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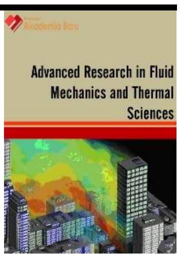

The Effects of Torrefaction on Lignocellulose Composition and Moisture Absorption Ability of Cocoa Pod Husk

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ABSTRACT

The weakness of biomass as a fuel can be minimized by torrefaction technology. Mass yield and enhancement factor are two of the parameters that can be used to evaluate the torrefaction process. Some of the important changes in the biomass properties after being torrefied are a reduction of moisture content and moisture absorption ability. This study was performed to determine the change of lignocel-lulose composition and moisture absorption ability of the cocoa pod husk (CPH) which was torrefied at 200, 250, and 300 °C and holding times of 0, 30, 60, and 90 min. The mass yield and enhancement factor of torrefied cocoa pod husk ranged from 54.6 % to 86.7 % and 1.09 to 1.34, respectively, depending on tem-perature and holding time. Hemicellulose fraction of torrefied CPH at 200 °C was 28.99 % then decreased to 8.39 % when torrefied at 300 °C. Amount of cellulose in CPH was in the range of 13.14 % (200 °C, 60 min) to 1.43 % (300 °C, 60 min). The lignin content increased from 28.99 % to 72.4 % with the temperature increased from 200 to 300 °C. Amount of hemicellulose in torrefied CPH tended to decrease along with the increasing of temperature and holding time, while lig-nin had the opposite trend. The moisture absorption was 11.5 % for raw CPH down to 5.5 % for torrefied CPH at 300 °C. The ability of CPH to absorb mois-ture decrease as increasing torrefaction temperature and holding time.

Keywords:
Cocoa pod husk; enhancement factor; lignocellulose; mass yield; torrefaction

1. Introduction

Indonesia has abundant biomass feedstock from agricultural wastes to generate sustainable energy. One of the biomass feedstocks that has the potential to be used as an energy source in Indonesia is cocoa pod husk (CPH) which is residue in harvesting of cocoa fruit. Indonesia was the third largest cocoa bean producer country in the world after Ivory Coast and Ghana. Indonesian Cocoa bean Production was 659.776 tons in 2017. The amount of cocoa bean is one third (33%) of the fruit weight, leaving behind 67% of the fruit as CPH as a waste by-product [1].

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Utilization of biomass as a fuel is limited by its characteristics such as low bulk density, high moisture content, inconsistent particle size, heterogeneous chemical composition, hydrophilicity, fibrous nature and relatively low calorific value [2,3]. One of the conversion technologies that can be applied to improve the properties of biomass is torrefaction. The torrefaction of biomass will change its physical and thermal properties [4]. Biomass will be changed from hydrophilic to hydrophobic by torrefaction [5]. The hydrophilic nature of biomass is a weakness that must be minimized because it is related to transportation costs and storage problems. Hydrophilic nature of biomass increases the moisture content of biomass even though it has been dried. Increasing of moisture content of biomass causes decreasing of heating value.

Moisture content and moisture absorption ability of biomass are two of the important changes in the biomass properties after being torrefied. The low moisture content of torrefied biomass is one of the factors that cause an increase in its heating value. Increasing heating value is caused by removing the components which do not and less contain energy. The heating value of biomass can decrease if the biomass increases the moisture content due to absorbing moisture from air. Moisture absorption ability of biomass correlates with the presence of OH groups in it [6].

It is known that biomass consists of three lignocellulose components, namely hemicellulose, cellulose, and lignin [7,8]. Torrefaction of biomass will cause changing of the percentage of each lignocellulosic component. Changing of the moisture absorption ability of biomass can be caused by changing of the lignocellulose composition of biomass. Among the three components of biomass, lignin has the lowest ability to absorb moisture, followed by cellulose and hemicellulose [6,9].

This study aims to determine the effectiveness of torrefaction of CPH under different experimental conditions, i.e. mass yield and enhancement factor were calculated based on mass and HHV of raw and torrefied CPH. The changing of the ligno-cellulose composition and the moisture absorption ability of the CPH which was torrefied also were investigated.

