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Influence of the chemical composition of kenaf bast and core on the alkaline pulping response

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Abstract The bast and core of kenaf, *Hibiscus cannabinus* L., have markedly different chemical components and alkaline cooking responses. The bast had about double the hot-water extractives content and only about half the lignin content of the core. The core contained a large amount of hemicellulose, mostly composed of xylan. The lignin structures of bast and core were also quite different: The former had a significant abundance of syringyl structures. Evidence showed that the bast was much more easily delignified than the core. When the bast and core were cooked together in alkaline condition, the pulp yields at the same kappa number were higher than those of the individual pulpings of bast and core. The bast-core pulping gave a positive effect on the yield of bast pulp in the soda-anthraquinone and kraft pulpings. On the other hand, kenaf was abundant in the hot water extractives. These extractives consumed alkali during cooking to a relatively large extent but acted as a protector of hemicellulose and slightly increased the pulp yields.

Key words Kenaf · Bast and core · Alkaline pulping · Lignin · Hot-water extractives

Introduction

Production of nonwood pulp in the world amounted to about 13.5% of the total worldwide pulp production in 1995. It had dropped to about 9.0% in 1996 but increased again to 10.6% in 1997.¹ The worldwide market share of nonwood pulp is rapidly and steadily expanding. The

recently increased production of nonwood pulp is mainly dependent on wheat and rice straws, bamboo, and baggasse,² but kenaf has drawn attention due to its rapid growth and good fiber quality.³

Kenaf (*Hibiscus cannabinus* L.) is an annual plant composed of bast and core, whose chemical components and fiber properties differ greatly from each other. For example, the bast lignin is different from the core lignin in respect not only to the content but also the chemical structure.^{4,6} Hence the delignification rates during alkaline cooking are also quite different.⁷ The bast and core (whole kenaf) are usually pulped together, but the effect of such pulping on each pulp yield and residual lignin content is not clarified. A large amount of hot-water extractives is another characteristic of kenaf and may also affect the alkaline pulping. This study tried to clarify the influence of these characteristics of kenaf on the alkaline pulping behaviors.

Materials and methods

Materials

Kenaf, Aokawa-3 cultivar, was planted on May 27 and harvested on November 9 in Kochi Prefecture in 1994. It was separated into bast and core by hand and then air-dried. Each dried sample was subjected to chemical analyses and pulping experiments.

Chemical analysis

The kenaf bast and core were respectively pulverized by a Wiley mill. The fine fractions, which passed 42 mesh (Tyler Standard Sieve, 351 μ m) and were retained on 100 mesh (147 μ m) of screens, was used for the analyses. The wood meals of akamatsu (*Pinus densiflora* Sieb. et Zucc.) and shirakaba (*Betula platyphylla* Sukatchev var. japonica Hara) were used as the reference samples.

The ash content was determined by incineration of the raw materials at 600°C for 1h. Extraction with alcohol-

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benzene (1:2) by Soxhlet's apparatus for 8h was carried out to determine the extractive content and to prepare the sample for chemical analysis. The lignin content was determined by the conventional Klason method⁸ and an additional method for acid-soluble lignin⁹ using the extractive-free sample. Holocellulose content of the extractive-free sample was determined by the acidic chlorite method¹⁰ and supplementary revision in which residual lignin after hydrolysis of holocellulose with sulfuric acid was deducted.⁸ α -Cellulose was measured as the residue after extraction of holocellulose with 17.5% NaOH solution.¹¹

The raw materials were extracted with hot water at 90–95°C for 7h. The extraction was repeated three times; then the water-extractives were combined, filtered with no. 2 filter paper, and evaporated. The water-soluble substances were dried and weighed.

Holocellulose was hydrolyzed with sulfuric acid, and the hydrolysates were neutralized with barium hydroxide solution. The neutral sugar composition of the hydrolysate was determined by an alditol acetate method.¹² The hydrolysate was converted to alditols with sodium borohydride and then acetylated with acetic anhydride and sulfuric acid. The resulting alditol acetates were analyzed by gas chromatography (GC), (Hitachi GC-163). The GC conditions were as follows: 3 mm i.d. \times 3 m stainless column, column packings (GL Science); Silicone XF-1150 (0.4%) + EGA (0.2%) + EGS (0.2%) on Gaschrom P (100–120 mesh), temperature 190°C, carrier gas nitrogen (30 ml/min), detector FID.

