

## Article

# Types and Composition of Biomass in Biocoke Synthesis with the Coal Blending Method

Erlina Yustanti <sup>1,2,\*</sup> , Endarto Yudo Wardhono <sup>3</sup>, Anggoro Tri Mursito <sup>4</sup> and Ali Alhamidi <sup>1</sup>

<sup>1</sup> Department of Metallurgical Engineering, Faculty of Engineering, Sultan Ageng Tirtayasa University, Jl. Jend. Sudirman KM. 03 Cilegon, Banten 42435, Indonesia; alhamidi@untirta.ac.id

<sup>2</sup> Centre of Excellence, Nanomaterial and Process Technology Laboratory, Faculty of Engineering, Sultan Ageng Tirtayasa University, Jl. Jend. Sudirman KM. 03 Cilegon, Banten 42435, Indonesia

<sup>3</sup> Department of Chemical Engineering, Faculty of Engineering, Sultan Ageng Tirtayasa University, Jl. Jend. Sudirman KM. 03 Cilegon, Banten 42435, Indonesia; endarto.wardhono@untirta.ac.id

<sup>4</sup> Research Center for Geotechnology, National Research and Innovation Agency (BRIN), Jl. Sangkuriang Kampus LIPI Bandung, Gd. 70, Bandung 40135, Indonesia; anggoro.tri.mursito@lipi.go.id

\* Correspondence: erlina.yustanti@untirta.ac.id; Tel.: +62-812-877-3791

**Abstract:** The steelmaking industry requires coke as a reducing agent, as an energy source, and for its ability to hold slag in a blast furnace. Coking coal as raw coke material is very limited. Studying the use of biomass as a mixture of coking coal in the synthesis of biocoke is necessary to reduce greenhouse gas coal emissions. This research focuses on biomass and heating temperature through the coal blending method to produce biocoke with optimal mechanical properties for the blast-furnace standard. The heating temperature of biomass to biochar was evaluated at 400, 500, and 600 °C. The blending of coking coal with biochar was in the compositions of 95:5, 85:15, and 75:25 wt.%. A compacting force of 20 MPa was employed to produce biocoke that was 50 mm in diameter and 27 mm thick using a hot cylinder dye. The green sample was heated at 1100 °C for 4 h, followed by quenching with a water medium, resulting in dense samples. Increasing heating temperature is generally directly proportional to an increase in fixed carbon and calorific value. Biocoke that meets several blast-furnace criteria is a coal mixture with coconut-shell charcoal of 85:15 wt.%. Carbonization at 500 °C, yielding fixed carbon, calorific value, and compressive strength, was achieved at 89.02 ± 0.11%; 29.681 ± 0.46 MJ/kg, and 6.53 ± 0.4 MPa, respectively. This product meets several criteria for blast-furnace applications, with CRI 29.8 and CSR 55.1.

**Keywords:** biomass; biocoke; coke; coal blending



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## 1. Introduction

Coal still plays a vital role in the increasing global energy demand. Even though it is a nonrenewable fuel, coal is the primary energy source for electricity generation and the principal heat supply in heavy industries. For example, in the metallurgical sector, the integrated iron and steel industry is one of the highest energy consumers, which generates a massive amount of CO<sub>2</sub> emissions due to its use of a considerable quantity of fossil-based carbon fuel, as either a reductant or fuel [1]. Energy saving and waste management are significant challenges facing this industry, because it is estimated that they are responsible for 26% of global industrial greenhouse gas emissions [2]. Concerning sustainability that meets climate targets and energy prices, iron and steel industries must improve their energy efficiency and promote environmentally friendly processes. Numerous strategies have been developed to replace unsustainable fossil fuels with renewable fuels [3]. Incorporating biocoke into coking coals is an excellent solution to both problems due to its renewability and carbon neutrality for net-zero CO<sub>2</sub> emissions.

Biocoke is a biofuel derived from carbonization biomass. It is organic matter that comes from living organisms such as plant residue and animal waste. Biomass is a porous

and fibrous material that consists of moisture, volatile matter, fixed carbon, ashes, and inorganic compounds such as Al, Si, K, Ca, and Na [4]. Biomass is a clean energy source that can partially substitute fossil fuels directly or be converted into gas, liquid, and solid fuels through different routes, namely, thermochemical and bioconversion. Combustion, gasification, and pyrolysis are techniques to extract energy from biomass through a thermochemical platform [5]. Pyrolysis is a process that converts biomass into biofuel by decomposing the organic content of materials into lighter substances under nonoxidative atmosphere conditions. A slow process of pyrolysis is called carbonization: the main products of carbonization are (a) biocoke, mainly composed of carbon; (b) tar, which contains water and oxygenated organic matter; and (c) gases that consist of carbon oxides, light hydrocarbons, and hydrogen. The yield of products depends on such operating conditions, including the type of biomass, temperature process, heating rate, and reactor design [6]. Carbonization products of biomass also strongly depend on the water content of the feed due to the large amount of water condensate formed in the tar.

As alternative energy, biocoke can be applied to large-scale industrial processes [7] because it has stable combustion at high temperatures [8]. Coke is the most crucial material fed in blast furnaces for iron production. This metallurgical coke acts as a primary energy source, reducing iron-ore agents and physical support.

Consequently, high-quality coke contributes to higher productivity and lower hot metal costs. The inclusion of biocoke in coking coals could reduce high-temperature gasification in iron production; thus, carbon consumption can be minimized [9]. According to Mousa et al., substituting about 20 wt.% of biomass in fuel consumption in a steelmaking blast furnace could reduce CO<sub>2</sub> emissions by 300 kg/tHM, representing 15% of the decrease in total greenhouse gas (GHG) emissions [2]. Simultaneously, adding biomass higher than 2 wt.% into coking coal deteriorates coke quality [1]. Furthermore, low density and weak mechanical strength cause a feeding problem in the feeding system. This induces health and safety risks during handling, storage, and transportation [10], whereas the presence of inorganic elements in ash increases char reactivity with CO<sub>2</sub> due to catalytic effects [11,12].

Briquetting under thermal compression is a method of improving the handling characteristics of coke production without a significant deterioration in quality. A fuel briquette is a compressed block typically consisting of coal dust used for fuel [13]. Briquettes from biomass are generally produced from a combustible material (coal, char, bagasse, agricultural waste, sawdust, etc.) and a binding agent. For industrial purposes, the most common materials used for binders are molasses, starch, coal tar, and wood tar [14,15]. A binding agent is necessary to improve the cohesion and bounding of the combustible materials to prevent the compressed material from crumbling. Compared to conventional coke, which has a value of 20–30 MJ/kg [16,17], the new, densified briquettes that were manufactured by Mizuno et al. under high thermal compression (20 MPa and 200 °C) exhibited better properties, such as higher density, improved mechanical strength, and high calorific value [18]. Yustanti et al. studied the maximal temperature of briquetting processes in order to generate maximal compressive strength. Biocoke briquettes with different compositions of rice husks and coconut shells with molasses as a binding agent were maintained at different temperatures under constant pressure of 20 MPa for 4 h. The charcoal of rice husks at 150 °C produced a compressive strength of about 2.09 MPa, whereas coconut shells were more suitable at 100 °C, with a compressive strength of 1.58 MPa [19]. The amount of biomass generally decreased the strength of coke and the swelling index. To improve mechanical properties, the feed size and binder type should be controlled. Mursito et al. obtained the best charcoal sizes from redwood and improved the coke-crushing strength of biocoke. Dry quenching helps to prevent the occurrence of cracks in the coke. Biocoke has a bulk density of 1071.44 kg/m<sup>3</sup> and generates an excellent compressive strength of 4.87 MPa with a fixed carbon content of 85.8% and a calorific value of 30.363 MJ/kg for a standard blast furnace [20]. However, this study did not characterize CSR and CRI.

Previous studies showed that the best mechanical endurance was achieved if 6 wt.% biomass was added to briquette production [21]. Calorific value, compressive strength,

fluidity, dilatation, and coke strength after the reaction generally decrease with the increase in the weight fraction of biochar added to the mixing process with coking coal. This study aimed to find the maximal value of the weight fraction of biochar added to coking coal, so that the mechanical and calorific properties of the produced biocoke met blast-furnace standards. This study analyzed the calorific value and compressive strength if the wt.% of biochar increased up to 25%, and how increased temperature and mixture composition affect biocoke properties. Shrinkage, binder types such as molasses, and surface morphology in biocoke are interesting to discuss regarding the prediction of compressive strength and heating value based on standard blast-furnace applications.

## 2. Materials and Methods

### 2.1. Materials

Raw materials for biocoke production were agricultural waste (coconut shells and rice husks) collected from the local market in Cilegon, Banten, Indonesia. The collected biomass was then dried in an oven at 110 °C for 5 h and coconut shells were crushed using a hammer to less than 1 × 1 cm in size; rice husks stayed their original size. Coking coals were obtained from Borneo, Indonesia, ground in a pulverizer mill, and sieved to <0.42 mm. The cone quartering method, used to determine the analyzed samples (biomass and coking coal), can be treated as representative [22,23]. Cone quartering is a type of sampling that uses a small and representative sample. This method is applicable for dry and moist materials of various sizes [23]. The particle size of the materials was kept constant for all the experiments. Commercial molasses were used as the binding agent, purchased from a sugar factory in Lampung, Indonesia, with their analysis shown in Table 1.

