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The Effect of Bio-Coal Agglomeration and High-Fluidity Coking Coal on Bio-Coke Quality

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Abstract: Metallurgical coke with high strength and low reactivity is used in the ironmaking blast furnace. Replacement of some coking coal with bio-coal was shown to result in lower strength and higher reactivity of produced coke due to introduction of reactive bio-coal carbon and ash components catalyzing the Boudouard reaction, but also due to lowering of the coking coal blend fluidity, which influences coke strength and reactivity negatively. The current study aims to investigate the possibility to counteract negative impact from bio-coal addition on fluidity and coke reactivity by using high-fluidity coking coal and by agglomeration of bio-coal before addition. Original bio-coal and micro-agglomerate of bio-coal was added at 10%, 15% and 20% to the coking coal blend. The influence of bio-coals on the coke reactivity was measured by using CO_2 in a thermogravimetric analyzer. Selected cokes and bio-cokes were produced in technical scale, and their reactivity and strength were measured in standard tests. The effect on dilatation of adding bio-coal or crushed agglomerates of bio-coal to the coking coal blends was measured in an optical dilatometer. The results show that by using a coking coal blend containing high-fluidity coal with agglomerated bio-coal, the max. contraction is increased, whereas the opposite occurs by using original bio-coal. The results show overlapping between contraction occurring before dilatation and during dilation, which affects max. dilatation. The bio-coke containing high-fluidity coal with agglomerated bio-coal has lower reactivity in comparison to bio-cokes with original bio-coal or bio-coke with agglomerated bio-coal produced from a coking coal blend without high-fluidity coal. The reactivity of coke produced in technical scale, as measured in CRI/CSR tests, shows a similar trend regarding reactivity, as measured by thermogravimetric analysis, on coke produced in laboratory scale.

Keywords: bio-coke; torrefied sawdust; agglomerated bio-coal; high-fluidity coking coal

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1. Introduction

Metallurgical coke is obtained by carbonization of coking coal blends up to ~1100 °C [1]. During carbonization, softening, swelling, evolution of volatiles, shrinking and, finally, re-solidification to obtain coke occur [2]. Within the plastic range of approximately 350–550 °C, fluidity is induced by breaking the carbon bonds and forming a plastic state, where coal particles soften, volatiles are released and swelling occurs, and solidification takes place to form a semi-coke. The plastic behavior is considered significant for coke quality, e.g., strength [3].

The effects from additives in coking coal blends have been investigated by Fernández et al. [4,5]. By the addition of coal tar pitch and benzenol, the fluidity was enhanced due to the presence of highly condensed aromatic structures and hydrogen donors that contribute to the stabilization of free radicals present during the coal plastic range. By addition of non-coking coals and recycled tires, the fluidity decreased due to the presence of heteroatoms, such as oxygen, which have a negative impact on the development of coal plasticity. The presence of oxygen promotes condensation and facilitates the re-solidification of the system.

The main purpose of using additives is to preserve the coking properties of the blend when replacing the prime coking coals, e.g., with poor or non-coking coals. The addition of carbonaceous material to coking coal blend has two effects: chemical interaction between devolatilization products from coal and additives during heating, and physical adsorption of products responsible for the thermoplasticity of coal [6–8]. To produce high-quality coke, it is required to have maximum fluidity and dilatation greater than 400 ddpm and 55%, respectively [9,10]. According to Kumar et al. [9], the fluidity of the coal blend influences bonding during cokemaking and affects the CSR (coke strength after reaction) of produced coke. Lowering of the fluidity can either be due to the presence of a higher amount of inert macerals in the coking coal blend than can be bound properly by plastic material, or due to the oxidation of coal during weathering causing loss of coal fluidity.

The substitution of coking coals with bio-coal (pre-treated biomass) in cokemaking could be a possible way to reduce fossil CO_2 emissions linked to BF ironmaking [11–13]. The biomass generation time is comparatively short, and effects on global warming can be reduced as the carbon cycle is closed [14]. When adding biomass or bio-coal to the coking coal blend and producing bio-coke (bio-coal containing coke), the fluidity of the coking coal blend is decreased [7,8,15,16]. Montiano et al. reported that the fluidity decreases with increasing raw sawdust addition from 0.7 to 3% [15], and pre-treated sawdust addition of 2% and 5% [7] caused a reduction in fluidity by up to 50% or 70%, respectively. Fraga et al. and Guerrero et al. found that charcoal addition (2, 5, 10 and 15%) to coking coals results in lower fluidity [8,16], which could be counteracted by the addition of coal tar. For charcoal fractions of mean size 12 µm, 60 µm and 189 µm, the reduction in fluidity increased with decreased particle size, likely due to the greater surface area of contact between coal particles and inert components [8]. Partial overlap of the temperature range for volatile matter (VM) release between charcoal having higher oxygen content in the volatiles and coal may also contribute to lower fluidity, as it promotes condensation [6].

Charcoal addition to coking coal blends resulted in a higher coke reactivity index (CRI) when 5% of charcoal with size <0.07 mm was added, compared to when coarse charcoal (2–9 mm) was used [17,18], and CRI further increased by 8% [19] and 10% charcoal addition [20]. The higher increase in CRI for fine charcoal was due to the fact that oxides of Ca, acting as a catalyst and promoting the reaction of carbon with CO_2, were more dispersed in the coke piece, compared to when using coarse charcoal [17,18,20].

Previous studies have shown that partial replacement of coking coals with different types of bio-coal reduced the fluidity of the coking coal blend and increased the coke reactivity [21]. It was indicated that compacted bio-coal and bio-coal with low content of catalytic oxides resulted in less negative impact, whereas high O_2 content impaired the plastic properties and resulted in higher coke reactivity.

This study aims to explore if an initial higher fluidity of the coking coal blend and agglomeration of bio-coal can counteract negative effects on the fluidity of the coking coal blend and the reactivity of bio-coke and, thereby, allow higher bio-coal additions, i.e., up to 20%. Therefore, the effect on the fluidity and bio-coke reactivity of adding original or agglomerated torrefied sawdust to two different coking coal blends consisting of three coking coals, as typically used in European industrial plants, has been investigated in laboratory scale. The coking coal blends differ in terms of the fluidity of the used high-volatile (HV) coking coal. To further validate the results, technical-scale carbonization was conducted with selected coking coal blends containing the high-fluidity HV coal.

