

Article

Influence of Modified Bio-Coals on Carbonization and Bio-Coke Reactivity

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Abstract: Substitution of coal in coking coal blend with bio-coal is a potential way to reduce fossil CO₂ emissions from iron and steelmaking. The current study aims to explore possible means to counteract negative influence from bio-coal in cokemaking. Washing and kaolin coating of bio-coals were conducted to remove or bind part of the compounds in the bio-coal ash that catalyzes the gasification of coke with CO₂. To further explore how the increase in coke reactivity is related to more reactive carbon in bio-coal or catalytic oxides in bio-coal ash, ash was produced from a corresponding amount of bio-coal and added to the coking coal blend for carbonization. The reaction behavior of coals and bio-coals under carbonization conditions was studied in a thermogravimetric analyzer equipped with a mass spectrometer during carbonization. The impact of the bio-coal addition on the fluidity of the coking coal blend was studied in optical dilatometer tests for coking coal blends with and without the addition of bio-coal or bio-coal ash. The result shows that the washing of bio-coal will result in lower or even negative dilatation. The washing of bio-coals containing a higher amount of catalytic components will reduce the negative effect on bio-coke reactivity, especially with acetic acid washing when the start of gasification temperature is less lowered. The addition of bio-coal coated with 5% kaolin do not significantly lower the dilatation-relative reference coking coal blend. The reactivity of bio-cokes containing bio-coal coated with kaolin-containing potassium oxide was higher in comparison to bio-coke containing the original bio-coal. The addition of ash from 5% of torrefied bio-coals has a moderate effect on lowering the start of gasification temperature, which indicates that the reactive carbon originating from bio-coal has a larger impact.

Keywords: bio-coals; washing; kaolin; ash; coking; volatile matter

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1. Introduction

Most of the iron units used for steelmaking are produced by reduction and smelting in the blast furnace (BF). The BF is a counter-current process where top-charged iron ore, coke and fluxes descending through the shaft meet ascending reducing gas generated in the lower part by partial combustion of tuyere-injected auxiliary reducing agents and some coke in oxygen-enriched hot blast air. Coke, as the only material being solid through the BF, will provide support to the burden, maintain bed permeability for ascending gases and produce hot metal and slag when other materials are softened and melted [1]. Additionally, the main part of hot metal carburization occurs through interaction between hot metal and coke.

A great challenge for steel producers is to lower the CO₂ emissions that are mainly related to the use of fossil coal for the injection or production of the coke to be used for reduction and smelting in the BF. Information from the World Steel Association shows that 7–9% of the total global CO₂ emissions originates from the iron and steel industry [2]. The European Union (EU) has set a target for 2030 with net greenhouse gas emissions reduction

with at least 55% compared to 1990 levels [3]. Biomass was pointed out as one possible way to decrease fossil CO₂ emissions in iron and steelmaking [4–6]. The biomass generation time is comparatively short, and as the carbon cycle is closed the contribution to global warming is lowered [7].

One of the features of biomass is contents of alkali metal and alkaline earth metal oxides (AAEMs), i.e., potassium oxide (K₂O), sodium oxide (Na₂O), calcium oxide (CaO) and magnesium oxide (MgO) in the ash [8]. The ash content in woody biomass is often less than 1%, but may be up to 15%, or more, in some herbaceous and forest residues [9], and by increasing the pre-treatment temperature a more pyrolysed bio-coal with higher ash content is formed [10]. High alkali input into the BF must be restricted due to its catalytic effect on the reaction of carbon (C) in coke with carbon dioxide (CO₂), i.e., gasification, which will increase coke consumption and cause the coke disintegration that may lower the BF permeability. The recirculation of alkalis in the BF increases the reducing agent consumption and may cause the formation of scaffolds, which can disturb burden descent [11].

Mineral matter in coke may influence the coke reactivity, as some oxides such as AAEMs and iron oxides catalyze the gasification reaction [12–14]. Increased coke reactivity with higher total amount of mineral phases containing calcium (Ca) was stated by Grigore et al. [12]. Nomura et al. [13,14] found that coke produced from a coking coal blend containing non-coking coal with high content of CaO had a high reactivity, and that oxides of iron (Fe) and Ca act as catalysts during gasification.

The effect of alkali oxide in bio-coke (bio-coal containing coke) on reactivity has been reported [15–20]. Ng et al. [15,18,19] studied the reactivity of bio-coke containing charcoal and concluded that the reactivity of bio-coke is influenced by alkaline metals that catalyze the gasification reaction. Ng et al. [18,19] stated that the increase in CRI (coke reactivity index [1]) was larger with fine charcoal, as catalyzing oxides of Ca were more dispersed in the coke piece compared to coke with coarse charcoal. Montiano et al. [16] studied the influence on CRI of adding sawdust from chestnut and pine and found that the catalytic effect of biomass ashes affects the coke reactivity. The higher amount of ash in chestnut than in pine, 1.5% and 0.3%, respectively, enhanced the coke reactivity more. MacPhee et al. [17] claimed that the presence of catalytic oxides, i.e., CaO, in charcoal resulted in a higher CRI in comparison to coke produced from coking coals only. The content of catalyzing ash compounds in bio-coal may limit the maximum amount of bio-coal that can be added to produce bio-coke. This could potentially be solved by washing bio-coals with water or acids to remove readily soluble oxides of AAEMs. Alternatively, kaolinite coating aiming to bind part of the catalytic compounds to alumina could be used to decrease their effect on bio-coke reactivity. Reid et al. [21] found that the coke reactivity decreased in the presence of kaolinite and quartz.

The washing of biomass with water or acid was shown to be a way to remove AAEMs in biomass [22–28]. Results from washing by different types of acids such as sulfuric acid (H₂SO₄), nitric acid (HNO₃) [22,23,27] and hydrochloric acid (HCl) [24–26] or weak acids, e.g., hydrofluoric acid (HF) [24,26] and acetic acid (CH₃COOH), is reported [22,28]. Water washing does not have a significant effect on the carbon structure of biomass, whereas acid washing may degrade components such as cellulose, hemicellulose and lignin in the cell walls of the biomass [23,26]. The washing of AAEMs is more efficient with a higher acidity [22,27,28]. Acetic acid treatment will introduce carbon, oxygen and hydrogen in comparison to hydrochloric, sulfuric acid and nitric acid, which may leave Cl, S and N, respectively [22]. Diluted acetic acid may be a feasible alternative due to its less negative effect on the structure of biomass and a higher potassium and sodium removal efficiency than deionized water [28].

Carbonization includes several chemical and physical changes such as softening, swelling, the evolution of volatiles, shrinking and, finally, re-solidification to obtain coke [29]. Individual coal particles fuse and form an expanding porous continuous mass that finally solidifies to semicoke, which is converted into coke after further heating. The properties of coke will depend on the thermoplastic properties of coal [30]. From bio-coke

research it is reported that the addition of any type of biomass results in the lower fluidity of the coking coal blend, as biomass acts as inert material during softening and melting and can bind plasticized components of coal [20,31–35].

