

Effect of Sewage Sludge Addition on Potassium Release and Ash Transformation during Wheat Straw Combustion

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Combustion of wheat straw for heat and power production is often challenging due to ash related problems such as fouling deposition and high temperature corrosion. Release and transformation of ash forming elements K, Cl and S directly respond to these problems. In this work, sewage sludge was tested as an additive to reduce potassium release during the wheat straw combustion. The wheat straw with and without sewage sludge addition (5 %, wt/wt) were combusted in a temperature range 700 °C to 1000 °C. The ash residues from each combustion test were analyzed with a combination of an inductively coupled plasma optical emission spectroscopy (ICP-OES), scanning electron microscopy equipped with energy dispersive X-Ray analysis (SEM-EDX) and X-Ray diffractometry (XRD). It was found that that release of potassium from the wheat straw started already at 700 °C. About 80 % of the potassium released from after the wheat straw combusted at 1,000 °C for 1 h. Most of the potassium evaporated as potassium chloride in the temperature range 700-900 °C as indicated by SEM-EDX and XRD analyses. Addition of sewage sludge considerably reduced potassium release from the wheat straw as temperature was over 800 °C. At 1000 °C, less than 60 % potassium released from the wheat straw and the rest retained in ash residues after combustion tests. The SEM-EDX and XRD analysis results revealed that aluminum silicates, phosphorus and calcium in the sewage sludge played critical roles in capturing potassium from the wheat straw, through forming different potassium aluminum silicates and phosphates. The results from current study indicate that addition of sewage sludge may be beneficial to reduce potassium release and thereby fouling deposits in wheat straw combustion applications.

1. Introduction

Combustion of wheat straw is the most widely applied way for converting such agricultural residue for energy and heat production (Wu et al., 2011a). The wheat straw is now combusting along or co-firing with other biomasses or coal in different scale combustion applications (Houshfar et al., 2013). However, ash related problems more than often take place in the combustor, as the wheat straw is used for different combustion applications. These problems mainly relate with presence and transformation ash forming elements K, Cl and Si. The potassium may react with Cl and release as KCl during combustion of the wheat straw (Boström et al., 2011). Formation of potassium salts such as KCl and K₂SO₄ is a main reason for ash fouling deposits and high temperature corrosion of the heat transfer sections of combustors or boilers. In addition, the K readily reacts with inherent and contaminated silica in the fuel, leading formation of low temperature melting potassium silicates. Continuous formation of the potassium silicates melts cause ash sintering/slagging in grate boilers and bed agglomeration in fluidized bed combustors. In addition, the potassium may react with phosphorus in the wheat straw or other P rich agricultural residues during combustion processes. Potassium phosphates are main products from such reactions, and part of them melt and promote ash sintering and bed agglomeration of the wheat straw ash (Wang et al., 2011). Different additives have been tested for abating ash related problems during combustion of the wheat straw (Wang et al., 2013). These additives may capture the problematic potassium containing compounds through chemical and physical reactions or combination of the two mechanisms (Wang et al., 2012).

Recently, sewage sludge has been tested as an additive to reduce ash related problems during combustion of the wheat straw or wheat straw contained fuel pellets (Skoglund et al., 2013). Addition of sewage sludge considerably increased the wheat straw ash melting points and decreased ash sintering degree as well. (Wang et al., 2013) In other studies, utilization of sewage sludge successfully reduced ash fouling deposits during combustion of wheat straw contained biomass pellets in a fluidized bed boiler (Elled et al., 2010). It was suggested aluminium silicates, sulphur, calcium and phosphorus may all involve in capturing potassium containing compounds (mainly KCl) and converting them into less troublesome potassium aluminium silicates, sulphates and calcium phosphates (Wu et al., 2013). However, addition of sewage sludge on the potassium release and ash transformation during the combustion of wheat straw has been rarely studied. In a recent study, sewage sludge was added in a typical Chinese straw to evaluate effect of the sludge on potassium retention during combustion process (Li et al., 2013). However, the focus of the work was more on interaction of phosphorus in the sludge with potassium in the wheat straw. In addition, a rather large amount of sewage sludge was added in this studied, and the smallest sewage sludge/wheat straw blending ratio is 30 wt%. Such an addition amount is more applicable for fluidized bed combustion application that has high tolerance ash rich fuels. However, addition of a large amount of sludge will cause difficulty of handling and disposing of ash residues during and after the combustion process, considering high ash content (> 30 wt%) of the sewage sludge (Pettersson et al., 2009). Therefore, a rather small addition amount of sewage sludge is more interesting for combustion technologies that are sensitive to in-going fuel ash content, such as grate combustion and pulverized combustion applications. On the other hand, the highest test temperature was 900 °C in the study as reported by Li et al (Li et al., 2013). This temperature is lower than combustion temperatures during combustion of wheat straw in certain combustors.

