



Article Influence of Bio-Coal Properties on Carbonization and Bio-Coke Reactivity

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Abstract: Coke corresponds to 2/3–3/4 of the reducing agents in BF, and by the partial replacement of coking coals with 5–10% of bio-coal, the fossil CO_2 emissions from the BF can be lowered by ~4–8%. Coking coal blends with 5% and 10% additions of bio-coals (pre-treated biomass) of different origins and pre-treatment degrees were carbonized at laboratory scale and with a 5% bio-coal addition at technical scale, aiming to understand the impact on the bio-coal properties (ash amount and composition, volatile matter content) and the addition of bio-coke reactivity. A thermogravimetric analyzer (TGA) connected to a quadrupole mass spectroscope monitored the residual mass and offgases during carbonization. To explore the effect of bio-coal addition on plasticity, optical dilatometer tests were conducted for coking coal blends with 5% and 10% bio-coal addition. The plasticity was lowered with increasing bio-coal addition, but pyrolyzed biomass had a less negative effect on the plasticity compared to torrefied biomasses with a high content of oxygen. The temperature for starting the gasification of coke was in general lowered to a greater extent for bio-cokes produced from coking coal blends containing bio-coals with higher contents of catalyzing oxides. There was no significant difference in the properties of laboratory and technical scale produced coke, in terms of reactivity as measured by TGA. Bio-coke produced with 5% of high temperature torrefied pelletized biomass showed a similar coke strength as reference coke after reaction.

Keywords: bio-coals; carbonization; gasification; reactivity; dilatation; fluidity

1. Introduction

The iron-ore-based blast furnace (BF) process is still the most dominant method for producing metallic iron units for steelmaking [1]. In the BF, the high-quality metallurgical coke that is used is considered crucial for the process. Besides working as a reducing agent for iron ore, coke also serves as the structural support for the burden in the furnace and provides passages for the upward movement of reducing gases [1]. The total consumption of coke is about 300 kg/t hot metal [1], depending on the amount of auxiliary reducing agents used (coke, coal, oil natural gas, etc.) [2]. The iron and steel industry aims to decrease the use of fossil carbon to minimize CO_2 emissions. According to the World Steel Association, the iron and steel industry accounts for approximately 7–9% of total world CO_2 emissions [3].

The use of pre-treated biomass (bio-coal) as a part of the raw material blend for cokemaking could be one possible way of reducing the fossil CO_2 emissions linked to the BF process. The advantage of replacing part of the fossil coal with bio-coal is that the biomass regeneration time is comparatively short [4] and the effects on global warming can be reduced as the carbon cycle is closed [5]. It has been reported that with the partial replacement of coking coals with 5–10% of bio-coal, the fossil CO_2 emissions at the BF can be lowered by ~4–8% [6]. Using bio-coke (bio-coal-containing coke) in the BF has the potential to lower the thermal reserve zone temperature (TRZT) of the BF, as the gasification reaction



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). (reaction of carbon in coke with CO_2) can proceed at a lower temperature in the more reactive bio-coke. A lowering in the TRZT shifts the gas composition in the equilibrium of FeO/Fe towards higher CO_2 and lower CO contents. This leads to higher utilization of the input carbon for the reduction of the iron ore and lowers the required carbon input [7]. A higher reactivity will, however, also reduce the coke strength after reaction, which is not desirable, as it may cause disintegration and have an impact on the permeability.

During cokemaking the coking coals go through chemical and physical changes including softening, swelling, shrinking, evolution of volatile matter (VM), and, finally, re-solidification to obtain coke [8]. The thermoplastic properties of the coals are important for the quality of the final coke [9]. In bio-coke research, several types of biomass-based materials have been studied for evaluation of their effect on coal fluidity. This material includes different raw biomasses, torrefied biomass, and pyrolyzed biomass. The addition of any type of biomass decreases the fluidity of the coal blend [10–14]. Ueki et al. [12] reported that the addition of raw woody biomass during carbonization results in the formation of voids between coal particles during carbonization, due to the release of biomass VM, and this results in brittle bio-coke. The coal particles were seen to be connected to woody biomass when they had a lower volatile content [12]. Diez et al. [11] reported that the thermal decomposition of raw biomasses (sawdust) occurs at low temperature ~150–400 °C and the majority of VM are released before the plastic stage of coking coal occurs at around 400–500 °C; this means that there is a lower amount of VM and remaining biomass that will interact with the coal during the fluidity development. On the other hand, Guerrero et al. [10] found that the devolatilization stages of coal and charcoal overlap partially and charcoal emits VM during carbonization that can block the fluidity, by establishing cross-linked O-C bonds. Fraga et al. [13] and Solar et al. [14] found that the addition of charcoal to coking coal blend caused a reduction in thermoplastic properties, and more so with increasing amounts. During the coal plastic stage charcoal acts as an inert material, which does not soften and melt, and as an active material that binds the components from the plasticized coal [11]. It was stated that chemically active additives, such as tar, petroleum residues, and oils, may act as fluidity enhancers or inhibitors, depending on their ability to donate or accept transferable hydrogen, respectively [9]. Generally, the blend of coal is required to have a maximum Gieseler fluidity and maximum dilatation greater than 400 ddpm and 55%, respectively, to produce high-quality metallurgical coke [15,16].

