Utilization of Charcoal Obtained from Woody Biomass in Metallurgical Processes Based on Solid–Gas Reactions

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Abstract: The high demand for carbon-based products within pyrometallurgy is placing the industry in an increasingly challenging position to meet stringent requirements. To transition away from fossil carbon carriers, biochar emerges as a sustainable and CO_2-neutral alternative, presenting a viable solution without necessitating fundamental adjustments to plant technology, unlike hydrogen as an alternative reducing agent. Prior investigations have underscored the potential of woody biomass pyrolysis products for CO_2-neutral metallurgy. Nonetheless, it is imperative to recognize that biochar must meet distinct requirements across various metallurgical processes. This paper conducts a comparative analysis between biochar and petroleum coke using thermogravimetric analyses, surface measurements, reactivity assessments, and scanning electron microscopy. Furthermore, the performance in a furnace for simulating the Waelz process, specifically regarding ZnO reduction, is scrutinized. The results illustrate the optical differences between petroleum coke and biochar and the significantly higher reactivity and specific surface area of biochar. When used in solid–gas reactors, it is observed that due to its high reactivity, biochar reacts more vigorously and carbon is completely consumed. However, during the reduction of ZnO, only minor differences were monitored, making biochar comparable to petroleum coke. Therefore, under certain constraints, biochar can be considered a potential substitute for metallurgical solid–gas reactions.

Keywords: biochar; alternative reducing agent; CO_2-neutral metallurgy

1. Introduction

In recent years, the issue of carbon emissions has become a prominent global concern due to its impact on the environment and climate change. The use of fossil fuels in metallurgical processes is one of the significant contributors to greenhouse gas emissions, mainly carbon dioxide (CO_2), which has led to an increased interest in alternative carbon sources. Biomass has emerged as a promising alternative to fossil fuels in metallurgical processes, given its potential to reduce CO_2 emissions. Biomass refers to any organic material derived from plants or animals that can be used as a source of energy [1]. When processed, biomass releases carbon dioxide, but this is offset by the fact that the carbon dioxide is reabsorbed by plants during their growth, creating a closed loop in which no net carbon is released [2]. This makes biomass a carbon-neutral fuel source.

The use of biomass in metallurgy can have additional environmental benefits, such as reducing the reliance on fossil carbon carriers, which are often associated with environmental pollution. Additionally, using biomass in metallurgy can help to reduce the demand for CO_2 certificates, which are needed to offset carbon emissions from fossil fuel use [2]. The reduced demand for CO_2 certificates can lead to lower costs for companies and create additional incentives for the use of biomass.

The direct use of biomass in metallurgical aggregates is not suitable for most applications. Thermal pre-treatment is therefore necessary to obtain an adequate product for reduction processes. In general, biomass undergoes thermochemical processes, specifically pyrolytic decomposition, resulting in combustible solid, liquid, and gaseous components.

This process is called pyrolysis and is usually realized in the absence of oxygen. Throughout the entire process, biomass components such as cellulose, hemicellulose, and lignin undergo splitting reactions, with large hydrocarbon molecules from the biomass being broken down into smaller hydrocarbon molecules during pyrolysis. Depending on temperature, residence time, and other reactor conditions, these reactions vary, consequently determining the yields of solid, liquid, and gaseous main products. This includes distinguishing between fast pyrolysis, primarily focused on producing liquids (such as pyrolysis oils), and slow pyrolysis, intended for generating primarily solid secondary energy carriers (like biochar) and gas. In the context of fast pyrolysis, both the so-called flash pyrolysis and intermediate pyrolysis are encompassed. Slow pyrolysis includes processes for biochar production and torrefaction. The shared primary goal of these procedures is mainly the generation of solid fuel with defined coal-like properties. Table 1 illustrates the yields of the three main product groups and presents the fundamental reaction parameters. The proportions of solid, liquid, and gaseous components also vary considerably across different pyrolysis variants [3–6].

Table 1. Typical process conditions and yields of main products in biomass pyrolysis [4,7,8].

Process	Conditions	Liquid [wt.%]	Solid [wt.%]	Gas [wt.%]
Fast				
Fast (flash)	~500 °C (450–600 °C) Hot gas retention time < 2–3 s High heating rate	~75	~12	~13
Medium fast (intermediate)	~500 °C (450–600 °C) Hot gas retention time 10–30 s Middle to high heating rate	~50	~25	~25
Slow				
Carbonization	~400 °C Hot gas retention time (h-d) Low heating rate	~30	~35	~35
Torrefaction	~250–290 °C Solid retention time 10–30 s Low to high heating rate	~5	~80	~20
Gasification	Up to 1250 °C	~6	~9	~85

Especially for the use of pyrolyzed biomass as an alternative reducing agent in metallurgy, the emphasis is on producing biochar with a high carbon content. This can be accomplished through an extended residence time and high temperatures. The elevated carbon content resulting from higher temperatures is achieved by reducing the oxygen and hydrogen content and the proportion of volatile matter, respectively [7,9–11]. This results in a suitable product for application in carbothermic reduction processes, although at the expense of yield [10,12,13].

Previous research conducted by the Chair of Nonferrous Metallurgy at the Montanuniversitaet Leoben has demonstrated that woody biomass offers the best potential for use as a substitute [10,12,13].

