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Factors Influencing Polyol Liquefaction of Nut Shells of Different *Camellia* Species

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The liquefaction rates and kinetics of nut shells of different *Camellia* species in PEG400/glycerol/H$_2$SO$_4$ liquefying solvent were investigated. Changes in major components including cellulose, hemicellulose, and lignin as well as cellulose crystallinity of the nut shells were determined. The compositions of the liquefaction residues were analyzed. Results indicated that, under the same conditions, the liquefaction rates of nut shells of different *Camellia* species were noticeably different and the PEG400/glycerol/H$_2$SO$_4$ liquefaction agent was not suitable for the liquefaction of the nut shells of all *Camellia* species. The burst liquefaction of *Camellia* nut shells (CNSs) that occurred during the first stage was due to the rapid degradation of hemicellulose, acid-soluble lignin, and amorphous cellulose. The liquefaction during the second stage became very slow, mostly because the swelling and decomposition of crystalline cellulose was very difficult to achieve with the liquefying agent and the liquefaction products inhibited liquefaction at later stages. The liquefaction residues of CNSs were composed of crystalline cellulose, small amounts of hemicellulose, acid-insoluble lignin, and ash. Ash was partially dissolved in the liquefying agent. The liquefaction rates of all CNSs tested in this study showed linear relationships with time, with coefficients of determination (R^2) greater than 0.7082, indicating that the liquefaction of CNS was a pseudo-first-order reaction.

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INTRODUCTION

Camellia spp. is an important oleiferous tree species in southern China. It is one of the most valuable oleiferous species in the *Camellia* family and is considered to be one of the four major oleifera tree species in the world, along with oil palm, olive, and coconut (Zhuang 2008). With the development of the tea oil processing industry, the cultivation area of *Camellia spp.* in China has reached ~5.5 million hm^2 (Jiang *et al.* 2011), with an annual production of nearly 10 million tons of *Camellia* fruit (Qiu *et al.* 2009; Shen *et al.* 2010; Jiang *et al.* 2010), 518,000 tons of tea oil, and nearly 8 million tons of *Camellia* nut shell (CNS) (Zhang *et al.* 2014). CNS is a hydroxyl-rich natural polymer primarily composed of cellulose, hemicellulose, and lignin. Theoretically, it can be used to replace petroleum-based polyethers or polyester polyols in nucleophilic addition reactions with isocyanate in order to produce polyurethane. Solid CNS can be converted into hydroxyl-rich liquid substances using liquefaction techniques to maximize its reuse at the molecular level and to improve its reuse efficiency and value. Therefore,

liquefaction has become a new research area in the all-component high-value utilization of CNS.

Currently, wood biomass liquefaction has been studied in terms of raw materials, liquefying agents, catalysts, heating, *etc*. Various biomasses, such as bamboo (Aysu and Küçük 2013), crop residues (Hassan and Shukry 2008; Wei *et al.* 2013), barks (D'Souza and Yan 2013), sawdust (Hui *et al.* 2012), poplar (Li *et al.* 2008), bamboo shells (Li 2014), bagasse (Ting *et al.* 2007), and palm shells (Omoriyekomwan *et al.* 2016), have been used as raw materials for liquefaction. Liquefying agents reported so far include phenol, polyethylene glycol, glycerin, ethylene glycol (Wei *et al.* 2011), ethylene carbonate (Xie and Chen 2005), and ionic liquids (Xie and Shi 2006; Zheng *et al.* 2014). Liquefaction reactions can be catalyzed using perchloric acid, sulfuric acid, and p-toluenesulfonic acid (Krzan and Zagar 2009). The reactions can be heated by a water bath, oil bath, salt bath, steam heating, microwave, and electric heating (Sequeiros *et al.* 2013). However, few reports have been found in the literature about the liquefaction of CNS.

In this study, we selected three *Camellia* species (*C. oleifera* Abel, *C. meiocarpa* Hu, and *C. polyodonta* How ex Hu) with greatly different chemical compositions and cellulose crystallinities among them, and conducted liquefactions of the nut shells of the three species with PEG400/glycerol as liquefying solvent and H_2SO_4 as catalyst to study the effects of the physical and chemical properties of CNS on its liquefaction.

EXPERIMENTAL

Materials

Camellia nut shells (CNSs) were provided by the Camellia Research and Development Center of the Chinese Academy of Forestry. Nut shells of *Camellia oleifera* Abel, *Camellia meiocarpa* Hu, and *Camellia polyodonta* How. ex Hu were respectively collected from Jinhua Township, Zhejiang Province, China; Nanping Township, Fujian Province, China; and Lingui County, Guangxi Zhuang Autonomous Region, China. All samples were dried in an oven at 105 °C until their weights became constant. They were then pulverized and sifted through a 40-mesh sieve and stored in a desiccator at room temperature.