Nitrobenzene oxidation was conducted by the method described by Chen.¹³ The wood meal (about 200 mg), 7 ml of 2M NaOH solution, and 0.4 ml nitrobenzene were placed in a stainless steel reactor (30 ml) and heated at 170°C for 2.5 h in an oil bath. The nitrobenzene oxidation products¹³ were trimethyl-silylated with *N,O*-bis(trimethylsilyl)-trifluoroacetamide and pyridine and then analyzed by GC (Hitachi GC G-5000A). GC conditions were as follows: capillary column TC-1 (GL Science); 0.2 mm i.d. \times 30 m, 150°C for 10 min, then programmed to 200°C with 2°C/min; carrier gas nitrogen (1 ml/min); split ratio 1:30; detector FID.

Uronic acid content was determined by the carbazole-sulfuric acid method.¹⁴

Alkaline pulping methods

The kenaf bast and core, which were same as the samples used for the chemical analyses, were pulped in the following conditions. Three types of alkaline pulpings: Soda, soda-anthraquinone (AQ), and kraft pulpings were conducted according to our previous study.¹⁵ The pulping conditions were as follows.

1. Dosage of active alkali (as Na₂O): 14.0%, 15.5%, and 17.0% based on the raw material material/liquor ratio: 1:5
2. Temperature: programmed to 170°C for 90 min, then held for 90 min at 170°C

3. Addition of AQ for soda–AQ pulping: 0.05% based on the raw material
4. Sulfidity in kraft pulping (as Na₂O): 25%

A miniautoclave with 125 ml volume and a rotary autoclave with 5 l capacity were used for cooking. Three miniautoclaves in which the samples (about 6 g oven-dried) and chemicals were stuffed and sealed were placed in the rotary autoclave and cooked at the same time.

The bast pulp was washed on a screen of 200 mesh, but the core pulp or the whole kenaf pulp were washed on a G3 glass filter because the core pulp was fine and partly passed through the usual screen of 200 mesh during pulp washing.

To clarify the individual behaviors of bast and core during cooking, the miniautoclave was partitioned off into two compartments by an 80-mesh stainless screen; and the bast and core were stuffed into different compartments and cooked together. The stainless screen of 80 mesh was able to preclude any mixing of bast and core pulps during the cooking. The resulting pulps were separately washed and analyzed for their pulp yields and kappa number.¹⁶

The hot water (HW) extractives of the kenaf samples and the HW extractive-free samples were cooked individually or together. For the latter cooking, the resulting pulp was washed and analyzed as above. The residual alkali in the waste liquor and washing effluent were determined by conventional potentiometric titration with 1N HCl.

Results and discussion

Chemical composition of kenaf bast and core

The chemical analysis data for kenaf bast and core are shown in Table 1. Each holocellulose content of bast and core was higher than that of akamatsu or shirakaba. The α -cellulose content of the bast was quite high, but the core had a content similar to that of akamatsu. The core seems to contain a lot of hemicellulose. The lignin contents of bast and core were 9.2% and 19.0%, respectively. The latter was close to that of shirakaba and about twice as large as the former.

The ash and alcohol-benzene extractive contents were about 1% and 3%, respectively; and there was only a small difference between bast and core. However, the HW extractives comprised about 16% of the bast and about 7.5% of the core; both values are high compared to that of wood.

Table 2 shows the monosaccharide composition of holocellulose determined by the alditol acetate method. Xylose was dominant in the holocellulose except for glucose; its contents were 18.1% for bast and 29.8% for core, which were similar to the results of Aorigele et al.¹⁷: 18.2% for bast and 27.7% for core. Although the arabinose content was 3%–5%, xylan predominated in the hemicellulose of kenaf bast and core. Neto et al.⁴ reported that hemicellulose of the kenaf consisted mainly of glucuronoxylan, and the xylose/uronic acid ratios were 3:1 to 5:1 for bast and 5:1 to 10:1 for core. In our experiment,

Table 1. Chemical composition of the samples

Constituent	Percent of oven-dried raw materials			
	Kenaf bast	Kenaf core	Akamatsu	Shirakaba
Holocellulose	79.6	77.6	65.8	76.8
α -Cellulose	69.8	45.3	43.6	56.4
Lignin	9.2	19.0	26.1	17.6
Ash	1.1	1.4	0.2	0.2
Alcohol-benzene extractives	3.4	3.0	4.1	2.0
Hot-water extractives ^a	15.9	7.5	2.6	5.3