2. Materials and Methods

2.1. Materials

In previous studies, the addition of 10% torrefied sawdust (TSD) provided by BioEndev AB in Sweden from pine/spruce pretreated at 296 °C had a significant effect on fluidity and coke reactivity [21]. Therefore, this bio-coal type was selected for this study to possibly counteract the negative effects by agglomeration of TSD and/or by use of a HV coal of higher fluidity in the coking coal blend.

TSD was agglomerated using a hydraulic laboratory press TP20 with compaction pressure 200 kN to produce agglomerates with a diameter of 4 cm and a length of 1 cm. Prior to cokemaking, the agglomerates were crushed, and agglomerated particles in fractions of around 20% 5.6–2.8 mm, 48% 2.8–0.5 mm and 32% less than 0.5 mm were achieved, i.e., in a similar size range to that of the coking coals, see Section 2.2.2. Four different types of coking coals, one low volatile (LV), one medium volatile (MV) and two different HV coals, were used in the coking coal blends, with or without the addition of TSD or crushed agglomerates of TSD (TSDa).

The proximate and ultimate analysis for TSD was conducted according to standard methods by ALS Scandinavia AB [22], and the analyses for coking coals were provided by the Swedish steel producer SSAB Europe, in Luleå [23]. Carbonaceous materials used in the study and their proximate and ultimate analyses are presented in Table 1. The TSD has high contents of VM and oxygen and low content of fixed carbon (C_{fix}); the opposite is the case for coking coals.

Table 1. Proximate, ultimate analysis results for carbonaceous materials and maceral composition of coal (dry base).

Carbonaceous Materials		Proximate Analysis (wt%)			Ultimate Analysis (wt%)					Maceral (%)	
		C_{fix}	VM	Ash	C_{tot}	H	N	S	O		
TSD	Torrefied sawdust	26.1	73.5	0.40	57.5	5.50	<0.1	<0.01	36.5	Vitrinite	Inertinite
HV1	HV coal 1	62.5	31.3	6.3	81.7	5.02	1.42	0.76	4.8	65.6	21.8
HV2	HV coal 2	59.9	32.6	7.5	80.0	5.11	1.50	1.09	4.9	66.1	24.1
MV	MV coal	67.4	24.0	9.0	81.4	4.46	1.86	0.50	3.1	59.0	35.8
LV	LV coal	70.0	19.4	10.6	79.7	4.27	1.79	0.63	3.2	66.1	28.0

C_{fix} Fixed carbon = 100 − (%ash + %VM); VM volatile matter; C_{tot} Total carbon; H hydrogen; N nitrogen; S sulfur; O oxygen.

The dilatometer test results supplied by SSAB showed that HV2 has a higher fluidity in comparison to HV1; the max. dilatation was 313% for HV2, compared to 205% for HV1. The maximum fluidity that was possible to measure in the Gieseler test was 30,000 ddpm, and this is the reason for the similar max. fluidity of 30,000 ddpm for both HV coking coals. The analysis of macerals is presented in Table 1 and shows that HV2 has a higher content of inertinite than HV1. The softening and re-solidification occur within temperature ranges of ~386–500 °C for the coking coals.

2.2. Methodology

2.2.1. Thermoplastic Properties of Coking Coal Blends

The coking coal blends used in technical-scale cokemaking were analyzed for dilatation and fluidity according to DIN 51739 and ASTM D 2369, respectively, and measurements of each sample were repeated twice.

Samples of the coking coal blends used for laboratory cokemaking were pulverized finely in a mortar and mixed with water to achieve smooth surfaces of the prepared briquette. The briquette was heated in air at a rate of 3 °C/min to a final temperature of 550 °C in an optical dilatometer from Leitz (Ernst Leitz Gmbh in Wertzlar, Germany) with an automatic image analysis system from Hesse Instruments (Hesse, Osterode am Harz, Germany). The changes in sample height and area with temperature were recorded, and the data evaluated for max. dilatation and max. contraction, as described in ISO 23873, and the swelling index was calculated from the change in sample area. The main difference in comparison to the standard method is the lack of applied load on the sample, and the significantly smaller sample size, 3 mm in diameter and 3 mm in height, compared to 60 mm in length and 8 mm in diameter in the standard method. Due to the small sample size and the inhomogeneity of coals and bio-coals, variations in measurements can be expected. To estimate the variation in the test method, measurements were repeated

three times for two different coking coal blends, and the standard deviation was about 0.98 and 2.00 for max. dilatation. The temperature readings were checked by conducting measurements on zinc metal wire of purity 99.996% and a thin piece of bismuth tin alloy. The melting points of the zinc and bismuth tin alloy were determined to be 409 °C and 137 °C, respectively, which can be compared with the known measurements of 419.3 °C and 137 °C.

2.2.2. Preparation of Coke

The recipes used are given in Table 2. The ratios among the HV, MV and LV coking coals were kept constant in all samples, and when 10%, 15% or 20% of bio-coal was added, the blend of coking coal was reduced correspondingly. The aimed particle size distribution of the coking coal blend was 19–21 wt% >2.8 mm fraction, 30–34 wt% <−0.5 mm, and the rest of the material was 2.8–0.5 mm. The coking coals and TSD/TSDa were mixed carefully, and water was added to reach ~7.5% moisture. The mix of moist carbonaceous materials was packed into a graphite crucible to achieve a wet bulk density of ~0.80 kg/dm^3 (0.74 kg/dm^3 on dry basis). By knowing the sample weight and the diameter of the crucible and by measuring the height of the coking coal bed, the volume and bulk density could be calculated; the dry bulk density for each blend is presented in Table 2. The crucible was placed in a Tamman furnace (RPT Ruhstrat power Technology GmBH, Bovenden, Germany), and the description of the test setup in the Tamman furnace was presented in detail in a previous publication [21].

Table 2. Mixing ratios of coals and bio-coal (wt%) for coking coal blends used in laboratory and technical-scale carbonization, achieved bulk density of packed bed and abbreviations of the sample names.

