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Improving Thermochemical and Physical Properties of Cocoa Pod Shell by Torrefaction and its Potential Utilization

Untoro Budi Surono*, #, 1, Harwin Saptoadi* and Tri Agung Rohmat*

Abstract – *Torrefaction process is one of the solutions to produce solid fuel from a cocoa pod shell (CPS). Fuel characteristics of CPS changed after torrefaction. Effects of torrefaction temperature and holding time on physical, thermal, and chemical properties of CPS were investigated in this study. The experiments were conducted in a tubular torrefaction reactor. Three different torrefaction temperatures of 200, 250, and 300 ℃ and four holding times of 0, 30, 60, and 90 min were considered in this investigation. It was found that the color of CPS changed from light brown to black due to the increasing content of fixed carbon and depend on the torrefaction temperature and the holding time. The decrease in the grayscale value of the torrefied CPS represented an increase in HHV. Fixed carbon content and - higher heating value (HHV) of the torrefied CPS increased up to 17.5% and 41.3% compared to the raw CPS, while the volatile matter decreased up to 19.4%. The O/C and H/C atomic ratio decreased from 0.79 and 1.68 to 0.37 and 1.01, respectively, which corresponded to the increase of carbon content and decrease of oxygen and hydrogen contents. The properties of severe torrefaction CPS resembled between lignite and peat. The grindability and hydrophobicity of CPS was improved. The CPS based biochar should be used as a substitute for solid fuel that has the same characteristic to reduce the unfavorable effects of its potassium content.*

Keywords – *cocoa pod shell (CPS), grindability, higher heating value, hydrophobicity, torrefaction*

1. INTRODUCTION

Biomass is a renewable energy source that has great potential to substitute fossil fuels because it is environmentally friendly. Biomass is regarded as carbon dioxide-neutral fuel because the carbon dioxide released during combustion is the carbon dioxide that was taken from the atmosphere during the continuous photosynthesis process for many years [1], [2]. However, utilization of raw biomass as a fuel is often difficult due to its unfavorable properties, such as high moisture and oxygen contents, low energy and heating values, flue gas emission [2], [3], sensitivity to biodegradation, and hydrophilicity [4]. High moisture content and low-density of biomass cause storage and transportation problems. High moisture content also makes biomass sensitive to biodegradation and needs additional pretreatment costs for drying process.

Gasification, carbonization, pyrolysis, torrefaction, and densification are technologies to convert biomass to favorable and useful energy sources. Combustion converts biomass directly into heat energy. Gasification converts biomass into cleaner gas fuel. Carbonization or torrefaction change biomass into better properties of solid fuels.

Torrefaction is one of the biomass pretreatment technologies that is currently attracting the attention of researchers in the last decade. It is a thermochemical process in an environment without oxygen or a very limited amount of oxygen where the biomass is heated in a slow heating rate at temperatures of 200-300°C and then held for a certain time. The maximum mass and energy yields are produced from biomass through the torrefaction process. Torrefaction temperature below 300°C prevents the loss of lignin in biomass. Furthermore, slow heating rate and torrefaction temperature below 300°C avoid cellulose cracking, so tar formation does not occur [5]. The main objective of torrefaction removes fibers in biomass so that biomass is easier crushed and milled.

One of the important things that distinguish between torrefaction and pyrolysis is slow heating rate of torrefaction (less than 50°C/min) [6]. This slow heating rate can affect the results of the process that will produce more solid fuel, while faster heating rate will produce more liquid fuel. In some cases, torrefaction is similar to carbonization. An important difference between carbonization and torrefaction is most of the volatiles is maintained in torrefaction, while most of the volatiles is removed in carbonization. The maximum amount of biomass energy is retained in torrefaction.

Several parameters influence the torrefaction process, such as temperature, holding time, type of biomass, biomass particle size, and type of reactor. Torrefaction temperature has the greatest influence on the torrefaction process because the level of biomass thermal degradation mainly depends on temperature. Higher torrefaction temperature results in lower mass and energy yields but produces a higher energy density. The fixed carbon fraction in the sample increases, while hydrogen and oxygen decrease with increasing torrefaction temperature [7].

The holding time of biomass in the torrefaction reactor affects the thermal degradation of biomass. The slow heating rate in the torrefaction process is one of the

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characteristics that distinguishes torrefaction with the pyrolysis process. With a slow heating rate, the holding time of the biomass in the torrefaction reactor becomes longer. The longer holding time will result in lower mass yield and higher energy density. The type of biomass is a parameter that can affect the results of torrefaction because each biomass has different composition. Biomass with high hemicellulose content will experience higher mass reduction because of the decomposition of hemicellulose according to the torrefaction temperature range.

The quality of torrefaction can be expressed in mass yield, energy yield, and energy density. Mass yield is the mass ratio of biomass after and before the torrefaction process, while energy yield is the ratio between energy in the biomass after torrefaction and energy in the original biomass. Energy density is heat energy contained in fuel per volume unit. Torrefaction increases biomass energy content but reduces the mass and volume of biomass, so the density and energy density of the torrefied biomass are higher. The information of the torrefaction effect on the density change is needed for the detailed design of torrefaction devices and process analysis.

Torrefaction is the choice of a solution to process biomass into fuel because it can improve the characteristics of biomass. The biomass cell structure becomes brittle, smooth, and less fibrous by torrefaction, so the energy required for grinding can be reduced. Biomass is naturally hygroscopic, so even though it had been dried, it tends to absorb moisture and becomes moist when stored. This property is related to the hydroxyl groups (-OH) contained in biomass [8]. After torrefaction was done, biomass nature changes to hydrophobic.

Indonesia as an agricultural country located in the equator has abundant biomass energy sources [10]. There are many kinds of potential biomass energy sources in Indonesia such as forest, plantation, and agricultural wastes. One of the plantation wastes that has the potential as an energy source is cocoa pod shell (CPS), which is a by-product of harvesting of cocoa fruit. Indonesia is the third-largest cocoa producer in the world after Cote de'Ivoire and Ghana according to the data on cocoa production in the last three years [10]. The plantation of cocoa is around 1,691,334 ha with cocoa bean production of 688,345 tons in 2017 [11]. The amount of cocoa pod shell generated can be estimated based on the balance of cocoa fruit mass. Wet cocoa fruit consists of about 70-75% pod shell and around 21% cocoa bean [12]. Whereas, in dry conditions, the percentage of pod shell is around 14.71% and cocoa bean is 10.93% [13]. Most of cocoa pod shell is only piled on the cocoa plantation after the cocoa bean is taken from the fruit. There are a few farmers who utilized it as supplements to animal feed.

