Organic acid-assisted catalytic wet torrefaction of oil palm trunks (OPT)

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Abstract. Oil palm trunks (OPT) are attractive bio-fuel sources given their abundant availability. Nonetheless, the inherent properties of these biomass can lead to their inefficient use as bio-fuel directly. This work utilizes four organic acids (i.e., acetic, formic, levulinic, and citric acid) as catalyst in wet torrefaction to enhance the fuel properties of OPT hydrochar. In this study, the effects of different catalysts, catalyst concentrations, and residence times on the fuel properties of OPT hydrochar are analyzed. To study the effect of residence time, 0.2M of acid concentration was used for all four acids at 220 °C for 3 hr and 24 hr. Meanwhile, study on the effect of catalyst concentration was performed at 220 °C for 24 hr at 0.2M and 1.0M for all four acids. Increasing the residence time decreased the solid yield of OPT hydrochar treated in deionized water, acetic, formic, and levulinic acid, while wet torrefaction in citric acid results in close solid yield value in both residence time. The energy yield was observed to decrease in all liquid medium with increasing residence time except for formic acid and citric acid. On the other hand, increasing the acid concentration increased the OPT hydrochar solid yield in all acids except formic acid and the highest energy yield of 77.08% was obtained from wet torrefaction in 1.0M of citric acid at 220 °C for 24 hr. In summary, citric acid is an environmentally friendly acid to be used as catalyst to enhance the fuel properties of OPT hydrochar. Further study on the reaction mechanisms that governs such fuel properties enhancement with citric acid is warranted.

1. Introduction

Renewable energy will always be of high demand especially in the near future due to the rapid depletion of fossil fuels owing to the growing industrialization and globalization. Biomass is an attractive option for renewable energy production since they are abundantly available and are carbon-neutral, in which plants take in as much CO₂ as it releases when burned [1]. Malaysia is one of the world’s largest palm oil producers coming second after Indonesia [2]. The plantation and processing of palm oil produce various types of biomass including oil palm trunks (OPT), oil palm fronds (OPF), empty fruit bunches (EFB), mesocarp fiber (MF), and palm kernel shell (PKS) [3]. Most studies focus on using EFB, PKS, MF, and OPF as feedstocks for renewable energy production. However, OPT accounts for up to 3.6 million tonnes of unused biomass, which are an attractive option for renewable energy conversion [4].

Direct utilization of biomass in thermochemical conversion processes, i.e., pyrolysis, gasification, and combustion suffer from various drawbacks due to the inherent properties of biomass such as high
moisture content, low energy value, high ash content, and hygroscopic nature, which can lead to increased cost for handling, storage, and transport as well as operational problems [5, 6]. Wet torrefaction is an attractive pre-treatment method for biomass prior to their thermochemical conversion to improve the biomass properties since it is performed in liquid medium and thus, pre-drying is not required [7]. Wet torrefaction is typically performed in hot compressed water at temperature between 180 and 260 °C [8, 9]. However, high temperature increases energy consumption and thus increases production cost. Therefore, introduction of catalyst is essential to reduce the temperature required to produce equivalent properties of hydrochar product at lower temperature.

In this preliminary study, four organic acids are selected, i.e., acetic acid, formic acid, levulinic acid, and citric acid to investigate their effects on the wet torrefaction of OPT and its resultant fuel properties. The effects of residence time and acid concentration are the focus of this study.

2. Materials and methods

2.1. Materials
In this study, the oil palm trunks (OPT) were obtained from a local oil palm plantation, i.e., Masranti Plantation at Serian, Kuching. The OPT were first chopped into smaller pieces and dried in a convection oven at 105 °C for 24 hours to remove the moisture. Then, the dried OPT were milled using a rotary miller (Fritsch, Pulverisette 14) and segregated into the desired size range of 0.5-1.0 mm by a mechanical sieve. The processed OPT were then kept in a sealed bag and placed in a desiccator for further use.

Four organic acids, i.e., acetic acid (AA), formic acid (FA), levulinic acid (LA), and citric acid (CA) were used in this study. Glacial acetic acid (R&M Chemicals), reagent grade of ≥ 95% formic acid (Sigma), 98% levulinic acid (Sigma), and citric acid monohydrate (Merck) were purchased from the major chemical suppliers. The four acids were diluted to 0.2M and 1.0M for use in the catalytic wet torrefaction of OPT.

