Application of Alkaline Ionic Liquids in the Pretreatment Process of Eucalyptus Kraft Pulping

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In order to explore the potential application of green solvent ionic liquids (ILs) in the kraft pulping process, eucalyptus wood was pretreated by [Mmim]DMP before normal pulping. The results showed that materials pretreated shortly by the ionic liquid had a higher yield and viscosity coupled with a lower potassium permanganate value and residual lignin content in the pulp, as a result of the cooking process. It was also inferred that alkaline [Mmim]DMP pretreatment could dissolve lignin effectively from fiber to result in a stronger binding force and more entangled properties. Paper tensile and burst strength were improved by about 40% and 60%, respectively. These results provide a new way for eucalyptus to be utilized in the kraft pulping process.

Keywords: [Mmim]DMP; Kraft pulping; Lignin; Paper properties

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INTRODUCTION

The essence of chemical pulping is to separate lignin from the cellulose content of lignocellulosic materials (Biermann 1993; Sahin 2003). Though kraft and sulfite processes are the oldest and most common technologies for commercial delignification of wood, high energy inputs and severe pollutants (sulfur-containing reagents) involved in the process have promoted the exploration of variety of new solvent pulping methods in recent decades. Some organic solvents such as glycols, ketones, dimethylsulfoxide, and aliphatic alcohols (Diebold *et al.* 1978; Hansen and April 1982; Paszner and Chang 1983) have been evaluated as pulping media (*i.e.* organosolv pulping) with some advantages such as higher removal rate and clean burning characteristics. However, thermal instability of the solvent and high cost for solvent regeneration (Chai *et al.* 2001; Zhao *et al.* 2009) are the major drawbacks of this technique. Additionally, poor pulp quality, chemical losses and recovery, and environmental problems have also plagued the further development of pulping processes relying upon organic solvents (Seoud *et al.* 2007; Araque *et al.* 2008).

Ionic liquids, generally defined as organic salts that melt below 100 °C, have been closely studied recently because of their designable nature, thermal stability, nonvolatile character, and capability of dissolving even polymeric compounds including cellulose under mild conditions (Swatloski *et al* 2002; Seoud *et al.* 2007; Yang *et al.* 2013; Achinivu *et al.* 2014). Though less attention has been paid to the use of alkaline ionic liquids as pulping agents, some studies have indicated that the solubility of lignin in [Mmim]DMP is stronger than other ionic liquids (Kilpeläinen *et al*. 2007; Pu *et al*. 2007). In this study [Mmim]DMP (1-methyl-3-methylimidazolium dimethylphosphate) was applied as a pretreatment solvent for eucalyptus wood in the kraft pulping process, and experiments were conducted to analyze the pretreatment effects of ionic liquids on the pulping and papermaking process.

EXPERIMENTAL

Materials

Eucalyptus robusta Smith as wood materials were collected from Guangdong Paper Company, Guangzhou, China. Before cooking, the eucalyptus wood was cut into small pieces (length along fiber direction): 4.8 mm to 20 mm; width: 4.8 mm to 20 mm; thickness: 2 mm to 8 mm). The main chemical compositions (wt.%) were analyzed as 75.19% total carbohydrates, 23.41% lignin, and 1.40% ash (Yang *et al.* 2013).

Ionic liquid [Mmim]DMP (≥ 99%) was made in the laboratory as previously described (Feng *et al.* 2011; Xu *et al.* 2014) with a yield of 97.5% and purity of 99.77%. The pK_b was measured as 10.6 (Song *et al.* 2012).

Pretreatment Conditions

A microwave extraction apparatus (XH-100B, XINGHU Microwave Beijing, China) was chosen to improve the efficiency of wood dissolution in ionic liquids (Han *et al.* 2009, 2012; Hui *et al.* 2013). The pretreatment conditions were as follows: microwave power, 500 W; temperature, 100 °C; reaction time, 10 min; and ratio of solid to liquid, 1:30. In each pretreatment process, 10 g of wood chips were immersed in the system; after pretreatment, the wood chips were washed several times with distilled water to ensure that ionic liquids were removed. In this paper all ionic liquid could be recycled 6 to 8 times according to preliminary studies. Untreated wood chips were used as the control sample. Methods employed for chemical composition of raw materials are shown in Table 1.

