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Investigation on Ash Slagging Characteristics during Combustion of Biomass Pellets and Effect of Additives

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ABSTRACT. This study reports a systematic investigation into ash slagging behaviour during combustion of barley straw and barley husk pellets with or without additives in a residential pellet burner. The slagging tendencies of the pellets were evaluated based on the amount, chemistry, mineralogy and morphology of inlet ash formed as slag and sintering degrees of residual ash. The barley straw and husk pellets showed high slagging tendencies with 39 wt % and 54 wt % ingoing ash formed as slag. Analyses using X-ray fluorescence (XRF) and scanning electron microcopy combined with Energy-dispersive X-ray spectroscopy (SEM/EDX) revealed high concentrations of K, Si, Ca but minor amount of P in barley straw slag. The slag mainly contained melted potassium silicates, directly observed by X-ray diffraction (XRD). For the barley husk, high ash slagging tendency was observed, mainly attributed to the formation and melting of potassium phosphates, potassium silicates and complex mixtures of the two mineral phases. Addition of marble sludge completely eliminated ash slagging during combustion of barley straw and husk pellets because it led to the formation of high temperature melting calcium potassium phosphates, calcium rich potassium silicates and oxides. Addition of calcium lignosulfonate showed a less pronounced ability to mitigate ash slagging issues during pellets combustion, although it promoted the formation of calcium rich silicates and phosphates (both with high-melting points) in barley straw and husk ash, respectively. This process was accompanied by considerable reduction in the amount and sintering degree of the formed barley straw and husk slag.

KEYWORDS: Biomass pellets, combustion, ash slagging, additives

1 INTRODUCTION

Utilization of agricultural and food processing wastes for energy purpose has attracted continuous attention in the past decades. It is increasingly important in response to the increasing energy demand, limited availability of stem wood assortment and great need for disposing these solid waste materials.[1] However, the use of agricultural and food processing wastes for energy applications is not straightforward. These fuels inherently often have undesired properties such as high moisture content, low energy and bulk density, diverse particle sizes and shapes.[2] Most of these drawbacks can be improved and/or overcome through pelletization. In contrast to the raw materials, the pellets produced from agricultural and food processing wastes have lower moisture contents and more uniform, consistent and standardized properties as solid fuel, resulting in better ignition/combustion behaviors and thereby higher energy efficiency and lower emission during combustion processes.[3] The increased volume and energy density reduces costs for transport and storage, while the uniform dimensions makes handling and feeding of biomass pellets easier and more controllable. Pellets of agricultural and food processing wastes are suitable for many industrial and residential applications, e.g. combustion in burners and grate furnaces.[4]

However, combustion of pellets prepared from agricultural and food processing wastes in small to medium scale combustion appliances may face challenges from ash sintering and slagging that interfere combustion processes, reduce combustion stability and decrease energy conversion efficiency consequently.[5, 6] The agricultural and food processing wastes often have high contents of ash forming matters, which can be 5-10 times of those of conventional woody biomass fuels.[5] Previous combustion experiments in residential combustion appliances showed that biomass fuels with high ash sintering and slagging tendency often contain large amounts of ash forming compounds.[7-11] Additionally, agricultural and food processing wastes contain abundant key ash-

forming matters (i.e., K, Si, P and Ca) which are also more heterogeneous than those in woody biomasses.[12] A general trend is that large amount of K and/or P can be found in agricultural and food processing wastes, together with other main ash-forming elements like Si and Ca.[13-15] Different than woody biomasses, relative concentrations of key ash forming elements (i.e., K, Si, P and Ca) vary significantly for agricultural and food processing wastes.[16-18] It was reported that the content of phosphorus in some agricultural wastes is even higher than that of silicon.[13, 17] Therefore, in addition to silicates, different phosphates are formed readily form and have been observed in the ash residues from combustion of agricultural and food processing wastes.[8, 13] Moreover, modes of occurrence of these elements in feedstock and ash have substantial effects on ash transformation reactions and amount/properties of formed ash residues.[17, 19, 20] Extensive chemical fractionation analyses for a wide range of biomass fuels showed that the association of ash forming matters in agricultural and food wastes is considerably different from that of other biomass fuels.[17, 21] The major fraction of K, Na and P in agricultural and food processing wastes are present as water-soluble salts or organic-bound forms.[17] These ash-forming elements with high solubility readily release during combustion and are active for further reactions to form compounds that initiate different ash related operational problems.[5, 19, 20] Predictions based on chemical fractionation analysis suggest that melting properties of ashes derived from agricultural and food processing wastes correlate well with the high content of soluble ash-forming elements in the feedstock.[17, 20] This correlation was also confirmed by experiments in combination with thermodynamic equilibrium calculations.[22] Due to the specific ash characteristics, ash sintering and slagging occur more often during the combustion of agricultural and food processing wastes. A previous study reported that up to 80% of the fuel ash entering the burner ended up as slag after the combustion of wheat straw.[10] For the combustion of cereal grains rich in phosphorus, 10-28% of incoming fuel ash formed slag.[8] These slags are often completely fused ash in the form of large

solid and hard blocks. Therefore, ash slagging causes great difficulties for achieving an efficient and clean combustion of pelletized agricultural and food processing wastes and hinders further utilization of such abundant biomass resources.

Utilization of additives is a promising and efficient way to abate ash sintering and slagging during combustion of biomass pellets.[23] Several studies investigated slagging characteristics and effect of additives during combustion of biomass pellets. Kaolin was found to be an efficient additive in different studies for eliminating or significantly reducing ash slag formation during biomass pellets combustion.[7, 9, 24] The kaolin chemically captures potassium compounds via different reaction routes, reducing the amount of potassium available for forming potassium silicates that have low-melting points.[9] As a consequence of this, both amounts of formed ash melts and ash slagging are reduced. However, utilization of additives like kaolin is not financially attractive because of relatively high costs. Different calcium-based additives were examined, including lime, limestone, and calcite.[8, 13, 24, 25] For the combustion of biomass fuel rich in silicon, potassium and calcium and with low content of phosphorus, addition of calcium leads to the formation of calcium rich silicates and oxides (both having high melting points) in the ash residues.[7, 25] This is accompanied by partial or even total elimination of ash sintering and slagging during combustion of these phosphorus-poor biomass fuels. On the other hand, addition of calcium based additives altered the ash chemistry and promoted the formation of potassium calcium phosphates that have high melting points as phosphorus rich biomass fuels were burned in various combustion appliances.[8, 10] This is considered as a main reason for the reduction in slag formation during the combustion of phosphorus rich biomass fuels. It is desirable to explore additive candidates from waste resources, which are available in a large amount at a relative low cost.[6, 26] In our previous work, addition of marble sludge, a waste from the marble refining process, eliminated slag formation during the

combustion of wood waste in a residential boiler.[25] This was mainly attributed to the reduced formation of alkali silicates (having low melting points), to more the increased formation of calcium rich alkali silicates (having high melting points) in ash residues.[25] However, the effect of marble sludge on ash slagging behavior during the combustion of agricultural and food processing wastes have not been well understood. The calcium rich additive can also be found in waste streams from the paper and pulp production process, in which significant amount of calcium carbonate is used. In this work, calcium lignosulfonate derived from a paper and pulp production plant was investigated. Calcium and sulfur are two dominating chemical elements of the calcium lignosulfonate. From the ash chemistry point of view, these two elements are favorable for mitigating ash related operational problems. However, no systematic study about the effect of calcium lignosulfonate on slagging behaviors of biomass ash have been reported.

The objectives of this work are to: i) investigate ash and slag forming processes during the combustion of barley straw and barley husk pellets and; ii) evaluate the effect of marble sludge and calcium lignosulfonate on slagging tendency and characteristics of the two fuels.

2 MATERIALS AND METHODS

2.1 Fuels and Additives

Two biomass fuels, i.e. barley straw and barley husk, were used in the experimental program. The barley straw was harvested in the county Hedmark in Norway and then stored indoors properly, in order to avoid further degradation and loss of water-soluble ash-forming elements due to rain. The barley husk was sourced from the same area, and so were wastes from the milling and refining process of barley grains. The received fuels were milled in a hammer mill to particles with size < 3 mm. The properties of two fuels are listed in Table 1. The marble sludge was obtained as slurry

from the marble processing company Hustadmarmor AS in Fræna, Norway. The received marble sludge was further air-dried to have a moisture content of ~10%. The calcium lignosulfonate was dry light-yellow and brown powders from Borregaard ASA. Both marble sludge and calcium lignosulfonate were further milled and sieved to a particle size < 20 μm.

The pellets of barley straw and barley husk with or without additive addition were produced using a pellets press (Kahl Akamat Herba-A/5K) equipped with a cascade mixer. The barley straw or barley husk was first milled and then transported to the mixer. For producing additive blended pellets, the fine additive powders were fed into the cascade mixer constantly through a feeding tube, which were stirred and blended with fuel particles by mixing paddles. After conditioning, the materials in the mixer passed through a rotating horizontal die and were pressed into pellets. The blending ratio of the additive to fuel was controlled by adjusting the mass of the additive fed into the mixer per unit time. In this way, fuel pellets with or without additive addition were produced under similar pelletizing conditions. Before pellets production, preliminary experiments were done for evaluating the effect of an additive on fuel ash melting behavior with respect to different additive-to-fuel ratios (0-5 wt%). Based on the assessment of ash melting behavior, marble sludge and calcium additive were added corresponding to approximately 3 wt% of each dry fuel. In addition, the calcium based additives lime and limestone were investigated as additive to reduce ash slagging during the combustion of cereal grains rich in phosphorus. It was reported that an additive-to-fuel ratio of 3 wt% dry substance was sufficient to eliminate slag formation during wheat grain combustion.[9,24] Therefore, the same additive-to-fuel ratio was also selected and studied in the present work for comparison purpose. Moreover, addition of 3 wt% dry substance additive to the fuel pellets only results in a small increase of amount of ingoing ash to the burner, which does not cause significant ash handling burdens. In this work, fuel pellets were also produced with

addition of both 3 wt% marble sludge and 3 wt% calcium additive. The two additives were added into one fuel to search for possible synergy effects from them on both pellets quality and ash slagging behaviors. In total, 8 types of pellets were produced for further combustion experiments.

