HYDROCHAR PRODUCTION FROM HYDROTHERMAL CARBONIZATION OF RAW PALM SHELL

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Abstract- Oil palm industry produces a large amount of biomass wastes in the form of EFB, fronds, trunks and palm shell. In this study, raw palm shell is converted into hydrochar using hydrothermal carbonization process. Hydrothermal carbonization of palm shell was carried out at 200 ^{o}C for 60 min with biomass to water ratio of 1:10 wt. %. The hydrochar product is further characterized using heating value, elemental, BET and FESEM analysis. The results show that heating value of raw palm shell was improved from 12.4 MJ/kg to 21.7 MJ/kg after hydrothermal carbonization. The results of elemental composition reveals that carbon content was increased whereas hydrogen and oxygen contents were decreased with hydrothermal carbonization temperature. The figures of FESEM show that the surface of raw palm shell was rough and didn't contain any pores while after hydrothermal carbonization, the pores were produced on the surface of hydrochar which shows that the palm shell was eroded significantly by hydrothermal carbonization.

Keywords- Oil Palm, Palm Shell, Hydrothermal Carbonization, Hydrochar

I. INTRODUCTION

Since last two decades, the conversion of biomass into biofuels has been increased significantly due to merits provided by using biofuels. Biomass comes from agricultural and industrial wastes. Oil palm industry is a largest producer of agricultural wastes in Malaysia. These wastes come in the form of fiber, trunk, palm shell and empty fruit bunch (EFB). Approximately 0.3 tons of palm shellis produced on the extraction of one ton palm oil. Similarly , 0.7 tons of palm fiber and 1 ton of EFB are produced as industrial wastes on the yield of one ton of oil palm(Dalimin 1995).

This fact shows the importance of utilization of biomass wastes of oil palm industry. Palm shell is a waste produced in oil palm mill and annual production of palm shell is about 2.4 million tons which might produce energy equal to 45.84 PJ (petajoule) (Md Kawser and Farid Nasir 2000, Sumathi, Chai et al. 2008, Abnisa, Daud et al. 2011). The major components of palm shell are: hemicellulose, cellulose and lignin (Abnisa, Daud et al. 2011). The paper will review higher heating value (HHV), ultimate, Brunauer Emmett and Teller (BET) and Field emission electron microscopy (FESEM) analyses of both raw palm shell and hydrochar. Moreover, the characteristics of char are compared to that of raw palm shell.

II. MATERIALS AND METHODS

The raw palm shell was collected from a local industry in Selangor, Malaysia. The raw palm shell was washed with tap water and then with distilled water for several times to remove dirt. The washed raw palm shell was kept in oven at 105 ^{o}C for 24 hours to drying purpose. The dried palm shell was ground and separated by sieving through different sieves and the average particle size determined is 0.5 – 2.5 mm.

The HTC experiments were conducted in a high pressure autoclave batch reactor with a volumetric capacity of 1 L. Reactor was fabricate dofstainless steel, SS 316, to withstand high temperature and pressure at 500 ^{0}C and 100 bars respectively with a stirrer speed of 100 to 1450 rpm to mix the reactants.

Hydrothermal carbonization was carried out at 200 ^{o}C with 1:10 wt.% biomass to water ratio for 60 min. The prepared feed sample and distilled water were mixed in the batch reactor at preset value of biomass to water ratio. The raw palm shell and distilled water were mixed uniformly at a stirrer speed of 400 rpm for 5 min and the stirrer speed was kept constant throughout the reaction.

Then the reactor was heated with an automatic proportional-integral-derivative (PID)controlled 2250 Watt ceramic heater up to preset value of temperature.

The reaction time was startedto count when the reactor obtained the set temperature value. After completion of the reaction, the reactor was cooled by circulating water through the joints of the reactor. After cooling reactor, the slurry of liquid and solid products was taken out of the reactor manually, while the gaseous products, being negligible, were vented. Slurry of solid and liquid product was filtered by using Fioroni Filter Paper Grade 601 and the solid and liquid product were separated. The solid product

was kept in the oven for the complete drying purpose at 105 ^{o}C for 24 hours, weighted and characterized.

III. RESULTS AND DISCUSSIONS

Raw palm shell was efficiently converted to hydrochar by hydrothermal carbonization. Hydrothermal carbonization effects the characteristics of raw palm shell also. It is observed that higher heating value of raw palm shell was improved from 12.4 MJ/kg to 21.7 MJ/kg. The improvement in heating value is due to temperature of hydrothermal carbonization. As temperature increases, the carbon content increases whereas hydrogen and oxygen contents decreases which results in improving the combustion properties (McKendry 2002, Oliveira, Blöhse et al. 2013).

