ASH TRANSFORMATION AND DEPOSITION BEHAVIOR DURING CO-FIRING BIOMASS FUELS WITH SEWAGE SLUDGE

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ABSTRACT

In the present work, the ash transformation and deposition behavior during wheat straw and wood waste combustion were investigated by combustion experiments in an entrained flow reactor. The influence of sewage sludge addition on ash chemistry and deposition tendency was also studied. During combustion wheat straw, fine fly ash particles smaller than 2.5 µm are mainly formed due to vaporization, nucleation and condensation of K, Cl, S and P species. Large fly ash particles consist of condensed potassium chloride crystals and molten/parti al molten spherical particles rich in K-silicates and K-Ca-silicates. The deposits formed on a well-controlled sampling probe are dominated by molten particles rich in K silicates. Over 70% of K in the fly ash is water soluble. The fine fly ash from wood waste combustion consists of mainly KCl and NaCl. Both ash clusters and molten spherical particles are found from the ash deposits, which mainly contain K-silicates, K-Al-silicates and K-Ca-silicates.

The sewage sludge addition significantly reduced the water soluble K and Na in the fly ash from wheat straw and wood waste combustion. Compared to pure wheat straw and wood waste, the ash deposition rates were increased due to sewage sludge addition. However, the ash deposition propensity decreased significantly. In addition, the content of water soluble K and Cl in the deposits reduced as a result of sewage sludge addition. The results from present work suggest co-firing of sewage sludge could alleviate deposit formation during suspension firing of risky biofuels.

Keywords: wheat straw, wood waste, sewage sludge, combustion, ash, deposition, EFR
1 INTRODUCTION

Suspension firing of biomass is a promising technology for large-scale biomass conversion with an aim of heat and power production.[1-3] Biomass suspension-fired plants potentially have higher load flexibility and electrical efficiency compared to traditional grate-fired systems.[4, 5] However, one great challenge for the suspension biomass firing is the deposition of ash on heat transfer surfaces. After fed into the boiler, a major portion of ash forming elements release from the burning biomass particles and interact with each other. This process is accompanied by the generation of vapors and fine aerosols. At the same time, large particles can also generate due to fusion of non-volatile elements and fragmentation of char residues.[6, 7] The inorganic vapors, fine and large particles carried by the flue gas can readily deposit on heat transfer surfaces through different mechanisms.[7] The critical ash forming elements such as potassium and chlorine play key roles in initiating and enhancing ash deposition and further sintering on heat transfer surfaces.[7, 8] After a long time build-up, the ash deposits can grow to an extent to bridge and block superheater tube bundles and the flue gas channels.[9] Ash deposition can considerably decrease efficiency and capacity of biomass combustion boilers. In addition, the formed deposits are normally corrosive to cause metal wastage and structural damage of the heat transfer tubes.[10] Biomass ash deposition and consequent corrosion may lead to unscheduled shutdowns of the facilities.

Utilization of additives and co-firing biofuels with other fuels with a 'cleansing' effect are two promising approaches to minimize ash deposition in biomass suspension combustion boilers.[11-18] The latter is more interesting since the trend in utilizing biofuels is towards co-firing to maximize the energy recovery and optimize combustion processes. By co-firing with a 'cleaner' fuel, vaporized ash forming matters from biofuels can be chemically converted to less harmful forms and/or physically elutriated out of the boiler.[13] This process reduces the concentrations of problematic ash species in the flue gas and abates ash deposition consequently.[17] Peat and coal are two well-known 'cleaner' fuels, which showed an ability to mitigate ash deposition during co-firing with different high fouling tendency biofuels.[1, 13, 14, 17, 19] Sewage sludge, a main by-product from the wastewater processing plant, has gained interests for using as a deposit inhibitor during combustion of risky biomass fuels.[20-23] Several studies have showed that co-combustion of sewage sludge with problematic biomass fuels significantly reduced the concentration of alkali chloride in the flue gas and restricted formation of deposits on heat transfer tubes decreased radically.[20-23] Furthermore, addition of sewage sludge decreased the contents of chlorine and potassium in the deposits. The beneficial effects are mainly attributed to destruction of alkali chloride from biomass fuels by sulfur and aluminum silicates from the sewage sludge. The phosphorus and calcium from the sewage sludge may also involve in the capture of potassium containing species from biomass fuels.[21, 22] In addition, potassium chloride from biomass fuels may also condense on the sewage sludge ash particle surfaces and elutriate out of the boiler with the flue gas.[22] It may decrease the concentration of vaporized potassium in the furnace and prevent deposits formation. However, most of the experiment studies were carried out in fluidized bed boilers. The results regarding co-firing biomass with sewage sludge in suspension combustion conditions are rare.
The object of this work was to study ash morphology, chemistry and deposition behavior during suspension combustion of straw and wood waste. In addition, the influence of sewage sludge addition on ash transformation and deposition properties of the two fuels was investigated.

