



Two strategies to reduce gaseous KCl and chlorine in deposits during biomass combustion – injection of ammonium sulphate and co-combustion with peat

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ABSTRACT

Combustion of a biomass with an enhanced content of chlorine can result in operational problems including deposit formation and superheater corrosion. The strategies applied to reduce such problems include co-combustion and the use of additives. In this work a mixture of wood pellets and straw pellets was fired in a circulating fluidised bed boiler. Two strategies were applied to decrease the risk of superheater corrosion by reducing gaseous KCl and content of chlorine in deposits: sulphation of KCl by injection of ammonium sulphate and co-combustion with peat. During co-combustion of biomass with peat both sulphation of KCl and capture of released potassium in ash components can be of importance. The results were evaluated by means of IACM (on-line measurements of gaseous KCl), deposit probe measurements (chemical composition in collected deposits, initial corrosion) and ash analysis (chemical composition in fly ashes). The best overall performance was achieved with ammonium sulphate, which significantly reduced KCl. Meanwhile almost no chlorine was found in the deposits. Only a minor reduction of gaseous KCl was obtained during co-combustion although the chlorine content in the deposits was greatly reduced. The resistance to initial corrosion was improved during both injection of ammonium sulphate and co-combustion with peat.

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1. Introduction

Certain biomass fuels such as straw contain high amounts of alkali (mainly potassium, K) and chlorine (Cl), and low amounts of sulphur (S). During combustion chlorine is released to the gas phase mainly as HCl and KCl. High levels of KCl in the flue gas often result in enhanced deposit formation whereas high content of chlorine in deposits causes accelerated superheater corrosion [1]. Combustion of such biomass fuels in a fluidised bed boiler can result in various operational problems including bed agglomeration, deposit formation and superheater corrosion [1,2]. These problems can be mitigated by either co-combustion or the use of additives. Peat, coal and municipal sewage sludge (MSS) are examples of fuels suitable for co-combustion with biomass [3–6]. The chlorine content in the deposits can be reduced by means of both capture of K in ash components from the additional fuel, and/or sulphation of KCl due to its sulphur content. The formation of alkali alumino silicates was identified as the dominant path to capture alkali during co-combustion of coal and Meat and Bone Meal (MBM) [5]. In this investigation, sulphur in the different coals was less relevant in preventing alkali chloride deposition. The content of Cl in

deposits was eliminated during co-combustion of a chlorine-rich biomass with MSS, whereas the content of K only decreased [3]. The KCl concentration in the flue gas was partly limited by sulphation, and partly by capture of K by the sludge ash. K captured was found in species mainly composed of silicon (Si), aluminium (Al), calcium (Ca), iron (Fe), and phosphorus (P). Especially important was the formation of potassium aluminium silicates, although the presence of Ca, Fe and P was also found to influence the alkali capture chemistry [7].

During co-combustion with peat both sulphation of KCl due to the sulphur content in peat and capture of released K in peat ash minerals can be of importance. Various peat fuels representing a wide range of ash-forming elements have been investigated [4,8,9]. Here the major ash-forming elements were Si, Al, Ca, Fe and S. It was proposed in [8] that the positive effects on deposit formation and composition during co-combustion with peat were capture of alkali in the gas phase via reactive peat ash. The composition of the reactive components in the peat ash remained unidentified since only small amounts of crystalline phases were detected by XRD (X-Ray Diffraction). Co-combustion of peat was one of the measures applied to reduce gaseous KCl and chlorine in the deposits during a large-scale investigation [6]. While only a minor reduction of gaseous KCl was obtained, the chlorine content in the deposits was greatly reduced. It remains unclear whether this reduction was due to heterogeneous sulphation or alkali capture on ash particles. Despite these efforts, the positive effects on deposit formation and superheater corrosion from peat are not yet

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fully understood. Aluminium silicates in peat ashes could possibly capture alkali from KCl by formation of alkali aluminosilicates. This formation is also important during co-combustion with coal [5], and during addition of clay minerals such as kaolin [10,11]. The main constituent of kaolin is kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$). Reactions between kaolinite and KCl to form leucite (KAlSi_2O_6) and kalsilite (KAlSiO_4) are presented in [11,12].

Elemental sulphur or other sulphur/sulphate-containing additives can be used for sulphation of alkali chlorides during biomass combustion. The additive reacts with KCl, converting it to a less corrosive alkali sulphate. Both homogeneous (gas phase) and heterogeneous (liquid or solid phase) mechanisms have been proposed for the formation of alkali sulphates from alkali chlorides found in deposits or in ash particles [13]. Two sulphur containing additives were evaluated in [14] for sulphation of gaseous KCl: elemental sulphur (S) and ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$). Ammonium sulphate reduced the amount of gaseous KCl and also the chlorine content in the deposits significantly better than sulphur. Thus the presence of gaseous SO_3 was of greater importance than that of SO_2 for sulphation of gaseous KCl. These results by Kassman et al. [14] support the proposal that sulphation of gaseous KCl takes place according to the reaction formula (R1):



Another possibility to extend the lifetime of superheater tubes in a boiler is to replace low-alloyed steels with more corrosion resistant materials. Chromia-forming austenitic stainless steels, high-alloyed FeCr steels and Ni based superalloys are among the alternative materials when firing biomass and waste fuels. The low-alloyed steels contain insufficient levels of chromium to form a protective chromia-rich oxide. Hence, low-alloyed steels are poorly protected already from the outset. The increased corrosion rate in the presence of alkali chloride rich deposits is often attributed to the so-called active oxidation mechanism in which $\text{Cl}_2(\text{g})$ acts as a catalyst in the corrosion attack [15]. Another mechanism, based on the inward diffusion of chlorine ions, has been proposed in recent years [16,17]. However, it has been shown that even though more chromium-rich materials are being used, the corrosion rates remain unsatisfactorily high [18–22]. One reason for this has been suggested to be due to chromium depleting reactions between the deposit/flue gas and the protective oxide [18,19]. It has previously been shown that oxygen-water vapour-mixtures can induce such a chromia depleting process [23]. Another process resulting in the breakdown of the protective oxide is the reaction between alkali salts (e.g. KCl, NaCl and K_2CO_3) and the chromia-rich oxide forming chromate [16,24–27].

