CO$_2$ Reactivity Assessment of Woody Biomass Biocarbons for Metallurgical Purposes

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Replacing the use of fossil reductants with biocarbons in metallurgical industries has a great potential with respect to reducing CO$_2$ emissions and the contribution from this industry to the increasing greenhouse gas effect. However, biocarbons are significantly different from fossil reductants and the biocarbon properties vary in a wide range depending on the raw biomass properties and the biocarbon production process conditions.

A key property of the biocarbons is their reactivity in the specific metallurgical process. The reactivity should be appropriate for the specific metallurgical process, to ensure an optimum reduction process. Especially important is the biocarbon reactivity towards CO$_2$, i.e. the CO$_2$ gasification of biocarbon fixed carbon. A standard method has earlier been developed by the metallurgical industry to test the CO$_2$ reactivity of coal and coke. This can be adopted also for biocarbons. However, a simpler and more cost-efficient reactivity test method is wished for. For the silicon industry, also SiO reactivity is important and a standard method has been developed. This is very expensive to carry out, and also here a simpler and more cost-efficient reactivity test method is wished for. If a qualitative correlation between SiO and CO$_2$ reactivity could be established as well, this would be very beneficial for this metallurgical industry.

In this study, the main objectives were to assess the CO$_2$ reactivity of biocarbons produced from different woody biomass in two experimental setups, a standardized setup and a thermogravimetric analyser (TGA), and to compare with the reactivity of fossil reductants. Spruce and birch stem wood and in addition their forest residues were tested. The results show that even if quantitatively different results were found in the two experimental setups, the qualitative results were the same, and hence the TGA test provides the opportunity of a simplified and cost-efficient CO$_2$ reactivity test method. The biocarbon from the forest residues showed a higher reactivity than stem wood biocarbon, probably due to the higher ash content in the forest residues and their biocarbons, giving a catalytic effect. Compared to coke the biocarbons were more reactive.

1. Introduction

Nowadays the metallurgical industry primarily use fossilised carbonaceous materials in their metal production processes. Due to energy intensive production processes, a large amount of fossilised carbonaceous materials (mainly coal and coke) are being consumed, producing a vast amount of greenhouse gases (GHG) consequently (Suopajärvi et al. 2013). The metallurgical industry faces increasing pressure to reduce their dependence on fossil carbon and GHG emissions from the production of metals. Renewable carbon from biomass has a great potential to substitute fossil carbon and radically reduce the net carbon emissions to the atmosphere from metallurgical processes. Compared to fossil carbon, biocarbon (or charcoal) can be produced from large amounts of available low cost biomass resources (Kuppens et al. 2014). It makes the use of biocarbon economically attractive. Additionally, compared to coal and coke, biocarbons have low contents of ash and some unwanted elements (e.g., sulphur and phosphorus), which will help to improve the purity of the produced metal (Antal et al. 2003). On the other hand, the fixed-carbon content in the biocarbon is normally lower than in coal and coke. The volumetric energy density and strength of biocarbons are also

rather poor, which might lead to some difficulties concerning the use of biocarbon in certain metal production processes (Myrhaug et al. 2004).

Biocarbon yield, fixed-carbon content and properties depend highly on the properties of the raw biomass materials and biocarbon production process conditions. Currently, biocarbon used for metal production is mainly produced from woody biomass. However, both the biocarbon yield and fixed-carbon content of biocarbon produced via present carbonisation technologies are rather low. Studies for tuning biocarbon production process conditions for optimizing biocarbon production efficiency and properties have been carried out (Wang et al. 2011). Even for biocarbons produced from woody biomass, properties of them can be considerably different. Therefore, assessment of biocarbon properties is critical for ensuring proper and efficient utilization of the biocarbon for metal production.

