Effects of Pectinase Treatment on Pulping Properties and the Morphology and Structure of Bagasse Fiber

Xiuyu Liu, a,b,1 Yan Jiang, a,b,1 Shuang Yang, a,b Xuemei Meng, a,b Xueping Song, a,b and Min Wu a,b,*

Bagasse was pretreated by pectinase, and both the control and pretreated bagasse were subjected to soda-anthraquinone (AQ) pulping. There were significant improvements in pulp properties after pectinase treatment, such as relative increases of brightness (5.5%), breaking length (17.1%), burst factor (16.5%), and tear factor (7.0%). The samples were analyzed by a fiber analyzer, scanning electron microscope (SEM), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR). The pectinase treatment changed the material properties, which would improve the efficiency of subsequent pulping, such as increasing the fiber length (20.0%), lowering the fines length (10.6%), and increasing the percentage of flexible fiber. Pectinase treatment removed some non-cellulose components; in particular, the pectin and alcohol-benzene extractives were decreased by 19.4% and 37.3% after enzymatic treatment. The hemicellulose and lignin were decreased by 5.5% and 1.9%, respectively. A bulkier and more collapsed fiber surface was observed in the treated fibers, which suggested greater pore volume and more accessible surface area. Treatment caused a slight incline by 4.8% in the crystallinity index. Some chemical structures in pectin, hemicellulose, and lignin were partly broken, showing the effect of pectinase treatment on the degradation of non-cellulose components. Pectinase treatment prior to pulping is therefore recommended, given its efficiency and eco-friendly nature.

Keywords: Pectinase treatment; Bagasse pulp; Fiber properties; Surface characterizations; Chemical components; Structures

Contact information: a: College of Light Industry and Food Engineering, Guangxi University, Nanning, 530004, PR China; b: Guangxi Key Laboratory of Clean Pulp & Papermaking and Pollution Control, Nanning 530004, PR China; 1: These authors contributed equally to this work; *Corresponding author: wumin@gxu.edu.cn

INTRODUCTION

Sugarcane bagasse, which is a fibrous residue of cane stalks left over after the juice has been extracted from sugarcane, is one of the largest cellulosic agro-industrial by-products (Pandey et al. 2000). However, while part of it is burned in sugar factories for energy purposes (heat and electrical), there is a considerable surplus of bagasse that can be used in pulp and paper production (Singhal et al. 2015).

Soda-AQ pulping produces a pulp with better properties, but at the same time it brings about some disadvantages, such as high chemical charge in pulping and bleaching and environmental pollution (Ates et al. 2008). Biopulping, which was used in fiber pretreatment prior to chemical pulping, would be a potential solution for some of the soda-AQ pulping problems, by, for instance, decreasing chemical consumption during pulping and bleaching (Liu et al. 2017), improving pulp strength properties, and reducing environmental pollution (Kaur et al. 2010; Martin-Sampedro et al. 2011). Biopulping can
result in better fiber qualities due to the superior flexibility, compressibility, collapsibility, and conformability of fibers produced using this method (Chen et al. 2010).

The enzymes used in biopulping include cellulases, hemicellulases, and ligninolytic enzymes such as lignin peroxidases, manganese peroxidases, and pectinases (de Souza-Cruz et al. 2004; Sittidilokratna et al. 2004; Martin-Sampedro et al. 2011). Of the enzymes mentioned above, pectinase has been applied in biopulping due to its selective removal of pectin. Pectic substances are common in the plant kingdom and form a major component of the middle lamella along with lignin, a thin layer of adhesive extracellular material found between the primary cell walls of adjacent young plant cells. Pectin is the protective barrier of the fiber, and the removal of pectin can promote the accessibility of certain chemicals and accelerate subsequent soda-AQ pulping (Pedrolli et al. 2009). In addition, pectinase is a multicomponent enzyme that includes pectin esterase, polygalacturonase, and lyase; it catalyzes the hydrolysis of the glycosidic bonds in pectic polymers and cleaves either at the end (exo-) or in the interior (endo-) of the pectin chain (Hoondal et al. 2002). Moreover, pectinases have been used in the treatment of plants to eliminate pectin, thus modifying the physical network of fibers and further affecting the properties of the fibers as well as separating the fibers (Evans et al. 2002). To date, there has not been a thorough study into the application of pectinase pretreatment prior to chemical pulping, which has implications for the improvement in pulping efficiency and quality.

