



The 8th International Conference on Applied Energy – ICAE2016

Release of potassium during devolatilization of spruce bark

Liang Wang^{*a}, Antero Moilanen^b, Jere Lehtinen^c, Jukka Konttinen^b, Berta Guell Matas^a

^{*a} SINTEF Energy Research, Sem Sælands vei 11, Trondheim, Norway

^bDepartment of Chemistry and Bioengineering, Tampere University of Technology, Korkeakoulunkatu 1, Tampere, Finland

^cAndritz AG, Stattegger Strasse 18, 8045 Graz, Austria

Abstract

The spruce bark with different particle sizes were devolatilized under various final temperatures and heating rates. The char yield and potassium release from the spruce bark at studied conditions were quantified. Lower char yields realized from the smaller fuel particles at high temperature and heating rate. It is mainly attributed to shorter residence time of volatiles in the fuel/char particles and less intensive secondary reaction of volatiles consequently. The devolatilization temperature has the most significant effects on alkali release from the studied spruce bark. At 600 °C, less than 5% of alkali released from the both small and large particles regardless of heating rate. However, at 850 °C, release of potassium from the small spruce bark particles sharply increased from 2.63 % and 4.71% to 12.87% and 17.89%, as they were heated under heating rate of 50 K/min and 500 K/min, respectively. Large fraction of alkali released from studied fuel particles as they were devolatilized under a high heating rate. Additionally, more potassium release from small particles ($125 < d < 180 \mu\text{m}$) than the larger ones ($500 < d < 600 \mu\text{m}$) and this tendency increased with devolatilization temperature. In brief, intensive devolatilization conditions may limit secondary reactions of potassium containing compounds in the volatiles and thereby formation of more stable phases. The results obtained in the present work are of importance for understanding of potassium release during thermal conversion of spruce bark and proposing measures for mitigating potassium related operational problems.

© 2017 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Peer-review under responsibility of the scientific committee of the 8th International Conference on Applied Energy.

Key words: Spruce bark, devolatilization, char, potassium; ICP-OES; SEM-EDX

1. Introduction

Woody biomass fuels including sawdust and chips are conventionally used for energy and heat production. These woody biomass fuels are traditionally mainly from stem part of the tree. Recently, nonconventional woody biomass such as bark and forest residues are the entering market for bioenergy production [1]. Compared to stem wood, the bark and forest residue normally have high ash content and concentration of certain ash forming elements like alkali metals. Transformation and reaction of alkali metals with other ash forming elements such as S, Si and P may cause ash related problems such as slagging, fouling and sintering during bioenergy production from the bark and forest residue [2]. The ash

related problems considerably reduce efficiency and profitability of power plants using bark and forest residue as fuel. During thermal conversion of biomass fuel, devolatilization is the first step to cause volatilization of organic and inorganic portion of the fuel whereas carbon-rich solid mass retains as the char [3]. The volatiles and solid char/ash generated during the devolatilization stage undergo further reactions. It has been reported that major fraction of the alkali metals volatilize during devolatilization of biomass particles and only minor fraction will further release from char/ash residues. The devolatilization reaction conditions have considerable effects on release and transformation of inorganic species and amount and property of the char. Previous studies showed that release of alkali metal K and Na strongly influenced by devolatilization temperature. The total alkali release increased at a higher devolatilization temperature [4,5]. In addition, the release of alkali metals from biomass particles heavily depends on concentration of ash forming elements in the fuel and ratio between these elements [6]. In general, the Cl is a main facilitator to cause alkali release as alkali chloride during thermal conversion of biomass fuel. Alkali metals have a high potential to release from the biomass fuels such as agricultural residues that are rich in Cl. However, because of relatively low content of Cl and K in the woody biomass, the alkali release from the woody biomass fuels should be dominated by different mechanisms. Previous studies focused on release of alkali metals during combustion of agricultural residues and conventional woody biomass like chip and sawdust [4-8]. Very few studies quantitatively investigated fate of alkali metals in the bark fuel during devolatilization at high heating rate and temperature. In this work, the release and transformation of K during devolatilization on spruce bark were quantitatively studied at different temperature and heating rate. The aim of this work is to reveal devolatilization parameters and fuel particles on the quantity of K released to the gas phase.