The influence of added minerals on coal fluidity has been reported [36–41]. Khan et al. [36] found that, with the addition of hematite (Fe_2O_3) or magnetite (Fe_3O_4) to coal, the thermo-plastic properties of coal deteriorate due to catalytic effects on the char-forming reaction during pyrolysis, which was also observed when adding K or Ca-containing compounds [37,38]. The addition of 5 wt% of sodium carbonate (Na_2CO_3) decreased the coal fluidity by 90% without changing the maximum fluidity temperature [39]. The addition of 5–20 wt% of silicon oxide (SiO_2) was shown to reduce the maximum swelling without affecting the fluidity temperature [40]. The addition of SiO_2 resulted in higher gas permeability and lower internal pressure, as SiO_2 particles present between softened coal particles may inhibit their fusion, and thus the swelling will decrease. The addition of 1–5 wt% of kaolinite was shown to increase the maximum fluidity, while further additions up to 10 wt% caused a fluidity decrease [41].

The effect of bio-coal addition on fluidity during carbonization [20,31–35] and coke reactivity [15–20] has been reported, but published results on the effect of washed bio-coal addition on the carbonization and bio-coke reactivity have not been found. The effects of ash composition on the reactivity of bio-coke when adding bio-coal have been reported [15–19], but the single effect from adding only bio-coal ash to a coking coal blend has not been investigated. The kaolinite addition to a coking coal blend was studied, aiming to reduce the effect from catalytic alkali oxides in the ash on coke reactivity [21], but there are no studies found about using this method to lower the effect of alkali oxides present in bio-coal ash on the reactivity of produced bio-coke.

To maximize the bio-coal utilization in cokemaking it is of importance to understand the impacts of bio-coal on carbonization and coke reactivity. The aim of this study is to find out if higher added amounts, with less effects on bio-coke reactivity, can be reached by using (1) washed bio-coals with lowered contents of catalytic ash oxides or (2) bio-coal coated with kaolin aiming to bind the catalytic oxides in the bio-coal ash. Further, the aim is to (3) understand the individual impact from ash or bio-coal structure by combining (1) and (2) with results on cokemaking and coke reactivity by only adding the bio-coal ash from a similar amount of bio-coals. In addition, the effect from kaolin coating of bio-coal with different contents of volatile matter (VM), ash composition and carbon structure and the effect of adding bio-coal ash to coking coal blend of three coking coals were also studied.

2. Materials and Methods

2.1. Materials

Based on tests with the addition of original bio-coals to the coking coal blend [42], three types of torrefied biomass having different VM and ash contents due to different origins and pre-treatment temperatures were selected. 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. The proximate and ultimate analyses as well as the ash composition for bio-coals and the coking coals were analyzed according to standard methods by ALS Scandinavia AB [43] and supplied by Swedish steel producer SSAB Europe in Luleå [44], respectively.

Carbonaceous materials used in the study, their origin, pre-treatment temperature, and suppliers were reported in a previous study [42]. HTT (biomass pre-treated at high temperature) consists of torrefied extruded pellets. The abbreviations corresponding to each carbonaceous material is presented together with the proximate and ultimate analyses in Table 1. The high content of VM and oxygen, and low content of C_{fix} , characterizes torrefied bio-coals, whereas the opposite is the case for HTT.

Table 1. Proximate and ultimate analysis results for carbonaceous materials (dry base) [42].

Abbreviation	Proximate Analysis (wt%)				Ultimate Analysis (wt%)				Description
	* C _{fix}	VM	Ash	C _{tot}	H	N	S	O	
TFR	25.1	72.7	2.2	58.0	5.30	0.48	0.03	34	Torrefied forest residue
TSD	26.1	73.5	0.4	57.5	5.50	<0.1	< 0.01	37	Torrefied sawdust
HTT	69.5	29.2	1.3	79.0	4.00	0.11	0.01	16	High-temperature torrefied pellets
HV	61.5	32.3	6.1	81.3	5.15	1.57	0.85	5	High Volatile coal
MV	67.4	24.0	9.0	81.4	4.46	1.86	0.50	3	Medium volatile coal
LV	70.0	19.4	10.6	79.7	4.27	1.79	0.63	3	Low volatile coal

* C_{fix} = 100% – (%ash + %VM) = fixed carbon; VM volatile matter; C_{tot}: Total carbon; H hydrogen; N nitrogen; S sulphur; O oxygen.

The ash compositions for bio-coals are stated in Table 2. TFR has higher contents of catalytic components in ash (K₂O, CaO, Fe₂O₃ and Na₂O) in comparison to TSD. The contents of the catalytic components are higher in HTT compared to that of TSD, but lower than for TFR. The analysis shows that TFR has a higher content of phosphorus than TSD and HTT.

Table 2. Oxide contents in the bio-coals (wt%, dry basis), based on selected data from ref. [42].

Bio-Coals	Al ₂ O ₃	CaO	SiO ₂	Fe ₂ O ₃	K ₂ O	MgO	MnO	Na ₂ O	P ₂ O ₅
TFR	0.006	0.71	0.062	0.009	0.23	0.10	0.005	0.02	0.11
TSD	0.005	0.16	0.028	0.007	0.07	0.02	0.017	-	0.01
HTT	0.020	0.31	0.259	0.086	0.14	0.06	0.039	0.02	0.03

Dilatometer and Gieseler data for coking coals showed that the maximum (max.) dilatation and max. fluidity were 278%, 107%, 69% and 30,000 ddpm, 1092 ddpm, 182 ddpm for HV, MV and LV, respectively. Softening and re-solidification temperature range according to Gieseler test was ~386–500 °C for these coking coals.

2.2. Pre-Treatment of Bio-Coals

The bio-coals were pre-treated by washing and kaolin coating aiming to lower the negative effect on carbonization and coke reactivity. Further, bio-coal ash was produced for studies on its effect on carbonization and coke reactivity.

2.2.1. Washing of Bio-Coal

TFR with a comparably high ash content and TSD with a low content of ash were selected for water and dilute acetic acid washing with the aim to lower the contents of catalytic oxides in their ash. The bio-coals washed by water and acid are labeled TFR_H₂O, TSD_H₂O and TFR_AC, TSD_AC, respectively. 100 g of bio-coal was washed in one liter of Milli-Q water or aqueous solution with 5 wt% of acetic acid at 80 °C or room temperature, respectively. The slurry was stirred during a two-hour washing time [28], and leachates and bio-coals were separated by vacuum filtration. Washed bio-coals were dried at 105 °C for 24 h before adding 5% of bio-coal to 95% of basic coal blend (BB) for carbonization. The filtrate was analyzed by ICP-OES (ICAP 7200, Thermo Fisher Scientific, Waltham, MA, USA) to determine the content of the dissolved elements.

