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Testing of Zeolite and Kaolin for Preventing Ash Sintering and Fouling during Biomass Combustion

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Formation and release of potassium chloride (KCl) during biomass combustion cause ash sintering and deposition during combustion of biomass fuels. In the present work, two mineral additives, zeolite 24A and kaolin, were tested in terms of their capacity for capturing KCl. This was done experimentally using a thermogravimetric method. The effects of zeolite 24A and kaolin on sintering behaviours of barley straw ash were also studied by a combination of laboratory sintering test, SEM-EDX and X-ray diffraction analyses. It was found that both zeolite 24A and kaolin have high capacities to capture KCl at elevated temperatures. Instead of evaporating into gas phase more than 50 wt% and 40 wt% of the tested KCl were retained in zeolite 24A and kaolin at 1,000 °C, respectively. The amount of KCl captured by zeolite 24A and kaolin decreased with increasing temperatures. Compared to kaolin, zeolite 24A was more effective for capturing KCl at the tested conditions. Both zeolite 24A and kaolin can react with KCl to form different potassium aluminium silicates. It indicates that chemical reactions play an important role in the overall capturing process. The barley straw ash melted severely at 1,000 °C due to formation and melting of potassium silicates. Addition of kaolin and zeolite 24A significantly reduced the sintering tendency of the barley straw ash. Together with SEM-EDX analysis, identification of high temperature melting potassium aluminium silicates by XRD partly explains the improved sintering behaviours of the ash-additive mixtures.

1. Introduction

Due to the development of bioenergy and the limited availability of virgin woody fuels, biomass materials such as residues from the agricultural sector are entering the market for heat and power production. Compared to woody biomass, the agricultural residues contain a high amount of ash forming matters. Ash forming elements such as K, P, Si and Cl are abundant in agricultural residues. These inorganic elements in biomass fuels are nutrients needed for plants growth and often enhanced as a result of utilization of fertilizers (Boström et al., 2011). The combustion of agricultural residues is often challenged by ash related operational problems, including ash sintering, fouling deposits and high temperature corrosion of heat transfer components. Potassium plays a critical role in initiating and boosting these problems during the combustion process (Hupa, 2011). During combustion, part of the potassium in agricultural residues readily releases as KCl gases causing fouling deposits on heat transfer tube surfaces. Potassium retained in solid combustion residues may react with silicon to form low temperature melting potassium silicates initiating ash sintering and slagging (Wang et al., 2012a). Utilization of additives have been investigated for binding and/or abating formation of problematic potassium chlorides during biomass combustion As a representative of aluminium silicates based additives, kaolin can bind potassium chloride in aluminium silicates and releases Cl in the form of HCl (Steenari and Lindqvist, 1998). Recent literature reports that zeolite, as a member of the aluminium silicates additives, can reduce fouling deposits during combustion of high potassium biomass fuels (Elled et al., 2010). In addition, zeolite is mainly used for washing powder production, and largely ends up in sewage sludge (De Filippis et al., 2013). Interactions of zeolites in the sewage sludge with problematic potassium species were also observed (Pettersson et al., 2009), opening the possibility of using sewage sludge as additive. These interactions reduced the concentration of KCl in flue gas and formation of fouling deposits on the sampling probe consequently. However, studies about

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the capturing of KCl by zeolite are rare. The purpose of this work is to characterize the capacity of zeolite to adsorb KCl by a thermogravimetric method. The possible mechanisms of KCl adsorption by zeolite were investigated. In addition, the effects of zeolite on sintering behaviours of ash from one agricultural residue, barley straw, were investigated. Kaolin was also tested in the current work for comparison purpose.

2. Experimental section

Barley straw was used in this study, and was combusted at 550 °C for 10 h to produce reference ash. Two additives, zeolite 24A and kaolin, were tested. With proven alkali getter capacity, the kaolin was used as a reference additive in this work. The zeolite 24A tested in this study is a widely used detergent zeolite with the chemical formula $(Na_2O \cdot Al_2O_3 \cdot 2SiO_2)2H_2O$, and has a particle size smaller than 2 μm. The particle size of kaolin powder is smaller than 10 μm. The chemical compositions of barley straw ash, zeolite 24A and kaolin were measured by X-ray fluorescence (XRF) and are presented as oxides in Table 1. Major mineral phases in barley straw ash, zeolite 24A and kaolin were analyzed by an X-ray diffractometry (XRD) spectrometer (Bruker D8 focus).

