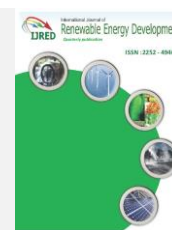




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Research Article

# The Effect of Wood Tar and Molasses Composition on Calorific Value and Compressive Strength in Bio-coke Briquetting

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**Abstract.** Biomass-based materials have the potential to replace conventional cokes for blast furnaces in the steel manufacturing study. Biomass as a renewable energy source can reduce the consumption of coking coal. The current challenge is saving fossil energy and waste management. The steelmaking industry with environmentally friendly processes and high energy efficiency is expected today. Many researchers have partially developed biomass as an alternative renewable resource to replace fossil fuels. This study aimed to determine the effect of composition the blending ratio of wood tar and molasses as a binder on the calorific value and compressive strength of bio-coke. The carbonization of redwood waste to produce high-quality charcoal was carried out at 500 °C with a kiln rotation speed of 20 rpm and a slope of 5°. The resulting charcoal showed a promising result with a 23.87 MJ/kg calorific value. The carbonization process of the redwood increased the fixed carbon value by up to 130% and the calorific value by 40%. The second part of this study focuses on bio-coke production by blending coking coal with redwood charcoal at 90:10 wt%. The coking coal and the redwood charcoal particle sizes were 40 and 50 mesh, respectively. A 15 wt% binder was added to increase the compressive strength of the bio-coke. The binder composition ratios of molasses: wood tar were 15:0, (12.5:2.5), and 10:5 wt%. The briquette was pressed using a cylinder die with a height: diameter ratio of 2.7:5.0 cm, then compacted up to 20 MPa followed by heating at 1100 °C for four hours. The bio-coke with a binder composition of 2.5 wt% wood tar + 12.5 wt% molasses produced a compressive strength of up to 5.57 MPa with a sulfur content of 0.8 wt% and produced a calorific value of 31.25 MJ/kg with an ash content of 9.6%. The study showed that the bio-coke produced meets some requirements for steelmaking industry.

**Keywords:** bio-coke, biomass, carbonization, charcoal, coking coal



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## 1. Introduction

Biomass is a renewable resource that can be converted to bio-coke and biofuel. Renewable energy resources are being continuously developed to replace dependence on fossil fuels. Biomass is a material derived from living organisms that contain carbon and oxygen, nitrogen, hydrogen, and trace amounts of other elements. Like fossil fuels, fuel from biomass also produces CO<sub>2</sub> through a combustion process. However, biomass fuel is known as carbon-neutral. Plants can absorb the CO<sub>2</sub> produced by biomass fuel. Carbon (C) is stored in wood tissue, and oxygen (O<sub>2</sub>) is released back into the atmosphere. Using biomass as an alternative energy resource is continuously being carried out. In the steel manufacturing industry, biomass has the potential to replace fossil fuels in blast furnaces. It can be blended with coking coal as fuel and partially replaced coal with biofuel in the pulverized coal injection (PCI) process (Norgate and Langberg, 2009).

Several countries—Brazil, Canada, Europe, the USA, and Australia—have many research institutes that focus on biomass to replace metallurgical coke (Wang *et al.*, 2013).

The physical and chemical properties of biomass as a precursor for the production of bio-coke, such as its high carbon content, low ash content, good compactness, compressive strength, and good co-firing characteristics, depending on its raw material and its processing. Raw biomass usually has a high moisture content of up to 30%, whereas the maximum moisture content of coke is 6%. One of the technologies used to improve the quality of biomass into bio-coke is pyrolysis (Wang *et al.*, 2013). Pyrolysis is the process of thermally decomposing biomass to produce solids (charcoal), liquids, and gases. If the desired product is solid (coke), the process is called carbonization. Under carbonization, the chemical properties of charcoal change compared to those of raw biomass. Increasing the carbonization temperature generally produces charcoal

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with a higher carbon content but a lower yield. Good-quality bio-coke has been produced using slow pyrolysis and pressure-assisted carbonation (Mansor *et al.*, 2018). The pyrolysis process of biomass decomposition begins at 350–400 °C and produces carbon-rich residues and volatile fractions rich in hydrogen. Its products are semicokes (char); tar, which consists of liquid hydrocarbons; gas; and light oil.

