Enhancement of Delignification by Ionic Liquids Pretreatment and Modification of Hardwood Kraft Pulp in Preparation for Bleaching

Jianmin Peng,a Guihua Yang,a,* Letian Qi,a,* Jinke Liu,a Fengfeng Li,a Jiachuan Chen,a and Lucian Luciaa,b

Ionic liquids (ILs) pretreatment is shown to improve the pulp bleachability and modify the physical strength of the hardwood pulp during the oxygen-chlorine dioxide-hydrogen peroxide (ODP) bleaching. The pretreatment enhanced lignin removal in ODP bleaching, resulting in decreased lignin content of the pretreated pulp. The brightness and strength properties were improved. In particular, the folding strength was increased by 153% relative to the control when the pulp was pretreated by [TEA][HSO4]. The analysis of scanning electron microscopy, Fourier transform infrared spectroscopy, and X-ray diffraction confirmed the enhancement of delignification in ILs pretreatment by the removal of hemicellulose and lignin on pulp fibers’ surface, and the well-preserved fiber framework of the hardwood pulp fibers during ODP-bleaching.

Keywords: Bleachability; Hardwood pulp; Ionic liquids; Pretreatment; Properties

Contact information: a: State Key Laboratory of Biobased Material and Green Papermaking, Qilu University of Technology, Shandong Academy of Sciences, Jinan, Shandong 250353, P.R. China; b: Department of Forest Biomaterials, North Carolina State University, Raleigh, North Carolina 27695, USA.
* Corresponding authors: ygh@qlu.edu.cn; lqi01@qlu.edu.cn

INTRODUCTION

Elemental chlorine free (ECF) bleaching has been widely adopted because of its environmental, economic, and social benefits (Zhu et al. 2017). The ECF bleaching can reduce pollution by replacing chlorine and hypochlorite-based chemicals (Kaur et al. 2018). Various ECF oxidants, such as oxygen (O) (Li et al. 2016), chlorine dioxide (D) (Acharjee et al. 2017), and hydrogen peroxide (P) (Loureiro et al. 2011) have therefore been commonly used. They efficiently degrade lignin by attacking all the phenoxy units (Wu et al. 2017). Yet, an undesired reduction in physical strength has been widely reported due to carbohydrate degradation (Zhao et al. 2018). Other approaches, for example, laccase pretreatment, have been applied to enhance brightness, but a reduction in physical strength and viscosity occur (Ravalason et al. 2012). In general, a loss of physical strength is noticed while elevating the bleachability of pulp. Therefore, the development of a novel approach improving the bleachability while modifying the physical properties of hardwood pulp is desirable.

During ECF bleaching, chlorine dioxide can selectively cleave lignin fragments by imparting hydrophilic carboxylic groups that allow for dissolution of lignin (Sjostrom 1993; Karim et al. 2011). Hydrogen peroxide enhances brightness via lignin-chromophore oxidation reactions (Brogdon and Lucia 2005). However, lignin compounds in plant fibers are not only on the surface but also inside. Thereby, during the penetration and diffusion of the oxidizing agent, unnecessary carbohydrate degradation always takes place.
Therefore, it is important to develop an approach to loosen the lignocellulosic fiber structure, promote the accessibility of bleaching agent to lignin compounds, and ultimately reduce the influence on fiber strength. Various studies have been reported for this purpose such as using enzyme, ionic liquids, and ultrasonication (Yu et al. 2018).

Ionic liquids (ILs) are attractive “green solvents” on account of their good solubility, chemical stability, and recyclability (Anthony et al. 2002; Khan et al. 2017). Thus, they are good candidates to pretreat lignocellulose. Their strong coulombic and H-bonding ability disrupts the H-bond network within plant fibers, facilitating lignin removal (Da et al. 2013; Xu et al. 2017). In previous work of Peng et al. (2019), [HSO₄⁻]-based IL pretreatment was applied to protect the fibers from depolymerization by improving pulp viscosity during the bleaching of eucalyptus kraft pulp. These ILs pretreatments notably reduced kappa number and improved the physical strength. In addition, they reduced fines content, decreased water retention value, and reduced the amorphous regions of the pulp fibers. [BMIM][HSO₄] has been reported for the processing of plant fibers, presenting mild modification over compositions (da Costa Lopes et al. 2013) and enhancing bleachabilities (Peng et al. 2019). [TEA][HSO₄] was recently reported to present similar lignin removal effect yet with higher tolerance to the water content. It presented similar effectiveness with up to 20% of water, which allows a significantly reduction in the cost of IL synthesis. A promising investigation by Brandt et al. (2017) reported that the cost of [TEA][HSO₄] reached the same level as to methanol ($1/kg), yet with high efficiency processing lignocellulosic biomass. Thereby in this work, enhancement of [BMIM][HSO₄] and [TEA][HSO₄] ILs pretreatment on the bleachability and properties of hardwood kraft pulp during ODP bleaching was studied through a comprehensive overview of the advantages of the ILs pretreatment in ODP bleaching. The objective was to use ILs pretreatment to swell the structure of lignocellulose and modify the bleachability and strength properties in ODP bleaching thereby improving the pulp quality.