**Table 1.** Analysis of commercial molasses \*\*.

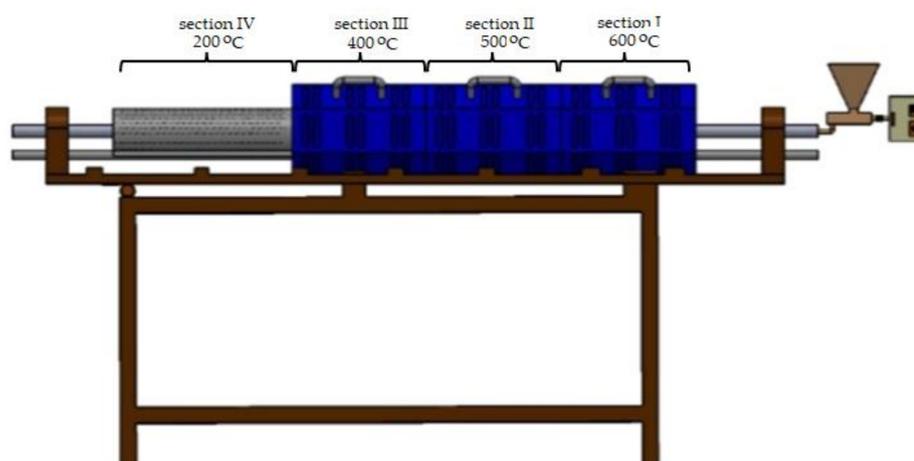
Parameter	Value
pH (25 °C)	7.91
Density, kg/m <sup>3</sup>	1221
Brix number, %	81.50
Polarization, %	48.86

\*\* Data given by the supplier.

### 2.2. Methods

#### 2.2.1. Biomass Carbonization

Biomass carbonization was conducted indirectly in a bench scale, with electrically heated rotary kiln pyrolysis in the axial and radial directions, and fabricated from a rolled mild steel plate, 5 mm thick, which was welded into a cylindrical form of 4 m length, 30 cm diameter, and 5° inclination angle. The main internal core reactor was designed with an ASTM 310 SS stainless-steel pipe with NQ size diameter for 0.7 L volume, and rotated by a controlled motor of Toshiba VF-S15 and sample hopper of a Danfoss VLT microdrive. The kiln was indirectly electrically heated by an AF Kanthal wire and Nikko 2 mL electrode, insulated by a Jarefu C-1 brick and Rockwool 96 fiber board, and controlled with a Fuji Electric controller, Mitsubishi S-T20 contactor, and regulated by Autonics TC4M, PXR-7 and PXR-9. The rotary kiln was supported with four heating-cooling zones: (1) heating at Zone 1, 600–400 °C; (2) 600–400 °C at Zone 2; (3) cooling at Zones 3 and 4, 300 and 200 °C, respectively, in which thermocouples carry out temperature control. The design of the indirectly electrically heated rotary kiln is shown in Figure 1. We set up our own pyrolysis reactor as per the design shown in Figure 1.



**Figure 1.** Rotary kiln for pyrolysis process.

The proximate and ultimate analyses of the used feed biomass are shown in Table 2. Experiments were carried out at three different temperatures, 400, 500, and 600 °C, under a rotation speed of 20 rpm. The ground feed was subjected to the cylinder kiln through a feed hopper at a rate of 1.2 kg/h for carbonization at 400–600 °C. As the kiln rotates, material gradually moves down towards the discharge end and may produce a certain amount of tar non-condensable gases. Carbonization ran for 2 or 4 h at each operational temperature, depending on the intake quantity for each process. Biomass carbonization with 3 kg of feed produced around 1 kg of biochar with a yield of around 35% to 40%, depending on biomass type. Biochar size was reduced with a mini jaw crusher and sieved to <6.35 mm using sieve 4 (in mesh). Operational time was selected on the basis of a preliminary study conducted by the authors.

**Table 2.** Proximate and ultimate analyses of raw materials.

Parameter	Raw Materials		
	Coconut Shells	Rice Husk	Coking Coal
Proximate (db)			
Equil. moisture (ar), %	8.35 ± 0.79	9.54 ± 0.50	1.23 ± 0.20
Volatile matter, %	69.47 ± 2.54	63.75 ± 1.75	30.02 ± 1.16
Ash, %	12.48 ± 0.92	22.16 ± 0.84	2.28 ± 0.29
Fixed carbon, %	18.05 ± 0.96	14.09 ± 0.56	67.70 ± 1.10
Gross calorific, MJ/kg	19.05 ± 0.31	12.89 ± 0.26	33.75 ± 0.99
Eff. calorific, MJ/kg	18.87 ± 0.27	12.69 ± 0.36	-
Ultimate (db)			
Carbon, %	53.01 ± 0.24	41.18 ± 0.37	81.07 ± 0.5
Hydrogen, %	6.25 ± 0.31	5.56 ± 0.38	5.10 ± 0.26
Oxygen, %	28.23 ± 0.32	31.08 ± 0.31	9.11 ± 0.33
Nitrogen, %	**	**	1.75 ± 0.08
Sulfur	0.03 ± 0.01	0.02 ± 0.01	0.69 ± 0.1

db = dry basis; ar = as received; (\*\*) undetected.

### 2.2.2. Coal Blending

Biocoke briquetting used a cylinder die with diameter and height of 5 and 5 cm, respectively. Coking coal, biochar, and molasses with variable composition were compressed in a laboratory hydraulic press, in a lighter procedure than described by previous authors [24], under 20 MPa pressure, 100 °C temperature, and 5 min holding time to conform briquettes of different compositions. On the basis of previous research, pressure of 20 MPa was confirmed for hot briquetting with a binder [25]. Blending samples after the compacting

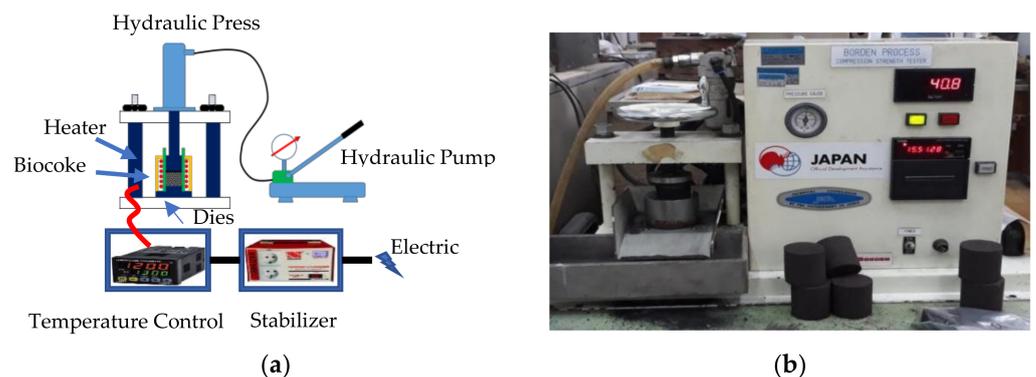
process were 54–56 g in weight with diameter and height dimensions of 5 and 2.5–2.7 cm, respectively. The briquette feed composition is given in Table 3. Briquettes were then hardened by heat treatment at 1100 °C for 4 h and quenched in water to increase their compressive strength. Quenching with water was performed by spraying water onto the red biocoke surface for 5 s [20].

**Table 3.** Proximate and ultimate analyses of biochar.

Parameter	Biochar					
	Rice Husks (°C)			Coconut Shells (°C)		
	400	500	600	400	500	600
Proximate (db)						
Eq. moisture (ar), %	7.71 ± 0.86	7.39 ± 0.84	7.12 ± 0.85	5.57 ± 0.81	5.6 ± 0.73	5.54 ± 0.66
Volatile matter, %	16.48 ± 0.45	15.31 ± 0.37	13.5 ± 0.33	39.08 ± 1.9	34.09 ± 1.5	28.37 ± 1.2
Ash, %	45.23 ± 1.81	45.43 ± 1.89	46.24 ± 1.4	1.19 ± 0.20	1.42 ± 0.18	1.69 ± 0.18
Fixed carbon, %	38.29 ± 1.26	39.26 ± 1.27	40.26 ± 1.2	59.73 ± 2.9	64.49 ± 2.1	69.94 ± 2.0
Gross calorific, MJ/kg	8.81 ± 0.34	12.27 ± 0.53	12.56 ± 0.2	27.68 ± 0.9	28.45 ± 0.8	29.79 ± 0.4
Eff. calorific, MJ/kg	12.17 ± 0.5	12.23 ± 0.4	12.53 ± 0.4	27.54 ± 0.9	28.33 ± 0.8	29.72 ± 0.3
Ultimate (db)						
Carbon, %	32.44 ± 0.28	34.24 ± 0.26	39.71 ± 0.3	76.98 ± 0.9	80.91 ± 0.3	83.98 ± 0.3
Hydrogen, %	2.48 ± 0.37	1.93 ± 0.29	1.58 ± 0.23	4.35 ± 0.3	4.04 ± 0.29	3.66 ± 0.28
Oxygen, %	19.28 ± 1.4	17.91 ± 1.57	12.01 ± 0.9	17.22 ± 1.5	13.42 ± 0.8	10.41 ± 0.8
Nitrogen, %	0.54 ± 0.07	0.47 ± 0.07	0.45 ± 0.06	0.24 ± 0.0	0.2 ± 0.02	0.25 ± 0.03
Sulfur, %	0.03 ± 0.01	0.02 ± 0.01	0.01 ± 0.01	0.02 ± 0.01	0.01 ± 0.01	0.01 ± 0.01

db = dry basis; ar = as received.

The schematic of the briquetting process is depicted in Figure 2. The coke compressive strength (CCS) was characterized according to the AFS 5202-09-S standard by using a Borden process compression strength tester Gun III-Borden (Koei Co. Ltd.). For accurate measurements to warrant the same condition in coke compressive strength testing, the briquette process was carried out at room temperature with a relative humidity (RH) of 70% to 75%. Furthermore, factors that affect compressive strength with ANOVA are discussed.



**Figure 2.** Coal blending process: (a) hot briquette process scheme; (b) compression strength machine.

### 2.3. Characterization

#### 2.3.1. Proximate and Ultimate Analysis

Proximate analysis was carried out on an LECO TGA 701 to determine moisture content, volatile matter, ash content, and fixed carbon according to American Standard Testing and Material methods, ASTM D3172-98; ASTM D5865 analyzed the heating value (gross calorific and effective calorific). Ultimate analysis for element components present in the samples, such as carbon (C), hydrogen (H), oxygen (O), and nitrogen (N), was conducted on ASTM D5373 using GCMS Shimadzu QP 500, and sulfur content by ASTM D2492. We used sigma-uncertainty analysis (standard error for finite population). We used an average value from three repetitions of every characterization method.

