

# Investigation of Liquefied Wood Residues Based on Cellulose, Hemicellulose, and Lignin

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**ABSTRACT:** Chinese eucalyptus was subjected to a liquefaction process using glycerol/ethylene glycol (EG) as liquefaction solvent. The effects of various liquefaction conditions, including reaction time, liquefaction temperature, acid concentration, and liquor ratio on the chemical composition of liquefied wood residues were studied. The results showed that the whole liquefaction process took place in two stages, the liquefaction yield of wood depended on the reaction temperature, acid concentration and liquor ratio. With increased acid concentration the

liquefaction yield, acid-insoluble lignin, and hemicellulose content of the residues were increased, and the relative content of cellulose was decreased. Fourier transform infrared (FT-IR) analyses of the residues showed that hemicellulose and lignin were almost decomposed at the initial stages of reaction. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 850–856, 2012

**Key words:** liquefied wood residue; cellulose; lignin; hemicellulose; polyhydric alcohol

## INTRODUCTION

The depletion of fossil fuels in the future is a major motive to hunting for alternative renewable resources which are sustainable in nature. Therefore, a large number of efforts have been made to develop novel techniques to convert renewable resource into useful products. The conversion technologies for utilizing biomass can be classified as follows: thermochemical processes, biochemical processes, and agrochemical processes.<sup>1</sup> Thermochemical processes are most commonly used and can be further subdivided into gasification, pyrolysis, supercritical fluid extraction, and direct liquefaction.<sup>1</sup> Two methods have been developed for direct liquefaction: one is noncatalyzed liquefaction at an elevated temperature (250–500°C) under high pressure. The other one is acid-catalyzed liquefaction, with a correctly selected solvent system and a catalyst, the biomass can be liquefied under atmospheric pressure at moderate temperature

(120–180°C).<sup>2–7</sup> Polyhydric alcohols, such as ethylene glycol and glycerol, are commonly used as the liquefaction solvent. Liquefied wood using polyhydric alcohols as solvent can be used to manufacture polyurethane and epoxy resins which have been reported to be more biodegradable than petrochemical polymers.<sup>8–11</sup>

Biomass consists of three main components (cellulose, hemicellulose and lignin) together with trace amount of extractives and minerals. Through the liquefaction process, the three major components decompose into small molecules. A model compound of cellulose powder, steamed lignin and the mixtures of these two components in the presence of polyhydric alcohol have been investigated.<sup>12</sup> The liquefaction of lignin with phenol has been studied using guaiacylglycerol- $\beta$ -guaiacyl ether as a model compound.<sup>13,14</sup> Pan<sup>15</sup> characterized the liquefied wood residues from different liquor ratios and cooking methods. Previous studies indicated that it was important to study the characteristics of the three components after liquefaction for a better understanding of biomass liquefaction process. However, a comprehensive study on the mechanism of wood liquefaction in the presence of polyhydric alcohol has not yet been performed, which is probably because the recondensation reaction occurred simultaneously among the wood components themselves during liquefaction. The overall rate of biomass liquefaction is considered as a sum of the individual rates of the three components, the degradation rate of each component could be significantly different,

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which in turn would cause the liquefaction rate to change as the reaction proceeds. Kim<sup>16</sup> found that newspaper liquefaction did not follow first order reaction kinetics, assumed this could be due to the different degradation rates of the various components. Previous studies<sup>16–18</sup> reported that there was a recondensation reaction between the liquefaction fragments resulting in an increased amount of residue, but the residual components content had not been studied well, which made it difficult to understand wood liquefaction accurately. In this article, we reported the effects of the reaction time, liquefaction temperature, acid concentration and liquor ratio on the wood liquefaction yield and the chemical compositions of liquefied wood residues. Quantitative analyses of major components of the residues were conducted, including cellulose, hemicellulose, lignin, and reducing sugar. The degree of crystallinity, which indicated the crystal and amorphous structure changed in cellulose of the residues, was studied by X-ray diffraction (XRD). The Fourier transform infrared spectrometry (FT-IR) was used to investigate the functional groups of the residues.

