Thermal Characteristics and Kinetics of Waste Camellia oleifera Shells by TG–GC/MS

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ABSTRACT: There is a large amount of Camellia oleifera shells generated as a waste product from industrial processes. Therefore, the high-value utilization of C. oleifera shells is a hotspot of current research. The thermal characteristics and kinetics of waste Camellia shells (WCOSs) were analyzed by thermogravimetry with gas chromatography–mass spectrometry (TG–GC/MS). The thermal behavior of WCOSs was studied at 10, 20, 40, and 60 °C/min, and the distributed activation energy model (DAEM) was used to research the kinetics and activation energies. The activation energies of WCOSs based on the DAEM ranged from 68.64 to 244.49 kJ/mol, corresponding to the conversion rate from 0.10 to 0.90. The correlation coefficient (R²) shows the best fit, and it ranged from 0.921 to 0.994. Pyrolysis products at four key temperature points (228, 296, 492, and 698 °C) were studied via GC/MS. Many compounds were detected at the different temperatures. With the increase of temperature, furans, benzene, and long-chain alkanes were produced successively. This data will help to expand the utilization of WCOSs.

1. INTRODUCTION

With the growing population and the developing economy, a large consumption of fossil fuels (coal, petroleum, and natural gas) has caused energy crisis and environmental problems.1 The release of large amounts of CO₂ into the atmosphere causes the greenhouse effect and climate change. In addition, combustion products like NOₓ and SO₂ cause air pollution, which damages human health.2 Renewable and environmentally friendly technologies have been developed for energy products, storage, and utilization. Among various renewable energy technologies, the utilization of biomass energy is a popular research topic.3 Thermochemical conversion technology of biomass is an effective method for biomass utilization. By this method, biomass can be converted into biochar, biogas, and biooil under limited or no oxygen, which can be used in the energy and chemical industries.4,5-8

Camellia oleifera is an important woody oil crop and is widely planted in South China, with more than 12 million acres in production.6 In recent years, the planting area of C. oleifera gradually increased because of the varieties of the functional components of the Camellia oil, such as vitamin E, squalene, phytosterols, and flavonoids.7 However, its processing produces a large amount of waste C. oleifera shells (WCOSs).8 Approximately, 0.54 tons of WCOSs are produced for each ton of processed C. oleifera.8 Burning and landfill are the traditional disposal methods for WCOSs, but they cause serious pollution to the environment. In the past decade, there have been various studies on the comprehensive utilization of WCOSs.10-13 These studies focused on the extraction and the property analysis of active substances, as well as the preparation and the property analysis of the chemicals from WCOSs.10-13 Recently, carbon materials derived from WCOSs have been produced via different technology, such as carbon microspheres with a controllable porous structure and functionalized aromatic carbon microspheres.14,15 These studies have broadened the utilization scope of WCOSs. However, these applications cannot consume many WCOSs at present. As a type of waste, WCOSs contain 22.6% hemicellulose, 17.8% cellulose, and 22.6% lignin and can be converted into biomass energy.9,16 Therefore, it is of great importance to analyze the pyrolysis characteristics of WCOSs.

Thermogravimetry (TG) is used to analyze the thermodynamic parameters of material decomposition under inert gases via mass change. Fourier transform infrared spectrometry (FTIR) and mass spectrometry (MS) are used to analyze the escaping gas during pyrolysis. However, identifying the compounds derived from the pyrolysis products is difficult because of numerous overlapping signals, which are produced by a wide range of low-molecular-weight compounds. The separation of released products is absent for TG–FTIR and TG–MS systems.20

Thermogravimetry with gas chromatography–mass spectrometry (TG–GC/MS) is an advanced technology for identifying volatile gases of pyrolyzed samples at a certain temperature.19 These methods quantitatively and qualitatively analyze the escaping gas during pyrolysis. However, identifying the compounds derived from the pyrolysis products is difficult because of numerous overlapping signals, which are produced by a wide range of low-molecular-weight compounds. The separation of released products is absent for TG–FTIR and TG–MS systems.20