The objectives of the present work were: 1) investigating effects of the sewage sludge on potassium release during combustion of the wheat straw, 2) studying the transformation chemistry of the wheat straw ash at elevated temperature with and without sewage sludge addition.

2. Experimental section

The wheat straw used in present work was a Danish wheat straw that is characterized as a problematic fuel in terms of ash sintering and fouling. The sewage sludge was received as granules from a waste water process plant in southern Norway. The received wheat straw and sewage sludge were air dried first and milled to particle size smaller than 1 mm, which were dried again at 105 °C to get stable weight. The ash content of the wheat straw and sewage sludge sample was measured through ashing one sample at 550 °C for 6 h. Chemical compositions of each ash sample were analyzed by an inductively coupled plasma optical emission spectroscopy (ICP-OES). The samples for ICP-OES analysis were prepared by following the standard CEN-TS 15920. About 50 mg ash sample produced at 550 °C was digested by a mixture of acid H₂O₂, HNO₃ and HF in the first stage, and H₃BO₃ in the second stage.

The combustion experiments were carried out with following steps: 1) to investigate potassium release behavior, the wheat straw without and with 5% (wt/wt of dry wheat straw) sewage sludge addition were combusted at temperature 700, 800, 900 and 1000 °C, respectively. Approximate 10 g sample was loaded in a Pt-Au crucible that was sent into a furnace and combusted at the desired temperature for 1 h. In order to ensure reproducibility of the experiment, the combustion experiments were repeated three times, and ash residues from each of them were analyzed by ICP-OES. Part of the ash residues were analyzed by a Bruker D8 Advance X-ray diffractometer using Cu k-alpha radiation and a LynxEye detector. Identification of the crystalline components in each sample was done by operating an instrument integrated TOPAS evaluation program and the ICDD-PDF2 database. The representative ash residues were analyzed by scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectrometry (EDX). The ash residues were embedded in resin, which were cut and polished before SEM-EDX analysis. EDX semi-quantitative spot/area analyses were carried out for interesting areas to get more detailed microchemistry information.

3. Results and discussion

3.1 Fuel analysis

Table 1 shows ash content and concentration of ash forming elements in the wheat straw and sewage sludge. The ash content of the wheat straw was 5.37 wt%, and the ash contains substantial amounts of K, Si, Cl and Ca. KCl and SiO₂ were two main crystalline phases detected from the wheat straw ash (550 °C). In addition, small amounts of K₂SO₄ and K₂CaP₂O₇ were also identified (Table 2). The similar crystalline phases in wheat straw ash have been reported before. The ash content of the sewage sludge was about

39.83 %. As shown in Table 1, the sewage sludge contains high contents of Si, Ca, P, Al and Fe. The high Fe content is due to use of phosphorus precipitate agent Fe_2SO_4 during waste water treatment (Wang et al., 2013). The SiO_2 and Fe_2O_3 were identified in the sewage sludge ash (550 °C), with detection of medium amount of $\text{Ca}_4(\text{Mg,Fe})_5(\text{PO}_4)_6$ and $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ as well.

