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COMPARATIVE CALORIFIC ANALYZES OF COCONUT SHELL AND DURIAN FRUIT PEEL BY USING DIFFERENTIAL SCANNING CALORIMETRY

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The production of coconut and durian means that it will produce a lot of waste from its shell. Indonesia is a country that produces a lot of them. The coconut shell (CS) and durian fruit peel (DFP) can be converted to briquette as new fuel from biomass. The objective of this research is to obtain the calorific briquette properties of CS and DFP using Differential Scanning Calorimetry (DSC). The material composition consist of 10 % and 15 % of starch for each CS and DFP. Thermal treatment was carried out in the temperature range of 28 °C to 600 °C at 5.4 °C/min. The addition of starch causes the heating temperature since it has thermoplastic properties. Additionally, it is difficult to burn and carries a lot of water so that the heat generated is used to evaporate the water first of all in the briquettes. The recommended material is CS with 10 % mass of starch. The optimum temperature reached was 578.97 °C with an enthalpy value of 0.42 J/g.

Keywords: *Coconut Shell, Durian Fruit Peel, DSC, Thermal Analyze.*

1. INTRODUCTION

Population, industry, and economic growth are the primary drivers of increased energy demand and carbon dioxide emission in Indonesia from electricity generation, industry, and transport sectors [1]. Energy consumption also increased significantly. These have led to the need to find efficient alternative and renewable energy sources. Indonesia has depended heavily on fossil fuels (crude oil, natural gas, and coal) as the primary energy source for the past ten years. Fossil fuels have been discouraged as people become more concerned about green energy and the environment. As a result, there is a pressing need for readily available alternative energy sources that are produced in large quantities. The alternative energy sources such as solar energy, wind energy, geothermal, hydropower, and biomass are viewed favorably as alternative energy sources (Fig 1).

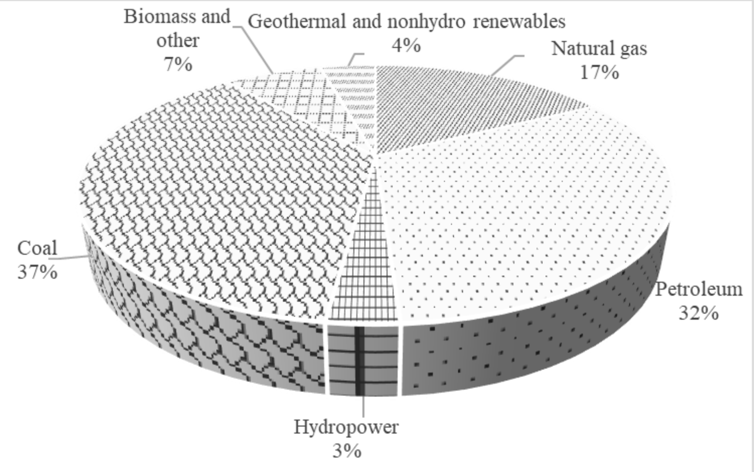

Figure 1. Energy consumption in Indonesia (Indonesia's Ministry of Energy and Mineral Resources) [1]

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Indonesia has a great potential for biomass that can be developed as briquette to support utilizing raw material of biomass. In North Sumatra Province, coconut production in 2019 was 99,132 tons, and durian reached 1,004,294 kW/qui in 2020 [2]. The production of coconut and durian means that it will produce a lot of waste from its shell. CS and DFP can be converted to briquette as new fuel from biomass. Biomass briquette made from CS and DFP is used for fossil fuels substitution [3] and offered as an environmentally friendly, clean and sustainable fuel [4]. The composition of cellulose, hemicellulose and lignin commonly found in CS and DFP can be used sustainably [5]. However, it is still untapped and underutilized. The technologies used are not efficient and environmentally friendly. There is also less innovation in its utilization. It shows that biomass is not used sustainably [6].

Calorie measurement is a thermal analysis technique which measures the flow of heat generated by either a chemical reaction of an element or a phase change process. Both methods can release or absorb heat and can cause significant changes in the temperature of the substance. Therefore, the calorific value measurement method measures the difference in heat flow between two samples at the same temperature during the phase transition [7].

