EFFECTS OF ALKALINE PRE-IMPREGNATION AND PULPING ON MALAYSIA CULTIVATED KENAF (*HIBISCUS CANNABINUS)*

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This study was carried out to identify an appropriate alkaline pulping condition for Malaysia cultivated kenaf *(Hibiscus cannabinus* L.*)*. The chemical composition of the kenaf bast and core fibers, and also whole stalk with different growing time were examined prior to pulping attempts. The results of various soda-AQ pulping showed that the degree of carbohydrate degradation and delignification increased with the increase of active alkali and cooking temperature, but decreased with the increase of liquor to material (L:M) ratio. The most satisfactory properties of pulp and handsheets from bast could be attained by employing soda-AQ pulping with 19.4% active alkali, 0.10% AQ, and L:M ratio of 7:1 cooked for 2 hours at 160˚C. Besides, it was also found that a mild alkaline pre-impregnation prior pulping improved the pulp viscosity and handsheets' strength properties, especially the tensile index and folding endurance effectively. Moreover, among the three alkaline pulping processes—kraft, kraft-AQ, and soda-AQ—the results of pulp and handsheet properties showed that the soda-AQ pulp was comparable or even slightly of higher quality than the kraft pulps. Between the unbeaten bast and core soda-AQ handsheets, the strength properties of the core were higher than the bast, as the thin-walled core fibers exhibited much better conformability than the thick-walled bast fibers.

Keywords: Hibiscus cannabinus (kenaf); Chemical compositions; Growing time; Soda-AQ pulping; Pulp and handsheets properties; Alkaline pre-impregnation

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INTRODUCTION

In Malaysia, kenaf was first introduced in the early 1970's and was recognized as a high potential alternative fibrous material for the production of panel products such as fiberboard and particleboard in the late 1990s under the 7th Malaysia Plan 1996-2000 (MP7) (Malaysian Timber Council 2005). Due to its potential commercial value, the research and development of the plant was continued under the 8th Malaysia Plan 2001-2005 (MP8), and the allocation from the government for this purpose was increased from RM 2 million under MP7 to RM 3.2 million under MP8 (New Straits times 2004; The star 2004).

The interest of the Malaysian government in kenaf has dramatically increased, as indicated by the great increase of allocation up to RM 35 million for a kenaf development

program under the 9th Malaysia Plan 2006-2010 (MP9). Under the plan, the National Kenaf and Tobacco Board (formerly known as the National Tobacco Board) contrived the development of kenaf cultivation in order to replace the current tobacco cultivation, especially in the state of Kelantan. Furthermore, instead of panel products, the government also has emphasized diversifying and commercializing the downstream kenaf-based industries including the pulp and paper industry with the cooperation of private sector (NST Business Times 2008; Malaysian National News Agency 2008).

Kenaf stem consists of two distinct parts, the long fiber bast and the short fiber core (Kaldor et al. 1990). Besides the fiber length, these two fibers are also greatly different in chemical compositions, and thus they are not recommended to be pulped together (Ohtani et al. 2001). Although many research studies on kenaf in the production of pulp and paper have been carried out extensively, studies based on the locally available kenaf for pulp and paper making are still very limited (Sharmiza et al. 2004; Latifah et al. 2007).

Moreover, it has been reported that the properties of the kenaf fibers, especially their chemical components, vary according to their different cultivars, years, climate, and soil (Webber 1992; Cook et al. 1998; Ashori 2006). Thus, the determination of the locally planted kenaf properties is essential because the differences of the kenaf fiber properties will directly affect the pulping properties. This means that even when under the same pulping conditions, the properties of the resultant pulps and handsheets could possibly be different. In order to identify an appropriate pulping method and condition to be potentially employed by local pulp mill, this study examined the chemical compositions of the bast and core as well as the whole stalk fibers of the locally planted kenaf. The effects of alkaline pre-impregnation and pulping variables on the kenaf bast pulp and handsheets properties were then investigated. Differences between kenaf bast and core soda-AQ pulp and handsheet properties were also examined.

EXPERIMENTAL

Materials

Kenaf was planted by Nibong Tebal Paper Mill Sdn. Bhd. in the district of Nibong Tebal, Penang, Malaysia in February and March 2007 and was harvested in June 2007. After stripping the flowers and leaves, kenaf as whole stalks and also kenaf bast and core were separated manually. They were air-dried to prevent the growth of mould and fungi during storage. All the kenaf stalks and the separated bast and core were then cut to the length of 2-3 cm.

Methods

Chemical analysis

The air-dried kenaf whole stalk, bast, and core fibers were ground into fine particles for chemical analyses according to TAPPI T 257 - Sampling and preparing wood for analysis. In order to obtain homogenous samples, the bast and core were sieved through 40- and 60-mesh screens to eliminate the fine and coarse fibers. For the whole stalks, in order to avoid obtaining false information, no sieving was applied. The

determination of extractives content was carried out based on TAPPI T 204 - Solvent extractive of wood and pulp with a minor modification, where instead of the mixture of ethanol-benzene, ethanol-toluene (1:2) was used as the solvent. The determination of holocellulose and α-cellulose contents were conducted according to the methods of Wise et al. (1946) and the Japanese Standard Method JIS 8101 - Determination of alpha-cellulose content, respectively. TAPPI Standard Methods were used for other determinations: T207 - Water solubility of wood and pulp, T211 - Ash in Wood, Pulp, Paper and Paperboard: Combustion at 525°C, T212 – One % Sodium Hydroxide Solubility of Wood and Pulp, T222 - Acid-Insoluble Lignin in Wood and Pulp, and T249 - Carbohydrates Composition of Extractive-Free Wood and Wood Pulp by Gas-Liquid Chromatography. Each analysis was carried out in triplicate.