Table 1: Ash content of wheat straw and sewage sludge

Fuel	Ash content ^a	K	Si	Ca	P	Al	Mg	Na	Fe	S	Cl
Wheat straw	5.37	1.14	1.50	0.43	0.07	0.005	0.07	0.01	0.008	0.11	0.88
Sewage sludge	39.83	0.34	4.45	3.23	3.66	1.58	0.59	0.21	5.56	1.24	0.06

a: dry basis.

Table 2: Major mineral phases observed in wheat straw ash and sewage sludge ash (550 °C)

Mineral phases	
Wheat straw ash	KCl, SiO_2 , K_2SO_4 , $\text{K}_2\text{CaP}_2\text{O}_7$
Sewage sludge	SiO_2 , Fe_2O_3 , $\text{Ca}_4(\text{Mg,Fe})_5(\text{PO}_4)_6$, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$

3.2 Effect of sewage sludge on potassium release during the wheat straw combustion

Potassium release during combustion of the wheat straw with and without sewage sludge addition is shown in Figure 1. The potassium release fraction was calculated by a mass balance of potassium in the raw fuel and in the ash residues after the combustion tests. It can be seen that, already at 700 °C, about 25 % of potassium has released during the wheat straw combustion. At 900 °C, almost 90 % of potassium was released. Fraction of released of potassium increased with increasing temperature, and around 85 % of potassium was vaporized after the wheat straw combusted at 1000 °C for 1 h. It was stated that Cl is a main facilitator for K release during combustion of the wheat straw through formation and sublimation of KCl (Knudsen et al., 2004). The K and Cl release curves shown in Figure 1 correlates well each other in the temperature range 700-900 °C. This finding agrees well with results from previous studies (Knudsen et al., 2004). At 800 °C, about 90 % Cl has released from the wheat straw, which almost completely release as the temperature was higher than 900 °C. For comparison purpose, the alkali release data (green circle) reported by Li et al were also illustrated in Figure 1a, in which the similar experiment were performed as those of the current work. It can be seen that our ICP results are quite close to those reported by Li et al (Li et al., 2013). In addition, the fractions of potassium (K-a) released at temperature range from 700 to 900 °C reported in Li's work higher than the data from the current study. The differences are probably due to higher content of K and Cl and use of rather small sample mass (3 grams) in Li's work. High Cl content is favourable for K release as reported in other studies. In addition, with a small sample mass, larger amount of K may release considering less intensive secondary capture of K by wheat straw char matrix/ash during the combustion process (Knudsen et al., 2004).

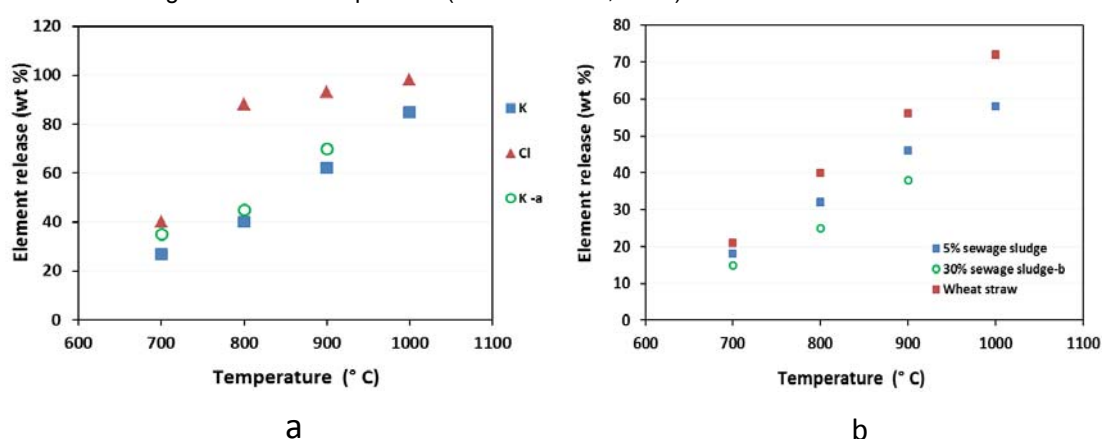


Figure 1: a) Release of K and Cl from the wheat straw, b) Effect of sewage sludge addition on K release during the wheat straw combustion. K-a and 30% sewage sludge -b: data from Li et al. 30 % sewage sludge: data from Li et al (Li et al., 2013)

