Valorization of tree leaves waste using microwave-assisted hydrothermal carbonization process

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Abstract
Fallen leaves of landscape trees, as an emerging biomass waste, were valorized using conventional hydrothermal carbonization (HC) and microwave-assisted hydrothermal carbonization (MHC) pretreatments, and were comparatively characterized for physicochemical properties and thermal degradation kinetics. The results show that MHC is superior to conventional HC operation, because at 200°C, the MHC process not only gives a higher hydrochar yield (45.09 vs. 39.47 wt%) with significantly reduced energy consumption (0.63 vs. 2.74 MJ g⁻¹), but also is more effective in removing K and Si. For isoconversional kinetic analysis, the FWO method provides better results than the KAS method as the latter failed to fit the tree leaves sample ($R^2 < 0.9$). The thermal degradation kinetics at high temperatures (>400°C) showed that the hydrochar obtained from the MHC process has a lower average activation energy of ~190 MJ kg⁻¹ than the conventional HC process (~260 MJ kg⁻¹). This study reveals the potential for valorization of the landscape tree wastes via the MHC process.

KEYWORDS
biomass, hydrochar, hydrothermal carbonization, isoconversional kinetic analysis, urban fallen leaves, valorization

1 | INTRODUCTION
Biomass energy can dramatically contribute to the mitigation of greenhouse gas emissions from heavily carbon-dependent sectors (Reid et al., 2020). Among the wide variety of biomass feedstocks, agricultural wastes and forestry residues are the most studied (Williams et al., 2016). However, fallen leaves from landscape trees cultivated in the urban area are a
novel alternative source of biomass, which, however, are often underestimated and disposed of together with other municipal solid wastes. Specifically, with rapid urbanization, many landscape trees are planted for greening, decoration, noise reduction, and air purification purposes (Trowbridge & Bassuk, 2004). Fallen leaves from these trees accumulate rapidly toward large quantities. However, different from those in the forest field, they are not subject to the natural microbiological digestion process as the ground in the urban area is often covered by non-soil materials such as brick, concrete, cement, or asphalt. Currently, for quick disposal, fallen leaves are often burnt, resulting in significant air pollution. The surged accumulation of fallen leaves calls for efficient valorization.

Although lignocellulosic biomass is often readily available, its pretreatment remains one of the most critical challenges to biomass utilization due to its complex hierarchical structure and recalcitrant nature (Hassan et al., 2018). Energy-efficient, environmentally friendly biomass valorization technologies are highly desirable. Without denying the advantages of biological or chemical processes, given the colossal quantity of fallen leaves a city can accumulate, thermochemical pretreatment seems to be more promising for energy recovery because it is fast, environmentally benign, and easily scalable (Adams et al., 2018; Patel et al., 2016).

Hydrothermal carbonization is a highly efficient thermochemical pretreatment technology, converting biomass feedstocks in the presence of subcritical water (Alper et al., 2020). After biomass pretreatment, the energy density, grindability, hydrophobicity, and ease of storage will be greatly improved (Dai et al., 2019; Wang et al., 2020). The hydrochars derived from the hydrothermal carbonization process are being studied for biofuels (Sharma et al., 2020), sorption of pollutants (Liu et al., 2021), soil amendment (Wang et al., 2020), soil C sequestration (Baronti et al., 2017), and its potential in climate change mitigation (Owsianiak et al., 2018). Based on the different heating methods, conventional hydrothermal carbonization (HC) and microwave-assisted hydrothermal carbonization (MHC) are under development. When compared to the widely studied HC process, the MHC process emerges as an attractive technology thanks to its unique benefits (Gao et al., 2021). First, microwave heating is less energy demanding and more cost-effective in producing various products such as hydrochars (Nizamuddin et al., 2018). Second, the MHC process reduces processing time because of its rapid volumetric heating. Third, it improves the processing capacity due to relatively lower residence time in converting the raw biomass into desired products (Afso1abi et al., 2017). In addition, microwave can promote new pathways during biomass valorization dependent on the unique properties of the feedstock being used (Lei et al., 2021; Liu, Zhong, et al., 2021).

Only a handful of reports give a direct comparison of hydrochars obtained from the HC and MHC processes. Dai et al. (2017) produced hydrochars from bamboo sawdust via the HC and MHC processes and compared the properties and pyrolysis behaviors of these hydrochars. They found that the HC hydrochars had higher thermal stability. Elaigwu and Greenway (2016) compared the chemical and structural properties of hydrochars produced from Prosopis africana shell. They concluded that the MHC process is faster in carbonization than HC, manifested by a higher level of conversion within a shorter time. The internal moisture content of the feedstock is favorable as the water molecules could couple with the electromagnetic field and promote microwave dielectric heating (Kannan et al., 2017). Previous studies showed that hydrochars could be produced from both processes and that, depending on the preparation conditions, the hydrochar properties might see significant variations. The structural change caused by microwave heating might have profound impact on thermal degradation behaviors of the hydrochars, which needs further elucidation. Furthermore, to determine the feasibility of using hydrochars as biofuels, the overall process efficiency and the thermochemical-kinetic properties need to be carefully assessed.