Polyethylene glycol 400 (PEG400, Sinopharm Chemical Reagent Co., Ltd., Shanghai) was of chemical grade. Glycerol (Sinopharm Chemical Reagent Co., Ltd., Shanghai), sulfuric acid (Zhejiang Eagle Chemical Reagent Co., Ltd., Lanxi, Zhejiang) and 1,4-dioxane (ChinaSun Specialty Products Co. Ltd., Changzhou, Jiangsu) were of analytical grade.

Previous studies showed that the liquefaction ratio for *C. oleifera* Abel in PEG400/ glycerol/ H_2SO_4 liquefying system was comparatively high when the PEG400/ glycerol ratio was 4/1 and the H_2SO_4 concentration was 3% (Zhang *et al.* 2012). Therefore, PEG400/ glycerol (4/1)/ 3% H_2SO_4 was used in this experiment.

Methods

Chemical composition analysis

Cellulose and hemicellulose contents were determined using the 72% sulfuric acid method and tetrabromide method (Zhang *et al.* 2002), respectively. The contents of

lignin, ash, and organic extractives were measured according to the National Standards of the People's Republic of China GB/T 2677.8 (1994), GB/T 2677.3 (1993), and GB/T 2677.6 (1994), respectively.

Liquefaction method

Approximately 80 g of PEG400, 20 g of glycerol, and 3 g of 98% sulfuric acid were mixed in a three-neck flask connected to a stirrer, a reflux condenser, and a thermometer, and heated to 100 °C in an oil bath. This was followed by the addition of 33 g of CNS powder sample. The reaction system was then heated at 160 °C for 15 to 150 min, and the reaction was subsequently terminated *via* cooling to room temperature in cold water.

The liquefaction 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 became clear. The residue was dried to a constant weight at 105 °C. The liquefaction rate was calculated as follows:

$$\text{Liquefaction rate} = \frac{1 - residue \cdot quality}{sample \cdot mass} \times 100\% \tag{1}$$

Fourier transform infrared spectroscopy (FTIR) analysis

The infrared (IR) spectra of CNS powder samples were recorded on an FTIR spectrometer (Nicolet 560, Thermo Nicolet Corporation, USA) to determine their functional groups. The samples were placed in a sample pool made using KBr. For each spectrum, a 32-scan adsorption interferogram was collected at a resolution of 4 cm^{-1} in the 400 to 4000 cm^{-1} region at ambient temperature. Each experiment was repeated three times, and crystallization indices were calculated.

X-ray diffraction analysis

Powdered CNS samples and liquefaction residues were sifted through a 40-mesh sieve, dried at 50 °C for 6 h, and compressed into thin slices at room temperature. Scanning was carried out on a Rigaku (Japan) D/max 2550PC X-ray diffractometer equipped with a Cu-target X-ray tube and nickel plate for CuK$_{\beta}$ radiation elimination under the following conditions: tube voltage 40 kV, current 40 mA, and 2θ/θ linkage scanning. The X-ray crystallography index was calculated as follows,

$$CrI = \frac{I_{002} - I_{am}}{I_{002}} \times 100\% \tag{2}$$

where *CrI* is the relative crystallinity (%), I_{002} is the maximum diffraction intensity at the angle of the (002) lattice, and I_{am} is the amorphous background scattering diffraction intensity at 2θ.

RESULTS AND DISCUSSION

Physical and Chemical Properties of Different *Camellia* Species' Nut Shells

Table 1 lists the chemical compositions, cellulose crystallinities, ash contents, and organic extractive contents of the nut shells of three *Camellia* species. The cellulose contents of the CNSs showed 2.33% to 5.49% variance. The nut shell of *C. polyodonta*

How. ex Hu showed 62.30% cellulose crystallinity, which was significantly higher than that of the other two species. *C. oleifera* Abel nut shell had the highest hemicellulose content, at 49.34%. The lignin contents of the CNSs followed the order *C. polyodonta* How. ex Hu > *C. meiocarpa* Hu > *C. oleifera* Abel. The organic extractive content of the *C. oleifera* Abel nut shell was 2.50%, nearly half of that found in the nut shells of the other two *Camellia* species. The CNSs of all three *Camellia* species showed IR absorption peaks at 1328, 1222, and 1124 cm^{-1} that were assigned to the syringyl of lignin. The absorption peak at 1268 cm^{-1} for all of the CNSs was attributed to the guaiacyl of lignin (Cui *et al.* 2011). As shown in Fig. 1, the activities of both syringyl and guaiacyl in the lignin were in the following order: *C. oleifera* Abel > *C. meiocarpa* Hu > *C. polyodonta* How. ex Hu.

