Effect of Anatomical Characteristics and Chemical Components on Microwave-assisted Liquefaction of Bamboo Wastes

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The epidermis layer waste (ELW) and the inner layer waste (ILW) were removed from *Phyllostachys pubescens* bamboo, and the anatomical characteristics and chemical components of these wastes were comparatively investigated. Both the ELW and ILW were subjected to a microwave-assisted liquefaction process to evaluate the relationship between bamboo properties and liquefaction behavior. The results indicated that higher vessel and parenchyma percentages and lower cellulose and lignin contents in ILW contributed to lower residue content, while higher fiber percentage and cellulose or lignin contents in ELW resulted in higher residue content. Recondensation took place during the liquefaction of ELW, which was indicated by small granules appearing on the liquefied residue surface according to SEM images. The intense bands corresponding to hemicellulose and lignin in the FT-IR spectrum of the liquefied ELW residue gave further evidence that the liquefaction of ELW is a complex solvolysis process involving simultaneous reactions of chemical degradation and recondensation.

Keywords: Bamboo; Anatomy; Chemistry; Liquefaction; Microwave

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INTRODUCTION

Compared to conventional heating, microwave energy penetrates and produces a volumetrically distributed heat source; heat is generated throughout the material and leads to faster heating rates and improved kinetics. Therefore, the development of a liquefaction process combining the greater microwave heating efficiency and the by-product glycerol from the bio-diesel production to replace petroleum-based solvents is a promising method to enhance economic viability of the process and benefit agricultural producers, bio-based processing industries, and the environment. According to the potential benefits of the microwave liquefaction system, lignocellulosic biomass residues have been subjected to microwave-assisted direct liquefaction processes for the production of alternatives to petroleum-based chemical feedstocks (Krzan and Zagar 2009; Pan *et al.* 2012; Xu *et al.* 2012; Zhuang *et al.* 2012).

However, the liquefaction processes in these studies cannot be directly used for the liquefaction of all lignocellulosic materials because of the differences in the characteristics, chemical components, and end applications of the liquefaction products. An example of this can be seen in the experimental results of the influence of wood species on the properties of biopolyurethane prepared from liquefied wood with residue, in which

the results showed that the liquefaction of softwood occurred in a shorter time than hardwood and that the biopolyurethane prepared from softwood was harder than that prepared from hardwood, which suggested that the properties of the liquefaction products and biopolyurethane were influenced by the chemical structure of lignin (Izumo and Fukushima 2010). It was also reported that the liquefaction residue content of cotton stalks was higher than that of bagasse under the same conditions, which indicated that bagasse is more susceptible to liquefaction than cotton stalks (Hassan and Shukry 2008). In the study of liquefaction of brown-rotted wood, wood samples with higher α-cellulose content were more difficult to liquefy and that lignin could be easily liquefied by phenol (Li *et al*. 2012).

In the liquefaction of lignocellulosic biomass, the most commonly explored solvents for liquefaction are phenol and polyalcohol. These solvents are effective, but they require large quantities and are costly. Phenol is derived from petroleum and as such is generally not considered as an environmentally green chemical. A by-product of the transesterification process to manufacture bio-diesel is the production of glycerol. For each kilogram of biodiesel produced, about 0.1 kg of a crude glycerol also is generated (Thompson and He 2006). Therefore, successful replacement of petroleum-based solvents, such as phenol by glycerol in a liquefaction process, should have potential to improve the economics.

Bamboo has become one of the most important non-timber forest products in China and other Asian countries. This is primarily due to its rapid growth rate, availability, renewable nature, high productivity, short maturity cycle, and multiple uses. Currently, bamboo has been used in the preparation of high-value added products such as, panel, parquets, furniture, and structural composites. However, in the manufacturing of bamboo-based materials, the epidermis and wax layer of bamboo usually are split off. This is because of the poor wettability or penetration of these portions for subsequent treatments, *e.g*., coating and preservative treatments, *etc*. Thus, large quantities of bamboo processing residues, such as epidermis, are cast aside as waste. Moreover, bamboo properties, such as anatomical and chemical characteristics, have been reported to differ with species, ages, locations, and portions; such differences can significantly affect its processing procedures and the performance of end products (Hisham *et al*. 2006). Thus, in order to maximize the utilization of bamboo processing residues to address problems concerning both waste disposal and resource wastage, microwave-assisted liquefaction of these wastes was carried out in a glycerol-based solvent. The anatomical characteristics and chemical components of the epidermis and wax layer wastes were first analyzed. The object of this study was to evaluate the effect of bamboo properties on their microwave liquefaction behaviors. The results in this paper would provide helpful information to realize an economically viable bamboo waste conversion technology.

