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The Effect of Feedstock Type and Slow Pyrolysis Temperature on Biochar Yield from Coconut Wastes

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***Abstract*—**The first objective of this study is to investigate the suitability of coconut frond (CF) and coconut husk (CH) as feedstocks using a laboratory-scale slow pyrolysis experimental setup. The second objective is to investigate the effect of pyrolysis temperature on the biochar yield. The properties of CF and CH feedstocks were compared. The properties of the CF and CH feedstocks were investigated using proximate and elemental analysis, lignocellulosic determination, and also thermogravimetric analysis (TGA). The CF and CH feedstocks were pyrolysed at 300, 400, 500, 600 and 700 °C for 2 hours at 10 °C/min heating rate. The proximate analysis showed that CF feedstock has 89.96 mf wt% volatile matter, 4.67 mf wt% ash content and 5.37 mf wt% fixed carbon. The lignocelluloses analysis showed that CF feedstock contained 21.46% lignin, 39.05% cellulose and 22.49% hemicelluloses. The CH feedstock contained 84.13 mf wt% volatile matter, 0.33 mf wt% ash content, 15.54 mf wt% fixed carbon, 28.22% lignin, 33.61% cellulose and 22.03% hemicelluloses. Carbon and oxygen are the major component of the CF and CH feedstock compositions. Both of CF and CH feedstocks contained very low percentage of sulfur, 0.77% and 0.33%, respectively. TGA analysis indicated that coconut wastes are easily degraded. It may be due to their high volatile content. Between the temperature ranges of 300 and 800 °C, the TGA curves showed that the weight percentage of CF feedstock is lower than CH feedstock by 0.62%-5.88%. From the D TGA curves, most of the weight loss occurred between 210 and 400 °C for both feedstocks. The maximum weight loss for both CF and CH are 0.0074 wt%/min and 0.0061 wt%/min, respectively, which occurred at 324.5 °C. The yield percentage of both CF and CH biochars decreased significantly as the pyrolysis temperature was increased. For CF biochar, the yield decreased from 49.40 wt% to 28.12 wt% as the temperature increased from 300 to 700 °C. The yield for CH biochars also decreased from 52.18 wt% to 28.72 wt%. The findings of this study indicated that both CF and CH are suitable feedstock for slow pyrolysis of biochar.

***Keywords*—**Biochar, biomass, coconut wastes, slow pyrolysis.

I. Introduction

BIOMASS is one of the major renewable energy resources. Generally, biomass refers to forestry, trees, plants and different type of waste such as organic, agricultural, agro-industrial and domestic wastes [1].

Plant biomass is made up of extractives, ash and cell wall components such as cellulose, hemicelluloses and lignin. Cellulose is linear and remarkable pure organic polymer, which consists solely of units of anhydroglucose. It degrades at around 240 to 350 °C to produce anhydrocellulose and levoglucosan [2]. The second major constituent is hemicelluloses, a mixture of various polymerized monosaccharides such as glucose, mannose, galactose, xylose, arabinose 4-*O*-methyl glucuronic acid and galacturonic acid residues. It consists of shorter chains, has amorphous structure with little strength, soluble in weak alkaline solutions and degraded at 200 to 260 °C, and thus tends to yield more gases (volatiles) and less tar than cellulose [3], [4]. Lignin is a complex polymer which is built of hydrophenylprophane units. It decomposes when heated in the temperature range of 280 to 500 °C [4]. It is known as the most thermally resistant component compare to cellulose and hemicelluloses due to its complex chemical composition. Biomass with higher lignin content was reported to produce a higher biochar yield as lignin preferably forms char during pyrolysis [5], [6].

The abundance and the improper management of biomass will lead to waste management problems. Usually biomass such as agricultural waste are not disposed properly. In many countries, agricultural waste such as stalks, leaves and husks are burned to reduce the residues from the agricultural activities [7]. Burning biomass produces pollutants including dust and the acid rain gases sulfur dioxide (SO_2) and nitrogen oxides (NO_x) [8]. The rest of biomass waste such as oil palm wastes are incinerated or dumped as organic fertilizer through natural decomposition [9]. The dumping of biomass which is left to rot also can lead to the emission of greenhouse gases such as methane (CH_4) and nitrous oxide (N_2O) [10]. The increment of greenhouse gases concentration in the atmosphere will consequently cause global warming. The impacts of global warming such as severe heat waves, more frequent drought, heavier rainfall and more powerful hurricanes are being felt across the globe [11].

