

## **DELIGNIFICATION OF POPLAR WOOD WITH LACTIC ACID-BASED DEEP EUTECTIC SOLVENTS**

LIFEN LI, LIPING YU, ZHIGANG WU  
GUIZHOU UNIVERSITY, COLLEGE OF FORESTRY  
GUIZHOU, P.R. CHINA

YINGCHENG HU  
NORTHEAST FORESTRY UNIVERSITY, COLLEGE OF MATERIAL SCIENCE AND ENGINEERING  
HARBIN, P.R. CHINA

(RECEIVED JULY 2018)

### **ABSTRACT**

A process for the delignification of poplar wood using lactic acid-based deep eutectic solvents (DESs) with different hydrogen bond acceptors (choline chloride, glycine) was studied. The effect of operational parameters on the yields of the pulps and the regenerated lignins, the chemical compositions of the pulps and the delignification extent was investigated with respect to several factors, such as the types of hydrogen bond acceptor, reaction temperature and time. The maximum delignification extent of approximately 90.4% was achieved with lactic acid-choline chloride DES at 120°C for 12 h, however only about 58.4% of lignin was removed with lactic acid-glycine DES under the same reaction condition. The structural characteristics of the pulps were subsequently investigated by Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), Thermogravimetric Analysis (TGA) and compared with original wood sample and microcrystalline cellulose.

**KEYWORDS:** Poplar, lactic acid, deep eutectic solvents (DESs), delignification, characterization.

### **INTRODUCTION**

With the increasing of polymer materials requirement and energy consumption, problems such as fossil resources exhaustion and greenhouse effect enhancement appeared recently. Lignocellulosic biomass, including agricultural residues, forestry wastes, energy crops, waste paper, etc. has received much attention, because it is the cheapest and most abundant natural resource on earth. Besides, it is renewable, relatively carbon-neutral and has traditionally been considered as a potential sustainable source for bio-polymers, bio-fuels and other value-added bio-based chemicals (Lee et al. 2009, Fu et al. 2010).

Lignocellulosic biomass is mainly composed of three major components, which are cellulose, hemicelluloses and lignin. Percentages of the three components may vary depending on factors such as plant species and plant parts (Tadesse et al. 2011). The cellulose has been researched to produce chemicals or materials via biological method for many years (Lee et al. 2009). However, the high costs and the excessive dosages of hydrolase have been considered to be the major bottleneck on the path to a commercial cellulose energy industry (Margeot et al. 2009). Especially, lignin is the major obstacle to enzyme attack on cellulose by preventing enzyme accessibility as well as irreversibly adsorbs cellulase (Lee et al. 2009, Loow et al. 2017).

Therefore, in order to realize the utilization of cellulose as value-added materials and chemicals, efficient means of separation of main composition of lignocellulosic biomass are required. Traditional separation methods such as kraft process, acid and steam explosion etc. are successful isolation of lignocellulosic components, but are chemically wasteful and expensive, and usually require high temperatures and pressures (Fu et al. 2010, Tan et al. 2009). In recent decades, ionic liquids (ILs), ionic compounds whose melting temperature generally below 100°C have attracted extensive attention worldwide in lignocellulosic biomass pretreatment, mainly due to its negligible vapor pressures, thermal stability over a wide range of temperatures, and tunable physicochemical properties by changing its anion and cation (Fort et al. 2007). Above all, lots of ILs show good solubility to biomaterials under relatively mild conditions, such as, chitin, cellulose, lignin, or even lignocellulose, etc. To date, many of ILs have been used to extract lignin from lignocellulosic biomass, mainly 1-allyl-3-methylimidazolium chloride, 1-butyl-3-methylimidazolium chloride, 1-ethyl-3-methylimidazolium chloride and 1-ethyl-3-methylimidazolium acetate, etc. (Mohan et al. 2018, Yang et al. 2013). However, these traditional imidazolium-based ILs have high toxicity and inferior biodegradability (Romero et al. 2008), and the feedstocks used are of petroleum origin. Besides, the treatment of lignocellulosic biomass using ILs usually requires the virtual absence of water, and then extensive drying of the substrates as well as the solvents is needed. Additionally, the pretreatment process usually need inert atmosphere, these may of course increase the pretreatment costs to a large extent (Tan et al. 2009).

Abbott et al. (2003) found that a range of quaternary ammonium salts and urea could form eutectic mixtures which are liquid at ambient temperatures and have unusual solvent properties, and named them deep eutectic solvents (DESs). Due to the similar physicochemical properties of DESs and ILs, DESs were also named deep eutectic ILs (Figueiredo et al. 2009). The advantages of DESs compared with traditional ILs are that they are biodegradable, sustainable, and the components of DES are inexpensive (Abbott et al. 2003). Particularly, the preparation of DESs is simple, by mixing different components according to a certain molar ratio, and then stirring under a certain temperature until a homogenous, clear liquid is formed. Recently, a series of DESs based on organic salt and natural carboxylic acid, mainly lactic acid, malic acid and oxalic acid, have been found to have high solubility to lignin while do not dissolve cellulose (Francisco et al. 2012, Lynam et al. 2017). Besides, the literatures revealed that DESs are promising solvent for the pretreatment of lignocellulosic material, such as corncob, corn stover, rice husk, rice straw, wheat straw, wood, etc., by isolating of lignin from biomass with conventional heating or microwave heating (Hou et al. 2012, Jablonsky et al. 2015, Kumar et al. 2016, Liu et al. 2017a, Loow et al. 2017, Muhammad et al. 2011). The mechanism of DESs extraction of lignin from lignocellulosic material was due to their ability to selectively cleave the ether linkages between lignin phenylpropane units (Alvarez-Vasco et al. 2016). Of which, lactic acid-based DESs have been proved to be an effective DES for lignin solubilization and biomass delignification compared with other carboxylic acid-based DESs (Alvarez-Vasco et al. 2016, Kumar et al. 2016). However, a very few studies compared the pretreatment effects of wood with lactic acid-based DESs of

different hydrogen bond acceptor, and very little attention is paid to the structure of delignified pulps treated with DESs.