EXPERIMENTAL

Materials and Chemicals

Three-year-old bamboo (*Phyllostachys pubescens*) was harvested from the Kisatchie National Forest in Pineville, LA, USA. Bamboo logs were transported to the laboratory and allowed to air-dry. The ELW and ILW were split off with a fine blade. A sketch of the process is shown in Fig. 1. The split blocks were sliced into match stick size

splints for the analysis of anatomical characteristics. Air-dried splits were screened to collect bamboo particles that passed through a 20-mesh sieve and were retained on a 40-mesh sieve and then dried to a constant weight in an oven maintained at 80 ^{o}C. The collected particles were used for the liquefaction process. All the reagents used in this study were of analytical grade and obtained from commercial sources.

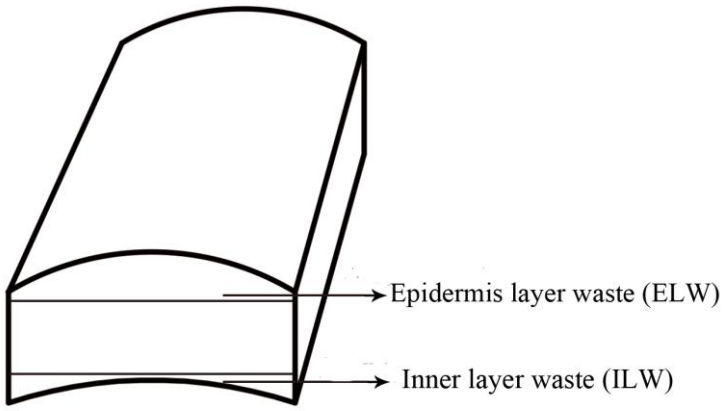

Fig. 1. Sketch for the removing of epidermis layer waste (ELW) and inner layer waste (ILW)

Liquefaction Reaction

Microwave liquefaction was carried out in a Milestone (Shelton, CT) MEGA laboratory microwave oven. A mixed glycerol and methanol ratio of 2/1 (w/w) was used as the solvent at a solvent to bamboo ratio of 4/1 (w/w). Sulfuric acid, at a content of 1.75% of solvent weight, was used as the catalyst. A typical reaction mixture consisting of 2 g of bamboo particles, 8 g of solvent, and 0.14 g of sulfuric acid was loaded in the Teflon vessels with a magnetic stirring bar. The Teflon vessels were then placed on the rotor tray inside the microwave cavity. The temperature was monitored using an ATC-400FO automatic fiber optic temperature control system. Based on monitored temperature, the output power was auto-adjusted during liquefaction. In this study, the temperature was increased from room temperature to 140 ^{o}C at a heating rate of 30 ^{o}C min^{-1} and then was kept constant for 3 min. After a cooling period of 30 min, the material was dissolved in 150 mL of methanol under constant stirring for 4 h. The liquefied solutions were then vacuum-filtered through Whatman No. 4 filter paper. The solid bamboo residue retained on the filter paper was oven-dried to a constant weight at 105 ^{o}C, and the residue content was calculated as follows:

$$\text{Residue content } (\%) = \left(\frac{\text{weight of residue}}{\text{weight of raw material}}\right) \times 100 \quad (1)$$

Analysis Methods

Measurement of bamboo properties

The anatomical characteristics of the ELW and ILW, such as vascular bundle dimensions, fiber and parenchyma morphologies, and proportions of cell types, were measured according to referenced methods (Wang *et al*. 2011; Ishiguri *et al*. 2009).

The holocellulose, alpha-cellulose, Klason lignin contents, hot-water extractive, and alcohol-toluene extractive contents were determined according to ASTM standards D1104-56, D1103-60, D1106-96, D1110-96, and D1107-96, respectively.

Fourier transform infrared spectroscopy (FT-IR)

The FT-IR analysis was performed using a Nicolet Nexus 670 spectrometer equipped with a Thermo Nicolet Golden Gate MKII Single Reflection ATR accessory. A small amount of sample was applied directly on the diamond crystal. Data collection was performed with a 4 cm^{-1} spectral resolution, and 32 scans were taken per sample.

Scanning electron microscope (SEM) analysis

The structure and the surface morphology of liquefied residues were observed using a scanning electron microscope (SEM, JCM-5000). Test samples were coated with gold using a vacuum sputter coater before subjected to the SEM analysis.

