Compactability and solubility of spruce wood derived biochar as an alternative to fossil carbon in metallurgy

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1. Abstract

Biochar serves as a viable alternative to fossil carbon in metallurgy while reducing the CO_2-content in the atmosphere. To enable the use of not only pulverized coal, for example in shaft furnaces, the agglomeration of biochar is needed. In this research briquetting of native German spruce wood was chosen as form of agglomeration and the different binders starch, bentonite and spruce wood ash were compared and tested in regard to the mechanical stability of the produced briquettes. Spruce wood ash proofed to form the most stable briquettes, but even those were not hard enough to perform mechanical testing on them. To determine their suitability for metallurgical application the carburization behaviour of the ash-bound briquettes in liquid iron was tested.

2. Introduction

The metallurgical industry is a major consumer of carbon, predominantly in solid form and from fossil origin. Its importance arose from processes that grew over centuries and relied on input materials that were plenty and readily available, which was the case for solid coal for large periods of time. Ultimately, many metallurgical processes rely on fossil coal or coke, not only as a reductant and energy producer but rather as an integral part of their internal mechanical structure [1]. Regardless of its purpose, most of the carbon consumption leads to direct CO_2 emissions; particularly when using fossil sources, the CO_2-content in the atmosphere will continue to rise indefinitely.

To counteract this effect the use of biochar is being heavily investigated, especially for processes which cannot be changed to the use of alternative reducing agents like hydrogen or electricity. Even though there will still be CO_2-emissions from processes using biochar, its origin is quite different to fossil coal: since biomass absorbed CO_2 from the atmosphere during its lifespan, the resulting CO_2 will not be added to the atmosphere but rather used circular, resulting in an anthropogenic carbon cycle [2].

To keep scope 2 and 3 emissions for the production of biochar low, it is preferable to use biomass which is native and close to the production site. In Germany’s case such a biomass is presented by spruce wood; a native tree species that was planted heavily after WW2 to produce building material for Europe. Nowadays, to avoid monocultures, those trees are being replaced by other tree species which result in large amounts of available spruce wood [3].

To enable a broader application of spruce wood biochar for metallurgical purposes, its briquetting was studied using various binders that were already used in other briquetting trials. By this it is also possible to use the biochar for applications like shaft furnaces where die carbon bearer plays a crucial role in stabilizing the burden.

3. Theoretical Assessment

3.1 Production process of biochar

The spruce wood biochar used in these trials was provided by CONVORIS, a German company currently producing biochar for agricultural purposes, such as fertilizer or cattle feed. In their production line spruce wood sawdust is treated by thermolysis, which enables an autothermal process. Products are pulverized biochar and an off-gas which is used for generation of electricity.

3.2 Briquetting of carbonaceous materials

Numerous metallurgical processes, such as the SAF process, depend on solid carbon not only as a reductant or for energy but rather as an integral part of the burden. The sole use of pulverized biochar is not possible in those cases. To enable those processes to become climate neutral, the agglomeration of pulverized biochar by pelletizing or briquetting is needed. Briquetting results in more uniform biochar compounds which proofs to be better for processes that depend on sufficient gas permeability of the burden. While the production of pellets does not require binders, briquetting without is only possible in rare cases, like with bituminous coal or anthracite, but not for biochar [4].

Binders can generally be divided into organic and inorganic. Examples are starches for organic binders, mineral compounds such as bentonite or ash for inorganics. Several advantages and disadvantages of industrial binders are listed in the Table 1 below.

While inorganic binders show a better thermal stability compared to organic binders like starch, they lead to larger slag amounts in metallurgical processes. Since thermal stability is a crucial property for pyrometallurgical processes, a larger slag amount is usually tolerated.