Scanning electron microscopy

The samples of kenaf bast and core fibers were cut into small pieces of 2 mm length. The micrographs were examined with a Leo Supra 50VP Field Emission Scanning Electron Microscope (SEM) equipped with an Oxford INCA 400 energy dispersive x-ray microanalysis system, operated at 5kV to observe the surface morphology of the samples at various magnifications. The specimens were stuck on aluminum stubs with double-sided adhesive tape and coated with a gold layer using a sputter coater before examination by SEM.

Chemical pulping

Pulping of kenaf (bast and core) was carried out in a 4-litre stationary stainless steel digester (without external circulation mixing) manufactured by NAC Autoclave Co. Ltd., Japan, fitted with a computer-controlled thermocouple. 200 grams of the material (oven-dry weight) was placed in the digestion vessel, and subsequently an appropriate amount of active alkaline (NaOH expressed as Na_2O) and 0.1% anthraquinone were added. Distilled water was added to achieve the liquor to material ratio of 6:1 or 8:1 (since kenaf core is very bulky, in order to have sufficient white liquor to completely immerse the material, the ratio of liquor to material was increased to 8:1 instead of 6:1 for kenaf bast). The material in the vessel was squeezed to ensure that all the materials were soaked in the cooking liquor for a homogenous cooking effect. The digester was then heated to the required temperature with a tolerance of 2°C within 90 min and maintained for 120 min at cooking temperature. All the pulping conditions are shown in Table 1.

Upon completion of the pulping, the resultant pulp and spent liquor were collected and re-mixed in a hydrapulper for 10 minutes in order to remove the degraded lignin, which was possibly adsorbed or adhered to the fibers' surfaces. After washing in a stainless steel mesh filter, the pulp slurry was mechanically disintegrated in a three bladed disintegrator for 1 minute at a pulp consistency of 2%, and subsequently it was screened on a flat-plate Sommerville screen with 0.15 mm slits. The screened pulp was spin-dried, and the yield was determined based on oven-dried material basis.

The viscosity and kappa number of the screened pulp were determined in duplicate according to TAPPI standard method T230 - Viscosity of pulp with minor

modifications, as explained elsewhere (Mazumder et al. 2000; and TAPPI Useful Method 246 - Micro Kappa).

Alkaline pre-impregnation

Alkaline pre-impregnation was carried out by soaking the kenaf bast for 15 hours in a desired concentration of alkaline (sodium hydroxide, NaOH) solution at room temperature with a ratio of liquor to wood of 6:1. Then, a higher concentration NaOH solution was directly topped up to the desired amount of active alkaline (25% AA) without washing the kenaf bast, and a ratio of liquor to wood increased to 7:1 was used in the pulping process. The pre-impregnation was carried at room temperature aimed to have a minimum dissolution of hemicellulose as verified by Sun et al. (1995) that the dissolution of hemicellulose increased with an increase of temperature, whilst a longer impregnation was used to achieve maximum chemical penetration and fiber swelling.

Handsheet making and testing

Without additional beating, each handsheet was made from the resultant pulps and tested according to TAPPI Standard Methods T 205 - Forming Handsheets for Physical Tests of Pulp, T 220 - Physical Testing of Pulp Handsheets, T 452 - Brightness of Pulp, Paper and Paperboard, and T 425 - Opacity of Paper.

Table 1. Pulping Conditions Used for Kenaf Bast and Kenaf Core

Pulping condition	Alkaline pre-impregnation, NaOH (M)	AA (%)	Sulfidity (%)	Cooking Temp. (°C)	(L:M)	AQ (%)
BS1	-	17.8	-	160	7:1	0.1
BS2	-	19.4	-	160	7:1	0.1
BS3	-	21.7	-	160	7:1	0.1
BS4	-	19.4	-	155	7:1	0.1
BS5	-	19.4	-	165	7:1	0.1
BS6	-	19.4	-	160	6:1	0.1
BS7	-	21.7	-	160	6:1	0.1
BS8	0.10	19.4	-	160	7:1	0.1
BS9	0.25	19.4	-	160	7:1	0.1
BS10	0.50	19.4	-	160	7:1	0.1
BK1	-	22.0	25	160	6:1	0.0
BK2	-	22.0	25	160	7:1	0.1
CS1	-	19.4	-	160	8:1	0.1
CS2	-	21.7	-	160	8:1	0.1
CS3	-	21.7	-	170	8:1	0.1

AA - active alkali as Na_2O; Cooking Temp. - cooking temperature; L : M - ratio of liquor to material; AQ – anthraquinone; BS - bast soda; BK - bast kraft; CS - core soda

RESULTS AND DISCUSSION

Chemical Analysis of Kenaf

Table 2 shows the results of chemical analyses for kenaf bast, core, and whole stalk with the plant age of 4.5 months. Besides, analyses were also carried out on the 3.5 months old kenaf whole stalk to examine the effect of harvesting time.

Extractive contents

As shown in Table 2, the organic solvent extractive content of kenaf bast and core were greatly different insofar as the core contained almost five times (4.9%) more extractives than the bast fiber (1%). In comparison to the published data of the extractive content, the bast was much lower, whereas the core was much higher than that reported by Ohtani et al. (2001), Khristova et al. (2002), and Ashori et al. (2006). On the other hand, a higher extractive content (4.4%) was observed in the 3.5 months whole stalk in comparison to the 4.5 months old whole stalk. The presence of the extractives will normally increase the consumption of chemicals during the pulping process, and also lower the pulp quality by giving the pitch problem during papermaking process (Khristova and Karar 1999). These findings indicated that the 4.5 months old kenaf with lower extractive levels is more favorable to pulp and paper production.