DSC analysis is a standard method to determine the quality of semi-crystalline polymers by defining pre-heating and cooling steps [8], the phase transition temperature and specific heat [9]. It also examines thermal degradation [10] or phase transitions [11,12] and quantify semi-crystalline thermoplastics [13]. The sample is heated at a specific temperature scan rate to determine heat capacity [14]. The temperature effects of glass transition were identified on the DSC thermogram [15] of CS and DFP. The DSC method can determine the temperature ranges at which physical-chemical transformations occur and properties in both fuels and wood [16]. In the previous study [17], the authors presented the research results related to the comparative analysis of biomass during its pyrolysis and combustion using DSC. The paper [18] presents the results of the relationship between the physical performance of briquettes performed by the use of DSC. Moreover, explored the calorific (heat) necessity for biomass pyrolysis utilizing TGA-DSC investigation [19]. In addition, the calorific prerequisite is the absolute intensity expected to warm the feedstock to the pyrolysis top temperature and complete the pyrolysis responses. It is a natural boundary in the plan, activity, and streamlining of biomass change gear. Notwithstanding, because of the intricacy and constraints of existing computation techniques, definite information on the calorific prerequisite of biomass is challenging to get. This research aims to obtain the calorific briquette properties of CS and DFP using DSC. Thermal treatment was carried out in the temperature range of 28 to 600 °C at 5.4 °C/min.

2. METHOD AND INSTRUMENT

2.1 Material

In this study, the calorific requirement of the CS and DFB was determined experimentally using DSC Analysis. The authors of the papers [16, 20, 21] presented techniques and methods for thermal analysis of various materials, as well as analyses of gaseous products released during thermal processes. The raw materials of this study consisted of two parts, CS and DFP, with a binder composition of 10% and 15% of starch, as shown in Table 1. The process of briquette production is shown in Figure 1.

Table 1: Composition of briquette.

No.	Biomass	Composition of starch (% mass)		Total of Mass Briquette
1	CS	10	15	35 Gram
2	DFP	10	15	35 Gram

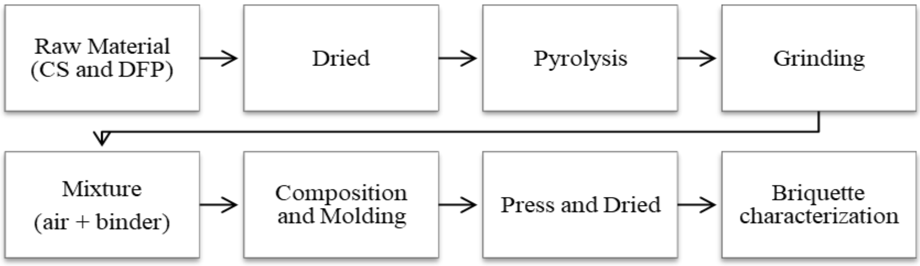

Figure 2. Schematic of Briquette Production

2.2 Instrumentation

The DSC test is a measurement of the physical and chemical properties of the material as a function of temperature for endothermic reactions, exothermic reactions and mass reduction. The principle of this test is to measure the reduction of mass material while heated from room temperature to high temperature. It shows the phase transition, thermal decomposition, and phase diagram of a material.

In this study, DSC-60 Plus Series is used for obtaining thermal properties. The thermal properties of a material are needed to determine its durability of the material. The process of experimental as shown in Figure 2.a-c. The briquette CS and DFP samples were placed in an aluminium crucible (Figure 2.a.) with a lid and heated in the DSC furnace (Figure 2.b.) at room temperature with a constant heating rate of 5.4°C/min using N_2 (gas flow rate of 25 ml/min) as sweeping gas (Figure 2.c.). After each process, the furnace is cooled, and the DSC results of each execution are analyzed in Microsoft Excel to determine the calorific requirements for each fuel during pyrolysis [22].

