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A Study on Bio-Coke Production—The Influence of Biochar Addition to the Coking Blend on Bio-Coke Quality Parameters

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Abstract: Carbon dioxide is emitted in several industrial processes and contributes to global warming. One of the industries that is considered a significant emitter is metallurgy. Therefore, it is necessary to search for and implement methods to reduce its emissions from metallurgical processes. An alternative option to the use of conventional coke, which is produced solely from fossil coal, is the utilization of bio-coke. The production of bio-coke involves the use of coking coal and the incorporation of biomass-derived substances such as biochar (charcoal). The article presents the results of the research on the influence of the biochar addition on the structural, textural, and technological properties of produced bio-coke. Research on the production and analysis of the properties of the obtained bio-coke aimed at assessing the potential possibilities of applying it in the process of a carbothermal reduction of manganese ore in order to smelt ferroalloys. Studies have shown that biochar addition to the coking blend in an amount of up to 20% allows a bio-coke characterized by properties enabling the mentioned use to be obtained. Bio-coke was characterized by higher CO_2 reactivity index (CRI), lower post-reaction strength (CSR), and higher reactivity to synthetic manganese ore than regular metallurgical coke. In the context of industrial applications of bio-coke, it is necessary to verify its production and use on a pilot and industrial scale.

Keywords: bio-coke; biomass; biochar; coke; coke-making; ferroalloys; carbon dioxide; steel

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1. Introduction

The iron and steel production sector is responsible for approx. 7% of global carbon dioxide emissions [1,2]. Iron ore is reduced in the blast furnace (BF), and the elemental carbon donor for reduction purposes is coke [3]. The main product resulting from this process is pig iron, which is directed to further processing in the basic oxygen furnace (BOF) where crude steel is produced [4,5]. This process, called the integrated steelmaking process (BF-BOF), currently accounts for about 70% of global steel production [6,7]. Coke plays a vital role in various industrial processes beyond steel production, including the foundry industry, the manufacturing of insulating wool, quicklime, ferroalloys, carbide production, and it is used as a heating fuel. In blast furnaces, coke serves a dual purpose: chemically, it acts as a reductant and carburizer, while physically, it functions as a gas-permeable grate that supports the charge material column, facilitating the proper flow of gasses and liquid products to the furnace's lower sections. Additionally, it provides heat energy essential for the process. Its specific role varies depending on the application. Given that coke is derived from fossil fuels, specifically coking coals, its usage is linked to carbon dioxide emissions, a greenhouse gas contributing to global warming. A potential solution to mitigate these emissions is the use of bio-coke, a hybrid reductant made from coking coal and biogenic raw materials which offers a source of renewable elemental carbon that is regarded as carbon neutral. Due to the addition of biomass into the coking blend, the elemental carbon of renewable origin is introduced into the reductant structure, which allows for the reduction of carbon dioxide emissions from its use. Therefore, in recent years, several research works have been observed, aimed at the use of the raw materials of biomass origin for partial substitution of coking coal in the production of bio-coke [8–12]. Two approaches are generally used—the addition of raw or thermally processed biomass. Due to the fact that coke is produced from coking coals, which are plasticized in a specific temperature regime (c.a. 350–500 °C), thus creating conditions for the formation of a well-sintered porous coke structure, the researchers focused on assessing both the impact of biomass addition on the coke-making properties of the coal/biomass blend and the most common coke quality indicators, i.e., CRI (coke reactivity index) and CSR (coke strength after reaction). In contrast to coking coals, the solid raw materials of biomass origin (raw biomass or thermally processed biomass) do not plasticize during the pyrolysis process, therefore their addition usually contributes to the deterioration of the rheological properties of the coking blend composed with their participation, consequently affecting the final quality of the coke [9–12]. Both the fluidity of the blend and its dilatation properties deteriorate. Deterioration is already observed in the case of a small addition of biomass, even up to 2%, and its degree depends on both the initial properties of the coal or coal blend and the type and physico-chemical properties of the added raw material. According to the literature reports, both chemical and physical properties are responsible for the deterioration of coking parameters. The decrease in fluidity is attributed to the harmful effects of oxygen groups present in the volatiles released during the pyrolysis process (chemical effect), but also due to the sorption of plasticizing coal components through the porous structure of the biomass, which also develops during the pyrolysis process (physical effect) [11,13]. The deterioration of the mentioned rheological parameters also worsens the sintering properties, which is evidenced by a decrease in the value of the sinterability index assessed according to Roga method (RI) [14]. The change in coke-making properties due to the addition of biomass substances has an impact on the technological properties of the bio-coke produced. To assess the usefulness of coke in technological processes, including the blast furnace process, indicators determined according to the Nippon Steel Corporation (NSC) method are used, i.e., the CRI and the CSR indices. The NSC test runs under conditions simulating the reaction of coke gasification with carbon dioxide in the high-temperature zone of a blast furnace. The value of the indices of this test reflects the coke's susceptibility to the gasification reaction with carbon dioxide, CO_2, (Boudouard reaction: $CO_2 + C = 2CO$) at a high temperature of 1100 °C (CRI), and the impact of this reaction on the mechanical properties of the coke (CSR). Generally, the addition of substances of biomass origin, including charcoal, leads to an increase in the coke reactivity index CRI, and, consequently, to a decrease in the post-reaction strength CSR [11,15]. There is also a decrease in the drum strength of bio-coke assessed by IRSID [16] and JIS [11]. For this reason, in order to maintain the qualitative indicators of coke at a satisfactory level, the share of biomass substance is usually small and does not exceed a small percentage of the mass share. Actions are also taken to increase the density of both the biomass additive (pelletization) and the coal-biomass mixture (partial briquetting). This makes it possible to compensate, to some extent, for the unfavorable impact of bio-components in comparison with introducing it in a mechanically unprocessed form.

MacPhee et al. [11] investigated the effect of the addition of commercial charcoal from hardwood (up to 10%) on CRI and CSR of obtained bio-coke. Charcoal was added to three different coal blends and in each case, a deterioration of the quality indicators was noted, i.e., an increase in CRI and a decrease in CSR. The changes were different depending on the base coal blend. According to the authors, the increase in CRI reactivity was due to the increase in the content of CaO and other ash components associated with the addition of charcoal. Moreover, the authors observed that the introduction of coarser-grained charcoal is more advantageous. Similar conclusions were reached by Dornelas et al. [17].