2.2 Characterization of Produced Pellets

The properties of barley straw and barley husk pellets with or without additives addition were further characterized. The melting characteristics of ashes from the produced pellets were determined by following procedures described in Standard ISO 540: 1995.[27] The ash from each type of pellet was produced through burning the sample at 550 °C for 12 hours according to ASTM D 1102.[28] The residue ash was then collected and shaped into a 3 x 3 mm cubical specimen. The ash specimens were loaded into an analyzer and heated from room temperature to 1500 °C at 6 °C/min in oxidizing atmosphere. Shape changes of each ash specimen were recorded as temperature increases via a high-speed video camera. According to the standard, four ash fusion characteristic temperatures were determined based on the shape changes of one sample, i.e. initial deformation temperature (IDT), softening temperature (ST), hemisphere temperature (HT) and fluid temperature (FT). Five tests were performed for each ash sample, and the average values are presented in Table 2.

2.3 Combustion Experiments

The combustion of the selected pellets was performed in a 25 kW horizontally-fired step-grate burner (CN-STOKER, type CN 250) connected to a 25 kW boiler (CN-boiler CN25) at full loads. The boiler consists of a furnace chamber and a 2-way heat exchanger, with all parts being water jacketed. Depending on the bulk densities of fuel pellets, a total of 50-60 kg for each fuel was combusted. Temperatures at different positions in the burner were measured by shielded type K thermocouples. One thermocouple was mounted approximately 50 mm over the grate for recording

combustion temperature. Continuous measurement of O_2, CO and NO in the flue gas was conducted online using a flue gas analyzer (TESTO 354/450 XL). After each combustion experiment, the amounts of ash residues in the burner and boiler were collected and quantified, and were then analyzed.

2.4 Visual Evaluation and Chemical Characterization of the Collected Ash Samples

The sintering degree of the ash residues was assessed both through visual inspection together with a simple strength by bare hand. The slag samples were classified according to a scale as follows: (1) non-sintered ash residues, (2) slightly sintered ash with a fragile structure that is easily broken, (3) very hard sintered ash that fused into small size and breakable slags and (4) completely melted ash that fused into large blocks and lumps. A similar scale for grading sintering degree of ash has been used in previous studies focusing on biomass pellets combustion applications.[7-9] The collected ash residues were further sieved and all melted ash particles larger than 0.3 cm were removed and classified as slag. The rest of the ash residues after sieving was considered as bottom ash. This assessment procedure was developed and used in various studies and proven to be an efficient way for evaluating slagging tendency and degree of different biomass fuels.[8-10, 24]

The chemical compositions of the bottom ash and slag were determined by X-ray fluorescence (XRF). A Bruker D8 Advance X-ray diffractometer using Cu k-alpha radiation and a LynxEye detector was used for identifying mineral phases in the bottom ash and slag. An instrument integrated TOPAS evaluation program and the ICDD-PDF2 database were used for processing obtained X-ray spectra. The morphology and microchemistry of the slag samples were examined by Scanning Electron Microscopy (SEM) equipped with Energy Dispersive X-ray Fluorescence spectrometry (EDX). Representative slag samples were mounted in resin, and then cut, ground and polished to obtain cross-sections with smooth surfaces. Back-scattered electron (BSE) images were

taken from scan areas. For the same areas, EDX spot analyses were performed using EDX, and element maps were also obtained to show the distribution and correlations of important elements in the sample.

3 RESULTS AND DISCUSSION

3.1 Characterization of Fuels, Additives and Produced Pellets

The fuel and additive analysis results are shown in Table 1. The barley straw and barley husk have high heating values around 19 MJ/kg$_{d.b.}$. Compared to conventional woody biomass, the ash content of the two fuels are rather high. Chemical analysis results showed that barley straw ash, produced at 550 °C according to standard ASTM D1102 in lab, has similar characteristics as other agricultural wastes such as rice and wheat straw.[10] Potassium, silicon and calcium are three dominant elements in the barley straw ash produced at 550 °C, with small contents of phosphorus and magnesium. The silicon content of the barley straw ash is 10% higher than that of the barley husk ash. For crop straw, silicon is a key element to form silicate skeleton on the surface of straw and strengthen the microstructure.[29] In addition, concentration of silicon in crop straw can also be enhanced due to soil contamination. Different from the barley straw, the barley husk has a substantially high phosphorous content that is almost three times of that in the barley straw. The abundance of phosphorous in the seed-originating biomass materials like wheat bran, cereal grain and meals was reported previously.[8, 13-15] Phosphorus is a vital nutrient for cell division and development of new tissues, which is essential for seeds formation and growth consequently.[14] Therefore, a large amount of phosphorous are found in seeds, cereals, grains, husks and grans.[11-13] Most of the phosphorous in the wheat gran is present as phytic acid or phytate, which convert to K-phosphates, Mg-phosphates, K-Mg-phosphates or phosphorus oxides.[13, 14, 30] These P-rich fuels are often related to high ash sintering and slagging tendencies.[8] The calcium lignosulfonate has an

ash content of 23.2 wt% on dry substance base, and is dominated by the elements calcium and sulfur. In addition to ash content, the heating value of the calcium additive is significantly high. It indicates that the burning of calcium lignosulfonate can also contribute to energy production during pellets combustion processes. Marble sludge contains calcium as a dominating element, and with a small amount of magnesium. As showed in Table 2, addition of calcium lignosulfonate improved the durability of barley straw and husk pellets. The calcium lignosulfonate contains certain amount of sulfonated random water-soluble polymers. As the calcium lignosulfonate encounters moisture in the studied biomass fuels, it becomes tacky and makes particles stick together.[31] Therefore, the lignosulfonate acts as a binder to improve durability and strength of biomass pellets. This will reduce weight loss related to the formation of fines during pellets transportation and storage.[32] On the other hand, addition of marble sludge only enhanced the durability of the barley husk pellets. As an inorganic additive, marble sludge might affect bonding of biomass fuel particles in different ways, which cause variation in pellets quality consequently. The barley husk ash started to melt at around 860 °C and completely melted at 1104 °C already. The barley straw ash has significantly higher ash fusion characteristics temperatures, and melts at about 964 °C and is fully fused at 1186 °C. In addition, for both the barley husk and barley straw, from initial melting to full fusion took a very short time interval, i.e. occurred in a narrow temperature range, with observation of clear swelling and bubbling of ash specimens during ash fusion tests. The ash fusion test results indicate high sintering and slagging tendency of both barley straw and barley husk at elevated temperatures. Addition of additives significantly increased fusion temperatures of barley straw and barley husk ashes by 90-200 °C. Addition of both calcium lignosulfonate and marble sludge has distinctive enhancing effects on the melting temperature of ashes from two fuels.

3.2 Combustion Experiments and Slagging Tendency

In all combustion experiments, combustion temperatures in the vicinity of the burner and flue gas compositions were continuously measured. The maximum temperature measured in the region above the grate was in the range of 1130 ºC and 1180 ºC. During combustion of barley straw and barley husk pellets with additive blended, the measured maximum temperatures only slightly increased, which should not give significant effects on the slag formation. The O_2 level in the flue gases was in level 5-7 volume%. The average CO emission levels increased from 20-50 ppm to 117-250 ppm as the barley straw and barley husk pellets with different additives blended were burned. The measured emission levels of NO_x were in a range of 370-470 ppm.

Each combustion experiment was planned to last 5 hours to produce enough representative ash samples. However, the combustion of barley straw and barley husk pellets only lasted around 30-40 minutes from starting the firing to stopping the fuel feeding due to intensive formation of ash slag. Most formed ash slag piled up on burner grate, causing severe clogging of primary air inlets and eliminating combustion of incoming fuel pellets consequently. Upon addition of calcium lignosulfonate, severe ash slagging was evidently reduced during combustion of barley straw and husk pellets. Only a few large hard slag blocks and many small lumps were formed. Marble sludge addition eliminated slag formation during the combustion of the two kinds of fuel pellets. The ash residues left in the burner were powders that traveled along the burner and fell down into the ash pan. There was also no slag formation during combustion of the barley straw and husk with addition of both calcium lignosulfonate and marble sludge. The slagging tendency of barley straw and barley husk pellets with or without additives addition were expressed as fraction of ingoing fuel ash that formed as slag. As shown in Figure 1, both barley straw and barley husk pellets have high slagging tendency, with 38% and 56% of ingoing ash forming slag during combustion tests. The slag from the combustion of barley straw and barley husk pellets were completely melted, and

classified as the highest sintering degree, i.e. a scale of 4. Figure 2 shows representative slag samples with similar sizes collected after combustion of barley straw and husk pellets with and without addition of calcium lignosulfonate. Figure 2a shows that the barley straw ash slag has continuous dense compact structure, which is hard as stone and cannot break with bare hand. On the other hand, the barley husk slag has a rather porous structure with many openings on the surface and in fractured areas. It indicates that the barley husk ash passed through a severe molten phase and acted as liquid with intensive bubbling. The 3% calcium lignosulfonate addition to the pellets had significant positive effect on the slagging tendency of two studied fuels. As shown in Figure 2, only about 21% and 34% of the ingoing ash formed as slag during combustion of barley straw and husk with addition of calcium lignosulfonate, respectively. The slag samples from the combustion of calcium lignosulfonate added pellets have different sintering degrees. The major fraction of them has low sintering degree, and are breakable structures that can be pressed into powders by fingers. There is also a minor fraction of slag formed due to sintering and aggregation of ash, which are rather hard to break into pieces as shown in Figure 2b and 2d.