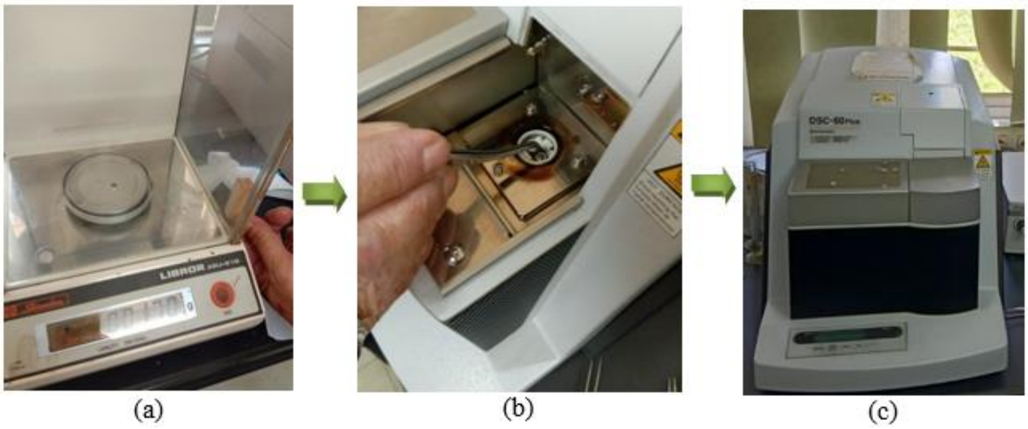

Figure 3: Experimental process of DSC

3. RESULT AND DISCUSSION

There are values of onset and endset temperatures as shown in Figure 4. The onset temperature is a phenomenon that begins with the formation of an endothermic peak and the occurrence of a decomposition reaction at a certain temperature. The endset temperature is a phenomenon that indicates the end of the decomposition reaction. Peak temperature indicates the peak of certain reactions.

In the DSC test, it can be seen the glass transition temperature (Tg), melting point, crystallization, heat of reaction and heat of fusion, heat capacity and specific heat, reaction kinetics, and purity. Table 2. shows the comparison of the thermal parameters of DSC on the briquette material with variations in the amount of tapioca adhesive against the two constituent materials. These parameters include melting temperature (Tl) and enthalpy of fusion (ΔHf).

Table 2: Peak of DSC Testing

Material	T_{onset} (°C)	T_{peak} (°C)	T_{endset} (°C)	Enthalpy (J/g)	Combustion heat (cal/g)	Identification	Refecences
CS+10% starch	68.26	100.00	116.05	-55.64	-13.29	Evaporation of water	[23, 24]
	331.20	339.35	357.45	0.40	0.10	Lignin decomposition	
	572.52	578.97	580.02	0.42	0.10	carbon purification	
CS+15% starch	65.66	80.81	92.15	-11.86	-2.83	Evaporation of water	
	302.58	318.21	341.34	2.46	0.59	Lignin decomposition	
DFP+10% starch	95.10	98.57	103.55	-3.59	-0.86	Evaporation of water	[25, 26]
	350.25	368.90	411.81	-90.74	-21.68	Lignin decomposition	
	538.41	557.91	560.88	7.25	1.73	carbon purification	
DFP+15% starch	60.87	84.81	95.63	-11.90	-2.84	Evaporation of water	
	311.63	337.33	356.31	18.00	4.30	Lignin decomposition	
	342.86	371.96	385.17	-9.38	-2.24	...	
	548.53	565.66	572.75	1.36	0.32	carbon purification	

There are 4 stages of the decomposition reaction in the DSC based on the test, a. Temperatures 100-120 °C evaporation of water occurs and at a temperature of 270 °C cellulose decomposition occurs, b. At 270–310 °C, an exothermic reaction will occur through the decomposition of cellulose in an incentive, c. At a temperature of 310–500 °C, lignin decomposition occurs, CO_2 gas decreases while CO, CH_4 and H_2 gases increase, and d. Temperature 500–1000 °C is the carbon content purification stage [27].

At the melting temperature, there are various values, 80–100 °C with the lowest value being CS + 15% starch (80.81 °C) and the highest value being CS + 10% starch (100 °C). While the enthalpy of smelting has different values between materials, the highest enthalpy was obtained at CS + 10% starch (55.64 J/g) and the lowest was at DFP + 10% starch (3.59 J/g). This result is similar to those reported for the other biomass residues [26]. The enthalpy of fusion indicates that there is an enthalpy change resulting from the change from the solid phase to the liquid phase at constant pressure.