Researchers examining the effect of the addition of charcoal in amounts up to 12% (fine fraction 100% < 2.83 mm and coarse fraction: 70% < 2.83 mm) found that CRI is significantly increased, and CSR is significantly reduced. For the 12% charcoal addition, an increase in CRI from 22.3 to 35.7 and 45.8 was observed for the coarser and finer fractions, respectively. In the case of CSR, there was a decrease from the level of 57.1 to the level of approx. 35. A slightly more favorable effect of coarser grain size was observed for less than 12% charcoal content. There was also a decrease in the drum index DI, but the decrease in this index was not as large as in the case of the above-mentioned parameters. For the coarser fraction, the DI value decreased from 79.7 to 72.8% and the fine fraction to 65.7%. Montiano et al. [18] studied the effect of the addition of waste sawdust on the thermoplastic properties of coal. The investigation was carried out for three different sawdust batches. It was found that a 2% addition of sawdust reduces the Gieseler fluidity c.a. 2 times. Diez and Borrego [18] evaluated CO_2-reactivity patterns in cokes from coal and woody biomass blends. Cokes were produced from blends made up of coking coal and lignocellulosic biomass—Eucalyptus and Olive woods and their charcoals. They found that cokes produced by adding 2 wt.% biomass were more reactive than the coke derived from the single coal. In addition, a decrease in the threshold temperature of the Boudouard reaction was observed. According to the authors, the increase in CO_2-reactivity of the cokes was related to oxygen content and its functionality, the ash chemical composition and isotropic porous nature of the biomasses, decreased fluidity in the carbonized blend, and the higher microporosity of the cokes produced with the use of biomass. In other work, Montiano et al. [15] explored the potential of incorporating waste sawdust into two industrial coal blends, with additions of up to 5%. Their findings revealed that the inclusion of biomass led to a significant reduction in the plastic properties of the coking blend, showing a decrease in Gieseler maximum fluidity of approximately 50% with 3 wt.% additions of both types of sawdust examined. Decreased in charge bulk density and in consequence, a deterioration of coke properties was observed. Coke reactivity to CO_2 (CRI) increased and JIS drum strength and CSR post-reaction strength decreased. In the work [19], the effect of biomass (0.3–2.25% of chestnut sawdust; directly added and incorporated into briquettes) was compared to the important parameters of the coking process and coke quality. The authors found that one of the problems associated with the use of biomass is its low bulk density. The direct addition of biomass to the charge resulted in a decrease in bulk density to level of c.a. 758 kg/m^3 for 1.5% chestnut addition (compared to coal alone: 776 kg/m^3), while the introduction of biomass incorporated into the briquettes (2–15% share of briquettes in coking blend) had a positive effect, i.e., a level slightly higher than for coal alone was obtained (c.a. 783–793 kg/m^3). They also found that the addition of biomass reduces the plasticity of the coking blend. In addition, it was observed that a direct addition of biomass worsens the coke properties: reduced $DI_{150/15}$ drum strength, increased CO_2 reactivity (CRI), and reduced CSR post-reaction strength of coke. The use of briquettes as a biomass carrier, due to the positive effect on bulk density, allows compensation for the adverse effect (to some extent). According to the authors, the coke quality results suggest that 10–15 wt.% of briquettes containing biomass can be included in coking blends. Florentino Madiedo et al. [20] studied the reactivity of biomass-containing briquettes. Different briquettes based on coal, four species of biomass, and four binders were produced (biomass: pine kraft lignin, pine sawdust torrefied at 300 °C for 30 min (SPT) and a commercial bio-coal derived from hydrothermally treated waste obtained from tree pruning). They found that depending on the biomass and used binder, coke had a different reactivity. In other research, the authors [21] studied the effect of briquette composition on coking pressure generation. It was found that coking pressure decreases with the addition of biomass-containing briquettes (up to 15% of briquettes which corresponds to 2.25% of the biomass in coking blend). In other works, the authors [22] observed that briquettes made from coking blends with the inclusion of various biomass materials and binders exhibited varying densities, resulting in cokes with different strength characteristics. They also discovered a correlation between the strength of the cokes produced from these briquettes and the density, volatile matter content of the briquettes, as well as the textural composition of the resulting coke. Matsumura et al. [23] studied the addition of biomass (cedar) to the strength of the bio-coke determined in the I-type drum. The authors found that the initial densification of biomass allows its addition in the amount of up to 1.5% without loss of strength of bio-coke. MacPhee et al. [11] studied the reactivity of bio-cokes produced with the use of charcoal (up to 5%). Reactivity toward CO_2 was examined using Thermal Gravimetric Analysis. It was found that mineral matter content plays an important role in the gasification characteristics of the bio-cokes. Bio-cokes with low mineral matter content behave very similarly to the referential coke. Flores et al. also studied the charcoal addition to the coking blend [24]. Charcoal was added to a vitrinite-rich medium volatile coking coal in three amounts (3, 5, and 8 wt.%) and in two different particle size ranges (below 1 mm and between 3 and 4 mm). The authors used thermogravimetric analyses (TGA) to assess coke reactivity towards CO_2 under isothermal and non-isothermal conditions. It was found that through controlling the amount and the particle size of charcoal added, the coke reactivity did not differ considerably from the reference coke. TGA indicated that the addition of charcoal tends to increase coke reactivity. The effect of a woody biomass (sawdust of Japanese cedar) addition on coke properties was studied by Ueki et al. [25]. Biomass was added in raw form (up to 10% in terms of fixed carbon) and in the form of biocarbon (up to 5%) produced at 300, 400, 500, and 1000 °C. The authors found that the addition of biomass reduces the connectivity of coal particles during carbonization, resulting in a drastic reduction in the Tumbling Index (TI). However, the most favorable effects were observed for the use of biocarbon produced at temperatures of 500 and 1000 °C, for which the decrease in the TI value was significantly smaller. Suopajärvi et al. [26] studied the effect of pine chips charcoal and kraft-lignin addition on coke compression strength and reactivity (up to 10%). The authors noted that the addition of charcoal increases the reactivity of bio-coke due to the addition of finer charcoal. The impact of kraft-lignin was slightly less. The optimization of the charcoal grain size allowed for the maintenance of the high strength of bio-coke with its 5% addition. Bio-cokes with the highest strengths were obtained for additives with a grain size of 0.125–0.15 mm.

Solar et al. [12] investigated the effect of the charcoal addition from waste woody biomass (*Pinus radiata*). According to the authors, when the charcoal is added (up to 2%), the quality of the bio-coke worsened, the $DI_{150/15}$ index was reduced from 76 to 66, and the CSR from 63 down to 56. CRI was at a similar level for the reference blend. A further addition of 5% resulted in a drop of $DI_{150/15}$ to below 25. Due to insufficient sample quantity, no CRI/CSR information is available for the 5% addition. The addition of biomass to coal was also studied by Tawil et al. [27]. The authors assessed the impact of a 5% addition of torrefied pine and spruce sawdust TSD5 (290 °C) and high temperature torrefied pelletized pine and spruce sawdust HTT5 (400 °C). A better result was obtained for the HTT5 additive, for which the CRI and CSR parameters did not differ much from the coke of the reference blend, i.e., 31.8 (CRI) and 57.8 (CSR); for the reference blend coke, it was 28.6 and 57.6, respectively. Bazaluk et al. [28] studied the effect of biomass addition on a number of different parameters of the obtained bio-coke. As a biomass additive, the Ukrainian industrial pellets with a diameter of 8 mm and a length of 4–22 mm were used in the amounts of 5, 10, 15, 30, and 45%. The authors found that the addition of biomass caused a decrease in structural and abrasion resistance but increased the electric resistivity of the bio-coke bed. Kieusch et al. [29] studied the effect of adding 5% of biomass pellets for different carbonization temperatures of 950 and 1100 °C. It was observed that the addition of pellets contributed to an increase in CRI reactivity and a decrease in CSR, but for bio-coke produced at a higher temperature, parameters similar to the reference coke produced at a lower temperature were obtained. Koskela et al. [30] investigated the effect of pyrolyzed and non-pyrolyzed lignin on the properties of the bio-coke produced (additive 5, 10, and 15%), including reactivity and compression strength. It was found that even a 5% addition of lignin caused a significant deterioration of coke strength—better results were obtained for pyrolyzed lignin. It also caused an increase in reactivity, with no differences between pyrolyzed and non-pyrolyzed lignin. Jayasekara et al. [31] studied the possibility of incorporating up to 10% of microalgae (*Chlorella vulgaris*) as a partial substitute for the coal blend. By adding microalgae to three different coals, the authors noted an increase in CRI and a decrease in CSR. However, the magnitude of this effect was different for different coals. For 2 out of 3 tested coals, even for a 10% addition of microalgae, bio-coke was obtained with a CSR value at a satisfactory level > 55, with a CRI not significantly different from single-coal coke. A slightly different way of producing bio-coke was proposed by Yustanti et al. [32]. Bio-coke was produced by carbonization of previously prepared briquettes from a blend of coking coal and rice husk and coconut shells charcoals (up to 25% addition). Depending on the type of charcoal, different results were obtained. Obviously, the addition of charcoal caused a decrease in CSR and an increase in CRI, but in the case of coconut shells charcoal, satisfactory values of these indicators were obtained, i.e., 29.8% (CRI) and 55.1% (CSR) and 23.9% (CRI) and 42.9 (CSR), respectively, for 15 and 25% of its content in the blend.

Based on the literature review, it should be stated that the issue of bio-coke production based on coking coal and additives of biomass origin is a relatively new topic—the first publication on this topic appeared in 2002 [8], while the vast majority of them have been published over the the last five years. Most publications concern the production of blast furnace coke, as this type of coke is dominant on the world market (approx. 90%). However, this process is the most demanding in relation to the quality of the coke used in it. According to the literature data, each addition of biomass, both raw and thermally processed, causes a significant increase in coke reactivity and a decrease in its post-reaction strength, which are parameters extremely important from the operational point of view of modern blast furnaces with a high volume (and height) of working chambers. Coke in such furnaces must withstand a load of charge materials with a height of up to several dozen meters, therefore it should be characterized by very high strength parameters. For this very reason, according to most authors, the permissible, acceptable addition of biomass is only a few percent. On the other hand, in addition to the blast furnace process as previously mentioned, coke is also used in a number of processes that are not so demanding in regard to coke strength. In the production of manganese ferroalloys, coke, in addition to the role of a reductant, also plays a physical role—support for the feedstock materials, while the height of the column of materials is much lower than those existed in blast furnaces (c.a. 4–8 m), thus the requirements as to its strength should be correspondingly lower. This means that if bio-coke is used for the smelting of ferroalloys in a submerged arc furnace, it is possible to potentially use bio-coke with a higher content of biomass additive.

The aim of this work is to determine the effect of the addition of charcoal in the amount of up to 20% on the parameters of the structure and texture of the produced bio-coke, which determines its quality parameters. All of the papers published so far focused on the production of bio-coke for the conditions of the gravity charging system (top charging), whose charge density is approx. 30–40% lower than in the stamp-charging system, which is currently the most dynamically developing coke-making technology [33,34]. The significantly higher batch density also offers additional potential, and in the authors' opinion, it is worth conducting comprehensive research. The presented research was also carried out both for the conditions of gravity charging system and for increased charge density corresponding to the stamp-charged technology for the purpose of comparing the capabilities of both methods.

2. Materials and Methods

The bio-cokes production tests were carried out using a reference coal blend with a composition similar to that used in production practice at the Czestochowa Nowa Coking Plant (Poland). Commercially available charcoal from the Polish company Ozen was used as a biomass additive—the charcoal is certified by FSC (Forest Stewardship Council) thus it is considered a bio-char. The moisture content of raw materials was assessed according to PN-ISO 11722:2009 [35] (coal) and PN-EN ISO 18134-1:2015-11 [36] (charcoal). Ash yield was evaluated following PN-ISO 1171:2002 [37] (for coal) and PN-EN ISO 18122:2016-01 [38] (for charcoal). The volatile matter content was measured according to ISO 562:2010 [39] (coal) and PN-EN ISO 18123:2016-01 [40] (charcoal). The contents of carbon, hydrogen, and nitrogen were determined in accordance with ISO 29541:2010 [41] (coal) and PN-EN ISO 16948:2015 [42] (charcoal). Total sulfur content was assessed based on ISO 19579:2006 [43] (coal) and PN-EN ISO 16994:2016 [44] (charcoal). Oxygen content was measured following PN-ISO 1928:2002 [45] (coal) and PN-EN ISO 16993:2016 [46] (charcoal). Ash chemical composition was assessed with the use of ICP-OES and the alkalinity index (*AI*) was assessed according to Formula (1).

$$AI = A^{ad} \times \frac{CaO + MgO + Na_2O + K_2O + Fe_2O_3}{SiO_2 + Al_2O_3} \tag{1}$$

The real density (ρ_t) and total pore volume (V_{TOTAL}) were measured using the AccuPyc II 1340 helium pycnometer from Micromeritics (Norcross, GA, USA). Apparent density (ρ_{app}) was determined with the GeoPyc 1350 density analyzer, also from Micromeritics. Total porosity (P) was calculated using Formula (2)—(ρ_t—real density of particle, g/cm^3; ρ_{app}—apparent density of particle g/cm^3):

$$P = \frac{\rho_t \ - \rho_{app}}{\rho_t} \times 100 \tag{2}$$

The results of the performed determinations for coals and blends are presented in Table 1.

