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Low Potassium Content Pellet Production by Hydrothermal-Washing Co-treatment

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Abstract: This study aims to produce a clean and durable pelletized fuel from palm empty fruit bunch (EFB) utilizing the combination of the hydrothermal treatment technology (HTT) and washing treatment. The EFB demerits in its energy extraction involves the moisture content, its bulk and energy density and shape that has negative effect on the combustion efficiency and transportation, in addition to its high content of potassium that often causing severe deposition problem in the biomass-fired plants. The HTT becomes key technology in improving the fuel characteristics as well as enhancing the washing and pelletization performance. The combination of the pelletization, HTT, and the washing co-treatment is promising for upgrading biomass into clean, energy dense, homogenous, friable, durable, and hydrophobic solid fuel.

Key-Words: Hydrothermal treatment, pellet, EFB, low-potassium, washing, combustion

1 Introduction

In Southeast Asia, one kind of biomass that being considered as the most potential for energy production is empty fruit bunch (EFB), a byproduct of palm oil industry. Indonesia, the world's largest palm oil producer, plans to double its current production of crude palm oil to 40 million tons by 2020, expecting the growing amount of EFB byproduct in each year [1]. This by-product is poorly utilized yet causing many problems associated with the improper disposal practices of EFB, such as the insufficient dumping spaces and bad odor, and hazardous methane gas from the decomposition processes [2]

The waste from the growing palm oil production needs immediate mitigation to fully utilize the waste and extract its potential energy for energy production. Despite its promising advantages to replace fossil fuels, there are many issues regarding raw EFB biomass [3]–[5], such as hydrophilic nature, high moisture content and low bulk density, thus lowering its calorific value and limiting its ease of use as fuel. EFB also contains high ash and alkali metal content especially potassium [5]. Considerable attention has been paid to ash deposition issues when combusting EFB in boilers. Therefore, improvement to obtain better characteristics is indispensable in the term of fuel use. Currently, several different approaches have been considered to improve the fuel properties of biomass. In this study, the combination of HTT, washing pre-treatment and pelletization will be employed in order to mitigate the issues.

Pelletization is one good way to deal with the handling and transporting issues of the EFB in its original form, especially when we intend to use it for domestic and international market. The pelletization of biomass could reduce the costs of transportation, handling and storage. Because of uniform sizes and shape, the pelletized biomass can be easily handled using the standard handling and storage equipment, and can be easily adopted in direct-combustion or co-firing with coal, gasification and in other biomass-fired plants. However, biomass pellets may still not be the ideal fuels because of the high moisture affinity and the relatively weak durability, especially for the pellets made from agricultural residues [6]. Therefore, the HTT and washing co-treatment is necessary before the pelletization; HTT can upgrade the raw biomass into more stable, more hydrophobic and more lignin containing feedstock; and washing treatment can deal with the ash deposition issue. The co-treatment is effective to produce more strong, durable and clean pellets.

The previous published literatures had conducted the various pre-treatments prior to pelletization, such as steam exploded biomass pellets, torrefied biomass pellets, and including the hydrothermally-carbonized biomass pellets. The steam treatment and hydrothermal treatment studies had shown that the pellets were more dimensionally stable and less hygroscopic [7], more resisted to higher breaking forces due to increased lignin content [8], and more durable compared to untreated one [6], [9], [10]. Nevertheless, there is no research focused on the washed treated pellets was found. Therefore, this study may give more clear information and knowledge on the effect of washing on the HT treated pellet

2 Material and Method

2.1 EFB samples

The EFB samples was harvested in 2010 and collected from private palm oil mill company, Waris Selesa Sdn. Bhd., in Sabah, Malaysia. The samples were received in milled and dried condition from the company, with a uniform particle size ranging from 10 - 20 mm. The samples were stored in sealed plastic bags at the room temperature until use for experiments.

2.2 Hydrothermal treatment

The HTT experiments were conducted using a commercially available batch type autoclave reactor (MMJ-500, Japan). The facility consists of a reactor equipped with an automatic stirrer, a controllable electrical heater, and a condenser. The detailed configurations of the facility can be found elsewhere [11]. In this experiment, 20 grams of EFB and distilled water in 1:10 biomass-water ratio was supplied to the reactor. The reactor temperature was set at 180 and 220°C, respectively, with the holding time of 30 minutes. After completed, the product was discharged from the reactor. The solid part was separated from the liquid by using the vacuum filtration, then oven dried at 105°C for 24 h, and stored in a sealed bag before further analysis. All HTT at four temperatures were repeated at least three times to ensure the reproducibility and consistency.