## EXPERIMENTAL

### Materials

Chinese eucalyptus from Guangxi province (Southern China) was used as a raw material. The wood sample was milled in a knife mill to pass through a 165- $\mu\text{m}$  sieve. Ethylene glycol and glycerol were used as the liquefaction reagents. Sulfuric acid (98%) was used as the acidic catalyst. All other chemicals in this study were reagent grade and were used without further purification.

### Liquefaction reaction

The wood was dried at 105°C for 24 h before use. The liquefaction was carried out in a three-neck flask equipped with a mechanical stirrer, reflux condenser, and thermometer. The mixture of liquefaction solvents and sulfuric acid was added to the flask. The concentration of sulfuric acid was calculated as weight content (%) based on the amount of the mixed solvent. The flask was immersed in an oil bath and preheated at a set temperature. A known quantity of wood powder was then added to the flask under stirring. The liquefaction was conducted under constant stirring and refluxing for a specified time. After the reaction, the flask was immersed in cold water to quench the reaction.

The sample was diluted with an excess of methanol,<sup>15</sup> the liquefied wood residue (LR) was separated by filtration, and then rinsed thoroughly with methanol. The LR was dried in oven at 105°C to constant

weight and weighed for the determination of the liquefaction yield (LY), LY was calculated with the following equation:

$$\text{Liquefaction yield (\%)} = \left(1 - \frac{\text{Mass of residue}}{\text{Mass of raw material}}\right) \times 100\% \quad (1)$$

### Chemical analyses

The amounts of hemicellulose, cellulose, and lignin in LR samples were determined according to the following method (the amounts of holocellulose and acid-insoluble lignin were determined by using the Chinese GB standard GB/T 2677, the percentages of cellulose, hemicellulose and acid-insoluble lignin were calculated based upon the mass of the extracted LR):

1. Analysis of extractives. The LR samples were extracted with ethanol-benzene mixture (2 : 1 in volume) for 6 h in a Soxhlet apparatus. After that, the sample was dried in an oven at 105°C until a constant weight was obtained. The weight difference of the LR before and after the extraction was the amount of the extractives.
2. Analysis of lignin. Extracted LR samples were hydrolyzed with 72% sulfuric acid at 18–20°C for 2 h (1 g of sample and 15 mL of sulfuric acid). The acid was diluted to a final concentration of 3% (addition of 545 mL of water) and the mixture boiled for 4 h. The residual material was cooled and filtered. The solids were dried to constant weight at 105°C and determined as the amount of acid-insoluble lignin.
3. Analysis of holocellulose and hemicellulose.<sup>19–21</sup> 0.6 g of NaClO<sub>2</sub>, 0.5 mL of acetic acid, and 65 mL of water were added to 2 g of extracted LR sample, and the temperature was held at 75°C for 1 h. After that, the mixture of NaClO<sub>2</sub> and acetic acid was added every an hour until the LR became white, the residual material was cooled and filtered. Hemicellulose was extracted from holocellulose using aqueous sodium hydroxide (NaOH) (0.5 mol/L) and the temperature was held at 80°C for 3.5 h. After that, the sample was washed using DI water until no more Na<sup>+</sup> was detected (indicated by the pH value of the solution approaching 7), and then it was dried to a constant weight. The difference between the LR sample weight before and after this treatment was the hemicellulose content.
4. Analysis of cellulose.<sup>22,23</sup> The content of cellulose was determined by the nitrate method. A solution of 25 mL of mixture of ethyl alcohol and nitric acid (4 : 1, v/v) was used as the solvent for 1 g of extracted LR, refluxing and

extracting for five times at 100°C and 1 h of each times.

5. Analysis of reducing sugar.<sup>24</sup> The 3, 5-dinitrosalicylic acid (DNS) spectrophotometric method was used by measuring the absorbance at 480 nm<sup>25,26</sup> in an 2550 UV-visible spectrophotometer (Shimadzu, Japan) provided with a UV-visible Chem Station software, the resulting value of reducing sugar content being expressed as the equivalent glucose content.