Table 2 provides a comparison of the characteristics of biochar and fossil coke utilized in metallurgical processes. The information reveals that specific varieties of high-quality biochar exhibit a superior fixed carbon value and reduced levels of volatile matter. As wood naturally possesses a comparatively high carbon content, corresponding pyrolysis processes can effortlessly attain carbon contents of >80 wt.% and <10 wt.% for volatile matter in biochar [13]. Consequently, equivalent proportions of carbon and volatile components can be attained compared to conventionally used coke. It is noteworthy that these findings underscore the potential of certain high-quality biochars as viable alternatives in metallurgical applications, offering comparable properties to conventionally used coke.

Biochar demonstrates markedly reduced sulfur levels when contrasted with fossil coke. Moreover, in certain processes, the ash content and ash basicity emerge as crucial parameters that require consideration. Here, as well, it is feasible to modify the selection of initial materials, as both basic and acidic ashes can be present in biochar.

Table 2. Comparison between biochar and fossil coke adapted from [14–19].

Parameter	Unit	Biochar	Petroleum Coke
C_{fix}	[wt.%]	65–93.8	84–90
Volatile matter	[wt.%]	3.8–35	11.8–1.7
Ash content	[wt.%]	0.4–5.9	0.4–10.89
Ash basicity	[CaO/SiO$_2$]	<1 and >1	<0.1
Sulfur content	[wt.%]	<0.1	0.45–7.9
Reactivity	-	Medium/high	Low/medium

Biochar, a carbon-rich material derived from the pyrolysis of biomass, exhibits diverse physical and chemical characteristics that influence its suitability for various industrial processes. The characterization of this sustainable product is a pivotal aspect in understanding its properties and optimizing its applications, particularly in the realm of metallurgical aggregates. In the context of this industry, precise characterization becomes imperative due to the partly stringent requirements of the applications, as factors such as specific surface area, reactivity, or chemical composition play a crucial role in determining the applicability of biochar. The knowledge of these characteristics aids in tailoring biochar to meet specific requirements, enhancing its performance as a sustainable carbonaceous material. As industries increasingly embrace sustainable practices, the accurate characterization of biochar becomes indispensable for ensuring its successful integration into metallurgical operations.

In this article, the potential application of biomass in metallurgical processes will be described with a focus on characterization and its use as an alternative reducing agent in solid–gas experiments. As biochar is intended to be an alternative reducing agent for fossil materials such as petroleum coke, a comparison of the fossil and renewable carbon sources is conducted during the characterization and process investigations.

2. Materials and Methods

The characterization methods used for the intended application are listed in the following sections.

2.1. Thermogravimetric Analysis

A modified and extended version of the TGA PT 1600 model from Linseis Messgeräte GmbH (Selb, Germany) was used as the analyzer. The software (Linseis TA Evaluation v2.3.3.178, Selb, Germany) for the system was provided by the manufacturer. Based on the standard for thermogravimetric analysis, the percentage content of moisture, volatile components, and ash was determined under changing atmospheres [20]. An N$_2$ atmosphere was applied for the heating phase and CO$_2$ was utilized to determine the ash content and the reaction behavior. Afterward, the amount of carbon (C$_{fix}$) can be calculated from the three values obtained by subtracting from the initial mass.

2.2. Specific Surface

The Brunauer–Emmett–Teller (B.E.T.) surface analysis is a crucial technique in characterizing biochar, offering insights into its specific surface area. In the context of biochar, B.E.T. is widely employed to quantify the available surface for adsorption and reactions, providing valuable information for diverse applications.

During the analysis, biochar samples are subjected to adsorption and desorption of a known gas, typically nitrogen, at varying pressures and temperatures. The resulting isotherms are then utilized to calculate the specific surface area based on the B.E.T. equation. Based on the research conducted by Brunauer, Emmett, and Teller, Langmuir's kinetic

theory of adsorption can be expanded to encompass multilayer adsorption. This expansion, commonly referred to as the B.E.T. theory, posits the existence of a dynamic equilibrium between the uppermost molecules in adsorbed stacks and the vapor phase. In cases where a surface is exclusively covered with a monolayer of adsorbate, an equilibrium is established between that layer and the vapor. When two or more layers are adsorbed, the highest layer consistently maintains equilibrium [21,22].

The analyses were conducted using a Quantachrome NOVA 2000e surface area analyzer (Boynton Beach, FL, USA). Following the manufacturer's recommendation and [23], CO_2 was employed as the measuring gas for the analysis. Unlike analyses with nitrogen as the adsorbate, CO_2 requires only a sample temperature of 0 °C $\pm$ 0.1. This temperature was achieved using a thermostat and a double-walled vessel filled with coolant inside and outside. Constant measurement of the temperature with a digital thermometer directly next to the immersed glass tubes made it possible to keep within the temperature limits.