2. Materials and Methods

2.1 Materials

The feedstocks used in these experiments was CPH that obtained from a plantation in Gunung Kidul Regency, Yogyakarta, Indonesia. As received CPH has very high moisture content (60-70%). The wet CPH is cut into pieces of 2-3 cm long and 0.5 cm thick, followed by drying in the sun for about 4 days. Furthermore, CPH was put into an airtight plastic bag for the raw material of the torrefaction process. Figure 1 shows the physical appearances of the feedstocks.

(a) (b) (c)

Fig. 1. The materials used in the experiments: (a) as received CPH; (b) after cutting up; (c) after drying

2.2 Equipment and Procedures

A tubular torrefaction reactor used in this study is depicted in Figure 2. It consists of a tubular reactor, gas preheater with a temperature controller, and a nitrogen supply system with a rotameter and a gas heater. A Nickeline electric heater with 1.8 kW isolated with ceramics ring was used to heat the furnace to the desired torrefaction temperature. In this study, three different torrefaction temperatures of 200, 250, and 300 °C for holding time of 60 min were done. Four different torrefaction durations of 0, 30, 60, and 90 min and torrefaction temperature 250 °C were done too. Nitrogen as inert gas flowed into the reactor tube at a constant rate of 10 l/min during the torrefaction process. K-type thermocouples were used to monitor the temperature in the reactor and to control the reactor and nitrogen heaters temperature. The sample that has been torrefied was weighed then stored in an airtight plastic bag for further testing.

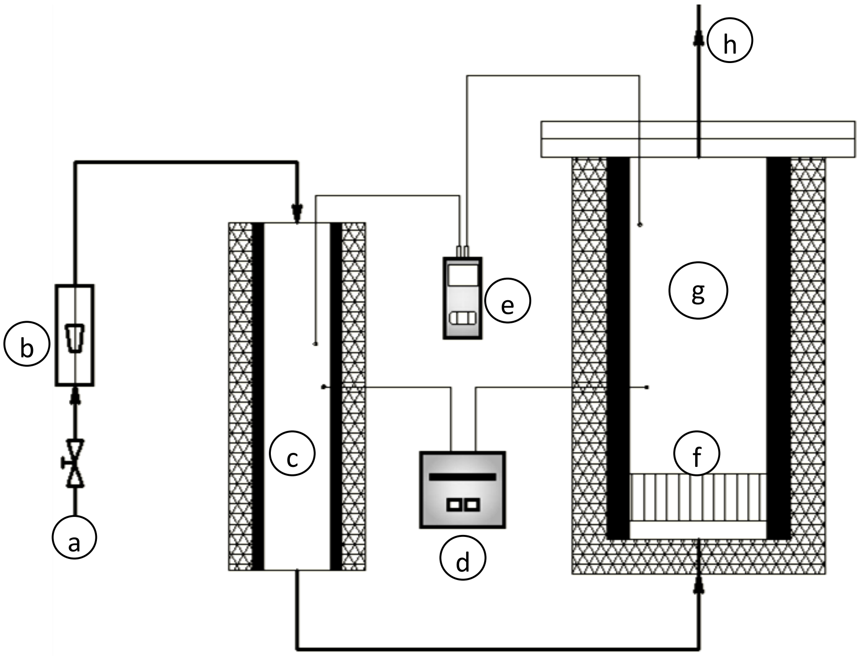


Fig. 2. Experimental setup of torrefaction reactor: (a) Nitrogen gas supply; (b) rotameter; (c) nitrogen preheater; (d) temperature controller; (e) data logger; (f) gas distributor; (g) reactor cylinder; (h) exhaust gas

Higher heating values (HHV) of the samples were measured using an IKA C6000 oxygen bomb calorimeter. Amounts of lignin, hemicellulose, and cellulose were determined. The mass yield and enhancement factor of raw and torrefied CPH were calculated using Eq. (1)-(2) adopted from Zhang *et al.,* [10].

$$\text{Mass Yield (\%)} = \left(\frac{mass\ of\ torrefied\ CPH}{mass\ of\ raw\ CPH}\right) \text{ x } 100\% \tag{1}$$

$$\text{Enhancement factor} = \left(\frac{HHV\ of\ torrefied\ CPH}{HHV\ of\ raw\ CPH}\right) \tag{2}$$