Reactivity towards CO_2 is one of the most important properties of the carbon materials used as reductants during metallurgical production processes (Huo et al. 2014). In the iron production process, the carbon reductant must be reactive towards CO_2 produced from the reduction of iron ore. The main product CO from the heterogeneous reaction between carbon reductant and CO_2 will react with the iron ore for producing iron (Suopajärvi et al. 2013). For the Si production industry, CO_2 reactivity of a carbon reductant is considered as an important indicator for evaluating its ability to react with SiO for generating SiC (Myrhaug et al. 2004). A standard test method has been developed for measuring the Coke Reactivity Index (CRI) in CO_2 at elevated temperature. However, there is no standard method for measuring the CO_2 reactivity of biocarbon. In addition, measuring the CO_2 reactivity demands significant time and resources (Myrhaug et al. 2004). Therefore, if the existing coke CO_2 reactivity test method can be further developed and improved, and also applied for biocarbon, it would be beneficial.

In the present work, the reactivity of fossil carbon, one industrial charcoal and biocarbon produced from Norwegian wood species are assessed by running CO_2 gasification experiments in two different setups. The two setups include a standardized furnace setup for determining the CRI, and a thermogravimetric analyser (TGA). The objectives of the present work are to assess the CO_2 reactivity of biocarbons produced from different woody biomass in the two experimental setups, and to compare with the reactivity of fossil reductants.

2. Experiment setups and methods

2.1 Char preparation

One type of coke and five kinds of biocarbons were used in this study. The biocarbons were produced at different carbonization conditions. The first one, an industrial charcoal, was produced at atmospheric pressure with slow heating rate and long residence time. The four other biocarbons were produced in a flash carbonizer at 21.7 bar pressure, for multiple research purposes. Norwegian spruce wood (SW), spruce forest residue (SFR), birch wood (BW) and birch forest residue (BFR) were carbonized in this flash carbonizer. In a flash carbonization experiment, 0.5-1 kg of raw material is loaded into a cylinder canister. The canister is then placed into a vertical pressure vessel and pressurized to 21.7 bar by air. Electrical power is delivered to two heaters at the bottom of the vessel, which ignite the materials in the canister. The ignition step creates a shallow bed of biocarbon at the bottom of the canister. Then air is delivered to the top of the reactor as the produced gas is vented out from the bottom of the reactor. The flame front moves upwards from the bottom against the flow of air and converts the biomass into biocarbon that is unloaded after cooling down the reactor. More details about the flash carbonization of biomass can be found in Antal et al. (2003). The coke and the five biocarbon samples were then ground and sieved to have particles with sizes of 1 mm for further studies.

2.2 CO_2 reactivity test

CO_2 reactivity of the samples was tested using a standardized furnace setup and a thermogravimetric analyser (TGA). For running the CO_2 reactivity test with the furnace setup, around 2g sample was loaded in a Pt-basket connected to a balance and lowered into the tube furnace before heating up the reactor. A thermocouple was then hung from the top of the furnace and inserted into the sample bed. Then the top of the furnace was sealed with a lid. The tube reactor was first purged by N_2 gas flowing upwards for 10 minutes at room temperature. Then the reactor was electrically heated to 850 $^{\circ}$C with a heating rate of 13 $^{\circ}$C/min in the presence of N_2. When the temperature reached 850 $^{\circ}$C, the N_2 flow was replaced by CO_2 and the sample was exposed to CO_2 at 850 $^{\circ}$C for 190 minutes. Continuous recording of sample weight loss starts automatically as the isothermal heating stage begins. After the isothermal heating stage, the gas flow shifts back to N_2 and the reactor cools down to room temperature.

The reactivity of the Norwegian biocarbon samples towards CO_2 was also assessed by using a thermogravimetric analyser (Mettler Toledo TGA 851^{e}). Before the start of one experiment, ground sample (around 10mg) was loaded in an alumina crucible that was heated up in the TGA using exactly the same

temperature program as described above. A 100 ml/min N_2 flow was used for purging the sample during the devolatilization stage while a 100 ml/min CO_2 flow was used during the CO_2 gasification at 850 °C.

