

Investigation of the Properties and Reactivity of Biocarbons at High Temperature in a Mixture of CO/CO₂

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The CO₂ gasification reactivity of biocarbons produced from birch wood chips under different atmospheric and pressurised conditions was investigated in this work. The reactivity tests were conducted by using a Macro-TGA at 1100°C in a gas mixture of 50% CO₂ and 50% CO to simulate the conditions in an industrial ferromanganese furnace. The results showed that biocarbons produced under different conditions have different CO₂ gasification reactivities. The biocarbon produced in an atmospheric fixed bed reactor has the highest reactivity. This biocarbon has a high surface area and content of catalytic inorganic elements, which favour the Boudouard reaction and consumes fixed carbon. Scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (EDS) showed that migration and transformation behaviours of inorganic elements in the studied biocarbons are different at the same gasification condition. Together with inductively coupled plasma atomic emission spectroscopy (ICP-OES) analysis, SEM-EDS analysis revealed that the most intensive transformation of inorganic elements occurred during gasification of the biocarbon sample produced at atmospheric conditions with slow heating rate and purging of N₂. Such pyrolysis condition promotes presence of catalytic inorganic elements on the biocarbon surface, which promotes the Boudouard reaction.

1. Introduction

Nowadays a large amount of fossil-based carbonaceous materials (mainly coal and cokes) are consumed by metallurgical industry, with emission of a vast amount of greenhouse gases (GHG) consequently. E.g., processes involving electric arc furnace (EAF) and submerged arc furnace (SAF) can generate approximately 1.83 kg CO₂ per kg of steel (World Steel Association, 2017), 1.04 to 1.15 kg CO₂ per kg ferromanganese (Olsen et al., 1998), 1.4 to 6.9 kg CO₂ per kg of silicomanganese and 2.5 to 4.8 kg CO₂ per kg ferrosilicon (Lindstad et al., 2007). It has been estimated that metal production accounts for approximately 10% of global GHG emissions (World Steel Association, 2017). Therefore, the metal production industry is challenged to realize decarbonization of the metal production processes and reduction of environmental impacts through different measures. Carbon from renewable biomass has gained continuous interest as an alternative to fossil carbon and has a great potential to reduce CO₂ emissions to the atmosphere from metallurgical processes.

As used in a metal production process, reactivity of the carbon reductant towards CO₂ is one of the most important properties to be assessed. A carbon material with high CO₂ reactivity has a high Boudouard reaction rate: CO₂ + C = 2CO, ΔG⁰ = 170.82 – 0.18T kJ/mol. The Boudouard reaction is a highly endothermic reaction with a reaction enthalpy of 172.5 kJ/mol. This reaction is undesirable in e.g. manganese alloy production, since it causes considerable consumption of carbon and heat in the upper part of the furnace (Kaffash et al., 2021). Additionally, there is a significant amount of CO₂ emissions from metal production that are due to the Boudouard reaction. It has been reported that about 500,000 tonnes of annual CO₂ emissions derived from FeMn and SiMn production are due to the Boudouard reaction, which is approximately 30% of the total annual emissions (Kaffash et al., 2021). For silicon production industry, CO₂ reactivity of a carbon reductant can give indications

to its ability to react with SiO for generating SiC as well. Compared coke, the biocarbon has low carbon content, bulk and energy density and mechanical strength. In addition, the biocarbon also has relatively high content of volatile matters and certain inorganic elements in comparison to the fossil reductants currently being used in metal production. On the other hand, the yield, properties and reactivity of biocarbon depend highly on the selection of biomass feedstock and biocarbon production conditions. Biocarbon produced from woody biomasses is currently used for metal production. To increase the fixed carbon content of the biocarbon, different production conditions have been tested including extending residence time of tarry vapours and increasing process pressure (Wang et al., 2016). Study results showed that both mass and fixed carbon yield of biocarbon can be significantly improved under these conditions. However, the CO₂ reactivity of biocarbon produced under these conditions has not been well studied. It is also important to test the CO₂ reactivity of carbon reductants under conditions close to those relevant to industrial production (Phounglamcheik et al., 2020). There is an American Society of Testing and Materials (ASTM) standard for testing CO₂ reactivity of biocarbon in a 100% CO₂ atmosphere at 1100 °C. With considering variation of gas atmosphere in industrial furnaces, methods have been developed by the Norwegian University of Science and Technology (NTNU) and SINTEF, where CO₂ reactivity tests are conducted in an atmosphere of 75% CO and 25% CO₂ or 50% CO and 50% CO₂ at 800–1100 °C (Kaffash et al., 2021).

