Combustion performance of hydrochars produced via citric-acid-assisted hydrothermal carbonization of pomelo peel at various temperatures

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Abstract. The shortage of fossil energy has become a worldwide problem. China has a vast land and a dense population, and the consumption of energy is becoming huge day by day. Biomass as a renewable and eco-friendly energy source has attracted extensive attention from researchers. In this study, biomass fuel was prepared by hydrothermal carbonization (HTC) technology with pomelo peel as feedstock. The combustion performance of citric acid (CA) assisted hydrochar based on pomelo peel was investigated under different treatment temperatures. The results show that the sample of PPH220-CA can become a good biomass fuel with excellent C content of 71.2%, HHV value of 27.7MJ/kg and combustion adequacy of 3.04%, so it is possible to play a role in the energy field in the future as an alternative fuel for coal.

1. Introduction
The energy structure of China is rich in coal, less oil and lack of gas, and coal has always occupied the leading position of energy consumption. However, over-reliance on coal has brought about a series of problems. One is the environmental pollution, a large number of pollutants such as CO₂, NOₓ, SO₂ and dust produced by coal combustion lead to increasingly serious ecological environment pollution. Second, the fossil fuels on which industrial societies depend are being consumed at a rapidly increasing rate [1]. Therefore, for the long-term development of human society, a clean and renewable fuel is urgently needed to replace the traditional fossil energy such as coal, oil and natural gas. Biomass, with its abundant organic matter and large yield, has attracted extensive attention from researchers and has the potential to play a role in the energy field as an alternative fuel [2].

Hydrothermal carbonization (HTC) technology improves feedstock and recovers energy in the presence of water, while avoiding excessive energy consumption during the drying process [3]. In this process, cellulose, hemicellulose and lignin undergo dehydration, decarboxylation and aromatization reactions initiated by hydrolysis reaction [4]. Lu et al.(2020) pointed out that citric acid could catalyze the fracture and recombination of cellulose, hemicellulose and lignin, thus increasing the carbon content of fuel [5]. Therefore, in this study, we use citric acid auxiliary agent, pomelo peel as raw material, using hydrothermal carbonization technology to explore the combustion performance of water heated carbon samples under different temperature conditions. The combustion performance of citric acid-assisted hydrochar of pomelo peel-based was evaluated by comparing the elemental content, HHV value, degree of dehydration and decarboxylation and combustion parameters of the samples.
2. Experimental Test

Hydrothermal carbonization (HTC) was carried out at 4 varying reaction temperatures (180°C, 200°C, 220°C, 240°C) and the same reaction time (6 hours) for each sample. Before HTC, about 8g pomelo peel powder was mixed with 50mL of citric acid solution (pH 3.61) and transferred to a closed reactor (autoclave), which was then placed in the oven. After that, the solid-liquid was separated, and the hydrochar was put into an oven for drying at 105 ℃ for 24 hours. The sample was labeled as PPHX-CA and X represented the HTC temperature.

An elemental analyzer (Vario EL CUBE, Elementar, Germany) was used to measure the C, H, N, contents of the sample. The O content was calculated by the differential method using Eq. (1):

\[
\%O = 100 - \%H - \%C - \%H
\]  

To understand the HTC process characteristics for the energy and mass balance, the High heating value (HHV; MJ/kg), Mass yield (MY), Energy yield (EY) were calculated by the following Eqs. (2,3,4) [4]:

\[
HHV = 0.335C + 1.423H - 0.154O - 0.145
\]  

\[
MY(\text{dry basis}) = \frac{W_f}{W_i}
\]  

\[
EY(\text{dry basis}) = \frac{W_f \times HHV_f}{W_i \times HHV_i}
\]

Where \(W_i\), \(W_f\), \(HHV_i\), \(HHV_f\) are the initial weight of the raw pomelo peel, the final weight of the hydrochars, the initial HHV of the raw pomelo peel and the final HHV of hydrochars, respectively.

STA2500 Simultaneous thermal analysis (STA) can be used to analyze hydrochar to obtain approximate analysis data- moisture(M), volatile matter (VM), fixed carbon and ash contents in accordance with ASTM standards [6]. The combustion performance is characterized by the weight loss curve and weight loss rate curve of the sample under air condition. The thermogravimetric analysis was carried out by the NETZSCH simultaneous thermal analyzer (STA2500 Regulus, Germany) to record the sample weight loss and weight loss rate under dynamic conditions as a function of temperature and time. For the test run, the samples each weighing between 2-5 mg were heated from 30°C up to 1000°C under a constant heating rate (10 °C/min) under a controlled (N₂:O₂ = 79:21) environment with a constant flow rate (30 mL/min). The data obtained by TG was analyzed using Origin Pro, a useful tool for analysis and graphing.

3. Results and Discussion

3.1 Physicochemical properties of PPHX-CA

The results of the elemental analysis are shown in Figure 1. With the increase of HTC treatment temperature resulted in an increase of the content of C and a reduction of H and O, ascribed to the occurrence of the dehydration and decarboxylation [7]. The dehydration reaction was usually defined as the elimination of hydroxyl groups, while decarboxylation was usually the thermal cleavage of long chain carboxylic acids [5].
Figure 1. C, H, O, N, S content of the raw pomelo peel and the corresponding hydrochars.

Van-Krevelen diagram can reflect the degree of dehydration and decarboxylation. From the Figure 2, it can be found that the PPH220-CA and PPH240-CA were closer to coal, meaning they had similar fuel properties to coal. High heating value (HHV) and Energy yield (EY) were two other critical fuel properties.

