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Characterization of Biochar Briquettes from Coconut Shell with the Effect of Binder: Molasses, Cow Manure and Horse Manure

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Abstract: The utilization of coconut shells as fuel still has several obstacles, including non-uniform size, low heating value, and low density. Pyrolysis of coconut shells into biochar is used to increase the calorific value and minimize the formation of smoke when burning. Biochar briquetting is needed to increase energy density and uniform size. The purpose of this study was to determine the effect of the type of binder and the concentration on the characteristics of biochar briquettes. The binder used were molasses, cow manure, and horse manure. Molasses is most suitable for use as a binder because it has sticky properties and sufficient moisture content. The ratio of biochar: molasses 70:30 produces briquettes with the best characteristics. In the drop test with a height of 1 m and 1.8 m, biochar briquettes with molasses binder still have 99% size stability.

Keywords: biochar, slow pyrolysis, briquettes, binder molasses

1. Introduction

Agricultural and livestock waste in developing countries has not been used optimally, most of it is only disposed of in landfills[1)]. Waste should be processed into useful materials and could reduce environmental pollution such as biofuels[2)]. Biomass has several disadvantages for direct use as fuel such as high moisture content, low heating value, and low energy density [3)]. Therefore, efforts are needed to improve the quality of biomass as an energy source by pyrolysis and processing pyrolysis products into briquettes. Pyrolysis is the thermal conversion of biomass to increase its calorific value[4)]. Pyrolysis consists of fast pyrolysis, intermediate pyrolysis and slow pyrolysis, which results in different product characteristics. Fast pyrolysis is carried out at a temperature of 500°C with a heating rate of more than 1000°C/s and solid residence time under 1 second. Meanwhile, intermediate pyrolysis is run at a temperature of 400-500°C with a heating rate of 1-1000°C/s and a solid residence time of 1-30 minutes. Slow pyrolysis is carried out at a temperature of 300°C to 500°C with a heating rate below 1°C/s and solid residence time from hours to days. Slow pyrolysis will produce biochar as the majority product[5)]. Biochar from pyrolysis can also be used as activated carbon for various applications[6-11)]. Compression of biomass or biochar into briquettes/ pellets is used to increase energy density[12)].

In the briquetting of coconut shell char required binder to improve physical and combustion characteristics of biochar briquettes[13, 14)]. Withot binder, biochar briquettes will crumbe more easily. Briquette binder affects the density, compressive resistance, calorific value, moisture content and ash content. Cassava starch and wheat starch are usually used as binders[15, 16)]. The use of this binder competes with food needs, so it is necessary to explore other materials that can be used as binders. According to a review of the literature, there has been no research employing cow and horse manure as a binder for briquettes generated from coconut shell char. Molasses, cow manure and horse manure have sticky characteristics that are considered suitable for use as a binder in the briquetting, not as the main component in the manufacture of briquettes[17, 18)]. Binders such as molasses and cow and horse manure are used to attract water and build a compact framework. With the addition of a binder, the particle arrangement will be better and denser after the pressing process. The heating value (HHV) of molases is 14 MJ/kg[19)], cow manure (dry basis) is 15-16 MJ/kg[20, 21)], while horse manure is 15-17.5 MJ/kg[22)]. The heating value of coconut shell is 18-20 MJ/kg, while coconut shell biochar has a heating value of 23-24 MJ/kg[23)]. In addition to briquette binders, molasses and animal dung can be processed into composites to increase combustion properties[15)]. Briquettes can be used directly for combustion in stoves and as raw materials for the gasification process[24-26]. Biochar briquettes can be used as raw material for gasification to produce tar-free syngas, a high H_2/CO ratio and reduce CO_2 emission[25]. Syngas with high H_2/CO ratio can be used as raw material for chemical synthesis such as methanol, DME etc[27]. The purpose of this study was to characterize briquettes from biochar using several binders: molasses, cow manure, and horse manure.

2. Material and method

2.1 Material

Coconut shells, horse manure, cow manure, molasses were obtained from Magetan, East Java, Indonesia. Coconut shells were cleaned from the rest of the coconut fiber, then sun-dried for a day. The proximate and ultimate of coconut shell are presented in Table 1. The moisture content of the molasses used was 20%, while cow and horse manure had moisture contents of 80% and 75%, respectively (without pre-treatment).