NaOH, and distilled water and then 1 ml of a solution of $NaClO_2$ and aquades to 1.25 g of extractive free powder placed in an Erlenmeyer. Erlenmeyer was put into hot water with a temperature of 70 ^{o}C for 4 hours and shaken every 30 min. At 45 min, 90 min and 150 min, add 1 ml of a solution of $NaClO_2$ and aquades, Erlenmeyer was put into ice water and 15 ml of distilled water was added aquades. The contents of the Erlenmeyer were filtered using a filter cup then dried in a furnace at a temperature of 100 – 105 ºC and weighed. Alfa-cellulose was determined by adding 12.5 ml of 17.5% NaOH to 0.5 g of holocellulose and then soaked with water for 5 min. Add 3 ml of 17.5% NaOH solution and leave it for 35 min. After that, the filter cup and holocellulose were washed with distilled water and drained and then added 10 ml of 10% acetic acid solution, stirred and drained again. The filter cup and its contents were dried in the furnace and weighed. Klason-Lignin was determined by heating 0.5 g of extractive free powder in 400 ml of water at 100 ^oC for 3 hours. Next, the sample was removed to a filter cup until dry. The sample was removed to the beaker and 15 ml of H_2SO_4 72% added while stirring. The filter cup and its contents were washed with hot water until free of acid, then dried in a furnace at 100-105 ºC and weighed. The amount of hemicellulose was obtained by the difference between the holocellulose and cellulose.

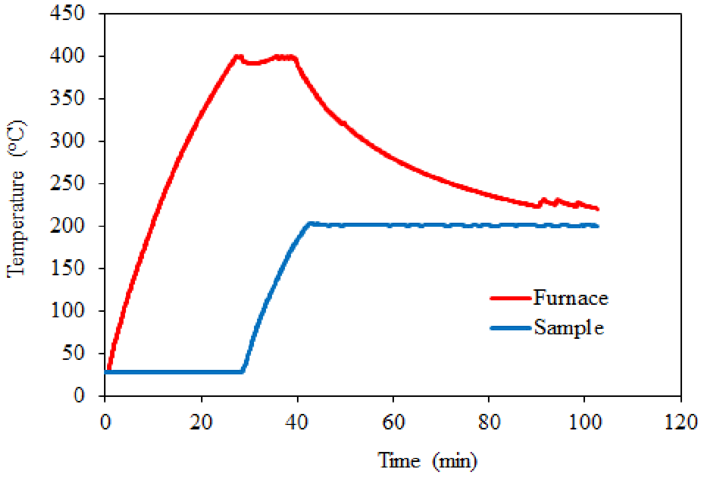
Equilibrium moisture content (EMC) was used to evaluate the hydrophobic properties of raw and torrefied cocoa pods husk. Analysis of hydrophobicity was conducted by letting 2 grams of the sample to absorb moisture in a container with relative humidity 70 – 75 % for 3 days.