2 MATERIALS AND METHODS

2.1 Experimental setup and procedure

The combustion experiments were conducted in an entrained flow reactor (EFR), which was designed to simulate environment of a suspension fired boiler.[11] Figure 1 shows a schematic drawing of the experimental setup. The complete setup consists of a fuel feeding system, a gas preheater, vertical tube reactor electrically heated by 7 thermal elements, a controlled gas and particle extraction system, a bottom chamber, a particle deposition system. Detailed information of the experimental setup can be found elsewhere.[5, 11, 17, 24] During the experiments, pulverized biofuel particles or premixed biofuel and sewage sludge particles were fed into the reactor by the primary air. The primary air and total air flow rates were kept at 13 and 95 NL/min in different tests, in order to achieve comparable residence time for different experiments. An excess air ratio was controlled at approximate 1.6 for different experiments by adjusting the fuel feeding rate. This air ratio was chosen to ensure a complete combustion of the fuel in the reactor.[17] After injection, the fuel particles were mixed with preheated secondary air on the top of the reactor and entrained in the reactor for combustion. For each experiment, the temperature of the preheater was controlled at 900 °C and the wall temperatures of the tube reactor were set from 1000 °C to 1300 °C, simulating the temperature profile in a boiler.[24] Ash residues from combustion flew together with the flue gas to a bottom chamber, where the bottom ash was collected. The flue gas was then separated into two fractions. A main part of the flue gas after reaching the bottom chamber was directed to an air cooled deposition probe.

Figure 1 Schematic drawing of the entrained flow reactor

The surface temperature of the probe was measured and registered by thermocouples mounted under the deposits probe tube wall. By adjusting the temperature of cooling air, the surface temperature of the tube wall was maintained at 550 °C during experiments. To obtain flue gas and fly ash particles samples, the minor part of the flue gas was drawn to
an extraction system though a water-cooled probe. The sampling point was located in the center of the reactor tube. The flue gas with a temperature about 600 °C was extracted and radically cooled to 100 °C in the water cooled probe. Part of the extracted ash particles, vapors and aerosols may condense and deposit on the probe surface due to significant temperature difference between flue gas and surface of water cooled probe.[11] After each experiment, the ash deposited on the water cooled probe surface was collected and counted as the cyclone ash. The sampled ash particles passing through the probe were firstly separated from the flue gas and collected by a cyclone with cutoff diameter size of 2.5 µm. After the cyclone, an aerosol filter using a polycarbonate filtration membrane with pore size of 0.1 µm was connected to gather remaining fine particles. During the experiments the cyclone, filters and extraction lines were heated to 95 °C to avoid condensation of water. The concentration of CO, CO₂, O₂, SO₂ and NO in the dry flue gas was continuously measured by two gas analyzer.

Before each experiment the reactor was preheated to the programed combustion temperature and kept overnight. The fuel feeding rate increased gradually to set point and continued for 40 minutes of prior to start of an experiment. A clean sampling probe was inserted into flue gas stream for deposits collection, which continued for 90 minutes. After each experiment, the deposits on the probe were photographed, scratching off and weighed. The ashes from the extraction tubes, cyclone, aerosol filter and bottom chamber were also collected and weighed. All ash samples were preserved carefully for further analysis. To minimize the deposit build-up on the reactor wall from previous experiments, high temperature cleaning was conducted after every experiment by heating up the reactor to 1400 °C for 20 h.