Demonstrated in this paper are two strategies to decrease the risk of superheater corrosion by reducing the amount of gaseous KCl in the flue gas and the content of chlorine in deposits. These strategies were co-combustion with peat and injection of ammonium sulphate both of which have previously been investigated in a large-scale circulating fluidised bed (CFB) boiler [6]. The main scope of this paper is to gain improved understanding of how gaseous KCl and chlorine in deposits are reduced during co-combustion of biomass and peat. This investigation was part of a larger project carried out in a full-scale CFB boiler used for research purposes. Results obtained in that particular CFB boiler focusing on co-combustion with sewage sludge and coal are presented in [3] and [28] respectively.

2. Materials and methods

2.1. The boiler and the operating conditions

The experiments were performed in the 12 MW CFB boiler at Chalmers University of Technology (CTH) shown in Fig. 1. This research boiler facilitates measurement campaigns in a full-scale boiler, while

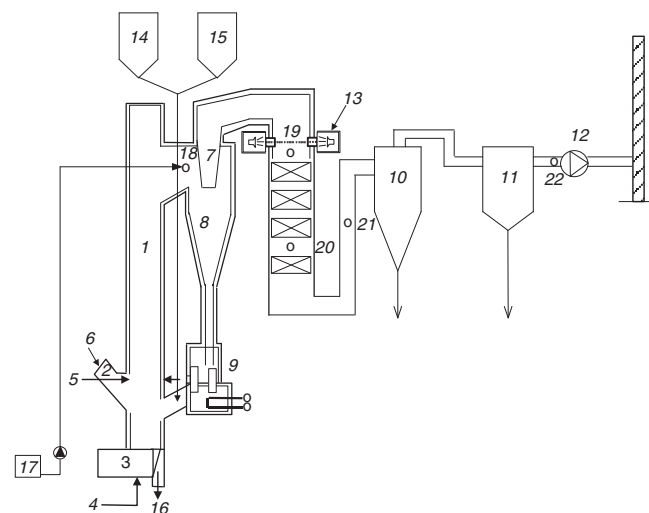


Fig. 1. The 12 MW CFB boiler. 1. furnace; 2. fuel chute; 3. air plenum; 4. primary air; 5. secondary air; 6. fuel feed and sand; 7. cyclone outlet; 8. primary cyclone; 9. particle seal; 10. secondary cyclone; 11. bag house filter; 12. flue gas fan; 13. IACM; 14. PVC; 15. kaolin; 16. bed material; 17. ammonium sulphate (AS); 18. injection of AS; 19–22. measurement positions; 19. before the convection pass; 20. in the convection pass, 21. after the convection pass; 22. before the stack.

maintaining control over important operation parameters such as load, air supply and composition of the fuel mix. The boiler has been described earlier in several publications including [3,14,28–30]. The combustion chamber has a square cross-section of about 2.25 m^2 and a height of 13.6 m. Fuel is fed from a fuel chute (located at the front of the boiler) to the lower part of the combustion chamber. The bed material is recirculated through the cyclone back to the combustion chamber, whereas the combustion gases enter the convection pass where the gases are cooled down to $150 \text{ }^\circ\text{C}$ before cleaning in a secondary cyclone and a bag house filter. Operating conditions typical of CFB boilers were selected. Silica sand ($d_p = 0.3 \text{ mm}$) was used as bed material.

The base fuel was wood pellets (made from saw-dust of stem wood of pine and spruce from the saw mill industry in Sweden). Straw pellets (made from wheat straw and manufactured in Denmark) were used as additional fuel to increase the level of gaseous KCl. Co-combustion was carried out with a mixture of straw pellets and peat. The peat selected had a medium degree of humidification and was dominated by sphagnum and carex. It came from a moss in Storuman in the north of Sweden and its composition was similar to the peat from Norrheden in [8] with a rather low calcium content. The major ash-forming elements were Al, Fe, Ca, Si and S.

The test plan consisted of four main test cases: Ref, Peat, RefCl, and ASCl. These test cases are described in more detail below. Table 1 presents the operating parameters for each of the test cases and the different fuel properties are given in Table 2. Each test was carried out according to the same procedure during a period of 12 h with stable

Table 1
Operating parameters.

Parameter	Ref	Peat	RefCl	ASCl
Load (MW)	6.4	5.9	6.5	6.4
Fraction of straw pellets, % of load	24	25	24	21
Bed temperature ($^\circ\text{C}$)	851	851	851	851
Temperature, top of furnace ($^\circ\text{C}$)	863	874	866	871
Temperature, cyclone outlet ($^\circ\text{C}$)	811	827	823	824
Temperature, after bag filter ($^\circ\text{C}$)	152	153	150	151
Pressure drop in furnace (kPa)	7.4	7.5	7.4	7.4
Excess air ratio	1.26	1.21	1.26	1.23
Primary air/total air flow (%)	57	56	54	56
Fluidisation velocity (m/s)	4.9	4.7	4.8	4.8

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