Upgrading of palm empty fruit bunch for solid biofuel production through hydrothermal carbonization

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Abstract. In this study, palm empty fruit bunch (EFB) was upgraded into solid fuel called biochar through hydrothermal carbonization process (HTC). The experiments were performed at different temperatures of 160, 180, 200 and 240 °C for 30 min. The properties of biochar products in terms of proximate and ultimate analysis, heating value and thermal decomposition were characterized. The results indicated that hydrothermal carbonization decreased the biochar yield from 79.2% at 160 °C to 39.5% at 240 °C. As the reaction temperature increased, the fixed carbon and heating value increased due to the decreasing of volatile matter and oxygen content involving dehydration and decarboxylation reactions. The heating value increased from 19.8 MJ/kg (raw EFB) to 23.0 MJ/kg at 240 °C. The H/C and O/C atomic ratios of biochar after treated with HTC decreased from 1.52 and 0.62 (at 160 °C) to 1.09 and 0.38 (at 240 °C) as similar to low rank coal. In addition, the potassium in the feedstock was extracted and removed to the aqueous phase during HTC. The maximum potassium removal efficiency reached up to 91.8% at reaction temperature of 240 °C. The removal of potassium led to lower deposition tendency of slagging and fouling indices. The results reveal that the HTC has the potential for upgrading EFB into energy–dense and durable solid fuel for use in energy generation.

1. Introduction

Oil palm tree is one of the economic crops in Thailand. The palm oil industry generates a large amount of biomass wastes which collected from both harvesting and replanting activities in plantation area and milling process in palm oil mill. Oil palm frond, oil plan trunk and oil palm leave are available at the plantation site in contrast empty fruit bunch (EFB), mesocarp fiber, palm kernel shell and palm oil mill effluent (POME) are generated during the production of palm oil. These oil palm wastes can be used as organic fertilizer and feedstock for biofuel production.

The abundant amount of EFB is generated from oil palm industries but poorly utilized. The drawback of EFB is high moisture content about 65%, low bulk density, low energy density as well as high inorganic element and ash content [1,2]. The high moisture content causes problem for fuel storage and transportation. The presence of inorganic component particularly potassium (K) is a major problem in thermochemical combustion that promotes the formation of slagging, fouling and corrosion in the boiler [3]. There are several techniques to improve the fuel properties of biomass such as hydrothermal treatment, torrefaction, and pyrolysis.
Hydrothermal carbonization (HTC) is a thermochemical technology that converts wet biomass into solid fuel (biochar) together with aqueous product and non-condensable gases without prior dewatering and drying. The process is performed under mild subcritical conditions by applying temperature of 150–250 °C under an autogenous water pressure for a residence time of 0.5–20 h. The chemical reactions occurred during HTC including hydrolysis, decarboxylation, condensation, polymerization, aromatization, and dehydration [4]. Besides, HTC can eliminate the portion of undesirable impurities and incombustible alkali materials [5,6]. The major product obtained from HTC is biochar with higher energy density, higher carbon content and higher hydrophobic properties than the feedstock. The biochar application includes solid biofuel, adsorbent, carbon–based catalyst and soil amendment [7–9]. Aqueous product (process water) can be utilized as fertilizer application and a feedstock for biogas production. The advantage of HTC compared to other thermal processes is the avoidance of energy–extensive in drying and dewatering, high conversion efficiency and relative low operation condition.

Many researchers have studied to investigate the effectiveness of HTC for improving the properties of various feedstock such as sewage sludge, moist agricultural wastes including empty fruit bunch, municipal wastes, low-rank coal, and woody biomass [11–15]. The results found that the heating value, carbon contents and fixed carbon content of solid products increased with reaction time and temperature. The H/C and O/C atomic ratios of solid part also decreased to become close to low rank coal like lignite and sub-bituminous coals. The liquid fraction obtained from HTC contained valuable chemicals such as furan compounds (furfural, hydroxymethyl furfural), fatty acids (acetic acid, levulinic acid, formic acid, and glycolic acid), phenolic compounds and sugar (glucose).

Most of research focused on the effect of HTC treatment on the physicochemical properties of biomass. However, there is limited literature concerning the removal of inorganic component particularly potassium in EFB that resulted in the combustion performance. Therefore, in this study, EFB was selected as the biomass because palm is one of the important crops in Thailand which is by-product from palm oil industries. The purposes of this study are to investigate the improving the fuel properties of EFB after HTC treatment as well as the focusing on the removal of potassium content that resulted in reducing the slagging and fouling indices. HTC experiments were carried out in batch reactor and the effect of temperature on the mass and energy yields were investigated. The fuel properties of solid product were also characterized by several techniques and discussed in detail.