3. Results and Discussion

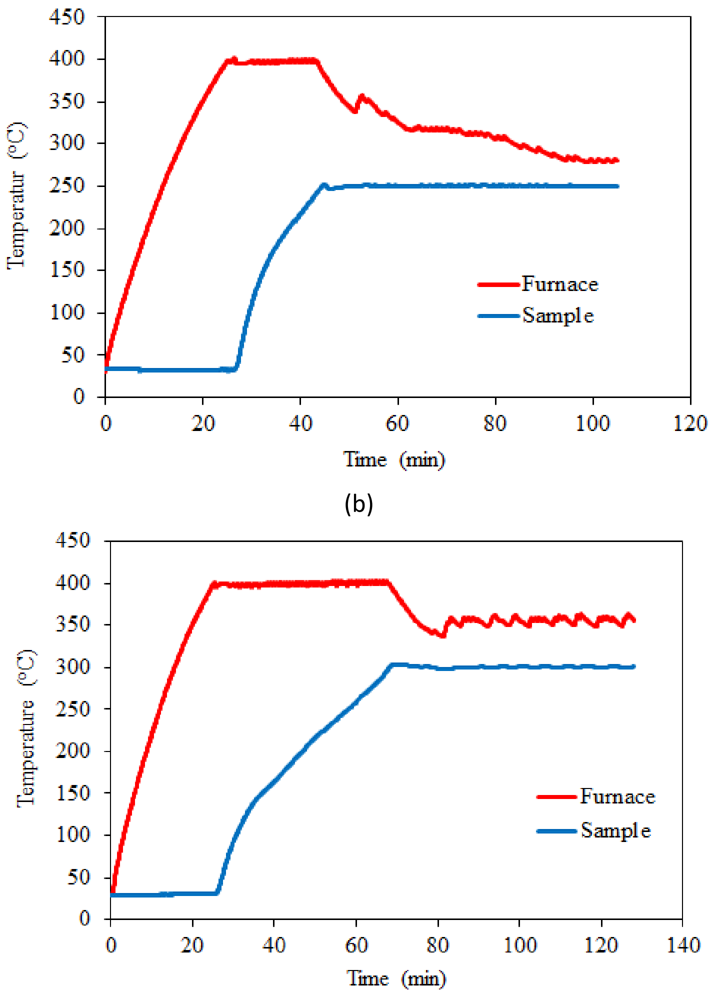
3.1 Temperature Profiles

The heat source in the torrefaction process is taken from an electric heater furnace. The furnace temperature is set to reach 400 ^oC before the reactor cylinder containing the sample is put into the furnace so that the temperature in the reactor cylinder can reach torrefaction temperature.

From Figure 3, it is obvious that the furnace takes about 25 min to reach the temperature of 400 ^oC, so the heating rate was around 15 ^oC/min. The sample heating rate from room temperature up to 150 ^oC was the same as the furnace heating rate, while from 150 ^oC to setting temperature decreases to 7 ^oC/min. The temperature of the furnace was kept at around 50 ^oC higher than the torrefaction temperature setting of the sample to keep it constant.



(a)



(b)

(c)

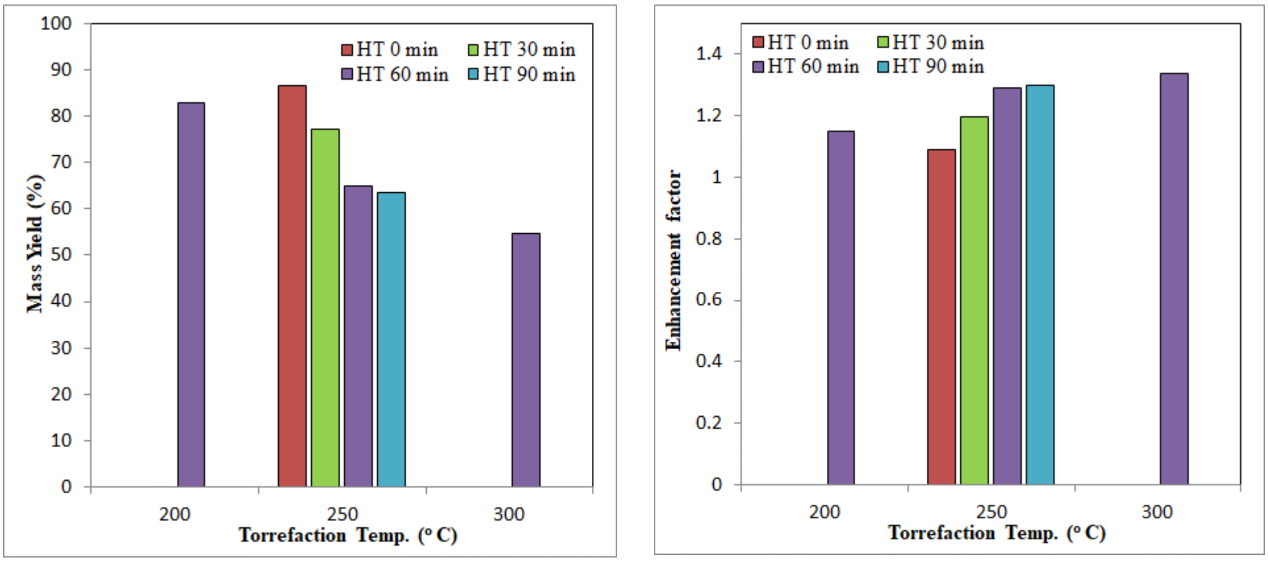
Fig. 3. Temperature profiles of reactor and sample on different torrefaction temperatures: (a) 200 °C; (b) 250 °C; (c) 300 °C

