Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 158 (2019) 1342–1347

Energy Procedia

www.elsevier.com/locate/procedia

10th International Conference on Applied Energy (ICAE2018), 22-25 August 2018, Hong Kong, China

Effect of fuel mixing on melting behavior of spruce wood ash

Liang Wang[a]*, Øyvind Skreiberg[a], Roger Khalil[a], Hailong Li[b]

[a]SINTEF Energy Research, Sem Saelands vei 11, Trondheim, Norway
[b]Mälardalens University, Energy Technology, Högskoleplan 1, Västerås 721 23, Sweden

Abstract

The aim of this work was to investigate effects of fuel mixing on melting behavior of spruce wood ash. Spruce bark was studied as additive fuel regarding its ability to lower the melting and flowing temperature of spruce wood ash. Standard ash fusion characterization tests were carried out on ashes from mixtures of spruce wood and bark after heating at 550 °C. The ash residues after the ash fusion tests were analyzed by using scanning electron microscopy-energy dispersive X-ray spectrometry (SEM-EDX). High melting temperature and low sintering tendency of spruce wood ash was observed. It is mainly attributed to formation of calcium rich silicates with high melting temperatures. Upon mixing with 10 wt% bark, the melting temperature of the spruce wood ash considerably decreased, which flowed completely after the ash fusion test. Compared to spruce wood ash, SEM images showed that the ash from the mixture of spruce wood and bark passed a molten stage with formation of slag. SEM-EDX revealed that the concentration of silicon in the spruce wood ash increased as a result of mixing with spruce bark. It favors formation of low temperature melting potassium silicates.

Keywords: Spruce wood, bark, ash, melting, gasification

1. Introduction

Woody biomasses have huge potential as sustainable and CO_2-neutral feedstocks for production of transportation fuels and vital chemicals. Production of syngas from the wood biomass through gasification is one of the most versatile conversion ways to exploit woody biomasses [1]. In comparison to other gasification technologies, entrained flow gasification of woody biomass can produce very high purity syngas with high fuel conversion degree

* Corresponding author. Tel.: +47-48064531
E-mail address: liang.wang@sintef.no

10.1016/j.egypro.2019.01.329

and hence provide competitive efficiency [2]. During the course of fuel conversion, both organic and inorganic elements in the biomass undergo chemical transformation reactions [3]. For maintaining a stable operation of an entrained flow biomass gasification process and producing high quality syngas, formation of a steadily flowing slag (molten ash) in the reactor is required [4]. A sufficient amount of woody biomass ash with proper melting behavior is critical to ensure coverage of the internal reactor wall with ash slag that protects the wall material against attack of corrosive gases. On the other hand, surplus ash formation and melting will cause ash accumulation on the internal wall, reducing heat transfer efficiency and causing blockage of the reactor outlet [5]. Hence, evaluation and understanding of ash chemistry and melting behavior are crucial to enable and ensure an effective entrained flow gasification process. Woody biomass, especially the stem part of trees, normally have low ash content with high melting temperature. Even with continuous feeding of fuel, the amount of inlet ash is not sufficient to form a protective layer of ash slag on the internal reactor wall, it does not melt intensively and is entrained in the gas flowing freely out of the reactor. Addition of fluxing agents is one measure to enhance ash melting and generate enough ash slag during entrained flow gasification of woody biomass. The purpose of addition of a fluxing agent is mainly to increase the amount of silicon into the reactor, which can react mainly with alkali metals in the woody biomass to form low temperature melting alkali silicates [3]. However, due to release of the alkali metals (mainly potassium) from the woody biomass during a high temperature gasification process, the amount of fluxing agent feeding needed together with the fuel is difficult to estimate and desired reactions between fluxing agent and wood ash might hardly be realized. It might cause deposition and accumulation of fluxing agent particles on the internal reactor wall, which disturbs gasification processes. Fuel mixing is the other promising way to positively affect the amount and melting behavior of the wood ash formed during entrained flow gasification. Additive fuel is mixed with the main fuel, the woody biomass, and they are gasified together in the entrained flow gasifier. It is expected that ash forming elements from the additive fuel can react with those in the woody biomass, promoting ash melting and lowering viscosity of the wood ash consequently. Additionally, mixing of additive fuel can help to keep the amount of alkali metals in the reactor and maximize the formation of alkali silicates with low melting temperatures. Ash fusion testing is a straightforward way to determine melting and flow temperature of biomass ash. The test results are considered as an initial indicator of ash fusion properties. The main objectives of this work are to investigate the effect of fuel mixing on the melting behavior, and the chemistry of woody biomass ash at high temperature.

