

A Comparative Study on Biochar from Slow Pyrolysis of Corn Cob and Cassava Wastes

Adilah Shariff, Nurhidayah Mohamed Noor, Alexander Lau, Muhammad Azwan Mohd Ali

Abstract—Biomass such as corn and cassava wastes if left to decay will release significant quantities of greenhouse gases (GHG) including carbon dioxide and methane. The biomass wastes can be converted into biochar via thermochemical process such as slow pyrolysis. This approach can reduce the biomass wastes as well as preserve its carbon content. Biochar has the potential to be used as a carbon sequester and soil amendment. The aim of this study is to investigate the characteristics of the corn cob, cassava stem, and cassava rhizome in order to identify their potential as pyrolysis feedstocks for biochar production. This was achieved by using the proximate and elemental analyses as well as calorific value and lignocellulosic determination. The second objective is to investigate the effect of pyrolysis temperature on the biochar produced. A fixed bed slow pyrolysis reactor was used to pyrolyze the corn cob, cassava stem, and cassava rhizome. The pyrolysis temperatures were varied between 400 °C and 600 °C, while the heating rate and the holding time were fixed at 5 °C/min and 1 hour, respectively. Corn cob, cassava stem, and cassava rhizome were found to be suitable feedstocks for pyrolysis process because they contained a high percentage of volatile matter more than 80 mf wt.%. All the three feedstocks contained low nitrogen and sulphur content less than 1 mf wt.%. Therefore, during the pyrolysis process, the feedstocks give off very low rate of GHG such as nitrogen oxides and sulphur oxides. Independent of the types of biomass, the percentage of biochar yield is inversely proportional to the pyrolysis temperature. The highest biochar yield for each studied temperature is from slow pyrolysis of cassava rhizome as the feedstock contained the highest percentage of ash compared to the other two feedstocks. The percentage of fixed carbon in all the biochars increased as the pyrolysis temperature increased. The increment of pyrolysis temperature from 400 °C to 600 °C increased the fixed carbon of corn cob biochar, cassava stem biochar and cassava rhizome biochar by 26.35%, 10.98%, and 6.20% respectively. Irrespective of the pyrolysis temperature, all the biochars produced were found to contain more than 60 mf wt.% fixed carbon content, much higher than its feedstocks.

Keywords—Biochar, biomass, cassava wastes, corn cob, pyrolysis.

I. INTRODUCTION

CLIMATE change globally caused many devastating impacts including heat waves, rise in sea level, and food insecurity [1]. Malaysia is likely to feel the force of climate events sooner, due to its climate and location [2]. Climate change happened largely due to the anthropogenic GHG emissions from the human activities. 78% of the total emission of GHG is carbon dioxide (CO₂) emissions from the fossil fuel

combustion and industrial processes. Rapid growth in economic and population continued to be the most important drivers for the rise in CO₂ emissions [3]. Efforts must be undertaken to rectify this global issue. Common renewable energy strategies can at best be carbon-neutral or off set the fuel emissions of CO₂, but they are unable to reverse the climate change. One promising approach to reduce the atmospheric CO₂ concentration is to convert biomass into biochar in combination with its utilization to the soil [4]-[6]. According to International Biochar Initiative (IBI), biochar production can displace fossil fuel use, sequester carbon in stable carbon pools, and reduce the emission of nitrous oxides. Biochar as a soil amendment can help improve the Earth's soil resource and water quality [7].

Biochar is a solid product from thermal decomposition of biomass under limited supply of oxygen [8]. The biochar components have high stability against decay compared to other soil organic matter and decomposed very slowly in soil [9], [10]. It has a chemical structure that make it very difficult to break down by physical, biological, and chemical processes [11]. Therefore, biochar allows carbon input into soil to be increased greatly compared to the carbon output. This is the basis behind biochar's possible carbon negativity that make the biochar as a potential tool to slow down the climate change [10]. The information about the volatile matter and fixed carbon content of biochars is important in order to evaluate its general stability in soil [12], [13] and to show its potential as the carbon sequester [14].