Table 1. Chemical Composition, Contents of Ash and Organic Extractives, and Crystallinity of the Three CNSs

| Components	*C. oleifera* Abel	*C. meiocarpa* Hu	*C. polyodonta* How. ex Hu
Cellulose (%)	18.62 $\pm$ 0.22	20.95 $\pm$ 0.24	15.46 $\pm$ 0.08
Hemicellulose (%)	49.34 $\pm$ 0.07	34.21 $\pm$ 0.15	35.15 $\pm$ 0.32
Lignin (%)	30.07 $\pm$ 0.14 (acid-soluble 3.33)	31.04 $\pm$ 0.06 (acid-soluble 3.64)	41.47 $\pm$ 0.07 (acid-soluble3.53)
Crystallinity Index	39.1	37.4	62.30
Organic Extractives (%)	2.50 $\pm$ 0.01	4.55 $\pm$ 0.02	4.65 $\pm$ 0.01
Ash (%)	2.57 $\pm$ 0.04	4.75 $\pm$ 0.01	2.95 $\pm$ 0.03
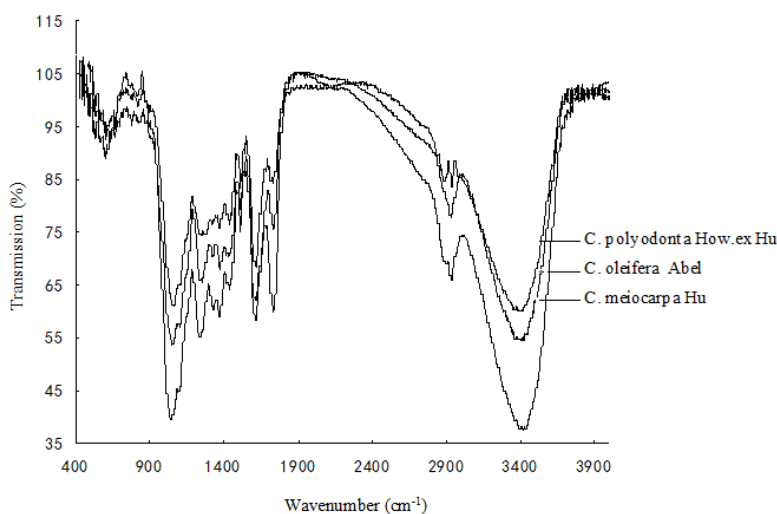
Fig. 1. Infrared spectra of the nut shells of three *Camellia* species

Liquefaction Rates of the Nut Shells of Different *Camellia* Species

The liquefactions of nut shells of the three *Camellia* species in PEG400/ glycerol/ H$_2$SO$_4$ solvent demonstrated similar tendencies (Fig. 2). *C. oleifera* Abel nut shell showed the highest liquefaction rate, followed by the *C. meiocarpa* Hu nut shells and *C. polyodonate* How. ex Hu nut shells. At the first liquefaction stage (0 to 15 min), 51.84% to 80.99% of the nut shells of all three *Camellia* species were liquefied. These liquefactions were attributed to the degradation of the CNS. During the second