Some studies on biomass torrefaction of various agricultural and plantation wastes such as rice straw [14], sawdust and rice straw [15], corn stalk [16], coffee residue [17], pinewood and coconut fiber [18], pomaces and peanuts [19], and wheat straw [20] can be seen in the literatures. However, published papers that investigated CPS waste are still a few. Besides, data of CPS utilization as a renewable energy source are still limited. Syamsiro *et al.* [21] studied combustion characteristics of bio-pellets from CPS and utilization of CPS as a renewable energy source through palettization and carbonization, while Forero-Nuñez *et al.* [22] investigated the effect of using cocoa pod shells as an additive to sawdust and coal pallets.

This research was conducted to complement the data of CPS pre-treatment by the torrefaction process as a renewable energy source. In this research, analyses of the influence of torrefaction temperature and holding time on changes in physical, thermal, and chemical properties of CPS were done. There are no previous researches evaluate color change by RGB model, hydrophobicity and the grindability of raw and torrefied CPS. In addition, an assessment of the potential utilization of torrefied CPS in combustion was carried out.

2. MATERIALS AND METHODS

2.1 Materials

The feedstock in this study was CPS. It was obtained from a plantation in the Gunung Kidul Regency, Yogyakarta, Indonesia. CPS is the by-product of the processing of cocoa fruit to obtain cocoa beans. As received, CPS is very high moisture content material (60-70%). The wet CPS was cut into pieces of 2-3 cm long and 0.5 cm thick, followed by drying under sunlight for about 4 days. Furthermore, CPS was weighed as much as 800 grams and put into an airtight plastic bag for the raw material of the torrefaction process.

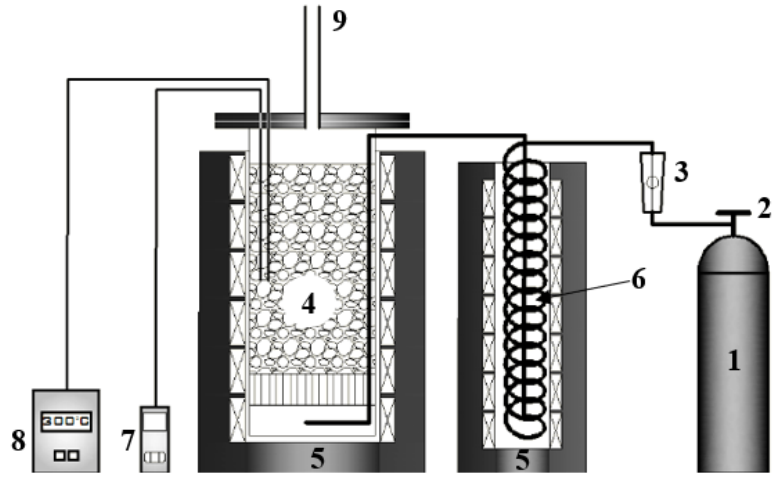

(a) (b) (c)

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

2.2 Description of the Apparatus

Figure 2 shows a schematic of the tubular torrefaction reactor used in this study. It consists of a tubular reactor, gas preheater with a temperature controller, and a nitrogen supply system with a rotameter and gas heater. The tubular reactor with 13.8 cm inner diameter and 46 cm high was made of galvanized steel plate. One K-type thermocouple connected to the data logger was used to monitor and record the temperature in the reactor. Two K-type thermocouples were used to control the reactor and nitrogen heater temperatures. Watt-hour meter was installed to monitor power supplied to electric heaters.

The torrefaction experiment was started by entering as much as 800 grams of biomass into the reactor. After being filled, the reactor was closed and connected to the nitrogen gas supply. Nitrogen as inert gas was flowed into the reactor tube at a constant rate of 10 l/min. A 1.8 kW Nichrome electric heater that isolated with ceramics ring was used to heat the furnace with a heating rate of about 16°C/min. The tubular reactor was put into the furnace once the desired torrefaction temperature setting was achieved. In this study, three different torrefaction temperatures of 200, 250, and 300°C, regarded as the light (200°C), mild (250°C), and severe torrefaction (300°C), respectively, combined with four different holding times of 0, 30, 60, and 90 min. After the torrefaction process, the reactor was removed from the furnace and left to cool down. Furthermore, the sample that has been torrefied was weighed then stored in an airtight plastic bag for further testing.



1. Nitrogen
2. Gas Regulator
3. Flowmeter
4. Biomass
5. Furnace
6. Gas Heater
7. Thermocouple Reader
8. Temperature Controller
9. Outlet Gas

Fig. 2. Experimental setup of the torrefaction reactor.

2.3 Material Analysis

Mass and energy yields are important parameters in the evaluation of torrefaction process. The mass and energy yields of raw and torrefied CPS was calculated using Equations 1 and 2.

$$\text{Mass Yield (\%)} = \frac{mass\ of\ torrefied\ CPS}{mass\ of\ raw\ CPS} \times 100\% \qquad (1)$$

$$\text{Energy Yield (\%)} = \frac{mass\ yield\ x\ HHV\ of\ torrefied\ CPS}{HHV\ of\ raw\ CPS} \qquad (2)$$

Proximate analysis was conducted to investigate the fraction of moisture, volatile matter, ash, and fixed carbon in the sample. Ash and volatile matter contents were determined using a muffle furnace (Carbolite AAF 1100), following ASTM 3174 and ASTM 3175, respectively, while moisture content analysis was performed by MFS oven (Carbolite) according to ASTM 3171. The fixed carbon content was calculated by subtracting the moisture, volatile, and ash contents from the total biomass on air-dry basis.

The elemental components (C, H, O, N, S) of the raw and torrefied CPS were determined by LECO CHN 628 elemental analyzer according to ASTM D5373, while sulfur content was analyzed using LECO S 632 elemental analyzer according to ASTM D4239. Oxygen content was determined by the difference. Higher heating values (HHV) of the samples are measured using an adiabatic bomb calorimeter IKA C6000. About 0.5 g of the sample with a particle size of less than 0.5 mm was placed in the crucible and ignited inside the bomb calorimeter using a pure cotton thread in the presence of pure oxygen (99.95%).The result of proximate and ultimate analyses and HHV of the raw CPS are shown in Table 1. The analysis was performed in duplicate to validate the measurement.