The utilization of biomass as renewable energy resources offers a lot of benefits towards our nature and environment. It is one of the ways to reduce carbon dioxide (CO_2) from the atmosphere and help to mitigate climate change by reducing greenhouse gases. This can be achieved because biomass is derived from living plants that need CO_2 for its growth. The planting of plants will absorb CO_2 from the atmosphere via photosynthesis process. However, withdrawal of CO_2 by photosynthesis process alone is not enough to cope with increasing CO_2 in the atmosphere. The production of biochar from biomass via pyrolysis process and the application of biochar into soil promote carbon negative effects because biochar systems can hold a substantial portion of carbon in soil, as compared to carbon neutral withdrawal by photosynthesis [12]. The utilization of biomass as a renewable

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energy resource helps to avoid the adverse environmental effects from the conventional methods of biomass residues disposal such as dumping and open air burning.

The utilization of biomass as the feedstock in the thermochemical conversion process has been intensively studied. Various types of biomass such as Rhodes grass and fronds of date palm [13], pine wood, wheat straw, green waste, dried algae [14], dry freshwater algae [15], cherry seeds, cherry seeds shells [16], oil palm wastes [17], [18], apricot stone, hazelnut shell, grape seed and chestnut shell [19] have been used as feedstock for thermochemical conversion such as the slow pyrolysis process to produce biochar.

Biochar is the solid carbon-rich product generated from the thermal decomposition process of organic materials such as biomass under limited supply or absence of oxygen at relatively low temperatures, approximately below 700 °C [20] and produced to be added into soils with the intention to improve soil functions and to reduce the emissions from biomass that would otherwise naturally degrade to greenhouse gases [21]. Production of biochar has attracted interest due to its potential to mitigate climate change. The utilization of biomass to produce biochar will prevent the release of harmful greenhouse gases such CO_2 and CH_4. The application of biochar into soil will lock up the carbon in the soil in more durable form for longer period [22]. In addition, during the conversion of biomass to biochar, around 50% of the original carbon is retained in the biochar. This offers a significant opportunity for creating such a carbon sink. The long persistence of biochar in soil makes it a main candidate for the mitigation of climate change as a potential sink for atmospheric carbon dioxide [23].

Slow pyrolysis is one of the thermochemical conversion processes. It favors the production of char as a major product besides liquid and gas. During the process, the feedstock will be heated at moderate temperature around 600 °C with the residence time varies from 5 min to 30 min [3], [24] and at low heating rate which is around 5 °C/min to 20 °C/min [25]. The proportion and composition of slow pyrolysis products such as biochar, bio-oil and gas are influenced by the pyrolysis conditions like temperature, heating rate and residence time. Temperature has been identified as the main factor that influences the properties of biochar [26], [27].

In Malaysia, the plantations of palm oil, rubber, cocoa, wood, timber, pineapple, coconut and pepper produce biomass residues [28]. Coconut is one of the oldest agro-based industries in Malaysia. It is also the fourth important industrial crop after oil palm, rubber and paddy. Coconut is known as the 'tree of life' because it has various parts that can be used for different purposes whether in commercial, domestic or industrial. Ministry of Agriculture and Agro-Based Industry Malaysia (MOA) reported that the total production of coconut in Malaysia is increasing from 2009 to 2013, albeit the reduction of total plantation area [29]. The decline of coconut cultivation area is caused by the conversion of land utilization to the industrial crop such as oil palm as well as other development such as housing and industry [30]. The decline of the total area also could be due to the infrastructure development, urbanization and the emergence of other more profitable crops [31]. Meanwhile, the total production of coconut shows increasing trends from 2009 to 2013, from 379,251 tons to 624,727 tons, and it is expected to continue to increase in the following years [29]. This increasing trend could be achieved through efficient agricultural practices, utilization of high yielding breeds, labor productivity improvement, application of latest technology and crop intensity enhancement. The higher percentages of coconut residues generated from the industry could be expected along with the increment of coconut production every year. According to [32], the total production of coconut biomass excluding coconut water is about 106,100 kiloton's and 60.5% are unprocessed. The coconut industry generates various types of wastes including CH, coconut fiber, coconut shell, coconut flesh, as well as CF and coconut trunk.

