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Effect of carbonization conditions on CO₂ gasification reactivity of biocarbon

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Abstract

Substituting fossil reductants with biocarbon is a promising way for reducing greenhouse gas emissions and increase sustainability of the metallurgical industry. Biocarbon can be produced from a wide range of raw biomass materials and carbonization conditions. Studies on the properties of biomass biocarbon are critical for further efficient utilization of the biocarbon in metallurgical industries. The purpose of this study was to study the impact of pyrolysis temperature and calcination treatment on properties of woody biomass biocarbon focusing on gasification reactivity under CO₂ atmosphere. The experimental work was carried out using Norway spruce biocarbon produced at two different carbonization temperatures (650 and 800 °C). In addition, pine wood biocarbon produced at 650 °C was also gasified for comparison purpose. Considering the possible negative effects of the volatile content on metallurgical processes, the studied biocarbon samples were also calcined at 1000 °C for 1 hour to eliminate the volatile matters. Both the uncalcined and calcined biocarbons were gasified in a furnace setup at 850 °C under CO₂ atmosphere with continuous monitoring of the weight loss. The results showed that the carbonization temperature has evident effects on CO₂ gasification reactivity of the studied biocarbons. The calcination treatment lowered the CO₂ gasification reactivity of the studied biocarbons. This is due to the higher temperature applied for the calcination compared to the carbonization, and additionally it might be due to loss of catalytic inorganic elements and structure reordering of the carbon matrix during the calcination that is accompanied by loss of active carbon sites. From this point view, calcination is an option to tune properties (i.e., remove volatiles, increase fixed carbon content, reduce reactivity etc.) of biocarbon, to better fit the requirements of metallurgical processes. In addition, different gasification behaviors were observed for the studied spruce and pine biocarbons produced under the same conditions. This is mainly attributed to the different nature of them, physical and chemical properties as well as the amount and composition of ash forming elements.

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1. Introduction

Currently metallurgical industry mainly use fossilized carbonaceous materials in their production processes. The metallurgical processes are energy intensive production processes and significant amounts of fossilized carbonaceous materials are being consumed as reductants. It causes emissions of a vast amount of greenhouse gases (GHG), mainly CO₂, consequently. Utilization of renewable carbon is a promising way to reduce the dependence of metallurgical industries on fossil carbon and GHG emissions to the atmosphere from metallurgical processes [1]. Biocarbon can be produced from a wide range of biomass sources, including low cost sources, which makes the use of biocarbon as reductant economically feasible and attractive. Additionally, compared to coal and coke, biocarbon normally has low contents of ash and some undesired inorganic elements that might negatively affect metallurgical processes and properties of produced metal, metalloid (e.g. Si) and alloy products as well. On the other hand, compared to coal and coke, the biocarbon normally has low fixed carbon content, compressive strength and volumetric energy density.

Biocarbon can be produced from different raw biomass materials and under various conditions. Nowadays, biocarbon produced from woody biomasses is mainly used in metallurgical processes, in addition to cooking and barbecuing. However, even for woody biomasses, there are considerable differences regarding physiochemical properties and conversion behaviors during carbonization processes. The properties of biocarbon produced from woody biomass can be very different, consequently. Furthermore, carbonization conditions have great effects on yield and properties of biocarbon from a certain biomass feedstock. Therefore, assessment of biocarbon properties is often the primary step to ensure proper and efficient utilization of the biocarbon in metallurgical processes. Moreover, assessment results are valuable for tuning and optimizing carbonization process parameters to produce biocarbon with the desired properties.

As biocarbon is used in metallurgical processes, reactivity of biocarbon towards CO₂ is one of the most important properties that has strong effects on productivity and specific energy consumption of metallurgical processes [1]. For example, intensive reaction of the carbon reductant with CO₂ in the pre-reduction zone in a manganese production furnace can result in significant increase of carbon and energy consumption [1]. Therefore, a less reactive carbon reductant is desired to enhance the energy efficiency of the manganese production process and ensure that the fixed carbon content of the reductant is available in the reduction zone. In comparison to coal and coke, the biocarbon normally has higher content of volatile matter that is often unwanted in metallurgical processes. The volatile matter released from the biocarbon can combust above the furnace charge, generating intensive heat and large gas amounts consequently. It results in severe heating of the upper structure of the furnace by radiation, causing e.g. possible water leakages from pipe joints. Volatile matter in liquid phase might release from the biocarbon and condense on electrode clamps and other parts of a furnace, and initiate and enhance corrosion of these components. Therefore, high volatile content in the biocarbon can lead to unexpected shutdowns of a furnace and costly maintenances. Upgrading of biocarbon via calcination is an efficient way to reduce or even eliminate volatile matter in the biocarbon, while providing other benefits, such as decreased reactivity, as well.