As a reducing agent in the metallurgical process for blast furnace application, bio-coke must have a fixed carbon content of above 85%, a gross calorific value of 28.47-30.15 MJ/kg, a maximum ash content of 10%, and a maximum sulfur content of 1.2% (Riazi and Gupta, 2016). Carbon content remains an essential factor in steelmaking because it is a carbon source for reducing iron oxide. The lower ash content of charcoal benefits hot metal production, as it will produce less slag. Previous researchers used 6 wt% of biochar at bio-coke synthesis for blast furnace applications (Rejdak *et al.*, 2020). In general, the ash content increased, but the compressive strength and calorific value decreased with increasing weight fraction of biochar added to the coal blending process with coking coal. This research analyzed coal blending's bio-coke ash content, compressive strength, and calorific value with a 10 wt% biochar composition. This study varied the composition of a mixture of wood tar and molasses as a binder to increase the compressive strength of coke from the minimum standard of 2.81 Mpa for blast furnaces (Riazi and Gupta, 2016) and the calorific value of bio-coke. Organic binders such as wood tar, molasses, and starch can be added to the briquette molding process (Amaya *et al.*, 2015; Florentino-Madiedo, Díaz-Faes and Barriocanal, 2020). This research focuses on the composition of the mixture (molasses: wood tar) as a binder to ensure that the bio-coke ash content, compressive strength, and calorific value meet the standard and efficiency of a blast furnace.

## 2. Materials and Methods

### 2.1. Materials

A certain 3 kg of redwood branches that size 1 cm was dried at 110 °C for 5 hours to reduce the moisture from the wood waste. Then the wood waste was carbonized through pyrolysis at 500 °C using a rotary kiln with a rotation speed of 20 rpm and a slope of 5° (Fig. 1).



**Fig 1.** Rotary kiln for the carbonization process

The rotary kiln was divided into four sections. The first and second sections had a temperature of 500 °C; the third section, 300 °C; and the fourth section, 200 °C. These temperature settings were intended to lower the temperature of the charcoal at the outlet of the rotary kiln.

### 2.2. Method

The coking coal and the redwood charcoal particle were 40-50 in mesh were blended at 90:10 wt% to synthesize bio-coke. Then a 15 wt% binder was added to the coal blending material to increase the compressive strength of the bio-coke. Three combinations of molasses: wood tar as binder ratios used to find out which would most significantly increase the compressive strength and calorific value of the bio-coke: 15:0, 12.5:2.5, and 10:5 wt%. The briquette process was performed in a cylinder die with a height: diameter ratio of 2.7:5.0 cm compacted at 20 MPa continues heated at 1100 °C for 4 h. The proximate and ultimate analyses were performed using standard ASTM D5142 and D5373-08 procedures. LECO TGA 701 was used as the proximate analyzer. The characteristics of coking coal can be seen in Table 1. This measurement is carried out with 3 repetitions using the sigma standard error analysis for finite elements.

The carbonized samples were subjected to chemical analyses such as ultimate and proximate analyses, calorific value analysis, hygroscopy, gravimetric thermal analysis, and Fourier-transform infrared spectroscopy (FTIR). Hygroscopic testing was conducted using an electric moisture analyzer (Kern MLB 50-30C) to obtain the equilibrium humidity value. Thermal analysis was performed to study changes in the material's physical properties with temperature changes. One of the thermal analysis techniques was used with thermal gravimetric analysis (TGA, 701 Shimadzu), which varies the weight as a function of the heating temperature. The changes in the structure and chemical composition of the biomass during its thermochemical conversion were analyzed using FTIR (IR Tracer-100 Shimadzu). The coke compressive strength (CCS) was mechanically tested using Japan's Borden process compressive strength tester. The inorganic element composition of the bio-coke ash was characterized using Bruker x-ray fluorescence (XRF) based on ASTM D 42326-04. The bio-coke surface appearance and porosity were characterized using a TESCAN VEGA 3 HiVac SEM.

**Table 1**

Characteristics of coking coal

Characterization	Coking Coal
Proximate (wt% <sup>db</sup> )	
- Fixed carbon	68.68
- Volatile matter	27.06
- Moisture	1.32
- Ash	4.26
Ultimate (wt% <sup>db</sup> )	
- C	81.92
- H	5.28
- N	1.82
- S	0.71
- O	6.01
Gross calorific value (MJ/kg <sup>db</sup> )	33.86
Net calorific value (MJ/kg)	32.67

### 3. Results and Discussion

#### 3.1 Biochar Production

The results of the biomass characterization before and after carbonization by the rotary kiln are in Table 2. The charcoal had high fixed carbon, low moisture, and ash contents. Thus, it can be used as a coke raw material. It also had low sulfur content, making it a good candidate for manufacturing blast furnace coke.

After the proximate analysis, the raw biomass sample had a fixed carbon content of 25.04 wt%. Previous research concluded that the wood carbon content was generally 15–20.5 wt% (Bridgwater, Czernik, and Piskorz, 2008). The insignificant difference in the carbon content was due to the type and parts of the wood used as the biomass. The raw biomass sample was carbonized to obtain charcoal with higher carbon content.

