## Jurnal Presipitasi

Media Komunikasi dan Pengembangan Teknik Lingkungan e-ISSN: 2550-0023

#### Original Research Article

# The Effect of Composition, Pyrolysis Temperature and Adhesive Concentration on the Proximate Content and Calorific Value of Biobriquettes from Durian Skin, Corn husk and Fish Bones Waste

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## Abstract

Briquettes are an alternative energy derived from biomass. Biomass material can be obtained from plantation waste such as durian peel, agricultural waste such as corn husk and waste from the fisheries sector such as fish bones. Waste of corn husks, durian peel and fish bones have the potential to become biomass material as an alternative energy. The aim of this research is to analyze the effect of variations in composition, pyrolysis temperature and adhesive concentration on the quality of biobriquettes and emissions resulting from the combustion process. The dried waste materials is then pyrolyzed for 4 hours at 350 °C and 500 °C. Proximate testing was carried out to determine the quality of the biobriquettes. The parameters analyzed in this test include moisture content, ash content, volatile matter content, bound carbon content and heating value. The results of the study revealed that the best sample variations were found in briquettes with a composition of 50% durian peel : 50% corn husk with a pyrolysis temperature of 350°C and an adhesive concentration of 7%. The level of CO emissions produced when burning briquettes is 1,700 mg/Nm<sup>3</sup> and SO<sub>2</sub> is 0.741 mg/Nm<sup>3</sup>.

Keywords: Briquettes; biomass; emissions; waste

#### 1. Introduction

The need for energy is increasing along with the increase in population. This increase makes fossil energy reserves dwindling so that alternative energy is needed to overcome this problem. The use of biomass energy is one alternative energy that can be applied. Biomass materials are very easy to find from agricultural, plantation, forestry, animal husbandry, fishery and other activities (Patabang, 2012). Plantation waste that can be used as raw material for biobriquettes is durian peel waste. Until now, the utilization of durian peel waste can be said to be still lacking. Durian peel waste contains 15.45% lignin, 13.09% hemicellulose and 60.45% cellulose. The presence of lignin and cellulose indicates that durian peel has the potential to be used as raw material for making biobriquettes (Irhamni et al., 2019). Durian peel in this study contained 80.04% moisture content, 85.54% volatile matter, 5.30% ash content, and 9.16% bonded carbon. Agricultural waste in the form of corn husks can also be used as raw material for making biobriquettes because corn husks are composed of 44.08% cellulose compounds. Corn itself is the second important food crop after rice and is found in almost all of the Indonesian archipelago. One way to process corn husk waste is to use it as raw material for biobriquettes. Corn husk contains 12.95% moisture content, 53.7% volatile matter, 10.99% ash content, and 35.31% bonded carbon. (Camalia, 2023). Waste from the fisheries sector in the form of fish bones can be processed into materials for making biobriquettes which, if successful, can become the latest innovation in utilizing fish bone waste. (Camalia,

2023). Indonesia is an archipelagic country that has abundant fish resources. Fish bones contain 6.32% moisture content, 48.16% volatile matter, 41.68% ash content, and 10.16% bonded carbon. (Camalia, 2023)

The waste of corn husks, durian peel and fish bones have the potential to become biomass material as an alternative energy. One of the products of biomass is briquettes, where briquettes themselves are solid fuels that can be used as an alternative energy source that has a certain shape. Making briquettes aims to obtain a quality fuel that can be used for all sectors as a substitute energy source (Haliza and Saroso, 2022). The raw material for making briquettes needs to be carbonized which will produce charcoal, one of the charcoal methods that can be used is the pyrolysis method. Pyrolysis is a chemical decomposition process using heating without the presence of oxygen (Ridhuan and Suranto, 2017). The pyrolysis temperature affects the quality of the briquettes where the higher the pyrolysis temperature, the higher the calorific value but the slower the burning rate. The type and concentration of adhesive can also affect the quality of the biobriquettes. The adhesive from tapioca flour is an organic adhesive that is often used in making briquettes. Tapioca flour has the potential to become a briquette adhesive because it has a low water and ash content and a high carbon content. The use of briquettes as fuel can cause emissions during combustion. If the resulting emission exceeds the established quality standards, it can pollute the environment if the bio-briquette-fired stove is not accompanied by gas and particulate treatment (Setiani et al., 2019).

