The Effect of Temperature on the Properties of Hydrochars Obtained by Hydrothermal Carbonization of Waste *Camellia oleifera* Shells

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**ABSTRACT:** Hydrothermal carbonization (HTC) is a thermochemical conversion technique that can produce renewable solid biofuel by all types of waste. Waste *Camellia oleifera* shells (WCOSs) can be used to produce hydrochars via HTC. The effect of HTC temperature on the physicochemical properties and combustion behaviors of hydrochars was analyzed by varying from 150 to 300 °C. The mass yield of hydrochars decreased from 72.45% at 150 °C to 41.88% at 300 °C with the increase in temperature, and the higher heating value increased from 19.22 MJ/kg at 150 °C to 29.97 MJ/kg at 300 °C. The H/C and O/C values reduced from 1.30 and 0.66 of HTC150 to 0.77 and 0.27 of HTC300, respectively. Fourier transform infrared spectroscopy analysis indicated that the functional groups of hydrochar have changed because of the dehydration and decarboxylation reaction. The surface structure of hydrochars was rougher, and many pore structures were found at 240−300 °C by scanning electron microscopy analysis. The combustion behaviors of WCOSs and their hydrochars are distinct via thermogravimetric analysis, and the stability of hydrochars was strengthened with the increase in HTC temperature.

1. INTRODUCTION

Energy demand is rapidly increasing with the rapid development of the economy and population.¹ Fossil fuel, the main type of energy consumption, cannot meet the current demand because of its nonrenewable and environmental pollution.² Accordingly, researchers have begun to pay close attention to the utilization of renewable energy as a replacement of fossil fuel.³,⁴ Biomass energy, a type of renewable energy, not only has a wide range of sources and huge reserves, which can alleviate the current energy crisis, but also reduces the emissions of CO₂, NOₓ, and SO₂, which plays a positive role in maintaining ecological balance.² However, many disadvantages of biomass energy, such as a low energy content, low density, and high water content, lead to expensive operation and transportation costs, which limit their popularization and utilization.⁵,⁶ At present, carbonization,⁷ gasification,⁸ and liquefaction⁹ have been successfully applied to produce products with higher energy density and easier transportation biofuel from different types of biomass raw materials, reducing the dependence on fossil energy. In these thermal conversion technologies, hydrothermal carbonization (HTC) has attracted the attention of many researchers.

HTC is a thermochemical conversion technique that can produce renewable solid biofuel via all types of wastes, such as kitchen wastes,⁹ animal droppings,¹⁰ agricultural and forestry wastes,¹¹ and sludge.¹² The operation of HTC is that raw materials are subjected to water at 150−300 °C of temperatures,¹³,¹⁵ a residence time from 15 min to 10 h,¹⁴,¹⁵ and a solid loading of 7−25%.¹⁶ HTC possesses many advantages (high conversion, efficiency, simplicity, without pre-drying, etc.) compared with other thermal techniques.¹⁷ During HTC, cellulose, hemicellulose, and lignin of raw materials experienced hydrolysis, dehydration, decarboxylation, aromatization, and condensation reactions.¹⁸ The produced hydrochar possesses higher dewaterability, drying performance, energy density, and porosity compared with raw materials.¹⁹ In recent years, many researchers have carried out hydrothermal carbonization of various biomasses and analyzed the properties of hydrochars. Keiller et al.²⁰ produced and analyzed hydrochars of Australian saltbush, and the results indicated that the hydrochars possessed numerous similarities to fossil coal, such as higher heating values (HHVs), ratios of C/O and H/C, contents of the volatile matter (VM), fixed carbon (FC), and ash. Samaksaman et al.¹¹ investigated the fuel characteristics of the hydrochars from macadamia nut shells and found...
that the HHV of the solid product ranged from 22 to 27 MJ/kg. The results indicated that the macadamia nut shell hydrochars can be used as solid fuel. Sliz and Wilk 21 analyzed the energy potential of the Virginia mallow hydrochars via the proximate analysis, ultimate analysis, and HHV. These findings indicated that HTC is a potential technique to convert agricultural and forestry wastes into solid fuel. A common finding of these studies is that the temperature is the main factor that affects the solid product properties during HTC.