2.3 Washing treatment

The washing process was studied applying several process parameters. Different hydrochars and solid-liquid ratios were applied. The washing processes were conducted by heating a certain ratio of distilled water to 60 °C and adding 3 g of the sample. The sample and water were mixed with a magnetic stirrer rotating at 600 rpm. Five samples; raw EFB, hydrochar produced at 100 °C (HTT- 100), HTT-150, HTT-180, and HTT-220 were used in the washing experiment. The biomass to distilled water ratio during the washing was 1:5, 1:8, 1:10, 1:20 and 1:50. The investigated leaching duration was 15 min. After the washing process, the mixture was separated using a vacuum filter. The solid was oven dried at 105 °C for 24 h, and stored in a sealed bag. HTW denotes for the hydrothermally treated and washed sample. The solid sample and liquid sample obtained after washing are designated as solid washing and liquid washing, respectively.

2.4 Pelletization

The pelletization of the raw EFB, hydrochar and washed hydrochar were conducted using a single pellet making device. The experiment was performed in the room temperature, and the pressure used was 150 MPa (approximately 7.5 kN). Then, approximately 1 g of samples was manually loaded inside the die and then compressed to a preset pressure. The pressing was performed using an Autograph Universal Testing Machine AG-IS (Shimadzu, Japan). The displacement speed was set at 0.1 mm/min. After holding for 30 s at the maximum pressure, the pressure was released and the plate was removed followed by pressing the formed pellet out from the die. The displacement for extrusion was set at the same speed and also using the same piston that used for the compression. The force-displacement data were logged during the compression-extrusion cycle of the pellet. The pellets were left undisturbed for 2 minutes and stored inside a sealed plastic bag for further measurements. More than 20 replicates were made from each treated and untreated EFB sample to ensure the reproducibility and consistency.

2.4 Analytical methods

2.4.1 Hydrochar characterization

The ultimate analysis (dry basis) of EFB was conducted using Vario Micro Cube Elemental Analyzer (Elementar, Germany), where oxygen content was determined by the difference. In this study, the correlation by Channiwala and Parikh was used to estimate the HHV of the samples [12]. The correlation is given below:

$$HHV = 0.3491\ C + 1.1783\ H + 0.1005\ S - 0.1034\ O - 0.0151\ N - 0.0211\ Ash \quad (1)$$

The potassium element was analyzed by atomic absorption spectrometry (AAS) method using Z-5010 Polarized Zeeman Atomic Absorption Spectrophotometer (Hitachi, Japan). The ash compositions of untreated and treated EFB material were analyzed using the X-ray fluorescence (XRF) technique by S2 Ranger energy dispersive X-ray fluorescence spectrometer (Bruker AXS, Germany). Trace elements including heavy metals in the sample are analyzed using ICPE-9000 (Inductively Coupled Plasma Emission Spectrometer) (Shimadzu, Japan).

2.4.2 Pellets characterization

The mass, length and diameter of each pellet were measured at once after extruded from the die cylinder to determine the pellet density.

The compression strength of the pellet was evaluated using an unconfined compression tester. The cylindrical pellet was horizontally placed between two plates, bottom plate and a disc shape metal probe (10 cm in diameter) attached to a 50 kN load cell. The test was carried out at a compression rate of 1.6 mm/min, and stopped after pellet failure. The value of the compression strength was defined as a maximum force a pellet could withstand, before the fracture of the pellet.

The moisture uptake test was measured by exposing the pellet samples to a controlled environment. The static desiccators technique [13] was adopted in this study in order to create a controlled humidity. Prior to the moisture uptake test, the pellets were dried at 105°C for 24 h. A pair of pellets was placed in the Petri glass dish and put inside the desiccators for at least 5 h. The weight of the pellets was measured every 15 min for the first hour followed by every 1 h for the following 5 h.

2.4.3 Pyrolysis analysis

The pyrolysis analysis was carried out by using a non-isothermal TGA analyser (Shimadzu D-50 simultaneous TGA/DTA analyser). Pyrolysis analysis was conducted by thermal decompositions under inert atmosphere (nitrogen gas). Approximately 10 mg samples were loaded into a crucible. Then the samples were heated at a constant heating rate of 10 °C/min to minimize the heat transfer limitation [14], [15]. The gas was used at a constant flow rate of 150 ml/min and the samples were heated from the ambient temperature to 900 °C. At least, three runs were completed for each sample to confirm the reproducibility. The mass loss (TG) and derivative curves (DTG) were continuously collected and represented as a function of time and temperature.

3 Results and Discussion

3.1 Charateristics of hydrochars

The fuel characteristics of the produced hydrochar and washed hydrochar were evaluated via ultimate analysis, and the results are presented in Table 1. The ultimate analysis of untreated EFB (Raw-EFB) is also presented as a comparison between the elemental values of the produced hydrochars (HTT-180 and HTT-220) and the washed hydrochars (HTW-180 and HTW-220).

