EFFECT OF FUEL ADDITIVE SORBENTS (KAOLIN AND CALCITE) ON AEROSOL PARTICLE EMISSION AND CHARACTERISTICS DURING COMBUSTION OF PELLETIZED WOODY BIOMASS

Boman C\textsuperscript{a}, Boström D\textsuperscript{b} and Öhman M\textsuperscript{b}

\textsuperscript{a} Energy Technology and Thermal Process Chemistry, Umeå University, SE- 901 87 Umeå, Sweden
\textsuperscript{b} Division of Energy Engineering, Luleå University of Technology, SE-971 87 Luleå, Sweden

ABSTRACT: The objective of the present work was to determine the effect of two fuel additive sorbents, i.e. kaolin and calcite (CaCO\textsubscript{3}) on the aerosol particle emission and characteristics during combustion of pelletized woody biomass fuels, i.e. bark and cleaning assortments in a residential pellet burner. The influence of adding 1-2 wt.-% of the additives to woody pellets was studied by sampling particles, size classify them and perform elemental analysis on the samples. A significant reduction of fine particles was seen by adding kaolin to both studied ash rich woody fuels. For calcite, this effect was only marginal. The formed fine particles during both bark and cleaning assortment as well as with the studied additives were in all cases dominated by K, Na, S, Cl and Zn. However, it was clearly shown that addition of kaolin significantly reduced the fraction of K and S in the particles. This implies for example that the Cl/S ratio in the fine particles was influenced by the kaolin additive. The present study shows that there is a potential of reducing fine inorganic particle emissions during combustion of woody biomass in residential pellets by using clay minerals, here illustrated by kaolin. However, the potential influence of different fuel additives on the complete ash transformation processes, e.g. slag formation and alkali volatilization has to be considered for specific fuels and fuel mixtures of different biomass raw materials.

Keywords: aerosols, wood pellets, additives

1 INTRODUCTION

A high technical and environmental standard is a prerequisite for enabling a significant introduction of new biomass technology as a competitive and realistic alternative. In parallel with the increased use of bioenergy, an increasing concern has been seen regarding combustion related aerosol particle and trace element emissions and their potential adverse health effects [1, 2]. More strict regulation of PM emissions within the EU, also for small-scale heating appliances, is therefore to be expected. Presently, the raw materials for fuel pellet production are mainly stemwood assortments, but other more ash rich forest and agricultural based feedstocks will most certainly be introduced. In modern optimized technology systems the fine (<1 µm) particulate matter is dominated by volatilized particle forming ash constituents (e.g. K, Na, S, Cl and P). A reduction potential therefore exists in capturing such elements in the bottom ash (i.e. minimize the release) and one way to affect these ash transformation processes is to use fuel additives.

Some mineral additives have been suggested and shown to bring positive effects to combat ash-related operational problems (e.g. slagging) as a result of a change of ash composition in the silicate-oxide systems relevant for many biomass ashes and a subsequent change in melting temperatures [3, 4, 5]. Addition of Ca-based fuel additives, e.g. CaCO\textsubscript{3} and CaMg(CO\textsubscript{3})\textsubscript{2}, to woody biomass fuels reduces the formation of melted ash (i.e. slag) considerably by formation of calcium silicates instead of potassium silicates [4, 5]. The use of the clay mineral kaolin has shown to influence the ash chemistry by acting as a strong sorbent for potassium according to the following reactions suggested in earlier studies, e.g by Tran et al. [6]:

\begin{equation}
\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \rightarrow \text{Al}_2\text{O}_3 + 2\text{SiO}_2 + 2\text{H}_2\text{O} \quad (1)
\end{equation}

\begin{equation}
\text{Al}_2\text{O}_3 + 2\text{SiO}_2 + 2\text{KCl} \rightarrow 2\text{KAlSiO}_4 + 2\text{HCl} \quad (2)
\end{equation}

\begin{equation}
\text{Al}_2\text{O}_3 + 2\text{SiO}_2 + 2\text{KCl} + 2\text{H}_2\text{O} \rightarrow 2\text{KAlSiO}_4 + 2\text{HCl} \quad (3)
\end{equation}

\begin{equation}
\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \quad (\text{kaolinite}) \quad \text{are the dominating mineral in kaolin clay and } \text{Al}_2\text{O}_3 + 2\text{SiO}_2 \quad (\text{meta-kaolinite}) \quad \text{is an amorphous mixture of alumina and silica when kaolinite loses water at high temperatures. KAlSiO}_4 \quad (\text{leucite}) \quad \text{and KAl}_2\text{Si}_2\text{O}_6 \quad (\text{kalsilite}) \quad \text{are high melting K-Al-silicate minerals formed during biomass combustion. Note that in reaction (3), in the formation of leucite, kaolinite reacts besides with KCl also with 2SiO}_2.
\end{equation}

The potential influence on the ash chemistry related to formation of aerosol particle emissions during combustion of biomass is less studied, although of great relevance for the evaluation of technical and environmental performance. One recent study showed the potential of using different additives, e.g. clay minerals, for reducing aerosol particle formation in straw combustion [7]. For woody biomass fuels, the content of different ash forming elements are significantly different from that in straw, e.g. illustrated by higher ratios of K/Si, Ca/K and S/Cl. Accordingly, the ash forming processes will differ based on fuel composition and therefore also the potential influence on the formation inorganic fine aerosol particles. The objective of the present work was therefore to determine the effect of two fuel additive sorbents (kaolin and calcite) on the aerosol particle emission and characteristics during combustion of pelletized woody biomass fuels (bark and cleaning assortments) in a residential pellet burner.

