Selective Liquefaction of Lignin from Bio-ethanol Production Residue Using Furfuryl Alcohol

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In order to obtain "clean" liquefied lignin, selective liquefaction of lignin from bio-ethanol production residue (BEPR) was conducted using an aromatic solvent, furfuryl alcohol. The effects of liquefaction time, temperature, and liquid ratio on the liquefaction yield were investigated. The results indicated that with the increasing of liquefaction temperature (120 to 170 °C) or liquid ratio (3 to 5:1), the liquefaction yield of lignin (LYL) increased, respectively. Liquefaction times of 15 to 120 min had no significant effect on the liquefaction yield. When liquefaction was conducted at 170 °C for 15 min with a ratio of 5/1 liquefying solvent to raw material, the LYL reached its highest level of 80.23%. Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Gel permeation chromatography (GPC) analyses confirmed that the liquefaction process had great selectivity for lignin. Ash and carbohydrates in the raw material could be removed as liquefied residue.

Keywords: Lignin; Bio-ethanol production residue; Furfuryl alcohol; Liquefaction; Selectivity

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INTRODUCTION

The bio-ethanol industry is developing rapidly due to the energy crisis and the global warming issue, and renewable lignocellulosic biomass has received great attention as a feedstock for producing fuel ethanol (Boopathy and Dawson 2008; Gonzalez *et al*. 2011). In this process, a large amount of residue is produced while the carbohydrates are converted into ethanol. The residue is mainly composed of lignin, ash, and some carbohydrates due to the incomplete bio-conversion, and usually the lignin content is around 60%. The residue amount accounts for almost 30% of the raw materials. Therefore, the efficient utilization of the residue would be helpful for the fuel ethanol industry to make profits and for plant resources to become competitive with petroleum fuels (Kleinert *et al*. 2009; Lü *et al*. 2011).

Liquefaction is a promising technique developed in the past few years to utilize the unused lignocellulosic resources (Liang *et al*. 2006; Niu *et al*. 2011; Zheng *et al*. 2012). Also, conversion of lignin into liquid would be an efficient way to utilize lignin waste. Such an approach may improve the reactivity of lignin and broaden its application in phenol formaldehyde resins, polyurethanes, and other fields. Liquefaction of biomass can be achieved in the presence of organic solvents, such as phenols and polyols (Briones *et al*. 2011; Lin 2004; Pan 2010; Tejeda-Ricardez *et al*. 2003). Using lignin as a substitute for phenol is very tempting because phenol is produced mainly from fossil fuels. Nevertheless, lignin's potential application is closely related to its purity, molecular size and distribution, and the amounts of different chemical functional groups (Buranov and Mazza 2008). The impurities, such as carbohydrates and ash, will act as obstacles in lignin's further application, such as lignin-based PF resin (Park *et al*. 2008; Zheng *et al*. 2007). Therefore, efficient selective liquefaction technologies of lignin from bio-ethanol production residue (BEPR) would be significant in the context of lignin application.

Furfuryl alcohol is a reduction product from furfural, which can be obtained from hydrolysis of pentosan-rich biomass. Due to its aromatic heterocycle, furfuryl alcohol could be used as a solvent for the separation of aromatic and aliphatic hydrocarbons (Morawski *et al*. 2002). Lignin was selectively liquefied from BEPR using furfuryl alcohol, and the liquefied products were characterized. The effects of different liquefaction conditions, such as liquefaction time, temperature, and liquid ratio (liquefying solvent/raw material) on the liquefaction yield are also discussed.

EXPERIMENTAL

Materials

Lumping BEPR was obtained from a large-scale pilot plant that converts cornstalk into bio-ethanol. Its lignin and ash content were determined to be 62.18% and 9.91% according to TAPPI T222 and TAPPI T211, respectively, and the remaining component was carbohydrates due to incomplete consumption in the enzymatic hydrolysis process. After being smashed and sieved, the material smaller than 80 mesh was oven-dried at 105 °C for 12 h and kept in a desiccator at room temperature before use. All chemicals used were analytical grade reagents.