^aThese were determined independently

Table 2. Monosaccharides of holocelluloses of kenaf bast and core

Monosaccharide	Bast (% of total sugars)	Core (% of total sugars)
Arabinose	3.2	4.8
Xylose	18.1	29.8
Mannose	1.5	1.3
Galactose	1.7	1.5
Glucose	75.5	62.6

Table 3. Yields and molar ratio of aromatic composition of nitrobenzene oxidation of bast and core kenaf lignins

Sample	G (% of KL)	S (% of KL)	H (% of KL)	S/G (molar ratio)
Bast	5.6	31.0	0.4	4.3
Core	14.1	26.6	1.1	1.5

G, guaiacyl unit; S, syringyl unit; H, *p*-hydroxy phenyl unit; KL, Klason lignin

the uronic acid contents were about 4% for both bast and core; therefore, the xylose/uronic acid ratios were 4.5:1.0 for the bast 7.5:1.0 for the core. It is obvious that the hemicellulose of the core is mostly xylan.

Syringyl/guaiacyl ratios of lignins from kenaf bast and core

It has been reported that the chemical structures of kenaf lignins, which have been analyzed by nitrobenzene oxidation,^{5,17,18} permanganate oxidation,^{4,6} and spectrometry,^{6,19–22} are significantly different based on their cultivars and parts of the kenaf plant as well as on the site of cultivation. Table 3 shows the results from nitrobenzene oxidation of bast and core lignins. The syringyl/guaiacyl (S/G) ratios were 4.3 for the bast lignin and 1.5 for the core lignin. Total yields of nitrobenzene oxidation products were 37.0% and 41.9% (w/w based on the lignin) for bast and core, respectively. Other researchers have reported about 4% for bast and about 2% for core^{5,17}; our results are similar. The kenaf lignin was abundant in the syringyl structure, which was especially marked in the bast lignin.

Quantitative ¹³C-NMR analysis indicated that the S/G ratios were 3.38 for bark and 1.55 for core.⁶ Pyrolysis-GC/

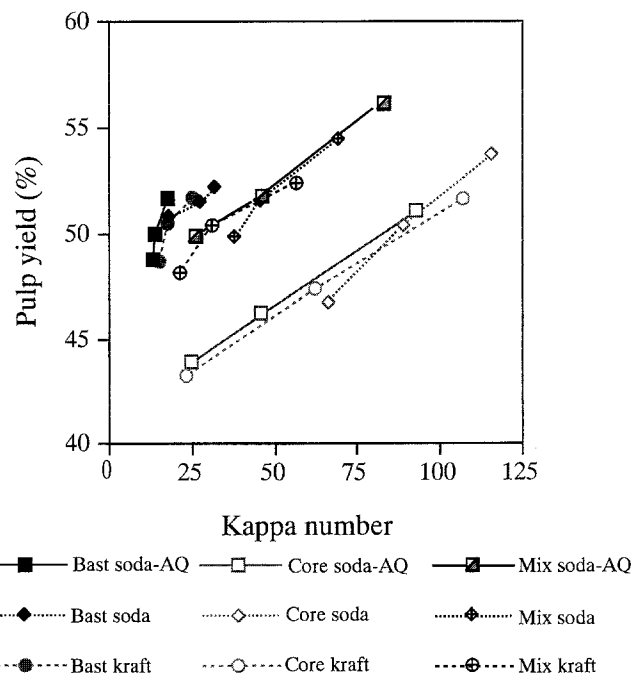


Fig. 1. Relations between pulp yields and kappa number obtained from the alkaline cookings of kenaf bast, core, and bast-core mixture. AQ, anthraquinone

mass spectrometry (MS) analysis indicated S/G ratios of 3.43 for bast and 1.53 for core.²² The nitrobenzene oxidation gives slightly larger S/G ratios than other methods because it cannot analyze the condensed structures¹³ and the guaiacyl units are usually more condensed than the syringyl unit. It may be concluded that the S/G ratios for bast and core are 3–4 and 1.5–2.0, respectively.