The properties of fibers, such as fiber length, fines content, and width, greatly affect the quality of pulp and paper. Moreover, the content of lignin, the lignin distribution, and the hemicellulose content in lignocellulosic substrates determine the subsequent pulping efficiency (Kumar and Wyman 2009). The pulping process is also greatly influenced by the exterior and interior characteristics of the substrates, including cellulose crystallinity, pore volume, and accessible surface area (Tozzi et al. 2013; Song et al. 2016). Therefore, it is important to study the variation in physico-chemical parameters that occur after pectinase pretreatment.

In this study, the effects of pectinase pretreatment on the pulp properties were evaluated, and the chemical components of bagasse and the fiber properties after pectinase pretreatment were measured. Scanning electron microscopy (SEM) was conducted to monitor the morphological changes occurring on the surface of the bagasse. Finally, the functional groups and crystalline structure of bagasse fiber were analyzed using Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD), respectively.

**EXPERIMENTAL**

**Materials**

The bagasse samples were supplied by Guangxi Huajing Group Co., LTD (Nanning, China). The enzymes used in this work contained 3000 IU/mL of pectinase, and a small amount of ligninase, xylanase, and mannase and were purchased from Sukehan Company (Weifang, China).

**Enzymatic Pretreatment**

Bagasse was pretreated with the pectinase in a 4 L reactor under the following conditions: temperature, 55 °C; pulp consistency, 10%; initial pH, 9.0 (adjusted with acetate buffer); pectinase dosage, 60 IU/g of oven-dried bagasse; and total time, 60 min (Liu et al. 2017). The control samples were subjected to the same treatment conditions
without the addition of the enzyme. After treatment, these pulps were filtered and thoroughly washed with distilled water.

Production of Pulps

All bagasse samples were subjected to soda-AQ pulping in an oil bath rotating digester. The conditions of cooking were as follows: alkali dosage, 13%; anthraquinone dosage, 0.05%; ratio of liquor to bagasse, 5:1 (v/w); maximum temperature, 158 °C; heating time, 100 min; and holding time, 100 min (Liu et al. 2017).

Analysis of Properties of Soda-AQ Pulps

Handsheets were prepared with pulp according to TAPPI T205 sp-02 (2002). The following properties of the handsheets were determined: brightness (TAPPI T217 wd-77 2004); breaking length (TAPPI T494 om-01 2001); burst factor (TAPPI T403 om-10 2010); and tear factor (TAPPI T414 om-04 2004). All experiments were carried out in triplicate, and the results are presented as the average values.

Measurement of Fiber Properties

A Kajaani FiberLab analyzer (Kajaani, Finland) was used to measure the fiber properties, including fiber length, fine, width, curl, and kink index according to the method of TAPPI T271 om-02 (2002) and the procedure of Metso paper company (FiberLab 2001). Values were given as the average of three independent determinations for each sample.

Pulp Chemical Components

The chemical components of the bagasse samples, before and after pectinase pretreatment, were determined as follows: cellulose (TAPPI T17 wd-70 2002), pentosan (TAPPI T223 cm-01 2004), acid-insoluble lignin (TAPPI T222 om-02 2004), ethanol-benzene extractives (TAPPI T204 cm-97 2004), and ash content (TAPPI T211 -02 2004). Values were given as an average of three independent determinations for each sample. Using gas chromatography, an analysis of the pectin degradation was performed to determine acidic sugars. Galacturonic acid was converted to acidic sugars by an acid methanolysis in which the depolymerized carbohydrates were silylated. The contents of the acidic sugars were determined using an Agilent 6890N HPLC (Agilent Technology, Palo Alto, CA, USA) equipped with FID detector and DB-1 (30 m × 0.32 mm × 0.25 μm) (Pakarinen et al. 2012). The conditions were as follows: oven temperature of 150 °C (5 min), 2 °C min⁻¹ to 186 °C, followed by 1 °C min⁻¹ to 200 °C and 20 °C min⁻¹ to 325 °C; injector temperature of 225 °C; and FID temperature of 280 °C. The injection volume was 2 μL with a split ratio of 1:30, and the flow rate of the carrier gas helium was 1 mL min⁻¹.