Statistical Analysis

Statistical analysis was carried out using SAS (version 9.1, SAS Institute, Cary, NC). Analysis of variance (ANOVA) was performed to determine significant difference (α=0.05) among the different samples.

RESULTS AND DISCUSSION

Anatomical Characteristics

Anatomical structure

Due to the fact that no radial cells exist in bamboos, only the transverse section was observed using the microscope, and the microstructural images of the ELW and ILW are presented in Fig. 2.

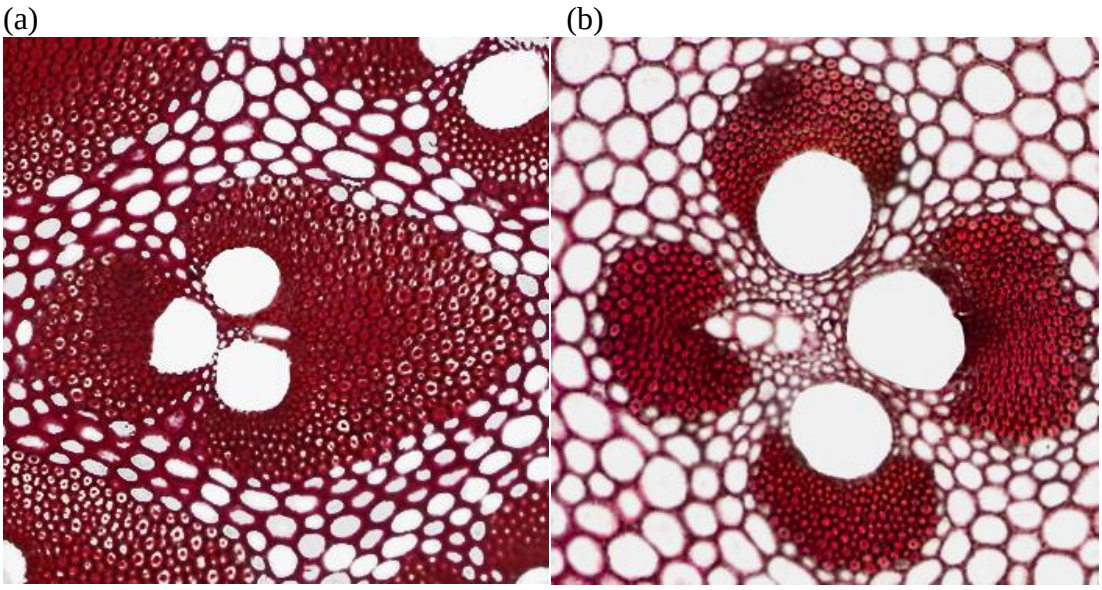

Fig. 2. Microstructure images of (a) ELW sample and (b) ILW sample

The structure of both the ELW and ILW is characterized by vascular bundles embedded in parenchyma cells. Differences in vascular bundle shape and size between the ELW and ILW were found. Compared to the ILW (Fig. 2b), the epidermis layer sample had denser vascular bundles and smaller size. The average concentration of vascular bundle and tangential diameter for the ELW and ILW were 7.0 and 1.7 bundle/mm^2, 320.4, and 611.3 μm, respectively. The vascular bundle consists of central vascular and fiber strands. Figure 2 also shows that the fiber strands accompanying the vascular bundle in ELW were larger than that in ILW.

Cell proportion and morphology

According to the microstructural images, the tissue of the ELW and ILW consists of parenchyma, fiber, and vessel cells. To further evaluate the structural difference between the ELW and ILW samples, cell proportions and morphologies were measured, and the results are shown in Fig. 3.

It can be seen from Fig. 3a that the ELW had higher fiber percentage (62.1%) and lower parenchyma percentage (29.2%) compared to those for the ILW (23.7 and 64.2% for fiber and parenchyma percentages, respectively). The vessel percentage for the ELW and ILW was 8.8 and 12.2%, respectively.

Significant differences were found in fiber and parenchyma percentages between the two samples. The fiber and parenchyma cell wall thickness in the ELW were greater than in the ILW, while the fiber and parenchyma lumen sizes of the ILW were larger than that of the ELW. The difference in fiber and parenchyma lumen size between the two samples was significant.