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pyrolysis of the specific condition. During TG–GC/MS experiments, TG is employed to analyze the mass change, and GC/MS is used to separate and identify the components of the released gases from the pyrolyzed samples via TG devices at specific temperature conditions. Thus, the results of TG–GC/MS are more accurate than those of TG–FTIR and TG–MS for the reaction of the pyrolysis products at a certain time. Fan et al. researched the pyrolysis products from walnut shells at different temperatures and analyzed the components of the pyrolyzed samples at different conditions. With the increasing pyrolysis temperature, furan, furfural, benzene, and long-chain alkanes were successively identified in different GC–MS experimental results. Fedelich confirmed that TG–GC/MS can be used to investigate the pyrolytic process by the quantification of low-content styrene–butadiene rubber in natural rubber. Strüggs et al. found that products of straw with absorbed glycerol thermal degradation during pyrolysis were gases, acrolein, and glycerol at low temperatures. Qin et al. investigated the thermal degradation of medical plastic waste by in situ FTIR, TG–MS, and TG–GC/MS coupled analyses, which improved the reliability of the results. Thus, it is feasible to study the pyrolysis products and characteristics of WCOs using TG–GC/MS. There are no known reports dealing with the pyrolysis products and the characteristics of WCOs by TG–GC/MS.

The kinetic models are used to study the complex pyrolysis kinetics. In numerous models, the distributed activation energy model (DAEM) is an effective method for analyzing pyrolysis kinetics of biomass. In the DAEM, the reaction process is assumed to be many independent reactions with different activation energies.

In this study, the pyrolysis behaviors and kinetics were researched with the DAEM by a TG experiment at different heating rates. The 20 °C/min heating rate was chosen during the TG–GC/MS experiment. The identification and regularity analysis of escaped products were carried out by GC/MS at important temperature points.

2. RESULTS AND DISCUSSION

2.1. Thermogravimetric Analysis. The pyrolysis characteristics and behavior of WCOs were investigated using TG and derivative thermogravimetry (DTG). Figure 1 shows the TG and DTG curves with different heating rates ranging from 10 to 60 °C. Thermogravimetric curves show the mass change with progressing temperatures, and DTG curves present the mass loss rate during the pyrolysis of WCOs. As shown in Figure 1, the first peak can be seen at approximately 150 °C. This is due to WCOs containing both extractive components (tea saponin, tannin, active polysaccharide, etc.) and water, which result in a low volatilization temperature. In addition, the front shoulder observed a weak peak because of tea saponin and tannin contents ranging from 15 to 30%. The main weight loss occurred in the pyrolysis temperature range of 200–450 °C, and this was attributed to the thermal degradation of cellulose, hemicellulose, and partial lignin.

The pyrolysis parameters of WCOs are given in Table 1. As shown in Figure 1 and Table 1, the peak temperatures increased from 283 to 355 °C when the heating rate was increased from 10 to 60 °C/min. Additionally, the maximum loss rate increased from 4.53 to 21.81% min⁻¹ when the heating rate was increased from 10 to 60 °C/min. In summary, the initial temperature, final temperature, and temperature for the maximum weight loss rate increased when the heating rate was increased. The peak shift due to the increase in the heating rate attributes to the increased thermal lag. The heating rate had no noticeable effect on the residual mass (Figure 2).

2.2. Kinetic Results by the DAEM Method. The DAEM method is often used to research the kinetic parameters of the pyrolysis process of biomass, and this type of isoconversional method is the most reliable method for the calculation of the kinetic parameters. In this work, four different heating rates of 10, 20, 40, and 60 °C/min were used in the DAEM method. For each heating rate, the Arrhenius plot of ln(β/β₀) vs 1/T was calculated from the slope and the correlation coefficient (R²) were calculated from the slope and intercept according to linear regression. The results showed that the activation energy ranged from 68.64 to 244.49 kJ/mol, which corresponded to the conversion rate ranging from 0.10 to 0.90. Compared with other biomass (e.g., walnut shells), the activation energy of WCOs was low at a low conversion rate (0.10–0.20). This may be due to WCOs containing more extractive components. When the conversion rate was 0.75–0.90, the activation energy increased sharply from 125.13 to 244.99 kJ/mol. The activation energy variation trend was attributed to various functional groups in the macromolecular structure. Their chemical bonds break under different activation energies in the various pyrolysis conditions.
analyzed to estimate the pyrolysis products. At 228 °C, residual lignin was pyrolyzed continuously. At 698 °C, samples was the fastest, and various products were produced. At 296 °C, the pyrolysis of cellulose were pyrolyzed. At 492 °C, the pyrolysis rate of the cellulose and hemicellulose in WCOSs. When the temperature increased, the product composition became more diverse. The reason is that the pyrolysis of lignin and the occurrence of secondary reactions produced complex products. Additionally, any former parts of pyrolysis products that were not completely discharged from the connecting pipe could still be observed in a later detection.

