Impact of biomass upgrading via hydrothermal treatment on slagging and fouling during cofiring with coal

Mi Yan 1, Dicka Ar Rahim2,*, Herri Susanto 2, Rahmad Dennie Agustin Pohan2, Dwi Hantoko 1,2

1 Institute of Energy and Power Engineering, Zhejiang University of Technology, Hangzhou 310014, People Republic of China
2 Department of Chemical Engineering, Institut Teknologi Bandung, Bandung 40132, Indonesia
*dicka@che.itb.ac.id

Abstract. Palm oil empty fruit bunch (EFB) is a by-product produced during palm oil processing. In South East Asian countries, EFB is abundant and can be utilized as a renewable energy source. Cofiring of EFB with coal can be beneficial for preserving coal and reducing CO2 emission. However, EFB has some weaknesses in its properties such as; low bulk density, high moisture content, high alkaline contents, etc. Moreover, high amount of silicon and potassium in EFB tend to increase ash agglomeration which causes slagging and fouling in the equipment. In this study, hydrothermal treatment (HT) was employed to improve the physicochemical properties of the EFB by turning into biochar. Biochars are obtained after EFB is treated hydrothermally at a temperature range of 200-300 °C for 60 minutes were characterized for their proximate and ultimate compositions, mineral composition, calorific values, and ash fusion temperature. The analyses showed that fixed carbon increased while volatile matter decreased after HT. These changes were more prominent with increasing reaction temperature. The calorific values of EFB increased from 19.05 MJ/kg to 29.31 MJ/kg after HT at 300 °C. The biochar was then mixed with coal at different ratios (1:1, 1:2, and 2:1) for cofiring. The results showed that the energy densification increased with increasing reaction temperature. XRF results showed that the contents of Na, K and Si in EFB decreased after HT, resulting in the increased ash melting temperature. Consequently, the fouling and agglomeration potential could be reduced. The optimum ratio for cofiring between biochar and coal was found to be 2:1, as the fouling and slagging indices were lowest. It can be concluded that HT is a promising method for upgrading EFB as a feedstock for cofiring with coal.

Keywords: Palm oil empty fruit bunch, hydrothermal treatment, biochar, fouling, slagging

1. Introduction

Palm oil empty fruit bunches (EFB) is the largest amount of biomass produced during palm oil processing. It is potential to be used as fuel with coal in coal-fired power plant boiler. Cofiring is one of the most advantageous method of utilizing biomass as an energy resource. Compared to direct combustion of biomass, cofiring offers the advantages of low investment and operation cost, and low dependence on fuel [1]. In addition, cofiring of biomass is capable of mitigating greenhouse gas by avoiding CH4 release from the otherwise landfilled biomass. CH4 is known to be 21 times more potent than CO2 in terms of global warming impact. Biomass also contains low level of sulfur and nitrogen. It contributes of SO2 reduction up to 75% [2].

At increasing biomass to coal ratio in cofiring system, several technical problems like slagging and fouling occur. Slagging and fouling are main problems in biomass utilization and threaten the economy of biomass power plant. In general, biomass-coal cofiring is technically feasible limited to 20% [3]. EFB as cofiring feedstock has inherent problems such as high moisture content, low calorific value, high ash content, high potassium content and other environmental issues. The high ash content and high potassium may cause slagging and fouling during biomass coal cofiring especially in boiler tube. The synergetic methods of pretreatment of biomass and cofiring have high potential for resolving...
problems on slagging and fouling during biomass coal cofiring. Therefore, the improvement on the fuel quality of EFB needs to be carried out.

The main cause on slagging and fouling during biomass combustion is alkali metal contained in biomass ash. Ash of EFB has high amount of silica and potassium, 44.80% and 24.70% respectively [4]. The presence of silica and potassium cause highly undesirable effects in terms of ash agglomeration, as their presence results in formation of compounds with low ash melting point, slagging, fouling, and tendency to corrode equipment [1]. The quantity of the alkali oxides in the fuel per unit of fuel energy is reflected by alkali index (AI) [1, 5]. Generally, to minimize occurrence of slagging and fouling during combustion, biomass require treatment prior to use. The treatment should be directed at lowering alkali metal content and increasing the ash fusion temperature of biomass fuel.

Recently, a study of hydrothermal treatment (HT) for improving fuel properties of empty fruit bunch at low temperature has been reported by our research group [6]. HT is one of the pretreatment method to convert high moisture content in biomass into carbonaceous solids under certain pressure and temperature [7]. The loss of volatile matter could be minimized during HT by fixing more organic substances into solid product compared to conventional drying [8]. Moreover, it also be able to remove inorganic components such as Na, Ca, K, Mg, K, Fe, and Mn in biomass [9]. HT may be used to decrease the volatile matter and increase the ash melting temperature to minimize the potential of ash agglomeration [7]. In this present work, the experiment is carried out at higher temperature.