Table 1: Advantages and disadvantages of binders for briquetting

Binder	**Advantages**	**Disadvantages**
Organic		Low thermal stability
Starch	Availability	Competition with food security
Lignin	Available waste product [5]	
Inorganic	High thermal stability	Larger amounts of slag
Wood ash	If from same source as biochar: no added pollutants	In competition with production of biochar
Bentonite	Well known binder [6]	competition with other industrial applications [7]
Slags	High availability	Possibly contain pollutants (S, P)

3.3 Dissolution of carbon in liquid iron

By the dissolution of carbon in liquid iron its melting point is significantly lowered from 1536° C to minimal 1147° C. As a result, lower processing temperatures and lower energy consumption are possible. The mechanism of dissolving solid carbon in molten iron proceeds according to the following scheme on the surface of the carbon particles [1]:

1. diffusion of the molten iron into the pores of the carbon particle
2. boundary reaction: dissolution of the carbon into the melt until saturation
3. removal of the saturated melt through the pores to the outside
4. transport of the carburized melt through the boundary layer surrounding the particle

This boundary layer referred to in point 4. consists of the melt directly surrounding the particle. According toFigure 1, a linear drop in concentration from the saturation concentration C_S to the melt concentration C(t) can be assumed in this boundary layer.

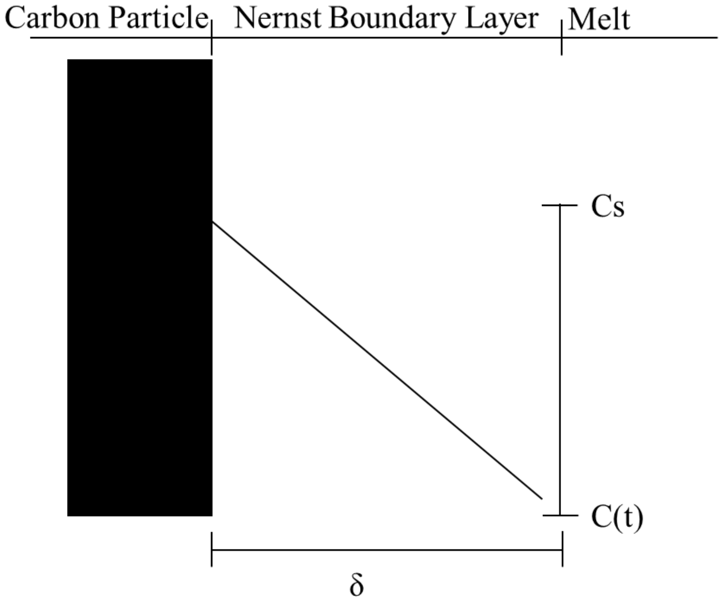

Figure 1: Concentration gradient of carbon within the Nernst boundary layer [8]

In various literary sources it has been shown that the rate of dissolution is limited by the mass transfer of carbon through the melt [9–13]. The mass transfer can be described by the first Fick's law using the following formula:

$$\mathrm{j} = -D * \frac{dC}{dx} \tag{1}$$

The material flow density is therefore dependent on the diffusion coefficient D. Assuming a linear concentration gradient over the distance δ from the carbon surface into the melt, $\frac{dC}{dx}$ corresponds to the concentration gradient. This results in the following relationship:

$$\frac{dC}{dx} = -\frac{C_s - C(t)}{\delta} \tag{2}$$

C_s describes the maximum carbon concentration on the surface of the carbon particle. C(t) is the carbon concentration after time t. Formulas (1) and (2) give the material flow density:

$$\mathrm{j} = -\frac{D}{\delta} * (C_s - C(t)) \tag{3}$$

The term $\frac{D}{\delta}$ is also referred to as the mass transfer coefficient k and is dependent on other variables such as the temperature or the current concentration gradient. Using the lastly derived equation (3), the total mass flow J can be calculated by taking the cross-sectional area A into consideration.

$$J = -A * k * (C_s - C(t)) \quad (4)$$

The carbon content of the melt increases as a result of the mass transfer. The change in the concentration of the volume corresponds to the change in the diffusion flow over time.

$$V * dC = J * dt \quad (5)$$

Formulas (4) and (5) give the speed of carburization:

$$\frac{dC}{dt} = -\frac{A}{V} * k * (C_s - C(t)) \quad (6)$$

The generally valid formula (7) for carburization can be formed from equation (6) by integration.

$$\frac{C_s - C(t)}{C_s - C_0} = exp - (\frac{A}{V} * k * t) \quad (7)$$

According to equation (7), the carburization rate depends on the concentration gradient between the melt and the saturation concentration, as well as the equilibrium constant k [1]. The concentration gradient can be maximized by convection in the system, e.g. by the use of gas bubbling or electromagnetic stirring, which, as well as the high temperature which increases *k*, accelerates carbon transfer within the system, leading to a fast dissolution reaction. Literature reports a significant carburization within the first 30 s after carbon charging and most of the carburization being complete after max. five minutes after charging [1, 14–16]

4. Methodology

4.1 Preparation of Input Materials

Spruce Wood Biochar

The composition of the biochar, according to CONVORIS, is shown in Table 2.