Table 1. Properties of raw materials.

Parameter	Coking Blend	Charcoal	Content in Ash, %	Coking Blend	Charcoal
Moisture content, M^{ad}, %	1.02	4.5	SiO_2	49.11	18.92
Ash yield, A^{ad}, %	8.35	4.8	Al_2O_3	26.04	1.43
Volatile matter, VM^{ad}, %	28.73	11.40	Fe_2O_3	6.67	2.24
Fixed carbon, %	61.9	79.3	TiO_2	1.17	0.04
Carbon content, C^{ad}, %	78.4	82.5	CaO	3.80	32.66
Hydrogen content, H^{ad}, %	4.89	2.33	MgO	1.74	2.83
Nitrogen content, N^{ad}, %	1.44	0.52	$P_4O_{10}(P_2O_5)$	1.34	2.54
Oxygen content, O^{ad}, %	5.4	5.3	SO_3	2.49	1.48
Total sulfur content, $S_T{}^{ad}$, %	0.50	0.02	Mn_3O_4	0.07	1.36
Real density, ρ_t, g/cm^3	1.357	1.502	BaO	0.23	0.19
Apparent density, ρ_{app}, g/cm^3	1.316	0.460	SrO	0.24	0.07
Total pore volume, $V_{TOTAL,}$ cm^3/g	0.023	1.510	Na_2O	0.96	0.61
Total porosity, P, %	3.0	69.4	K_2O	1.67	9.03
Alkalinity index, -	n/a	n/a	AI	1.6	11.6

The bio-coke production tests were carried out for 2, 6, 10, and 20% charcoal addition for gravity charging conditions (low density) and compacted coking chamber filling system (high density). To achieve proper homogenization of coal/biomass blend, both coking blends and charcoal were crushed to the grain size of c.a. 95% < 3.15 mm. Before carbonization tests, all blends were moisturized to the fixed moisture content of 10%. Carbonization tests were carried out with the use of Karbotest installation designed to simulate the industrial coking process. The Karbotest installation (Figure 1) is an electric heated vertical tubular oven designed for producing metallurgical coke under laboratory conditions that closely mimic industrial processes. A blend of coal and biomass, weighing approximately 4 kg, is charged into a steel retort (with a depth of 850 mm and an inner diameter of 150 mm) by either gravity- or stamp-charging methods. The retort is then placed in the hot oven, where it is heated until the temperature at the center of the charge reaches 950 °C. The bio-coke is maintained at this final coking temperature until gas production falls below 0.5 dm^3/min. Following this, the oven is turned off, and the retort remains inside for self-cooling to ambient temperature. The next day, the bio-coke is extracted and prepared for further analysis.

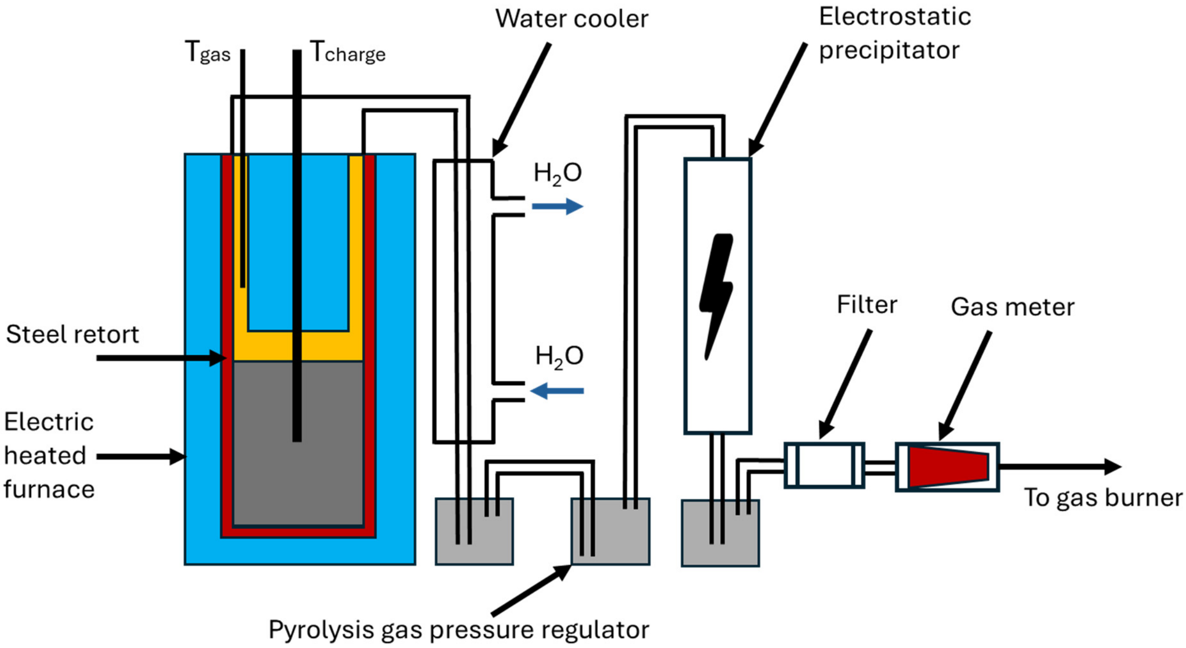

Figure 1. Scheme of the Karbotest apparatus.

The Nippon Steel Corporation (NSC) parameters CRI and CSR were determined based on ISO:18894:2006 [47]. CRI (coke reactivity index) is a quantity mass loss of coke (bio-coke), resulting from the reaction of carbon dioxide with carbon in a coke matrix molecular structure at the temperature of 1100 °C for 2 h. It is expressed in mass percentage. CSR is the ratio of the mass of grains larger than 10 mm remaining after subjecting a sample of gasified coke to mechanical treatment (I-type tumbler) to a mass sample of coke subjected to tumbling, expressed in mass percentage. The principle of the method is based on the gasification of a 200 g coke sample of a grain size 19–22.4 mm in a carbon dioxide atmosphere (flow 300 dm^3/h) at a temperature of 1100 °C for 2 h. The coke reactivity index is calculated based on the amount of weight loss. Then, a sample of the coke remaining after gasification was subjected to treatment is mechanically processed in a rotating drum under conditions specified in the standard (600 revolutions, 20 rpm), after which the mass of grains with dimensions above 10 mm is determined in order to determine the CSR index. tumbling strength TS600 and Abrasion Index AI600 assessment. The TS600 measurement principle is to determine the tumbling residue (600 revolutions, 20 rpm) of a 50 g coke sample of a grain size of 10–19 mm. The TS600 indicator is the quotient of the mass remaining on the 5 mm sieve to the initial mass of the sample, expressed in mass percentage. AI600 indicator is the ratio of the grains' mass passed through the 0.5 mm sieve to the initial mass of the sample subjected to tumbling. The results of proximate and ultimate analysis of the bio-cokes are presented in Table A1 (Appendix A).

3. Results

3.1. Bulk Density of Coal/Charcoal Blends and Yield of Bio-Coke

In coke-making technology, charge density plays a very important role, affecting both the course of the process (i.a. specific energy consumption, coking pressure), its performance (yields of individual products, productivity of the chamber), and the parameters shaping the quality of the coke produced. The influence of charcoal addition to the coking blend on bulk density (calculated on dry basis) is presented in Figure 2. As it is clear from the results presented, the addition of charcoal to the coking blend significantly affects the final density of the charge. With the increase in the addition of charcoal, the charge density is significantly reduced. In the case of a gravity charging system, the density decreases from 721 kg/m^3 to 590 kg/m^3 for a 20% charcoal addition whereas, for the stamp charging system, the density decreased from 990 to 870 kg/m^3. It is a decrease of 18.1% and 16.6%, respectively. This decrease is mainly caused by the differences in the apparent density of coal particles and charcoal particles. The apparent density for coal is 1.316 g/cm^3, while the apparent density of tech charcoal is 0.460 g/cm^3. Therefore, the higher the proportion of raw material with lower apparent density, the lower the bulk density. Nevertheless, a decrease in the bulk density will potentially result in a decrease in the unit productivity of the chamber in the coke oven battery. Importantly, it should be noted that in the case of the stamp charging system, even despite the additional stamping of the mass, it was not possible to maintain the assumed high density, but even for 20% of the additive, the density of the charge was significantly higher than in the case of the base reference blend loaded by gravity.

