TCF BLEACHING OF KENAF (*HIBISCUS CANNABINUS*) PULP FOR PAPERMAKING APPLICATIONS

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ASHORI, A., JALALUDDIN, H., MOHD. NOR, M. Y., WAN ROSLI, W. D., WAN MD. ZIN, W. Y. & KHAIRUL ZAMAN, M. D. 2004. TCF bleaching of kenaf (*Hibiscus cannabinus*) pulp for papermaking applications. Non-wood fibres are increasingly being used in the pulp and paper industry to help meet the increasing world demand for pulp and paper. Due to its short growth period, high yield and comparable physical and optical properties, kenaf is a viable and attractive non-wood fibre source alternative for soft- and hardwood fibres. Currently very little information is available on totally chlorine free (TCF) bleaching. The aim of this study was to bleach pulps to high brightness, while retaining sufficient strength properties. Peroxide reinforced oxygen (PO) and hydrogen peroxide (P) were used in the TCF bleaching of different fractions and blends of kenaf kraft pulps. A brightness of 82.4–90.4% ISO was achieved with moderate charge of peroxide. Final brightness and viscosity values showed that by using a Q_1(PO)Q_2P sequence, bast, core and all blend fibres can be bleached to high

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brightness while retaining sufficient viscosity. It was seen that bast, core and all blend fibres exhibited great strength characteristics that were suitable for papermaking.

Key words: Kraft pulp – strength properties – selectivity – pulp viscosity – fibre morphology – non-wood – bast fibre

ASHORI, A., JALALUDDIN, H., MOHD. NOR, M. Y., WAN ROSLI, W. D., WAN MD. ZIN, W. Y. & KHAIRUL ZAMAN, M. D. 2004. Pelunturan TCF pulpa kenaf (*Hibiscus cannabinus*) untuk aplikasi membuat kertas. Gentian bukan kayu semakin banyak diguna dalam industri pulpa dan kertas untuk memenuhi permintaan pulpa dan kertas sedunia. Oleh sebab tempoh pertumbuhannya yang singkat, hasil yang tinggi serta ciri fizikal dan optik yang memuaskan, kenaf dianggap sumber bukan kayu alternatif yang berdaya maju dan menarik untuk gentian kayu konifer dan kayu keras. Pada masa ini, maklumat tentang pelunturan yang bebas klorin (TCF) tidak banyak didapati. Tujuan kajian ini adalah untuk meluntur pulpa sehingga mencapai kecerahan tinggi, sambil mengekalkan ciri kekuatan yang mencukupi. Peroksida diperkuat oksigen (PO) serta hidrogen peroksida (P) diguna dalam pelunturan pecahan serta adunan pulpa kraft kenaf yang berbeza. Kecerahan sebanyak 82.4–90.4% ISO dicapai apabila menggunakan jumlah peroksida yang sederhana. Nilai kecerahan akhir serta kelikatan menunjukkan bahawa jika menggunakan langkah $Q_1(PO)Q_2P$, gentian basta, gentian teras dan semua gentian adunan dapat diluntur sehingga kecerahan tinggi sambil mengekalkan kelikatan yang mencukupi. Gentian daripada basta, teras dan semua adunan menunjukkan ciri kekuatan yang tinggi dan sesuai untuk pembuatan kertas.

Introduction

Paper consumption has increased by 50% worldwide during the last decade. This has happened in spite of the generation of computer and audio-visual technologies. The demand for raw materials for papermaking is continuously increasing as a result of the increase in paper consumption. Non-wood plants could alleviate the shortage of fibrous raw materials for pulping since it is possible to produce any paper by properly selecting the plant and pulping conditions (Atchison 1996). Kenaf is considered one of the most promising alternatives to virgin soft- and hardwoods for paper production in countries experiencing shortages of wood raw material. It is a dicotyledon, which means its stalk has an outer bast fibre and an inner core fibre (Figure 1).