### 2.3.2. Mechanical Test

Biocoke with the highest coke compressive strength was investigated with coke reactivity index (CRI) and coke strength after reaction (CSR) according to ASTM D 5341-99. A 200 g sample of biocoke was gasified with a grain size of 19–22 mm and heated to 1100 °C for 2 h in atmospheric CO<sub>2</sub> with a flow rate of 300 dm<sup>3</sup>/h. CRI corresponds to the biocoke weight loss during the process. The amount of weight loss indicated the biocoke reactivity index based on Equation (1). Then, the gasification product was fed into the drum for a total of 600 revolutions at a speed of 20 revolutions/minute. The CSR value was calculated on the basis of Equation (2), the ratio of the weight of biocoke with a particle size above 10 mm to the total weight of gasified biocoke.

$$CRI = \frac{m_0 - m_1}{m_0} \cdot 100 \quad (1)$$

$$CSR = \frac{m_2}{m_1} \cdot 100 \quad (2)$$

where  $m_0$  is the initial mass of biocoke (g),  $m_1$  is biocoke mass after reaction at atmospheric CO<sub>2</sub> (g), and  $m_2$  is the mass of particle size biocoke over 10 mm after the spinning drum (g).

The coking properties of biocoke were characterized using Gieseler fluidities based on ASTM D 2639-04, and Ruhr dilatations were characterized according to ASTM D 5515-97.

### 2.3.3. Chemical Structure

The biomass's primary components and chemical structure were analyzed by Shimadzu Fourier-transform infrared spectroscopy (FTIR; IRTracer-100) using the ATR method, and JASCO IR Mentor Pro 6.5 software was used for spectral analysis. Other analytical methods were previously described with detailed operational techniques, and band assignments can be found elsewhere [26–29].

### 2.3.4. Morphology Analysis

Biocoke morphology was observed via scanning electron microscopy (SEM). Samples were dispersed onto carbon tape and imaged using a HiVac TESCAN Vega III SEM.

## 3. Results and Discussion

### 3.1. Biochar Characteristics

#### 3.1.1. Proximate and Ultimate Analyses

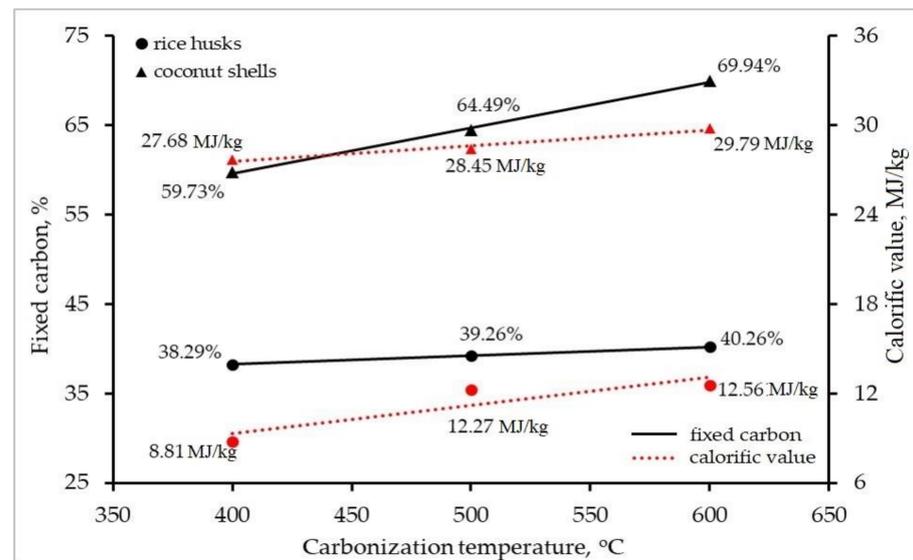
The characteristics of coking coal and biomass are presented in Table 2.

Coking coal had a high fixed carbon content of about 67.70%, low impurities, moisture content of 1.23%, and a low ash content of 2.28% [30,31]. Sulfur content was 0.69%, which was lower than the standard of the blast furnace (<1%) [32]. This provided an excellent starting point for the coal blending process. The biomass rice husks exhibited fixed carbon of 14.09% and volatile matter content of 63.75%. Coconut shells had higher fixed carbon and volatile matter, 18.05%, and 69.47%, respectively, according to a previous study [33]. The proximate analysis of biomass in Table 2 is in accordance with previous studies [34]. The calorific value of coconut shells in this study was 19.05%, very close to the 19.04% from previous research [34]. Ultimate analysis showed that coking coal contained 81.07% carbon, 5.10% hydrogen, and 9.11% oxygen. For the raw materials, rice husks contained 41.18% carbon, 5.56% hydrogen, and 31.08% oxygen, whereas coconut shells had a better carbon content of 53.01%, 6.25% hydrogen, and 28.23% oxygen. Carbon, hydrogen, and oxygen contents in the study were close to those in a previous study [35]. The fixed carbon content from coconut shells in this study was 53.01% higher than that of previous research (21.8%) [34]. Rice husks have higher hygroscopic properties than coconut shells, and thus absorb water more efficiently. The moisture content of both looked quite similar between the different heat-treatment temperatures. The equilibrium moisture content (EMC) raw-material values of rice husks and coconut shells in charcoal were not very different from the moisture found in proximate analysis. Analysis of proximate and ultimate biomass in

Table 2 is in accordance with previous research; therefore, both biomass types entered the carbonization stage through slow pyrolysis using a rotary kiln.

### 3.1.2. Carbonization

Carbonization was conducted to produce biochar in the rotary kiln at different temperatures (400, 500 and 600 °C) for 6 h. The basic parameters of the obtained biochar are presented in Table 3 and described in Figure 3.



**Figure 3.** Effect of heating temperature on fixed carbon and calorific value of biochar.

The products of biomass carbonization are biochar, gases, and tar. This slow pyrolysis is effective. Biochar yield was 34.7% from rice husks, approximately in line with a previous study [36], and 40.6% from coconut shells. Biochar yield in this study was slightly higher than that of previous research [33,37,38]. Factors affecting the outcome of pyrolysis include the type of biomass, temperature, heating rate, pyrolysis duration, reactor type, and pretreatment [33].

The moisture contents of the two biochar types were better because they were smaller (5.54–7.71%) compared to previous research (~10%) [2,35]. Volatile matter from the biochar had approximately the same levels (13.5–39.8%) as those in previous research (20–25%) [2]. The favorable property of coconut-shell charcoal in this study was a lower average ash content of 1.19–1.69% compared to that of 3–4% in a previous study [2,39]. Ash content determines the quality of biomass [40]. Although biochar from rice husks was very high (45.23–46.24%), previous studies have reported values up to 75.35% [37]. Fixed carbon biochar from coconut shells was 59.73–69.94%, compared to ~70% according to the results of previous research [2]. Fixed biochar carbon from rice husks was lower (38.29–40.26%). The calorific value of biochar from coconut shells (27.68–29.79 MJ/kg) was close to the value from previous research (30–32 MJ/kg) [2]. The calorific value of biochar from rice husks was 50% less than that of coconut shells (8.81–12.56%). Overall, rice-husk biochar did not meet the criteria for blending with coking coal because it has very high ash content and low fixed carbon and calorific values. A literature review showed that the carbon content from rice-husk carbonization is generally 38–44% [37,41], whereas the carbon content in this study was 32.44–39.71%. Carbon content decreases with increasing carbonization temperature. The quality of coking coal in this study with 67.7% fixed carbon was better because it had a higher content than that of a previous study (50–55%) [2]. The calorific value of coking coal in this study was 33.75 MJ/kg, above the previous research's minimal limit of 23 MJ/kg [2]. Coking coal's high fixed carbon value has a high chance of blending with biochar from coconut shells.

The different fixed carbon (solid black line in Figure 3) biochar varied, ranging from 38.29% to 40.26% for rice husks (black circle in Figure 3), and from 59.73% to 69.94% (black triangle in Figure 3) for coconut shells. The higher carbonization temperature increased the fixed carbon of most biochar. The biochar of the rice husks had a lower fixed carbon compared to that of the coconut shells. Water content and volatile matter decreased by increasing the temperature.

The calorific values of biochar produced from both biomass types and the different temperatures are presented in Figure 3 (red dotted line). The calorific value ranged from 8.81 to 12.56 MJ/kg for rice husks and 27.68 to 29.79 MJ/kg for coconut shells. Temperature treatment increased the calorific values of both types of biochar, and coconut-shell-based biochar had a higher value than that of rice husks. The coal blending method that uses coking coal produced a higher calorific value when compared with previous research without coking coal [42,43]. Coconut-shell charcoal with the highest calorific values is more suitable for mixing in biocoke production compared to rice-husk charcoal.

### 3.1.3. Coalification Band

The elemental composition (C, H, O) of the raw materials influences product characteristics, in which the atomic ratios of each component are generally correlated with the degree of aromaticity and the polarity of biochar. The comparisons of hydrogen to carbon (H/C) and oxygen to carbon (O/C) ratios against each other are plotted in Figure 4.