The objective of the present work is to assess impacts of pyrolysis temperature and calcination treatment on gasification reactivity of woody biomass biocarbon under CO₂ atmosphere. The experimental work was carried out using Norway spruce biocarbon produced at two different carbonization temperatures (650 and 800 °C). In addition, pine wood biocarbon produced at 650 °C was also gasified for comparison purpose. All biocarbons were produced with a holding time of 10 min. The studied biocarbon samples were also calcined at 1000 °C for 1 hour and the CO₂ gasification reactivity of the calcined biocarbon was investigated.

2. Experiment setup and methods

Three kinds of biocarbon produced under different conditions were used in this study. Norway spruce and pine wood chips were carbonized in a screw carbonizer. The spruce wood chips were carbonized at 650 and 800 °C, while the pine wood chips were carbonized only at 650 °C. The sample was held at the carbonization temperature for 10 minutes. The proximate analysis results of the studied biocarbons are listed in Table 1. The carbonized spruce and pine wood chips were crushed and ground, and the particles with size in the range of 1-2 mm were used for further CO₂ gasification tests. The CO₂ gasification of the biocarbon particles were carried out with a tube furnace setup. First around 1 gram sample was loaded in a Pt-basket connected to a balance that is lowered into the tube furnace. Then a

thermocouple was hung from the top of the furnace and inserted into the middle of the sample bed. Afterwards, the furnace was sealed with a lid, and was purged with pure N₂ for 10 minutes at room temperature. Then the furnace was electrically heated up to 850 °C with a heating rate of 13°C/min in the presence of N₂. As the temperature reached 850 °C, the purge gas was shifted from N₂ to CO₂. The sample was kept at this temperature in presence of CO₂ for 190 minutes, with continuous recording of the sample weight loss. After the isothermal heating stage, the gas flow was shifted back to N₂ and the reactor cooled down to room temperature. The weight loss measured by the balance was recorded automatically. The conversion degree, as an increasing fractional weight loss, of the sample is calculated by the following equation:

$$X = \frac{m_0 - m}{m_0 - m_{ash}} \quad (1)$$

where m_0 is the initial dry weight of the biocarbon sample, m is the weight of the sample at a given time, and m_{ash} is the residual mass of the sample at the end of the gasification test. Effect of calcination treatment on CO₂ gasification reactivity of biocarbon was also studied. The biocarbon sample was first loaded into a graphite calcination crucible, which was covered with a lid and placed in a graphite container that was filled with petrol coke and covered with a lid. The container was then placed in a furnace (Nabertherm N161) and preheated to 1000 °C for 1 hour in the presence of N₂. After the calcination, the furnace was cooled down to room temperature, before the crucible in the container was removed. The morphology and microstructure of the biocarbon samples with and without calcination treatment were examined by scanning electron microscopy (SEM, ZEISS SUPRA-55).

Table 1. Properties of studied biocarbons.

Sample	Volatile matter (dry, wt %)	Fixed carbon content (dry, wt %)	Ash content (dry, wt %)
Spruce 650-10	8.91	89.52	1.57
Pine 650-10	9.43	89.15	1.32
Spruce 800-10	6.52	91.43	2.05

Table 2. Concentration of major catalytic elements in raw spruce and pine (mg/kg).