Table 1. Pyrolysis Characteristic Parameters of WCOSs

| Heating rate | Initial temperature (°C) | Final temperature (°C) | Temperature for maximum weight loss rate (°C) | Maximum weight loss rate (% min⁻¹) | Residual mass (%) |
|--------------|--------------------------|------------------------|-----------------------------------------------|-----------------------------------|------------------|
| 10           | 164                      | 690                    | 283                                           | 4.53                             | 29.91            |
| 20           | 173                      | 698                    | 296                                           | 8.32                             | 30.79            |
| 40           | 188                      | 718                    | 326                                           | 19.83                            | 30.89            |
| 60           | 197                      | 720                    | 355                                           | 21.81                            | 29.95            |

Figure 2. Parameters of the DAEM for WCOSs.

Figure 3. Activation energy and correlation factor from the DAEM for WCOSs.

temperatures. The correlation coefficient for all lines at various conversions was greater than 0.90, and the values ranged from 0.921 to 0.994, which showed the best fit.

2.3. GC/MS Series Analysis. During the pyrolysis process, the products were pyrolyzed continually during the TG experiment. Gas chromatography–mass spectrometry can only analyze the pyrolysis products from a given time point because of the long analysis period for GC/MS. According to the pyrolysis characteristics, temperature at mass losses of 10% (228 °C), the maximum mass loss rate (296 °C), mass losses of 90% (492 °C), and mass losses of 98% (698 °C) were analyzed to estimate the pyrolysis products. At 228 °C, the extractive components, partial cellulose, and partial hemicellulose were pyrolyzed. At 296 °C, the pyrolysis rate of the samples was the fastest, and various products were produced. At 492 °C, the main pyrolysis reaction tends to end and residual lignin was pyrolyzed continuously. At 698 °C, the pyrolysis reaction was over except for a few secondary reactions.

Figure 4 and Table 2 exhibit both the GC/MS fingerprint and the produced components of WCOSs at different selected pyrolysis temperature points. A matching degree higher than 75% was accepted in the detected products, excluding the last four products in Table 2. During testing, the last four products had a matching degree of 60–65%. The pyrolysis fingerprint of the WCOSs was obviously different from that of the previously studied walnut shells, and the products were simpler. The reason may be that the lignin, cellulose, and hemicellulose in WCOSs and walnut shells have different effects on each other during the pyrolysis process.

Table 1 shows that the pyrolysis products of WCOSs were rich and different in composition at different temperatures. When the temperature increased, the product composition became more diverse. The reason is that the pyrolysis of lignin and the occurrence of secondary reactions produced complex products. Additionally, any former parts of pyrolysis products that were not completely discharged from the connecting pipe could still be observed in a later detection.

In the initial stage of pyrolysis (228 °C), the results of GC/MS indicated that the main pyrolysis products of WCOSs were low-carbon (C ≤ 5) compounds, including 2-butene, acetic acid methyl ester, 2-methylfuran, and furfural. The results showed that the unstable branched chain of hemicellulose and cellulose from WCOSs broke. Furfural was detected to originate from the pyrolyzed cellulose of WCOSs. The pyrolysis temperature of cellulose and hemicellulose was low, and their initial pyrolysis temperature was generally considered to be below 200 °C. Therefore, parts of cellulose, hemicellulose, and the extractive components were pyrolyzed at 228 °C. The main pyrolysis products at this stage were CO₂, CO, and H₂. In addition, the products showed that nitrogen- and sulfur-containing compounds in WCOSs were pyrolyzed at a lower temperature.