### FT-IR spectroscopy

Infrared spectra of the LR samples were investigated by using Fourier Transform Infrared Spectrophotometer (Perkin-Elmer, Spectrum one). All measurements were carried out using the KBr disc technique.

### X-ray measurements

The LR samples from different liquefaction conditions were pressed into disks and analyzed by a D/max-1200 (Rigaku, Japan) Diffractometer with Ni-filtered CuK $\alpha$  radiation ( $\lambda = 0.1541$  nm) generated at 40 kV and 20 mA. The X-ray diffractograms (XRD) were recorded from 0° to 40° at a scanning speed of 1°/s and sampling rate of 2 data/s. The degree of crystallinity was determined from the ratio of the integral intensity of crystalline portions to the total intensity of the sample over a range of  $2\theta = 4\text{--}60^\circ$ .<sup>23,27</sup>

$$\text{CrI, \%} = \frac{I_{002}}{I_{002} - I_{am}} \times 100\% \quad (2)$$

where  $I_{002}$  is the intensity of the diffraction from the (002) plane at  $2\theta = 22.5^\circ$ , which represents diffraction intensity of crystallizing area,  $I_{am}$  is the intensity of the amorphous background scatter measured at  $2\theta = 18^\circ$ .

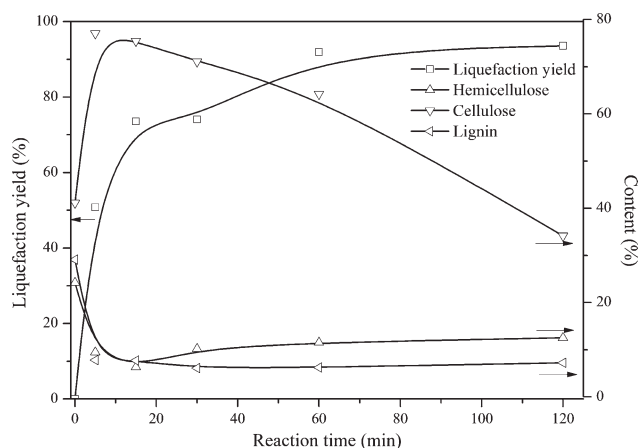
### Scanning electron microscopy

The structure and the surface morphology of the liquefied wood residues and original wood powder were taken with FEI Quanta400 SEM without coating.

## RESULTS AND DISCUSSION

### Effect of time

The composition of the three major components of the eucalyptus powder was 41% cellulose, 31% hemicellulose, 29% acid-insoluble lignin, and 5.1% reducing sugar. The average values of acid-insoluble lignin, hemicellulose, and cellulose contents of the LR and the liquefaction yield at different liquefaction



**Figure 1** The effect of the reaction time on the liquefaction yield and chemical composition of liquefied wood residues. Note: liquor ratio = 4 : 1, H<sub>2</sub>SO<sub>4</sub> 3%, 160°C.

time are shown in Figure 1. The liquefaction was initiated immediately from the beginning of the process. Up to 73% of the wood components were removed and converted to soluble components within 30 min, and the reaction rate thereafter decreased. The reducing sugar content of the LR is presented in Table I. The value found for LR increased first then decreased as the liquefaction time increased. Some researchers have reported that free-radical fragments are formed in the degradation of lignin under acidic conditions, and are easily condensed to form char when the concentration of the degradation fragments is high enough.<sup>28,29</sup> However, both the liquefaction yield and the content of lignin from the LR did not change much, and condensation reaction was not observed within 120 min, since lignin condensate and lignin cannot be separately determined in the analytical method adopted. This could be due to the reaction between the hydroxyl groups of glycerol and lignin which can hinder the recondensation of the free-radical fragment, and increasing the liquefaction yield.<sup>7,16</sup> A significant amount of lignin and hemicellulose were liquefied during the liquefaction process, so the relative cellulose content increased. Figure 2 shows X-ray diffractograms of the wood and the LR under different reaction time. The major diffraction signals of cellulose occur at around 14.8, 16.7, 20.7, and 22.5°, normally assigned to the diffraction planes 101, 10 $\bar{1}$ , 002, and 040, respectively.<sup>30</sup> Because there were still small amounts of hemicellulose and lignin in the LR, the peaks of 101 and 10 $\bar{1}$  diffraction planes in the X-ray diffractograms of LR overlapped each other and formed one broad peak.<sup>30</sup> It is important to note that the crystallinity index (CrI) is used to indicate the relative rather than the absolute amount of the crystalline region in cellulose.<sup>30</sup> The X-ray crystallinity index of the LR from different liquefaction conditions are also presented in Table I. The CrI of the LR

