Chemical and Physical Characteristics of Cellulosic Materials Obtained from Kenaf (*Hibiscus Cannabinus* L.) Plants of Different Ages

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Abstract: The chemical and physical characteristics of kenaf plants (Zhejiang No.1 cultivar from China) grown in Japan, 1996 and their cellulosic materials of different plant ages were investigated, and their bast (outer bark) was compared with their inner core.

The ash content of the bast and the core of the kenaf plant of different ages decreased with the plant aged, however, the percent of the holocellulose content for the bast and the core of the kenaf plants at different ages was almost constant, similar to the kenaf plants grown in U.S.A., though its weight was different. The alpha-cellulose content, the sorption of basic dye, the degree of polymerization and the birefringence for the bast pulp fibers were higher than those for the core pulp fibers, however, the content of lignin, hot water extract, 1% NaOH solution extract and carboxyl group for the bast fibers was lower than that for the core fibers. The content of the hot water extract and 1% NaOH solution extract for the bast and core fibers increased with plant ages. However, there were only slight effects of the kenaf plant ages and the differences between the bast and the core fibers on the moisture content, the sorption of direct dye, the crystallinity, the crystallite size and the orientation. Therefore, these results indicate that kenaf (Zhejiang No.1) can be harvested at about 140-150 days in Japan.

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1. Introduction

Kenaf plants, which are annuals and rapidly grow, are tropical crops native to Africa, however, they have now widely been planted from the tropical regions to the temperate regions. They have been noted as sources not only for non wood paper, but also for biomass.

Annual plants used for paper and composites are generally harvested at the end of the growing season. However, in order to increase the effective application of kenaf plants, it is important to investigate the chemical and physical characteristics of the kenaf plants and their cellulosic materials of different ages because of their rapid growth in height of about 2 - 4 meters, and both the physical and chemical characteristics dependence on their fiber quality.

The characteristics of the kenaf plants (Tainung, Everglades and Cuba 108 cultivars) of different ages, which were planted in U.S.A., were investigated by R.M. Rowell, J. S. Ham [1], and T.F. Clark et al. [2,3], however, the cultivar (Zhejiang No.1 from China) and the location of growth (Japan) of kenaf in this study were different from those of their study. The physical and the chemical characteristics of the cellulosic

materials from the kenaf plants of different ages have also hardly been investigated such as the degree of polymerization, the degree and the size of crystallinity, the orientation, the birefringence, and the sorption of moisture, water and dyes.

Therefore, kenaf plants, which were planted and harvested at 77 days, 148 days and 218 days after seeding in Kochi (latitude: 33° 33' N, longitude 133° 31' E, altitude: 2.5m), Japan, in 1996, were pulped from the bast and the core of the kenaf by a kraft method. The previously mentioned chemical and physical characteristics of their cellulosic materials were also investigated, and their bast (outer bark) fibers were compared with their inner core fibers.

2. Experimental

2.1. Materials

The kenaf plants (Zhejiang No.1) were planted on May 18, 1996 in Kochi, Japan and were harvested on August 2, October 12 and December 21, namely, 77 days, 148 days and 218 days, respectively, after planting. The stems were manually separated into the bast fraction and core fraction, and they were both cut to a length of about

4 cm, then cooked by a kraft method. The cooking conditions were as follows; dosage of active alkali (as Na₂O), 16% based on the raw material, sulfidity in kraft pulping (as Na₂O) 25%, material/liquor ratio, 1:5, cooking temperature, 170°C, rising time, 1.5 hours, and holding time, 1.5 hours. The crude bast and core pulp fibers were washed and bleached at 70-80°C with sodium chlorite, acetic acid and sodium acetate. The bleached bast and core pulp fibers were then washed, dried, and evaluated.

2.2. Analysis of materials

The bast and the core of the kenaf plants and fibers were separately analyzed for ash, hot water extracts, 1% NaOH solution extracts, holocellulose, α -cellulose, carboxyl groups and Kappa number according to the normal method for pulp and wood analysis [4].

The crystallinity ($I_{002}/(I_{002} + I_{002B})$), crystallite size (Scherrer equation) and orientation (I_{101}/I_{002}) of the bast and the core samples were measured by X-ray diffractometry (Rigaku Denki Co., Ltd.) using a random assembly of shortly chopped fibers of each material with Cu K α radiation[5], and the birefringence of the bast and the core fibers was measured using a polarized microscope (Olympus BH-2) and a Berek compensator [6].