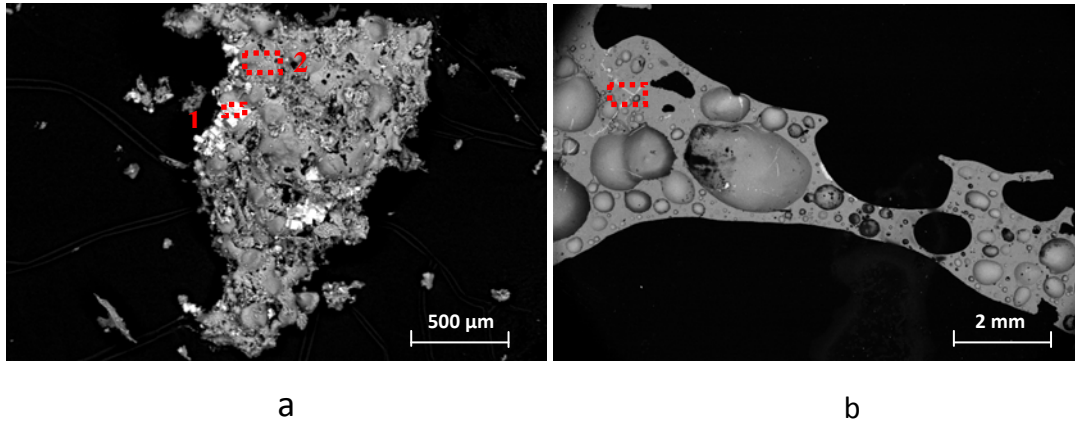


Figure 2: SEM-EDX analyses of wheat straw ash produced at a) 800 °C, b) 1000 °C

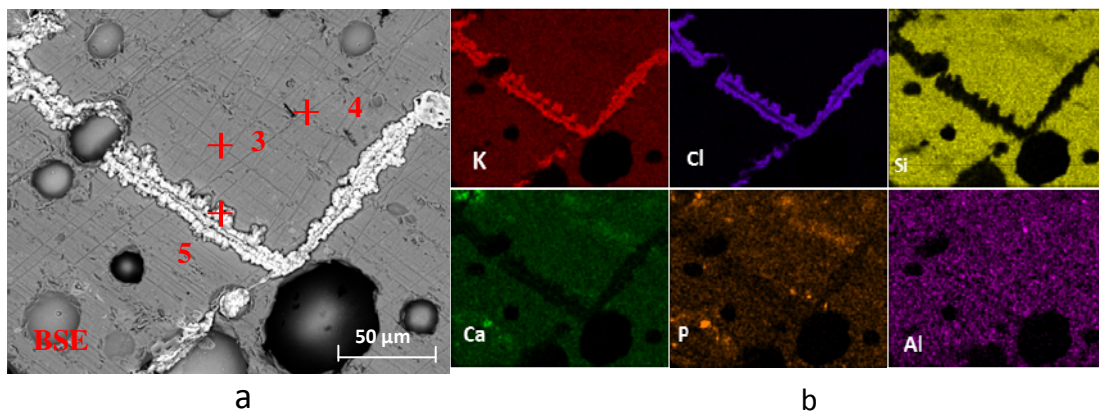


Figure 3: SEM-EDX spot and mapping analyses of the wheat straw ash produced at 1000 °C