Methods

Liquefaction of BEPR

The liquefaction was carried out in a 100-mL, three-neck flask equipped with a stirrer, refluxing condenser, and thermometer. Furfuryl alcohol was added according to varying liquefying solvent/raw material ratio (3:1, 4:1, 5:1) in the flask and preheated to 120–170 °C with a variable transformer. Then 3 g of BEPR was added to the flask under stirring, and this time was considered to be the starting point of liquefaction. After the presetting time of 15 to 120 min, the flask was immersed in ice water to quench the liquefaction reaction. The acid catalyst would promote the decomposition of cellulose (Yamada and Ono 2001; Zhang *et al*. 2006) and improve the liquefaction yield, but in the meantime lignin fragments are more apt to condense in acid medium (Chen and Lu 2009; Ge *et al*. 2003; Jasiukaitytė *et al*. 2010), which is adverse to the selective liquefaction of lignin. Moreover, furfuryl alcohol tends to polymerize under acidic circumstances. Consequently, acid catalyst was not used in the furfuryl alcohol system. Also, the liquefaction of bio-ethanol residue in polyols (polyethyleneglycol/glycerol cosolvent) was conducted as a furfuryl alcohol case for comparison. The ratio of PEG to glycerol was fixed at 80/20 (w/w) (Jin *et al*. 2011).

Measurement of liquefied residue content (LRC) and liquefaction yield of lignin (LYL)

The liquefaction yield was evaluated by two indexes: liquefied residue content (LRC) and liquefaction yield of lignin (LYL). The resultant was diluted by an excess amount of 80% 1,4-dioxane. Then the dilution was separated to residue and filtrate with a Toyo GA100 glass filter. The residue was rinsed thoroughly with the dioxane and oven-dried at 105 °C to a constant weight. LRC and LYL were calculated with the following equations:

$$\text{LRC (\%)} = \text{Mass of liquefied residue}/\text{Mass of raw material} \times 100 \quad (1)$$

$$\text{LYL (\%)} = (1 - \text{Liquefied residue content})/\text{Lignin content of BEPR} \times 100 \quad (2)$$

Measurement of lignin content and ash content

The lignin and ash contents of liquefied product from furfuryl alcohol liquefaction in the range 120 to 170 °C were determined according to TAPPI T222 and TAPPI T211 standards, respectively.

Characterizations

Sample preparation

The filtrate was dried in a vacuum oven at 70 to 80 °C to remove furfuryl alcohol, dioxane, and water, and then the sample was obtained as the liquefied lignin. Another sample was the liquefied residue. Polyols had a very high boiling point and could not be removed in this way. Thus, the liquefied product in polyols liquefaction was not characterized.

Fourier transform infrared (FTIR) measurements

IR analysis was performed on a Magna 560 FT-IR spectrometer, which was made by Nicolet Company, and a KBr press method was used.

X-ray diffraction (XRD) analysis

The BEPR and the liquefied residue were scanned by using a D/max-2200VPC X-Ray Diffraction machine (Rigaku, Japan) to evaluate the crystallographic structure. The sweep range was set at 5° to 70° with a step size of 0.02°. The scans proceeded at 1° per second. The relative crystallinity index was calculated based on the Segal formula (Segal *et al*. 1959) as follows,

$$\mathrm{C_rI}(\%) = (I_{002} - I_{\mathrm{am}})/I_{002} \times 100 \quad (3)$$

where $\mathrm{C_rI}$ is the percentage of the relative crystallinity index. I_{002} is the diffraction intensity of the 002 side at 22.5° and I_{am} is the diffraction intensity due to the non-crystalline background at near 18°.

X-ray photoelectron spectroscopy (XPS) analysis

The BEPR, the liquefied residue, and the liquefied lignin were analyzed on a K-Alpha X-ray photoelectron spectroscopy machine (Thermo Fisher Scientific, USA), using a monochromatic Al Ka X-ray source (hv = 11254 keV) with a beam current of 6 mA and voltage of 12 kV. The measurements were conducted under a high vacuum of 10 to 8 Pa at room temperature. The atomic percentages of the elements presented were derived from high-resolution spectra run with a pass energy of 50 eV and a step of 0.1 eV.