2.3 Characterization of biocarbon samples

The morphology of the samples was examined by a scanning electron microscopy (SEM, Hitachi S-3400N). The sample powders were first attached to a carbon tape fixed on a sample tab that was put into the SEM for scanning. In addition, the four biocarbons produced from Norwegian wood species were also analysed by inductively coupled plasma optical emission spectrometry (ICP-OES, Thermo Scientific iCAP 6300 Duo View Spectrometer), to determine the concentration of inorganic elements in the samples. One sample was dissolved in an aqueous solution of H_2O_2, HNO_3 and HF (30%: 65%: 40%). The major inorganic element contents were determined according to standard CEN/TS 15290:2006.

3. Results and discussions

3.1 CO_2 reactivity test using the standardized furnace setup

Figure 1 shows weight loss behaviors of the coke and the five biocarbons as a function of conversion time. One should note that the weight loss caused by devolatilization in the first 65 minutes is not shown in Figure 1, only the weight loss recorded in the isothermal gasification stage. Therefore, Figure 1 displays conversion behaviors of highly carbonized samples after the release of volatiles in the devolatilization stage. It can clearly be seen that the coke reacts much slower compared to the biocarbon samples, which exhibit a much higher CO_2 gasification reactivity. The CO_2 gasification reactivity of chars derived from different carbonaceous materials are influenced by their physical and chemical properties. These properties include pore volume, surface area, ash content, alkali content, crystalline structure, etc. As shown in Figure 2(a), the coke particles have very compact structure and intact surface. The biocarbons have completely different microstructures. As shown in Figure 2(b), the industry biocarbon has more coarse surfaces and many pores can be found on the surfaces of the particles. In addition, it can clearly be seen in Figure 2(c) and Figure 2(d) that biocarbon particles retain the porous fiber structures from their parental biomass. Some of the particles show a clear cellular structure with a large amount of open pores. Based on the SEM analyses, the coke sample should have much smaller pore volume and specific surface area in comparison to the biocarbon samples. The petroleum coke normally has a surface area in the range of 0.5-3 m^2/g that is significantly smaller than those of biocarbon with surface area around 300-400 m^2/g (Huo et al. 2014, Kawakami et al. 2004). Reaction of coke with CO_2 is significantly restricted due to poor diffusion of CO_2 gas into the particle. Therefore, coke has a much lower CO_2 gasification reactivity compared to biocarbon.

Figure 1(a) also shows evident differences between the five tested biocarbon samples in terms of CO_2 gasification behaviors. For the spruce forest residue biocarbon (SFR), the weight loss is stable after around 125 minutes testing time. It indicates a close to complete conversion, with mainly ash left. However, complete conversion of spruce wood biocarbon happens around 20 minutes later. Complete conversion of birch wood biocarbon and birch forest residue biocarbon happens significantly later compared to their spruce counterparts, as shown in Figure 1(a). In addition, the conversion of industry biocarbon continues until the end of the reactivity test. It suggests that the SFR biocarbon has the highest CO_2 gasification reactivity of the biocarbon samples. Figure 1(b) shows in more detail the weight loss in the first 30 minutes only. It can clearly be seen that from the beginning the weight loss trend of the samples develops consistently towards the final result. The differences in the weight loss behaviors of the four samples gradually increase along the reaction time. This might relate to pore structure and total surface area differences of the tested samples as the CO_2 gasification reaction proceeds (Kawakami et al. 2004). No conclusions regarding the influence of carbonization pressure can be drawn from these results.
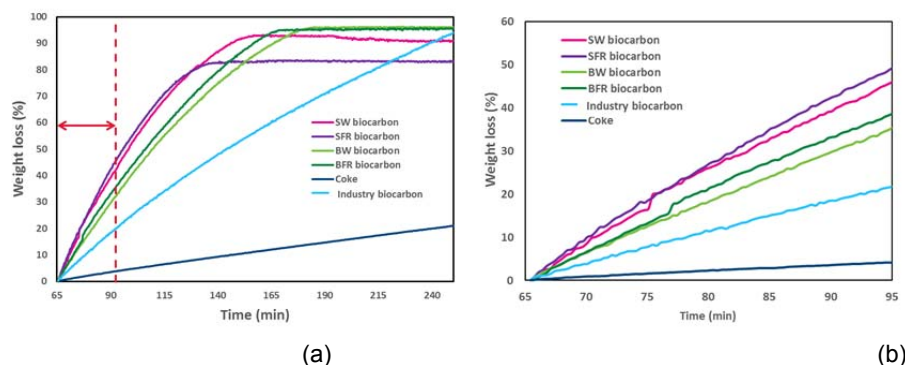