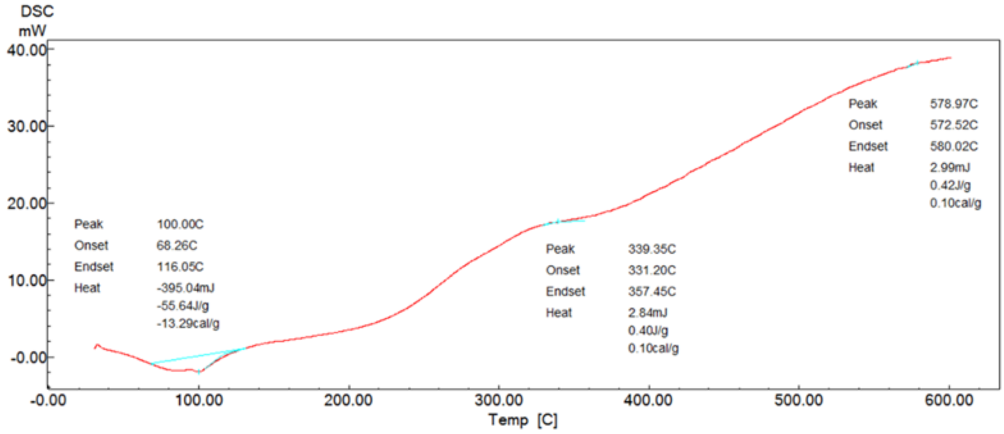

Figure 4: DSC thermogram of CS + starch 10%

The results of DSC on CS + 10% starch composition as shown in Figure 4. get the melting temperature (T_l) occurs at 100 °C with an enthalpy of fusion (ΔHf) of 55.64 J/g. At a temperature of 339.35°C crystallization occurs with an enthalpy of 0.40 J/g. Meanwhile, at a temperature of 578.97 °C oxidation occurs with an enthalpy of 0.42 J/g.

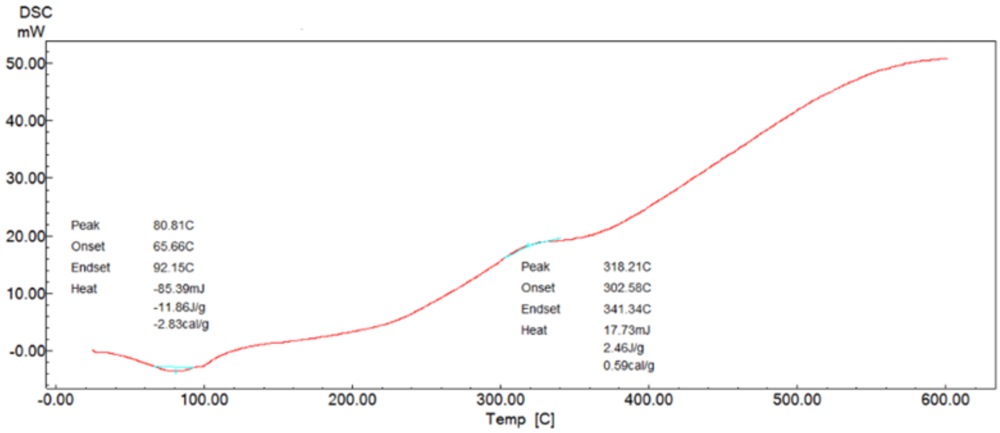

Figure 5: DSC thermogram of CS + starch 15%.

Figure 5. shows the CS + 15% starch composition, there are only two peaks, namely the melting and crystallization sections. The melting temperature (T_l) occurs at 80.81 °C with an enthalpy of fusion (ΔH_f) of 11.86 J/g. At a temperature of 318.34 °C crystallization occurs with an enthalpy of 2.46 J/g.