Gel permeation chromatography (GPC) analysis

In order to improve the solubility, the samples were acetylated with a pyridine/ acetic anhydride (1:2, v/v) mixture for 72 h at room temperature without light or air. The solution was added dropwise into ether during stirring, then the acetylated product was precipitated and filtered with a G3 glass filter. After being dried in a vacuum oven at 40 to 50 °C, the acetylated product was dissolved in tetrahydrofuran (THF).

Molecular weight distributions of the BEPR and the liquefied lignin were determined by GPC (Agilent, USA) equipped with a JASCO UV-1575 detector at 254 nm and a tandem system of two columns (79911GP – 101 and 79911GP – 104). The mobile phase was THF, which had a flow rate of 1.0 mL/min. The column temperature was 30 °C, and the injection size was 20 μL. The molecular weights of the samples were calibrated by monodisperse polystyrene standards.

RESULTS AND DISCUSSION

Effect of Liquefying Solvents on the Liquefaction Yield

In the case of PEG and glycerol cosolvent, liquefied residue content was 58.40% (Table 1) when liquefaction was conducted at 140 °C for 15 min with the liquid ratio of 5:1. When furfuryl alcohol was used as the liquefying solvent, the liquefied residue content was 52.67%, lower than that of PEG/glycerol. However, both liquefaction methods had a highly liquefied residue content, which may be attributed to the high content of ash (9.91%, text 2.1) and crystalline cellulose (35.94%, text 3.4) in the raw material BEPR.

Table 1. Effect of Different Liquefaction Processes on the Liquefaction Yield

Solvent	Time min	Temperature °C	Liquid Ratio wt/wt	Residue Content %	LYL %
PEG + glycerol	15	140	5:1	58.40	--
Furfuryl alcohol	15	140	5:1	52.67	76.12
Furfuryl alcohol	30	140	5:1	53.33	75.06
Furfuryl alcohol	60	140	5:1	52.88	75.78
Furfuryl alcohol	90	140	5:1	52.39	76.57
Furfuryl alcohol	120	140	5:1	53.70	74.46
Furfuryl alcohol	15	120	5:1	57.06	69.06
Furfuryl alcohol	15	140	5:1	52.67	76.12
Furfuryl alcohol	15	160	5:1	51.39	78.18
Furfuryl alcohol	15	170	5:1	50.11	80.23
Furfuryl alcohol	15	170	3:1	55.51	71.55
Furfuryl alcohol	15	170	4:1	51.88	77.39
Furfuryl alcohol	15	170	5:1	50.11	80.23

Effect of Liquefaction Conditions on the Liquefaction Yield

The influence of different liquefaction conditions on the liquefaction yield is given in Table 1. It can be seen that the liquefied residue content (LRC) and liquefaction yield of lignin (LYL) showed no obvious differences among the liquefaction time of 15 to 120 min when furfuryl alcohol was used as a solvent. The data revealed that the lignin liquefaction in furfuryl alcohol system was very efficient in the beginning short time. Therefore, liquefaction time was fixed at 15 min.

LYL increased markedly as liquefaction temperature increased from 120 to 140 °C. Further increases in the liquefaction temperature resulted in a slow increase in the liquefaction yield of lignin. It was found that LYL reached the highest level of 80.23% at a temperature of 170 °C. The decrease of liquefied residue content indicated that the re-condensation reactions were almost non-existent at a liquefaction temperature of 120 to 170 °C in this system. It was clear from the data that LYL increased with the increasing of liquid ratio. When the liquid ratio was 3:1, its minimum LYL was 71.55%. This may be attributed to the higher susceptibility of degraded and liquefied components to undergo re-condensation reactions in insufficient amounts of liquefying solvent (Hassan and Shukry 2008). A liquid ratio of 5:1 was considered to be the suitable concentration for the selective liquefaction of lignin with a higher LYL of 80.23%.