Table 1. Methods Used to Determine Chemical Composition

Chemical compositions	References
Ash in wood	TAPPI Test T15wd-80
Cellulose in wood	TAPPI Test T17wd-70
Holocellulose in wood	TAPPI Test T 9wd-75
Acid–soluble lignin in wood	GB/T 2677.8-1994
Acid–insoluble lignin in wood	TAPPI Test T18wd-76

In this paper all determinations were conducted with at least 3 replicates, and the data were expressed as the average.

Cooking Conditions

The cooking conditions are shown in Table 2. To maximize the protection of holocellulose and avoid it being degraded by alkali, which would reveal the extraction effect of lignin in ionic liquid, low alkali was applied to avoid eucalyptus pulp overcook (Huang *et al.* 2008; Sahin and Young 2008). In the heating stage, temperature and pressure increased uniformly and maintained stability at the end.

Table 2. Pulping Conditions

Pot Weight (dry) (g)	Active alkali dosage(%)	Sulfidity (%)		Liquid Ratio	Maximum Temperature (ºC)	Heating-up Time (min)
350	20	25		1:4	165	90
Soaking Time (min)	Actual loading capacity	Dosage		Total liquid amount (L)	Supplementary water (L)	Moisture Content (%)
		NaOH (g)	Na_2S (g)			
60	388.9	52.5	17.1	1.4	1.3	10

XRD Spectra analysis

X-ray diffraction spectra were obtained on a Bruker D8 Advance X-ray diffractometer (Karlsruhe, Germany) equipped with Ni-filtered Cu Kα_1 radiation at room temperature. The scattering angle range was 4 to 50°, and scans were collected at 40 kV and 40 mA with a step size of 0.04° every 35.4 s.

The Fiber Quality Analysis

The fiber was determined to range from 0.5 to 3.5 mm. The fiber quality analysis was determined in accordance with TAPPI T 233 cm-06 (2006) by the fiber quality analyzer (US61M/LDA02, Danbell, China).

Pulping and Papermaking

The pulp was beaten in a stainless steel PFI (M-PTB508A, Shenzhen, China) mill under standard conditions (TAPPI T 248 sp-00 2000) until the freeness of the pulp reached an appropriate value (~300 mL CSF). All the PFI revolutions were the same, as 3500r. The pulp was then disintegrated with a British disintegrator (DSG-2000, Regmed, Brazil) for 75,000 revolutions. The freeness of unbleached eucalyptus pulp was determined in accordance with TAPPI T 227 om-99 (1999). Handsheets were formed using a sheet machine in accordance with the TAPPI T 205-sp-95 (1995); the sheets had a basis weight of 60 g/m^2. These handsheets were conditioned at 23 ± 1 °C and 50% relative humidity. The handsheets was tested according to TAPPI standard methods. The tensile index (L&W CE062, ADEV, Sweden), burst index (L&W 180, ADEV, Sweden), and thickness (L&W 250, ADEV, Sweden) were determined according to TAPPI T494 om-96 (1996), TAPPI T 403 om-97 (1997), and TAPPI T 411 om-98 (1998), respectively.

RESULTS AND DISCUSSION

Comparison of Main Chemical Composition

Comparisons of main chemical composition are shown in Table 3. The absolute dry weight was slightly decreased because of the removal of part of the lignin. The relative content of holocellulose was increased by ionic liquid extraction, which showed that the dissolution of cellulose and hemicellulose in ionic liquid was low, and most of those components were still in the solid phase materials. The relative content of lignin was decreased, which showed that the solubility of lignin in alkaline ionic liquid was significantly higher than that of cellulose. Extraction of alkaline ionic liquid can effectively remove some lignin from eucalyptus.

Table 3. Comparison of Main Chemical Composition

	Control sample	Ionic liquid sample
Bone dry weight/g	400	377
Holocellulose content	75.2%	82.1%
Lignin content	23.4%	17.8%

XRD Spectra

In the spectra of native eucalyptus (1), there are diffraction peaks of (1 $\bar{1}$0) and (1 10), planes merging together at 16.3°, and a strong peak at 22.3°. Corresponding to the (200) plane of crystals are the features of cellulose I. Figure 1 shows that ionic liquid pretreated pulp slurry still had the characteristic peak of cellulose I, which is similar to the shape of the control sample. This indicates that the pretreatment process of ionic liquid had no effect on the crystalline structure of cellulose.

