfaces enhancing fouling and corrosion. Subsequent deposition of silica-rich ashes leads to the formation of low temperature melting eutectics, especially alkali/earth alkali-silicates (K/Ca-Si), and creates compact and strong deposits. Condensing chlorides/sulfates and low melting eutectics both reduce boiler performance and its availability.

Two different woody biomass fuels and their mixture with two different kinds of aluminosilicate base additives were combusted during this study. Deposits were sampled using two different kinds of probes; cooled deposit probe and un-cooled deposit probe. The macroscopic and microscopic observations and chemical composition of deposit samples are compared using electron microscopic image analysis (EMPA) for both deposit samples. The additive significantly changes the morphology and composition of the deposit samples. The difference in morphology and composition can be explained by the change in potassium chemistry between two cases.

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1. Introduction

Biomass boiler issues regarding slagging, fouling and corrosion are coupled with high temperature chemistry of ash; i.e. its melting and volatility at different temperatures [1,2]. The most significant ash-forming elements in biomass are Si, Al, Fe, Ca, Mg, Mn, K, Na, P, S and Cl, normally making up the majority of ash forming elements [1,3,4]. Among them silicon (Si), alkali earth metal (Ca, Mg), alkali metals (K, Na), sulfur (S) and chlorine (Cl) play a vital role regarding slagging, fouling and corrosion [4–6]. In woody biomass, silicon (Si), calcium (Ca) and potassium (K) are significantly present. This paper focuses on the understanding of the role of potassium (K) and to identify its impact on deposit formation.

In most of the biomass potassium (K) is expected to occur in the form of chloride, sulfates, carbonates and phosphate salts. Potassium (K) can also occur as metal ions organically associated with biomass fibers. In pulverized fuel combustion where temperature reaches relatively high (≥ 1300 °C), potassium is expected to release in gaseous phase as KOH and KCl. K_2SO_4 having a very low vapor pressure is more stable in condensed phase (solid or liquid). The amount of chlorine limits the amount of KCl and the remaining potassium is probably released as KOH at higher temperature.

Subsequent interaction of released potassium species with silicon leads to the formation of low melting silicates. This has a considerable

impact on the deposit formation and growth. The presence of molten deposits creates a significant risk of un-controlled deposit growth and requires frequent soot blowing operations. Additionally, alkali chlorides/sulfates may later condense on cool boiler surfaces which have direct impact on fire side corrosion. The condensing chlorides/sulfates and low melting silicates both reduce boiler performance and its availability.

The use of various mineral additives during biomass combustion has been extensively discussed as an attractive solution to mitigate slagging, fouling and corrosion related issues [7]. The effectiveness of aluminosilicate base additives to capture gaseous potassium species formed during biomass combustion has been previously studied, mostly with kaolinite [5,8–10]. Some previous studies are also found using coal fly ash as an additive instead of kaolinite mineral [5,8,9]. It should be noted that the basic idea of using coal fly ash is also the abundance of aluminosilicate found in coal fly ash. The positive role of coal ash composition has been also discussed in many biomass co-firing studies [8].

The amorphous aluminosilicate called meta-kaolin ($Al_2O_3 \cdot 2SiO_2$) formed during the thermal decomposition (endothermic de-hydroxylation) of kaolinite is responsible to capture gaseous alkali species as the high melting potassium aluminosilicate component [8]. Kalsilite ($KAlSiO_4$) and leucite ($KAlSi_2O_6$) have been identified among the products [8,9]. Tran et al. [10] studied the capture efficiency of gaseous potassium species by kaolin in air (water vapor content no more than 20 ppm) at 850 °C and concluded that kaolin captures potassium irreversibly. The capture efficiency was similar for KCl and KOH but less effective for K_2SO_4 . Most of the published previous studies [5,8–10] are done at 900 °C or below and discuss gas–solid interaction of alkali species and with kaolin. However, few studies have been performed

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Table 1

Proximate and elemental analyses of the wood pellets used in this study [percentages on a weight basis; W: water; A: ash; V: volatiles; FC: fixed carbon].

Wood Pellets	W [% ad]	A [% db]	V [% daf]	FC [% daf]	C [% daf]	H [% daf]	N [% daf]	S [% daf]	Cl [% daf]
WP-1	2.9	1.2	81	19	48	5.4	0.34	0.016	0.015
WP-2	6.5	2.6	80	20	52	5.0	0.02	0.087	0.021

to understand the behaviour of mineral additive when feed together with biomass at higher temperature relevant to pulverized fuel combustion [11–14].

This study focuses on the formation of deposits during pulverized wood pellets combustion and the impact of the additive on deposit formation. Deposit samples during various combustion tests were evaluated using electron microscopic image analysis (EMPA). Both, morphology and composition of deposit samples are discussed to evaluate the influence of the additive. The equilibrium calculations were performed to discuss the major reactions pathways to explain the difference in deposition mechanism.

2. Material and method

2.1. Fuel and additive

Table 1 shows the proximate and elemental composition of the wood pellets combusted during this study. The analysis represents the composition of pulverized wood pellets (milled and sieved through 400 μm sieve).