The first step to measure color differences, that was each sample was pulverized by using a hammer mill and passed through an 80-mesh sieve to homogenize. The sample was spread over a 5 cm diameter plastic cup lid prior to imaging. Images were captured using a Fujifilm® digital camera (Model X A5). All images were captured using the same camera settings: 75 mm focal length, ISO 200, 1/50 s shutter speed, and f/8.0 aperture setting. Samples for imaging were placed at 7.5 cm from the camera. All images were captured under the same lighting conditions and continued by analysis in the RGB color model use an open-source image editor (GIMP 2.10.18). The RGB color model has three color components, Red, Green, and Blue [23]. The RGB image values then converted to greyscale image value that has one color component by using the formula [24]:

$$I = 0.299 * R + 0.587 * G + 0.114 * B \qquad (3)$$

Grindability test, based on particle size distribution, was done to determine the effect of torrefaction temperature and holding time on the grindability of raw and torrefied CPS. Grinding in the grindability test was carried out in two stages, namely pre-grinding and fine grinding. In the pre-grinding stage, each of samples was ground using a hammer mill then sieved to get particle size of 8 - 20 mesh. This stage was carried out to reduce and homogenize the size before fine grinding is done. Fifty grams of the first grinding stage were taken then continued by the second grinding stage. Fine grinding was done using a ball mill. A cylindrical pan with an inner diameter of 12 cm and a height of 10 cm was used to place samples and alumina balls.

The rotational speed of the mill was 70 rpm. Forty alumina balls with diameter of about 20 mm and mass of 1075 grams were used as grinding media. Milling with the ball mill was carried out for 30 min. After grinding, the sample was sieved to get the particle size distribution with a series of sieves of 200 (75 μm), 100 (150 μm), 40 (425 μm), and 30 (600 μm) mesh sizes. Sieving was carried out by a sieve shaker with a frequency of 20 Hz. Particle size distribution was determined by weighing the material on each sieve. After that, the cumulative weight was calculated after the shaking was completed.

Table 1. The fuel properties of raw CPS.

Analysis	Value
Proximate analysis (wt% adb)[a]	
Moisture	10.65
Volatile	60.78
Fixed carbon[b]	21.74
Ash	6.82
Ultimate analysis (wt% adb)	
C	41.94
H	5.87
O[a]	44.27
N	0.93
S	0.16
Higher heating value (MJ/kg)	16.35

[a] adb – air-dried basis
[b] calculated by difference

Equilibrium moisture content (EMC) was used to evaluate the hydrophobic properties of raw and torrefied CPS. Preparation for the hydrophobicity test was started by grinding the sample to a size of less than 177 μm (80 meshes) followed by drying the sample at 105°C for one hour. Analysis of hydrophobicity was conducted by putting 2 grams of each of the samples in a closed plastic container. A saturated solution of sodium chloride (NaCl) was used to control relative humidity in the container of about 75% [25]. A digital thermo-hygrometer HTC-2 (Yueqing Kampa Electric Co., Ltd.) was used to monitor the relative humidity and temperature in the container. Each sample was weighed every 24 hours until there is no more increase in weight.

3. RESULTS AND DISCUSSION

3.1 Color Changes of Torrefied CPS

Raw and torrefied biomass showed different physical appearances. Color was the change in biomass that can be directly seen after the torrefaction process. Biomass changed from light brown to dark brown either to black depending on the temperature and the holding time of the torrefaction. Figure 3 showed the color-changing of raw and torrefied CPS at the various torrefaction temperatures and holding times. It was evident that the higher the torrefaction temperature and the longer the holding time, the darker the color of the torrefied CPS. It was observed that torrefaction with different temperatures at the same holding time resulted in more prominent color-changing than torrefaction at a different holding time with the same temperature.

The darker torrefaction products indicated that carbon content in the solid fuel was getting higher. The previous study conducted by Pimchuai *et al.* [3] only showed the change in color of biomass before and after torrefied with a temperature of 250°C and a holding time of 1 hour. The color of torrefied products was more brownish than the raw biomass. The other literature [26] exhibited raw and torrefied of three types of oil palm waste. The color of EFB and mesocarp fiber changed to black, particularly at torrefaction of 300°C, while the change in color of kernel cell was not prominent with the increasing of torrefaction temperature. Gucho *et al.* [27] also obtained the same color change in beech and mischanthus woods biomass after being torrefied at four different torrefaction temperatures and three holding times. Changing the color was caused by decomposing and evaporating some of the components in the fuel, which results the increasing fixed carbon content. As the severity of torrefaction increased, the fuel color changed from light brown to dark brown and finally to black.

These visual observations are only descriptive evaluation hence it is difficult to distinguish nearly identical color samples. Therefore, quantitative evaluation needs to be presented to compare different colors of torrefied products. The RGB values of the images were in the range from 0 to 255 for each Red, Green, and Blue. The greyscale images value of the samples calculated by Equation 3 were in the range of 0 for black to 255 for white. The results listed in Table 2 presents the RGB and a greyscale images pixel value of the samples. The results showed that torrefaction had an influence on RGB and greyscale values of the torrefied CPS. The RGB and greyscale values of torrefied CPS decreased with the increasing torrefaction temperature and holding time, and the decrease of the values were trivial at holding times of 60 and 90 min. The greyscale value of raw CPS decreased from 129 to 99 at torrefaction of 200°C and holding time of 0 min and to 34 at torrefaction of 300°C and holding time of 90 min.

A smaller greyscale indicates a darker sample color due to higher carbon content.

The previous study conducted by Saito *et al.* used the term hue angle (h_{ab}) derived from the L*a*b* color model to evaluate the properties of carbonized wood biomass. The results showed that the hue angle value of the sample could be used to estimate the fixed carbon of carbonized wood biomass [28]. In this study, the grayscale value was used to evaluate the HHV of torrefied CPS. The relationship between the grayscale value and the HHV of each sample is shown in Figure 4. When the torrefaction conditions get more severe, the grayscale value became lower and the HHV became higher. Figure 4 also shows that the effect of the decreasing grayscale value at severe torrefaction is more significant than that of mild and light torrefaction. The decrease in the grayscale value of the torrefied CPS did not only describe an increase in fixed carbon but also represented an increase in HHV.