2. Materials and method

In this work, Norway spruce trees were harvested in southern Norway. After debarking, the stem wood collected was chipped and tested, as a largely available woody biomass species in Nordic countries. The bark from the same trees was tested as additive fuel to improve the melting behavior of the wood ash. Both spruce wood chips and bark were first air-dried and ground to particles with size less than 1 mm. The ground spruce wood and bark were further dried at 105 °C for 12 hours to remove the moisture content. The chemical compositions of spruce wood and bark were analyzed by using inductively coupled plasma atomic emission spectroscopy (ICP-AES). To investigate the effect of bark mixing on melting behavior of the spruce wood ash, fusion tests were performed on ash produced from spruce wood, bark and a mixture of them. First the ground spruce wood was well mixed with bark at a mass ratio of 90%/10%. After blending, the mixture of spruce wood and bark was heated at 550 °C for 12 hours. Ash residues obtained from the 550 °C heating treatment of spruce wood, bark and the mixture of the two were further subject to fusion test according to ISO standard 540:1995. Each ash sample was shaped into a 3 x 3 mm cubical specimen and sent into an ash fusion analyzer. The ash specimen was then heated up to a temperature of 1500 °C at a heating rate a 2 °C/min in an oxidizing atmosphere. Upon heating, sintering and melting of the ash specimen cause changes to the outer shape that were recorded by a high-speed camera. Through following standard procedures described in ISO 540:1995, the shape changes of one ash specimen were assessed to determine four ash fusion characteristic temperatures: initial deformation temperature (IDT), softening temperature (ST), hemisphere temperature (HT) and fluid temperature (FT). For each sample, at least five tests were performed for obtaining reproducible results, and average values of these tests are presented in Fig. 1. The ash from spruce wood, bark and the mixture of them were also sintered at 1200 °C for 1 hour in a muffle furnace. After the ash sintering test, the ash residues remaining on the alumina sample holder surface were visually evaluated regarding sintering degree, and then were examined by a scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy

(EDX). For selected samples and scan areas, EDX semi-quantitative spot/area analyses and element mapping were performed.

3. Results and discussion

Table 1 presents ash content and concentration of main ash forming elements in the spruce wood and bark. It can be seen that the ash content of spruce wood is quite low compared to that of bark. Continuous flowing ash slag often does not generate due to the limited amount of ash formed, as the spruce wood is gasified in an entrained flow gasifier. In this study, the ash content of the spruce wood increased to 0.71% when mixing with 10% (w/w) of bark, which is close to two times higher than the initial spruce wood ash content. The main elements in the spruce wood ash is Ca, K, Mg and Si. However, as indicted in Table 1, the amount of Si in the spruce wood is not sufficient to react with K to form K-silicates. Compared to the spruce wood, the bark contains a considerably higher content of K and Si, and P. Therefore, mixing with a certain amount of bark can change the composition of the spruce wood ash, which can alter ash transformation reactions and melting behavior consequently.

Table 1. Ash content and concentration of main ash forming elements in spruce wood and bark.

	Ash content (wt%, d.b.)	Concentration of main ash forming elements (mg/kg, d.b.)									
		Ca	K	Si	P	Na	Al	Mg	Fe	S	Zn
Spruce wood	0.38	1743	554	105	54	12	5	126	11	60	12
Spruce bark	2.53	7803	2011	3602	407	47	67	807	41	301	159

The characteristic fusion temperatures of the spruce wood ash are shown in Fig. 1. It can be seen that the spruce wood ash have high fusion temperature, and starts to melt at around 1380 °C, and the ash sample was completely fused at around 1480 °C. During the ash fusion test, the outer shape of the ash specimen changed slowly and the ash residues remaining after heating to 1500 °C is a black deposit with solid structure. Upon addition of the bark, the melting of the spruce wood ash commenced at 1250 °C, and it was completely melted at 1378 °C. Clear swelling and further shrinking of the ash specimen from the mixture of spruce wood and bark were observed. The ash residues are more transparent with light brown color and flow as a thin layer on the alumina sample holder. The ash sintering evaluation results agreed with the ash fusion tests results. After sintered at 1200 °C for 1 hour, the spruce wood ash kept a loose structure without observation of melting. However, the ash from the mixture of spruce wood and bark sintered together has a partial molten structure. The ash fusion test and sintering assessment results clearly show that mixing of spruce bark with spruce wood can considerably reduce the fusion temperature and promote melting of the spruce wood ash at elevated temperatures.