This study aimed to improve the physicochemical properties of the EFB in the form of biochar and to evaluate the cofiring performance of coal-biochar. It is expected that this work would provides efficient pretreatment of biomass to improve its physicochemical properties and cofiring performance, especially in minimizing occurrence of slagging and fouling tendency during combustion.

2. Material and methods

2.1 Materials

EFB was obtained from a palm oil processing plant in Riau Province, Indonesia. The sample was shredded to 2–3 cm strands and then dried at 105 °C for 24 h in a hot air oven. Coal sample consisted of Indonesian lignite obtained from Zhejiang Energy Group, China. The proximate and ultimate analyses of EFB and coal are presented in Table 1.

2.2 Experimental set-up

2.2.1 Biochar preparation. The HT experiments were performed in a 500 mL batch digester at temperatures 200–300 °C. The digester pressure depended solely on the volume of water, and was measured by the pressure gauge in a range of 1.6 to 9.4 MPa. Twenty grams of EFB were used in each experiment with the ratio of biomass to water at 1:5 (w/w). At first, nitrogen was passed through the digester to purge oxygen. The digester was then heated to the desired temperature and maintained for 60 minutes. After the completion of each experiment, the digester was cooled down to room temperature by cooling water for 30 minutes. The hydrothermally treated EFB were collected from the reactor. The solid part (biochar) was separated from the liquid by using vacuum filtration 0.45 μm PVDF membrane and then dried at 105 °C in the oven before further analysis. The detailed configuration of the digester was described in our previous work [6].

2.2.2 Cofiring. The experiments of cofiring were conducted in the laboratory furnace. Five grams of feedstock were used in each experiments with the ratios of biomass to coal: 1/1; 1/2; and 2/1 (w/w). The cofiring experiments were carried out at 900°C, and the temperature was hold for 3 hours. Air was flowed naturally into the furnace at atmospheric pressure. After the completion of each experiment, the furnace was cooled down to room temperature naturally. The ash was collected and stored in a sealed container for further analysis.

2.3 Characterization and data analysis

The properties of the biochar were examined by several characterization techniques. The proximate analysis was analyzed based on ASTM D.3172 and ultimate analysis was determined using CHNS analyzer. Calorific value of biochar was analyzed using Bomb Calorimeter. The mineral composition of ash was analyzed using X-ray fluorescence spectrophotometer (ARL ADVANT’X Thermo Electron
Corp. Slagging and fouling characteristics, such as base/acid ratio, slag viscosity index, Si-Al ratio, fouling index, slagging index, and alkali index were evaluated by empirical equations based on composition of ash [1].

\[
\text{Base/acid (B/A)} = \frac{(\text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O})}{(\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2)} \quad \text{Eq. (1)}
\]

\[
\text{Slag viscosity (G)} = \frac{\text{SiO}_2}{(\text{SiO}_2 + \text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO}) \times 100} \quad \text{Eq. (2)}
\]

\[
\text{Si-Al ratio} = \frac{\text{SiO}_2}{\text{Al}_2\text{O}_3} \quad \text{Eq. (3)}
\]

\[
\text{Fouling index (Fu)} = \text{B/A} \times (\text{Na}_2\text{O} + \text{K}_2\text{O}) \quad \text{Eq. (4)}
\]

\[
\text{Slagging index (Rs)} = (\text{B/A}) \times S_d, (S_d = \% \text{ of S in dry fuel}) \quad \text{Eq. (5)}
\]

\[
\text{Alkali index (AI)} = \text{Na}_2\text{O} + \text{K}_2\text{O} \quad \text{Eq. (6)}
\]

3. Results and Discussion

3.1 Biochar characterization

The properties of biomass, biochar, and coal are shown in Table 1. Thermal degradation of biomass could be observed from the significant changes in volatile matters and fixed carbon. HT proved capable of upgrading proximate and ultimate compositions of biochars. The volatile matter decreased while the fixed carbon increased with increasing reaction temperature. Generally, biomass has a very high volatile matter content, resulting in low combustion efficiency and release harmful emissions when directly combusted [9]. While, fixed carbon content contributed to improve the energy density of fuel. The upgraded compositions of volatile matter and fixed carbon brought the properties of biochar to be more similar to coal. It was worth noting that HT at 280°C, the fixed carbon and volatile matter composition of biochar became better than coal.