3.3 Chemical Composition of Bottom Ash and Slag Formation without Additives

The chemical compositions of the formed slag and bottom ash are presented in Figures 3-5. The dominating elements in the slag from combustion of barley straw pellets are silicon, potassium, and calcium, indicating that the presence of various silicates. The chemical analyses results showed that major elements in the barley husk slag are silicon, potassium and phosphorus, with lower contents of calcium and magnesium as well. The concentration of phosphorus in the barley husk slag is significantly higher than that of barley straw slag. Additionally, the calcium content in the barley husk slag is 15% less than that of barley ash slag. Differences in the concentrations of dominating elements in the slags imply different ash transformation reactions and slag forming

mechanisms during combustion of the barley straw and husk pellets. In comparison to the barley husk, the content of potassium in the barley straw slag and bottom ash are considerably higher. Amounts of silicon and chlorine in the raw biomass, among other factors, is a crucial factor to determine retention of potassium in the ash residues. During combustion of biomass fuel, chlorine is a key inorganic element facilitating potassium release that is limited by the quantity of available chlorine.[33, 34] For chlorine rich biomass fuel, a larger fraction of potassium releases together with chlorine through sublimation of KCl during the devolatilization of fuel particles [33]. During the char burnout stage, the residual potassium has great affinity to react with silicon containing species (i.e., silica and silicates) to form K-silicates.[5] As seen in Table 1, compared to barley husk, the barley straw contains evidently higher concentration of silicon and lower concentration of chlorine. This ash composition favors formation of K-silicates, retaining in the solid combustion residues and which partially explain the higher potassium content in the barley straw ash slag and bottom ash (see Figures 3 and 4). This finding agrees well with that potassium is readily retained in silicon rich straw ash and slag as reported in previous studies.[5, 29]

Figures 3 and 4 show that the addition of calcium lignosulfonate resulted in a distinct increase of calcium concentration in both slags and bottom ashes formed during combustion of barley straw. Enrichment of calcium is evident for the slag collected from combustion of barley straw, which increased from 22% to 35% upon calcium lignosulfonate addition. On the other hand, the concentration of potassium in slag from the combustion of calcium lignosulfonate added barley straw pellets are evidently lower than that from the combustion of non-additive pellets (see Figure 3). Upon addition of calcium lignosulfonate, a great amount of calcium is introduced to barley straw ash. Enhancement of calcium will limit incorporation of potassium into the silicates structure, which releases to gas phase instead.[30] In addition, it was also reported that calcium, either inherent

or from an external source, might substitute K in the molten depolymerized K-silicates to promote release of K during biomass combustion.[9, 10, 13, 35] Therefore, addition of calcium lignosulfonate reduces retention of the potassium in the ash and formation of low temperature melting K-silicates consequently. This is accompanied with decrease in ash melts formed and hence slagging tendency, as observed in this work. As displayed in Figures 3 and 5, phosphorus is enriched in both slag and bottom ash upon combustion of barley husk with addition of calcium lignosulfonate. Release of phosphorus is presumably related to formation and volatilization of K-phosphates (i.e., KPO_3) during combustion of phosphorus rich biomass fuels, which normally end up as fine particles in the flue gas.[9, 14] In presence of alkali earth metals, chemical transformation reactions of phosphorus is rather different and more solid ternary phosphates are preferably formed hence remain in ash residues.[5] Addition of calcium lignosulfonate introduces additional calcium to the barley husk ash that reduce the extent of phosphorus volatilization and promotes formation of nonvolatile K-Ca-phosphates. It partially explains enrichment of the phosphorus in the slag and bottom ash from combustion of calcium lignosulfonate added barley husk pellets. It is worth to note that, upon addition of calcium lignosulfonate, the contents of sulphur in all analyzed slag and bottom ash samples are increased considerably. The sulfur should be initially from the calcium additive, and might also be involved in ash transformation reactions during the combustion of the studied fuel pellets. As expected, the addition of marble sludge alone or together with calcium lignosulfonate increased the content of calcium in the barley straw bottom ash dramatically. On the other hand, the concentrations of silicon and potassium decrease evidently.

The crystalline phases in the collected slag and bottom ash samples were further identified by XRD and the result is listed in Table 3. One should note that the slag and bottom ash contain materials that are in crystalline or amorphous phases, and the later one cannot be directly observed by XRD.

The ratio between crystalline and amorphous phases is strongly affected by fuel chemical composition, thermal conversion temperatures and ash cooling history etc.

As listed in Table 3, only three crystalline phases SiO_2, $K_2CaP_2O_7$ and $KMgPO_4$ are identified in the barley straw slag. During combustion of biomass, potassium may involve in the formation of both phosphates and silicates but the phosphorus has a higher thermodynamic affinity than silicon to react with potassium and that the K-phosphates may form prior to the K-silicates.[5] As the initially formed K-phosphates encounter the alkali earth metals, ternary K-Ca/Mg-phosphates are readily formed and remain in the ash residues. Similar observations of $K_2CaP_2O_7$ and $KMgPO_4$ can be made in the barley straw slag in this study. Formation of K phosphates and K-Ca/Mg-phosphates reduces the amount of potassium available to react with silicon during combustion of biomass. As seen for the ash composition (Table 1) of the barley straw, the content of phosphorus and the molar ratio of Si/K are both rather high. The results suggest that a certain portion of the silicon in the barley straw, either organically bound or from external sources, keeps unreacted and ends up in the ash residues as silica. This is consistent with the observation of SiO_2 as a main crystalline phase in the slag.

Compared to barley straw slag, more K-Ca/Mg-phosphates were identified as major crystalline phases in the barley husk slag as shown in Table 3. This is related to high content of P in the barley husk, which favors formation of K-Ca/Mg-phosphates. Again, the SiO_2 was identified as the other major crystalline phase in the barley husk ash. Similar crystalline phases have been identified in the slag from combustion of phosphorus rich barley grains.[8] The results reported in this study, together with those in in previous work [11], confirm that different ash transformation chemical reactions during the combustion of phosphorus-rich and -poor biomass fuels have important effect on the mechanisms and severity of ash slagging.

As seen in Table 3, compared to slag formed from the combustion of pellets without additives, there are evident differences of mineralogical phases identified from the slags collected after combustion of barley straw and barley husk pellets with addition of additives. Upon addition of calcium lignosulfonate, new mineral phases Ca_2SiO_4 and $Ca_2Mg(Si_2O_7)$ were observed from the barley straw slag, with no crystallized SiO_2 detected in the same sample. For the agricultural wastes such as crop straws, silicon and potassium in the fuel are abundantly available and readily react during combustion. Products from such reactions are normally K-silicates that readily melt, initiating and enhancing ash sintering and slagging. As the molten K-silicates encounter the alkali earth metal oxides, reactions will take place and the latter will dissolve into the melts, resulting in evaporation of K and formation of Ca/Mg-silicates and/or K-Ca/Mg-silicates. The formed Ca/Mg-silicates and/or K-Ca/Mg-silicates normally have much high melting temperature compared to the initially formed K-silicates.[8] Formation of these melting phases of high melting points resulted in reduction of ash melts amount in the slag and slag sintering degree as well. The other possible explanation for this is that calcium oxide contained in the calcium lignosulfonate might directly react with the silica in the barley straw ash, leading to the formation of Ca_2SiO_4 and $Ca_2Mg(Si_2O_7)$ both of which have high melting points and are thermally stable. Since silica in the barley straw can react with calcium oxide from the additive, less amounts of silica in fuel will be available to form molten K-silicates that are key sources for producing ash melts. It explains decreased slag sintering degrees during barley straw combustion with addition of the calcium additive.

As can be observed in Table 3, the addition of calcium additive resulted in a general shift from potassium rich phosphates (i.e., $K_2Ca_2P_2O_7$) to calcium rich phosphates [i.e., $Ca_{10}K(PO_4)_7$ and $KCaPO_4$] in the slags from the combustion of barley husk pellets. As aforementioned, intensive formation of potassium phosphates may take place during the combustion of the barley husk

pellets, considering the high contents of both phosphorus and potassium in the fuel. The addition of calcium lignosulfonate provides calcium oxide to react with K-phosphates formed initially to produce Ca rich K-Ca-phosphates. The latter ones normally have higher melting points and can explain the improved slagging behavior of the barley husk ash. Similar ash transformation chemistry was also observed during the combustion of phosphorus rich cereal grains with addition of 2 wt% of lime.[8] In addition to K-Ca-phosphates, a small amount of $Ca_2Mg(Si_2O_7)$ was also observed from slag collected from the combustion of barley husk pellets with addition of calcium lignosulfonate. The results suggest that a redistribution of Si from potassium silicates to calcium silicates that have high melting points. This might also contribute to the reduction in the amount and sintering degree of ash slag formed during the combustion of the barley husk pellets with prior blending of the calcium additive.

Table 3 also lists the crystalline phases observed from the bottom ash samples. In addition to the K-Ca-phosphates and SiO_2, there are also crystalline phases KCl and K_2SO_4 detected from bottom ashes from the combustion of barley straw and husk pellets. These two major crystalline phases are presumably formed and vaporized during initial combustion of the biomass fuel pellets produced from agricultural and food processing wastes.[10] During the shutdown and cooling stages of the combustion experiments, these phases may be crystallized out from the flue gas and condensed on the surfaces of bottom ash particles.[8] It should be noted that the amount of K_2SO_4 in the bottom ashes increased during combustion after the addition of calcium lignosulfonate into the barley straw and husk pellets. While the exact mechanism is unknown, one possible interpretation is that the calcium lignosulfonate contains a high content of sulfur that will be oxidized first and then react with potassium in the fuel pellets during the combustion tests. This leads to a subsequent increase of the $K_2SO_4(g)$ concentration in the flue gas, which condense on bottom ash particle

surfaces, as detected by XRD. Compared to those from the combustion of pellets without additives, significant amounts of $CaCO_3$ and CaO were identified in the bottom ash samples from pellets combustion with the addition of either calcium lignosulfonate or marble sludge. This is more evident for the bottom ashes from the combustion of marble sludge blended pellets. The presence of $CaCO_3$ and CaO indicates there is surplus marble sludge in the system. Therefore, a dilution effect from the marble sludge on the barley straw and husk ash during combustion should be taken into account regarding slag formation. In addition, $Ca_5(PO_4)_3(OH)$ was also observed from the bottom ash samples collected from combustion of fuel pellets with marble sludge blended. Formation of $Ca_5(PO_4)_3(OH)$ is probably due to reactions between calcium rich phosphates and water vapors from fuel pellets.[8] Similar phase compositions have been observed in bottom ashes from combustion of cereal crops with addition of lime.[8]

3.4 SEM-EDX analysis of slag

Figure 6 shows the representative back-scattered electron images of cross-sections of slag samples collected from combustion of barley straw and barley husk with and without addition of calcium lignosulfonate. It can be seen that both barley straw and husk slag have a continuous and dense structure with inclusion of many voids with round rims (see panels a and b of Figure 6). The round voids represent formation of bubbles due to release of gases from the barley straw and husk ash that melted severely in a liquid phase with high surface tensions. The slag samples formed upon addition of calcium lignosulfonate (see panels c and d of Figure 6) have rather heterogeneous structure with reduced number of round voids. There are also areas and patches with higher brightness, which are absent in the BSE images of slag from combustion of non-additive pellets. It indicates that different compositional phases exist in slag formed with or without additive addition.