2.3. Reactivity

Basically, the reactivity of carbonaceous materials refers to the chemical behavior and the conversion rate of carbon at high temperatures with different gases such as O_2 or CO_2, respectively. The reaction with CO_2 is particularly important for metallurgical applications, as the resulting CO (Equation (1)) acts as an additional reducing agent. The reaction of solid carbon with CO_2 gas is known as the Boudouard equilibrium and is an essential equation in metallurgy. In addition, this gas has the advantage of a slower reaction and thus enables simpler and more accurate measurement compared to a reactivity determination with O_2. The reactivity of biochar can be determined by calculating the Coke Reactivity Index (CRI) according to Formula (2).

$$C + \{CO_2\} = 2\{CO\} \tag{1}$$

$$CRI[\%] = \frac{\text{initialweight} - \text{outputweight}}{\text{initialweight}} \cdot 100 \tag{2}$$

However, the standard specified for this procedure requires a grain size of 19–22.4 mm for the samples to be analyzed [24]. Since most of the samples used for this work had a smaller grain size, an adapted method based on the specified standard was employed. This involved preparing the samples only by drying them at 105 °C and analyzing them without altering the grain size. The use of such adapted procedures has been common in past scientific analyses conducted at the Chair of Non-ferrous Metallurgy (see [12,13]). The equipment utilized was the STF 15/450/E/301 tube furnace from Carbolite (Sheffield, UK), with an additional stopper, including a connector for gas purging. The furnace heated the material to 1000 °C under nitrogen gas, followed by a 15 min treatment with a CO_2 gas stream. Afterward, the microgranules cooled down to room temperature in a nitrogen atmosphere.

2.4. Scanning Electron Microscope

A scanning electron microscope (Jeol JSM-IT300, Tokyo, Japan) was used for an optical comparison of the carbon carriers and analyses of the material treated in the TBRC. The following settings were selected for all analyses on the scanning electron microscope (SEM):

- Acceleration voltage: 20 kV;
- Working distance: 10 mm;
- Beam current: 60–80 pA;
- Aperture: ø 30 μm.

A secondary electron (SE) detector provided by Jeol (Freising, Germany) was used especially for the comparison of the carbon carriers since the topography of the material surfaces can be better visualized. For the analyses using an EDX detector from Oxford Instruments (Abington, UK), semi-quantitative measurements were carried out at three points on each sample. An average value was then calculated from the results for further evaluation.

2.5. Microgranulation

The feed material for the Waelz process is usually mixed with slag formers and a reducing agent followed by pelletizing or granulation. A compulsory mixer (type Eirich EL1, Stuttgart, Germany) with a capacity of one liter was used to ensure that the feed material was comparable to the industrial feedstock. The steel mill dust for the trials, which was already blended with slag formers, was mixed with the calculated quantity of carbon carrier (stoichiometric factor: 1.15) and converted into a microgranulate by adding water. The amount of water added depends largely on the moisture of the feed materials and was in the range of 70 mL to 120 mL per batch (600–800 g). The manufacturer of the system recommends a maximum filling volume of 80 % of the nominal volume of the mixing container for granulation tasks. Other parameters, in addition to the details in Table 3, for the production of microgranules according to the manufacturer's recommendations are as follows:

-   Mixing tool: Z swirler;
-   Mixing vessel speed: 0.5 m/s (stage 1);
-   Mixing vessel angle: 30°.

Table 3. Parameters for microgranule production with an Erich mixer type EL1.

Processing Steps -	Rotational Speed [m/s]	Rotation Direction -	Treatment Time [min]
Dry mixing	15–25	Countercurrent	1–2
Addition of water	20–30	Countercurrent	1–2
Granulation	20–30	Countercurrent	1–2

2.6. Furnaces for Trials

In addition to the main unit, the Top Blown Rotary Converter (TBRC), a smaller unit was applied to compare the fossil and alternative carbon carriers. These preliminary tests formed the basis for the subsequent TBRC tests. The Carbolite STF 15/450/E/301 tube furnace was used for initial investigations into solid–gas processes. As the results of the tube furnace tests showed that it was not possible to simulate a Waelz process on this scale, a switch was therefore made to the TBRC. With the larger amount of feed material (20 kg), it was possible to achieve rolling via rotation similar to a Waelz process. Figure 1 shows the schematic setup for the TBRC experiments to investigate the biochar behavior in solid–gas reactors. The temperature was controlled by a O_2/CH_4 burner and the flow rate, respectively. The trials were based on the temperature measured on the oven cover and additional measurements with a hand-held device. The angle of the aggregate was set to 10.5 ° at a speed of 1–2 rpm for the solid–gas tests.

Table 4 shows the parameters for the trials conducted in the TBRC with petroleum coke, biochar, and a mixture of both. Since biochar 2 had a very high carbon content and was already available as a fine fraction, it was used for the production of microgranules and the simulation of the heating phase in the TBRC. The heat-up time to maximum temperature was about three hours, with a starting temperature of 650 °C. One holding point with a duration of 30 min was at 650 °C and the other three points with the same duration were at the final temperature.