**TABLE I**  
The Content of Reducing Sugar (%) and X-ray Crystallinity Index (CrI, %) of the LR from Different Liquefaction Conditions

|                | Liquefaction time (min) <sup>a</sup> |       |       |       |       | Acid concentration (%) <sup>b</sup> |       |       |       |
|----------------|--------------------------------------|-------|-------|-------|-------|-------------------------------------|-------|-------|-------|
|                | 5                                    | 15    | 30    | 60    | 120   | 1                                   | 2     | 3     | 6     |
| CrI            | 61.05                                | 54.79 | 43.25 | 38.47 | 34.65 | 60.65                               | 61.51 | 54.79 | 30.58 |
| Reducing Sugar | 5.2                                  | 3.2   | 4.5   | 4.81  | 4.02  | 1.9                                 | 2.1   | 3.2   | 6.3   |

<sup>a</sup> The liquefaction temperature is 160°C, polyhydric alcohol/wood = 4 : 1 (w/w), H<sub>2</sub>SO<sub>4</sub> 3 %.

<sup>b</sup> The liquefaction temperature is 160°C, polyhydric alcohol/wood = 4 : 1 (w/w), liquefaction time is 15 min.

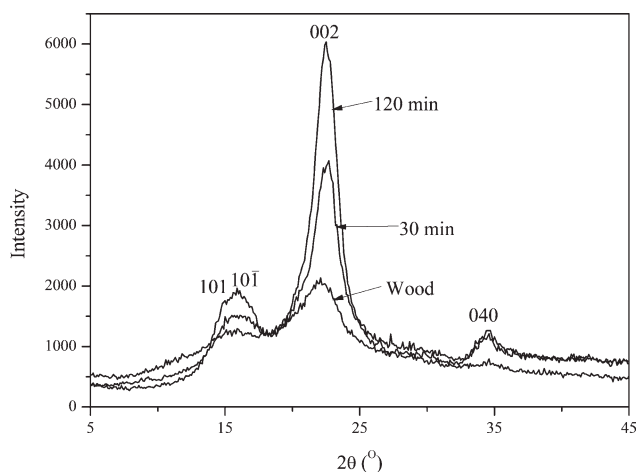
was higher than that of the original wood powder (28.78) because the relative portion of the crystalline region of cellulose increased when the lignin in the amorphous region decreased, and decreased as the liquefaction time increased. It can be seen that the whole reaction process took place in two stages, the rapid liquefaction stage could be attributed to the susceptible components in the wood (lignin, hemicellulose, and amorphous zones of cellulose) reacted with polyhydric alcohols,<sup>8,17</sup> while the second stage, which is characterized by a slow decrease of LR content, mainly depended upon degradation of the crystalline regions of the cellulose.

Figure 3 shows the FT-IR spectra of the LR obtained under different reaction times. The strong bands observed at 1596 and 1506 cm<sup>-1</sup> are attributable to the aromatic skeletal vibration of lignin,<sup>31</sup> and the band at 1216 cm<sup>-1</sup> corresponds to the methoxyl groups of lignin.<sup>32</sup> The intensities of the bands at 1596, 1506, 1458, and 1236 cm<sup>-1</sup> weakened and then disappeared as the liquefaction time increased. It is suggested that the lignin in the wood should be completely transferred into the liquid phase. Both bands corresponding to the methylene group (1430 and 1370 cm<sup>-1</sup>) and the stretching of C—O of cellulose (1163 and 1058 cm<sup>-1</sup>) were weaker but still can