The Camellia oleifera growth is one of the important agricultural activities in the world and produces waste C. oleifera shells (WCOSs) from its production to processing. 22 In this study, WCOSs were used to prepare all kinds of products. Zhao et al. 23 obtained high concentration tea saponin via extraction and purification from WCOSs and analyzed the antibacterial activity of tea saponin. Zhang et al. 24 designed an efficient catalytic route for the conversion of WCOS into furfural, and the results provide an attractive utilization option to WCOSs. You et al. 25 explored the transformation of WCOSs for the production of xylooligosaccharides (XOS), and the solid residues derived from the production of XOS were used to prepare activated carbons. Li et al. 26 prepared a carbon microsphere with a controllable porous structure from WCOSs with an activation technique. However, these studies cannot be applied in industrialization at present. A large number of WCOSs are discarded or burned, causing harm to the environment. The preparation of WCOS biofuel by pyrolysis technology is an important method for the effective utilization of WCOSs. Xu et al. 27 evaluated the biochar performance of WCOSs under different pyrolysis temperatures. Wang et al. 28 researched the combustion characteristics and kinetics of heavy tar from pyrolysis of WCOSs. However, few studies correlated the evolution of hydrochars of WCOSs from its production to processing. 22 In this study, the hydrochars of WCOSs were produced via HTC at different temperatures (150, 180, 210, 240, 270, and 300 °C). The properties of hydrochars were analyzed via the mass yield, proximate, ultimate analysis, HHV, scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR). The combustion characteristics of WCOSs and their hydrochars were investigated by thermogravimetric analysis (TG). This research aims to investigate the effect of HTC on different temperatures, determine the best HTC temperature for the high quality hydrochars, and provide

| Table 1. Proximate Analysis, Ultimate Analysis, and HHV of Raw WCOSs and Their Hydrochars |
|----------------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| materials | VM (%) | FC (%) | ash (%) | HHV (MJ/kg) | C | H | O | N | S | mass yield (%) | energy yield (%) | H/C | O/C |
| WCOSs   | 72.16  | 24.64 | 3.19   | 17.15 | 45.79 | 5.01 | 45.38 | 0.33 | 0.30 | 1.31          | 0.74          |
| HTC150  | 74.16  | 24.88 | 0.95   | 19.22 | 49.77 | 5.39 | 43.51 | 0.21 | 0.17 | 72.45          | 81.10         | 1.30 | 0.66 |
| HTC180  | 71.85  | 27.00 | 1.15   | 19.60 | 51.04 | 5.23 | 42.14 | 0.28 | 0.16 | 61.13          | 69.77         | 1.23 | 0.62 |
| HTC210  | 66.30  | 32.85 | 1.35   | 22.22 | 57.33 | 5.03 | 35.83 | 0.30 | 0.16 | 55.52          | 71.45         | 1.05 | 0.47 |
| HTC240  | 58.25  | 49.97 | 1.49   | 24.13 | 62.55 | 4.67 | 30.82 | 0.35 | 0.12 | 49.79          | 69.67         | 0.90 | 0.37 |
| HTC270  | 53.47  | 45.72 | 0.82   | 25.98 | 67.05 | 4.57 | 27.05 | 0.40 | 0.11 | 44.28          | 66.90         | 0.82 | 0.30 |
| HTC300  | 46.32  | 52.89 | 0.79   | 26.97 | 69.55 | 4.46 | 24.66 | 0.43 | 0.11 | 41.88          | 65.68         | 0.77 | 0.27 |
| XOS     | 48.76  | 40.98 | 10.26  | 26.04 | 61.64 | 5.72 | 19.87 | 1.74 | 0.77 | 1.11           | 0.24          |
| sub-bituminous coal* | 46.60  | 48.04 | 5.36   | 28.67 | 70.68 | 5.01 | 17.35 | 1.42 | 0.18 | 0.85           | 0.18          |
| bituminous coal* | 34.45  | 58.32 | 7.23   | 30.94 | 76.25 | 4.73 | 10.58 | 1.07 | 0.14 | 0.74           | 0.10          |

*VM, volatile matter; FC, fixed carbon; and HHV, higher heating value. The oxygen content was calculated by difference based on dry ash free basis. *Lignite, sub-bituminous coal, and bituminous coal are chosen for comparison. 24,29

