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An SEM-EDX Study of Forest Residue Chars produced at High Temperatures and High Heating Rate

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Abstract

This work investigated morphology, structure and chemical transformation of forest residue chars devolatilized in a drop tube reactor at high heating rates and high temperature conditions. Produced forest residue chars were analyzed by SEM to examine morphology and structure variations. Compared to parent forest residues, char residues obtained from devolatilization experiments have significant smaller particle sizes. At 1200 °C, the char particle underwent plastic deformation, developing a structure with smooth and compact surfaces. EDX analyses of the char surfaces revealed migration and coalescence of inorganic elements (mainly Ca, K and Si) during devolatilization processes. It was found that vaporization of calcium from char particles is more intensive at 1200 °C compared to that of 800 °C char. Meanwhile, part of calcium retained the char residues and incorporated into silicates structures.

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Keywords: Biomass, devolatilization, heating heating, char, SEM-EDX

1. Introduction

Forest residues are gaining continuous interests and entering market for renewable energy production. Large amounts of forest residues are produced annually during harvest of forest and outtake of timber. With further improvement of collecting and bundling technologies, more forest residues will be available for energy production [1]. Gasification is a promising and efficient way for converting forest residues into energy and different valuable products [2]. Gasification can be conceptually divided into two steps where devolatilization is the first step that biomass fuel particles experience. Volatiles and solid char are two main products from the fuel particles devolatilization stage. Properties of char residues heavily depend on

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devolatilization conditions, including heating rate, residence time, final temperature, gas atmospheres, etc [3]. Consequently, characteristics of char residues such as morphology, micro- structure, size variations, and concentrations of inorganic elements have critical impacts on char gasification reactivity and energy conversion efficiency of the overall gasification process. Studies of chars derived from devolatilization processes under different operation conditions have been reported [2, 3]. However, few data about properties of chars from forest residues, especially for those obtained from high temperature and high heating rate, are available in the open literature.

The aim of the present work is to characterize forest residues chars produced in a drop tube reactor under high temperature and high heating rate conditions. Transformation of char morphology, structure and inorganic elements under different conversion temperatures were evaluated.

2. Experiment Section

2.1. Fuel

Forest residues (FR), mainly tops and branches from spruce forest in Southern Norway, were collected and studied in the present work. In order to homogenize the studied fuel, raw forest residues were first dried, milled and pelletized, and the pellets were then ground and sieved. The fuel particles with size in the range of 212 to 300 μm were used for further devolatilization experiments. Fuel characteristics and chemical compositions are listed in Table 1 and Table 2.

Fig 1 shows a schematic sketch of the electrically heated drop tube reactor (DTR) used for realizing fuel devolatilization experiments. The DTR features a 1.5 m long vertical reactor section with a diameter of 5.08 cm and a 1.0 m long horizontal gas preheater section. As illustrated in Fig 1, the fuel particles were carried by 4 standard liters per minute (slpm) room temperature N_2 gas and fed into the reactor from the top with a mass flow rate of approximate 50 g/h. The main bulk gas stream of 182 slpm was heated in the preheating sections and entered the reactor, generating the desired experiment temperature in the reactor. Fuel particles were injected into the reactive section of the reactor and devolatilized at 800 °C and 1200 °C. Once fed into the reactor, the fuel particles were heated up to a given temperature with a very high heating rate, in the range of 10^4 °C/s – 10^5 °C/s. The residence time of the fuel particles in the reactor was in the range of 150-200 ms. The char residues produced during the devolatilization process were extracted by a water-cooled sampling probe and finally collected by a cyclone. Char residues were examined by a scanning electron microscopy (SEM) equipped with an energy-dispersive X-ray spectroscopy (EDX). SEM images were taken from representative samples. Semi-quantitative EDX area analyses were performed for selected areas to obtain detailed micro-chemistry information.