EXPERIMENTAL

Materials

Hardwood chips were obtained from a paper mill in China. 1-Butyl-3-methylimidazolium hydrogen sulfate ([BMIM][HSO₄], >95%) was obtained from Rhawn Chemical Co. Ltd. (Shanghai, China).

Triethylammonium hydrogen sulfate ([TEA][HSO₄], 83% in water solution) was synthesized following the method of Brandt-Talbot et al. 2017. The structure and purity of both ILs were confirmed with NMR. The ClO₂ (1 vol%) was obtained from Dahua Special Environmental Engineering Co. Ltd. (Shandong China), H₂O₂ (30%) and H₂SO₄ (98%) were purchased from Chemical Co. Ltd. (Laiyang China). Triethylamine (99%), anhydrous magnesium sulfate (99%), NaOH (>96%), and Na₂S (>98%) were obtained from Fuyu Fine Chemical Co. Ltd. (Tianjin China). All chemicals used were analytically pure.

Methods

Pulp preparation

The hardwood pulping conditions used were 21% active alkali, 25% sulfidity, 170 °C, and 90 min. The pulp chemical composition was: cellulose = 81.77 wt%, lignin = 15.30%, and hemicellulose = 3.52%. The properties of the pulp were kappa number of 20.04, brightness of 28.24 %ISO, and pulp viscosity of 1015 mL/g.
Ionic liquid pretreatment

Approximately 25 g of oven-dried pulp was mixed with 2.5 g of ILs in a sealed polyethylene bag, then water was added into the mixture to keep 10% of consistency. The pretreatment was conducted in a water bath at 60 °C for 60 min.

ODP bleaching

First, the pretreated pulp was adjusted to 10% of consistency in a polyethylene bag, and bleached in an ODP bleaching sequence. The conditions of ODP bleaching sequence were 0.5 MPa of oxygen pressure, 4% of Na₂O, 100 °C for 60 min in an oxygen stage (O); 9 kg/t pulp of ClO₂ dosage, pH value in the range 2 to 3, 70 °C for 30 min in chlorine dioxide stage (D), 12 kg/t pulp of H₂O₂ dosage, 5 wt.% of NaOH dosage for adjusting pH to the range 11 to 12, and 90 °C for 60 min in hydrogen peroxide stage (P).

Ionic liquid recovery

The effluent after oxygen delignification stage was collected and filtered to remove insoluble content. The filtrate was collected and dehydrated under rotary evaporation, followed by centrifugation and filtration. The filtrate was again collected and dehydrated under reduced pressure with Schlenk line at 70 °C for 24 h. The structure and purity of the recycled ILs was checked by NMR.

Pulp analysis

The content of cellulose, hemicellulose, and lignin were determined according to TAPPI T 201 wd-76 (2004), T 223 cm-01 (2004) and T 222 om-11 (2011), respectively. Analysis of pulp viscosity was obtained using the method of ISO 10650 (1999), and the degree of polymerization (DP) of pulp was calculated based on the pulp viscosity (η). The DP was calculated according to the Eq. 1 (Mazumder et al. 2000):

\[ DP^{0.905} = 0.75 [\eta] \]

Pulp yield was calculated as the mass ratio of pulp sample before and after bleaching. Kappa number of pulp was determined according to the ISO 302 (2004) method. The water retention value (WRV) of pulp was determined according to the ISO 23714 (2013) method. The weight mean length, weight mean width, and fines content of pulp fibers were measured using a fiber quality analyzer (FQA-LDA02, OpTest Equipment Inc., Ontario, Canada).