In the light of these findings, the aims of this study were: (a) to clarify the feasibility of delignification of poplar wood using lactic acid-choline chloride (LC) and lactic acid-glycine (LG) DESs; (b) to explore the effect of process parameters such as temperature and time on the yields of the pulps and the regenerated lignins on the composition of the pulps and on the delignification extent; (c) to explore the structural features of the pulps by several instrumental methods and compared with original poplar wood and microcrystalline cellulose (MCC).

## MATERIALS AND METHODS

### Materials

Air-dried poplar wood (*Populus ussuriensis*) xylem was grounded to 100 ~ 120 mesh size and dried at 90°C for 12h prior to use. Choline chloride (ChCl, C<sub>5</sub>H<sub>14</sub>ClNO, >98%), glycine (C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub>, >98.5%) and MCC ((C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>)<sub>n</sub>) were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. L-Lactic acid (C<sub>3</sub>H<sub>6</sub>O<sub>3</sub>, >80%) and other chemicals were analytical grade, and were obtained from local commercial supplier and were used without further purification. Distilled water was used in all of the experiments. Owing to the strong hygroscopic nature of choline chloride, it was vacuum dried at 80°C overnight before used.

### Preparation of DESs

DESs were prepared according to the procedures of the previous study (Francisco et al. 2012), and the flow chart was shown in Fig. 1. Briefly, starting materials, lactic acid/choline chloride with a molar ratio of 10:1 and lactic acid/glycine with a molar ratio of 9:1 were added to closed glass vials, the mixtures were magnetic stirred under 60°C until clear liquid was formed. The glass transition temperatures of LC and LG were -66.3°C and -54.5°C, respectively.

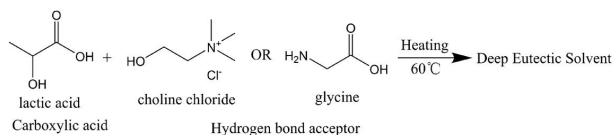


Fig. 1: Lactic acid reacted with hydrogen bond acceptor to produce DESs.

### Delignification process

Five percent mass fraction of wood in DESs was prepared by adding 0.75g of oven-dry wood fiber into 15g of preheated DES and then stirred at temperatures of 90°C, 100°C, 110°C, 120°C (oil bath) for 3h, 6h, 9h and 12h. When the designed reaction time had elapsed, the reaction mixture was poured into 150 mL acetone/water (7:3, v/v), and then the mixtures were stirred rapidly 1h at room temperature (Muhammad et al. 2011). Afterwards, the precipitated pulps was separated by gentle vacuum filtration with 0.45 μm nylon filter paper, repeated washed the pulps with 150mL acetone/water (7:3, v/v) twice to ensure remove lignin and DES completely.

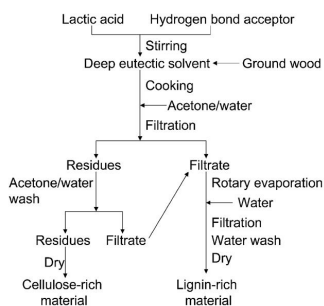


Fig. 2: Flowchart for the process of delignification of poplar wood in lactic acid-based DESs.

Collected the three times filtrates, removed of the acetone by rotary evaporation at 50°C, added 150 mL water to regenerate lignin, the precipitation was separated by vacuum filtration and washed with 300 mL water to ensure complete DES removal. Subsequently, the pulps and the regenerated lignins were dried at 80°C for 12 h, and then stored in a desiccator. The flow chart was shown in Fig. 2.

### Compositional analysis

The chemical components of original wood and the partially delignified pulps were subjected to analysis according to Datta's method with modification (Cheng et al. 2018, Datta 1981). (1) To determine the amount of extractives in the samples, Soxhlet extraction was used with acetone, and kept at 90°C for 2 h (Datta 1981). After the extraction, the sample was dried till constant weight was achieved, and the loss was considered as extractives part. (2) To determine the hemicelluloses content, 30 mL 0.5M H<sub>2</sub>SO<sub>4</sub> solution was added to 0.1 g of dried biomass, and the mixture was refluxed at 100°C for 2 h. The residues were subsequently washed with distilled water until the pH value of the solution approached 7 and dried to a constant weight, the hemicellulose content was obtained as the loss in weight. (3) To determine the amount of lignin, 2 mL 72wt% H<sub>2</sub>SO<sub>4</sub> was added to the hemicellulose-free biomass, followed by 4h of stir at room temperature, and then the mixture was diluted up to 4% concentration of H<sub>2</sub>SO<sub>4</sub>. The resulting mixture was stirred at 100°C for 2 h with recycled water. The weight of the dried residue was represented as the acid-insoluble lignin content, while the amount of acid-soluble lignin was determined based on the absorbance of filtrate at 205 nm using 4% H<sub>2</sub>SO<sub>4</sub> as the control. (4) Finally, the cellulose content was calculated by difference, assuming that the entire wood is composed only of extractives, hemicellulose, lignin and cellulose.

The main components of the starting materials were as follows: 49.6 wt% cellulose, 25.7 wt% hemicelluloses, and 23.8 wt% lignin and 0.9 wt% extractives. The yields (in percent) of the pulps and the regenerated lignins as well as the components of the pulps were reported as the corresponding mass recovered after pretreatment compared to the weight of original wood on a dry mass basis. The delignification extent was calculated as the reduction of the lignin content in the pulps compared to the lignin content in original wood.

### Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of original and the pulps obtained at 120°C for 12 h were recorded with the FT-IR spectrometer (Nicolet 6700, Thermo Fisher Scientific, USA) within the wavelength range of 4000-650 cm<sup>-1</sup> at 4 cm<sup>-1</sup> resolution and 128 scans per sample.

### X-Ray diffraction (XRD)

X-Ray Diffraction spectra of raw wood and the pulps obtained at 120°C for 12 h were obtained on X-Ray Diffraction (D/max-2200, Rigaku, Tokyo, Japan) equipped with Ni-filtered Cu K $\alpha_1$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) at 40 kV and 30 mA. The scattering angle range was  $5 \sim 30^\circ$  at a scan rate of  $4^\circ \cdot \text{min}^{-1}$ . The crystallinity index ( $CrI$ ) was calculated according to peak height method, which is the most popular and useful method to compare relative differences in the  $CrI$  of cellulose (Segal et al. 1959, Park et al. 2010). The  $CrI$  was calculated using the Eq. 1.

$$CrI_{(\%) } = \frac{I_{002} - I_{am}}{I_{002}} \times 100\% \quad (1)$$

where:  $I_{002}$  - the diffraction intensity at  $2\theta \approx 22^\circ$  which corresponding to the (002) lattice diffraction,

$I_{am}$  - the minimum intensity between the 101 (the broad peak at about  $16^\circ$ ) and the 002 peaks at  $2\theta \approx 18.5^\circ$  (Park et al. 2010).