2. Materials and methods

2.1. Material
Palm empty fruit bunch (EFB), obtained from an oil palm mill in Thailand, were used as a raw material in the experiment. The raw EFB were dried at 105 °C for 24 h and then crushed to obtain the size less than 10 mm before HTC experiment.

2.2. Experimental method
HTC experiments were conducted in a high pressure reactor (Parr reactor) equipped with an automatic stirrer and a controllable electric heater. The HTC set up was shown in Figure 1. During HTC process, the raw EFB was loaded into the reactor and mixed with deionized water at a ratio of 1:10 to ensure that feedstock was entirely submerged underneath the water level. The reactor was purged three times with nitrogen to remove the residual air. The operating temperatures ranged from 160–240 °C with 20 °C temperature intervals and maintained at the desired temperature for 30 minutes. After complete reaction, reactor was cooled to room temperature and the product was discharged from the reactor. The solid and liquid products were separated using filtration under vacuum. The solid product was dried in an oven at 105 °C for 24 h and stored in a sealed bag before further analysis.
Figure 1. The schematic diagram of reactor used for hydrothermal carbonization

The proximate analysis for determining the percentage of volatile matter, fixed carbon and ash content was carried out in TGA–701 (LECO). The ultimate analysis, including the percentage of carbon, hydrogen, nitrogen, and sulfur was conducted using TruSpec CHNS elemental analyzer (LECO). The heating value of EFB and biochar were analyzed using a Bomb calorimeter (Parr 6300). Thermal decomposition behaviors of feedstock and biochar were determined by TGA–STA449F3 (NETZSCH) operated at the heating temperature from room temperature to 800 °C. The analysis done was with heating rate of 10 °C/min. Moreover, inorganic elements including P, K, Ca, Mg and Na in feedstock and biochar were analyzed using Inductively Coupled Plasma Emission Spectrometer (ICP-OES) (PerkinElmer).

The mass yield of biochar was calculated by using the following equation:

\[
Mass \ yield \ (\%) = \frac{m_{\text{Biochar, dry}}}{m_{\text{Raw EFB, dry}}} \times 100
\]  

where:

- \( m_{\text{Biochar}} \) = the mass of biochar products
- \( m_{\text{Raw EFB}} \) = the mass of empty fruit bunch feedstock

The energy yield of biochar was calculated by using the following formula:

\[
Energy \ yield \ (\%) = Mass \ yield \times \left( \frac{HHV_{\text{Biochar}}}{HHV_{\text{Raw EFB}}} \right) \times 100
\]  

where:

- \( HHV_{\text{Biochar}} \) = higher heating value of biochar products
- \( HHV_{\text{Raw EFB}} \) = higher heating value of empty fruit bunch feedstock

The HHV increased was defined according to equation:

\[
HHV_{\text{increased}} \ (\%) = \left( \frac{HHV_{\text{Biochar}} - HHV_{\text{Raw EFB}}}{HHV_{\text{Raw EFB}}} \right) \times 100
\]  

3. Results and Discussion

3.1. Colour appearance

The physical appearance of EFB feedstock and solid product (biochar) were shown in Figure 2. The EFB feedstock is brown colour. Increasing HTC temperature influenced the colour of biochar. The colour of biochar slightly changed from brown to dark brown and became darker with HTC temperature increasing. The darkest brown colour was observed when HTC was performed at 240 °C.
3.2. Mass and Energy yields
The mass and energy yields of biochar produced at different reaction temperatures are illustrated in Figure 3. The results indicated that mass yield of biochar obviously decreased with increasing temperature. The biochar yield slightly decreased from 79.2% to 57.6% and significantly dropped to 37.5% when HTC temperature reached at 240 °C. This decreased of mass yield was attributed to primary decomposition or secondary decomposition of the solid residue at higher temperature. The biomass consists of three major components including cellulose, hemicellulose, and lignin. These components were decomposed as temperature increased. Hemicellulose and some of cellulose were decomposed into liquid and gaseous by-products during HTC [16,17]. The energy yield also presented as the same trend with mass yield. Energy yield of biochar decreased from 71.2% to 43.3% as HTC temperature increased. The energy yield is an important parameter as it indicates the total energy remained in biochar.