Coal Blends		Composition, (wt%)					Bulk Density (Dry), kg/dm^3		Sample Abbreviations	
		HV1	HV2	MV	LV	Bio-Coal	Tech. Scale	Lab. Scale	Tech. Scale	Lab. Scale
Coke based on BB1	Basic coal blend (BB1)	28.0	-	32.0	40.0	-		0.74		BB1
	BB1 +10% TSDa	25.2	-	28.8	36.0	10.0		0.74		BB1_10TSDa
	BB1 + 15% TSDa	23.8	-	27.2	34.0	15.0		0.74		BB1_15TSDa
	BB1+ 20% TSDa	22.4	-	25.6	23.0	20.0		0.71		BB1_20TSDa
Coke based on BB2	Basic coal blend (BB2)	-	28.0	32.0	40.0	-	0.73	0.74	BB2^T	BB2
	BB2 + 10% TSDa	-	25.2	28.8	36.0	10.0	0.73	0.74	BB2_10TSDa ^{T}	BB2_10TSDa
	BB2 + 20% TSDa	-	22.4	25.6	23.0	20.0		0.71		BB2_20TSDa
	BB2 + 10% TSD	-	25.2	28.8	36.0	10.0	0.73	0.71	BB2_10TSD ^{T}	BB2_10TSD
	BB2 + 15% TSD	-	23.8	27.2	34.0	15.0	0.73	0.68	BB2_15TSD ^{T}	BB2_15TSD
	BB2 + 20% TSD	-	22.4	25.6	23.0	20.0		0.63		BB2_20TSD

The coal blends were heated under inert conditions in nitrogen gas (purity 99.996% and a flow rate of 10 L/min). The temperature increase was initially slow, ~5 °C/min, and the samples were kept for ~1.5 h at 100 °C, then the samples were heated up to 1050 °C at a rate of ~15 °C/min, and then kept at this temperature for 1.5 h before the furnace was turned off and coke was allowed to cool in N_2 atmosphere. Produced coke was discharged from the crucible, crushed, screened into a fraction of 1–2 mm and kept in a desiccator until characterization was carried out.

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

For technical-scale cokemaking, in the 11-kg retort at DMT [24], similar particle size distribution and bulk density was aimed for as in the laboratory tests, but the moisture content was 9.0%, which results in the lower bulk density of 0.73 kg/dm^3 on dry basis. Each coking coal (HV2, MV, LV) and bio-coal (TSD and TSDa) was crushed separately and blended according to the recipe, and water was added to reach 9.0% moisture. The mixed coal for the technical-scale samples, as stated in Table 2, was filled into the steel tube, placed into the carbonization furnace and pre-heated to 1050 °C. After four hours of coking, the steel tube was removed from the furnace. At this point, the temperature in the coke bed was approximately 1020 °C. After cooling, the coke quality was determined.

2.2.3. Coke Reactivity and Strength

For evaluation of the reactivity of laboratory-scale-produced coke, a thermogravimetric analyzer (TGA), Netzsch STA 409 with graphite furnace, cf. reference [2], was used. Approximately 40–50 mg of each coke sample in the fraction 1–2 mm was placed in an alumina crucible with low edges to avoid accumulation of formed CO when heated in CO_2 atmosphere at a flow rate of 300 mL/min. The sample was heated at a rate of 20°C/min from room temperature up to 600 °C, and at 3 °C/min between 600–1100 °C. Interrupted tests at up to 1050 °C were conducted under similar conditions, but with cooling in argon (flow rate 100 mL/min) using bio-coke samples containing 10% TSDa and HV coking coals with different fluidity (BB1_10TSDa and BB2_10TSDa) and for BB2_10TSD containing 10% TSD and high-fluidity coal HV2.

Technical-scale-produced coke was analyzed for CRI and CSR by DMT, in accordance with ISO 18894, after stabilization of produced coke by letting the coke fall from 4 m height on a 45° inclined steel plate. From drum tests (ISO 556), the results for JIS 15/150 and I_{40} and I_{10} were obtained, and Micum 40 (M40) and Micum 10 (M10) were calculated using conversion factors determined by DMT [24].

3. Results

3.1. Bio-Coal and Coal Properties

3.1.1. Structure of Bio-Coals

Figure 1 shows LOM images for original and agglomerated TSD. TSD is characterized by duct structure, but due to the agglomeration of TSD, the pores of TSDa became compacted, as seen in Figure 1.

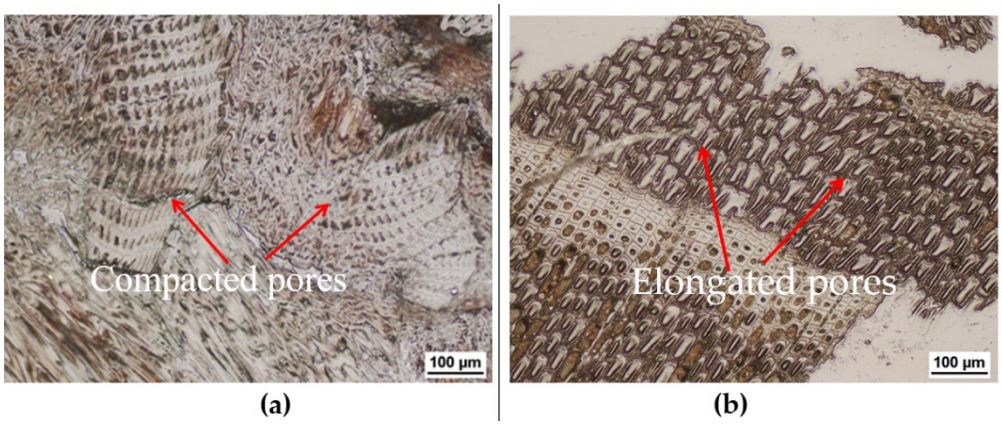

Figure 1. Microstructure images of (**a**) TSDa and (**b**) TSD. Red arrows indicate compacted and elongated pores in (**a**) and (**b**), respectively.

3.1.2. Plastic Properties of Coking Coal Blends

The results of optical dilatometer tests for BB1 and BB2 and these base blends with the addition of 10–20% of TSD and TSDa are stated in Table 3, and the plasticity parameters are explained in Figure 2. The results show that the max. dilation, max. contraction and swelling index (SI) are higher for BB2 containing a high-fluidity coking coal in comparison

to BB1. BB2 is the only sample with a max. contraction detected before max. dilatation; all other samples reach the max. contraction at 500 °C after max. dilatation.

Table 3. Thermoplastic parameters determined by optical dilatometer tests for BB1 and BB2 with different addition of TSD and TSDa.

Coal Blends		Max. Contraction		Max. Contraction Before Dilatation (a)		Max. Dilatation (b)		SI	Δ Height
		°C	%	°C	%	°C	%	%	%
Coking coal blend based on BB1	BB1	500	7.4	405	3.3	432	4.8	3.0	8.1
	BB1_10TSDa	500	12.8	393	3.7	395	2.9	0.8	6.6
	BB1_15TSDa	500	6.1	392	0.8	419	5.1	0.6	5.9
	BB1_20TSDa	500	6.9	380	−0.9	428	6.2	1.4	5.3
Coking coal blend based on BB2	BB2	410	3.8	410	3.8	439	8.3	4.2	12.0
	BB2_10TSDa	500	14.0	399	2.7	419	0.8	1.4	3.6
	BB2_20TSDa	500	10.1	328	1.1	421	2.8	1.1	3.9
	BB2_10TSD	500	3.6	357	−0.2	432	4.7	2.9	4.4
	BB2_15TSD	500	2.4	284	0.2	418	10.1	1.5	10.3
	BB2_20TSD	500	2.5	391	−2.1	431	14.7	3.3	12.7

SI= swelling index = %change in sample area, Δ height = (a) + (b).