### 2.2 Fuels

Two biomass fuels used in the present work were Danish wheat straw and wood waste. The wood waste is a mixture of different woody residues derived from furniture manufacturing industries[12]. The sludge is dewatered municipal sewage sludge, which was received as granular form.

<table>
<thead>
<tr>
<th>Property</th>
<th>Wheat straw</th>
<th>Wood wastes</th>
<th>Sewage sludge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash (wt %, dry)</td>
<td>6.3</td>
<td>0.6</td>
<td>46.7</td>
</tr>
<tr>
<td>Cl (wt %, dry)</td>
<td>10.68</td>
<td>6.36</td>
<td>0.10</td>
</tr>
<tr>
<td>S (wt %, dry)</td>
<td>0.28</td>
<td>0.14</td>
<td>1.05</td>
</tr>
<tr>
<td>K (wt %, dry)</td>
<td>28.22</td>
<td>12.53</td>
<td>0.58</td>
</tr>
<tr>
<td>Na (wt %, dry)</td>
<td>0.99</td>
<td>8.81</td>
<td>0.36</td>
</tr>
<tr>
<td>Si (wt %, dry)</td>
<td>21.25</td>
<td>6.12</td>
<td>12.61</td>
</tr>
<tr>
<td>Al (wt %, dry)</td>
<td>0.53</td>
<td>3.46</td>
<td>16.85</td>
</tr>
<tr>
<td>P (wt %, dry)</td>
<td>3.02</td>
<td>1.06</td>
<td>7.49</td>
</tr>
<tr>
<td>Ca (wt %, dry)</td>
<td>5.09</td>
<td>26.57</td>
<td>9.45</td>
</tr>
<tr>
<td>Mg (wt %, dry)</td>
<td>1.25</td>
<td>3.64</td>
<td>0.65</td>
</tr>
<tr>
<td>Fe (wt %, dry)</td>
<td>0.50</td>
<td>1.52</td>
<td>4.84</td>
</tr>
<tr>
<td>Ti (wt %, dry)</td>
<td>0.40</td>
<td>1.81</td>
<td>0.28</td>
</tr>
</tbody>
</table>
The ash content of each fuel was determined by following the standard ASTM D 1102. Main chemical compositions of three fuels ashes were analyzed by ICP-OES, which are given in Table 1. Before combustion experiments, all pure air-dried fuel samples were milled in an Alpine pin mill. The 50% sieve passing sizes \( d_{50} \) of straw, wood waste and sewage sludge are about 250, 220 and 100 µm, respectively. Biofuels and sewage sludge mixtures were prepared by mixing each pulverized biofuel with sludge in correct proportions in a special designed mixer.

2.3 Ash and deposits analysis

The fuel properties were characterized by following ASTM standards. The main ash forming elements K, Na, Si, Al, P, Ca, Fe, Mg, Ti, S and Cl in fuel ash (prepared at 550 °C) and the collected ash samples were analyzed by Inductive coupled plasma optical emission spectrometry (ICP-OES). The content of water soluble K, Na, Cl and S in cyclone ash, bottom ash, deposits and aerosol was also determined by ICP-OES/IC. The collected ash and deposits were dissolved in ultrapure water, heating at 120 °C for 1 hour. Then the solution were filtered and sent to ICP-OES/IC analysis. Same procedures applied in previous study were followed to prepare samples for water soluble content analysis.[11, 17] Supplementary scanning electron microscopy and dispersive X-ray spectroscopy (SEM-EDX) analyses were performed to examine the morphology and the chemical composition of filter ash, cyclone ash and deposits.

3 RESULTS

3.1 Ash transformation during wheat straw and wood waste combustion

Figure 2 shows the elemental compositions of bottom ash, cyclone ash and the filter ash collected from wheat straw and wood waste combustion tests. In addition, the fuel ash compositions are also displayed for a comparison purpose.

