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Characterization of ashes from *Pinus Sylvestris* forest biomass

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Abstract

Efficient and profitable biomass combustion is often limited by ash related operational problems. Knowledge of the ash melting and sintering is of important, in terms of predict and reduce ash-related problems in biomass-fired boilers. In this study, chemical composition and melting behaviors of ashes from the four parts of *P. sylvestris* trees were investigated. The four parts from *Pinus sylvestris* trees are stem wood, bark, branch base and twigs. A simultaneous thermal analyzer (STA) was used to characterize the melting behavior of selected biomass fuels in oxidizing atmosphere. Ash melting process was identified as the distinctive endothermic peaks on recorded DSC curves. The results showed that the stem wood of pine contains higher contents of most of the ash forming matters than other tree parts. Chemical composition of ashes from four parts of the pine tree is dominated by element Ca, K, Mg, Mn, P and Si. The K, Na and P contents in the twigs are significantly higher than that of stem wood, bark, and branch base indicating high tendency of ash melting and slagging. STA experiments indicated that the melting process of the studied fuel ashes start in the temperature range of 930-965 °C. Scanning electron microscopy (SEM) equipped with an energy dispersive X-ray spectrometry (EDX). Analyses results showed that the stem wood ash remains loose structure even after 1000 °C sintering treatment. But the ashes originated from top branch show sign of sintering at 1000 °C. The obtained results of present work can be considered as useful information within an industry interest for a prediction of the forest biomass ash melting behavior.

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Key words: Pinus sylvestris; Ash, melting behaviour; Simultaneous thermal analysis (STA); SEM-EDX

1. Introduction

In Norway, utilization of forest residues for production of heat and power has become more common in recent years. Thermochemical conversion method, such as direct firing, is the current major technology of biomass utilization nowadays [1]. However, efficient and profitable biomass combustion applications are often limited by ash related operational problems such as fouling and slagging, which reduce the efficiency and profitability biomass power plants [2, 3]. High concentration of K in the biomass fuel

causes formation of compounds (i.e., potassium salts and silicates) with low melting points. Deposition and accumulation of ash particles lead to slagging and fouling in furnaces and on surfaces of heat transfer component [4, 5, 6, 7, 8]. Cl can facilitate the release of K in the form of KCl. The condensation of vapor-phase alkali compounds generates deposits on the heat transfer surfaces [9]. Si, Al, and S can trap potassium compounds before being deposited, thereby reducing the potassium content in flue gas [10]. Characteristics of biomass ashes are affected by many factors including fuel species, growing and harvest conditions and utilizing of fertilizer. Consequently, the ash fusion characteristics (AFC) of various biofuels differ from each other [11]. Residues from forest sector are largely available and are promising fuels for combustion applications. Forest residues are often mixture of bark, twigs, tops and branches of trees. The knowledge of characteristics of ash derived from forest residues is important for combusting the forest residues efficiently and economically.. The objectives of the present study were to: 1) characterize of ashes from different parts of *Pinus sylvestris* trees, 2) investigate of the ash melting behaviors based on the STA measurement, and 3) study the ash sintering chemistry through SEM-EDX analysis.

2. Experimental

2.1. Material

The stem wood and forest residues was obtained from *P. sylvestris* trees harvested during spring period 2014 in East Norway (Hobøl, Latitude 59°43 'N and Longitude 10°52 'E). Three felled trees were divided into three crown levels (bottom, middle, top), based on the corresponding tree height. The crown base was defined to be the lowest living branch towards to tree top. One branch whirl was selected from the middle crown level (corresponding to about 60% of the tree height) and three branches including the needles were randomly cut. Cross-sectional discs, 5 cm thick, were cut from each tree in the vertical direction of the stem at given 60% tree height level. Branches were divided into two parts including base section and top branch section (mainly twigs with needles).

2.2. Measurement

All fuel samples were air dried first, which were milled to particle size smaller than 1 mm and dried again at 105 °C in order to get stable weight. The ash content of each fuel sample was measured according to ASTM standard D 1102. Chemical composition of each ash sample was analyzed by an inductively coupled plasma optical emission spectroscopy (ICP-OES). The samples for ICP-OES analysis were prepared by following the standard CEN-TS 15920. The ash melting behavior of samples expressed as the differential heat was measured simultaneously by a differential heat balance (Netzsch STA 449 F1 Jupiter). The DSC were carried out under an oxidizing atmosphere (N₂/O₂ 80:20 vol.%) at a heating rate of 10 °C /min. During one combustion experiment, 10 mg samples loaded in an aluminum oxide crucible was heated from room temperature to 1500 °C in the STA and the mass loss was monitored continuously. The onset and ignition temperatures of combustion were recorded by the analyzer for each sample. Melting of on one sample has been identified as a single endothermic peak in the DSC signal curve. The experimental measurement for each sample was repeated three times in order to ensure the reproducibility. In order to obtain knowledge of transformation chemistry of the studied fuel ash, about 10 g of each fuel sample was burned at 1000 °C for 1 hour in a muffle furnace. Ash residues from each sample were analyzed by a scanning electron microscopy (SEM) equipped with an energy dispersive X-ray spectrometry (EDX). Representative ash residue samples were stick on a carbon tape on a sample holder, which was sent into SEM for analysis. The SEM was operated in a backscattered electron mode