| Table 1. Properties of biomass, biochars, and coal |
|---|---|---|---|---|---|---|
| | EFB | Hydrothermal temperature (°C) | Coal |
| | 200 | 220 | 240 | 260 | 280 |
| Moisture content | 9.45 | 3.00 | 2.61 | 7.36 | 4.47 | 1.40 | 2.22 | 20.81 |
| Volatile matter | 77.55 | 69.98 | 65.47 | 51.49 | 47.71 | 44.69 | 44.34 | 51.57 |
| Fixed carbon | 17.91 | 26.59 | 30.15 | 44.49 | 48.71 | 50.47 | 50.35 | 44.69 |
| Ash | 4.54 | 3.44 | 4.38 | 4.02 | 3.90 | 4.85 | 5.30 | 3.74 |
| Ultimate analysis (wt%, dry ash-free basis) | | | | | | | | |
| C | 50.35 | 60.25 | 50.63 | 60.57 | 53.61 | 51.67 | 70.93 | 66.58 |
| H | 7.03 | 6.63 | 6.85 | 4.06 | 5.94 | 7.16 | 5.73 | 9.27 |
| Oa | 37.29 | 17.66 | 26.82 | 25.10 | 28.60 | 23.95 | 15.79 | 20.01 |
| N | 0.98 | 5.80 | 5.75 | 4.40 | 4.44 | 3.09 | 1.91 | 0.94 |
| S | 0.24 | 6.33 | 5.69 | 2.14 | 3.66 | 9.36 | 0.46 | 0.25 |
| O/C | 0.74 | 0.29 | 0.53 | 0.41 | 0.53 | 0.46 | 0.22 | 0.30 |
| H/C | 0.14 | 0.11 | 0.14 | 0.07 | 0.11 | 0.14 | 0.08 | 0.14 |

*aOxygen content is calculated by balance.

The energy content of solid fuels strongly depends on the chemical composition, which is obtained to evaluate the characteristics of the fuel [1]. The energy content in biochar was improved after HT which associated with a decrease in the number of low energy bond H/C and O/C ratios and an increase in high energy bond C-C [10]. The effect of removing oxygen was responsible for increasing the energy content of biochar. Actually, HT of lignocellulosic material involves dehydration, condensation, hydrolysis, demethanation, and decarboxylation processes [10]. Thus, HT produced not only solid and gaseous products, but also various compounds dissolved in the liquid residue.
Figure 1. Effect of HT temperature on calorific value and energy yield of biomass.

3.2 Mineral composition of ash

Generally, biomass has lower ash content than coal. However, several types of biomass, especially agricultural wastes (EFB, sugarcane bagasse, etc.), contain high alkali metal in their ash, resulting in slagging and fouling problems. Table 2 shows the effectiveness of HT to upgrade the mineral composition of biomass. After cofiring of biochar and coal with several ratio (1:1, 1:2, and 2:1) the ash were analyzed using XRF.

| Compounds | EFB | Coal | Biochar : Coal (mass ratio) |
|-----------|-----|------|-----------------------------|
|           |     |      | 1:2 | 1:1 | 2:1 |
| SiO₂      | 37.29 | 32.09 | 45.32 | 41.69 | 43.91 |
| Al₂O₃     | 4.12  | 11.76 | 11.14 | 13.27 | 15.45 |
| Fe₂O₃     | 4.41  | 28.28 | 6.01  | 9.24  | 8.65  |
| K₂O       | 19.06 | 0.33  | 6.03  | 6.33  | 4.73  |
| Na₂O      | 0.20  | 2.03  | 2.66  | 2.32  | 1.32  |
| CaO       | 25.78 | 15.72 | 16.044 | 13.44 | 13.37 |
| MgO       | 9.15  | 8.83  | 12.80 | 13.73 | 12.56 |

HT of biomass could provide a treatment option for improving mineral composition of ash and further decreased slagging and fouling tendency during combustion. The presence of hot compressed water as reaction medium in HT might dissolve potassium and metal ions in biomass ash. From Table 2, it can be observed that the composition of K₂O decreased and Al₂O₃ increased with increasing biochar ratio in the cofiring system. The change in K₂O and Al₂O₃ compositions resulted in the improvement of ash properties. Higher potassium content in fuel tended to lower the melting points of ash, which led to slagging and fouling tendency during combustion, whereas high aluminium content prevent these problems.