Pyrolysis is a promising biomass conversion process, in the context of biochar production. Pyrolysis is taken from the Greek words, where "pyro" means fire, while "lysis" means decomposition [15]. Despite the types of biomass feedstock, the operating parameters during pyrolysis affect the physical properties of the biochar product. Temperature is the most important pyrolysis parameter studied because the fundamental physical changes are all temperature dependent [16]. Temperature is also an important factor for the product distribution of pyrolysis. Low temperatures and high residence times favor the production of solid biochar product, while the higher temperatures and short residence times lead to high liquid production [17]. Slow pyrolysis is a type of pyrolysis which favor the biochar yield up to 35% [15], [18]. Slower heating rates and longer residence times during slow pyrolysis make the biomass feedstock to continue reaction with each other, which convert most condensable organic compounds into solid biochar and condensable liquid product [17], [19].

Biomass is a promising feedstock for pyrolysis since it is abundantly available around the world. Biochar should be

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made from biomass waste materials to avoid the competition with any other land use. The abundant of wastes can also be reduced if they were used as the feedstocks for biochar production [20]. Corn and cassava are two types of the world's staple food [21]. The agricultural wastes from corn and cassava are high-potential biomass feedstock for biochar production because their production quantity and harvested area increased yearly. According to Food and Agriculture Organization, the production quantity of corn in Malaysia alone increased from 47,602 tonnes in 2010 to 86,643 tonnes in 2014. Meanwhile, the production quantity of cassava also increased by 40.94% from 2010 to 62,967 tonnes in 2014 [22].

In this study, corn cob from corn kernel industry and the cassava wastes from cassava plantation have been chosen as the feedstocks for biochar production via slow pyrolysis process. The aim of this study is to understand and compare the characteristics of the feedstocks and investigate the effect of pyrolysis temperature on the percentage of biochar yield and its characteristics.

II. METHODOLOGY

A. Biomass Feedstocks Preparation

Biomass from agricultural wastes which are corn cob, cassava stem, and cassava rhizome were used as the feedstocks to produce biochar via slow pyrolysis process. The corn cobs were obtained from a corn farm in Kedah, Malaysia. Meanwhile, the cassava stem and cassava rhizome samples were collected from a local cassava plantation in Penang, Malaysia. They were leftover on the plantation after its tubers were harvested. The feedstocks had undergone the pre-drying treatment which was conducted in a conventional oven at 105 °C. The drying process was continued until the feedstock is retained at a constant weight. The feedstocks were cut into smaller sizes where the length of cassava stems and corn cob feedstocks ranged from 3 cm to 4 cm. The cassava rhizomes which had non-uniform shapes were cut into dimension of 4 cm length, 4 cm width, and 3 cm thick. All the feedstocks were kept neatly in labeled plastic containers.

B. Characterization of Biomass Feedstocks

The feedstocks were characterized by using the proximate and elemental analyses as well as calorific value and lignocellulosic determination. The proximate analysis involved the determination of moisture content, volatile matter, and ash content according to the standard test method ASTM E1756-01 [23], ASTM E872-82 [24], and ASTM E1755-01 [25], respectively. The elemental analysis was conducted by using Perkin Elmer 2400 elemental analyzer to determine the amount of carbon, hydrogen, nitrogen, sulphur, and oxygen content of the feedstocks. The calorific value of feedstocks was determined by using an adiabatic bomb calorimeter, Yoshida Seisakusho 1013-B. The ASTM standard procedures to determine the lignocellulosic contents of the feedstocks were performed in sequence starting from determination of alcohol-toluene solubility (ASTM D1107-96) [26], Klason lignin (ASTM D1106-96) [27], holocellulose

(ASTM D1104-56) [28], and lastly alpha-cellulose (ASTM D1103-60) [29].

C. Slow Pyrolysis Experiment

The slow pyrolysis for biochar production was conducted using a fixed-bed slow pyrolysis set-up as shown in Fig. 1. The experimental set-up consists of a cylindrical stainless steel pyrolyzer equipped together with the condensing system. The dimension of the pyrolyzer is 50 mm diameter × 170 mm length.

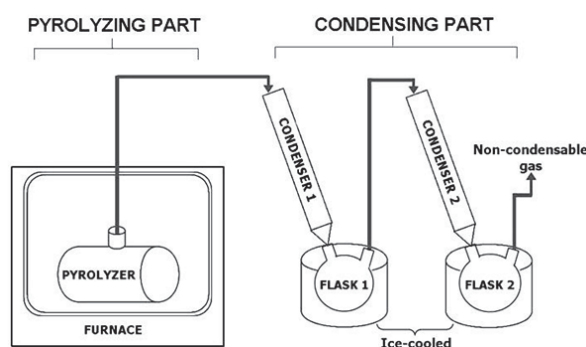


Fig. 1 Schematic diagram of slow pyrolysis set-up

The experiment was conducted at five different pyrolysis temperatures for each feedstock. The pyrolysis temperature or terminal temperature ranged from 400 °C to 600 °C, while the heating rate was fixed at 5 °C/min. Once the experiment reached the terminal temperature, it was maintained for an hour until no further significant release of gas was observed. About 100 g of feedstock was used for each run of the experiment. Experiment was repeated three times for each varied temperature and feedstock.