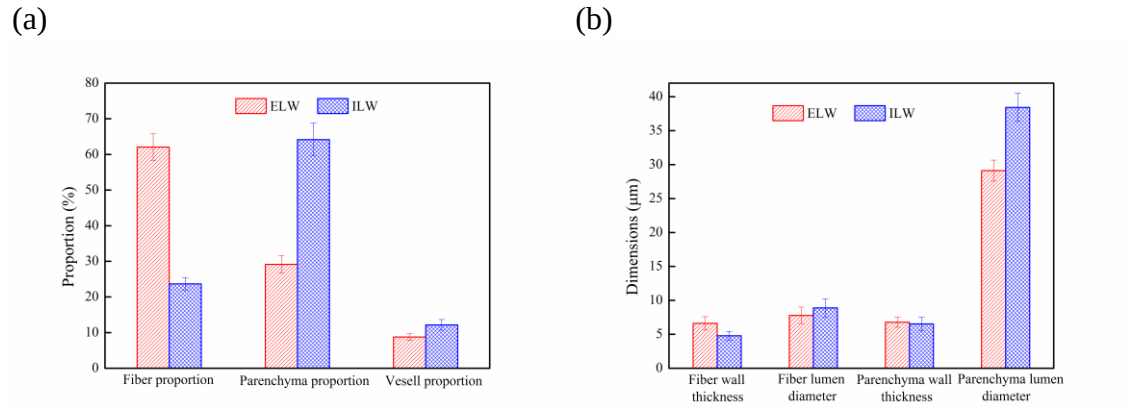

Fig. 3. Variation in (a) cell proportions and (b) morphologies between the ELW and ILW samples

Chemical Components

The chemical components of bamboo residues were compressively analyzed in a previous study by the authors (Qi *et al.* 2013). The results for the ELW and ILW were as follows: the holocellulose, cellulose, and lignin for the ELW and ILW were 69.6, 49.3, and 25.2% and 61.1, 36.6, and 20.1%, respectively. The hot-water and alcohol-toluene extractives for the ELW and ILW were 4.3, 3.9%, and 13.8, 8.8%, respectively. Significant differences were observed in the chemical components between the ELW and ILW. The results revealed that the ELW had higher holocellulose, cellulose, and lignin contents, and the ILW had the highest extractive content.

Liquefaction and Characteristics of Liquefied Residue

Residue content

To explore the difference in liquefaction behaviors between the ELW and ILW, liquefaction reaction was carried out in glycerol/methanol binary solvent with sulfuric acid (1.75%) as catalyst for 7 min. As shown in Fig. 4, at 140 °C, the residue content for the ELW and ILW were 17.6 and 10.5%, respectively. For comparison, the residue contents for extractive-free wastes were higher than that for controlled samples after liquefaction. The residue content increased dramatically when the liquefaction temperature was increased to 180 °C. This may be due to the recondensation reactions taking place in the liquefaction of both the ELW and ILW. It was clear from Fig. 4 that the residue content for ELW was much higher than that for ILW, and significant difference was found between the ELW and ILW.

