

Physicochemical characterization of different treatment sequences on kenaf bast fiber[☆]

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Abstract

Three different processing sequences for pulping kenaf (*Hibiscus cannabinus* L.) bast fibers were investigated, and the chemical composition (cellulose, hemicellulose and lignin content) and physical properties (viscosity, degree of polymerization and crystallinity index) of the extracted pulp were determined. Three processing steps were employed: treatment with (a) ammonium oxalate, (b) sodium hydroxide, and (c) acidic chlorite. Variations in the order, conditions and duration of their application resulted in three different pulping methods. The kenaf fiber treated sequentially with acidified sodium chlorite, 0.5% ammonium oxalate and 1% sodium hydroxide (AC–AO–SH₁) generated the greatest yield and highest kappa number; whereas the sample treated sequentially with 0.5% ammonium oxalate, 15% sodium hydroxide and acidic chlorite (AO–SH_{1.5}–AC) developed the highest viscosity. No significant difference in hemicellulose content was observed between pulping methods. While Fourier Transform Infra Red spectra (FT-IR) and X-ray diffractometry of all extracted pulp samples revealed the same chain conformation, mean hydrogen bonding, and crystallinity index were apparent. X-ray diffractograms indicated the presence of residual oxidized lignin between the (110) planes of the fibers subjected to AC–AO–SH₁ processing sequence that were absent from fibers processed differently. From CP/MAS ¹³C NMR spectra of extracted pulp, weak shoulder peaks at 57 and 110 ppm were observed in sample treated by AC–AO–SH₁ sequence that confirm the presence of oxidized lignin. Lignin content may adversely affect the viscosity of treated kenaf bast fiber.

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1. Introduction

Kenaf (*Hibiscus cannabinus* L.) is an annual herbaceous crop of the Malvaceae family, of which cotton and okra are also members. Kenaf is believed to have had its origin in ancient Africa (Western Sudan) and to have been cultivated in Egypt as early as 4000 BC (Kobayashi, 1991). The traditional uses of kenaf focus on its production for fiber used in making rope, sacks, canvas and carpets (Kaldor, 1992; Kaldor, Karlgren, & Verwest, 1990; Li, 1980). The length of kenaf bast fibers, critical for textile preparation and non-woven processing, varies significantly according to plant population density,

variety, size, and portion (Cheng, Li, Ohtani, Sameshima, & Mei, 1995, 1997, 1998). In view of recent global environmental issues and inadequate raw fiber resources, scientists worldwide have begun to show interest in exploiting the full potential of kenaf and its diverse uses (AKS, 2000). New applications for kenaf have been developed in the pulp and paper industry, for oil absorption, as a potting medium, in the manufacture of broadcloth, in filtration, and as an additive in animal feed (Sellers & Reichert, 1999). In the case of kenaf bast fibers, loss of viscosity, a measure of pulp damage under processing, has been found to be highly sensitive to the conditions under which the pulping process occurs (Chark, Nelson, Nieschlag, & Wolff, 1962; Nezamoleslami, Suzuki, Nishida, & Ueno, 1998). When a series of normal pressure pulping procedures were compared, the alkaline hydrogen peroxide pulping of kenaf bast fiber pretreated with ammonium oxalate provided a pulp with comparatively good brightness and mechanical properties (Mazumder, Ohtani, Cheng, & Sameshima, 2000; Mazumder, Ohtani, & Sameshima, 1998). Likewise, a combination of ammonium oxalate pretreatment, soda pulping under normal pressure and acidic chlorite treatment yielded an excellent pulp

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with extraordinarily high viscosity and highly desirable mechanical properties (Mazumder et al., 2000). On the other hand, Cheng, Fujiwara, Ohtani, and Sameshima (2000) using a sequence of acidified sodium chlorite, ammonium oxalate and 1% sodium hydroxide treatment generated good quality kenaf bast fiber, which, however, exhibited lower viscosities than those reported by Mazumder et al. (2000). The present study sought to establish whether modifying the ammonium oxalate treatment applied under reflux (Mazumder et al., 2000), to a more mild treatment would affect the viscosity of the fiber. The influence of these two processing sequences and an additional sequence derived from them on pulp yield, Kappa number and pulp viscosity were investigated. Moreover, FT-IR spectroscopy, X-ray diffractometry and CP/MAS ^{13}C NMR spectroscopy of pulp generated from these processing sequences gave further information on fiber characteristics.