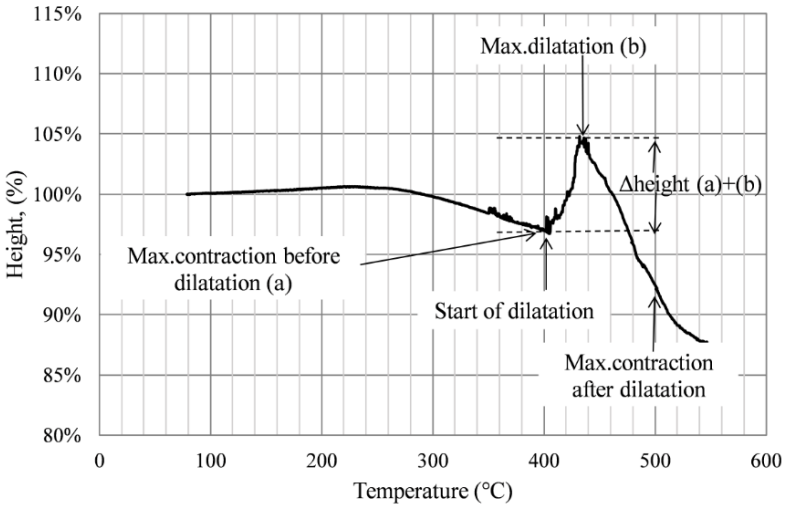

Figure 2. Illustration of the thermoplastic parameters deduced from optical dilatometer tests presented in Table 3.

Addition of TSD or TSDa results, in general, in a decrease in max. contraction before dilatation, more so when adding TSD. Moreover, the SI is generally lower for all bio-coal-containing blends in comparison to the corresponding base blend. Plots of the data indicate that the dilatation generally starts at a lower temperature with the addition of bio-coal. The overlap between contraction and dilatation contributes to reduced Δheight with the addition of TSDa, and this is more significant with addition to BB2. When adding TSD to BB2, the contraction before max. dilatation drops, but the max. dilatation and Δheight are not significantly changed compared to BB2.

The dilatometer and Gieseler test results for the coking coal blends used in technical-scale cokemaking are shown in Table 4. When adding bio-coal to the blends, only contraction is recorded, as seen in Figure 3. The max. contraction is 29% and similar for all coking coal blends containing bio-coal, and the temperature for max. contraction increases slightly with increased addition of TSD. Reference coke, $BB2^T$, has a lower max. contraction of 24% at around 430 °C, and the dilatation of 69% is reached at 462 °C. The plastic range for the reference blend is 81 °C, whereas the bio-coal-containing blends have no detected plastic range.

Table 4. Dilatometer and Gieseler test data for the coal blends before carbonization in technical scale at DMT. All blends contain HV2 coal, i.e., $BB2^T$.

Parameter	$BB2^T$	BB2_10TSD ^{T}	BB2_15TSD ^{T}	BB2_10TSDa ^{T}
Plastic range Dilatometer [°C]	81	–	–	–
Max. Contraction [%]	24	29	29	29
Max. Contraction temp. [°C]	430	469	492	481
Max. Dilatation [%]	69	–	–	–
Plastic range Gieseler [°C]	73	29	25	63
Max. Fluidity [ddpm]	217	4	3	19
Max. Fluidity [°C]	443	419	436	452

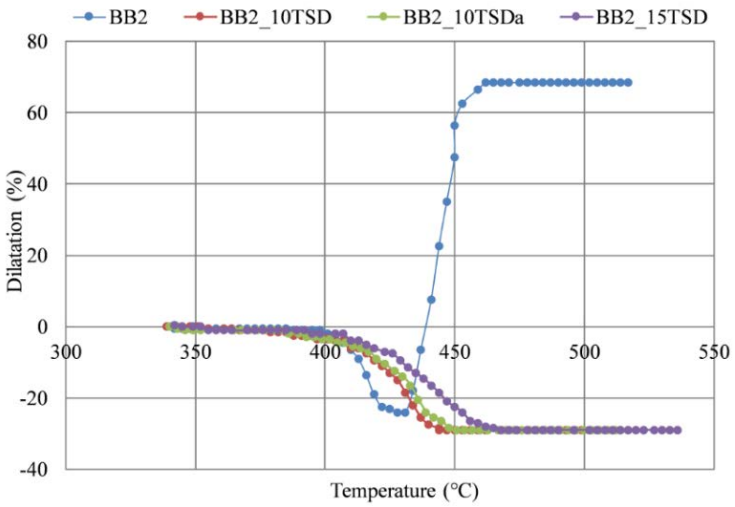

Figure 3. Dilatation for the blends carbonized in technical scale, average of two tests.

In the Gieseler tests, see Table 4 and Figure 4, all blends with bio-coal addition show low fluidity compared to the $BB2^T$ reference blend (217 ddpm), which contains HV2, a coal with high fluidity. However, the fluidity of BB2_10TSDa^T with 10% TSDa is significantly higher (19 ddpm) than when adding 10% or 15% TSD (4 and 3 ddpm). In addition, the maximum fluidity temperature is closer to the reference blend than for BB2_10TSD ^{T} and BB2_15TSD ^{T}.

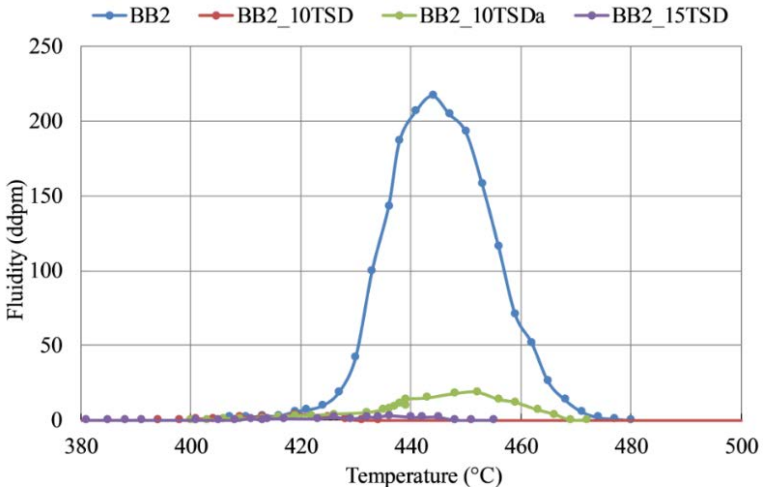

Figure 4. Gieseler test result for the blends carbonized in technical scale, average of two tests.