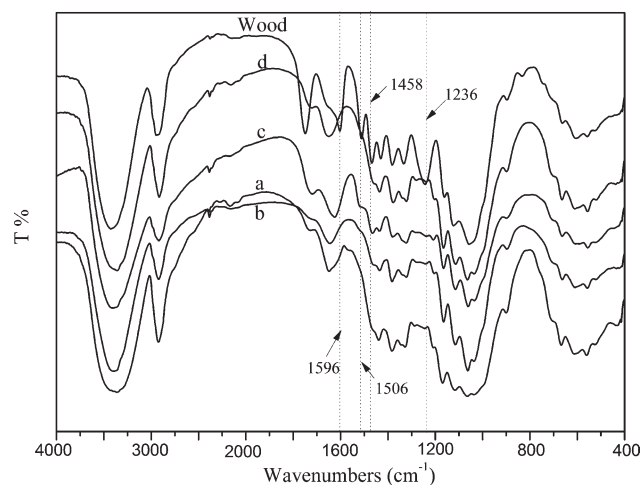
be observed, which indicated that the degradation of cellulose was not completed.

### Effect of temperature

The liquefaction yield increased as the liquefaction temperature increased from 140 to 180°C. As showed in Figure 4, the hemicellulose, cellulose, and acid-insoluble lignin contents for the LR decreased with increasing liquefaction temperature. Lignin and hemicellulose were the most reactive wood components in the liquefaction reaction, and were almost completely decomposed in 15 min (Fig. 1). It is clear from the Figure 4 that the degradation rate of cellulose was the lowest, with about 12% of it being degraded from 140 to 180°C, the CrI of the LR decreased with increasing liquefaction temperature (data not shown). Glycerol could reduce the surface tension of the liquefaction solvent at high temperature,<sup>33</sup> thus not only promoting penetration of the sulfuric acid into the wood samples especially the crystalline regions of the cellulose but also accelerating diffusion of small molecules from the wood into the liquefaction solvent, causing a uniform distribution of the reagents within the wood. Furthermore, as the reaction temperature is raised, the vapor pressure of the system is also increased, especially for low boiling point alcohols.

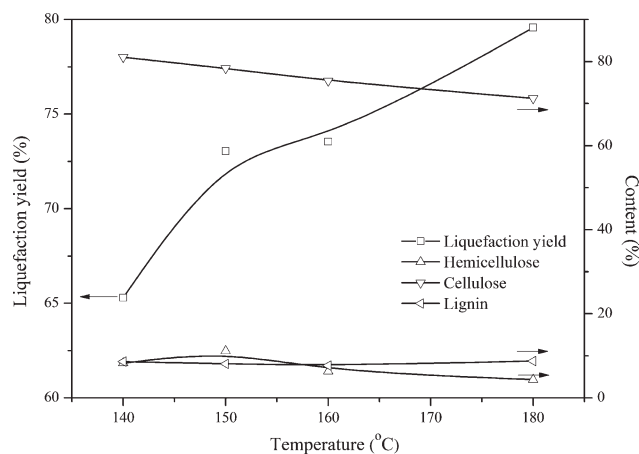


**Figure 2** X-ray diffractogram of wood and the liquefied wood residue under different reaction time. Note: liquor ratio = 4 : 1, H<sub>2</sub>SO<sub>4</sub> 3%, 160°C.



**Figure 3** FT-IR spectra of residues at different reaction times. Liquefaction time: a, 5 min; b, 15 min; c, 30 min; d, 60 min. Note: liquor ratio = 4 : 1, H<sub>2</sub>SO<sub>4</sub> 3%, 160°C.