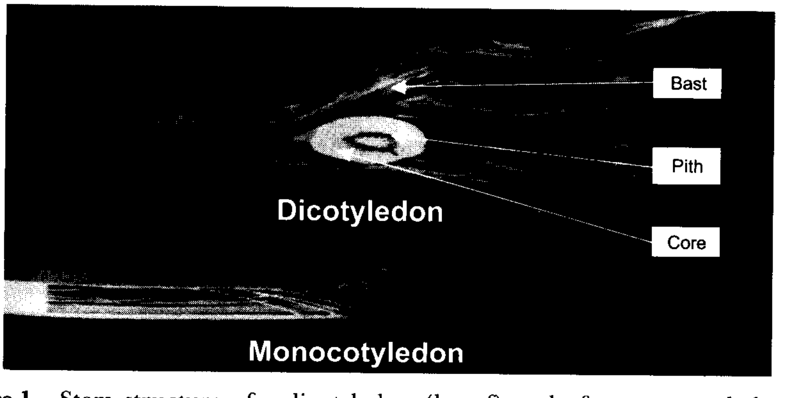


Figure 1 Stem structure of a dicotyledon (kenaf) and of a monocotyledon for comparison (Touzinsky 1993)

A kenaf stalk consists of approximately 35% bast fibre and 65% core fibre (Mohta *et al.* 2004). The two fractions in kenaf are very different chemically (Table 1) and morphologically. Bast fibres are long, slender and thick-walled, while core fibres are much shorter, wider, thin-walled and with large lumen; they are comparable with soft- and hardwoods respectively. Therefore, different fractions of kenaf produce pulps with completely different properties (Karakus & Roy 1998). Kenaf grows quickly, rising to a height of 3.7–5.5 m with a diameter of 25–51 mm in as little as four to five months under suitable temperature and tropical climate conditions (Kaldor *et al.* 1990). The yield per acre is notably different. It has been commonly reported that kenaf yield ranged from 14–22 tonne ha^{-1} or more (Touzinsky 1993), depending on location, growing conditions and kenaf variety.

Conventional pulp bleaching processes involve the use of many chlorine-containing compounds, which can react with lignin by electrophilic aromatic substitution, producing chlorinated structures. The organochlorine compounds generated in the bleaching stages may be harmful to the environment and may cause a problem for the pulp and paper industry (Bright *et al.* 1998). The increasing demand for pulps bleached without chlorine compounds contributes to the development of alternative pulping and bleaching processes. Chlorine use has been drastically reduced and elemental chlorine free (ECF) and totally chlorine free (TCF) bleaching processes are being developed.

In TCF bleaching the compounds of choice are oxygen, hydrogen peroxide, ozone and peracids (Taylor *et al.* 1998). Hydrogen peroxide is a versatile bleaching agent that can be used in a variety of roles. Traditionally, hydrogen peroxide was used as a brightening agent in mechanical pulp bleaching. Depending on its position in a bleaching sequence, peroxide can either delignify or brighten the pulp. For delignification of kraft pulps, the conditions (temperature, concentration and pH) are usually much harsher than in peroxide brightening of mechanical pulps, so that lignin removal becomes possible. In recent years, several developments have been made to increase the effectiveness of hydrogen peroxide bleaching. One of the most significant process developments in peroxide bleaching is the advent of the pressurised peroxide (PO) stage. In pressurised peroxide bleaching,

Table 1 Chemical composition of kenaf fractions from various sources in the literature

Chemical components (%)	Bast[1]	Bast[2]	Whole[2]	Whole[3]	Core[1]	Core[2]
Holocellulose	79.5	57	80.5	76.5	77.2	51
Alpha-cellulose	-	42	50.6	44.1	-	34
Hemicellulose	14.3	-	29.9	32.4	16.5	-
Lignin	13.8	8	19.5	16.2	22.4	17
A-B extractive	1.4	4	14.2	3.2	2.0	3
Hot water extract	8.6	14	-	-	8.2	8
Ash	3.5	6	2.1	2.1	2.2	3

[1] Shi *et al.* (1988)
[2] Karakus and Roy (1998)
[3] Touzinsky *et al.* (1972)

the temperature of the process is raised from 80 or 90 °C to 105 °C and higher, and oxygen pressure is applied in the mixer to allow the bleach liquor to remain in the liquid phase (Anderson & Amini 1996).