(a) (b)

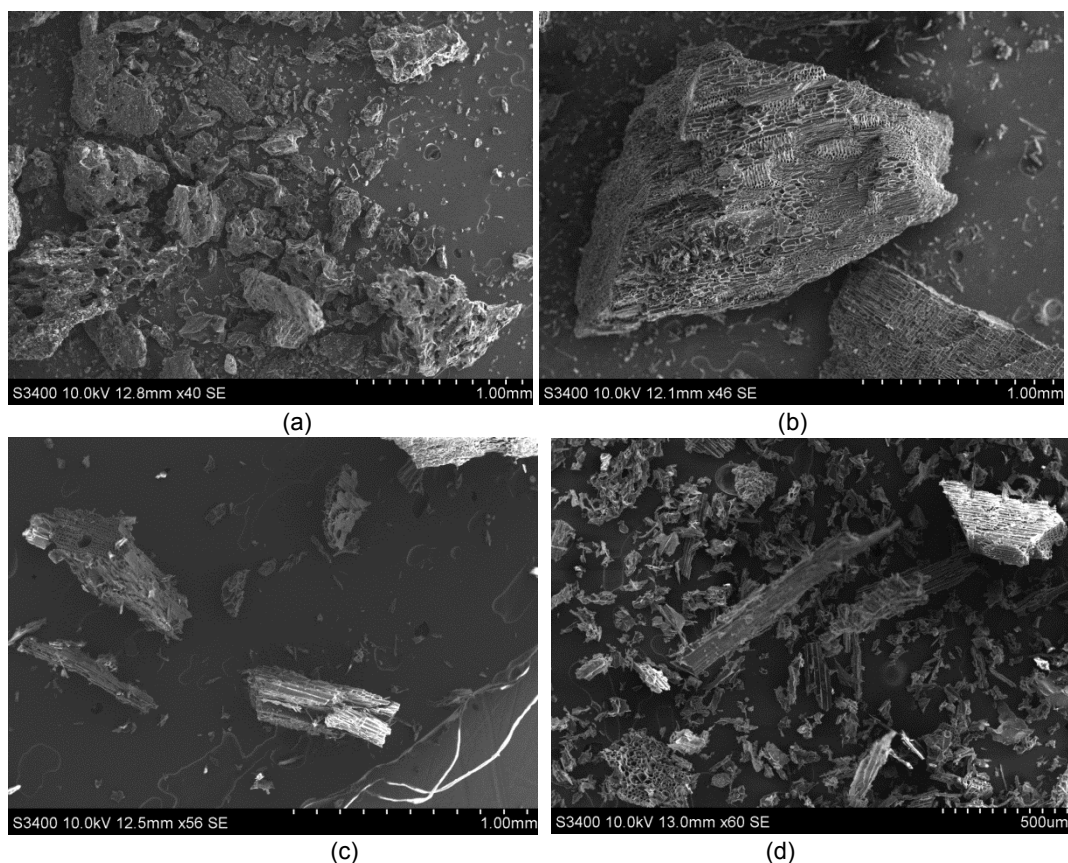*Figure 1: Conversion of coke and biocarbon samples in the furnace setup*