FTIR Analysis

Figure 1 gives the IR spectra of the BEPR and its products in PEG/glycerol or furfuryl alcohol liquefaction. The liquefaction conditions were set at a liquefaction time of 15 min, a temperature of 140 °C, and a liquid ratio of 5:1. From the IR spectra, the broad band at about 3410 cm^{-1} was the characteristic stretching vibration of aliphatic and aromatic -OH; the band at 2920 cm^{-1} was due to the C-H stretching vibration of the aliphatic CH_3, CH_2, and CH groups; and the band at 1650 cm^{-1} could be attributed to the stretching vibration of conjugated carbonyl (Cheng and Liu 2006). All the samples had characteristic bands of benzene rings at 1510 cm^{-1}. The band of liquefied residue in furfuryl alcohol liquefaction at 1510 cm^{-1} was much weaker than that of BEPR but stronger in the responding liquefied product, which indicated the lignin was well-liquefied in furfuryl alcohol. The spectrum of BEPR had a characteristic band of C-O stretching vibration at 1035, 1050, and 1100 cm^{-1}, which reflects the existence of carbohydrates (Pérez and Samain 2010; Zhang *et al*. 2007). Both the liquefied residue and product in PEG/glycerol had an absorption band in the 1000 to 1100 cm^{-1} region, which showed that a part of carbohydrates was hard to liquefy at the early stage of liquefaction and a part of carbohydrates was already dissolved in the polyols. When furfuryl alcohol was used as the liquefying solvent, the band at the 1000 to 1100 cm^{-1} region was observed only in the liquefied residue and disappeared in the liquefied product. This indicated that the liquefaction of carbohydrates did not occur in furfuryl alcohol. Thus, it can be concluded that furfuryl alcohol had great selectivity for the liquefaction of lignin.

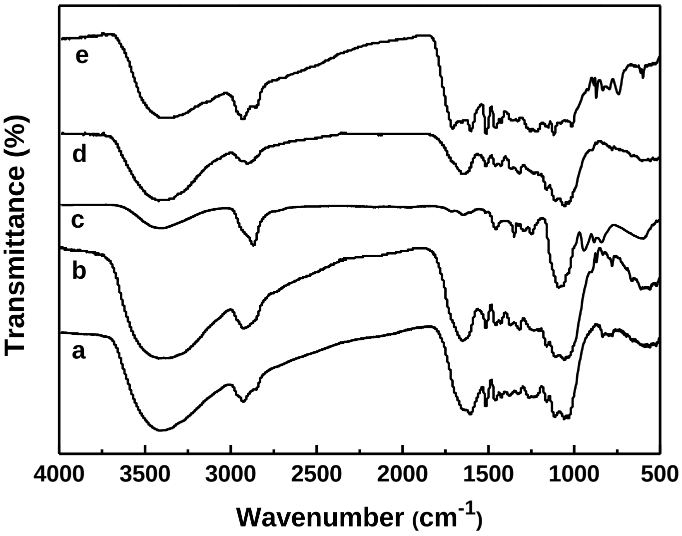

Fig. 1. FTIR spectra of (a) BEPR, (b) residue in PEG/glycerol, (c) liquefied product in PEG /glycerol, (d) residue in furfuryl alcohol, and (e) liquefied product in furfuryl alcohol