2.2. Wet torrefaction and catalytic wet torrefaction
The wet torrefaction of OPT in deionized water (DI) and the four organic acids were performed with a 200 mL polytetrafluoroethylene (PTFE)-lined acid digestion vessel (Parr Instrument Company, 4748A). The biomass and liquid medium were loaded into the vessel at a 1:25 biomass to liquid ratio by weight. After sealing the vessel tightly, it is placed into the convection oven to be heated to the desired temperature of 220 °C and maintained isothermally until the desired residence time reaches. To investigate the effects of residence time, wet torrefaction was heated at 220 °C for 3 and 24 hours with 0.2M acid concentration. Meanwhile, 0.2 and 1.0M of acid concentrations were used to study the effect of acid concentration and processed at 220 °C for 24 hours for all samples. Once the heating is completed, the acid digestion vessel is taken out from the oven and left to cool down to room temperature. The resultant hydrochar with liquid medium is filtered and rinsed with distilled water until the wash water reaches pH 7 and the solid hydrochar is dried in the convection oven at 105 °C for 24 hours. The dried solid hydrochar is weighed and stored in a plastic sealed bag, which is placed in the desiccator for storage until further analysis. The energy content, i.e., higher heating value (HHV) of the solid hydrochar is measured with a bomb calorimeter (IKA, C200). The solid yield, energy density, and energy yield are calculated following equations 1-3 [10]:

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\text{Hydrochar yield (\%) = } \frac{\text{Hydrochar mass}}{\text{Raw biomass mass}} \times 100\% \tag{1}
\]

\[
\text{Energy density, } ED = \frac{\text{Hydrochar HHV}}{\text{Raw biomass HHV}} \tag{2}
\]

\[
\text{Energy yield, } EY (\%) = \text{Hydrochar yield } \times ED \tag{3}
\]
3. Results and discussion

3.1. Effect of residence time

Figure 1 depicts the effect of two different residence times on the resultant non-catalyzed and catalyzed OPT hydrochar based on their solid yield, energy content presented as HHV, and energy yield. As expected, increasing the residence time from 3 to 24 hours led to decreased solid hydrochar yield from 45.29 to 30.88%, 49.05 to 32.13%, 45.05 to 35.40%, and 55.73 to 35.02% that is treated with deionized water, acetic acid, formic acid, and levulinic acid, respectively (figure 1(a)). Nonetheless, it was observed that increasing the residence time from 3 to 24 hours did not cause significant change in the solid yield when treated in 0.2M of citric acid, where the solid yield was 41.02% in 3 hours residence time and 41.00% for 24 hours residence time.

Lignocellulosic biomasses are generally composed of hemicellulose, cellulose, and lignin. Relative to cellulose and lignin, hemicellulose is the least thermally stable component followed by cellulose and subsequently, lignin. This is since hemicelluloses are amorphous structures of polysaccharides that comprises of various pentose and hexose sugars that can hydrolyze easily in the presence of weak acid or base [11, 12]. The hemicellulose is attached to cellulose microfibrils, which is a strong crystalline structure made of long polymer chain of glucose [11, 12]. Lignin, on the other hand, is a phenylpropene polymer that strongly cross-links the cellulose and hemicelluloses together and has the highest thermal stability [11]. The major cause for the weight loss in OPT during wet torrefaction is due to the decomposition of hemicellulose and parts of the cellulose. Increasing the residence time allows the liquid medium to further hydrolyze the hemicellulose and cellulose. The solid yield of the hydrochar treated in citric acid in both residence times, i.e., 41.00-41.02% is between that of the 3 and 24 hours of the average solid yield of deionized water, acetic acid, formic acid, and levulinic acid (i.e., the average solid yield of the four samples with 3 hours residence time is 48.78%; the average solid yield of the four samples with 24 hours residence time is 33.36%; the average between 33.36 and 48.78% is 41.07%, which is close to that of the solid yield of the hydrochar treated in citric acid). This implies that in citric acid liquid medium, the hydrolyses of hemicellulose and cellulose in OPT can only reach a certain point only, unlike the other liquid mediums that can further hydrolyzes the cellulose component in OPT to a higher extent with increasing reaction time. Thus, further increasing the residence time cannot decrease the solid yield much further in citric acid medium.

The HHV of raw OPT is 16.40 MJ kg⁻¹. Subjecting OPT to wet torrefaction in general, can enhance its energy value content. In addition, increasing the residence time from 3 to 24 hours increases the HHV of the resulting hydrochar from 20.30 to 26.70 MJ kg⁻¹, 18.18 to 26.30 MJ kg⁻¹, 18.25 to 26.37 MJ kg⁻¹, 18.13 to 26.15 MJ kg⁻¹, and 18.64 to 26.32 MJ kg⁻¹ that is treated with deionized water, acetic acid, formic acid, and levulinic acid, respectively (figure 1(b)). It is observed that the OPT hydrochars from all acid-catalyzed liquid mediums for 3 hours residence time have lower HHV than those from deionized water. However, the HHV of the OPT hydrochar is relatively same in all liquid mediums when treated at 24 hours. This implies that the change in energy value when acid catalyst was added was highly influenced by the residence time. Wet torrefaction is a densification process whereby low HHV components, i.e., hemicellulose and cellulose are completely or partially decomposed to form a lignin-rich hydrochar, which has a high energy content where lignin is the main contributor to the HHV [13].