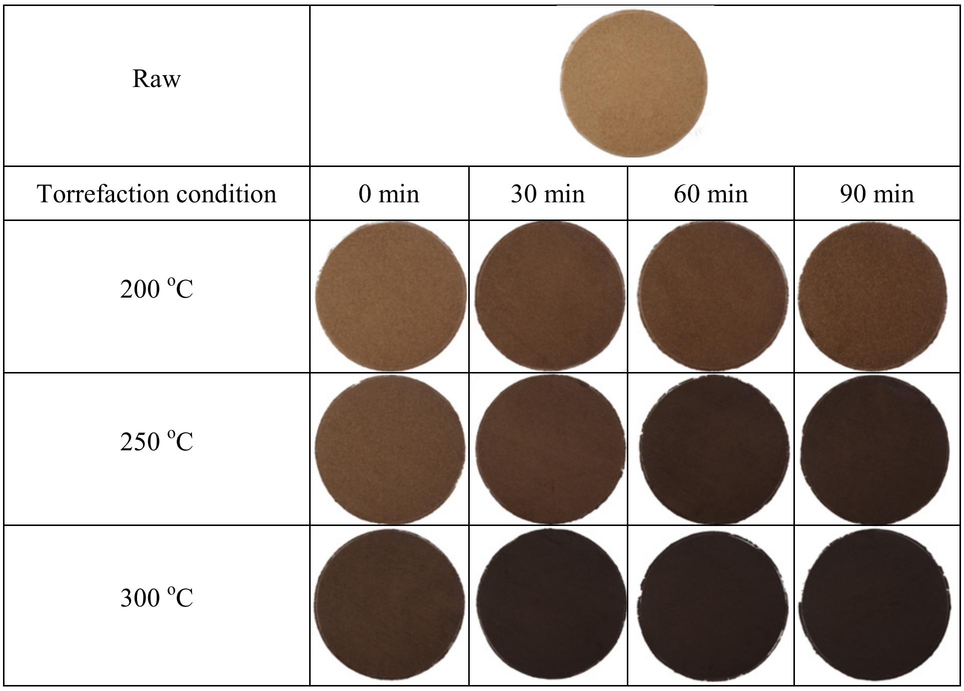


Fig. 3. True color appearance of CPS and its torrefied products.

Table 2. RGB and Greyscale color parameter of raw and torrefied CPS.

Torrefaction temperature	Color parameter	Holding time (min)			
		0	30	60	90
RM	R	159			
	G	122			
	B	84			
	Greyscale	129			
200°C	R	127	97	93	92
	G	92	66	62	61
	B	63	46	42	41
	Greyscale	99	73	69	68
250°C	R	104	82	53	56
	G	74	56	37	39
	B	52	41	30	31
	Greyscale	80	62	42	40
300°C	R	72	46	45	42
	G	50	34	33	31
	B	38	29	28	28
	Greyscale	55	37	36	34

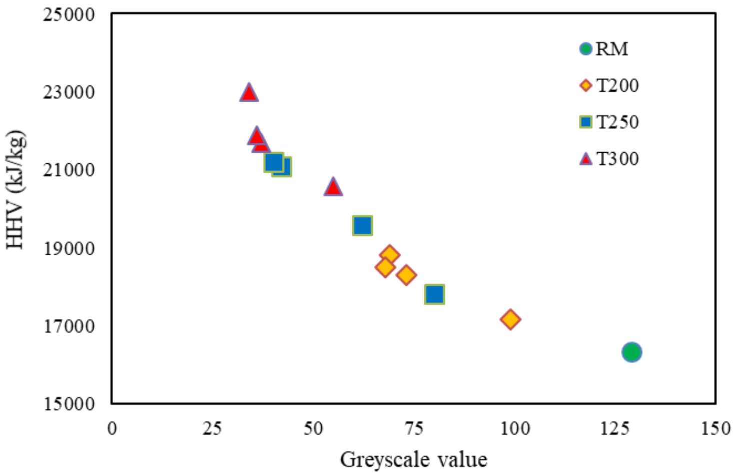


Fig. 4. Relationship between the greyscale value and HHV of CPS and its torrefied products.

3.2 Ultimate Analysis and Higher Heating Value

Table 3 presents the ultimate analysis and HHV of CPS based biochar produced at different temperatures and holding times, showing that increasing temperature and holding time of torrefaction produced increasing carbon content and HHV but decreasing oxygen and hydrogen content. The carbon content of CPS underwent rise from 41.94% (raw CPS) to 42.94 - 56.53% when torrefaction was performed at 200 to 300^{o}C. Once CPS was torrefied, the hydrogen and oxygen content decreased from 5.87% and 44.27% to 4.74% and 28.18% (TT 300, HT 90 min). Meanwhile, the effect of torrefaction on HHV can be seen from the enhancement of HHV from 16.35 MJ/kg (raw CPS) to the range of 17.17 MJ/kg to 23.11 MJ/kg. The highest heating value of all the samples was achieved at 300°C due to the higher carbon content of the samples [29] and the loss of oxygenated compounds during torrefaction [30].

Figure 5 is the Van Krevelen diagram that plots the atomic O/C and H/C ratios calculated from Table 3. The atomic O/C and H/C ratios decreased due to torrefaction temperature and holding time increased. These facts were due to the reduction of O and H content and addition C content after the torrefaction process. The atomic O/C and H/C ratios of raw CPS were 0.79 and 1.68, respectively. The product of torrefaction still in the area of biomass when the torrefaction temperature of 200 and 250^{o}C for the holding time less than 60 min. The torrefaction resulted in the significant diminishing of the atomic O/C and H/C ratio, especially at the torrefaction temperature of 300^{o}C with the holding time more than 30 min, *i.e.* 0.37 and 1.01, respectively. In this condition, the product nearly resembled between lignite and peat.

Table 3. Ultimate analysis and higher heating value of torrefied CPS at various temperatures and holding times.