The degree of polymerization of the bast and the core pulp fibers was determined as follows; the trinitrocellulose samples were prepared from both fibers [7] and dissolved in acetone. Their viscosity was then measured by a viscometer at 20 °C and their degree of polymerization was calculated by equation $[\eta] = 11 \times 10^{-4} P$ [8].

2.3. Sorption of moisture, water, direct and basic dyes

About 0.5 g of the oven dry sample was kept in a desiccator (67.4% RH and 92.3% RH) to sorb moisture at 20 °C for about 4 weeks, and then the moisture content of the samples was calculated as the grams of moisture per gram of dry sample (g/g).

The dry samples of about 1 g were put into 100 mL water for 24 hours at 20 °C, then they were filtered and centrifuged at 3000 rpm for 5 minutes. The amount of their water sorption was calculated as already mentioned.

About 0.25 g of the oven-dry bast and core fibers were added to 25 mL of aqueous direct and basic dye solutions of 100 mg/L and 200 mg/L, respectively, and after the mixture solutions were stirred for 24 hours and the dyed fibers were filtered, the concentration of the direct and the basic dyes in the filtrate was measured

using a 100-10 type Hitachi Spectrophotometer at 475 nm and 645 nm, respectively. The amounts of their sorption of the direct and basic dyes were then calculated as the grams of dye per gram of dry sample (g/g). C.I. direct yellow 12 (Chrysophenine G) and C.I. basic blue 9 (Methylene blue) were used as the direct and basic dyes, respectively.

3. Results and discussion

3.1 Characteristics of kenaf stalks at different ages

The rate of kenaf plant growth will vary significantly depending on the kenaf cultivars, day of seeding, growing places, fertilizer, temperature, rainfall, and so on. Table 1 shows the kenaf plant height, diameter and oven - dry weight ratio of the kenaf core to bast fiber.

Table 1 Plant height, diameter and oven-dry weight ratio of core to bast fiber.

Days after seeding	Height (cm)	Diameter (cm)	Volume factor ^a	Volume fraction (%) ^b	Ratio ^c
77	196	1.53	300	0.64	1.45
148	223	1.91	426	0.90	1.63
218	284	1.66	471	1.00	2.18
The data for the kenaf grown in Wisconsin, U.S.A[1]					
77	173	1.9	329	0.2	1.03
155	375	2.7	1013	0.7	1.71
175	400	3.7	1480	1.0	1.81

a Volume factor=height x diameter

b Volume fraction= volume factor for days/volume factor at maturity

c Ratio=oven-dry weight ratio of kenaf core to bast fiber

These data increased with planting days, however, they were lower than those for the kenaf grown in Wisconsin, U.S.A. by R.M. Rowell et al [1], except for the volume fraction (volume factor (height x diameter) for days/volume factor at maturity) and ratio (oven-dry weight ratio of kenaf core to bast fiber). Especially, the volume factor was one-third that of the kenaf grown in the U.S.A [1], namely, the height and the diameter of kenaf Zhejiang No.1 were lower than those of the kenaf grown in the U.S.A. except at 77 days.

The volume fraction for Zhejiang No.1 at 77 days and 148 days after seeding was about 0.64 and 0.90, respectively, whereas that of the U.S.A. grown kenaf at 77 days and 155 days was 0.2 and 0.7, respectively. Therefore, Zhejiang No.1 significantly grew at the early

stage, and then gradually grew, however, the oven-dry weight ratio of the kenaf core to bast for Zhejiang No.1 was almost the same as that of the U.S.A.-grown kenaf. The volume fraction is able to be used to calculate the yield of plant mass at any given time after seeding.

Table 2 Chemical composition of kenaf plants.

Day after seeding and bast or core	Ash content (%)	Hot water extractive (%)	1%NaOH soln. extractive (%)	Holo-cellulose content (%)
77 bast	9.4	17.0	21.4	79.1
148 bast	8.9	16.7	30.5	72.6
218 bast	5.8	12.7	14.0	77.7
77 core	5.8	9.3	9.7	73.3
148 core	4.8	9.1	11.2	74.8
218 core	1.0	10.0	19.5	75.2

%, oven-dry basis

Table 2 shows the chemical composition of the kenaf plants. The contents of ash, hot water extracts, 1% NaOH solution extracts and holocellulose for the kenaf bast were greater than those for the core. The ash content for both the bast and core and the hot water extracts, and 1% NaOH solution extracts for the kenaf bast generally decreased after seeding, whereas those for the kenaf core increased after seeding as shown in Table 2. However, the holocellulose content for both the bast and core harvested at different days were almost constant.