To the best of our knowledge, converting landscape tree leaves into biofuel via hydrothermal pretreatment has rarely been studied. The effect of heating methods and carbonization temperature on yield and physicochemical properties of fallen leaves hydrochar has not yet been discussed. Moreover, the impact of different heating methods on hydrochar thermochemical kinetics is not compared for the HC and MHC processes. The kinetic analysis will provide insight into the hydrochar thermal degradation mechanism, allowing selection and optimization of the subsequent conversion process, and providing a valuable reference for subsequent reactor design (Cai et al., 2019; Damartzis et al., 2011).

Therefore, this study aims to (1) comparatively study the yield and physicochemical properties of hydrochars produced from tree leaves using two different heating methods, each with four different reaction temperatures, (2) to compare energy consumption of the HC and MHC processes for the pretreatment of tree leaves, and (3) to compare the thermal degradation kinetics of hydrochars produced by different hydrothermal processes using different isoconversional analysis methods. Results reported in this study will provide important reference for how to valorize fallen tree leaves via the different carbonization pretreatments, and facilitate the design of subsequent hydrochar utilization process.

## 2 EXPERIMENTAL PROCEDURES

### 2.1 Materials

Tree leaves (TLs) of Fraxinus chinensis Roxb, a widely cultivated landscape tree species in China, were collected...
on the ground along the pedestrian walk near the College of Mechanical and Electronic Engineering at the Northwest A&F University in Fall 2018. After collection, the TLs were stored under ambient temperature and air-dried for 1.5 months. The TLs were then pulverized using an ultracentrifugal grinder mill (ZM 200, Retsch), giving a particle size smaller than 0.18 mm. The biomass powders were subject to characterization or hydrothermal pretreatments.

2.2 Hydrothermal carbonization

Either HC or MHC process was applied to pretreat the TLs. Before hydrothermal carbonization, a certain amount of TLs was dispersed into distilled water while maintaining a fixed biomass loading of 1 g per 10 mL H₂O. For increased mixture, homogeneity agitation was applied using a magnetic stirrer (Model MS-H-S, Scilogex LLC) at 600 rpm for 5 min. The mixture was then transferred into reactors. For HC or MHC experiments, the heating ramp rate and reaction duration were both set at 10 ℃ min⁻¹ and 1 h (excluding the heating period), respectively.

The HC experiments were performed using an autoclave reactor with an inner volume of 25 ml (KH-25, Yikai Instrument Equipment Co.), which was made with polytetrafluoroethylene liner covered by a 304 stainless steel shell. Five autoclave reactors were placed simultaneously in a muffle furnace (SX-2-4-10G, Jinan Laibao Medical Equipment Co., Ltd.). After carbonization, the reactors were removed from the furnace for sample collection when cooled down to the ambient temperature.

The MHC experiments were performed using a multifunctional microwave synthesizer (Model XH-8000 Plus, Beijing Xianghu Science and Technology Development Co., Ltd.). Its schematics are depicted in Figure 1, and the detailed specifications are available in our previous report (Kang et al., 2019). The reaction vessel was made of polytetrafluoroethylene (PTFE), protected by a polyether ether ketone (PEEK) shell, with upper limits of temperature and pressure being 260 ℃ and 4.0 MPa, respectively. The microwave power input was auto-adjusted based on the temperature setting. After carbonization, sample collection was performed at the ambient temperature. The mixture of hydrochar and liquid phase products was transferred into a clean beaker, then separated through Whatman™ grade 2 qualitative filter paper (8 µm particle retention at 98% of efficiency). The hydrochars were washed with de-ionized water and dried in an oven at 105 ℃ for 12 h and then stored in glass bottles for further analyses.

To investigate the influence of reaction temperature, hydrochars were prepared at 110, 140, 170, and 200 ℃, respectively. Temperatures higher than 200 ℃ were not attempted due to the safe operation requirements of the reactor, and for practical applications, converting large quantity of biomass through hydrothermal process at higher than 200 ℃ is difficult. For reproducibility and characterization needs, five batches of hydrochars were produced for each temperature. During the carbonization experiments, energy consumption was measured using an electric meter (model SZDX-D01, Wenzhou Longwan Guoguang Electric Control Equipment Co.) connected to the muffle furnace or microwave synthesizer dependent on the pretreatment process being used. The hydrochars were named after their producing method (HC or MHC) and reaction temperature, for example, “MHC-110” refers to hydrochar produced with MHC at 110 ℃. The carbonization experiments for each condition has been triplicated.