2. Experimental

The biomass fuel studied in present work is spruce bark pellet. The spruce bark pellets were milled to particle size smaller than 1 mm and were then sieved and the particles with size in the range of 125-180 μm and 500 - 600 μm were obtained for further study. A novel thermogravimetric analyzer (TGA) (TA Q5000, TA Instrument) was used for devolatilization of the fuel particles under well controlled conditions. Before each experiment, approximate 10 mg sample was loaded on a sample pan. The sample particles were tried to be evenly spread on bottom of the sample pan, in order to avoid limitation of heat and mass transfer. After loaded into the TGA furnace, the sample was purged for half hour with pure N (purity>99.9999%) for weight stabilizing and flushing away remained air in the furnace. Then, the sample was heated up from 25 $^{\circ}\text{C}$ to a prescribed temperature 600, 850 and 1000 $^{\circ}\text{C}$, respectively. Each sample was devolatilized under heating rate of 50, 200 and 500 K/min to the desired final temperature without further holding. The weight loss of one sample was continuously monitored by the TGA and char yield was calculated by dividing the final weight of char with the initial sample weight. After each devolatilization experiment, the char residues left were collected. For one sample, at least devolatilization under one condition were performed for checking reproducibility of experiment and collecting rather large amount char residues for further analysis. Chemical composition of the char residues produced from one sample under same conditions were 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 sample analyses were done for raw fuel particles with different particle sizes. Fraction of potassium release during devolatilization of one sample were calculated based on the concentrations of element in the raw sample and char residue and the weight raw sample and its char after devolatilization experiment. The microstructure and microchemistry of selected samples were examined by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX).

3. Experimental

3.1. Fuel properties

Table 1 presents chemical composition of spruce bark with different particle sizes. It can be seen K, Ca and Si are main ash forming elements in the case of the two studied samples. In addition, concentration of main inorganic elements in small particles are generally higher than those of large ones. It has been reported presence of certain ash forming elements may have considerable effects on volatility of potassium that during thermal conversion of biomass fuels. Cl and S are two key elements that facilitate release of potassium through formation and volatilization of potassium chloride and sulfate at elevated temperatures. On the other hand, as the K release from the fuel and char particles, potassium and potassium oxides might incorporate into silicate networks in the fuel to form potassium silicates, causing volatility reduction of potassium [5-7]. As the potassium silicates encounter the alkali earth metal Ca and Mg, reactions will take place with formation of Ca/Mg silicates and K can be driven out consequently [9]. The molar ratios of key elements are listed in the Table 1. For large spruce bark particles, the (Ca+Mg)/Si molar ratio is higher than that of the small particles. It indicates that more Ca and Mg are available in the large particles to associate with Si, which will limit amounts of K incorporate in the silicate matrix and enhance release of K.

Table 1. Chemical compositions of spruce bark (mg/kg, dry fuel) and molar ratio of key elements

Sample	Al	Ca	Fe	K	Mg	Na	P	S	Si	Si/K	S/K	(Ca+Mg)/Si
125 < d < 180 μm	373	8191	477	2720	718	254	477	386	3710	0.20	0.17	1.77
500 < d < 600 μm	321	8067	324	2229	659	227	422	332	3380	0.21	0.19	1.89

3.2. Char yields

Table 2 lists char yields of the studied small and large spruce bark particles as function of devolatilization of temperature and heating rate. The results showed that char yields of the spruce bark have great dependences on particle size and devolatilization conditions. The char yields of both small and large particles decreased with increasing devolatilization temperature due to continuous release of volatiles and conversion of solid residues at a high temperature. In addition, high char yields were obtained at low heating rate for two samples devolatilized under elevated temperatures. Degradation of fuel particles and release of volatiles tend to slow at low heating rate. Consequently, residence time of volatiles in the particles might be longer. It increases possibility of the volatiles or tarry vapors to crack and re-polymerize within particles to form secondary carbon, enhancing char yields as compared to higher heating rates [9]. In addition, condensation of tarry vapors on surfaces of solid char can lower reactivity of the char and hinder further conversion of the char. For all studied devolatilization conditions, higher char yields were obtained from the large particles. This can be due to several reasons. For the large particles, the heat and mass transfer resistance is much higher than that in smaller ones.