3.2. Properties of Coke

3.2.1. Structure of and Chemical Composition for Cokes Produced in Laboratory

It was not possible to reach aimed bulk density during production of some bio-cokes, especially for the bio-cokes containing TSD, but also to some extent for bio-cokes with 15–20% of TSDa, see Table 2, which may influence the structure of these bio-cokes. Further, BB2 showed significant swelling, and the coking coal bed was extended above the crucible during this carbonization test.

The structures of the produced coke and bio-cokes with 10% addition of TSD and TSDa were examined in LOM. Images of bio-coke samples containing agglomerated and original TSD show that the bio-coal is fixed in a matrix originating from coking coals. TSDa retains its compacted structure in bio-coke as, e.g., in BB2_10TSDa, seen in Figure 5a, and TSD retains its open duct structure as, e.g., in BB2_10TSD, shown in Figure 5b. In the bio-cokes BB2_10TSDa and BB2_10TSD, collected after interrupted reactivity tests up to 1050 °C, shown in Figure 5c,d, structures of bio-coal are still present. As seen in Table 5, the weight loss up to 1050 °C for bio-cokes BB2_10TSDa and BB2_10TSD are 5.9% and 6.6%, respectively.

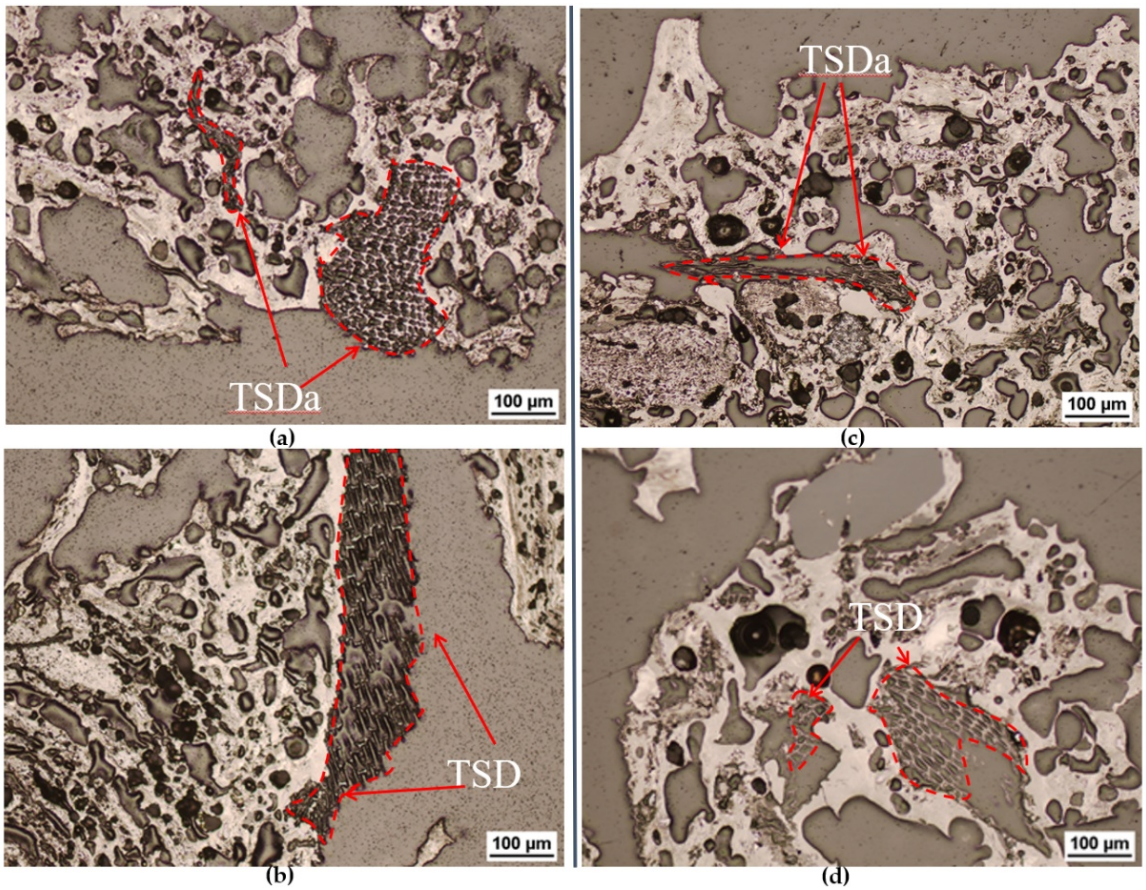

Figure 5. LOM images showing the microstructure for bio-cokes based on BB2 and containing 10% bio-coal, produced bio-cokes are (**a**) BB2_10TSDa and (**b**) BB2_10TSD. Subfigures (**c**) and (**d**) show bio-cokes collected after interrupted reactivity tests in CO_2 atmosphere up to 1050 °C, (**c**) BB2_10TSDa and (**d**) BB2_10TSD. Red arrows and lines indicate the bio-coal structure in the bio-coke.

Table 5. Start of gasification temperatures and accumulated mass loss of laboratory-produced cokes up to different temperatures as measured in TGA.

Cokes and Bio-Cokes		Start of Gasification Temperature, °C	Accumulated Mass Loss (%), up to Each Temperature (°C)			
			950 °C	1000 °C	1050 °C	1100 °C
Coke based on BB1	BB1	985	0.2	1.9	5.8	12.3
	BB1_10TSDa	899	0.9	3.1	7.1	13.5
	BB1_15TSDa	877	2.7	5.9	10.3	17.0
	BB1_20TSDa	871	3.1	5.7	10.2	16.9
Coke based on BB2	BB2	963	—	0.7	3.2	7.8
	BB2_10TSDa	891	1.4	3.0	5.9	11.0
	BB2_20TSDa	876	2.3	4.5	8.6	15.1
	BB2_10TSD	892	1.5	3.4	6.6	12.1
	BB2_15TSD	892	1.0	2.8	6.5	12.8
	BB2_20TSD	884	3.0	6.4	10.8	17.9

The XRF analyses of coke shows that the addition of 10–20% of bio-coal to the coking coal blend results in higher CaO content and basicity B2 (CaO/SiO_2) increase with increased amounts added, see Figure 6. The ratio of SiO_2/Al_2O_3 is quite similar for all cokes, based on the similar base blend, as the contribution from bio-coal to these elements are negligible. The ash content is also lowered when bio-coal with low ash content replaces the coking coal blend.