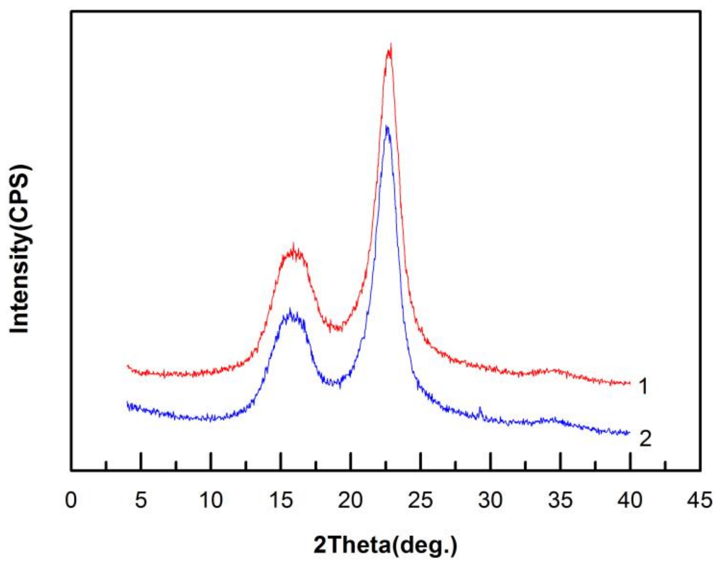

Fig. 1. XRD analysis chart of ionic liquid pretreated pulp and control sample. (1, untreated pulp; 2, ionic liquid pretreated pulp)

Influence of Pretreatment on Black Liquor

As shown in Table 4, the COD_{Cr} of black liquor with pretreatment was much greater than the blank sample, which means that more lignin was separated from fiber into black liquor during the cooking process. This is beneficial for the subsequent bleaching process with decreased chemical pollution load and greater alkali recovery efficiency with increased COD. Higher pH and EA content in the black liquor with ionic liquid pretreatment showed that less residual lignin remaining in the pulp led to a lower alkali consumption. The ionic liquid pretreatment process extracted more solid lignin, so the amount of alkali needed for cooking was decreased. Additionally, the cooking conditions can be optimized to be milder with lesser chemical consumption, which is economical and advantageous for the development of the pulping and paper-making industry.

Table 4. Test Results from Eucalyptus Pulping Black Liquor

Sample	Ionic Liquid Treatment of Pulp Black Liquor	Control Sample
pH	13.4	13.1
SS (%)	14.5	14.2
Inorganic substance (%)	9.7	8.8
Organics (%)	4.8	5.5
EA (NaOH) (g/L)	6.3	2.2
COD_{Cr} (mg/L)	114,000	83,000

Pulp Properties

Table 5 shows that after the pretreatment, the crude pulp weighed 1020.9 g with the yield of 44.9%, which is greater than the control sample with yield of 40.8%. Greater yield pulp of pretreatment with ionic liquid will be beneficial for the utilization of raw material. The permanganate number of pulp has been reported to be related to the lignin contents, compared with control sample, the pretreated pulp with lower permanganate number means more lignin have been separated from cellulose effectively, which will be favor for the subsequent beating and bleaching process.

Table 5. Properties of Eucalyptus Pulp

Sample	Crude Pulp Weight (g)	Yield (%)	Permanganate Number	Viscosity (cP)
Pretreated pulp	1020.9	44.9	12.9	871.2
Untreated pulp	861.4	40.8	14.6	809.4

Analysis of the Fiber Quality of the Pulp and the Control Sample in the Pretreatment of Ionic Liquids

The fines composition of the pulp is an important part of the paper fiber material that can affect the physical properties of the paper. Figure 2 shows that the ionic liquid pretreatment pulp's fines component content was higher than that of the blank sample.