Table 2. Chemical Composition of Kenaf Fractions

	Extractives			Ash (%)	Klason lignin (%)	Holo-cellulose (%)	α – cellulose (%)
	Organic solvent (%)	Hot-water (%)	1% NaOH (%)				
Penang							
4.5 months							
Bast	1.0 ± 0.1[a]	3.8 ± 0.3	22.0 ± 0.2	4.4 ± 0.1	10.4 ± 0.2	88.3 ± 1.2	67.3 ± 0.2
Core	4.9 ± 0.5[a]	8.2 ± 0.5	30.3 ± 0.3	2.3 ± 0.1	21.1 ± 0.2	85.2 ± 0.7	46.3 ± 0.2
Whole stalk	2.5 ± 0.1[a]	6.5 ± 0.1	29.4 ± 0.2	4.2 ± 0.1	19.3 ± 0.6	79.6 ± 0.5	54.4 ± 0.3
3.5 months							
Whole stalk	4.4± 0.1[a]	12.1± 0.1	33.9± 1.6	4.4± 0.1	16.0 ± 0.2	83.6± 1.2	54.9± 0.2
Selangor*							
Bast	2.7	3.4	14.5	2.2	14.7	82.6	56.4
Core	2.2	3.9	20.6	1.6	22.1	75.8	46.1
Whole stalk	2.3	3.6	17.3	1.8	19.9	77.2	48.7
Kochi**							
Bast	3.4	15.9	N/a	1.1	9.2	79.6	69.8
Core	3.0	7.5	N/a	1.4	19	77.6	45.3
Sudan***							
Bast	2.0[b]	6.7	26.1	4.0	8.1[c]	N/a	N/a
Core	3.0[b]	4.4	29.3	2.9	19.6[c]	N/a	N/a
Whole stalk	2.9	9.5	28.4	3.4	15.6[c]	78.9	49.5
France***							
Whole stalk	5.6	9.3	32.2	5.9	19.3[c]	N/a	N/a
USA***							
Whole stalk	3.1	10.2	54.4	4.1	19.7[c]	N/a	37.4

All values presented as percent of oven-dry raw materials
N/a = Not available; [a]Alcohol-toluene (1:2); [b]Alcohol-cyclohexane (1:2); [c]Corrected for ash; *Ashori et al. 2006; **Ohtani et al. 2001; ***Khristova et al. 2002.

The hot water solubility of the core fiber (8.2%) was more than two-fold higher than that of the bast fiber (3.8%). The solubility presented by Ashori et al. (2006) demonstrated the same trend; however their solubility value for the core was far lower. Although the results obtained illustrated a reverse trend in comparison to those reported by Khristova et al. (2002) and Ohtani et al. (2001), where the hot water solubility of the core was much lower than that of the bast (Table 2), these publications actually showed the same trend for both the organic solvent and 1% NaOH solubility as in this study. Similar to the organic solvent solubility, the 3.5 months old kenaf whole stalk presented higher hot water solubility (12.1%), which was almost double in comparison to the 4.5 months one (6.5%). The results revealed that the hot water solubility of kenaf decreased with an increase of plant age. A similar trend of results was also reported by Rowell and Stout (1998), but their solubility was relatively much higher than ours. The low hot water solubility of the kenaf, especially of the bast fibre is a good indicator for its potential to be used in the production of chemical pulp with higher pulp yield.

On the other hand, the one percent sodium hydroxide (1% NaOH) solubility of bast and core fibers were 22.0% and 30.3%, respectively. These results were in agreement with those published by Khristova et al. (2002) but about 50% higher than those reported by Ashori et al. (2006). Furthermore, similarly to the other two types of solubility, the increase of harvesting time from 3.5 months to 4.5 months also reduced the 1% NaOH solubility from 33.9% to 29.4%.

Solubility is an essential parameter that enables us to estimate the dissolution of the material during the pulping process. Hence, in the production of chemical pulp from kenaf, which involves a substantial dissolution of lignin, the estimated loss of yield would be more than 40%, and the yield loss during chemical pulping for the core is expected to be higher than the bast as well.

Ash content

Based on Table 2, it can be seen that the ash content of bast fiber (4.4%) was higher than that of core fiber (2.3%). These results were quite similar to those reported by Khristova et al. (2002). However, a remarkable difference was observed in comparison to the data reported by Ashori et al. (2006) and Ohtani et al. (2001). The comparison between the kenaf whole stalk with different plant ages indicates that the effect of harvesting time was not obvious, since the difference of the ash content between the 4.5 months (4.2%) and 3.5 months old kenaf (4.4%) was only 0.2%. Basically, the high ash content of the material may increase the consumption of pulping chemicals and also poses difficulty to the spent black liquor recovery system by increasing the spent liquor viscosity.

Acid-insoluble lignin

Acid-insoluble lignin or more commonly known as Klason lignin values obtained from both kenaf bast and core were 10.4% and 21.1%, respectively. Obviously, the lignin content of the bast was only half of the core content for most of the cases, as shown in Table 2. With the increase of plant age, the lignin content increased from 16.0% at 3.5 months to 19.3% at 4.5 months. Low lignin content is normally more favorable for papermaking due to lower the production costs and water pollution. Nevertheless, earlier

harvesting of kenaf may not only lead to lower lignin content, but also to substantial losses in biomass yields (Webber and Bledsoe 2002).

By virtue of low lignin content, kenaf exhibited superiority in the production of pulp and paper, since milder pulping conditions in terms of time, chemicals, and temperature can be adopted to lower the production cost. At the same time, by employing milder pulping conditions, carbohydrate degradation can be minimized, resulting in higher strength properties for both pulp and paper.