Based on the description above, this research was conducted to utilize waste in the form of corn husks, durian peel, and fish bones as materials for making briquettes. The aim of this research is to analyze the effect of variations in composition, pyrolysis temperature and adhesive concentration on the quality of biobriquettes and emissions resulting from the combustion process.

## 2. Methods

#### 2.1 Material and equipment

The main material of bio briquettes in this study was durian peel waste, corn husks and fish bones. In another hand, the equipment in this study was pyrolysis reactor and manual briquette press.

#### 2.2 Determination of Variation and Production of Bio briquettes

Variations in this study consisted of variations in composition, pyrolysis temperature and adhesive concentration. The raw materials used in this study were durian peel waste, corn husks and fish bones. Pyrolysis temperature variations used in this study are 350 °C and 500 °C. Variations in the concentration of the adhesive used were 7% and 10% by weight of the briquettes per sample. Sample variations can be seen in Table 1.

Material Composition	350°C		500°C	
(CH : DS : FB)	7%	10%	7%	10%
Durian Peel (DS)	Sı	S4	S7	S10
(100%)				
Durian Peel (DS) : Corn Husk (CH)	S2	S5	<b>S8</b>	S11
(50% : 50%)				
Durian Peel (DS) : Fish Bones (FB)	S3	<b>S</b> 6	S9	S12
(50% : 50%)				

Tabel 1. Variation of composition, pyrolysis temperature and adhesive concentration

The process of making briquettes :

a. The CH, DS and FB were cut into smaller sizes of  $\pm$  5cm. Material cutting is done to speed up the drying process of the material which is carried out using an oven at 115°C until the moisture content is  $\leq$  15%. (Bot et al., 2023).

- b. The dried material is then pyrolyzed for 4 hours at 350°C and 500°C. The charcoal from the pyrolysis results is then ground into a fine powder and then filtered using a 60 mesh sieve. The sieving process is carried out so that the particle size of the charcoal powder is equally distributed (Purwanto and Sofyan, 2014).
- c. The filtered charcoal is then mixed according to the variations specified in Table 1, the mixture of ingredients is then added with tapioca flour adhesive solution according to the predetermined concentration to form a briquette dough (Wahyudi et al., 2022).
- d. The finished briquette dough is then printed using a manual briquette press, then the briquette samples are dried using an oven at 105°C (Saeed et al., 2021).

## 2.3 Proximate Testing and Calorific Value

Proximate testing in this study aims to determine the quality of bio briquettes from The CH, DS and FB. The parameters analyzed in this test include moisture content, ash content, volatile matter content, bound carbon content and heating value. The test standards carried out in this study can be seen in Table 2.

8					
Parameters	Value	Unit	Reference		
Moisture Content	$\leq 8$	%	SNI 1-6235-2000		
Ash Content	$\leq 8$	%	SNI 1-6235-2000		
Volatile Matter	$\leq 15$	%	SNI 1-6235-2000		
Fixed Carbon	≥77	%	SNI 1-6235-2000		
Calorific Value	≥ 5000	Cal/gr	SNI 1-6235-2000		

Table 2. Proximate Parameter Testing Standard and Calorific Value

## 2.4 Statistical analysis

The research data that has been obtained is then analyzed using the Multivariate Analysis of Variance (MANOVA) test. MANOVA is a statistical technique used to calculate the simultaneous mean difference significance test between groups for two or more dependent variables (Sutrisno and Wulandari, 2018). Statistical analysis in this test was carried out to analyze the effect of variations in material composition, pyrolysis temperature and adhesive concentration on the proximate value and calorific value test results.

## 2.5 Selection of the Best Variation Samples

Determination of the best variety of briquettes in this study was carried out using the scoring method. This scoring method consists of 2 criteria, where the sample gets a score of 1 if it has a value according to SNI 1-6235-2000 and will get a score of 0 if the parameter value does not match SNI 1-6235-2000. The selection of this scoring value was carried out in accordance with the research conducted by Dewilda and Maryam (2017).