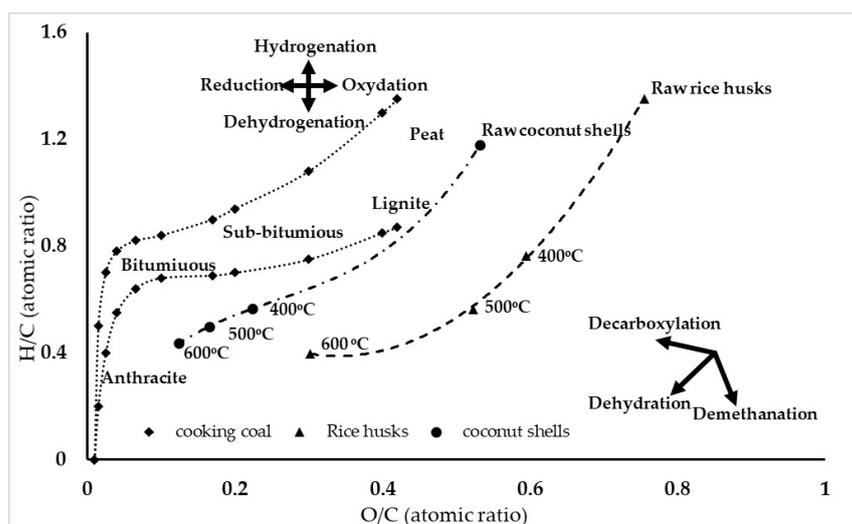
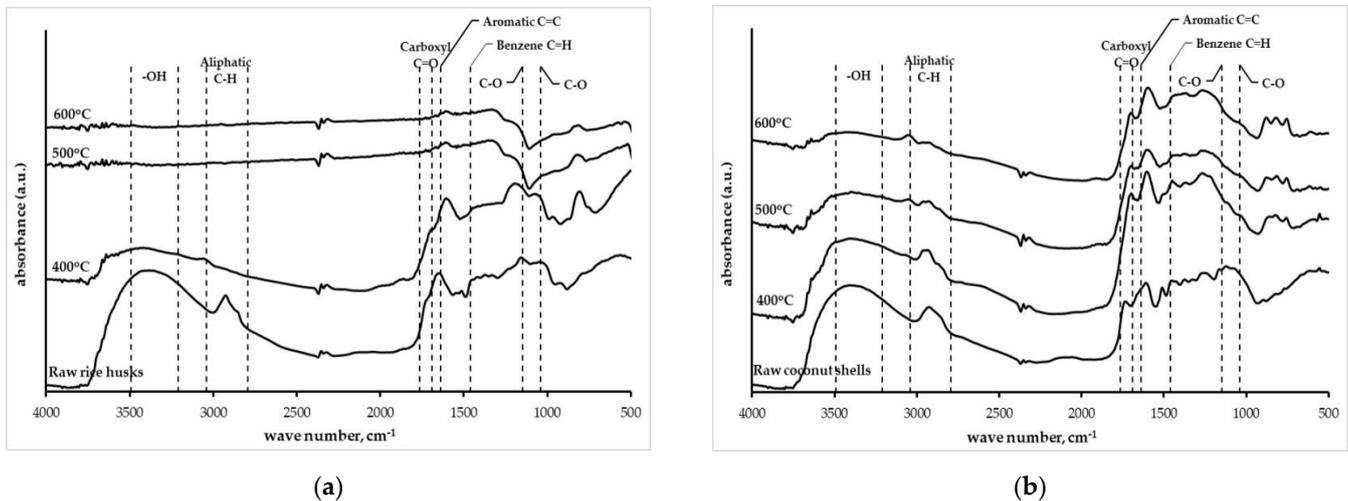


Figure 4. Van Krevelen diagram of coal and biochar.

As shown in Figure 4, the van Krevelen diagram confirms the coalification rank of coking coal and the sample biochar samples at different temperature ranges. Coalification is a gradual change in biochar's physical and chemical properties during thermal carbonization, which assists in determining the reaction mechanism from raw materials into biocoke. The figure shows that H/C and O/C atomic ratios decreased as the reaction temperature increased from 400 to 600 °C. H/C ratio generally decreases less than the O/C ratio does because oxygen content is 4–8 times higher than the hydrogen content. Heating significantly shifted the O/C ratio of both biochar types depending on the level of their moisture content, where rice husks have higher moisture (9.54%) compared to that of coconut shells (8.35%). The temperature increase also caused the oxygen level and the hydrogen of the raw materials to decrease to close to bituminous coal characteristics, in which the O/C and H/C ratios of the coconut shells were lower than those of the rice husks.

### 3.1.4. Functional Groups

FTIR spectra of the produced biochars are presented in Figure 5. FTIR analysis was conducted to compare the organic functional groups in the raw biomass to those in the biochars, and was interpreted using publication data [44,45].



**Figure 5.** FTIR spectra of biochar of (a) rice husks and (b) coconut shells.

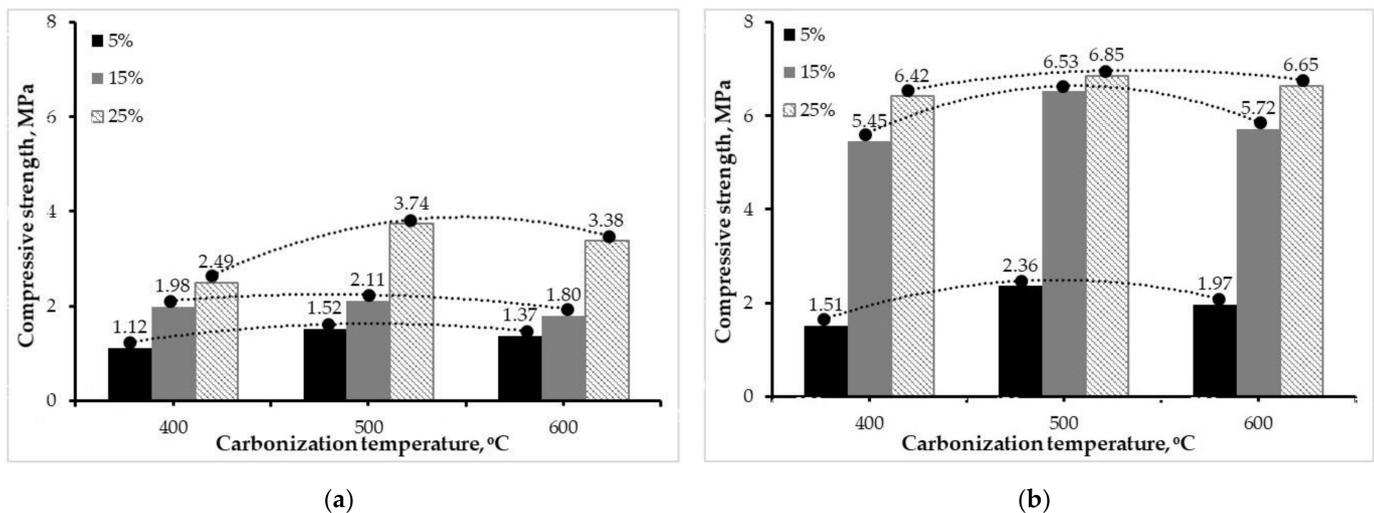
The functional groups of the raw materials of rice husks (Figure 5a) and coconut shells (Figure 5b) showed the same characteristics, in which they were entirely changed during thermal treatment. O–H stretching modes from both materials appeared as a broad peak around  $3200\text{--}3500\text{ cm}^{-1}$ , and became less intense after carbonization because dehydration broke the hydroxyl and carboxyl groups. In addition, the low-intensity peak at  $1640\text{ cm}^{-1}$  appeared to decrease, corresponding to the aromatic C=C structure of carboxylic groups. The decrease in this peak was intense after heating, which was identified as carbon content being converted into  $\text{CO}_2$ . The disappearing peak at  $1040\text{ cm}^{-1}$  in both spectra indicated that the primary carboxyl C–O bond was likely damaged due to decarboxylation. The medium peak between  $3040$  and  $2800\text{ cm}^{-1}$  was related to aliphatic C–H stretching. At the higher temperatures of  $500$  and  $600\text{ }^\circ\text{C}$ , the shoulder disappeared in both samples. The small intensity at  $1702\text{ cm}^{-1}$  was linked to the absorption of C=O bonds. Spectra also indicated that the carbonization temperature had induced fewer C–O and aliphatic C–H functional groups in both produced biochar types, but with a more aliphatic structure C–H in the form of  $\text{CH}_x$  and carbonyl C=O functional groups, which suggested that some carbon had been converted into  $\text{CO}_2$ .

## 3.2. Biocoke Characteristics

### 3.2.1. Compressive Strength

There are three stages of briquetting: high pressure of  $110\text{--}250\text{ MPa}$ , medium pressure of  $50\text{--}100\text{ MPa}$  with heating, and low pressure of  $20\text{--}50\text{ MPa}$  with a binder. Heating is to activate the natural adhesives (lignin and hemicellulose) in biomass [25]. This study used low pressure because it a binder and hot briquetting were used. The compacted material was not total biomass, but  $75\text{--}95\text{ wt.}\%$  coking coal that had swelling and caking properties, and  $5\text{--}25\text{ wt.}\%$  biochar. On the basis of previous research, pressure of  $20\text{ MPa}$  was confirmed used for hot briquettes with a binder [25].

The compressive strengths of biocoke from the briquettes as a function of biochar proportion and carbonization temperature are shown in Figure 6.