2.2 Pyrolysis of coconut shell

6 kg of coconut shell was put into the autothermal pyrolyzer with diameter of 35 cm and a height of 43 cm. Pyrolysis was carried out by burning part (about 5%-10%) of the coconut shell until the pyrolyzer temperature reached 600°C, immediately the pyrolyzer was closed so that it was airtight for 24 hours. Separate the biochar from the coconut shell and grind it using a miller and sieve it on a 50 mesh size.

Table 1. Proximate and ultimate analysis of Coconut shell

Characterization of Coconut Shell		
1	Proximate analysis (adb)	
	Moisture	10.66%
	Volatile matter	69.89%
	Fixed Carbon	19.65%
	Ash	0.80%
2	Ultimate analysis (adb)	
	Carbon	48.10%
	Hydrogen	6.47%
	Oxygen	43.72%
	Nitrogen	0.80%
	Sulfur	0.11%
3	Heating value, HHV (kJ/kg)	18376

2.3 Production of briquettes

Briquetting was done by mixing 35 grams of biochar with a binder in certain variations then the dough was put into a briquette mold with the size of 4 cm x 4 cm x 7 cm (length x width x height) (Fig. 1) and pressed with a pressure of 3.5 tons/in^2 using a hydraulic press and hold for 10 minutes. The biochar briquettes were dried in an oven at 60°C for 24 hours. Experiments were carried out on mixing biochar with various binder concentrations to determine the optimum composition as presented in Table 2.

Table 2. Biochar-binder ratio

Variation	Biochar (gram)	Binder (gram)		
		Molasses	Cow Manure	Horse Manure
72%:28%	35	14	-	-
72%:28%	35	-	14	-
72%:28%	35	-	-	14
70%:30%	35	15	-	-
70%:30%	35	-	15	-
70%:30%	35	-	-	15

2.3 Briquettes Characterization

2.3.1 Moisture

The method of testing the water content of briquettes is in accordance with SNI-06-3730-1995. Drying was carried out at a temperature of 105°C in the oven for 24 hours. Calculation of water content is as follows

$$\text{Moisture } (\%) = \frac{\text{b}-\text{c (gram)}}{\text{b}-\text{a (gram)}} \text{ x } 100\ \% \qquad (1)$$

a = empty cup weight (gram)
b = cup weight + sample before drying (gram)
c = cup weight + sample after drying (gram)

Fig. 1: Briquette Mold

2.3.2 Density

The density of briquettes was determined by weighing the briquettes, measuring the length, width, and height of the briquettes, and calculating the volume of briquettes according to ASTM D2395-17.

2.3.3 Drop test

The drop test aims to determine the strength of the briquettes. The mass of the briquettes to be tested was measured first. Briquettes were lifted and dropped from a height of 180 cm according to ASTM D440-49 procedure. The remaining briquettes (large pieces) were weighted. The calculation procedure related to the drop test uses the formula:

Size stability % = (100 x s)/S (2)

Friability % = 100 – size stability (3)

S= weight of briquettes before dropping (gram)

s = weight of briquettes after dropping (gram)

2.3.4 Combustion rate

The combustion rate test was carried out by burning the briquettes into ashes, then calculating the burnt briquette weight and burning duration. The weight of the burned briquettes was calculated from the initial weight of the briquettes minus the weight of the ash resulting from the combustion. Burning duration was measured using a stopwatch. The equation used to determine the rate of combustion is as follows.

$$\text{combustion rate (g/s)} = \frac{\text{burnt briquette weight (g)}}{\text{burning duration (s)}} \quad (4)$$

3. Result and discussion

3.1 Pyrolysis

The temperature of the pyrolyzer is measured to reach 500-600°C during the autothermal pyrolysis process, which begins with a partial combustion starter. The pyrolyzer is then closed to prevent air from entering, and the temperature decreases at a rate of less than 1°C/s. To maximize the pyrolysis process, the pyrolyzer is left for one day. This pyrolysis process is slow pyrolysis. The lower heating rate will produce biochar as the main product, while at a higher heating rate, it will tend to produce pyrolysis oil or tar. The heating rate affects the composition and yield of the pyrolysis process. The yield of the pyrolysis products are presented in Table 3. The results of the pyrolysis process obtained a yield of 21.9% of the amount of coconut shell 30 kg.