#### 2.6 CO and SO<sub>2</sub> Emission Tests

Emission testing in this study was conducted to determine the levels of CO and SO<sub>2</sub> emissions produced during the burning process of briquette samples. Emission testing in this study was carried out referring to the Government Regulation of the Republic of Indonesia No. 41 of 1999 concerning National Ambient Air Quality Standards. The method used to analyze CO emission levels is NDIR using the NDIR Analyzer tool. SO<sub>2</sub> parameters were analyzed using pararosaniline using a spectrophotometer.

## 3. Result and Discussion

#### 3.1 Analysis of Proximate Test Results

## a. Moisture Content

The parameter of water in the briquettes is one of the important elements because it is related to the amount of smoke produced, the ignition of the briquettes and the durability of the briquettes. The results of testing the water content of each sample variation can be seen in Figure 1.



Figure 1. Moisture content of bio briquette samples

Figure 1 shows that the water content of the variations in the composition of the durian peel bio briquettes increased with the amount of adhesive concentration, namely the water content of the samples with 10% adhesive concentration was greater than the 7% adhesive concentration. The concentration of tapioca adhesive affects the value of the water content because the higher the concentration of the adhesive, the more water ratio used. Bio briquettes with a composition of 100% durian peel and 7% adhesive concentration at 500°C have a lower water content than 350°C. The high pyrolysis temperature can also be the cause of the decrease in the water content in the briquettes, because the higher the temperature, the water content in the raw material will decrease and produce charcoal with a low water content. (Purwanto and Sofyan, 2014).

The highest water content of 5.88% was obtained from a variation of 50% durian peel: 50% corn husk with an adhesive concentration of 10% at a pyrolysis temperature of 500°C. The cause of the high water content, variations in the composition of durian peel and corn husks, is due to the water content in durian peels of 82.26% and corn husks containing a moisture content of 20%, while the water content of fish bones is 6.32%. High water content can make briquettes difficult to light and will also break easily. In addition, briquettes with high water content are very susceptible to mold growth (Chusniyah et al., 2022).

#### b. Ash Content

Ash is the remaining part of the combustion products, the main element of ash is silica mineral and has a bad effect on the resulting calorific value, so the higher the ash content produced, the lower the quality of the briquettes. (Ajimotokan et al., 2019).

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Figure 2. ash content of bio briquette samples

Figure 2 shows that the higher the adhesive concentration, the greater the ash content. This is in line with the research conducted (Sofyana et al., 2021) where the higher the adhesive content, the higher the ash content produced, due to the addition of ash from starch adhesive which is completely burnt. Pyrolysis temperature is also a factor causing the high value of the ash content. It can be seen in Figure 3.2 that the ash content at 350°C is lower than at 500°C. The high value of the ash content can be caused by the high temperature and the length of the pyrolysis process. The higher the temperature and pyrolysis time, the higher the ash content. This is because the carbon particles that burn to ashes are increasing (Ajimotokan et al., 2019).

#### c. Volatile Matter

The volatile matter content affects the completeness of combustion and the intensity of the flame. Testing for volatile matter levels in this study was carried out according to procedures based on SNI o6-3730-1995. The results of testing the levels of volatile substances can be seen in Figure 3.

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Figure 3. Volatile matter content of bio briquette samples

Figure 3 shows that all sample variations have very large values because they exceed the value based on SNI, which is 15%. The highest levels of volatile matter were found in samples with variations of 100% durian peel with a pyrolysis temperature of 350°C and an adhesive concentration of 10%. The higher the concentration of the adhesive, the greater the level of volatile matter. The increase occurred due to the presence of volatile substances contained in the adhesive, such as CO, CO<sub>2</sub>, H<sub>2</sub> and CH<sub>4</sub>. The higher the level of adhesive, the content of these substances is increasing (Yuliah et al., 2017). The addition of adhesive concentration is also the reason for the high levels of volatile matter in briquettes, this is because the amount of adhesive that has not been carbonized will have a higher volatile matter than charcoal, so the more adhesive concentration the higher the volatile matter content. (Deglas and Fransiska, 2020).