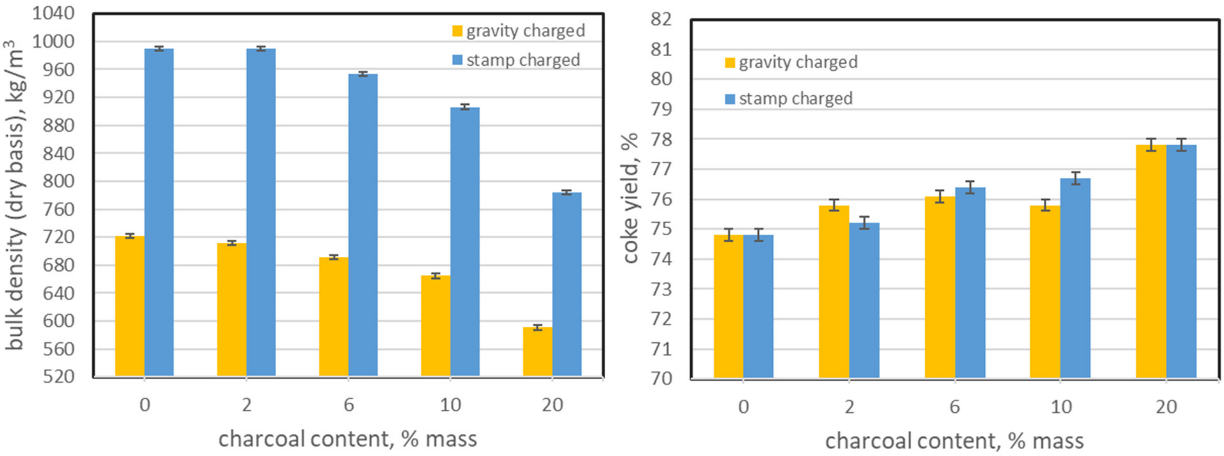

Figure 2. Influence of charcoal addition on charge bulk density and coke yield.

The yield of coke/bio-coke is important primarily from the point of view of the operation of coke batteries and production economics. The higher the percentage of coke yield, the higher the unit production from a single coking chamber. Of course, this applies only to the constant bulk density of the charge in the coking chamber. As can be seen from the data presented in Figure 2, the addition of charcoal to the coking blend increases the yield of bio-coke. In the studied range of the charcoal addition, an increase in the percentage yield of bio-coke in the range of 74.8–77.8% was noted. The method of charging the coking blend had no significant impact on the yield value, but due to the higher density of stamped batches, it would result in a higher unit production per chamber. However, since the increase in bio-coke yield is much lower than the decrease in bulk density caused by the addition of charcoal, the final unit production from one chamber will be lower than in the case of classic coke production— the more charcoal is used in the blend, the lower the mass yield from one chamber. Obviously, the increase in the percentage yield of bio-coke is due to the addition of charcoal with a much lower content of volatile matter than the coal mixture (charcoal VM^{ad} = 11.40%; coking blend VM^{ad} = 28.73), which, after degassing at the final temperature, leaves more solid residue than results from the mathematical calculation.

3.2. Bio-Coke Porous Structure

This part of the research aimed to determine the influence of charcoal addition on the coke structure and texture parameters affecting its quality parameters. According to the literature reports, the volume and surface area of micropores correlate with the reactivity of carbon materials [18,48]. Some dependencies between coke reactivity and BET surface area were also noted [49,50]. The character of the porous structure, including the pores morphology, total volume, and size distribution has a significant influence on the reactivity and strength of the coke [51,52]. In general, the coke strength tends to be decreased with an increase in the total pore volume [53] while reactivity tends to be increased when the total pore volume and average pore size are higher [52]. The degree of development of the texture of carbon materials is the way in which the basic structural units (BSU) are rearranged, creating larger spatially ordered objects called LMO (Local Mollecular Orientation) or MOD (Molecular Oriented domains). The thermal energy supplied to the pyrolysis process breaks the bonds between them, which enables their rearrangement and the creation of larger areas with a local orientation. These objects can vary in size from a few nanometers to several micrometers or larger. Objects measuring approximately 0.3–1 µm and above can be identified using optical microscopy. The degree of texture ordering can be evaluated through qualitative and quantitative analyses of the optical textures, as well as by assessing the reflectance of the coke matrix [54–57]. The degree of optical anisotropy corresponds well with reactivity (CRI) and post-reaction strength (CSR). It is generally recognized that a higher degree of anisotropy is associated with lower reactivity and higher post-reaction strength. Based on the analysis of optical textures, appropriate indicators can be determined to make the interpretation of results clearer, e.g., OTI (optical texture index), Wx (fibrosity index), or CMSI (Coke Mosaic Size Index) [54–58].

To assess the micropore volume and surface area, CO_2 sorption method was used. The range of estimated volume and surface area of the micropores was 6.2–49.4 $\times$ 10^{-4} cm^3/g and 14.4–106.1 m^2/g, respectively. It is clearly visible that the addition of charcoal caused a significant increase in the volume of micropores in bio-coke, which is associated with the increase in their summary surface area (Figure 3). There were no significant differences between the method of loading the retort both for the gravity and stamp charging system and for the specific content of charcoal; values within the expanded uncertainty. However, it should be noted that the increase in the value of both parameters is tremendous. Already for the 10% of the charcoal addition, the values of determined parameters were more than twice as large, while for 20% of the value they were five times higher. An even higher increase in specific surface area was noted in work [59] where a 20% addition of yellow poplar caused more than 13 times increase (bio-coke produced in 700 °C). This indicates a very developed charcoal microporosity concerning the microporosity of a coke substance derived from the resolidified coal plastic mass. An increase in surface area measured with N_2 and CO_2 was also observed by Flores et al. [24]. In the case of CO_2, the values obtained were several times lower than in the case of our study. Kieush et al. [29] also observed some increase in BET surface (measured by N_2 sorption) with the addition of 5% wood pellets. The differences in the obtained surface area results most likely stemmed from the use of a different type of charcoals and a different type of coal mixture, whose properties and behavior during the pyrolysis process determine the unique nature of the microstructure of coke or bio-coke. As a rule, the charcoal's surface area and micropore volume is much larger than other reductants of fossil origin, including coke [24,60,61]. In addition, the structure of the micropores could be additionally developed (increased) during the co-pyrolysis process because the final temperature of the production of the classic charcoal (used in our study) is within 500–550 °C, while during the co-pyrolysis process, the final temperature of the bio-coke production was 950 °C. The literature reports indicate that with the increase in the final temperature of pyrolysis, the surface area of the chars produced also increases [62], which suggests that the charcoal used, which initially had a much higher surface area, developed it even further during the pyrolysis process. The increased micropore surface increases the accessibility of the bio-coke matrix for CO_2 molecules during the gasification reaction (Boudouard reaction), which may suggest that bio-cokes produced will be characterized by increased reactivity compared to coke produced from the reference blend. Generally, the results in the form of surface area growth along with the addition of biomass substances follows the literature reports [26,61].

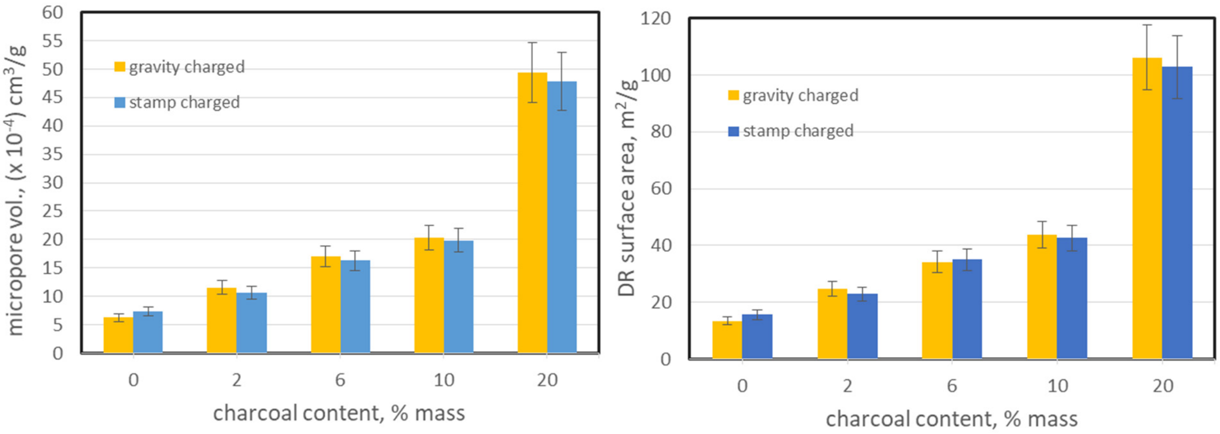

Figure 3. Influence of charcoal addition on micropore volume and surface area of bio-cokes.

Figure 4 shows the influence of the addition of charcoal on the real and apparent density of particles of the bio-coke produced. In general, the range of determined true densities was in a relatively narrow range from 1.811 to 1.839 g/cm^3. For bio-coke produced from feedstocks with a higher density (stamp charged), a slightly higher real density was observed for the share of 2, 6 and 10% charcoal addition, but despite the fact that the differences go beyond the uncertainty range, they are very small and should not be of great importance from the technological point of view. Theoretically, taking into account the values of real densities for coal and charcoal (Table 1), it would be expected that the addition of charcoal should increase the real density of bio-coke due to the fact that it is characterized by a noticeably higher real density than the coal blend. However, it must be taken into account that the coal structure during the pyrolysis process from the ambient temperature to the temperature of about 950 °C undergoes a strong transformation (polymerization, condensation, and cyclization reactions), which means that the true density of the carbon matrix also increases, as evidenced by the values of the true density of cokes with no added charcoal. These values are significantly higher than the value obtained for the raw coal blend. Obviously, the real density of charcoal introduced into the coal blend is also increased because of temperature, which is confirmed by the literature reports [63]. However, despite the undoubted increase in the real density of both raw materials (during the pyrolysis process), the final real density of bio-coke is at a similar level for all produced bio-cokes (regardless of the charcoal content), it means that the post-pyrolytic residues of both raw materials, together forming a conglomerate bio-coke, have a similar real density.