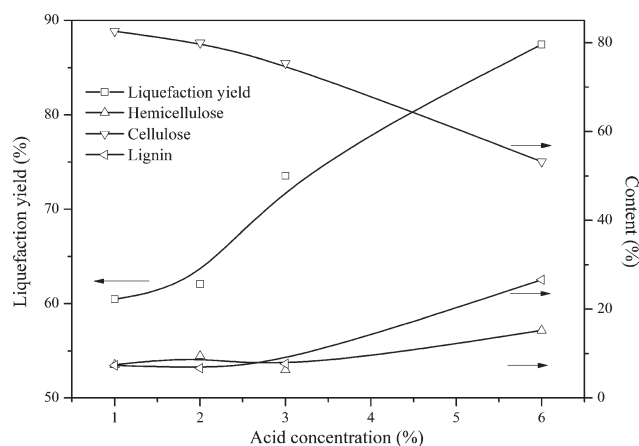




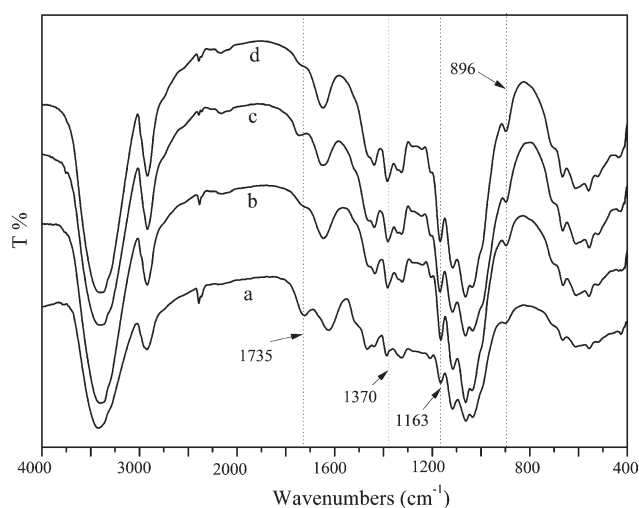
**Figure 4** The effect of the liquefaction temperature on the liquefaction yield and chemical composition of liquefied wood residues. Note: liquor ratio = 4 : 1,  $\text{H}_2\text{SO}_4$  3%, 15 min.

### Effect of catalyst

It is apparent that the liquefaction yield increased with increasing content of the sulfuric acid. It is known that the liquefaction of wood in the presence of organic solvents is a solvolysis process and solvents play important roles in the decomposition of wood.<sup>34</sup> Therefore, the presence of a catalyst is very important not only to accelerate liquefaction reaction but also to reduce the liquefaction temperature and residue. It is evident from the Figure 5 that the liquefaction yield increased drastically with an increase of the catalyst dosage. The cellulose content of the LR decreased rapidly with an increase in acid concentration, but the mean hemicellulose, lignin and reducing sugar content of the LR and the liquefaction yield increased. It was also noted that the LR with a sulfuric acid concentration of 6% had the lowest CrI (Table I). Apparently, the CrI result of the LR was consistent with the cellulose content of



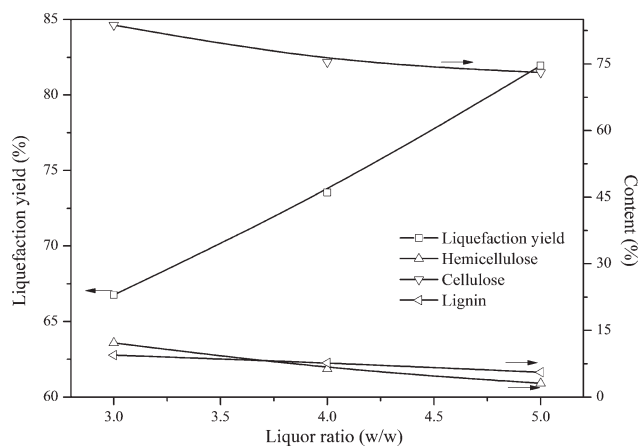
**Figure 5** The effect of the acid concentration on the liquefaction yield and chemical composition of liquefied wood residues. Note: liquor ratio = 4 : 1, 160°C, 15 min.