**Figure 6.** Compressive strength of biocoke from briquettes of (a) rice husks and (b) coconut shells.

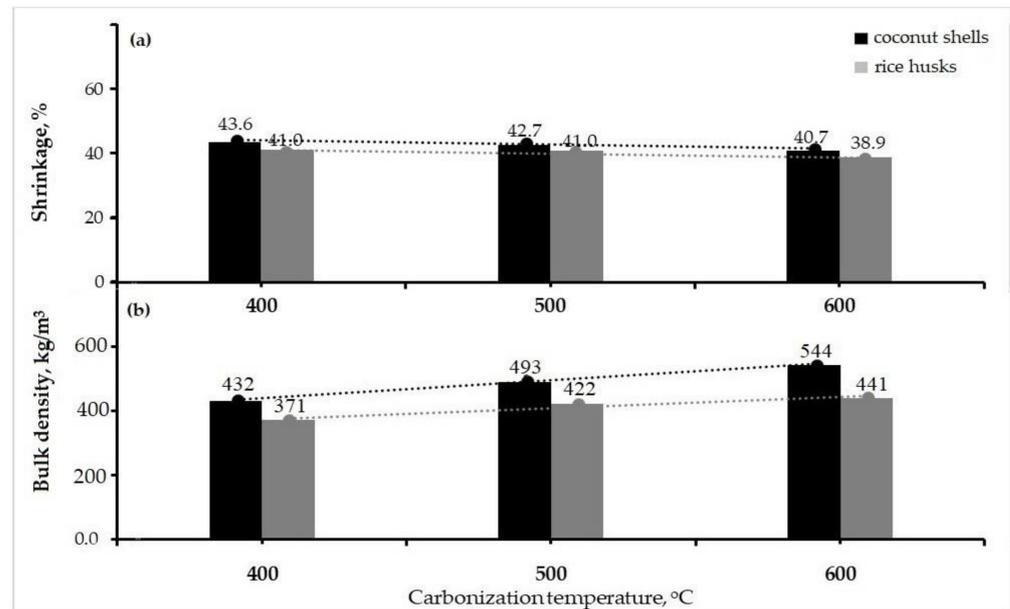
The compressive strength of the biocoke improved when the quantity of biochar increased from 5 to 25 % wt. at the same temperature treatment. In Figure 6a, for example, the rice-husk biocoke with a 25 wt.% proportion of biochar exhibited the highest strength values of 2.49, 3.74, and 3.38 MPa at formation temperatures of 400, 500, and 600 °C, respectively. Additionally, coconut-shell biocoke (Figure 6b) with a 25% wt. proportion of biochar also exhibited high strength: 6.42 MPa for 400 °C, 6.85 MPa for 500 °C, and 6.65 MPa for 600 °C. Increasing the temperature carbonization induced the brittleness of the biocoke; biocoke produced at 600 °C exhibited lower compressive strength compared to that produced at 500 °C. Both types of biocoke exhibited the highest compressive strength value at 500 °C, where rice-husk strength was 3.74 MPa, and that of coconut shells was 6.85 MPa. By considering the different carbon forms of coke when treated by different temperature carbonization instances, the strength of coke improves with increasing temperature [46]. ANOVA statistics were used to observe the factors that affect the compressive strength of biocoke, as shown in Figure 6. In this study, analysis of variance was performed with  $\alpha = 0.05$ , and results confirmed that the F test of temperature and humidity strongly affected the compressive strength.

Thus, compressive strength decreased as temperature increased over 500 °C of the thermal treatment. This indicates that the biocoke had lost ductility, which made it more brittle. Biocoke lost its moisture content during the heating process, which increased the glass transition temperature and reduced the interdiffusion of the polymer compounds (cellulose, lignin, and hemicellulose) between particles in the biocoke [47]. According to Arman (2019) [48], moisture is a softening agent of those biopolymers during the densification process. Moreover, the strength value is both determined by the composition ratio of the blending coal, and influenced by the physical (weight loss, particle size, and reactivity) and chemical (ultimate and proximate) properties of the biomass coking coal. The increase in biocoke strength during carbonization is due to the attained maximal connectivity of coking coal and biochar. In all proportions and operational temperatures, the strength of the coconut-shell briquettes showed a better value than that of rice-husk briquettes. The presence of tar was predicted to enhance mechanical performance due to its binder capacity, and cellulose influences biochar formation, which helps in the formation of tar [49]. In general, rice husks are composed of 35% cellulose, and coconut shells are composed of 65% cellulose.

### 3.2.2. Mass Shrinkage and Bulk Density

In this study, the method for increasing the shrinkage and bulk density of the resulting biocoke was applied by briquetting under thermal pressure. Figure 7 shows the variation in mass shrinkage and briquette density at the optimal composition of biocoke (15 wt.% of

biochar) as a function of the carbonization temperature. Black bars represent the briquettes prepared with coconut shells, and the grey bars are rice husks.



**Figure 7.** (a) Mass shrinkage and (b) bulk density of biocoke briquettes at optimal composition as a function of carbonization temperature.

Figure 7a shows the mass shrinkage from different types of biochar. Carbonization led to product shrinkage due to water and volatile evaporation loss. The biocoke from rice husks did not exhibit a significant difference in shrinkage during carbonization. At the same time, the coconut-shell sample decreased the percentage of shrinkage with increasing temperatures. Figure 7b shows the bulk density characteristics of the coal blend briquettes during increasing temperature from 400 to 600 °C. Coconut shells gave higher densities when blended with coking coal, where the densities of the briquettes increased from 432 kg/m<sup>3</sup> (400 °C) to 544 (600 °C) kg/m<sup>3</sup> compared to the briquettes containing the rice husks, which increased from 371 kg/m<sup>3</sup> (400 °C) to 441 kg/m<sup>3</sup> (600 °C). The increased temperature made the fiber biomass softer and more fluid, acting as a binding agent within the coke [50], whereas mechanical compression increased adhesion between particles and generated intermolecular bonds within the contact area [51]. Moreover, the moisture content of the biomass plays an important role in briquette densities. A lower moisture content produces denser briquettes, whereas a higher one decreases compact density. Increasing bulk density is followed by an increase in compressive strength [52]. Figure 6 shows that the compressive strength of biocoke from the briquettes of coconut shells is better than that of rice husks.

### 3.2.3. CSR and CRI Tests

The quality of the coking blend for its application in the blast furnace was investigated with two indices, namely, CSR and CRI. The CRI represents the loss of weight, whereas the CSR is the percentage of partially reacted coke. All samples corresponding to the optimal carbonization temperature in the mechanical test (500 °C) were tested with variations in the amount and type of biochar, as shown in Figure 8.

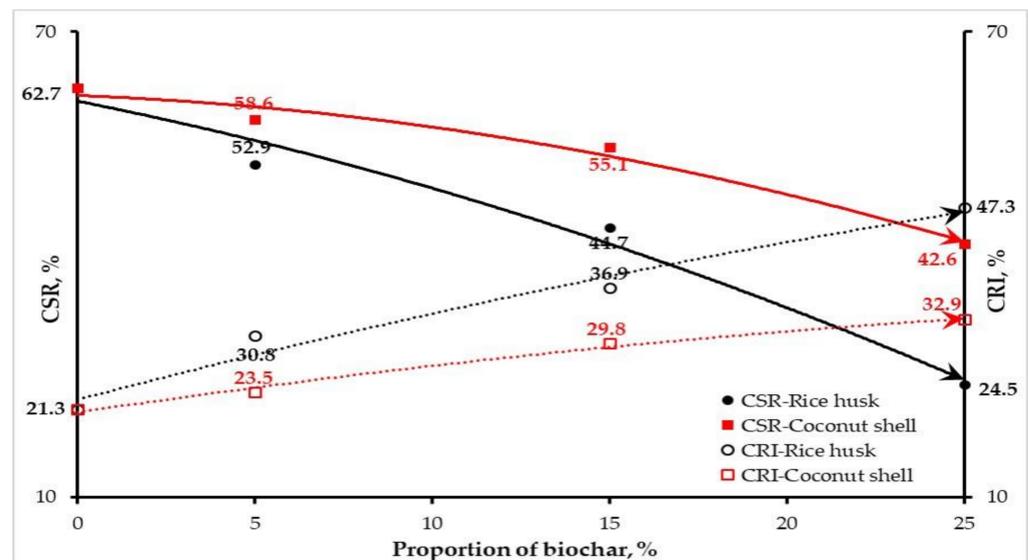


Figure 8. CSR and CRI of coking blends containing various amounts of biochar.

Results show that the two coking blends produced similar trends. The increase in biochar proportion (0 to 25 wt.%) led to downgrading the coke quality, in which with an increasing amount of biochar, the CSR index decreased from 62.7% to 24.5% for the rice husks (black line), and from 62.7% to 42.6% for the coconut shells (red line); the CRI index increased from 21.3% to 47.3% for the rice husks (black dotted line), and from 21.3% to 32.9% for the coconut shells (red dotted line). However, the CSR index of the coke containing coconut shells was slightly higher than that of the rice husks for the same amount in the coking coal. In general, for good-quality coke, the CSR index must be high, whereas the CRI is low [53]. In this work, up to 15 wt.% of the coconut shells, CSR index (55.1%), and CRI index (29.8%) remained at workable-level biocoke for blast-furnace applications, which is CSR 74–50 and CRI 19–30 [2,31,39,54].

In blast-furnace applications, coke strength after reaction of biocoke with carbon dioxide at 1100 °C depends on the coking condition. The factors of coal rank, coal rheology, organic inert, and inorganic inert influenced the coking conditions [53]. Coal blending with biochar combined with hot briquetting improved the quality of the biocoke. Two processes impacted the strength and reactivity of the biocoke. The reduction in strength was hence dependent on the rank of the coal. From proximate analysis and optimal calorific values, samples were taken in the six most influential samples to discuss biocoke suitability used in a blast furnace. The first three samples resulted from coal blending with coconut-shell charcoal; the three other resulted from coal blending with rice-husk charcoal. Thus, six samples resulted from coal and biochar blending in a composition of 15 wt.%, followed by a hot briquette process of 100 °C. The use of molasses as a binder increased the compressive strength of coke coal briquettes [55]. Previous researchers reported that the binder function in coal blending improved coke quality, as the coke's strength significantly increased [56]. Molasses are organic binders, and previous research found that briquettes with the most favorable mechanical properties such as durability were obtained using organic binders [21].

### 3.2.4. Thermal Rheology

The effect of biochar on the thermal rheological properties of the coal blend is shown in Figure 9. Fluidity was found to not change much with the addition of biochar, which is different with dilatation.