2.2.2. Kaolin Coating

Two different bio-coals, TSD with a high VM and low ash content and HTT with low VM and slightly higher ash content, were coated with 5% or 10% of kaolin. The kaolin was analyzed in D-LAB AB [45] and is presented in Table 3. The prepared coated bio-coals are labeled TSD_5KC, TSD_10KC, HTT_5KC and HTT_10KC, and the numbers indicate the percentage of kaolin added for coating. The used kaolin had a relatively high content of potassium oxide.

Table 3. Main chemical components in kaolin, (wt%) and determined loss of ignition (LOI).

CaO	MgO	SiO ₂	Al ₂ O ₃	K ₂ O	P ₂ O ₅	Fe ₂ O ₃	LOI
0.05	0.17	57.1	38.5	3.15	0.14	0.79	12.3

2.2.3. Bio-Coal Ashing

To evaluate the impact of ash from bio-coal on cokemaking, ash was produced from TFR and TSD. The bio-coals were placed in alumina crucibles and heated in air in a muffle furnace. The sample was heated at a rate of 15 °C/min to 500 °C and kept for 30 min, the heating continued with 15 °C/min up to 850 °C. The sample was kept at 815 °C for 2 h before the furnace was turned off and the material was allowed to cool in the furnace. The prepared ash was used in preparation of coke samples. Bio-coke samples containing bio-coal ash are labeled as TFR_ash and TSD_ash.

2.3. Methodology

2.3.1. Thermoplastic Properties of Coking Coals Evaluated by Using Optical Dilatometer

A small briquette (3 mm in diameter and height) was produced from BB with and, without the addition of 5% of original, washed and kaolin-coated bio-coals or bio-coal ash, were heated in an optical dilatometer from Leitz (Ernst Leitz GmbH, Wetzlar, Germany) with an automatic image analysis system from Hesse Instruments (Hesse, Osterode am Harz, Germany). To achieve a smooth sample surface, the blends of coal and bio-coal were ground finely in a mortar and mixed with water before making a small briquette. The sample was heated at a rate of 3 °C/min to a final temperature of 550 °C. As previously reported [42], to secure correct temperature readings, zinc metal wire and a thin piece of bismuth tin alloy were heated above their known melting points of 409 °C and 137 °C.

The change of sample height and area were recorded during heating. The maximum contraction and maximum dilatation were evaluated according to ISO 23873. The swelling index, SI (%), was calculated from the area change of the sample according to (1).

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

In comparison to the standard method, the sample size in this study is smaller and no load is applied on the sample. The samples, according to the standard, are 60 mm in length and 8 mm in diameter. Due to the inhomogeneity of coals and bio-coals in combination with the small sample size in this study, variations in measurements can be expected. The standard deviation for max. Dilatation was determined to be 2:00 and 0.98, when repeating the analysis for BB and HTT5_5KC, three times, respectively.

2.3.2. Preparation of Coke

The recipes for coking coal blend with the addition of original, washed and kaolin-coated bio-coal as well as ash produced from bio-coal are given in wt% in Table 4. The amount of ash added to the BB corresponded to the ash in 5% of bio-coal. For the coking coal blend containing kaolin-coated bio-coals, the added amount of bio-coal corresponded to 5 wt% before coating with 5% or 10% kaolin. The blends with and without different bio-coal types are presented in Table 5. The particle size distribution of coking coal blend was controlled by having 19–21% of particles > 2.8 mm, 45–51% between 2.8 and 0.5 mm and 30–34% < 0.5 mm. Water was added to reach ~7.5% moisture. Further information on methodology for coking test are found in [42]. The produced coke was crushed and particles in between 1 and 2 mm was used in the reactivity test. Each sample was kept in a desiccator until characterization was carried out.

Table 4. Mixing ratios of coking coals and bio-coals in coking coal blends (wt%).

Coal Blend	Mixing Ratio (wt%)				
	HV	MV	LV	Bio-Coal	Ash
Basic coal blend (BB)	28.0	32.0	40.0	-	-
BB + 5% bio-coal	26.6	30.4	38.0	5.0	-
BB + ash from 5% TSD/TFR	26.6	30.4	38.0	-	0.02%/0.11%

Table 5. Abbreviations of evaluated coking coal blends and cokes.

Base Blend and Added Bio-Coal	Blend Composition	Abbreviation
BB	HV, LV and MV	BB
TFR	BB + 5%TFR	TFR5
	BB + 5%TFR_H ₂ O	TFR5_H ₂ O
	BB + 5%TFR_AC	TFR5_AC
	BB + 0.11%TFR_Ash	TFR_Ash
TSD	BB + 5%TSD	TSD5
	BB + 5%TSD_H ₂ O	TSD5_H ₂ O
	BB + 5%TSD_AC	TSD5_AC
	BB + 0.02% TSD_Ash	TSD_Ash
	BB + 5%TSD_5KC	TSD5_5KC
	BB + 5%TSD_10KC	TSD5_10KC
HTT	BB + 5% HTT	HTT5
	BB + 5%HTT_5KC	HTT5_5KC
	BB + 5%HTT_10KC	HTT5_10KC

A light optical microscope (LOM, Nikon ECLIPSE E600 POL, Tokyo, Japan) was used for studies of textures in bio-coal, coke and bio-cokes. The samples were mounted in epoxy resin, and the surface was polished, before studies in LOM. The chemical composition of coke was analyzed by SSAB Luleå using a Thermo ARL 9900 X-ray fluorescence (XRF) instrument (Thermo Fisher Scientific Inc., Waltham, MA, USA) with a rhodium tube at 50 kV and 50 mA.

2.3.3. Thermogravimetric Analysis

The thermal behavior of original and washed bio-coal during conditions corresponding to carbonization was studied in a thermogravimetric analyzer (TGA, Netzsch STA 409, Netzsch, Selb, Germany) instrument (sensitivity $\pm 1 \mu\text{g}$) attached to a Quadruple Mass Spectrometer (QMS, Netzsch, Selb, Germany). The test was conducted in an inert atmosphere of N₂ gas (purity 99.996%) with a flow rate of 200 mL/min. The sample was heated at 2 °C/min from room temperature up to 100 °C; after 15 min the heating continued with 15 °C/min up to 1050 °C and kept for 30 min; then, the sample was cooled with 20 °C/min to room temperature.

Reactivity tests of coke samples were conducted in TGA Netzsch STA 409 with a graphite furnace [29] using a CO₂ flow rate of 300 mL/min. The weight of the sample was about 40–50 mg and the heating rates were 20 °C/min up to 600 °C and 3 °C/min between 600 and 1100 °C. The test was repeated three times for one sample, BB, to check the influence of possible inhomogeneity in the coke sample, and the standard deviation for mass loss was $\pm 1\%$.