![Figure 2: Elemental composition of bottom ash, cyclone ash, filter ash and fuel ash of (a) wheat straw and (b) wood waste.](image)

It can be seen that the bottom ash from wheat straw combustion mainly contains K, Si and Ca. The Cl and S are almost depleted in the bottom ash, which is associated with high volatility of the two elements during combustion. The cyclone ash element composition is
quite close to the fuel ash composition, which is dominated by K, Si, Ca and Cl. However, the concentrations of elements K, S and Cl are slightly lower than those in fuel ash. The dominating elements in the filter ash are K, Cl, S and P. It indicates that the formation and condensation of KCl, K₂SO₄ and potassium phosphates play a dominating role for aerosol formation.[11] As shown in Figure 2-b, nonvolatile Si, Al and Ca are three main elements remained in the bottom ash from wood waste combustion, along with the depletion of S and Cl. The cyclone ash composition generally represents the fuel ash compositions, whereas the elements K, Na, S and Cl are considerably depleted. Significant amounts of K, Na, S and Cl were detected from the filter ash. It indicates that the filter ash primary consists of alkali chloride and sulfate.

Figure 3-6 display the morphology and micro-chemical compositions of the fly ash particles from wheat straw and wood waste combustion in the EFR. The filter ash (Figure 3-a) from wheat straw combustion consists of fine particles that are in cubic and irregular shape (spots 1 and area 2) and with K and Cl as two main elements. Therefore these particles are probably particles formed from nucleation, condensation and aggregation of KCl released from the wheat straw. The similar particles have been observed during straw combustion in other studies.[25, 26] In agreement with Figure 2-a, particles (spots 3, 4 and area 5, Figure 4-a) containing P and S were also observed.

As shown in Figure 3-b, the morphology of the cyclone ash is totally different than the filter ash. The cyclone ash is dominated by spherical particles in different sizes. The spherical shape and smooth surface imply they have been experienced a molten stage.[27] The large particles (spots 2 and 5, Figure 4-b) contain K-silicates and K-Ca-silicates as indicated by the compositions. Whereas, in addition to the Si, K and Ca, relatively higher content of P were detected from small spherical particles (spot 6, Figure 4-b). Some flake-shaped particles can be found in the cyclone ash. Compared with spherical particles, typical higher Si content was detected from the flake-shaped particles (spot 3), which indicates presence of silicon oxide.[11] Since the melting temperature of the silicon oxide is significantly high, these particles were just partially melted instead of fused as droplike particles.[28] A needle-like particle can be easily seen in Figure 3-b (spot 1), which is KCl crystal according to EDX analysis. The deposits from wheat straw combustion consists of much bigger particles, as indicated by the scale bar 100 µm in Figure 3-c. A large particle is clearly displayed in white color, which consists of mainly KCl (spot 1, Figure 4-c). Some of the ash particles have been agglomerated due to partial
molten. On the other hand, some of the smaller spherical particles (spot 3, Figure 4-c) are aggregated due to the presence of KCl (spot 2, Figure 4-c). It agrees with previous studies that formation of KCl is one of the main reasons for aggregating and sintering of deposited ash particles during straw combustion. As implied by the EDX analysis, K-sulfate was also formed and stick on particle surfaces (spot 7, Figure 4-c).

Figure 4: EDX analysis (a) filter ash, (b) cyclone ash and (c) deposits results of the spots and areas shown in Figure 3.

Figure 5-a shows the filter ash collected from the wood waste combustion, which appear to contain three kind of particles with considerable different sizes. Several large round particles can be clearly seen, which are dominated by Ca, Si Al and Mg. Particles with similar appearance and chemical compositions were observed in previous study during combustion of high potassium saw dust in down-fired tunnel furnace.[29] These particles are probably originated from small mineral particles in the original wood waste, which may have been fragmented and melted during fuel conversion. A large amount of particles are found in smaller sizes, which are identical as single ones (spot 4, in Figure 5-a) or aggregated together (area 5, Figure 5-a). These particles have an almost round gavel-like appearance, and appear as molten-like rounding morphology under higher magnification. Except K and Cl, Na and S were also detected from these particles. This elemental composition suggests they are alkali chloride and sulfate formed due to direct condensation.[6] There are also very fine particles (area 3, Figure 5-a) that aggregate together and contain mainly K, Na, Cl and S. This type of particles is associated with direct condensation of vaporized alkali aerosols.