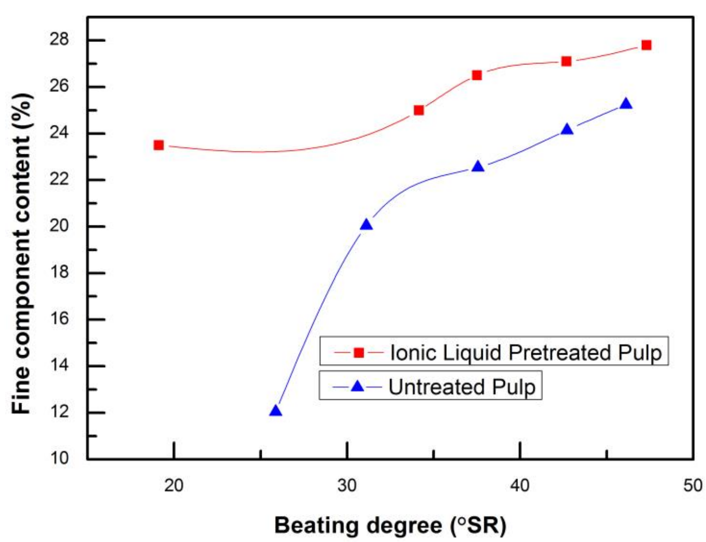

Fig. 2. Fines component content

Both samples showed an upward trend and then tended to plateau. The beating process of ionic liquid pretreatment pulp fine component content was less affected; the influence of small components in the ionic liquid pretreatment process increased the strength of pulp fibers and improved the resistance to shearing action. The ionic liquid pretreatment pulp fine component content was high, which is helpful for the retention of the wet part of the paper.

In the papermaking process, moderate amounts of fines can be filled between the long fibers to achieve an interwoven fiber structure with bridging effects, leading to enhanced sheet strength. However, too many fines will lead to the poor performance of the drainability of pulp. In the present work a slight increase in fines with ILs pretreatment mainly resulted in the enforcements in paper strength with little impact on performance of pulp drainability.

Fiber roughness affects the flexibility, adhesion, and physical strength of the paper. It also has an effect on the permeability of the paper, the smoothness of the air permeability, and the degree of smoothness. Figure 3 shows that at the same beating degree, the roughness of ionic liquid pretreatment pulp was slightly higher than untreated pulp. With the increase in beating degree, the degree of roughness first increased and then decreased after 42.3 °SR.

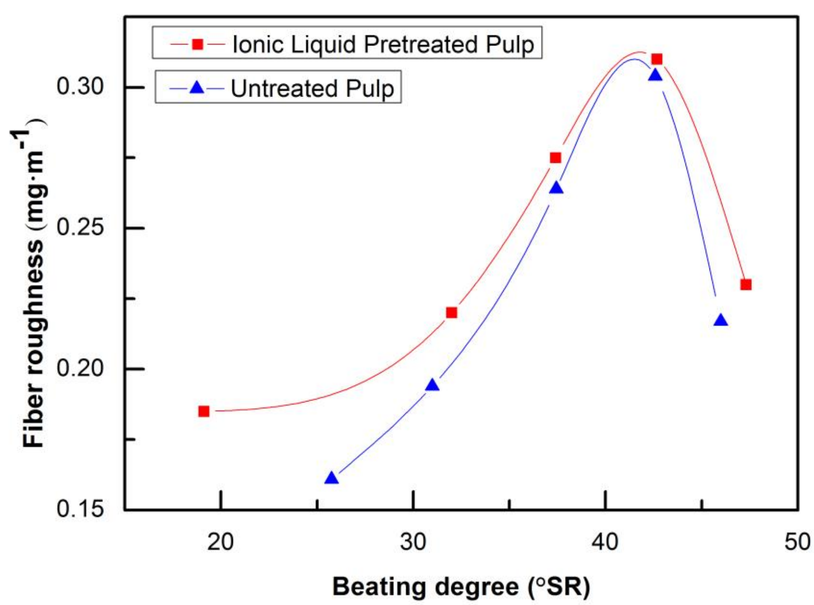

Fig. 3. Fiber roughness

In the process of beating, the friction between the fiber and beating equipment for fiber shear force can cause fiber deformation, changing the curl index and kink index. Figures 4 and 5 show that, in the condition of the same beating degree, the curl index and kink index of alkaline ionic liquid pretreatment sample were lower than that of untreated pulp. Because part of the lignin is extracted from the pulp in the pretreatment process of ionic liquids, the pulp fiber can better absorb water swelling and fibrillation, which reduces the fiber curl index and kink index.