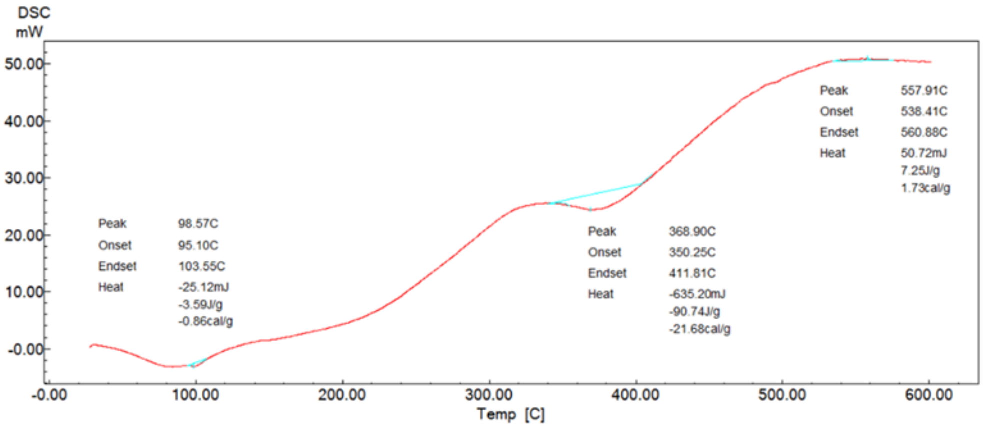

Figure 6. DSC thermogram of DFP + starch 10%

Figure 6. shows the results of DSC on DFP + 10% starch composition that the melting temperature (T_l) occurs at 98.57 °C with an enthalpy of fusion (ΔHf) of 3.59 J/g. At a temperature of 368.90 °C crystallization occurs with an enthalpy of 90.74 J/g. Meanwhile, at a temperature of 557.91 °C oxidation occurs with an enthalpy of 7.25 J/g.

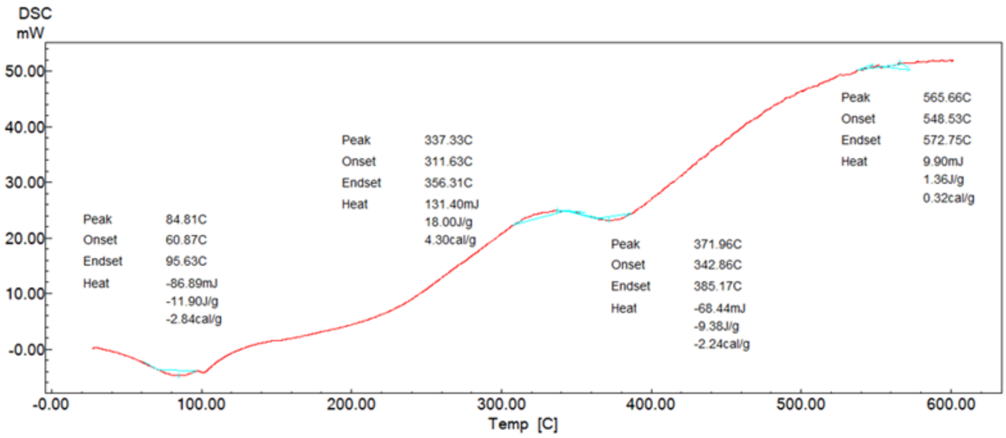

Figure 7. DSC thermogram of DFP + starch 15%

The results of the DSC on DFP + 15% starch composition as shown in Figure 7. show the melting temperature (T_1) occurs at 84.81°C with an enthalpy of fusion (ΔHf) of 11.90 J/g. At a temperature of 337.33°C, a crystallization event occurs with an enthalpy of 18.00 J/g. However, there is one peak outside. Meanwhile, at a temperature of 565.66 °C oxidation occurs with an enthalpy of 1.36 J/g.