Table 3. Coconut shell pyrolysis yield

Run	Coconut shell feed (kg)	Biochar (kg)	Yield
1	6.02	0.96	15.95%
2	6.02	1.23	20.43%
3	6.02	1.39	23.09%
4	6.02	1.49	24.77%
5	6.12	1.55	25.33%

3.2 Briquetting

In the early stages, the levels of molasses-based binders were investigated. There are four composition levels: low (83:17), medium (72:28 and 70:30), and high binder content (54:46). The mixture of biochar: molasses 83:17 obtained brittle briquettes (Fig. 2(a)), while the mixture of biochar: molasses 54:46 obtained flabby briquettes (Fig. 2(d)). At a mixture of 72:28 and 70:30, briquettes with physical quality are stronger and more stable (Fig. 2(b) & (c)). After pressing, briquettes with a medium binder content are more stable. Then it was tested on different types of binders. Briquettes on a mixture of biochar with a binder of molasses, cow manure, and horse manure are presented in Fig. 3.

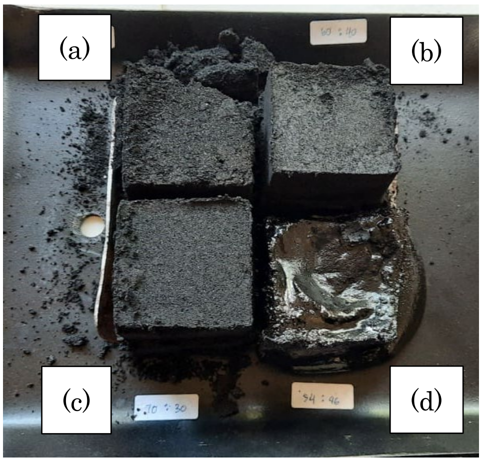
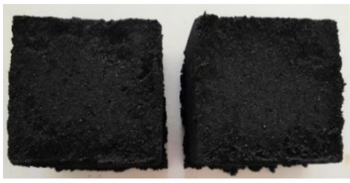
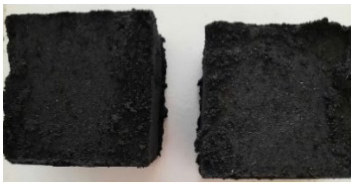


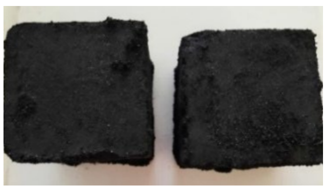
Fig. 2: Briquette with biochar: molasses (a) 83:17 (b) 72:28 (c) 70:30 (d) 54:46



(a)



(b)



(c)

Fig. 3: Biochar briquettes with binder at variation 70:30 (a) molasses (b) cow manure (c) horse manure

3.3 Moisture content

The moisture content of briquettes affects the calorific value. In general, the lower the moisture content, the higher the calorific value of the briquettes. Biochar has high hygroscopic properties, so it is necessary to measure the water content. Hygroscopic properties are inverse to the strength of briquettes, so the moisture content of the mixture of biochar and binder needs to be studied. Measurement of the moisture content of briquettes on various binders is presented in Fig. 4.

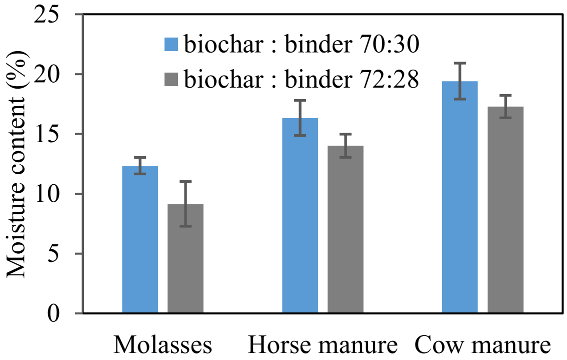


Fig. 4: Moisture content of briquettes at variations in binder concentration

Based on the measurement of water content in biochar briquettes, the highest water content was obtained by 19.41% from a mixture of biochar with cow manure binder at a concentration of 30%. The lowest water content of briquettes is found in molasses binder at a concentration of 28% with a moisture content of 9.15%. Molasses is suitable for use as a binder in briquettes because molasses has a sticky nature with a low moisture content of 15% – 25% [28]. While the water content of cow manure is 80% and horse manure is 73%.