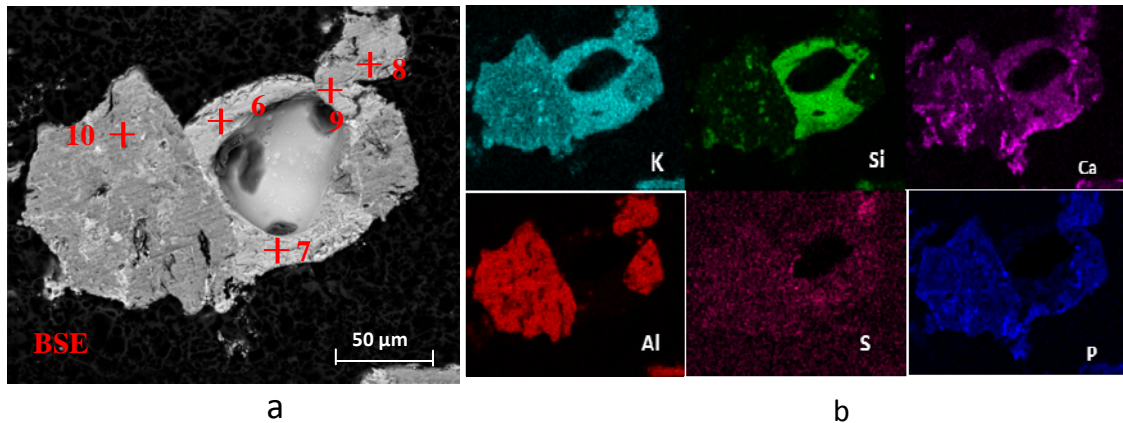


Figure 4: SEM-EDX spot and mapping analyses for the mixture of sewage sludge and wheat straw combusted at 1000 °C

Figure 1b shows, with addition of the sewage sludge, fractions of K released from the wheat straw decreased in the studied temperature range. It confirms potassium capturing ability of the sewage sludge. At 700 °C, capturing effect of the sewage sludge on potassium in the wheat straw is not evident. However, considerable reduction of K release about 13 % was observed, indicating a rather strong potassium binding capacity of the sewage sludge even at 1000 °C. This finding is constant with results reported (Li et al., 2013). It also indicates a larger sewage sludge addition may enhance potassium retaining in the ash residues instead of releasing to gas phases.

3.3 Effect of sewage sludge addition on wheat straw ash transformation

Figure 2 shows variations of particle shape, structure and morphology of the wheat straw ash produced at 800 and 1,000 °C. Figure 2a shows one representative SEM image of the wheat straw ash with partial melting structure and intact surface. The Si and K were detected from the area 2 (Table 3), indicating formation of potassium silicates melts in the ash. From the area 1 (Table 3), K and Cl were detected as two dominating elements. It reveals that the white cubical particles are KCl crystals, and observation of these crystals agrees well with previous studies. It has been reported that release of KCl from the wheat straw starts at about 700 °C and progressed gradually at elevated temperatures (Wang et al., 2011). Figure 2b shows a BSE image took from the cross sectioned wheat straw slag produced at 1000 °C. It is clear to see that the wheat straw has been melted completely and has a dense and continuous structure after cool down. There are also bubbles with different sizes can be seen from the Figure 2b, indicating the wheat straw has passed a molten stage and acted as liquid. Figure 3 shows SEM-EDX analyses of one area marked with red rectangle in the Figure 2b. EDX spot analyses (spot 3 and 4) revealed that the melted wheat straw ash contains mainly K and Si, with small amounts of Ca and P. The K and Si also correlate well in the element maps. It confirmed that severe fusion of the wheat straw was attributed to formation and melting of potassium silicates during the fuel combustion process. The mineral phases in the ash residues after combustion of wheat straw combustion at 1,000 °C were identified by XRD. As agreed with SEM-EDX analysis, the wheat straw ash (1,000 °C) has a very poor crystallinity with only trace amounts of SiO₂ detected. Major fraction of the wheat straw ash (1,000 °C) is in amorphous phase that appears as a hump in the baseline of the spectrum.