It is well known that KCl is directly responsible for biomass ash related problems. One main objective of this study is to test the capacity of zeolite 24A and kaolin to capture KCl. This was achieved by performing a simple thermogravimetric method. In the tests, one additive was thoroughly mixed with solid KCl particles in a platinum crucible in a molar ratio 1:2. This molar ratio represents the amount of the additive that could react with added KCl according anticipated stoichiometric reactions. KCl will be mostly vaporized after a long enough time at a temperature higher than 850 °C (Steenari and Lindqvist, 1998). The sample mixtures were then heated at 900 °C and 1,000 °C for 1 h under oxidizing atmosphere in a muffle furnace. During the heating, the KCl may vaporize and the additive retains the KCl through physical adsorption and/or chemical reactions. After heating, the residues of the sample mixtures were weighed while they still were warm to avoid adsorption of moisture from the ambient air. The weight differences between initial and final mass of the sample mixtures were calculated, with subtraction of weight loss of raw additives at the same condition. The final results were considered as amount of KCl captured by one additive, which were described as retention mass fraction of KCl initially blended in the additive.

To investigate the effects of additives on barley straw ash sintering behaviors, the reference fuel (550 °C) and ash-additive mixtures were heated at 1000 °C for 1 h. The stoichiometric amount of additive to theoretically capture all potassium in the barley straw ash was added. Therefore, 4 % (w/w) additive was added to the reference barley straw ash. After cooling down to room temperature, sintering behaviors of residues from reference ash and ash-additive mixtures were visually evaluated. Then the solid residues were collected for further analyses. Part of the collected solid residues was embedded in resin and cross-sectioned for SEM-EDX analysis. The SEM was operated in a backscattered electron mode for illustrating distribution of detected elements in a scanned area. EDX semi-quantitative spot/area analyses were carried out for interesting areas to get more detailed microchemistry information. In addition, residues from reference ash and ash-additive mixtures after heating treatment were also grinded into powder and analyzed by XRD.

3. Results and discussion

3.1 Fuel and additives

The elemental compositions and crystalline compounds of the barley straw ash and the two additives are listed in Table 1 and Table 2. Abundance of K, Cl, Si and P in the barley straw ash strongly indicates the existence of K containing chlorides, silicates and phosphates. This assumption was proved by XRD analysis results. As shown in Table 2, KCl and K_2SO_4 were detected together with $KCa(PO_3)_3$ and $K_4Ca_3SiO_4$ in the barley straw ash.

Table 1: Chemical compositions of barley straw ash and additives used in this study

Ash analysis (wt %. db[a])	K_2O	SiO_2	CaO	P_2O_5	Al_2O_3	MgO	Na_2O	Fe_2O_3	SO_3	Cl
Barley straw ash[c]	33.64	27.50	16.43	8.07	0.18	2.91	0.38	1.73	4.90	3.28
Kaolin	0.2	46.12	0.07	n[b]	34.08	0.16	0.04	0.87	0.06	n[b]
Zeolite 24A	0.03	34.26	n[b]	n[b]	26.35	n[b]	11.74	0.01	0.01	n[b]

a: dry basis; b: not detected; c: ash produced at 550 °C

Table 2: Major mineral phases observed in barley straw ash (550 °C) and raw additives

Major mineral phases	
Barley straw ash	KCl, K_2SO_4, $KCa(PO_3)_3$, $K_4Ca_3SiO_4$, SiO_2, $CaCO_3$
Kaolin	$Al_2Si_2O_5(OH)_4$, SiO_2
Zeolite Doucil 24A	$(Na_2O)(Al_2O_3)(SiO_2)_2{\cdot}5H_2O$

The KCl and K_2SO_4 have rather low melting temperatures, about 770 and 850 °C, respectively. Melting of these potassium salts is one of the dominating mechanisms causing sintering of ash during biomass combustion. Table 2 shows that kaolinite ($Al_2Si_2O_5(OH)_4$) is a major component of the kaolin used in the current work. Zeolite 24A contains $(Na_2O)(Al_2O_3)(SiO_2)_2{\cdot}5H_2O$ as a major compound.

3.2 Adsorption of KCl by additives

Retention of KCl by the two additives at 900°C and 1,000 °C are shown in Figure 1. It can be seen that both zeolite 24A and kaolin have high capacities to capture KCl. Even at 1000 °C, about 50 % and 40 % of the added solid KCl were retained in zeolite 24A and kaolin, respectively. However, less KCl was captured by the two additives at 1,000 °C compared to 900 °C. The capturing of KCl by additive particles involves physical and chemical adsorption (Kyi et al., 1999). Decreased KCl capturing capacities of the two additives at a higher temperature are probably due to loss of reactive surface areas on the additive particles, which restrains physical adsorption and chemical reactions of additive particles with the KCl vapor (Wang et al., 2012b). In addition, the porosity of the additive particles decreases at a higher temperature. It will limit the amount of KCl vapor diffusing into additive microstructure and reacting with active compounds in the additive (Tran et al., 2005). On the other hand, the chemical incorporation of KCl into additive particles may become difficult due to the transformation of main active compounds such as metakaolinite into rather inert new phases at elevated temperatures (Zheng et al., 2008).