The quality of coke affects the performance of the BF; thus, it must be strictly controlled. Mechanical strength, coke reactivity index (CRI), and coke strength after reaction (CSR) are the most important parameters used to define coke quality, which are measured according to ISO standards 1889-4 and 556, respectively. It has been reported that there is a strong correlation between CRI and CSR. When the CRI is low, the CSR is maintained at a high level [17].

Ash components such as oxides of alkali and alkaline earth metal and iron are known to act as catalysts in the gasification reaction [18–20]. Nomura et al. [7,21] found that coke containing a high content of Ca in non-coking coal has a high reactivity and that Fe and Ca act as catalysts during gasification. Grigore et al. [20] reported that the coke reactivity increased with the increasing total amount of mineral phases containing Ca. Babich et al. [22] found that coke with a higher porosity has a higher reactivity, which was explain by the fact that microporosity also affects the reactivity, because it enables the access of CO_2 molecules to the inner part of the coke.

The effect of bio-coal particle size on the quality of bio-coke, in terms of CRI and CSR values, is reported in the literature [23–27]. The addition of 0.3–5% [14], 2–5% [23,24], 5% [25], 2–10% [26], 8% [27], and 5–25% [28] charcoal or (4.5–9%) lignite [29] to the coking coal blend was studied. It was found that the CRI of bio-coke is higher in comparison to reference coke, and vice versa for CSR. The increase in the CRI was more pronounced with fine charcoal, due to the presence of calcium oxide, which acts as a catalyst that promotes the reaction of carbon with CO_2 , being more dispersed in the coke pieces compared to when using coarse charcoal [14,23,24,26]. It was shown that bio-coke has a higher reactivity

when charcoal with a size <0.07 mm was added, compared to when coarse charcoal (2–9 mm) was used, with 5% charcoal addition [23,24], and further increased with 8% [27] and 10% charcoal additions [26]. The cold strength of bio-coke was strongly affected by the addition of coarse charcoal, while the coke strength was preserved when adding fine charcoal [23–27]. The main drawbacks related to bio-cokes are the lower mechanical strength and strength after reaction compared to cokes produced from coking coals only. The low mechanical strength of bio-coke contributes to difficulties during handling and charging, as well as higher dust formation in the upper part of the BF. A low strength after reaction may result in the generation of fines within the BF, especially in the lower part.

The carbonization behavior of coking coal blends containing raw or pre-treated biomass was reported in [12,14,23,24,26,28,30–33]. Matsumura et al. [30] studied the carbonization of raw biomass with one type of coking coal. Montiano et al. [32,33] studied the carbonization of industrial coal blends, containing more than six different coals, with the addition of two types of raw woody biomass: chestnut sawdust and pine sawdust. Solar et al. [14] studied the carbonization of an industrial coking coal blend with the addition of 0.3–5% of one type of charcoal. Ueki et al. [12], Florenonti et al. [31], and Yustanti et al. [28] studied the carbonization of coking coals with bio-coals produced from woody raw biomass or agricultural waste pre-treated at different temperatures and, therefore, with different VM and ash contents. Others [23,24,26] have studied the carbonization of charcoal with different types of coals. No studies were found in which the aim was to understand the effect on carbonization and coke reactivity from bio-coal with different origins (different ash composition and cell structure) and different pre-treatments (pyrolysis degree, compaction through pelletizing) when adding up to 10% of the bio-coal in a coking coal blend consisting of three typical coking coals in the ratio used at industrial coking plants for the production of high-quality coke. Such a study would give information about the relative impact of applying bio-coal additions at an industrial coking plant.

In this study the effect on carbonization from the addition of different types of pretreated biomass to coking coal blends consisting of three coking coals, as typically used in European industrial plants, was investigated. The bio-coals used were of different pyrolysis degrees and origin, therefore, their properties differed, e.g., in terms of structure, VM, and ash composition, and this may influence their individual effects during coking and the properties of the produced bio-coke. The aim was to understand the impact of different bio-coal types on the carbonization and quality of bio-coke, depending on their properties, i.e., cell structure and reactivity, at added amounts of 5% or 10%.

2. Materials and Methods

2.1. Materials

Three different types of coking coals, i.e., with low, medium, and high content of VM, were used in the coking coal blend, with or without the addition of bio-coal. Four types of bio-coals were selected based on their differences in VM and ash contents due to different pre-treatment temperatures and the origin of materials. The proximate and ultimate analysis, as well as the ash composition, for the bio-coals and the coking coals was analyzed according to the standard methods of ALS Scandinavia AB [34] and Swedish steel producer SSAB Europe in Luleå [35], respectively.