The sintering behavior and microchemistry of the spruce wood ash, bark ash and ash residues after sintering tests were examined by SEM-EDX and the results are shown in Figures 2-5. Fig. 2 shows a SEM image of the spruce wood ash produced at 550 °C. The spruce wood ash has porous structure. According to the EDX spot and area analyses, Ca and K are two main elements and only a small amount of Si is detected. It indicates presence of calcium rich carbonates and oxides. Fig. 3 shows that the bark ash has more dense structure, which are grains of different sizes. The EDX analyses results reveal that Ca, K and Si are the three main elements in the bark ash, with only a small amount of P. As shown in Fig. 3, part of the bark ash melted with smooth surface. The EDX analysis results showed that Si and K are the two dominating elements (K+Si > 80%) from spot 4 and area 5, implying formation and melting of K rich silicates.

Fig. 4 shows SEM-EDX analysis of the spruce wood ash after sintered at 1200 °C. The ash has rather loose structure, which is formed with aggregated fine grains and particles. According to the EDX analysis, Ca is the dominant element in the ash with detection of a small amount of Si and Al. In comparison to the ash produced at 550 °C, the K content in the ash sintered at 1200 °C is considerably reduced. It is mainly due to release of K during the sintering test. Fig. 5 displays SEM-EDX analysis of the spruce wood-bark mixture after the 1200 °C sintering test. It is clearly visible that part of the ash is already melted, exhibiting a smooth and continuous surface (spot 1 and area 2, Fig. 5). The K and Si contents detected in this melted ash fraction are evidently higher than that of the spruce wood ash (spot/area 1-6, Fig. 4). The rest of the ash shown in Fig. 5 has a clear sintered structure and some grains with round shapes can be seen (spot 3, Fig. 5). Again, the Si content detected from the sintered ash (spot 3 and area 4, Fig. 5) is considerably high. It indicates that, because of mixing with bark, more K and Si were introduced in the spruce wood ash. This altered ash transformation reactions and promoted formation of low temperature melting K-silicates. This process was observed through the increases of ash melts and sintering degree as well.

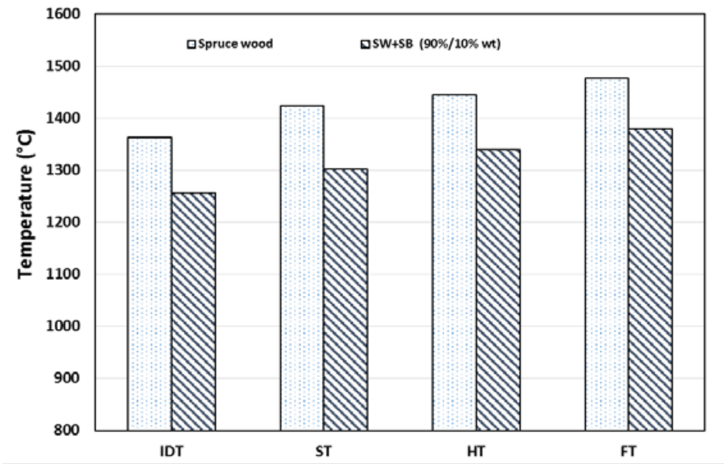

Fig. 1. Melting temperature of spruce wood ash with and without mixing with bark.