Table 2: Biochar composition, water free

Compound	C_{tot}	H_2	O_2	N_2	S	Ash
Weight %	93,50	0,31	2,37	0,51	< 0,03	4,20

Firstly, the grain size distribution was determined, the result is shown in Figure 2. It should be noted that a representative sampling proofed difficult as the biochar was delivered in a big bag in which particle separation by size took place due to the handling. The biochar was then fractioned using 500 µm, 125 µm and 80 µm sieves, resulting in four fractions of biochar.

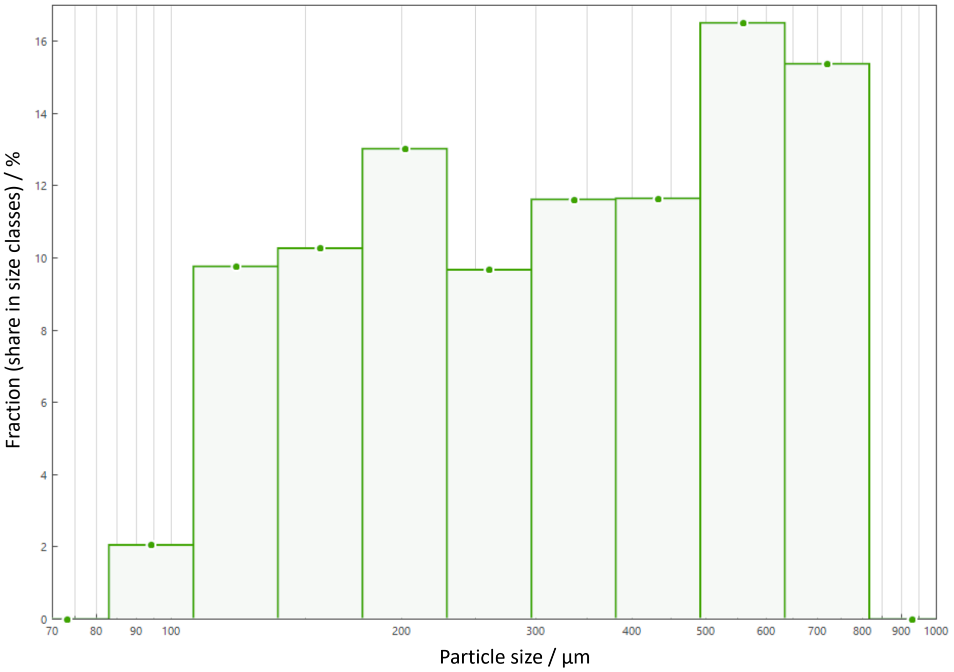

Figure 1: Grain size distribution in fractions of biochar sample

Spruce Wood Ash

Spruce wood ash was produced by roasting the > 500 µm biochar fraction at 450° C for 24 h. The product was a fine beige and very light material, shown in Figure 2.

Figure 2: Spruce wood ash, left: ashed >500 µm fraction; right: partially ashed < 80 µm fraction

Iron

Since iron has a relatively high solubility for carbon of up to 4,5 % at 1600° C and is easily available it was chosen for the solubility trials. The composition of the used iron is shown in Table 3 below. Each six kg block of input material was cut into roughly 250 g pieces.

Table 3: Composition of input metal in %weight, rest is iron

C	Si	Mn	P	S	Cu	Sn	Al	Cr	Mo	Ni	N
0,014	0,003	0,050	0,002	0,003	0,006	0,001	0,004	0,020	0,007	0,019	0,003

4.2 Briquetting

For these trials, fraction < 80 µm was chosen and agglomerated using a hydraulic tablet press by the company Herzog. To enhance handling and thermal stability of the produced briquettes, binders were chosen according to literature. Five kinds of briquettes were produced using a briquetting pressure of 150 kN and a holding time of one minute. The briquette compositions are shown in Table 4 below.