### X-ray photoelectron spectrometer (XPS)

Surface chemical characterization of raw wood, MCC, LC pulp and LG pulp obtained at 120°C for 12 h was carried out with a K-Alpha XPS (Thermo Fisher Scientific, USA) with monochromatic Al K $\alpha$  ray.

Using the Gaussian-Lorentz fitting, the XPS-C1s region can be divided into four small peaks, which represent four types of chemical bonds of carbon in lignocellulosic biomass that are expressed as C1-C4 (Gustafsson et al. 2003, Xing et al. 2013, Zhang et al. 2007). C1 peak (centred at 284.8eV) was assigned to unoxidized carbon atoms (i.e., C-C or C-H), which was associated with the presence of lignin and extractives.

C2 peak (centred at 286.5eV) was attributed to carbon atoms bound to a single oxygen (i.e., C-O), which was mainly derived from cellulose and hemicelluloses. C3 signal (centred at 288eV) was due to carbon atoms with two oxygen bond (i.e., O-C-O or C=O) originating from the groups in hemicelluloses or lignin. C4 signal (centred at 289.2eV) corresponds to carbon atoms with three oxygen bond (i.e., O=C-O) that has been shown to be mainly refers to carboxylic acid from hemicelluloses and extractives.

The theoretical surface coverage of lignin ( $\phi_{(lignin)}$ ) was calculated from the O/C ratio according to the following equation (Gustafsson et al. 2003):

$$\phi_{(lignin)} = \left( O/C_{(sample)} - O/C_{(cellulose)} \right) / \left( O/C_{(lignin)} - O/C_{(cellulose)} \right) \quad (2)$$

Where  $O/C_{(sample)}$  is the O/C ratio of the measured sample,  $O/C_{(cellulose)}$  and  $O/C_{(lignin)}$  are 0.83 and 0.33, respectively, which represent the theoretical O/C ratios of pure cellulose and lignin (Gustafsson et al. 2003).

### Thermal gravimetric (TG)

The thermogravimetric measurements of the pulps were performed by using a thermal analyzer (PerkinElmer, STA 6000) and compared with original wood as well as MCC. Samples weighted about 10 mg were heated in an aluminum crucible under a temperature range of 40 to 800°C at a heating rate of  $10^\circ \text{C} \cdot \text{min}^{-1}$ , high purity nitrogen was used as shielding gas at a flow rate of  $20 \text{ mL} \cdot \text{min}^{-1}$ .

## RESULTS AND DISCUSSION

## Chemical composition of the pulps

It is well-known that the delignification efficiency depended on the nature of process conditions (Alvarez-Vasco et al. 2016, Padmanabhan et al. 2012, Tan et al. 2009). Therefore, the influence of process variables such as delignification temperature and time with LC and LG DESs on the yields of the pulps and the regenerated lignins, the chemical components of the pulps as well as the delignification extent was studied.

As can be seen in Fig. 3, the extraction process is very temperature dependent and time dependent for both DESs. Higher delignification efficiencies would obtain with both elevated temperatures and extended extraction time, but at the same time, the conditions that promoted the removal of lignin also decreased the yield of solid residues. This is because that under more severe conditions (higher temperature, longer reaction time) of wood delignification, higher part of hemicelluloses and amorphous cellulose converted to low molecular mass soluble products, which could not be recovered as solid material. Therefore, as a general fact, the higher the cellulose purity was the lower yield of the pulps was observed, which was also observed in biomass delignification with formic acid-ChCl and lactic acid-betaine DESs (Guo et al. 2018).

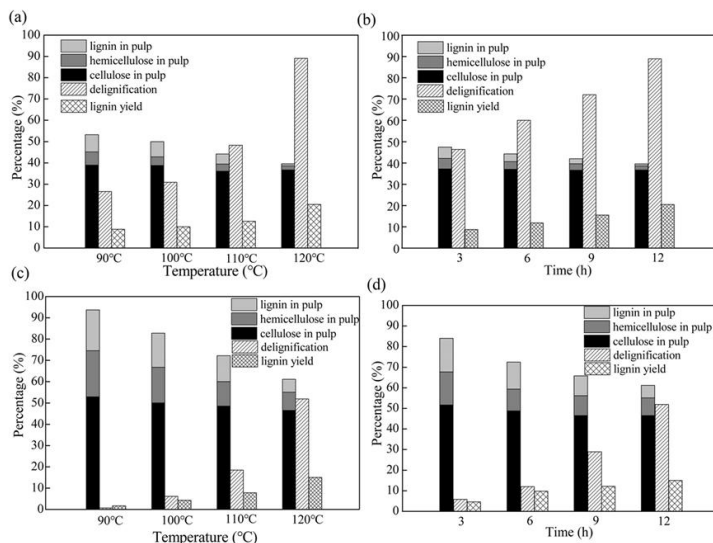


Fig. 3: Influence of reaction conditions on the yields of the pulps and the regenerated lignins, the composition of the pulps, and the delignification extent: (a) LC process at different temperature for 12 h, (b) LC process at 120°C for different reaction time, (c) LG process at different temperature for 12 h, (d) LG process at 120°C for different reaction time.

Solvent dependent study of lignin content in the pulps and the corresponding yield of the pulps was also investigated (Fig. 4).

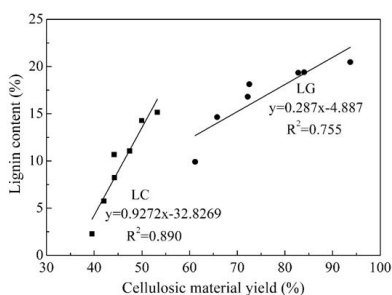


Fig. 4: The change of lignin content in pulps versus change in pulp yield. (■) represents lactic acid-choline chloride and (●) represents lactic acid-glycine.