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liquefaction stage, the liquefaction rates of all three CNSs slowly increased for the first 15 to 90 min, when the degradation rate of CNS was higher than the polymerization rate of the liquefaction products and then became stable at 90 to 120 min, when the degradation rate was close to the polymerization rate. During the third stage, starting at 120 min, the liquefaction rates of CNSs for two of these three species decreased due to the increased polymerization rate, which probably resulted in the macromolecular substance generated with the reaction among the liquefied products or between the liquefied product and the liquefying agent. These results are consistent with conclusions drawn about the liquefaction of woody species in polyhydric alcohols, previously reported by Kurimoto *et al* (1999).
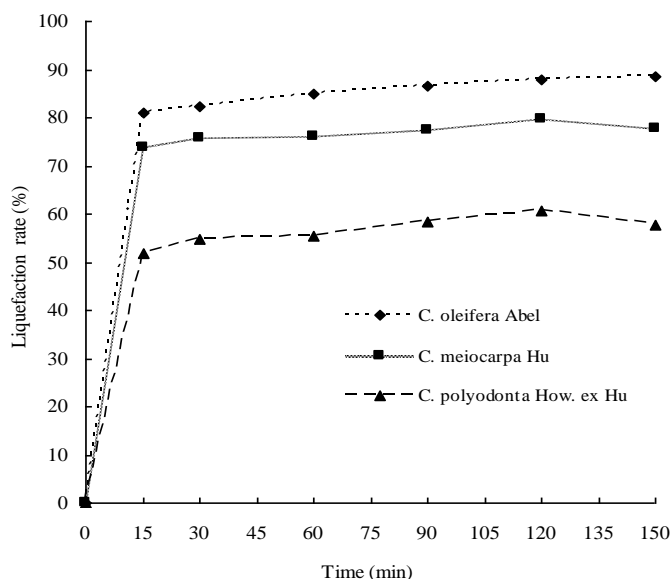
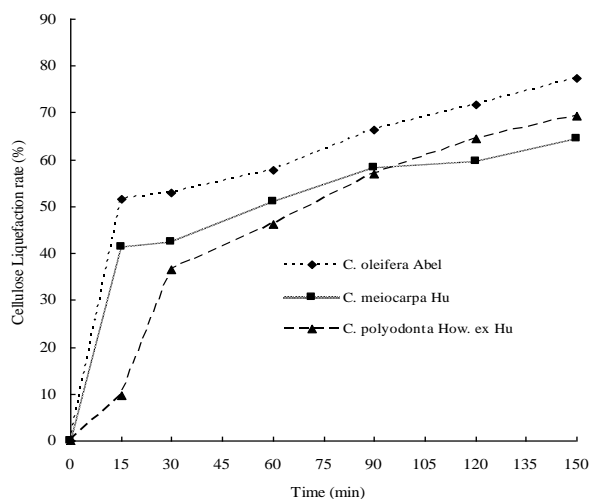**Fig. 2.** Liquefaction rate of three *Camellia* nut shells

In all, the liquefaction rates of the nut shells of different *Camellia* species in PEG400/glycerol/H_2SO_4 solvent under the same conditions were noticeably different. This may be attributed to their different cellulose, hemicellulose, and lignin contents, cellulose crystallinities, and cellulose distributions in the cell wall (Kurimoto *et al.* 1999). Therefore, a PEG400/glycerol/ H_2SO_4 liquefying agent is not suitable for the nut shells of all *Camellia* species.

## Liquefaction Processes of the Nut Shells of Different *Camellia* Species

CNS is primarily composed of cellulose, hemicellulose, lignin, organic extractives, and ash. The organic extractives are mostly proteins, polysaccharides, saponins, polyphenols, *etc.* (Chen *et al.* 2011), which have no obvious effect on the liquefaction of CNS because they can be degraded along with cellulose, hemicellulose, and lignin into lower-molecular weight substances. The composition of organic extractives has no obvious influence on the liquefaction products of CNS for the production of pre-polyurethane.

Figures 3 and 4 show the cellulose liquefaction rates and cellulose crystallinities of the nut shells of different *Camellia* species during their liquefactions. As can be seen, the cellulose liquefaction rates of *C. oleifera* Abel, *C. meiocarpa* Hu, and *C. polyodonta* How. ex Hu nut shells reached 51.46%, 41.28%, and 9.8%, respectively, in the first 15

min. During a liquefaction time between 15 to 150 min, the cellulose liquefaction rates of *C. oleifera* Abel and *C. meiocarpa* Hu nut shells slowly increased. The cellulose crystallinities of their liquefaction residues increased from 15 to 60 min because of the degradation of amorphous components, and decreased from 60 to 120 min because of the degradations of both amorphous components and crystalline components. The cellulose crystallinities of the liquefaction residues increased again from 120 to 150 min. This can be explained by the fact that all the amorphous components were liquefied, leaving highly crystalline cellulose in the residues. *C. polyodonta* How. ex Hu nut shells showed a different cellulose liquefaction process. Its cellulose liquefaction rate increased rapidly from 15 to 30 min, and the liquefaction during this period of time mostly involved its amorphous components. At 90 to 150 min, the cellulose liquefaction rate became higher than that of the *C. meiocarpa* Hu nut shell, and liquefaction primarily affected the crystalline components.
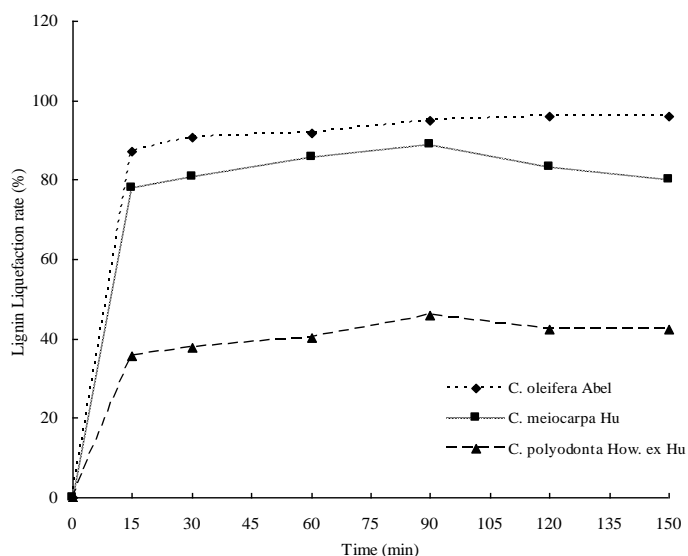