Figure 5: SEM images of (a) filter ash, (b) cyclone ash and (c) deposits collected from wood waste combustion.

The cyclone ash from wood waste combustion consists of molten or partial particles, which have spherical appearance and contain K/Na-silicates and K/Na-Ca-silicates. Particles containing alkali chloride present as fine white particles (spot 1 and 2, Figure 5-
b) on the surface of other particles. Different than the ash deposit from wheat straw combustion, large clusters is evidently shown in SEM image taken from wood waste ash deposits. EDX analysis results (spot 4 and 5, Figure 6-c) suggest these clusters formed due to melting and sintering of K-Ca-silicates and Na-Ca-silicates. Particles with spherical appearance can also be found in Figure 6-c, which consist of alkali calcium silicates and alkali aluminum silicates. Needle-like materials attach on the cluster surface, which are alkali chloride.

Figure 6: EDX analysis (a) filter ash, (b) cyclone ash and (c) deposits results of the spots and areas shown in Figure 5.

3.2 Effect of sewage sludge on fly ash chemistry

The impact of sewage sludge addition on the fate of alkali species during combustion of the wheat straw and wood waste was investigated. It has been well documented that the water soluble alkalis such as KCl and K$_2$SO$_4$ are critical for the fly ash and deposits formation in biomass combustion applications. For this reason, the content of water soluble K and Na in the fly ash was calculated as the wheat straw and wood waste combusted with and without sewage sludge addition.[11] One should note this calculation was based on an assumption that all alkali species in filter ash are water soluble. This assumption is supported by the fact that most alkalis are found as chlorides, sulfates and phosphates in the filter ash. The results are presented in Figure 7.

Figure 7: Fraction of K and Na present as water soluble form in fly ash from (a) wheat straw and (b) wood waste combustion.

It can be seen that content of water soluble K and Na reduces as a result of sewage sludge addition. One of the reasons responding this is the reaction of active compounds from sewage sludge with vaporized alkali species from biofuels. This process results in conversion of water soluble alkali species to water insoluble form. Aluminum silicates...
has been considered as the main compound in the sewage sludge, which can bind KCl from biofuels and form K-aluminum silicates with high melting temperatures.[22] Sulfur is the other key element in the sludge, which can destroy the alkali chloride with formation of less troublesome alkali sulfate and depresses ash deposition as well.[20] However, considering the high reaction temperature and short residence time of fuel particles, sulfur might be less important than aluminum silicates in terms of alkali capturing. In addition, sulfur from sewage sludge can also be captured by calcium contain in the fuel. It may reduce amount of sulfur available for reacting with alkali chloride.[22, 30]

### 3.3 Effect of sewage sludge on ash deposition

The effect of sewage sludge on wheat straw and wood waste ash deposition behavior was assessed by using an air-cooled deposit probe. Two parameters, deposit flux and deposit flux/ash flux (%), were calculated based on collected ash during EFR combustion tests. The deposit flux represents fraction of the input ash flying against the probe. Influence of sewage sludge addition on deposition behaviors of the two biofuels are shown in Figure 8.

![Figure 8: Influence of sewage sludge on (a) deposition flux (gram/hour/centimeter) and (b) deposition flux/ash flux during EFR combustion tests.](image)

As shown in Figure 8-a, deposition fluxes of both wheat straw and wood waste are increased due to addition of sewage sludge. This is probably due to high ash content of the sludge, which considerably increased the ash flux toward the probe. Since the wood waste has a low ash content about 0.62 wt %, enhancement of sewage sludge addition on ash flux is more evident for combustion of blends of wood waste and sludge. In comparison with pure wood waste combustion, the ash flux is tripled as a result of 10 wt% sewage sludge addition. The deposit flux/ash flux indicates the tendency of the fly ash depositing on the probe.[11] As shown in Figure 8-b, addition of sewage sludge reduced both wheat straw and wood waste ash deposition propensity. Different mechanisms have been proposed to explain biomass ash deposition, which are inertial impaction, thermophoresis and condensation.[7] Based on previous studies conducted with this EFR reactor, the ash deposition is mainly related to inertial impaction of ash particles.[11] The propensity of one ash particle captured by probe is mainly controlled by stickiness of the particle and surface of the deposits, which is associated with the concentration of alkali chloride in the flue gas. Therefore, the lower deposition
propensities shown in Figure 8-b are probably because that sewage sludge addition has reduced the amount of alkali chloride formed during the wheat straw and wood waste combustion. This was also confirmed by visual observation on appearance of ash deposits on the sampling probe. As the wheat straw combusted along, the sampling probe was initially covered by a layer of white fine particles, which is potassium chloride as proved by EDX. However, with sewage sludge addition, this white ash deposition layer almost disappeared, indicating consumption of potassium chloride by sewage sludge addition.