There have been many studies on the slow pyrolysis of biomass using various kinds of feedstocks. However, a limited amount of work has been reported for slow pyrolysis of coconut wastes such as coconut frond and coconut husk. The objective of this paper is to investigate the suitability of CF and CH as feedstocks for a laboratory-scale slow pyrolysis experiment. This study is also carried out to investigate the effect of pyrolysis temperature on the biochar yield for both CF and CH feedstock. The comparison of the CF and CH feedstock properties and the correlation between the type of feedstock and yield percentage of the biochar are also discussed in this paper.

II. Methodology

A. Sample Collection and Pre-Treatment

CF and CH feedstocks originate from a plantation in Penang, Malaysia. The feedstocks were collected and dried in a conventional oven at 105 °C for 24 hours. Both of the feedstocks were cut into smaller sizes of around 2-5 cm.

B. Analysis of CF and CH Feedstock

TABLE I
STANDARD METHODS USED FOR PROXIMATE AND LIGNOCELLULOSES ANALYSIS

Analysis	Test	Unit	Method
Proximate Analysis	Moisture Content	mf wt%[a]	ASTM E871
	Volatile Matter	mf wt%	ASTM E872
	Ash Content	mf wt%	ASTM E1755-01
	Fixed Carbon	mf wt%	By difference
Lignocellulosic Determination	Lignin	%	ASTM D1106-96
	Cellulose	%	ASTM D1103-60
	Hemicellulose	%	By difference

[a]mf wt % - moisture free weight percentage.

The characterization of CF and CH feedstock were carried out via proximate and elemental analysis, lignocellulosic determination and TGA. The proximate and lignocellulosic analysis were performed according to the American Standard Test Method (ASTM), as listed in Table I. Perkin Elmer 2400 elemental analyzer was used to perform the elemental analysis. TGA was carried out using Mettler Toledo TG analyzer at 5 °C/min heating rate and 100 ml/min nitrogen gas flow rate.

C. Slow Pyrolysis Experiment

The slow pyrolysis experiment was performed using a laboratory-scale system. Fig. 1 shows the setup of the laboratory scale slow pyrolysis system which consists of a muffle furnace, sample holder and condensers.

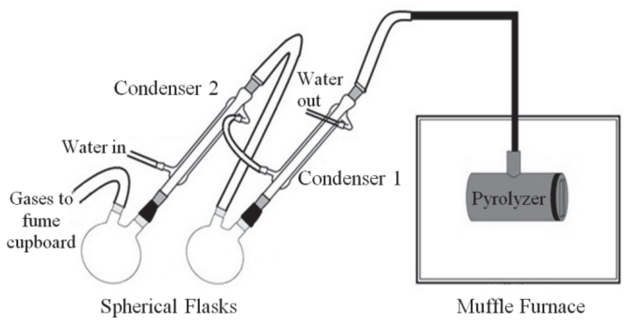

Fig. 1 Slow Pyrolysis Apparatus Setup

The feedstock was tightly packed in the sample holder to minimize the air inside the sample holder. The sample holder and the feedstock were weighed. The pyrolysis temperature was set at 300°C. The heating rate was fixed at 10°C/min. Then the feedstock was heated from 30°C to 300°C and the terminal temperature was on hold for two hours. Later, the sample holder was removed from the muffle furnace and allowed to cool down for approximately one hour. The sample holder was weighed again to determine the percentage of biochar yield, as shown by (1). The experiment was repeated at 400, 500, 600 and 700 °C pyrolysis temperature. The experiment was performed three times for each pyrolysis temperature and the average of biochar yield was determined.

$$\text{Biochar Yield (wt \%)} = (\text{Mass of biochar (g)} / \text{Mass of feedstock (g)}) \times 100 \quad (1)$$

III. Results and Discussion

A. Properties of CF and CH Feedstock

A preliminary study of the feedstock characterization provides details and fundamental understanding regarding the feedstock properties and how these properties influence the pyrolysis process and its products. The result of the proximate, elemental and lignocellulosic analysis of the CF and CH feedstocks are presented in Table II.