Holocellulose content

Based on the results obtained (Table 2), there was only a small difference of holocellulose content between the bast (88.3%) and core (85.2%) fibers, but they were relatively higher than those reported by Ashori et al. (2006) and Ohtani et al. (2001). As a function of harvesting time, the holocellulose content seemed to decrease from 83.5% to only 79.6% with the increase of plant age from 3.5 months to 4.5 months. However, the difference was not as large as reported by Miyata (2003) and Karakus and Roy (1998). As compared to wood, kenaf generally has a rather high holocellulose content, which is mainly attributed to its relatively low lignin content.

α-Cellulose content

High α-cellulose content is preferable in pulp production because it implies that a higher yield will be obtained from the pulping process. Table 2 demonstrates that the α-cellulose content of bast fiber was higher than that of core fiber, which was 67.3% and 46.3%, respectively, and they were actually in good agreement with the results presented by Ohtani et al. (2001). It is interesting to see that even though there was only a small difference (ca. 2%) in the holocellulose content between the core and the bast, the α-cellulose content of the bast was about 40% higher than that of the core. This indicated that the core fiber basically has higher hemicellulose content, and this is also the reason why the core had a higher value of 1% NaOH solubility.

By comparing the 3.5 months and 4.5 months old kenaf, it was found that the harvesting time did not show any effect on the α-cellulose contents, which were valued at 54.4% and 54.9%, respectively. Although the level of the α-cellulose content in raw materials does not directly affect their pulping properties, high pulp yield after the pulping and bleaching process can normally be a reflection of the presence of high α-cellulose content in the material.

Carbohydrate composition by gas chromatography

The carbohydrate composition (Table 3) of kenaf fibers was determined based on the holocellulose. Since glucose is the monomer for the cellulose chain, as expected the content of glucose was the highest in both bast and core fibers, which accounted for 76.32% and 64.88%, respectively.

Since the hemicellulose of kenaf is mainly from xylan, the second most abundant monosaccharide in kenaf was xylose, of which the composition levels were determined as 16.87% and 27.95% for the bast and core fibers, respectively. The amounts of both the glucose and xylose were in good agreement with those reported by Ohtani et al. 2001 (Table 3), wherein the only noticeable differences were the amounts of arabinose and

mannose. For different plant ages, the results of gas chromatography did not show any significant differences in the carbohydrate compositions. Thus, the effect of harvesting time on the carbohydrate composition was considered negligible.

Table 3. Polysaccharides of Holocelluloses of Kenaf Fractions

Sample	% Polysaccharide					
	Kochi*		4.5 months old (Penang)			3.5 months old (Penang)
	Bast	Core	Bast	Core	Whole stalk	
Glucose	75.5	62.6	76.32	64.88	68.22	68.73
Xylose	18.1	29.8	16.87	27.95	24.92	24.85
Arabinose	3.2	4.8	0.9	1.24	1.29	1.36
Mannose	1.5	1.3	4.26	3.5	4.89	4.55
Galactose	1.7	1.5	0.75	-	0.68	0.51
Rhamnose	N/a	N/a	0.9	2.43	-	-
*Ohtani et al. 2001						

Alkaline Chemical Pulping

The increase of plant age from 3.5 to 4.5 months decreased the extractive contents. However, it adversely increased the lignin content, and as a result, countered the effect on the holocellulose and α-cellulose contents to a small extent. Hence, for the subsequent study on soda-AQ pulping, 4 months old kenaf was chosen to compromise the positive and negative effects of harvesting time on the chemical composition.

Although Han and Rymsza (1999) have reported that the minimum soda-AQ pulping condition for the kenaf bast was 12% AA with 0.15% AQ cooked for 2 hours at 160°C, and the kappa number of its resultant pulp was 16, the employment of the same condition to the locally planted kenaf has resulted in uncooked pulp with a rejection rate of more than 50%. Thus, in order to produce chemical pulp from kenaf bast and core with a substantially low kappa number, several attempts have been tried as shown in Table 1.

Effect of soda-AQ pulping variables on kenaf bast fiber: Active alkali (AA)

The influences of AA in the range of 17.8% to 21.7% on kenaf bast soda-AQ pulp and its handsheet properties were investigated, and results are presented in Tables 4 and 5. The results show that the rejects yield, kappa number, viscosity, and CSF decreased clearly with an increase of AA. Based on the results of screened yield, it was positively increased from 50.8% to 52.7%, with an increase of AA from 17.8% (BS1) to 19.4% (BS2) and a subsequent increase of AA to 21.7% (BS3) caused a decrease of the yield to 51.3%. This revealed that the alkali concentration of BS1 (17.8% AA) was insufficient to fully cook the kenaf bast fibers, whereas excessive AA in BS3 (21.7%) led to yield loss due to inevitable carbohydrate degradation.

Moreover, a high concentration of OH- ions for 21.7% AA markedly increased the delignification rate as indicated by a lower kappa number (10.7). However, an increase of AA from 19.4% to 21.7% was accompanied by a significant reduction in viscosity from 43.7cP to 35.2cP. Hence, the best active alkali for the kenaf bast in this study was 19.4%.

