Physicochemical Properties of Camellia Nut Shell and its Thermal Degradation Characteristics

Jinping Zhang,* Zhioulian Wang, Menghao Du, Xiaohua Yao, and Lisong Hu

Camellia nut shell (CNS) is known as an important bio-resource that has great potential as a biomaterial. The elemental composition, chemical structure, crystallinity, and pyrolysis characteristics were analyzed in this paper for six species of CNS. The concentration of organic carbon, N, K, and Na in CNS ranges from 44.40 to 48.60%, 2.91 to 4.42 mg.g⁻¹, 7.67 to 13.80 mg.g⁻¹, and 0.02 to 0.26 mg.g⁻¹, respectively. The content of lignin, cellulose, hemicellulose, and ash varies between 30.07 and 36.23%, 13.87 and 20.95%, 35.15 and 49.34%, as well as 2.00 and 4.75%, respectively. Camellia nut shell cellulose crystalline structure belongs to typical cellulose type I, and the cellulose crystallinity index for the six species ranges from 37.4 to 62.3%. The CNS pyrolysis process can be divided into three phases, and the substantial degradation occurs within the temperature range of 200 to 430 °C, with nearly 60% loss of weight. The temperature could be reduced greatly during pyrolysis under acidic conditions with PEG 400/glycerol as a solvent. The degradation rate was impacted by K concentration. Increasing cellulose crystallinity negatively affected the degradation rate.

Keywords: Camellia nut shell; Elemental analysis; Chemical composition; Crystallinity index; Thermal degradation

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INTRODUCTION

Resources, environment, and sustainable development are major concerns that have attracted substantial attention worldwide (Bensaid et al. 2012). One of the sources for these problems is the extensive use of non-renewable fossil fuels that cause serious environment pollution. Bio-resources, due to their renewability, easy degradability, and wide availability, have drawn great attention (Guo et al. 2012). Green plant photosynthesis is one of the most available renewable resources on earth. As much as 2 × 10¹¹ tons of carbon is sequestered annually on earth through photosynthesis. In other words, about 3 × 10¹⁸ kJ in solar energy is trapped in biomass each year. Exploitable biomass energy is about 10 times the total annual energy consumption worldwide. Therefore, biomass has been widely considered as a major source for unconventional energy and as an ideal substitute for high value-added chemicals. Farming and forestry residues, as a major form of bio-resources, consist of cellulose, hemicellulose, and lignin. They contain numerous active groups such as hydroxyl groups, which makes the residue a good source for polyurethane materials (Lemus and Lal 2005; Xiao et al. 2011). Farming and forestry residues are insoluble and infusible composite materials, and cannot be processed by means of heating or pressuring. However, it is possible to convert these materials into liquid micromolecules with high reaction activity by thermochemical...
processing and to generate new polymer materials for manufacturing adhesives and molding (Hassan and Shukry 2008; Chen et al. 2009). The ratio of multipurpose utilization for farming and forestry residues can reach 100% by using thermochemical conversion technology, which will open up a new era for its high-value utilization.

Camellia refers to a group of species belonging to the *Camellia* genus under the Theaceae family, with high oil content in their nuts (Zhang et al. 2012). Camellia has been known as one of the top four woody oil crops in the world, the other three being oil palm, olive, and coconut, and it has been cultivated for about 2000 years for oil production in China and other East and Southeast Asia countries such as Japan, Myanmar, and Vietnam (Zou and Wu 2009). China has 3.67 million hectares of camellia plantations that are mainly distributed in 18 provinces in the Yangtze River Basin and Southern China (Zhou et al. 2013a). The annual production of camellia nut exceeds 3 million tons, with nut shell production accounting for about 60% in weight. Camellia nut shell (CNS) can be used to extract tannin (Xu et al. 2009), saponin (Hu et al. 2012), anthocyanin (Xue et al. 2012), brown pigment (Qiu et al. 2009), antioxidants (Jin 2012), furfural (Yang et al. 2011), and biosorbents (Lu et al. 2011).