2. RESULTS AND DISCUSSION

2.1. Effect of HTC Temperatures. The effect of HTC temperatures on the proximate analysis, ultimate analysis, HHV, mass yield, and energy yield of the hydrochars is shown in Table 1. The mass yield, energy yield, and HHV ranged from 72.45 to 41.88%, 81.10 to 65.68%, and 19.22 to 26.97 MJ/kg, respectively. The results indicated that the HTC temperature had a significant effect on the mass yield, energy yield, and HHV of WCOS hydrochars. The mass and energy yield gradually decreased with the increase in temperature. However, the HHV of hydrochars increased from 17.15 MJ/kg for WCOSs to 19.22 MJ/kg for HTC150 and further to 26.97 MJ/kg for HTC300. The HHV of HTC270 and HTC300 can be comparable to that of lignite and slightly lower than those of the sub-bituminous coal and bituminous coal. 29,30 This phenomenon is attributed to the hydrolysis, dehydration, decarboxylation, aromatization, and condensation reactions of hemicellulose, cellulose, and a portion of lignin. 18 The organic compounds of WCOSs are more easily dissolved with the increase in HTC temperature, which resulted in the decrease in the mass and energy yield and the increase in HHV.

The proximate analysis of hydrochars showed that the fuel characteristics increased with the increase in the HTC temperature. The raw WCOSs exhibited 72.16% of VM, 24.64% of FC, and 3.19% of ash. After HTC at 300 °C, the VM content decreased to 46.32%, which was lower than those of lignite and sub-bituminous coal. The FC content increased to 52.89%, which was higher than those of lignite and sub-bituminous coal. These results are in accordance with the literature. 21,51

The ash content increased first and then decreased as the temperature increased, and its values ranged from 0.79 to 1.49%, which are lower than those of the raw WCOSs. The reason is that the organic components of WCOSs decrease, and the proportion of ash increases with the increase in temperature. However, when the temperature exceeds 240 °C, the degradation of organic components promotes ash to the decomposition of inorganics into water. 15 The low ash content
of hydrochars can effectively avoid the deposition of the inorganic substance in the boiler and prevent scaling and corrosion, which is an advantage of hydrochar as solid fuel. Table 1 illustrates no regular between the rise of temperature and the change of the ash content. The results are in accordance with the literature. However, some research results showed that the ash content increases with the increase in temperature.1

The C, H, N, and S contents of hydrochar from different HTC temperatures were measured, and the oxygen content was calculated by difference according to dry ash free basis. The ultimate analysis indicated that hydrochars of WCOSs had a higher C content than those of raw WCOSs, with a range from 49.77 to 69.55%. The C content gradually increased with the increase in the HTC temperature, indicating that the increased temperature enhanced the carbonization degree of hydrochars because of hydrolysis, dehydration, and decarboxylation of samples.18 Meanwhile, the H and O contents exhibited a gradual decrease. The H content gradually decreased with a range from 5.39% of HTC150 to 4.46% of HTC300. The O content gradually decreased with a range from 43.51% of HTC150 to 24.66% of HTC300. The sulfur content decreased after HTC. The value of the S content decreased to 0.12% at 240 °C of HTC temperature, reducing by 60.00% compared with the raw WCOSs. These results are in accordance with the literature.32 However, some researchers also reported that the change of the S content has nothing to do with temperature.13,34 The reason may be that the content of S in the samples and the washing times of solid products affect the experimental results. The same result was found in the N content.

To further analyze the HTC, the Van Krevelen diagram was used to exhibit the dehydration and decarboxylation reaction.16,22,35 The atomic ratios of H/C and O/C of the raw WCOSs and their hydrochars were plotted in the Van Krevelen diagram, and lignite, sub-bituminous coal, and bituminous coal were also plotted for comparison. In Figure 1, the raw WCOSs had the highest H/C and O/C values of 1.31 and 0.74, respectively. The atomic ratios of all hydrochars tended to the zero point with the increase in temperature. At 210 °C, the H/C value of HTC210 was less than that of lignite, indicating that HTC210 showed similar properties to lignite.22 Moreover, the values of H/C and O/C are close to those of sub-bituminous coal and bituminous coal at 270 and 300 °C, respectively. The results indicated that HTC270 and HTC300 were more suitable to be used as solid fuel because of the lower atomic ratio.

2.2. FTIR Analysis. The FTIR spectra of raw WCOSs and their hydrochars at different HTC temperatures are shown in Figure 2. The spectra indicated that the HTC temperatures have an obvious effect on the functional groups of raw WCOSs and their hydrochars. Thus, the chemical transformation information can be obtained during HTC.