Fig. 3. Liquefaction rate of cellulose in nut shells of three *Camellia* species
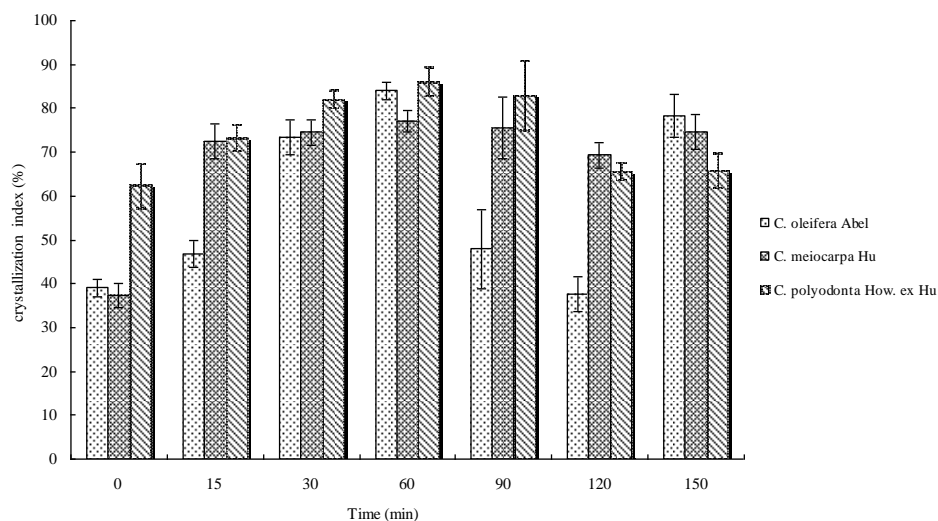
Fig. 4. Crystallization index of cellulose in nut shells of three *Camellia* species

The lignin liquefaction rates of *C. oleifera* Abel, *C. meiocarpa* Hu, and *C. polyodonta* How. ex Hu nut shells reached 87.30%, 78.05%, and 13.83%, respectively, in the first 15 min, and increased gently later. At 90 min, the lignin liquefaction rates of the

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nut shells for two of these three species reach the peaks, and decreased thereafter (Fig. 5). The low lignin liquefaction rate of the *C. polyodonta* How. ex Hu nut shell can be attributed to the insoluble residues produced by the reactions between the levulinic acid derivatives and aromatic derivatives that were respectively generated by the degradations of cellulose and acid-soluble lignin (Kobayashi *et al.* 2004). In addition, cellulose degradation occurred *via* a nucleophilic substitution reaction of the hydroxyl group of lignin (Kobayashi *et al.* 2004) and thus was affected by the content, distribution, and reactivity of lignin and cellulose crystallinity. Lignin acts as a physical barrier that hinders cellulose degradation and conversion caused by the liquefying solvent (Santos *et al.* 2012). In all, the low lignin liquefaction rate of *C. polyodonta* How. ex Hu nut shell may have been a result of its high lignin content and inappropriate acid liquefaction solvent, or the high contents and low reactivity of syringyl and guaiacyl in the lignin (Kurimoto *et al.* 1999).

Fig. 5. Liquefaction rate of lignin in nut shells of three *Camellia* species

Hemicellulose in the nut shells was rapidly liquefied within 15 min, with the highest liquefaction rate of 97.87% found in the *C. oleifera* Abel nut shell, and the lowest rate of 72.38% found in the *C. polyodonta* How. ex Hu nut shell (Fig. 6).
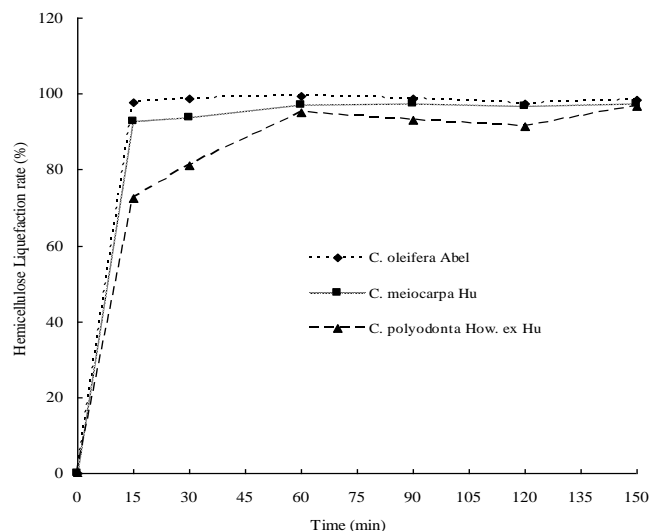
Fig. 6. Liquefaction rate of hemicellulose in nut shells of three *Camellia* species