Figure 2. Van-Krevelen diagram of atomic ratios of the raw pomelo peel and the corresponding hydrochars.

Figure 3. Mass yield, Energy yield and High heating value contents of the raw pomelo peel and the corresponding hydrochars.

The red curve in Figure 3 showed that the raw pomelo peel with a low HHV of 13.1MJ/kg, while the hydrochars with a higher HHV in the range of 18.5-27.7MJ/kg, this verified that HTC treatment was an effective way to obtain value-added hydrochars. Compared to the HHV value, it can be found that the HHV values of PPH220-CA and PPH240-CA were similar and significantly higher than those of the hydrochars at the other two temperature conditions. The column bar graphs represented the Mass yield and Energy Yield of hydrochars. The Energy yield of PPHX-CA samples were in the range of 59.4-82.9%, as can be seen from the figure, with the increase of the hydrothermal treatment temperature, the EY value first increased and then decreased, reaching the maximum value at 220°C.
3.2 Combustibility of PPHX-CA

In order to investigate the combustibility of raw pomelo peel and prepared PPHX-CA, the TG and DTG curves were displayed in Figure 4 and Figure 5. The combustion profile of raw pomelo peel (PP) was divided into three stages. The first stage extended from 204.5°C to 262.5°C, what happened in this phase was the release and combustion of light volatile matter. The second stage was in the range of 262.5°C to 362.5°C, attributing to the combustion of heavy volatile matter. The third stage was the fixed carbon combustion phase with the temperature from 362.5°C to 443.9°C. After HTC treatment, the combustion performance of hydrochars derived from pomelo peel changed significantly. The second DTG peaks increased while the first peaks disappeared because light volatile matter were decomposed into liquid phase, H₂O and CO₂ during the HTC process.

The values of ignition temperature (Ti) and burnout temperature (Tf) can be obtained from the Figure 4 and Figure 5. The Ti and Tf value of raw pomelo peel were 204.5°C and 424.6°C, those of PPHX-CA were in the range of 271.3°C - 282.2°C and 499.7°C - 512.0°C. Although these two values increased with the increase of treatment temperature, the difference was very slight. Therefore, the HTC temperature had little influence on the combustion parameters of pomelo peel-based hydrochars.

Figure 4. TG curves of raw pomelo peel and the produced hydrochars at 10°C/min.

Figure 5. DTG curves of raw pomelo peel and the produced hydrochars at 10°C/min.

The remaining ash contents can reflect the degree of fuel combustion. The results of remaining ash contents for raw pomelo peel and the produced PPHX-CA were shown in Figure 6. Based on the results, with the increase of the temperature of hydrothermal treatment, the residual ash content also changed significantly. The value of raw pomelo peel was 4.93%, after the HTC treatment, the value was in the range of 3.04-8.74%. From the column bar, an interesting phenomenon was that when the temperature of HTC treatment was higher than 220°C, the hydrochar samples will burn more fully and the PPH220-CA was the superior fuel with lowest residual ash content of 3.04%.

Through thermogravimetric analysis, the HTC temperature had little effect on the ignition temperature and burnout temperature of pomelo peel-based hydrochar, but it can obviously affect the degree of combustion. Among them, PPH220-CA burns the most fully, so the combustion performance is the best.
4. Conclusion
Energy-intensive hydrochars assisted by critic acid (CA) were prepared by hydrothermal carbonization (HTC). Due to the high carbon content of 53.24-71.20% and HHV value of 18.6-27.7 MJ/kg, the prepared hydrochars (PPHX-CA) exhibited excellent combustion behaviour. The results of thermogravimetric analysis show that the ignition temperature and burnout temperature of the hydrochars have little influence on the hand temperature, but there is a significant difference in the degree of combustion.

PPH220-CA sample becomes a good biomass fuel because of its excellent carbon content, HHV value and combustion adequacy, so it is possible to play a role in the energy field in the future as an alternative fuel for coal, but the environmental impact such as ash release and gas emission behaviour, has not been studied, so it needs more time to be used in the energy field.

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References
[1] Zhao P, Shen Y, Ge S, Chen Z, Yoshikawa K. Clean Solid Biofuel Production from High Moisture Content Waste Biomass Employing Hydrothermal Treatment. Applied Energy. 131(2014):345-366.
[2] Zhuang X, Zhan H, Huang Y, Song Y, Yin X, Wu C. Denitrification and desulphurization of industrial biowastes via hydrothermal modification. Bioresource Technology.254(2018):121-129.
[3] Wang L, Zhang L, Li A. Hydrothermal treatment coupled with mechanical expression at increased temperature for excess sludge dewatering: influence of operating conditions and the process energetics. Water Research. 65(2014):85-97.
[4] Yao Z, Ma X. Characteristics of co-hydrothermal carbonization on polyvinyl chloride wastes with bamboo. Bioresource Technology. 247(2018):302-309.
[5] Lu X, Ma X, Chen X, Yao Z, Zhang C. Co-hydrothermal carbonization of polyvinyl chloride and corncob for clean solid fuel production. Bioresource Technology. 301(2020):122763.
[6] Cassel B, Menard K. Proximate Analysis of Coal and Coke using the STA 8000 Simultaneous Thermal Analyzer. 2012.
[7] Funke A, Ziegler F. Hydrothermal carbonization of biomass: A summary and discussion of chemical mechanisms for process engineering. Biofuels, Bioproducts and Biorefining. 4(2010):160-177.