When 5 % sewage sludge was added, Fe₂O₃ and SiO₂ were the two main crystalline phases identified in the resulting ash residues from mixture of the wheat straw and the sludge. In addition, mineral phases KAlSi₂O₆, CaAl₂Si₂O₈, Ca₁₀K(PO₄)₇ and KCa₉Mg(PO₄)₇ were also identified. Identification of KAlSi₂O₆ is possibly due to reactions of aluminum silicates in sewage sludge with potassium-containing compounds in the wheat straw ash. The KAlSi₂O₆ has a high melting temperature, which was also observed in ash residues from other wheat straw and sewage sludge co-firing experiment (Elled et al., 2010).. New phosphates Ca₁₀K(PO₄)₇ and KCa₉Mg(PO₄)₇ were identified due to adding of sewage sludge. The potassium has a high affinity to react with phosphorus in the biomass fuel with formation of K-phosphates as a result (Wu et al., 2011b). The potassium phosphates will further interact with alkali earth metals (Ca and mg) in the ash to form different K-Ca-phosphates consequently. Therefore, identification of the two phosphates indicates that phosphorus and calcium in the sewage sludge also play certain roles in binding K into more stable ternary phosphate structures. Figure 4a shows a SEM image of an aggregate collected from combustion of wheat straw with 5 % sewage sludge addition. The wheat straw ash is the part in the middle with smooth surface, which has been melted due to formation of potassium silicates (spot 6, Table 3). There are several big grains connect with the melted ash. A medium size grain in the upper right corner of Figure 4a is bonded to the melted ash. In this grain, the Al and Si were detected as two dominant elements (spot 8, Table 3), which exhibit correlations in the element maps. Therefore, this grain consists of aluminum silicates. Higher K and Si contents and a lower Al content were detected in the neck (spot 9) between the grain and the melted ash. This indicates that the aluminum silicate rich grain (spot 8) had reacted with the melted ash, leading to formation of potassium aluminum silicates and contributing to potassium capturing. One large grain (spot 10) in dark gray color was attached to the molten wheat straw ash. The high Al, P and Ca content of the grain implies that is a sewage sludge ash particle bond with melted wheat straw ash.

Table 3: Chemical compositions of barley straw ash and additives used in this study

Element (Norm, wt %)	K	Si	Ca	P	Al	Mg	Na	S	Cl
Area 1	56.9	0.5	0.2	0.0	0.1	0.1	0.3	1.0	41.0
Spot 2	32.9	42.6	9.6	6.4	1.0	3.8	2.4	0.4	0.2
Spot 3	37.2	46.2	5.3	3.6	0.9	0.8	1.4	2.4	1.2
Spot 4	36.2	47.2	4.3	4.6	0.8	0.9	1.1	2.9	0.9
Spot 5	53.9	0.3	0.3	0.0	0.0	0.1	0.2	0.9	44.0
Spot 6	24.0	58.2	12.5	1.3	1.3	1.2	1.1	0.1	0.2
Spot 7	22.1	42.6	22.9	7.7	0.5	1.9	1.8	0.0	0.4
Spot 8	5.2	37.7	8.0	5.7	35.1	0.8	0.6	6.8	0.2
Spot 9	18.0	40.0	4.0	3.0	32.0	1.0	0.5	2.0	0.1
Spot 10	7.0	14.9	9.2	10.2	56.0	1.5	0.9	0.1	0.2

Table 4: Major mineral phases observed from barley straw ash with and without additive addition

Major mineral phases	
Wheat straw ash	trace amount SiO ₂ , mainly amorphous phases
+ 5% sewage sludge	SiO ₂ , Fe ₂ O ₃ , KAlSi ₂ O ₆ , CaAl ₂ Si ₂ O ₈ , Ca ₁₀ K(PO ₄) ₇ , KCa ₉ Mg(PO ₄) ₇

4. Conclusions

The ability of sewage sludge in reducing potassium release from wheat straw combustion has been investigated. The potassium in the wheat straw has a high propensity to release together with Cl as temperature higher than 700 °C. At 1,000 °C, over than 80 % of potassium has been released from the wheat straw. Addition of sewage sludge considerably decreased potassium release in the studied temperature range from 700 to 1,000 °C. SEM-EDX and XRD analyses indicate that reactions occurred between aluminum silicates, phosphorus and calcium contained in the sewage sludge and alkali-containing species in the wheat straw ash. As results of these reactions, the potassium in the wheat straw was captured and consumed, instead of release to gas phase. Moreover, addition of the sewage sludge significantly reduced sintering the wheat straw ash, due to formation of high temperature melting potassium aluminum silicates and phosphates.

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