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# Characterization of renewable reductants and charcoal-based pellets for the use in ferroalloy industries

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## Abstract

This study investigates the effect of high-temperature pyrolysis and post-treatment processes on spruce and oak charcoal yields and CO<sub>2</sub> reactivity in a slow pyrolysis reactor. Post-treatment processes such as co-pyrolysis of biomass and recirculated tar mixture with that to the distillation of the charcoal-tar blend gave similar increase in charcoal yields. From a technological standpoint, co-pyrolysis of charcoal and tar mixture decreased the CO<sub>2</sub> reactivity of the charcoal approaching that of fossil-based coke. This emphasize the importance of tar addition and high temperature treatment on charcoal properties. Moreover, the findings of this work show the potential use of the tar organic fractions as a binder that can be used for the charcoal pellet preparation. The results are promising as they show that the charcoal-based pellets have comparable properties of pellets from herbaceous biomass

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leading to the cost reduction in charcoal transportation and storage.

*Keywords:* ferroalloy industry, charcoal, high temperature pyrolysis, secondary heat treatment, pelletization

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## 1. Introduction

The reduction of anthropogenic greenhouse gas emissions is one of the greatest challenges in coming decades [1]. Carbon dioxide is considered as the main source for anthropogenic climatic change. Metallurgy is one of the most energy intensive industries, which is responsible for about 10% of the global anthropogenic CO<sub>2</sub> emissions [2, 3]. The use of biomass and its derivatives as CO<sub>2</sub> neutral reduction agents in metallurgical processes can be a possible solution to decrease emissions. However, the metallurgical production nowadays is based on the use of fossil-based fuels due to the limited knowledge of charcoal properties and its high costs.

Ferroalloys are defined as iron-rich alloys which contain high proportions of Si, Mn, C, Cr, etc. which improve tensile strength, wear, corrosion resistance and toughness [4]. Ferroalloys are mainly produced in submerged-arc furnaces at temperatures  $> 1500^{\circ}\text{C}$ . A three-phase electrode is inserted into a mixture consisting of ferroalloys and carbonaceous reductants [5, 6]. The carbonaceous material acts as a reducing agent to form the base metal [7]. The most important properties of carbonaceous reductants are high reactivity, high conversion rates, low levels of impurities (such as sulphur and phosphorus), high bulk density and energy density [8, 9]. The high reactivity of charcoal reductant may be advantageous in some cases within the ferroalloy industries. However, the use of a reductant more reactive than fossil-based

coke may increase maintenance costs due to the decreased electrical conductivity [10, 11]. Previous studies have examined distillation of bio-oil and charcoal blends which increased the char yields by over 15% and decreased the reactivity of remaining post-distilled solid residue [12–14]. Likewise, the low bulk density and energy density of charcoal necessitate relatively large equipment for handling and storage. Thus, the cost of charcoal reductants is not competitive with fossil-based coke [15]. Pelletization of charcoal using recycled tar as a binding agent has potential to increase the charcoal mechanical strength and bulk density leading to the reduction in transportation and storage cost [16]. However, there is little data in the literature that describes the effects of tar used as a binding agent on resulting charcoal pellet properties that impact metallurgical applications. This adds uncertainty to the use of recycled tar addition as an approach to increase the mechanical strength and decrease charcoal reactivity. In order to increase the solid char yield and adjust the charcoal reactivity, metallurgical industries strive to understand how charcoal properties are correlated with heat treatment temperatures and composition of pyrolysis products.

In this study, the impact of heat treatment temperature, secondary heat treatment, feedstock origin, and co-pyrolysis with tar on the product yields, CO<sub>2</sub> reactivity and charcoal-based pellet properties were investigated. The specific objectives of this study were to: (1) determine the treatment conditions which decrease char reactivity and increase the yield of charcoal for the further use in pellets production and (2) understand the influence of post-pyrolysis processes on the charcoal properties.

## 2. Materials and methods

### 2.1. Raw biomass characterization

Norway spruce (*Picea abies*) and oak (*Quercus petraea*) from Dømmesmoen (Grimstad, Norway) were harvested in 2012 and 2016. The age of the Norway spruce was 39 years, whereas oak was 46 years. Feedstock selection was based on the differences in ash composition and plant cell compounds (cellulose, hemicellulose, lignin, extractives) of softwood and hardwood. Norway spruce is low in ash and with lower potassium and calcium contents than oak, whereas oak is low in lignin content. Both spruce and oak samples were chipped by a disc chipper to 5-20 mm and dried at 60°C before storage. Prior to the wood characterization, biomass samples were divided into six equal fractions using a riffler. A vibrating EFL2000 sieve shaker (ENDECOTTS, United Kingdom) comprising ten sieves ranging from 2 to 20 mm in opening size and a bottom pan (< 2 mm) was used (EN ISO 17827-2:2016) to determine the particle size distribution.

### 2.2. Slow pyrolysis reactor

The charcoal samples were generated in the slow pyrolysis reactor, as shown in Figure 1.