At 296 °C, the maximum mass loss rate of WCOSs reached 8.32% min⁻¹, and many products from the pyrolyzed WCOSs were detected, including 2-methylfuran, 2,5-dimethylfuran, furfural, and 4-cyclopentene-1,3-dione. Compared with the pyrolysis products for the maximum mass loss rate of walnut shells, the pyrolysis products of WCOSs were simple. No benzene-containing compounds were detected at this temperature point, indicating that only a small amount of unstable carboxyl and carbonyl chains in lignin side chains was broken.

At 492 °C, the mass loss of WCOSs was reduced by 90%. Table 2 shows that the pyrolysis products were complex and diverse, including 2-methylfuran, furfural, benzene, toluene, ethylbenzene, 1,3-dimethylbenzene, and α-xylene. The product contained benzene ring compounds because of the pyrolyzed lignin, and furan compounds in the product were due to residues from previous pyrolysis products in the pipelines.

At 698 °C, the pyrolysis of WCOSs was completed. The product contained many benzene compounds because of the aromatic ring of lignin had side chain breaking, condensation, etc. In addition, long-chain alkanes were detected in the
products. The aliphatic long-chain in lignin continued to break, and the aromatic properties of biochar increased.

3. CONCLUSIONS

An increase in the pyrolysis peak temperatures of WCOs was observed ranging from 283 to 355 °C, corresponding to the heating rate ranging from 10 to 60 °C/min. The activation energies based on the DAEM ranged from 68.64 to 244.49 kJ/mol, corresponding to the conversion rate from 0.10 to 0.90. The pyrolysis products at four key temperature points (228, 296, 492, and 698 °C) were studied via GC/MS.

Table 2. GC–MS Analysis of WCO Components at Different Pyrolysis Temperatures

| retention time (min) | name                  | chemical formula | 228 | 296 | 492 | 698 |
|----------------------|-----------------------|------------------|-----|-----|-----|-----|
| 2.49                 | 2-butenone            | C4H8              | +   | +   | +   | +   |
| 2.60                 | sec-butylamine        | C4H11N            | +   | +   | +   | +   |
| 2.68                 | acetic acid methyl ester | C3H6O2        | +   | –   | –   | –   |
| 2.86                 | urea                  | CH4N2O           | +   | +   | –   | –   |
| 2.93                 | 2-methyl-furan        | C5H6O            | +   | +   | +   | +   |
| 3.32                 | benzene               | C6H6             | –   | –   | +   | +   |
| 3.65                 | heptane               | C7H16            | –   | –   | +   | +   |
| 3.74                 | 2,5-dimethylfuran     | C5H8O2           | –   | +   | –   | –   |
| 4.26                 | dimethyl disulfide    | C6H8S2           | –   | –   | –   | –   |
| 4.66                 | toluene               | C6H5             | –   | –   | +   | +   |
| 5.39                 | 3-ethylhexane         | C8H14            | –   | –   | +   | +   |
| 6.26                 | furfural              | C5H4O2           | +   | –   | –   | –   |
| 7.23                 | ethylbenzene          | C8H10            | –   | –   | +   | +   |
| 7.53                 | 1,3-dimethylbenzene   | C10H10           | –   | –   | +   | +   |
| 8.15                 | 4-cyclopentene-1,3-dione | C10H10     | –   | –   | +   | –   |
| 8.39                 | o-xylene              | C8H10            | –   | –   | +   | +   |
| 27.95                | 1-methylene-1H-indene | C10H6           | –   | –   | +   | –   |
| 39.22                | tridecane             | C13H26           | –   | –   | +   | +   |
| 47.48                | 2-methyldecano        | C11H14           | –   | –   | +   | –   |
| 52.24                | 7-methylpentadecano   | C16H34           | –   | –   | +   | –   |

“+” indicates the presence of substance, and “−” indicates the absence of substance.
alkanes were produced successively when the pyrolysis temperatures were increased.

4. MATERIALS AND METHODS

4.1. Materials. WCOs were collected from Yunnan Province, China. The WCOs were washed with deionized water and then dried at 105 °C for 24 h. The dried WCOs were shredded to smaller than 0.075 mm (approximately 200 mesh) for the TG–GC/MS test. The proximate analyses for the volatile, fixed carbon, and ash of WCOs were 72.68, 23.95, and 3.37%, respectively. The ultimate analyses for the chemicals C, H, N, S, and O were 44.85, 5.01, 0.48, 0.21, and 46.08%, respectively. The O content was calculated with a dry ash-free base by difference.