For either HC or MHC process, its hydrochar mass yield (Y) and energy consumption (EC) were calculated using Equations (1) and (2):

\[
Y \text{ (wt. %)} = \frac{\text{Mass of hydrochar produced}}{\text{Mass of tree leaves loaded}} \times 100\%, \quad (1)
\]

\[
EC \text{ (MJ/g hydrochar)} = \frac{\text{Electric energy consumed}}{\text{Mass of hydrochar produced}} \times 100\%. \quad (2)
\]
2.3 | Characterizations

2.3.1 | Proximate and ultimate analyses

The proximate analysis of TLs and hydrochars was performed following the ASTM 1762-84 and 3173-87 standards. The ultimate analysis was conducted using an elemental analyzer (vario Macro cube, Elementar). Based on the elemental composition, the HHV of hydrochar was estimated using the Mendeleev formula (Krysanova et al., 2019):

$$HHV(\text{MJ/kg}) = 339[C] + 1256[H] + 109[S] - 109[O]. \quad (3)$$

2.3.2 | X-ray diffraction (XRD) analysis

The XRD analysis was performed with a D8 ADVANCE X-ray diffractometer (Bruker) equipped with a Cu Kα radiation source, using a scanning 2θ range of 10–90°.

2.3.3 | FTIR and SEM analyses

The functional groups present in the TLs and hydrochars were detected using a Nicolet iS10 FT-IR spectrophotometer (ThermoFisher Scientific). The powdered samples were scanned under transmittance mode in the range of 400–4000 cm⁻¹ at the resolution of 4 cm⁻¹, and 16 accumulations were used to obtain each spectrum. Surface morphological characteristics of the samples were investigated using a scanning electron microscope (SEM) (TM 3030 Tabletop Microscope, Hitachi Ltd.).

2.3.4 | Inorganic elemental analysis

The inorganic elements present in the TLs and hydrochars were measured following the procedures described in the LY/T 1270-1999 standard (Zhang & Yang, 1999). The contents of metals were determined using a flame atomic absorption spectrometer (Z-2000, Hitachi Ltd.). For each test, 0.5 g of dry sample passing through a 0.5-mm sieve was placed in a glass tube and was used to determine the K, Na, Ca, Mg, and Fe content. The residue on the filter paper was used to determine the Si content by weighing.

2.3.5 | TG/DTG analysis

The thermogravimetric (TG) and derivative thermogravimetric (DTG) analyses of TLs and hydrochars were performed using a simultaneous thermal analyzer (TGA 55, TA Instruments). For each run, powdered sample of 15–20 mg was heated from room temperature to 800°C with a nitrogen flow of 20 ml min⁻¹, and the tests were conducted at different thermal ramp rates of 5, 10, 20, 30, and 40°C min⁻¹, respectively. Weight loss and weight loss rate were recorded continuously as a function of temperature.

2.4 | Kinetic analysis

The TG/DTG data provide essential information on physicochemical changes during the thermal degradation process and are widely used for kinetic analysis (Cai et al., 2018). For this purpose, the degree of conversion (α) is defined as

$$\alpha = \frac{w_0 - w_t}{w_0 - w_f} \times 100\%, \quad (4)$$

where $w_0$, $w_t$, and $w_f$ are sample weight at the initial stage, at time $t$, and at the completion of the reaction/process, respectively. The general kinetic equation is given as

$$\frac{d\alpha}{dT} = k(T)f(\alpha), \quad (5)$$

or

$$\frac{d\alpha}{dT} = \frac{k(T)}{\beta}f(\alpha), \quad (6)$$

where $d\alpha/dT$ is the mass conversion rate, $k(T)$ is the thermal degradation rate constant, and $f(\alpha)$ is the differential form of the kinetic model function. The solid sample was heated at a constant ramp rate of $\beta$ (K/min). The temperature dependence of the rate constant $k(T)$ is described using the Arrhenius equation:

$$k(T)A\exp\left(-\frac{E_a}{RT}\right), \quad (7)$$

where $A$ is the pre-exponential factor, $E_a$ is the activation energy (kJ mol⁻¹), and $R$ is the gas constant, 8.3145 J mol⁻¹ K⁻¹. Combining Equations (6) and (7) leads to the fundamental expression to calculate kinetic parameters from the TG results:

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\exp\left(-\frac{E_a}{RT}\right)f(\alpha). \quad (8)$$

For solid-state reactions, $f(\alpha)$ can be generalized as
where \( m, n, \) and \( p \) are empirically obtained exponential factors, with one of them always being zero (Hao et al., 2017). By separating variables and integrating, Equation (7) can be transformed into:

\[
g(\alpha) = \frac{a}{f(a)} \int \frac{A}{\beta} \exp\left(-\frac{E_a}{RT}\right) dT,
\]

where \( g(\alpha) \) is the integral form of the reaction model function. The right side of Equation (10) is a well-established temperature integral function that has no analytical solution but can be determined by using either numerical methods or approximations.

In this study, two highly successful isoconversional model-free methods (Hao et al., 2017; Wu et al., 2020), that is, the Flynn–Wall–Ozawa (FWO) method and the Kissinger–Akahira–Sunose (KAS) method, were chosen to calculate the kinetic parameters. The FWO method can be presented as

\[
\log\beta = \log\left(\frac{A E_a}{R g(\alpha)}\right) - 2.315 - 0.4567 \frac{E_a}{RT},
\]

The KAS method can be presented as

\[
\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{E_a g(\alpha)}\right) - \frac{E_a}{RT}.
\]

As shown in Equations (11) and (12), for a certain degree of conversion, by plotting data points of \( \log\beta \) or \( \ln(\beta/T^2) \) versus \( 1/T \) obtained at different heating ramp rates, the \( E_a \) value can be calculated from the slope of the linear regression.