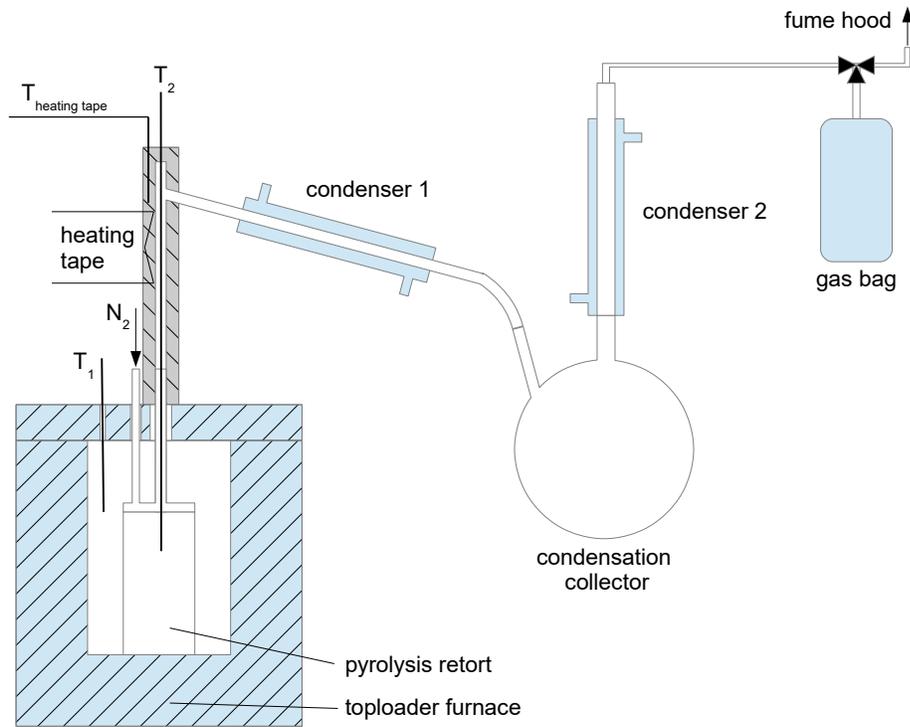


Figure 1: Slow pyrolysis reactor.

The reactor can be operated at temperatures up to  $1350^{\circ}\text{C}$  and heating rates up to  $20^{\circ}\text{C min}^{-1}$ , as reported by Surup et al. [17]. The pyrolysis retort (inner diameter: 75 mm, height: 150 mm, wall thickness: 2 mm) is made of SiC material. The sample temperature was monitored by a thermocouple type S (max.  $1600^{\circ}\text{C}$ ). The pyrolysis setup encloses a two-stage cooling system with a condensation collector and a pyrolysis gas sampling unit. The connection pipes (inner diameter: 16 mm) between the retort and the condensation unit were made of quartz glass. The connection pipes were heated up to  $350^{\circ}\text{C}$  by a heating tape HBQ (Hillesheim, Germany) and a temperature

regulator MC1 (HORST GmbH, Germany) to minimize the condensation and thermal decomposition of tars. The volume flow of the N<sub>2</sub> gas was measured by the flowmeter HFC-202 (Teledyne, USA). The reactor was continuously purged by nitrogen at a defined flow rate of 100 ml min<sup>-1</sup>. The temperature control system was based on the LabView software (Version 8.6). A sample mass of 60 g for each experiment was selected. The wood sample was distributed homogeneously in the reactor's retort, pre-heated in nitrogen at 10°C min<sup>-1</sup> up to 160°C and kept at that temperature for 30 min. The dried wood was further heated at 10°C min<sup>-1</sup> to temperatures ranging from 500 to 1300°C and kept at the final temperature for about 1 h to ensure the complete conversion. After the heating program was finished, the furnace was turned off and the charcoal sample was cooled overnight in N<sub>2</sub> (0.3 l min<sup>-1</sup>). Samples were stored in sealed plastic containers.

### *2.3. High-temperature furnace*

The charcoal samples were further treated in the high-temperature furnace LHTG 200-300/20-1G (Carbolite Gero, Germany). The furnace can be operated at temperatures up to 1800°C and at heating rates up to 20°C min<sup>-1</sup>. Prior to each experiment, 5 g of the char sample were loaded into the A<sub>2</sub>O<sub>3</sub> crucible (Almath Crucibles Ltd, UK) placed in the graphite retort middle. Prior to pyrolysis, the furnace was repeatedly evacuated and purged by argon. The char sample was heated at 10°C min<sup>-1</sup> up to 700, 1000, 1300, and 1600°C and kept at that temperature for 2 h. The sample was cooled to room temperature at a heating rate of 20°C min<sup>-1</sup> and stored in sealed plastic containers.

#### 2.4. Pyrolysis product analysis

*Sample preparation.* The charcoal samples were crushed to a fine powder in a mortar with a ceramic pestle and sieved to a particle size  $\leq 0.25$  mm for the elemental and thermogravimetric analysis.

*Fixed carbon yield.* The fixed carbon yield of charcoal samples was determined in equation 1 [18]:

$$\gamma_{uc} = \gamma_{bc} \cdot \frac{FC_{\text{biochar}}}{1 - ash_{\text{biomass}}} \quad (1)$$

In equation 1,  $\gamma_{bc}$  and FC are the char yield and fixed carbon content as described in BS ISO 15148:2009.

*Elemental analysis.* The elemental analysis of raw biomass and charcoal was performed on Elemental Analyser 2400 CHNS/O Series II (Perkin Elmer, USA). Acetanilide was used as a reference standard. The ash content was determined using a standard ash test at 550°C, according to the procedure described in DIN EN 14775.

*SEM microscopy.* SEM/EDS analysis of char was conducted on a high-resolution field emission microscope SU-70 (Hitachi, Japan) under high vacuum in order to understand char structural properties. Prior to the analysis, char samples were coated with a thin layer of gold (2 min, 20 mA) using an Edwards S150B Sputter Coater to avoid sample charging.