3.2 Mass Yield and Enhancement Factor

The mass yield (Figure 4(a)) of torrefied CPH ranged from 54.6 % to 86.7%, depending on temperature and holding time. The higher the torrefaction temperature and the longer the holding time, the lower the mass yield because more biomass components decomposed and evaporated. Decreasing of mass yield from torrefaction temperature of 200 to 250 °C (83.0 to 65.0 %) was higher than from 250 to 300 °C (65.0 to 54.6 %) in the same holding time (60 min). This shows that most CPH components have decomposed at temperatures between 200 and 250 °C. Figure 4(a) also showed that decreasing of mass yield in holding time from 60 to 90 min (65.0 to 63.6 %) was not as large as from 0 to 30 min (86.7 to 77.1 %) and from 30 to 60 min (77.1 to 65.0 %). This means that the addition of time of more than 60 min is no longer effective in the CPH decomposition process.

Enhancement factor (Figure 4(b)) of torrefied CPH ranged from 1.09 to 1.34. This result is in accordance with the enhancement factor of spent coffee grounds torrefaction that was in the range of 1.03 – 1.37 [10], while it was higher than enhancement factor of torrefied poplar and fir that was in the range of 1.021–1.124 [11]. The higher enhancement factor was resulted by torrefaction of Madagascar almond. Its enhancement factor was 1.36 and 1.54 with torrefaction temperatures of 250 and 300 °C, respectively [12]. Enhancement factor depended on the result of raw and torrefied

CPH heating values. Even though the mass yield got lower with higher temperature and longer holding time, the enhancement factor tent to be higher because increasing heating value was higher than decreasing mass yield. The profile of enhancement factor illustrated in Figure 4(b) shows that the higher temperature and the longer holding time the lesser the raising of enhancement factor.



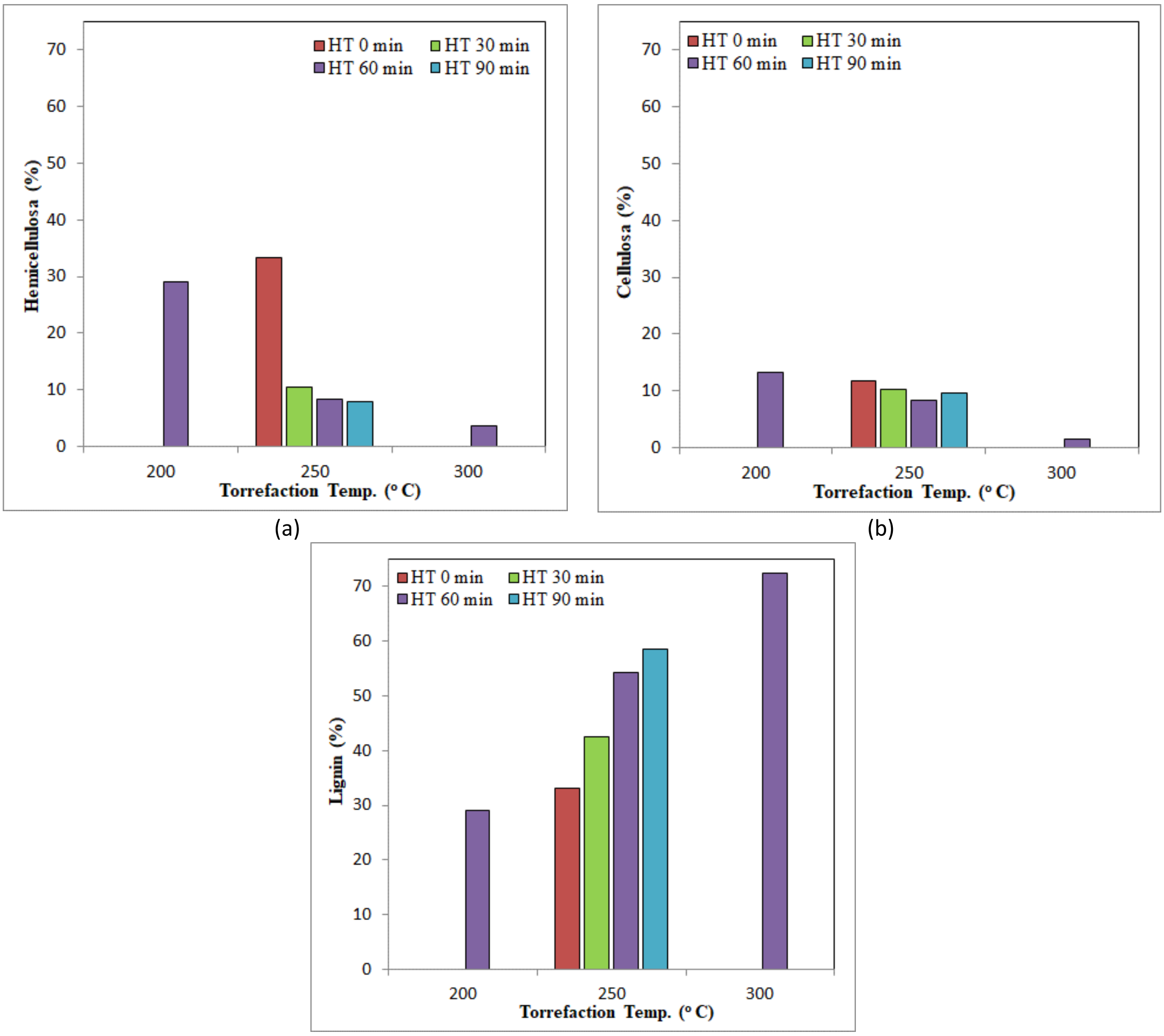
(a) (b)