Table 4:Briquett compositions

	Binder	Water content
B1	Corn starch, 10 $\%_{\text{weight}}$ [17]	0.50 ml / g biochar
B2	Bentonite, 2 $\%_{\text{weight}}$ [18]	0.42 ml / g biochar
B3	Spruce wood ash, 10 $\%_{\text{weight}}$ [19]	0.44 ml / g biochar

Firstly, all of the binders were mixed with the biochar powder in dry state in plastic bags to ensure homogenous mixing. Afterwards, water was added, beginning with 0,3 ml / g biochar followed by manual mixing. Water was added batch wise until the mixture turned doughy and did not dust anymore. 8,0 g of the mixture were measured for each briquette and pressed, according to the aforementioned conditions.

One trial was performed with starch-bound briquettes to burn them at 110° C under Nitrogen atmosphere for 15 h. In another trial all briquettes, including unburned starch briquettes, were left to cure for 5 days at room temperature. Both processes were done to increase the briquettes’ stability.

4.3 Solubility trials

The solubility trials were done in a 4 kHz induction furnace, the set-up is shown in Figure 3 below. Melting was done inside an alumina crucible which was placed inside a clay-graphite crucible to protect against melt leakages. The crucibles were placed inside the induction coil on top of a chamotte brick to protect the furnace against the experimental temperature of 1550° C. For temperature measurement a type B thermocouple was used which was placed in the crucible within a protective alumina shell. To keep oxygen out of the system, 10 l/ min argon was blown using a lance. Furthermore, the system was covered using refractory materials.

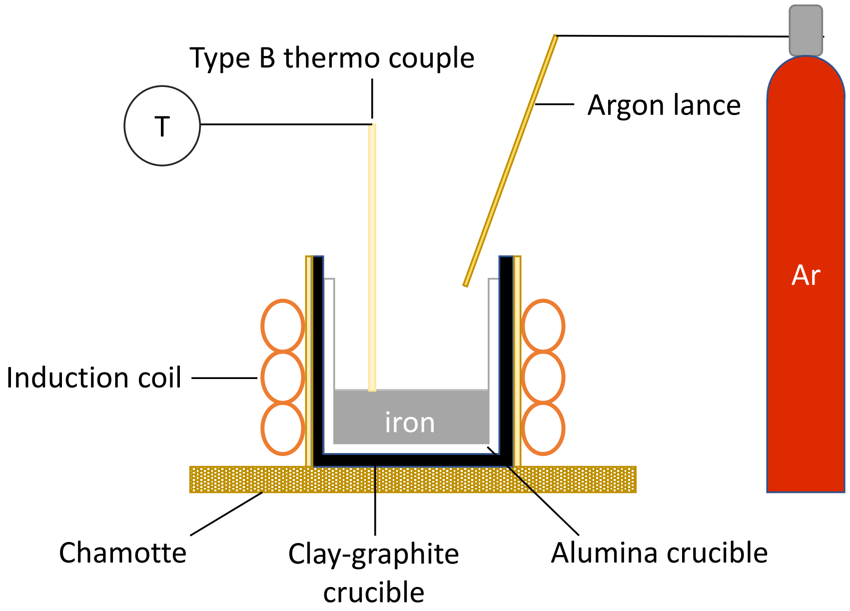

Figure 3: Set-Up for solubility trials

In the beginning, 505,5 g of iron were charged into the crucibles which were then covered and the system was heated to process temperature over the course of 2:40 h. With full power of 28 kW in the last 15 minutes of heating, 1550° C within the crucible were reached and power was lowered to 5 kW to keep the melt at 1550° C. The refractory material on top of the crucible was removed and 16,3 g of cured biochar briquettes were added and samples were taken with vacuum pipettes after 10 s, 30 s, 60 s and 120 s. 2,5 g more of briquettes were charged and samples were taken after 300 s after the first charge and 600 s.

5. Results and Discussion

5.1 Briquetting Trials

The starch-, bentonite, and ash-bound briquettes after their curing time are shown in Figure 4 below. An initial visual inspection shows obvious differences in the strength of the briquettes, which were confirmed by applying manual, external pressure. The starch briquettes showed lowest stability and a layered structure, both after burning, where it was more severe, and curing, as is shown in Figure 5.

The originally planned tests of mechanical strength in accordance with BS ISO 616:2021-10-29 could not be carried out as the briquettes did not develop the required strength [20].