The peak at 3440 cm\(^{-1}\) was attributed to the stretching vibration of \(\mathrm{O}−\mathrm{H}\) in the hydroxyl and carboxyl groups. The peak became less intense with the increase in temperature because of the dehydration reaction during HTC.18 The same results were found for the C−H stretching vibration (2946 and 2858 cm\(^{-1}\)) in the aliphatic and aromatic structures because of the demethylation reaction.5 The peak at 1732 cm\(^{-1}\) is due to the C=O stretching vibration in the FTIR spectra of raw WCOSs and disappears after HTC treatments, except for HTC150.22 The results indicated that the decarboxylation reaction at low temperature is less. The peak at 1608 cm\(^{-1}\) was attributed to the C=C stretching vibration in the benzene ring skeleton of lignin, and their intensities were the same. The peaks at 1389 and 1015 cm\(^{-1}\) are due to the C=C and C−O−C stretching vibration, respectively, and the change in the regular pattern of the intensity was consistent with that at 1732 cm\(^{-1}\) (C=O).

2.3. SEM Analysis. The micrographs of raw WCOSs and their hydrochars at different HTC temperatures have been analyzed by SEM, and the results are shown in Figure 3. The HTC temperatures can change the surface structure of the hydrochars. The raw WCOSs had a compact structure and smooth surface without pores. The fragment retains the original structure of the sample (Figure 3a). The fragment began to disappear with the increase in temperature, and the surface cracks and becomes rougher (Figure 3b–d). This situation occurs because the temperature is not sufficient to destroy the structure of WCOSs, and only a part of the hydrolysis reaction can occur on the surface of the sample.5 When the temperatures reach 240, 270, and 300 °C, a large number of pore structures and small fragments were observed on the surface of the samples. These phenomena are attributed to the dehydration, decarboxylation, and condensation of the samples.5,18 The microsphere or carbon microsphere is rarely

![Figure 1. Van Krevelen diagram.](https://doi.org/10.1021/acsomega.1c01787)
2.4. Combustion Behaviors of Raw WCOSs and Their Hydrochars. The TG and derivative thermogravimetry (DTG) curves of raw WCOSs and their hydrochars are presented in Figure 4, and their combustion parameters are summarized in Table 2. The combustion behaviors of raw WCOSs and their hydrochars were divided into three stages. A small DTG peak in stage I was observed at 85−100 °C, which is due to the moisture evaporation in the samples. A sharp
DTG peak in stage II was observed at 229.1–274.3 °C because of the VM combustion of the samples. The stage III peak is derived from the FC combustion. Stages II and III of the DTG curves showed opposite peak intensities due to the difference in the contents of VM and FC in hydrochars. The DTG curves of raw WCOs showed a wider range of stage II because of the complex components compared with hydrochars. The peak in stage II gradually flattened out with the increase in HTC temperature. By contrast, the peak intensity becomes strong at stage III. This phenomenon resulted in the increase in $T_i$ with the increase in the HTC temperature.

Table 2 illustrates that the $T_i$ and $T_m$ of hydrochars were higher than those of WCOs. The $T_i$ increased from 260.6 °C of HTC150 to 306.2 °C of HTC300 because of the decrease in the high reactivity VM with the increase in the HTC temperature. Meanwhile, $T_m$ reached the maximum value at 240 °C and then gradually decreased. Table 2 shows that HTC300 possesses the highest ($dw/dt)_\text{max}$ (9.43%/min) and ($dw/dt)_\text{mean}$ (4.14%/min). The reason may be that HTC300 has the highest FC content compared with other hydrochars. These results indicated that a higher HTC temperature enhanced the intensity of carbonization, and the stability of hydrochars increased.

### 3. CONCLUSIONS

The WCOs hydrochars were produced via HTC at different temperatures (150, 180, 210, 240, 270, and 300 °C), and the effect of HTC temperature was investigated by hydrochar properties. The results indicated that hydrochars that derived higher temperatures showed superior properties compared with the raw WCOs. The C content and HHV of hydrochars gradually increased, and the O content in H/C and O/C values decreased with the increase in the HTC temperature. At 300 °C, the C and O contents and the HHV, H/C, and O/C values were 69.55 and 24.66% and 26.97 MJ/kg, 0.77, and 0.27, respectively. The FTIR analysis showed that the dehydration and decarboxylation reaction occurred, which can be inferred from the change trend of functional groups of hydrochars. The surface structure of hydrochars was rougher, and many pore structures were found at 240–300 °C. The TG and DTG curves of raw WCOs and their hydrochars showed that the combustion behaviors were distinct, and hydrochars had a more stable combustion process with a higher $T_i$ temperature.