2 EXPERIMENTAL PROCEDURE

2.1 Fuels and Additives

Two different woody raw materials, bark from pine and a cleaning assortment consisting of whole young conifer trees, were used to produce the different pelletized fuels. These fuels represent typical future, increasingly relevant and more ash rich woody biomass fuels that may be utilized for fuel production to a larger extent than today. All pellets were produced by conventional pellet equipment with a production capacity of 500-800 kg/h. The additives used was a calcite (CaCO\textsubscript{3} slurry (78 wt-% d.s.) and a kaolin slurry (66 wt-% d.s.) with a particle size of 1-2 µm, as described
Öhman et al. [4]. The additives were additionally diluted in water and added to the raw material with nozzles during the pelletizing process in a conditioning step for good stirring and mixing. The additive-to-fuel ratio in all the four pellets containing additives, determined by elemental composition by scanning electron microscopy (SEM) combined with energy-dispersive X-ray analysis (EDS).

<table>
<thead>
<tr>
<th>Ash content</th>
<th>Si</th>
<th>Al</th>
<th>Ca</th>
<th>Fe</th>
<th>K</th>
<th>Mg</th>
<th>Mn</th>
<th>Na</th>
<th>P</th>
<th>S</th>
<th>Cl†</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bark</td>
<td>4.4</td>
<td>3400</td>
<td>1550</td>
<td>6980</td>
<td>769</td>
<td>2640</td>
<td>884</td>
<td>433</td>
<td>379</td>
<td>558</td>
<td>273</td>
</tr>
<tr>
<td>C.A.‡</td>
<td>4.7</td>
<td>7850</td>
<td>2080</td>
<td>4560</td>
<td>1240</td>
<td>2150</td>
<td>593</td>
<td>225</td>
<td>749</td>
<td>326</td>
<td>384</td>
</tr>
</tbody>
</table>

†Cleaning assortment, ‡% of fuel, †% of d.s.

2.2 Combustion procedure

The combustion experiments were performed in a commercial under fed residential pellet burner installed in a reference boiler used for the national certification test (P-marking) of residential pellet burners in Sweden. The burner operated at a continuous fuel feeding (i.e. heat output) of ~10 kW. Combustion temperatures were measured continuously with three shielded type N thermocouples on and in the vicinity to the burner grate. The concentrations of O₂, CO and NO were continuously measured in the exhaust gas after the boiler with electrochemical sensors (Testo 350XL) to monitor and evaluate the combustion performance. The combustion conditions were in all cases rather stable with flue gas temperatures at ~120 °C. The filter sampling system was equipped with a pre-cyclone with a cut-off of ~1 µm (aerodynamic diameter), and the total particle mass sampling is therefore referred to as PM₁₀ measurements. The PM₁₀ sampling was performed during a period of 15-30 minutes for each combustion experiment. After at least 12 hours of conditioning in a desiccator, the filters were analyzed gravimetrically before and after sampling with an analytical balance (<10 µg).

The particle mass size distributions were determined by isokinetic sampling, using a 13 stage low-pressure cascade impactor from Dekati Ltd. The impactor size classifies particles according to aerodynamic diameter in the range of approximately 0.03-10 µm. The impactor and sampling probe were kept at ~120 °C during the measurements. Un-greased Al-foils were used as substrate in the impactor. For comparison, one measurement with greased foils was also performed during combustion of bark pellets. The impactor measurements were performed during 3 minutes (6*30 s) for each experiment.

Specific particle samples, i.e. stage 3 (D₉₀=0.108 µm) and/or 4 (D₉₀=0.194 µm), from the impactor measurements were analyzed by area analysis (100*100 µm) for standard ashing procedure was 1-2 wt-% d.s. In table I, the characteristics and concentration of ash forming elements of the different raw materials (pure bark and cleaning assortment) used, are given.

2.3 Aerosol particle measurements and characterization

The particle emissions were characterized regarding; mass and number concentration, size distribution and elemental composition. All particle sampling was performed in the exhaust gas pipe approximately 3 m after the boiler at a flue gas temperature of ~120 °C. Total particle mass concentrations was measured according to principles in standard method SS-EN 13284-1 using conventional equipment with 90 mm glass fibre filters heated to ~120 °C. The filter sampling system was equipped with a pre-cyclone with a cut-off of ~7 µm (aerodynamic diameter), and the total particle mass sampling is therefore referred to as PM₁₀ measurements. The PM₁₀ sampling was performed during a period of 15-30 minutes for each combustion experiment. After at least 12 hours of conditioning in a desiccator, the filters were analyzed gravimetrically before and after sampling with an analytical balance (<10 µg).