XRD Analysis

Figure 2 shows the X-ray diffraction curves of the BEPR, the liquefied residue, and the liquefied product in furfuryl alcohol that were obtained at the liquefaction time of 15 min, temperature of 170 °C, and liquid ratio of 5:1. From the XRD pattern, it can be seen that the 2θ diffraction curves for BEPR and liquefied residue were similar. For both XRD curves, there were peaks appearing at about 17°, 22.5°, and 26.5°, in which 17° and 22.5° can be attributed to the 101 side and 002 side of cellulose, respectively, and 26.5° was the diffraction peak of SiO_2 originating from the ash of the raw material. There was a minimum value peak appearing at about $2\theta = 18°$ for the 021 side and a small absorption at $2\theta = 35°$ for the 040 side. All the characteristic peaks show that cellulose crystals in the raw material had the typical cellulose I structure, in good agreement with a previous report (Reddy and Yang 2005). The curve of the liquefied product was quite similar to that of the original lignin due to its amorphous and highly cross-linked morphology (Rohella *et al*. 1996). The relative crystallinity index for the BEPR was 35.94%, while for the liquefied residue it was 53.18% according to the Segal formula. The remarkable increase of the crystallinity index for the liquefied residue was attributed to the liquefaction of lignin in furfuryl alcohol, which resulted in the decrease of lignin content and the increase of cellulose content in the liquefied residue. These results implied that furfuryl alcohol played an important role in the selective liquefaction of lignin.

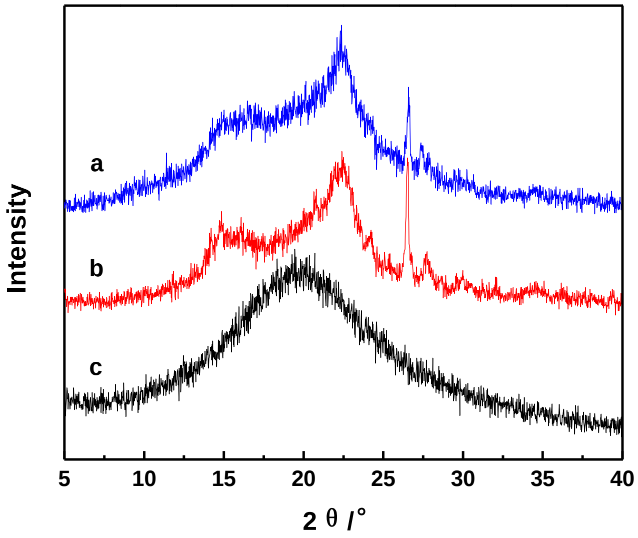

Fig. 2. XRD patterns of BEPR (a), the residue (b), and the liquefied product (c) in furfuryl alcohol

XPS Analysis

Figure 3 presents a typical XPS survey spectra of BEPR, the liquefied residue, and the liquefied product in furfuryl alcohol that was obtained at the liquefaction time of 15 min, temperature of 170 °C, and liquid ratio of 5:1. The curves of the liquefied residue and the liquefied product were shifted for better reading. It was clear that BEPR was mainly composed of carbon (C1s) and oxygen (O1s) along with small amounts of nitrogen (N) and silicon (Si). After liquefaction, the peaks of N and Si were observed only in the liquefied residue and disappeared in the liquefied product. The percentage of Si in the liquefied residue increased from 1.35% to 1.99%, but it was not detected in the liquefied product (Table 2), which signified that ash in the raw material could be removed as liquefied residue during the furfuryl alcohol liquefaction process. The O/C ratio decreased markedly from 0.50 to 0.19 because the removed residue was very rich in oxygen and the lignin was not. The O/C ratio of 0.19 is lower than the average O/C ratio of lignin (0.33) (Laine *et al*. 1994). This is a sign of the high content of *p*-hydroxyphenyl lignin in the liquefied product because the theoretical O/C ratio of *p*-hydroxyphenyl lignin is around 0.15, guaiacyl lignin is around 0.27, and syringyl lignin is around 0.36. In the meantime, the O/C ratio of the liquefied residue increased to 0.77, which approached the theoretical O/C ratio of cellulose (0.83) (Laine *et al*. 1994). This indicated that the carbon/oxygen–containing compounds of the liquefied residue were mainly carbohydrates, which were not liquefied by furfuryl alcohol. This result was consistent with FTIR and XRD analyses.