In order to obtain reproducible and meaningful measured values, the TBRC vessel was temporarily stopped, and the extracted samples (~100 g) were cooled to room temperature in a small vessel with N_2 purging. Through cooling with inert gas, it was possible to prevent further reactions with the atmosphere.
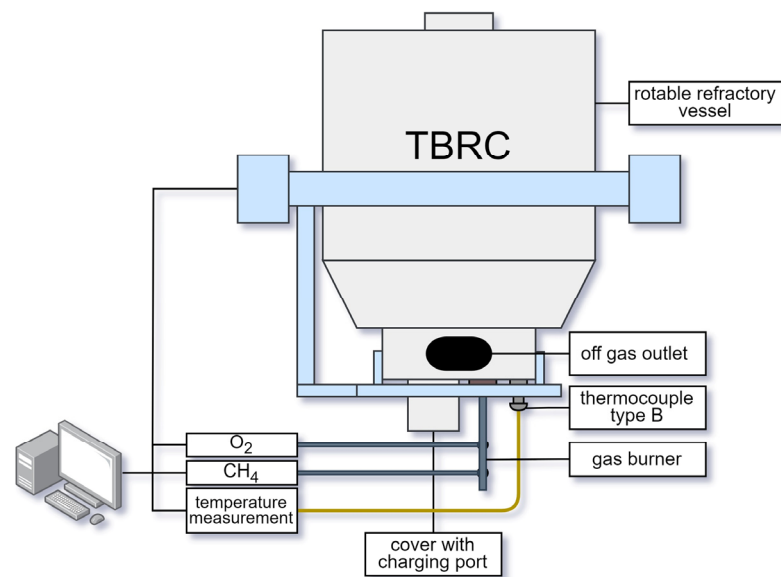
Figure 1. Schematic top view of the test setup for simulating the heating phase of a Waelz process in a TBRC.

Table 4. List of the parameters for the TBRC trials.

Trial No.	Petroleum Coke [%]	Biochar [%]	Max. Temperature [°C]	Holding Point [°C]
1	-	100	1050	650
2	-	100	1050	1050
3	100	-	1050	1050
4	50	50	1050	1050

3. Results

This section lists the results of the characterization of the carbon carriers and the tests performed in the TBRC.

3.1. Thermogravimetric Analysis

The thermogravimetric analysis conducted revealed distinctive thermal degradation patterns among the various biochar samples (Figure 2). Initially, upon heating to 200 °C under a nitrogen atmosphere, the first step observed was the evaporation of moisture from the samples. After heating to 200 °C, the temperature was held for 20 min to remove the water and achieve a constant mass. By heating the device to 950 °C in the presence of N_2, the volatile components were removed from the biochar samples in the second step of the analysis. After reaching 950 °C, the temperature was maintained until mass stability was achieved after the removal of volatile components. The sample was also held at the maximum temperature to determine the ash content upon reaching mass stability. Biochar 2 was noticeable because it was characterized by a high moisture content and a low content of volatile components. This combination resulted in the mass being very similar to the other biochar samples when it reached 950 °C after the two components had evaporated. In contrast, biochar 4 had a minimal moisture content and a low amount of volatile matter, which resulted in the highest mass level under nitrogen purging conditions at 950 °C. Following the 950 °C holding point, the samples underwent flushing with CO_2 to observe their combustion behavior and to determine the ash content. Interestingly, all biochar samples exhibited a comparable mass loss during this phase. To further elucidate the differences among the samples, a separate diagram (Figure 3) was generated.
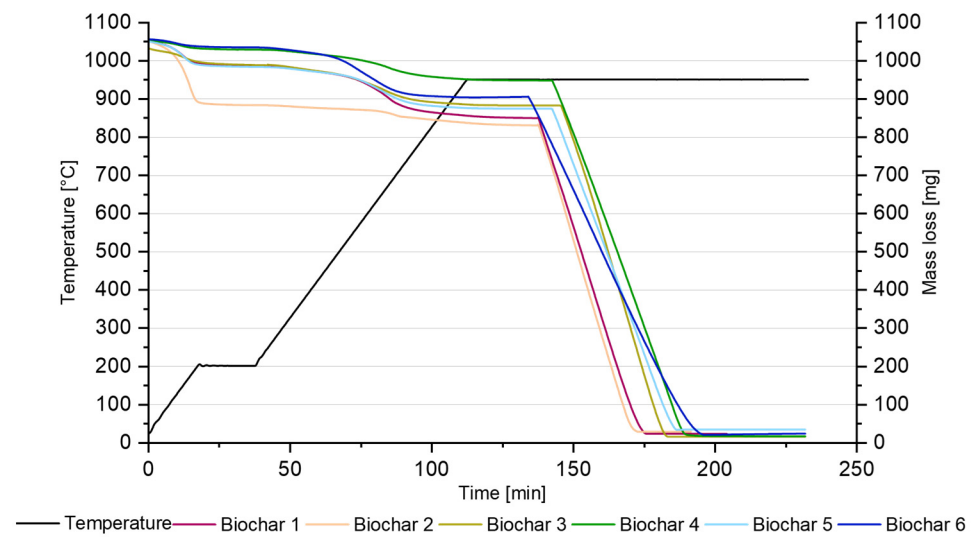
Figure 2. Thermogravimetric analyses of the biochar with the temperature curve and the mass losses.
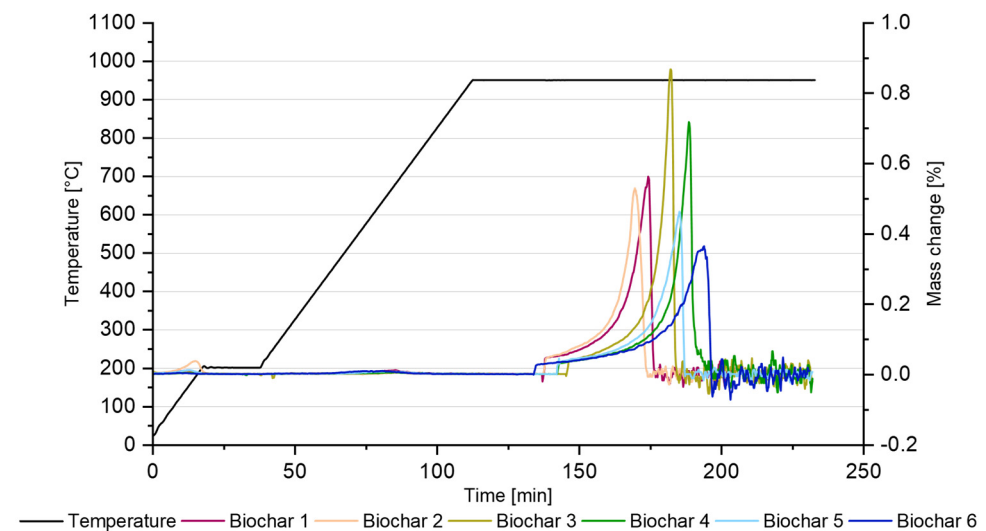

