Hydrothermal carbonization of biomass waste under low temperature condition

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Abstract. In this paper, the use of banana peel for energy purposes was investigated. Banana peel is a lignocellulosic waste since it is the most widely produced and consumed fruit in Indonesia. Among the others, hydrothermal carbonization (HTC) was chosen as alternative thermochemical process, suitable for high moisture biomass. Through a 1 L stirred reactor, hydrothermal treatments were performed under low temperature condition (190, 210 and 230 °C), residence times (30 and 60 min), and biomass to water ratio (1:3, 1:5, and 1:10). Three of product were collected from the process with primary material balance. Solid phase (hydrochar) was evaluated in terms of calorific value, proximate and ultimate analysis. The results suggested that the hydrothermal carbonization of banana peel gave high heating value (HHV) of 20.09 MJ/kg for its char after dried naturally.

1 Introduction

Biomass is one of the most abundant sources of renewable energy. Agricultural and forest residues, and even industrial biomass waste are cheap and non-edible feedstock. They can be an important part of more sustainable future energy system. One of promising technology that can be used for energy purposes is hydrothermal carbonization (HTC).

HTC is a thermochemical process which imitates the natural coalification of biomass. Compare to the natural process which requires some hundred (peat) to some million (black coal) years, HTC only needs less than a half day for the transformation of biomass into a material quite similar to brown coal. Its technique uses liquid sub-critical water as a reaction medium for conversion of wet biomass. According to several researchers [1-3], HTC comprises a series of hydrolysis, condensation, decarboxylation and dehydration reactions. It utilizes subcritical water to heat feedstock at temperature typically ranging from 180 to 350 °C [4], even though the effect of carbonization can be achieved under temperature below 300 °C [5]. Not only process temperature, the type of feedstock is also important parameter to be considered in terms of sustainability. The application of HTC process to several typologies of biomass has been discussed by many researcher [6-9].

In Indonesia, bananas are the most widely consumed fruit. In 2013, based on *Angka Tetap (ATAP)*, the production of bananas reached 6.28 million tons. More than 50% of Asian banana production is produced by Indonesia [10]. Most residual of consumed banana is still found as wet ligno-

cellulosic residue, which must be properly disposed of. HTC could be an effective technology to handle wet feedstock. Considering that HTC is performed at lower temperature. This process has been investigated in this paper.

In this paper, the results of HTC of banana peel performed in a lab scale batch reactor were presented. Several reaction conditions such as reaction temperature, feed to water ratio, and residence times were determined. Three of product were collected from the process with primary material balance. Solid phase (hydrochar) was evaluated in terms of calorific value, proximate and ultimate analysis.

2 Materials and Methods

2.1. Experimental Setup

Banana peels (*Musa spp*) were purchased locally. Approximate size of it, in all dimensions, is <1 mm. The peels were air-dried prior to use in the carbonization experiments. Banana peels were used to represent cellulose and hemicellulose component. It comes from household residue. Banana is very popular fruit in Asia.

HTC of banana peels was carried out using 1 L batch reactor. Reactor, equipped with electrical heater and agitator, was made from stainless steel SS-304 as shown in insert in Figure 1. To analyze the effect of operating condition on feedstock, the experiments were performed at the different holding time period (30 and 60 minutes), feed to water ratio 1:3, 1:5, 1:10, and reaction temperatures (190, 210, and 230 °C) as

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subcritical temperature for hydrolysis starts at 180 °C [11]. Nitrogen gas was passed through the reactor for 5-10 min to ensure oxygen free in the system. Figure 1 showed scheme of HTC experimental system.

Figure 1. Experimental setup

50 gram of sample was loaded into reactor in every single run. Samples were mixed with deionized water with same amount to ensure complete soaking. Reactor was heated up in around 50 min and maintained at desired temperature for 30 and 60 minutes. Once the inside temperature of reactor dropped to room temperature, the pressure valve was released under fume hood to discharge gaseous products. Solid and liquid product were separated using filter paper (2 µm). Both gas and liquid were collected without further evaluation. Solid fuel (hydrochar) were dried naturally more than 24 hours before analysis.