	Ash content (dry, wt %)	K	Ca	Na	Mg	Fe	P	Mn	Zn
Spruce	0.2	361	1511	101	157	73	49	89	13
Pine	0.3	153	1178	81	129	13	42	27	5

3. Results and discussion

The weight loss curves obtained from uncalcined and calcined biocarbon samples are shown in Fig. 1. It can be seen for uncalcined biocarbon, that around 7-10 wt% weight loss occurred in the devolatilization stage as the sample was heated from room temperature up to 850 °C. On the other hand, no weight loss was recorded for the calcined biocarbon samples. I.e. calcination at 1000 °C efficiently reduced the volatile matter content of the samples. Fig. 2 shows carbon conversion behaviors of the six tested samples as a function of time. For the uncalcined spruce biocarbon, one should note that the one produced at 800 °C reacts faster compared to that produced at 650 °C. The CO₂ gasification reactivity of biocarbon produced at different temperatures has been studied and reported previously [3-6]. The general perception is that the biocarbon produced at higher temperatures are less reactive than those produced at lower temperatures are. E.g. it was reported that chars produced from Acacia wood and Eucalyptus wood at increasing carbonization temperatures have lower reactivity and higher activation energy [3]. Fig. 2 also shows that biocarbon from pine produced at 650 °C reacts considerably slower than that of spruce biocarbon prepared at the same temperature. Moreover, it can be seen in Fig. 2 (a) that all calcined biocarbon samples convert evidently slower than those of the counterpart uncalcined biocarbon samples do. In order to evaluate the reactivity of the different biocarbon samples, the time of half conversion of them ($t_{0.5}$) was calculated and compared as shown in Fig. 2 (b). In agreement with the observed weight loss behaviors, less time is needed to complete the half conversion for spruce biocarbon

produced at 800 °C than that prepared at 650 °C. Furthermore, conversion of uncalcined biocarbon samples takes considerably shorter time than those after calcination treatment. It is interesting to see that differences in $t_{0.5}$ of uncalcined and calcined biocarbon samples increase for those prepared at higher carbonization temperature.

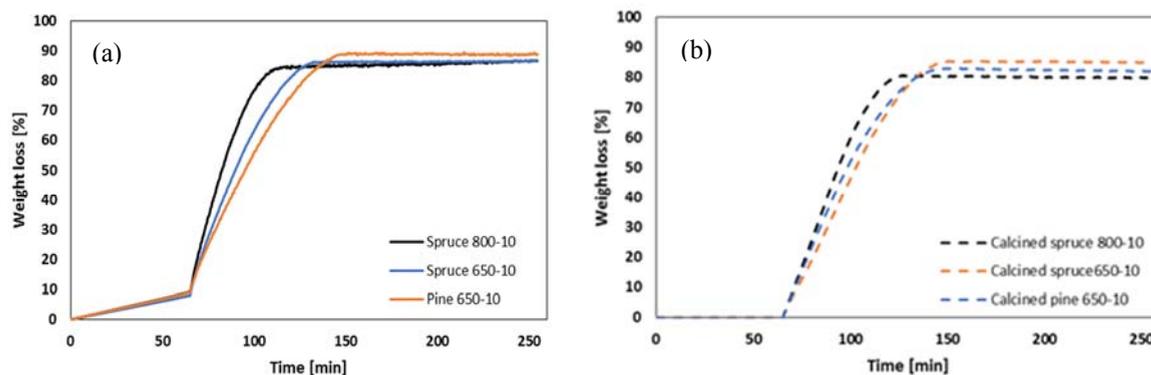


Fig. 1. Gasification behaviors of (a) uncalcined biocarbon and (b) calcined biocarbon in the furnace setup.

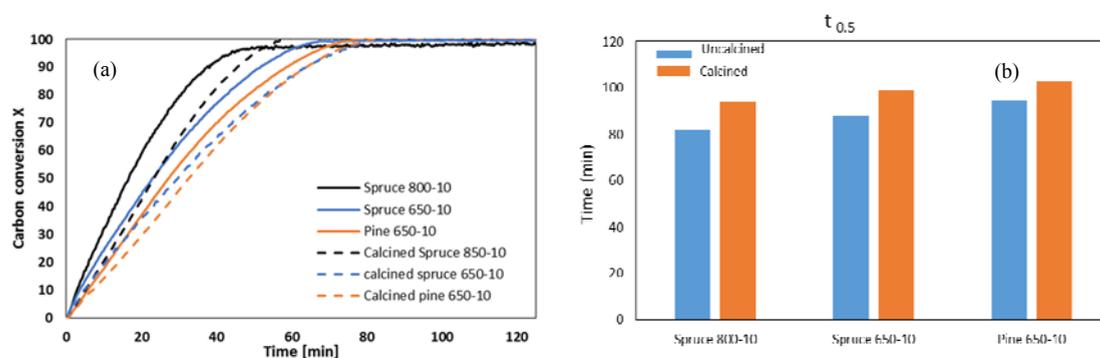


Fig. 2. (a) Conversion degree of biocarbon; (b) the reactivity index $t_{0.5}$ of biocarbon