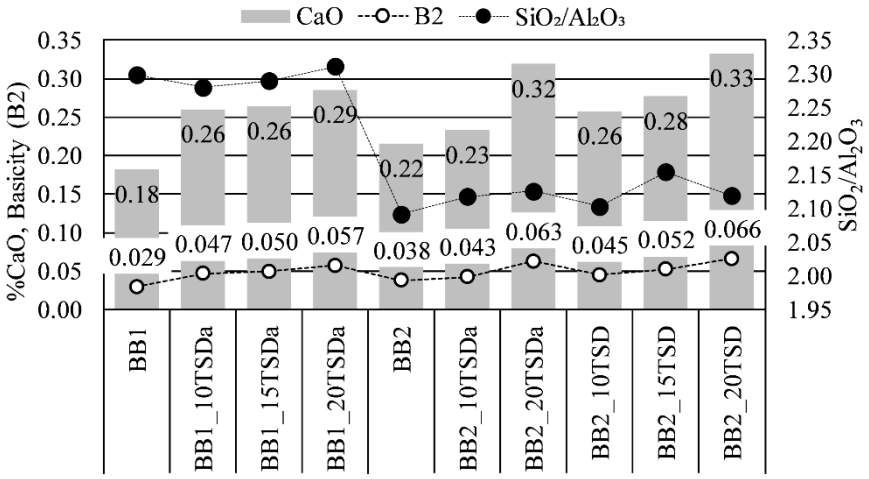

Figure 6. CaO, basicity B2 and ratio of SiO_2/Al_2O_3 for laboratory-produced coke.

3.2.2. Reactivity of Laboratory Coke, CRI/CSR and Mechanical Strength of Technical-Scale Coke

Table 5 shows the mass loss of the sample during the reactivity test of all laboratory-scale-produced coke and bio-coke samples. The TGA results show that the reactivity of bio-cokes increases with bio-coal addition. All bio-cokes are more reactive than the corresponding reference coke, and the start of the reaction temperature for gasification is lower. The reactivity of references coke BB1 is higher compared to BB2, and BB2 with addition of 10% of TSDa (BB2_10TSDa) also has lower reactivity in comparison to BB1. The reactivity of bio-cokes based on BB2 is lower when comparing bio-cokes based on BB1 and BB2 with the same addition of agglomerated TSDa.

The addition of 10% of agglomerated TSDa to BB1 (BB1_10TSDa) does not result in significantly higher reactivity, but the addition of 15% and 20% TSDa to BB1 (BB1_15TSDa and BB1_20TSDa) results in equal and significantly higher reactivity up to 1100 °C. With addition of 10%, 15% and 20% original TSD to coking coal blend BB2, the reactivity of

bio-cokes increased with added amounts, and also more, compared to when TSDa is added at corresponding amounts.

The start of the gasification temperature is lower for BB2 than for BB1 and decreases more with a higher amount of bio-coal added. The lowest start of the gasification temperature is found for bio-cokes with a 20% addition of TSD or TSDa.

CRI, CSR and mechanical strength for the coke carbonized in technical scale are shown in Table 6. For coke produced in technical scale, CRI increases and CSR decreases with an added amount of TSD, and BB2_10TSD^T has lower CRI and higher CSR than BB2_15TSD^T. At a 10% addition of TSDa, as in BB2_10TSDa^T, the CRI is lower and the CSR is higher, compared to when adding TSD, as in BB2_10TSD^T. A corresponding effect on reactivity by bio-coal addition was found for laboratory-produced coke tested in TGA. Figure 7 shows the CRI for cokes produced in technical scale plotted as a function of the reactivity measured in TGA for coke produced in laboratory scale. R^2 of 0.99 shows that CRI correlates well with the mass loss at 1100 °C. The mechanical strength shows a similar trend as CSR, for example, M40, I40 and JIS 15/150 are highest and M10 and I10 are lowest for BB2^T, followed by BB2_10TSDa^T, BB2_10TSD^T and BB2_15TSD^T.

Table 6. Coke Reactivity Index, CRI, and Coke Strength after Reaction, CSR, and mechanical strength according to different standards for the coke carbonized in technical scale.

Coke and Bio-Cokes	CRI	CSR	M40	M10	I40	I10	JIS 15/150
BB2^T	22.2	66.3	78.6	7.1	55.0	20.5	95.7
BB2_10TSD^T	32.1	45.6	71.8	9.7	44.6	26.3	93.5
BB2_15TSD^T	34.0	40.6	60.1	14.1	27.1	36.2	88.9
BB2_10TSDa^T	30.6	51.7	73.6	9.0	47.4	24.8	94.1

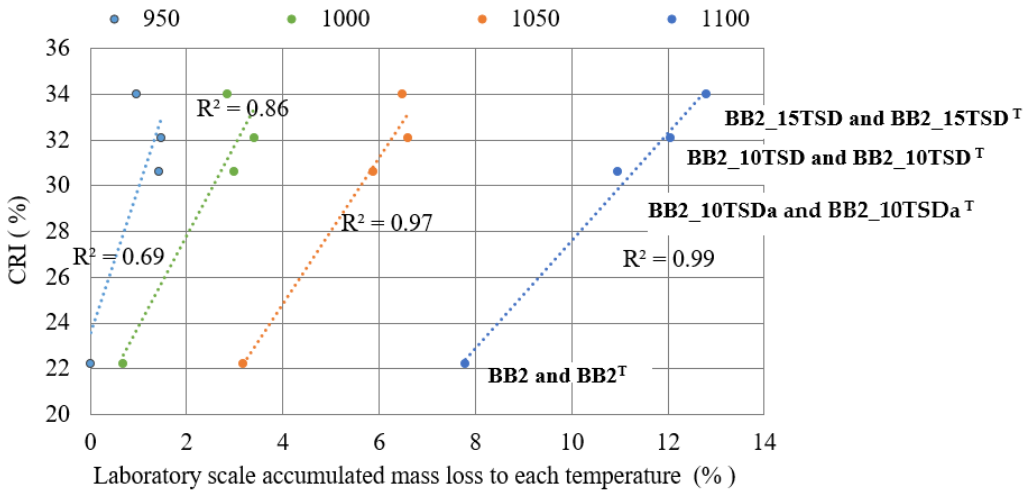

Figure 7. Correlation between CRI for coke produced in technical scale and mass loss up to 950, 1000, 1050 and 1100 °C in TGA tests for coke produced in laboratory scale.