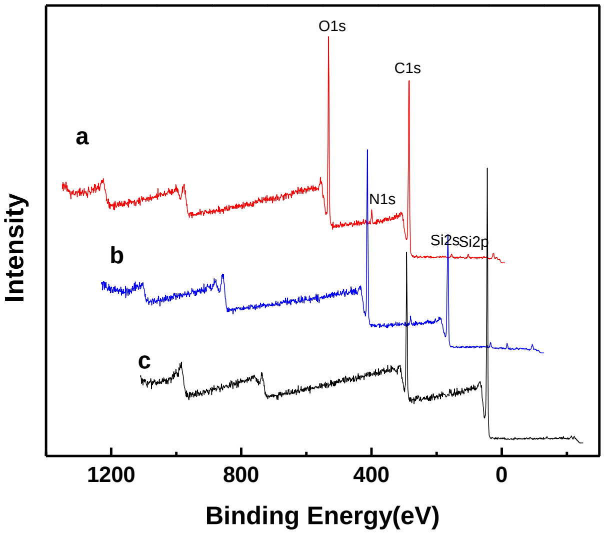

Fig. 3. XPS survey spectra of BEPR (a), the residue (b), and the liquefied product (c) in furfuryl alcohol

Table 2. Experimental Atomic Composition and O/C Ratio Obtained by XPS Analysis for All Samples

Sample	C %	O %	Si %	O/C
BEPR	63.58	31.99	1.35	0.50
Residue	54.50	41.77	1.99	0.77
Liquefied product	82.50	15.47	0	0.19

Figure 4 shows the deconvoluted high-resolution XPS spectra of the C1s peaks for the samples. The relative area of each peak was calculated and is listed in Table 3. According to the literature (Zhao and Boluk 2010), the C1s peak of lignocellulosic materials can be deconvoluted into four Gaussian peaks which correspond to four types of carbon atoms, respectively. The C1 corresponds to C-C or C-H originating from lignin and extractives. The C2 component is due to C-O, which has been shown to be mainly derived from lignin and cellulose. The C3 peak represents C=O or O-C-O arising from lignin, cellulose, and hemicellulose. The C4 represents O=C-O which is due to acidic polysaccharose, organic acid, and esters. However, there was no C4 peak in Fig. 4 because these components did not exist in the raw BEPR after the enzyme hydrolysis process. From the deconvoluted data, after liquefaction, the percentage of C1 increased from 53.45% to 71.61% and both C2 and C3 decreased. The increasing relative amount of C1 and the decreasing O/C atomic ratio indicated an increasing amount of lignin. Both C2 and C3 decreased, meaning that the content of cellulose decreased (Pang *et al*. 2012).

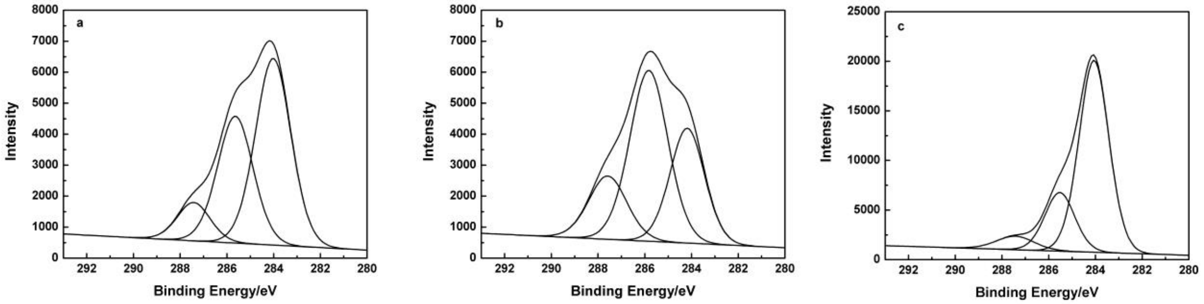

Fig. 4. The deconvoluted high resolution XPS spectra of the C1s peak for BEPR (a), the residue (b), and the liquefied product (c) in furfuryl alcohol

Table 3. Relative C1–C3 Peak Areas of the Deconvoluted C1s for All Samples

Sample	C1 %	C2 %	C3 %
BEPR	53.45	36.34	10.21
Residue	30.77	50.48	18.75
Liquefied product	71.61	21.92	6.47

GPC Analysis

Gel permeation chromatography was applied to obtain the molecular weight distributions of the BEPR and the liquefied product in furfuryl alcohol. Tests were carried out with a liquefaction time of 15 min, a temperature of 170 °C, and a liquid ratio of 5:1. The molecular weight distribution of the samples ranged from 100 to 40000 g/mol (Fig. 5). For the raw material, the peak from 300 to 8500 g/mol was the main molecular weight distribution corresponding to low molecular weight (LMW) lignin and some oligosaccharides; the peak at 16000 g/mol was attributed to high molecular weight (HMW) lignin.