During the slow pyrolysis process, the pyrolyzer was externally heated in an electrical muffle furnace, Thermolyne F62700. The emissions from the pyrolyzer were led out to the first water-cooled condenser attached to the first ice-cooled spherical flask. The condensation process continued in the second water-cooled condenser attached to the second ice-cooled spherical flask. The incondensable gases were not collected and discharged out from the laboratory through the fume cupboard.

The weight of biochar is the weight of solid residue remained in the pyrolyzer after the pyrolysis process. The biochar yield was calculated based on moisture free feedstock. Consequently, it was defined on moisture free basis (mf wt.%) and averaged over three results. The percentage of biochar yield was calculated using (1):

$$\frac{\text{Weight of biochar (g)}}{\text{Weight of moisture free feedstock (g)}} \times 100 \quad (1)$$

D. Biochar Characterization

The procedure to determine the biochar composition such as volatile matter, ash content, and fixed carbon were done according to the amended ASTM D1762-84. The modification

was done as to meet the application of biochar as a soil amendment, not as a fuel source [13].

III. RESULTS AND DISCUSSION

A. Characteristics of Raw Biomass Feedstocks

Table I enlisted the characteristics of three types of biomass feedstocks used in this study. The results from the proximate and elemental analysis were presented in weight percentage on moisture free basis (mf wt.%). From the proximate analysis results, the moisture contents of all the pre-dried feedstocks were below 10 mf wt.%. These values are acceptable for the slow pyrolysis process because high moisture content in the feedstock cause less effective heating process during pyrolysis [30]. Cassava rhizome contained the highest ash content of 7.28 mf wt.% compared to the cassava stem and corn cob. Ash content of biomass originates from minerals present in the structure of the biomass tree, shrubs, and any soil contamination [31]. Since cassava rhizome originally located under the ground, we assumed its high percentage of ash content is due to the excess soil attached on its surface area.

Table I clearly shows that the percentage of volatile matter is found to be the highest composition in all the three feedstocks. The cassava stem, cassava rhizome, and corn cob contained more than 80 mf wt.% of volatile matter and have relatively high calorific value, more than 16 MJ/kg. This suggested all the feedstocks are suitable to be converted via thermochemical process such as slow pyrolysis.

TABLE I
CHARACTERISTICS OF BIOMASS FEEDSTOCKS

Characteristics	Cassava stem	Cassava rhizome	Corn cob
Proximate analysis (mf wt.%)			
Moisture	2.08	3.53	7.14
Volatile matter	81.51	83.64	87.76
Ash	2.42	7.28	1.05
Fixed carbon ^a	16.07	9.08	11.19
Elemental analysis (mf wt. %)			
Carbon, C	44.47	41.78	43.81
Hydrogen, H	5.82	5.97	6.54
Nitrogen, N	<0.01	0.26	0.77
Sulphur, S	0.83	0.92	0.69
Oxygen, O ^a	48.88	51.07	48.19
Molecular formula	CH _{1.56} O _{0.83}	CH _{1.70} O _{0.92}	CH _{1.77} O _{0.83}
Calorific value (MJ/kg)	18.39	18.01	16.46
Lignin (%)	32.26	26.18	11.32
Cellulose (%)	47.67	47.27	45.88
Hemicellulose (%)	27.79	35.83	39.40

^aCalculated by different

Results from the elemental analysis showed that carbon and oxygen are the major elements in all the three feedstocks. The percentage of carbon ranged from 41.78 mf wt.% to 44.47 mf wt.%, while the percentage of oxygen ranged from 48.19 mf wt.% to 51.07 mf wt.%. All the feedstocks are relatively environmental friendly as their nitrogen and sulphur contents were very low of less than 1 mf wt. %, which indicated that they will only give off very low rate of nitrogen oxides and

sulphur oxides during the slow pyrolysis process. The molecular formulas derived from the elemental analysis were found to be CH_{1.56}O_{0.83}, CH_{1.70}O_{0.92}, and CH_{1.77}O_{0.83} for the cassava stem, cassava rhizome, and corn cob, respectively.