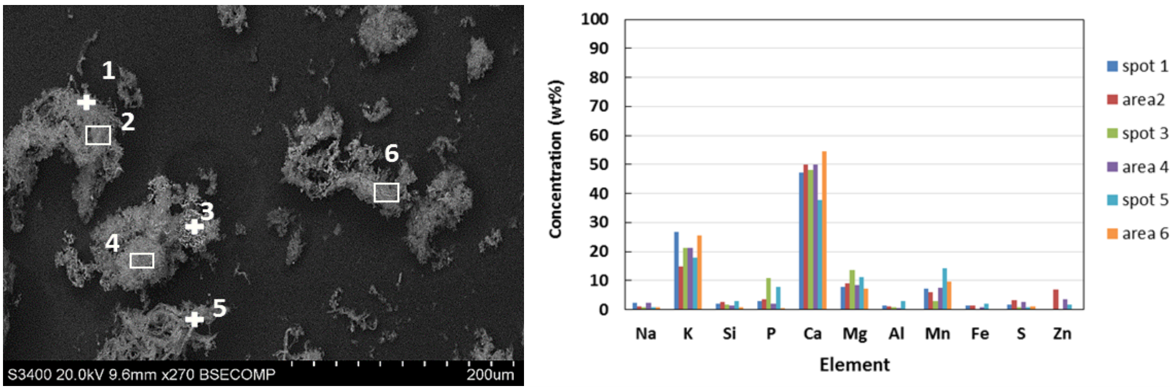

Fig. 2. SEM-EDX analysis of spruce wood ash produced at 550 °C.

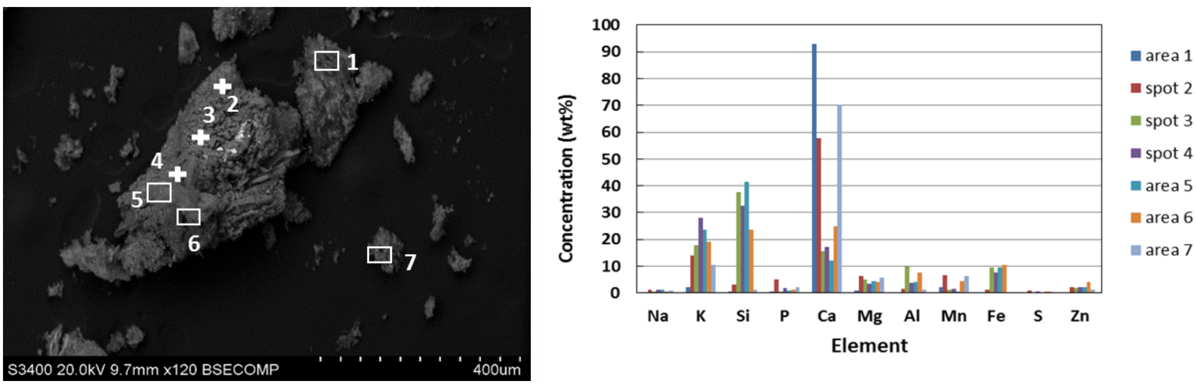

Fig. 3. SEM-EDX analysis of spruce bark ash produced at 550 °C.

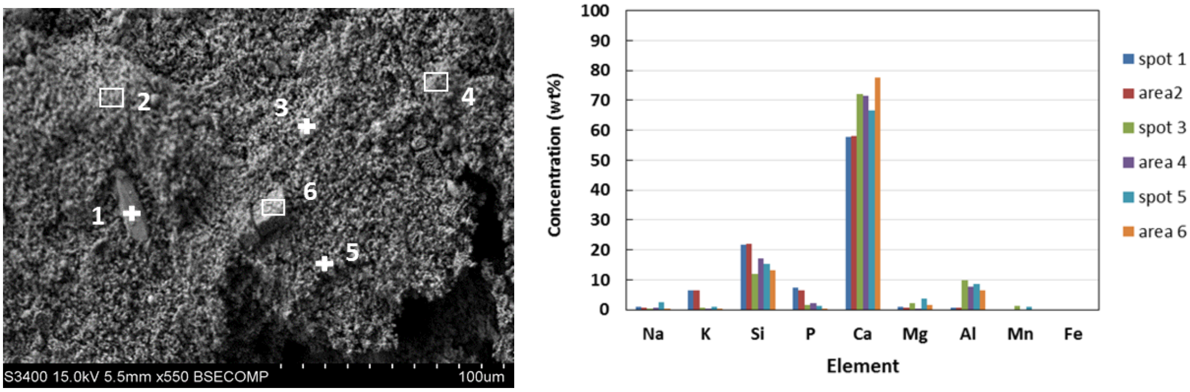

Fig. 4. SEM-EDX analysis of spruce wood ash residues after ash sintering test at 1200 °C.