SEM Analysis

The scanning electron microscope (SEM) images of bagasse fibers were obtained using an S-3400N-II microscope (Hitachi, Tokyo, Japan). Gold was sputtered on the samples (one cycle of 120 seconds) before they were examined in secondary electron mode at a beam current of 100 mA and an accelerating voltage of 10 KV.

XRD Analysis

The cellulose crystallinity of bagasse fiber was characterized using powder X-ray diffraction (XRD). The X-ray source was Cu target, and the Kα-ray was generated at 40 KV and 40 mA. The CuKα radiation was filtered with nickel filters, and its radiation
wavelength was 0.15418 nm. Scans were obtained from 5 to 50 degrees 2θ in 0.02 degrees steps for 0.1 seconds per step. The XRD spectra were further analyzed using Jade 8 software (Livermore, USA), through which crystallinity data were obtained. The crystallinity index (CI) is typically used to illustrate the relative amount of crystalline material in cellulose. It was calculated from the height ratio between the intensity of the crystalline peak ($I_{002}$-$I_{am}$) and the total intensity ($I_{002}$) according to Segal's method as follows (Segal et al. 1959),

$$\text{CI} = \frac{I_{002} - I_{am}}{I_{002}} \times 100$$

where $I_{002}$ is the maximum intensity of the crystalline peak at 2θ between 22° and 23° for cellulose I (between 18° and 22° for cellulose II) and $I_{am}$ is the minimum intensity of the amorphous cellulose at 2θ between 18° and 19° for cellulose I (between 13° and 5° for cellulose II) (Roncero et al. 2005).

**FTIR Spectra Analysis**

The analysis of the samples was performed using a Perkin-Elmer 2000 spectrometer (Phoenix, USA). A total of 100 scans, at a resolution of 2 cm$^{-1}$, were taken for each sample. The fibers were cut in an IKA MF10 cutting mill and then sieved to produce fibers in a size range from 106 to 212 mm. A mixture of 5.0 mg dried sample and 200 mg KBr was pressed into a wafer for the FTIR measurement.

**RESULTS AND DISCUSSION**

**Effects of Pectinase Pretreatment on Soda-AQ Pulps Properties**

The enzyme-treated and control bagasse samples were subjected to soda-AQ pulping under the same conditions. The brightness and physical strength properties of the handsheets prepared with the soda-AQ pulps are shown in Table 1.

**Table 1. Effects of Pectinase Pretreatment on Pulps Properties**

<table>
<thead>
<tr>
<th></th>
<th>Brightness (% ISO)</th>
<th>Breaking Length (km)</th>
<th>Burst Factor (kPa·m$^2$/g)</th>
<th>Tear Factor (mN·m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>35.00 ± 0.05</td>
<td>1.87 ± 0.04</td>
<td>3.22 ± 0.02</td>
<td>6.25 ± 0.03</td>
</tr>
<tr>
<td>Pretreatment</td>
<td>36.91 ± 0.07</td>
<td>2.19 ± 0.03</td>
<td>3.75 ± 0.04</td>
<td>6.69 ± 0.05</td>
</tr>
</tbody>
</table>

Compared with the control, the pulps from bagasse pretreated with pectinase had higher ISO brightness (about 2% ISO higher). After pectinase pretreatment, some properties of physical strength of the pulps were improved, such as breaking length by 17.1%, burst factor by 16.5%, and tear factor by 7.0%. These results revealed that pretreatment with pectinase before pulping could yield further improvements in the paper quality. The results were similar to findings form other researchers (Pulkkinen et al. 2006; Garmarood et al. 2011). The pectinase pretreatment may facilitate an increase in fiber average length and variations in the level of fiber bonding (Bajpai 1999). A longer average fiber length could lead to a higher tear index for pulps. Moreover, the higher level of fiber bonding could lead to a higher breaking length and better burst factor. Additionally, the pulp brightness was slightly improved by pectinase pretreatment. This result might reflect the decrease in residual lignin content in the pulps. A thorough study into the properties
and morphology of bagasse fiber after pectinase treatment would promote a deeper understanding about the effects of pectinase pretreatment on soda-AQ pulping.