Carbonaceous materials are shown in Table 1; namely, torrefied biomass (TSD and TFR) from BioEndev AB (Holmsund, Sweden) [36] and Sveaskog AB (Stockholm, Sweden) [37], respectively, high-temperature torrefied biomass (HTT) from BioEndev AB and pyrolyzed biomass (CC) from Vindelkol AB (Vindeln, Sweden) [38], and three types of coking coals provided by SSAB Europe in Luleå, Sweden. HTT was densified through pelletizing before torrefaction.

Carbonaceous Materials	Biomass Type	Temperature (°C)	Abbreviation
Torrefied forest residue	Wood chips of tops and branches of	270	TFR
Torrefied sawdust	Pine/Spruce	290	TSD
High temperature torrefied	Pelletized saw dust of pine/spruce	400	HTT
Charcoal	Mixture of pieces of pine, birch, alder, aspen	550	СС
High Volatile coal	-	-	HV
Medium volatile coal	-	-	MV
Low volatile coal	-	-	LV

Table 1. Selected carbonaceous materials with abbreviations and their approximate pre-treatment temperatures.

The proximate and ultimate analyses are presented in Table 2. The pre-treatment temperature of biomass affects their properties, e.g., VM, oxygen, and fixed carbon (C_{fix}). The bio-coals prepared at low temperature (TFR and TSD) had a high content of VM and a low content of C_{fix} ; the opposite was the case for biomass pre-treated at high temperature (HTT and CC). The ash compositions are stated in Table 3. TFR has higher contents of catalytic components in terms of K₂O, CaO, Fe₂O₃, and Na₂O in comparison to TSD. The content of the catalytic components K₂O, Fe₂O₃, and Na₂O is higher in HTT than in CC.

Table 2. Proximate and ultimate analysis for carbonaceous materials (dry base).

	Proximate Analysis (wt%)			Ultimate Analysis (wt%)				
Abbreviation	*C _{fix}	VM	Ash	C _{tot}	Н	Ν	S	0
TFR	25.1	72.7	2.20	58.0	5.30	0.48	0.029	34.0
TSD	26.1	73.5	0.40	57.5	5.50	< 0.1	< 0.01	36.5
HTT	69.5	29.2	1.30	79.0	4.00	0.11	0.008	15.5
CC	80.7	18.6	0.70	87.0	3.40	0.25	< 0.004	8.30
HV	61.5	32.3	6.10	81.3	5.15	1.57	0.85	4.96
MV	67.4	24.0	9.0	81.4	4.46	1.86	0.50	3.10
LV	70.0	19.4	10.6	79.7	4.27	1.79	0.63	3.16

 $\overline{C_{\text{fix}}}$ fixed carbon; VM volatile matter, C_{tot} total carbon; H hydrogen; N nitrogen; S sulfur; O oxygen. * $C_{\text{fix}} = 100\% - (\%Ash + \%VM)$.

Fable 3 . Oxide content in the carbonaceous materials (wt% dry back)

Abbreviatior	h Al ₂ O ₃	CaO	SiO ₂	Fe ₂ O ₃	K ₂ O	MgO	MnO	Na ₂ O
TFR	0.006	0.71	0.062	0.009	0.23	0.10	0.0053	0.018
TSD	0.005	0.16	0.028	0.007	0.073	0.023	0.017	-
HTT	0.020	0.31	0.26	0.086	0.14	0.058	0.039	0.02
CC	0.006	0.32	0.028	0.009	< 0.002	0.11	0.044	< 0.009
HV	1.79	0.074	3.28	0.507	0.010	0.049	-	0.0015
MV	2.85	0.11	4.68	0.482	0.007	0.067	-	0.0033
LV	3.11	0.12	6.25	0.409	0.012	0.069	-	0.0070

The true density of the bio-coals was measured in a Micrometric Accupyc 1340 pycnometer (Micromeritics Instrument Corporation, South San Francisco, CA, USA). The sample was placed in a cell with a volume of ~37.67 cm³ and the pores were filled with helium gas. The prepared sample had a particle size of 1–2 mm and was dried before measurements. The true densities were 1.34, 1.41, 1.44, and 1.51 g/cm³ for TFR, TSD, HTT, and CC, respectively, and the trend was for increasing density with higher pre-treatment temperature. The received data for the three different types of high-quality coking coals generated from Gieseler and dilatometer tests showed a max. dilatation and max. fluidity of 278%, 107%, and 69% and 30,000 ddpm, 1092 ddpm, and 182 ddpm, for HV, MH, and LV coals, respectively. The Gieseler softening and re-solidification temperature for these coking coals was within the temperature range of ~386–500 °C.

2.2. Methodology

2.2.1. Thermoplastic Properties of Coking Coals Evaluated Using an Optical Dilatometer

The heating of a basic coal blend, BB, with and without a 5% and 10% addition of bio-coals was performed in an optical dilatometer from Leitz (Ernst Leitz Gmbh, Wertzlar, Germany), with an automatic image analysis system from Hesse Instruments (Hesse, Osterode am Harz, Germany). To secure the correct temperature readings, measurements were also conducted on zinc metal wire, of purity 99.996%, and a thin piece of a bismuth-tin alloy, with known melting points of 419.3 °C and 137 °C, respectively. The measured melting points were 409 °C and 137 °C, respectively.