4.2. TG Experiment and Pyrolysis Kinetics. Thermogravimetric analysis was used to study the pyrolysis characteristics of WCOs. The kinetic parameters of pyrolysis provide information that helps to design and optimize the thermal-chemical system. In this paper, the DAEM was selected to estimate the kinetics of WCOs and has been proved to be a useful and reliable model during biomass pyrolysis.

During the biomass pyrolysis, the DAEM assumed that the reaction is an independent parallel-first-order reaction, and each reaction has its own activation energy, which is continuously distributed. The DAEM was represented as follows in eq 1

\[
\frac{V}{V^*} = 1 - \int_0^\infty \exp\left[-k_0 \int_0^T \exp\left(-\frac{E}{R \times T}\right) dT\right] \cdot f(E) \times dE
\]

where \( V \) is the volatile content at temperature \( T \) (g), \( V^* \) is the effective volatile content of the sample (g), \( k_0 \) is the pre-exponential factor (m/s), \( \beta \) is the heating rate (K/min), \( T \) is the absolute temperature (K), \( E \) is the activation energy (kJ/mol), and \( R \) represent the universal gas content (8.314 J/(mol·K)), and \( f(E) \) is the distribution curve of the activation energy representing the difference in the activation energies (units), calculated as shown in eq 2

\[
\int_0^\infty f(E) = 1
\]

A simple integral model for estimating the kinetic parameters based on the DAEM was presented by Miura and is expressed as shown in eq 3

\[
\ln \frac{\beta}{T} = \ln \left(\frac{k_0 \times R \times E}{E}\right) + 0.6075 - \frac{E}{R \times T}
\]

where the Arrhenius plot of \( \ln \frac{\beta}{T} \) vs \( \frac{1}{T} \) is a straight line whose slope and intercept are calculated as \( E \) and \( k_0 \), respectively.

The pyrolysis of WCOs was studied using a TG (SETSYS Evo; SETARAM, Caluire, France), with temperatures starting from room temperature to 900 °C at a heating rate of 10, 20, 40, and 60 °C/min under 50 mL/min of the high purity helium. For each experiment, 20 mg of the sample was used.

4.3. TG–GC/MS Experiment. A GC/MS system (ISQ, LT; Thermo Fisher Scientific, Waltham, MA) coupled with a TG (SETSYS Evo; SETARAM, Caluire, France) was used to carry out the TG–GC/MS experiment. The evolved gas was collected via an Automation Autoinjector system (TC3, ITEM; SETARAM, Caluire, France), and the transmission line was maintained at 280 °C to prevent the condensation of the evolved gas. A heating rate of 20 °C/min was chosen for the TG–GC/MS experiment. Data were collected at four temperature points, namely 228, 296, 492, and 698 °C according to the mass losses of 10%, the maximum mass loss rate, mass losses of 90%, and mass losses of 98%, respectively.

When the WCOs were pyrolyzed by TG at the specific temperatures, the evolved gas was then separated through GC and detected in the MS system. A TraceGOLD TG-SMS GC Column (Thermo Fisher Scientific, Waltham, MA) was chosen with a 30 m length, 0.25 mm inner diameter, and 0.25 μm film thickness. The oven temperature was held at 40 °C for 1 min and then increased from 40 to 100 °C at a rate of 1.5 °C/min. It was then maintained for 2 min, increased from 100 to 150 °C at a rate of 5 °C/min and maintained for 1 min, then increased again from 150 to 230 °C at a rate of 20 °C/min, and finally it was increased from 230 to 280 °C at a rate of 20 °C/min. High purity helium gas (99.999%) was used as the carrier gas at a flow rate of 1.3 mL/min. The electron impact mass spectra were obtained with 70 eV of ionizing energy, and the scanning range was from 50 to 600 m/z with a frequency of 4 scans/s. The ion source temperature was held at 280 °C. Every injection was collected from the repeated TG experiments at the same set temperature because of a lack of time at different set temperatures for the GC/MS analysis during a single TG experiment. MS E.02.01.1177 Chemstation system software was used to identify the separated compound of MS with NIST 11 library data.

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Notes

The authors declare no competing financial interest.

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