Figure 3. Thermogravimetric analyses of the biochar with the temperature curve and the percentage mass changes.

Upon closer examination, it was observed that biochar 3 displayed the fastest reaction kinetics, whereas biochar 6 exhibited the slowest. Compared with the results of petroleum coke, similar values of moisture, volatile components, and ash content could be determined. However, the major difference was the rate of reaction of the carbon carrier with CO_2 (Figure 4). As can be seen in the diagrams, the reaction according to Boudouard was almost 10 times slower. This is also evident in the gradient of the percentage mass decrease during the experiments (Figure 5). These reactivity results highlight the clear differences between the carbon carriers and illustrate their high importance for various applications in metallurgy.

The composition of the tested carbon carriers after calculation of the carbon content is shown in Table 5. The values indicate that biochar 2 had the highest water content and biochar 6 the lowest. However, the widely differing water content makes it difficult to compare the materials. It is therefore advisable to convert to dry matter. When comparing the dry substances, all tested biochars exhibit similar carbon values to petroleum coke. The ash content also falls within a comparable range, so the greatest difference, aside from moisture content, lies in the proportion of volatile components.
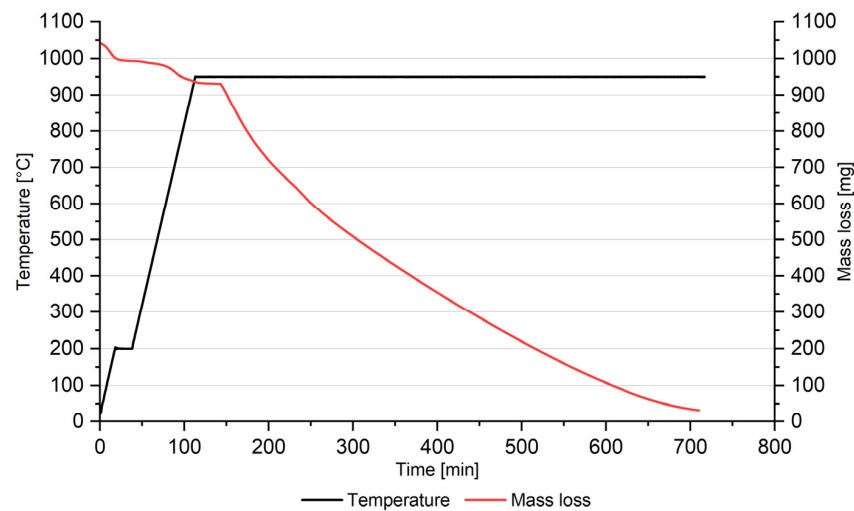
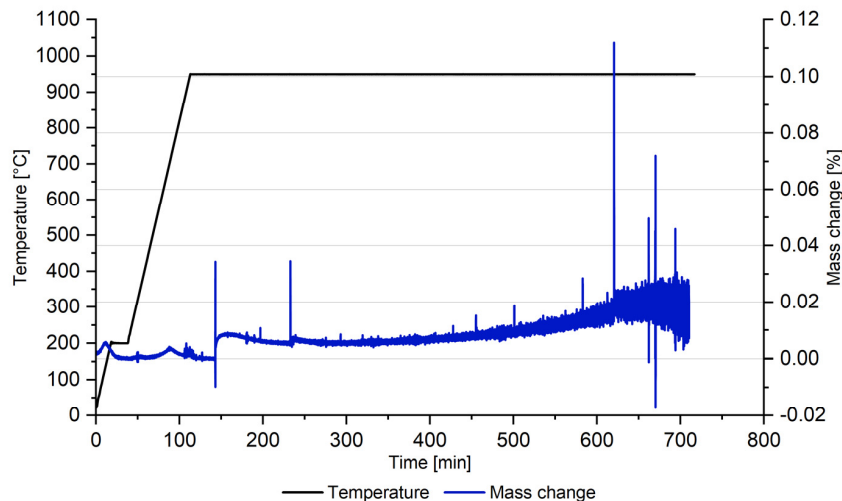**Figure 4.** Thermogravimetric analyses of the petroleum coke with the temperature curve and the mass loss.