Utilization and consumption of fossil-based reductants cause significant emissions of CO₂ from metallurgical industry. There is a continuous need and interest to produce and use green biocarbon, which can be produced from low cost and highly available renewable biomass sources. However, in comparison to the conventional fossil reductants, biocarbon has considerably different physiochemical properties and reactivity, which are affected by both properties of raw feedstock and production conditions. More detailed and systematic studies are required to assess and characterize properties of the biocarbons to reveal their feasibility and estimate their performance as alternatives to fossil reductants for metal production. In this work, biocarbon was produced from Norwegian birch wood under different production conditions. The CO₂ reactivity of the produced biocarbon was measured and assessed by conducting macro-TGA experiments in an atmosphere of 50% CO and 50% CO₂ at 1100 °C. SEM-EDS and chemical analyses were conducted to examine the microstructure of the reacted biocarbons and identify the presence and possible role of inorganic elements with catalytic effects.

2.1 Biomass feedstock

Birch stem wood chips was used in the present work. The birch trees were harvested from a Norway birch forest (Latitude 59°55'N, Longitude 10°89'E) in South Norway. After debarking, the stem wood was further chipped. The produced birch wood chips were dried at 105 °C for 24 hours before pyrolysis experiments. Proximate and ultimate composition of the birch wood chips are shown in Table 1.

Table 1: Proximate and ultimate composition of the birch wood chips

Volatile matter ^a	Ash ^a	Fixed carbon ^{a,c}	C ^b	H ^b	N ^b	S ^b	O ^{b,c}
84.4	0.8	14.8	45.93	6.01	0.13	0.02	47.91

^a: wt%, dry basis, ^b: wt%, dry ash free basis, ^c: by difference

2.2 Production of biocarbon

Pyrolysis was conducted using an apparatus comprising of a tubular fixed bed reactor, a condenser and a gas monitoring system. The pre-dried birch wood chips were placed into the reactor tube that was then sealed and connected to a gas monitoring system and a condenser. The reactor tube was placed into and heated by an electrical furnace with three heating zones. Control and monitoring of the temperature in the reactor were enabled by three pairs of thermocouples along the length of the tubular reactor. Before start of one experiment, the reactor was purged by N₂ from the bottom of the tube with a flow rate of 2 L min⁻¹ as carrier gas to flush away residual air. After the initial purging step, the reactor with the birch wood chips were in the experiment with continued purging of N₂ further heated up to a temperature of 500 °C with a heating rate of 10°C min⁻¹ and maintained at this temperature for 1 h before gradual cooling (with N₂ flow) until reaching 50°C. During the pyrolysis experiment, the condensable volatiles and gases pass through the condenser and cools down to 50 °C and are further collected in a tank. The non-condensable product fraction further flows through two filters, and the flow was monitored by a rotameter, and also sampled and analysed by a micro-GC in terms of main composition. After pyrolysis, the biocarbon was unloaded from the reactor and stored for further testing and analysis. A staged pyrolysis experiment was also carried out with the same tubular reactor. After the initial purging with N₂, the loaded birch wood chips were then first heated with a heating rate of 10°C min⁻¹ to 350 °C with a residence time of 1 h at this intermediate temperature. Then, the temperature was further increased to 500 °C. However, after the initial purging period, there was no purging of N₂ during the staged pyrolysis experiment. As the temperature reached 500°C, the sample was heated at this temperature for 60 minutes, then the power