### 3 | RESULTS

#### 3.1 | HC/MHC process efficiency

For the HC or MHC process, its efficiency was compared on the basis of hydrochar mass yield (Y) and energy consumption (EC), with results presented in Figure 2. For either HC or MHC process, the hydrochar mass yield decreases with an increasing pretreatment temperature, which can be attributed to the ever-increasing partial decomposition of hemicellulose and cellulose. One exception is that, for the HC process, the hydrochar yield is barely changed when the reaction temperature increases from 110 to 140\(^\circ\)C, indicating that for the conventional HC process, such low reaction temperatures are insufficient to noticeably destruct the biomass matrix. As for energy consumption, for reaction temperatures ranging from 110 to 200\(^\circ\)C, the HC process is consistently higher than that of the MHC process, showing that the MHC process is able to produce a significantly higher amount of hydrochar with less energy consumption.

#### 3.2 | Physiochemical characteristics of the hydrochars

##### 3.2.1 | Basic properties

The results of the proximate and ultimate analysis of the hydrochars as well as the biomass feedstock are listed in Table 1. As a general trend, the fixed carbon content in the hydrochars increased with reaction temperature due to the increasing loss of volatile matters. The ash content was increased when the reaction temperature was increased from 100 to

![Figure 2](image-url)
140°C and then stabilized for both HC and MHC samples derived from the TLs.

Furthermore, we analyzed the inorganics present in the TLs and hydrochars produced under 200°C, and the contents of select elements are plotted in Figure S1 of the supplementary data. As shown in the figure, some of the inorganic components might have dissolved and were leached out during the hydrochar formation, resulting in reduced amounts of Mg, Fe, K, and Na in the hydrochar. However, the content of some other inorganic elements (e.g., Ca) in the hydrochar increases mostly because of the removal of volatile matters.

### 3.2.2 Spectroscopic analyses

The XRD patterns of the TLs and hydrochars are given in Figure 3. For the TLs feedstock, only two peaks at the 2θ of 24.2° and 38.0° are obviously visible, which peaks could be attributed to the cellulose structure (Farrow et al., 2015) and the mineral phase of CaCO₃ (Xiao et al., 2017), respectively. Two new peaks were observed at the 2θ of 14.8° and 29.8° on the spectra of hydrochars. The first peak at 14.8° is regarded as plane 101 of cellulose (Jiang et al., 2013), and the second peak at 29.8° derives from calcite crystallization (Yuan et al., 2011). The intensification of the first peak suggests that with the increase in reaction temperature, harsher hydrothermal pretreatments cause more severe damage to the biomass particle surface, and the crystal structure of cellulose gets more exposure. The increase in the intensity of the second peak confirms the increase in the Ca content of the hydrochar, which is consistent with the ICP-MS results (Figure S1). Therefore, the enrichment of Ca might improve the fuel characteristics of the hydrochar.

The FT-IR spectra of the HC and MHC hydrochars are shown in Figure 4a,b, respectively. Hydrochars produced from both HC and MHC processes are rich in functional groups. Based on the literature (Kim et al., 2011, 2013; Xiao et al., 2017; Yuan et al., 2011), the multiple peaks presented on the spectra may be assigned to O–H stretching vibration of hydroxyl (3200–3400 cm⁻¹), C–H stretching vibration of the fatty chain structure (2800–3000 cm⁻¹), C = C stretching vibration of the ethylenic bond (1608–1630 cm⁻¹), C–O stretching vibration of the aromatics (1450–1600 cm⁻¹), C–H bending vibration of aliphatic structure (1420–1480 cm⁻¹), O–H/C–H bending vibration of olefins, alkyd, acids, phenols, and alcohol (1360–1430 cm⁻¹), C–O stretching vibration of unsaturated ether (1200–1300 cm⁻¹), C–H bending vibration of aromatics (1140–1200 cm⁻¹), and C = O bonds and alcoholic C–O bonds (950–1150 cm⁻¹), and torsion or bending modes of the six-membered ring concerning the glycosidic bonds (400–800 cm⁻¹).

### 3.2.3 Surface morphology

The SEM images of the TLs and hydrochar surfaces were taken at the magnification of 1000x and are shown in Figure 5. For the TLs sample, the particle surface showed naturally formed cracks without any pore structure exposed. For both HC and MHC hydrochars, the change in surface structure is strongly dependent on the reaction temperature. Specifically, at 110 and 140°C, the changes were not significant when compared to the TLs, and a limited number of pores were observed on the surface of MHC-140 hydrochar, but not HC-140. Moreover, the pattern of particle surface destruction is influenced by heating methods. For example, comparing the images recorded for hydrochars prepared at 170 and 200°C, all hydrochars showed an increased extent of surface destruction, but the MHC-200 showed a more exposed porous structure than HC-200. For the HC hydrochars, the pores underneath the particle surface start to emerge with the increase in surface decomposition. For the MHC hydrochars, however, the fiber surface and part of the inner fraction of the plant tissue are degraded simultaneously.