However, the majority of CNS is not efficiently utilized at present. Nearly three million tons of CNS is burned or discarded each year, resulting in great waste and environmental pollution. Camellia nut shell is in a solid state with low chemical activity. Its main contents include cellulose, hemicellulose, and lignin as well as a small amount of saponin, tannins, pigments, and ash (Jin 2012). The content and structures of these substances in CNS play a great role in the selection of liquid agents and catalysts in CNS thermochemical conversion processing. Camellia nut shell components and their percentage have big effects on the structure of liquefied products. For example, the concentration of K, Na, and N directly affect the application of liquefied products (Tong 2005; Ye 2005). The content of cellulose, hemicellulose, and lignin, as well as their thermal degradation characteristics, determine the selection of reaction parameters in liquefaction processing (Kim 2010). Thermal decomposition of cellulose seems to be more complicated since the amorphous zone is more active than the crystalline zone, and the degree of polymerization of the native celluloses depends on the raw materials. In this study, six camellia species were selected, i.e., *Camellia oleifera* Abel, *C. eticulate* Lindl, *C. semiserrata* Chi, *C. mairei* (Levl.) Melehir, *C. meiocarpa* Hu, and *C. polyodonta* How, which are widely cultivated in camellia production areas in China. The elemental composition, chemical component, cellulose crystal structure, and thermal degradation characteristics of their nut shells were analyzed. This study will provide a fundamental understanding for the liquefaction of CNS and its thermochemical conversion technology.

**EXPERIMENTAL**

**Materials**

Camellia nut shell samples were obtained from Jinhua, Zhejiang province and provided by the Camellia Research and Development Center of Chinese Academy of Forestry. All samples were placed in an oven at 105 °C until the weight became constant. They were then crushed and sifted through an 80-mesh sieve and stored in a desiccator for further analysis.
Methods

Elemental analysis

Approximately 5 g of CNS samples for each species were dried by placing them in an oven at 65 °C for 24 h and then in a desiccator for 20 min. The samples were weighed with the subtraction method, transferred to a 150-mL Erlenmeyer flask (0.0001 g accuracy), and then boiled with 30 mL of mixed acid. After separation of silicon dioxide, the concentration of K and Na in the filtrate with constant volume was measured by atomic absorption spectroscopy SolaaM6 (Thermo Scientific Co., USA) according to the China Forestry Industry Standards LY/T 1270 (1999) and Su et al. (2013).

For the measurement of N concentration, 0.3-g samples for each species were dried by placing them in oven at 65 °C for 24 h, weighed with the subtraction method, and transferred into a Kjeldahl flask (0.0001 g accuracy). Then, 1.0 g of mixed catalyst was put into the flask and shaken well. Then, 5 mL of concentrated sulfuric acid was added to the mixture, which was boiled after being set overnight. After cooling, 20 mL of water was used for dilution and the mixture was set until the liquid was clear. The N concentration of the liquid was measured using a FOSS Kjeldahl determination apparatus (FOSS, Denmark) according to the China Forestry Industry Standard LY/T 1269 (1999) and Su et al. (2013).

For the measurement of organic C concentration, a 0.5-g sample for each species was weighed with the subtraction method and put into a test tube. Then, 0.1 g of powdered silver sulfate was added, followed by 5 mL of 0.800 M potassium dichromate standard solution and 5 mL of concentrated sulfuric acid. After being shaken well, the mixture was boiled. The solution was used for titration to determine the organic C concentration according to China Forestry Industry Standards LY/T 1237 (1999) and Peng et al. (2014). All experiments were repeated three times, and the average values were used.

Chemical composition analysis

The concentrations of organic extractives, cellulose, hemicellulose, lignin, and ash were determined based on the national standards GB/T 2677.6 (1994), GB/T 2677.10 (1995), GB/T 2677.9 (1994), GB/T 2677.8 (1994), and GB/T 2677.3 (1993) and the work of Zhou et al. (2008).