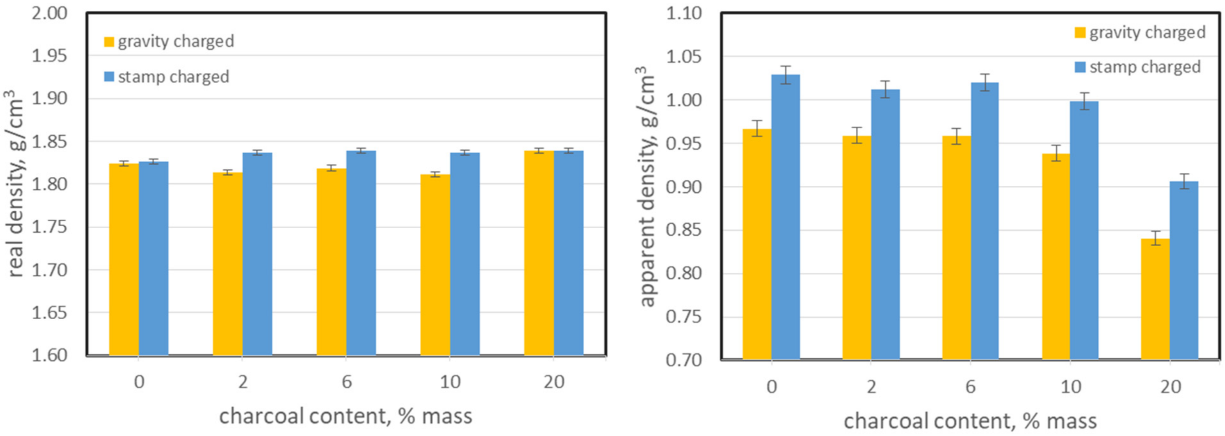

Figure 4. Influence of charcoal addition on real and apparent density of bio-cokes.

An interesting thing was observed in the case of the effect of charcoal addition on the total pore volume and total porosity of the obtained bio-cokes. Considering the significantly higher total pore volume of charcoal (1.510 cm^3/g—Table 1) in relation to the total pore volume of coke produced from the coal blend without the charcoal addition (0.425–0.486 cm^3/g—data in Figure 5) and significantly higher porosity (69.4% for charcoal; 44–47% for pure coke), it was expected that the addition of charcoal with a much higher total pore volume and porosity would cause a significant increase in both parameters. Meanwhile, although a slight trend can be seen, the increase in both parameters is relatively small in up to 10% of the supplement. Only for the content level of 20% can a big difference be observed. Considering the significantly lower apparent density of charcoal (0.460 g/cm^3—Table 1) compared to the density of coke produced from the charge mixture without the addition (0.96–1.04 g/cm^3—data in Figure 6) and significantly higher porosity (69.4% for charcoal; 44–47% for pure coke), it was expected that the addition of charcoal would cause a significant increase in both parameters. Obviously, one should also take into account a certain increase in porosity and thus total pore volume along with an increase of carbonization temperature. According to the literature reports, an increase in the carbonization temperature causes an increase in the porosity of charcoal [64,65]. The aforementioned increase in the porosity of charcoal should increase the effect of increasing the porosity of bio-coke with the addition of charcoal. However, in up to a 10% addition of charcoal, an increase in porosity of only about 1.2–2 percentage points was observed. A greater increase in porosity should also be caused by a decrease in the bulk density of the charges (in particular for gravity charging charges) because as it is known, the decrease in the bulk density of the coking charge is associated with an increase in the porosity of the coke produced [34]. In the case of our research, such a small change in porosity observed in up to 10% of the charcoal content is caused by the penetration of the plastic mass coming from the coal part, the charcoal porous structure. This is very visible in the optical microscope images in polarized, reflected light (Figure 6). The plastic mass during the coal's transition through the plastic state in a specific temperature range (approx. 350–500 °C) flows inside the charcoal structure, thus impregnating some of the pores, which consequently causes their closure (Figure 6). In Figure 6, it can also be observed that some charcoal particles are more (Pictures no. 3, 4, 6) and some less impregnated (Pictures no. 1, 2, 4) by the surrounding, penetrating, and consequently solidified plastic mass. This is most likely due to several factors such as the size of the particles, the morphology of their pores, their arrangement in relation to the moving plastic mass, as well as the rheological properties (fluidity) of the plastic mass itself.

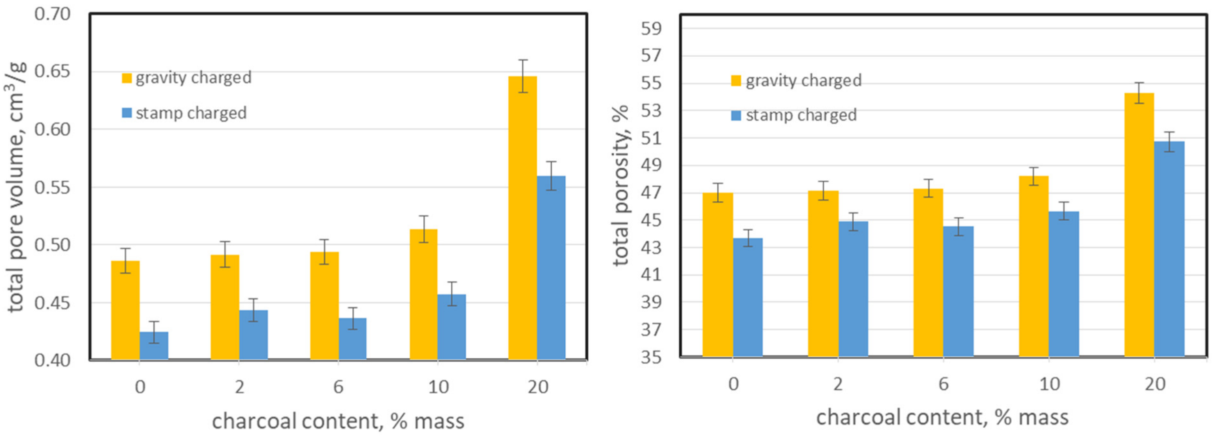

Figure 5. Influence of charcoal addition on total pore volume and total porosity of bio-cokes.

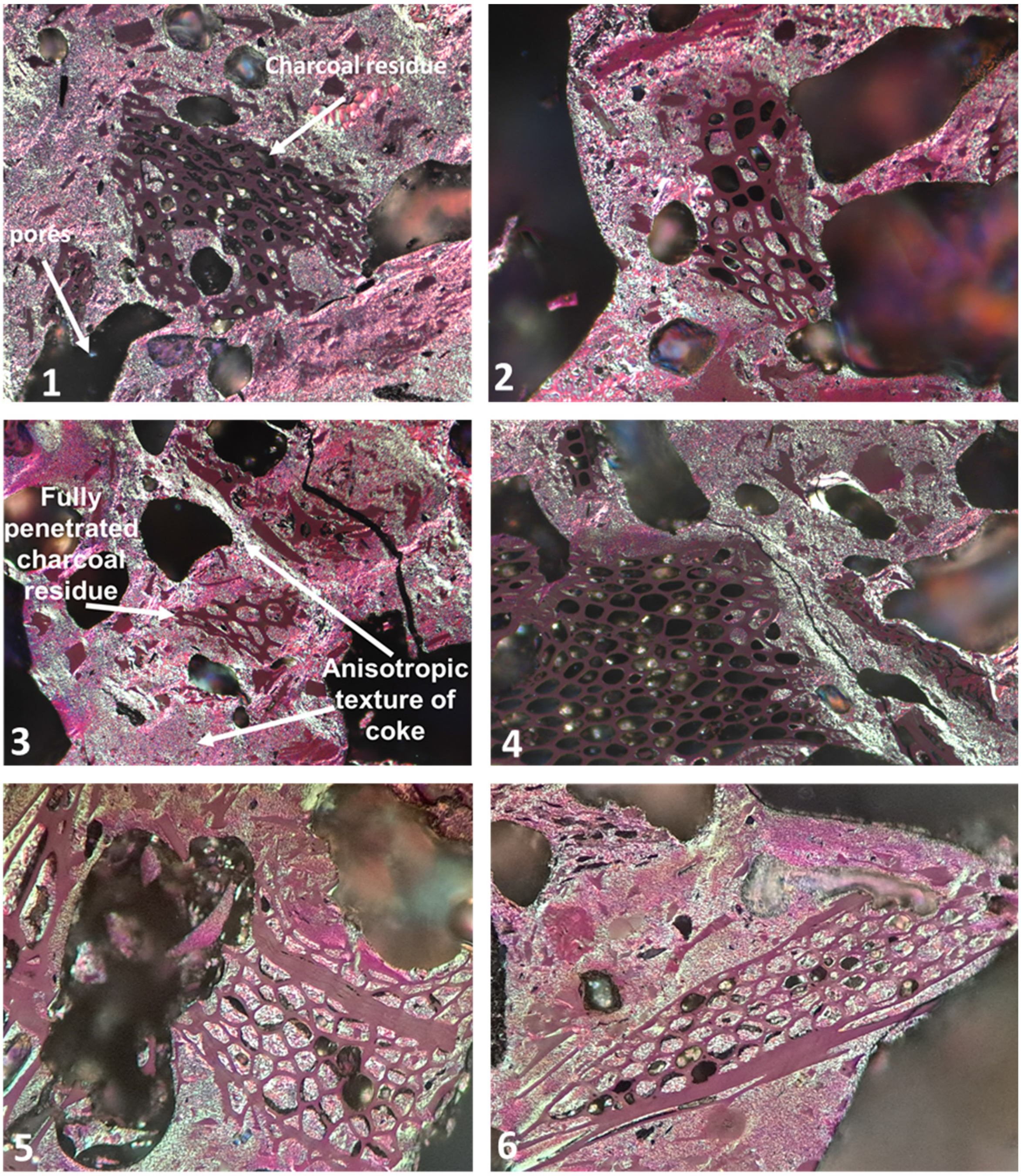

Figure 6. Photomicrographs (magnification × 500) of produced bio-cokes.