Table 1. Ultimate and HHV analysis of the hydrochars

Element	Weight Percentage (wt%), dry				
	Raw-EFB	HTT-180	HTW-180	HTT-220	HTW-220
Ash	4.9	2.2	0.9	4.1	2.7
Carbon	43.6	46.4	46.8	50.0	50.7
Hydrogen	5.3	5.6	5.9	5.4	5.5
Nitrogen	0.6	0.4	0.3	0.8	0.7
Sulfur	0.11	0.03	0.04	0.09	0.06
Oxygen**	45.5	45.4	46.1	39.7	40.3
Chlorine	0.7	0.2	0.2	0.5	0.3
O/C ratio	0.78	0.73	0.74	0.60	0.60
H/C ratio	1.47	1.44	1.51	1.29	1.29
HHV, dry (MJ/kg)	16.8	18.0	18.5	19.6	20.0

*) 1:10 ratio, temperature 60°C, duration 15 minutes

**) by difference

The elemental composition and the HHV of hydrochars were apparently shifted by HTT, particularly at the HTT temperature of 220°C. The HTT severity degree linearly affected the carbon content which steadily increase with a higher HHT temperature. HTT-220 hydrochar shows the maximum increase of the carbon content, with an increase of 14.7%, compared to the Raw-EFB. The highest decrease of oxygen was also observed for HTT-220, as a result of the carbonization process. These changes led to the significant reduction of the O/C ratio compared to other lower operating temperatures. This result shows that the hydrochar obtained by 220°C HTT was energetically denser since the degradation of hemicelluloses and all extractives at HTT above 200°C enhanced the densification [16]. HHV is also an important characteristic to evaluate a fuel. The calculated HHV increases with the rise of the HTT temperature, as seen in Table 1. The increasing of HHV is mainly related to the increase of the carbon fraction and the decrease of the ash content in hydrochars. HTT-220 hydrochar has a heating value which almost equals to a low-grade sub-bituminous coal (approximately 20 MJ/kg [17]).

The ash content was seen to be significantly reduced after HTT, progressively with the increase of the temperature. The inorganic material in the form of either loose dirt from harvesting or loosely bonded in a cross-linked matrix is removed during the HTT process leading to the decrease of the ash content. There is also some expectation that additional acidity produced in HTT may solubilize and remove inorganics [18]. The inorganic solubilization from EFB was increasing with the increase of the severity of the HTT conditions. Nonetheless, HTT-220 hydrochar exhibited a higher ash content compared to HTT-180 hydrochar. Under a higher temperature HTT, EFB becomes more porous as all the hemicelluloses and extractives will be reacted, and much of the cellulose will be reacted as well [19]. The porous structure might absorb some inorganics, which might explain the increase in the ash content of HTT-220 hydrochar, as compared to HTT-180 hydrochar.

The results showed here implied that the fuel qualities of the hydrochars are improved compared to its parent biomass, having decreased oxygen and ash contents, and increased carbon content and HHV. The resulting hydrochar has the potential to be a satisfactory solid fuel for either direct combustion or co-combustion with coal. A higher reaction temperature produced relatively higher HHV especially at 220°C, but considering the energy yield and the ash content of the product, HTT at 180°C seems more favorable for the large-scale production of solid fuel from EFB. Moreover, the HTT reaction at a lower temperature and lower pressure results in less energy requirement and lower capital/operating costs.

3.2 Effect of HTT and washing co-treatment

3.2.1 Fuel properties

The distinct compositional alterations observed from the washed hydrochars were seen in the ash content and the chlorine content. From Table 1, the ash content of HTT-180 dropped to less than 1% with the additional washing process. The ash content of the hydrochar becomes important considering its end-use as a fuel. In the European pellet industries, the accepted pellets in the market must have an ash content of less than 2% [20]. The reduction of chlorine about 72% after employing HTT and washing was also observed, leading to a better fuel property for combustion since it can lower the deposition tendency in boilers 18. As chlorine is commonly found in the form of water-soluble salts and low quantities of organic compounds, it could be easily removed during HTT and washing processes.

Beside the changes in ash and chlorine content, other elemental elements like C, H, O, and N are seen only has a slight changes after washing. The carbon fraction seems to increase slightly for all the washed samples, probably as the consequence of the decrease in the ash content due to washing. The other possible reason might be due to a substantial amount of sugar would enter water during washing of biomass as pointed out by He et al. [21]. The significant reduction in the ash also caused the HHV of the samples increase modestly. After washing, the HHV increases with a percentage varied from 2.04% in the case of HTT-220 to 2.78% in HTT-180 sample. This also pointed out by Jenkins et al (1996) that stated the increase in HHV may be correlated to the decrease in the ash content of the washed straws [22].