### 3.3 Thermal degradation characteristics of the hydrochars

#### 3.3.1 Thermal degradation behavior

To understand the influence of hydrothermal carbonization temperature and the two different heating methods, TG/DTG curves of the hydrochars were obtained at the heating ramp rate of 10°C min⁻¹ and plotted in Figure 6. On the TG curves of both HC and MHC hydrochars, two general trends could be observed. First, the main weight loss stage is shifted to higher temperatures when the pretreatment temperature is increased. Second, hydrochars prepared at 200°C exhibit higher weight retain rates at the analyzing temperature of 800°C.

More detailed interpretation may be illustrated using the DTG curves, that is, weight loss peaks occurred at different temperatures can be attributed to the decomposition of different constituents of the hydrochar sample. In Figure 6c,d, the first peak occurred at around 130°C may be assigned to water evaporation. The second one, which is a shoulder peak located at approximately 266°C, is associated with the decomposition of hemicellulose (Naik et al., 2010). Regardless of the heating method, this peak gradually disappears when the hydrothermal carbonization temperature reaches 170°C, indicating that both the HC and MHC processes effectively remove or destroy the hemicellulose in the TLs. The third peak is of the highest intensity and located at the temperature range of 332–351°C, which can be attributed to cellulose decomposition (Shi et al., 2019). The fourth peak at 460–470°C has the smallest area and cannot be well separated from the
third one. This peak might be associated with lignin decomposition (Kabir et al., 2018; Vamvuka et al., 2003). The fifth peak is observed at about 650 °C, which is possibly caused by the degradation of mineral containing compounds, for example, carbonates (Idris et al., 2010).

### 3.3.2 Kinetic analysis

For kinetic analysis, the TG/DTG curves of TLs, HC-200, and MHC-200 hydrochars under different ramp rates (5, 10, 20, 30, and 40 °C min\(^{-1}\)) were plotted in Figure S2. Thermal lag can be observed for all three TG curves (subplots a, c, and e), that is, when the heating ramp rate is increased, thermal degradation is delayed and the initiation of de-volatilization is shifted to higher temperatures because of heat transfer limitations from the sample surface to the particle core (Damartzis et al., 2011). When comparing the DTG profiles at subplots b, d and e, the shoulder peak at 240–270 °C disappears for HC/MHC hydrochars, indicating that hemicellulose is completely removed during the pretreatment process. The last peak showed varied temperatures in the range of 630–720 °C, and no direct dependency can be linked to the increase in heating ramp rate. This is due to the complicated interactions among different inorganic components and the interaction between minerals and carbonaceous residues.

The activation energy (\(E_a\)) and corresponding \(R^2\) values are given in Table 2, showing that the two isoconversional

| Sample  | Proximate analysis (wt%) | Ultimate analysis (wt%) |     |
|---------|--------------------------|-------------------------|-----|
| Sample  | Moisture | Volatile matter | Ash | Fixed carbon | C | H | N | S | O\(^a\) | HHV (MJ kg\(^{-1}\)) |
| TL  | 6.20 ± 0.14 | 79.19 ± 0.27 | 8.56 ± 0.50 | 6.05 ± 0.76 | 43.82 | 6.17 | 0.95 | 0.06 | 49.01 | 17.26 |
| HC-110 | 6.36 ± 0.53 | 78.83 ± 0.00 | 8.38 ± 0.39 | 6.43 ± 0.39 | 44.62 | 6.23 | 1.04 | 0.04 | 48.07 | 17.72 |
| HC-140 | 6.05 ± 0.10 | 78.39 ± 0.01 | 9.46 ± 0.09 | 6.10 ± 0.72 | 45.43 | 6.04 | 1.06 | 0.03 | 47.44 | 17.82 |
| HC-170 | 4.29 ± 0.13 | 76.97 ± 0.00 | 9.38 ± 0.15 | 9.36 ± 0.74 | 47.58 | 6.16 | 1.07 | 0.03 | 45.17 | 18.94 |
| HC-200 | 3.63 ± 0.17 | 73.23 ± 0.00 | 9.22 ± 0.37 | 14.06 ± 0.47 | 51.18 | 6.05 | 1.04 | 0.04 | 41.69 | 20.41 |
| MHC-110 | 6.13 ± 0.08 | 78.95 ± 0.01 | 7.25 ± 0.22 | 7.67 ± 0.24 | 44.45 | 6.10 | 1.03 | 0.06 | 48.36 | 17.47 |
| MHC-140 | 5.75 ± 0.41 | 77.55 ± 0.01 | 8.24 ± 0.19 | 8.45 ± 0.77 | 44.43 | 6.04 | 1.06 | 0.05 | 48.42 | 17.37 |
| MHC-170 | 3.58 ± 0.29 | 76.14 ± 0.00 | 8.16 ± 0.30 | 12.22 ± 1.29 | 48.00 | 6.12 | 1.07 | 0.03 | 44.79 | 19.08 |
| MHC-200 | 3.69 ± 0.45 | 73.58 ± 0.01 | 8.61 ± 0.11 | 14.11 ± 1.65 | 51.60 | 5.98 | 1.06 | 0.04 | 41.31 | 20.51 |

\(^a\)The oxygen content was calculated by difference.