2. Materials and methods

2.1. Source material

A frost-killed kenaf variety, Tainung-2 was grown in Nankoku, Kochi, Japan (latitude 33°N) and was harvested in November 2000 (180 days after planting). The stems were separated manually into bast and core. The bast fibers were cut into 30 mm lengths prior to treatment.

2.2. Pulping methods

Various chemical combinations and conditions were employed for processing kenaf bast fiber (Table 1). Treatment AO-SH₁₅-AC used a sequence of ammonium oxalate, sodium hydroxide and acidic sodium chlorite (Mazumder et al., 2000). Treatment AC-AO-SH₁ used a sequence of acidic sodium chlorite, ammonium oxalate and sodium hydroxide (Cheng et al., 2000). The AO-SH₁-AC processing sequence was a combination of the other two sequences, with the series of steps being those of the AO-SH₁₅-AC processing sequence, and the conditions those of AC-AO-SH₁ processing sequence

2.3. Viscosity measurements

Following different processing sequences kenaf fiber viscosity was measured according to the TAPPI test method (TAPPI T 230 om-89, 1994) using cupriethylenediamine (CED) as a solvent and a capillary viscometer three times. The degree of polymerization (DP) of the fibers was calculated as

$$\text{DP} = [0.75[(954 \log \mu) - 325]]^{-0.905} \quad (1)$$

where, μ is the TAPPI viscosity (cP).

2.4. Chemical analysis

Kappa number and cellulose content (as α -cellulose) were determined by the TAPPI test methods (TAPPI T 236 cm-85, 1994 and TAPPI T203 om-93, 1994) three times. Lignin and

Table 1
Protocols of three experimental processing sequences for kenaf bast fiber

Processing sequence	Steps ^a	Treatments		
		Conditions	Liquor ratio	Remarks
AO-SH ₁₅ -AC	(1) 0.5% Ammonium oxalate	Refluxing, 1 h	1:25	
	(2) 15% NaOH (on pulp)	Refluxing, 1 h	1:10	
	(3) NaClO ₂ + CH ₃ COOH ^b	1 h at 75°		Added three times
AC-AO-SH ₁	(1) NaClO ₂ + CH ₃ COOH ^b	1 h at 75°		Added three times
	(2) 0.5% Ammonium oxalate	8 h at 85°	1:30	
	(3) 1% NaOH (aq. soln.)	50 min at 60°	1:10	
AO-SH ₁ -AC	(1) 0.5% Ammonium oxalate	8 ha at 85°	1:30	
	(2) 1% NaOH (aq. soln.)	Refluxing, 1 h	1:10	
	(3) NaClO ₂ + CH ₃ COOH ^b	1 h at 75°		Added three times

^a Thorough tap water rise was applied between each step.

^b Wise treatment.

hemicellulose contents were calculated as

$$\text{Lignin content (\%)} = 0.13 K \quad (2)$$

Hemicellulose content (%)

$$= 100 - \text{cellulose (\%)} - \text{lignin (\%)} \quad (3)$$

where, K is the Kappa number (unit less)

2.5. FT-IR spectroscopy

FT-IR spectra were measured with a Bruker FT-IR IFS 66 spectrophotometer, to investigate the physical structure of processed pulp samples. Samples were ground and mixed with KBr powder according to Abbott, Palmer, Gordon, and Bagby (1988). The mean strength of H-bonds (MHBS) calculated as

$$\text{MHBS} = (A_{\text{OH}})/(A_{\text{CH}}) \quad (4)$$

where,

A_{OH} is the absorbance of the stretching vibration of -OH groups and A_{CH} is the absorbance of the stretching vibration of C-H bonds.

The IR crystallinity index CI was calculated as the ratio of the absorbance at 14.30 m^{-1} to that at 9.00 m^{-1} (Nada, Shabaka, Yousef, & Nour, 1990).