**Effects of Pectinase Pretreatment on Fiber Properties of Soda-AQ Pulps**

Table 2 shows the effects of pectinase pretreatment on the soda-AQ pulp fiber properties, such as average fiber length, average fines length, average fiber width, fiber curl, and fiber kink index. The pectinase-pretreated samples had greater fiber lengths than the controls. This result could partly be explained by a reduction in the fines fraction due to the decrease in F(l) and F(n). Compared with the control, slight increases in the fiber curl and kink indices were observed after pretreatment. Also, an increase in the fiber flexibility would be beneficial to the improvement of fiber length due to the increase in the curl and kink index. These findings were in agreement with other results (Evans et al. 2002).

**Table 2. Effects of Pectinase Pretreatment on Fiber Properties of Soda-AQ Pulps**

<table>
<thead>
<tr>
<th></th>
<th>Fiber Length (mm)</th>
<th>Fines Length (%)</th>
<th>Width (μm)</th>
<th>Curl (%)</th>
<th>Kink Index</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L(l)</td>
<td>L(w)</td>
<td>L(n)</td>
<td>F(l)</td>
<td>F(n)</td>
</tr>
<tr>
<td>Control</td>
<td>0.92 ± 0.03</td>
<td>1.57 ± 0.03</td>
<td>0.45 ± 0.02</td>
<td>7.10 ± 0.06</td>
<td>28.28 ± 0.04</td>
</tr>
<tr>
<td>Pretreatment</td>
<td>1.03 ± 0.02</td>
<td>1.68 ± 0.04</td>
<td>0.54 ± 0.01</td>
<td>6.19 ± 0.05</td>
<td>25.27 ± 0.06</td>
</tr>
</tbody>
</table>

L(l), length-weight fiber length; L(w), weight-weight fiber length; L(n), arithmetic fiber length; F(l), length-weight fiber fines; F(n), arithmetic fiber fines.

However, both the length-weight fiber fines (Fine (l)) and the arithmetic fiber fines (Fine (n)) of the bagasse soda-AQ pulp were reduced. In this respect, after pretreatment, the lower content of fine length and the higher percentage of flexible fiber with more collapsibility in the soda-AQ pulp could produce a paper with improved qualities (Hoondal et al. 2002), which agreed with the results of the superior pulp physical properties displayed in Table 1. The higher fiber curl and kink indices in the pulp could be explained by their higher fiber coarseness and higher cell wall flexibility, and that the effect of pectinase treatment on the chemical components of fibers was also responsible for this result.

**Table 3. Effects of Pectinase Pretreatment on Chemical Components of Bagasse**

<table>
<thead>
<tr>
<th></th>
<th>Cellulose (%)</th>
<th>Pentosan (%)</th>
<th>Acid-insoluble Lignin (%)</th>
<th>Alcohol-benzene Extractive (%)</th>
<th>Ash Content (%)</th>
<th>Galacturonic Acid (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>46.85 ± 0.05</td>
<td>26.48 ± 0.05</td>
<td>20.84 ± 0.05</td>
<td>2.71 ± 0.03</td>
<td>3.33 ± 0.06</td>
<td>0.98 ± 0.02</td>
</tr>
<tr>
<td>Pretreatment</td>
<td>47.98 ± 0.04</td>
<td>25.02 ± 0.06</td>
<td>20.44 ± 0.04</td>
<td>1.70 ± 0.05</td>
<td>2.98 ± 0.03</td>
<td>0.79 ± 0.03</td>
</tr>
</tbody>
</table>

**Effects of Pectinase Pretreatments on Chemical Components of Bagasse**

The main chemical components of the enzymatic pretreated and control bagasse samples are shown in Table 3. The galacturonic acid and pentosan contents after enzyme treatment were decreased by 19.4% and 5.5%, respectively, compared with the control.
These results indicated that the pectin bound to the hemicellulose was partly reduced, which led to the disintegration and rupture of the fiber network and the dissolution of part of the hemicellulose. George et al. (2014) and Zhang et al. (2013) found similar results that hemicellulose was partly removed after pectinase pretreatment by XPS and HPLC analysis.