3. Results

3.1. Bio-Coals and Coal Properties

3.1.1. Chemical Analysis of Washed Bio-Coals

The leachate from washing with water and acetic acid was investigated by ICP analysis. A higher concentration of elements in the leachate was achieved by acid washing in comparison to water washing. By water washing, the TSD leachate had a higher content of Ca, Mn and Mg in comparison to TFR. However, by acid washing, the TFR leachate had a higher content of Ca, Mg and K. In both cases the TFR leachate had a higher content of phosphorus. The washing efficiency calculated according to Equation (2) is presented in Table 6. The acid washing had a significant effect on washing alkaline earth metal i.e., Ca and Mg, in comparison to water washing. However, there was no significant difference for washing alkali metal as Na by acid or water in case of TFR_H₂O and TFR_AC or K in the case of TSD_H₂O and TSD_AC. According to the calculation, all phosphorus was removed during washing. After washing a substantial amount of liquid (e. g., ~31% in case of washing TFR by water), remains in the filter cake and during the drying the mineral dissolved in the leachate will precipitate and be part of the bio-coal.

$$\text{Washing efficiency (\%)} = \frac{\text{Amount of element present in leachate, (g)}}{\text{Amount of element present in original bio-coal, (g)}} \times 100 \quad (2)$$

Table 6. Washing efficiency (%) for major elements present in bio-coal.

Washed Bio-Coals	Ca	Si	Mn	Mg	Na	K
TFR_H ₂ O	2.10	3.48	0.73	3.55	53.2	37.0
TSD_H ₂ O	17.4	3.59	13.1	19.8	-	53.2
TFR_AC	56.4	2.52	59.9	53.4	45.8	60.7
TSD_AC	31.7	18.4	71.0	37.9	-	46.1

3.1.2. Thermal Behavior of Original and Washed Bio-Coals under Carbonization Conditions

The thermal behavior of original and washed bio-coal was evaluated by TGA. The TGA results for original and washed TFR and TSD are shown in Figure 1a,b, respectively. The original and washed samples had their major mass loss in the first devolatilization step within the temperature range of 200–400 °C. Original and washed TSD had a higher mass loss than the original and washed TFR. The total mass loss for the original and washed TSD is quite similar, about ~70%, while the total mass loss of TFR, TFR_H₂O and TFR_AC was 61%, 65% and 63%, respectively.

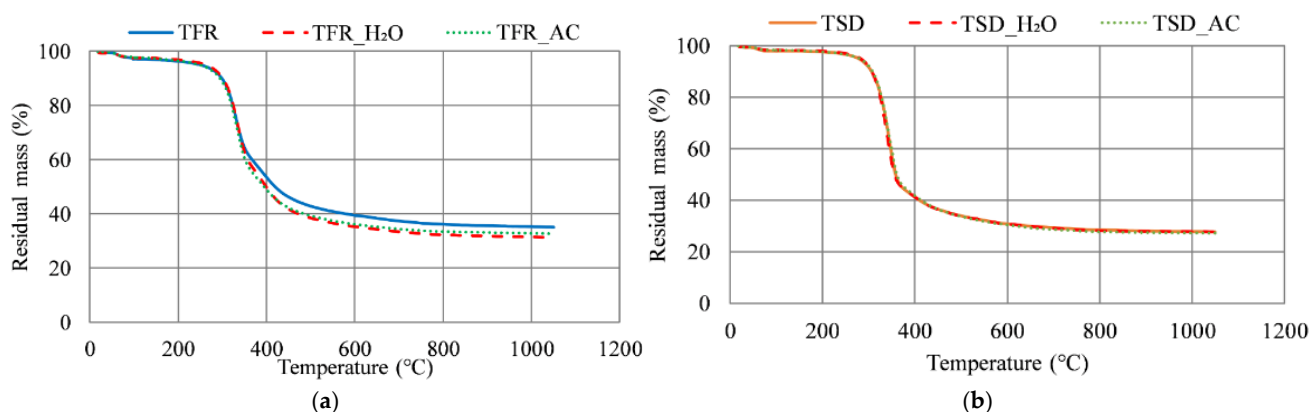


Figure 1. Residual mass under carbonization condition in N₂ atmosphere in TGA for (a) original and washed TFR and (b) original and washed TSD.

During the thermal decomposition of the original and washed bio-coals, H_2 , H_2O , CO_2 and CH_3^+ were released. The recorded ion currents as measured in the QMS are shown in Figure 2. The release of gases and hydrocarbons showed quite similar behavior for original and washed TFR and TSD. Hydrocarbons, such as CH_3^+ , was detected from $\sim 290^\circ C$ to $\sim 650^\circ C$, see Figure 2a. The presence of H_2 was detected in the range of $\sim 310^\circ C$ – $1050^\circ C$, as shown in Figure 2b. CO_2 and H_2O were detected between 119 – $770^\circ C$ and 115 – $770^\circ C$, with higher intensity peaks around at $350^\circ C$ and $340^\circ C$, respectively; see Figure 2c,d.

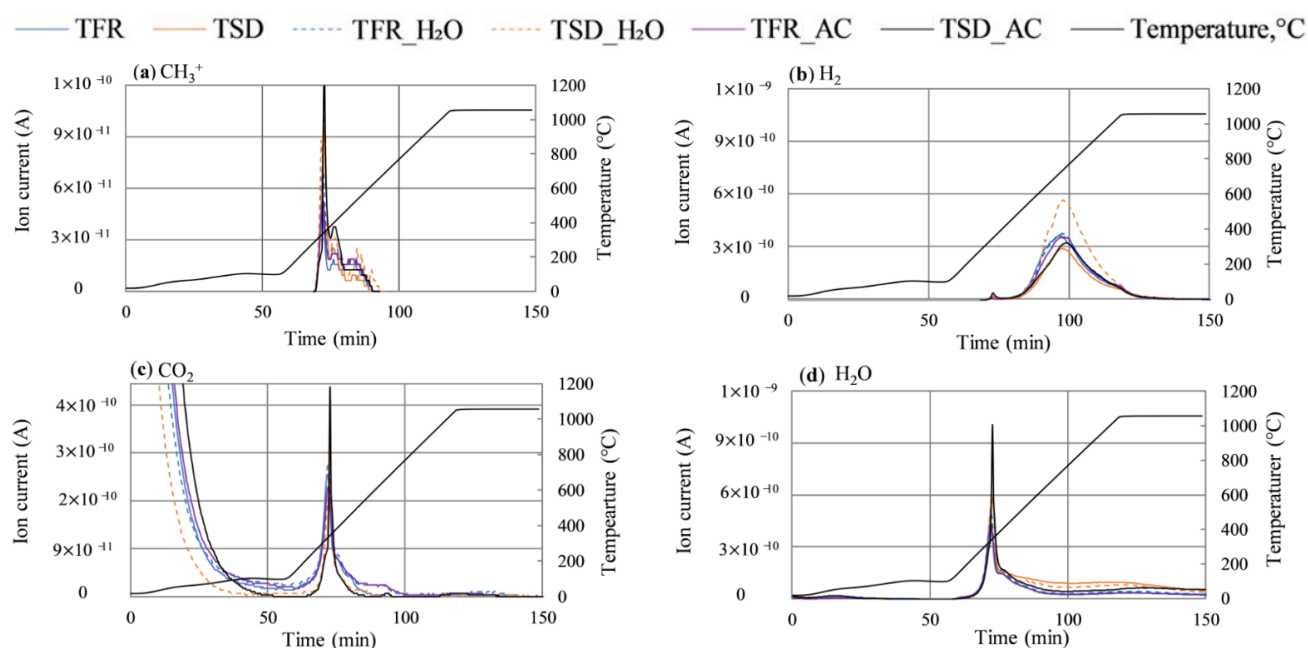


Figure 2. Ion current for (a) CH_3^+ ; (b) H_2 ; (c) CO_2 and (d) H_2O in off gases released during heating original and washed bio-coals under carbonization condition in N_2 atmosphere in TGA.