The change in sample height and area with temperature was recorded and evaluated for similar parameters, as described in the standard ISO 23873. The main difference in comparison to the standard method is the lack of an applied load on the sample and the significantly smaller sample size. Due to the sample size and inhomogeneity of coals and bio-coals, variations in measurements can be expected. The variation test was repeated three times for two different coking coal blends with bio-coal, the standard deviation and standard error for the max dilatation were 0.98 and 0.56, respectively, for the first sample, and for the second sample 2.00 and 1.15, respectively. The samples in these tests were 3 mm in diameter and 3 mm in height, compared to 60 mm in length and 8 mm in diameter in the standard method. The raw materials were finely pulverized in a mortar and mixed with water to achieve smooth sample surfaces. The sample was heated at a heating rate of 3 °C/min to a final temperature of 550 °C. Based on the area measurement of the sample, the swelling index, SI (%), was calculated according to Equation (1).

$$SI(\%) = \frac{Change in area}{Original area} \times 100$$
(1)

2.2.2. Preparation of Coke

The recipes with relative additions of coking coals and bio-coal in the coal blend given in percentage weight are presented in Table 4. As seen, the ratios of bio-coals added were 5% or 10%. The blends with different bio-coal types added and the reference blend are presented in Table 5. The carbonaceous materials used were sieved and added to the coal blend in the proportions 19–21 wt% of +2.8 mm fraction, 30–34 wt% of a fraction -0.5 mm, and the rest of the material was in between, +2.8–0.5 mm. The coking coals and bio-coal were mixed carefully, and water was added to reach ~7.5% moisture. The mix was transferred into a graphite crucible with an inner diameter of 70 mm and an inner height of 210 mm, and the crucible was then placed in a Tamman furnace (Berlin, Germany), as shown in Figure 1. Two-thirds of the crucible were packed with moist carbonaceous materials to achieve a bulk density of ~800 kg/m³. Furthermore, to record the temperature of carbonaceous materials during the coking, a thermocouple (k-type) in a protection tube of alumina was placed in the middle of the sample bed. A thermocouple (s-type) was used between the graphite crucible and the graphite tube to monitor the heating of the Tamman furnace.

Cool Pland	Recipe (wt%)				
Coal Diellu —	HV	MV	LV	Bio-Coal	
Basic coal blend (BB)	28.0	32.0	40.0	-	
BB + 5% bio-coal	26.6	30.4	38.0	5.0	
BB + 10% bio-coal	25.2	28.8	36.0	10.0	

Table 4. The mixing ratio of coal blend with bio-coal (wt%).

Table 5. Added bio-coals and abbreviations of coking coal blends for carbonization in the Tamman furnace and the produced cokes.

Bio-Coals	Coking Coal Blend	Coke
-	HV, LV and MV	BB
TED	BB + 5% TFR	TFR5
IFK	BB + 10%TFR	TFR10
TCD	BB + 5%TSD	TSD5
ISD	BB + 10%TSD	TSD10
τταντ	BB + 5% HTT	HTT5
HII	BB + 10% HTT	HTT10
66	BB + 5% CC	CC5
	BB + 10% CC	CC10



Figure 1. Schematic setup for cokemaking in the Tamman furnace.

The coal blends were heated under inert conditions using nitrogen gas (purity 99.996% and a flow rate of 10 L/min), according to the heating profile stated in Figure 2. The temperature increase was initially slow, and the samples were kept for ~1.5 h at 100 °C, then the sample was heated up to 1050 °C, and the sample was maintained for 1.5 h at 1050 °C, and finally the furnace was turned off and the coke was allowed to cool in N₂ gas atmosphere. The produced coke was discharged from the crucible, crushed, and screened into a fraction of 1–2 mm and kept in a desiccator until characterization was carried out.

The coke yield was calculated according to Equation (2) and is presented in Table 8.

Coke yield (%) =
$$\frac{m_1}{m_0(1 - \text{moisture } \% \times 0.01)}$$
 (2)

 m_1 is the remaining mass of coking coal blend after carbonization and m_0 is the amount of coking coal blend before carbonization.

Selected coal blends, BB, TSD5, and HTT5, were also carbonized in a 10-kg-retort at DMT GmbH & Co. KG in Essen, Germany [39]. The carbonaceous materials used were sieved to achieve the proportions 18–20 wt% of +3.15 mm a fraction, and 30–34 wt% of a fraction -0.5 mm, and the rest was between 3.15 and 0.5 mm. The small-scale coking test retort that was charged with approximately ~11 kg of coking coal blend had a height of 50 mm and a diameter of 180 mm [40,41]. The set points for moisture content and bulk density (wet) were ~9% and 800 kg/m³, respectively. The duration of carbonization at DMT was approximately 4 h, and the final coke temperature was ~1020 °C. The coke was analyzed for CRI, CSR (ISO 1889-4), and mechanical strength, using the Micum test, according to ISO556, but modified for smaller sample sizes according to [40]. CRI corresponds to the weight loss due to the carbon solution loss reaction of carbon in coke under a CO_2 atmosphere at 1100 °C for 2 h. Due to the gasification reaction consuming carbon, the outer layer of coke particles becomes porous and the mechanical strength against abrasion drops. To measure this effect, the reactivity test was followed by determination of CSR in a tumbler test, which corresponds to the percentage of particles that remain larger than 10 mm after 600 rotation [1]. The M40 and M10 deduced from the Micum test describe the resistance to physical degradation and were calculated from the percentage material remaining of +40 and -10 mm, respectively, after 100 revolutions. In Europe, the Micum (M40/M10) test for cold mechanical strength is commonly used and the acceptable ranges are M40 > 80% and M10 < 7% [17].