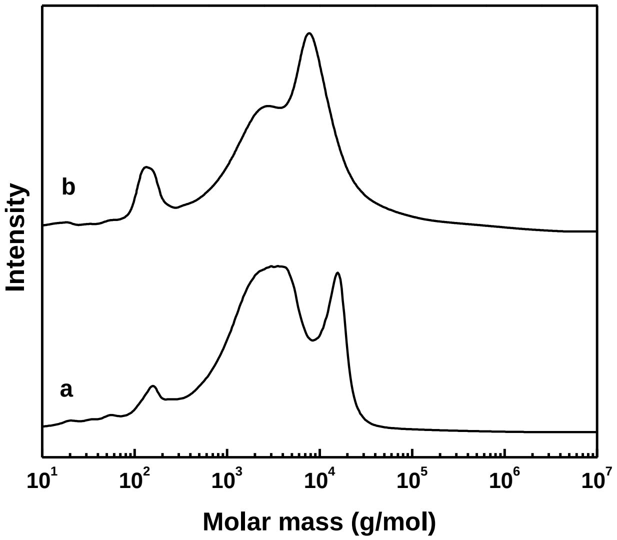

Fig. 5. GPC spectra of BEPR (a) and the liquefied product in furfuryl alcohol (b)

After liquefaction, the distribution at around 16000 g/mol shifted to a lower molecular weight of 7700 g/mol. This may be attributed to the decomposition of HMW lignin and the possible condensation between LMW lignin and furfuryl alcohol (Saw *et al*. 2011). After the selective liquefaction, the peak from 300 to 8500 g/mol of the raw material BEPR was substantially decreased, which is relevant to the non-liquefied oligosaccharides in furfuryl alcohol (Egüés *et al.* 2012; Shi *et al.* 2013).

Composition Analysis of Liquefied Product

As shown from the FTIR, XRD, XPS, and GPC analyses, furfuryl alcohol was selective for the liquefaction of lignin. In order to illustrate the purity of lignin in the liquefied product, the lignin content and ash content of the liquefied product were determined, and the results are listed in Table 4. It can be seen that liquefaction temperature barely affected the composition of liquefied product. Within the liquefaction temperature range of 120 to 170 °C, the lignin content reached 92% to 96%, and the ash content was no more than 1%. The high lignin content and low ash content revealed the selectivity of the liquefaction process for lignin and is in good agreement with the above analytical characterizations.

Table 4. Lignin and Ash Contents of Liquefied Product

Liquefaction temperature °C	Lignin content %	Ash content %
120	92.89	0.99
140	93.84	0.82
160	93.19	0.92
170	95.55	0.89

CONCLUSIONS

1. BEPR was successfully liquefied in furfuryl alcohol without any catalyst. The liquefied residue content was lower than that of the liquefaction in polyols. However, both of the two liquefactions produced much liquefied residue due to the high content of ash and crystalline cellulose in the BEPR.
2. With the increasing of liquefaction temperature or liquid ratio, LYL increased. Liquefaction time of 15 to 120 min had no significant effect on the liquefaction yield. When the liquefaction was conducted at 170 °C for 15 min with 5/1 furfuryl alcohol to raw material, LYL reached the highest level of 80.23%.
3. Based on the FTIR, XRD, XPS, and GPC analyses, it can be concluded that furfuryl alcohol had great selectivity for the liquefaction of lignin. Ash and carbohydrates in the raw material could be removed as liquefied residue.

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