Similarly, the ethanol-benzene extractives and ash were decreased by 37.3% and 10.5%, respectively. The main reason for this was that pectinase degraded some of the pectin in the bagasse, which made the loosened waxes on the surface fibers more easily removable and decreased the ethanol-benzene extractives (Abdel-Halim et al. 2008). Additionally, the pretreatment with the crude pectinase enzyme had degraded some resin and fatty compounds of the bagasse, leading to a decrease in the ethanol-benzene extractive content and ash content.

The lignin linked with ethanol-benzene extractives, ash, and pentosans in bagasse was also induced to fracture, resulting in a slight removal of acid-insoluble lignin. Importantly, harmful pectin in the aqueous phase of pulp would be depolymerized by the pectinase pretreatment, and consequently rendered harmless to the papermaking process by lowering the cationic demand (Ricard and Reid 2004). Simultaneously, the results may partially explain the differences in the pulping results between pectinase-pretreated bagasse and the control.

Although the effect of pectinase treatment on the removal of non-cellulose components was not obvious, the treatment was still beneficial to the subsequent pulping (as shown in Table 1). Therefore, the pectinase pretreatment made the pulping process not only economically feasible but also eco-friendly.

Effects of Pectinase Pretreatments on Fiber Surface Morphologies of Bagasse

SEM images of bagasse fibers at magnifications between 500 and 1000 were obtained. The fiber sections were randomly selected. The SEM observation in Fig. 1 revealed that the surface of the controls were relatively smooth and rigid, and fewer damages and pores were observed on the exterior epidermis due to its wax-like hydrophobic covering on the fiber surface (Fig. 1a). However, the fiber surfaces pretreated by pectinase were decomposed, collapsed, and uneven (Fig. 1b).

Serious exfoliations emerged on the exterior area of the epidermis after the pectinase treatment, and some fragments were still present on the surface of the fibers, which indicated the incomplete activity of the pectinase to break down or depolymerize the pectin molecules in the partial areas of the fibers.

Additionally, these looser and bulkier surface characters in Fig. 1b might also have been caused by the removal of some characteristic structures by the pectinase treatment, such as the releasing of silica, the breaking of the intra-molecular hydrogen bonding of microfibril, and the dissolution of hemicellulose and lignin (Table 3). The changes in the fiber morphologies after pectinase treatment were conducive to improving pore volume and accessible surface area, and then promoting the entry of chemicals into the interior fiber during the pulping process.

Moreover, a more efficient lignin removal process with milder pulping conditions, less degradation of hemicelluloses and cellulosics, higher pulp yield, and inexpensive and environmentally attractive option, were expected to be realized by pectinase treatment prior to pulping.
Effects of Pectinase Pretreatments on Fiber Crystallinity of Bagasse

Changes in the crystallinity of undissolved cellulose due to chemical/mechanical/biological treatment would greatly influence the cellulose dissolution, accessibility, and elastic state (Park et al. 2010). X-ray diffraction is an effective way to analyze cellulose crystallinity. The crystallinity changes in the samples, corresponding to both pectinase-pretreated and control test samples, are shown in Table 4.

Table 4. XRD Parameters for Control and Pretreated Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>$I_{101}$, a.u.</th>
<th>$I_{002}$, a.u.</th>
<th>CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>1643</td>
<td>2413</td>
<td>31.92</td>
</tr>
<tr>
<td>Pretreatment</td>
<td>2870</td>
<td>4312</td>
<td>33.45</td>
</tr>
</tbody>
</table>

The crystallographic planes were labeled to indicate their crystal lattice assignments based on the observations of Ouajai and Shanks (2005). Reflections from the 16.0 ° 2θ (assigned to the 101 crystallographic plane), 19.0 ° 2θ (assigned to amorphous phase), and 22 ° 2θ (assigned to the 002 crystallographic plane of cellulose I) were obtained in both the control test and pectinase-pretreated sample. Hence, there was no crystalline transformation of the crystalline structure, as the typical crystallographic pattern of cellulose I was acquired in the cellulose of bagasse fiber treated by pectinase.