Figure 2: SEM images of (a) coke, (b) industry biocarbon, (c) birch wood biocarbon, (d) birch forest residue biocarbon

3.2 Comparison of CO_2 reactivity test in two setups

The CO_2 gasification reactivity tests for biocarbon produced from Norwegian wood species were also carried out using a TGA. Figure 3 display weight changes of the four tested biocarbon samples obtained by the TGA together with those from the standardized furnace tests. As mentioned before, the volatile content of biocarbon might influence on their reactivity towards CO_2. Therefore, the devolatilization behaviours of the biocarbon in the furnace and TGA are first compared. Figure 3 shows that, for the four tested biocarbon samples, the weight loss curve shapes in the devolatilization stage obtained from the furnace setup and TGA are generally similar. The weight losses of the four biocarbon samples at the end of the devolatilization stage are shown in Figure 4. The amount of volatiles released from the biocarbon samples in the furnace setup are higher, in comparison to those obtained in the TGA, with an exception of the SFR biocarbon.

After the devolatilization stage, the CO_2 gasification of the four biocarbons starts and the weight losses develop as shown in Figure 4. For BW, BFR and SW biocarbons, the weight loss curves obtained from the TGA are quite similar to those obtained in the furnace setup. As described above, the furnace setup has a different design and as well purge gas flow pattern than the TGA. In addition, sample mass and purge gas flow rate used in the furnace setup is significantly higher than those applied in the TGA. Therefore, the heat and mass transfer rates exhibited by a biocarbon sample towards CO_2 should be different due to differences in experimental setup, sample mass and purge flow pattern/rate. It will consequently influence the conversion behaviours of the biocarbon samples in the presence of CO_2 in the two setups. However, as shown in Figure 3, the similarity between the weight losses curves of three of the biocarbon samples are surprisingly high. It is most evident for BW and SW biocarbons as the gasification of them complete in a narrow time slot range of 154 to 158 minutes. It indicates that TGA could be a reliable alternative to the furnace setup for assessing CO_2 reactivity of biocarbons.

Figure 3 shows that, during the isothermal gasification stage, the weight loss rate of BW, BFR and SW biocarbons in the TGA are generally larger in comparison to those in the furnace setup. In the TGA CO_2 reactivity test, 10mg biocarbon powders were loaded in a crucible as a thin bed. The CO_2 can rather easily diffuse into the sample bed. In addition, the reaction products from reactions between the biocarbon powder and CO_2 can also rather easily be transported out of the sample bed. This will be quite different in the furnace

setup. The sample bed in the basket is larger and can be more compact due to the large amount of sample used. It will limit both diffusion of CO_2 into and release of gas products out from the centre of the sample bed (Teixeira et al. 2014), creating concentration gradients. Additionally, there might be temperature gradients in the sample bed in the basket. The temperature in the centre region of the sample bed might be significantly lower than that of the rim of the bed. This together with concentration gradients may restrict the conversion rate of biocarbon in the centre region.
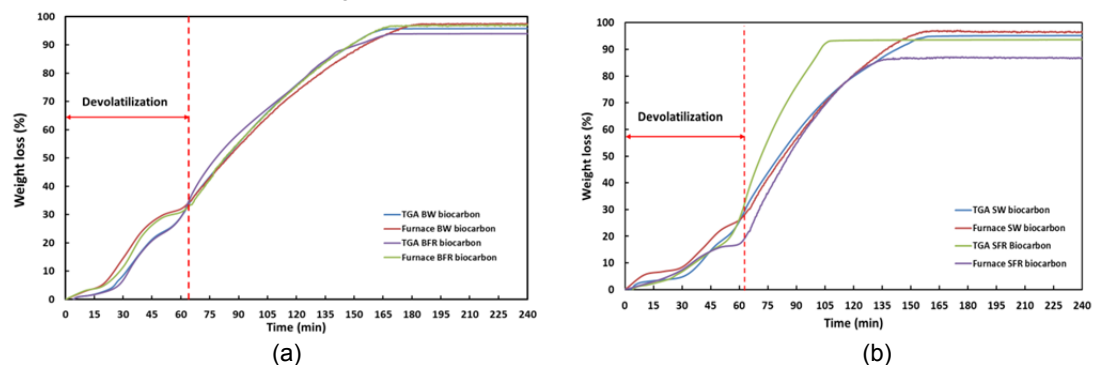