3.2.2 Potassium removal efficiency

A high concentration of potassium in biomass fuel tends to result in the easy formation of compounds with low melting points. Thus, the potassium content in particular is important to indicate potential ash fusion or ash deposition. Potassium content of the raw-EFB was found relatively high with approximately 32.4 g/kg of biomass or around 3.2 wt%. Potassium is usually present in biomass in the form of ionic K^+ and highly soluble in water [23], also forms weak complexes with organic acid ions [24]. Hence, potassium is easily leached from the biomass.

The quantification of potassium species for the raw-EFB and the resulting hydrochars before and after water washing are presented in Fig. 1. It is evident that various extents of removal of potassium content can be achieved via water washing. By washing raw-EFB with 1:10 biomass-water ratio, up to 54.9% of potassium content in the raw-EFB can be removed (see Fig. 2). However, when the biomass was treated with HTT process prior to washing process, the removal efficiency can be enhanced to above 80%, even 92% in the case of HTT-180. Potassium was released mostly during HTT, with the removal efficiency increase with the increase of the HTT temperature. From Fig. 2, it can be seen that HTT at 180°C optimally removed most potassium to the liquid fraction with the removal efficiency of 74.1%. In contrast, Reza et al (2013) reported that the hydrothermal carbonization at 200°C (5 min holding time) can be very effective in removing inorganics, such as Ca, S, P, Mg and K, from corn stover, mischantus, switch grass and rice hull biomass [19]. The different biomass feedstock could explain these observations. For HTT-220, the efficiency of the washing stage is found lower than other cases, which might be due to the re-absorption by porous structure produced from HTT under the reaction at 220°C.

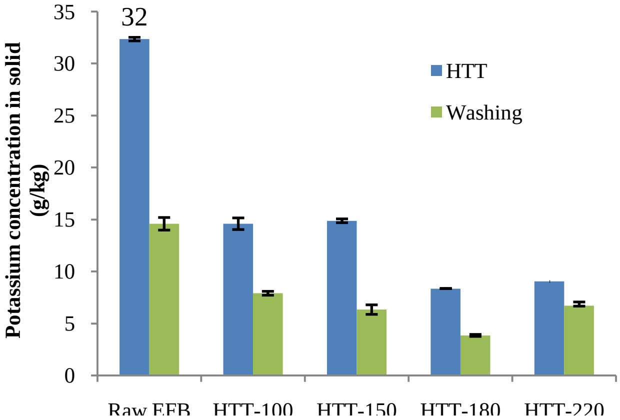

Fig 1. Potassium concentration of EFB after HTT and washing

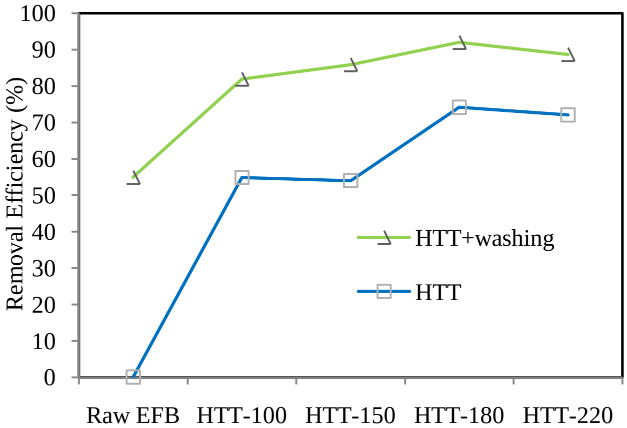

Fig 2. Potassium removal efficiency of EFB after HTT and washing

3.2.3 Ash composition and deposition tendency

Table 2 presents the ash elemental percentage obtained by the XRF analysis. The elemental species in ash was generally found as an oxide [25]. It was observed that the alkali levels are quite high in raw-EFB; with potassium oxide appear as dominant species with the percentage of 49.1%, showing its nature tendency to cause slagging and fouling. Employing HTT and the washing processes were able to significantly change the relative composition in ash, where the alkali values were much reduced. A total decrease as high as 72% in K_2O was observed after the pretreatments. This result also proved that a high fraction of potassium was released to the aqueous side, and remained only small fraction in the ash. However, some species such as SiO_2 and Al_2O_3 only have a slight change after both processes. Si is found to be very stable which is covalently bonded within biomass organic matrix [19].