Samples		Ultimate Analysis (wt%, adb)					HHV (MJ/kg)
TT (^{o}C)	HT (min)	Carbon	Hydrogen	Nitrogen	Total Sulfur	Oxygen^a	
200	0	42.94	5.58	1.09	0.15	40.37	17.17
200	30	45.66	5.49	1.02	0.16	38.71	18.31
200	60	46.52	5.44	0.96	0.16	38.11	18.80
200	90	45.15	5.47	1.12	0.17	39.32	19.00
250	0	44.17	5.59	1.05	0.11	40.21	17.81
250	30	48.42	5.46	1.09	0.12	38.64	19.58
250	60	53.09	5.22	1.17	0.12	32.70	21.08
250	90	52.93	5.21	1.13	0.15	33.65	21.20
300	0	48.70	5.52	0.94	0.09	36.56	20.57
300	30	55.50	4.98	1.04	0.14	28.68	21.68
300	60	55.90	4.92	1.05	0.13	28.33	21.87
300	90	56.53	4.74	1.22	0.11	28.18	23.11

^{a} calculated by difference

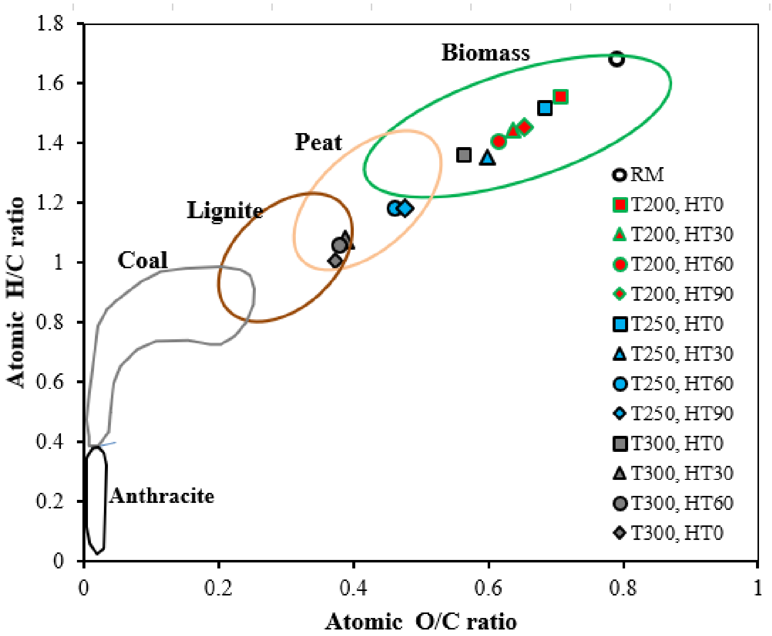


Fig. 5. Van Krevelen diagram of raw and torrefied CPS at different temperatures and holding times.

3.3 *Mass and Energy Yields*

Two of the main parameters in the evaluating of the torrefaction process are the mass and energy yields. Part of biomass component encounter decomposition and devolatilization then left solid component, *i.e.* biochar. Moisture was released first then followed by volatile matter. The volatile matter was not released completely during the torrefaction process. The quantity of biochar depends on the amount of volatile matter that raised, which was affected by holding time and torrefaction temperature.

The effect of the torrefaction temperature on the mass and energy yields at different holding times can be seen in Figure 6 and Figure 7. Increasing torrefaction temperature from 200°C to 300°C resulted in decreasing mass and energy yields. Besides the torrefaction temperature, the holding time has also influence on mass and energy yields. The mass and energy yields decreased from 92.5% ± 1.70% and 97.19% ± 1.79% (200°C, 0 min) to 52.5% ± 1.28% and 74.22% ± 1.81% (300°C, 90 min). At holding time of 0 and 30 min, the increasing of the torrefaction temperature from 200°C to 250°C had little effect on mass and energy yields while at holding time of 60 and 90 min, the effect of increasing torrefaction temperature from 200°C to 250°C had a more significant effect on the mass and energy yields. This phenomenon was the opposite of increasing the torrefaction temperature from 250°C to 300°C.

In general, the longer the holding time, the lower the mass yield. The results are similar to previous investigations carried out by Correia *et al.* for Arundo donax L. and Phoenix canariensis. Mass yields of Arundo donax L., Phoenix canariensis trunk, and Phoenix canariensis leaf sheaths are 85.5% to 3%, 82.6% to 38%, and 77.3% to 40% when torrefied at temperatures 200°C to 350°C [31]. Torrefaction of wood and dried sewage sludge at temperatures from 230°C to 290°C resulted in mass yields from 90.5% to 44.6 % and 72.5% to 60.3%, respectively [32]. In the investigation of Laminaria japonica [33] and Leucaena [34] torrefaction, it was found that the solid yield decreased, while liquid and gas yields increased with increasing torrefaction severity. The charring and devolatilization reactions were harder at longer holding time, thus forming of vapors, which consisted of tar and condensable gases were more [17].

At the torrefaction temperatures of 200°C and 300°C, mass and energy yields decreased sharply at holding time from 0 to 30 min while at holding time from 30 to 90 min mass and energy yields changed just slightly. It means that at temperatures of 200°C and 300°C the addition of a holding time of more than 30 min did not have a significant effect on CPS decomposition. This was likely due to the component of biomass decomposed at light torrefaction (200°C) was very limited. Mass reduction at this temperature was still dominated by evaporation and devolatilization of light gases, while at severe torrefaction (300°C), the biomass component decomposed rapidly until 30 min. At torrefaction temperature of 250°C, a decrease in mass yield at 0 to 60 min was significant, whereas it was not significant from 60 to 90 min. It implies that at a reaction temperature of 250°C, the addition of holding time of more than 60 min had little effect on CPS decomposition. In general, from Figure 7, it can be concluded that the change of mass and energy yields were not significant for holding time more of than 60 min.

As seen in Figure 6 and Figure 7, the energy yield was greater than the mass yield. It means that energy addition in biomass is greater than the mass reduction of biomass. According to the study of Gucho *et al.* for Beech Wood and Miscanthus torrefaction, it was due to the loss of water and carbon dioxide, which do not contribute to the final energy content of the torrefied product [27].

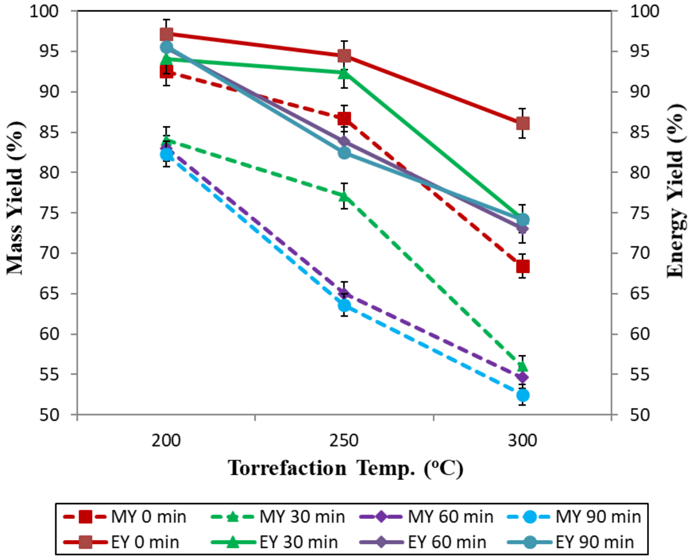


Fig. 6. Influence of torrefaction temperature on the mass and energy yield for different holding times.