Table 4. Results of Pulp Properties of Kenaf Fibers

Pulping condition	Screened yield (%)	Rejects (%)	Kappa No	Viscosity (cP)	CSF (ml)
BS1	50.8 ± 0.3	3.9	14.2	54.4	596
BS2	52.7 ± 0.5	0.8	13.3	43.7	573
BS3	51.3 ± 0.5	0.3	10.7	35.2	541
BS4	50.3 ± 0.8	4.9	16.4	71.5	585
BS5	50.7 ± 0.6	0.3	11.9	27.7	541
BS6	51.9 ±1.3	0.6	12.7	34.9	595
BS7	52.1 ± 0.4	0.4	10.5	24.7	612
BS8	53.0 ± 0.9	0.4	13.5	45.2	556
BS9	54.3 ± 0.7	0.5	13.7	49.4	542
BS10	53.9 ± 0.6	0.5	13.9	47.5	555
BK1	53.2 ± 0.9	0.9	13.2	33.1	583
BK2	54.2 ± 1.1	0.2	12.3	41.1	564
CS1	36.0 ± 0.6	5.0	24.0	37.1	305
CS2	39.6 ± 0.4	0.3	15.6	28.8	293
CS3	38.2 ± 0.5	0.3	11.0	16.0	286

For the handsheets's properties, apart from the tear index, the tensile and burst indices, folding endurance, and brightness increased with the increase of AA from 19.4% AA to 21.7% AA, as shown in Table 5. This indicated that the intrinsic fiber strength of all the pulps was still strong enough and did not negatively affect most of the paper strength properties. Hence in this case, the principal factor affecting the folding endurance, tensile, and burst indices is fiber-fiber bonding ability, which was increased when the flexibility and hydrophylicity of fibers were increased due to better lignin removal. The only negative effect observed was on tear index, which was mainly attributed to the decrease of pulp viscosity (fiber strength) with the increase of AA.

Table 5. Results of Handsheet Property Tests for Kenaf Pulps

Pulping condition	Density (g/cm^3)	ISO brightness (%)	TAPPI opacity (%)	Tensile index (Nm/g)	Bursting index ($kPa.m^2/g$)	Tear index ($mN.m^2/g$)	Folding endurance
BS1	0.4005	28.80	93.96	52.4	7.2	14.7	225
BS2	0.4164	29.96	91.92	57.8	7.9	13.0	315
BS3	0.4181	34.40	91.70	59.6	8.0	13.5	626
BS4	0.4125	28.64	91.97	52.8	7.8	14.2	419
BS5	0.4066	33.79	91.34	50.1	7.6	12.8	334
BS6	0.4534	31.98	91.94	56.1	8.0	15.3	291
BS7	0.4470	28.99	93.92	54.6	6.8	12.0	212
BS8	0.4302	31.82	89.93	63.6	8.2	13.7	607
BS9	0.4375	31.26	90.69	66.2	8.8	14.3	514
BS10	0.4336	30.04	92.16	65.7	8.5	21.3	519
BK1	0.4374	27.28	94.84	52.5	7.9	12.0	317
BK2	0.4066	29.28	93.33	55.8	8.0	13.9	424
CS1	0.8167	25.51	90.88	76.9	9.1	4.6	>1000
CS2	0.8402	28.62	90.61	87.5	9.4	4.7	>1500
CS3	0.8830	31.23	89.77	96.5	9.1	4.4	>1500

Effects of cooking temperature

As shown in Table 4, the best screened yield (52.7%) was obtained when the cooking temperature was 160˚C (BS2). The relatively low screened yield (50.3%) and relatively high uncooked rejects yield (4.9%) of condition BS4 indicated that 155˚C was not quite adequate to fully cook the material, while cooking at 165˚C (BS5) caused significant yield loss, maintaining only 50.7% of screened yield. Meanwhile, the increase of cooking temperature from 155˚C to 160˚C and 165˚C reduced the kappa number from 16.4 to 13.3 and 11.9. Concurrently, the pulp viscosity dropped from 71.5cP to 43.7cP and 27.7cP.

As shown in Table 5, the handsheet properties of BS2 with 160˚C were the best among the three conditions. It was very interesting to note that even though the BS4 yielded the highest pulp viscosity, its handsheets's strength properties were lower than those of BS2. This might mainly due to the fact that its resultant pulp contained lots of tiny bundles of under-cooked fiber, which was detrimental to the handsheet formation. Furthermore, as expected, with the highest cooking temperature (165˚C, BS5), a negative effect to the pulp strength was observed, which was strongly related to its substantially lower pulp viscosity (fiber strength).

Effects of the ratio of liquor to material (L: M)

The influences of different L: M ratio (6 and 7) at different AA level (BS2 vs. BS6 and BS3 vs. BS7) on kenaf bast soda-AQ pulp and its handsheet properties are presented in Tables 4 and 5. It was found that the screened yield was less dependent on the L: M ratio. Besides, the kappa number was also independent of changes of L: M ratio either with the AA of 19.4% or 21.7%. However, there was a remarkably decrease of pulp viscosity with the decrease of the L: M ratio at both AA levels. This indicates that the pulp viscosity was more dependent on the L: M ratio in comparison to the kappa number. From here, it was obvious that the pulp viscosity was not only affected by AA, but also by the alkali concentration, which was controlled by the L: M ratio.

From Table 5, it was surprisingly noted that even though the pulp viscosity of the four pulps was greatly different, excluding the tearing index, their handsheets' strength properties were not really affected. This might be explained based on a hypothesis that the intrinsic fiber strength of all these pulps was still strength enough and thus did not impart a detrimental effect on the paper strength properties. On the other hand, at a constant AA of 19.4%, the brightness increased from 29.96% to 31.98% with the decrease of the L: M ratio, while when the AA was 21.7%, a reverse result was obtained; the brightness decreased from 34.40% to 28.99%. This phenomenon was most probably related to the darkening effect caused by a higher concentration of OH^- ion in the lower volume of liquor.