The percentage of cellulose crystallinity was calculated by the area method. The degree of crystallinity (CI) was slightly higher for the cellulose of bagasse fiber with pectinase treatment (33.4%) than for that of the control sample (31.9%). This may have been due to the partial removal of pectin, amorphous hemicellulose, and lignin from bagasse as observed in Table 3, which brought about a relative increase in the degree of crystallinity. Additionally, the ordered crystalline and less ordered amorphous regions were

two-phase of cellulose models. The amorphous regions were more susceptible to the enzymes or chemical reagents than were the crystalline regions (Marcovich et al. 2001). To some extent, the increased degree of crystallinity (CI) would decrease the accessibility of subsequent chemical reagents to internal fiber. However, in addition to the CI, there were some other factors that also affected the accessibility of the chemicals to the fiber. The other characteristics of the substrate such as available particle size, surface area, and degree of polymerization could all have affected the accessibility of substrate (George et al. 2014). However, larger scale structures in cellulosics may have drastically impacted the accessibility of enzymes and chemicals to the fiber (Dong et al. 1998). For instance, chemicals could barely attack the amorphous component packed sufficiently by the adjoining crystallites. Moreover, since the transition region of paracrystalline cellulose existed in between the crystalline and amorphous zones, assessment of the accessibility of the substrate by CI amount was even more difficult (Larsson et al. 1997). Therefore, the effects of pectinase treatment on bagasse fiber must be considered compositely.

**FTIR Analysis of Bagasse Fiber**

Infrared spectra of the bagasse fiber are shown in Fig. 2. The 1500 cm\(^{-1}\) band corresponding to the stretching vibration of benzene rings, which had a stable intensity in the infrared spectra, was employed as the base band to identify the intensity of the other bands. The relative intensities of characteristic peaks are shown in Table 5.

![FTIR spectra of bagasse fibers: (A) Control, (B) Pectinase-pretreated](image)

In Fig. 2, the spectrum of the treated bagasse fiber is similar to that of the control fiber, which indicated that pectinase treatment did not obviously change the chemical structures of the bagasse fibers. However, some peak intensities such as those at 895 cm\(^{-1}\), 830 cm\(^{-1}\), 1037 cm\(^{-1}\), and 3340 cm\(^{-1}\) were remarkably reduced, by 45.3%, 27.2%, 26.0%, and 24.0%, respectively, which was attributed to the OH and C=O stretching vibration of...
Table 5. Relative Intensity of Characteristic Peaks

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Relative Intensity (control) A/(A_{1500})</th>
<th>Relative Intensity (treated) A/(A_{1500})</th>
<th>Reduction Rate (%)</th>
<th>Corresponding Structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>3338-3348</td>
<td>1.7576</td>
<td>1.3364</td>
<td>23.96</td>
<td>OH stretching vibration</td>
</tr>
<tr>
<td>2916-2922</td>
<td>1.0379</td>
<td>0.8864</td>
<td>14.60</td>
<td>CH stretching vibration</td>
</tr>
<tr>
<td>1724-1730</td>
<td>1.2348</td>
<td>1.1000</td>
<td>10.92</td>
<td>C=O stretching vibration</td>
</tr>
<tr>
<td>1640-1642</td>
<td>0.2841</td>
<td>0.2722</td>
<td>4.19</td>
<td>antisymmetric COO- stretching</td>
</tr>
<tr>
<td>1602-1603</td>
<td>1.5833</td>
<td>1.3272</td>
<td>16.18</td>
<td>Benzene ring stretching vibration</td>
</tr>
<tr>
<td>1509-1511</td>
<td>1.2045</td>
<td>1.1955</td>
<td>0.75</td>
<td>Benzene ring stretching vibration</td>
</tr>
<tr>
<td>1418</td>
<td>1.5833</td>
<td>1.3364</td>
<td>15.60</td>
<td>Benzene ring stretching vibration</td>
</tr>
<tr>
<td>1370-1371</td>
<td>1.8636</td>
<td>1.5227</td>
<td>18.30</td>
<td>CH stretching vibration</td>
</tr>
<tr>
<td>1314-1315</td>
<td>1.9621</td>
<td>1.5727</td>
<td>19.85</td>
<td>C=O stretching vibration of phenolic ether; syringyl and guaiacyl lignin</td>
</tr>
<tr>
<td>1240-1243</td>
<td>3.1742</td>
<td>2.4363</td>
<td>23.25</td>
<td>C-O-C stretching vibration</td>
</tr>
<tr>
<td>1158-1161</td>
<td>3.0303</td>
<td>2.4091</td>
<td>20.50</td>
<td>C-O-C symmetric bending</td>
</tr>
<tr>
<td>1035-1037</td>
<td>7.2576</td>
<td>5.3727</td>
<td>25.97</td>
<td>C=O stretching vibration</td>
</tr>
<tr>
<td>895-898</td>
<td>2.7424</td>
<td>1.5000</td>
<td>45.30</td>
<td>C=C stretching vibration; the anomeric carbon (C1) vibration of hemicelluloses</td>
</tr>
<tr>
<td>800-850</td>
<td>2.5833</td>
<td>1.8818</td>
<td>27.16</td>
<td>CH bending vibration of aromatic ring</td>
</tr>
</tbody>
</table>