The lignin content in the pulps and the yield of the pulps showed a strong correlation ( $R^2=0.890$ ) for LC process and a relatively poorer correlation ( $R^2=0.755$ ) for LG process. As can be seen from Fig. 3 and Fig. 4, for LC process, approximately 90.4% reduction of lignin content in the pulps has been achieved, lignin extraction yields of 78.5% from poplar and 60% from rice straw have been reported by previous studies (Alvarez-Vasco et al. 2016, Kumar et al. 2016), demonstrated the efficiency of LC DES in the dissolution of lignin from biomass. But at the same time, the mass of recovered pulps was only between 53.23% and 39.54%. Therefore, LC process could obtain high quality cellulosic product containing small amount of residual lignin and hemicelluloses, which indicates that LC has higher selectivity towards the lignin isolation, but at the same time, the cleavage of lignin-hemicelluloses bonds favored the hydrolysis of polysaccharose during the delignification process (Keskar et al. 2012). The yield of the pulps from LG process was high (between 61.16% and 93.7%) with a relatively high amount of residual lignin, and the maximum delignification extent was obtained at 120°C for 12h, with only about 58.4% of lignin removed from the original lignin content. The possible explanation for the difference between LC process and LG process may be that, LC has higher lignin solubility (Francisco et al. 2012). Besides, the presence of halide ions in LC could enhance its ability to penetrate the lignocellulosic material, thus caused the high efficacy of delignification. Analogous affinity toward lignin has also been achieved by using chloride-containing ionic liquids (George et al. 2011). Based on the results described above, it can be seen that though there was some lignin remained in the pulps, the ratio of lignin to carbohydrate was significantly below that in the untreated poplar wood. It also demonstrated that it may be feasible to design different delignification processes using lactic acid-based DESs by the choice of different hydrogen bond acceptors. In this way, one can selectively extract components from poplar wood to obtain high yield pulps with relatively high lignin residue or to make almost pure cellulosic fraction with relatively low yield.

### FTIR analysis

The FTIR spectra of the pulps obtained by LC and LG processes at 120°C for 12h were compared with that of original wood and MCC (Fig. 5). All spectra had broad adsorption band at about 3331  $\text{cm}^{-1}$ , which is attributed to O-H stretching vibration in phenolic and aliphatic hydroxyl. The band at 2887  $\text{cm}^{-1}$  is related to the C-H stretching in methyl and methylene. The adsorption band at 1732  $\text{cm}^{-1}$  is assigned to C=O stretching vibration of acetyl groups (Sirviö et al. 2016), which was still present in the spectra of the pulps, indicating that hemicelluloses-containing pulps was obtained or the pulps might react with lactic acid during the delignification

process, which has also been founded in previous researches when wood pretreatment with lactic acid-based and oxalic acid-based DES (Dou et al. 2010, Sirviö et al. 2016). The absorption band at  $1640\text{ cm}^{-1}$  is attributed to the bending mode of the absorbed water (Luo et al. 2014). The reduction in intensity of the peaks at  $1592\text{ cm}^{-1}$ ,  $1503\text{ cm}^{-1}$  and  $1456\text{ cm}^{-1}$ , corresponding to phenylpropane skeleton aromatic stretching vibration (Tejado et al. 2007) after DESs treatment suggested lignin removal. The adsorption peak at  $1233\text{ cm}^{-1}$  is due to the C-O stretching in lignin and hemicelluloses, the reduction of this peak from the spectra of the pulps was attributed to the cleavage of ester linkages in lignin and hemicelluloses, as well as to the cleavage of lignin side chains (Li et al. 2011). The intensity of peak at  $898\text{ cm}^{-1}$ , attributed to the  $\beta$ -(1 $\rightarrow$ 4)-glycosidic linkages between the sugar units in polysaccharides (De Rosa et al. 2011) has increased in the spectra of the residues, demonstrating that more cellulosic material was present in the pulps. On the whole, the changes observed in FTIR spectra indicated the efficiency extraction of lignin and hemicelluloses, and implied that the residues were richer in cellulosic material.

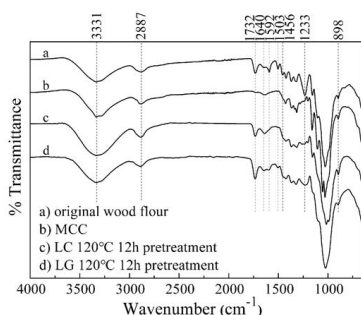


Fig. 5: FTIR spectra of (a) raw wood, (b) MCC, (c) LC pulp and (d) LG pulp obtained at  $120^{\circ}\text{C}$  for 12h.

### Crystallinity analysis

X-ray diffraction (XRD) measurement can be used to qualitatively or semi-quantitatively estimate the relative amount of crystalline cellulosic component in total biomass (Pinkert et al. 2011). Fig. 6 shows the wide-angle XRD curves of original poplar wood, MCC and the pulps obtained by LC and LG processes at  $120^{\circ}\text{C}$  for 12h. As can be seen, all the patterns show two main peaks, the first broad peak at around  $16^{\circ}$ , corresponding to (101) plane of crystals, is a composite peak of two peaks from cellulose allomorphs  $I_{\alpha}$ ,  $I_{\beta}$  or both. The second peak of (002) plane at around  $22.2^{\circ}$  is indicative of the distance between H-bonded sheets in cellulose I. The third small peak (040) at around  $34.5^{\circ}$  corresponds to  $1/4$  of the length of one cellobiose unit and arises due to its ordering along the fiber direction (Cheng et al. 2011, Pinkert et al. 2011). All of the XRD patterns showed the native crystalline state (cellulose I), and no signs of cellulose II were found.

As can be seen from Fig. 6, the XRD patterns of the pulps are similar to that of native wood, although the diffraction intensity was increased, which indicates that the relative amount of crystalline structure in the pulps increased after delignification treatment. *CrI* of the cellulose samples is calculated by the aforementioned peak height method. The native wood and MCC were calculated to have *CrI* of 48.1 and 78.3, respectively, and the *CrI* was 54.9 and 56.6 for the LC and LG pulps, correspondingly. The slight increase of *CrI* of the pulps compared with raw wood may be explained by partially removing of amorphous materials like lignin, hemicelluloses and the amorphous cellulose, thus the proportion of crystalline cellulose was increased. During this delignification process, the highly crystalline structure of wood cellulose has not been



destroyed, this is because that LC and LG have high solubility for lignin, but cannot dissolve the crystalline region of cellulose. A positive correlation between crystallinity and the strength of cellulosic-rich pulp has been demonstrated (Pinkert et al. 2011).

