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# Alkali transformation during single pellet combustion of soft wood and wheat straw



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#### ARTICLE INFO

#### ABSTRACT

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Keywords: Biomass Combustion Ash Alkali Release Single pellet Controlling slag and deposit formation during thermochemical fuel conversion requires a fundamental understanding about ash transformation. In this work, a macro-TGA reactor was used to determine the release of ash forming elements during devolatilization and char combustion of single pellets. Soft wood and wheat straw were combusted at two temperatures (700 °C and 1000 °C) and the residual ashes were collected and analyzed for morphology, elemental and phase composition. The results showed that the single pellet combustion exhibit similar release character as in grate boilers. The temporal release was found to be both temperature and fuel dependent. For wood, the release of potassium occurred mostly during char combustion regardless of furnace temperature. Similar results were found for straw at 700 °C, but the temperature increase to 1000 °C implied that the release occurred already during devolatilization. The differences are presumably explained by different fuel phase compositions. The residual ash were composed of three different categories of phases; crystalline compounds, molten ash (glass) and char, and the work concludes that K was captured by crystalline K/Ca-carbonates as well as in amorphous glassy silicates for wood, and by almost fully molten ash of glassy silicates for straw. The fuel conversion processes occurring on a grate influence the fuel combustibility in terms of e.g. burnout, slag formation and release of fine particle and deposit forming matter, and the present work has given novel insights into the specific alkali behavior during biomass fuel conversion.

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#### 1. Introduction

Ash related operational problems, like slag and deposit formation in combustion appliances as well as fine particle emissions, are major concerns in biomass combustion that decreases the performance and may hinder an extension of the biomass resource base for heat and power production. The phenomenon of fouling is described in general terms by e.g. Bryers [1], and specifically for grate boilers by Yin et al. [2] and Bashir et al. [3]. The mechanisms of slag formation in grate boilers are not covered to the same extent in the literature but Näzelius et al. [4] depict the present understanding.

The distribution and transformation of alkali metal compounds within the burner and boiler during biomass combustion determines to a large extent the type of operational problem and degree of severity. Deposit formation on heat transfer surfaces and formation of fine particle (PM<sub>1</sub>) emissions is mainly influenced by the release of alkali species. Suppressing the release, i.e. capturing alkali metals to the bottom ash as non-volatile compounds, is thus one way to control fouling and PM<sub>1</sub> emissions. However, a drawback of capturing alkali metals to the bottom ash during fixed bed combustion is an increased risk of slagging

\* Corresponding author. *E-mail address:* jonathan.fagerstrom@umu.se (J. Fagerström). due to the potential formation of sticky ash melts [4–5]. Controlling both slag and deposit formations during biomass combustion requires a fundamental understanding about ash transformation, especially when the fuel resource base is extended towards new ash rich assortments and biomass mixtures for co-combustion situations.

To elucidate the underlying phenomenon and mechanisms related to these ash chemical effects, controlled studies in lab-scale reactors are a useful approach. For wood and straw fuels, some experimental work has been performed in specific reactor set-ups to elucidate the effect of temperature on the release of mainly K, S, and Cl by analyzing the elemental composition of the residual ash after full conversion of powder samples [6–8]. The experimental procedure applied in these studies included a step-wise thermal treatment of the fuel/ash with different atmospheres that resulted in long (200 min) conversion times. The capturing mechanisms for certain ash forming elements were discussed through the support of thermodynamic equilibrium calculations. In a recent study, the same experimental approach was used to study the release behavior of K, Cl, S and P during combustion of the energy crops poplar and brassica [9]. Furthermore, the composition of wood ash during thermal treatment has been studied in a similar manner and reactor also by other authors [10]. Another approach to study the alkali release behavior is by measuring alkali species in the evolving gas during thermal treatment, which has been performed for small biomass powder samples [11–12]. However, the composition of the residual ashes in those experiments was not analyzed and considered in relation to the release behavior of certain elements, and total quantifications of the released fractions during different fuel conversion stages have so far not been presented in the literature.

Thus, a detailed understanding of the time-resolved quantitative release behavior of critical ash forming elements in relation to the fuel conversion process, are to a large extent still lacking. Such information are vital for the development of generally applicable models of the ash transformation that can be applied on different biomass fuels to predict technical and emission related problems. The objective with the present study was therefore to determine the release of major ash forming elements after both the devolatilization phase and the char combustion using single pellets of soft wood and wheat straw. The phase compositions of the residual ashes were further determined after full conversion to study the capturing mechanism of alkali metals and to explore the overall ash transformation processes on a single fuel pellet level.