Alkaline cooking of kenaf bast and core

Relations between pulp yield and kappa number for the soda, soda-AQ, and kraft pulpings of bast, core, and bast-core mixture (1:1) are shown in Fig. 1. The pulp yield of soda-AQ pulping was somewhat higher than that of kraft pulping compared at the same kappa number, so the former pulping was slightly superior to the latter for obtaining the higher pulp yield and lower kappa number. Although the pulps of a bast-core (1:1) mixture would be expected to give the middle values between the individual bast and core

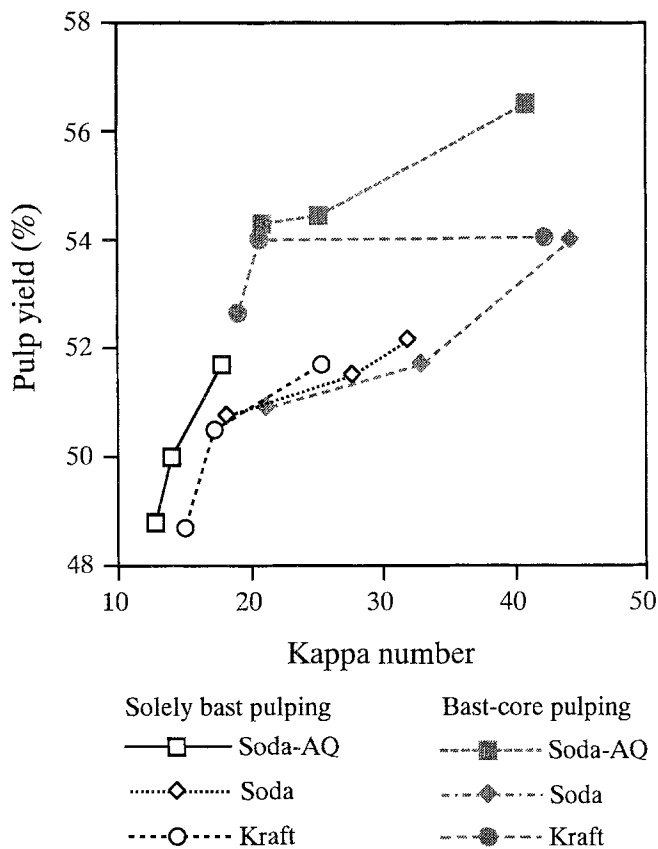


Fig. 2. Relations between yields and kappa number of the kenaf bast pulps obtained from bast or bast-core pulpings

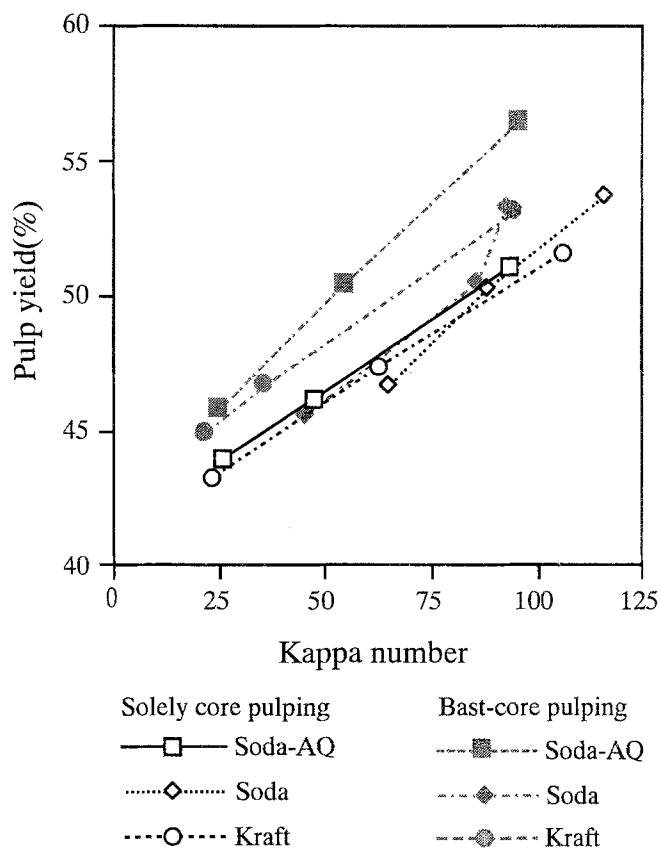


Fig. 3. Relations between yields and kappa number of the kenaf core pulps obtained from core or bast-core pulpings

pulps, the position of their data on Fig. 1 was rather close to that of the bast.