Table 2. Char yield (wt %) of studied samples at different devolatilization temperatures and heating rates

Sample	125 < d < 180 μm			500 < d < 600 μm		
	50 K/min	200 K/min	500 K/min	50 K/min	200 K/min	500 K/min
600	35.9	35.7	32.3	36.1	36.0	34.1
850	30.2	29.9	26.8	31.6	30.7	28.2
1000	28.9	28.8	24.6	29.1	28.9	26.8

It causes extension of residence time of the tarry vapors in the large particles, promoting contacting and recombination of tarry vapors with the solid char surfaces [9]. As a result of this, conversion of tarry vapors back to solid carbon can be more intensive for large particles and reduces the weight loss of the char. Additionally, the temperature gradients from the surface to the center of the large particles can be more pronounced due to large heat transfer resistance [3].

3.3. Release of potassium

Quantitative release of potassium was obtained for spruce bark under different devolatilization conditions. The experimental results showed that the release of potassium was strongly dependent on the devolatilization temperature and heating rate. Figure 1 shows that only minor fraction of potassium released from both small (2.6-4.7%) and large particles (1.7-3.0%) as samples were devolatilized at 600 °C. At 850 °C, the potassium release significantly increased up to 12.9-17.9% and 8.3-16.2% for small and large particles, respectively. There was further increase of potassium release as the studied fuel particles devolatilized at 1000 °C. It was reported that potassium release during rapid pyrolysis of birch wood includes two parts [4]. At temperature lower than 600 °C, the potassium release occurred solely due to pyrolysis of the fuel particles, which vaporizes together with volatiles to gases. As temperature higher than 800 °C, the potassium is mainly emitted from char and/or ash residues remained after pyrolysis of fuel particles. Compared to the potassium release from the char and/or ash, the fraction of the potassium emitted during wood pyrolysis reactions in the temperature lower than 600 °C is significant smaller [4]. It explains the much less potassium release from studied spruce bark particles as shown in Figure 1. Figure 1 also shows that the release of potassium from studied spruce bark was heavily influenced by heating rate. There is significant difference in release of potassium between fast heating and slow heating experiments carried under 850 °C and 1000 °C. As the heating rate increases, a larger fraction of spruce bark becomes volatilized and thereby release more pyrolysis potassium. In addition, at a high heating rate, more volatiles including tar and light hydrocarbons will produce and lead to forming of free radicals (mainly H radicals) [3]. The interactions of free radicals and char will cause break of bonds between alkali and alkali earth metals and char matrix, causing release of alkali and alkali earth containing species [4]. Considering more intensive devolatilization of spruce bark at a high heating rate, production of free radicals and interactions of them with char matrix will be to a larger extent [10]. As a result of this, release of potassium from the studied spruce bark is more substantially as they are devolatilized at high heating rate and higher temperatures. As shown in Figure 1, more potassium released from small particles under studied devolatilization conditions in comparison to large particles. This trend increases with increasing temperature.

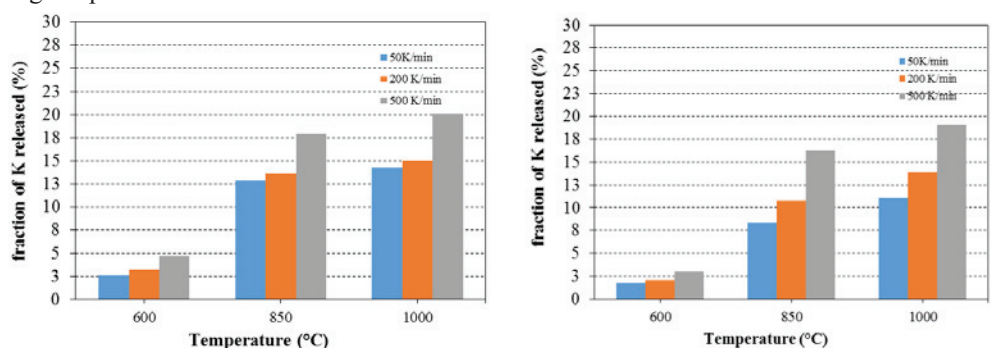


Fig 1. Release of K during devolatilization as function of temperature and heating rate for spruce bark particles with size (a) $125 < d < 180 \mu\text{m}$ and (b) $500 < d < 600 \mu\text{m}$

It is partially related to faster evolution and evaporation of volatiles and inorganic species in the small particles, due to less mass transfer resistance by the char matrix. It means shorter residence time of the volatiles and inorganic species in the char matrix and less secondary reactions on their way out of the particle.