3.2. Plastic Properties of Coking Coal Blends

The results of optical dilatometer tests for BB with and without 5% addition of original, washed and coated bio-coals, as well as a sample with the ash corresponding to 5% of bio-coal added, are stated in Table 7. For 5% original bio-coal addition, the results show that the max. dilatation of HTT5 was almost similar to BB, but it was lower for TFR5 and TSD5. For the coking coal blend containing 5% washed bio-coal, the max. dilatation was significantly lower in comparison to that of coal blends with original bio-coal, whereas for 5% kaolin-coated bio-coals, the dilatation was not much lower than for BB. With the ash addition, the max. dilatation for TFR_Ash and TSD_Ash blends was quite similar to that of BB. The swelling index, SI, decreased more with additions of washed bio-coals in comparison to BB and when adding original bio-coals or bio-coal ash. The max. contraction, according to standard ISO 23873, was determined at $500^\circ C$ for most of the samples except HTT5_5KC, and the contraction decreased with the addition of bio-coal and bio-coal ash.

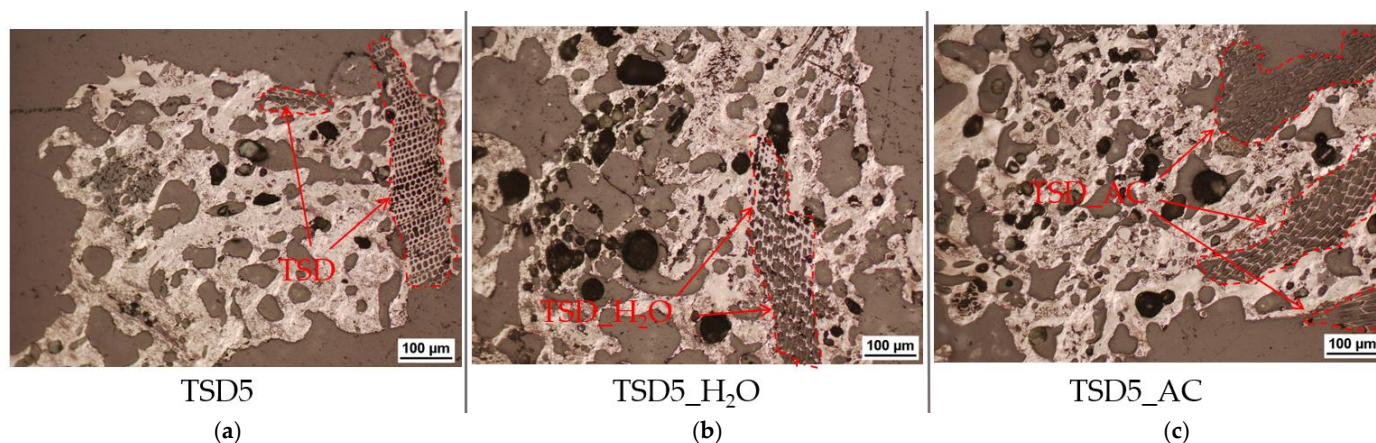
3.3. Properties of Coke

The structure of produced bio-cokes was examined in LOM. Figure 3 shows that the original and washed bio-coal in the coke matrix kept their structure after carbonization. Elongated duct cells originating from original and washed TSD were found in the coke, as seen in Figure 3a–c. The image of bio-coke with the original bio-coal TSD5 was presented in the previous publication [42].

Table 7. Thermoplastic parameters for BB compared with different addition of coated, washed or original bio-coals and ash.

Coal Blend		Max Contraction		Max Dilatation		SI
		°C	%	°C	%	%
Basic coal blend	BB	500		436	15.8	68.3
5% original bio-coal	TFR5	500	5.7	425	10.4	22.1
	TSD5	500	2.1	430	8.3	19.9
	HTT5	500	−0.6	422	15.3	20.4
5% washed bio-coal	TFR5_H ₂ O	500	12.4	431	0.6	0.67
	TSD5_H ₂ O	500	12.1	429	0.2	0.9
	TFR5_AC	500	10.7	424	−0.8	0.6
	TSD5_AC	500	11.2	431	1.2	2.5
Ash from 5% of bio-coal	TFR_Ash *	500	−3.3	432	13.3	28.4
	TSD_Ash **	500	−1.6	434	12.4	25.5
5% bio-coal coated by kaolin	TSD5_5KC	500	5.0	437	14.1	15.8
	TSD5_10KC	500	8.2	430	8.7	5.9
	HTT5_5KC	412	2.3	455	12.6	8.7
	HTT5_10KC	500	8.2	429	8.7	5.9

SI: Swelling index, * 0.11 of TFR ash, ** 0.02% TSD ash.

**Figure 3.** LOM images showing the microstructure for bio-coke samples (a) TSD5 [42], (b) TSD5_H₂O and (c) TSD5_AC.

The contents of different inorganic elements in coke were analyzed by XRF, but no significant difference in the overall chemical composition of bio-cokes was found, and the ash amount was quite similar. The effect of ash can be more significant for local ash composition where the bio-coal particle with more basic ash is located.

3.4. Reactivity of Coke

Table 8 shows the mass loss of the sample during reactivity tests of coke produced from BB and bio-cokes containing 5% of the original, washed or kaolin-coated bio-coals, or bio-coal ash corresponding to the amount present in 5% bio-coal. The TGA results show that all bio-cokes containing 5% bio-coal, except for HTT5, are more reactive than BB coke, and the start of reaction temperature for gasification is lower for all bio-cokes compared to that of BB coke.

Table 8. Start of gasification temperatures and accumulated mass loss of coke up to different temperatures as measured in TGA.