Handsheet preparation

Pulp handsheets were prepared according to the literature (Chen et al. 2017). The grammage of the prepared pulp handsheet was 80 g/m², and they were conditioned at 23 °C and 50% humidity for 24 h prior to analysis. The properties include of tensile index, tear index, folding endurance, and brightness of the pulp handsheets were measured according to the TAPPI standard methods TAPPI T494 om-01 (2004), TAPPI T414 om-04 (2004), TAPPI T511 om-02 (2004) and TAPPI T452 om-02 (2004), respectively.

Scanning electron microscopy (SEM)

The surface observations of pulp fibers were done using a scanning electron microscope (Regulus 8220, Hitachi, Tokyo, Japan). The oven dried samples were thoroughly scanned at 5 kV accelerating voltage and 2000 times magnification.
Fourier transform infrared spectroscopy (FTIR)

The FT-IR analysis of the pulp samples were conducted using a Bruker FT-IR (Vertex70, Bruker, Karlsruhe, Germany) and the scanning range was 4000 to 500 cm\(^{-1}\), with a resolution ratio of 4 cm\(^{-1}\) and a scanning speed of 32 s\(^{-1}\).

X-ray diffraction (XRD) analysis

The degree of crystallinity of the pulp was evaluated using a X-ray diffraction (D8-Advance, Bruker, Karlsruhe, Germany). The scan mode used was 2\(\theta\) at 35 mA. Angles ranged from 5° to 60°. The crystallinity index of various samples was determined according to (Segal et al. 1959) Eq. 2:

\[
CrI (%) = 100 \times \frac{(I_{002}-I_{am})}{I_{am}}
\]

where \(CrI\) was the crystallinity of cellulose, \(I_{002}\) was the scattering intensity of the diffraction of 002 plane, \(I_{am}\) was the diffraction intensity at 2\(\theta\) =15.6°.

RESULTS AND DISCUSSION

Effect of ILs Pretreatment on the Chemical Compositions and the Bleachability of the Hardwood Pulp

Effects of ILs pretreatment on the composition of bleached pulp during ODP bleaching are shown in Table 1, while the effect of ILs pretreatment on the bleachability of the kraft pulp during ODP bleaching process is listed in Table 2. Table 1 shows that ILs pretreatment protected the pulp fibers by increasing the cellulose content and viscosity, and enhanced lignin removal during ODP bleaching. The lignin content and kappa number of the pulp pretreated by [TEA][HSO\(_4\)] were decreased by 18% and 69%, while the brightness increased by 1.33 %ISO compared to the control. Thereby ILs pretreatment can enhance and modify bleachability. As shown in Table 2, the ILs pretreatment also increased pulp yield, demonstrating the protection effect of ILs pretreatment for pulp fibers, which did not influence the drainability as shown in a stable water retention value (WRV).

Table 1. Compositions of the Pretreated and Unpretreated Pulp during ODP Bleaching Process

<table>
<thead>
<tr>
<th>ILs Pretreatment</th>
<th>Cellulose (%)</th>
<th>Hemicellulose (%)</th>
<th>Lignin (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>95.27±0.21</td>
<td>2.44±0.08</td>
<td>1.97±0.07</td>
</tr>
<tr>
<td>[BMIM][HSO(_4)]</td>
<td>95.45±0.13</td>
<td>1.87±0.13</td>
<td>1.83±0.06</td>
</tr>
<tr>
<td>[TEA][HSO(_4)]</td>
<td>96.23±0.12</td>
<td>2.25±0.12</td>
<td>1.62±0.03</td>
</tr>
</tbody>
</table>

Table 2. Effect of ILs Pretreatment on the Bleachability of Hardwood Pulp during ODP Bleaching Process

<table>
<thead>
<tr>
<th>ILs Pretreatment</th>
<th>Brightness (%ISO)</th>
<th>Kappa number</th>
<th>Yield (%)</th>
<th>WRV (g/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>79.17±0.05</td>
<td>1.54±0.08</td>
<td>96.76</td>
<td>1.50±0.04</td>
</tr>
<tr>
<td>[BMIM][HSO(_4)]</td>
<td>79.80±0.03</td>
<td>0.67±0.08</td>
<td>97.09</td>
<td>1.41±0.05</td>
</tr>
<tr>
<td>[TEA][HSO(_4)]</td>
<td>80.50±0.02</td>
<td>0.48±0.08</td>
<td>97.23</td>
<td>1.49±0.02</td>
</tr>
</tbody>
</table>
Effect of ILs Pretreatment on Fiber Qualities and Strength Properties of the Pulp