to the electrically heated furnace was switched off and the pyrolysed material cooled down naturally to 50 °C with purging of N₂. The birch wood chips were also carbonized in a flash carbonization reactor at university of Hawaii. The birch wood chips were placed in a canister that was loaded into a reactor vessel. The vessel was then pressurized with air to 7.9 bar. Then the loaded birch wood chips were ignited by an electrical heating coil at the bottom of the pressurised vessel, which was turned off after 6 minutes of ignition time. Following the ignition, compressed air was fed into the top of the reactor and flowed downwards through the feedstock bed. The ignition caused a flash fire of the feedstock and a flame front moved upward, triggering the carbonization of feedstock into charcoal. During the carbonization process, the pressure in the reactor was continuously monitored and maintained at 7.9 bar by a valve located downstream of the reactor. More details about the reactor and operational procedures for producing biocarbon through the flash carbonizer can be found in our previous work (Van Wesenbeeck et al., 2016).

2.3 Macro-TGA reactivity test

The CO₂ reactivity of the produced biocarbons was tested by conducting macro thermogravimetric analyzer (Macro-TGA) experiments. A sample of about 20-30 grams was first loaded into a stainless-steel crucible that was suspended from a scale (Mettler Toledo PB 1502 balance with an accuracy of 0.1 g) and loaded into the cylindrical furnace that is electrically heated. For one experiment, argon was first fed to the furnace to sweep away the residual air in the furnace. Then the temperature was increased to 1100 °C with a heating rate of 10 °C min⁻¹. As the temperature reached 1100 °C, the sample was held at this temperature for 30 minutes to further eliminate volatile matters, with mainly fixed carbon left. After this calcination stage, the inlet gas was shifted to a gas mixture of 50% CO₂ and 50% CO with a total flow of 4 L min⁻¹. The reactivity test was stopped as a weight loss corresponding to 20% fixed carbon loss was reached. The fixed carbon content was calculated based on proximate analysis, i.e. including ash. Once the desired weight loss was reached, the purge gas was shifted back to the inert gas and the sample was withdrawn from the hot zone. After cooling down, the reacted sample was collected and stored for further analysis. The same method has been used for testing CO₂ reactivity of different carbonaceous materials in previous work (Kaffash et al., 2021; Kaffash et al., 2022; Monesn et al., 2007).

2.4 Analysis of raw and reacted biocarbon

Microstructure and microchemistry of untreated and calcinated pellets were examined by using a scanning electron microscope (Zeiss Ultra 55, Limited Edition), equipped with energy-dispersive X-ray spectroscopy (EDS, Bruker XFlash). The raw and reacted samples were also analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES) to measure concentration of main inorganic elements.

3. Results and discussion

3.1 Weight loss and reactivity

Figure 1 shows the fraction of fixed carbon reacted as a function of time for of the CO₂ gasification tests of the three studied biocarbon samples. It can be seen that the birch biocarbons produced at atmospheric pressure and with a slow heating rate has higher reactivity than that produced from the pressurized reactor. It took about 440 s to get a weight loss corresponding to 20% fixed carbon loss for the sample BW 500 P that was produced from pyrolysis experiment with purging of N₂. On the contrary, 600 s was needed for the biocarbon produced under pressure to realize this.