Base Blend and Additives	Samples	Start of Gasification Temperature (°C)	Accumulated Mass Loss (%), Up to Each Temperature			
			950 °C	1000 °C	1050 °C	1100 °C
Basic coal blend	BB	947	0.23	1.6	4.9	11.2
5% original bio-coal	TFR5	895	2.7	5.3	10.8	19.8
	TSD5	912	1.4	3.3	7.7	15.4
	HTT5	905	1.4	3.3	6.4	11.9
5% washed bio-coal	TFR5_H ₂ O	898	1.8	4.3	9.4	18.5
	TSD5_H ₂ O	868	1.5	4.5	10.9	20.5
	TFR5_AC	928	1.5	3.4	8.8	17.9
	TSD5_AC	918	1.2	3.6	8.9	17.3
Ash from 5% of bio-coal	TFR_Ash	943	0.3	2.2	6.9	15.4
	TSD_Ash	930	0.5	2.6	7.6	16.3
5% bio-coal coated by kaolin	TSD5_5KC	891	1.5	3.6	8.7	17.0
	TSD5_10KC	890	1.3	3.6	8.5	16.8
	HTT5_5KC	895	2.6	5.8	10.5	18.4
	HTT5_10KC	894	1.7	4.0	8.1	15.3

The bio-cokes containing water-washed bio-coals had a lower start of gasification temperature than bio-cokes containing acetic-acid-washed bio-coals. By comparing the reactivity of bio-coke containing original and washed TFR, it is seen that reactivity decreases in the order TFR5 > TFR5_H₂O > TFR5_AC, and by comparing the reactivity for bio-cokes containing original and washed TSD, it is shown that the reactivity decreases in the order TSD_H₂O > TSD5_AC > TSD5.

Cokes containing ash of TSD and TFR had a quite similar mass loss at different temperatures, but both with a higher reactivity and a slightly lower start of gasification temperature in comparison to BB coke. The bio-cokes containing kaolin-coated bio-coal had a higher reactivity compared to bio-cokes with original bio-coal. There is no significant difference in reactivity or start of gasification temperature with the amount of kaolin used for bio-coal coating.

4. Discussion

The effects of original, washed and kaolin-coated bio-coals as well as bio-coal ash additions to a basic coal blend on carbonization and coke reactivity were investigated. The thermal behavior of coking coals and bio-coals under carbonization conditions was studied in TGA/QMS in a N₂ atmosphere. To evaluate the impact of bio-coal addition on bio-coke reactivity, tests in a CO₂ atmosphere were conducted in TGA, and the microstructure was examined by LOM.

4.1. Influence of Modified Bio-Coal Addition on Thermoplastic Properties of Coking Coal

By adding bio-coal, the max. dilatation and max. contraction is in general decreased. However, the effect is not significant when adding 5% of original HTT or 5% kaolin-coated TSD or HTT. The main difference between added original bio-coals, HTT, TFR and TSD in terms of cell structure, VM and ash content during carbonization and reactivity has been discussed in [42].

There are several parameters influencing the maximum dilatation for coking coal blends in general and also for those containing washed bio-coal. Firstly, washing by H₂O or CH₃COOH leave remains that contribute to a higher content of oxygen in the solid material. It was found that oxygen has a deleterious effect on the plastic properties of coal [46,47]. Secondly, it was reported that acid or water washing of raw biomass increases

the surface area [24,48] due to the hydrolysis of hemicellulose and cellulose into smaller organic molecules. According to Loison et al. [49], fine inert particles with a higher surface area adsorb more primary decomposition products of coking coal and bind the plasticizing part of the coal, which will inhibit the fluidity development. It has also been reported that the addition of biomass or bio-coal causes a reduction in plasticity [31–33]. Thirdly, an overlap between contraction and dilatation will result in lower maximum dilatation. Fourthly, any presence of precipitated catalytic compounds in the bio-coal after washing and drying will contribute to lower dilatation [37].

Dilatometer test results show that there is no significant change in the maximum dilatation for samples with 5% biomass coated with 5% kaolin, while a slight drop in maximum dilatation occurred by adding 5% bio-coal with 10% kaolin coating. According to Meng et al. [41], thermal decomposition in the presence of kaolin involved the cleavage of aryl-alkyl bonds and formation of lower molecular weight molecules, radicals, H_2 release, etc. Meng et al. [41] found that by a 5% kaolin addition, the maximum dilatation increased due to increasing content of active methylene groups. It was also reported that the formation of active methylene groups favors the decomposition reaction of naphthenic rings and the release of H_2 , which stabilizes thermally generated radicals produced during the plastic stage of carbonization, and by that, the fluidity is enhanced [50]. However, the release of crystalline water from kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) occurs at temperatures above 450 °C [51] and will, according to Mochizuki et al. and Tsubouchi et al. [46,47], influence the plasticity negatively due to contribution with oxygen; this effect will be higher with a 10% kaolin coating of bio-coal.

4.2. Influence of Modified Bio-Coal Addition on Coke Reactivity

The addition of washed bio-coal increased the reactivity of bio-coke in comparison to the original one if the initial ash content is low, as in TSD, but is slightly decreased, especially if acetic acid is used, if the ash content is higher, as in TFR. After washing with water, a substantial part of the catalytic oxides remains in the bio-coal, especially CaO and MgO. This has a larger impact for TFR having a higher initial content of these oxides. There is a trend of lower reactivity in the order $TFR5 > TFR5_{H_2O} > TFR5_{AC}$. After acetic acid washing, the increase in reactivity from adding TFR or TSD to the BB is quite equal. TSD contributes with a small amount of bio-coal ash (0.4 wt% ash in TSD) and, therefore, a low amount of catalytic compounds to be removed, and at the same time, TSD has a duct structure, possibly being more affected by the washing agent. The structure of TFR is more compact, and the ash content in TFR is 5.5 times higher compared to that of TSD. The increased surface area due to the hydrolysis of organic bio-coal structure during washing is reported for raw biomass [24,48]. This increases the number of active carbon sites that can be attacked by CO_2 , which enhances the gasification. Flores et al. [52] and Xing et al. [53] reported that a higher surface area of bio-coal and a greater number of active sites enhance bio-coke gasification. The combination between active carbon sites and remaining catalytic elements in the bio-coal promotes the gasification of bio-coke due to the formation of intermediate complexes, as claimed by others [54–56]. The presence of a catalyst (M) would destroy the $C=O$ of CO_2 and form $M(O)$, which transfers oxygen to the active carbon site and forms the active intermediate complex $M-C-O$. Thus, the catalysts increase the concentration of active intermediates and enhance the gasification reactivity significantly.

Bio-coke containing kaolin-coated TSD or HTT had in general higher reactivity and lower start of a reaction temperature than bio-cokes with original bio-coals. The presence of the active carbon structure of bio-coal with the additional K_2O supplied via kaolin enhances the gasification in accordance with what has been stated in literature [12–20]. From the result of this study, it is recommended to use kaolin with a low alkali content to lower the role of the catalytic effect.

The addition of TFR_Ash and TSD_Ash gives only a slightly reduced temperature for the start of carbon gasification, at 943 °C and 930 °C, respectively, in comparison to 974 °C for the BB. Thus, the addition of ash at the amounts present in 5% of TSD or TFR

did not have a significant effect on coke reactivity when more reactive bio-coal carbon was not present. However, the total weight loss up to 1100 °C was higher, being approximately at similar level as when adding 5% of TSD to the coking coal blend.

5. Conclusions

This study aims to understand the impact of washing, kaolin coating and ash addition on the carbonization and quality of bio-coke, i.e., reactivity.