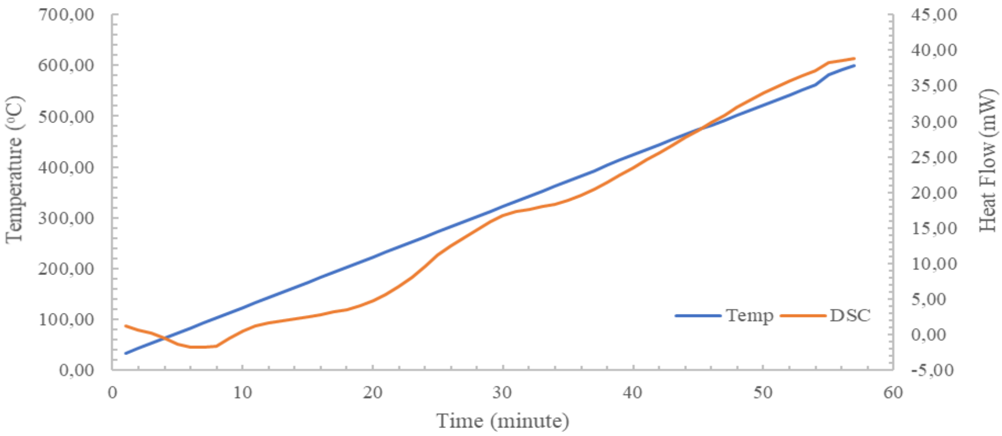

Figure 8: DSC curve of CS + starch 10%

From Figure 8., it is known that at 7th minute and a temperature of 92.97℃ there is a peak decrease until a heat flow of -1.78 mW is obtained dehydration phase. The peak of the glass transition was obtained at 333.09℃, 31st minute, and 17.31 mW of heat flow. Crystallization peak was obtained at 581.85℃, 55 minute, and heat flow 38.26 mW.

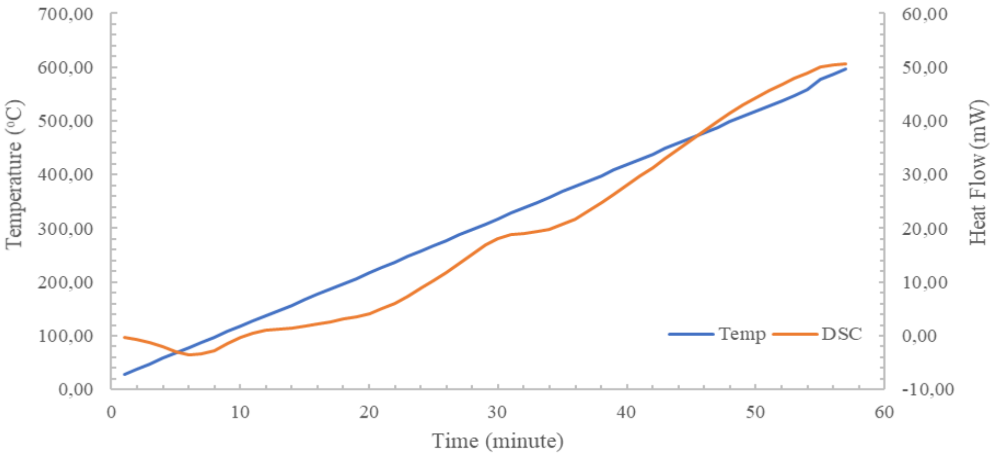

Figure 9: DSC curve of CS + starch 15%

Figure 9. shows the 6th minute and at a temperature of 77.90℃ there is a peak decrease until the heat flow is -3.58 mW dehydration phase. The peak of the glass transition was obtained at 318.13℃, 30 minutes, and a heat flow of 18.16 mW.

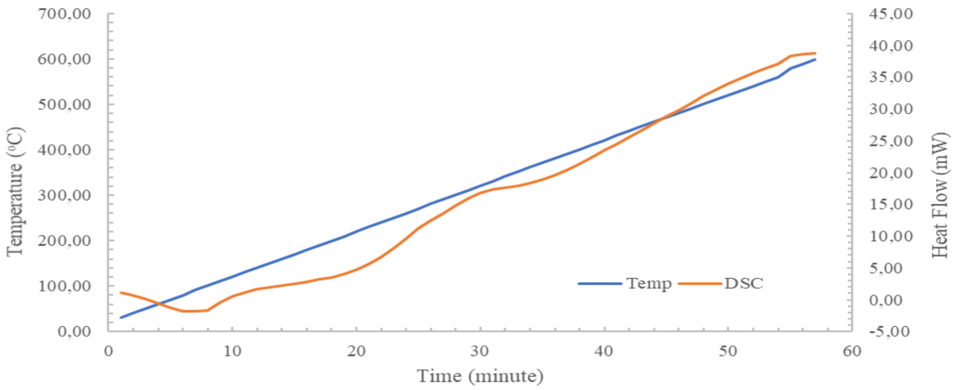

Figure 10: DSC curve of DFP + starch 10%.