Figure 5. Thermogravimetric analyses of the petroleum coke with the temperature curve and the percentage mass change.

Table 5. Results of the thermogravimetric analysis of the different biochar and the petroleum coke.

	C_{fix} [wt.%]	Volatiles [wt.%]	Ash [wt.%]	H_2O [wt.%]
Biochar 1	78.81	13.03	1.98	6.18
Biochar 2	76.60	5.04	2.38	15.98
Biochar 3	84.17	10.25	1.23	4.35
Biochar 4	88.53	7.61	1.67	2.19
Biochar 5	80.01	10.37	3.15	6.47
Biochar 6	83.38	12.31	2.32	1.99
Petroleum coke	86.95	5.64	2.40	4.60

3.2. Specific Surface

Table 6 depicts the results obtained from the B.E.T. surface measurements. The data obtained varied from 343 m^2/g to 425.2 m^2/g for biochar. As expected, a lower value for petroleum coke was measured. Since no valid measurement could be performed for biochar 6, a value from the literature for this specific type of wood-based biochar was used. However, it aligned well with the overall picture of the higher specific surface area of

biochar compared to petroleum coke. Due to the structure of biomass derived from wood, resulting biochar possesses an open-pore structure. The numerous pores contribute to a very large surface area. Conversely, petroleum coke has a closed surface with few pores, leading to a smaller surface area.

Table 6. Results of the specific surface measurements of the different biochar and the petroleum coke. Value for Biochar 6 reprinted from [25].

	Petroleum Coke	Biochar 1	Biochar 2	Biochar 3	Biochar 4	Biochar 5	Biochar 6
[m^2/g]	260.1	398.0	369.6	425.2	405.0	391.6	343.0

3.3. Reactivity

Table 7 shows the data from the reactivity measurements in the tube furnace. Similar to the results for the specific surface area, the values for biochar are significantly higher than for petroleum coke. Biochar 3 shows the highest reactivity and petroleum coke the lowest.

Table 7. Results of the reactivity measurements of the different biochar and the petroleum coke.

	Petroleum Coke	Biochar 1	Biochar 2	Biochar 3	Biochar 4	Biochar 5	Biochar 6
[%]	16.21	44.74	50.76	53.04	43.36	47.61	43.14

3.4. Scanning Electron Microscope

Figure 6 displays images of all carbon carriers utilized, captured with the SE detector in the SEM (strewn slide samples). While all biochar exhibited a similar open-pore structure, the surface of the petroleum coke appears closed. Additionally, petroleum coke possesses a globular shape, whereas the structure of biochar is attributed to its woody or fibrous composition.
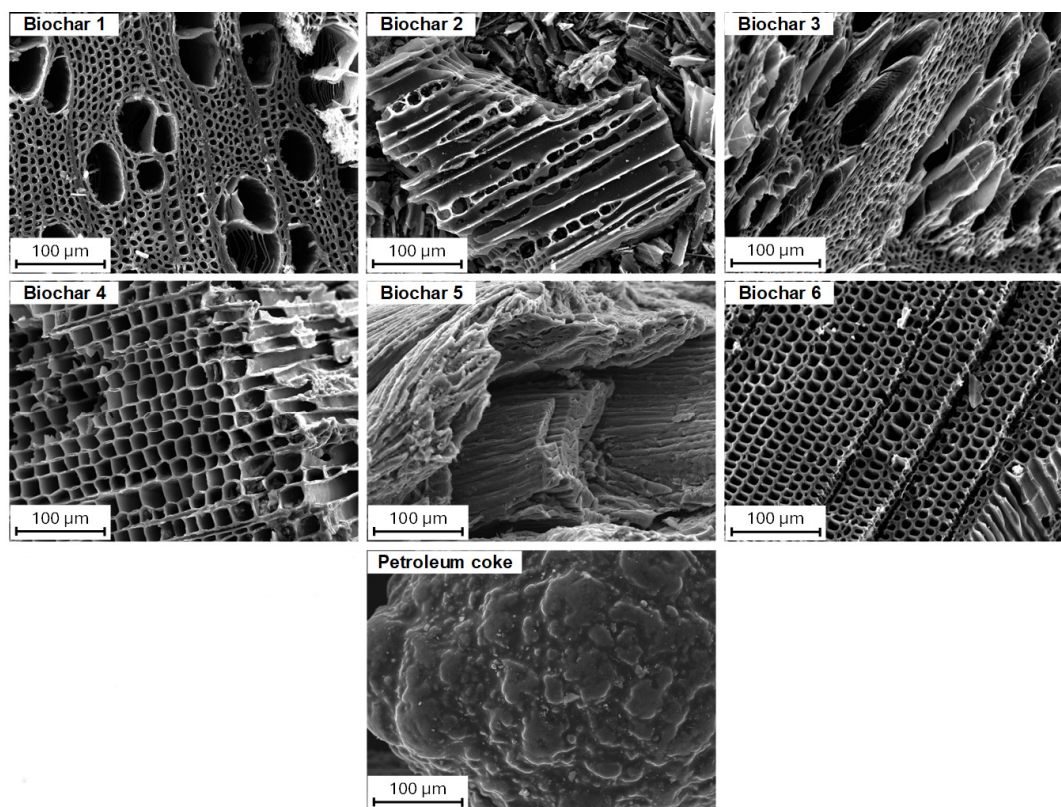

Figure 6. SEM-SE images of different carbon carriers prepared as strewn slide samples. Own unpublished data and reprinted from [26].