Table 2. Ash composition of raw-EFB and hydrochars

Element (%wt of ash)	Raw EFB Un-washed	Raw EFB Washed	HTT-180 Un-washed	HTT-180 Washed 1:10	HTT-180 Washed 1:50
K_2O	48.9	50.9	27	13.5	10.9
SiO_2	19	32.1	28.6	33.9	38.4
CaO	7.9	N/A	10.7	9.3	9.3
Fe_2O_3	5.5	1.9	6.6	4.5	3.1
MgO	4.4	7.4	5.9	8.2	8.7
SO_3	4	7.4	4.9	6	7.4
Na_2O	3.9	N/A	6.1	11.9	12.9
P_2O_5	3	N/A	2.5	2.8	N/A
Al_2O_3	2.5	N/A	6.8	9.5	8.4
TiO_2	0.7	N/A	0.7	0.4	0.5

The evaluation of slagging and fouling tendencies of the raw-EFB, HTT-180 and washed HTT-180 is presented in Fig. 3. The calculated slagging and fouling indices were defined from the literature [26]. Except for SI, all the indices clearly showed that raw-EFB exhibited high tendency of deposition. The high content of basic group compounds, in particular alkali, apparently is the main cause of the high tendency presented in the indices. The SI value for raw-EFB was 0.4 exhibiting a low deposition probability due to low sulfur content in the biomass. However, it was observed from Fig. 3 that the effects of HTT and the washing process are more pronounced for AI, FI, and Cl indices, where they can considerably lower the tendency of fouling. After HTT at 180°C, the FI and Cl values of EFB can be reduced to low probability regime showing the low deposition tendency. The additional washing process affects in the improvement of the AI value, shifts the initially high occurrence of slagging and fouling to probable occurrence. From the calculated slagging and fouling indices, it could be concluded that raw-EFB originally has high tendency of fouling and this risk was significantly eased after pretreatment using HTT and washing.

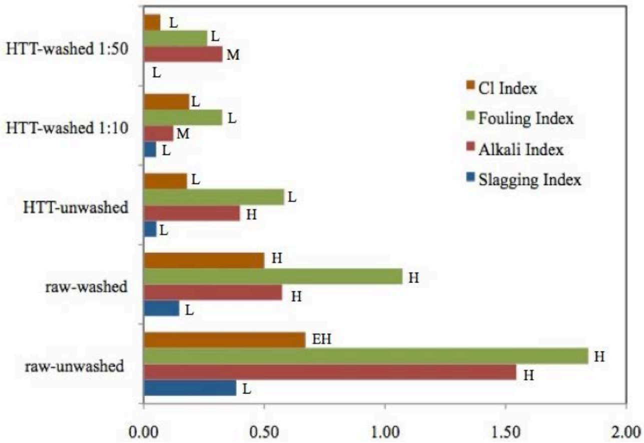

Fig. 3. Slagging and fouling indices for raw-EFB and pretreated products (EH= extremely high, H = high, M = medium, L = low deposition)

3.3 Treated pellet evaluation

3.3.1 Pellet characteristics

Fig.4 shows the pellet products after the compaction process. The color of the raw EFB feedstock is less dark color than the hydrochars. The color became darker brown color as the HTT temperature increased. These color change was due to Maillard reactions of mono-saccharides and extractives degradation after steam treatment [27]. As can be seen, the hydrochar pellets has smoother and glassy surface compared to raw-EFB pellets. It can also be seen that the surface of the hydrochar pellets were very compact and uniform without visible voids. Contrary, obvious voids and gaps were seen on the surface of the raw-EFB pellet. These gaps were reported to able to reduce the pellet resistance to deformation and promote the movement of the particles within matrix that leads to weak mechanical durability [6]. The bigger gaps were also indicating poor adhesion between the biomass particles [28].

From Fig. 4, it also can be seen that the pellet made from treated EFB had a shiny surface on its outer side. An external shine on the pellet surface is tought to be caused by lignin coating. It indicated that lignin came out from the wood cell inside the EFB fibres and melted on the pellet surface. Lignin presence in biomass acts as a natural binder that bonds the biomass particles together and initiates the solid bridge binding force to form [29]. Because solid bridge has been known as the strongest binding force, it was expected that the treated EFB pellet will have higher mechanical strength.

Fig 4. Appearance of the pellets

The particle size distribution of all the samples is presented in Fig. 5. Larger particle sizes were found for the raw-EFB. While smaller particle size portion was seen to increase with the increasing severity of HTT. HTT was seen shifted the particle distribution into smaller size. The effect of washing was evidently seen for the hydrochar at HTT-220. Originally, the smaller particle size is already dominantly present in the HTT-220 hydrochar particles. Hemicelluloses removal at the HTT temperature of 220°C, changed the products to become brittle and easy to break, sincehemicellulose acts as a binding structure among other biomass components (lignin and cellulose). Therefore, the mixing process during washing experiment might break the hydrochar particles further, resulting in smaller size particles compared to the unwashed ones. On the other hand, washing process had only slight effect on the HTT-180 hydrochars.