Figure 7 shows a BSE image of a scanned area (100 x 100 μm) of cross-sectioned barley straw ash slag. Three zones can easily be distinguished according to brightness. The zone with dark gray color dominates the whole scanned area. EDX spot analyses (spots 1 and 2, Figure 8) revealed that potassium and silicon are two main elements, with clear correlations in the elemental maps (Figure 7). It manifests that slag from barley straw combustion contains melted potassium silicates. This finding agrees well with the previous work.[10, 29] It was reported that the potassium silicates chemistry plays a critical role in ash slagging during the combustion of silicon rich agricultural residues.[10, 29] The zones with light gray color (spots 3 and 4, Figure 8) with round edge can easily be distinguished in the elemental maps. High contents of potassium and phosphorus and minor amounts of calcium were detected in these zones, representing the formation potassium-rich phosphates in the slag. The dark gray zone represents a sand particle trapped by the melted ash, in which silicon is detected as the main element (spot 5, Figure 8). For the barley straw slag, significantly high contents of silicon and potassium were detected by both XRF and SEM-EDX analyses. However, only the SiO_2, $K_2CaP_2O_7$ and $KMgPO_4$ are mineral phases containing silicon and potassium, as detected by XRD. There is evident deficiency of silicon and potassium detected in the XRD analysis compared to those detected by XRF and SEM-EDX analyses. Together with the clear correlation between silicon and potassium shown in Figure 7, the barley straw slag presumably contains considerable amount K-silicates that are in glass phases and which cannot be directly observed by XRD. Actually, for all XRD patterns obtained from the analyzed samples, the typical scattering distribution from an amorphous material was observed, implying presence of a significant amount of glass phase.

Figure 9 shows BSE image and element mapping of a scanned area (100 x 100 μm) of barley husk slag. From the dominating dark gray color zone (spot 1 and 2, Figure 10), silicon, potassium and

phosphorus were detected as major elements and the phosphorus content is considerably higher than that of barley straw slag. It indicates coexistence of potassium-rich silicates and phosphates in the examined area. It was suggested that phosphates are miscible with silicate melts, leading to formation of a complex mixture containing both phosphates and silicates.[22, 36] The formed phosphate-silicate mixture has even lower eutectic points than the parental silicates and phosphates.[22] Therefore, the formation and melting of a phosphate-silicate mixture could be one reason for the severe slagging of the barley husk ash observed in this study. There are also some zones (spots 4-7, Figure 9) with irregular shapes showing in the Figure 9. Potassium, phosphorus, calcium and magnesium were detected as dominating elements that show clear correlations in element maps. Therefore, these zones indicate the presence of K-Ca/Mg-phosphates that agree with XRD analysis results. An extremely high silicon concentration was detected from one of the dark zones (spot 3, Figure 9), which was easily distinguished due to its high brightness in the right corner of the elemental Si map (Figure 11). Therefore, this zone represents sand/soil particles trapped in the melted ash. The SiO_2 is the main mineral composition of these sand/soil particles. The observation from these sand/soil particles might correlate with identification of SiO_2 in the slag sample by XRD analysis.

Figures 11 and 12 present SEM-EDX analyses of the slag formed during the combustion of barley straw with addition of calcium lignosulfonate. The results showed that, compared to slag from barley straw combustion (Figure 8), the slag from the combustion of barley straw with addition of calcium lignosulfonate (Figure 12) has considerably higher calcium content and lower potassium content. The EDX analyses results agree well with the bulk chemical composition analysis (XRF) results shown in Figure 3. The differences in potassium and calcium content shown in Figures 3, 8 and 9 imply reactions between calcium from calcium lignosulfonate and the molten K-silicates in

barley straw ash, which enhances potassium release consequently. As shown in the BSE image in Figure 11, there are many light gray patches distributed across the scanned area. The calcium was detected as a dominant element (more than 50 %) together with potassium and silicon (spots 3 and 4, Figure 12) and there are clear correlations between the three elements shown in the elemental maps. Therefore, these light gray patches represent the formation of calcium rich silicates in the barley straw ash upon addition of calcium lignosulfonate. Figures 13-14 present SEM-EDX analysis of the slag formed during the combustion of calcium lignosulfonate blended barley husk pellets. Large amounts of light gray patches and areas are clearly shown in the BSE image in Figure 13, which cannot be found from that of barley husk slag (Figure 9). A significantly high content of calcium was detected in these patches with relatively small amounts of potassium and phosphorus (spots 5-9, Figure 14). With addition of calcium lignosulfonate, more calcium is available for incorporation into K rich phosphates during combustion of barley husk, yielding calcium rich phosphate with high melting temperatures, as identified by XRD. Considering this, these patches represent the existence of calcium rich phosphates in the slag.

4 CONCLUSIONS

The study results showed high slagging tendency during combustion of barley straw and barley husk pellets. The barley straw slag consisted of mainly potassium rich silicates and high temperature melting potassium calcium phosphates. SiO_2 was also identified from the slag sample. For barley husk, the collected slag presumably consists of a mixture of potassium rich silicates and phosphates. Addition of marble sludge or a mixture of it with calcium lignosulfonate eliminated slag formation during combustion of barley straw and husk pellets. Upon marble sludge addition, the main composition of the barley straw and husk slag and bottom ash shifted from low melting

points silicates and phosphates to high temperature melting calcium silicates, phosphates and oxides. The significant amount of calcium oxide and calcite carbonate observed in the ash residues, indicates a surplus of marble sludge that gave a diluting effect and presumably restrains ash slagging. Addition of calcium lignosulfonate gave a less pronounced effect on mitigation of barley straw and husk ash slagging. However, as a result of the addition of calcium additive, the slagging tendencies of the two studied fuels were reduced to certain extents. The size and sintering degree of the formed slag were considerably decreased. Addition of calcium additive promoted formation of high temperature melting calcium rich silicates and phosphates in barley straw and husk pellets ash, respectively. The effect of calcium lignosulfonate addition on barley straw and husk pellets ash transformation is supported by coherence between the SEM-EDX, XRF and XRD analyses.

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Tables and Figures

Table 1. Proximate, Ultimate and Ash Composition of Fuels and Additives

	barley straw	barley husk	calcium lignosulfonate	marble sludge
Proximate analysis (wt %, d.b.[a])				
Volatiles matter	79.2	81.5	57.6	nd[c]
Fixed carbon[a]	17.6	14.4	20.2	nd[c]
Ash content	3.2	4.1	22.2	98.0
Ultimate analysis (wt %, d.b.)				
C	48.4	46.4	42.5	nd[c]
H	5.8	6.0	4.5	nd[c]
N	0.72	2.0	0.13	nd[c]
S	0.08	0.14	6.46	nd[c]
O[b]	45.0	45.46	46.41	nd[c]
High Heating value (MJ/Kg d.b.)	19.36	18.92	15.42	nd[c]
Ash forming elements (wt %)[d]				
CaO	13.43	6.89	65.32	95.12
SiO_2	41.50	30.95	0.12	0.20
K_2O	29.22	32.13	0.99	0.02
P_2O_5	8.07	23.76	0.51	0.02
MgO	1.91	0.15	0.01	2.99
SO_3	3.90	1.97	32.78	0.05
Al_2O_3	0.18	1.43	0.03	0.80
Na_2O	0.38	0.01	0.07	0.22
Fe_2O_3	0.43	0.65	0.12	0.52
Cl	0.98	2.06	0.05	nd[c]

[a] dry basis; [b] by difference; [c] not detected; [d] the values are in weight percentage of dry ashes produced at 550 °C.

Table 2. Physical Properties and Ash Fusion Behavior of Fuels and Additives

	Standard	barley straw	+ 3% CL	+3% MS	+ 2% CL + 2% MS	barley husk	+ 3% CL	+ 3% MS	+ 2% CL + 2% MS
Physical properties of produced fuel pellets									
Particle density (kg/m^3)	CEN/TS 15405:2006	1.25	1.23	1.29	1.32	1.24	1.25	1.27	1.28
Bulk density (kg/m^3)	NS-EN 15103	0.67	0.64	0.69	0.71	0.68	0.69	0.70	0.68
Durability (%)	NS-EN 15210-1:2009	95.91	98.7	90.08	94.64	88.07	93.43	93.26	94.28
Moisture (wt %)	NS-EN 14774-2	8.42	9.96	6.59	7.03	10.98	10.65	9.88	9.98
Ash fusion behavior of pelletized barley straw and husk with and without additives [a]									
Initial deformation temperature, IT (°C)	ISO 540: 1995	964	1058	1108	1189	860	980	1022	1058
Softening temperature, ST (°C)	ISO 540: 1995	1014	1102	1208	1289	972	1068	1148	1204
Hemispherical temperature, HT (°C)	ISO 540: 1995	1098	1188	1302	1346	1050	1098	1264	1342
Fluid temperature, FT (°C)	ISO 540: 1995	1186	1258	1378	1388	1104	1128	1348	1386

[a] the ash was produced at 550 °C according to ASTM Standard D1102.