*Thermogravimetric analysis.* The reactivity of charcoal was analyzed by exposing samples to a reactive gas consisting of 100 % volume fraction CO<sub>2</sub> in a thermogravimetric instrument TGA/DSC 1 STARe System (Mettler Toledo,

USA). In each experiment, 5 mg of the crushed sample were loaded into an  $\text{Al}_2\text{O}_3$  crucible. The charcoal samples were firstly heated up to  $110^\circ\text{C}$  and kept for 30 min isothermally for drying. The dried samples were subsequently heated up to  $1100^\circ\text{C}$  at a constant heating rate of  $10^\circ\text{C min}^{-1}$  and kept at the final temperature for 10 min. The reaction threshold is the temperature that corresponds to the appearance of the sample mass decrease [19]. Simultaneous non-isothermal thermogravimetric measurements of char were carried out in  $\text{N}_2$  to determine the mass loss.

*Karl Fischer titration.* Karl Fischer titration was carried out using a KF1000 volumetric titrator (Hach, Germany). Tar samples were first dissolved in anhydrous methanol and then injected into the titration cell. All titrations were carried out at room temperature and the experiments had an error of  $\pm 0.5\%$  water content.

*Single pellet preparation.* Prior to pelletization, the water fraction of tar was removed by distillation and the heavy fraction was used as a binding agent. A single pellet press tool (Fistreem International Ltd, UK) similar to that described by Rudolfsson et al. [20] was used, that consists of a metal cylinder with a press channel and a backstop, as shown in Figure 2. The char particles were comminuted to a particle size of  $< 0.4$  mm. A 3 g pellet with an diameter of 12 mm and a height of 20 mm was made from charcoal particles, tar binder and water in the wt. % ratio of 65:30:5. The mixture was dried for 30 min at room temperature before feeding into the mold of a single pellet press. Once the pellet was pressed, the backstop was removed and the pellet was extruded from the steel die. The charcoal pellets were dried for 24 h at  $30^\circ\text{C}$

in an oven desiccator. In addition, a number of pellets were heat treated at 400°C in a tubular furnace to study the influence of heat treatment on the pellet hardness and durability.

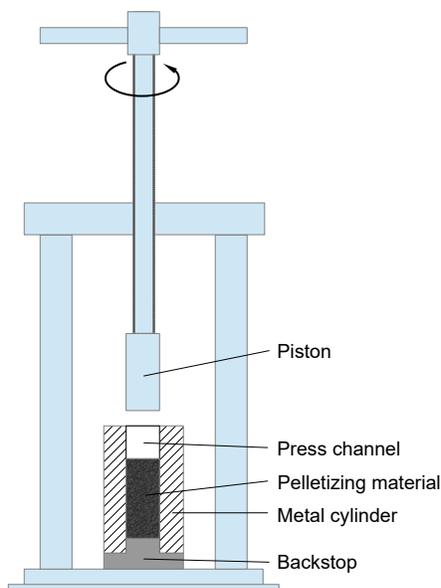


Figure 2: Single pellet press tool.

*Pellet hardness.* The hardness analysis of a single charcoal pellet was performed using a pellet hardness tester (AMANDUS KAHL, Germany). A charcoal-based pellet was placed between a die and a punch. The force was applied on the pellet until it breaks. The result was reported as a destructive force in newtons. The measurements were repeated three times.

*Pellets ligno durability.* Ligno durability of charcoal pellets was determined by treating 100 g of pellets for 60 s in a pressurized air-steam with 70 mbar in a Ligno tester (Borregaard, Norway) [21]. The fine particles were separated by a 3.15 mm sieve. The ligno durability of charcoal pellets was calculated as

the weight percentage of treated pellets remaining on the sieve to the initial sample weight, as reported by Larsson et al. [22].

*Electrical conductivity.* Electrical conductivity measurements were performed using a 34470A 7 1/2 Digit Multimeter (Keysight Technologies, USA). The connection between the four probes of the source meter and microelectrodes was established using a socket. Two adjacent electrodes were connected to the voltmeter (Fluke, USA), whereas the other two electrodes were connected to the current source (ISO-Tech IPS 3303) (constant current) of the source meter, as it was reported by Sun et al. [23]. A charcoal pellet was connected by four different electrodes to the source meter based on the van der Pauw electrode geometry [24]. The electrical conductivity was determined according to equation 2:

$$\sigma = \frac{L}{R \cdot A} \quad (2)$$

In equation 2,  $\sigma$  is the electrical conductivity,  $A$  is the cross-sectional area,  $L$  is the length of the resistor, and  $R$  is the resistance between two Ti-Au electrodes.

### **3. Results and discussion**

#### *3.1. Biomass characterization*

The ultimate and proximate analysis of metallurgical coke and wood was carried out at Eurofins Lidköping and shown in Table 1.

Table 1: Proximate, ultimate and ash analyses of feedstocks.

| Fuel   | Norway spruce | Oak  | Metallurgical coke |
|--|---------------|------|--------------------|
| Proximate analysis   |               |      |                    |
| Moisture, (wt. % as received)                                  | 8.6           | 7.6  | 0.6                |
| Ash at 550 °C, (wt. % dry basis)                               | 0.8           | 1.6  | 11.8               |
| Volatiles, (wt. % dry basis)                                   | 80.6          | 82.6 | 3                  |
| Fixed carbon content (wt. % dry basis)                         | 18.6          | 15.8 | 85.2               |
| HHV, (MJ kg <sup>-1</sup> )                                    | 20.3          | 19.3 | 27.9               |
| LHV, (MJ kg <sup>-1</sup> )                                    | 18.5          | 17.5 | 27.8               |
| Ultimate analysis, (wt. %, dry basis)                          |               |      |                    |
| C  | 53.2          | 50.6 | 85.6               |
| H  | 6.1           | 6.1  | 0.3                |
| N  | 0.1           | 0.2  | 1.8                |
| S  | 0.06          | 0.02 | 0.6                |
| Cl   | 0.04          | 0.02 | 0.03               |
| Ash compositional analysis, (mg kg <sup>-1</sup> on dry basis) |               |      |                    |
| Al   | 40            | 20   | 12000              |
| Ca   | 2300          | 3600 | 6400               |
| Fe   | 200           | 50   | 6300               |
| K  | 800           | 1500 | 1700               |
| Mg   | 250           | 300  | 1300               |
| Na   | <50           | <50  | 1100               |
| P  | 200           | 250  | 400                |
| Si   | 550           | 550  | 27000              |
| Ti   | 50            | 50   | 550                |

The compositional analysis of biomass (cellulose, hemicellulose, acid-soluble lignin, acid-insoluble lignin, and extractives) was conducted by Celig-nis Analytical according to NREL technical reports [25–27] and Thammasouk et al. [28], and is shown in Table 2.