Fourier transform infrared (FT-IR) spectroscopy analysis

The infrared spectra of the CNS powder samples were measured using an FT-IR spectrometer (Nicolet 560, Thermo Nicolet Corporation; USA), to determine the functional groups of the CNS. The samples were placed in the sample pool, which was made from KBr. For each spectrum, a 32-scan adsorption interferogram was collected with a resolution of 4 cm⁻¹ in the 400 to 4000 cm⁻¹ region at ambient temperature. Experiments were repeated three times, and crystallization indices were calculated.

X-ray diffraction analysis

Camellia nut shell powder samples passed through an 80-mesh sieve were dried at 50 °C for 6 h and made into thin slices at room temperature. The scanning was carried out on a Rigaku D/max 2550PC X-ray diffractometer (Japan), with the following experimental conditions: Cu-target X-ray tube, the nickel plate for CuKβ radiation elimination, 40 kv tube voltage, 40 mA current, and the 2θ/θ linkage scanning. The X-ray crystallography index was calculated using Eq. 1,
where \( C_rI \) is relative crystallinity (%), \( I_{002} \) is (002) lattice diffraction maximum intensity angle, and \( I_{am} \) represents \( 2\theta \) the amorphous background scattering diffraction intensity. \( I_{am} \) and \( I_{002} \) have the same units.

**Thermogravimetric analysis**

An SDT Q600 (TA Instruments, USA) simultaneous thermal analyzer was used for analysis of the loss weight of CNS. The experimentation settings were as follows: CNS powder samples passed through 80- to 100-mesh sieves, 8 mg in weight, heating rate at 10 °C·min⁻¹, 99.99% nitrogen atmosphere with a flow rate of 50 mL·min⁻¹, initial temperature of 30 °C, and termination temperature of 600 °C.

**Liquefaction methods**

Approximately 80 g of the liquefying agent PEG 400, 20 g of glycerin, and 3 g of concentrated sulfuric acid were put into a three-necked flask with a stirrer, a reflux condenser, and a thermometer. The mixture was heated in an oil bath to 100 °C, and then 33 g of powder sample was added. The heating continued until reaching 160 °C and was maintained for 15 to 150 min, after which the reaction was terminated by cooling the mixture in cold water.

The liquefied product was dissolved in 80% 1,4-dioxane, filtered with a No. 3 sand core funnel, and washed with 80% 1,4-dioxane until the filtrate was clear. Residue was dried to a constant weight by placing it in an oven at 105 °C. The liquefaction rate was calculated using Eq. 2:

\[
\text{Liquefaction rate} = \frac{1 - \text{residue quality}}{\text{sample mass}} \times 100\% 
\]

**RESULTS AND DISCUSSION**

**CNS Elemental Concentrations**

The concentrations of K, Na, and N in CNS significantly impact the thermal degradation characteristics and the application of the degradation products. K and Na elements are the common catalysts in the degradation process of CNS that can reduce the activation energy required by CNS pyrolysis, and these make the process more complicated (Xu et al. 2012). Furthermore, the concentrations of K and Na in CNS determine the elemental concentrations in the degradation products. High concentrations of K⁺ and Na⁺ in products may cause a reaction between these ions and isocyanate. In the preparation process of polyurethane foam, the alternative reaction of polyether polyols and isocyanates could result in agglomeration and scorching in products. Therefore, determining the concentrations of K and Na would provide useful information for their removal from the degradation product (biological polyether polyols). Among the six species, *C. meiocarpa* Hu had the highest K concentration (13.80 mg·g⁻¹) and *C. eticulate* Lindl had the lowest (7.67 mg·g⁻¹). Sodium concentrations ranged from 0.02 to 0.26 mg·g⁻¹ among the six species. Higher concentrations of K in CNS could catalyze the
thermal degradation; however, the total content of $K^+$ and $Na^+$ in degradation products should be less than 0.02 mg.g$^{-1}$ (Tong 2005; Ye 2005). It is necessary to remove $K^+$ and $Na^+$ from the degradation products (Table 1). The degradation product containing N is a good flame retardant, and the degradation product that originated from N-containing materials can be used to replace the flame retardant polyether polyol. Camellia nut shell of six species all contained certain amounts of N (Table 1), with the highest concentration occurring in $C. eticulate$ Lindl (4.42 mg.g$^{-1}$) and the lowest in $C. semiserrata$ Chia (2.91 mg.g$^{-1}$), implying that the degradation products of all of these six species CNS could substitute for the flame retardant polyether polyol. The organic C concentrations of CNS were similar among the six species, with a range from 44.40% to 48.60% (Table 1).