Next, the bast and core were put separately into the compartments of the miniautoclave partitioned with stainless steel net, then pulped by soda, soda-AQ, and kraft cooking. The relations between pulp yield and kappa number for the bast pulps are shown in Fig. 2. The filled symbols indicate the data of bast pulps in the bast-core pulping. The open symbols indicate the data of bast pulps in the solely bast pulping. The soda pulping did not show any difference between bast-core and solely bast pulpings. In the other experiment, soda-AQ pulping of solely bast with 13.6% active alkali was carried out, but its datum point is not plotted on Fig. 2. It gave a pulp yield of 52.6% and a kappa number of 26.0. This datum point was positioned much lower than those of the bast pulps obtained from bast-core pulpings. The kraft and soda-AQ pulpings, however, showed that the pulp yields at the same kappa number were more than 2% higher with the bast-core pulping than those with the solely bast pulping. The bast-core pulping had a positive effect on the yield of bast pulp in the soda-AQ and kraft pulpings.

The relations between pulp yield and kappa number for the core pulps are shown in Fig. 3. Specification of the symbols is similar to that of Fig. 2. The core pulps were also effectively delignified in the soda-AQ and kraft pulpings of bast and core together. In this case, the soda pulping also

showed slightly effective delignification, which was different from the result of bast in Fig. 2. Delignification efficiency was the highest with soda-AQ pulping, the second with kraft pulping, the lowest with soda pulping.

The activation energy of soda pulping⁷ was reported as 68 kJ/mol for bast, 91 kJ/mol for core, and 75 kJ/mol for whole kenaf, composed of bast (35%) and core (65%). These activation energies were much lower than those of wood,^{23,24} usually 130–150 kJ/mol. Values calculated tentatively for the whole kenaf, bast (35%) and core (65%), is 83 kJ/mol; then 8 kJ/mol may correspond to the increment of delignification efficiency in the soda pulping by mixing bast and core. For the soda-AQ and kraft pulpings, decreased activation energy is considered to be larger than 8 kJ/mol for the soda pulping.

Influence of HW extractives on alkaline pulping

As shown in Table 1, the contents of HW extractives were high. These extractives are dissolved in the cooking liquor during the early stage of pulping and so would affect the subsequent pulping reaction.

Figure 4 shows the relations between pulp yield and kappa number of the pulps obtained by soda-AQ and kraft pulpings of the raw samples or the HW extractive-free samples. These pulpings were conducted using the same

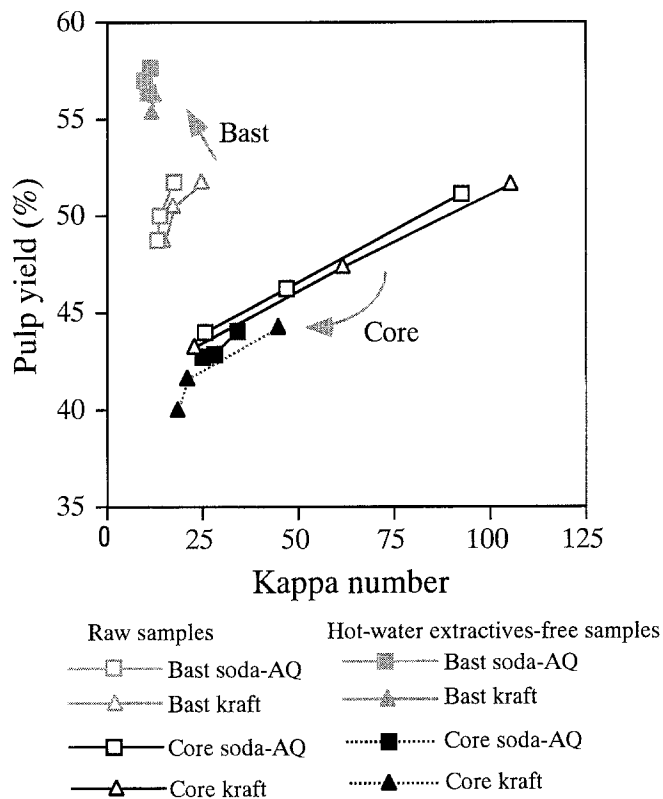


Fig. 4. Relations between pulp yields and kappa number obtained from the alkaline cookings of raw samples or hot-water extractives-free samples

weight of the samples, so the HW extractive-free sample would be expected to give a larger pulp yield. The bast and core, however, exhibited quite different delignification behavior from each other; the pulp yields of the former increased 7%–8% by removal of HW extractives, but the pulp yields of the latter slightly decreased. If the pulp yields are calculated based on the weights of HW extractive-free samples corresponding to the initial raw samples, the pulp yields of bast would not be different for the raw samples and the HW extractive-free samples; but those of core were about 3% lower in the HW extractive-free samples than those in the raw samples. The core had about a twofold larger content of hemicellulose than the bast, so the presence of HW extractives seemed to suppress strongly the decomposition and loss of hemicellulose. The HW extractives are assumed to exert protection for hemicellulose during alkaline cooking.