Table 2: Composition of Norway spruce and oak, calculated in percentage based on dry basis (wt. %).

| Biomass       | Cellulose | Hemicellulose | Lignin          |              | Extractives |
|---------------|-----------|---------------|-----------------|--------------|-------------|
|               |           |               | acid in-soluble | acid soluble |             |
| Norway spruce | 37.8      | 25            | 27.9            | 0.7          | 7.8         |
| Oak           | 36.7      | 18.7          | 19.4            | 2.5          | 11          |

### 3.2. Elemental analysis

Figure 3 shows a Van Krevelen plot of original spruce and oak, their charcoals, and metallurgical coke.

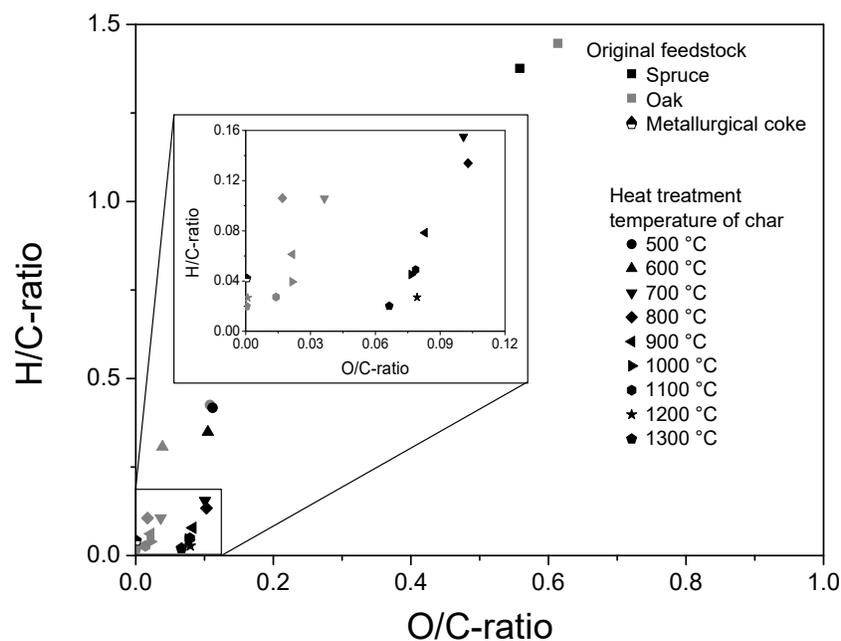


Figure 3: Van Krevelen plot of metallurgical coke, original spruce and oak samples and their charcoals from pyrolysis in the temperature range from 500 to 1300°C.

The results indicate that the oxygen content in all char samples decreased with the higher heat treatment temperature. The spruce charcoal contained less carbon and more oxygen than oak charcoal. A point of note is that the elemental composition of oak samples obtained from pyrolysis at 1300°C was comparable to the composition of metallurgical coke.

### 3.3. Product yields

The product yields from pyrolysis of spruce and oak with respect to char and major liquid products (water and organic fraction) are shown in Figure 4.

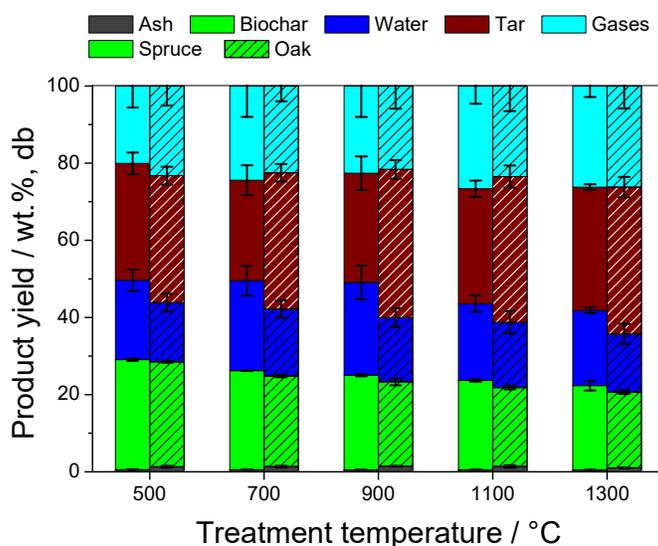
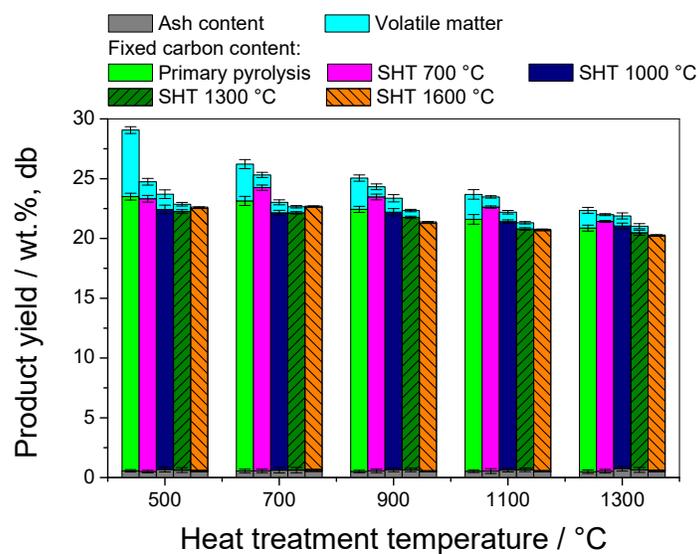
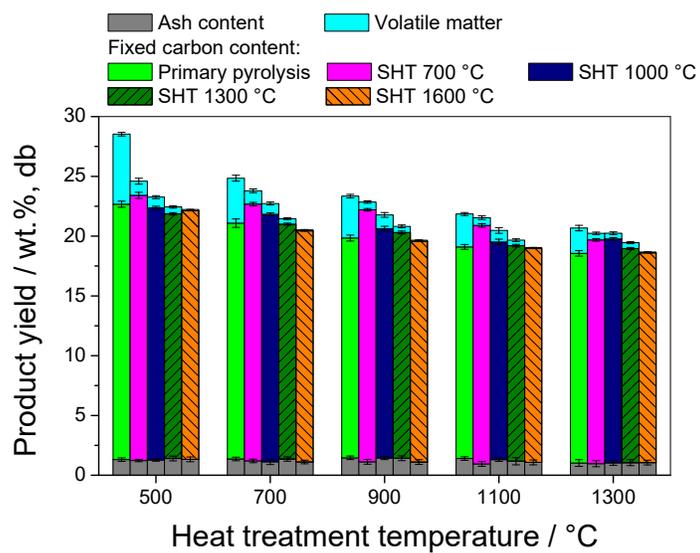