3.5. Microgranulation

It was possible to successfully produce the microgranules shown in Figure 7 using the Eirich mixer type EL1. The agglomerates produced with water as a binder have an average diameter of 0–4 mm and correspond to the grain sizes typically used in industry. By mixing and granulating, the carbon carrier particles were almost completely coated with steel mill dust. This ensured that the two materials were in the highest possible contact with each other.

Figure 7. Microgranules made of steel mill dust, slag former, carbon carrier, and water in an Eirich mixer type EL1.

3.6. TBRC Trials

Due to the numerous and complex reactions within a Waelz kiln, a precise downscaling to laboratory scale in a tube furnace was not possible. Nevertheless, an approximate simulation of single zones of the Waelz kiln on a small scale is feasible. Whereas the reduction of ZnO worked well, the heating zone proved to be problematic. Due to the high reactivity of the biochar, a significant proportion of the ZnO was already reduced during heating despite nitrogen purging. Even when using petroleum coke, there was a significant reduction effect during heating up. Experiments were carried out on a larger scale (TBRC) to solve this problem. Figure 8 shows the selected curves of the ZnO from the test series with 30 min holding points at ~650 °C and ~1050 °C. Whereas the different holding points had no influence on the behavior of the biochar, all experiments showed a similar reduction of ZnO. The lowest value was achieved with the mixture containing biochar and petroleum coke.
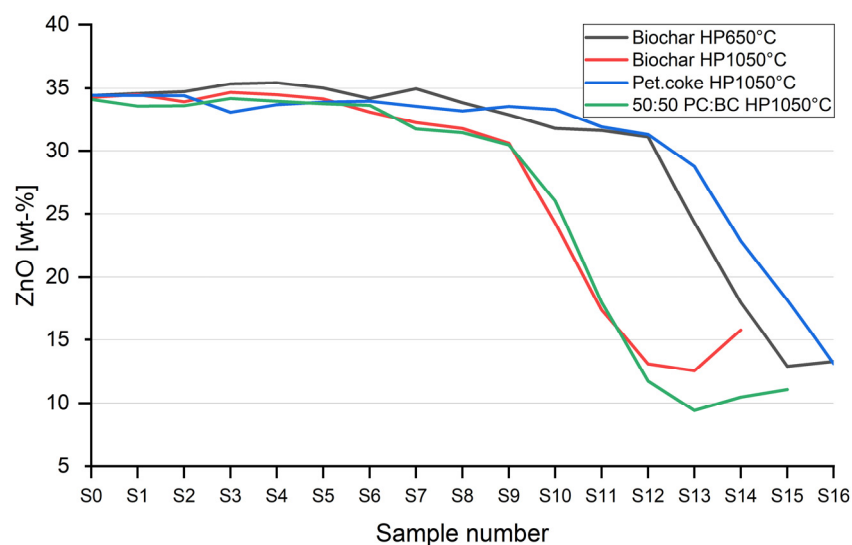

Figure 8. ZnO profiles of the simulation for the heating phase of the Waelz process in the TBRC. HP: holding point; PC: petroleum coke; BC: biochar; S: sample.

Figure 9 shows the carbon content profiles across the experiment duration of 3.5 to 4 h. When using biochar, it appears that no carbon remains in the material at the end of the tests, whereas a small amount is still present in the trials with petroleum coke. Although the trial parameters differed, such as holding point and carbon carrier, the carbon contents decreased similarly over time. The carbon analyses were conducted by the accredited laboratories Activation Laboratories Ltd. (Ancaster, ON, Canada) and Aufbereitung, Recycling, und Prüftechnik GmbH (Leoben, Austria).
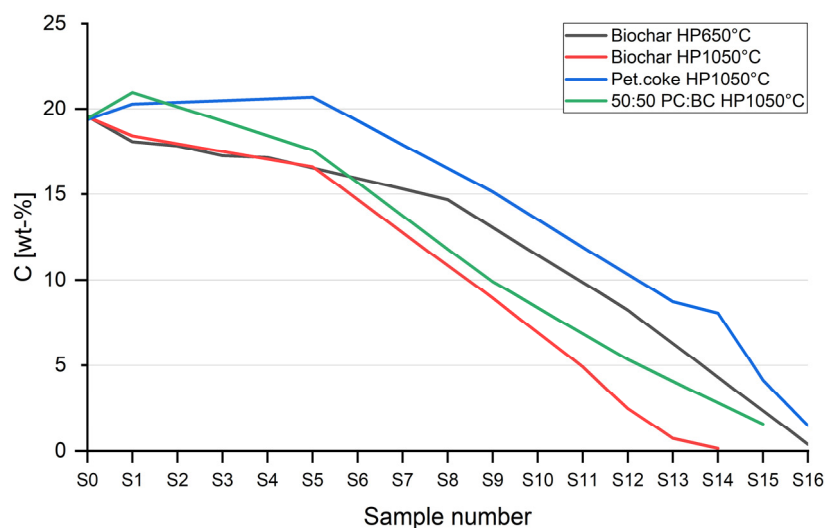

Figure 9. C profiles of the simulation for the heating phase of the Waelz process in the TBRC. HP: holding point; PC: petroleum coke; BC: biochar; S: sample.