The biomass carbonization was carried out at 500 °C using a rotary kiln with a 20 g/min feeding rate. In the carbonization stage with limited oxygen, the devolatilization process occurred. The biomass was decomposing into a residue rich in carbon and a volatile fraction like hydrogen. The products of biomass carbonization were charcoal, gas, and tar, which are liquid hydrocarbons. This de-volatilization process was very effective because it increased the fixed carbon content up to 130% but low yield (33.95%). The carbonization result showed a blackish color that indicates the formation of carbon residues. Based on proximate analysis of the charcoal, the biomass carbonization resulted in carbon content of 58.14 wt%. The calorific value of the biomass also increased by 40%, from 17.12 MJ/kg to 23.87 MJ/kg.

One of the properties of biomass that must be considered is its moisture content. Biomass has natural properties, one of which is hygroscopicity. This property enables biomass to reabsorb moisture in the atmosphere (Ninov, 2010). Even though the biomass has been dried and placed in a room, it would still have moisture absorbed from the surrounding environment. Hygroscopic testing was performed to determine the biomass's equilibrium moisture content (EMC). The EMC value of the biomass decreased after carbonization, from 10.75% to 8.64%.

**Table 2**  
Characteristics of the carbonization sample

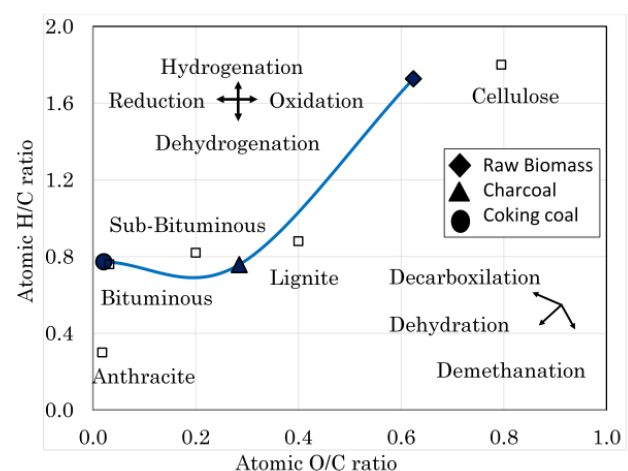
Characterization	Biomass 25°C	Biochar 500°C
Proximate (wt% <sup>db</sup> )		
- Fixed carbon	25.04	58.14
- Volatile matter	71.74	35.89
- Moisture	10.75	8.64
- Ash	3.22	5.97
Ultimate (wt% <sup>db</sup> )		
- C	50.28	76.76
- H	7.23	4.80
- N	0.41	0.89
- S	0.03	0.08
- O	38.38	11.50
Gross calorific value (MJ/kg <sup>db</sup> )	17.12	23.87
Net calorific value (MJ/kg)	15.43	22.83

The carbonization effectively removed the moisture and volatile content of the biomass. Van Krevelen's coalification diagram ranks the coal samples using the ultimate analysis data. The coal sample was confirmed to have been in the bituminous rank shown in the coalification diagram in Fig. 2. The redwood waste was in the biomass rank between cellulose and lignite.

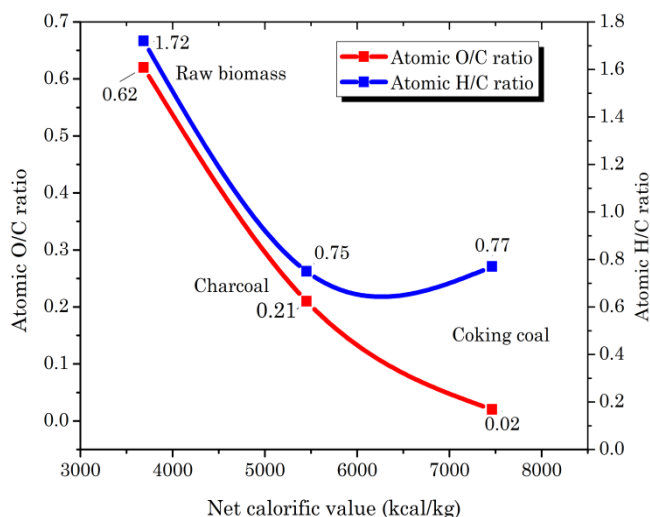
The product of the wood waste carbonization in the form of charcoal approached the sub-bituminous area in the coalification diagram. The quality of the charcoal was almost the same as that of the sub-bituminous coal due to the reduced levels of hydrogen and oxygen after the carbonization, which reduced the O/C and H/C ratios. The raw biomass had high levels of hydrogen and oxygen of 7.23 and 38.38 wt%, respectively. The carbonization of the biomass into charcoal reduced the hydrogen content to 4.80% and the oxygen content 11.5 wt%, but these are still higher than those of coking coal.