The energy yield in figure 1(c) is related to both the solid yield and the energy density, which is calculated as shown in equation (2). Increasing the residence time from 3 to 24 hours decreased the energy yield of the OPT hydrochar from 56.08 to 50.29%, 54.37 to 51.54%, and 61.63 to 55.84% treated in deionized water, acetic acid, and levulinic acid, respectively. The decrease in energy yield in these three samples might be due to the large solid yield loss during wet torrefaction. However, the energy yield increases with increasing residence time from 3 to 24 hours from 50.15 to 56.92% and 46.62 to 65.82% treated in formic acid and citric acid, respectively. This indicates that the formic acid and citric acid catalyzed liquid mediums can cause further reaction with increasing residence time. However, the reactions and mechanism that occur need further investigation.
3.2. Effect of acid concentration

The effect of acid concentration on the fuel properties of OPT hydrochar is depicted in figure 2. It is observed in figure 2(a) that increasing the acid concentration from 0.2 to 1.0M increased the solid yield from 32.13 to 33.89%, 35.02 to 40.72%, and 41.00 to 46.67% treated in acetic acid, levulinic acid, and citric acid, respectively, except for that in formic acid, where the solid yield decreased from 35.40 to 24.10% when concentration increased from 0.2 to 1.0M. During wet torrefaction, the hemicellulose and cellulose decompose and hydrolyze into the liquid medium as intermediate hydroxymethylfurfural (5-HMF) [14–16]. The increased solid yield may be due to the increased acid concentration that helps to catalyze the repolymerization reaction of the intermediate 5-HMF components in the liquid medium onto the solid hydrochar. García-Bordejé, Pires [17] studied the wet torrefaction of cellulose in HCl and reported that the presence of 2M HCl promotes cellulose microfibrils fragmentation and formation of carbon spheres, i.e., microspheres. Qi, Song [18] investigated the effects of formic acid and levulinic acid addition to wet torrefaction of sucrose. They reported that the 5-HMF microspheres contain several reactive groups including hydroxyl groups that can actively react with the carboxyl groups of levulinic acid to promote microspheres formation and growth. They also found that in the case where formic acid was added, the liquid phase had much lower levulinic acid concentration at the initial stage since the addition of formic acid suppressed 5-HMF rehydration to levulinic acid. Thus, it is postulated that the increased in formic acid concentration from 0.2 to 1.0M in this study hinders the formation of levulinic acid during wet torrefaction of OPT that can assist in increasing the solid yield by promoting microspheres formation onto the surface of the hydrochar.
The HHV of raw OPT and OPT hydrochar treated in deionized water was 16.40 and 26.70 MJ kg\(^{-1}\), respectively. Increasing the acid concentration increased the HHV of OPT hydrochar treated in formic acid, levulinic, and citric acid from 26.37 to 26.63 MJ kg\(^{-1}\), 26.15 to 26.99 MJ kg\(^{-1}\), and 26.32 to 27.08 MJ kg\(^{-1}\), respectively, except in acetic acid where the HHV decreases from 26.30 to 25.08 MJ kg\(^{-1}\). The increased acid concentration primarily helped to catalyze hydrolysis reaction and carbonized the OPT to further densify the energy content.

Figure 2(c) depicts the energy yield obtained from the OPT hydrochar at different liquid medium and acid concentration. The energy yield of OPT hydrochar produced with deionized water was 50.29%. Meanwhile, increasing the acid concentration from 0.2 to 1.0M obviously increased the energy yield of OPT hydrochar treated in acetic acid, levulinic acid, and citric acid from 51.54 to 51.85%, 55.84 to 67.02%, and 65.82 to 77.08%, respectively, which is mainly contributed by the increased solid yield as discussed. Nonetheless, the reduced solid yield with increasing formic acid concentration led to decreased energy yield from 56.92 to 39.15%, which is the lowest energy yield obtained in this study. The highest energy yield was obtained from wet torrefaction of OPT in 1.0M of citric acid at 220 °C for 24 hours. Thus, citric acid is the most desired acid to catalyze wet torrefaction of OPT. In actual application nonetheless, optimum energy yield is desired when low acid concentration and residence time is used to minimize cost and downstream effluent processing. Therefore, levulinic acid is also a considerable candidate since a reasonably high energy yield of 61.63% was obtained when treated at 0.2M concentration at 220 °C and 3 hours residence time (figure 1(c)).

![Figure 2. (a) Solid yield, (b) HHV, and (c) energy yield of OPT hydrochar treated at 220 °C for 24 hours in deionized, acetic acid, formic acid, levulinic acid, and citric acid at 0.2M and 1.0M concentration.](image-url)
4. Conclusion
Organic acid is an excellent medium as catalyst to promote and enhance the fuel properties during wet torrefaction of OPT. Nonetheless, this study concludes that there is a close relationship between various operating parameters, i.e., acids type, residence time, and acid concentration. Therefore, further parametric study and optimization study including response surface methodology (RSM) is necessary to optimize the performance. Citric acid is a good candidate to achieve high energy yield given higher acid concentration and longer residence time. On the other hand, levulinic acid is a good candidate for low concentration and residence time that can help to reduce cost and effluent handling in actual application.

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