Table 1. Fuel properties

	Proximate analysis (wt %)			Elemental analysis (wt %)				
Forest residues	Volatile content	Ash content	Fixed carbon	C	H	N	S	O
	76.5 (dry ash free basis)	2.2	21.5	52.1	6.1	0.5	< 0.02	41.3 (by difference)

Table 2. Chemical compositions of studied forest residues

	Amount of ash-forming matter (wt %)									
Forest residues	Si	Ca	K	Na	Mg	Al	Fe	Mn	P	Ba
	12.82	47.86	20.51	1.71	5.13	1.71	2.56	5.13	2.56	12.82

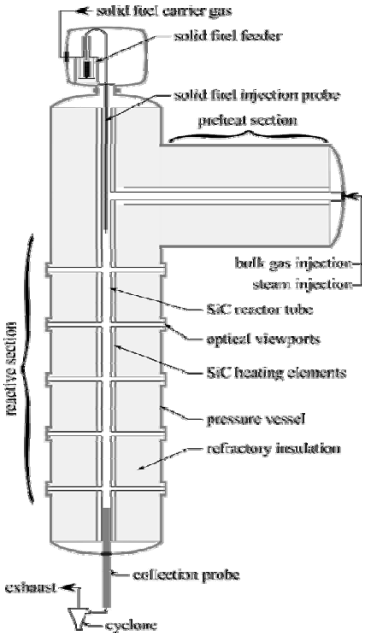

Fig 1. Schematic sketch of the drop tube reactor

3. Results and Discussions

3.1. Morphology of raw forest residues and char obtained from devolatilization experiments

SEM images of virgin forest residues particles and char residues obtained at 800 °C and 1200°C are shown in Fig 2. Fig 2(a) shows flaky parent forest residue particles with a fibrous structure and oblong shape. Compared to the parent fuel, dimensions of 800 °C char particles have been evidently reduced as shown in Fig 2(b). There are several large particles that maintain the original cell and texture structure but with deeper openings and/or slits that are associated with intensive release of volatiles. Fig 2(c) shows forest residue char obtained at 1200 °C, which mainly contains particles with sizes smaller than 30 μm. This is partially attributed to intensive conversion and fragmentation fuel particles at 1200 °C.

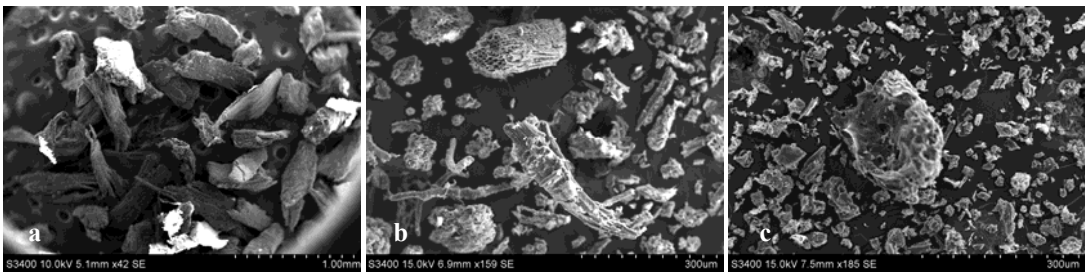

Fig 2. SEM image of (a) raw forest residues; (b) char collected at 800 °C; (c) char collected at 1200 °C

The 1200 °C char particles have significantly different structure and morphology than those of parent fuel and 800 °C char. The 1200 °C char particles have a more compact structure and smooth surfaces, showing a sign of melting. In the middle of Fig 2(c), a large particle with more spherical shape and smooth surface can be seen. The lack of cell structure and voids of this particle can be attributed to melting of certain fuel contained compounds. It causes break of fibrous cell structure, closing of the pores and formation of plastic surfaces. At severe devolatilization conditions (i.e., high heating rate, high temperature and high pressure), plastic transformation of char particles might occur due to softening of the solid matrix, melting of the cell structure, leading to clog of pores [2, 3]. The gases and volatiles from decomposition of carbonaceous materials generate overpressure in the particle, causing swelling of the particle [4].