**Figure 6** FT-IR spectra of residue at different acid concentration: a, 6%; b, 3%; c, 2%; d, 1%. Note: liquor ratio = 4 : 1, 160°C, 15 min.

the LR. High concentrations of acid enhanced the recondensation reactions for the liquefied fragments resulting in an increase in the amount of insoluble residue (repolymerization) after liquefaction.<sup>18</sup> However, polyhydric alcohol not only reduced the amount of undissolved residue but also retarded recondensation for free-radical fragment (degradation).<sup>7</sup> When the acid concentration was less than 3%, degradation became dominant. As a result, the residue percentage decreased rapidly. When the acid concentration was increased to 6%, the concentration of liquefied fragments became higher and the repolymerization reaction took precedence. From these results, it can be concluded that 3% acid concentration is the optimum concentration in this system.

Figure 6 shows the FT-IR spectra of the LR with different acid concentration. It is clear that the bands of different functional groups of cellulose such as 1430, 1370, 1163, 1058, and 896  $\text{cm}^{-1}$  are still found after liquefaction, which indicates that most of the LR is presented as nonreacted cellulose. The peak intensities of the functional groups of cellulose decreased as the amount of sulfuric acid increased. The band at 1735  $\text{cm}^{-1}$  corresponding to carbonyl groups of uronic acid esters, which were formed from the reaction between the acid and hemicellulose during the liquefaction process.<sup>15,17,32</sup> The intensity of the carbonyl peak (1735  $\text{cm}^{-1}$ ) in these compounds may reflect the degree of repolymerization of decomposed components of hemicellulose. The strong absorption at 1735  $\text{cm}^{-1}$  which occurred in spectra of untreated wood became a small shoulder in the spectra of LR as the reaction proceeded. However, the intense absorbance at 1735  $\text{cm}^{-1}$  decreased first and then increased. It is suggested that more and more decomposed components of hemicellulose could be repolymerized in the late



**Figure 7** The effect of the liquor ratio on the liquefaction yield and chemical composition of liquefied wood residues. Note:  $\text{H}_2\text{SO}_4$  3%, 160°C, 15 min.

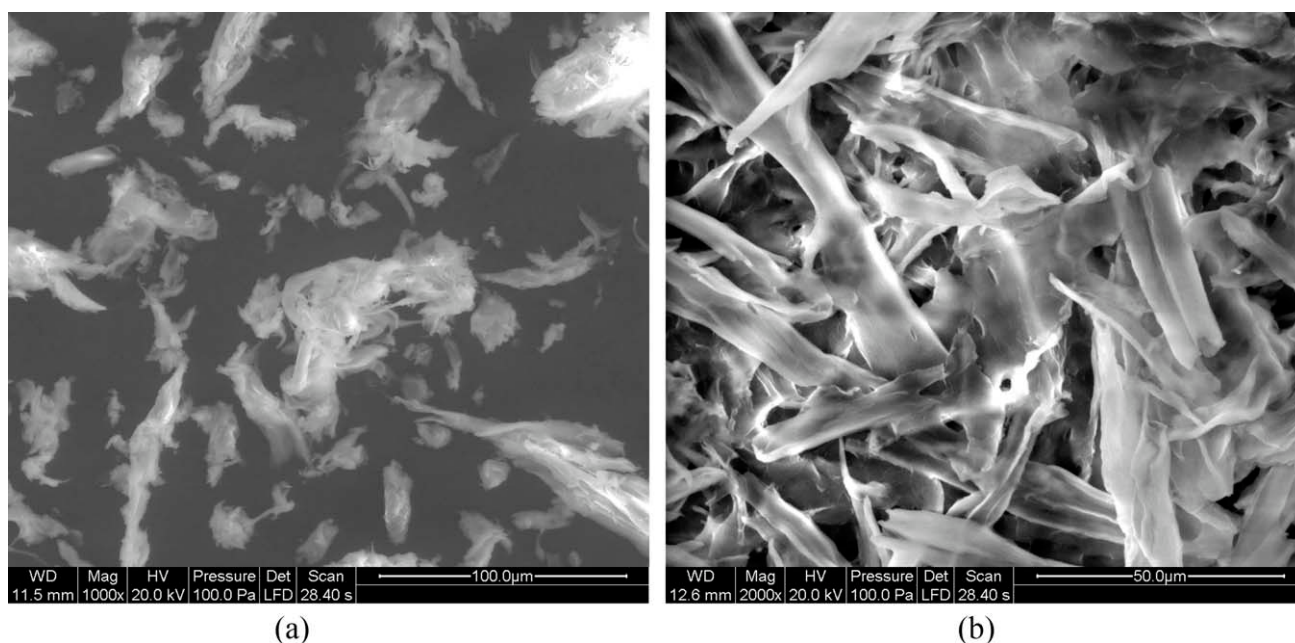
liquefaction stage. The absorbance at 1596 and 1506  $\text{cm}^{-1}$  corresponding to aromatic skeletal vibrations (lignin)<sup>31</sup> disappeared which is inconsistent with the data from Figure 5. One plausible explanation was that the LR contained many kinds of acid-insoluble substances other than acid-insoluble lignin. Another possible reason was that the dehydration of carbohydrates resulted in acid insoluble residues which were sometimes calculated as acid-insoluble lignin.<sup>17</sup> Thus, it is suggested that these residues could mainly be derived from cellulose in acid-catalyzed liquefaction, cellulose mainly underwent acid hydrolysis reactions in addition to other side reactions, such as oxidation, which led to the decomposition of cellulose into small compounds.