The hemicellulose liquefaction rates of all three CNSs peaked at 60 min and decreased thereafter, indicating that the polycondensation of hemicellulose occurred as liquefaction proceeded. The hemicellulose liquefaction rate increased slightly during the liquefaction period between 120 and 150 min and reached again the similar level at 150 min as it was at 60 min for C. *polyodonta* How. This can be explained by the fact that the polycondensation reaction precipitated some degradation products of cellulose and lignin (Wei *et al.* 2013), thereby reducing the concentrations of the hemicellulose liquefaction products in favor of hemicellulose liquefaction.

The rapid liquefaction of CNSs that occurred during the first stage was due to the rapid degradations of hemicellulose, acid-soluble lignin, and amorphous cellulose. During the second stage, liquefaction became much slower because the liquefying agent could not effectively swell and degrade the crystalline cellulose and the liquefaction products inhibited the reaction. Hemicellulose and acid-soluble lignin were easier to degrade using PEG400/ glycerol/ H_2SO_4 liquefying agent than cellulose. The liquefaction rate of cellulose depended on the liquefaction rate of lignin, and the content and activity of the phenolic hydroxyl groups within lignin, which together decide the liquefaction rate of CNSs, consistent with conclusions reported by Wei *et al.* (2013) on the liquefaction of crop residues using polyols (Wei *et al.* 2013). The liquefaction products of cellulose and lignin can react with each other in PEG400/ glycerol/ H_2SO_4 solvent, affecting the liquefaction of CNSs. The liquefied hemicellulose was subjected to polycondensation at the liquefaction time of 60 min under optimal experimental conditions.

Liquefaction Residues of the Nut Shells of Different *Camellia* Species

The liquefaction residues of CNSs were mostly composed of cellulose, a small amount of hemicellulose, lignin, and ash. The ash contained minerals, including K, Na, Si, Fe, Al, and trace elements that were very difficult to liquefy. The ash was partially dissolved in liquefied solvent, while the rest remained in the residue, which is consistent with conclusions reported by Li *et al.* (2014) that the liquefaction ash of bamboo shoot shells was partially dissolved in PEG400/ EG/ acid liquefying solvent.

The cellulose contents and crystallinities of liquefaction residues increased dramatically in the first 15 min because of the rapid degradation of most of the

hemicellulose, and some lignin and amorphous cellulose. The cellulose crystallinities of the liquefaction residues of different CNSs changed differently during the liquefaction. The cellulose crystallinities of the liquefaction residues of both *C. oleifera* Abel and *C. meiocarpa* Hu nut shells peaked at 60 min, while that of *C. polyodonta* How. ex Hu nut shell peaked at 90 min, indicating that the residues were mostly composed of crystalline cellulose. Further liquefaction led to a decline in the cellulose crystallinity of their liquefaction residues and partial degradation of crystalline cellulose. The cellulose crystallinities of the residues increased at 150 min because of the degradations of the amorphous and partial crystalline cellulose. Crystalline cellulose was the predominant cellulose in the liquefaction residues (Fig. 7 and Fig. 4).