The CO₂ gasification reactivity of biocarbon derived from different biomass materials are influenced by many factors, including biocarbon physical and chemical properties, gasification reaction conditions, heat transfer and mass transfer of gas products, etc. [3-6]. In the present work, the gasification experiments were carried out under the same reaction conditions (i.e., purge gas flow rate, heating rate during the devolatilization stage) in the same test setup. Therefore, the differences in gasification reactivity observed from different samples may mainly relate to the different properties of them, which then should mainly be affected and determined by the carbonization conditions. These properties include volatile matter content, surface area, porosity, content of catalytic inorganic elements, biocarbon carbon structure etc. Upon increase of carbonization temperature, the contents of volatile matter and inorganic elements of a biocarbon sample decrease. During the gasification process, the remaining volatiles in the biocarbon particles release with formation of e.g. significant amounts of H₂ [5]. Reactions of e.g. H₂ with biocarbon enhance the release of catalytic inorganic elements in the biocarbon, which also results in conversion of the carbon structure, from small aromatic rings systems into large and less reactive ones. Therefore, volatile-biocarbon reactions around and inside biocarbon particles can be intensive and significantly reduce the reactivity of biocarbon [6]. This could partially explain the low reactivity of the spruce biocarbon produced at 650 °C, which has a relatively high content of volatile matter compared to the one produced at 800 °C as shown in Table 1. In addition, the CO₂ gasification reaction reactivity of biocarbon is heavily associated with concentration and form of catalytic inorganic elements remaining in the biocarbon after the carbonization process. It was reported that inorganic elements, mainly alkali and alkali earth metals, in the biocarbon can act as catalysts to promote gasification conversion of biocarbon [4-6]. Table 2 shows that spruce wood generally contains higher concentrations of catalytic inorganic elements than pine wood. It implies that

the concentration of these elements in the spruce wood biocarbon produced at 650 °C might be higher than that of pine wood biocarbon. The higher concentration of catalytic elements could cause the conversion of spruce wood biocarbon to become relatively faster than that of pine wood biocarbon, as shown in Fig. 2. For the calcined biocarbon samples, they have been heated at 1000 °C for 1 hour. It is known that release of catalytic inorganic elements continues with increase of carbonization temperature and extension of heat treatment time. Moreover, the catalytic inorganic elements in the biocarbon can react with other elements to form new chemical forms or mineral phases. For example, the alkali and alkali earth metals in the raw biomass transform to oxides and salts such as sulphates and chlorides during a carbonization process. At a high carbonization temperature, the alkali and alkali earth metal oxides and salts will further react with Si and Al organically bound to the biomass carbon matrix or quartz and clay minerals to form non-volatile silicates and aluminosilicates [6]. The formed silicates and aluminosilicates are catalytically inactive species, in comparison to oxides, chlorides and sulphates. Therefore, the low gasification reactivity observed from the calcined biocarbon samples can be partially attributed to loss of catalytic inorganic elements and catalytic effects from these elements. Additionally, calcination cause release of remaining volatiles and transformation of amorphous carbon structure into larger aromatic ring systems that are less reactive and hence need higher activation energy for the gasification reaction to occur [6]. The present findings regarding reduction of biocarbon reactivity after calcination of the studied biocarbon samples are in good agreement with results reported in other work [5,6]. The gasification reactivity of a biocarbon sample is also heavily related to the initial microstructure (i.e., surface area and porosity) of them. Figs. 3 and 4 show SEM images of spruce wood biocarbon produced at 650 and 800 °C with and without calcination treatment, respectively. Compared to uncalcined biocarbon samples, more openings and cavities can be seen for the calcined biocarbon surfaces. It indicates further decomposition of the biocarbon and increase of porosity. The reactivity of biocarbon generally positively correlates with increasing surface area and porosity. However, as discussed above, the gasification reactivity of biocarbon is affected by a combination of different factors. For the present work, reordering of the carbon structure and loss of catalytic elements should be the two dominating factors rather than increase of porosity, resulting in lower reactivity of the calcined biocarbon samples.