### 4. MATERIALS AND METHODS

#### 4.1. Material

WCOs were obtained from the Yunnan Province (China). The raw material was washed with tap water, which ensured that the sample is free of sludge and stains. Then, WCOs were dried in an oven at 105 °C for 24 h to remove water and crushed to 100 meshes (0.16 mm) as the experimental samples. The powder samples were stored with the sealed bags in a dry environment.

#### 4.2. HTC Process

A high-pressure batch reactor (Anhui Kemi Machinery Technology Co., Ltd., China) was employed for HTC. The volume of the batch reactor was 50 mL. The reactor was equipped with a temperature controller. The HTC experiments were consistent with the literature and are presented in Figure 5. The temperatures of the HTC experiments were 150, 180, 210, 240, 270, and 300 °C for 150, 200, 210, 240, 270, and 300 °C/min of the heating rate and maintained for 30 min with a 150 rpm stirring rate. The WCO hydrochars were designated as “HTCXXX”, where “XXX” represented the HTC temperature.

#### 4.3. Hydrochar Property

The ultimate analysis (C, H, N, and S) was determined with an elemental analyzer (Vario EL III, Germany), and the oxygen content was calculated by difference on the basis of eq 1. The VM was measured according to ASTM D3175. Thereafter, the ash content (dry basis) was obtained at 750 °C for 4 h in an oxygen environment. The FC was calculated on the basis of eq 2. The HHV of the samples was calculated on the basis of eq 3.

\[
O(\%) = 100 - C(\%) - H(\%) - N(\%) - S(\%)
\]

\[
\text{ash}(\%) = 100 - \text{FC}(\%) - \text{ash}(\%)
\]

\[
\text{HHV(MJ/kg)} = 0.3491C + 1.1783H + 0.1034O - 0.015N - 0.0211A
\]
The mass and energy yields were calculated on the basis of eqs 4 and 5, respectively.  

\[
\text{mass yield (\%) } = \left( \frac{m_{\text{hydrochar}}}{m_{\text{WCOSS}}} \right) \times 100
\]  

(4)

\[
\text{energy yield (\%) } = \left( \frac{\text{HHV}_{\text{hydrochar}}}{\text{HHV}_{\text{WCOSS}}} \right) \times \text{mass yield}
\]  

(5)

The functional groups of the samples were estimated by the FTIR spectra (Magna-IR 560 ESP Thermo Nicolet Waltham, MA, USA). The absorption spectra ranged from 400 to 4000 cm\(^{-1}\). SEM (JEOL, Japan) was used to analyze the change of the surface structure from WCOSS hydrochars at different HTC temperatures.

4.4. Combustion Characteristics. The combustion experiments of the samples were performed via TG (Netzsch, Germany) within a temperature range of 30–900 °C at a heating rate of 10 °C/min. The atmosphere was chosen as the carrier gas, and the flow rate was 60 mL/min.

TG–DTG was performed to analyze the ignition temperature \(T_i\), burnout temperature \(T_h\), maximum combustion rate temperature \(T_{\text{max}}\), maximum rate of mass loss \((\text{dw}/\text{dt})_{\text{max}}\), and mean rate of mass loss 

\[
\frac{(\text{dw}/\text{dt})_{\text{max}}}{T_i}, \frac{(\text{dw}/\text{dt})_{\text{mean}}}{T_i}, \frac{(\text{dw}/\text{dt})_{\text{mean}}}{T_h}
\]

in accordance with the previous literature.\(^3,30\,37\)

The comprehensive combustibility index \((S_N)\) was used to determine the combustion characteristics of the WCOSSs and their hydrochars.\(^31\,37\)

\[
S_N = \frac{(\text{dw}/\text{dt})_{\text{max}}}{(\text{dw}/\text{dt})_{\text{mean}}} \times \frac{T_i}{T_h}
\]

(6)

where \((\text{dw}/\text{dt})_{\text{max}}\) and \((\text{dw}/\text{dt})_{\text{mean}}\) represented the maximum and mean rates of mass loss (wt %/min), respectively, \(T_i\) and \(T_h\) were the ignition and burnout temperatures (K), respectively.

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Notes

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