3.3 Fouling and slagging

As mentioned in section 3.2, coal cofiring with biochar could improve the ash properties and further prevent slagging and fouling. Cofiring with biochar and coal ratio 2:1 showed the lowest slagging and fouling indices of 0.27 and 4.14 respectively. Alkali index showed decreasing trend with increasing biochar ratio in the cofiring system. Cofiring with biochar and coal ratio 2:1 also showed the lowest alkali index of 6.05. It can be confirmed that combination of cofiring and pre-treatment via HT can reduce slagging and fouling tendencies.
Table 3. Slagging, fouling, and ash fusion temperature

|                        | EFB | Coal | Cofiring (Biochar : Coal) |
|------------------------|-----|------|---------------------------|
|                        |     |      | 1:2 | 1:1 | 2:1 |
| Base/acid ratio (B/A)  | 1.42| 1.26 | 0.77| 0.82| 0.68|
| Slag viscosity index (G)| 48.66| 37.79| 56.53| 53.39| 55.94|
| Fouling index (Fu)     | 27.26| 2.97 | 6.71| 7.09| 4.14|
| Slagging index (Rs)    | 0.35| 0.33 | 0.25| 0.30| 0.27|
| Alkali index (AI)      | 19.26| 2.36 | 8.70| 8.65| 6.05|

Ash fusion temperature (oxidizing atmosphere) °C

|                          |       |
|--------------------------|-------|
| Deformation temperature  | 1185  |
| Spherical temperature    | 1214  |
| Hemispherical temperature| 1218  |
| Flow temperature         | 1223  |

To further determine evidence to support the slagging and fouling characteristics, the same samples were analyzed using ash fusion temperature test. The results are presented in Table 3. Ash fusion temperature (AFT) are largely influenced by mineral composition of ash. The measurement of AFT is an important indicator of the solid fuel behaviour during combustion, gasification, liquefaction, or ash utilization. Thus, the mineral composition of ash affected AFT, which can be described by initial deformation temperature, softening temperature, hemispherical temperature and flow temperature. The mentioned parameters are regarded as important indicators for slagging and fouling during combustion. Compared to the coal ash, raw biomass usually possesses low ash fusion temperature around 900 °C [6].

4. Conclusions

Hydrothermal treatment (HT) has been utilized to improve the properties of biomass as solid fuel with respect to energy densification and ash composition. The improvement in EFB properties were more prominent with increasing reaction temperature. Thus, the physicochemical properties of biochar were much different from those of EFB, while more similar to coal. The change in K₂O and Al₂O₃ compositions in ash could be favourable to reduce the potency of fouling and slagging during cofiring with coal. The potassium contents in EFB decreased after HT, resulting in the higher ash fusion temperature. The optimum ratio for cofiring between biochar and coal was found to be 2:1, which gave the lowest fouling and slagging indices. Therefore, HT is a promising method for upgrading EFB as a feedstock for cofiring with coal as the fouling and slagging potential could be reduced.

References

[1] Zhu Y, Niu Y, Tan H and Wang X 2014 Short review on the origin and countermeasure of biomass slagging in grate furnace. Front. Energy Res. Fenerg(2014)00007
[2] Sahu SG, Chakraborty N, Sarkara P 2014 Coal–biomass co-combustion: An overview. Renewable and Sustainable Energy Reviews 39:575-586
[3] Hansson J, Berndes G, Johnsson F, Kjarstad J 2009 Co-firing biomass with coal for electricity generation—An assessment of the potential in EU27. Energy Policy 37(4): 1444-1455
[4] Yan M, Hantoko D, Susanto H, Ardy A, Wahuyo J, Weng Z, Lin J 2019 Hydrothermal treatment of empty fruit bunch and its pyrolysis characteristics. Biomass Conversion and Biorefinery https://doi.org/10.1007/s13399-019-00382-9
[5] Wang Y, Wang D, Dong C, Yang Y 2017 The behavior and reactions of sodium containing minerals in ash melting process. Journal of the Energy Institute 90:167-73
[6] Hantoko D, Yan M, Prabowo B, Susanto H 2018 Preparation of empty fruit bunch as a feedstock for gasification process by employing hydrothermal treatment. Energy Procedia 152:1003–1008
[7] Novianti S, Nurdjawati A, Zaini IN, Prawisudha P, Sumida H, Yoshikawa K 2015 Low-
potassium fuel production from empty fruit bunches by hydrothermal treatment processing and water leaching. *Energy Procedia* **75**:584–589

[8] Moon J, Mun T-Y, Yang W, Lee U, Hwang J, Jang E, Choi C 2015 Effects of hydrothermal treatment of sewage sludge on pyrolysis and steam gasification. *Energy Convers Manag* **103**:401–407

[9] Khan AA, de Jong W, Jansens PJ, Sliethoff H 2009 Biomass combustion in fluidized bed boilers: potential problems and remedies. *Fuel Process Technol* **90**(1):21–50

[10] Hu X, Li X, Luo G, Yao H 2016 Homogeneous and heterogeneous contributions of CO₂ and recycled NO to NO emission difference between air and oxy-coal combustion. *Fuel* **163**:1-7.

**Acknowledgments**

This work was financially supported by P3MI 2018 Research Grant in Institut Teknologi Bandung, Indonesia; The State International Cooperation Project (2016YFE0202000, 2017YFE0107600), China; and Zhejiang Natural Science Foundation Project (LY17E060005), China.