3.4. SEM-EDX analysis

Figure 2 shows SEM images of the char residues produced from devolatilization of spruce bark particles ($500 \mu\text{m} < d < 600 \mu\text{m}$) from 25°C at a heating rate of 50 K/min (Figure 1 (a) and (b)) and 500 K/min ((Figure 1 (a) and (b)), respectively. Semi-quantitative EDX analyses (Table 3) were carried out on selected spots and areas as indicated by numbers and rectangles shown in Fig 2 (b) and (c). Many small white grains (spot 1, Table 4) can be found on surface of one char particle, which have cubic shape and size of $5\text{-}10 \mu\text{m}$. EDX analysis revealed that main composition of these grains is calcium. Therefore, these grains are formed due to transformation, migration and coalescence of calcium from the fuel matrix to surfaces during devolatilization process [11]. Minor amount of K was detected from one grain (spot 2, Table 3) and Ca is still detected as major element. This grain represents formation of potassium carbonate. In Figure 2 (c) and (d), cluster of the calcium rich white grains can not be found, indicating more intensive release calcium oxides at 500 K/min devolatilization experiments. During fast pyrolysis of biomass particles, release of carboxyl groups like char-COOM takes place, where M can be Ca and Mg. At a higher rate, more intensive decomposition of char-COOM occurs, leading to forming of solid char and release of CO_2 and M in the gas phases [3]. It can partially explain decrease of the calcium rich grains on surfaces of spruce bark particles devolatilized at 500 K/min . The EDX analyses revealed that chemical compositions spruce char particles are dominated by Ca, Mg, K and Na (Table 3).

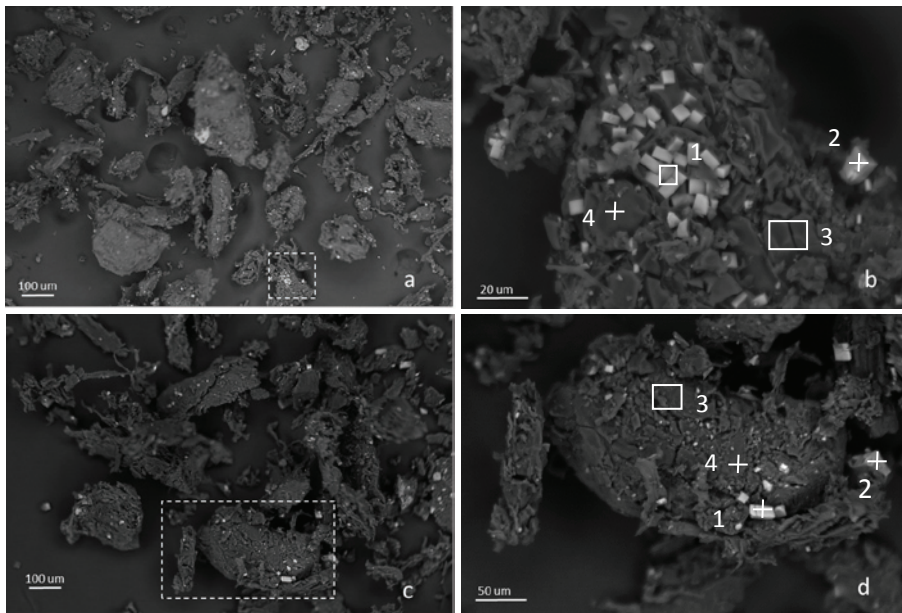


Fig 2. SEM images of char residues after spruce bark particles ($500 \mu\text{m} < d < 600 \mu\text{m}$) devolatilized from 25°C at a heating rate of: (a) and (b) 50 K/min , (c) and (d) 500 K/min

Table 3. EDX analyses of areas referred to Fig 1.