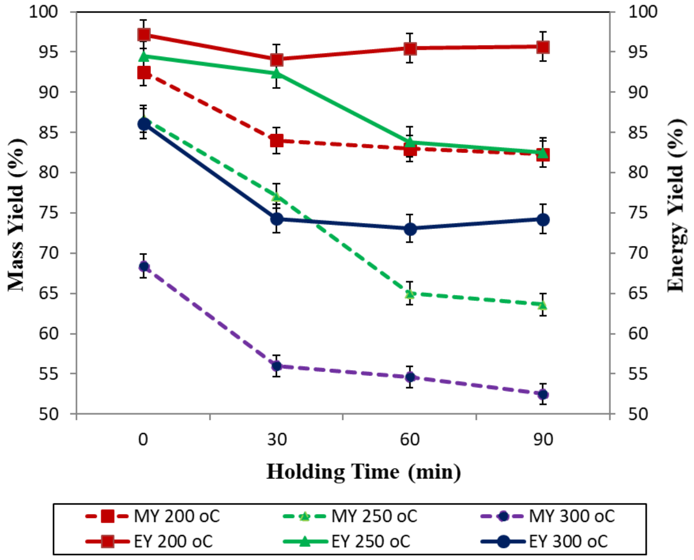


Fig. 7. Influence of holding time on the mass and energy yield for different torrefaction temperatures.

3.4 Fixed Carbon and Volatile Matter Content

The fixed carbon and volatile matter contents at different torrefaction temperatures are plotted in Figure 8 and Figure 9. This figure shows that increasing a holding time of more than 30 min did not have a significant effect on increasing fixed carbon. The torrefaction temperature presented a notable effect on the fixed carbon of CPS, especially at holding time of 60 and 90 min. This was probably only part of the biomass component decomposed until the 30 min. The fixed carbon was increased from 24.61% ± 1.05% at 200°C to 39.24% ± 0.4% at 300°C for holding time 90 min. The fixed carbon content of biomass increased with increasing torrefaction temperature was due to high carbonization and reduction in the O–H and C–O bonds, which increased C–C bonds [35].

The volatile matter content of torrefied CPS at 200°C was almost unchanged on different holding times. The significant change of VM was obtained at the torrefaction temperature of 300°C, *i.e.* from 60.78% ± 0.06% for raw CPS to 41.39% ± 0.05% at 300°C, 90 min. This was maybe due to the fact that in torrefaction of the 200°C, biomass components that released mainly of moisture and a little of hemicellulose, while at 250°C and 300°C, most of the hemicellulose has already released and part of cellulose, as well as lignin, has started to decompose.

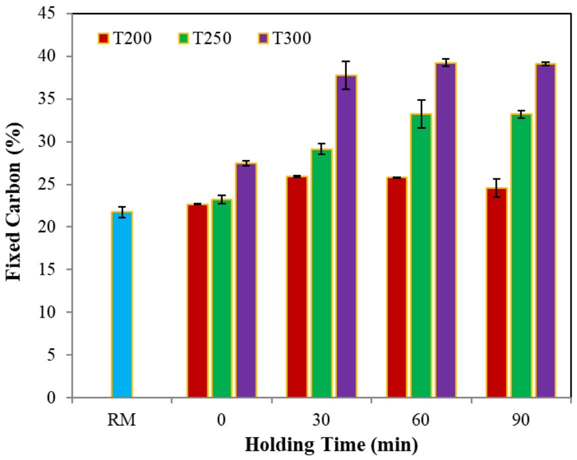


Fig. 8. The effect of holding time on fixed carbon content for different torrefaction temperatures.

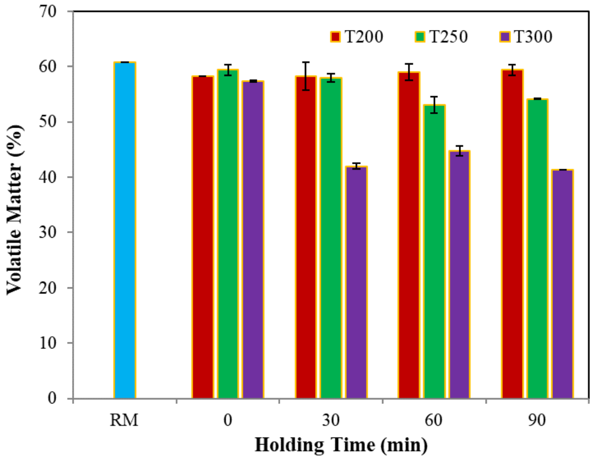


Fig. 9. The effect of holding time on volatile matter content for different torrefaction temperatures.

3.5 Hydrophobicity

One of the disadvantages of biomass is prone to absorb moisture from air. The higher the ability to absorb moisture means that the moisture content in biomass increases again when stored in open air even though it has been dried. Increasing moisture content in biomass reduces the calorific value, grows fungus more easily, and increases transporting and handling costs [5]. Torrefaction process changes the nature of biomass from hydrophilic to hydrophobic.

A comparison of the ability to absorb water vapor from air between raw and torrefied CPS can be seen in Figure 10. The hydrophilicity of the sample was indicated by the increase of the sample mass when the sample was exposed in open air until the moisture in the sample achieves equilibrium. The sample mass did not change after the second day. It means that after two days, the sample got equilibrium and stopped in absorbing moisture. After torrefaction process, CPS has decreased ability to absorb moisture from surrounding air.

Before being torrefied, the CPS powder absorbed moisture from air by 11.5% of the initial mass, while the increasing mass of the torrefied CPS powder resulted in moisture absorption depended on the torrefaction temperature and holding time. Moisture absorptions of torrefied CPS at 200°C, 250 C, and 300 C for 0 min to 90 min were 11.5% ± 0.25% to 9 % ± 0.25%, 9% ± 0.25% to 5.5% ± 0.25%, and 8.5% ± 0.25% to 4.5% ± 0.25% of the initial mass, respectively. Figure 10 indicates that the raw CPS absorbed moisture more than the torrefied CPS and the longer the holding time, the less moisture absorption. The decrease of moisture absorption was not significant at torrefaction the temperature of 200°C for holding time more than 30 min. Hydrophobicity of torrefied CPS changed prominently for holding time from 0 min to 30 min.