Effects of alkaline pre-impregnation on kenaf bast fiber

The effect of pre-impregnations with three different alkali concentrations (BS8, BS9 & BS10) on pulp properties is shown in Table 4. The analysis of variance tabulated in Table 6 verified that pre-impregnation contributed a significant positive effect on both the screened yield and pulp viscosity but slightly increased the kappa number. Even though the effect of alkali pre-impregnation on pulp properties was rather small, it was

surprising to see that the handsheet properties of the resultant pulp showed a substantial improvement, especially the tensile index as presented in Table 5 and verified by analysis of variance as shown in Table 6. This was probably due to the decrease of the rate of carbohydrate degradation, especially hemicellulose, after applying the pre-impregnation, since the alkali concentration during the subsequent pulping process was relatively lower.

In order to seek for further verification, determination of γ-cellulose (hemicellulose) content of pulps (BS1, BS2, BS8, BS9, and BS10) was carried out. As shown in Table 7, with pre-impregnation, BS8, BS9, and BS10 retained more γ-cellulose content in comparison to BS2. The fact that BS1 retained rather high γ-cellulose content was basically due to insufficient AA to fully cook the material; thus there was less carbohydrates degradation.

The scanning electron micrograph (SEM) shown in Fig. 1 illustrates that fibers in the handsheet were bonded by a kind of membrane. Between the two pulps—without pre-impregnation (1a and 1b) and with pre-impregnation (2a and 2b), the handsheet of the latter exhibited more membrane-bonded area, and thus it was suspected that the major constituent of the membrane is hemicellulose. This indicated that the more hemicellulose content remains in its resultant pulp, the more inter-fiber bonding can be achieved, thereby increasing the strength properties of the handsheet. Since 0.25M NaOH pre-impregnated pulp retained the highest pulp viscosity and hemicellulose, it gave better handsheet strength properties. Based on this view, it may be expected that there is an opportunity to improve paper strength by using pre-impregnation with a suitable alkali concentration.

Table 6. Analysis of Variance (ANOVA) of Pulp and Handsheet Properties between Pulps Produced With and Without Pre-impregnation

	Screened Yield		Kappa number		Pulp Viscosity		Tensile Index	
*Groups**	With	Without	With	Without	With	Without	With	Without
Count	3	5	3	5	3	5	3	5
Sum	161.2	258.7	41.1	59.1	142.1	166.2	195.5	278.2
Average	53.73	51.74	13.70	11.82	47.37	33.24	65.17	55.64
Variance	0.44	0.59	0.04	1.49	4.42	54.91	1.90	13.08

	Screened Yield		Kappa number		Pulp Viscosity		Tensile Index	
Source of Variation	Btwn. Groups	Within Groups	Btwn. Groups	Within Groups	Btwn. Groups	Within Groups	Btwn. Groups	Within Groups
SS	7.45	3.24	6.63	6.05	374.18	228.48	170.17	56.14
df	1	6	1	6	1	6	1	6
MS	7.45	0.54	6.63	1.01	374.18	38.08	170.17	9.36
F	13.802		6.574		9.826		18.187	
P-value	0.010		0.043		0.020		0.005	
F crit	5.987		5.987		5.987		5.987	

* With – with impregnation; Without – Without impregnation

Comparison between soda-AQ, kraft and kraft-AQ pulping on kenaf bast fiber

As can be seen in Table 4, kenaf bast fibers were successfully cooked by kraft pulping (BK1 and BK2) with a rather high AA (22%) and 25% sulfidity with and without 0.10% AQ. Although the AA used for kraft pulping was slightly higher than soda-AQ (BS2) pulping with an AA of 19.4%, based on the pulp properties, the remaining screened yield, kappa number, and pulp viscosity were not extremely low, which verified that the AA used by kraft pulping was actually not really overdosed. This indicated that soda-AQ pulping with lower AA could produce higher or comparable quality of pulp properties in comparison to the kraft pulps.

Although the soda-AQ pulp gave slightly lower screened yield, its pulp offered much higher viscosity than kraft pulps. Besides, the resultant handsheets from soda-AQ also imparted higher brightness, tensile, and tear indices, as well as similar burst index in comparison to kraft pulps, as presented in Table 5. Only the kraft-AQ (BK2) pulp showed higher values in folding endurance. With regards to its relatively high pulp viscosity and pulp brightness, it was confirmed that the sulfur free soda-AQ pulping was suitable to be employed for kenaf bast fibers to produce pulp with better bleachability and environmental compatibility.