### FIGURE 3

XRD patterns of the tree leaves and hydrochar samples
methods have varied suitability of application on different samples. For TLs feedstock, the FWO method gives satisfactory regression results for the conversion range of $\alpha = 0.2–0.7 \ (R^2 > 0.9)$, whereas the KAS method is obviously not applicable. The relatively low $R^2$ values from the KAS method can be explained by the inhomogeneity of the TLs sample, causing distorted temperature profiles. Since the KAS method plots $\ln(\beta/T^2)$ versus $1/T$, even small disorder in the reaction temperature will be mathematically enlarged.

4 | DISCUSSION

4.1 | MHC gives higher production efficiency for hydrochar

In a biomass carbonization process, three important factors need to be considered, including energy consumption, hydrochar yield, and properties. Generally, using less energy to produce high-quality hydrochars is highly desirable. The mass yields of hydrochar from the MHC process are higher than those of HC, which was also observed by other...
researchers in their comparison of the two processes using peanut shell or bamboo sawdust as the feedstock (Chu et al., 2017; Dai et al., 2017). The results indicate that the MHC process caused less loss of the organic components due to a reduced extent of decomposition. The reduced energy consumption of the MHC process is closely associated with the advantages of microwave heating, such as high efficiency and selective heating over conventional heating methods (Dai et al., 2019).

4.2 | MHC improves fuel properties of the hydrochar

One of the most important applications of the hydrochar is to be used as a solid biofuel. In this study, comprehensive characterization results were acquired to understand the evolution of fuel-related properties during the carbonization process. An increase in ash content of the hydrochars was observed between 100 and 140°C. A similar increase was reported by other researchers (Dai et al., 2017; He et al., 2013; Kalderis et al., 2014), but different from what we had observed when applying the MHC process on corn stalk (Kang et al., 2019). The difference in feedstocks and operation conditions might account for such a difference in the effect of reaction temperature on the change of ash content.

Fortunately, from a fuel production point of view, other than Ca, the contents of most alkali metals (e.g., Na and K) present in the biomass precursor were all reduced—these alkali metal salts typically have a lower melting point and tend to cause severe issues during hydrochar combustion. We also see that the MHC process is more effective in reducing the Si concentration in the hydrochar than the HC process. This is beneficial because when combined with a large amount of K, the formation of K₂O-SiO₂ can cause tenacious surface deposits on firesides and heating surfaces due to its low-melting point of 550°C (Niu et al., 2016). The enrichment of carbon content and improvement in the hydrochar HHV are not adversely affected by applying microwave-assisted heating. These properties were found to be highly dependent on the reaction temperature, and 200°C provided a fair compromise between hydrochar yield and fuel quality. The changes of HHV with temperature in both processes are similar and are not significant till the temperature is increased to 170°C, indicating that effective
removal of hemicellulose and enrichment of carbon occur at this temperature or above.

As shown in Figure S1, compared to the raw TL, the Ca element is enriched in the hydrochars. Calcium salts have low mobility and a high melting point, causing less significant deposition problems, and an increase in the Ca content might help decrease the slagging (Niu et al., 2016). Therefore, the enrichment of Ca improves the fuel characteristics of the hydrochar.

The MHC-200 showed a more exposed porous structure than HC-200. This may be associated with the different heat transfer patterns of the two different processes. For HC, the heat was first transferred to the water, then to the surface of the biomass particles. In contrast, in MHC, this inward heat transfer was accompanied by the outward heat transfer from the inner layer to the outer layer of the plant tissues since the biomass itself adsorbed microwave and was heated. However, it should be noted that due to the uneven distribution of the biomass components, including hemicellulose, cellulose, and lignin in the TLs, and their differed microwave adsorption capabilities, the heat transfer mechanism can vary at different spots even on a single biomass particle.