### Effect of liquor ratio

Figure 7 shows the effect of the liquor ratio on the liquefaction yield and chemical composition of LR. In general, the liquefaction yield is sensitive to the liquor ratio (solvent/wood, w/w). The liquefaction yield increased along with the increase of the liquor ratio. A solvent to wood ratio of 4/1 has generally been used for woody and herbaceous plants. From Figure 7, the results indicate that the acid-insoluble lignin contents of the LR consistently decreased as the liquor ratio increased. The liquefaction yield was lowest when the liquor ratio was 3/1, which indicated that the liquefaction was incomplete. It is probably because solvolytic capability of liquefaction solvent decreased and viscosity dramatically increased when the liquor ratio decreased, which would limit reaction rates and present a challenge to mixing. Therefore, with an increase in liquor ratio, the excess amount of polyhydric alcohols can hinder the recondensation reaction of the lignin. Furthermore, it is possible that the polyhydric alcohols reacted with the free-radical lignin's fragments to form an intermediate insoluble new substance that was retained in the residue in the process of solvolysis during wood liquefaction, which in turn affected the acid-insoluble lignin determination. However, an increase in liquor ratio means that more chemicals are used and, accordingly, higher capital investments are required.

### Scanning electron microscopy

Figure 8 shows the micrographs of the untreated wood and the liquefied wood residue after the



**Figure 8** SEM micrographs of wood (a) and liquefied wood residues (b). Liquefaction conditions: liquor ratio = 4/1,  $\text{H}_2\text{SO}_4$  3%, 160°C, 120 min.

reaction. The starting material (a) consisted of a mix of torn fibers, many small fragments of cell wall components, while the remains left after the liquefaction (b) showed many large fibers of uniform size. This indicated that broken fibers and most small fragments attached on the surface of the wood powder were completely removed during the reaction and that only the most resistant fibers remain in the residue.

### CONCLUSIONS

The mean value of acid-insoluble lignin, hemicellulose, cellulose content of the LR and the liquefaction yield were carried out to understand the liquefaction process of wood in the system using ethylene glycol as liquefaction a liquefaction solvent. The whole liquefaction process took place in two stages. The rapid liquefaction stage due to removal of lignin, hemicellulose and amorphous zones of cellulose, and another stage that was characterized by the slow decrease of residue content, mainly depended upon the crystalline regions of the cellulose. The sulfuric acid concentration and liquor ratio had a greater influence on the liquefaction yield rather than the reaction temperature. The characteristic of the LR was influenced by many factors such as liquefaction temperature, amount of the sulfuric acid and liquor ratio. With increase in acid concentration, the liquefaction yield, the hemicellulose and acid-insoluble lignin contents of LR increased, content of cellulose of the LR, by contrast, decreased. The degrees of wood liquefaction depended on the degradation of crystalline regions of the cellulose in the wood.

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