Figure 1 shows that, compared to kaolin, more KCl was retained in zeolite 24A at the two tested temperatures. It is probably related to the different microstructure of kaolin and zeolite 24A. Zeolite 24A has a channel pore structure and intracrystalline voids. Vaporized KCl may diffuse into the channels and voids followed by reactions with aluminum silicates contained in zeolite 24A. At a certain high temperature, the original structure of zeolite 24A may partially collapse and occlude all KCl vapor into the structure. On the other hand, KCl easily desorbs from kaolin particles with a flake like structure, when they are heated at high temperature or for long enough time. In brief, zeolite 24A has a microstructure that is more favorable for capturing KCl vapor.

The mineral phases in the solid residues from additive-KCl mixtures were analyzed by XRD. $KAlSiO_4$ was observed in residues from the kaolin-KCl mixture, which has also been observed as a main product from reactions of kaolin with KCl in other study (Steenari and Lindqvist, 1998). Formation of $KAlSiO_4$ was also observed from the zeolite 24A-KCl mixture sintered at 1000 °C. In addition, the mineral phases $KAlSi_3O_8$, $KNa_3Al_4Si_4O_{16}$, $(K,Na)Si_3AlO_8$ and $KNa_3(Al,Si)_4O_8$ were identified from the heated zeolite 24A-KCl mixtures. Formation of these potassium aluminum silicates indicates that zeolite is chemically active to react with KCl via different reaction paths. These chemical reactions are normally irreversible and favorable to bind KCl vapor, which can abate KCl initiated ash sintering and fouling deposits consequently.

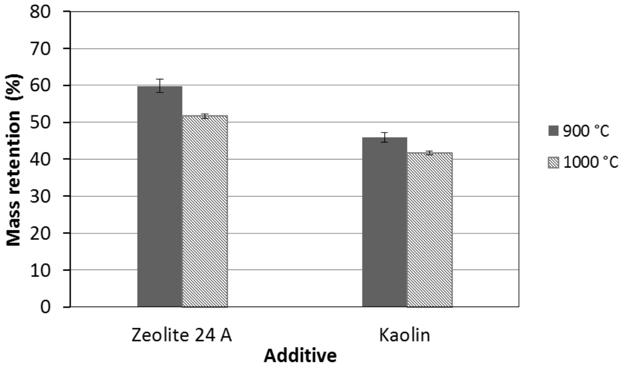

Figure 1: Retention of KCl within zeolite 24A and kaolin at different temperatures

3.3 Effect of additives on sintering behaviour of barley straw ash

The effects of the additives on sintering behaviour of the barley straw ash were evaluated by performing laboratory scale sintering tests. The reference barley straw ash and mixtures with additives were heated at 1,000 °C for 1 h. After the heating treatment, the barley straw ash melted completely on the bottom of the crucible. Broken bubbles were observed from the melted ash residues. It implies that the ash passed through an intensive melting stage and behaved as liquid. With addition of additive, severe melting of the barley straw ash was mitigated. The residues from the mixture of barley straw ash and kaolin heated at 1000 °C are slightly sintered with formation of fine aggregates that are easily broken. However, the residue from the mixture of the barley straw ash and zeolite 24A was sintered with the formation of large ash aggregates. Part of the residues was melted and formed a solid layer on top of the residues after the heating treatment. The sintering tests in this study showed that kaolin is more effective than zeolite 24A for reducing sintering tendency of the barley straw ash. Similar findings have been reported in a previous study. Kaolin has the ability to eliminate sintering of ash from wheat straw in the temperature range 700-1,000 °C. However, as zeolite 24A was added, wheat straw ash partially agglomerated as the heating temperature became higher than 900 °C (Wang et al., 2012b).