According to the literature reports, a decrease in the rheological properties of the coking blends is observed with an increase in the amount of added substance of biomass origin. Even a small addition of this type of substance significantly reduces fluidity so that the penetration ability may be limited. For the case study, the effect of the addition of various biomass substances on the coke-making properties of blends, including Gieseler fluidity, was also investigated. The results were published in the paper of Rejdak et al. [14]. In the case of the addition of 10 and 20% charcoal, the maximum fluidity decreased from 699 ddpm to the level of 208 ddpm and 30 ddpm, respectively. While the level of 200 ddpm can be considered as a satisfactory result, the level of 30 ddpm is a very low result, meaning that the fluidity of the blend is very low. In fact, in the case of bio-coke made from a blend of 20% charcoal, a much lower degree of charcoal residues with impregnated pores was observed. In addition to the undoubtedly limited fluidity, the smaller amount of penetrated charcoal residue pores also result from greater content of charcoal (and thus the number of pores to be penetrated)—a lower ratio of plastic mass to inert. For this reason, the insufficient amount of plastic mass caused a significant part of the pores of the charcoal residue to remain empty, which contributed to a significant increase in the total porosity and total pore volume of the obtained bio-coke. In general, the observed trend of increasing the total porosity with the addition of charcoal is consistent with the literature reports for the addition of raw biomass—the increase in porosity was observed in the work of Kieush et al. [29] and Montiano et al. [15].

3.3. Bio-Coke Optical Texture

The degree of arrangement of the texture of carbon materials, including coke or bio-coke, is an extremely important factor affecting its properties. The unique feature of coking coals, which is the ability to go into a plastic state, allows the reorganization and ordering of the molecular carbon structure. Its final degree of organization depends on many factors, including, above all, the degree of coalification of coal/coal coking blend, petrological composition, and rheological properties, in particular fluidity. A certain role is also played by the coking process conditions, such as time and temperature as well as charge density. The composition and distribution of minerals play a minor role, although their local influence is observed, e.g., a less ordered texture around pyrite or clay inclusions. When the coke microtexture consists of larger objects (texture types), a greater number of carbon atoms are contained within them, making access for CO_2 molecules more challenging. This type of texture is associated with lower reactivity (CRI) and higher strength (CSR). In contrast, if the texture is formed from smaller domains, most carbon atoms are situated at their edges, enhancing accessibility to carbon dioxide, thereby increasing their reactivity [66].

As mentioned, the degree of ordering of the coke texture is one of the factors determining its technological properties. Unlike coking coal, materials of biomass origin, including thermally processed biomass, do not have thermoplastic properties, therefore they are an inert material during the co-pyrolysis process. Therefore, this type of material is a precursor of low-ordered isotropic textures, which are characterized by higher reactivity towards CO_2. In addition, due to the fact that the introduction of biomass substances also deteriorates the fluidity of the blend, it potentially contributes to the deterioration of the conditions for ordering the texture. Bio-coke microtexture analysis has not been the subject of many analyses so far. A reduction in the degree of semi-coke texture ordering with the addition of charcoal (up to 15%) was also observed by Guererro et al. [67], while McPhee et al. [11] did not report any major differences in the degree of texture ordering (charcoal addition up to 10%). In the work [15], Montiano et al. found that the addition of 5% sawdust from chestnut and pine causes a decrease in the content of the anisotropic component and an increase in the isotropic component while increasing the amount of organic inerts. However, in the work of Flores et al. [24], the addition of charcoal (up to 8%) did not significantly affect the share of individual types of textures of the binder phase, while an increase in coarse organic inerts was noted. As can be seen, the type and magnitude of the effect of the additive depends on several factors, most likely including the physical and chemical properties of coals, coal blends and charcoal, including its amount and morphological features.

Figure 7 shows the influence of charcoal content on the types of optical textures occurring in bio-coke for gravity charging (left) and stamp-charging bio-cokes (right). Obviously, the addition of charcoal caused an increase in organic inerts, because generally this type of addition behaves inertly during the transition of carbon to the plastic state and in the microscopic image it constitutes an organic inert clearly distinguishable from other textures. Moreover, a decrease in circular textures was also observed. In the case of bio-cokes from the gravity charging system, there are slightly more circular textures than from stamp charging bio-cokes. The content of other types of textures does not show any clear trends.

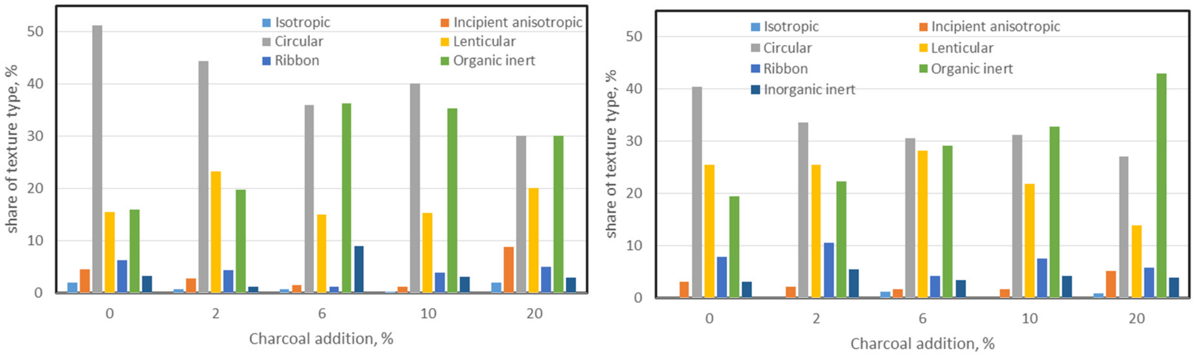

Figure 7. Optical textures of produced bio-cokes.

To illustrate the impact of the addition of charcoal on the conditions of texture formation, the CMSI (Coke Mosaic Size Index) was used to describe the coke texture using one indicator, which greatly facilitates the interpretation of the results (Figure 8). However, it should be remembered that the use of this indicator applies only to the so-called binder phase, i.e., coke textures formed from plasticizing macerals of coking coal. On the other hand, it allows us to assess how the significantly reduced fluidity of the coking blend (due to the addition of charcoal [14]) influenced the final degree of ordering of the bio-coke matrix. Interestingly, the addition of charcoal did not significantly affect the CMSI value, which allows us to assume that in the examined case, the reduction in the fluidity of the plastic mass as a result of the use of charcoal addition (F_{max} decreased from 699 ddpm to 30 ddpm for 20% addition [14]) did not significantly worsen the conditions for creating the bio-coke texture. The only thing that can be observed is slightly higher CMSI values for bio-cokes from the stamp-charged feeds, which confirms the positive effect of increased charge density (and higher pressure in the plastic layer) on the degree of texture order. This leads to the conclusion that the addition of charcoal may have primarily a physical effect. It reduces the fluidity of the sample mass as a mixture of coking coal and charcoal, but most likely the coking coal part itself may have sufficient high fluidity for the texture to become well organized. There may be some reduction in fluidity due to the sorption of the plastic mass components by the porous structure of the inert additive or increased friction forces on the stirrer from unplasticized charcoal particles, but the final fluidity is sufficient and, as previously mentioned, it does not significantly worsen the conditions for texture organization (up to 20% addition).

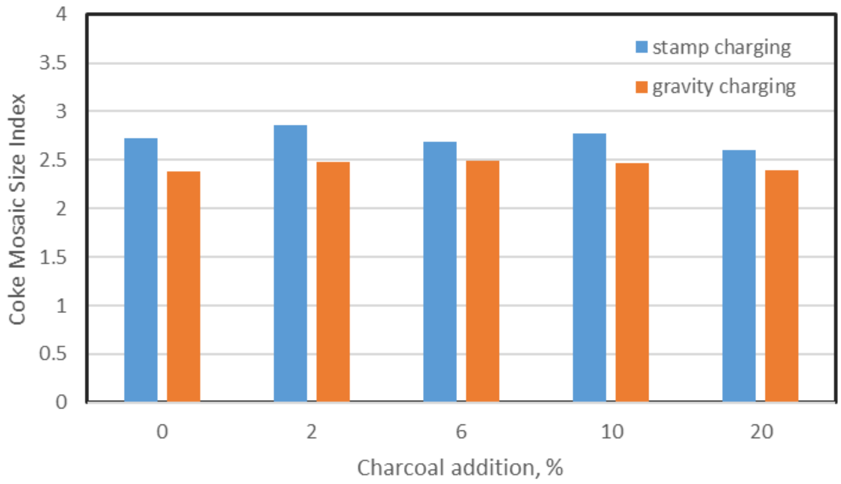

Figure 8. Influence of charcoal addition on CMSI of bio-cokes.