Table 3. XRD analysis on collected slag and bottom ash samples

	Slag				Bottom ash							
	barley straw	+ 3% CL	barley husk	+ 3% CL	barley straw	+ 3% CL	+ 3% MS	+ 2% CL + 2% MS	barley husk	+ 3% CL	+ 3% MS	+ 2% CL + 2% MS
SiO_2	**		**		**				**			
$CaK_2P_2O_7$	**		**		**				***			
$Ca_5(PO_4)_3(O$						**	**	**			**	**
$Ca_{10}K(PO_4)_7$				**						*	**	**
$KMgPO_4$	*		**	**								
$KCaPO_4$		**	**	***								
Ca_2SiO_4		***										
$CaCO_3$						*	***	***		**	***	***
CaO						**	**	**			**	**
CaK_2CO_3						*	*	*	*			
$K_2Mg_2(SO_4)_3$		*		*								
MgO										*	**	
$Ca_2Mg(Si_2O_7$		**		*								
KCl					*	*			*	*	*	
K_2SO_4					**	***			**	***		

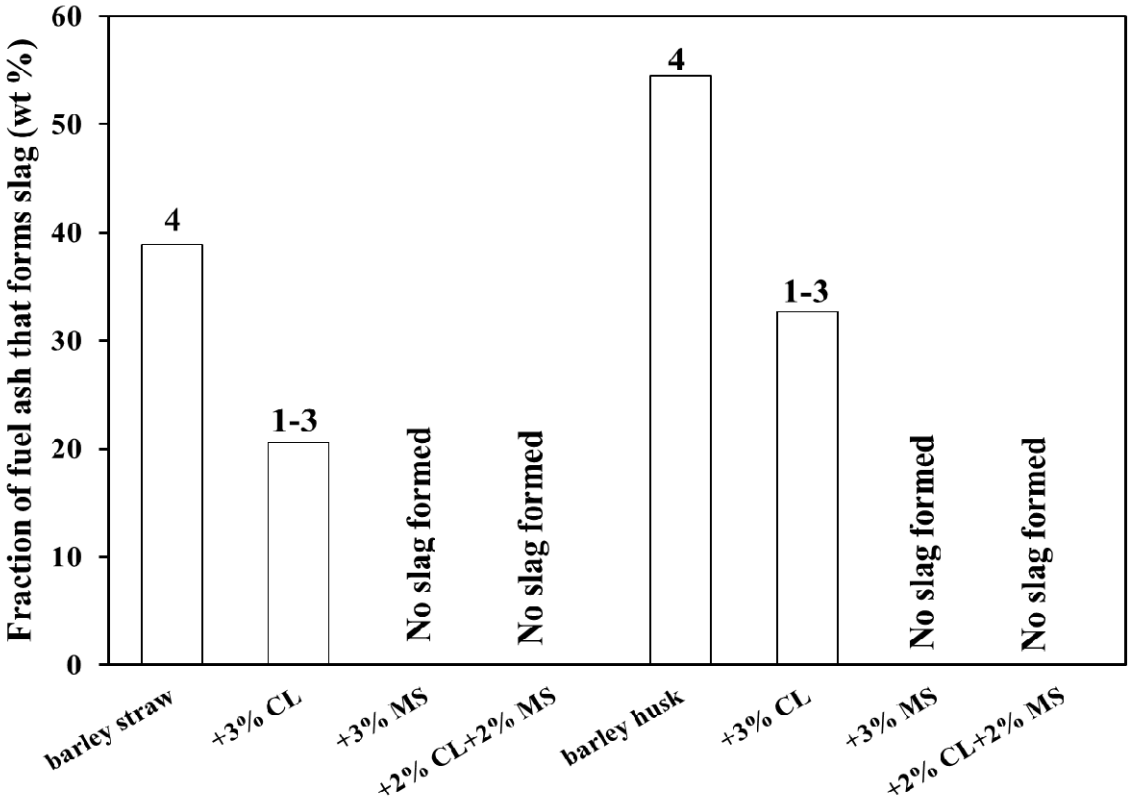

Figure 1. Fraction of fuel ash that forms slag during the combustion of barley straw and barley husk pellets with and without addition of calcium lignosulfonate and marble sludge.

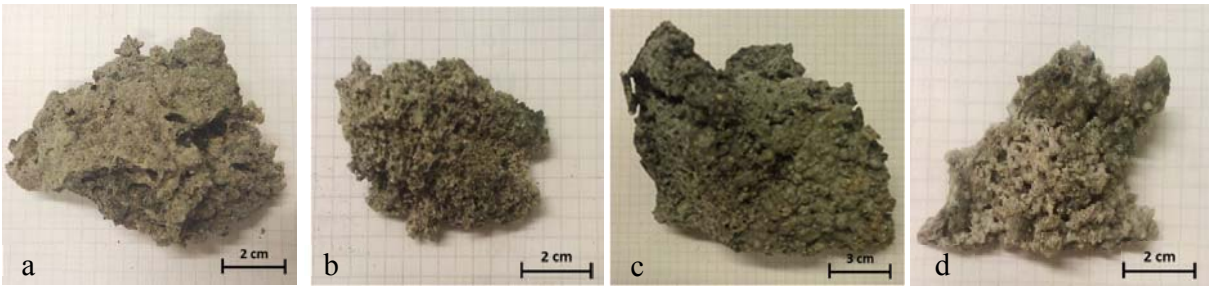

Figure 2. Slag samples collected from combustion of (a) barley straw pellets, (b) + 3 wt % calcium lignosulfonate, (c) barley husk pellets, (d) + 3 wt % calcium lignosulfonate.