4. Discussion

The possibility to counteract negative effects from bio-coal on fluidity and coke reactivity by using crushed agglomerates of bio-coal and/or high-fluidity coal in the coking coal blend was investigated through cokemaking in laboratory and technical scale, followed by CRI/CSR and TGA tests on the produced coke. The thermoplastic properties for coking coal blends used in laboratory were studied in a modified optical dilatometer test, whereas standardized dilatometer and Gieseler tests were performed for coking coal blends used in technical scale. The microstructure of bio-coal and bio-cokes was examined by LOM.

4.1. Influence of TSD and TSDa on the Plastic Properties of Coking Coal Blend

There are several parameters, i.e., type of coking coals, maceral components, the cell structure of bio-coal, amount of bio-coal present in coking coal blend, etc., that affect the plastic properties of coking coal blend, and it is difficult to conclude precisely which parameter has the dominating effect.

The max. dilatation does not change significantly for some of the coking coal blends containing bio-coal due to lower max. contraction before dilatation and greater overlap between the contraction and dilatation due to the start of dilatation at a lower temperature with increased addition of bio-coal. The lower max. contraction indicates the less suitable plastic properties of the coking coal blend.

The larger drop in max. contraction before dilatation and the higher max. dilatation with TSD, in comparison with TSDa, for coking coal blends based on BB2 are not clear. However, the remaining TSD with open and duct structure (Figure 1) enables adsorption of the plastic phase present at a larger amount during the carbonization of blends based on BB2. Further, TSD likely occupies a larger volume of the test briquette than TSDa, and the test briquette containing TSD will have lower density, as was found in the laboratory carbonization tests. Compacted TSDa has a denser cell structure and higher density; therefore, it has less ability to adsorb the plastic phase. In TSDa containing bio-coke based on BB1, less plastic phase is formed, and the max. dilatation is not significantly changed when adding TSDa.

In standardized tests for the dilatation of coking coal blends (Table 4) used in technical-scale carbonization, a significant impact due to addition of TSD and TSDa is found. There is no dilatation detected for samples containing either TSD or TSDa. In Gieseler tests (Table 4), the max. fluidity is significantly lower for samples containing bio-coal in comparison to BB2 (217 ddpm). However, the samples containing TSDa show higher max. fluidity (19 ddpm), compared to those containing TSD (4 and 3 ddpm, respectively), which indicates that TSDa could be advantageous to use in cokemaking.

Data deduced from the standard test and the modified test for dilatation in the optical dilatometer are not directly comparable; however, the relative difference between individual samples can be compared. In the modified dilation tests conducted without load on the sample, the contraction will be lower when inert bio-coal without contraction properties is added to the coking coal blend. This indicates a negative impact on the plastic properties. During dilatation, the sample can extend more in height without a load hindering the growth; additionally, with lower contraction, the starting point for dilatation is less, below 100% of the height or even more than 100% of the height of the sample.

4.2. Influence of TSD and TSDa Addition and High-Fluidity Coking Coal on Bio-Coke Reactivity

The TGA results (Table 5) show that the reactivity of the bio-coke samples is generally higher than for the reference coke. In addition, the temperature for the start of the carbon gasification reaction (Boudouard reaction) is lowered with higher bio-coal addition, and this is due to an increase in the content of reactive bio-coal carbon gasified at a lower temperature, in comparison to carbon originating from coking coals.

The increase in measured reactivity when adding TSDa is higher for BB2 than for BB1. The reactivity of bio-coke based on BB2 will have lower reactivity compared to that based on BB1 with the similar added amount of TSDa. According to Lin et al. [25], the reactivity of coke is lowered by the addition of high-fluidity coal, and Hayashizaki et al. [26] reported that high-fluidity coal fills the voids between coal particles and will be tightly bonded together, which increases coke strength. It is well known that there is a strong linear correlation between reactivity and strength after reaction; when CRI is low, CSR is at a high level [27].

The start of the gasification temperature (Table 5) is quite similarly affected by TSD and TSDa added to BB2, whereas the reactivity increases more with the addition of TSD. The larger reactivity with TSD could be partly explained by the fact that the oxides catalyzing the Boudouard reaction and the reactive carbon from bio-coal are spread more in the coke

sample. An effect on the ash content and overall chemical composition, especially the CaO content (Figure 6) by bio-coal addition, is clear and similar for TSDa and TSD addition. Most likely, the ash oxides from bio-coal are not as dispersed in the coke containing TSDa as in that containing TSD. Further, with increasing added amounts, the bulk density of coking coal bed for carbonization is lowered, especially when adding TSD, which increases the porosity of coke. Moreover, TSDa has a more compact cell structure (Figure 1) that may hinder the CO_2 diffusion and, therefore, result in lower reactivity compared to TSD.

The increase in the measured reactivity of the coke produced on technical scale is also slightly less if agglomerated bio-coal is used. The CRI measured for the coke produced on technical scale correlates well with the weight loss reached up to 1100 °C in the TGA for the corresponding series of coke (Figure 7). With 10% addition, the CRI increases by 8.4 and 9.9% for TSDa and TSD, respectively, whereas the CSR is reduced by 14.6 and 20.7%, respectively (Table 6). Considering the reported higher CRI of 4% and lower CSR of 6% between coke produced in small retort or on industrial scale [24], coke containing 10% TSDa could potentially obtain a CRI and CSR of 26.6% and 57.7%, respectively, if coke was industrially produced from a similar coking coal blend. It will, furthermore, be possible to optimize the coking coal blend composition.

5. Conclusions

- Addition of bio-coal lowers the max. contraction before dilatation and the temperature for start of dilatation; thus, the overlap between max. contraction and dilatation becomes larger.
- Bio-coke based on a base blend containing high-fluidity coal with different addition of agglomerated bio-coal shows less reactivity than bio-coke based on the blend containing high-volatile coal with a lower fluidity, but the rise in reactivity due to addition of agglomerated torrefied sawdust is roughly similar. The high fluidity did not counteract increased reactivity, but as the initial reactivity is lower, the bio-coke with a lower addition of agglomerated sawdust still may have acceptable reactivity for BF use.
- Bio-coal agglomeration counteracts the negative effect from added bio-coal on the coke reactivity, which is seen when comparing the effect from torrefied sawdust and agglomerated torrefied sawdust added to a similar type of coking coal blend. The effect was seen from the CRI/CSR test for coke produced on technical scale and from the thermogravimetric analyses of coke produced in laboratory scale.