3.2. SEM-EDX analysis

Fig 3 and Fig 4 present SEM images of chars obtained at 800 °C and 1200 °C at different magnifications, with indication of selected areas for EDX analysis. For both chars EDX area analyses were also carried out for selected areas as indicated by white rectangles and numbers showing in Fig 3 and Fig 4. Summary of the EDX area analyses results is presented in Fig 5. In general, Ca, K, and Si are three dominant elements detected in the two kinds of char, which agree well with the bulk chemical composition analysis of the parent fuel. However, as shown in Fig 5, evident differences in concentration of individual element were observed from grains with different morphologies.

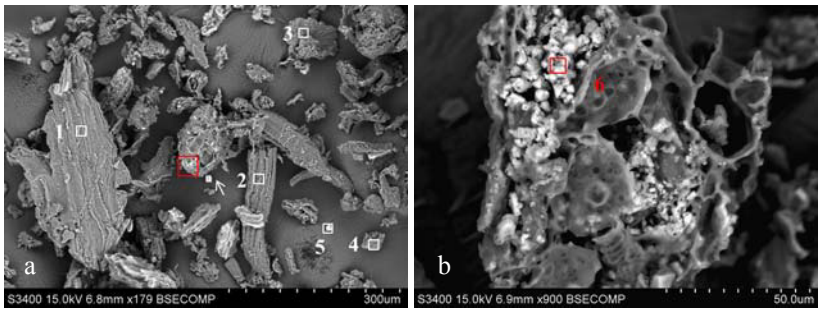

Fig 3. SEM-EDX analysis of 800 °C char (a) general view ; (b) details of migration and coalescence of calcium

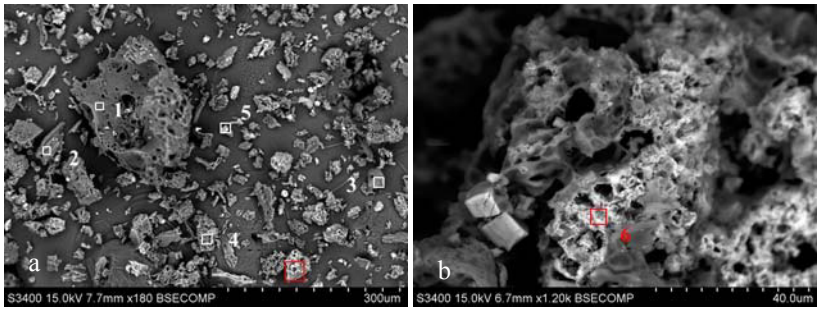

Fig 4. SEM-EDX analysis of 1200 °C char (a) general view ; (b) details of coalescence and vaporization of calcium

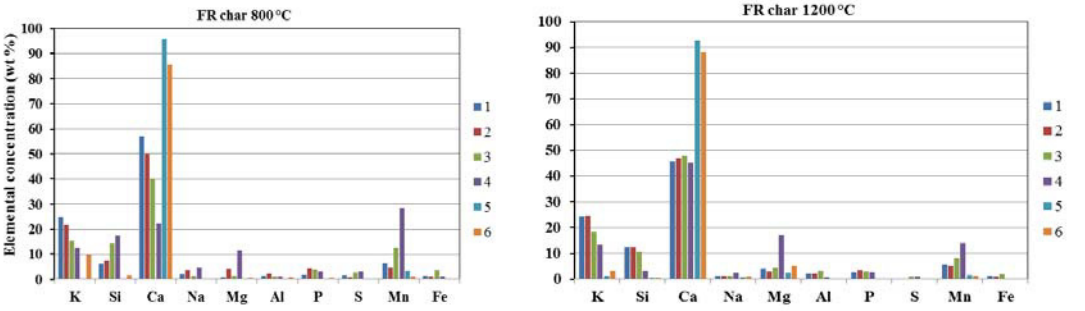

Fig 5. Summary of EDX analysis on (a) forest residue char 800 °C; (b) forest residue char 1200 °C