Figure 4: Product yields of tar and char (wt.% relative to the original biomass) of spruce (left) and oak (right), reacted at 500-1300°C in the slow pyrolysis reactor. The char yield is separated in ash and organic matters. The tar yield was separated in organic fraction and water content. The error bars characterize the standard deviations between the total yields of products.



5(a): Spruce



5(b): Oak

Figure 5: Char yields (wt. % relative to the original biomass) from pyrolysis of spruce and oak after secondary heat treatment at 700, 1000, 1300 and 1600°C in the high temperature furnace. The total char yield is separated in ash, fixed carbon and volatile matter.

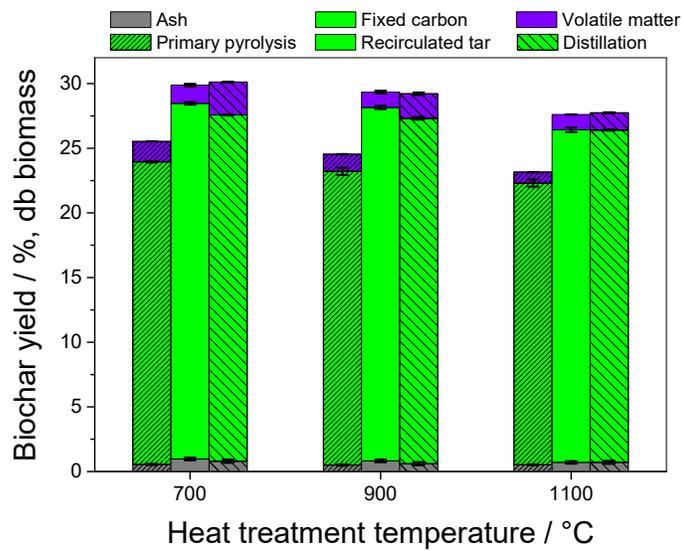
The gas yield was determined by the difference between the total weight loss and the non-devolatilized tar and solid fractions. The char yield from pyrolysis of both spruce and oak decreased with increasing heat treatment temperature, from about 29 to 22 % for spruce and from 27 to 20 % for oak in the temperature range from 500 to 1300°C. The ash content remained only slightly changed with the increasing heat treatment temperature in pyrolysis of both feedstocks. The yields of tar organic fraction in pyrolysis of oak increased slightly from 33 to 38 % in the temperature range from 500 to 900°C and remained constant at higher temperatures. It was observed that almost similar yields of tar organic fractions were determined in pyrolysis of spruce, whereas the water content in spruce tar was 5 % points greater than in oak pyrolysis. Spruce and oak charcoal samples were subjected to an additional heat treatment in the high temperature furnace. The fixed carbon content and volatile yield of non-treated charcoal and samples from pyrolysis in the temperature range from 500 to 1300°C are shown in Figure 5. The additional heat treatment led to the further decrease in fixed carbon content of both charcoal samples by about 1 % point with the increasing temperature from 700 to 1600°C. It was found that the fixed carbon content of spruce and oak charcoal samples produced at temperatures  $\geq 700^\circ\text{C}$  increased after additional heat treatment at 700 and 1000°C. The proximate analysis of charcoal samples showed that the mass loss in the additional high-temperature pyrolysis was mainly caused by the volatile matter release. The ash content of spruce and oak charcoal samples remained unchanged after additional heat treatment. The experiments in the slow pyrolysis reactor demonstrated that the maximum heat treatment temperature exerted greater influence on the