### 4.3 MHC enhances thermal degradation reactivity of the hydrochar

The investigation of thermal degradation behavior is necessary for the comprehension of phenomena that occurred during thermolysis of hydrochars as a biofuel (Giudicianni et al., 2013). The information contained in DTG curves could be used to better understand the reactivity of the tested hydrochars because the peak positions (temperature) and heights in the DTG curves are closely associated with the reactivity of the biofuel samples. The peak temperature is inversely proportional to its reactivity, whereas the peak height is directly proportional to the reactivity (Zheng & Koziński, 2000). Therefore, when the hydrothermal carbonization temperature increases, the peak of cellulose decomposition is shifted to a higher temperature, but the height is also increased. This shows that a higher level in the removal of volatile matters causes carbon enrichment, which makes it

| Sample  | Conversion (°) | Temperature range (°C) | FWO method $E_a$ (kJ mol$^{-1}$) | $R^2$ | KAS method $E_a$ (kJ mol$^{-1}$) | $R^2$ |
|---------|----------------|------------------------|----------------------------------|------|---------------------------------|------|
| TL 0.1  | 130.1–143.7    | 104.05                 | 0.3188                           |      | 122.32                          | 0.2433|
|         | 0.2            | 225.0–235.9            | 288.03                           | 0.9333| 489.84                          | 0.8710|
|         | 0.3            | 253.5–263.1            | 477.30                           | 0.9261| 620.50                          | 0.8617|
|         | 0.4            | 278.3–293.9            | 288.03                           | 0.9426| 362.66                          | 0.8379|
|         | 0.5            | 291.3–311.5            | 253.37                           | 0.9351| 316.66                          | 0.8245|
|         | 0.6            | 318.2–337.7            | 270.06                           | 0.9554| 341.52                          | 0.8631|
|         | 0.7            | 342.0–358.8            | 361.45                           | 0.9308| 459.16                          | 0.8379|
|         | 0.8            | 399.8–416.2            | 275.27                           | 0.3434| 376.71                          | 0.3530|
| HC-200 0.1 | 227.6–245.1    | 216.45                 | 0.7693                           |      | 219.16                          | 0.7556|
|         | 0.2            | 281.2–300.8            | 268.53                           | 0.9606| 273.01                          | 0.9580|
|         | 0.3            | 308.5–330.2            | 266.89                           | 0.9750| 270.80                          | 0.9732|
|         | 0.4            | 324.3–348.6            | 252.77                           | 0.9816| 255.68                          | 0.9802|
|         | 0.5            | 335.7–362.1            | 243.96                           | 0.9868| 246.21                          | 0.9858|
|         | 0.6            | 347.4–375.0            | 244.03                           | 0.9925| 246.09                          | 0.9919|
|         | 0.7            | 374.6–395.2            | 354.31                           | 0.9974| 361.65                          | 0.9972|
|         | 0.8            | 424.1–441.3            | 471.44                           | 0.9965| 484.02                          | 0.9963|
| MHC-200 0.1 | 220.0–242.8    | 166.45                 | 0.9582                           |      | 166.65                          | 0.9541|
|         | 0.2            | 268.0–294.5            | 178.95                           | 0.9618| 178.97                          | 0.9580|
|         | 0.3            | 296.2–325.7            | 181.82                           | 0.9548| 181.49                          | 0.9501|
|         | 0.4            | 313.4–344.9            | 184.85                           | 0.9549| 184.38                          | 0.9502|
|         | 0.5            | 327.3–359.3            | 191.60                           | 0.9652| 191.24                          | 0.9616|
|         | 0.6            | 343.6–374.0            | 212.05                           | 0.9859| 212.48                          | 0.9845|
|         | 0.7            | 385.0–408.8            | 280.19                           | 0.7445| 283.49                          | 0.7294|
|         | 0.8            | 446.7–473.5            | 97.53                            | 0.1126| 90.40                           | 0.0897|
less reactive at lower temperatures but can release heat more intensively once it starts to decompose.

To calculate the activation energy, linear regression plots according to the FWO or KAS methods are presented in Figure S3, together with their equations and determination correlation coefficients ($R^2$). Telling from low $R^2$ values, the regressions using either method typically fail at conversion (α) lower than 0.1 or higher than 0.9. This phenomenon has been reported by other researchers (Damartzis et al., 2011; Ma et al., 2019; Ren et al., 2013). At a low conversion (α) of 0.1, the corresponding temperature range is 130.1–143.7°C for TLs under different heating ramp rates, which is mainly for moisture removal. This occurs at the temperature ranges of 227.6–245.1°C and 220–242.8°C for HC-200 and MHC-200 hydrochars, respectively. The greatly elevated temperature of achieving 10% of conversion shows that moisture removal has been accomplished during hydrochar formation, confirmed by results in Table 1. This is desirable for fuel utilization as less heat will be required for demoisturization before ignition. At a high conversion (α) of 0.9, the corresponding temperatures are 508.8°C for TLs, 532.8°C for HC-200 hydrochar, and 608.6°C for MHC-200 hydrochar at the heating ramp rate of 5°C min$^{-1}$. Under these temperatures, lignin, carbonaceous residues, and mineral phase of the TLs or hydrochars may undergo complicated reactions, affecting the linearity of the apparent regression relation. In addition, the low $R^2$ values may result from the methods being used, as it has suggested that the accuracy of both FWO and KAS methods will decrease in predicting the biomass activation energy when lignin decomposition occurs (Álvarez et al., 2016). This is because the lignin decomposition process combines complicated exothermal and endothermal reactions with competitive pathways, restricting the application of model-free analysis methods (Kawamoto, 2017; Opfermann et al., 2002).