for illustrating distribution of detected elements in a scanned area. EDX semi-quantitative analyses were carried out especially for interesting areas to get more detailed microchemistry information.

3. Results and discussion

3.1. Ash content

Table 1 presents ash content of different parts of *P. sylvestris* tree. Compared to stem wood and branch base samples, other tree parts contain much higher contents of ash. The ash content of the stem wood was 0.2% and branch base has ash content of 0.48%. The ash content of the bark is 1.78%, which is about 10 times higher than the one of stem wood. The branch twigs have high ash content about 1.56%. With needles included, the ash content of branch tops is evidently higher than that of the branch base. In addition, applied combustion process of stem bark performed under the oxidative atmosphere resulted in higher residue ash mass produced at 550 °C compare to that of the stem wood. Similar results about the ash content of different parts of tree were reported [12]. Stem bark is well-known for its high ash content, including unburned organic materials and significant amount of mineral matters [13]. This fact can explain larger amount of combustion residue obtained from stem bark than one from other tree parts.

Table 1. Ash content of fuel samples from *P. sylvestris* different tree parts

| | Stem wood | Stem Bark | Branch base | Branch twigs |
|---------------------------|-----------|-----------|-------------|--------------|
| Ash content (% dry basis) | 0.22 | 1.78 | 0.48 | 1.56 |

3.2. Ash forming elements

Samples of stem wood, stem bark, branch base and branch top were collected from the same tree height level. The branch top refers to thinner twigs together with attached foliage and needles on top of the branch. The concentration of main ash forming elements in each fuel samples presents Table 2. As shown in Table 2, the stem wood has the highest concentration of most of the ash forming elements.

Table 2. Concentration of the major ash forming elements (mg/kg dry weight) in *P. sylvestris* fuel samples

| Sample | Al | Ca | Fe | K | Mg | Mn | Na | P | S | Si | Zn |
|-------------|------|--------|------|--------|-------|-------|-------|-------|-------|-------|------|
| Stem wood | 2372 | 294618 | 6307 | 58298 | 70199 | 39433 | 13152 | 28050 | 30555 | 18202 | 3811 |
| Stem bark | 860 | 239749 | 2425 | 72739 | 37481 | 47704 | 10608 | 37942 | 20460 | 3712 | 3057 |
| Branch base | 115 | 241309 | 2757 | 64150 | 45526 | 25575 | 7201 | 33092 | 18133 | 7210 | 3297 |
| Twigs | 779 | 125095 | 3648 | 174887 | 33486 | 19467 | 19233 | 81096 | 18052 | 14725 | 2383 |

3.3. Ash melting behavior

The characteristic TG and DSC values occurred during the thermal degradation of four *P. sylvestris* fuels are shown in Table 3. Biomass ash fusion temperature of samples varied depending on the diversity of biomass fuels. The decomposition of stem wood, stem bark, branch base and branch top under the oxidizing atmosphere is characterized by four DSC peaks, observed for all tested *P. sylvestris* fuels (Table 3). The first (P1) relatively small one at temperatures about 320-340 °C, a second large peak (P2) at 415-445 °C, a small third peak (P3) at 930-965 °C and a small endothermic peak (P4) at 1300-1315 °C. Observed first peaks (P1) are attributed to the thermal decomposition of holocellulose and less stable organic structures present in woody biomass.