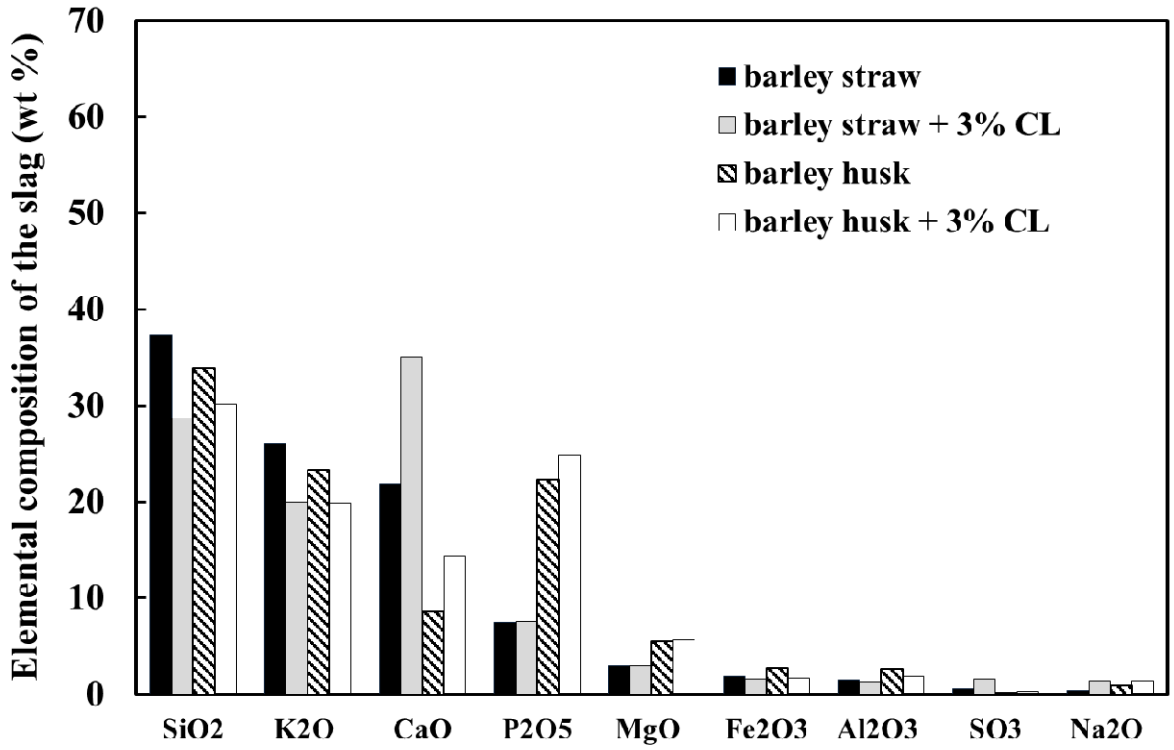

Figure 3. Elemental compositions (given as oxides) of the formed slag samples

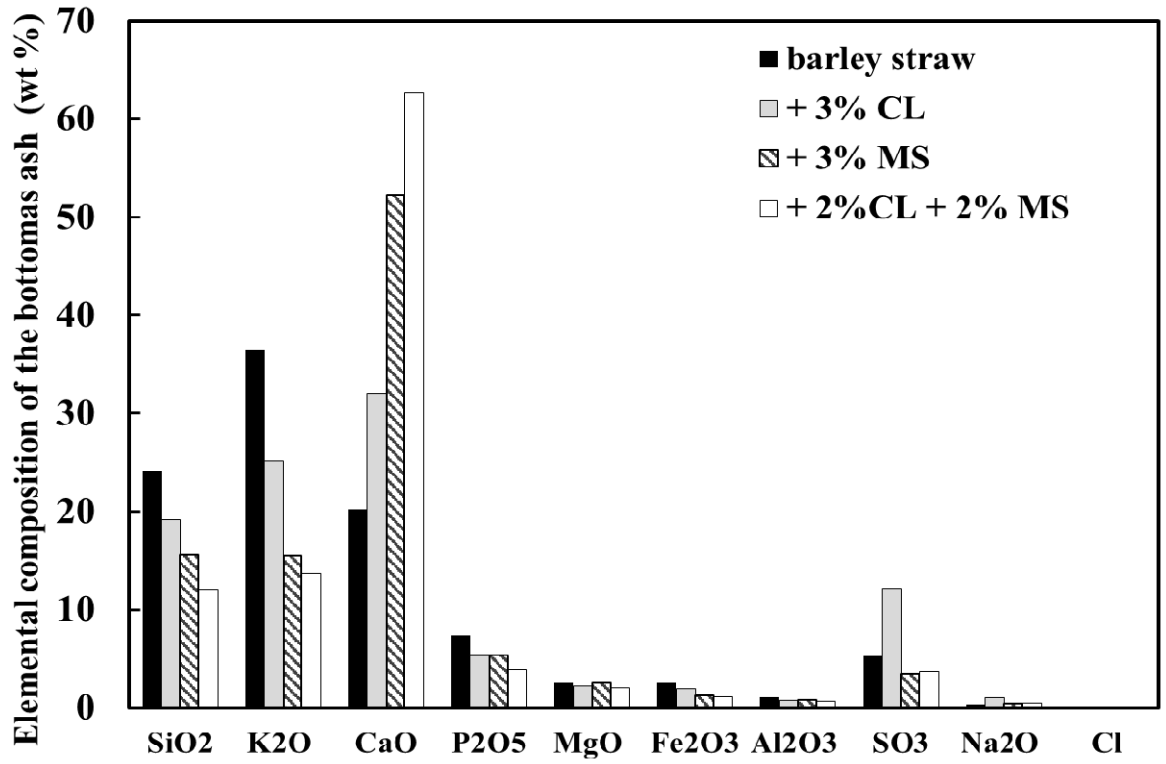

Figure 4. Elemental compositions (given as oxides) of the formed bottom ash from combustion of barley straw with and without additive addition

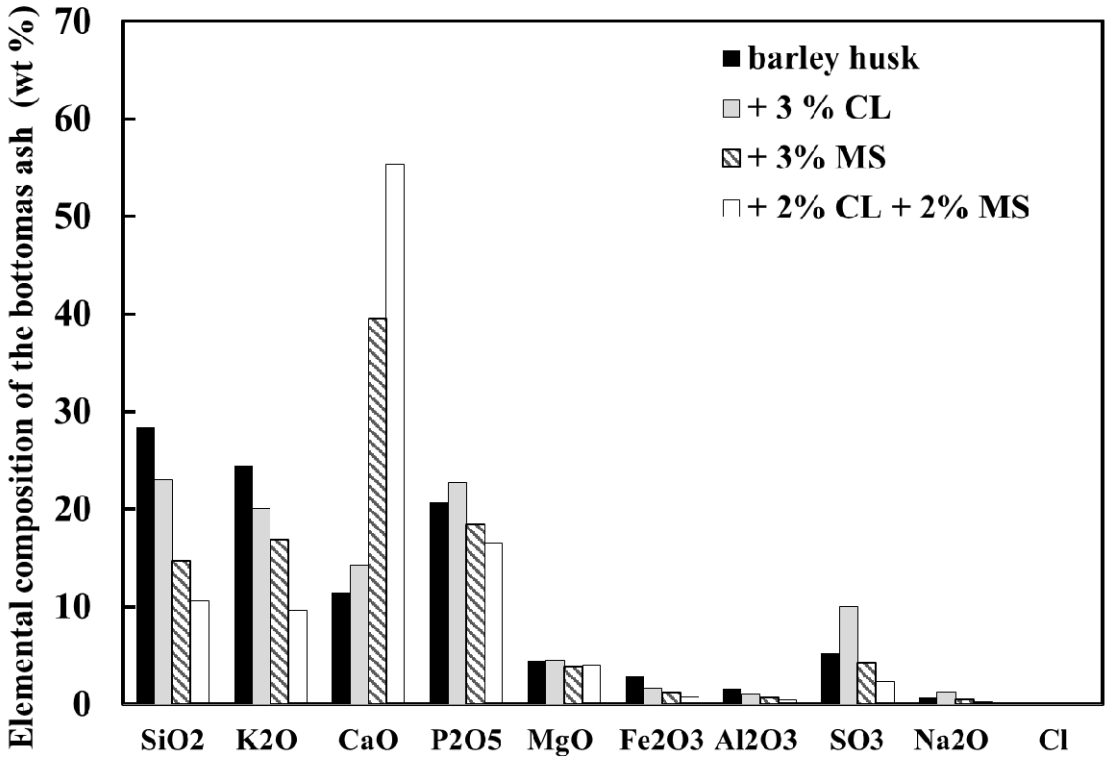

Figure 5. Elemental compositions (given as oxides) of the formed bottom ash from combustion of barley husk with and without additive addition

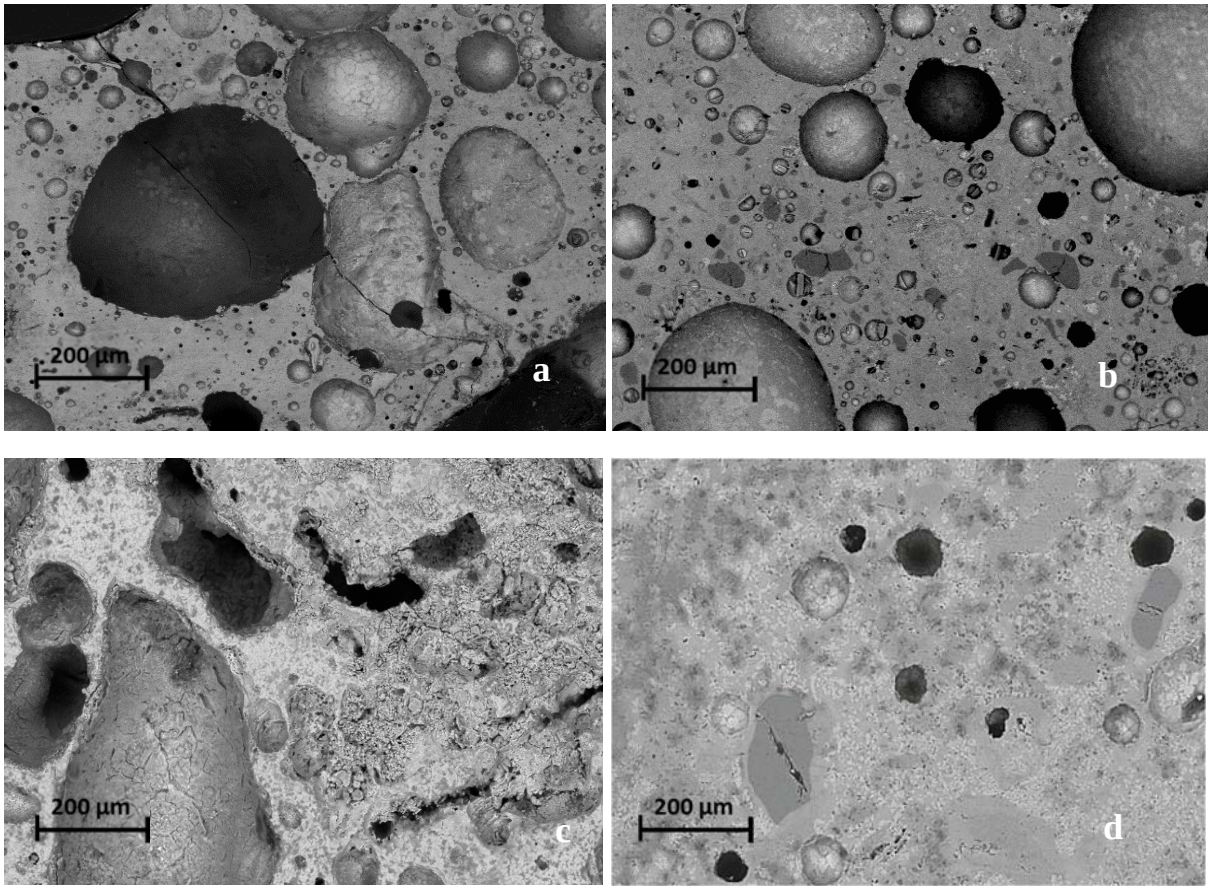

Figure 6. Back-scattered electron image of typical polished cross-section of slag samples from combustion of barley straw and barley husk pellets with and without additives: (a) barley straw, (b) barley husk, (c) barley straw + 3% calcium lignosulfonate and (d) barley husk + 3% calcium lignosulfonate

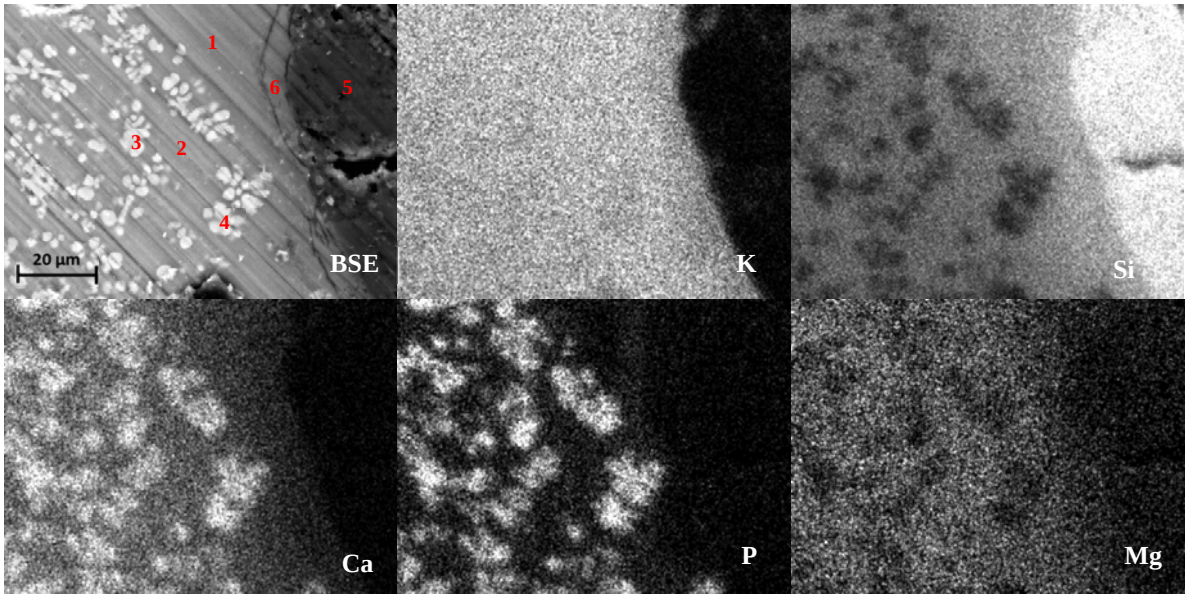

Figure 7. Back-scattered electron image and elements mapping of slag sample formed during the combustion of barley straw pellets