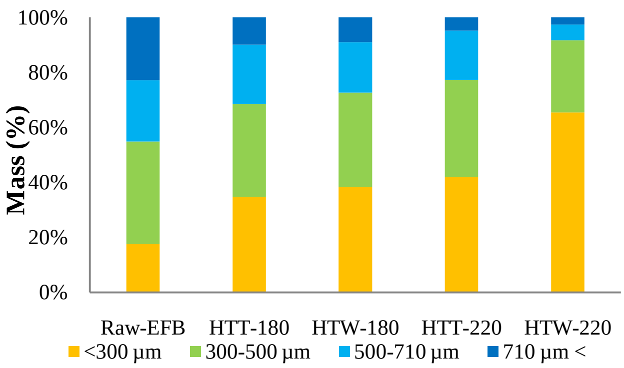

Fig 5. Particle size distribution of produced pellets

During measurement of the physical dimension of the pellets, the diameter and the length of the pellets were recorded 2 times; immediately after extrusion from the cylinder and after resting them for 24 h, thus the initial density and relaxed (final) density could be calculated. The length expansion happened during the relaxation of pellets was also calculated. Fig. 6 presents the initial and final pellet density, and also the expansion rate of all the pellet samples observed. The bulk density of the feedstock particles prior to pelletization were recorded at approximately 160 kg/m3 and 180-240 kg/m3 for raw-EFB and hydrochars, respectively. From the figure, the initial pellet density increased with the severity of HTT. This is also in line with the previous studies on the HT pretreated pellet [7], [9]. However, in this study, the initial pellet density of HTT-180 hydrochar decreased after the washing process, while it was increasing for HTT-220 hydrochars. The smaller particles of the washed HTT-220 hydrochar that has been discussed previously might be the reason of the higher mass density of the washed HTT-220 hydrochar compared to the washed HTT-180 hydrochar pellet. A similar trend was observed for the final pellet density measured after 1 day rest.

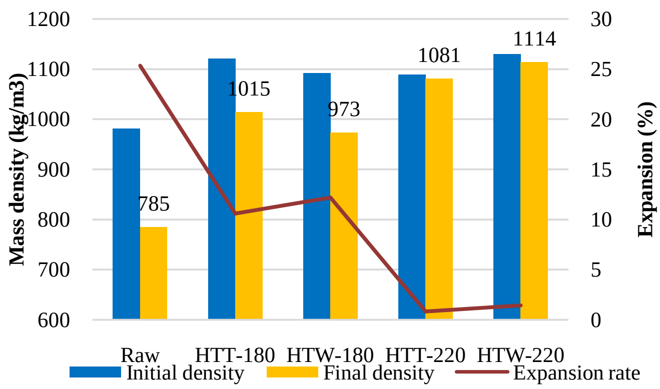

Fig. 6. Initial, final, and expansion of the raw EFB, hydrochar and washed hydrochar pellets

The pellet density of the raw-EFB decreased from 982 kg/m3 to 785 kg/m3 due to 25% length expansion, as can be seen in Fig. 6. In contrast, for the hydrochar pellets, the expansion is less, particularly for the HTT-220 hydrochar pellet. Stelte et al. (2012) reported on the phenomenon where the biomass has tendency to expand after palletization, which is known as “spring back effect”[28], [30]. The expansion rate also can be a measure for the bonding quality between the biomass particles within a pellet. If there is poor adhesion, the particles do not bind well together and the pellet expands like a spring [28].

3.3.2 Mechanical strength

The mechanical strength test is a good way to know the pellet strength and quality in holding its shape without being disintegrate during transportation and storage.

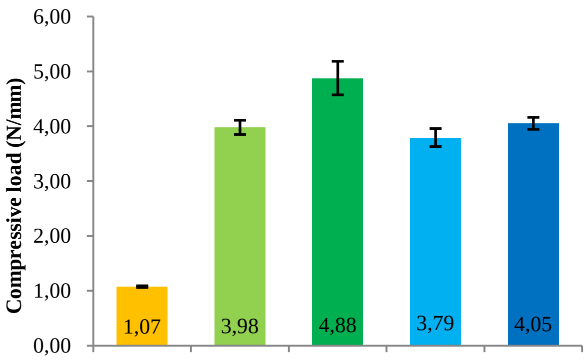

Fig. 7. The compressive strength of the raw EFB, hydrochar and washed hydrochar pellets

The compressive strength of pellet is the measure of internal bonding strength of the maximum force a pellet can withstand before its rupture during transportation and storage [9]. Fig. 7 presents the compressive strength of the produced pellets divided by the pellet length (N/mm). The maximum load required to break the pellet slightly decreased for the hydrochar pellet with the increasing of the HTT severity; 3.98 N/mm and 3.79 N/mm for HTT-180 and HTT-220 pellets, respectively. The increase of the lignin content caused by the thermal degradation of hemicelluloses contributed to the increase in the compressive strength [7], [31]. However, too high percentage of lignin present, as in the hydrochar produced from HTT-220, can act as a natural binder, but at the same time can make the pellets highly brittle [9], [10]. The less lignin in hydrochar pretreated at lower temperature (180°C) compare to higher one (220°C) make the pellet more elastic; therefore it requires more compressive load to break the pellet [10]. The hemicelluloses degradation and the increase in the cellulose content might also result in more brittle pellet after HTT at a higher temperature. Washing the hydrochar could increase the strength of the pellets. The highest compressive strength was obtained from the washed HTT-180 hydrochar. The higher strength of washed hydrochar pellets might be due to the removal of metal content during washing process that might exposed more lignin for binding, thereby increasing the pellet strength.