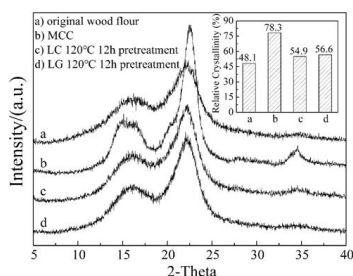


Fig. 6: The X-ray diffraction patterns of (a) raw wood, (b) MCC, (c) LC pulp and (d) LG pulp obtained at 120 °C for 12 h.

Therefore, this task-specific behaviour of DESs delignification makes it possible to extract and isolate lignin while retaining the crystalline integrity of the pulps. Furthermore, the excellent mechanical properties of the cellulosic-rich pulps can transfer to cellulose-based bio-composites, such as cellulose nanofibrils and cellulose nanocrystals (Li et al. 2017, Liu et al. 2017b, Pinkert et al. 2011, Sirviö et al. 2016).

### XPS analysis

XPS has been proven to be a very effective technique to analyze the surface specific of a solid, although it detects only about 5 ~ 10 nm deep, it can be used to qualitatively or semi-quantitatively determine the element composition of the sample surface (Tenhunen et al. 2018, Xu et al. 2007).

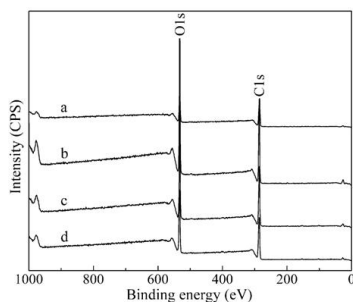


Fig. 7: XPS survey spectra of (a) raw wood, (b) MCC, (c) LC pulp and (d) LG pulp obtained at 120°C for 12h.

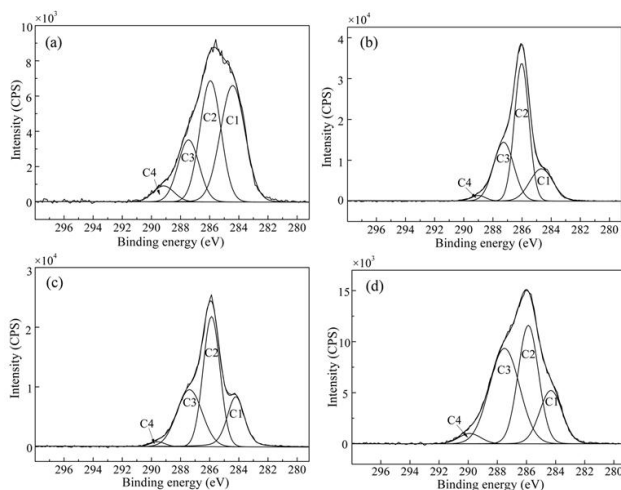


Fig. 8: Deconvolution of the C1s emission line of (a) raw wood, (b) MCC, (c) LC pulp and (d) LG pulps obtained at 120°C for 12h.

Recently, researches have shown that the O/C atomic ratio and the relative amount of the types of chemical bonds of carbon in the pulps surface directly correlate to the amount of surface lignin (Xu et al. 2007, Zhang et al. 2007). As a rule of thumb, a higher O/C ratio and lower relatively amount of C1 indicates a higher cellulose concentration. Fig. 7 shows the XPS wide scan (0 ~ 1000 eV) spectra for poplar wood, MCC, LC pulp and LG pulp obtained at 120°C for 12 h, Fig. 8 shows a deconvolution of the C1s emission line of the corresponding samples, and Tab. 1 shows the results of XPS-peak-differentiating analysis.

Tab. 1: XPS analysis of original wood, MCC, DESs pulps obtained at 120°C for 12h.

Substrate	O/C	$\phi_{(lignin)}$ (%)	Decomposition of C1s							
			C1(eV)	C2(eV)	C3(eV)	C4(eV)	C1(%)	C2(%)	C3(%)	C4(%)
Cellulose <sup>a</sup>	0.83	-	-	-	-	-	-	83	17	-
Hemicellulose <sup>a</sup>	0.80	-	-	-	-	-	-	83	17	-
Lignin <sup>a</sup>	0.33	-	-	-	-	-	-	49	49	2
Wood	0.37	0.92	284.42	285.95	287.45	289.16	41.11	35.88	18.34	4.67
MCC	0.67	-	284.67	286.03	287.23	289.00	18.67	49.63	29.78	1.93
LC pulp	0.60	0.46	284.21	285.87	287.39	289.57	21.22	46.67	30.63	1.48
LG pulp	0.52	0.62	284.32	285.87	287.51	289.90	18.12	36.06	42.46	3.36

<sup>a</sup> The theoretical values of O/C atomic ratios and the relative peak areas of the C1-C4 as calculated from the chemical composition of the compounds (Gustafsson et al. 2003).

As can be seen, the measured O/C atomic ratios were 0.37, 0.67, 0.60, and 0.52 for original wood, MCC, LC pulp and LG pulp, correspondingly. The measured value of O/C atomic ratio of MCC was lower than that of pure cellulose deduced from the theoretical formula ( $C_6H_{10}O_5$ , 0.83), this can be possibly attributed to C-rich molecular segments were deposited at the surface of the solid under study (Missoum et al. 2012). As shown in Tab. 1, the O/C atomic ratios of

the pulps were higher than that of original poplar wood, while lower than that of MCC. To illustrate the results in a more intuitive way, the theoretical surface coverage of lignin ( $\phi$  (*lignin*)), as calculated from the O/C ratio according to Eq. 2, was 0.92, 0.46 and 0.62 of raw wood, LC pulp and LG pulp, correspondingly, indicating that the surface lignin concentration has been decreased after DESs delignification treatment. Besides,  $\phi$  (*lignin*) of LC pulp was lower than that of LG pulp, this implied that LC process extracted more lignin when compared with LG process, which was consistent with the results estimated by composition analysis and FTIR analysis.