From Figure 10. is known that in the 8th minute and at a temperature of 100.66℃ there is a peak decrease until the heat flow is -2.81 mW dehydration phase. The peak of the glass transition was obtained at 321.27℃, 30 minutes, and a heat flow of 24.73 mW.

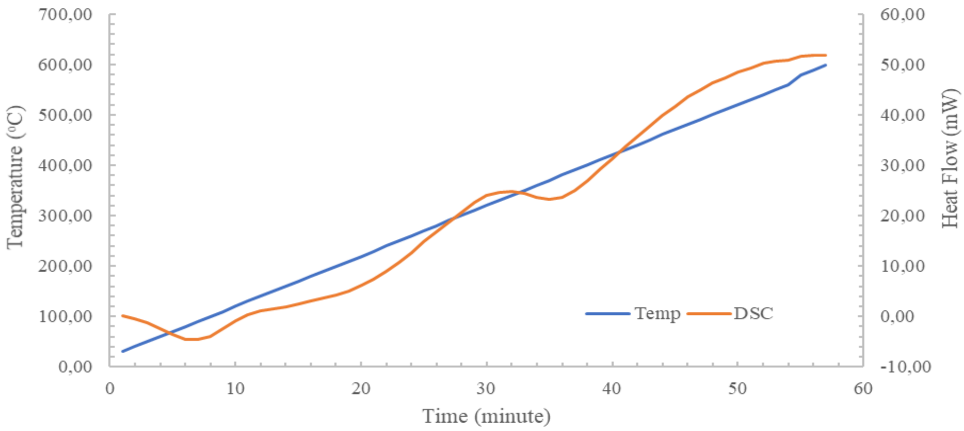

Figure 11: DSC curve of DFP + starch 15%.

From Figure 11. is known that at the 6th minute and the temperature of 77.90°C there is a peak decrease until the heat flow is -3.58 mW dehydration phase. The peak of the glass transition was obtained at 308.05°C, 29 minutes, and a heat flow of 16.97 mW.

Burning time of briquettes is a quality parameter for briquettes as solid fuel. The longer the briquettes burn, the better the quality. From the combustion analysis, it was found that increasing the amount of tapioca used can reduce the burning time. There was a decrease in the melting point of CS and DFP when tapioca flour was increased to 15%. The higher the tapioca content, the adhesion between the charcoal particles will increase but it has a high solvent content (liquid) in the form of water. Meanwhile, at 10% tapioca concentration, it has not as much solvent content as other concentrations, so that it makes the material harder and takes longer to burn. This has an impact on the amount of combustion energy produced. This combustion depends on several factors, namely particle size, material compound content, and ambient atmospheric conditions. The previews study [28] said that DFP contains 50-60% cellulose, 5% lignin, and low starch so that is has a problem when it is made into briquettes, the fast-burning rate so that it will quickly burn to ashes. While CS waste is generally used as an ingredient for making activated charcoal. Besides, the difference composition and type of briquette composition have various effects on the characteristics of briquette itself, such as calorific value, burning time, and burning speed of wrought charcoal [29].

4. CONCLUSION

Based on the analysis of research results regarding the DSC value of CS and DFP briquettes with variations in the amount of tapioca adhesive, it can be concluded that the quality of briquettes is strongly influenced by the amount of adhesive used. One of the reasons is the water content that is too high can cause the heating temperature to decrease. The addition of adhesive causes the heating temperature to decrease because the adhesive material has thermoplastic properties and is difficult to burn and carries a lot of water so that the heat generated is used to evaporate the water first in the briquettes. The recommended material is CS with 10% mass of starch. The optimum temperature reached was 578.97°C with an enthalpy value of 0.42 J/g.

5. ACKNOWLEDGEMENT

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