(a) (b)

Figure 3: Comparison of biocarbon CO_2 reactivity in the furnace setup and the TGA
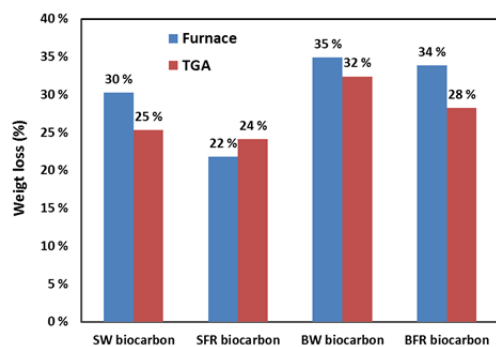

Figure 4: Devolatilization related weight losses of biocarbon samples in the furnace setup and the TGA

3.3 Gasification of biocarbons in the TGA

Figure 5 shows the conversion of the four biocarbons in the presence of CO_2 in the TGA. It can clearly be seen that forest residue biocarbon have a more intensive weight loss during the isothermal gasification stage. It suggests that biocarbons produced from forest residues have higher reactivity than those produced from stem wood. Compared to SW and BW biocarbon, the concentrations of ash and inorganic elements in the SFR and BFR are considerably higher, as shown in Table 1. The inorganic elements K, Ca, Na and Mn can act as catalysts for the gasification of biocarbons (Wang et al. 2013), and the SFR has the highest content of these. It can partially explain the high CO_2 gasification reactivity of the forest residues biocarbons, whereof the SFR has the highest reactivity.
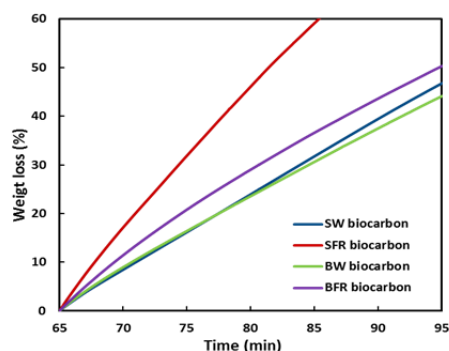

Figure 5: Conversion of biocarbon samples in the TGA

Table 1: Concentrations of ash (wt%) and inorganic elements (mg/kg) in the biocarbon samples

Sample	Ash content	Ca	Fe	K	Mg	Mn	Na	S	P
SW biocarbon	1.1	8043	45	2172	759	824	27	293	158
SFR biocarbon	3.7	9968	68	3407	1153	1595	64	426	329
BW biocarbon	1.4	3332	70	1508	682	344	13	253	210
BFR biocarbon	5.0	5010	342	1965	741	374	109	498	404

4. Conclusions

CO_2 reactivity of coke and biocarbons were assessed in the present work by using a standard furnace setup and a TGA setup. The results showed that biocarbons are more reactive than coke. Comparison of CO_2 reactivity test results realized in the two experimental setups shows that the qualitative results were the same for the four tested biocarbons. It suggests that a TGA test can be a simple and cost-efficient alternative to a standardised furnace setup test for assessing the CO_2 reactivity of carbon reductants. The TGA tests revealed that biocarbon from forest residues showed a higher reactivity than stem wood biocarbon, probably due to higher content of ash and inorganic elements in the forest residues and their biocarbons. Presence of some of these elements might give a catalytic effect and promotes conversion of the biocarbon in the presence of CO_2.

Acknowledgments

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