Figure 2. Typical temperature profile during carbonization in the Tamman furnace.

The textures of bio-coal, coke, and bio-cokes were investigated using a light optical microscope (LOM, Nikon ECLIPSE E600 POL, Tokyo, Japan). The samples were mounted in epoxy resin and the surfaces were polished before the studies. The chemical composition of coke prepared in the laboratory and technical scale was determined by SSAB Luleå using Thermo an ARL 9900 X-ray fluorescence (XRF) instrument (Zagreb, Croatia) with a rhodium tube at 50 kV and 50 mA.

2.2.3. Thermogravimetric Analysis

In this study two thermogravimetric analyzers were used. A TGA, Netzsch STA 409 instrument (sensitivity $\pm 1 \mu$ g, Columbus, OH, USA) attached to a Quadruple Mass Spectroscope (QMS, Netzsch, Selb, Germany) was used to monitor the mass loss and off-gas analysis, respectively, during the pyrolysis of carbonaceous materials. The TGA/QMS used in this study is described in detail in reference [42]. A TGA equipment Netzsch STA 409, with graphite furnace [8], was used when studying the reactivity of the coke and bio-coke.

Carbonization was done using TGA/QMS equipment. A sample of ~150 mg was placed in an alumina crucible and heated according to the heating profile presented in

Figure 3. The carbonization was performed in an inert atmosphere of N_2 gas (purity 99.996%) having a flow rate of 200 mL/min.

Reactivity tests were performed using a CO₂ atmosphere at a rate of 300 mL/min for the coke and bio-coke samples that were carbonized in the Tamman furnace and at DMT. Particles of 1–2 mm size were used. Approximately 40–50 mg of the sample was placed in an alumina crucible with low edges, to avoid accumulation of formed CO in the sample and heated in TGA equipment and heated at 20 °C/min from room temperature up to 600°C, and at 3 °C/min between 600 and 1100 °C.



Figure 3. Heating profile used for the carbonization of carbonaceous materials in the TGA tests.

The accuracy of the balance and temperature for the graphite furnace was checked using calcium oxalate and gold in an argon atmosphere up to 1000 °C and 1100 °C, respectively. The mass loss for calcium oxalate was 12.3%, 19.1%, and 30.3% up to 300 °C, 600 °C and 1000 °C, respectively, which can be compared with the reference data of 12.3%, 18.9%, and 30.2%, with a tolerance of ± 0.2 %. The known melting point for gold is 1064 °C, and the measured one was 1069 °C. The influence of the possible inhomogeneity in the coke sample was checked in a TGA, Netzsch STA 409 Spectroscope (QMS, Netzsch, Selb, Germany), and three reactivity tests was performed for one sample, while the TGA result showed consistent results without significant variations; the standard deviation for mass loss was ± 1 %.

3. Results

3.1. Bio-Coals and Coal Properties

3.1.1. Structure of Bio-Coals

Figure 4 shows LOM images of the four different types of bio-coals used in the coking coal blend. It is noted that the structure of the TFR is characterized by a spherical and compact structure, while samples of TSD showed a duct structure with elongated pores, as seen in Figure 4a and 4b, respectively. From the areas studied with the microscope, it was indicated that the TSD sample contained cells of larger size, $26-48 \mu m$, compared to TFR, which had cells of sizes around 9–24 μm . The structure of CC had a regular distribution of pores in a size between 40 and 79 μm , and it had a duct structure, as seen in Figure 4d. The texture of the HTT sample contained more collapsed pores, with a pore size between 6 and 11 μm , as seen in Figure 4c.

3.1.2. Carbonization Behavior of Single Coals or Bio-Coals

Table 6 shows the mass loss for carbonaceous materials at different temperatures. TSD and TFR had the most mass loss in the temperature range 200–400 °C, while the CC and HTT had a main mass loss above 500 °C. It is seen that TSD had a higher mass loss than TFR at 200–400 °C. At temperatures above 400 °C, TFR had a slightly higher mass loss than TSD. In general, the mass loss of bio-coals is higher than for coals. The maximum mass loss for coals occurs in the temperature range 400–500 °C.



Figure 4. Microstructure images of bio-coals (a) TFR, (b) TSD, (c) HTT, and (d) CC.