- Washing of bio-coals will contribute to decreased max. dilatation and higher max. contraction of coking coal blend due to the changing of bio-coal structure during washing and possible presence of precipitated free minerals in the bio-coal after drying.
- For the specific bio-coals used, the removal of catalytic ash oxides by washing from bio-coal with higher contents of them lower bio-coke reactivity. Contrarily, the washing of bio-coal with a low content of catalytic ash oxides results in increased reactivity due to the changed bio-coal structure.
- The reactive carbon structure of bio-coal in bio-coke contributes to lowering the start of the gasification temperature; therefore, the start of reaction temperature is higher if only bio-coal ash is present.
- Kaolin coating stabilizes plastic properties by a 5% addition, but types with substantial contents of K₂O should be avoided, as its catalytic effect enhances gasification of bio-coke.

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References

1. Geerdes, M.; Chaigneau, R.; Kurunov, I. *Modern Blast Furnace Ironmaking: An Introduction*, 3rd ed.; IOS Press: Amsterdam, The Netherlands, 2015; ISBN 1614994994.
2. World Steel Association. Available online: <https://www.worldsteel.org/publications/bookshop/product-details~Steel-s-contribution-to-a-low-carbon-future--update-version-coming-shortly~-PRODUCT~contribution-low-carbon-pp~.html> (accessed on 18 September 2020).
3. European Commission. 2050 Long-Term Strategy. Available online: https://ec.europa.eu/clima/eu-action/climate-strategies-targets/2050-long-term-strategy_en (accessed on 16 November 2021).
4. Mandova, H.; LeDuc, S.; Wang, C.; Wetterlund, E.; Patrizio, P.; Gale, W.; Kraxner, F. Possibilities for CO₂ emission reduction using biomass in European integrated steel plants. *Biomass Bioenergy* **2018**, *115*, 231–243. [CrossRef]
5. Babich, A.; Senk, D.; Fernandez, M. Charcoal Behaviour by Its Injection into the Modern Blast Furnace. *ISIJ Int.* **2010**, *50*, 81–88. [CrossRef]
6. Feliciano-Bruzual, C. Charcoal injection in blast furnaces (Bio-PCI): CO₂ reduction potential and economic prospects. *J. Mater. Res. Technol.* **2014**, *3*, 233–243. [CrossRef]
7. Gupta, R.C. Woodchar as a sustainable reductant for ironmaking in the 21st century. *Miner. Process. Extr. Met. Rev.* **2003**, *24*, 203–231. [CrossRef]

8. Keown, D.; Favas, G.; Hayashi, J.; Li, C.-Z. Volatilisation of alkali and alkaline earth metallic species during the pyrolysis of biomass: Differences between sugar cane bagasse and cane trash. *Bioresour. Technol.* **2005**, *96*, 1570–1577. [\[CrossRef\]](#)
9. Agblevor, F.A.; Besler, S. Inorganic Compounds in Biomass Feedstocks. 1. Effect on the Quality of Fast Pyrolysis Oils. *Energy Fuels* **1996**, *10*, 293–298. [\[CrossRef\]](#)
10. Phanphanich, M.; Mani, S. Impact of torrefaction on the grindability and fuel characteristics of forest biomass. *Bioresour. Technol.* **2011**, *102*, 1246–1253. [\[CrossRef\]](#) [\[PubMed\]](#)
11. Dastidar, M.G.; Sarkar, B.K.; Mitra, M.K.; Dey, R. Effect of alkali on different iron making processes. *Mater. Sci Eng.* **2018**, *2*, 304–313. [\[CrossRef\]](#)
12. Grigore, M.; Sakurovs, R.; French, D.; Sahajwalla, V. Influence of Mineral Matter on Coke Reactivity with Carbon Dioxide. *ISIJ Int.* **2006**, *46*, 503–512. [\[CrossRef\]](#)
13. Nomura, S.; Ayukawa, H.; Kitaguchi, H.; Tahara, T.; Matsuzaki, S.; Naito, M.; Koizumi, S.; Ogata, Y.; Nakayama, T.; Abe, T. Improvement in Blast Furnace Reaction Efficiency through the Use of Highly Reactive Calcium Rich Coke. *ISIJ Int.* **2005**, *45*, 316–324. [\[CrossRef\]](#)
14. Nomura, S.; Kitaguchi, H.; Yamaguchi, K.; Naito, M. The Characteristics of Catalyst-coated Highly Reactive Coke. *ISIJ Int.* **2007**, *47*, 245–253. [\[CrossRef\]](#)
15. Ng, K.; MacPhee, J.; Giroux, L.; Todoschuk, T. Reactivity of bio-coke with CO₂. *Fuel Process. Technol.* **2011**, *92*, 801–804. [\[CrossRef\]](#)
16. Montiano, M.; Díaz-Faes, E.; Barriocanal, C.; Alvarez, R. Influence of biomass on metallurgical coke quality. *Fuel* **2014**, *116*, 175–182. [\[CrossRef\]](#)
17. MacPhee, J.; Gransden, J.; Giroux, L.; Price, J. Possible CO₂ mitigation via addition of charcoal to coking coal blends. *Fuel Process. Technol.* **2009**, *90*, 16–20. [\[CrossRef\]](#)
18. 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.
19. 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 CO₂ Reduction in the Steel Industry, Session 9, Düsseldorf, Germany, 27 June–1 July 2011.
20. Solar, J.; Caballero, B.; Barriocanal, C.; Lopez-Uribebarrenechea, A.; Acha, E. Impact of the Addition of Pyrolysed Forestry Waste to the Coking Process on the Resulting Green Biocoke. *Metals* **2021**, *11*, 613. [\[CrossRef\]](#)
21. Reid, M.H.; Mahoney, M.R.; Monaghan, B.J. A Coke Analogue for the Study of the Effects of Minerals on Coke Reactivity. *ISIJ Int.* **2014**, *54*, 628–633. [\[CrossRef\]](#)
22. Liu, X.; Bi, X.T. Removal of inorganic constituents from pine barks and switchgrass. *Fuel Process. Technol.* **2011**, *92*, 1273–1279. [\[CrossRef\]](#)
23. Mourant, D.; Wang, Z.; He, M.; Wang, X.S.; Garcia-Perez, M.; Ling, K.; Li, C.-Z. Mallee wood fast pyrolysis: Effects of alkali and alkaline earth metallic species on the yield and composition of bio-oil. *Fuel* **2011**, *90*, 2915–2922. [\[CrossRef\]](#)
24. Das, P.; Ganesh, A.; Wangikar, P. Influence of pretreatment for deashing of sugarcane bagasse on pyrolysis products. *Biomass-Bioenergy* **2004**, *27*, 445–457. [\[CrossRef\]](#)
25. Mayer, Z.A.; Apfelbacher, A.; Hornung, A. Effect of sample preparation on the thermal degradation of metal-added biomass. *J. Anal. Appl. Pyrolysis* **2012**, *94*, 170–176. [\[CrossRef\]](#)
26. Eom, I.-Y.; Kim, K.-H.; Kim, J.-Y.; Lee, S.-M.; Yeo, H.-M.; Choi, I.-G.; Choi, J.-W. Characterization of primary thermal degradation features of lignocellulosic biomass after removal of inorganic metals by diverse solvents. *Bioresour. Technol.* **2011**, *102*, 3437–3444. [\[CrossRef\]](#) [\[PubMed\]](#)
27. Asadieraghi, M.; Daud, W.M.A.W. Characterization of lignocellulosic biomass thermal degradation and physiochemical structure: Effects of demineralization by diverse acid solutions. *Energy Convers. Manag.* **2014**, *82*, 71–82. [\[CrossRef\]](#)
28. Jiang, L.; Hu, S.; Sun, L.-S.; Su, S.; Xu, K.; He, L.-M.; Xiang, J. Influence of different demineralization treatments on physicochemical structure and thermal degradation of biomass. *Bioresour. Technol.* **2013**, *146*, 254–260. [\[CrossRef\]](#)
29. Lundgren, M. Development of Coke Properties during the Descent in the Blast Furnace. Ph.D. Thesis, Luleå Tekniska Universitet: Sustainable Process Engineering, Department of Civil, Environmental and Natural Resources Engineering, Luleå, Sweden, 2013.
30. Fernández, A.; Barriocanal, C.; Díez, M.; Alvarez, R. Influence of additives of various origins on thermoplastic properties of coal. *Fuel* **2009**, *88*, 2365–2372. [\[CrossRef\]](#)
31. Díez, M.A.; Alvarez, R.; Fernández, M. Biomass derived products as modifiers of the rheological properties of coking coals. *Fuel* **2012**, *96*, 306–313. [\[CrossRef\]](#)
32. Guerrero, A.; Díez, 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**, *147–148*, 105–114. [\[CrossRef\]](#)
33. Ueki, Y.; Nunome, Y.; Yoshiie, R.; Naruse, I.; Nishibata, Y.; Aizawa, S. Effect of Woody Biomass Addition on Coke Properties. *ISIJ Int.* **2014**, *54*, 2454–2460. [\[CrossRef\]](#)
34. Yustanti, E.; Wardhono, E.Y.; Mursito, A.T.; Alhamidi, A. Types and Composition of Biomass in Biocoke Synthesis with the Coal Blending Method. *Energies* **2021**, *14*, 6570. [\[CrossRef\]](#)
35. 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. [\[CrossRef\]](#)