Figure 3. The mass and energy yield of biochar from HTC at different temperatures

3.3. Chemical composition
The proximate and ultimate analysis of dry EFB and biochar is presented in Table 1. The fixed carbon and volatile matter contents of EFB feedstock were 15.3 wt.% and 78.5 wt.%, respectively. At higher temperature, the results indicated that the fixed carbon content enhanced to 28.7 wt.% in contrast the volatile matter content reduced to 69.0 wt.% at 240 °C due to the decomposition of some volatile organic matter [18]. The carbon content of biochar was observed to increase while the oxygen content decreased as the reaction temperature increased. Reducing of the oxygen content led to improve the energy density. The hydrogen and nitrogen contents slightly decrease. This was attributed to the dehydration and decarboxylation reactions during the HTC [19]. Biochar at the highest reaction temperature exhibited the maximum carbon content with an increase of 20% compared to raw EFB. The ash content in the biochar had lower than raw EFB. It was observed that the ash content obviously
decreased from 6.3 wt.% (raw EFB) to 1.2 wt.% (at 200 °C) and then slightly increased to 2.5 wt.% (at 240 °C) due to some inorganic might be reabsorbed in the porous structure of biochar [20].

The higher heating value (HHV) is an important parameter in the fuel characterization of biochar. Regarding the HHV, a slightly increase was observed after HTC treatment. The HHV of raw EFB was measured as 19.8 MJ/kg while the HHV of biochar increased to a high as 23.0 MJ/kg for the highest reaction temperature, as shown in Figure 4. The biochar at HTC 240 °C had the heating value almost equivalent to low−grade coal such as lignite coal (15−20 MJ/kg) and sub-bituminous coal (19−26 MJ/kg) [21]. The HHV of biochar after HTC treatment at 220 °C and 240 °C were 14.9% and 16.2%, respectively increased in comparison to raw EFB. The increased of heating value was mainly related to increase of carbon content and fixed carbon content involving dehydration and decarboxylation reactions [9].

Table 1. Characteristics of raw EFB and biochar at various temperatures

| Temperature | EFB | 160 °C | 180 °C | 200 °C | 220 °C | 240 °C |
|-------------|-----|--------|--------|--------|--------|--------|
| Proximate analysis (wt.%, dry) |     |        |        |        |        |        |
| Volatile matter | 78.52 ± 0.39 | 83.72 ± 0.07 | 84.65 ± 2.38 | 81.54 ± 1.55 | 78.60 ± 0.71 | 69.03 ± 0.98 |
| Fixed carbon | 15.27 ± 0.08 | 14.58 ± 0.18 | 14.11 ± 0.71 | 17.27 ± 0.59 | 19.97 ± 0.92 | 28.72 ± 0.45 |
| Ash | 6.25 ± 0.31 | 1.71 ± 0.13 | 1.24 ± 0.25 | 1.19 ± 0.97 | 1.43 ± 0.59 | 2.25 ± 0.32 |
| Ultimate analysis (wt.%, dry) |     |        |        |        |        |        |
| C | 50.49 ± 0.01 | 52.05 ± 0.28 | 53.62 ± 2.02 | 54.79 ± 1.80 | 55.86 ± 0.58 | 60.75 ± 0.70 |
| H | 6.34 ± 0.20 | 6.34 ± 0.34 | 6.18 ± 0.68 | 6.05 ± 0.48 | 6.00 ± 0.24 | 5.57 ± 0.53 |
| N | 0.78 ± 0.09 | 0.07 ± 0.04 | 0.05 ± 0.32 | 0.11 ± 0.30 | 0.19 ± 0.07 | 0.37 ± 0.12 |
| S | 0.14 ± 0.06 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.00 ± 0.00 |
| Oa | 36.05 ± 0.25 | 39.83 ± 0.61 | 38.91 ± 0.79 | 37.85 ± 0.05 | 36.53 ± 1.37 | 31.06 ± 0.87 |

EFB = Empty fruit bunch
*a By different: O% = 100% - ash% - C% - H% - N% - S%
The conversion of biomass carbon rich materials is represented using van Krevelen diagram. This diagram provides the information about the H/C and O/C atomic ratios of raw EFB, biochar and different types of coal, as shown in Figure 5. The biochar contained low H/C and O/C ratios compared to raw EFB due to decarboxylation and dehydration reactions during HTC. The H/C and O/C ratios of biochar decreased from 1.52 to 1.09 and 0.62 to 0.38, respectively, as the reaction temperature increased from 160 °C to 240 °C. As given in Figure 5, the H/C and O/C ratios were compared to four types of coal such as anthracite, bituminous, sub-bituminous, and lignite, the H/C and O/C ratios of biochar at 240 °C were in the lignite region that was presented the H/C ratio of 0.9−1.3 and O/C ratio of 0.28−0.4, respectively [22]. Therefore, HTC process could improve the fuel properties of biochar in terms of higher heating value, lower oxygen content and higher carbon content that were similar to low rank coal such as lignite.