**Table 1. Elemental Composition in Nut Shell of Six Camellia Species**

<table>
<thead>
<tr>
<th>Camellia species</th>
<th>K (mg.g$^{-1}$)</th>
<th>Na (mg.g$^{-1}$)</th>
<th>N (mg.g$^{-1}$)</th>
<th>Organic carbon (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C. oleifera$ Abel</td>
<td>8.54</td>
<td>0.03</td>
<td>4.19</td>
<td>48.60</td>
</tr>
<tr>
<td>$C. eticulate$ Lindl</td>
<td>7.67</td>
<td>0.02</td>
<td>4.42</td>
<td>46.90</td>
</tr>
<tr>
<td>$C. semiserrata$ Chi</td>
<td>8.89</td>
<td>0.05</td>
<td>2.91</td>
<td>44.40</td>
</tr>
<tr>
<td>$C. mairei$ (Levl.) Melehi</td>
<td>8.10</td>
<td>0.16</td>
<td>3.53</td>
<td>45.40</td>
</tr>
<tr>
<td>$C. meiocarpa$ Hu</td>
<td>13.80</td>
<td>0.06</td>
<td>3.86</td>
<td>45.60</td>
</tr>
<tr>
<td>$C. polycodonata$ How</td>
<td>8.64</td>
<td>0.26</td>
<td>4.16</td>
<td>45.50</td>
</tr>
</tbody>
</table>

**CNS Chemical Components**

Camellia nut shell degradation was carried out using acidic, alkaline, or metallic salt as catalysts or liquid agents under normal pressure (Lu et al. 2013; Tekin and Karagoz 2013; Zhou et al. 2013b). Low cellulose and high lignin/hemicellulose content could facilitate the CNS liquefaction in the liquefaction and catalyst system (Kurimoto et al. 1999). Therefore, the chemical compositions of raw materials would have great impacts on the liquefaction process.

The main components of CNS were cellulose, hemicellulose, and lignin (Table 2). The cellulose content of CNS ranged from 13.87% to 20.95%, which is lower than that of bamboo timber, which ranges from 45% to 69% (Jiang et al. 2008). The content of CNS hemicellulose varied between 35.15% and 49.34%, which is higher than that of bamboo timber, which ranges from 15% to 23%. Lignin content varied between 30.07% and 36.23%, higher than that of bamboo timber which ranges from 20% to 25% (Jiang et al. 2008). $C. oleifera$ Abel had the highest content of hemicellulose and lignin combined (79.41%). The organic extractive accounted for around 2.36 to 4.65% in weight except for in $C. mairei$ (Levl.) Melehi, which accounted for 7.76%. The ash content in CNS of six species ranged from 2.00% to 4.75%, which is higher than that in wood (less 1%) and approximately equivalent to that in bamboo timber (2 to 3%) (Jiang et al. 2008).