36. Khan, M.R.; Walker, P.L., Jr.; Jenkins, R.G. Swelling and plastic properties of coal devolatilized at elevated pressures of H₂ and He: Influences of added iron oxides. *Fuel* **1988**, *67*, 693–699. [CrossRef]
37. Khan, M.R.; Jenkins, R.G. Influence of added calcium compounds on swelling, plastic, and pyrolysis behaviour of coal devolatilized at elevated pressures. *Fuel* **1986**, *65*, 1203–1208. [CrossRef]
38. Khan, M.; Jenkins, R.G. Influence of K and Ca additives in combination on swelling, plastic and devolatilization properties of coal at elevated pressure. *Fuel* **1989**, *68*, 1336–1339. [CrossRef]
39. Patrick, J.; Shaw, F. Influence of sodium carbonate on coke reactivity. *Fuel* **1972**, *51*, 69–75. [CrossRef]
40. Khan, M.; Jenkins, R. Swelling and plastic properties of coal devolatilized at elevated pressures of H₂ and He Influence of potassium and silicon additives. *Fuel* **1986**, *65*, 1291–1299. [CrossRef]
41. Meng, F.; Gupta, S.; Yu, J.; Jiang, Y.; Koshy, P.; Sorrell, C.; Shen, Y. Effects of kaolinite addition on the thermoplastic behaviour of coking coal during low temperature pyrolysis. *Fuel Process. Technol.* **2017**, *167*, 502–510. [CrossRef]
42. 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]
43. ALS Scandinavia AB. Available online: <https://www.alsglobal.se/en> (accessed on 15 September 2020).
44. SSAB. Available online: <https://www.ssab.se/ssab-koncern/om-ssab/produktionsorter-i-sverige/lulea> (accessed on 15 September 2020).
45. D-LAB AB. Available online: <https://www.degerforslab.se/en-us/> (accessed on 15 June 2021).
46. Mochizuki, Y.; Naganuma, R.; Tsubouchi, N. Influence of Inherently Present Oxygen-Functional Groups on Coal Fluidity and Coke Strength. *Energy Fuels* **2018**, *32*, 1657–1664. [CrossRef]
47. Tsubouchi, N.; Mochizuki, Y.; Naganuma, R.; Kamiya, K.; Nishio, M.; Ono, Y.; Uebo, K. Influence of Inherent Oxygen Species on the Fluidity of Coal during Carbonization. *Energy Fuels* **2016**, *30*, 2095–2101. [CrossRef]
48. Xu, W.; Wei, J.; Chen, J.; Zhang, B.; Xu, P.; Ren, J.; Yu, Q. Comparative Study of Water-Leaching and Acid-Leaching Pretreatment on the Thermal Stability and Reactivity of Biomass Silica for Viability as a Pozzolanic Additive in Cement. *Materials* **2018**, *11*, 1697. [CrossRef] [PubMed]
49. Loison, R.; Foch, P.; Boyer, A. *Coke: Quality and Production*; University Press: Cambridge, UK, 2014; ISBN 1483165272.
50. Kidena, K.; Murata, A.S.; Nomura, M. Studies on the Chemical Structural Change during Carbonization Process. *Energy Fuels* **1996**, *10*, 672–678. [CrossRef]
51. Xu, L.; Liu, J.; Kang, Y.; Miao, Y.; Ren, W.; Wang, T. Safely Burning High Alkali Coal with Kaolin Additive in a Pulverized Fuel Boiler. *Energy Fuels* **2014**, *28*, 5640–5648. [CrossRef]
52. Flores, B.D.; Flores, I.V.; Guerrero, A.; Orellana, D.R.; Pohlmann, J.G.; Diez, M.A.; Borrego, A.G.; Osorio, E.; Vilela, A. Effect of charcoal blending with a vitrinite rich coking coal on coke reactivity. *Fuel Process. Technol.* **2017**, *155*, 97–105. [CrossRef]
53. Xing, X. Pore Structure and Integrity of a Bio-Coke under Simulated Blast Furnace Conditions. *Energy Fuels* **2019**, *33*, 2133–2141. [CrossRef]
54. Yang, H.; Song, H.; Zhao, C.; Hu, J.; Li, S.; Chen, H. Catalytic gasification reactivity and mechanism of petroleum coke at high temperature. *Fuel* **2021**, *293*, 120469. [CrossRef]
55. Wang, Q.; Wang, E.; Li, K.; Husnain, N.; Li, D. Synergistic effects and kinetics analysis of biochar with semi-coke during CO₂ co-gasification. *Energy* **2019**, *191*, 116528. [CrossRef]
56. Malekshahian, M.; Hill, J. Potassium catalyzed CO₂ gasification of petroleum coke at elevated pressures. *Fuel Process. Technol.* **2013**, *113*, 34–40. [CrossRef]