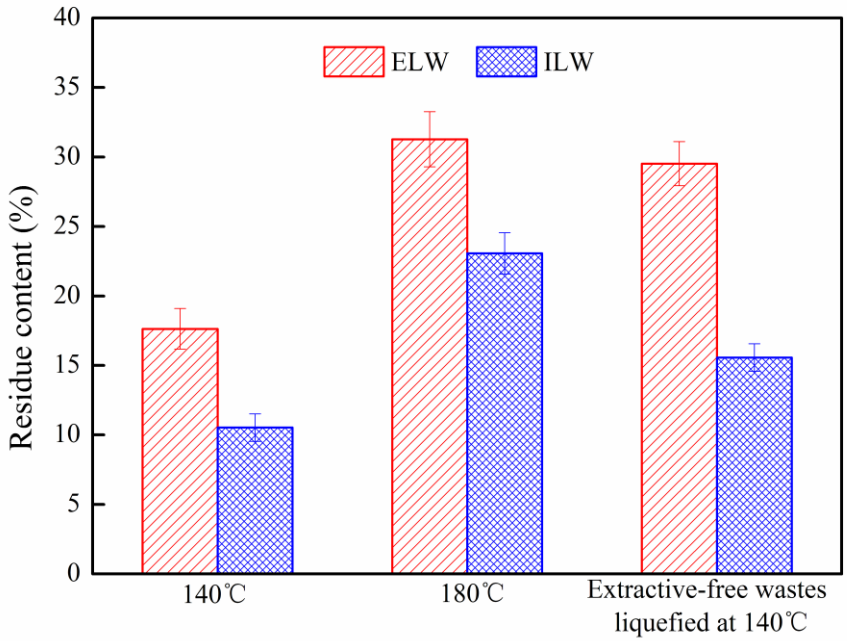

Fig. 4. Residue content for ELW and ILW at various liquefaction conditions

Residue characteristics

The SEM images of the liquefied residues are shown in Fig. 5. The liquefied residue for the ELW (Fig. 5a) showed broken fiber bundles with many small granules (0.2 to 0.3 μm) on the smooth surface. In the image of residue for the ILW, broken parenchyma cells as well as fibers were observed, resulting in a larger surface area. No granules were observed in the relatively homogeneous texture, as shown in Fig. 5b. In terms of the granules observed in this study, Xiao *et al.* (2011) also observed many granules on the surface of microwave-assisted liquefied corn stover residue.

FT-IR was used to further characterize the liquefied residues obtained in this study. As shown in Fig. 6, significant differences were found in the four characteristics absorption bands (peaks at 1735, 1596, 1506, and 1456 cm^{-1}) of hemicellulose and lignin between spectra for the liquefied ELW and ILW residues.

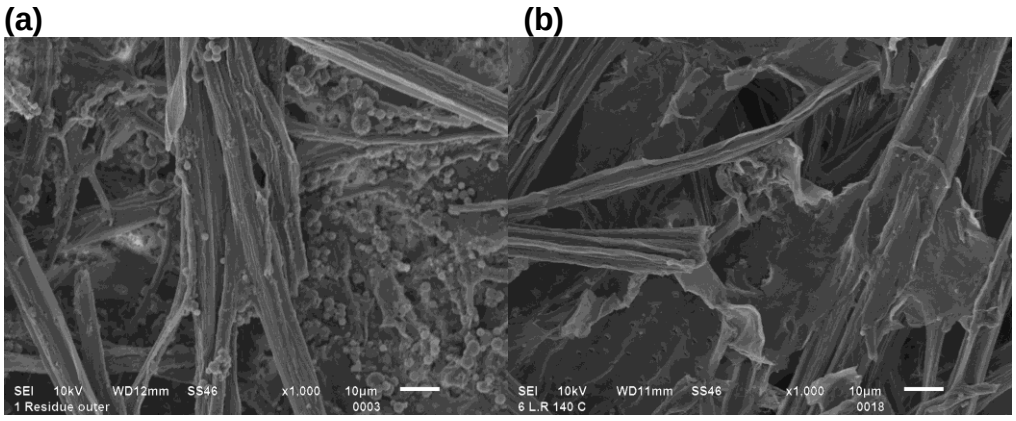

Fig. 5. SEM images of (a) liquefied ELW residue and (b) liquefied ILW residue. Liquefaction condition: time, 7min; temperature, 140 °C

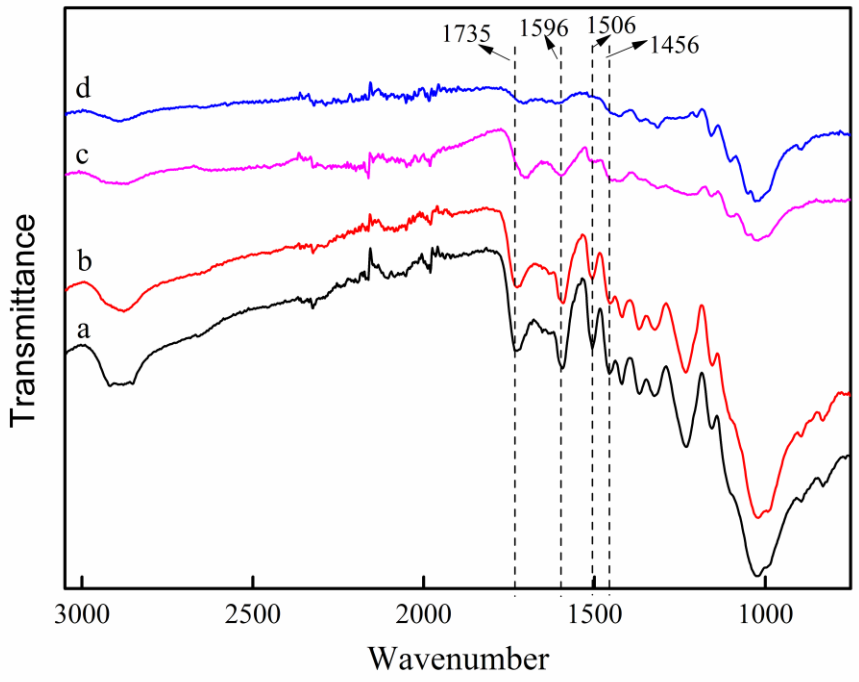

Fig. 6. FT-IR spectra of the (a) ELW, (b) ILW, (c) liquefied ELW residue, and (d) liquefied ILW residue. Liquefaction condition: time, 7min; temperature, 140 °C