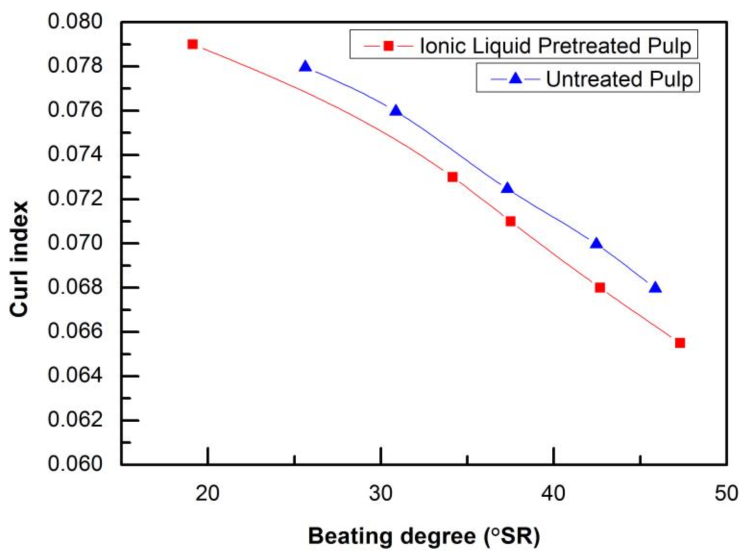

Fig. 4. Curl index

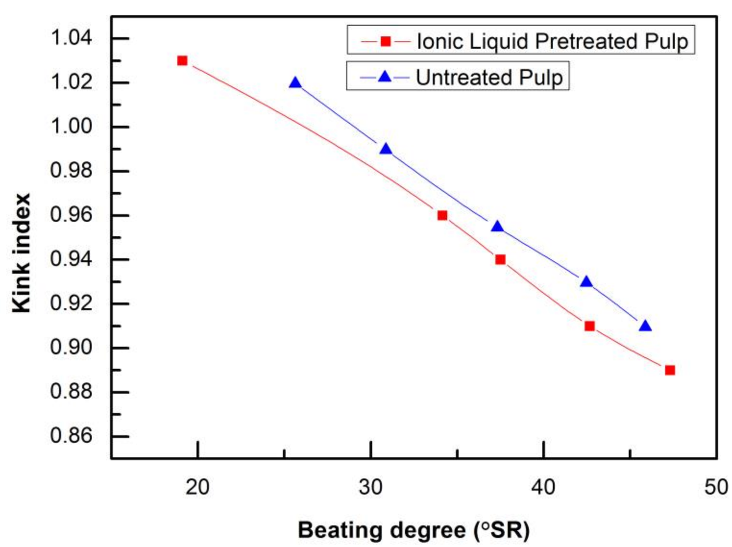

Fig. 5. Kink index

Different Beating Degree of Ionic Liquid Pretreatment Physical Properties of Pulp Samples and Control Samples of Handsheet

Handsheet density is an important index for paper properties. From Fig. 6(a), the handsheet density increased with increasing beating degree. This may result because the ionic liquid pretreatment renders the fibers more conformable following the beating process, leading to a more interwoven structure. The binding force between fibers increases with the extent of beating, such that the fibers have an even tighter structure after drying of the paper. In the condition of the same beating degree, the alkaline ionic liquid extract slurry internal splitting and fiber interior swelling proceed easily due to the removal of part lignin in the raw materials. A large number of fiber fines are released, and these fines can fill the gaps among the long fibers in the paper.