2.2 Analysis

Proximate analysis (ash, volatile matter, and fixed carbon) was measured using Leco TGA-601. Ultimate analysis (carbon (C), hydrogen (H), oxygen (O), nitrogen (N), sulphur (S)) was determined using Elementar Vario Macro and for high heating value (HHV) were measured using bomb calorimeter. All of analysis was under supervised by Research and Development Center of Mineral and Coal Technology (Tekmira). Mass yield (Eq.1), energy densification ratio (eq.2), and energy yield (eq.4) are three parameters that were calculated in the study and are expressed as:

$$\text{mass yield} = \frac{\text{mass of dried hydrochar}}{\text{mass of dried feedstock}} \times 100 \quad (1)$$

$$\text{energy densification ratio} = \frac{\text{HHV of hydrochar}}{\text{HHV of feedstock}} \times 100 \quad (2)$$

$$\text{energy yield} = \text{mass yield} \times \text{energy densification ratio} \quad (3)$$

3 Results and Discussion

3.1 Effect of Operating Condition

Table 1 and Figure 2 showed that the experimental design that was completed in this study. Two kind of different operating condition; feed to water ratio and reaction temperature, during HTC process and their effect on calorific properties of each paper, banana peel, and sawdust. The results were presented in Table

2 and Figure 2, showed that both reaction temperature and holding time period, have influenced the properties of hydrochar mass yield, energy yield and high heating value.

Table 1. Experimental design of feedstock and hydrochar

Temp. (°C)	Feed to Water Ratio	Residence time	Energy yield	Mass Yield
190	1/3	30 min	67.62	64.21
		60 min	68.29	64.11
	1/5	30 min	67.14	63.54
		60 min	67.47	63.28
	1/10	30 min	66.42	62.87
		60 min	67.12	62.76
210	1/3	30 min	70.56	63.25
		60 min	70.25	62.04
	1/5	30 min	69.42	61.43
		60 min	70.96	60.95
	1/10	30 min	69.08	60.06
		60 min	69.99	59.55
230	1/3	30 min	68.02	59.26
		60 min	70.47	59.21
	1/5	30 min	68.30	59.12
		60 min	68.81	58.86
	1/10	30 min	67.46	58.46
		60 min	69.47	57.85

Figure 2. HHV from HTC biomass waste

The results suggest that even mass yield decreased, both energy yield and heat heating value increased along temperature rises. Banana peel contains cellulose and hemicellulose, it were easier to decompose than lignin feedstock during hydrothermal carbonization. It also explains the reason of the calorific value and carbon content increase of the most of feedstock after the hydrothermal treatment whose major component is cellulose. More than 90% hemicellulose starts to decompose in the temperature range 180-220 °C. Temperature of biomass hydrolysis starts at 180 °C

[11]. Lignin behaviour is different, less than 10% of lignin decomposed at below 250 °C [11,12].

From Figure 2 also shows the effect of reaction time and temperature on the mass yield of different feedstock during HTC. As expected, the mass yield less reduces with an increase in the holding time period and temperature. Banana peel showed very low in mass yield. Banana peel is one of biomass with high cellulose and hemicellulose content. Because of low thermal stability, banana peel tend to loss its mass easily [13].

The removal of hemicellulose via degradation and depolymerisation reactions during the thermal pre-treatment of a biomass results into the loss of structure [1]. The destroyed structure has improved friability. The example structures of the raw and hydrochar samples from banana peel have been observed under Scanning electron microscope (SEM) was shown in the Figure 3. The images show the variation in the structure a hydrochar with an increase in the process reaction temperature. For the raw feedstock, a clearly well-defined structure can be observed. However, in case of the hydrochar samples the unwrapping and rupture of polymer bundles and opening of pores is clearly noticeable. Almost complete loss of the structure can be observed for the samples pre-treated at 230°C.