Figure 4: Biochar briquettes after curing time; left to right: starch bound bentonite-bound, ash-bound

Figure 5: Starch-bound briquette after burning

Since the ash-bound briquettes showed the highest stability they were chosen for the following solubility trials. They were weighed before the trial and were 4.2, 4.1, 4.5 and 3.5 g each. This results in a weight loss ranging from 43.75% to 56.25%. A portion of this loss can be attributed to water evaporation: with an average of 0.44 g of water per gram of biochar and accounting for 10% ash content in the dry mixture, each briquette contains approximately 2.3 g of water which is equivalent to $28.75\%_{weight}$. Consequently, the remaining weight loss of 1.5 - 2.2 g or 15.00 – 27.5 $\%_{weight}$ per briquette may be attributed to the disintegration of loose coal particles or fragments breaking off during the curing process, since the briquettes were stable but not sufficiently strong.

5.2 Solubility results of ash bound briquettes in iron

Overall, 18.8 g of dry briquettes were added. The dry briquettes have a biochar content of 90 % which has a total carbon content of 93.5 %. This results in 15.8 g of carbon which have been added to the system, resulting in a theoretical carbon content of 3.62 % in the carburized iron.

The iron samples were measured after ISO 15350, the resulting carbon contents are shown in Figure 6 below. As can be seen, the carbon content rises quickly within the first 10 s to a maximum carbon content 140 to 640 ppm which is in line with literature [1, 14–16].The resulting speed of carburization is 50 ppm/s within this period. After 10 s the carbon content decreases at a decreasing rate until it reaches a final carbon content of 124 ppm five minutes after charging.

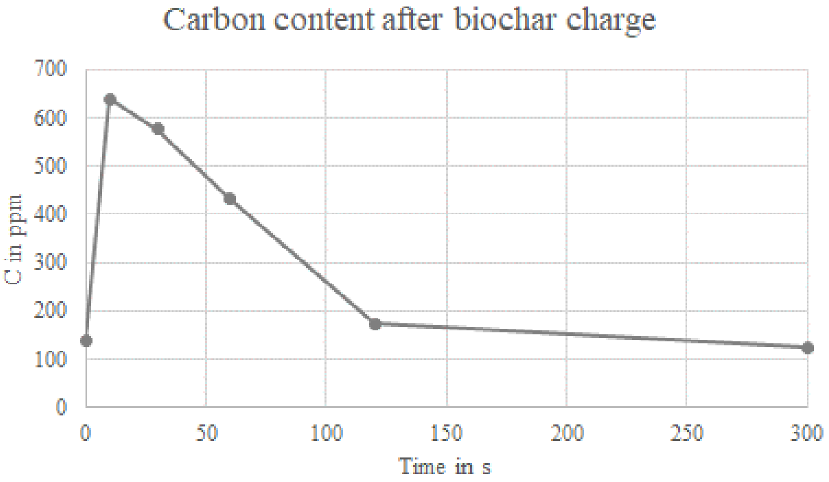

Figure 6: Measured carbon contents during solubility trials with ash-bound biochar briquette

One reason for the large discrepancy between theoretical maximum carbon content and the actual carbon content lies in the relatively open system. The argon blowing proofs insufficient in keeping oxygen away from the melt and the carbon, which is supported by the appearance of flames during charging of the briquettes. Also, some biochar was observed beside the crucible which is due to instability of the briquette while charging and could be prohibited by an improved briquetting process.

Summary and Outlook

It was possible to form briquettes with different binders, where the spruce wood ash-bound one was the most stable, yet not stable enough for metallurgical purposes. In the future, the briquetting process will be improved in order to produce briquettes that will withstand handling and can uphold the burden. Once those are produced, their metallurgical suitability will be further investigated. Those trials will be performed in a more shielded environment, to protect the biochar from outside oxygen.

The ultimate goal is to produce biochar briquettes which properties are optimized for industrial processes like the climate neutral production of hot metal in SAFs or the recycling of copper slag, preferably with native raw materials. This includes mechanical stability while handling, thermal stability during the process and an adequate reactivity. Furthermore, the use of inorganic binders as slag formers is to be investigated, decreasing the amount of added fluxes in industrial processes or making them obsolete.

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