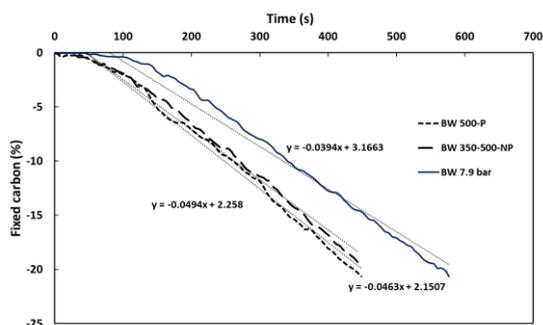


Figure 1: Fixed carbon loss of birch wood (BW) biocarbons produced at different conditions (500 P: atmospheric at 500°C with N₂ purge; 350-500: two-stage atmospheric without N₂ purge; 7.9 bar: pressurised, flash carbonisation at about 600°C)

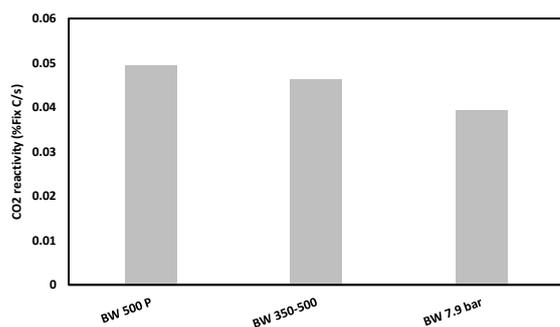


Figure 2: CO₂ reactivity of the birch wood biocarbons produced at different conditions

By using the slope of the weight loss curves obtained during CO₂ gasification of the biocarbon, the fraction of reacted fixed carbon per time can be calculated. The slope is considered as the CO₂-reactivity for comparison purpose. As shown in Figure 2, the birch wood biocarbon produced under atmospheric pressure with purging of N₂ has the highest reactivity, followed sample BW 350-500 produced by two-stage pyrolysis without purging of N₂, whereas the biocarbon produced from the pressurized reactor has the lowest reactivity.

It has been reported that higher yield of biocarbon can be realized by carbonizing biomass under restrained conditions, with increase of fixed carbon content of the produced biocarbon as well (Van Wesenbeeck et al., 2016). Such enhancement of biocarbon and fixed carbon yields is mainly attributed to extended residence time of tarry vapours in the reactor and promotion of secondary reactions of them. In our previous study, micro-TGA experiments showed that the biocarbons produced at higher pressures have lower CO₂ reactivity than those produced at atmospheric pressure (Bui et al., 2016). Results obtained in the current work showed a similar decreasing trend of reactivity for the biocarbon produced at elevated pressure.

3.2 Analysis of raw and reacted biocarbon

The studied biocarbons before and after CO₂ gasification reactivity tests were analysed in terms of concentration of inorganic elements and microstructure/chemistry. Figure 3 shows concentration of main inorganic elements in the raw and reacted biocarbons, which can play catalytic roles for the Boudouard reaction. The ICP-OES analysis results showed that K, Ca, P and Mg are four major inorganic elements that are abundant in raw and reacted biocarbons. It can be seen that the concentration of these four elements in the biocarbon produced from the pressurized reactor are higher than in those produced at atmospheric pressure. During a pressurized carbon production process, cracked tarry vapours might deposit and condensate on the charring biomass particles surfaces, which block pores and limit migration of inorganic elements from the inner structure to the external surface. On the other hand, for a slow heating rate carbonization process, the continuous release of volatiles and decomposition of the carbonaceous structure favour formation of biocarbon with a porous structure. Under such circumstance, more intensive heat and mass transfer within and at the external surface of charring biomass particles can cause greater loss of inorganic elements. It can partially explain the lower concentrations of K, Ca, P and Mg in the sample BW-500-N₂, as shown in the Figure 3.

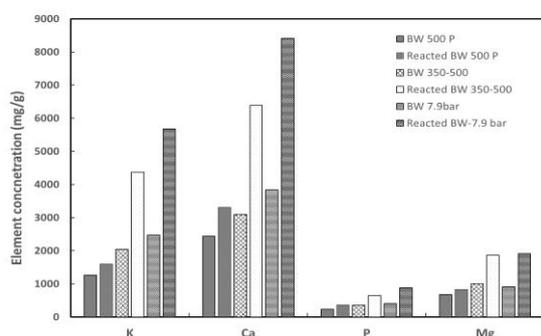


Figure 3: Concentration of main ash forming elements in the raw and reacted biocarbons