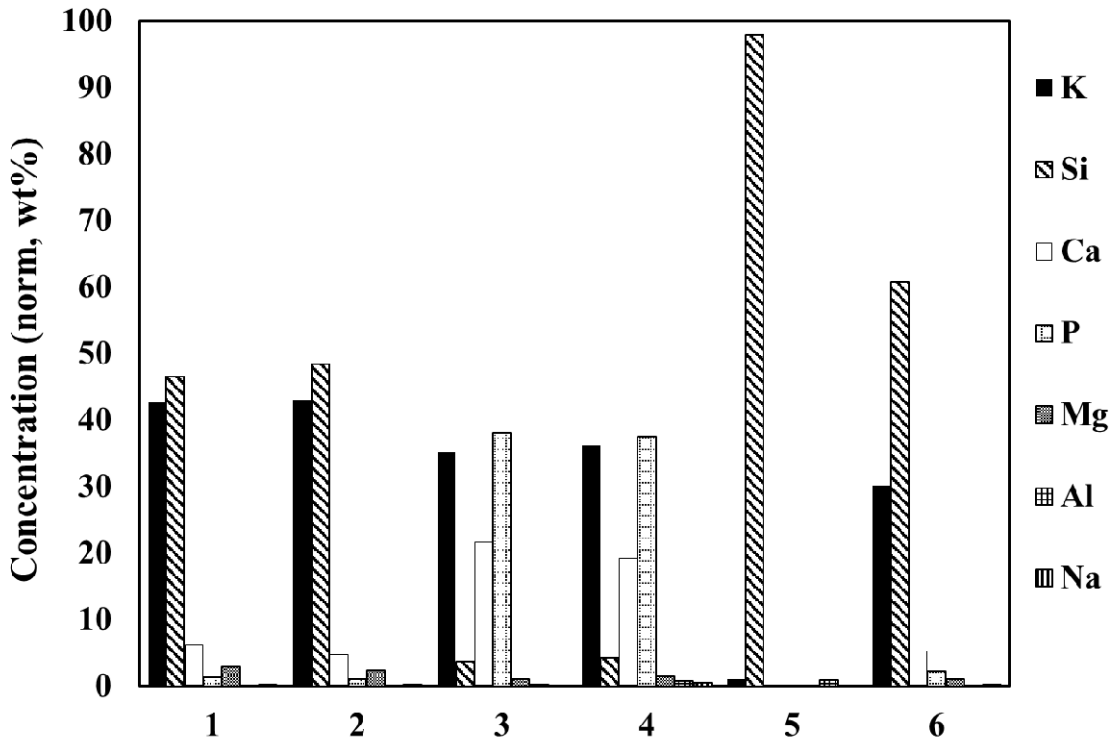

Figure 8. Element composition on C- and O-free basis of slag collected from combustion of barley straw pellets (marked spots in Figure 7)

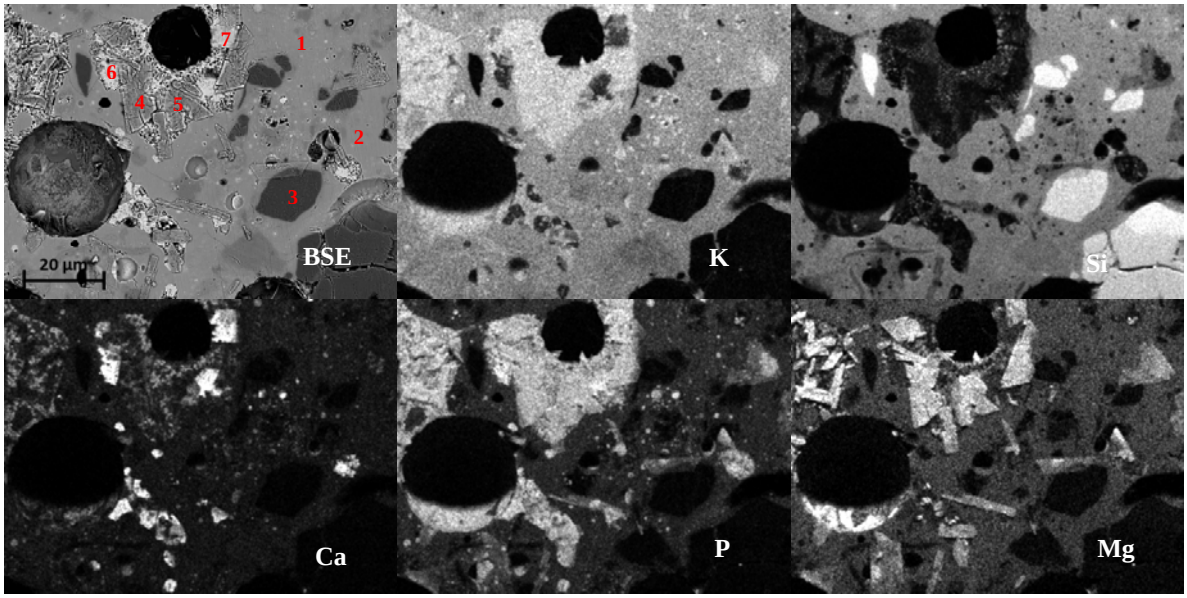

Figure 9. Back-scattered electron (BSE) image and elements mapping of slag sample formed during the combustion of barley husk pellets

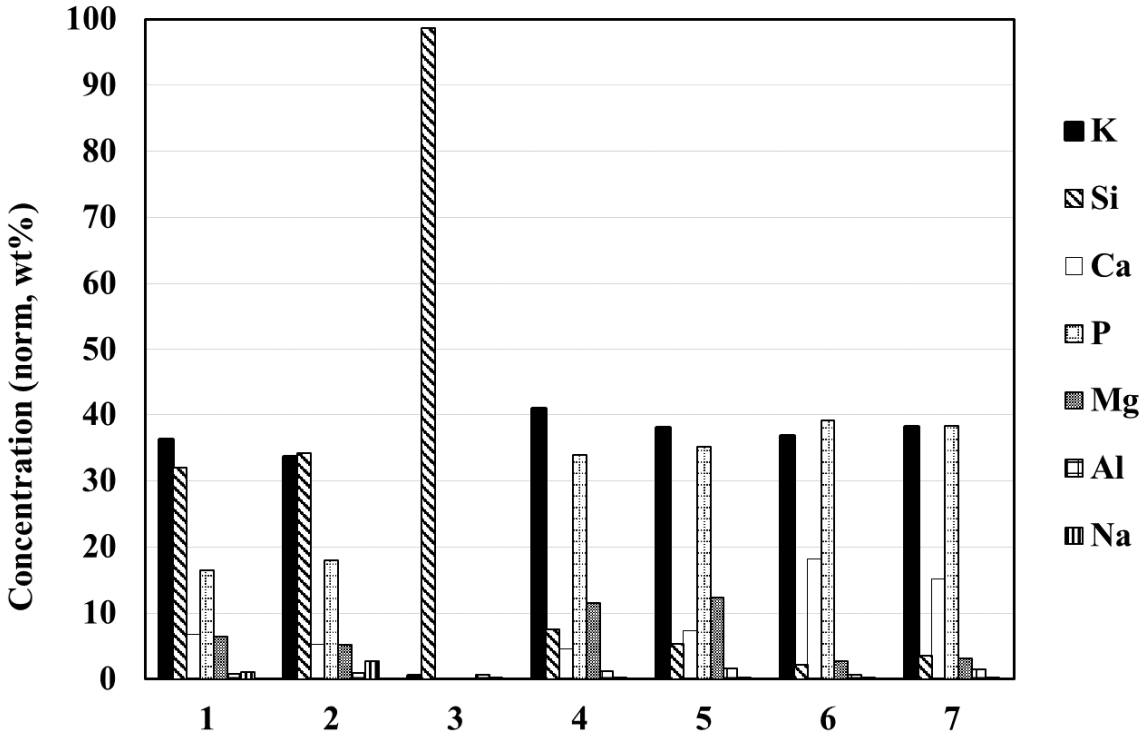

Figure 10. Element composition on C- and O-free basis of slag collected from combustion of barley husk pellets (marked spots in Figure 9)