Table 3 Chemical composition of kenaf bast and core pulp fibers.

Days after seeding and bast or core	Ash content (%)	Hot water extractive (%)	1%NaOH soln. extractive (%)	Holo-cellulose content (%)	α -cellulose content (%)	Lignin content (%)	Carboxyl group content (meq/100g)	Kappa number
77 bast	0.7	0.9	4.4	90.4	76.8	4.7	2.6	31.2
148 bast	0.6	1.0	4.6	84.3	72.5	4.3	4.2	29.0
218 bast	0.8	1.3	5.1	76.2	64.8	4.9	4.9	32.9
77 core	0.1	1.9	8.0	73.7	48.9	13.3	13.3	88.4
148 core	0.8	2.8	9.0	78.9	52.9	11.5	11.5	77.0
218 core	0.6	4.0	10.0	80.0	54.7	9.9	6.4	66.1

T.F. Clark et al. reported that the percent of ash content for the kenaf stalks generally decreases with increasing plant maturity, however, the percent of α -cellulose and M.E.A. cellulose (monoethanolamine procedure) contents are almost constant in the kenaf stalks harvested at various times at each locations (Florida and Illinois)[3]. Moreover, Poo Chow et al. reported that the percent of holocellulose content of 4 kenaf cultivars (Everglades 41, Everglades 71, Tainung 2

and Cuba 108) and 3 tree species (cotton wood (*Populus deltoides*), hard maple (*Acer* spp.) and hickory (*Carya* spp.) is almost constant, however, the percent of the α -cellulose content for these kenaf basts is greater than that of the 3 tree species [9].

In conclusion, the percent of the holocellulose content for the bast and the core of the kenaf stalks harvested at different days in Japan is almost constant, similar to the kenaf plants grown in U.S.A. though the weight of the holocellulose content is different.

3.2 Characteristics of kenaf bast and core fibers at different plant ages

Table 3 shows the chemical composition of the kenaf bast and core pulp fibers of different ages. The contents of ash, hot water extracts and 1% NaOH solution extracts for the kenaf bast and core fibers were lower than those for the bast and core of the kenaf plants, however, the holocellulose content for the kenaf bast and core fibers was greater than that for the bast and core of the kenaf stalks, as shown in Tables 2 and 3. This is due to the differences between the original kenaf stalks and alkaline cooked pulp fibers.

The contents of the hot water extracts, 1% NaOH solution extracts and the carboxyl group for the kenaf bast and the core fibers increased with planting days, however, these results for the kenaf bast fibers were lower than those for the kenaf core fibers as shown in Table 3. These results indicate that the short chains of the glucose and hemicellulose content for the kenaf

bast fibers were smaller than those for the kenaf core fibers though they increased with planting days. However, the contents of the holocellulose and the α -cellulose for the kenaf bast fibers were greater than those for the kenaf core fibers and no significant changes in these contents were associated with plant maturity.

Table 3 also shows the Kappa number for the cellulose of the bast and the core fibers obtained from the kenaf plants of different ages. The core fibers were distinctly

greater in the Kappa number, and therefore, the lignin contents in the core fibers were greater than those in the bast fibers. However, there was only slight differences in the Kappa number of the kenaf bast fibers at the different plant ages.

Fig. 1 Degree of polymerization of trinitrocellulose and birefringence.

Fig.1 shows the degree of polymerization of trinitrocellulose made from the bast and the core cellulose fibers at the different plant ages and the birefringence of these mentioned fibers. The degree of polymerization of trinitrocellulose was about 1500 - 1800 and the birefringence of these fibers was about 0.05-0.07, and both the degree of polymerization and the birefringence of the bast fibers were greater than those of the core fibers, and both of them slightly increased with planting days.

The degree of polymerization of the cellulose of the kenaf bast and the core fibers is almost the same as that of wood pulp (1500-2000 [10]), however, it is lower than that of cotton (2000-3000 [10]), ramie (6500-9000 [10]). The birefringence of the kenaf bast and core fibers is greater than that of cotton (0.041-0.051 [11]), wood pulp (0.02 [12]) and regenerated cellulose (polynosic, 0.03-0.05 [11]), respectively, and it is almost the same as that of ramie (0.057-0.068 [11]).