3.3.3 Hydrophobicity

The biodegradation of biomass pellets was strongly influenced by its moisture content. The moisture content of the biomass largely depends on the surrounding atmosphere but it also depends on the composition of biomass [10], [13].

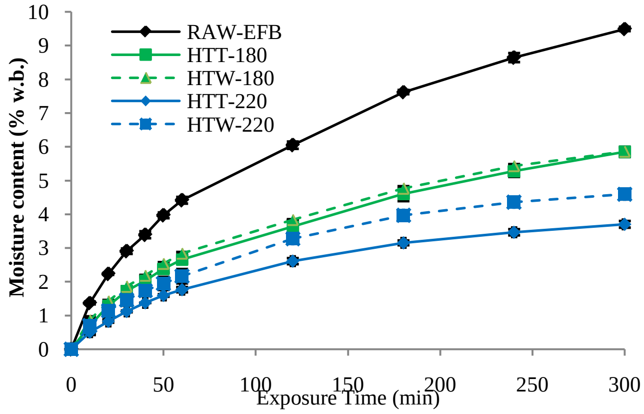

Fig 9. The moisture uptake of raw EFB, hydrochar and washed hydrochar pellets at 26-28°C and 75-80% relative humidity.

Fig. 9 shows the moisture content of the pellets against the exposure time for 5 h. Pellet produced from the raw-EFB exhibited the highest moisture uptake of 9.49% after being exposed to the high humidity for 5 h, showing the hygroscopic behavior. On the other hand, the moisture uptake of the hydrochar pellets was seen decreased significantly compared to the corresponding raw-EFB pellet. The lowest moisture uptake was observed for the HTT-220 hydrochar pellet for which the increase of the moisture content is only 3.70% after 5 h exposure. The hydrochar pellets indeed presented the hydropobic nature compared to the raw-EFB pellet. The hydrophobic nature of hydrochar is coming from the lignin content. Among the biomass component, hemicelluloses have the greatest capacity of water absorption, while lignin has only little tendency to absorb water [9], [13]. Therefore, the removal of hemicelluloses from the biomass will increase its hydrophobicity. Alternatively, the presence of pores on the surface of raw EFB pellets might increase the tendency to absorb moisture content (free water) from the atmosphere [32].

In case of HTT-180 hydrochar, the unwashed and washed hydrochar has no difference in moisture uptake behavior. While, the washed HTT-220 hydrochar pellet showed slightly higher uptake than unwashed, exhibiting a lower moisture resistance. Hence, washing was seen to decrease the moisture resistance slightly. The possible reason for this phenomenon is that the introduction of water during washing experiment may reduce the hydrophobic nature of the hydrochar. The moisture uptake test results indicated that the pretreated EFB pellets has a good resistance against moisture and highly hydrophobic in nature. Therefore, the pellets can be safely stored for long time without being afraid of biological deterioration. Moreover, the transportation cost will be less expensive, since there will be less water to transport along with the biomass [9].

3.4 Thermal degradation of hydrochars

Series of thermogravimetric analysis (TGA) were performed to investigate the effect of HTT and the water washing combination on the thermal decomposition of EFB. Fig. 10 presented a comparative analysis of the TG and DTG curves of raw EFB, HTT EFB and washed HTT EFB (HTW). The contour of the curves showed that all samples have similar decomposition mechanism. Their significant mass loss occurred in the temperature range of 250-350 °C with only one maximum rate of decomposition observed at around 320 °C to 360 °C. This pattern illustrates that there was, at least, one major reaction occurring during the thermal decomposition of inert atmosphere for EFB. After completion of the primary weight loss, the reaction was followed by a continuous gradual weight loss. The steeper first step was due to the primary devolatilization. The next decomposition level was attributed to the degradation of heavier chemical structures in the solid matrix, which can be also produced from the primary devolatilization [33].