#### 2. Material and methods

#### 2.1. Fuels

Two biomass fuel pellets were used, softwood without bark consisting of a spruce/pine mixture from northern Sweden, and wheat straw delivered from Denmark. The pellets were 8 mm in diameter and weighed 700  $\pm$  50 mg. The ash content and the concentration of ash forming elements in the two fuels is presented in Table 1 together with reference data for the two fuels. As seen in Table 1, the composition of the two fuels is similar to the previously reported reference data. Thus, both of the included fuels, i.e. softwood and wheat straw, can be considered to be representatives. Besides the fuel bulk analysis (Table 1), additional fuel analysis was performed to determine the deviation of moisture and ash content within the pellet batch. 12 different pellets were placed in different ceramic containers and inserted into a muffle furnace at room temperature. The moisture contents were achieved (7.9  $\pm$  0.2% and 13.5  $\pm$  0.4% for soft wood and wheat straw respectively) by heating the pellets at 105 °C until no weight loss could be detected. The ash contents (0.33  $\pm$  0.02% and 4.63  $\pm$  0.09% for wood and straw respectively) were achieved by increasing the temperature to 550 °C in 1 h and keeping it at 550 °C for an additional1 h or until no unburned material was visible. The low standard deviation for the ash contents indicated that the ash matter was evenly distributed within the pellet batch and consequently that a good consistency could be achieved for the replicates during fuel conversion.

#### 2.2. Macro-TGA reactor

The macro-TGA reactor was recently described by Biswas et al. [13] and in previous studies [14–17] a similar reactor has been applied. The furnace was resistively heated by two side panels controlled by PID

#### Table 1

Total ash content (wt-% of ds) and the concentration of ash forming elements (mg/kg of ds) in the soft wood and wheat straw fuels. Reference mean and standard deviation values adapted from [37].

	Softwood	<sup>a</sup> Reference (11)	Wheat straw	<sup>a</sup> Reference (7)
Ash content	0.40	n.a.	4.48	n.a.
K	564	$561 \pm 157$	6970	$8658 \pm 6881$
Na	22	$39 \pm 46$	201	$359 \pm 1080$
Ca	751	$1118\pm351$	3010	$3910 \pm 2287$
Mg	140	$178 \pm 39$	688	$1099 \pm 1072$
Al	34	$135\pm198$	217	$358 \pm 403$
Si	420	$662 \pm 1307$	11100	$18,960 \pm 27,066$
Р	44	$71 \pm 28$	385	$1283 \pm 2600$
S	72	n.a.	913	n.a.
Cl	59	n.a.	2300	n.a.
Zn	12.7	n.a.	6.6	n.a.

<sup>a</sup> Number in parenthesis denote number of samples.

regulators and a type N thermocouple situated 10 mm above the grate and 30 mm below the fuel sample. The internal dimensions of the furnace were  $200 \times 130 \times 130$  mm and a cylindrical quenching tower was separated from the furnace zone by a slide hatch to enable the use of different atmospheres in the quenching tower and furnace. A pneumatic cylinder underneath the furnace was used to lower and raise the furnace into position of combustion or quenching. The sample basket, made of platinum to avoid interactions between the fuel ash and sample holder, was hung from an on-line analytical balance with resolution of 1 mg. A window on the front side facilitated visual inspection and video monitoring of the fuel conversion stages. The gas supply consisted of two sources, N<sub>2</sub> and air, both controlled by calibrated volume flow meters. A schematic sketch is presented in Fig. 1.

#### 2.3. Combustion experiments

#### 2.3.1. Experimental procedure

Three replicates were performed for each experiment. The experiments were performed with an oxygen concentration of 10 vol-%, a total gas supply of 15 l per minute (0 °C and 100 kPa), and at furnace temperatures of 700 °C and 1000 °C. The combustion temperature, i.e. the temperature in the pellet, was measured with a type N thermocouple ( $\emptyset$  1.5 mm) inserted into a drilled hole in the pellet. These measurements were performed for both fuels and for both furnace temperatures prior to the release experiments since the set-up did not enable simultaneous temperature and gravimetric analysis.

The ash release was determined for two fuel conversion stages by performing two separate experimental procedures. The experiments involving the first stage (devolatilization) was quenched before the char combustion started, i.e. when the fuel pellet stopped flaming and turned glowing red by char oxidation. The extinction of the flame coincided with the "break", i.e. deflection point, of the weight curve (Fig. 3) and



Fig. 1. Schematic sketch of the macro-TGA reactor.

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