As the biocarbon is heated from room temperature to 1100 °C and during further isothermal gasification at 1100 °C, the absolute concentration of inorganic elements in the biocarbons increases as a result of consumption of carbon. Therefore, much higher concentrations of K, Ca, P and Mg are detected in the reacted biocarbons, as displayed in Figure 3. Enrichment factors of the four elements K, Ca, P and Mg were calculated as the ratio

between the absolute concentration of them in reacted and raw biocarbons, as shown in Table 2. It is interesting to see that the calculated enrichment factor for the sample BW-500-P are lower than for the other two samples. One explanation to this can be that more intensive release of inorganic elements took place during heating up and further gasification of the biocarbon BW-500-P. Brunauer–Emmett–Teller (BET) surface analysis on sample BW-500-P and BW-350-500 were conducted in the current work. It was found that BW-500-P has a BET surface area of $423 \text{ m}^2 \text{ g}^{-1}$, whereas the BET surface area of BW-350-500 is $262 \text{ m}^2 \text{ g}^{-1}$. Considering this, the inorganic elements might easier migrate and release from the biocarbon particles with high surface area and porosity due to more intensive heat and mass transfer.

Table 2: Enrichment factor of critical inorganic elements in the biocarbon after reactivity test

Element	BW 500 P	BW 350-500	BW 7.9bar
K	1.5	2.1	2.3
Ca	1.8	2.1	2.2
P	1.5	1.9	2.2
Mg	1.2	1.9	2.1

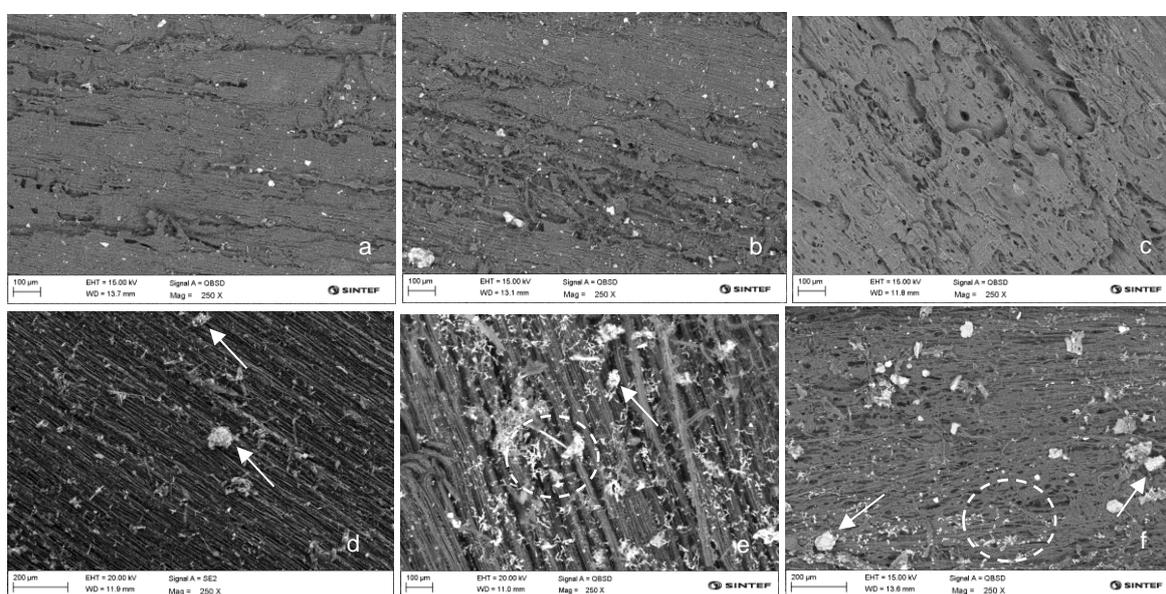


Figure 4: Scanning electron microscopy image of raw (a-c) and reacted (d-f) biocarbon BW-500-N₂, BW-350-500 and BW 600-7.9bar, respectively