Cellulose, of which the degree of polymerization and the birefringence are high, generally has higher strength properties, and therefore, it can be understood from these results that the strength properties of the

kenaf pulps were comparable to those of commercial softwood bleached kraft pulp as reported by Sameshima et al. [13].

Fig.2 shows the crystallinity, the crystallite size and the orientation for the bast and the core fibers at the different plant ages. Their crystallinity, the crystallite size and the orientation were about 73-78%, about 3.2 nm and about 0.7, respectively, and the effects of the kenaf plant maturity were slight. Their crystallinity and their crystallite size were almost the same as that of wood pulp (79% [14]) and that of kenaf (Everglades 41 planted in Mississippi, U.S.A., 2.6-3.2 nm), respectively [15].

P.K. Ray et al. reported that the crystallinity index of 120-day-old mesta (*Hibiscus sabdariffa*) and 150-day-old mesta were 39 and 45, respectively, and the latter was about 1.2 times the former [16]. However, there was no reference to the crystallite size and the orientation of the kenaf cellulose fibers for different planting days.

Fig. 2 Crystallinity, crystallite size and orientation for the bast and the core fibers at the different plant ages.

T.F.Clark et al. reported that the strength values and the pulp quality of the kenaf pulps decreased between pulps from the 90-day harvests and those from later harvests, e.g., 120 days, however, it did not significantly change after 120 days.

In conclusion, the degree of polymerization and the birefringence for the bast and the core fibers of the kenaf plants harvested at different days are almost

constant, and the effects of the kenaf plant maturity on their crystallinity, their crystallite size and their orientation were slight though the weight of the holocellulose content is different.

3.3 Sorption of moisture, water, direct and basic dyes on kenaf bast and core fibers at different plant ages

Fig. 3 Moisture content of bast and core fibers at different plant ages at 67.4%RH and 92.3%RH.

Fig. 4 Water sorbency of kenaf bast and core fibers at different ages after filtration or centrifugation.

Fig. 3 shows the moisture content of the kenaf bast and core fibers at the different plant ages. The moisture contents of the kenaf bast and core fibers at the different ages were about 0.08 g/g - 0.12 g/g and 0.18 g/g - 0.23 g/g at 67.4%RH and 92.3% RH at 20 °C, respectively, and they were greater than those of cotton (0.075 g/g and 0.171 g/g, respectively) and wood pulp (0.107 g/g and 0.194 g/g, respectively) [14]. The moisture content of the kenaf bast fibers was almost the same as that of the kenaf core fibers, and both moisture contents increased from the 77-day harvest to the 148-day harvest, however, that of the 218-day harvest decreased.

Fig. 4 shows the water sorbency of the kenaf bast and core fibers of different ages after filtration or centrifugation. Their values were about 4.1-6.0 g/g and 1.2-2.5 g/g, respectively. There were only slight differences between the water sorbency of the bast fibers and that of the core fibers, and both the water sorbency increased from the 77-day harvest to the 148-day harvest, however, that of the 218-day harvest decreased similar to the moisture content described above.

Fig. 5 Sorption of direct and basic dyes on bast and core fibers at different ages.

Fig.5 shows the sorption of the direct and basic dyes on the kenaf bast and core fibers of different ages. The sorption of the direct dye on the kenaf bast and core fibers decreased with planting days, and that of the direct dye on the kenaf bast fibers was greater than that of kenaf core fibers, however, the sorption of the basic dyes on them did not significantly change after the 77-day

harvest and that on the kenaf bast and core fibers was almost same.

4. Conclusions

The chemical and physical characteristics of the cellulosic materials obtained from different aged kenaf plants (Zhejiang No.1 cultivar from China) grown in Japan were investigated, and their bast was compared with their inner core. The ash content of the bast and core of the kenaf plants at different ages decreased, however, the percent of holocellulose content was almost constant. The moisture content, the sorption of the direct dye, the crystallinity, the crystallite size and the orientation for the bast and core fibers at different plant ages were almost constant. Therefore, these results indicate that kenaf (Zhejiang No.1 cultivar) can be harvested at about 140-150 days in Japan.

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