Figure 3. SEM of banana peel at (a) Raw, (b) HTC temperature 230 °C

Figure 4. Carbon distribution in hydrochar

Mass balance analyses indicate that carbonization of the feedstock results in a significant fraction of carbon retained within the char (Figure 4). Carbonization of offie banana peel results in the smallest fraction of carbon remaining in the solid-phase. Hydrothermal process breaks the physical and chemical structure of material into smaller molecules. Biomass feedstock usually have high volatile matter and oxygen content. With the increase of the

hydrothermal reaction temperature, the volatile matter and oxygen content decreased while the fixed carbon and high heating value slightly increased that influenced by hydrolysis reaction. The results suggested that the hydrothermal treatment of biomass waste to solid fuel gave high heating value (HHV) with value of 20.09 MJ/kg for fruit peel respectively after product dried naturally.

3.2. Proximate and Ultimate Analysis of Hydrochar

The proximate analysis is used to determine the quality of coal and other solid fuels. The analysis comprises the measurement of fixed carbon, volatile matter, and ash content. The carbon content of the produced hydrochar ranges from 42-73%. According to many literature [14-17], carbon contents of hydrochar from the carbonization process were vary depend on other compounds. So, it is very hard to compare between carbon-contents measured in this study with reported in other literature. There are so many factors, such as the different of temperature, pressure, reaction time, reactor design, feed/water ratio, water stream, and catalyst.

Fixed carbon is the combustible residue after volatile matter burned. Organic samples have high volatile matter content and low fixed carbon, but high moisture content. Increasing of volatile matter and fixed carbon contents after hydrothermal process will lead to increase calorific value. Figure 5 showed that the fixed carbon of each feedstock was increasing during the HTC process. The increasing of fixed carbon can influence the increasing of HHV.

Figure 5. Fixed carbon of HTC of banana peel

Figure 6 showed that decreasing of volatile matter content in sample after process might lead to increase fixed carbon content. Increasing of volatile matter content in sample after process probably leads to increase calorific value. This is because volatile matter is combustible element and produce high flame. It can be seen that volatile matter content in feedstock decreases after hydrothermal process. This is because some volatile matters were probably evaporated and released into the air. In addition, it can be seen that using less process water will result lower volatile matter content in sample.

Figure 6. Volatile matter of HTC of banana peel

Figure 7 showed that ash content increases after process for feedstock. This because lignin content from banana peel is less than other wood feedstock. Lignin tends to decomposed at temperature more than 250 °C. Ash is the inorganic residue remaining after the sample is completely burned. Ash characteristics play an important role in system design in order to minimize slugging, fouling, erosion, and corrosion.

Figure 7. Ash content of HTC of banana peel

Figure 8. Coalification diagram

The hydrothermal carbonization or the coalification process that happen can be described (Figure 8) by the van Krevelen diagram or coalification diagram [18]. During carbonization as a result of demethylation,

decarboxylation, and dehydration reaction, there is a reduction of hydrogen and oxygen content in the feedstock. It can be described by the molar ratios of H/C and O/C. In the coalification diagram, those ratios move from upper right to lower left as the carbonization advance. The process goes from cellulose and wood, peat and lignite to the various forms of brown coal and finally to coal and anthracite. From the preliminary test of HTC, hydrochar from banana peel fall in the region of lignite brown coal.

4 Conclusion

The results, both in terms of hydrochar yield and hydrochar chemical and thermal properties, showed that HTC represents a suitable way to energetically valorise the banana peel. The resulted showed that increasing reaction temperature and holding time period during hydrothermal carbonization tend to increasing carbon content. Due to there was decreasing polarity and increasing temperature is associated with molecule breaking. In this perspective, high temperatures tend to increase the heating values of the hydrochar, although the yields resulted lowered. Thus, further experiments are required to assess the optimal values of the process parameters. In particular, a detailed reaction kinetics study could be useful to optimize the process and thus to obtain its maximum performance. Moreover, several parameters such as pure substances usage, variation of ratio feed to water, and catalyst is required in view of an actual assessment of the HTC potentiality for large-scale applications. Characteristic of liquid and gas product should be determined to gain more accurately about process and other carbonization products.

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