Abbreviation	200–400 °C	400–500 °C	500–800 °C	800–1050 °C
TFR	42.7	10.8	6.69	1.10
TSD	56.3	7.36	5.46	0.80
HTT	4.30	5.66	14.9	1.20
CC	3.63	3.93	13.3	1.22
HV	2.27	14.5	7.87	1.40
MV	1.79	11.1	8.83	1.17
LV	1.11	7.14	8.54	1.25

Table 6. Mass loss (wt%) for coals and bio-coals during carbonization.

During the thermal decomposition of bio-coals and coals the gases H₂, CO, CO₂, H₂O, and ionized hydrocarbons such as CH_4^+ , $C_2H_5^+$ were detected. However, the lengths of the carbon chains in the released hydrocarbons were probably initially longer, before thermal decomposition and excitation in the QMS. The highest ion currents recorded by QMS were for m/z of 2, 18, 15, 29, and 44; judged to represent H₂, H₂O, CH_4^+ , $C_2H_5^+$, and CO₂, respectively. The recorded ion currents for H₂, H₂O, CO₂, and CH_4^+ are shown in Figure 5. Hydrocarbon such as CH_4^+ was detected at 290 °C for torrefied biomass (TFR and TSD) and at 455 °C for pyrolyzed biomass (HTT and CC), see Figure 6a. Overlapping between the peaks for ionized hydrocarbons CH_4^+ was seen within the temperature range 430–630 °C for coals and all types of bio-coals. The release of H₂ started at 310 °C for TFR and TSD, while it started at 500 °C for pyrolyzed bio-coals and coals, see Figure 5b. CO₂ was detected only for TFR and TSD within a temperature range of 119–770 °C, with a slightly higher intensity peak at 350 °C for TSD, see Figure 5c. H₂O was detected from 115 °C until 1050 °C for all types of bio-coals, but TFR and TSD had a higher intensity peak at 340 °C, see Figure 5d.



Figure 5. Off gas analysis of (a) CH_4^+ ; (b) H_2 ; (c) CO_2 ; and (d) H_2O for different types of bio-coals and coals at carbonization conditions in N_2 atmosphere.

3.2. Carbonization of Selected Coking Coal Blends in TGA

The TGA results for the carbonization of BB and coal blend with a 10% addition of TFR and TSD are presented in Figure 6. The total mass loss achieved for TFR10 and TSD10 was higher than for BB. The devolatilization of TFR10 and TSD10 started at ~290 °C and 340 °C, respectively, compared to at ~400 °C for the BB. DTG analysis shows that the TFR10 and TSD10 had two devolatilization steps, while the main devolatilization for BB occurred in one step, above 400 °C.

Hydrocarbon, such as $C_2H_5^+$, was detected at 300 °C for TFR10 and TSD10, while it was detected at 400 °C for BB, as seen in Figure 7a. CH_4^+ was detected in the temperature range of ~400–600 °C, and the release of H₂ started at ~430 °C for all coking coal blends, see Figure 7b and 7c, respectively. The release of CO₂ was negligible in all coking coal blends and is therefore not presented.

Plastic Properties of Coking Coal Blends

The results from the optical dilatometer tests for BB and blends with 5 or 10% addition of bio-coals are shown in Table 7. The results show that the max. dilatation of CC5 and HTT5 was quite similar to BB but dropped for the other coking coal blends. The drop in max. dilatation was more pronounced for coking coal blends containing 10% of bio-coals, especially when using the torrefied bio-coals TSD and TFR. The swelling index, SI, decreased with the addition of bio-coals to the BB, and the decrease was more significant for the addition of TFR, TSD, and HTT in comparison to CC. The coking coal blends produced from the mixtures BB, TSD5, and HTT5 were also analyzed at DMT using DIN 51739. The max. dilatation was found to be 48, -10, and 41 for BB, TSD5, and HTT5, which was a similar trend as in the modified tests in the optical dilatometer.



Figure 6. (a) TGA (b) DTG for TFR10, TSD10, and BB at carbonization conditions in N2 atmosphere.



Figure 7. Off gases detected by QMS when testing coking coal blends at carbonization conditions in the TGA, (**a**) $C_2H_5^+$, (**b**) CH_4^+ , and (**c**) H_2 ; for TFR10, TSD10, and BB.

	Max. D	SI	
Coal Blend —	°C	%	%
BB	436	15.8	68
TFR5	425	10.4	22
TSD5	430	8.29	19
HTT5	423	15.2	20
CC5	421	16.3	31
TFR10	346	-0.38	-
TSD10	406	-1.50	2
HTT10	417	8.03	2
CC 10	428	9.77	18

Table 7. Thermoplastic parameters for the basic coal blend, BB, and coal blends with the addition of bio-coals, deduced from optical dilatometer tests.

SI: Swelling index.

3.3. Properties of Coke

3.3.1. Laboratory Cokemaking

Table 8 shows the coke yields for the produced coke and bio-coke. As could be expected, the coke yield was lower for bio-coke-containing torrefied bio-coals, TFR, and TSD, in comparison to bio-coke containing the pyrolyzed ones, HTT and CC.

Table 8. Coke yield (%) of coke and bio-coke.