**Table 2. Chemical Components and Their Percentage in Nut Shell of Six Camellia Species**

<table>
<thead>
<tr>
<th>Camellia species</th>
<th>Organic extractives</th>
<th>Cellulose</th>
<th>Hemicellulose</th>
<th>Lignin</th>
<th>Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C. oleifera$ Abel</td>
<td>2.50</td>
<td>18.62</td>
<td>49.34</td>
<td>30.07</td>
<td>2.57</td>
</tr>
<tr>
<td>$C. eticulate$ Lindl</td>
<td>2.36</td>
<td>13.95</td>
<td>42.97</td>
<td>36.23</td>
<td>2.00</td>
</tr>
<tr>
<td>$C. semiserrata$ Chi</td>
<td>3.53</td>
<td>14.62</td>
<td>45.57</td>
<td>33.82</td>
<td>2.13</td>
</tr>
<tr>
<td>$C. mairei$ (Levl.) Melehi</td>
<td>7.76</td>
<td>13.87</td>
<td>39.25</td>
<td>34.15</td>
<td>2.44</td>
</tr>
<tr>
<td>$C. meiocarpa$ Hu</td>
<td>4.55</td>
<td>20.95</td>
<td>34.21</td>
<td>31.04</td>
<td>4.75</td>
</tr>
<tr>
<td>$C. polycodonata$ How</td>
<td>4.65</td>
<td>15.46</td>
<td>35.15</td>
<td>30.88</td>
<td>2.95</td>
</tr>
</tbody>
</table>
Infrared Spectra and X-ray Diffraction Analysis of CNS

Camellia nut shell infrared spectral peak assignments can be used to infer the type and number of chemical bonds in CNS, and indicate the degree of CNS cellulose crystallinity (Kosikova et al. 1995; Davy and Nada 2003; Röder et al. 2006). As Fig. 1 shows, the CNS infrared spectroscopy characterization of absorption peaks was similar among the six Camellia species. The peak at 3420 cm\(^{-1}\) was generated by the hydroxyls of cellulose, hemicellulose, and lignin. The peaks at 2942 cm\(^{-1}\), 1452 cm\(^{-1}\), and 1378 cm\(^{-1}\) were the characteristic absorption peaks of cellulose. The absorption peaks at 1615 cm\(^{-1}\), 1508 cm\(^{-1}\), and 1436 cm\(^{-1}\) were generated with the vibration of a benzene ring skeleton which served as the criteria of presence of lignin group. The peak at 1051.19 cm\(^{-1}\) was attributed to the stretching vibration of C-O (cellulose and hemicelluloses) and the stretching vibration of alkoxy oxygen bond in acetyl group in hemicelluloses. The peak at 1743 cm\(^{-1}\) indicated the stretching vibration of C=O in acetyl and carboxyl groups, which can be used to differentiate the hemicellulose from other components. The absorption peak at 3420 cm\(^{-1}\) intensity of hemicellulose and cellulose was the strongest for C. oleifera Abel, implying the highest content of hemicellulose and cellulose existed in C. oleifera Abel, consistent with the data shown in Table 2 and Fig. 1.

![Fig. 1. Infrared spectra of nut shell of six Camellia species](image)

The infrared spectroscopy analysis indicated that the main components of CNS were cellulose, hemicellulose, and lignin, which were consistent with the results from chemical analysis. Infrared spectroscopy can determine the degree of crystallinity of cellulose.
The degree of crystallinity of cellulose can be expressed as the proportion of crystalline region of the cellulose to its total area, which is one of the major factors of cellulose degradation. The ratio between the intensities at 1373 cm\(^{-1}\) and 2898 cm\(^{-1}\) (A1373/A2898) is defined as the relative crystallinity of cellulose type I and II (Baldinger et al. 2000; Dawy et al. 2003). The ratio between the intensities at wavenumbers 1436 cm\(^{-1}\) and 898 cm\(^{-1}\) also indicates the relative crystallinity of cellulose type I and II. The calculated relative crystallinities are given in Table 3, where the crystallinity of \textit{C. polyodonta} How was the largest, followed by \textit{C. semiserrata} Chi, \textit{C. mairei} (Levl.) Melehior, \textit{C. eticulate} Lindl, \textit{C. oleifera} Abel, and \textit{C. meiocarpa} Hu, successively.