The increase of the biomass hydrophobicity after torrefaction was also evident in studies conducted by Medic *et al.* [25], Supramono *et al.* [36], Li *et al.* [39] and Chen *et al.* [38] who researched with raw materials of corn husk biomass, bagasse, bamboo, and cotton tree trunks. In these studies, it was known that the increased hydrophobic nature of biomass was related to the reduced content of hemicellulose in biomass. According to Tumuluru *et al.* [39], hemicellulose has many hydroxyls (-OH) groups that trigger biomass to be polar and easy to form hydrolytic bonds with water molecules.

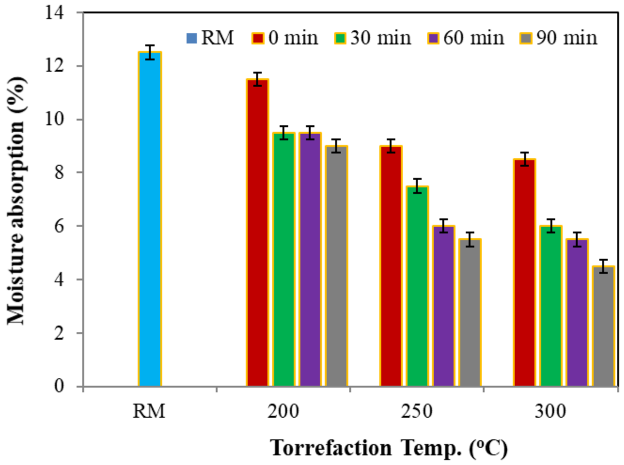


Fig. 10. Moisture absorption of raw and torrefied CPS at various torrefaction temperatures on different holding time.

3.6 Particle Size Distribution

The other important advantage of torrefaction is the change of biomass characteristic from fibrous to brittle, which makes it easier to grind. Grindability of biomass is very important, especially in pulverized combustion systems. The original nature of fibrous biomass causes higher energy consumption for grinding. By improving the physical properties of biomass after being torrefied, biomass processing equipment becomes smaller, simpler, and cheaper so that the capital and operational costs become lower [8].

The general grindability testing method for coal is the HGI standard. There is no grindability testing standard for charcoal. There are several methods used to evaluate the grindability by previous researchers, including the volumetric HGI test [40], the energy consumption [41],[42], and particle size distribution method [29],[43].

In this work, the particle size distribution method was used. The effect of holding time on the particle size distribution for different torrefaction temperatures and raw material are presented in Figure 8 and Figure 9. As observable from the figures, just 5.43% of raw CPS particles passed through the 75 µm sieve size. In addition, the figures reveal that the longer the holding time, the proportion of smaller size particles increased.

Figure 11 shows the effect of torrefaction temperature on particle size distributions of raw and torrefied CPS at different torrefaction temperatures for the same holding times. The particles of torrefied CPS at 200, 250, and 300°C for 60 min holding time that passed through the 75 µm sieve size were 17.89%, 39.57%, and 58.59%, respectively. It is clear that the higher the torrefaction temperature, the more particle passes through the series of sieves. The torrefaction broke down the cell wall and fiber structures of biomass so that the grindability was improved [44]. According to previous studies [43], [44], the reduction of particle size after the torrefaction process principally due to the reduction of particle length, thus the shape of particles became more spherical.

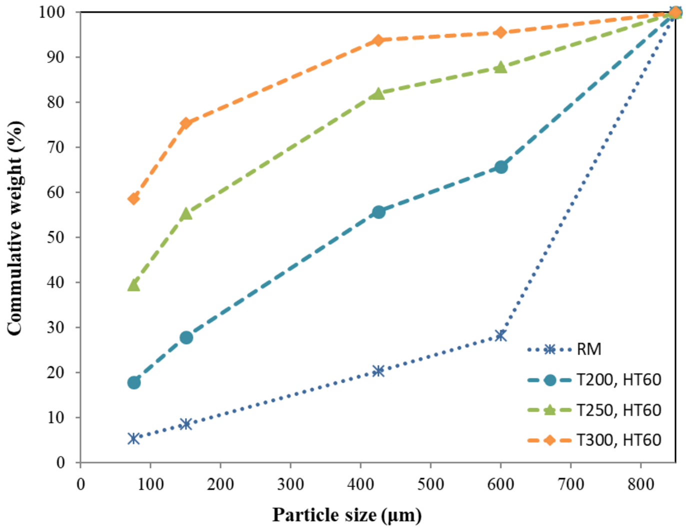
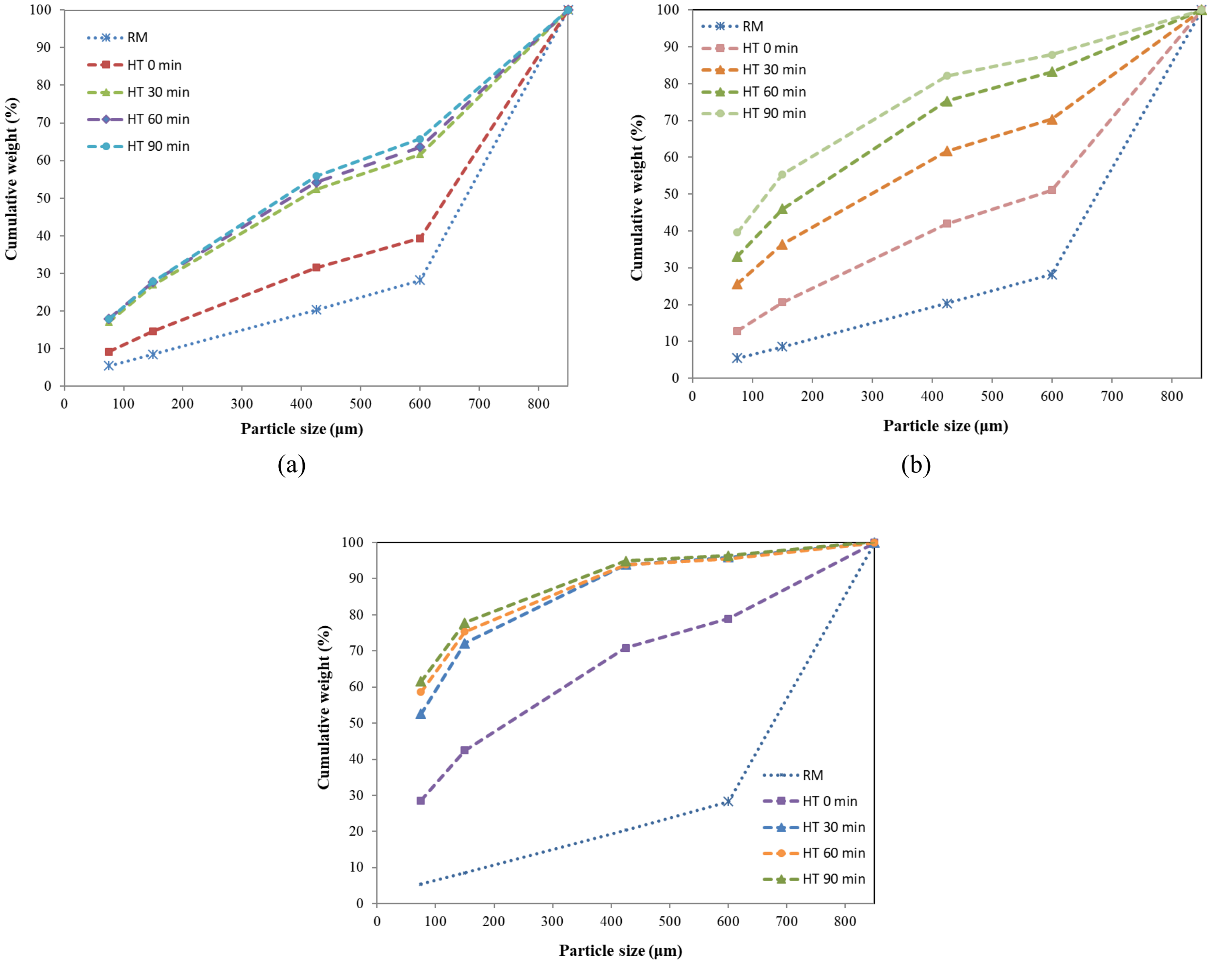