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References

1. Ryan, B.; Gransden, J.; John Price, C. Fluidity of Western Canadl4n coals and its relationship to other coal and coke properties. In *Geological Fieldwork*; Paper 1998–1; British Columbia Geological Survey Branch: Victoria, BC, USA, 1997; p. 27.
2. Lundgren, M. Development of Coke Properties during the Descent in the Blast Furnace. Ph.D. Thesis, Luleå University of Technology, Luleå, Sweden, 2013.
3. Loison, R.; Foch, P.; Boyer, A. *Coke: Quality and Production*; Elsevier: Amsterdam, The Netherlands, 2014; ISBN 1483165272.
4. Fernández, A.M.; Barriocanal, C.; Díez, M.A.; Alvarez, R. Influence of additives of various origins on thermoplastic properties of coal. *Fuel* **2009**, *88*, 2365–2372. [CrossRef]
5. Fernandez, A.M.; Barriocanal, C.; Díez, M.A.; Alvarez, R. Evaluation of bituminous wastes as coal fluidity enhancers. *Fuel* **2012**, *101*, 45–52. [CrossRef]
6. Diez, M.A.; Alvarez, R.; Fernández, M. Biomass derived products as modifiers of the rheological properties of coking coals. *Fuel* **2012**, *96*, 306–313. [CrossRef]
7. Montiano, M.G.; Barriocanal, C.; Alvarez, R. Effect of the addition of waste sawdust on thermoplastic properties of a coal. *Fuel* **2013**, *106*, 537–543. [CrossRef]
8. Guerrero, A.; Diez, M.A.; Borrego, A.G. Influence of charcoal fines on the thermoplastic properties of coking coals and the optical properties of the semicoke. *Int. J. Coal Geol.* **2015**, *147*, 105–114. [CrossRef]
9. Kumar, P.P.; Barman, S.C.; Singh, S.; Ranjan, M. Influence of coal fluidity on coal blend and coke quality. *Ironmak. Steelmak.* **2008**, *35*, 416–420. [CrossRef]
10. Coking Coal. Available online: https://www.ispatguru.com/coking-coals/ (accessed on 21 June 2021).
11. Mandova, H.; Leduc, S.; Wang, C.; Wetterlund, E.; Patrizio, P.; Gale, W.; Kraxner, F. Possibilities for CO_2 emission reduction using biomass in European integrated steel plants. *Biomass Bioenergy* **2018**, *115*, 231–243. [CrossRef]
12. Babich, A.; Senk, D.; Fernandez, M. Charcoal Behaviour by Its Injection into the Modern Blast Furnace. *ISIJ Int.* **2010**, *50*, 81–88. [CrossRef]
13. Feliciano-Bruzual, C. Charcoal injection in blast furnaces (Bio-PCI): CO_2 reduction potential and economic prospects. *J. Mater. Res. Technol.* **2014**, *3*, 233–243. [CrossRef]
14. Gupta, R.C. Woodchar as a sustainable reductant for ironmaking in the 21st century. *Miner. Process. Extr. Metall. Rev.* **2003**, *24*, 203–231. [CrossRef]
15. Montiano, M.G.; Díaz-Faes, E.; Barriocanal, C.; Alvarez, R. Influence of biomass on metallurgical coke quality. *Fuel* **2014**, *116*, 175–182. [CrossRef]
16. Fraga, M.; Flores, B.; Osório, E.; Vilela, A. Evaluation of the thermoplastic behavior of charcoal, coal tar and coking coal blends. *J. Mater. Res. Technol.* **2020**, *9*, 3406–3410. [CrossRef]
17. Ng, K.W.; Giroux, L.; MacPhee, T.; Todoschuk, T. Incorporation of charcoal in coking coal blend—A study of the effects on carbonization conditions and coke quality. In Proceedings of the AISTech 2012—Iron & Steel Technology Conference, Atlanta, GA, USA, 7–10 May 2012; pp. 225–236.
18. Ng, K.W.; Giroux, L.; MacPhee, T.; Todoschuk, T. Biofuel Ironmaking Strategy from a Canadian Perspective: Short-Term Potential and Long-Term Outlook. In Proceedings of the 1st International Conference on Energy Efficiency and CO_2 Reduction in the Steel Industry, Düsseldorf, Germany, 27 June–1 July 2011.
19. Flores, B.D.; Flores, I.V.; Guerrero, A.; Orellana, D.R.; Pohlmann, J.G.; Diez, M.A.; Borrego, A.G.; Osório, E.; Vilela, A.C.F. Effect of charcoal blending with a vitrinite rich coking coal on coke reactivity. *Fuel Process. Technol.* **2017**, *155*, 97–105. [CrossRef]
20. MacPhee, J.A.; Gransden, J.F.; Giroux, L.; Price, J.T. Possible CO_2 mitigation via addition of charcoal to coking coal blends. *Fuel Process. Technol.* **2009**, *90*, 16–20. [CrossRef]
21. El-Tawil, A.A.; Björkman, B.; Lundgren, M.; Robles, A.; Sundqvist Ökvist, L. Influence of Bio-Coal Properties on Carbonization and Bio-Coke Reactivity. *Metals* **2021**, *11*, 1752. [CrossRef]
22. ALS Scandinavia AB. Available online: https://www.alsglobal.se/en (accessed on 15 September 2020).
23. SSAB. Available online: https://www.ssab.se/ssab-koncern/om-ssab/produktionsorter-i-sverige/lulea (accessed on 15 September 2020).
24. Gajic, D.; Kaiser, M. New findings from the DMT small-scale coking test retort regarding coke quality and coke oven wall safety. In Proceedings of the 2012 AISTech—Iron & Steel Technology Conference, Atlanta, GA, USA, 7–10 May 2012; pp. 237–246.
25. Lin, M.-F.; Hong, M.-T. The effect of coal blend fluidity on the properties of coke. *Fuel* **1986**, *65*, 307–311. [CrossRef]
26. Hayashizaki, H.; Hayashi, Y.; Kubota, Y.; Uebo, K.; Nomura, S. *Development of Coal Blending Technology for Improvement of Coke Quality*; Nippon Steel: Tokyo, Japan, 2020.
27. Díez, M.A.; Alvarez, R.; Barriocanal, C. Coal for metallurgical coke production: Predictions of coke quality and future requirements for cokemaking. *Int. J. Coal Geol.* **2002**, *50*, 389–412. [CrossRef]

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