Fig 3 shows that 800 °C FR char contains mainly two types of particle with distinctive shapes and sizes, including large oblong particles with fibrous texture and smaller ones with more spherical shape and cavities. From the surface of large oblong particles, high contents of Ca and K are detected, which are due to migration of these two elements from the fuel matrix to the surface. Compared to those detected in the large oblong particles, evident increase of contents of Si and decrease of Ca and K are observed when characterizing the smaller particles with spherical shapes and cavities. Two white cubic grains can be clearly seen in the Fig 3(a), as indicated by an arrow and rectangle 5. EDX analysis revealed that these grains contain mainly Ca with certain amount of carbon and oxygen, implying presence of calcium carbonate or calcium oxide crystal. Fig 3(b) shows a zoom-in view of the area selected (as indicated by the red rectangle) in Fig 3(a). Large amounts of white grains can be seen from the surface, with a Ca-dominant composition, representing migration and coalescence of Ca rich species, mainly oxide and/or carbonate, from the fuel matrix to surface during the devolatilization.

Fig 4 shows SEM images for the 1200 °C FR char took at different magnifications. Partial melting of char particles is evident displayed in Fig 4(a) as indicated by rectangles 1 and 2, from which significant high concentrations of K, Ca and Si were detected. During the conversion process, K in the biomass particles will vaporize in the form of oxide, salts and hydro carbonates. Upon encountering silicon in the fuel matrix, potassium silicates might be formed, and some of them have melting temperature as low as 600 °C [5]. The widely dispersed alkali earth metals like Ca and Mg in the fuel matrix mostly present as oxides and incline to react with molten K-silicates. Formation of K-Ca-silicates in the biomass chars at temperatures of 1000 °C to 1400 °C has been reported [5, 6]. Fig 4(b) shows again the presence of calcium rich grains on the char surface. However, in contrast to the 800 °C char, the amount of Ca rich grains is reduced, as observed by the more visible cavities in different sizes. This indicates more intensive vaporization of Ca at the higher conversion temperature (1200 °C). Studies addressing the effects of heating rate and temperature on dispersion of Ca in carbonaceous species have reported that more intensive calcium dispersion occurs at higher heating rates [6]. Increase of pyrolysis temperature will promote vaporization of calcium containing species, mainly $CaCO_3$ and CaO, leaving cavities on carbonaceous surfaces [6].

4. Conclusions

Forest residue chars produced under different devolatilization conditions were characterized by SEM-EDX in terms of morphology and inorganic chemistry. Compared to the parent fuel, sizes of char particles produced from the high heating rate devolatilization process were significantly reduced. It is attributed to consumption and fragmentation of fuel particles at more severe conversion conditions. The

forest residues char produced at 800 °C partially remain fibrous structure and show a low ability to melt. In contrast, melting of the char particles occurred mainly when the devolatilization was conducted at 1200 °C, leading to forming of swelling chars with smooth surface and round voids. EDX analyses revealed that Ca, K and Si were the most dominant elements on the surface of char particles, due to vaporization and migration of these elements during conversion of the fuel particles. Detection of these three elements, i.e., Ca, K and Si, indicates formation of K-Ca-silicates on the char surfaces, probably as a result of the incorporation of CaO into the K-silicates. Besides, evident formation and coalescence of calcium rich species on char surfaces was observed. The calcium containing species vaporized more intensively at 1200 °C and contributed to the large porosity of the char particles.

5. Copyright

Acknowledgements

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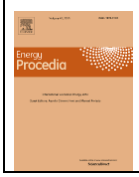

Biography

The corresponding author of this paper Dr. Wang Liang is now working as a research scientist in Thermal Energy Department in SINTEF Energy Research Norway. Main research interests of Dr. Wang are thermal conversion of biomass and wastes to energy.