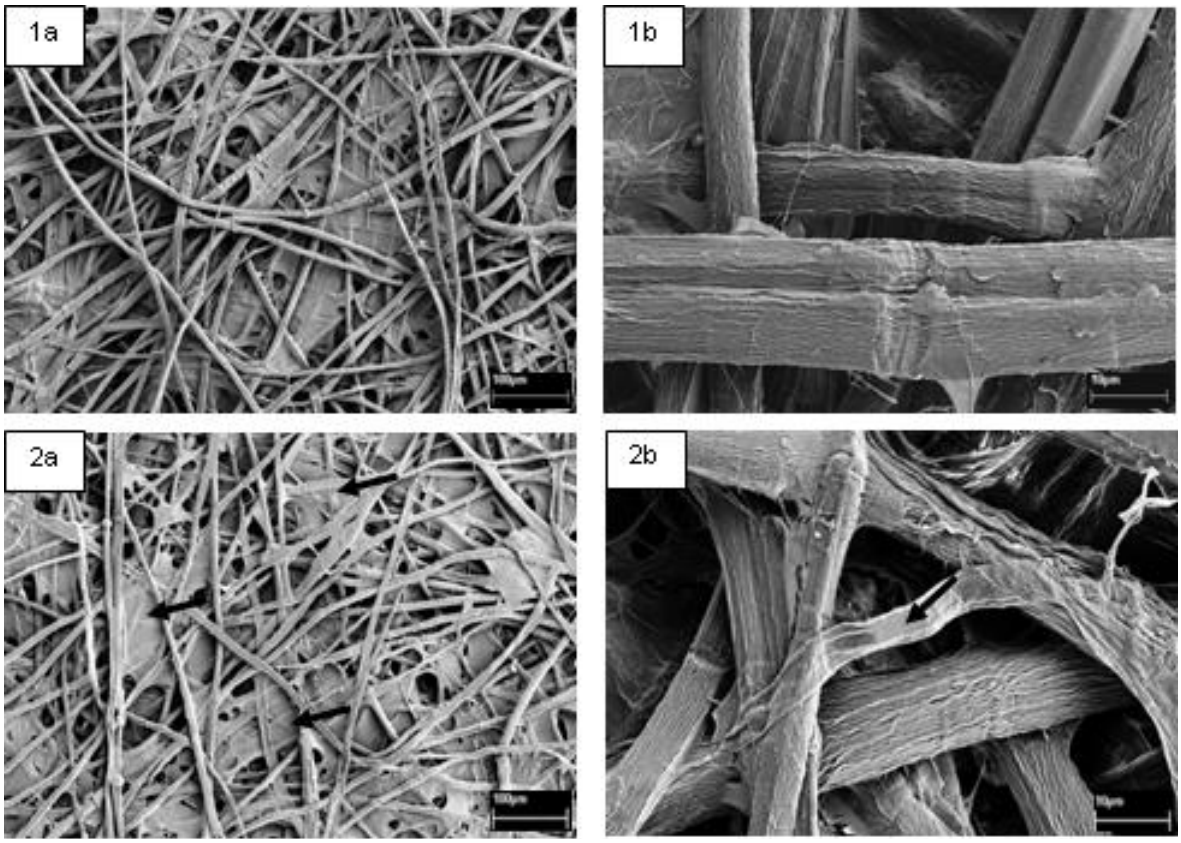

Fig. 1. SEM micrographs of the kenaf bast's handsheet: (1a) and (1b) without pre-impregnation; (2a) and (2b) with 0.25M NaOH pre-impregnation. Magnification = 100x for (1a) and (2a); 1.0k for (1b) and (2b)

Table 7. Results of Cellulose Contents of Kenaf Bast Pulps With and Without Pre-impregnation

Pulping condition	Without pre-impregnation		With pre-impregnation		
	BS1	BS2	BS8	BS9	BS10
Impregnation concentration, M, mol/L	-	-	0.10	0.25	0.50
Active alkali as Na_2O, %	17.8	19.4	19.4	19.4	19.4
α-cellulose, %	94.46	93.38	94.03	94.35	94.58
β-cellulose, %	3.93	6.15	5.37	4.05	4.77
γ-cellulose, %	1.61	0.47	0.60	1.60	0.65

Between the two kraft pulps, it was noticed that the kraft-AQ (BK2) pulp with the addition of 0.10% AQ during pulping resulted in an increase in both the screened yield and pulp viscosity. Besides, it also decreased both the reject yield and kappa number as compared to the kraft pulp without the addition of AQ (BK1). Furthermore, the kraft-AQ (BK2) pulp produced a much stronger handsheet with markedly favorable strength properties as compared to ordinary kraft pulp. The brightness of the pulp was also improved through the increase of the delignification rate.

Effects of soda-AQ pulping on kenaf core fiber

As is noticeable in Table 4, the kenaf core was partially uncooked, with conspicuously high reject yield (5%) and relatively low screened yield at 19.4% AA (CS1). Since the L:M ratio for kenaf core was 8:1, the increase in the volume of white liquor tends to lower the concentration of OH^-, which may decrease the pulping efficiency. By increasing the AA to 21.7% for CS2, lignin dissolution and fiber liberation were improved. Thus the reject rate dropped to 0.3% and the screened yield increased to 39.6%. The increase of AA decreased the kappa number from 24.0 to 15.6, but at the same time the pulp viscosity dropped from 37.1cP to 28.8cP.

CS3 had the most severe conditions, with a cooking temperature of 170^{o}C and an AA of 21.7%. Even though the screened yield dropped imperceptibly, in comparison to CS2, the kappa number decreased 4.6 points and the pulp viscosity remarkably dropped 12.8 points. Although the pulp of CS3 can be considered as overcooked, its impact on handsheet strength properties was also yet to be noticeable (Table 5). The highest tensile index of CS3 also indicated that the effect of better delignification on enhancing the interfiber bonding strength was more predominant than the deleterious effect of cellulose degradation on fiber strength.

Comparison between kenaf bast and core fibers on soda-AQ pulping

Regardless of the pulping conditions employed (BS5 vs CS2 and BS3 vs CS1), it was noticeable that for pulps with similar viscosity, the bast pulp showed lower kappa numbers than the core pulp, as presented in Table 4. The main factor was most probably attributable to the intrinsic quality of the bast, which originally has lower lignin content in comparison to the core. Besides that, a great difference of screened yield could also be observed between the bast and core pulps. This is in agreement with the result of 1%

NaOH solubility stated earlier, where the core (together with the soft tissues of the pith) basically contains more alkaline soluble material than the bast.

Apart from pulp properties, a remarkable difference in unbeaten pulps handsheet properties was also noticeable, as shown in Table 5. Surprisingly, the handsheet density of the core pulp was almost double the density of the bast pulp. Core pulp handsheets also exhibited excellent strength properties, although they were slightly lower in brightness. The distinct strength properties between the two pulps can be understood by referring Fig. 2, the SEM of the handsheets at different magnifications.