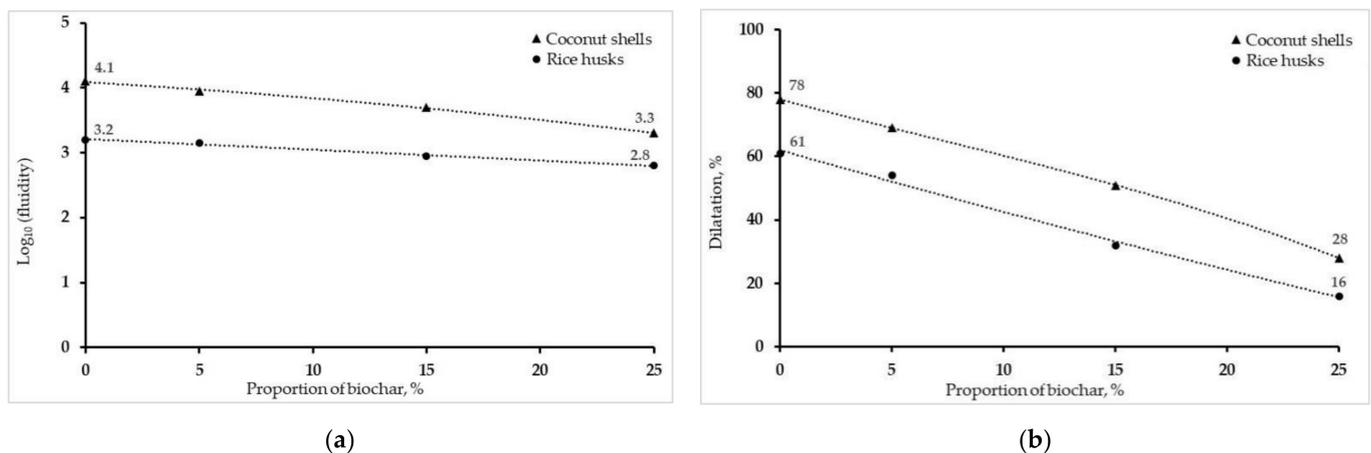


Figure 9. Thermal rheology of coal blends: (a) fluidity; (b) dilatation.

A slight decrease was observed in the fluidity (Figure 9a) of the coking blends with the proportion of biochar up to 25 wt.%, namely, from 4.1 to 3.3 for the coconut shells, and from 3.2 to 2.8 for the rice husks. These results are supported by dilatation, which is demonstrated in Figure 9b. The percent dilatation of the sample coconut shells decreased from 78% to 28%, whereas that of the rice husks decreased from 61% to 16%. Fluidity is a coal property that affects the particle bonding and pore structure of metallurgical coke. A decrease in fluidity decreases the tensile strength and reactivity to carbon dioxide in blast furnaces [57,58]. Dilatation studies the effect of coking coal, which experiences swelling and softening due to heating [59]. The addition of biochar in a blending process causes the swelling ability to decrease. In biocoke synthesis, sufficient swelling and softening are required so that the biocoke will develop good strength. In all cases, there is a reduction in fluidity and dilatation with the addition of biochar. Even at 15 wt.% added biochar, fluidity and dilatation remain at a workable level for biocoke [39]. The type of biomass affects the fixed carbon, and the calorific value of biochar varies significantly (Figure 3), resulting in a significant difference in compressive strength (Figure 6). The temperature effects were generally not very significant (Figures 3, 6 and 7). The type and composition of biomass (Figures 8 and 9) had a more significant influence than that of temperature.

### 3.2.5. Surface Morphology

Figure 10 presents the SEM micrographs of the coal blends with 15 wt.% of two types of biochar prepared at a carbonization temperature of 500 °C.

Both images indicate that biochars did not form a chemical bond or react with the host matrix of coking coal after the briquetting process. Some void structures were formed at the core, as was a denser structure at the periphery, which tended to generate fragile products. Figure 10a shows the structure of the biocoke briquette prepared with 15 wt.% rice-husk biochar. The distributed axis showed a more extensive area but shallow depth. Figure 10b is the structure of the coke that was prepared with 15 wt.% coconut shells. It shows that the axis morphology had a small number and shallow depth, similar to that in previous research [30,35]. Both samples displayed a homogeneous structure. The SEM micrograph of coal blends exhibits the general surface deformation. The morphology of biocoke from rice-husk biochar had many deeper and broader pores on the surface than the coconut-shell biochar, according to a previous study [60]. This is correlated with mechanical testing, in which coconut shells had higher compressive strength. The addition of biochar caused degradation by gasification, caused by losing the biochar particles' preferred solution, leaving a vacuum that holds the pores in the coke together [61]. Coal blending through briquetting improves the quality of coke [62].

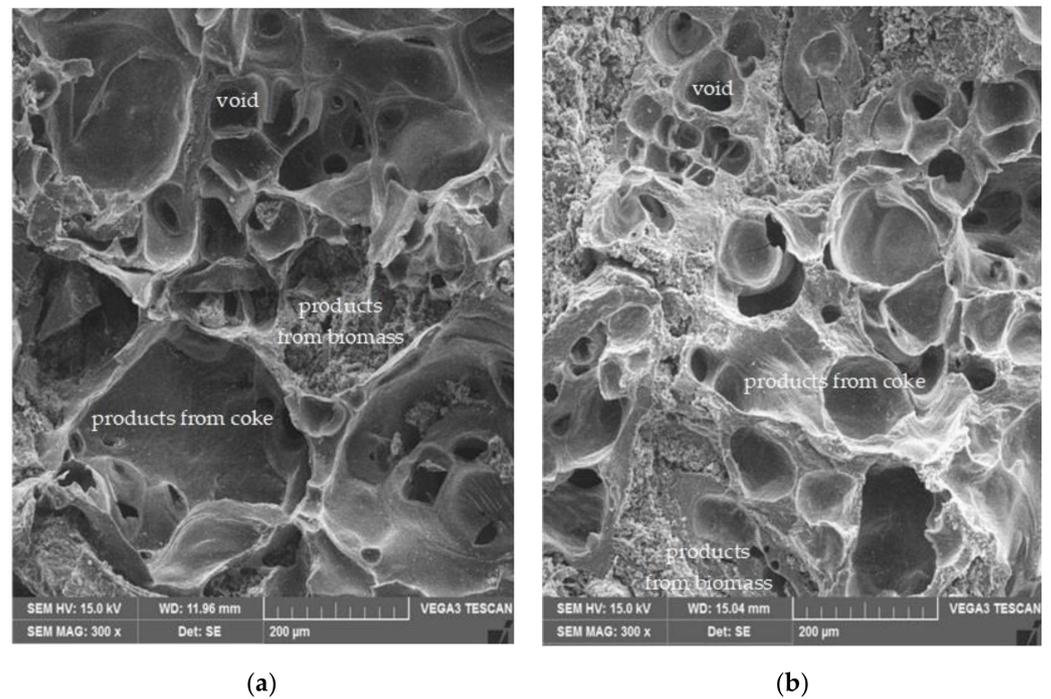


Figure 10. SEM micrograph of coal blends containing (a) rice husks and (b) coconut shells.

### 3.2.6. Rheological Properties

Table 4 shows that the biocoke was of good quality according to the CSR and CRI, applicable for blast-furnace operation when the blending composition of coking coal and biochar was 85:15 wt.%. According to the literature, excellent metallurgical coke has more than 85% fixed carbon and a calorific value of 28.451–30.125 MJ/kg [32]. We obtained a minimal calorific value of 29.648 MJ/kg, which was higher than the minimum reported in the literature. Table 4 shows that the biocoke using coconut-shell charcoal produced the highest fixed carbon,  $89.23 \pm 0.14\%$ , whereas the biocoke using rice-husk charcoal only produced fixed carbon of  $73.44 \pm 0.65\%$ . The blend using coconut-shell charcoal exhibited excellent calories when used as metallurgical coke in a blast furnace. Biocoke produced at 400, 500, and 600 °C showed overall calorific values of more than 28.451 MJ/kg. Blends using rice-husk charcoal produced the highest calorific value of only  $24.970 \pm 0.51$  MJ/kg. These rice husks are not recommended as a blending material for metallurgical coke due to consideration of their volatile matter, ash, fixed carbon, gross calorific, and compressive strength. Table 4 shows the averaged values from three experiments using sigma standard errors.

Table 4. Biocoke analysis.

Analysis	Rice Husk Charcoal *			Coconut Shell Charcoal *			Unit
	RHB 4	RHB 5	RHB 6	CSB 4	CSB 5	CSB 6	
Moisture (ar)	$1.21 \pm 0.16$	$1.03 \pm 0.14$	$1.12 \pm 0.16$	$1.26 \pm 0.18$	$1.01 \pm 0.12$	$1.13 \pm 0.11$	%
Volatile Matter (db)	$3.54 \pm 0.28$	$3.46 \pm 0.28$	$3.36 \pm 0.28$	$1.79 \pm 0.29$	$1.56 \pm 0.26$	$1.64 \pm 0.22$	%
Ash (db)	$29.12 \pm 0.54$	$26.21 \pm 0.42$	$23.20 \pm 0.49$	$9.41 \pm 0.25$	$9.42 \pm 0.17$	$9.13 \pm 0.12$	%
Fixed Carbon (db)	$67.34 \pm 0.57$	$70.33 \pm 0.60$	$73.44 \pm 0.65$	$88.80 \pm 0.12$	$89.02 \pm 0.11$	$89.23 \pm 0.14$	%
Gross Calorific (db)	$22.506 \pm 0.54$	$23.029 \pm 0.57$	$24.970 \pm 0.51$	$29.648 \pm 0.53$	$29.681 \pm 0.46$	$30.033 \pm 0.49$	MJ/kg
Sulfur (db)	$0.62 \pm 0.02$	$0.62 \pm 0.02$	$0.62 \pm 0.02$	$0.68 \pm 0.03$	$0.68 \pm 0.02$	$0.68 \pm 0.02$	%

(\*) Note: RHB 4–6 of biocoke result from blending coking coal with rice-husk charcoal at 400, 500, and 600 °C, respectively. CSB 4–6 of biocoke result from blending coking coal with coconut-shell charcoal at 400, 500, and 600 °C, respectively. ar = as received; db = dry basis.

We conducted sulfur and proximate analysis on the biocoke results from blending coking coal with coconut-shell charcoal at a composition of 85:15 wt.%. volatile matter,

ash, fixed carbon, gross calorific, and compressive strength were assessed in accordance with blast-furnace standards. Coal blends using coking coal produced a higher calorific value of  $30.033 \pm 0.49$  MJ/kg when compared with previous research without coking coal (20.778 MJ/kg) [42,43]. The study showed that the blending composition of coking coal:coconut-shell charcoal at 85:15 wt.% produces high-quality biocoke with fixed carbon of  $89.23 \pm 0.14\%$ . Previous research confirmed that blending coal:biochar at 90:10 wt.% produces 65.34% of fixed carbon content [39]. According to previous research, this research shows that CCS is influenced by the type of biomass, blending composition, and carbonization temperature [21,63]. The CCS can be increased through the use of molasses and tar as binders [55,56], briquetting [62], and hot briquetting [64]. The CCS in this study can be increased by adding pressure during briquetting from 30 to 250 MPa [65]. Further investigations are needed to increase biomass utilization in biocoke production without impairing the quality of the biocoke product.