In order to get a better understanding of ash deposits chemistry, the content of water soluble K, Cl and S is analyzed and listed together with that of the fly ash in Table 2. Generally, the content of water soluble K and Cl in deposits from wheat straw and wood waste combustion is decreased upon sewage sludge addition. Reduction of K and Cl can be caused by chemical reaction discussed above and dilution effect of sewage sludge ash. The lower Cl content in the deposit with the sludge addition implies reduction of corrosion potential of the deposited ash. The contents of water soluble S in fly ash from wheat straw and wood waste combustion decreased with sludge addition. However, the water soluble S content in deposits is considerably higher than that in fly ash. It is probably linked to condensed phase sulfation in the deposits. The similar sulfur distributions in the fly ash and ash deposit have been reported by other studies.[17, 20] In addition, for the different fly ash, the content of water soluble S in the deposits generally increased with sewage sludge addition. One of the reasons for this sewage sludge addition increased content of S in the input fuel, promoting condensed phase sulfation in the ash deposits.

Table 2: Content of water soluble K, Cl and S in deposits and fly ash collected from EFR combustion tests

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Water soluble element in fly ash (dry, wt %)</th>
<th>Water soluble element in deposit (dry, wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K</td>
<td>Cl</td>
</tr>
<tr>
<td>Wheat Straw</td>
<td>14.25</td>
<td>8.10</td>
</tr>
<tr>
<td>WS+5 wt % SS</td>
<td>6.09</td>
<td>4.52</td>
</tr>
<tr>
<td>WS+10 wt % SS</td>
<td>4.52</td>
<td>3.97</td>
</tr>
<tr>
<td>Wood Waste</td>
<td>6.31</td>
<td>9.27</td>
</tr>
<tr>
<td>WW+5 wt % SS</td>
<td>3.10</td>
<td>3.78</td>
</tr>
<tr>
<td>WW+10 wt% SS</td>
<td>1.62</td>
<td>1.46</td>
</tr>
</tbody>
</table>

4 CONCLUSIONS

General ash transformation processes and deposition behavior during wheat straw and wood waste combustion with and without sewage sludge addition have been studied in an entrained flow reactor, and the work led to following conclusions:

- During the wheat straw combustion, a major fraction of K, S and Cl partitioned to the fly ash. The filter ash is dominated by K, Cl and S, which is probably formed due to nucleation and condensation of these volatile species. The cyclone ash
contains both KCl crystals and molten/partial molten spherical particles. About 75 percent of K in the fly ash is water soluble. These spherical particles consist of K-silicates and K-Ca-silicates. The deposited ash composes of condensed potassium chloride particles and melted potassium silicate rich particles.

- Due to relatively high content of K, Na and Cl in the ash, the wood waste shows high a fly ash formation tendency. The filter ash mainly consists of alkali chloride and sulfate. Over 80 percent of K in the fly ash is water soluble. In addition to molten spherical particles, clusters of ash particles are also observed from the deposited ash.

- Addition of sewage sludge showed significant influences on ash chemistry and deposition propensity during wheat straw and wood waste combustion. The content of water soluble K and Na in the fly ash from two fuels combustion is considerably decreased due to sewage sludge addition. This is probably due to both a dilution effect and chemical reactions between active compounds in the sludge with alkali species from the biofuel. At the same time, the ash deposition tendencies of two fuels are significantly depressed. The chlorine content of the deposits is also considerably decreased, indicating a reduced corrosion potential on the probe.

5 ACKNOWLEDGEMENTS

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6 REFERENCES