From Table I, the lignocellulose content of cassava wastes and corn cob showed to have an apparent differentiation, especially on their lignin content. Cassava stem and cassava rhizome possessed higher lignin content of 32.26% and 26.18% respectively, while the lignin of corn cob is 11.32%. All the feedstocks contained high and comparable percentage of cellulose content in the range between 45% to 48%. Since lignin and cellulose mainly contribute to the biochar production [32], it is suggested that all the feedstocks can give fairly high yield of biochar and thus are suitable feedstocks for slow pyrolysis.

B. Biochar Yield

Fig. 2 presents the graph of percentages of biochar yield from five different slow pyrolysis temperatures ranged from 400 °C to 600 °C.

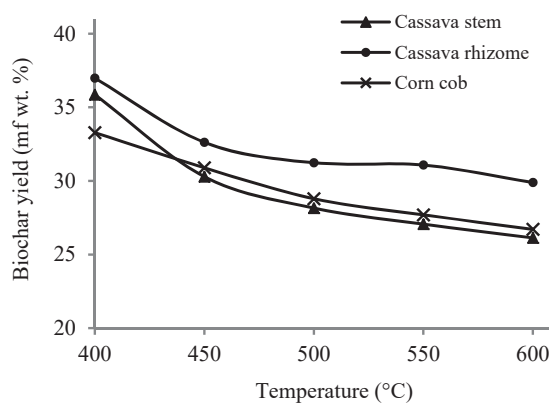


Fig. 2 Effect of temperature on biochar yield

The graph trend shows that the biochar yield from cassava stem, cassava rhizome, and corn cob is inversely proportional to the pyrolysis temperature. As the pyrolysis temperature increased from 400 °C to 600 °C, the percentage yield of cassava stem biochar, cassava rhizome biochar, and corn cob biochar decreased by 27.13%, 19.17%, and 19.74%, respectively. The same effect was also found from many other slow pyrolysis experiments using different types of feedstocks such as softwood pellets [14], cogon grass [33], pomegranate seeds [34], oil palm empty fruit bunch, and rice husks [35]. The decrement of the biochar yield with increasing temperature could be either due to higher primary decomposition of the feedstocks or secondary decomposition of the biochar residue [36].

The comparison of biochar yield from three feedstocks in Fig. 2 showed that the highest biochar yield from each varied temperature is from slow pyrolysis of cassava rhizome. This is maybe due to the high ash content in the cassava rhizome, compared to the other two feedstocks (refer Table I). During slow pyrolysis process, the alkali metals from the ash such as

sodium and potassium will favor the secondary reaction and catalyze some re-polymerization reactions of the heavier fraction of the products (tar) that increased the biochar yield [37].

C. Characteristics of Biochar

Figs. 3-5 summarized the composition of cassava stem biochar, cassava rhizome biochar, and corn cob biochar respectively. All the three graphs represent the percentage of moisture, volatile matter, ash, and fixed carbon content of biochars produced at 400 °C, 500 °C, and 600 °C.

Figs. 3-5 show that pyrolysis temperature gives more significant impact on the percentage of fixed carbon and volatile matter compared to the moisture and ash content of the biochars. The results in all the three figures showed that higher pyrolysis temperature produced biochar with higher fixed carbon content. The same trend of results was also obtained from many other studies including pyrolysis of woodchips [14], pomegranate seeds [34], and cherry sawdust [38]. The increment of pyrolysis temperature from 400 °C to 600 °C increased the fixed carbon content of cassava stem biochar by 10.98%, from 78.39 mf wt.% to 87.00 mf wt.%. Meanwhile, Figs. 4 and 5 showed that the fixed carbon content in cassava rhizome biochar and corn cob biochar increased by 6.20% and 10.33% respectively, as the pyrolysis temperature increased from 400 °C to 600 °C.