Figure 3 shows a graph of the correlation of the O/C and H/C ratios with the calorific value. The decreases in the oxygen and hydrogen levels increased the calorific value of the sample. The lower the O/C and H/C ratios were, the higher the fuel heating values were. The mechanism in Fig. 3 corresponds to the Van Krevelen coalification band from a previous study (McKendry, 2002). The oxygen losses during the heating to up to 500°C reduced the equilibrium water content. This phenomenon shows that the maximum effectiveness of the devolatilization exceeded 48%. Thus, it is clear that the devolatilization increased the calorific value from 3686.30 kcal/kg to 5452.20 kcal/kg. The high heating value of the biomass makes it a high-quality fuel.

Wood tissue is composed of natural polymer materials in lignin, cellulose, and hemicellulose. These polymer components are the primary components of the wood cell wall, in addition to extractive substances in the form of organic and inorganic compounds. During pyrolysis, biomass is decomposed from wood to charcoal. FTIR analysis is one of the methods of measuring changes in the structure and chemical composition of biomass during its thermochemical conversion. The FTIR spectroscopic method is based on differences in the absorption of infrared radiation.



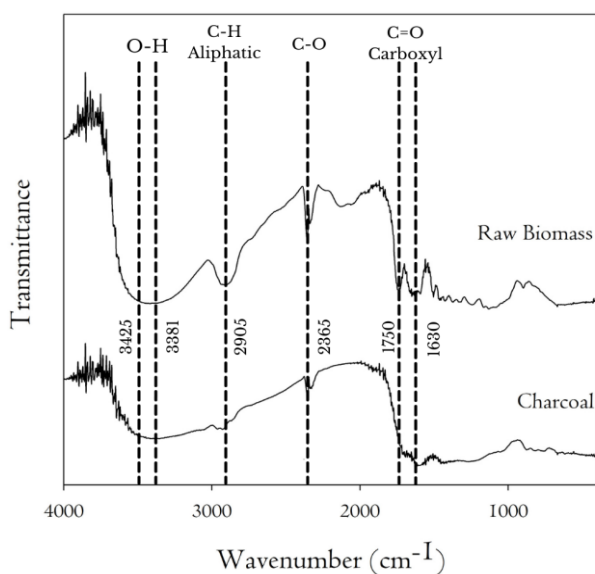
**Fig. 2** Correlation of the atomic O/C and H/C ratios based on the Van Krevelen coalification band



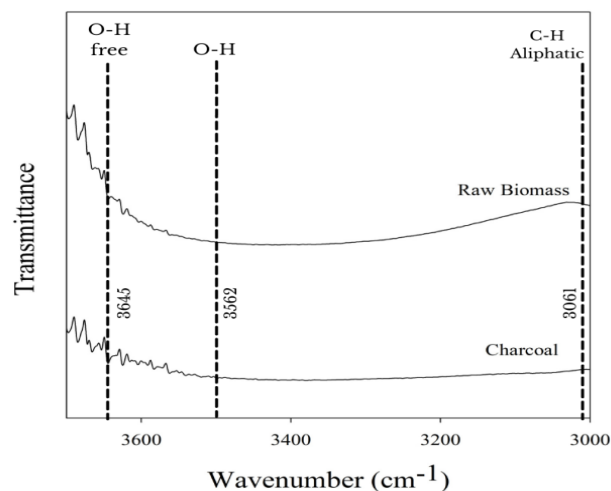
**Fig. 3** Correlation of the calorific value of the biomass with its atomic O/C and H/C ratios.

As shown in Table 2, biomass carbonization increased the fixed carbon and calorific values but decreased the volatile matter by 49.97%. The decrease in the volatile matter was confirmed by releasing functional groups like OH, C-H, C-O, and C=O during the carbonization. Many volatile matters from lignins such as phenol were lost as CO, CO<sub>2</sub>, and CH<sub>4</sub> at 500 °C. OH and CH<sub>3</sub> decreased gradually with increasing temperature (Huang et al., 2014). The results of the FTIR analysis are plotted in the graph in Fig. 4.

The characteristics of biomass carbonization can be seen from the difference in the shape of the biomass curve before and after the carbonization. The hydrogen bonds, OH group, and OH-free groups in the raw biomass are visible in 3000-3700 cm<sup>-1</sup> with a peak of 3425 cm<sup>-1</sup>. The charcoal samples have a smaller hydrogen bond absorption area than the raw biomass at the peak of 3381 cm<sup>-1</sup>. The biomass sample can be seen releasing the OH group during the pyrolysis.