As can be seen from Tab. 1, lignin contains much more amount of C1 than polysaccharose, while polysaccharose has a higher contribution from C2 and C3 peaks compared to lignin. According to Tab. 1, a definite decrease of the relative peak area of C1 is noted after LC and LG treatment (from 41.11% to 21.11% and 18.12%), simultaneously, the relative amount of C3 increased extensively (from 18.34% to 30.63% and 42.46%), while the change in the relative peak area of C2 and C4 is not significant. Consequently, the significant decreasing of relative amount of C1 and increasing of relative amount of C3 of the pulps with the increasing of O/C ratio refers to the decrease in the amount of lignin in the pulps surface.

### Thermal analysis

Thermogravimetry is one of the most widely used techniques to monitor the change of the main components of wood dependence on the thermal degradation (Saravanakumar et al. 2014). Furthermore, in order to expand the application of the cellulosic-rich pulps, it is imperative that the issues related to their thermal stability be addressed (Lin et al. 2008).

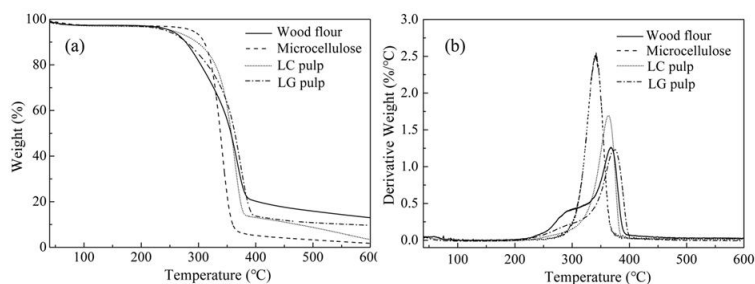


Fig. 9: TG and DTG curves of raw wood, MCC, and DESs pulps obtained at 120°C for 12h.

Fig. 9 displays the TG and DTG results of original wood, MCC and the pulps obtained using LC and LG DESs at 120°C for 12 h.

In the case of original wood, it can be seen that the weight loss in the temperature range 40 ~ 600°C can be divided into four stages. An initial weight loss of the wood powder occurs below 100°C corresponding to the vaporization of absorbed water. The second weight loss at around 250 to 320°C due to the decomposition of hemicelluloses (Yang et al. 2007). It should be highlighted that this peak decreased to some different extent from the DTG curve of the LC pulp and LG pulp, which indicates that different amount of hemicelluloses were removed during delignification process. Subsequently, the rapid decline of weight occurred at around 320 to 390°C (the third stage) was mainly attributed to the decomposed of cellulose (Yang et al. 2007). The temperature for the maximum rate of decomposition ( $T_{max}$ ) in this stage was 1.21% / °C at 366°C for original wood, while the main degradations of MCC, LC pulp and LG pulp took place was 2.46% / °C at 342°C, 1.98% / °C at 363°C and 1.46% / °C at 374°C, respectively.

The fourth weight loss occurred at 390 to 600°C was mainly attributed to the further decompose of lignocellulosic components. As can be seen, the amount of residue at 600°C in MCC and the pulps were remarkably lower than that of original wood, which was 12.99%, 1.75%, 3.40% and 9.68%, respectively, for original wood, MCC, LC pulp and LG pulp. It has been reported that when temperature was higher than 600°C, the solid residue was mainly lignin and small amount of hemicelluloses (Yang et al. 2007). Therefore, the lower content of solid residue in the pulps than in original wood indicated that lignin and hemicelluloses has been removed during the delignification processes, and LC pulp contained nearly pure cellulosic material, which was consisted with the foregoing FTIR spectra. The similar thermogram patterns have also been reported on pretreatment of cellulose pulp with acidic DESs (Sirviö et al. 2016).

## CONCLUSIONS

Delignification of poplar wood using LC and LG DESs was successfully achieved at atmospheric pressure. The results indicated that elevated temperature and prolonged time both can improve the delignification extent. Compared with LG process, LC process extracted more lignin under the same reaction conditions though at the sacrifice of more carbohydrates, thus obtained a high purity of cellulosic product with relatively low yield. The effective delignification has been proven through FTIR analysis, but the derivatisation of the pulp was observed during the lactic-based DESs treatment. X-ray diffraction analysis showed that DESs treatment has been found to have no influence on the native cellulose I crystal lattice. The O/C atomic ratios of the pulps increased and the theoretical surface coverage of lignin decreased compared with that of original wood as measured by XPS surface elemental analysis, the same conclusion can be drawn from the C1 percentage. TG analysis indicated that the pulps exhibited reduced thermal stability over untreated one, but the thermal stability was relatively higher than MCC. These findings should facilitate the efficient utilisation of the pulp treated with lactic acid-based DESs.

## ACKNOWLEDGEMENTS

This project was supported by the National Natural Science Foundation of China (NO. 31470581 and 31800481), Science and Technology Plan of Guizhou Province (NO. Qiankehe Platform Talent [2017]5788), Scientific and Technological Research Project of Guizhou Province (NO. Qiankehe NY [2015]3027), Forestry Department Foundation of Guizhou Province of China (No. [2017]14, [2018]13), Education Department Foundation of Guizhou Province of China (No. [2017]114), and Introduction of Guizhou University Scientific Research Grants Project of China (NO. [2015]66).

## REFERENCES

1. Abbott, A.P., Capper, G., Davies, D.L., Rasheed, R.K., Tambyrajah, V., 2003: Novel solvent properties of choline chloride/urea mixtures. *Chemical Communications* 9(1): 70-71.