The fixed carbon content is dependent on the percentage of volatile matter. According to [39], the fixed carbon content of biochar is the carbon remained after evaporating the volatile matter from the biochar. The volatile matter in the feedstock transformed into the gas phase during the pyrolysis process. Therefore, at higher pyrolysis temperature, more volatile matter have been forcibly expelled out of the biochar particles which resulted in less volatile matters but more fixed carbon left in the biochar product [39]. Fig. 3 showed that the percentage of volatile matter in cassava stem biochar decreased by 61.44% as the pyrolysis temperature increased from 400 °C to 600 °C. Meanwhile, Figs. 4 and 5 showed that the increment of temperature from 400 °C to 600 °C decreased the percentage of volatile matter in cassava rhizome biochar and corn cob biochar by 50.68% and 93.91%, respectively.

It can be seen clearly in Figs. 3-5 that irrespective of the type of feedstock and pyrolysis temperature, the highest composition in all the biochars is the fixed carbon content. The cassava stem biochars produced from 400 °C to 600 °C contained 78.39 mf wt.% to 87.00 mf wt. % of fixed carbon, cassava rhizome biochars contained 79.20 mf wt.% to 84.11 mf wt.% of fixed carbon, while corn cob biochars contained 84.88 mf wt. % up to 93.65 mf wt. % of fixed carbon content.

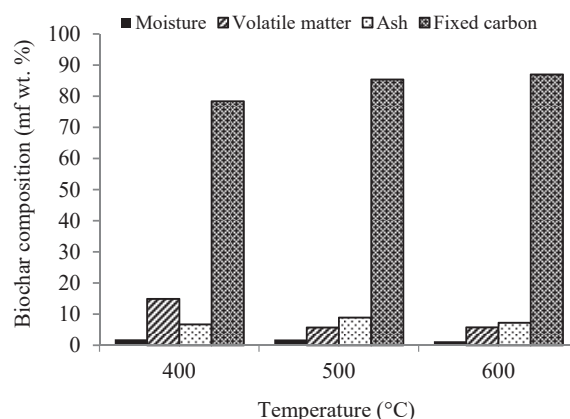


Fig. 3 Composition of cassava stem biochars

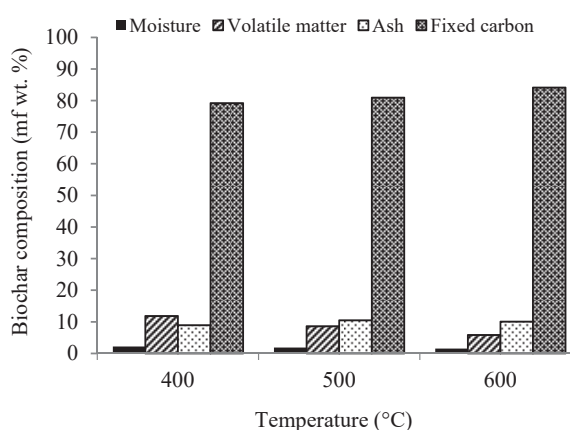


Fig. 4 Composition of cassava rhizome biochars

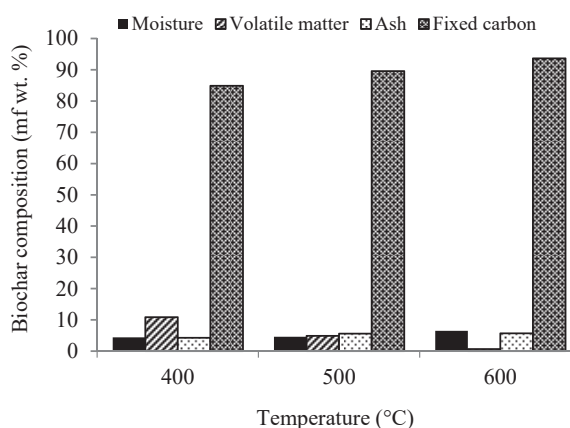


Fig. 5 Composition of corn cob biochars

By comparing the fixed carbon content of biochars in Figs. 3-5 with the fixed carbon content of feedstocks in Table I, it can be clearly seen that all the biochars produced at any pyrolysis temperature possessed higher fixed carbon content compared to their raw feedstocks. The cassava stem biochar produced at 600 °C has five times higher fixed carbon content, compared to its raw feedstock. Meanwhile, cassava rhizome

biochar and corn cob biochar produced at 600 °C have respectively nine times and eight times higher fixed carbon content compared to their raw feedstocks. This suggested that it is beneficial to convert the cassava rhizome, cassava stem, and corn cob into biochar products as biochar with high fixed carbon content has great potential to be used for soil amendment to sequester carbon and mitigate the climate change.

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