solid product yield than the feedstock origin and secondary heat treatment. The solid product yield can be affected by differences in lignocellulosic composition of biomass, ash content, heat treatment temperature and secondary heat treatment. Proximate analysis of the solid residue showed that the ash content of spruce and oak char samples from pyrolysis in the temperature range from 500 to 1300°C were not affected by the mass loss, whereas the yield of an organic matter decreased with the increasing heat treatment temperature. The ash content of the original spruce (0.8 wt. %) was half that in the original oak. Alkali metal ions ( $K^+$  and  $Ca^{2+}$ ) catalyze the conversion of bridges into char links and enhance cross-linking/polymerization, leading to the greater char yield [29]. Thus, based on ash content alone it might be expected that oak char yield should be greater than char yield from spruce pyrolysis. However, the yields of spruce and oak charcoal were similar. In addition, the yield of spruce char organic fraction was 2 % point greater than that of oak char, whereas original oak contained less lignin and hemicellulose than spruce, indicating that lignocellulosic biomass composition had a minor influence on the biomass devolatilization. Spruce and oak char yields decreased by 7 wt.% in primary pyrolysis with the further char yield decrease during secondary heat treatment. The proximate analysis showed that after removal of volatile matter a fixed carbon yield was in the range from 20 to 23 wt.% and from 18 to 21 wt.% for spruce and oak charcoal, indicating only a minor influence of secondary heat treatment and feedstock origin on the char yield. In addition, the fixed carbon content of charcoal obtained at different temperatures in primary pyrolysis varied only slightly at 1600°C of secondary treatment. The increase in heat treatment temperature during

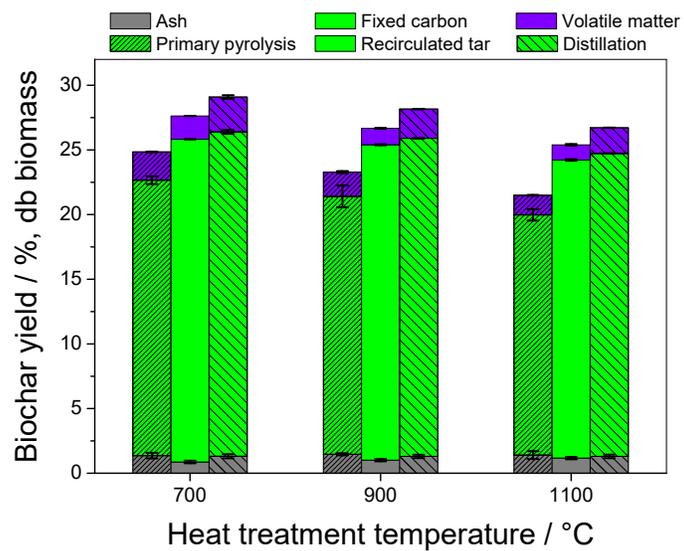
primary pyrolysis significantly decreased the char yield, emphasizing a key role of temperature on the biomass devolatilization.

#### *3.4. Co-pyrolysis with liquid products*

The char and volatile yields of co-pyrolysis of original feedstocks with recirculated tar and post-distilled residues are shown in Figure 6. Co-pyrolysis of both original spruce and oak samples with recirculated tar increased the char yield by approximately 4% points at 700, 900, and 1100°C, indicating that the feedstock had no influence on the product yields. The addition of recirculated tar to charcoal probably promoted secondary reactions which led to greater char yields than in primary pyrolysis. Moreover, the yields of remaining post-distilled solid product were similar to char yields from co-pyrolysis of original biomass with recirculated tar. The volatile matter content in the post-distilled product was 1 to 2% points greater than the amount of volatiles remaining in charcoal from co-pyrolysis. Temperatures greater than 700°C in co-pyrolysis of charcoal with tar products led to the predominance of secondary reactions forming larger size tar products and more cross-linked char fractions with less volatile compounds than in distillation of tar and charcoal mixture at 450°C. The fixed carbon yield obtained in co-pyrolysis of both charcoals with tar varied only slightly indicating that no tar decomposition occurs. In general, the differences in total char yields from both post-treatment processes were small. The increase in total solid yield of spruce charcoal from co-pyrolysis and distillation was nearly similar ( $\approx 4\%$  points), whereas the increase in total solid yield from co-pyrolysis of oak charcoal with tar was 1% less than the yield after distillation.



6(a): Spruce



6(b): Oak

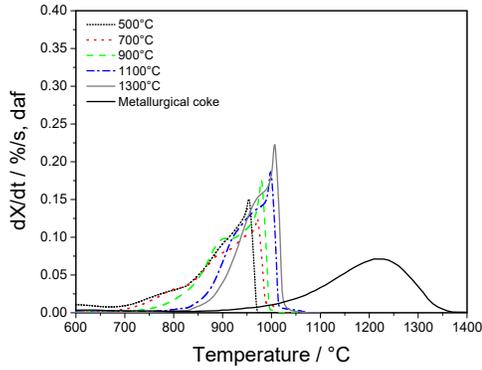
Figure 6: Char yields (wt.% relative to the original biomass) of spruce and oak from co-pyrolysis of charcoal with tar. The total char yield is separated in ash, fixed carbon and volatile matter.

Both post-treatment processes led to the formation of an additional carbon layer on the charcoal particle surfaces that had only small influence on the solid product yield, confirming the previous results of Elkasabi et al. [30]. In addition, an increase in the solid residue yield from both post-treatment processes varied only slightly between feedstocks suggesting that the additional carbonaceous layer was formed from tar with similar aromatic/phenolic composition [12]. The results showed that co-pyrolysis and distillation of charcoal with tar significantly increase the solid char yield in the entire process and thus, emphasize the potential use of biocarbon-based reductants in ferroalloy industries.