2. Alvarez-Vasco, C., Ma, R., Quintero, M., Guo, M., Geleynse, S., Ramasamy, K.K., Wolcott, M., Zhang, X., 2016: Unique low-molecular-weight lignin with high purity extracted from wood by deep eutectic solvents (DES): a source of lignin for valorization. *Green Chemistry* 18(19): 5133-5141.
3. Cheng, F., Zhao, X., Hu, Y., 2018: Lignocellulosic biomass delignification using aqueous alcohol solutions with the catalysis of acidic ionic liquids: A comparison study of solvents. *Bioresource Technology* 249: 969-975.
4. Cheng, G., Varanasi, P., Li, C., Liu, H., Melnichenko, Y.B., Simmons, B.A., Kent, M.S., Singh, S., 2011: Transition of cellulose crystalline structure and surface morphology of biomass as a function of ionic liquid pretreatment and its relation to enzymatic hydrolysis. *Biomacromolecules* 12(4): 933-941.
5. Datta, R., 1981: Acidogenic fermentation of lignocellulose-acid yield and conversion of compounds. *Biotechnology and Bioengineering* 23(9): 2167-2170.
6. De Rosa, I.M., Kenny, J.M., Maniruzzaman, M., Moniruzzaman, M., Monti, M., Puglia, D., Santulli, C., Sarasini, F., 2011: Effect of chemical treatments on the mechanical and thermal behaviour of okra (*Abelmoschus esculentus*) fibres. *Composites Science and Technology* 71(2): 246-254.
7. Dou, Y.Y., Li, X.B., Ye, J.D., Gao, Q.W., Zhu, L.Y., Hong, G.J., 2010: Degradation and structural changes of wheat straw pulp cellulose in lactic acid medium. *Journal of Anhui Agriculture Science* 38(27): 15449-15452.
8. Figueiredo, M., Gomes, C., Costa, R., Martins, A., Pereira, C.M., Silva, F., 2009: Differential capacity of a deep eutectic solvent based on choline chloride and glycerol on solid electrodes. *Electrochimica Acta* 54(9): 2630-2634.
9. Fort, D.A., Remsing, R.C., Swatloski, R.P., Moyna, P., Moyna, G., Rogers, R.D., 2007: Can ionic liquids dissolve wood? Processing and analysis of lignocellulosic materials with 1-n-butyl-3-methylimidazolium chloride. *Green Chemistry* 9(1): 63-69.
10. Francisco, M., Bruinhorst, A.V.D., Kroon, M.C., 2012: New natural and renewable low transition temperature mixtures (LTTMs): screening as solvents for lignocellulosic biomass processing. *Green Chemistry* 14(8): 2153-2157.
11. Fu, D., Mazza, G., Tamaki, Y., 2010: Lignin extraction from straw by ionic liquids and enzymatic hydrolysis of the cellulosic residues. *Journal of Agricultural and Food Chemistry* 58(5): 2915-2922.
12. George, A., Tran, K., Morgan, T.J., Benke, P.I., Berruoco, C., Lorente, E., Wu, B.C., Keasling, J.D., Simmons, B.A., Holmes, B.M., 2011: The effect of ionic liquid cation and anion combinations on the macromolecular structure of lignins. *Green Chemistry* 13(12): 3375-3385.
13. Guo, Z., Ling, Z., Wang, C., Zhang, X., Xu, F., 2018: Integration of facile deep eutectic solvents pretreatment for enhanced enzymatic hydrolysis and lignin valorization from industrial xylose residue. *Bioresource Technology* 265: 334-339.
14. Gustafsson, J., Ciovica, L., Peltonen, J., 2003: The ultrastructure of spruce kraft pulps studied by atomic force microscopy (AFM) and X-ray photoelectron spectroscopy XPS. *Polymer* 44(3): 661-670.
15. Hou, X.D., Smith, T.J., Li, N., Zong, M.H., 2012: Novel renewable ionic liquids as highly effective solvents for pretreatment of rice straw biomass by selective removal of lignin. *Biotechnology and Bioengineering* 109(10): 2484-2493.
16. Jablonsky, M., Skulcova, A., Kamenska, L., Vrska, M., Sima, J., 2015: Deep eutectic solvents: fractionation of wheat straw. *BioResources* 10(4): 8039-8047.

17. Keskar, S.S., Edye, L.A., Doherty, W.O.S., Bartley, J.P., 2012: The chemistry of acid catalyzed delignification of sugarcane bagasse in the ionic liquid trihexyl tetradecyl phosphonium chloride. *Journal of Wood Chemistry and Technology* 32(1): 71-81.
18. Kumar, A.K., Parikh, B.S., Pravakar, M., 2016: Natural deep eutectic solvent mediated pretreatment of rice straw: bioanalytical characterization of lignin extract and enzymatic hydrolysis of pretreated biomass residue. *Environmental Science and Pollution Research* 23(10): 9265-9275.
19. Lee, S.H., Doherty, T.V., Linhardt, R.J., Dordick, J.S., 2009: Ionic liquid-mediated selective extraction of lignin from wood leading to enhanced enzymatic cellulose hydrolysis. *Biotechnology and Bioengineering* 102(5): 1368-1376.
20. Li, C., Cheng, G., Balan, V., Kent, M.S., Ong, M., Chundawat, S.P.S., Sousa, L.D., Melnichenko, Y.B., Dale, B.E., Simmons, B.A., Singh, S., 2011: Influence of physico-chemical changes on enzymatic digestibility of ionic liquid and AFEX pretreated corn stover. *Bioresource Technology* 102(13): 6928-6936.
21. Li, P., Sirviö, J.A., Haapala, A., Liimatainen, H., 2017: Cellulose nanofibrils from nonderivatizing urea-based deep eutectic solvent pretreatments. *ACS Applied Material and Interfaces* 9(3): 2846-2855.
22. Lin, Z., Renneckar, S., Hindman, D.P., 2008: Nanocomposite-based lignocellulosic fibers 1. Thermal stability of modified fibers with clay-polyelectrolyte multilayers. *Cellulose* 15(2): 333-346.
23. Liu, Y., Chen, W., Xia, Q., Guo, B., Wang, Q., Liu, S., Liu, Y., Li, J., Yu, H., 2017a: Efficient cleavage of lignin-carbohydrate complexes and ultrafast extraction of lignin oligomers from wood biomass by microwave-assisted treatment with deep eutectic solvent. *ChemSusChem* 10(8): 1692-1700.
24. Liu, Y., Guo, B., Xia, Q., Meng, J., Chen, W., Liu, S., Wang, Q., Liu, Y., Li, J., Yu, H., 2017b: Efficient cleavage of strong hydrogen bonds in cotton by deep eutectic solvents and facile fabrication of cellulose nanocrystals in high yields. *ACS Sustainable Chemistry & Engineering* 5(9): 7623-7631.
25. Loow, Y., New, E.K., Yang, G.H., Ang, L.Y., Foo, L.Y.W., Wu, T.Y., 2017: Potential use of deep eutectic solvents to facilitate lignocellulosic biomass utilization and conversion. *Cellulose* 24(9): 3591-3618.
26. Luo, X., Liu, J., Wang, H., Huang, L., Chen, L., 2014: Comparison of hot-water extraction and steam treatment for production of high purity-grade dissolving pulp from green bamboo. *Cellulose* 21(3): 1445-1457.
27. Lynam, J.G., Kumar, N., Wong, M.J., 2017: Deep eutectic solvents' ability to solubilize lignin, cellulose, and hemicellulose; thermal stability; and density. *Bioresource Technology* 238: 684-689.
28. Margeot, A., Hahn-Hägerdal, B., Edlund, M., Slade, R., Monot, F., 2009: New improvements for lignocellulosic ethanol. *Current Opinion in Biotechnology* 20(3): 372-380.
29. Missoum, K., Bras, J., Belgacem, M.N., 2012: Organization of aliphatic chains grafted on nanofibrillated cellulose and influence on final properties. *Cellulose* 19(6): 1957-1973.
30. Mohan, M., Deshavath, N.N., Banerjee, T., Goud, V.V., Dasu, V.V., 2018: Ionic liquid and sulfuric acid-based pretreatment of bamboo: biomass delignification and enzymatic hydrolysis for the production of reducing sugars. *Industrial and Engineering Chemistry Research* 57(31): 10105-10117.