The X-ray diffraction curves of cellulose in CNS of six species are given in Fig. 2. The maximum crystal plane diffraction peak of (002) plane was observed at around 2\(\theta\) = 22.6\(^{\circ}\). The amorphous region was around 18\(^{\circ}\). The half cone angle (2\(\theta\)), 18\(^{\circ}\), 22.6\(^{\circ}\) and 35\(^{\circ}\) of the diffraction peaks position of CNS were consistent with the six species, and they were the same as that of cotton fiber (18\(^{\circ}\), 22.6\(^{\circ}\), and 34.7\(^{\circ}\)) (Lin et al. 2013), indicating that they would belong to the typical cellulose type I. Table 3 showed the consistency of results obtained from X-ray diffraction and infrared spectrum. There was a big difference in crystallinity among the six \textit{Camellia} species, with CNS of \textit{C. polyodonata} How having the highest crystallinity (62.3\%), while \textit{C. meiocarpa} Hu the lowest (37.4\%). CNS for the species with low crystallinity in cellulose contains a more extensive amorphous region, which makes the CNS cellulose more easily absorb water or other chemicals, and results in mildew on CNS (Mortazavi and Moghaddam 2010).

![Fig. 2. X-ray patterns of nut shell of six Camellia species](image-url)
Table 3. Crystallinity Extent of Nut Shell of Six Camellia Species

<table>
<thead>
<tr>
<th>Camellia species</th>
<th>A1373/A2898</th>
<th>A1436/A898</th>
<th>X-ray/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C. polyodonta How</td>
<td>0.9001</td>
<td>0.8042</td>
<td>62.3</td>
</tr>
<tr>
<td>C. semiserrata Chi</td>
<td>0.8966</td>
<td>0.7888</td>
<td>58.4</td>
</tr>
<tr>
<td>C. mairei (Levl.) Melehior</td>
<td>0.8880</td>
<td>0.7875</td>
<td>49.4</td>
</tr>
<tr>
<td>C. oleifera Abel</td>
<td>0.8683</td>
<td>0.7565</td>
<td>39.1</td>
</tr>
<tr>
<td>C. eticulate Lindl</td>
<td>0.8795</td>
<td>0.7583</td>
<td>45.2</td>
</tr>
<tr>
<td>C. meiocarpa Hu</td>
<td>0.8354</td>
<td>0.6850</td>
<td>37.4</td>
</tr>
</tbody>
</table>

Thermal Degradation Characteristics of CNS

The pyrolysis process of CNS for six species was analyzed with TG and DTG, and the corresponding curves are given below (Figs. 3 and 4). The pyrolysis characteristic curves trends of CNS for the six camellia species were similar. Essentially, the pyrolysis behavior of CNS is pyrolysis processing of the three major components, i.e., cellulose, hemicellulose, and lignin, which corresponds to the pyrolysis behavior of other biomass (Ye et al. 2014). In detail, the pyrolysis temperature of hemicellulose ranged from 200 to 300 °C. The pyrolysis of cellulose, where the crystalline and amorphous coexist, occurred at temperatures between 300 and 400 °C. The pyrolysis temperature range of lignin was wide, with its weight loss occurring at temperatures from 300 through 700 °C (Cao et al. 2014). The pyrolysis could be divided into three phases, i.e., water loss (loss of free water, crystal water, and adsorbed water as well as small terpene molecules), fast weight loss, and slow weight loss. The pyrolysis of pine sawdust was reported to have a similar process (Ulloa et al. 2009). The water loss period occurred at temperatures between 30 and 150 °C, with CNS weight reducing by 10%. As the temperature continued to rise, the second phase, fast loss weight, approached. During this period, CNS lost 60% weight at temperatures between 200 and 430 °C. In this period, the glycosidic bonds in cellulose and hemicellulose started to break. Meanwhile, some C-O and C-C bonds in cellulose, hemicellulose, and lignin also began to break, generating new compounds, including volatile substances with low molecular weight (Yin 2012).
The third phase of pyrolysis came after the temperature continued to rise to 800 °C, when the mass loss rate was slow and the residue of lignin and carbon was slowly degrading. That is to say, lignin was the most difficult to be pyrolyzed and the hemicellulose was the easiest. Dawy et al. (2003) reported a similar result. As Fig. 4 shows, the CNS weight loss for the all six species occurred at temperature between 200 and 430 °C, and the maximum weight loss occurred at 300 °C. Around the temperature of 300 °C, the rate of weight loss for C. eticulate Lindl and C. oleifera Abel was remarkably higher than the others. The high weight loss rate for C. oleifera Abel could be caused by high concentration of hemicellulose (49.34%) and cellulose (18.62%), as well as low crystallinity (39.1%). Low crystallinity (45.2%) for C. eticulate Lindl could be the reason that it had a high weight loss rate at 300 °C also. The weight loss rate for C. meiocarpa Hu was the lowest at the temperature between 330 and 450 °C because it had the highest concentration of cellulose. Therefore, the weight loss rate of CNS was affected by the concentration of cellulose, hemicellulose, and lignin as well as crystallinity.