**Fig. 4** FTIR spectrum of the biomass



**Fig. 5** FTIR spectrum of the 3700-3000 cm<sup>-1</sup> biomass

The spectrum at 3700-3000 cm<sup>-1</sup> in Fig. 5 shows the change in the hydrogen bonding. Several peaks were detected in the hydrogen bond absorption area in the raw biomass. The OH functional group was no longer visible at the peak of 3562 cm<sup>-1</sup>, and the OH-free uptake area at the peak of 3645 cm<sup>-1</sup> decreased after the carbonization. In addition to the OH group, the aromatic hydrogen (C-H) group was detected at the peak of 3061 cm<sup>-1</sup> but was lost during the pyrolysis.

Thermal analysis was performed to study the changes in the material's physical properties with temperature control. One of the thermal analysis methods is TGA. TGA is a measurement method that uses weight loss (%) to function time and the heating temperature. This characterization was carried out to determine how much mass the charcoal sample lost (through steam emission) or gained (through gas fixation). This method can determine decomposition behavior, thermal degradation, and chemical reactions that involve changes in the mass of matter due to adsorption, desorption, and chemical kinetics. Each shape of the TGA curve has a meaning.

The data from the TGA analysis of the charcoal in terms of weight loss (%) against time and temperature are shown in Fig. 6. From the TGA analysis, there are several stages of the combustion process. The moisture evaporation stage (a) is under 140 °C. The combustion began with the decomposition or release of the volatile matter (b-c) at 279.8–950 °C. The charcoal mass decreased significantly (b) until the temperature reached 950 °C, at which the moisture and volatile matter contents decreased.

Meanwhile, the fixed carbon and ash contents increased. The charcoal samples were still decomposed but with a lower mass reduction rate when the temperature was kept at 950 °C for a few minutes and then lowered to 593.9 °C (c). The charcoal was oxidized to ash at the second ignition stage (d). This combustion occurred at the temperature range of 693–750 °C.

The charcoal sample was lost in mass when it was oxidized to ash. Then its burning was stopped, marked by a constant sample period that meant there was no more reaction. Fig. 6 shows that the TGA analysis curve for the charcoal correlates with the increase in the bio-coke ash during the heating process at 1100 °C. The total burning time of the charcoal until it was fully decomposed was 1.38 hours, and the yield was 4%.

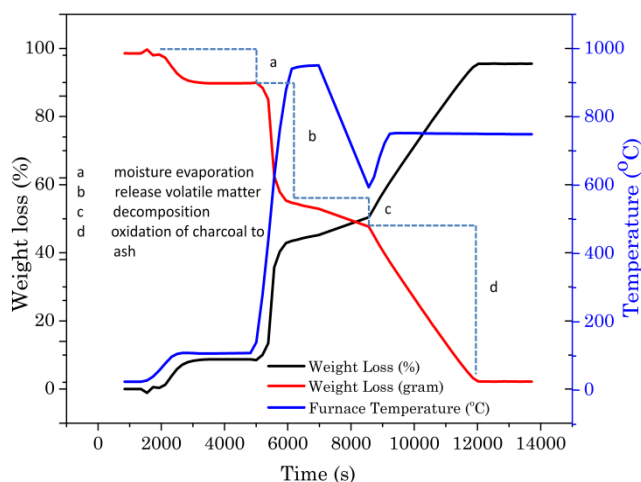


Fig. 6 TGA analysis curve of the charcoal

This condition illustrates that the amount of charcoal blended with the coal must be controlled because it has the potential to increase the ash content significantly. When charcoal is blended with coking coal, it partly replaces the coking coal. It contributes to an increase in the fixed carbon and calorie contents, but the charcoal to be added is limited to 10 wt% because the ash content of bio-coke is a maximum of 10 wt% (Gupta, 2003; Riazi and Gupta, 2016). The slightly critical ash performance confirmed the feasibility of predicting the biomass quality index (Liu *et al.*, 2020). Bio-coke synthesis is expected to be effective at a temperature of 1100 °C with a holding time of 4 hours.

### 3.2 Bio-coke Production

The binder function strengthened the briquettes. A previous study reported that 15 wt% tar is very effective as a binder in the manufacture of coke briquettes (Montiano, Faes, and Barriocanal, 2016). Some researchers use various binders to increase the strength of the material. Among these binders are starch (5–10) wt% and cellulose (15–25) wt% (Raju *et al.*, 2014), wheat, potato-based starches, and cellulose derivatives (Rejda *et al.*, 2020). The use of up to 15 wt% molasses as a binder significantly increases the strength of briquettes (Zhong *et al.*, 2017). Tar, molasses, and organic binders (starch and cellulose) serve to bind and strengthen briquettes. Coal tar and pitch were also binders and improved coal's caking properties and coking strength (Nomura and Arima, 2017).