	Spruce bark				Spruce bark			
	1	2	3	4	1	2	3	4
Ca	97.00	96.95	53.82	51.77	96.81	0.21	61.94	63.94
K	0.01	0.02	11.53	10.94	0.01	0.59	6.67	5.90
Si	0.45	0.43	2.36	3.73	0.43	96.87	3.32	3.25
P	0.24	0.42	3.12	2.54	0.32	0.01	2.27	2.17
Al	0.60	0.42	5.72	5.10	0.42	1.25	6.20	5.96
Mg	0.82	0.68	13.50	17.97	0.77	0.68	14.98	14.22
Na	0.56	0.72	8.31	7.02	0.92	0.38	4.02	4.23
S	0.21	0.27	1.18	0.56	0.27	0.01	0.43	0.31

4. Conclusions

The potassium released during devolatilization of spruce bark was studied. Particle size, devolatilization temperature and heating rate varied and release of potassium from studied spruce bark were quantified with these parameters. Potassium release during devolatilization of spruce bark increases with significantly with temperature. More potassium released from spruce bark at a high heating rate and this trend become stronger as the temperature increases. Compared to large spruce bark particles, larger fraction of potassium released from the small ones. This is mainly due to faster evolution and transport of potassium out of fuel and char particles. It limits reactions between potassium and char matrix to form more stable potassium containing compounds.

Acknowledgements

The study was financed by Nordic Energy, the Research Top-level Research Initiative for supporting this work through the Nordsyngas project. The authors also acknowledge the financial support by the Bioenergy Innovation Centre (CenBio), which is funded by the Research Council of Norway.

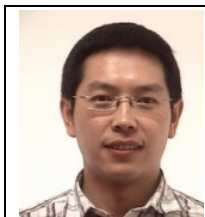
References

- [1] Dibdiakova J, Wang L, Li H. Characterization of Ashes from Pinus Sylvestris forest Biomass. *Energy Procedia*; 2015.
- [2] Wang L, Dibdiakova J. Characterization of ashes from different wood parts of norway spruce tree. *Chemical Engineering Transactions* 2014; 37-42.
- [3] Li C-Z. Importance of volatile-char interactions during the pyrolysis and gasification of low-rank fuels – A review. *Fuel*. 2013;**112**:609-23.
- [4] Davidsson KO, Stojkova BJ, Pettersson JBC. Alkali emission from birchwood particles during rapid pyrolysis. *Energy and Fuels*. 2002;**16**:1033-9.
- [5] Wei X, Schnell U, Hein KRG. Behaviour of gaseous chlorine and alkali metals during biomass thermal utilisation. *Fuel* 2005;**84**:841–48.
- [6]. Van Lith SC, Alonso-Ramírez V, Jensen PA, Frandsen FJ, Glarborg P. Release to the Gas Phase of Inorganic Elements during Wood Combustion. Part 1: Development and Evaluation of Quantification Methods. *Energy & Fuels*. 2006;**20**:964-78.
- [7] Knudsen JN, Jensen PA, Dam-Johansen K. Transformation and Release to the Gas Phase of Cl, K, and S during Combustion of Annual Biomass. *Energy & Fuels*. 2004;**18**:1385-99.
- [8] Wang L, Skjevraak G, Hustad JE, Skreiberg O. Investigation of biomass ash sintering characteristics and the effect of additives. *Energy and Fuels*. 2014;**28**(1):208-18.

[9] Wang L, Skreiberg O, Gronli M, Specht GP, Antal MJ. Is elevated pressure required to achieve a high fixed-carbon yield of charcoal from biomass? Part 2: The importance of particle size. *Energy and Fuels*. 2013;27:2146-56.

[10] Keown, D. M., Hayashi, J.-i., Li, C.-Z. Effects of volatile-char interactions on the volatilisation of alkali and alkaline earth metallic species during the pyrolysis of biomass. *Fuel* 2008, **87**: 1187-1194.

[11] Perander M, DeMartini N, Brink A, Kramb J, Karlström O, Hemming J, Moilanen, A., Kontinen, J.b, Hupa, M. Catalytic effect of Ca and K on CO₂ gasification of spruce wood char. *Fuel*. 2015;150:464-72.



Biography

Liang Wang is a research scientist at SINTEF Energy Research in Trondheim Norway. His research focuses on characterization of biomass and wastes using combined analytical instruments and techniques, advanced biomass carbonization technology, experimental and kinetic study of torrefaction, pyrolysis, gasification and combustion, of biomass and charcoal, ash chemistry during biomass and waste thermal conversion.