Alkali consumption of HW extractives occupied 23% of total alkali consumption for the bast and 11% of the total for the core. The contents of HW extractives were 16% for the bast and 7.5% for the core; therefore alkali consumption of the extractives was higher than that of the extractive-free residues. It is suggested that the water extractives of kenaf were composed mainly of organic acids,²⁵ which may consume alkali considerably during the alkaline cooking.

Figure 5 shows the influence of the HW extractives on soda-AQ pulplings. The circle and square symbols indicate the results from the raw samples and the HW extractive-

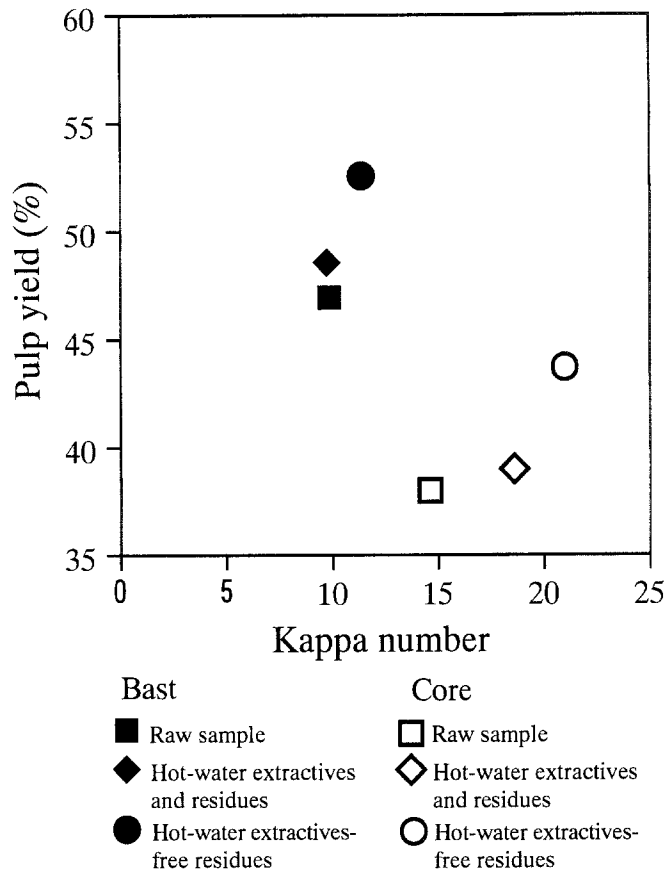


Fig. 5. Pulp yields and kappa numbers obtained from the soda-anthraquinone pulplings of raw samples, hot-water extractives-free samples, and a mixture of hot-water extractives and residues

free samples corresponding to the raw samples, respectively. The diamond-shaped symbols indicate the results from the combined samples of HW extractives and HW extractive-free residues whose ratios were the same as for the raw samples. The pulp yields was slightly enhanced by the addition of HW extractives, but it was still low compared to the raw samples. This result suggests that the influence of HW extraction on the alkaline pulping could not be explained only by the alkali consumption of HW extractives. It is thought that other physicochemical effects, such as swelling and softening of the cell walls, may be important. Further investigation should be carried out on this point.

Conclusions

Kenaf bast and core were quite different in respect to their chemical components and alkaline cooking responses. The lignin content of the bast was about half that of the core, but the HW extractives content of the bast was about three times that of the core. The core contained a large amount of hemicellulose, which was mostly composed of xylan. Syringyl/guaiacyl ratios of the lignins from bast and core were 4.3 and 1.5, respectively; and kenaf lignin,

especially bast lignin, was significantly abundant in syringyl structures.

The alkaline pulping of whole kenaf, including bast and core, demonstrates rather efficient delignification compared to the individual pulpings of bast and core. These effects are particularly observed with the soda-AQ and kraft pulpings.

The HW extractives consumed alkali per unit weight more than the HW extractive-free residues during the alkaline cooking, but they acted as a protector of hemicellulose. In the presence of HW extractives, the pulp yields were higher at the same kappa number than that of the HW extractive-free samples.

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