The addition of wood tar affected the strength of the bio-coke, as shown in Fig 7. The compressive strength of the bio-coke with 2.5 wt% wood tar increased compared to the bio-coke without wood tar. The coking value of the wood tar was 28.7–33.7%, but it was below that of the coal tar pitch (CTP), which was 54.1% (Lis *et al.*, 2016). The addition of 5 wt% wood tar reduced the compressive strength of the bio-coke. The wood tar's water content and compounds with low boiling points can affect the characteristics of the binder such that the particles between the coal and the charcoal would not bind to each other. This condition is supported by the indications of fissure in the pressed briquettes after 5 wt% wood tar was added to them, which were not seen after the 2.5 wt% wood tar was added to the briquettes. These show that a pretreatment process has to be done to remove the water and low boiling point

compounds. The addition of 5 wt% of tar decreases the coke strength because the specific gravity of tar (1.1 g/cm<sup>3</sup>) is lower than molasses (1.22 g/cm<sup>3</sup>). Thus, adding the 5 wt% tar to the sample made the sample more difficult to compact and bind. The yield of the bio-coke was 53.7 wt%, and of the briquette sample before it was heated, 54±1.3 g, and after it was heated to 1100 °C, 29±1.6 g.

The addition of a binder also affects the chemical properties of bio-coke and its mechanical properties. The composition of the binder plays an essential role in the characteristics of the bio-coke and thus, determines its feasibility as a substitute for blast furnace coke. This research combined two types of binders: molasses and wood tar. Molasses is an industrial liquid waste of sugar cane that contains a monosaccharide compound (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>), and wood tar is an aromatic hydrocarbon compound from biomass carbonization products.

The compressive strength was affected by the diameter of the briquettes. When the diameter of the briquettes was reduced, the compressive strength increased (Mizuno *et al.*, 2016). Table 3 shows the proximate and ultimate analyses based on different binder compositions. They demonstrate that the bio-coke with binders of 0, 2.5, and 5 wt% had fixed carbon contents above 87 wt%. The fixed carbon content of blast furnace coke is 85–88 wt% (Gupta, 2003; Riazi and Gupta, 2016).

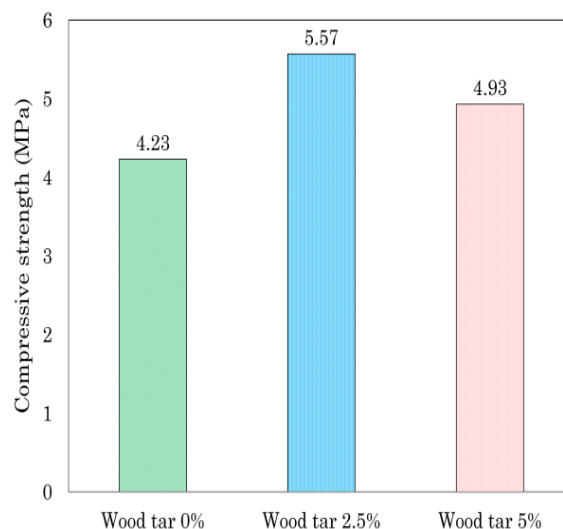


Fig. 7 Coke compressive strength diagram based on the addition of wood tar

Table 3  
Bio-coke characteristics

Sampel	Proximate (wt% <sup>db</sup> )			Ultimate (wt% <sup>db</sup> )					MJ/kg	
	M	A	VM	FC	C	H	N	O	S	NCV
BC0T	1.23	10.8	2.11	87.1	82.9	0.5	1.2	3.8	0.8	29.66
BC2.5T	1.59	9.6	1.91	88.5	85.4	0.4	1.2	2.6	0.8	31.25
BC5T	1.66	9.8	1.94	88.3	84.4	0.4	1.2	3.4	0.8	29.96

M:moisture; A:ash; VM:volatile matter; FC:fixed carbon; NCV:net calorific value

The bio-coke with 0 wt% wood tar had the lowest fixed carbon content of 87.1 wt% but the highest volatile matter. The volatile matter came from the coal, binders, and charcoal. The molasses binder had a higher volatile matter (88.4 wt%) than the wood tar (67.9 wt%) and a low fixed carbon of 6.1 wt% (Amaya *et al.*, 2015). The binder's fixed carbon and volatile matter contents significantly affected the quality of the bio-coke.