BB	TFR5	TFR10	TSD5	TSD10	HTT5	HTT10	CC5	CC10
76.5	70.4	74.0	75.1	73.6	78.5	77.0	77.7	76.5

3.3.2. Structure of Bio-Cokes and Chemical Composition

The structure of the produced coke at laboratory and technical scales was examined in LOM. Figure 8 shows the TSD5 sample, which indicates that bio-coals possibly retained their structure after carbonization. The elongated duct cell shape seen for the TSD was also found in the coke, as seen in Figures 8a and 8b, respectively.

Coke prepared in Tamman furnace

Coke prepared at DMT



Figure 8. LOM images showing the microstructure for coke and bio-coke samples for (**a**) TSD5 and (**b**) TSD5-DMT.

Analyses using XRF of bio-coke ash showed that there was no significant difference in the ash amount or composition between the produced bio-cokes when 5 or 10% biocoal was added, as the coals in the basic blend were mainly influencing the average ash composition. However, local variations in ash composition due to the presence of bio-coal ash can still be important.

3.3.3. Reactivity of Coke Prepared at Lab and Technical Scale

Table 9 shows the mass loss of the sample during the reactivity test of coke produced from BB and bio-coke containing 5% and 10% bio-coal. The TGA analysis showed that bio-coke containing 5% and 10% bio-coal is more reactive than the BB. HTT5 is an exception, with similar gasification as BB. TFR5 had a higher mass loss than other bio-cokes, with 5% bio-coal addition. Bio-coke TSD5 and CC5 had quite similar mass losses. HTT10 had a higher mass loss than the other bio-cokes with 10% bio-coal addition, already occurring at lower temperatures. The gasification of bio-coke containing 5% bio-coal started at lower temperatures in comparison to BB and the start of reaction temperature further decreased with 10% bio-coal in the coking coal blend.

Table 9. Temperature for the start of gasification and accumulated mass loss at different temperatures, as measured in TGA.

Tupos	Samplas	Samples Start of		Accumulated Mass Loss (%), Up to Each Temperature			
Types	Samples	Gasification (°C)	950 °C	1000 °C	1050 °C	1100 °C	
	BB	953	0.00	0.96	4.36	11.5	
lechnical scale coke produced	TSD5	943	0.86	3.13	7.69	15.9	
in retort at DMT	HTT5	908	1.80	4.25	7.94	14.5	
	BB	964	0.23	1.63	4.94	11.2	
	TFR5	895	2.72	5.30	10.8	19.8	
	TSD5	912	1.42	3.34	7.65	15.4	
	HTT5	905	1.49	3.30	6.36	11.9	
Laboratory coke produced	CC5	919	1.50	4.31	9.65	17.9	
in a Tamman furnace	TFR10	869	3.45	6.51	12.1	20.2	
	TSD10	888	2.00	4.48	9.90	18.9	
	HTT10	884	4.49	8.68	13.2	20.7	
	CC10	875	2.44	6.07	12.0	20.9	

The quality of coke carbonized at technical scale was analyzed for CRI, CSR, and Micum test, see Table 10. The results showed a higher mass loss for TSD5 compared to HTT5. The same trend was found for the reactivity measured by TGA for lab and technical scale produced coke.

Table 10. Quality of coke prepared at technical scale.

	CRI/CS	SR Test	Drum Test/Micum		
Abbreviations —	CRI	CSR	M40	M10	
BB	28.6	57.6	80.7	7.0	
TSD5	36.5	46.6	76.4	7.7	
HTT5	31.8	57.8	78.5	7.8	

The drum test results for bio-cokes prepared at DMT showed that the M40 for bio-coke with 5% bio-coal addition of HTT was quite similar to BB, and this indicates that HTT5 had a high strength. The true density was measured for bio-coke samples carbonized at laboratory and technical scales, and the results were quite equal, 1.89 and 1.82 g/cm³, respectively.

4. Discussion

4.1. Influence of Bio-Coal Carbonization on the Thermoplastic Properties of Coking Coal

The maximum dilatation for coking coal blends decreased with 5% bio-coal addition of torrefied bio-coals (TFR, TSD), whereas it was not significantly changed for CC and HTT. The maximum dilatation decreased further with a 10% bio-coal addition, especially for TFR and TSD. It has been stated in the literature that the release of H_2 [9,43,44] can influence fluidity. However, the release of H_2 from bio-coals occurred in a similar temperature range as for coking coals, and can, thus, not explain the impact on fluidity from bio-coal addition. From the results, it is noted that the release of hydrocarbons (for example CH_4^+ detected in

QMS) from HTT and CC occurred in the plasticity temperature range for the coals, possibly contributing to the better development of plasticity in these blends.

In comparison to HTT or CC, a significantly larger effect on max dilatation was seen when adding TSD and TFR, especially at 10% addition, which could have been due to the higher O₂ content in TFR and TSD, 34% and 36.5%, respectively, compared to 15.5% and 8.3% for HTT and CC. Mochizuki et al. and Tsubouchi et al. [45,46] found that heteroatoms such as oxygen have a deleterious effect on the plastic properties of coal. From these results, the VM released from bio-coals including a high amount of oxygen is likely to inhibit the thermoplastic properties of the coal, which was discussed in [13,14]; however, the use of charcoal with a low oxygen content mainly has effects as an inert material. It was reported that the addition of inert materials to coking coal may cause a reduction in thermoplastic properties, due to the effect from the high surface area of bio-coals acting as adsorbents of the primary decomposition products of coking coal, which binds the plasticizing part of the coal, favoring the inhibition of fluidity development [47].