The degradation of main woody component such as hemicellulose and cellulose started at the temperature range between 180 °C and 390 °C (breaking of C-C and C-O bonds of holocellulose) and the release of CO at higher temperatures is mainly due to the lignin, possibly through the release of COOH groups and the breaking of C-O groups [14]. Whereas the second peaks (P2) shown in DSC curves correspond to the combustion of char at temperature range around 415 °C and 445 °C. Some studies explain appearance of this peak by the decomposition of the remaining lignin and combustion of residual volatiles and char [15, 16]. Further, the DSC curves show exothermic peaks (P3) in the temperature range of 930-965 °C, which are primarily attributed to the transformation of silicates slag. The mass loss above 900 °C may be explained by decomposition of K_2CO_3 , which is characteristic for ashes with low silicon contents [17, 18]. In this temperature range, simultaneously, the initial melting of the ash of all biomasses occurs. The endothermic peaks (P4) at 1300 °C can be assigned to release of CO_2 from K_2CO_3 , $CaCO_3$ decomposition and different stages of ash melting.

Table 3. Characteristic TG and DSC peak values and ignition temperatures of *P. sylvestris* biomass derived at the heating flow 10 °C/min under oxidizing atmosphere (N_2/O_2)

| Sample | TG _{Peak} (°C) | | | | DSC _{Peak} (mW/mg) | | | |
|----------------------|-------------------------|-------|-------|--------|-----------------------------|--------|--------|-------|
| | P1 | P2 | P3 | P4 | P1 | P2 | P3 | P4 |
| Stem wood | 333.9 | 445.6 | 941.3 | 1309.4 | -9.635 | -27.29 | -1.162 | 0.591 |
| Stem bark | 323.4 | 415.9 | 955.5 | 1314.5 | -10.29 | -14.10 | -1.234 | 0.156 |
| Branch base | 327.0 | 436.5 | 932.6 | 1301.0 | -10.33 | -32.58 | -2.531 | 0.782 |
| Top branches (twigs) | 322.8 | 442.1 | 964.5 | - | -9.782 | -13.03 | -1.795 | - |

3.4. SEM-EDX analysis

Fig 1. shows morphology and structure of ashes from stem wood, bark, branch base and top branch produced at 1000 °C. Stem wood ash (Fig 1(a)) has fibrous structure and much smaller grain sizes compared to those of other ashes. No clear sign of sintering and agglomeration is observed from the stem wood ash displayed in the Fig 1. The ashes originated from bark, base branch and top branch aggregate and sinter into grains with large sizes and individual ash grains are rarely seen in the Fig 1 (b), (c) and (d). Semi-quantitative EDX area analyses (Table 4) were carried out on selected areas as indicated by numbers and rectangles shown in Fig 1. EDX analyses revealed that chemical compositions of the loose stem wood ash are dominated by alkali earth metals (Table 4). There are many small white grains that can be found on surface of one ash particle, which are $CaCO_3$ crystal according to EDX analyses (area 1, Table 4). It presents transformation, migration and coalescence of calcium from the fuel matrix to surfaces during combustion process. The ashes from bark and base branch show rather similar morphology, containing evidently higher content of K compared to stem wood ash. The ash of top branch displayed in Fig 1(d) is formed due to aggregating of grains with different morphologies. The long stick like grain (area 1) has a smoother surface and round outer shape, indicating melting of it at 1000 °C. Elemental concentration of P and K of this grain (area 1, Table 4) are considerably higher compared to other grains. In addition, there is part of ash grains that has loose structure and is rich in calcium (Figure 1(d), area 2 and Table 4). The top branch is a mixture of twigs and needles. Transformation behaviors of ash from each composition of the top branch are different during combustion processes, resulting ash residues with various morphology and chemical compositions as revealed by SEM-EDX analyses. Fig 2. shows elemental composition in the formed ashes, which are average values of elemental compositions detected from 10 areas scanned with size 1 × 1 mm of each sample. As shown in Fig 2, concentrations of K and P are significantly higher than those of other three ashes. Therefore, melting of this ash grain might occur due to the formation of low temperature melting K-Ca-phosphates.