3.4 Density

The higher the density of the briquettes, the longer the effect on the combustion time. Measurement of the density of briquettes on the variation of the binder as shown in Fig. 5. Based on the measurements, the highest density of 0.85 gram/cm^3 was obtained in molasses binder briquettes at a concentration of 30%. The lowest density of 0.65 gram/cm^3 was found in cow manure binder briquettes with a concentration of 28%.

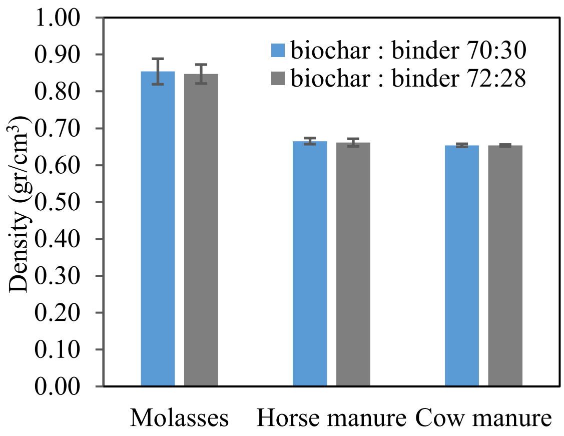


Fig. 5 Density of briquettes at variations in binder concentration

Biochar briquettes from coconut shells are still in accordance with the ASTM D2395-17 standard. The briquette density value according to ASTM D2395-17 is a maximum of 1 gram/cm^3 [29]. This is because the bond between coconut shell biochar powder is more cohesive and stronger affects the homogeneity of the briquette constituents.

3.4 Drop test

Drop test as an index of the destruction of briquettes, the degree of destruction or release of briquette particles due to impact after being dropped at the height of 1.8 meters. Drop test values were analyzed from size stability and friability (lost particles). The smaller the drop test value means, the less mass is lost. The maximum friability limit (lost particles) is <4% [30]. The results of the drop test of coconut shell biochar briquettes as presented in Table 4. Molasses has a higher adhesion than manure in the production of biochar briquettes. The high adhesion is due to the presence of hydroxyl groups in the molasses. It causes briquettes with molasses binder to stick more tightly between the particles. So that the resulting briquettes are still strong after a drop test. Briquettes made from manure are weaker because their adhesive power is lower.

Table 4. Drop test briquettes with variations in binder concentration at the height of 1 Meter

Biochar - Binder ratio	Binder	Size stability	Friability
70 : 30	Molasses	99.28%	0.72%
	Horse Manure	79.28%	20.72%
	Cow Manure	62.10%	37.90%
72 : 28	Molasses	99.28%	0.72%
	Horse Manure	59.27%	40.73%
	Cow Manure	48.45%	51.55%

The friability test on molasses is still below 4% on the drop test at 1 meter for molasses binder concentration, both 30% and 28%. To ensure the best durability and strength of the briquettes according to ASTM D440-49, drop them at the height of 1.8 meters, as shown in Table 5. Based on the drop test of molasses binder biochar briquettes with a height of 1.8 meters, the concentration of particles lost at 30% concentration was 0.59% and at 28% concentration was 1.44%. These results indicate that the briquettes have complied the ASTM D440-49.