The residues from barley straw ash and corresponding mixtures with additives after heating treatment were analysed by SEM-EDX and XRD. Figure 2 shows representative SEM images taken from cross-sectioned barley straw ash sintered at 1000 °C. It can be seen that the barley straw ash has completely melted, showing continuous phases. Voids with round rims of different sizes are visible in the melted ash. The voids represent formation of bubbles as the gases (mainly from carbonates) are released from liquid ash melts. One zone in Figure 2-a marked with a white rectangle was further examined by EDX. It was found that the chemical compositions in area 1 and 2 are dominated by K and Si, with small amounts of Ca and P. This element distribution confirms that melted barley straw ash contains mainly potassium silicates. It is well documented that potassium readily reacts with silica in the biomass ash to form different potassium silicates (Boström et al., 2011). Some of the potassium silicates have low melting temperature and may fuse as viscous liquids leading to the bonding of ash grains. Continuous formation and melting of potassium silicates may result in bridging of ash aggregates and loss of individual particles (Boström et al., 2011). With a longer combustion time, ash will be melted completely with a homogeneous and continuous structure as shown in Figure 2. Compared to the mineral phases contained in ash produced at 550 °C, only trace amounts of silica were observed from barley straw ash sintered at 1,000 °C. Poor crystallinity of the barley straw ash sintered at 1,000 °C implies that it has melted into amorphous phases that can not be directly observed by XRD. A broad hump was observed in the XRD spectrum, which confirms presence of amorphous phases in the barley straw ash.

Figure 3-a shows a typical SEM image of residues from the mixture of barley straw ash and kaolin after heating at 1,000 °C. Contrary to barley straw ash, the residues from barley straw ash-kaolin mixture shown in Figure 3-a have a porous structure and no clear melting can be observed. The big grain illustrated in Figure 3-a is formed due to agglomeration of fine particles with different sizes. As revealed by EDX analyses, K and Si are still dominating elements in areas 3 and 4 (Table 4). However, the content of Al detected in the same area is significantly higher than that of melted barley straw ash (area 1 and 2, Figure 2). It suggests that kaolin addition has introduced more Al in the barley straw ash. This will promote the formation of high temperature melting potassium aluminium silicates instead of low temperature melting potassium silicates.

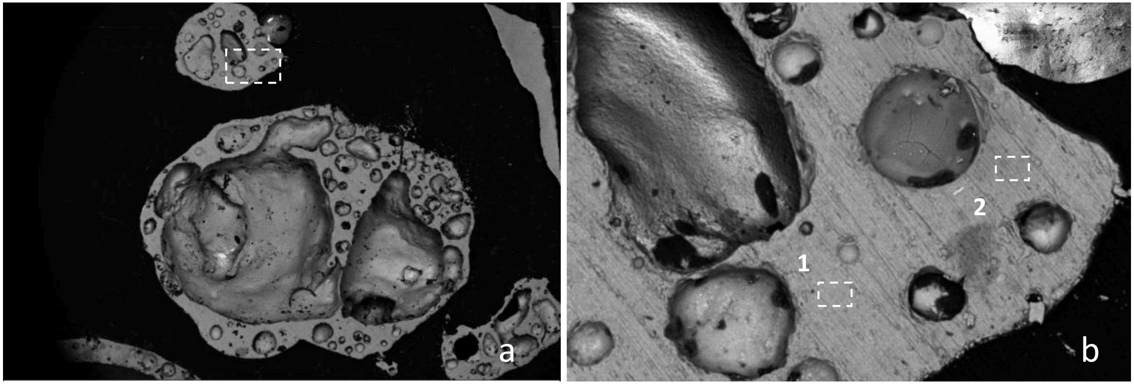

Figure 2: SEM-EDX analyses of barley straw ash sintered at 1000 °C

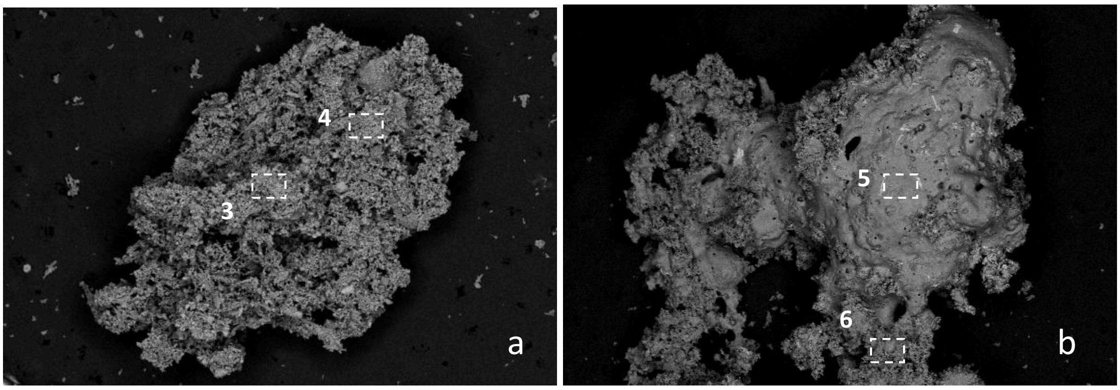

Figure 3: SEM-EDX analyses of mixtures of (a) barley straw ash-kaolin and (b) barley straw ash-zeolite 24A sintered at 1000 °C