3.4. Technological Properties of Bio-Cokes: CRI, CSR, TS600, and AI600

As could be expected, the changes in structure and texture observed with the introduction of charcoal to the coking blend resulted in significant changes in the quality indicators of the produced bio-coke. Currently, the most widespread and most frequently used indicators for the technological assessment of coke are the NSC (Nippon Steel Corporation) indices, i.e., CRI (coke reactivity index), and CSR (coke strength after reaction). The value of the indices of this test reflects the susceptibility of coke to the gasification reaction with CO_2 carbon dioxide (Boudouard reaction: $CO_2 + C = 2CO$) at a high temperature of 1100 °C (CRI) and the impact of this reaction on the mechanical properties of coke (CSR). These indicators have been developed to assess the technological suitability of coke in a blast furnace. However, due to the fact that approximately 90% of the world's coke production is coke used in the blast furnace [68], they have become a standard for evaluating coke, regardless of its application, and are often a parameter shaping its price in commercial contracts. From the technological point of view, it is advantageous for coke to be characterized by possibly low reactivity (low CRI value) and high post-reaction strength (CSR). It is generally recognized that good quality coke has a CSR of min. 55–58% [69–71]. The required value increases as the working chamber volume of the blast furnace increases. As mentioned before, the working height of the modern blast furnace chamber reaches several dozen meters (c.a. 30 m), so the coke forming the bed (permeable support) must withstand the pressure of a column of materials several dozen meters high, hence the high requirements as to the value of the CSR parameter. As part of the currently conducted research, the produced bio-coke is to be used as a carbon reductant in the process of carbothermic reduction of manganese ores, which takes place in submerged electric arc furnaces. At present, the aforementioned process uses blast furnace coke fraction with a grain size of 5–25 (10–30) mm. The height of the working chamber of such a furnace is usually about 4–8 m, so we assume that coke with a lower CSR (and higher CRI) should also meet the technological requirements. However, it is necessary to verify this at least on a pilot scale and then on an industrial scale.

The results of the impact of charcoal addition on the value of CRI and CSR indices are presented in Figure 9. It is clearly visible that the addition of charcoal significantly affects the value of both parameters. For the charge in the case of CRI, it was observed the increase in value from 34.6 (pure coke without additive) to 58.1% for 20% charcoal addition. We can observe that the use of a higher charge density (stamp charged) did not significantly affect the value of the achieved parameters. For 20% of the additive, the CRI increased from 33.0 to 58.4%. The observed trends, both for CRI and CSR, are consistent with the literature reports. An increase in reactivity (according to CRI or other methods) and decrease in CSR with the addition of charcoal was observed in works [11,15–17,20,26,32]. In the paper of Solar et al. [12], no significant changes in reactivity were noted, but the share of charcoal in the charge mixture intended to produce bio-coke was only 2% and the alkalinity index of the added charcoal was lower than those of coking blend. Similar trends were also observed when adding raw biomass—not thermally processed [19,28,29,31]. Higher values of the bio-coke reactivity index may be caused by several factors. First, as previously mentioned, the texture of the coke produced from the coals is ordered during the plastic state to form highly ordered textures that are low in reactivity. In the case of the addition of charcoal, we are dealing with the introduction of a carbon material with an isotropic texture of a low level of ordering. This was confirmed by assessing the optical textures in the produced bio-cokes (Figure 7), where an increase in the content of organic inerts was found. The increase in organic inerts was simultaneously accompanied by a decrease in anisotropic textures (less reactive), which also contributed to the increase in the reactivity of bio-coke. The isotropic textures, including organic inerts, are much more reactive, so an increase in their share results in a gradual increase in the reactivity of the composite bio-coke. Moreover, changes in structural parameters, including total porosity and micropore surface, also contributed to the increase in reactivity. The significantly higher micropore surface area observed with the increase in the amount of charcoal added (Figure 3) results in a much larger contact surface available for CO_2 molecules, which intensifies the gasification reaction. The aforementioned increase in total porosity and total pore volume also contributes to the increase in reactivity. Greater pore volume and porosity also mean more paths for CO_2 molecules to penetrate the bio-coke structure consecutively. In addition to the aforementioned factors, an additional factor increasing the reactivity could be the increase in the content of alkaline compounds of the mineral substance, which is confirmed by the chemical composition of the ash and the increase in the value of the AI (Table 1). It is a well-known and proven fact that alkaline components act catalytically in Boudouard reactions [70,72,73]. In the case studied, we can observe that the introduced charcoal contained significant amounts of calcium and potassium. The influence of increased alkali content on the reactivity of bio-coke was also suggested by [11,15,16,26].

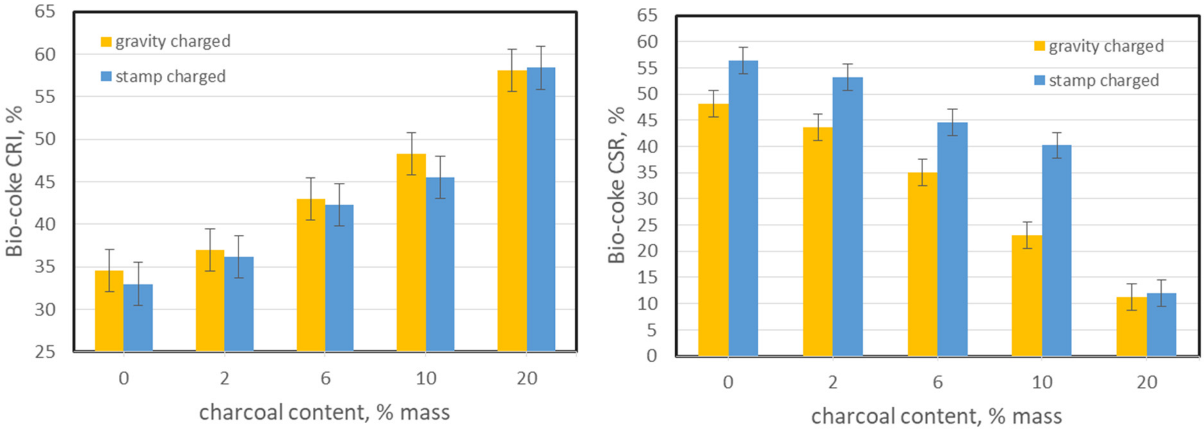

Figure 9. Influence of charcoal addition on CRI and CSR of bio-cokes.

The influence of the addition of charcoal on the CSR value is also more complex. On the one hand, it results from the use of a material with much lower structural strength (brittleness) in the bio-coke structure, on the other hand, it is the result of degradation of the bio-coke structure during the CRI test. In fact, after the CRI test, it is to be expected that there is practically no charcoal residue left in the bio-coke structure. Since charcoal residues are more susceptible to gasification and their gasification takes place preferentially in relation to the structure of bio-coke derived from coal, they leave empty spaces behind, which further intensifies the structural weakening of bio-coke, resulting in a significant decrease in the CSR value. In general, the decrease in CSR along with the increase in CRI is obvious because the bio-coke structure weakened by CO_2 (structural destruction) is more susceptible to mechanical impacts occurring during the CSR test, which in turn causes a significant decrease in the value of the aforementioned indicator.

The relations between CRI and CSR presented in Figure 10 are also consistent with the literature [74], but in the described case, it can be clearly observed that for stamp-charged bio-cokes, the CSR values are slightly higher than for gravity-charged, for a constant CRI value (except for 20% charcoal content, where they are practically the same). Higher CSR values for stamp-charged bio-cokes may result from their lower porosity (Figure 5), making them less susceptible to mechanical impacts. The behavior of the sample of 20% charcoal content is not entirely clear where, despite the lower porosity, CSR improvement with increased charge density was not noted. The effect of increased CSR strength for the same CRI value results from the higher density of the charge, which contributed to the reduction in the total porosity of the bio-coke. As it is known, lower total porosity is associated with higher mechanical strength [34,51–53]. The increase in the density of the coal charge, apart from the decrease in porosity itself, also causes an increase in the thickness of the pore walls, which also has a positive effect on the mechanical strength. Such a phenomenon was noted in the works of [75,76]. The mentioned parameters also affect the values of TS600 and AI600 (Figure 11). In the case of bio-cokes from the feedstock, a decrease in the tumbling strength TS600 value and an increase in the abrasivity index AI600 were observed. The values of these parameters are more favorable for bio-cokes made from rammed feedstocks, thanks to their higher density and lower total porosity.