The bio-coke with 0 wt% wood tar did not meet the quality standards for blast furnace application because sample BC0T has the highest ash content. The ash requirement for coke blast furnace was <10 wt%, whereas sample BC0T has ash content reached 10.8 wt%. The ash content in coking coal (4.26 wt%) increased after blending with the biomass. The ash from the charcoal and the coal contributed to the increase in the ash content of the carbonized bio-coke. Based on previous studies, the molasses had 1.3 times higher ash content than wood tar (Amaya *et al.*, 2015), so the bio-coke without tar had the highest ash content. The sulfur content of the bio-coke was 0.8 wt%, which meets the quality standard for blast furnace coke of <1%. The caloric value of the coal reached 33.86 MJ/kg but decreased after it was blended with the biomass. The caloric value of the bio-coke exceeded the calorific standard for coke for the blast furnace, which is > 28.47 MJ/kg (Riazi and Gupta, 2016).

The synthesized bio-coke was tested to determine the strength of the coke. The coal blending with the redwood charcoal and the 15 wt% binders (12.5 wt% molasses to 2.5 wt% wood tar) resulted in the highest compressive strength of 5.57 MPa. In our previous study, the mixture of coking coal with 50 mesh charcoal at 90:10 wt% with a 15 wt% binder (molasses and wood tar) was added, resulting in a bio-coke compressive strength up to 4.87 MPa (Mursito, Muharman, and Yustanti, 2020). Previous researchers have reported that charcoal with too fine particles resulted in low compressive strength (MacPhee *et al.*, 2009; Mursito, Muharman, and Yustanti, 2020). Fig. 8 shows the correlation between the bulk density and the compressive strength of bio-coke on various binder compositions.

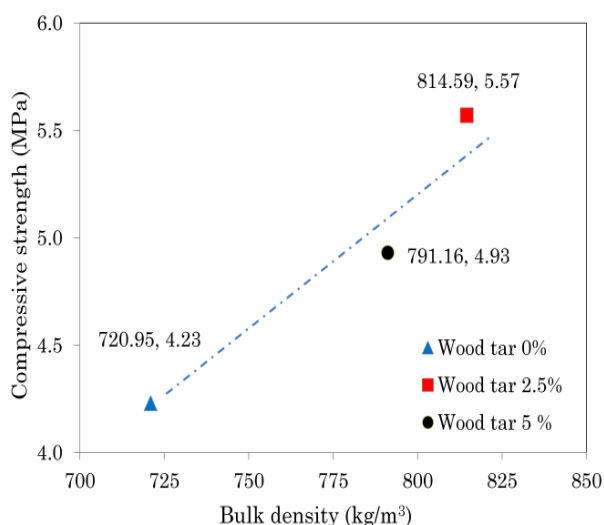


Fig. 8 Correlations of bulk density and coke compressive strength

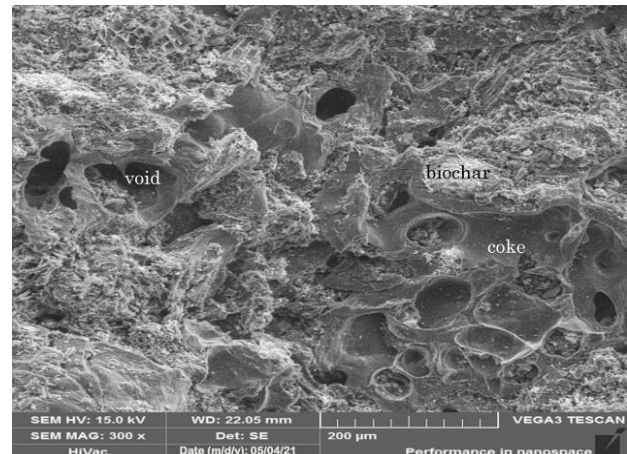


Fig. 9 Microphotograph of the bio-coke, 300x magnification

Coke with a low bulk density was identified as having more cracks and pores in its matrix (Xing *et al.*, 2017). The CCS of the disintegrated coke increased with the increase in the bulk density of the bio-coke. The Bio-coke sample with the highest bulk density and CCS was that to which a binder with 2.5 wt% wood tar + 12.5 wt% molasses was added. The high bulk density indicated that particle density increased, so fewer gaps and porosity were formed. Bio-cokes with more gaps and greater porosity break more easily when a load is applied to them. The bio-coke with the highest bulk density of 814.59 kg/m<sup>3</sup> could retain loads better than the bio-coke with a bulk density of 720.95 kg/m<sup>3</sup>. Bio-coke with a high density usually has high compressive strength to be used as an alternative to coal coke (Kamal Baharin *et al.*, 2020).

Fig. 9 shows the microphotograph of the bio-coke at 300x magnification at the binder composition of 2.5 wt% wood tar mixed with 12.5 wt% molasses. The strength of the bio-coke was influenced by the type (Yustanti *et al.*, 2021), size of the biochar, and composition of the binder. The bio-coke with a binder composition of 2.5 wt% wood tar + 12.5 wt% molasses had a compressive strength of 5.57 MPa.