The liquefying agent reached hemicellulose on the inner cell wall through the channels formed by the degradation of partial cellulose and lignin, swelled, and then liquefied the hemicellulose, leading to a rapid decrease in the residual hemicellulose content and an increase in residual cellulose content during the first 15 min (Yang *et al.* 2013). During the liquefaction period between 15 and 60 min, the residual hemicellulose content was in the following order: *C. polyodonta* How. ex Hu > *C. meiocarpa* Hu > *C. oleifera* Abel (Fig. 8). The high residual hemicellulose content of *C. polyodonta* How. ex Hu nut shell was caused by its high crystallinity and the low liquefaction rate of amorphous cellulose (Fig. 4) that hindered the liquefying agent's entry into cells to contact the hemicellulose. After 60 min of liquefaction, the residual hemicellulose contents slightly increased due to polycondensation of the liquefied hemicellulose.
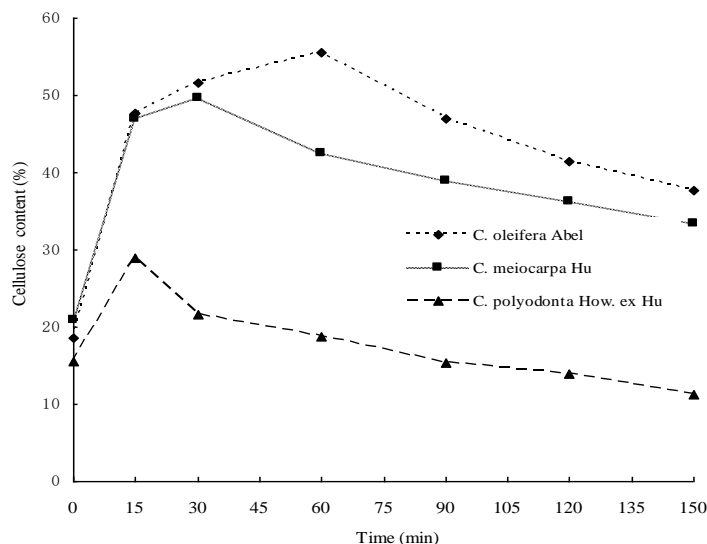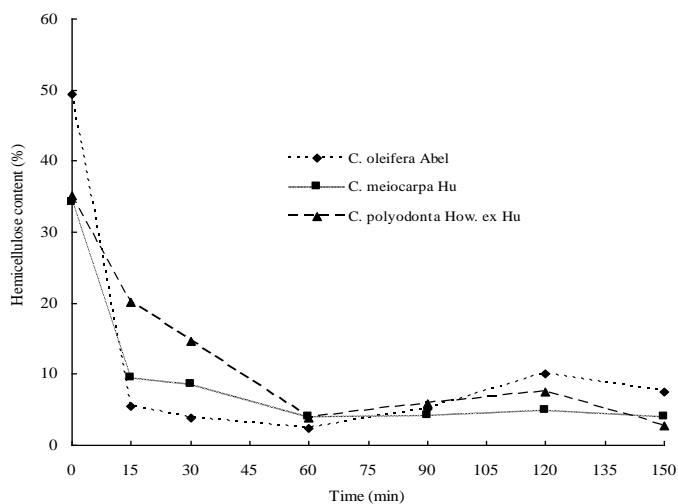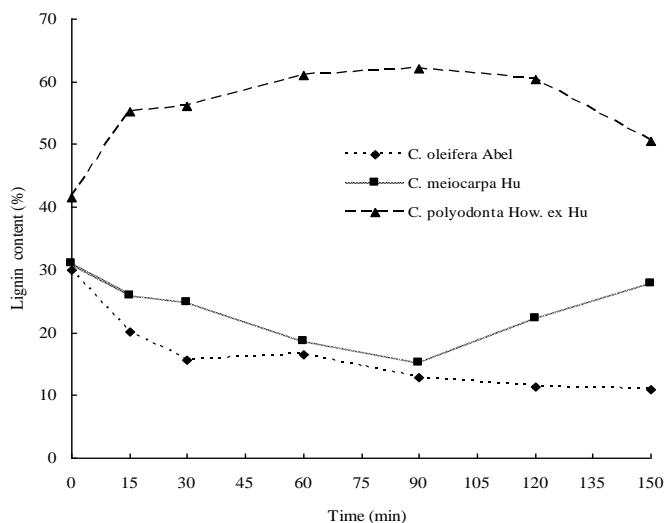

Fig. 7. Cellulose content of the liquefied residues of three *Camellia* nut shells

Fig. 8. Hemicellulose content of the liquefied residues of three *Camellia* nut shells

The residual lignin contents of the nut shells of all three *Camellia* species were very high, which may have been due to the recondensation of the liquefaction products of lignin under acidic conditions (Kobayashi *et al.* 2004.), resulting in only acid-soluble lignin being liquefied. This is consistent with the conclusion mentioned above that the lignin liquefaction rates of the nut shells of all three *Camellia* species in PEG400/glycerol/H_2SO_4 liquefying solvent were low. In particular, the residual lignin content of *C. polyodonta* How. ex Hu nut shell increased from the beginning of liquefaction (Fig. 9), which may be attributed to its high lignin content or the low activity of its syringyl and guaiacyl under acidic conditions (Kurimoto *et al.* 1999). Therefore, the degradation of lignin plays an important role in the liquefaction of CNSs (Yao *et al.* 1993).