Both FWO and KAS methods accurately described the thermal decomposition of the HC hydrochars in the conversion range of α = 0.2–0.8, which is consistent with the trends reported by a previous study (Ma et al., 2019). When compared to the TLs, generally higher $R^2$ values with hydrochars also indicate that the hydrothermal carbonization process converts the thermochemically unstable raw material into more homogenous fuel with higher predictability in terms of thermal degradation behavior.

Both methods also work well on the MHC data; however, the best-fitting range is shifted to lower conversions of 0.1–0.6, and regressions at the conversion of 0.7 and 0.8 give low $R^2$ values. A close examination of the data reveals that the FWO and KAS methods performed the best in describing the decomposition characteristics in the temperature range of 230–360°C for TLs, 280–440°C for HC-200 hydrochar, and 220–370°C for MHC-200 hydrochar. Therefore, it is reasonable to deduce that the thermal degradation mechanism of MHC-200 hydrochar is the same as TLs in this specific range, whereas for HC hydrochar, this shared decomposition behavior is shifted to higher temperatures. This phenomenon also shows that the HC process is more efficient than MHC in decomposing hemicellulose in the TLs.

Based on the satisfactory regression results ($α = 0.2–0.6$), the average activation energies and $R^2$ values were calculated. Even in this select $α$ range, the KAS method does not work well for TLs, providing an average $R^2$ of only 0.8516. As mentioned before, the high inhomogeneity of TLs makes the KAS method ineffective in describing the thermal degradation of this biomass feedstock (Ma et al., 2017). Moreover, the results show that the average activation energy is decreased in the hydrochar samples, suggesting that the hydrochars are more active than the TLs during thermal degradation. This is because, to a different extent, the hydrothermal carbonization process destroys the complex lignocellulosic matrix of TLs, which enhances the thermochemical reactivity of the hydrochars. The MHC-200 hydrochar shows lower activation energy than the HC-200 hydrochar (~190 kJ mol$^{-1}$ vs. 260 kJ mol$^{-1}$). During pyrolysis, high activation energy means that the reaction requires more energy from the surroundings to proceed (Liu et al., 2004). Therefore, at the preparation temperature of 200°C, the MHC process performs better than the HC process in reducing the energy demand for subsequent hydrochar thermal degradation.

To sum up, under tested conditions for carbonization pre-treatment of tree leaves waste, the MHC process is more effective than HC in producing a significantly higher amount of hydrochar with less energy consumption. At the pretreatment temperature of 200°C, the resulting MHC hydrochar has improved fuel properties, giving an increased HHV of 20.51 MJ kg$^{-1}$ (17.26 MJ kg$^{-1}$ for TLs feedstock and 20.41 MJ kg$^{-1}$ for the HC hydrochar), reduced K and Si content, and reduced activation energy for subsequent thermal degradation (~190 MJ kg$^{-1}$ vs. ~260 MJ kg$^{-1}$ for HC hydrochar). The isoconversional analysis also reveals that the FWO method is applicable to characterize the TLs feedstock and HC/MHC hydrochars, while the KAS method is not suitable for the characterization of TLs due to its high inhomogeneity. These results reveal how the fuel properties and thermal degradation mechanism of hydrochars were influenced by the HC and MHC processes, therefore, allowing the optimization of the valorization process of landscape tree leaves as an alternative biomass resource.

**ACKNOWLEDGMENTS**

This work was supported by the Natural Science Basic Research Program of Shaanxi [2020JQ-243], Key Laboratory of Energy Resource Utilization from Agriculture Residue, Ministry of Agriculture and Rural Affairs, China [KLERUAR2018-02], the National Key Research and Development Program of China [2018YFE0127000],
Key Research and Development Program of Shaanxi [2020NY-105], Fundamental Research Funds for the Central Universities [2452017299], Shaanxi Provincial Department of Science and Technology [2018ZDXM2-01, 2020QFY10-03], and Start-up Fund from the Northwest A&F University for Dr. Dongbing Li.

AUTHOR CONTRIBUTIONS
Kang Kang involved in conceptualization, methodology, formal analysis, data curation, writing—original draft, and writing—reviewing and editing. Tianle Zhang involved in investigation, data curation, and software. Guotao Sun involved in data curation and writing—reviewing and editing. Mingqiang Zhu and Kankan Li involved in resources and visualization. Dongbing Li involved in methodology, formal analysis, writing—original draft, and writing—reviewing and editing. Tianle Zhang involved in resources and visualization. Dongbing Li involved in methodology, formal analysis, writing—original draft, and writing—reviewing and editing.

DATA AVAILABILITY STATEMENT
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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**SUPPORTING INFORMATION**

Additional supporting information may be found online in the Supporting Information section.

**How to cite this article:** Kang, K., Zhang, T., Sun, G., Zhu, M., Li, K., & Li, D. (2021). Valorization of tree leaves waste using microwave-assisted hydrothermal carbonization process. *GCB Bioenergy*, 13, 1690–1703. [https://doi.org/10.1111/gcbb.12882](https://doi.org/10.1111/gcbb.12882)