Table 5. Drop test briquettes with molasses binder variations at the height of 1.8 Meters

Binder	Biochar - Binder ratio	Size stability	Friability
Molasses	70 : 30	99.40%	0.59%
Molasses	72 : 28	98.56%	1.44%

3.5 Combustion rate

Test the rate of combustion briquettes to determine the effectiveness of briquettes as fuel. The combustion rate test was carried out by measuring the length of time the briquettes burned to ashes. The longer the briquettes burn to ashes, the better the quality and efficiency of the briquettes. The rate of combustion of briquettes with variations in the concentration of binder is presented in Fig. 6. The highest combustion rate was obtained from briquettes with horse manure binder at a concentration of 30% at 0.197 g/minute. While the lowest combustion rate was obtained in briquettes by binding cow manure at a concentration of 28% at 0.162 g/minute. Briquettes with horse manure binder have a faster combustion rate because the composition inside affects the diffusion of oxygen to the fuel's surface and pore matrix, resulting in a higher combustion temperature and faster oxidation[22). According to Cong et al. (2019), horse manure still contains organic content and lignocellulose, which will easily degrade at temperatures ranging from 200 to 400 degrees Celsius, causing the weight to drop by up to 80%[31). Another factor influencing the rate of combustion is the high volatile matter component in horse manure, which is more than 50%, making the briquettes more combustible and increasing the rate of burning[32). According to Liu's (2021) experiment on the characteristics of burning briquettes using thermogravimetric analysis, the heating rate has a major influence on improving combustion performance[33). A high volatile content can assist in increasing the heating rate. As a result, the combustion rate of briquettes containing horse manure was higher than that of the others.

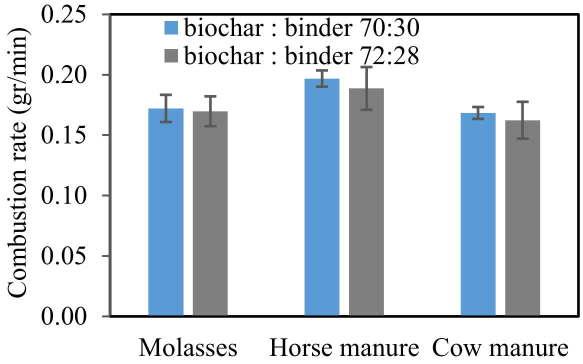


Fig. 6 Combustion rate of briquettes at variations in binder concentration

3.6 Water boiling test

The Water Boiling Test is a rough simulation of the cooking process to determine the quality of the heat energy of biochar briquettes transferred to cooking utensils compared to using a general cooking stove. The boiling time test was carried out by measuring the boiling time of 1000 ml of water on a biomass stove with biochar briquettes as fuel. The water boiling test on combustion briquettes at variations in binder concentration is presented in Fig. 7.

The boiling time of water using molasses binder briquettes is shorter than the concentration of binder in cow manure and horse manure. The slowest time on horse binding briquettes with a concentration of 28% was 19 minutes and 47 seconds. Meanwhile, the shortest time for molasses binder briquettes with a concentration of 30% was 13 minutes and 3 seconds. The concentration of the binder affects the density and calorific value of the briquettes. Horse manure binder briquettes and cow manure binder briquettes have brittle resistance when put into a biomass stove. The same amount of briquettes placed in the gasification stove has a different heating value for each variation of the binder, resulting in a different boiling time of water.

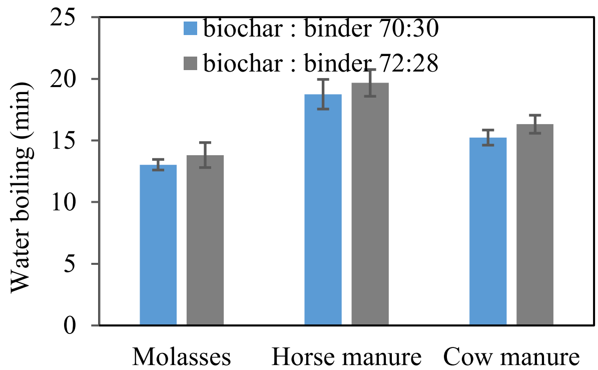


Fig. 7 Water boiling test on combustion briquettes at variations in binder concentration

4. Conclusion

The type of binder affects the characteristics of biochar briquettes. Molasses is most suitable for use as a binder because it has sticky properties and sufficient moisture content. The ratio of biochar: molasses 70:30 produces briquettes with the best characteristics. This mixture produces briquettes with the best size stability, density, and water boiling test. Briquettes' most essential properties are their size stability and combustion process, which are reflected by the rate of degradation of the briquettes as well as their volatile and moisture content.. In the drop test with a height of 1 m and 1.8 m, biochar briquettes with molasses binder still have 99% size stability.

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