The decrease in the moisture from the biochar to the bio-coke reduced the voids between the bio-coke particles. The swelling properties of the coking coal, combined with the number of pores heated at 1100 °C, resulted in a better plastometric layer. Also, the coking coal caking index increased (Xuehong *et al.*, 2019).

Ash is a mineral oxide produced when coal or coke is burned. A high ash content results in lower coke energy, resulting in decreased blast furnace productivity. Maximum ash content for coke in blast furnace application has 9–10% (Riazi and Gupta, 2016). Coke ash usually contains acidic compounds (SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>), bases (CaO and MgO), bases (K<sub>2</sub>O and Na<sub>2</sub>O), and sulfur. Other compounds in coking ash are sulfate (SO<sub>4</sub><sup>2-</sup>), sulfide (S<sup>2-</sup>), carbonate (CO<sub>3</sub><sup>2-</sup>), and titanium oxide (TiO<sub>2</sub>) (Olofsson, 2017).

Table 4 shows the inorganic compounds of the bio-coking ash obtained from the XRF analysis. The dominant compounds detected by XRF were SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and CaO. Alkali metals such as potassium (K) affect operations in blast furnaces. The increase in the alkaline content in blast furnace operation has been shown to accelerate the gasification of coke. Oxides from iron (Fe<sub>2</sub>O<sub>3</sub>), calcium (CaO), and potassium (K<sub>2</sub>O) play a role in reducing the

melting point of ash. In turn, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> increase the melting point of ash (Golovko, 2015). The comparison of the acid/base oxides (Al<sub>2</sub>O<sub>3</sub>+SiO<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub>+CaO+MgO) shows the ash fusion temperature and the blast furnace efficiency. The lower the acid/base ratio, the lower the ash fusion temperature, resulting in less slag volume. Such conditions increase the efficiency of the furnace. The acid/base ratios of the bio-coke with 0:2.5 and 0:5 wt% wood tar were 7.52:7.44 and 7.52:7.56, respectively. The bio-coke met the smallest ratio of 7.44 with 2.5 wt% wood tar.. All types of bio-coke with various binder compositions had a constant CaO/SiO<sub>2</sub> ratio of 0.05, consistent with previous studies (Gupta, 2003; Mousa *et al.*, 2016). The basicity index (BI), the total ash content and the ratio of the base to the acidic oxide were calculated in all the bio-coke compositions.

$$BI = \text{ash} \frac{Fe_2O_3 + MgO + CaO + Na_2O + K_2O}{SiO_2 + Al_2O_3}$$

According to a previous researcher, the highest BI index was 1.61 for the bio-coke with 2.5wt% wood tar, which had the highest reactivity to CO<sub>2</sub> (Montiano *et al.*, 2014).

One way to increase the efficiency of the blast furnace is to reduce the volume of slag by increasing the alkaline content, such as the presence of the elements Ca and Fe. Table 4 shows that the bio-coke sample with 2.5 wt% wood tar had the highest Fe content of 7.85 wt% compared to the samples without wood tar and with 5 wt% wood tar, whose Fe contents were only 7.79 wt% and 7.73 wt%. These suggest that producing bio-coke with 2.5 wt% wood tar is advantageous in blast furnace operations. Several requirements for blast furnace application were met by bio-coke with an added binder of 2.5 wt% wood tar + 12.5 wt% molasses). The low CCS of the bio-coke in this study can be increased by increasing the compaction pressure from 20 to 250 MPa because it effectively increases the durability of briquettes (Kaur, 2017).

**Table 4**  
Characterization of the bio-coke ash using XRF

Compound (wt%)	Wood tar 0%	Wood tar 2.5%	Wood tar 5%
Al <sub>2</sub> O <sub>3</sub>	31.91	31.98	32.04
SiO <sub>2</sub>	50.62	50.66	50.71
MgO	0.81	0.83	0.8
Na <sub>2</sub> O	0.58	0.59	0.61
Fe <sub>2</sub> O <sub>3</sub>	7.79	7.85	7.73
SrO	0.13	0.12	0.14
P <sub>2</sub> O <sub>5</sub>	0.72	0.7	0.71
CaO	2.38	2.43	2.41
K <sub>2</sub> O	1.61	1.58	1.59
SO <sub>3</sub>	1.08	1.09	1.1
TiO <sub>2</sub>	1.6	1.59	1.61
LOF	0.77	0.58	0.55

#### 4. Conclusion

Carbonization of biomass increases fixed carbon and calorific value very significantly. The addition of biochar in coal blending is possible to reduce dependence on fossil fuels and reduce CO<sub>2</sub> emissions. The addition of wood tar increases the biocoke's fixed carbon and mechanical strength. Bio-coke with a binder composition of 2.5 wt% wood tar and 12.5 wt% molasses fulfills several criteria for the steelmaking industry.

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