3.4. Combustion characteristic

The thermal decomposition behaviour of raw EFB and biochar obtained from thermal gravimetric (TG) and different thermal gravimetric (DTG) is illustrated in Figure 6. The decomposition behaviour of biomass could be divided into three stages. The first stage was the dehydration taken place at temperature below 120 °C. The second stage was the degradation of hemicellulose and cellulose occurred at 200–300 °C and 250–350 °C, respectively and the last stage was the degradation of lignin occurred slowly over broader at 250–550 °C [19]. The raw EFB showed the decomposition in two stages; the first stage is in the range of 180–250 °C and the second stage is between 250–350 °C. The maximum mass loss rate is defined by the position of peaks in the DTG curve. The DTG peak of raw EFB was observed at 250 and 300 °C due to the decomposition of hemicellulose and cellulose. The DTG peak of biochar was shifted to higher temperature in comparison with the raw EFB, suggested that the thermal stability increased at higher temperature. The maximum decomposition rate of biochar was observed at 350 °C. This implied that HTC led to lower content of hemicellulose and the decomposition is dominated by the cellulose and lignin. It can be concluded that the thermal stability of biochar was better than raw EFB as well as led to improve combustion performance.

3.5. Potassium removal behaviour

The inorganic component and potassium removal efficiency of biochar after HTC treatment and raw EFB is presented in Figure 7. The raw EFB had high inorganic element particularly potassium with approximately 1.74 wt.%. The potassium content significantly reduced to as low as 0.14 wt.% as the reaction temperature rise to 240 °C. The potassium removal efficiency achieved to above 86.8% (at 180 °C) and as high as 91.8% (at 240 °C). In addition, hydrothermal carbonization can be effective for
removing other inorganic elements such as Ca, Mg, P, and Na from raw EFB. The presence of potassium in biomass is in forms of ionic K$^+$ and highly soluble in water [23]. It was found that the potassium in raw EFB can be extracted and dissolved into the aqueous phase during HTC, as shown in Figure 8. The aqueous product contained high potassium content that is an important macronutrient. Novianti S et al. [56] found that the quality of aqueous phase was still considered to use as fertilizer due to low pH value, low N and low germination index.

![Figure 7](image-url) ![Figure 8](image-url)

**Figure 7.** The inorganic element and potassium removal efficiency of raw EFB and biochar after HTC treatment.

**Figure 8.** The potassium content in solid and aqueous products.

Based on the results, it is proposed that HTC is an attractive alternative to upgrade low quality of biomass to cleaner or higher quality of solid fuel. Solid fuel with higher energy density can be blended with coal for heat and power generation application. There are several applications of the solid product including carbon–based materials, soil amendment and adsorbent. The liquid and gaseous by–product also obtains from HTC. The liquid product contained value added chemicals can be used as intermediated for other chemical platforms. However, the limitation in terms of resource availability, production cost and transportation cost should be considered for developing large scale HTC system.

4. Conclusion

HTC treatment significantly upgraded the fuel qualities of biochar produced from raw EFB. The mass yield of biochar decreased as the reaction temperature increased because of the decomposition of volatile matters. The heating value increased as the fixed carbon and carbon contents increased due to dehydration and decarboxylation reactions. The highest heating value of biochar reached 23 MJ/kg that almost equivalent to sub-bituminous coal. As shown in the van kreveken diagram, the H/C and O/C atomic ratios reached to as low as 1.09 and 0.38 at the highest reaction temperature which caused the characteristic of biochar similar to lignite coal. The biochar exhibited great thermal stability at higher decomposition temperature in comparison with the raw EFB that resulted in the improvement of combustion performance. In addition, HTC clearly achieved to remove the inorganic component and ash content in raw EFB. The potassium removal efficiency enhanced to above 91.8% as the highest reaction temperature. A large amount of potassium in raw EFB was extracted and dissolved into aqueous phase. The lower potassium and ash content could be reduced the formation of slagging and fouling during combustion. Regrading to the results of this study, solid fuel produced from HTC is suitable for used as co–firing with coal for energy generation.

All these findings showed that HTC is a promising technology for converting the wet biomass into alternative solid fuel with improving its energy density, the heating value and higher hydrophobic properties as well as lower potassium and ash content. The limitation of HTC in terms of energy requirement and economic feasibility should be considered. Nevertheless, solid fuel could be utilized as blending with coal for heat and power generation and HTC system should be integrated
with the existing co-firing system in the power plant. The heat from coal power plant is utilized for power generation and generating steam in boiler. The rest of heat can be utilized for HTC system. This is an attractive option for reducing the energy consumption of HTC.

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