Fig. 4. Effect of torrefaction temperature and holding time on (a) mass yield, (b) enhancement factor

3.3 Changing of Lignocellulose

The composition of the three main components of CPH namely cellulose, hemicellulose and lignin depended on the torrefaction temperature and holding time. Figure 5 shows that hemicellulose tended to decrease along with increasing the temperature and the holding time, whereas lignin has the opposite trend. These results indicate that hemicellulose decomposes when torrefaction was performed, while most of the lignin did not decompose. Cellulose changed slightly with increasing torrefaction temperature. This fact corresponded to different degradation temperature of each component. Hemicellulose degrades from 130–260 °C, while cellulose breakdowns at a temperature between 240 to 350 °C, and lignin decomposes between 280 and 500 °C [13].

Figure 5(a) display that hemicellulose fraction of CPH decreased from 28.99 % to 8.39 and then to 3.68 related to torrefaction temperature 200 °C, 250 °C, and 300 °C in the holding time of 60 min. Increasing of holding time at the torrefaction temperature of 250 °C was able to reduce hemicellulose from 33.3 % to 7.95 % when CPH was torrefied in 0 min to 90 min. Moreover, changing of cellulose fraction in CPH due to thermal decomposition was demonstrated in Figure 5(b). Amount of cellulose in CPH was in the range of 13.14 % (200 °C, 60 min) to 1.43 % (300 °C, 60 min). A relative increase in the lignin content of torrefied CPH is shown in Figure 5(c). The lignin content increased relatively from 28.99 % to 72.4 % with the temperature increased from 200 to 300 °C and rose from 33.07 % to 58.57 % with the holding time increased from 0 to 90 min. The increase in lignin was not caused by the increasing amount of lignin in the sample, but other components, especially hemicellulose, decrease more. These results reveal that hemicellulose is the easiest be thermally degraded, while lignin is a biomass component that is more resistant to thermal degradation compared to hemicellulose and cellulose. This is consistent with the statement of Gong *et al.,* [14].



(a) (b)

(c)