Table 2 shows the composition of ash oxides in respective fuel. As typical wood pellets fuel, SiO_2 , CaO and K_2O , account for the majority of ash oxide composition.

Two different kinds of aluminosilicate based additives were used during this study. ICP-OES analysis confirmed that SiO_2 and Al_2O_3 are the major oxides present in both additives. The water (moisture, 105 $^\circ\text{C}$) content in additive A is around 1% and in additive B was around 13%. The loss on ignition (950 $^\circ\text{C}$) was 11.44 and 10.28 for additive A and additive B, respectively. It is expected to be due to the release of combined water present in the mineral additive. The composition of additive (as oxides in db, normalized, ICP-OES analysis) is shown in Table 3. The XRD analysis confirms that the kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) is the major mineral constituent present in both additives.

Both additives were used as fine powder. The d_{10} , d_{50} and d_{90} of additive A were in the ranges 1.0 μm , 4.0 μm and 13 μm and for additive B they were in ranges of 1.6 μm , 7.9 μm and 61.3 μm respectively (determined by laser diffraction). The additive mixed with WP-1 is referred as additive 'A' and additive mix with WP-2 is referred as additive 'B'. The pulverized fuel was mixed with the respective additive (fine powder) prior to the combustion test. The mixture was prepared in small batches (amounts) to insure homogenous distribution of the additive with fuel as much as possible. The average mixing ratio was 1.5 wt.% of additive A with WP-1 and 2 wt.% of additive B with WP-2. The mixing ratio represents the average mixing ratio in dry basis.

2.2. Combustion test

The combustion tests were performed at the combustion test facility at IFK, University of Stuttgart. The functionality of BTS is similar to an

atmospheric drop tube facility. Fig. 1 shows the schematic outline of the BTS combustion reactor. Five different temperature zones can be established along the height of the furnace. The vertical oil cooled sampling probe can move up and down along the vertical axis of the furnace which facilitates sampling at desired location inside the furnace.

The combustion parameters were kept constant for all the combustion cases. For the combustion test with additive, the respective amount of additive was pre-mixed with fuel. The feeding rate of fuel and pre-mixture fuel both were around 2 kg/h. The combustion air was chosen to keep the excess O_2 (3–3.5 vol.%, dry) at the end of furnace (2.5 m down the combustion chamber), for each combustion test.

For WP-1 and WP-1 + A all temperature zones (T1–T5) were set to 1300 $^\circ\text{C}$ i.e. the temperature at the deposit sampling point was also \sim 1300 $^\circ\text{C}$. The temperature zone in the upper temperature zone (T1–T2) for WP-2 and WP-2 + A was set at 1300 $^\circ\text{C}$ while T3, T4 and T5 were respectively set at 1200 $^\circ\text{C}$, 1150 $^\circ\text{C}$ and 1100 $^\circ\text{C}$. It means that the temperature at the deposit sampling point was \sim 1200 $^\circ\text{C}$.

Two different deposition probes were used for deposit sampling, namely cooled and un-cooled deposit probe. Uncooled deposit was sampled over a half circle ceramic surface. The temperature of ceramic surface remains equal (in equilibrium) with the surrounding temperature at the sampling location. While the cooled deposit was sampled using the temperature control probe. It is equipped with a replaceable metal probe attached with a thermocouple. The temperature of the metal probe is maintained by the air flow. The temperature at the surface of the replaceable metal probe was kept at \sim 550 $^\circ\text{C}$. Both deposits were sampled for \sim 3 h in a stable operating condition. The sampling location was 1.5 m down the burner for both deposits. The residence time (calculated from the total flue gas) from the burner mouth to the deposit sampling location is around 3 s.

The cooled probe simulates the boiler heat exchanger surfaces. The condensable ash species in the surrounding hot flue gas, fine fly ash particles and aerosols transported to the cooled surface due to thermophoresis and molten/semi-molten & solid fly ash particles collected due to inertial impaction represent the deposit developed over the cooled probe. It represents the initial deposit layer. The temperature of the surface of the uncooled probe is similar to the surrounding flue gas and represents the outer deposit layer that would develop on boiler heat exchanger surfaces over time. The uncooled deposit also represents the high temperature slagging deposits. The molten/semi-molten and solid fly ash particles collected mostly due to inertial impaction form the uncooled deposit. The deposit samples collected during the experiment were prepared for electron microscopic image analysis. The BSE image of the deposit sample cross-section was generated to visually evaluate the morphology of deposits. SEM-WDX analysis was performed to generate element maps to evaluate the quantitative distribution of major elements present in the deposits. Additionally, SEM-EDS analysis was performed to quantify the major elements present in deposits.

Table 2

Analysis of wood pellets by ICP-OES for main ash forming elements [percentages on a weight basis].

Ash (550 $^\circ\text{C}$)	Al_2O_3 [% db]	CaO [% db]	Fe_2O_3 [% db]	K_2O [% db]	MgO [% db]	Na_2O [% db]	P_2O_5 [% db]	SO_3 [% db]	SiO_2 [% db]	TiO_2 [% db]
WP-1	2.6	18	1.5	6.6	4.7	1.4	2.0	1.9	32	1.0
WP-2	6.4	11	3.5	5.8	4.1	1.2	1.6	1.0	56	0.3

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