Fig. 9. Lignin contents of the liquefied residues of three *Camellia* nut shells

Liquefaction Kinetics of the Nut Shells of Different *Camellia* Species

The liquefaction system of CNS using PEG400/glycerol/H_2SO_4 includes two or more liquid and solid phases. Therefore, the liquefaction kinetic equilibrium is affected

by the physicochemical properties of different compounds. At the beginning of the reaction, the liquefying agent (PEG400/glycerol/H_2SO_4) was in excess, and it showed no noticeable changes during the liquefaction. Thus, the dependence of the rate upon *Camellia* nut shells residues can be isolated, and the rate law could be written as a pseudo-first-order reaction model (Wei *et al*. 2013),

$$R = A \exp(-kt) \tag{3}$$

where k is the rate constant, R is the mass of unliquefied component, and A is a constant determined by the fitting date.

Equation 3 can also be written as:

$$\ln R = \ln A - kt \tag{4}$$

The value of R at different time t could be obtained from experiment curves (Fig. 2). Plotting in R against time gave six points corresponding to date mentioned in Fig. 2. The six points created a straight line with slope k. The rate constant k was used to evaluate the liquefaction reaction rate of different CNSs in the present study.

Figure 10 shows the relationships between the logarithm residue rate and time ($\ln R \sim t$) of the CNSs established within the experimental data. As can be seen, the logarithm of residue rate linearly changed according to time for all *C. oleifera* Abel, *C. meiocarpa* Hu, and *C. polyodonta* How. ex Hu nut shells, with equations as follows:

$$y = -0.0067x + 3.0726 \; (R^2 = 0.9927) \tag{5}$$

$$y = -0.0016x + 3.2766 \; (R^2 = 0.8589) \tag{6}$$

$$y = -0.001x + 3.8491 \; (R^2 = 0.7082) \tag{7}$$

All of the coefficients of determination (R^2) of CNSs residues were above 0.7082. The reaction constant k followed the order *C. oleifera* Abel> *C. meiocarpa* Hu > *C. polyodonta* How. Ex Hu. The results suggested that the species of *CNS*s affect the liquefaction rate. *C. polyodonta* How . Ex Hu was difficult to liquefy, and *C. oleifera* Abel was easy to liquefy in PEG400/ glycerol/ H_2SO_4.
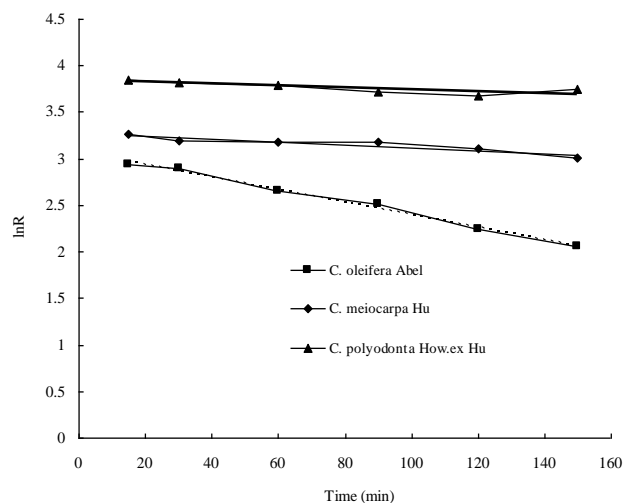

Fig. 10. The value of R at different times

CONCLUSIONS

1. The liquefaction of the nut shells of different *Camellia* species showed similar tendencies but different rates. Therefore, the PEG400/ glycerol/ H_2SO_4 liquefying solvent is not suitable for the nut shells of all *Camellia* species.

2. The rapid degradations of hemicellulose, acid-soluble lignin, and amorphous cellulose led to a burst in liquefaction during the first 15 min. The liquefaction became slower thereafter because the liquefying agent could not effectively swell and degrade crystalline cellulose, and the liquefaction products inhibited the liquefaction. Hemicellulose and acid-soluble lignin were easier to liquefy using PEG400/ glycerol/ H_2SO_4 solvent.

3. The liquefaction rates of cellulose and lignin decided the liquefaction rate of CNSs. Under acidic conditions, partially liquefied lignin was subjected to polycondensation, which reduced the lignin liquefaction rate. The liquefaction rate of CNS is affected by the liquefying agent, the contents and distributions of cellulose, hemicellulose and lignin, and cellulose crystallinity.

4．The liquefaction rates of CNSs showed linear relationships according to liquefaction time with correlation coefficients (R^2) greater than 0.7082, indicating that the liquefaction was a pseudo-first-order reaction.

ACKNOWLEDGMENTS

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