According to the literature [48], the presence of a higher content of catalytic components, e.g., K_2O and CaO, in TFR, as mentioned in Table 3, could also have an impact on lowering the dilatation in TFR5 and TFR10. However, as the maximum dilatation is always lower for TSD, the oxygen content seems to be of greater importance. The low O_2 content in CC and HTT could be the reason for CC5 and HTT5 having similar maximum dilatations to BB. The CC5 results agree with Ng et al. [23], who found that the presence of a 5% charcoal addition to the blend did not affect the development of a plastic layer of coking coal.

4.2. Influence of Bio-Coal Addition on Coke Quality

There are many parameters, i.e., cell structure of bio-coal, amount of reactive carbon originating from bio-coal present in coke, and contribution of catalytic oxides in the ash, that simultaneously affect bio-coke reactivity. Therefore, it is difficult to make a precise conclusion about which parameter is most important.

The TGA results show that the start of the carbon gasification reaction was lowered by a higher bio-coal addition, and this could have been due to an increase in the content of reactive bio-coal carbon that was gasified at a lower temperature in comparison to carbon originating from coking coals. The lowering of the start of gasification temperature for bio-coke, in comparison to a reference coke, was reported in [18,25,27], and according to Suopajärvi et al. [25] it was lowered by 30–50 °C for bio-coke containing 5% charcoal. In this study, the temperature was lowered by 45 °C for a corresponding addition of CC. As expected, in bio-cokes containing bio-coal with a higher content of catalytic components in the ash, the start of gasification occurred at lower temperature and the reactivity was higher, as seen for TFR5 and TFR10, in comparison to TSD5 and TSD10.

The cell structure, i.e., open or closed, may also affect bio-coke reactivity, as it has an impact on the gas diffusion. The compact cell structure of HTT could be the reason for HTT5 having almost the same behavior as BB; but with a higher content of carbon originating from HTT in HTT10, the reactivity is higher than for BB coke, which reflects the complex set of parameters influencing coke reactivity. The CRI and CSR test results for the cokes produced at technical scale show that the difference between HTT5 and BB is minor, and this indicates that it could be possible to maintain the properties of industrial coke with a 5% HTT addition. The CRI test results for cokes produced at technical scale showed that the CRI values increased in the order BB < HTT5 < TSD5, and vice versa for CSR. The higher CRI for TSD5 could have been due to the difference discussed above; high VM and oxygen content may contribute to the higher porosity of produced bio-coke, which enhances the diffusion of CO₂. The low mechanical strength of TSD5 produced at technical scale could have been due to the higher oxygen content in TSD, and this will have a deleterious effect on the plastic properties of coal. The CRI results for the technical scale coke followed the same trend as the reactivity tests conducted in TGA. Hayashizaki et al. [49] reported that the coke strength largely correlated to the dilatation. When the coal dilatation is insufficient, the voids between coal particles will not fill up and coal particles will not be tightly bonded together, which decreases the coke strength. This could have also influenced the diffusion of gas within the coke piece.

5. Conclusions

This study aimed to understand the impact of different bio-coal types from different origins and pyrolysis degrees, with added amounts of 5% or 10% to an industrially used coal blend, on carbonization and quality of bio-coke structure and reactivity. The following conclusions can be drawn:

- Pyrolyzed bio-coals, such as charcoal and high temperature torrefied bio-coal having a devolatilization behavior such as coking coals, did not have a significant effect on the fluidity up to a 5% addition; while they had a moderate effect on lowering the fluidity at 10% addition.
- Torrefied bio-coals, such as forest residue and sawdust, with a high content of volatile matter releases hydrocarbons, such as CH₄⁺, at lower temperature than coking coals and have a high O₂ content. These properties of bio-coals lead to deleterious effects on the plastic properties of coking coal blends, especially at 10% addition. However, for bio-coals with a low volatile and oxygen content, the plastic properties, as shown in the optical dilatometer test, are less influenced.
- All addition of bio-coal in cokemaking lowers significantly the starting temperature for gasification, in comparison to reference coke; with differences in the content of catalyzing compounds having a smaller effect.
- Coke produced at laboratory and technical scales from coking coal blends with 5% addition of high-temperature torrefied pelletized sawdust or 5% torrefied sawdust show a similar trend in reactivity as measured using thermogravimetric analysis.
- Technical scale produced types of bio-coke showing low reactivity in the thermogravimetric analysis also showed a high quality in standard tests for reactivity, strength after reaction, and mechanical strength, when technical scale produced bio-coke was tested. This indicates that the coking coal blend with a 5% high temperature torrefied bio-coal could be suitable for industrial use.

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