Formation of potassium aluminium silicates was confirmed by XRD analysis. Kalsilite ($KAlSiO_4$) and leucite ($KAlSi_2O_6$) were observed in the residues from the mixture of the barley straw ash and kaolin. These two mineral phases have previously been identified as main products from the residues from mixtures of kaolin and biomass ashes heated at 1,000 °C (Steenari et al., 2009). Kalsilite and leucite have significantly high melting points over 1,100 °C. Therefore, formation of these two phases is the main cause for the reduction of barley straw ash sintering tendency with kaolin addition.

Figure 3-b shows that the residues from the sintered mixture of barley straw ash and zeolite 24A contain both melted ash and agglomerated particles. The former is clearly visible as a smooth and intact surface. From the melted ash, EDX revealed that K and Si are two dominating elements. Therefore, formation and melting of potassium silicates is the main reason for fusion of this part of the ash. However, Figure 3-b shows that part of the ash in the residue also contains fine particles agglomerated together, with loose structure. Significant amounts of Al together with Si and K were detected (area 6, Figure 3-b). During the thermal conversion process, the zeolite decomposes and transforms into different silicates and aluminium silicates at high enough temperature (Aranda et al., 2012). Some of the aluminium silicates can further react with potassium containing species in the barley straw ash, leading to formation of high temperature melting potassium aluminium silicates (Pettersson et al., 2009). Therefore, this part of the ash represents presence of potassium aluminium silicates such as kalsilite ($KAlSiO_4$) and leucite ($KAlSi_2O_6$) identified in the barley straw ash-zeolite 24A mixture. Formation of these high temperature inert phases improved the sintering behaviours of barley straw ash with zeolite 24A addition.

Table 4: Chemical compositions of barley straw ash and additives used in this study

Element (wt %)	K	Si	Ca	P	Al	Mg	Na	S	Cl
Area 1[a]	29.8	45.1	14.2	3.4	0.7	2.3	3.2	0.7	0.2
Area 2 [a]	33.1	14.8	39.6	5.4	1.0	2.8	2.4	0.4	0.3
Area 3[b]	27.2	35.7	9.8	1.7	19.8	2.2	2.1	0.2	1.1
Area 4[b]	25.3	37.2	9.2	2.1	21.2	3.1	1.2	0.4	1.2
Area 5[c]	30.3	38.6	7.9	1.8	8.2	1.9	8.9	0.3	1.3
Area 6[c]	24.8	40.2	3.4	2.4	16.5	4.3	7.4	0.2	1.0

a: barley straw ash sintered at 1000 °C; b: mixture of barley straw ash and kaolin; c: mixture of barley straw ash and zeolite 24A

Table 5: Major mineral phases observed from barley straw ash with and without additive addition

Major mineral phases	
Barley straw ash	amorphous material, trace amount of SiO_2, trace amount of $CaSiO_3$
+ Kaolin	SiO_2 (cristobalite), $KAlSiO_4$, $KAlSi_2O_6$, $CaSiO_3$,
+ Zeolite 24A	$KAlSiO_4$, $KAlSi_2O_6$, $(Na,K)AlSiO_4$, $Na_4Al_2Si_2O_6$, trace amounts of SiO_2 and $CaSiO_3$

4. Conclusions

The ability of kaolin and zeolite 24A to capture KCl was investigated via a thermogravimetric study. It was found that a significant fraction of KCl can be retained in the kaolin and zeolite 24A particles at the tested temperatures. High melting temperature potassium aluminium silicates were observed from the mixtures of additives and KCl. It indicates that chemical reactions occurred in the overall capturing process. The barley straw ash severely sintered at 1,000 °C due to formation and melting of potassium silicates. The intensive sintering of the barley straw ash was reduced through addition of kaolin or zeolite 24A. Kaolin and zeolite 24A reacted with potassium containing compounds in the barley straw ash. High temperature melting potassium aluminum silicates were formed, which can partially explain improved sintering behaviors of the barley straw ash. The results from the current work show that both kaolin and zeolite 24A can be used for mitigating ash fouling and sintering in biomass combustion applications.

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