#### 4. Conclusions

Several biocoke requirements for blast-furnace applications are met by biocoke from blending coal using coking coal with coconut-shell charcoal at 85:15 wt.%. The composition of this mixture produces fixed carbon, calorific value, and compressive strength of  $89.02 \pm 0.11\%$ ,  $29.681 \pm 0.46$  MJ/kg, and  $6.53 \pm 0.4$  MPa, respectively. This product allows for blast-furnace applications with CRI 29.8 and CSR 55.1. Carbonization temperature did not have a significant effect on the increase in fixed carbon and calorific value. The type of biomass, and composition mixing between biochar and coking coal determine the CSR and CRI values applicable to a blast furnace.

**Author Contributions:** E.Y. was responsible for the conceptualization, methodology, experimental laboratory works, manuscript preparation, writing—review and editing, and project administration. E.Y.W. was responsible for the integrity of the analytical data laboratory and data curation. A.T.M. contributed to the validation, conceptualization, supervision, and writing—original draft preparation. A.A. contributed to the formal analysis, and resources. All authors have read and agreed to the published version of the manuscript.

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#### References

1. Montiano, M.G.; Diaz-Faes, E.; Barriocanal, C.; Alvarez, R. Influence of biomass on metallurgical coke quality. *Fuel* **2014**, *116*, 175–182. [CrossRef]
2. Mousa, E.; Wang, C.; Riesbeck, J.; Larsson, M. Biomass applications in iron and steel industry: An overview of challenges and opportunities. *Renew. Sustain. Energy Rev.* **2016**, *65*, 1247–1266. [CrossRef]
3. Gielen, D.; Boshell, F.; Saygin, D.; Bazilian, M.D.; Wagner, N.; Gorini, R. The role of renewable energy in the global energy transformation. *Energy Strateg. Rev.* **2019**, *24*, 38–50. [CrossRef]
4. Perea-Moreno, M.A.; Samerón-Manzano, E.; Perea-Moreno, A.J. Biomass as renewable energy: Worldwide research trends. *Sustainability* **2019**, *11*, 863. [CrossRef]
5. El Naggari, A.M.A.; El Sayed, H.A.; Elsalamony, R.A.; Elrazak, A.A. Biomass to fuel gas conversion through a low pyrolysis temperature induced by gamma radiation: An experimental and simulative study. *RSC Adv.* **2015**, *5*, 77897–77905. [CrossRef]
6. Adrados, A.; Lopez-Uribebarrenechea, A.; Solar, J.; Requies, J.; De Marco, I.; Cambra, J.F. Upgrading of pyrolysis vapours from biomass carbonization. *J. Anal. Appl. Pyrolysis* **2013**, *103*, 293–299. [CrossRef]
7. Fuchigami, Y.; Hara, K.; Kita, T.; Uwasu, M.; Kurimoto, S. Analysis of effect on CO<sub>2</sub> emission reduction and cost estimation for the use of Bio-coke: A case study of Osaka, Japan. *J. Wood Sci.* **2016**, *62*, 93–100. [CrossRef]
8. Takeshi, U.; Keiichi, O.; Hajime, A. Reduction of coke consumption in high-temperature gasifying and direct melting system. *JFE Tech. Rep.* **2014**, *19*, 145–152.
9. Hanrot, F.; Sert, D.; Delinchant, J.; Pietruck, R.; Burgler, T.; Babich, A.; Fernandez, M.; Alvarez, R.; Diez, M.A. CO<sub>2</sub> Mitigation for Steelmaking Using Charcoal and Plastics Wastes as Reducing Agents and Secondary Raw Materials. 1st Spanish National Conference on Advances in Materials Recycling and Eco-Energy, Madrid, Spain, 12–13 November; 2009.

10. Gil, M.V.; Oulego, P.; Casal, M.D.; Pevida, C.; Pis, J.J.; Rubiera, F. Mechanical durability and combustion characteristics of pellets from biomass blends. *Bioresour. Technol.* **2010**, *101*, 8859–8867. [[CrossRef](#)]
11. Lin, Y.; Ma, X.; Peng, X.; Yu, Z.; Fang, S.; Lin, Y.; Fan, Y. Combustion, pyrolysis and char CO<sub>2</sub>-gasification characteristics of hydrothermal carbonization solid fuel from municipal solid wastes. *Fuel* **2016**, *181*, 905–915. [[CrossRef](#)]
12. Zaini, I.N.; García López, C.; Pretz, T.; Yang, W.; Jönsson, P.G. Characterization of pyrolysis products of high-ash excavated-waste and its char gasification reactivity and kinetics under a steam atmosphere. *Waste Manag.* **2019**, *97*, 149–163. [[CrossRef](#)]
13. Speight, J.G. *The Chemistry and Technology of Coal*; CRC Press: Boca Raton, FL, USA, 2012.
14. Florentino-Madiedo, L.; Díaz-Faes, E.; Barriocanal, C. Mechanical strength of bio-coke from briquettes. *Renew. Energy* **2020**, *146*, 1717–1724. [[CrossRef](#)]
15. Amaya, A.; Corengia, M.; Cuña, A.; Vivo, J.D.; Sarachik, A.; Tancredi, N. Preparation of Charcoal Pellets from Eucalyptus Wood with Different Binders. *J. Energy Nat. Resour. Resour.* **2015**, *4*, 34–39. [[CrossRef](#)]
16. Mansor, A.M.; Theo, W.L.; Lim, J.S.; Ani, F.N.; Hashim, H.; Ho, W.S. Potential commercialisation of biocoke production in Malaysia—A best evidence review. *Renew. Sustain. Energy Rev.* **2018**, *90*, 636–649. [[CrossRef](#)]
17. Ito, H.; Sakai, Y.; Ida, T.; Nakamura, Y.; Fujita, O. Combustion of Bio-coke (Highly Densified Biomass Fuel) Block in High-Temperature Air Flow. In Proceedings of the ASME/JSME 2011 8th Thermal Engineering Joint Conference AJTEC2011, Honolulu, HI, USA, 13–17 March 2011; pp. 1–10.
18. Mizuno, S.; Ida, T.; Fuchihata, M.; Namba, K. Effect of specimen size on ultimate compressive strength of Bio-coke produced from green tea grounds. *Mech. Eng. J.* **2016**, *3*, 15-00441. [[CrossRef](#)]
19. Yustanti, E.; Kusumawati, H.; Partuti, T.; Mursito, A. The effects of hot briquetting on the coke strength in the biocoke making process with coal blending method. *Mater. Sci. Eng.* **2019**, *478*, 012025.
20. Mursito, A.T.; Muharman, A.; Yustanti, E. Producing bio-coke by redwood charcoal blending for blast furnace application. In Proceedings of the 3rd International Seminar on Metallurgy and Materials Tangerang Selatan (ISMM2019), Tangerang Selatan, Indonesia, 23–24 October 2019; Darsono, N., Thaha, Y.N., Ridhova, A., Rhamdani, A., Utomo, M.S., Ridlo, F.M., Prasetyo, M.A., Eds.; America Institute of Physics AIP: Tangerang Selatan, Indonesia, 2020; Volume 2232, p. 060004-1.
21. Rej dak, M.; Robak, J.; Czardybon, A.; Ignasiak, K.; Fudała, P. Research on the Production of Composite Fuel on the Basis of Fine-Grained Coal Fractions and Biomass—The Impact of Process Parameters and the Type of Binder on the Quality of Briquettes Produced. *Minerals* **2020**, *10*, 31. [[CrossRef](#)]
22. Brittain, H. Particle-Size Distribution, Part II The Problem of Sampling Powdered Solids. *Pharm. Technol.* **2002**, *26*, 67–73.
23. Campos-M, M.; Campos-C, R. Applications of quartering method in soils and foods. *Int. J. Eng. Res. Appl.* **2017**, *7*, 35–39. [[CrossRef](#)]
24. Mori, A.; Yuniati, M.D.; Mursito, A.T.; Kudo, S.; Norinaga, K.; Nonaka, M.; Hirajima, T.; Kim, H.S.; Hayashi, J.I. Preparation of coke from Indonesian lignites by a sequence of hydrothermal treatment, hot briquetting, and carbonization. *Energy Fuels* **2013**, *27*, 6607–6616. [[CrossRef](#)]
25. Grover, P.D.; Mishra, S.K. *Biomass Briquetting: Technology and Practices*; FAO: Rome, Italy, 1996.
26. Mursito, A.T.; Hirajima, T.; Sasaki, K. Upgrading and dewatering of raw tropical peat by hydrothermal treatment. *Fuel* **2010**, *89*, 635–641. [[CrossRef](#)]
27. Mursito, A.T.; Hirajima, T.; Sasaki, K. Alkaline hydrothermal de-ashing and desulfurization of low quality coal and its application to hydrogen-rich gas generation. *Energy Convers. Manag.* **2011**, *52*, 762–769. [[CrossRef](#)]
28. Mursito, A.T.; Hirajima, T.; Listiyowati, L.N.; Sudarsono, S. Surface physicochemical properties of semi-anthracitic coal from Painan-Sumatra during air oxidation. *Int. J. Coal Sci. Technol.* **2018**, *5*, 156–166. [[CrossRef](#)]
29. Mursito, A.T.; Widodo, D.N.; Arifin, D.N. Characterization of bio-coal briquettes blended from low quality coal and biomass waste treated by Garant<sup>®</sup> bio-activator and its application for fuel combustion. *Int. J. Coal Sci. Technol.* **2020**, *7*, 796–806. [[CrossRef](#)]
30. Seo, M.W.; Jeong, H.M.; Lee, W.J.; Yoon, S.J.; Ra, H.W.; Kim, Y.K.; Lee, D.; Han, S.W.; Kim, S.D.; Lee, J.G.; et al. Carbonization characteristics of biomass/coking coal blends for the application of bio-coke. *Chem. Eng. J.* **2020**, *394*, 124943. [[CrossRef](#)]
31. Kokonya, S.; Castro-Díaz, M.; Barriocanal, C.; Snape, C.E. An investigation into the effect of fast heating on fluidity development and coke quality for blends of coal and biomass. *Biomass Bioenergy* **2013**, *56*, 295–306. [[CrossRef](#)]
32. Riazi, M.R.; Gupta, R. *Coal Production and Processing Technology*, 1st ed.; Riazi, M., Gupta, R., Eds.; CRC Press: Boca Raton, FL, USA; Taylor and Francis Group LLC: Boca Raton, FL, USA, 2016; ISBN 9781482252187.
33. Azeta, O.; Ayeni, A.O.; Agboola, O.; Elehinafe, F.B. A review on the sustainable energy generation from the pyrolysis of coconut biomass. *Sci. Afr.* **2021**, *13*, e00909. [[CrossRef](#)]
34. Kabir Ahmad, R.; Anwar Sulaiman, S.; Yusup, S.; Sham Dol, S.; Inayat, M.; Aminu Umar, H. Exploring the potential of coconut shell biomass for charcoal production. *Ain Shams Eng. J.* in press. **2021**. [[CrossRef](#)]
35. Promdee, K.; Chanvidhwatanakit, J.; Satitkune, S.; Boonmee, C.; Kawichai, T.; Jarernprasert, S.; Vitidsant, T. Characterization of carbon materials and differences from activated carbon particle (ACP) and coal briquettes product (CBP) derived from coconut shell via rotary kiln. *Renew. Sustain. Energy Rev.* **2017**, *75*, 1175–1186. [[CrossRef](#)]
36. Vieira, F.R.; Romero Luna, C.M.; Arce, G.L.A.F.; Ávila, I. Optimization of slow pyrolysis process parameters using a fixed bed reactor for biochar yield from rice husk. *Biomass Bioenergy* **2020**, *132*, 105412. [[CrossRef](#)]
37. Jia, Y.; Shi, S.; Liu, J.; Su, S.; Liang, Q.; Zeng, X.; Li, T. Study of the effect of pyrolysis temperature on the Cd<sup>2+</sup> adsorption characteristics of biochar. *Appl. Sci.* **2018**, *8*, 1019. [[CrossRef](#)]