Table 2
Characterization of kenaf bast fibers following three different processing sequences

Parameter	Processing sequence		
	AO-SH ₁₅ -AC	AC-AO-SH ₁	AO-SH ₁ -AC
<i>Chemistry</i>			
Yield (%)	55.80	57.90	55.91
Viscosity (cP)	109	63	102
Degree of polymerization	2559	2165	2511
Kappa no.	3.37	6.81	3.93
% Lignin	0.44	0.88	0.51
% α -Cellulose	84.86	85.06	84.77
% Hemicellulose	14.70	14.06	14.72
<i>IR spectroscopy</i>			
Mean strength H-bonds	1.16	1.00	1.12
IR Crystallinity index	1.30	1.20	1.27
A_{C-O-C}/A_{CH_2}	2.33	2.27	2.30
$A_{1^{\circ}OH}/A_{CH_2}$	3.25	2.68	2.78
<i>X-ray diffractometry</i>			
X-ray crystallinity index	78.0	70.5	75.0
$2\theta/d(110)$	15.10 (5.88)	14.04 (6.25)	15.16 (5.86)
$2\theta/d(110)$	16.01 (5.53)	15.98 (5.55)	15.98 (5.74)
$2\theta/d(020)$	22.64 (3.93)	22.77 (3.89)	22.60 (3.91)

2.6. Wide-angle X-ray diffractometry

The diffractogram of processed fiber samples was recorded at room temperature with a Shimadzu XD-D1_w diffractometer using Ni-filtered Cu K α radiation ($\lambda=1.54$ Å) obtained from a Shimadzu VG-207RII generator. The operating voltage and current were 40 kV and 20 mA, respectively. Each sample was measured as a sheet on a specimen carrier. Data were collected at 0.008° 2θ intervals and treated by the diffract DP-D1 (Shimadzu) software. Crystallinity was calculated from the diffracted intensity data using the method of Segal, Creely, and Conrad (1959).

2.7. CP/MAS ¹³C NMR Spectroscopy

The CP/MAS ¹³C NMR spectra were recorded (at 292 ± 1 K) on Joel CMX-300 instrument operating at 7.0 T. A double

air-bearing probe and a zirconium oxide rotor were used. The MAS rate was in the 4–5 kHz range. Acquisition was performed with a standard CP pulse sequence using a 5 μ s proton 90 pulse, a 1200 μ s contact pulse and 3 s delays between repetitions. Adamantine was used as an external standard for the chemical shift scale relative to tetramethylsilane. The crystallinity of the extracted pulp was calculated from C4 crystalline part in the resolution enhanced spectra after deconvolution (Maunu, Liitia, Kauliomaki, & Sundquist, 2000).

3. Results and discussion

Differences in the processing sequences and conditions used in the preparation of kenaf bast fiber pulp are outlined in Table 1. The yield and kappa number for treatment AC-AO-SH₁ were the highest of all processing sequences (Table 2). The viscosity and degree of polymerization for treatment AO-SH₁₅-AC were greater than those of either the AC-AO-SH₁ or AO-SH₁-AC processing sequences (Table 2). Assuming that the difference in viscosity between processing sequences was affected by lignin content, these differences may be attributed to the greater lignin content in the sample subjected to the AC-AO-SH₁ processing sequence, than the AO-SH₁₅-AC or AO-SH₁-AC sequences (Table 2). Raw kenaf bast generally consists of coarse bundles of single fibers held together by lignin and pectin (Moreau, Bel-Berger, & Tao, 1995). When the lignin and hemicellulose contents decrease during pulping, the pore volume increases, until the pore structure finally collapses (Stone & Scallan, 1968). The fiber surface becomes more open and porous with well-defined fibril aggregates as the lignin and hemicelluloses are removed, even though both porous and compact regions may be seen adjacent to one another (Duchesne & Daniel, 2000). Under processing sequence AC-AO-SH₁ sodium chlorite and acetic acid were applied directly to pectin-containing raw kenaf bast, allowed the sodium chlorite to penetrate and oxidize all the lignin. On the other hand, under the AO-SH₁₅-AC and AO-SH₁-AC