Compared with the control sample, the band intensity at 1730 cm⁻¹ that was attributed to the C=O stretching of methyl ester and carboxylic in pectin (Ouajai and Shanks 2005) decreased by 10.9% after treatment, indicating that the pectin had been removed after the treatment. This result was also consistent with the observation in Table 3.

Additionally, the degree of methylation in pectin was clearly indicated (Bociek and Welti 1975). Generally, both esterified and carboxylic groups exist in the structure of pectin. However, the removal of the carboxylic section in pectin could not be explained by the information on the C=O band alone due to the close original position between carboxylic acid and esterified pectin bands. Moreover, the acetyl group of the hemicelluloses also causes disturbances because of the absorbance in the same region (Himmelsbach et al. 2002). Fortunately, the band at 1642 cm\(^{-1}\) assigned to the antisymmetric COO-stretching is a characteristic band for the carboxylate ion in the water-extracted pectin (Synytsya et al. 2003), leading to a good separation of the carboxylate and ester bands. As shown in the spectra, an increase in the 1642 to 1730 cm\(^{-1}\) ratio was obtained, suggesting a high degree of methyl ester content after pectinase treatment. The specific action of the enzyme on the nonesterified fraction might be responsible for this consequence. Also, the decreased intensity of the OH stretching band was caused by the higher content of methyl ester. The peak intensities at 1602 cm\(^{-1}\), 1418 cm\(^{-1}\), and 1314 cm\(^{-1}\) assigned to the stretching vibration of the lignin benzene rings and to the syringyl and guaiacyl lignin were reduced by 16.2%, 15.6%, and 19.8%, respectively. There was also reduced band intensity at 1240 and 1158 cm\(^{-1}\), which was attributed to C-O-C stretching vibration and C-O-C symmetric bending. As shown in Fig. 2, the pectinase treatment caused an 18.3% reduction in the peak intensity at approximately 1370 cm\(^{-1}\), which was attributed to the C-H bending vibration of the celluloses and hemicelluloses. These results confirmed that part of lignins and hemicelluloses were degraded or removed after pectinase treatment.

CONCLUSIONS

1. Pectinase pretreatment has potential for improving the efficiency and environmental-friendliness of bagasse soda-AQ pulping. The brightness and physical strength properties of the pulp were noticeably improved by the pectinase pretreatment.

2. The properties of the pulp fibers after pretreatment, such as higher fiber length, lower fine length, and higher percent of flexible fiber, would be beneficial to subsequent pulping. The ash, organic solvent extractives, and pectin were partly removed, and the hemicellulose and lignin were slightly degraded by the pretreatment, leaving the fibers with a relatively high cellulose content as measured from Fourier transform infrared spectroscopy (FTIR). The scanning electron microscopy (SEM) study exhibited that the fiber surfaces became looser and collapsed after pretreatment, and X-ray diffraction (XRD) demonstrated that the pectinase treatment was conductive to a slightly higher crystallinity degree of the celluloses. Some structural changes in pectin, hemicellulose, and lignin occurred after pretreatment.

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