4. Discussion

The thermogravimetric analysis provides a good opportunity to gain an initial impression of the main properties and composition data. Biochar has a hygroscopic character, which can cause a highly fluctuating moisture content. This was observed during extended storage of biochar 2. The moisture contents of different batches also vary. Therefore, storage and transportation are crucial for their use in pyrometallurgical aggregates. In addition to the negative effect of the additional energy required to vaporize the water, an increased moisture content has a positive effect on the handling of the biochar, too. As a very dry material has a greater tendency to dust, this can lead to a higher proportion of losses. The negative influence on work safety should also be mentioned, as the inhalation of biochar dust is classified as harmful to health and the potential risk of dust explosions also increases. The moisture content in biochar furthermore complicates direct comparisons among different samples and with petroleum coke. Hence, it is advisable to always consider the dry substance.

For the investigations mentioned here, biochar with a carbon content ranging from 84 wt.% to approximately 91 wt.% shows a comparable proportion to petroleum coke (~91 wt.%). Since the ash content is also at a very similar level, the volatile component content shows the greatest variation.

The production of an agglomerated feedstock for the tests in relation to the Waelz process led to a good result. A very homogeneous agglomerate could be produced which hardly required any improvements. The setting of defined grain fractions of the feed products for the Eirich mixer could lead to even better and more consistent granules. However, as the final microgranules already exhibit better agglomeration than the material used in industrial Waelz processes, further optimization does not appear to be necessary.

The most significant difference between petroleum coke and biochar lies in their reaction rate with CO_2. Petroleum coke requires significantly more time for conversion following the Boudouard reaction. This manner is due to its lower reactivity and smaller specific surface area. The results of measurements regarding specific surface area and reactivity precisely reflect this behavior. Furthermore, the difference in structure is clearly

visible in the scanning electron microscope images. The numerous pores in biochar result in an enormously large surface area, which subsequently leads to increased contact with CO_2 and thus enhanced reactivity. The closed surface of petroleum coke reduces gas penetration, leaving only a smaller surface area for solid–gas reaction.

The difference in the final carbon contents between biochar and petroleum coke should be noted. In all experiments, ZnO was present in the charge at the end, indicating that the reduction was not fully completed. Since petroleum coke was still available at the end of the experiments, further reduction of ZnO could be expected with a longer duration of the trial. Since it can be assumed that in the test with the mixture of petroleum coke and biochar, mainly the petroleum coke remained in the bed, the correlation of further reduction by extending the test duration also applies to this test. The presence of the fossil carbon carrier in the treated material can be explained by its low reactivity. This is confirmed by the results from thermogravimetry and reactivity measurement.

In general, a trend can be observed at the beginning of the reduction in carbon content. In the experiments, the reduction started from sample 5 at a temperature of 700–800 °C. This region marks the beginning of the reaction where CO_2 from combustion is converted according to Boudouard and explains the beginning of the reaction in most cases. The experiment with the holding point at 650 °C delays the heating phase by 30 min, resulting in a temperature of 700–800 °C for sample 8. A fast decrease in the carbon content can also be observed from this point onwards.

Even though the application delivered a positive result for the substitution of petroleum coke with biochar, there were still various difficulties during the implementation. Heating via the CH_4/O_2 burner proved to be problematic. Although the flame was orientated as far away from the bed as possible, the large amount of gas caused strong turbulence in the furnace chamber. As a result, no distinct reducing and oxidizing gas layers could form, as is usually the case in a Waelz process. It should be mentioned that the mixing of CH_4 and O_2 did not take place in a specific chamber outside the furnace. It only occurs after the outlet from two concentric tubes in the vessel during the trials. This means that non-stoichiometric combustion cannot be excluded.

5. Summary and Outlook

The application of biochar in metallurgy earned a lot of interest many years ago when the price for CO_2 credits was high. With decreasing prices, the interest decreased as well and nearly froze completely. With the again increasing prices nowadays, biochar receives more and more attention. Based on successful previous work, new promising data were generated. However, there is still a lot of research required, at least in some areas, such as the Waelz kiln. The main limiting factor seems to be the high reactivity. Here, a solid basis for improvements has been made.

Future work will focus further on reducing the reactivity by using additives and by mechanically changing the structure of the biochar. This will be carried out, for example, by milling and agglomeration. The larger furnace (TBRC) proved to be a good scale for investigations, and it was possible to create adequate conditions for the first optimization of the Waelz process. Besides the modifications concerning the reactivity, different kinds of woody biomass and mixtures of biochar with petroleum coke will be evaluated before moving forward on an industrial scale.

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Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors on request.

Conflicts of Interest: The authors declare no conflicts of interest.

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