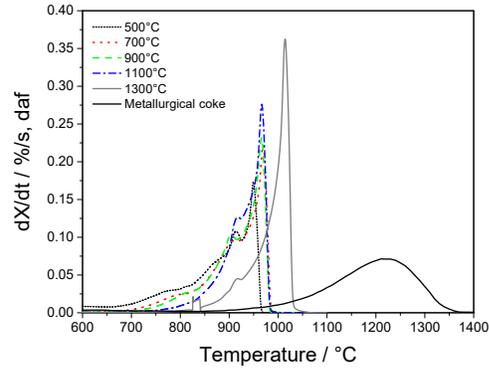
### 3.5. Charcoal reactivity

Figure 7 shows the differential weight loss curves (DTG) for the 100 % volume fraction CO<sub>2</sub> gasification of spruce and oak char samples. The DTG curves show a double peak in CO<sub>2</sub> gasification, indicating a heterogeneous char mixture with respect to the composition that leads to the differences in reactivity of two constituents with less reactive carbon structure that approaches the reactivity of metallurgical coke (maximal reaction rate is at 1220°C) [31]. The maximal reaction rates of both woody chars varied from 800 to 1030°C. The CO<sub>2</sub> gasification of spruce chars from pyrolysis ranging from 700 to 900°C and oak chars generated from 700 to 1100°C took place at nearly the same temperature of 960°C, indicating a minor effect of feedstock origin on the char reactivity. The maximum reaction rates of spruce and oak chars reacted at 1300°C were the highest and nearly identical. The results show that differences in heat treatment temperature have more influence on char reactivity than the residence time, feedstock composition or additional

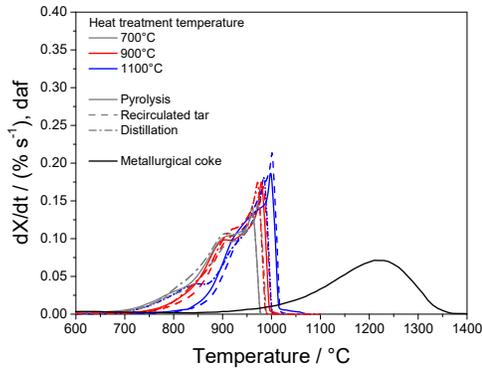
heat treatments.



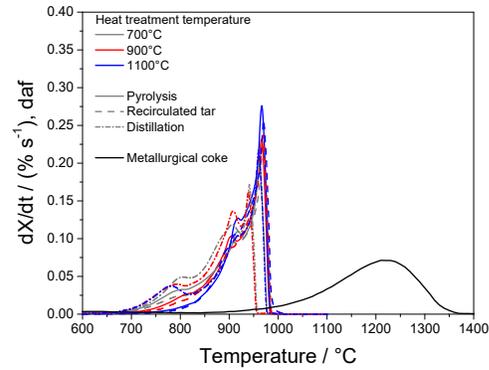
7(a): Spruce



7(b): Oak



7(c): Spruce



7(d): Oak

Figure 7: DTG curves of spruce and oak charcoals from pyrolysis (a,b) at 500, 700, 900, 1100, and 1300°C and (c,d) samples from co-pyrolysis of charcoal with recirculated tar and post-distilled solid fraction reacted in 100 % volume fraction CO<sub>2</sub>.

Figure S-4 from the supplemental material showed that spruce char samples exhibited a double peak, whereas oak char samples exhibited a triple peak after co-pyrolysis with recirculated tar and distillation. It was observed that the maximal reaction rate of spruce and oak charcoal after distillation

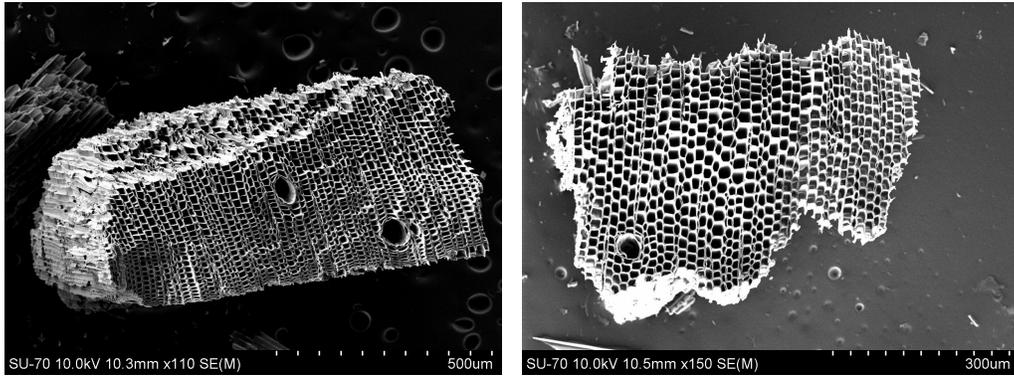
shifted to the lower temperatures, indicating the increase in CO<sub>2</sub> gasification reactivity. In comparison, the maximum reaction rate of both charcoal samples from co-pyrolysis with the recirculated tar shifted to higher temperatures, indicating a decrease in CO<sub>2</sub> gasification reactivity. The reactivity of spruce and oak charcoal from co-pyrolysis at 1100°C was similar to that of non-treated charcoal samples, whereas the maximum reaction rate of spruce and oak charcoal from co-pyrolysis with recirculated tar at 700 and 900°C was about 50 and 20°C lower than that of non-treated charcoal samples. This emphasizes that heat treatment temperature is the more important factor determining CO<sub>2</sub> gasification reactivity in co-pyrolysis with recirculated tar than the feedstock origin. The maximal reaction rate of spruce and oak chars from pyrolysis at 500°C after additional heat treatment at 1000, 1300, and 1600°C in a high-temperature furnace was about 60°C greater than that of non-treated char samples. This is probably due to the further proceeded pyrolysis and catalytic effect of remaining alkali metals in the non-treated char structure. It was observed that the CO<sub>2</sub> reactivity of both charcoal samples remained unchanged at higher temperatures of additional heat treatment.