Figure 5 shows the CNS degradation rates of six species with PEG 400/glycerol as solvent and 98% H₂SO₄ as catalyst. More than 50% of the CNS was degraded within 30 min, and this period could be regarded as the first stage of CNS degradation. The second stage was the period from 60 to 90 min when the changes of degradation rates were slow. The CNS degradation process in PEG 400/glycerol system was similar for the six species. Between 70 and 80% of the CNS was degraded after 30 min for C. oleifera Abel and C. meiocarpa Hu, with the degraded components being mainly hemicellulose and lignin, and the residue consisting of the crystalline region of cellulose. The cellulose was wrapped by hemicellulose and lignin, making it difficult to be reached by the degradation agent, thus generating the low degradation rates. After 90 min degradation, the degradation rates decreased a little and, accordingly, the residue mass increased.
which can be attributed to the recondensation and reprecipitation of degraded CNS components (Yao et al. 1993). It can be concluded that a higher content of hemicellulose and lignin and lower degrees of crystallinity would lead to a higher degradation rate, and the type degradation agent and catalyst may reduce the temperature of thermal degradation of cellulose, hemicellulose, and lignin. Efficient degradation of CNS and the degradation mechanism remain to be studied further.

![Graph showing the time-course of degradation rate of CNS using PEG 400/glycerol system](image)

**Fig. 5.** Time-course of degradation rate of CNS using PEG 400/glycerol system

**CONCLUSIONS**

1. The contents of cellulose, hemicellulose, and lignin in the nut shells of six *Camellia* species were 13.87 to 20.95%, 35.15 to 49.34%, and 30.07 to 36.23%, respectively.
2. Concentrations of K, Na, and N were 7.67 to 13.80 mg.g⁻¹, 0.02 to 0.26 mg.g⁻¹, and 2.91 to 4.42 mg.g⁻¹, respectively.
3. Infrared spectra and X-ray diffraction analysis showed that there is a great difference in crystallinity among *Camellia* species. *Camellia polyodonta* How had the greatest crystallinity (62.3%), while *C. meiocarpa* Hu had the lowest (37.4%).
4. The most rapid degradation for camellia nut shells occurred at temperatures around 200 to 430 °C, with 60% of weight loss in a thermogravimetric analyzer. The weight loss rate of CNS was affected by the concentration of cellulose, hemicellulose, and lignin as well as the cellulose crystallinity, and degradation rate is negatively related to cellulose crystallinity significantly.
5. The degradation system containing PEG 400/glycerin and catalyst could reduce the temperature of thermal degradation of cellulose, hemicellulose, and lignin. The degradation rate was related to hemicellulose concentration and cellulose crystallinity in PEG400/Glycerol system, and higher hemicellulose concentration and lower cellulose crystallinity lead to higher degradation rates.
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