31. Muhammad, N., Man, Z., Azumi Bustam, M., Abdul Mutalib, M.I., Wilfred, C.D., Rafiq, S., 2011: Dissolution and delignification of bamboo biomass using amino acid-based ionic liquid. *Applied Biochemistry and Biotechnology* 165(3-4): 998-1009.
32. Padmanabhan, S., Zaia, E., Wu, K., Blanch, H.W., Clark, D.S., Bell, A.T., Prausnitz, J.M., 2012: Delignification of miscanthus by extraction. *Separation Science and Technology* 47(2): 370-376.
33. Park, S., Baker, J.O., Himmel, M.E., Parilla, P.A., Johnson, D.K., 2010: Cellulose crystallinity index: measurement techniques and their impact on interpreting cellulase performance. *Biotechnology for Biofuels* 3: 10.
34. Pinkert, A., Goeke, D.F., Marsh, K.N., Pang, S., 2011: Extracting wood lignin without dissolving or degrading cellulose: investigations on the use of food additive-derived ionic liquids. *Green Chemistry* 13(11): 3124-3136.
35. Romero, A., Santos, A., Tojo, J., Rodríguez, A., 2008: Toxicity and biodegradability of imidazolium ionic liquids. *Journal of Hazardous Materials* 151(1): 268-273.
36. Saravanakumar, S.S., Kumaravel, A., Nagarajan, T., Ganesh Moorthy, I., 2014: Investigation of physico-chemical properties of alkali-treated *Prosopis juliflora* fibers. *International Journal of Polymer Analysis and Characterization* 19(4): 309-317.
37. Segal, L., Creely, J.J., Martin, A.E., Conrad, C.M., 1959: An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer. *Textile Research Journal* 29(10): 786-794.
38. Sirviö, J.A., Visanko, M., Llimatainen, H., 2016: Acidic deep eutectic solvents as hydrolytic media for cellulose nanocrystal production. *Biomacromolecules* 17(9): 3025-3032.
39. Tadesse, H., Luque, R., 2011: Advances on biomass pretreatment using ionic liquids: An overview. *Energy & Environmental Science* 4(10): 3913-3929.
40. Tan, S.S.Y., MacFarlane, D.R., Upfal, J., Edey, L.A., Doherty, W.O.S., Patti, A.F., Pringle, J.M., Scott, J.L., 2009: Extraction of lignin from lignocellulose at atmospheric pressure using alkylbenzenesulfonate ionic liquid. *Green Chemistry* 11(3): 339-345.
41. Tejado, A., Peña, C., Labidi, J., Echeverria, J.M., Mondragon, I., 2007: Physico-chemical characterization of lignins from different sources for use in phenol-formaldehyde resin synthesis. *Bioresource Technology* 98(8): 1655-1663.
42. Tenhunen, T.-M., Lewandowska, A.E., Orelma, H., Johansson, L.-S., Virtanen, T., Harlin, A., Österberg, M., Eichhorn, S.J., Tammelin, T., 2018: Understanding the interactions of cellulose fibres and deep eutectic solvent of choline chloride and urea. *Cellulose* 25(1): 137-150.
43. Xing, Y., Yu, H., Zhu, L., Jiang, J., 2013: Efficient enzymatic hydrolysis of bamboo by pretreatment with steam explosion and alkaline peroxide. *BioResources* 8(4): 5392-5408.
44. Xu, Y., Li, K., Zhang, M., 2007: Lignin precipitation on the pulp fibers in the ethanol-based organosolv pulping. *Colloids and Surfaces a Physicochemical and Engineering Aspects* 301(1-3): 255-263.
45. Yang, D., Zhong, L.X., Yuan, T.Q., Peng, X.W., Sun, R.C., 2013: Studies on the structural characterization of lignin, hemicelluloses and cellulose fractionated by ionic liquid followed by alkaline extraction from bamboo. *Industrial Crops and Products* 43: 141-149.
46. Yang, H., Yan, R., Chen, H., Lee, D.H., Zheng, C., 2007: Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel* 86(12-13): 1781-1788.
47. Zhang, M., Xu, Y., Li, K., 2007: Removal of residual lignin of ethanol-based organosolv pulp by an alkali extraction process. *Journal of Applied Polymer Science* 106(1): 630-636.

LIFEN LI, LIPING YU, ZHIGANG WU  
GUIZHOU UNIVERSITY  
COLLEGE OF FORESTRY  
GUIYANG 550025  
GUIZHOU  
P.R. CHINA

\*YINGCHENG HU  
NORTHEAST FORESTRY UNIVERSITY  
COLLEGE OF MATERIAL SCIENCE AND ENGINEERING  
HARBIN, 150040  
HEILONGJIANG  
P.R. CHINA

\*Corresponding author: [yingchenghu@163.com](mailto:yingchenghu@163.com)