The inorganic elements might promote the Boudouard reaction through acting as catalysts, providing active sites on the biocarbon surfaces, consequently resulting in high reactivity since the presence of the catalytic inorganic elements lower the activation energy of gasification reactions that take place on the carbon surface. Considering this, migration and transformation of inorganic elements to the biocarbon surface are critical for them to act as catalysts. Figure 4 shows SEM images taken in Backscattered-Electron (BSE) imaging mode. The images show contrast between areas with different chemical compositions. The areas and spots with high brightness indicate presence of elements with high atomic number. As shown in Figure 4 (a) and (b) for the biocarbons produced at atmospheric conditions, a few brightness spots can be observed from the darker background that shows the part of the surface of the biocarbon sample with carbon as the dominant element. Energy-dispersive X-ray (EDS) spectroscopy analyses revealed that Ca is a main element detected from these spots together with small amounts of O and C, indicating presence of Ca oxide and carbonates. In contrast, there are no such bright spots that can be observed from the biocarbon produced at pressurised conditions, in Figure 4 (c). It implies different transformation behaviours of inorganic elements in the biomass as it is carbonized under different conditions. Figure 4 (d)-(f) show BSE images of the biocarbons after the macro-TGA CO₂ gasification tests. Compared to the other two biocarbon samples, there are very few bright spots or areas that can be observed from Figure 4 (d), the BSE image taken of the reacted biocarbon BW-500-P. There are two agglomerates as indicated by two arrows, one in the middle and the other in the top of the image. The EDS analyses results revealed that Ca, C and O are dominant elements, together with Fe and Mg, indicating presence of carbonates. Large size of the agglomerates indicates accumulation, reaction and sintering of

contained inorganic elements. On the other hand, for the reacted biocarbons BW-350-500 and BW 600-7.9 bar, in respectively Figure 4 (e) and (f), there are quite many small white grains, and a few large solid gray particles can be observed from the BSE images taken. EDS analysis results showed that Ca, K, O and C are dominant elements detected from the white grains that might be Ca and K carbonates. For the large grey particles with irregular shapes, Si was detected as the main element, with additional small amounts of K, Fe and O, which can be due to soil and sand particles contaminated into the wood chips. Together with ICP-OES analysis on the reacted biocarbon samples, the SEM-EDS analyses implies that more inorganic elements like K and Ca migrate and transfer to the surface and volatilize away from biocarbon BW-500-N₂ during the gasification process. Transformation and especially presence of these elements on the biocarbon surface will enhance the Boudouard reaction and consume carbon consequently, which increases the reactivity of the biocarbon BW-500-N₂. Additionally, for both the raw and reacted biocarbon BW 600-7.9bar, the SEM analysis revealed that it has more compact structure and intact surface than the other two samples. It indicates lower surface area and porosity of this sample compared to the other two, which results in lower CO₂ gasification reactivity.

4. Conclusions

In this work, biocarbon was produced from birch wood chips under atmospheric and pressurized conditions. The CO₂ gasification reactivity of the produced biocarbons was studied by using a Macro-TGA at conditions relevant to those of industrial furnaces. The raw and reacted biocarbons were analyzed in terms of concentration of inorganic elements and microstructure/chemistry. It was found that biocarbons produced under different conditions have different CO₂ gasification reactivities. The biocarbon produced from an atmospheric slow heating rate carbonization process has the highest CO₂ reactivity, followed by the biocarbons produced from staged pyrolysis and in a pressurized carbonization process. It was also found that transformation and release behaviors of inorganic elements in the studied biocarbons are different. In the current work, the reactivity of the studied biocarbons is related to their physio-chemical properties (i.e., surface area and concentrations of inorganic elements) and transformation behaviors and catalytic effects of the inorganic elements during the gasification process.

Acknowledgments

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