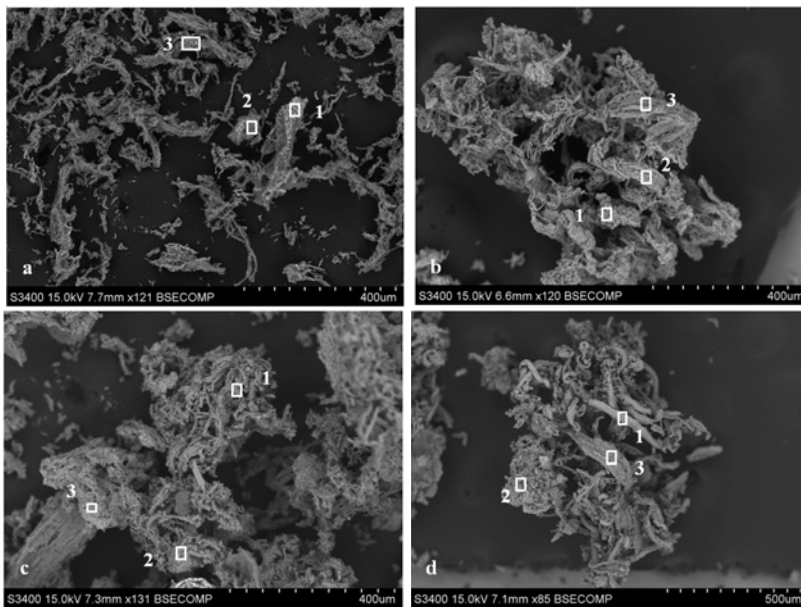


Fig 1. SEM images of ash from *P. sylvestris* (a) stem wood, (b) stem bark, (c) base branch, and (d) top brach (twigs)

Table 4. EDX analyses of areas referred to Fig 1.

| | Stem wood | | | Stem bark | | | Base branch | | | Top branch | | |
|----|-----------|------|------|-----------|------|------|-------------|------|------|------------|------|------|
| | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 |
| Ca | 70.5 | 54.1 | 64.1 | 74.3 | 65.0 | 48.2 | 89.5 | 71.0 | 63.6 | 41.1 | 59.0 | 40.8 |
| K | 0.1 | 0.1 | 0.1 | 6.2 | 5.9 | 7.4 | 3.2 | 9.1 | 12.2 | 19.2 | 5.2 | 14.2 |
| Si | 0.1 | 0.1 | 0.2 | 0.1 | 0.2 | 0.2 | 0.1 | 1.6 | 0.2 | 0.1 | 0.6 | 0.3 |
| P | 5.2 | 0.5 | 4.7 | 2.1 | 8.4 | 9.4 | 0.8 | 3.4 | 8.0 | 14.4 | 8.0 | 11.4 |
| Al | 0.5 | 0.4 | 0.7 | 3.7 | 6.5 | 9.4 | 0.8 | 2.1 | 1.4 | 0.9 | 2.3 | 6.0 |
| Mg | 13.3 | 17.6 | 13.7 | 6.0 | 6.8 | 14.9 | 1.0 | 6.1 | 5.8 | 3.2 | 10.2 | 18.0 |
| Na | 0.1 | 0.7 | 2.0 | 1.8 | 1.5 | 1.6 | 0.7 | 1.6 | 0.4 | 1.4 | 1.3 | 3.3 |
| S | 1.9 | 16.5 | 1.8 | 1.8 | 1.9 | 2.6 | 0.3 | 1.5 | 1.5 | 0.2 | 0.1 | 0.1 |
| Fe | 0.1 | 0.1 | 0.2 | 0.7 | 0.8 | 1.7 | 0.3 | 0.5 | 1.2 | 0.6 | 1.0 | 0.9 |

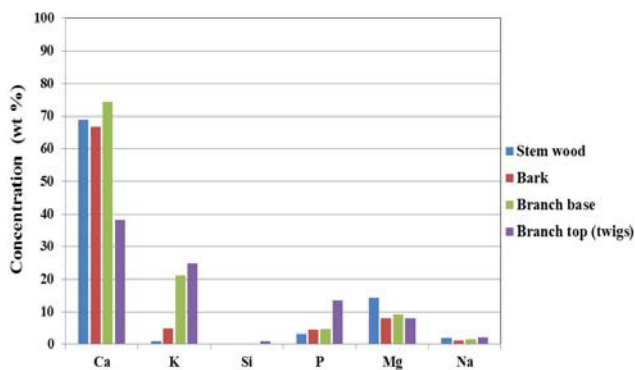


Fig 2. Average elemental composition in the formed ashes (presented on a carbon- and oxygen-free basis, 10 areas with size 1× 1 mm were scanned and analyzed)

4. Conclusions

The chemical compositions and fusion behaviors of ashes from stem wood, bark, base branch and top branch were characterized with ICP-OES, STA and SEM-EDX. Compared to other three ashes, top branch ash contains considerably high content of K and P, and is rich in Ca and Si as well. STA analyses on four kinds of fuels indicate that melting of them might start in the temperatures range from 930 °C to 960 °C. In comparison to ash originated from stem wood, SEM-EDX analyses confirm that the ashes from stem bark, base branch and top branch have high sintering tendency. Top branch ash contains substantially high concentration of K and P elements. These two typical mobile elements in plants are often found in twigs containing a large amount of young and biologically active tissues. Abundance of K and P, together with Ca, may cause formation of low temperature melting K-Ca-phosphates, partially explaining high sintering tendency of the top branch ash.

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