The peaks at 1596 and 1456 cm^{-1} in the spectrum for the liquefied ILW residue disappeared, and bands at 1735 and 1506 cm^{-1} became a shoulder, indicating the cleaving of the functional groups in lignin/hemicellulose, such as syringyl and guaiacyl units, with the microwave liquefaction process. Absorption bands at 1735, 1596, and 1506 cm^{-1} in the spectrum for the liquefied ELW residue were observed, and the band at 1456 cm^{-1} consisted of a small shoulder. This was mainly due to the occurrence of recondensation and repolymerization resulting from interactions among decomposed hemicellulose and lignin fragments (uncondensed C-5 position at guaiacyl units). The difference in FT-IR spectra indicated that hemicellulose and lignin in the ILW were almost completely

decomposed through liquefaction; meanwhile, some hemicellulose/lignin compounds were still retained in the residue of the ELW after liquefaction.

Accordingly, the liquefaction rate of the wood components follows a decreasing order of hemicellulose, lignin, and cellulose. Though, hemicellulose and lignin could be easily decomposed at the initial reaction stage, they could also easily undergo recondensation under critical conditions (Pan *et al.* 2007; Zhang *et al.* 2012). Thus, the granules observed in this study may be attributed to the recondensed hemicellulose/lignin derivatives. These observations were similar to findings in the case of aqueous ethanol autocatalytic organosolv pulping, for which Zhang (2003) noticed some spherical sediment on the fiber surface, and she argued that the spherical granule was a lignin scrap fraction. Usually, the recondensation reactions of hemicellulose/lignin have been found to occur under critical liquefaction conditions such as higher temperature (160 to 180 ^{o}C) and longer reaction time (Niu *et al.* 2011). However, with the same liquefaction conditions, recondensation reactions were non-existent in the liquefaction of ILW in the present study. This may be due to the difference in bamboo characteristics and chemical components between the bamboo wastes.

Analysis of Liquefaction Behavior

As for the three cell types in bamboo, vessels have the largest lumen size (120 to 125 μm), followed by parenchyma (29.1 to 38.4 μm), then fiber (7.8 to 8.9 μm) according to the analysis of anatomical characteristics. It is generally considered that the lumen size of cells has a strong relationship with the permeability of bamboo. Thus, compared to the ELW, the ILW which has higher vessel and parenchyma percentages could provide much more pathways of solvent absorption, resulting in a much more uniform distribution of the reagents within the bamboo. Thus, the uniform distribution of reagents along with the uniform temperature distribution induced by microwave heating enhanced the liquefaction extent of the ILW. Moreover, because cellulose is the main resistance to solvolysis, the lower cellulose content in the ILW may also accelerate the liquefaction rate and contribute to lower residue content.

For comparison, the compact structure of the ELW had a negative effect on the solvent absorption. Meanwhile, the higher cellulose and lignin content resulted in multiple solvolysis processes involving degradation and recondensation in the liquefaction of ELW. Therefore, the complex chemical reactions because of the poor permeability and high cellulose and lignin contents attributed to the higher residue content of the ELW. However, there was no obvious evidence in this experiment that the extractive-free raw materials had higher residue content than that for the control samples.

CONCLUSIONS

1. Significant difference was found in anatomical characteristics between the ELW and ILW. The ELW tissue consists of smaller vascular bundles accompanied with larger fiber structures compared to the ILW.
2. The ILW had higher vessel and parenchyma proportions, while the ELW had higher fiber proportion. The lumen size of the parenchyma and fiber in the ILW was larger, resulting in a porous tissue with better permeability.

3. The holocellulose, cellulose, and lignin contents for the ELW were higher than those for the ILW. The ILW had higher hot-water and alcohol-toluene extractives.
4. The residue content for the ELW was much higher than that for the ILW; recondensation took place during the liquefaction of ELW.
5. The results of porous tissue with better permeability of the ILW obtained in this study may provide possible explanations to the lower liquefied residue content.
6. The results of the anatomical characteristics and chemical components may affect the reaction kinetics of the ELW, which resulted in multiple solvolysis processes.

ACKNOWLEDGMENTS

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