Fig. 11. Particle size distributions of raw and torrefied CPS at 200 to 300°C obtained in 60 min holding time.

At the torrefaction temperature of 200°C and holding time of more than 30 min, only a slight difference of the cumulative particles passed through the series of sieves was observed. This fact was similar to the torrefaction temperature of 300°C. At the 200°C, the decomposition of biomass has been reduced at the holding time of more than 30 min because of the temperature was insufficient for further decomposition. While at 300°C, this fact was probably due to the decomposition occurred effectively until the 30 min. From Figure 12, it can be seen that torrefied CPS was easier ground than that of raw CPS, and the longer the holding time, the better the grindability. According to Arias *et al.* [45], raw biomass was more difficult to grind caused by its highly fibrous nature.



(a)

(b)

(c)

Fig. 12. Particle size distributions of raw and torrefied CPS at (a) 200°C, (b) 250°C, and (c) 300°C that obtained at holding time 0 to 90 min.

Table 4. Proximate and ultimate analyses and higher heating value of torrefied CPS and coals.

Material	Proximate analysis (%, adb)				Ultimate analysis (%, adb)					HHV (MJ/kg)	Ref.
	M	A	V	FC	C	H	N	S	O		
Torrefied CPS	6.34	9.66	44.76	39.24	56.53	4.74	1.23	0.11	28.18	23.11	
Anthracite	2.88	8.94	8.970	79.21	81.68	2.88	1.77	1.70	0.15	30.38	[46]
Bituminous coal	1.51	9.20	32.37	56.92	72.36	4.52	0.95	11.06	0.40	28.867	[47]
Sub-bituminous coal	11.55	3.84	27.30	57.31	66.68	3.08	1.05	13.43	0.37	24.828	[48]
Lignite	7.50	23.7	27.50	41.30	55.00	4.00	2.00	5.99	1.81	23.211	[49]
Peat	21.38	0.32	48.86	29.44	55.20	5.00	1.30	38.40	0.10	22.037	[50]

Note: adb = air dry basis. M = moisture content. A = ash content. V = volatile content. FC = fixed carbon.
Qnet = net calorific value

3.7 Assessment of Potential Utilization

The purpose of biochar utilization is to reduce the use of coal, which is less environmentally friendly. The feasibility of biochar utilization as a solid fuel needs to consider several things including its physical, chemical, and thermal properties so that its utilization does not reduce the performance of the existing coal power plant. Table 4 shows the comparison of CPS based biochar with anthracite, bituminous coal, sub-bituminous coal, lignite, and peat. It is seen that CPS based biochar has a heating value and fixed carbon, which is almost the same as lignite. The advantage of CPS based biochar compared to lignite is lower ash and sulfur contents.

In terms of thermal properties, CPS based biochar can be used to substitute lignite, but in terms of its chemical content, it is reported that CPS contains high potassium (K) which is 8.74% by weight [51] and its combustion ash contains K_2O to 61.4% by weight [52]. This high potassium content increases the tendency for slagging and fouling on the boiler heat exchanger surface, so CPS is not suitable for combustion alone. Alternatively, it can be mixed with other solid fuels which have nearly the same characteristics, *i.e.* lignite. Amirabedin *et al.* [51] reported that the content of potassium in lignite is low, so CPS should be used as fuel by being mixed with lignite. Further research on co-combustion of biochar CPS and lignite needs to be done to determine the characteristics and combustion performance for a variety of ratios of a mixture of both solid fuels

4. CONCLUSIONS

In this study, the effects of torrefaction on the improving of CPS properties were investigated. It was found that temperature and holding time were influential factors in the torrefaction process. The physical appearance of torrefied CPS changed from light brown to black caused by releasing volatile matter, with the result that the fixed carbon content increased. The lower the grayscale value, the higher the HHV of the torrefied CPS. The carbon and fixed carbon contents, as well as higher heating value increased, while the volatile matter, hydrogen and oxygen contents, as well as the mass and energy yields decreased with increasing of the torrefaction temperature. The product of torrefaction nearly resembles between lignite and peat especially at the torrefaction temperature of 300°C with the holding time more than 30 min. Changing mass and energy yields were not significant for holding times of more than 60 min. The torrefaction process changed the nature of biomass from hydrophilic to hydrophobic and the higher the torrefaction temperature the less the moisture absorption. The higher the temperature and the longer the holding time, the better the grindability of torrefied CPS, so that it was easier ground than that of raw CPS. CPS based biochar is recommended for co-combustion with other solid fuels which have almost the same characteristics, *i.e.* lignite.

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