CF feedstock contained 89.96 mf wt% of volatile matter, 4.67 mf wt% of ash content and 5.37 mf wt% of fixed carbon. CH feedstock has higher fixed carbon, 15.54 mf wt% and lower volatile matter and ash content compared to CF feedstock, 84.13 mf wt% and 0.33 mf wt%, respectively. The volatile matter of the biomass usually ranges between 65% and 85% [33]. Both CF and CH feedstocks are suitable to be used as the feedstock in the slow pyrolysis experiment due to the high composition of volatile matter.

Elemental analysis shows that carbon and oxygen are the main elements of CF and CH feedstocks. CF feedstock contained 42.81% of carbon and 49.19 of oxygen, while CH feedstock contained 47.36% of carbon and 44.16% of oxygen. The sulfur composition is very low for both of CF and CH feedstocks, 0.77% and 0.03%, respectively. Consequently, these feedstocks will produce lower SO_2 emissions during the pyrolysis process. However, it was found that CH feedstock contained high percentage of nitrogen, 7.02%, compared to normal range of sulfur in biomass 0.15-2.70% as reported by [33]. In contrast, the nitrogen content in CF feedstock is negligible and below detection limit of the elemental analyzer.

TABLE II
PROPERTIES OF CF AND CH FEEDSTOCK

Analysis	CF	CH
Proximate analysis (mf wt%)		
Moisture content	0.37	0.18
Volatile Matter	89.96	84.13
Ash Content	4.67	0.33
Fixed Carbon[b]	5.37	15.54
Elemental Analysis (%)		
Carbon	42.81	47.36
Hydrogen	7.23	1.43
Nitrogen	BDL[c]	7.02
Sulfur	0.77	0.03
Oxygen[b]	49.19	44.16
Lignocellulosic determination (%)		
Lignin	21.46	28.22
Cellulose	39.05	33.61
Hemicellulose	22.49	22.03

[b]Calculated by difference
[c]BDL – below detection limit

The lignocelluloses analysis shows that the CF feedstock comprised of 21.46% of lignin, 39.05% of cellulose and 22.49% of hemicelluloses. CH feedstock has higher lignin percentage, 28.22% and lower cellulose and hemicelluloses, 33.61% and 22.03% respectively compared to CF feedstock.

The thermal degradation behavior of CF and CH feedstock is presented by thermogravimetric (TG) and derivative thermogravimetric (D TG) curves in Fig. 2.

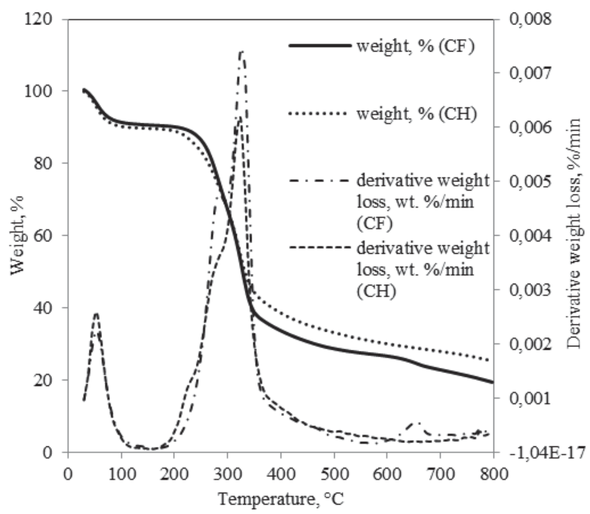

Fig. 2 TG and D TG curves of CF and CH feedstock

Fig. 2 shows the thermal degradation behavior of the CF and CH feedstock which were represented by the TG and D TG curves. TG curve indicates the fractional weight loss of the feedstock as a function of temperature. D TG curve is a plot of the rate of mass change, dM/dt versus temperature. It can be observed from the TG curve that the weight loss of the CF feedstock was prominent between 230 and 350 °C. Meanwhile, the weight loss of the CH feedstock was prominent between 220 and 340 °C. When the temperature is greater than 350 °C, the weight loss is insignificant for both CF and CH feedstock. It also can be observed from the TG curve that after 300 °C, the weight percentage of CH feedstock is higher than CF feedstock which implies that the percentage of CH biochar will be higher than CF biochar. It is due to higher lignin percentage composition in the CH feedstock which is responsible for char formation.