Figures S-4 and S-5 from the supplemental material show that the additional heat treatment at temperatures > 1000°C affected the reactivity of charcoal samples significantly less than the post-treatment using co-pyrolysis and distillation with tar, confirming the previous results of Hussein et al. [32]. It was found that the maximum reaction rate of charcoal from additional pyrolysis at 1300 and 1600°C was shifted to temperatures about 40°C lower than for charcoals from primary pyrolysis at 1300°C. The TEM analysis showed that the mean separation distance of oak char graphene layers was similar to

graphite, whereas spruce char contained different types of amorphous carbon structures [31]. However, in the present study the CO<sub>2</sub> reactivity of spruce and oak charcoal samples was similar after the additional heat treatment. Co-pyrolysis with tar and distillation of charcoal with tar showed a minimal influence on the CO<sub>2</sub> reactivity, confirming the results of Veksha et al. [33]. The post-treatment using distillation with tar slightly increased the reactivity due to the cross-linking of hydroxyl groups with carbonyls, increasing the molecular weight of solid residues [34]. The reactivity of charcoal after co-pyrolysis with tar remained similar to the non-treated charcoal due to the similar porosity and composition [33]. In addition, the CO<sub>2</sub> reactivity of charcoal after all post-treatment processes was about 250°C lower than that of metallurgical coke.

### *3.6. Charcoal-based pellets*

Figure 8 illustrates the structure of a char particle from pyrolysis at 900°C using original spruce and wood with the addition of tars. Both char particles preserved the structure of an original biomass particle with the longitudinal tracheids and resin vessels. Figure 9 shows that the heat treated spruce char pellet obtained a structure with the visible cracks on the outer surface, whereas the non-treated spruce pellet exhibited a smooth external surface. The heat treatment increased the hardness of a spruce char pellet from 455 to 490 N, whereas the durability of the spruce pellet decreased from 98.4 to 95.7%. The previous studies showed that the durability of high quality pellets is required to be  $\geq 97.5\%$  [35]. The secondary heat treatment of charcoal pellets improved the hardness that was similar to that of alfalfa straw pellets using hydrated lime as a binding agent ( $\approx 471$  N) [36].



8(a): Spruce char

8(b): Spruce char from pyrolysis with the tar addition to the raw wood

Figure 8: SEM images of char from pyrolysis at 700°C using (a) original spruce and (b) wood with the addition of tars.

The increase in heat treatment temperature improved the hardness of charcoal pellets during pyrolysis, confirming the previous results of Li et al. [37]. The electrical resistivity of the heat treated charcoal pellets increased from 0.8 to 1.5  $\Omega\cdot\text{m}$ , whereas the electrical resistivity of metallurgical coke and single spruce char particle was about 0.01 and 0.03  $\Omega\cdot\text{m}$ , emphasizing the importance of tar addition on the charcoal pellet electrical properties. In addition, the electrical resistivity of metallurgical coke and single charcoal particle in the present study was similar to that of coke ( $\approx 0.01 \Omega\cdot\text{m}$ ) measured by the four-point-probe setting, as reported by Eidem et al. [38]. This indicates that the heat treatment improves the mechanical strength and electrical resistivity of charcoal pellets for the use in metallurgical processes. The improvement of charcoal pellet durability using other types of binding agents and different concentrations is a significant task that can be proposed

for future studies.

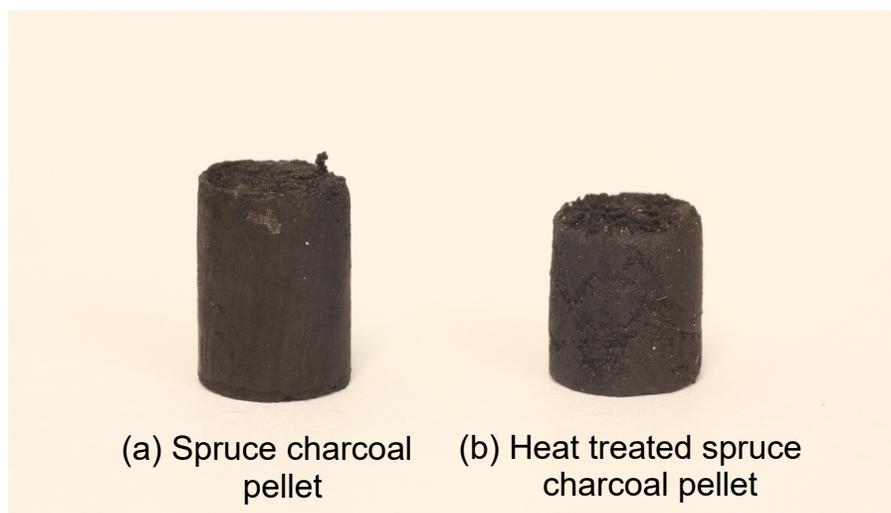


Figure 9: Single spruce charcoal pellets (a) non-treated and (b) heat treated.

#### 4. Conclusion

The novelty of this work relies on the fact that the reactivity, char yield and electrical resistivity of charcoal can be improved by the addition of recirculated tar. Softwood and hardwood were converted into renewable carbonaceous reductants using pyrolysis treatment. The experiments in the slow pyrolysis reactor showed that the char yield depends mainly on heat treatment temperature in primary pyrolysis and less on the feedstock origin and secondary heat treatments. The co-pyrolysis of charcoal with recirculated tar and distillation increased significantly the char yield. However, both spruce and oak charcoal samples remained more reactive than fossil-based coke after secondary heat treatment, co-pyrolysis with tar and distillation.

In addition, the tar organic fraction showed properties of a binder that increase the electrical resistance and hardness of charcoal pellets. The findings of this study emphasize the potential use of biocarbon-based pellets in the ferroalloy industry with concomitant improvement in charcoal transportation and storage.

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