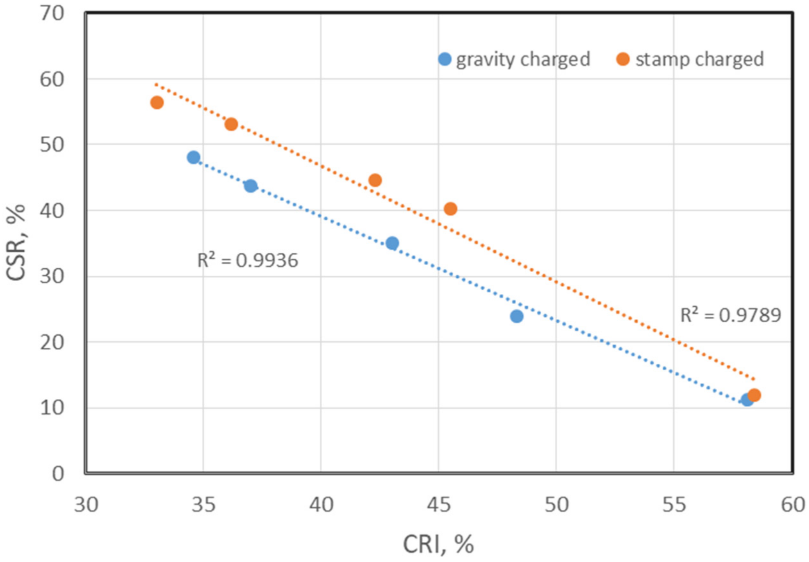

Figure 10. Relation of CSR and CRI values of bio-cokes.

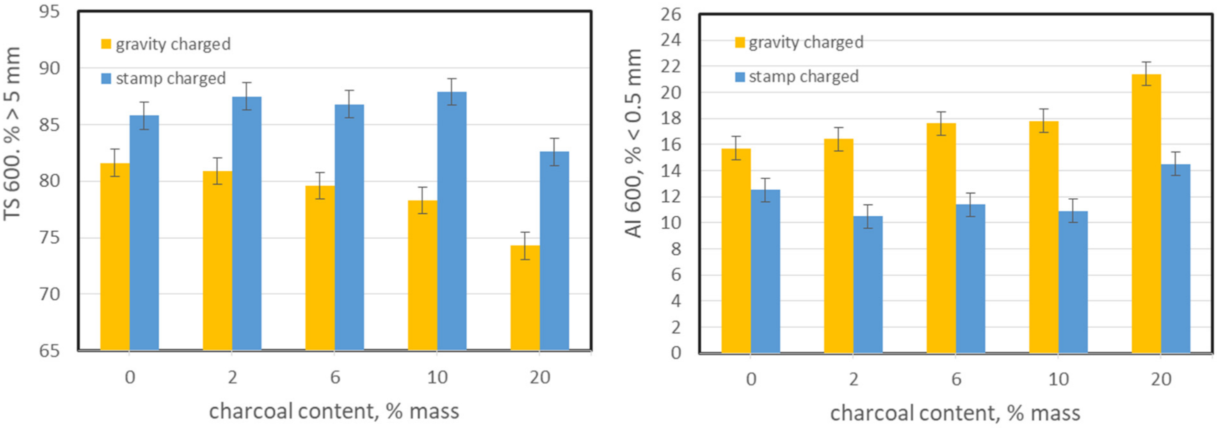

Figure 11. Influence of charcoal addition on tumbling strength TS600 and abrasivity index AI600 values of bio-cokes.

However, the decrease is not as drastic as in the case of CSR. TS600 dropped from 81.6% to 74.3% in the case of the gravity-charging system, while for a stamp-charging system to a content of 10%, the TS600 values are even higher than for the blend without the addition of charcoal. Only for 20% content there was a slight decrease from 85.8% to 82.6%. Obviously, for bio-cokes made from stamped charges, the values are noticeably higher than for gravity-charged ones. In the case of rammed batches, the higher resistance to tumbling may result from the fact, that with the addition of charcoal, a substance with a much lower apparent density, the batches were stamped to maintain an assumed fixed density (which was actually achieved only for 2% of the content—see Figure 2). Therefore, with the increased charcoal content, the compacted charges, despite their lower density, were more compacted—especially the coking coal part. This resulted in an increase in its structural strength, which is reflected in the high TS600 values. Opposite trends were observed in the case of abrasivity index AI600. The noticed value and increase in bio-cokes from the gravity charging system was clearly higher than for bio-cokes from the stamp charging system. Based on the above information, it can be concluded that the obtained bio-cokes were characterized by relatively good cold mechanical properties.

In the case of using bio-cokes in submerged electric arc furnaces (SEAF) for the production of manganese ferroalloys, the important parameters are electrical resistivity and so-called slag-resistance, i.e., the reactivity of the material towards synthetic manganese ore. The produced bio-cokes were also tested to assess the aforementioned parameters, and the detailed results and description of the research procedures can be found in the publication [77]. The appropriate electrical resistivity is important from the point of view of the proper heat distribution in the furnace, in particular in the coke bed, where the direct reduction of manganese oxide MnO to metallic manganese on the surface of the carbon reductant takes place. On the other hand, the proper reactivity towards MnO is necessary for the effective course of the reduction process to metallic manganese. As it results from the data presented in the publication [77], in the temperature range of approx. 1500–1600 °C (temperatures prevailing in the coke bed in the SEAF), the electrical resistivity values of bio-cokes produced with the addition of up to 20% are at a relatively similar level. For the final measurement temperature of 1600 °C, they were in a rather narrow range of 6.4 to 8.3 mΩm, similar to that obtained for other carbon materials, including classic metallurgical coke [78]. In the case of tests of bio-coke reactivity towards synthetic manganese ore (slag-reactivity) it was observed that the more bio-additive in the structure of bio-coke, the higher the reactivity expressed in %MnO/min with a simultaneous greater fluctuation of values when repeating the test [78]. For coke without any additive, values of 0.8 to 1.9 (%Mn/min) were obtained, while for bio-cokes produced with the addition of charcoal up to 20%, the values were in the range of 0.9–5.1 (%MnO/min). The fluctuations can result from the fact that, in contrast to classic metallurgical coke, bio-coke is not so structurally homogeneous (inclusions of charcoal particles) and encountering (by MnO particles) particles of bio-component incorporated into the bio-coke matrix causes a significant increase in the reaction rate. This also indicates a greater reactivity of bio-coke elements originating from the added charcoal in relation to the part of the matrix originating from coking coal. Nevertheless, higher reactivity values towards MnO obtained for bio-coke should be considered as technologically beneficial; however, this requires verification in tests on a larger scale.

4. Conclusions

This study aimed to assess the influence of biochar (charcoal) addition on the structural, textural, and technological properties of bio-cokes produced. Based on the research carried out, the following conclusions can be drawn:

- The addition of biochar in amounts up to 20% (wt.%) caused a decrease in the bulk density of the coking charge.
- With the addition of biochar, a decrease in apparent density and an increase in the total porosity were noted.
- An increase in the volume and surface area of micropores was observed.
- Changes in the optical anisotropy of bio-cokes were observed, expressed by an increase in organic inerts and a decrease in circular textures. No significant changes in the CMSI (Coke Mosaic Size Index) values were observed.
- A significant increase in the CRI and a decrease in the CSR of bio-cokes produced with the addition of biochar were observed. Slightly more favorable parameters were obtained in the case of stamp-charged blends.
- In the case of tumbling strength (TS 600), the changes were less severe than for CRI and CSR—a decrease in several percentage points was noted. The use of stamped charges had a positive effect on the values of TS 600.
- In the case of the abrasivity index AI 600, a clear upward trend was noted only for bio-cokes produced by the gravity charged method. For stamp-charged bio-cokes, the AI600 values did not show clear trends, although an increase in these values should be expected—the effect of increased charge density compensated the effect of adding a more brittle substance.
- Relatively favorable properties of bio-coke from the point of view of producing ferroalloys in SEAF (i.e., appropriate electrical resistivity and higher reactivity towards MnO

than classical coke), with the possibility of regulating the final quality parameters of bio-coke (through the amount of biochar used) bode well for potential industrial application. Both the production and application of bio-coke require verification on a pilot scale and then on an industrial scale.

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Appendix A

Table A1. Proximate and ultimate analysis of bio-cokes.

Chargé Type (Gr—Gravity; St—Stamp)	**Gr**	**St**	**Gr**	**St**	**Gr**	**St**	**Gr**	**St**	**Gr**	**St**
Charcoal share, %	0	0	2	2	6	6	10	10	20	20
Moisture content, M^{ad},%	0.8	0.7	0.6	0.5	0.5	0.6	0.7	0.5	0.7	0.7
Ash yield, A^{ad}, %	11.7	11.5	11.3	11.4	11.1	11.2	10.9	10.7	9.3	9.7
Volatile matter, VM^{ad}, %	0.32	0.51	0.54	0.38	0.57	0.49	0.57	0.52	0.43	0.5
Fixed carbon, %	87.2	87.3	87.6	87.7	87.8	87.7	87.8	88.3	89.6	89.1
Carbon content, C^{ad}, %	85.0	85.2	85.4	85.2	85.7	85.8	85.3	86.4	87.6	87.4
Hydrogen content, H^{ad}, %	0.24	0.25	0.28	0.27	0.28	0.28	0.26	0.28	0.33	0.34
Nitrogen content, N^{ad}, %	1.11	1.03	1.09	1.01	1.07	0.98	0.99	0.96	0.97	0.95
Oxygen content, O^{ad}, %	0.74	0.90	0.92	1.19	0.94	0.73	1.44	0.75	0.72	0.53
Total sulfur content, $S_T{}^{ad}$, %	0.40	0.41	0.40	0.39	0.39	0.38	0.39	0.37	0.37	0.37

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