The value of the volatile matter content also decreased due to the increase in temperature. The temperature and the length of time of pyrolysis are factors for the rise and fall of the volatile matter content in the briquettes. The large amount of wasted volatile matter occurs due to the increasing temperature and pyrolysis time so that when tested it will yield low levels of volatile matter (Anizar et al., 2020). The higher the temperature, the lower the volatile matter content, this is because the volatile matter content in the raw material is running out so that if the calculation is carried out, a small volatile matter content will be obtained. The results of testing the levels of volatile substances in this study still do not meet the minimum standard of SNI 1-6235-2000 which is 15%.

The highest volatile matter content in this study was produced by briquettes composed of 100% durian peel with an adhesive concentration of 10% at 350°C. This is due to the content of volatile substances in the durian peel of 85.54%. The lowest volatile matter content in this study was found in variations in the composition of 50% durian peel and 50% fish bones with an adhesive concentration of 7% at 500°C. In addition to the low concentration of adhesive and high temperature, the low level of volatile matter can also be caused by the content of volatile matter in the composition of the material, where fish bones have a volatile matter content of 48.16% while corn husk is 53.70%. This is in line with research conducted by (Deglas and Fransiska, 2020). The content of volatile matter in raw materials can affect the value of the volatile matter content of briquettes.

#### d. Fixed Carbon Content

The fixed carbon content will be of high value if the value of the ash content and the decomposition rate of volatile compounds is low. The results of testing the fixed carbon content can be seen in Figure 4.



Figure 4. Fixed carbon content of bio briquette samples

Figure 4 shows that the fixed carbon content in this study is still below the minimum limit based on SNI. The highest fixed carbon content was found in samples with variations of 50% durian peel and 50% corn husk with a pyrolysis temperature of 350°C and an adhesive concentration of 7%. The concentration of the adhesive affects the size of the fixed carbon content, the higher the adhesive concentration, the lower the fixed carbon content. The decrease was due to the higher concentration of adhesive, the greater the need for water as a solvent. Given the high content of fixed carbon when the water content, ash content and volatile matter in briquettes are low (Norhikmah et al., 2021).

The higher the pyrolysis temperature, the lower the fixed carbon content. As in briquettes with a pyrolysis temperature of 350 °C has a greater fixed carbon content than a temperature of 500 °C. This is probably due to the carbonation process with high temperatures for a long time can damage the walls of the carbon pores so that the carbon burns and leaves ashes (Erwin Junary et al., 2015). This fixed carbon value depends on the ash and volatile matter content in the briquettes, where the higher the ash and volatile matter content in the briquettes.

The test results for the volatile matter content of all variations are still far below the minimum standard of SNI 1-6235-2000 which is 77%. The highest bonded carbon content of 30.22% was obtained from a sample with a composition of 50% durian peel: 50% corn husk with an adhesive concentration of 7% at a pyrolysis temperature of 350°C, this is because the carbon content in the durian peel is 9.16% and corn husk was 35.31%, while the carbon content bound to fish bones was 10.16%. Good briquettes have a high carbon content. The presence of bound carbon in charcoal briquettes is influenced by moisture content, ash content and volatile matter content. The level will be of high value if the water content, ash content and volatile matter content. The level will be of high value if the bonded carbon value of burning charcoal briquettes. The calorific value of charcoal briquettes will be high if the bonded carbon value is also high. The level of bound carbon or fixed carbon shows the amount of carbon element content present in the bio briquette (Saputra et al., 2021).

## 3.2 Calorific Value Yield Analysis

The heating value is the most important quality parameter for charcoal briquettes as fuel so that the heating value greatly determines the quality of charcoal briquettes. The higher the burning value of charcoal briquettes, the higher the quality of the resulting briquettes (Lukum et al., 2012).



Figure 5. Bio briquette Sample Calorific Value

The highest calorific value in this study was found in variations of 50% durian peel and 50% corn husk with 10% adhesive concentration at 350°C which is 5404.4 cal/gr. The lowest calorific value was found in variations of 50% durian peel and 50% fish bones with 10% adhesive at 500°C which was 2868.2 cal/gr. This difference can be influenced by the ash content in each material, where the ash content of fish bones is 35.91%. (Mismawati et al., 2022), while the ash content of corn husk was 11.67%. Ash is the remaining part of the combustion products, the main element of ash is silica mineral and has a bad effect on the resulting calorific value, so the higher the ash content produced, the lower the quality of the briquettes (Situmorang and Kusmartono, 2022).