Effect of ILs pretreatment on fiber qualities and strength properties of the pulp during ODP bleaching are shown in Tables 3 and 4. Table 3 showed an increase of length, width, viscosity, and DP of the pretreated pulp fibers. As can be seen, the viscosity and DP increased by 17.8% and 19.8%, respectively, while fines content decreased compared to the control. Table 4 showed that the tensile index, tear index, and folding endurance of the pretreated pulp during ODP bleaching were all improve. In particular, the folding endurance of the pulp pretreated by [BMIM][HSO₄] and [TEA][HSO₄] increased by 100% and 153%, respectively, compared to the control pulp. These results are consistent with increase of length, viscosity, and DP of the pretreated pulp fibers showing an enhancement of ILs pretreatment on the bleachability and strength properties of hardwood pulp.

Both ILs pretreatment in this work facilitated the dissolution of lignin during the bleaching process, which contributed to the swelling of the pulp fibers, and possibly led to the higher fiber width within pretreated samples. It should be admitted that only minor difference in lignin content was found in the final ODP bleached samples, which could be attributed to the mild pretreatment conditions. ILs dispersed into the vast aqueous phase allowing a desirable mild modification over the pulp fibers, by the meantime avoided ILs attaching on the surface of pulp fibers. Therefore the recycling of the ILs was easily achievable.

On the other hand, the IL pretreatment dissolved hemicellulose component and modified the micro-fiber compositions. The mild process conditions allowed the modification of micro-fiber to take place while keeping the cellulose framework untouched. Hence, the fiber length of pulp increased, resulting in an increase of viscosity and DP of the pulp fibers. All these effects mentioned above contributed to the enhancement of the physical strength in the handsheets.

In addition, the ionic liquids used in the pretreatment process could be recycled by collecting the effluent after oxygen delignification stage, where up to 98% of ILs could be recovered. These ILs could be reused after purification to process handsheet with similar physical strength upto 3 cycles.

### Table 3. Effect of IL Pretreatment on Pulp Fibers Qualities during the ODP Bleaching Process

<table>
<thead>
<tr>
<th>ILs Pretreatment</th>
<th>Fiber length (mm)</th>
<th>Fiber width (μm)</th>
<th>Fines (%)</th>
<th>Viscosity (mL/g)</th>
<th>DP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$L_c$ (n)</td>
<td>$L_c$ (w)</td>
<td>13.50</td>
<td>4.19</td>
<td>684±3</td>
</tr>
<tr>
<td>--</td>
<td>0.631</td>
<td>0.793</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[BMIM][HSO₄]</td>
<td>0.632</td>
<td>0.796</td>
<td>13.61</td>
<td>4.02</td>
<td>721±4</td>
</tr>
<tr>
<td>[TEA][HSO₄]</td>
<td>0.639</td>
<td>0.795</td>
<td>13.60</td>
<td>3.24</td>
<td>806±4</td>
</tr>
</tbody>
</table>

Definitions: $L_c$ (n) = number mean length; $L_c$ (w) = weight mean length

### Table 4. Effect of IL Pretreatment on the Physical Strength of Pulp Handsheet

<table>
<thead>
<tr>
<th>ILs Pretreatment</th>
<th>Tensile index (N·m·g⁻¹)</th>
<th>Tear index (mN·m²·g⁻¹)</th>
<th>Folding endurance (times)</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>52.75±0.25</td>
<td>6.93±0.24</td>
<td>126±12</td>
</tr>
<tr>
<td>[BMIM][HSO₄]</td>
<td>57.13±0.50</td>
<td>7.60±0.06</td>
<td>252±6</td>
</tr>
<tr>
<td>[TEA][HSO₄]</td>
<td>60.13±0.13</td>
<td>7.87±0.13</td>
<td>319±10</td>
</tr>
</tbody>
</table>
SEM Analysis

The fibers morphology of the ODP bleached pulp were accessed from SEM analysis, as shown in Fig. 1. According to Fig. 1(a), the control pulp fibers showed a smooth surface during bleaching illustrating the removal of the wax and encrusting substances on the fiber surface (Mohtar et al. 2017). Figures 1(b) and 1(c) displayed cracks and holes on fiber surface including small fragments were observed after ILs pretreatment, which validated successful removal of hemicellulose and lignin on pulp fibers’ surface.