Obviously, the bast pulp has long and slender thread-like fibers. However, they are relatively thick-walled and less flexible (Villar et al., 2009); hence the fiber-to-fiber contact within the handsheets was considerably poorer (Fig. 2a and 2b). In contrast to the bast, the core fibers were relatively short, but due to their thin cell wall, the core fibers were easily to collapse to form broad ribbon-like fibers (Fig. 2c and 2d) even though there was no additional beating taken place, and thus displayed great conformability and gave higher tensile and burst indices, in addition to extremely high folding endurance. Nevertheless, these factors also adversely caused a decrease of the tear index. Similar results have been reported by Touzinsky et al. (1977).

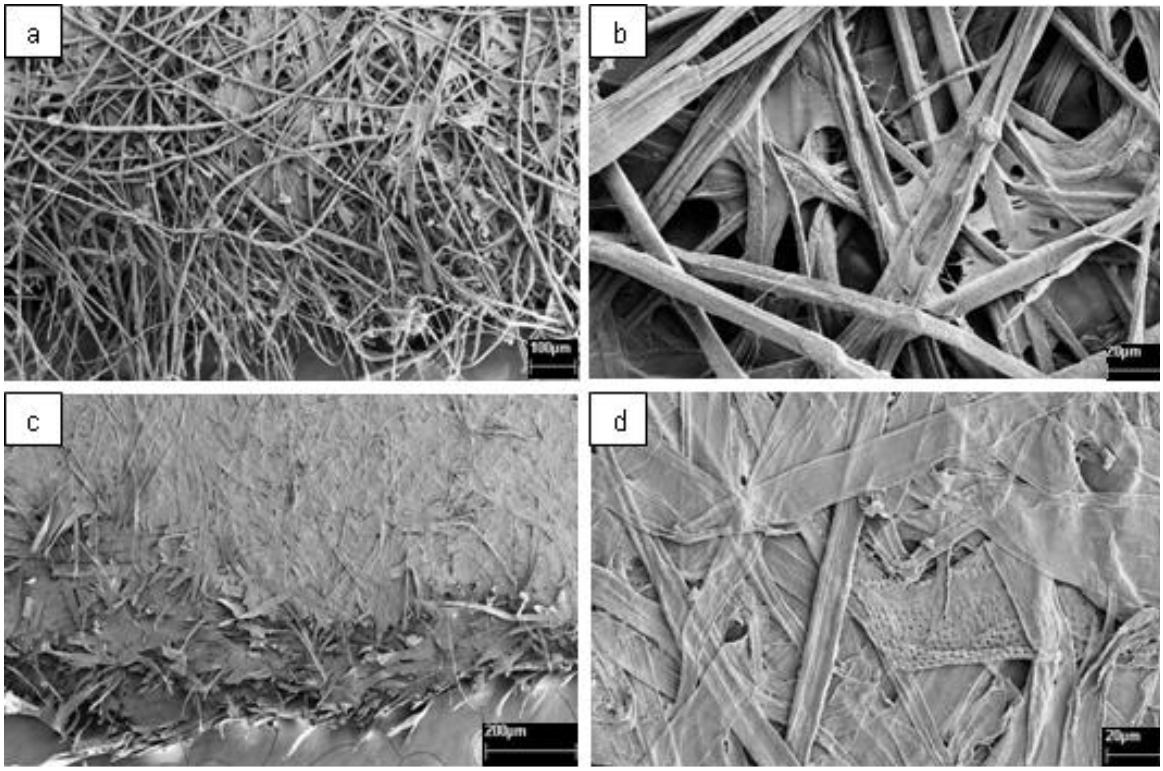

Fig. 2. SEM micrographs of handsheets made from soda-AQ pulps for kenaf bast (a, 50x and b, 300x) and kenaf core (c, 50x and d, 300x)

CONCLUSIONS

Kenaf bast has a relatively lower extractive content, lower 1% NaOH solubility, lower lignin content, and higher α-cellulose content in comparison to kenaf core. For whole stalk kenaf intermediate results are obtained. At the same time, the increase of plant age from 3.5 to 4.5 months has a positive effect on decreasing the extractive contents, but it also increases the lignin content and slightly decreases the holocellulose content. Thus it is recommended that kenaf be harvested at 4 months of age for utilization in papermaking.

AA higher than 19.4% not only accelerates the degree of delignification, but it was also accompanied by a reduction in pulp viscosity. The cooking temperature for kenaf bast soda AQ pulping should be not above 160°C in order to avoid serious carbohydrate degradation. The decrease of the L:M ratio from 7 to 6 led to a substantial reduction in pulp viscosity, while only a very small reduction of kappa number was observed with the increase of AA from 19.4% to 21.7%. The optimum condition for kenaf bast soda-AQ pulping was 19.4% AA with 0.10% AQ and an L:M ratio of 7:1 cooked for 2 hours at 160˚C.

The quality of soda-AQ pulp and handsheets, especially relative to tensile index, could be effectively improved by applying alkaline pre-impregnation prior to the pulping process, where 0.25M NaOH was the optimum concentration.

Kraft and kraft-AQ pulping produced slightly lower or comparable quality pulp than soda-AQ pulping. However, when taking account of the environmental impacts of the pulping process, soda-AQ pulping was a better choice to be employed for the kenaf bast.

Regardless of the pulping conditions employed, for the unbeaten pulps with similar viscosity, the bast pulps showed lower kappa numbers than the core pulps. In spite of lower tear strength, other strength properties from core pulps were higher than those from bast pulps due to better fiber collapsibility and conformability. However, the pulp yield of kenaf core was substantially lower than that of kenaf bast.

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