Temperature affects the calorific value of briquettes, where briquettes with a pyrolysis temperature of 350°C are greater than those with a temperature of 500°C. This incident was caused by the length of time the material was written so that it increased the ash content in the charcoal (Purwanto and Sofyan, 2014). The ash content will increase because the carbon will burn out and leave ash which is the result of combustion. The carbon content will decrease if there is an increase in the ash content because the carbon content is a reduction in the amount of water content, ash content and volatile content contained in the charcoal. If the carbon content decreases, the heating value will also decrease because the carbon content is directly proportional to the calorific value produced (Erwin Junary et al., 2015).

The calorific value of 100% durian peel with 7% adhesive has a greater calorific value than durian peel briquettes with 10% adhesive concentration. The greater the adhesive, the greater the need for water as a solvent. This is in line with research Sofyana et all., (2021) The greater the concentration of the adhesive, the lower the calorific value of the briquettes. Considering that tapioca flour as an adhesive is an insulator and its calorific value is very low. The higher the adhesive concentration, the greater the ash content produced. The higher the ash content, the lower the calorific value produced (Aziz et all., 2019).

#### 3.3 MANOVA Statistical Analysis

The MANOVA test is a statistical technique used to calculate the significance test of the mean difference simultaneously between groups for two or more dependent variables (Sutrisno and Wulandari, 2018). The independent variables in this MANOVA test are material composition, pyrolysis temperature and adhesive concentration while the dependent variable is the proximate test parameter and calorific value. The MANOVA test results can be seen in Table 3.

Independent Variable	Sig	Sig	Hypothesis	Information	
	Value	Limit			
Composition					
Moisture Content	0.003	<0.05	$H_1$ accepted		
Ash Content	0.001				
Volatile Matter	0.020			Influential	
Fixed Carbon	0.021				
Calorific Value	0.024				
Temperature					
Moisture Content	0.046	<0.05	H1 accepted	Influential	
Ash Content	0.025				
Volatile Matter	0.001				
Fixed Carbon	0.001				
Calorific Value	0.001				
Adhesive					
Moisture Content	0.001	<0.05	H1 accepted	Influential	
Ash Content	0.023				
Volatile Matter	0.000				
Fixed Carbon	0.001				
Calorific Value	0.006				
Composition, Temperature and Adhesive					
Moisture Content	0.002	<0.05	H1 accepted	Influential	
Ash Content	0.006				
Volatile Matter	0.003				
Fixed Carbon	0.005				
Calorific Value	0.017				

Table 3. MANOVA Test Results

Table 3 is the result of testing using MANOVA which aims to determine whether or not there is an effect of material composition, pyrolysis temperature and adhesive concentration on the proximate test results and calorific value. Table 3 shows that variations in composition, pyrolysis temperature and adhesive concentration can affect the results of testing for moisture content, ash content, volatile matter content, carbon content and heating value. this is because the value of the P-value <0.05.

## 3.4 Selection of the Best Varieties

Determining the best variation of briquettes in this study was carried out using the scoring method. The determination of the scoring value is carried out based on the criteria for the maximum and minimum parameter values in SNI 1-6235-2000. This scoring method consists of 2 criteria, where the sample gets a score of 1 if it has a value according to SNI 1-6235-2000 and will get a score of 0 if the parameter value does not match SNI 1-6235-2000. The selection of this scoring value was carried out in accordance with the research conducted by Dewilda and Maryam (2017). The scoring of each variation can be seen in Table 4.