Fig. 1. SEM images of the ODP bleached pulp: (a) Control pulp; (b) [BMIM][HSO₄] pretreated pulp; and (c) [TEA][HSO₄] pretreated pulp.

FTIR Analysis

The FTIR spectra of the pulp samples are shown in Fig. 2, where the peak at 3400 cm⁻¹ corresponded to stretching vibration of O-H groups, the absorbance at 2940 cm⁻¹ to 2850 cm⁻¹ for C-H stretching vibration (Mohtar et al. 2017), the peaks at 1437 cm⁻¹ and 1335 cm⁻¹ were characteristic absorption peaks of lignin (Bouchard and Douek 1993), the absorbances at 1160 cm⁻¹ and 1060 cm⁻¹ were associated with C-O-C tensile vibrations and C-O-C pyranose ring skeletal vibration, and the peak at 898 cm⁻¹ was a β-type glycosidic bond vibration, indicating that the xylan units were linked by a β-type glycosidic bond (Sun et al. 1996). As shown in Fig. 2, there was no new characteristic peak appearing for the pretreated pulp fibers, which confirmed that ILs pretreatment can only change the physical structure of pulp fibers, but did not alter the chemical structure such as functional groups.

Fig. 2. FTIR analysis of the ODP bleached pulp: (a) Control pulp; (b) [BMIM][HSO₄] pretreated pulp; and (c) [TEA][HSO₄] pretreated pulp.
XRD Analysis

Figure 3 shows the XRD patterns of the ODP bleached pulp. In Fig. 3, the cellulose fraction indicated two peaks corresponding to \(I_{101}\), \(I_{002}\), which appeared at 15.6° and 22°, respectively. As shown in Fig. 3, the crystallinity of the control pulp was 36.2%, while that of the pulp pretreated by [BMIM][HSO\(_4\)] and [TEA][HSO\(_4\)] were 48.8% and 50.3%, respectively. In other words, an increase of crystallinity by 35% and 39%, compared to the control pulp was observed, which further indicated the enhancement of ILs pretreatment on the bleachability and properties of hardwood kraft pulp due to removal of hemicellulose and lignin during ODP bleaching. Meanwhile, the protection of ILs on the pulp fibers resulted in retaining cellulose with a higher degree of crystallinity (Rosli et al. 2013).

![Figure 3](image_url)

**Fig. 3.** XRD analysis of the ODP bleached pulp: (a) Control pulp; (b) [BMIM][HSO\(_4\)] pretreated pulp; and (c) [TEA][HSO\(_4\)] pretreated pulp

CONCLUSIONS

1. Ionic liquids pretreatment enhanced the bleachability and properties of hardwood kraft pulp during ODP bleaching.
2. A decrease of lignin content and increase of brightness and strength properties of the pretreated pulp were obtained compared to the control; especially the folding strength of the pulp pretreated by [TEA][HSO\(_4\)] considerably increased by 153%.
3. The crystallinity of the pulp pretreated by [BMIM][HSO\(_4\)] and [TEA][HSO\(_4\)] increased by 35% and 39%, respectively.
4. The analysis of SEM and FTIR confirmed the enhancement of delignification in ILs pretreatment by the removal of hemicellulose and lignin on pulp fibers surface, and the well-preserved fiber framework of the hardwood pulp fiber during ODP-bleaching.
ACKNOWLEDGMENTS

The authors are grateful for the financial support received from the National Natural Science Foundation of China (Grant No. 31770628), the Provincial Key Research and Development Program of Shandong (Grant No. 2019JZZY010326, 2019JZZY010328) and the Taishan Scholars Program.

REFERENCES CITED


TAPPI T201 wd-76 (2004). “Cellulose in pulp (Cross and Bevan method),” TAPPI Press, Atlanta, GA.


TAPPI T223 cm-01 (2004). “Pentosans in wood and pulp,” TAPPI Press, Atlanta, GA.


TAPPI T452 om-02 “Brightness of pulp, paper and paperboard (Directional reflectance at 457 nm),” TAPPI Press, Atlanta, GA.

TAPPI T511 om-02 “Folding endurance of paper (MIT Tester),” TAPPI Press, Atlanta, GA.


Article submitted: December 5, 2019; Peer review completed: January 24, 2020; Revised version received and accepted: April 8, 2020; Published: July 1, 2020.
DOI: 10.15376/biores.15.3.6299-6308