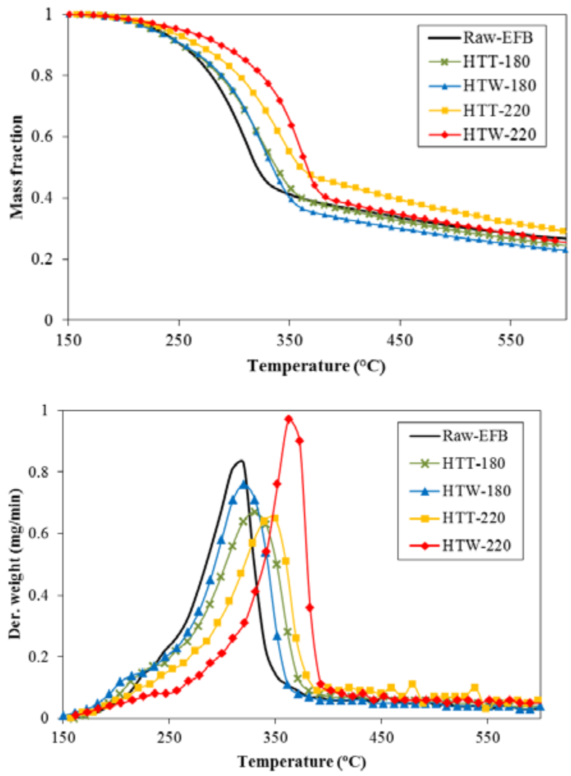

Fig. 10. Mass fraction (top) and derivative weight (bottom) profiles of untreated and treated EFB under an inert atmosphere.

There was quite an important variance in the maximum decomposition rate and the total conversion that indicate the effect of HTT and the washing process on the reactivity of the EFB samples during the pyrolysis reaction. It is clearly shown that the maximum decomposition rate (Rmax) was shifted to a higher temperature (Tmax) for both unwashed and washed hydrochars compared to Raw-EFB. Raw-EFB has the lowest Tmax at around 317 °C. The highest Tmax was observed when EFB was HTT treated at 220 °C followed by the water washing. The shifted scheme might be caused by the hemicellulose content alteration within EFB. An experimental study was carried out by Biagini, et al. (2006) to investigate the devolatilization parameters of biomass components during pyrolysis. The study pointed out that the behavior of biomass materials during devolatilization is mainly affected by the behavior of the cellulose, hemicellulose and lignin components [33].

Raw EFB relatively has more hemicellulose content than the treated EFB; hence, its primary devolatilization takes place at a lower temperature near the range of hemicellulose devolatilization temperature. As explained before, HTT decreased the hemicellulose content in EFB. The more severe condition of HTT will lead to the lower content of hemicellulose. Then the weight loss curve of the pyrolysis reaction will be shifted to a higher temperature at which devolatilization is mainly dominated by cellulose and lignin degradation.

The DTG curve comparison indicated that the washing process apparently affected the reactivity of hydrochars. The maximum weight loss rate of HTW-220 sample was recorded at about 0.97 mg/min, significantly higher than the maximum rate of HTT-220 (0.64 mg/min). Hydrochar products from HTT at 180 °C also showed similar phenomenon which represents the elevated decomposition rate of the washed HTT-180 hydrochar. Moreover, the washed hydrochar simultaneously yielded smaller solid residue than the unwashed hydrochars since HTT and the washing process removed a considerable amount of the alkali content especially potassium as shown in the previous study [34]. A study was performed by Shebani et al. (2008) to investigate the effect of extractives presence on the thermal stability of various wood samples. It was found out that after extractives removal, the maximum decomposition rate (Rmax) during the pyrolysis reaction was lower than the untreated sample [35]. The Rmax reductions of the washed hydrochars in this study probably also related to the extractives content.

4 Conclusion

The fuel qualities of the product was improved after HTT; such as a higher carbon content, a higher energy density, lower O/C and H/C ratios compared with the raw feedstock. The calorific value of the hydrochar is equal to low-grade sub-bituminous coal. Considering the energy consumption and fuel property, HTT at 180°C is found to be most favorable for large-scale production of solid fuel from EFB. From the HTT-washing co-reatment results, the major removal of potassium was attributed to the HTT process. The 92% potassium removal can be achieved by the HTT and washing co-treatment. The combination also lowered the ash content and the chlorine content of EFB down to 0.9% and 0.19%, respectively. It was found that 180°C was the optimum HTT temperature for the effective potassium removal. Combination of HTT and the water washing improved the slagging and fouling indices, exhibiting positive results in the term of the deposition tendency, thus clarified that the removal of potassium may lead to lower deposition tendency.

The pellets treated by the HTT and washing has better quality; such as high mechanical strength, and high resistance to the atmospheric moisture. In addition, it also has lower ash and alkali metal contents. It was found that the changes in the composition of EFB biomass by HTT and the washing process regulates the pelletization behavior and affects the bonding mechanism during the pelletization. Finally, the combination of the pelletization, HTT, and the washing co-treatment is promising for upgrading abundant EFB biomass into clean, energy dense, homogenous, friable, durable, and hydrophobic solid fuel that is ready for domestic and international markets, while dealing with the waste EFB problem in the plantation.

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