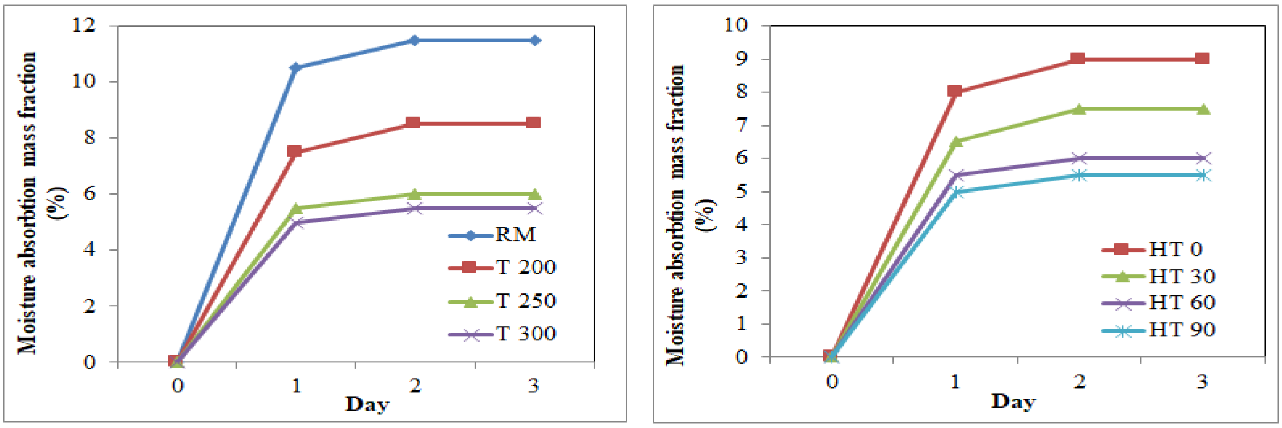
Fig. 5. Effect of torrefaction temperature and holding time on (a) hemicellulose, (b) cellulose, and (c) lignin

3.4 Moisture Absorption

Moisture absorption ability illustrated the hydrophobicity of the sample. Comparison of the ability to absorb moisture from air between torrified CPH for various torrefaction temperatures and same torrefaction temperature at various holding times can be seen in Figure 6. The moisture absorption ability of the sample was indicated by the increase of sample mass compared to the initial sample mass in dry basis condition. From Figure 6, it reveals that moisture absorption after one day was quite significant, but the sample did not absorb moisture anymore after two days. This means that after two days the sample terminated in moisture absorption.

Increasing of torrefaction temperature as well as holding time resulted in decreasing moisture absorption ability of CPH. Compared with raw CPH, moisture absorption ability of torrefied CPH greatly changed at torrefaction temperature of 250 °C, then only slightly decreased again at 300 °C. The moisture absorption was 11.5 % for raw CPH down to 6,0 % and 5.5 % for torrefied CPH at 250 °C and 300 °C. The effect of holding time on moisture absorption can be shown in Figure 6(b). It revealed that increasing holding time from 0 min to 30 min and 60 min have a significant effect on moisture absorption ability, but no substantial enhancement when holding time was prolonged to 90 min.

It is known that among the chemical composition in lignocellulose, hemicellulose and cellulose showed a great tendency for moisture absorption (hydrophilic), whereas lignin is a hydrophobic [9]. Moisture absorbed by the hemicellulose and cellulose is mainly due to the containing free hydroxyl groups (~OH) which easy to attract and hold water molecules through hydrogen bond [15,16]. The previous discussion stated that the content of hemicellulose and cellulose in torrefied CPH tended to decrease Therefore, the decreasing moisture ability of CPH may be due to the loss of hydroxyl groups within hemicellulose and cellulose caused by torrefaction process. This result is in accordance with the research conducted by Iroba *et al.,* [17] with biomass of woody construction demolition waste and grass clippings.



(a) (b)

Fig. 6. Moisture absorption ability of torrefied CPH (a) at various torrefaction temperatures and holding time of 60 min (b) at 250 °C and various holding times

4. Conclusions

The higher the torrefaction temperature and the longer the holding time, the lower the mass yield because the more biomass components decomposed and evaporated. The mass yield of torrefied CPH ranged from 54.6 % to 86.7%. Enhancement factor depends on the heating value before and after torrefaction. The enhancement factor of torrefied CPH ranged from 1.09 to 1.34. Amount of hemicellulose in torrefied CPH tends to decrease along with increasing the temperature increases and the holding time, whereas lignin has the opposite trend. Hemicellulose fraction of CPH decreased from 28.99 % to 3.68 related to torrefaction temperature 200 and 300 °C in the holding time of 60 min. Amount of cellulose in CPH was in the range of 13.14 % (200 °C, 60 min) to 1.43 % (300 °C, 60 min). The lignin content increased from 28.99 % to 72.4 % with the temperature increased from 200 to 300 °C. Hemicellulose is the easiest be thermally degraded, while lignin is more resistant to thermal degradation. The ability of CPH to absorb moisture from air decrease as increasing torrefaction temperature and holding time. The moisture absorption was 11.5 % for raw CPH down to 6,0 % and 5.5 % for torrefied CPH at 250 °C and 300 °C.

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