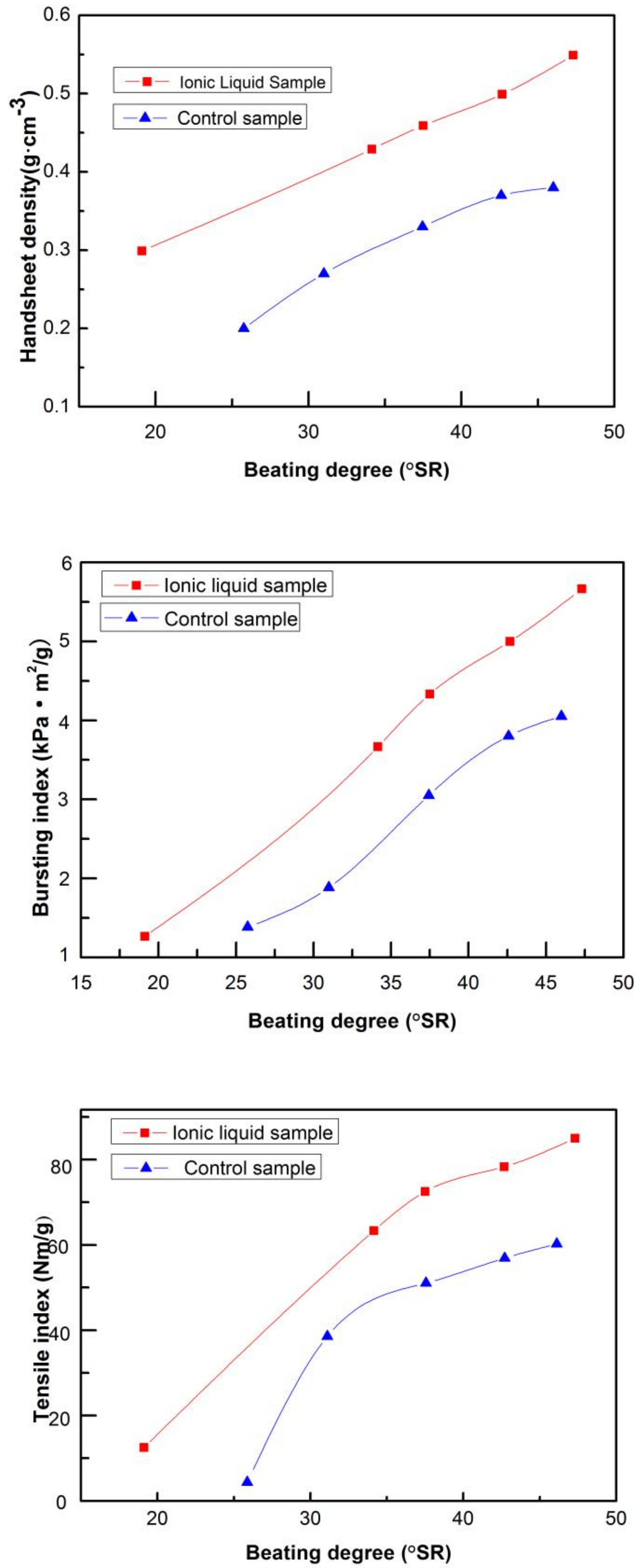

Fig. 6. Comparison of physical properties of handsheets in different beating degree after the treatment with ionic liquids: a) handsheet density, b) bursting index, c) tensile index

Moderate amounts of fines can fill in spaces between the long fibers to make the fibers more closely interwoven, due to bridging effects, such that the sheet strength can be enhanced. The hydrogen bonding between the fibers increases, and the bond strength between the fibers is improved. This makes the handsheet density of the ionic liquid pretreatment sample higher than that of the untreated sample.

Tensile index and bursting index increased due to the stronger weaving force between fibers. Tensile index and bursting index are important properties of paper. From Fig. 6(b) and (c), and in the condition of the same beating degree, the tensile index and bursting index of the ionic liquid pretreatment pattern were significantly higher than the corresponding untreated samples. In the alkaline ionic liquid pretreatment process, most of the lignin is removed from the fibers; as a result, internal delamination and interior fiber swelling proceed easily. Therefore, the bonding between the fibers improved remarkably. The tensile index and bursting index of paper were also greatly improved. Paper properties were optimized.

CONCLUSIONS

1. Alkaline ionic liquids [Mmim]DMP were applied to pretreat eucalyptus chips before traditional pulping process. The results showed that short-time pretreatment with [Mmim]DMP could promote the separation of lignin with higher pulp yield and lower lignin content in pulp, which will be beneficial to subsequent alkali recovery and bleaching.
2. The fiber with pretreatment with [Mmim]DMP showed an improvement in pulping and beating properties with better fiber curl index and kink index. Paper tensile strength and burst strength were improved by about 40% and 60%, respectively. Alkaline ionic liquid pretreatment of biomass materials provides a new technical route for improving the conditions of pulping and papermaking while reducing the production cost and pollution load.

ACKNOWLEDGMENTS

The authors are grateful for the support of State Key Laboratory of Pulp and Paper Engineering (Project Number 2015C02). The authors also appreciate the financial support from the Science and Technology Planning Project of Guangdong Province (grant number 2015A020215009), National Natural Science Foundation of China (grant number 21476091, 21206046), and Science and Technology Planning Project of FoShan in Guangdong Province (grant number 2015AG10011).

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Article submitted: July 12, 2016; Peer review completed: August 14, 2016; Revised version received and accepted: August 28, 2016; Published: September 7, 2016.
DOI: 10.15376/biores.11.4.9036-9046