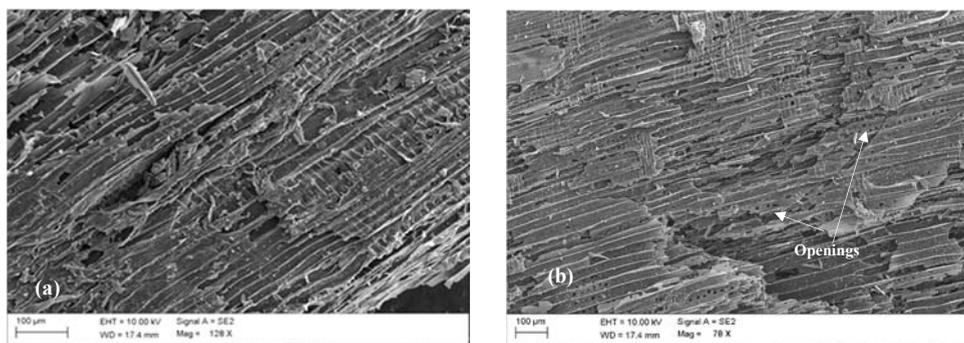


Fig. 3. SEM image of (a) uncalcined spruce 650-10 biocarbon; (b) calcined spruce 650-10 biocarbon.

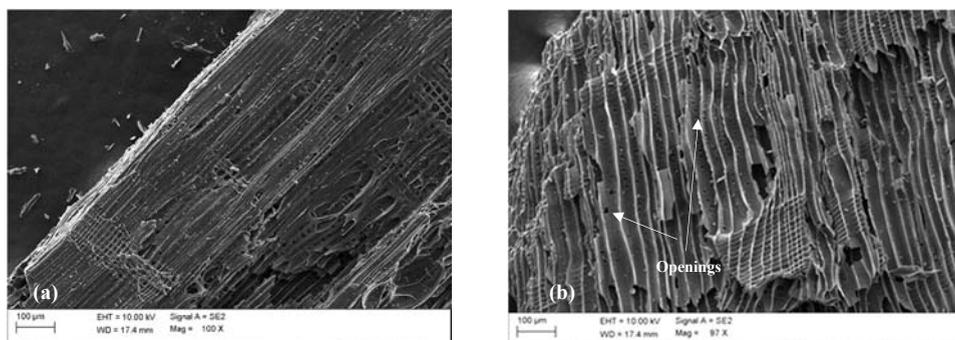


Fig. 4. SEM image of (a) uncalcined spruce 800-10 biocarbon; (b) calcined spruce 800-10 biocarbon.

Results from the present work have important implications for the use of the biocarbon as a reductant in metallurgical processes. The biocarbon reactivity is closely related to carbonization conditions and further calcination. If biocarbon with low volatile content and reactivity is required, the initially produced biocarbon can be further treated by calcination at a high temperature. Another benefit of the calcination treatment is further release of inorganic elements from the biocarbon, reducing effects of inorganic elements on purity and quality of the final products of the metallurgical processes.

4. Conclusions

In the present work, CO₂ gasification reactivity of biocarbon produced at different temperatures and from different wood species were studied. In addition, the effect of calcination treatment on biocarbon CO₂ gasification reactivity was also assessed. It was found that spruce biocarbon produced at 800 °C had higher reactivity compared to that produced at 650 °C. The lower reactivity of the latter one can be partially related to a higher content of volatiles in the biocarbon sample produced at lower carbonization temperature. Intensive volatile-biocarbon reactions might cause reduction of catalytic inorganic elements and reactivity of the biocarbon consequently. Calcination affected the biocarbon reactivity significantly. The calcination is normally coupled with loss of heteroatoms, with formation of increasingly ordered carbon structure. Moreover, during a calcination process, the concentration of catalytic inorganic elements in the biocarbon decreases, as they are also transformed into new and much less catalytically active forms. Therefore, calcination is a promising way to tune biocarbon CO₂ gasification reactivity for producing less reactive biocarbon for certain metallurgical processes.

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Biography

Liang Wang is a research scientist at SINTEF Energy Research in Trondheim Norway. His research focus 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.