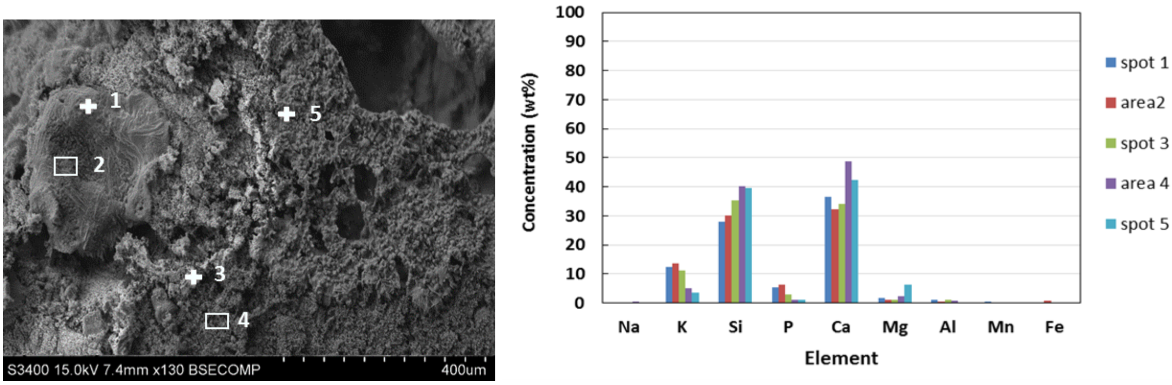

Fig. 5. SEM-EDX analysis of spruce wood-bark ash residues after ash sintering test at 1200 °C.

4. Conclusions

Spruce wood has a low ash content and a high concentration of Ca in the ash, and has high melting temperature and poor sintering behaviors. SEM-EDX analyses results indicate that the high melting temperature of spruce wood ash is mainly attributed to formation of high temperature melting calcium carbonates and oxides. Mixing spruce bark with the spruce wood considerably reduce the melting temperature of the spruce wood ash, according to ash fusion and sintering test results. SEM-EDX analyses indicated that mixing with bark introduced K and Si to the spruce wood ash. It leads to more reactions between K and Si in the fuel mixture and formation of low temperature melting K-silicates. This explains the more severe ash melting and sintering of spruce wood upon mixing with bark. The results obtained in this work suggests that fuel mixing can be an efficient way to alter the chemical composition and further transaction reactions of the spruce wood ash. As a result of fuel mixing, the melting temperature and severity of the spruce wood ash can be improved, ensuring a smooth and efficient spruce wood entrained flow gasification process.

Acknowledgements

This work was supported the Research Council of Norway and a number of industrial partners through the project Gasification and FT-Synthesis of Lignocellulosic Feedstocks (GAFT).

5. References

[1] Wang L, Várhegyi G, Skreiberg Ø. CO_2 Gasification of Torrefied Wood: A Kinetic Study. Energy & Fuels 2014;28:7582–7590.
[2] Moilanen A, Öhman M, Backman R, Wiinikka H, Wang L, Lehtinen J, Kurkela M, Muhola M, Tuomi S, Carlsson P, Guell BG, Sandquist J, Lundgren J, Andersson J, Umeki K, Ma C, Kurkela E. Biomass gasification fundamentals to support the development of BTL in forest industry. Final scientific report of Nordsyngas project. 2015.
[3] Wang L, Hustad J.E., Grønli M. Sintering Characteristics and Mineral Transformation Behaviors of Corn Cob Ashes. Energy & Fuels. 2012;26(9):5905-16.
[4] Coda B, Cieplik M, de Wild P, Kiel J. Slagging behavior of wood ash under entrained flow gasification conditions. Energy & Fuels 2007;21:3644–3652.
[5] Ma C, Weiland F, Hedman H, Boström D, Backman R, Öhman M. Characterization of reactor ash deposits from pilot scale pressurized entrained flow gasification of woody biomass. Energy & Fuels 2013;27:6801–6814.