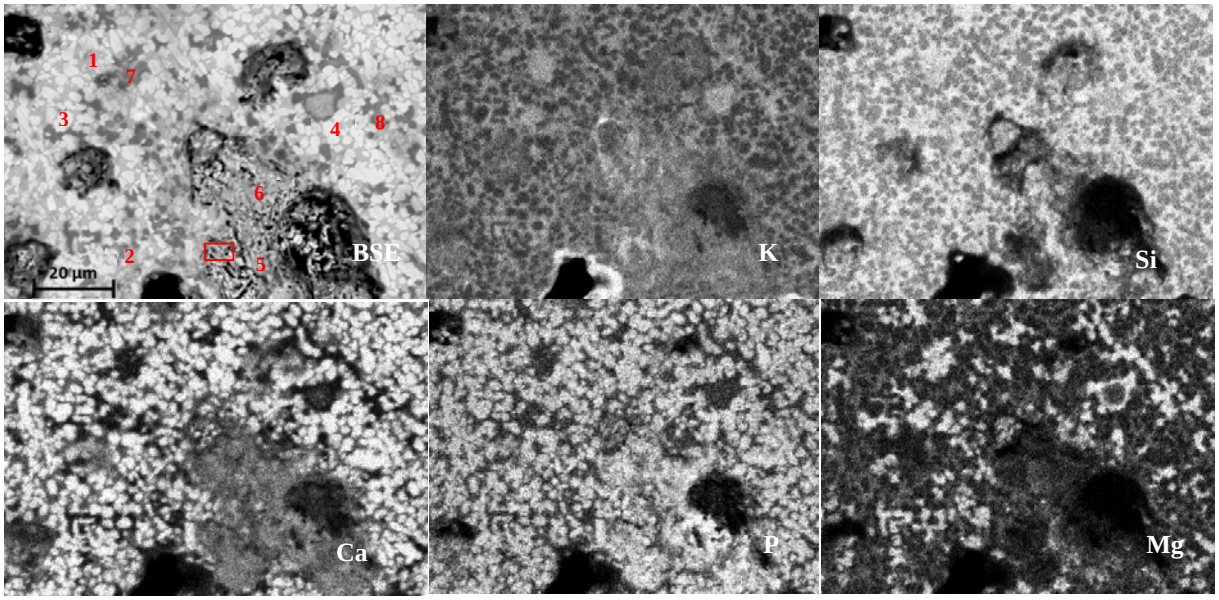

Figure 11. Back-scattered electron (BSE) image and elements mapping of slag sample formed during the combustion of barley straw with and without additive addition

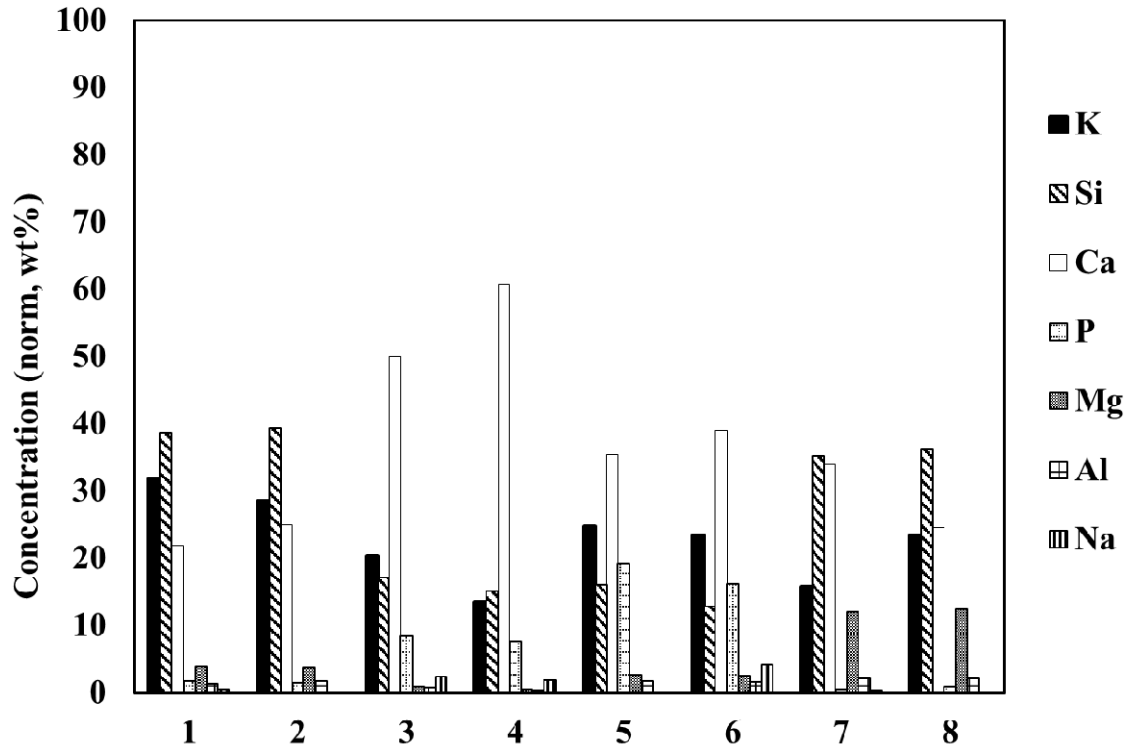

Figure 12. Element composition on C- and O-free basis of slag collected from combustion of barley straw pellets with addition of 3 % calcium lignosulfonate (marked spots in Figure 11)

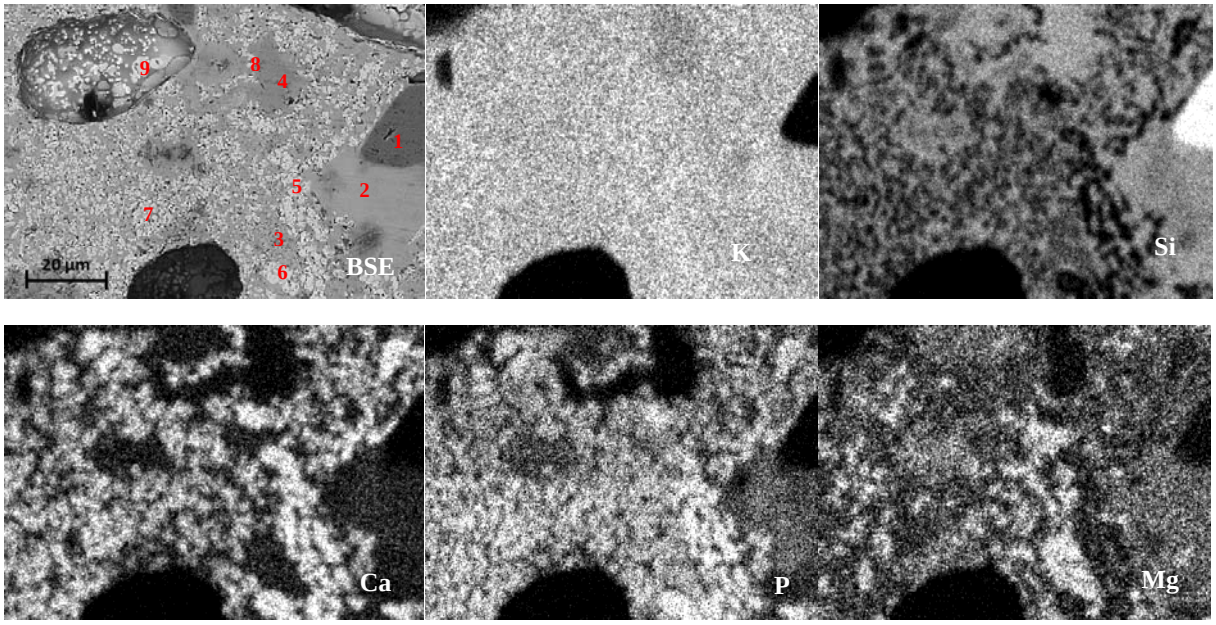

Figure 13. Back-scattered electron (BSE) image and elements mapping of slag sample formed during the combustion of barley husk pellets addition of 3 % calcium lignosulfonate

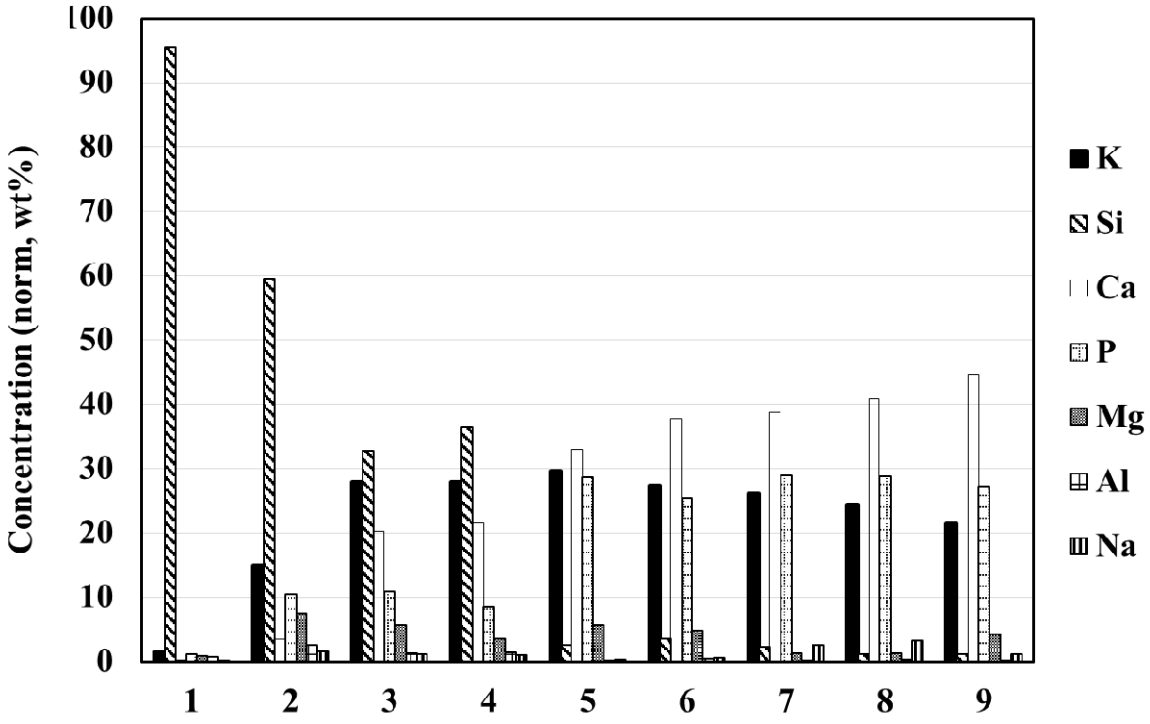

Figure 14. Element composition on C- and O-free basis of slag collected from combustion of barley husk pellets with addition of 3 % calcium lignosulfonate (marked spots in Figure 13)