Variation	Parameter					Score
	Moisture Content (%)	Ash Content (%)	Volatile Matter (%)	Fixed Carbon (%)	Calorific Value (kal/g)	
S1	2.77	16.51 (a)	52.50	30.99 (a)	4971.1	1
S2	(1) 4.03 (1)	(0) 18.55 (0)	(0) 44.64 (0)	(0) 36.81 (0)	(0) 4488.2 (0)	1
S3	3.13 (1)	(0) 34.14 (0)	(0) 41.96 (0)	23.90 (0)	3889.3 (0)	1
S4	3·33 (1)	23.72 (0)	55.19 (o)	21.09 (0)	4749·9 (o)	1
S5	2.47 (1)	20.50 (0)	53·93 (o)	25.58 (0)	5404.4 (1)	2
<b>S</b> 6	1.87 (1)	36.97 (o)	47.70 (o)	15.33 (o)	3909.2 (0)	1
<b>S</b> <sub>7</sub>	1.66 (1)	23.65 (0)	46.06 (0)	30.29 (0)	4628.6 (0)	1
<b>S</b> 8	3.08 (1)	24.09 (0)	44·33 (o)	31.57 (o)	3339·7 (o)	1
S9	4.25 (1)	39.58 (o)	40.76 (o)	19.67 (0)	3524.2 (o)	1
S10	4.9 (1)	29.10 (0)	51.82 (0)	19.08 (0)	4018.4 (0)	1
S11	5.88 (1)	31.21 (0)	53·53 (o)	15.27 (0)	4762.9 (0)	1
S12	4·37 (1)	43.18 (o)	42.38 (o)	14.44 (o)	2868.2 (o)	1

## Table 4. Determination of the best variation using the scoring method

Table 4 shows that the sample variation that has the highest score is the S5 sample variation. Sample S5 is a briquette made from variations in the composition of durian peel: corn husk with an adhesive concentration of 7% at a pyrolysis temperature of 350°C. This is because these variations have met the values in SNI 1-6235-2000 on the parameters of water content and heating value.

## 3.5 Analysis of Emission Test Results

The use of bio-briquettes as fuel certainly goes through a combustion process that allows emissions to form. Emission testing in this study was carried out in order to determine the levels of CO and SO<sub>2</sub> emissions produced during the bio briquette burning process. The sample used for this test is the best sample made from a composition of 50% durian peel: 50% corn husk with a pyrolysis temperature of 350°C and an adhesive concentration of 7%. The results of emission testing can be seen in Table 5.

No	Parameters	Result	Standart	Unit	
1.	SO <sub>2</sub>	0.741	800	mg/Nm <sup>3</sup>	
2.	СО	1700	726	mg/Nm <sup>3</sup>	

Table 5 shows that the sample produces emissions in the form of carbon monoxide (CO) whose values exceed the quality standards based on Pergub Jatim No. 10 Tahun 2009 tentang baku mutu udara ambien dan emisi sumber tidak bergerak. Incomplete carbon combustion results in the formation of CO emissions. The high CO content occurs due to the lack of oxygen during combustion. The high CO

content can also be attributed to the high lignin content of the briquette composition (Senila et al., 2022). Bio briquettes are composed of chemical compounds C, H, O, N and sulfur. Durian peel has a C content of 48.95% and 38.75% O (Brunerová et al., 2017). Meanwhile, corn husk has a C content of 31.06% and O content of 32.63% (Maj et al., 2019). The content of carbon, nitrogen and sulfur in bio briquettes when in contact with oxygen during combustion will form gaseous compounds such as carbon monoxide and others.

SO<sub>2</sub> emissions produced in the process of burning bio-briquettes are still below the quality standards based on the Minister of Energy and Mineral Resources Regulation of 2006 Emission Standards for Coal-Fired Stoves and Coal-Based Solid Fuel Stoves. This is due to the high or low levels of SO<sub>2</sub> depending on the sulfur content present in the raw material (Setiani et al., 2019). The sulfur content in durian peel is 0.13% (Brunerová et al., 2017), while corn husk has a sulfur content of 0.48% (Maj et al., 2019).

## 4. Conclusions

Based on the research that has been done in this study it is known that the best sample variation is found in briquettes with a composition of 50% durian peel, 50% corn husk with a pyrolysis temperature of 350°C and an adhesive concentration of 7%. It is known that the emission levels generated when burning briquettes CO emissions exceed the established quality standard of 1700 mg/Nm<sup>3</sup>, while the SO<sub>2</sub> content produced is still below the established quality standard of 0.741 mg/Nm<sup>3</sup>. To improve the quality of bio briquettes that do not meet the standards, it can be rearranged the percentage of the ingredients by increasing the composition of corn husks instead of durian peels.

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