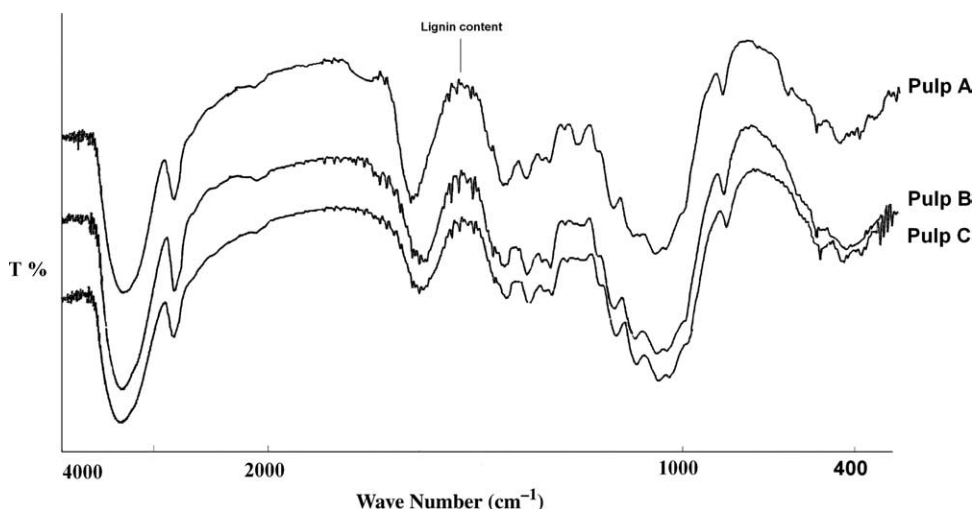


Fig. 1. Infrared spectra of kenaf bast fiber following processing sequence: (a) AO-SH₁₅-AC; (b) AC-AO-SH₁; (c) AO-SH₁-AC.

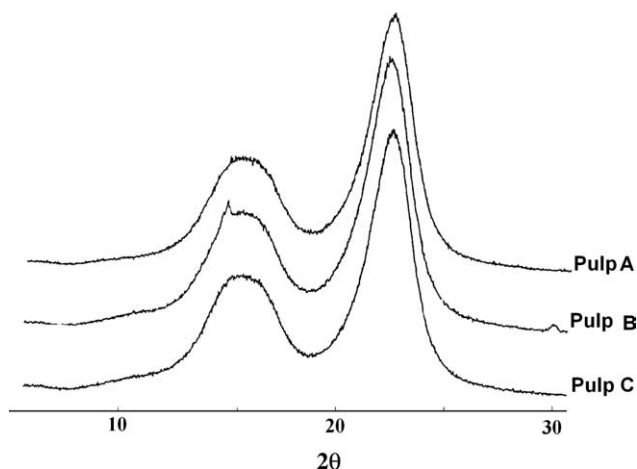


Fig. 2. X-ray pattern of kenaf bast fiber following processing sequence: (a) AO-SH₁₅-AC; (b) AC-AO-SH₁; (c) AO-SH₁-AC.

sequences, penetration enhancement was the result of pectin removal through the action of ammonium oxalate. The use of sodium hydroxide prior to sodium chlorite is best, as the former dissolves the non-lignin materials that otherwise waste chlorine dioxide, rendering the subsequent removal of lignin by the latter much more efficient.

Infrared spectra showed the physical structure of processed pulp samples to be remarkably unchanged (Fig. 1). The absorption at 33.97 m^{-1} is due to the stretching of -OH groups and the absorption $29.02\text{--}29.18\text{ m}^{-1}$ is due to C-H stretching. Each spectrum also presented peaks at 14.30 and 9.00 m^{-1} , representing crystalline and amorphous regions, respectively (Nada et al., 1990). The absorbance at 13.28 m^{-1} is associated with the C-H rocking of the ring, whereas the peak at 11.60 m^{-1} corresponds to ether linkages. There were no significant differences in both MHBS and crystallinity index between samples (Table 2). Furthermore, the relative absorbance of ether linkages (A at $11.60/13.25\text{ m}^{-1}$) in sample of AO-SH₁₅-AC sequence show a smaller difference than that of either AC-AO-SH₁ or AO-SH₁-AC samples. The relative absorbance of primary OH (A at $10.35/13.25\text{ m}^{-1}$) is relatively the same in all samples (Table 2). Fig. 1 in particular showed a distinct increase in absorbance at $15.50\text{--}15.93\text{ m}^{-1}$, related to lignin content (Abbott et al., 1988). This was most apparent in sample AC-AO-SH₁, and less so in samples AO-SH₁₅-AC and AO-SH₁-AC. This result was confirmed by the kappa number measurement (Table 2).