The differences between CF and CH feedstock also could be seen in their D TG curves. The D TG curve of CF feedstock has two distinct peaks occur at 285 and 325 °C. Meanwhile for the CH feedstock, a small hump and a high peak could be observed between 270 and 330 °C. According to [34], the decomposition of hemicelluloses occur around 220 to 315 °C. Thus, it can be concluded that the formation of first high peak for CF feedstock and small hump for CH feedstock are due to the degradation of hemicelluloses. As shown in Table II, CH feedstock contained lower percentage of hemicelluloses, 22.03% compared to CF feedstock which contained 22.49% of hemicelluloses. This could explain the formation of a small hump and a peak which represent the degradation of hemicelluloses for CH and CF feedstock, respectively. Meanwhile, cellulose degraded between 315 and 400 °C [34]. Thus, the high peaks of D TG curves for both CF and CH feedstock which occur around 325°C represent the degradation of cellulose. Cellulose is the main lignocellulosic component for both feedstocks. According to [35], it can be considered that the prominent weight loss during the analysis is caused by the degradation of cellulose.

B. Biochar Yield

The percentages of CF and CH biochar yield produced at different temperatures are presented in Fig. 3.

Fig. 3 shows the percentage of CF and CH biochar yield produced at 300, 400, 500, 600 and 700 °C. It could be observed that for both CF and CH biochar, the percentage yield decreased with the increasing temperature. The CF biochar decreased from 49.40 wt% to 28.12 wt% as the temperature increased from 300 to 700 °C. Meanwhile, the CH biochar decreased from 52.18 wt% to 28.72 wt%. The reduction of biochar yield may be attributed to the increase in the devolatilization of the organic material [36]. The dehydration of hydroxyl groups and decomposition of the lignocelluloses structure are expected to increase with increasing temperature [37].

From Fig. 3, it also can be observed that the different type of feedstock influence the percentage of biochar yield. This is due to the variation of lignocellulosic component and ash content in the feedstock. The high lignin composition in the feedstock will result in higher char formation [6]. Fig. 3 shows that CH biochar produced higher biochar yield compared to CF biochar at certain temperature. For example, at 300°C, CH biochar produced 52.18 wt%, while CF biochar produced 49.4 wt%. The higher percentage of CH biochar is due to the higher lignin content in the CH feedstock; 28.22% compared to CF feedstock which contained 21.46% of lignin. According to [38], ash content of the feedstock is another factor that influences the percentage yield of biochar. More char will be formed from the feedstock which contained higher ash content [39]. However, in this study it was found that CF biochar yield is lower than CH biochar yield produced at various pyrolysis temperatures even though CF feedstock contained higher ash content; 4.67 mf wt% compared to CH feedstock which contained 0.33 mf wt%. This could be due to the lower differences of ash content percentages of these two feedstocks compared to the differences of lignin percentages.

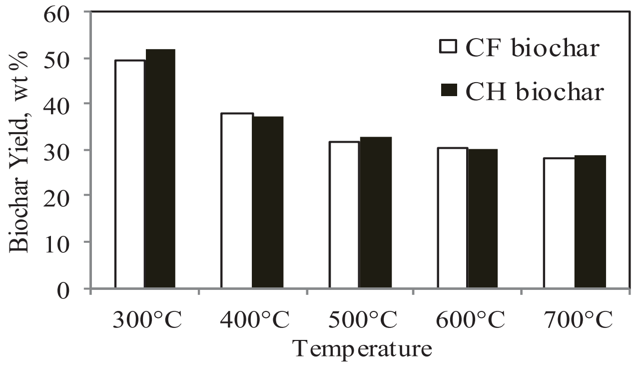

Fig. 3 CF and CH biochar yield produced at various temperatures

It also can be seen from Fig. 3 that the difference of biochar yield between CF biochar and CH biochar is insignificant as the temperature increased.

IV. Conclusion

The findings in this study showed that the CF and CH are suitable feedstock for slow pyrolysis. Types of feedstock and pyrolysis temperature influence the percentage of biochar yield. Results show that the biochar yield decreased with increasing temperature for both CF and CH biochar. CF biochar decreased from 49.40 wt% to 28.12 wt% as the temperature increased from 300 to 700 °C, while CH biochars decreased from 52.18 wt% to 28.72 wt% for the same temperature range. CH biochar produced higher biochar yield at most of temperatures due to the higher lignin composition in the CH feedstock. Further research will be directed towards the characterization of CF and CH biochar for soil benefits. More detailed research is needed to evaluate and understand the ability and performance of CF and CH biochar as soil enhancer.

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