38. Singh Karam, D.; Nagabovanalli, P.; Sundara Rajoo, K.; Fauziah Ishak, C.; Abdu, A.; Rosli, Z.; Melissa Muharam, F.; Zulperi, D. An overview on the preparation of rice husk biochar, factors affecting its properties, and its agriculture application. *J. Saudi Soc. Agric. Sci.* **2021**. [[CrossRef](#)]
39. MacPhee, J.A.; Gransden, J.F.; Giroux, L.; Price, J.T. Possible CO<sub>2</sub> mitigation via addition of charcoal to coking coal blends. *Fuel Process. Technol.* **2009**, *90*, 16–20. [[CrossRef](#)]
40. Liu, X.; Feng, X.; Huang, L.; He, Y. Rapid Determination of Wood and Rice Husk Pellets' Proximate Analysis and Heating Value. *Energies* **2020**, *13*, 3741. [[CrossRef](#)]
41. Muthukrishnan, S.; Gupta, S.; Kua, H.W. Application of rice husk biochar and thermally treated low silica rice husk ash to improve physical properties of cement mortar. *Theor. Appl. Fract. Mech.* **2019**, *104*, 102376. [[CrossRef](#)]
42. Nazari, M.M.; San, C.P.; Atan, N.A. Combustion performance of biomass composite briquette from rice husk and banana residue. *Int. J. Adv. Sci. Eng. Inf. Technol.* **2019**, *9*, 455–460. [[CrossRef](#)]
43. Yuliah, Y.; Kartawidjaja, M.; Suryaningsih, S.; Ulfi, K. Fabrication and characterization of rice husk and coconut shell charcoal based bio-briquettes as alternative energy source. In Proceedings of the International Conference on Biomass: Technology Application, and Sustainable Development, Bogor, Indonesia, 10–11 October 2016; IOP Publishing: Bristol, UK, 2017; Volume 65, p. 012021.
44. Kim, D.; Lee, K.; Bae, D.; Park, K.Y. Characterizations of biochar from hydrothermal carbonization of exhausted coffee residue. *J. Mater. Cycles Waste Manag.* **2017**, *19*, 1036–1043. [[CrossRef](#)]
45. Ibarra, J.V.; Muñoz, E.; Moliner, R. FTIR study of the evolution of coal structure during the coalification process. *Org. Geochem.* **1996**, *24*, 725–735. [[CrossRef](#)]
46. Grant, M.G.K.; Chaklader, A.C.D.; Price, J.T. Factors affecting the strength of blast furnace coke. *Fuel* **1991**, *70*, 181–188. [[CrossRef](#)]
47. Baharin, N.S.K.; Koesoemadinata, V.C.; Nakamura, S.; Azman, N.F.; Yuzir, M.A.M.; Akhir, F.N.M.; Iwamoto, K.; Yahya, W.J.; Othman, N.; Ida, T.; et al. Production of Bio-Coke from spent mushroom substrate for a sustainable solid fuel. *Biomass Convers. Biorefinery* **2020**, 1–10. [[CrossRef](#)]
48. Arman, M.A. *An experimental study of the improvement of mechanical properties of blended bio-coke.*; Kindai University: Higashiōsaka, Japan, 2019.
49. Tomczyk, A.; Sokołowska, Z.; Boguta, P. Biochar physicochemical properties: Pyrolysis temperature and feedstock kind effects. *Rev. Environ. Sci. Biotechnol.* **2020**, *19*, 191–215. [[CrossRef](#)]
50. Stevens, C.; Verhe, R. Renewable Bioresources Scope and Modification for Non- Food Applications. *Ind. Crops Prod.* **2006**, *23*, 223–224. [[CrossRef](#)]
51. Song, Y.; Tumuluru, J.S.; Iroba, K.L.; Tabil, L.G.; Xin, M.; Meda, V. Material and operating variables affecting the physical quality of biomass briquettes. In *XVIIth World Congress of the International Commission of Agricultural and Biosystems Engineering*; Canadian Society for Bioengineering: Québec City, QC, Canada, 2010; pp. 13–17.
52. Gendek, A.; Aniszewska, M.; Malat'ák, J.; Velebil, J. Evaluation of selected physical and mechanical properties of briquettes produced from cones of three coniferous tree species. *Biomass Bioenergy* **2018**, *117*, 173–179. [[CrossRef](#)]
53. Diez, M.; Alvarez, R.; Barriocanal, C. Coal for metallurgical coke production: Predictions of coke quality and future requirements for cokemaking. *Coal Geol.* **2002**, *50*, 389–412. [[CrossRef](#)]
54. Sundqvist Ökvist, L.; Lundgren, M. Experiences of bio-coal applications in the blast furnace process—opportunities and limitations. *Minerals* **2021**, *11*, 863. [[CrossRef](#)]
55. Zhong, Q.; Yang, Y.; Li, Q.; Xu, B.; Jiang, T. Coal tar pitch and molasses blended binder for production of formed coal briquettes from high volatile coal. *Fuel Process. Technol.* **2017**, *157*, 12–19. [[CrossRef](#)]
56. Nomura, S.; Arima, T. Influence of binder (coal tar and pitch) addition on coal caking property and coke strength. *Fuel Process. Technol.* **2017**, *159*, 369–375. [[CrossRef](#)]
57. Prachethan Kumar, P.; Barman, S.C.; Singh, S.; Ranjan, M. Influence of coal fluidity on coal blend and coke quality. *Ironmak. Steelmak.* **2008**, *35*, 416–420. [[CrossRef](#)]
58. Diez, M.A.; Alvarez, R.; Fernández, M. Biomass derived products as modifiers of the rheological properties of coking coals. *Fuel* **2012**, *96*, 306–313. [[CrossRef](#)]
59. Jenkins, D.R.; Mahoney, M.R. A mechanistic model for the softening of coking coal and its use for predicting the dilatation of blends. *Fuel* **2015**, *153*, 585–594. [[CrossRef](#)]
60. Ketov, A.; Rudakova, L.; Vaisman, I.; Ketov, I.; Haritonovs, V.; Sahmenko, G. Recycling of rice husks ash for the preparation of resistant, lightweight and environment-friendly fired bricks. *Constr. Build. Mater.* **2021**, *302*, 124385. [[CrossRef](#)]
61. Xing, X.; Rogers, H.; Zhang, G.; Hockings, K.; Zulli, P.; Deev, A.; Mathieson, J.; Ostrovski, O. Effect of charcoal addition on the properties of a coke subjected to simulated blast furnace conditions. *Fuel Process. Technol.* **2017**, *157*, 42–51. [[CrossRef](#)]
62. Rejda, M.; Pawłowski, P.; Rodź, A.; Ignasiak, K.; Helt, I. The Study of Influence of Fine Coal Fraction Addition to Coking Blend and Its Partial Briquetting on Coke Quality Parameters. In Proceedings of the Mineral Engineering Conference (MEC 2019), Kocierz, Beskid Mały, Poland, 16–19 September 2019; IOP Publisher: Bristol, UK, 2019; Volume 641.
63. 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](#)]

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64. Matsumura, T.; Ichida, M.; Nagasaka, T.; Kato, K. Carbonization Behaviour of Woody Biomass and Resulting Metallurgical Coke Properties. *Iron Steel Inst. Jpn. Int.* **2008**, *48*, 572–577. [[CrossRef](#)]
  65. Kaur, A.; Roy, M.; Kundu, K. Densification of Biomass by Briquetting: A Review. *Int. J. Recent Sci. Res.* **2017**, *8*, 20561–20568. [[CrossRef](#)]