The particle mass size distributions were determined by isokinetic sampling, using a 13 stage low-pressure cascade impactor from Dekati Ltd. The impactor size classifies particles according to aerodynamic diameter in the range of approximately 0.03-10 µm. The impactor and sampling probe were kept at ~120 °C during the measurements. Un-greased Al-foils were used as substrate in the impactor. For comparison, one measurement with greased foils was also performed during combustion of bark pellets. The impactor measurements were performed during 3 minutes (6*30 s) for each experiment.

Specific particle samples, i.e. stage 3 (D₉₀=0.108 µm) and/or 4 (D₉₀=0.194 µm), from the impactor measurements were analyzed by area analysis (100*100 µm) for standard ashing procedure was 1-2 wt-% d.s. In table I, the characteristics and concentration of ash forming elements of the different raw materials (pure bark and cleaning assortment) used, are given.

Table I: Fuel characteristics and main ash forming elements (by ICP-AES) of the studied bark and cleaning assortment raw material. All units are in mg/kg of d.s. if not otherwise indicated.

<table>
<thead>
<tr>
<th>Element</th>
<th>Bark</th>
<th>C.A.‡</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash (%)</td>
<td>4.4</td>
<td>4.7</td>
</tr>
<tr>
<td>Si</td>
<td>3400</td>
<td>7850</td>
</tr>
<tr>
<td>Al</td>
<td>1550</td>
<td>2080</td>
</tr>
<tr>
<td>Ca</td>
<td>6980</td>
<td>4560</td>
</tr>
<tr>
<td>Fe</td>
<td>769</td>
<td>1240</td>
</tr>
<tr>
<td>K</td>
<td>2640</td>
<td>2150</td>
</tr>
<tr>
<td>Mg</td>
<td>884</td>
<td>593</td>
</tr>
<tr>
<td>Mn</td>
<td>433</td>
<td>225</td>
</tr>
<tr>
<td>Na</td>
<td>379</td>
<td>749</td>
</tr>
<tr>
<td>P</td>
<td>558</td>
<td>326</td>
</tr>
<tr>
<td>S</td>
<td>273</td>
<td>384</td>
</tr>
<tr>
<td>Cl†</td>
<td>0.028</td>
<td>0.027</td>
</tr>
</tbody>
</table>

†Cleaning assortment, ‡% of fuel, †% of d.s.
The fine particles were in all cases dominated by K, Na, S, Cl and Zn, which is in line with previous presented data regarding inorganic particles from woody biomass combustion [8, 9, 10]. The relative distribution of those five major elements in the particles is accounted for in figure 3 and 4 for bark and C.A., respectively. As can be seen, the composition and influence/non-influence of the fuel additives of the particles where almost identical for bark and C.A. It was clearly shown that addition of calcite significantly reduced the fraction of K and S in the particles, while the fraction of the other three elements (Na, Cl and Zn) increased. No similar effect was, however, seen for addition of calcite. The molar ratio (K+Na)/(2S+Cl) for the bark fuels was; 1.05 for pure bark, 1.19 for bark+kaolin and 1.10 for bark+calcite. For the cleaning assortment fuels the same ratios were; 1.09 for pure C.A., 1.14 for C.A.+kaolin and 0.99 for C.A.+calcite. Thus, if Zn is assumed to be present as ZnO, the major part of the volitized (fine particle forming) alkali (i.e. K+Na) prevails as sulfates and chlorides in all cases. A small amount of the fine particles may also be consist of some other components, presumably carbonates, especially in the case where kaolin was added to both the bark and cleaning assortment fuels.

The ash formation in general and slagging potential/characteristics in specific, are expected to be responsible for the observed effects concerning reduced volatilization of K, although not the major topic of the present study. The slagging tendencies and ash transformation mechanisms during combustion of woody biomass fuels are instead accounted for in more detail elsewhere, e.g. Öhman et al (2004) and Lindström et al (2005) [4, 5].

4 CONCLUSIONS

A significant reduction of fine particles was seen by adding kaolin to both studied ash rich woody fuels. For calcite, this effect was only marginal, and it seems like the addition of extra Ca in the form of calcite to the studied fuel had no influence on the ash transformation processes. The formed fine particles during both bark and cleaning assortment as well as with the studied additives were in all cases dominated by K, Na, S, Cl and Zn. However, it was clearly shown that addition of kaolin significantly reduced the fraction of K and S in the particles. This implies for example that the C/S ratio in the fine particles was influenced by the kaolin additive. The present study shows that there is a potential of reducing fine inorganic particle emissions during combustion of woody biomass in residential pellet appliances by using clay minerals, here illustrated by...
kaolin. However, the potential influence of different fuel additives on the complete ash transformation processes, e.g. slag formation and alkali volatilization has to be considered for specific fuels and fuel mixtures of different biomass raw materials.

5 ACKNOWLEDGEMENT

This work was financially supported by the Swedish Energy Agency which is gratefully acknowledged.

6 REFERENCES