Elemental analysis results reveal that the carbon content was increased from 26.5 % to 46.2 % while oxygen and hydrogen contents decreased from 57.2 % and 5.8 % to 40.1 % and 4.7 % respectively. The increase in carbon content is because of dehydration and decarboxylation reactions taking place during the HTC process (Berge, Ro et al. 2011).

It is observed that O/C and H/C atomic ratios were decreasing gradually in hydrochar with increasing temperature of hydrothermal carbonization.

The decrease in O/C and H/C atomic ratios are because of dehydration and decarboxylation reactions taking place during hydrothermal carbonization(Akhtar and Amin 2011).

Dehydration reaction carbonizes biomass significantly by lowering the H/C and O/C ratios of biomass (Funke and Ziegler 2010).The results show that the BET surface area, total pore volume and average pore diameter of hydrochar products are increased as compared to raw oil palm shell and it is totally dependent on parameters of hydrothermal carbonization process, reaction times and temperatures.

An increase in temperature causes widening of pore structure resulting in increase of BET surface area (Rashid, Reddy et al. 2014).Lower surface area and lower porosity of hydrochars has limited the use of hydrochars as a catalysts and absorbent(Xu, Qian et al. 2013). Porosity and surface area of hydrochars could be improved by chemical and thermal activation for catalytic and energetic applications. Higher particle size and higher reaction times also may increase surface area of hydrochars(Xu, Qian et al. 2013).

The higher heating value, elemental composition (C, H, O, N, and S), O/C,H/C atomic ratiosand BET results of palm shell and hydrochar are listed and compared in Table 1.FESEM results show that some morphological changes were perceived in hydrochar produced by hydrothermal carbonization as compared to raw palm shell representing the damage of palm shell structure.

The Fig 1 (a) and (b) indicate clearly that hydrothermal carbonization has altered the structure of palm shell significantly. It can be observed by FESEM images that the raw palm shell has rough surface with very few pores. After hydrothermal carbonization process, the surface porosity of the hydrochar products was increased, resulting in large surface area with small voids on the surface. These voids make easier the release of volatile matter from biomass (Thanapal, Chen et al. 2014).

CONCLUSION

Raw palm shell was successfully converted to hydrochar by using hydrothermal carbonization process. It is observed that heating value and carbon contents were increased whereas hydrogen and oxygen contents were decreased with hydrothermal carbonization.

BET analysis results show that BET surface area, average pore diameter and total pore volume were also incremented with hydrothermal carbonization. Although, these values were low.

According to FESEM results, there were no pores on the surface of raw palm shell and were produced on the surface of hydrochar after hydrothermal carbonization process.

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Table 1. Elemental analysis, O/C, H/C atomic ratios, heating value and BET results of raw palm shell and hydrochar.

	C %	O %	H %	N %	O/C	H/C	HHV (MJ/kg)	Surface area (cm^2/g)	Total pore volume (cm^3/g)	Av. Pore diameter (nm)
Palm shell	26.5	57.2	5.8	0.2	2.2	0.2	12.4	0.3106	0.001292	45.1133
Hydrochar	46.2	40.1	4.7	0.3	0.9	0.1	21.7	10.9022	0.0392	143.8311

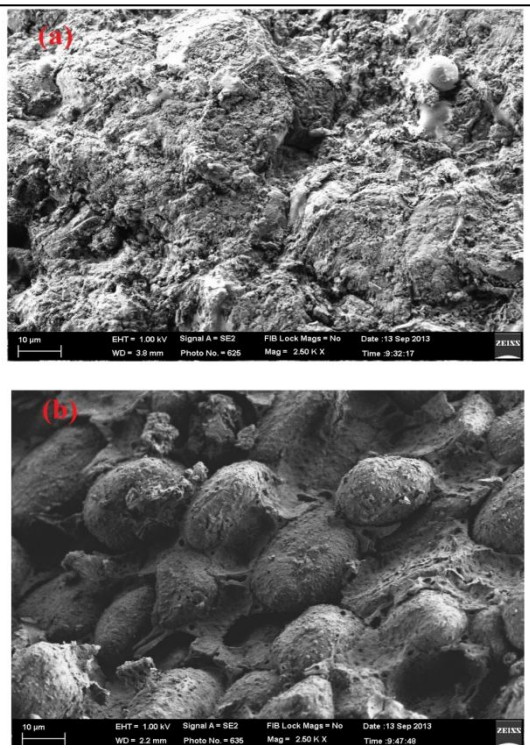


Figure 1. FESEM images of (a) raw palm shell and (b) hydrochar.

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