X-ray diffraction patterns of the processed pulp samples (Fig. 2) were well resolved. The X-ray crystallinity index values of AO-SH₁₅-AC, AC-AO-SH₁ and AO-SH₁-AC processing sequence samples were 78.0, 70.5 and 75.0, respectively. The diffractive angle ($2\theta^\circ$) and d-spacing of the corresponding plane are presented in Table 2. Fibers processed according the AC-AO-SH₁ sequence showed a diffraction plane of ($1\bar{1}0$) appearing at a lower angle side with broader d-spacing plane, while the diffractions plane of (020) appeared at higher angle side with a smaller d-spacing plane than those of the other processing sequences. Moreover, there were two additional small peaks in the X-ray pattern of pulp from this

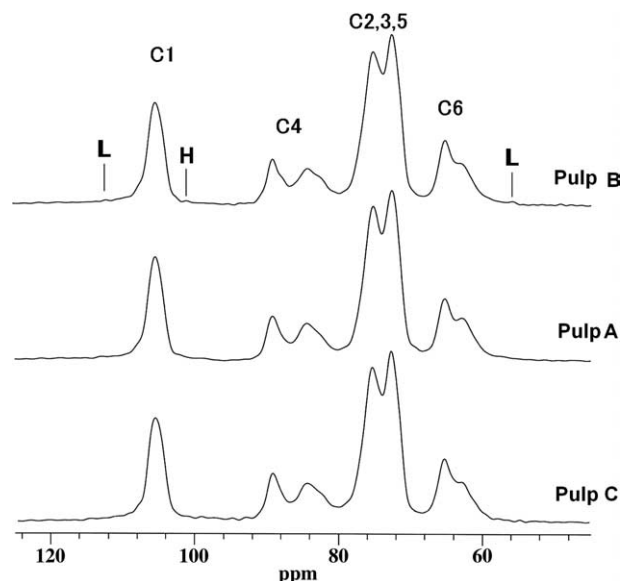


Fig. 3. CP/MAS ^{13}C NMR kenaf bast fiber following processing sequence: (a) AO-SH₁₅-AC; (b) AC-AO-SH₁; (c) AO-SH₁-AC. L, lignin content, H, hemicellulose content.

treatment at $2\theta = 15^\circ$ and 30° , which are attributable to hydromolysite (iron) and sodium hydroxide with hydromolysite, respectively (ASTM data). This may be a result of residual oxidizable lignin or pectin, which chelates the iron that is present in sodium hydroxide during the last processing stage. This can be attributed more to a relatively greater inclusion of residual oxidized lignin in the ($1\bar{1}0$) plane following processing sequence AC-AO-SH₁ than following the other two processing sequences. The presence of such residue would lead to a little expansion of that plane and a decrease the in d-spacing of the (020) plane, accompanied by a greater angle shift. Owing to the inclusion of lignin and hemicellulose in the ($1\bar{1}0$) plane, the intermolecular hydrogen bonding between the sheets might be prevented, lowering the crystallinity index in all sequences but appear clearly in sequence AC-AO-SH₁.

The CP/MAS ^{13}C NMR spectra of the pulp samples are presented in Fig. 3. The degree of crystallinity (CrI) is not different as seen from the size of the signals centered at 89 and 84 ppm presenting the crystalline and amorphous phase, respectively. The CrI percentage was 57, 54 and 56% for AO-SH₁₅-AC, AC-AO-SH₁ and AO-SH₁-AC processing sequence samples, respectively. The low crystallinity of kenaf fiber affects the sharpness of the signals as shown in Fig. 3. The presence of hemicellulose in the samples increases the area of the amorphous cellulose signal at 84 ppm, due to the presence of C-4 of xylose residues in well-ordered xylan chains (Mitikka, Teeaar, Tenkanen, Lain, & Vuorinen, 1995). Furthermore, the presence of a weak shoulder peak that appear clearly in case of AC-AO-SH₁ sequence at 102 ppm (assigned to C1 of mannose residues in relatively well-ordered glucomannan chains) that reflects a small amount of hemicelluloses (Kim & Newman, 1995). On the other hand, the presence of weak peaks at 56 ppm (assigned to methoxyl carbon in lignin) and 110 ppm (assigned to lignin aromatic

carbon) that appear clearly in sequence AC–AO–SH₁, indicate the presence of a relatively higher lignin than that from the other sequences. From these results, the hemicellulose content affects the crystallinity of the kenaf fiber whereas the lignin content affects the viscosity of these samples.

4. Conclusions

Kenaf bast fibre processed according to the AO–SH₁₅–AC sequence (Table 1) showed the greatest viscosity and lower kappa number values than either of the other processing sequences tested. Consequently, the AO–SH₁₅–AC sequence was the best of the three sequences tested. Treatments presented no significant differences in hemicellulose content, but they did differ relatively in lignin content. Overall, the AO–SH₁₅–AC sequence is the best processing option, generating a good viscosity pulp.

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