Due to the awareness of the dangers associated with the utilisation of chlorine and chlorine derived bleaching chemicals, it is necessary to use ECF and TCF bleaching sequences. In this paper, a Q_1(PO)Q_2P bleaching sequence was utilised to bleach core and bast fibres to high brightness, while retaining sufficient strength properties for subsequent papermaking applications. Historically, soft- and hardwood pulps are mixed together to get suitable properties. As mentioned earlier, bast and core fibres are similar to soft- and hardwood morphologically and chemically respectively. Various blends of bast and core (70:30, 50:50, 30:70) pulps were used in this study. The resulting bleached fibres were subjected to burst, tensile and tear index strength tests to determine the papermaking properties.

Materials and methods

Raw materials

The unbleached pulps used in this study were produced in the laboratory by kraft cooking using the following operating conditions: effective alkali = 17% based on Na_2O on oven dry (o.d.) fibre, sulphidity = 25%, liquor-to-wood ratio = 7:1, and maximum temperature = 170 °C. Due to the different activation energy of bast and core fibres, they were pulped separately. Prior to bleaching, the bast and core fibres were evenly blended in 70:30, 50:50 and 30:70 ratios. The blend of 30:70 was the ratio of bast and core fibres in the whole stem. Initial viscosities and Kappa numbers of samples were determined on the well-washed unbleached pulps, and the values are as in Table 2. Different fractions (pure bast and core) and homogenised blends of kenaf fibres were used to study the bleachability and papermaking properties.

Pulp bleaching procedures

A four-stage bleaching sequence, Q_1(PO)Q_2P, was applied as TCF bleaching for all samples. An amount of 15 g (oven dry) of pulp was used for bleaching. In each stage, after addition of the specified chemical, the pulp was stirred with a

Table 2 Properties of unbleached and bleached pulp

Fibre	Kappa No.			Viscosity			Selectivity	Yield %
	Before bleaching	After bleaching	Drop (%)	Before bleaching (cP)	After bleaching (cP)	Drop (%)		
Bast	13.48	1.7	87.39	26.72	12.85	51.91	1.68	96.7
70:30	14.38	1.4	90.26	24.83	13.18	46.92	1.92	94.6
50:50	16.73	1.4	91.63	21.64	10.48	51.57	1.78	93.8
30:70	15.52	1.1	92.91	22.17	11.65	47.45	1.96	93.9
Core	17.81	0.9	94.95	20.39	11.54	43.40	2.19	95.5

glass rod to ensure even mixing. The pulp mass was periodically mixed during the entire treatment. At the end of each stage, the pulp was collected on a filter mesh and thoroughly washed with deionised water. Finally, the bleached pulp was placed in a muslin cloth and spin-dried and homogenised for 10 minutes.

Chelation (Q)

Chelation was done in two types, Q_1 and Q_2. Chelation Q_1 consisted of two parts. In the first part, the pH was adjusted to 3 using sulfuric acid. The pulp was sealed in a plastic bag and immersed in a water bath at 50 °C for 30 min. In the second part, the pH was raised to 5 using sodium hydroxide after which diethylene triamin penta acetic acid, DTPA (1% o.d. pulp basis), was added. The mixed slurry was placed in a sealable plastic bag and heated in a water bath at 50 °C for 30 min. The pulp consistency was 3% during the entire treatment.

For the Q_2 method, pulp was treated with ethylene diamine tetra acetic acid, EDTA (0.5% o.d. pulp basis) at 3% pulp concentration in heat-proof polyethylene bags maintained in a water bath at 70 °C for 90 min. The pH of pulp was adjusted to 4.5–5 during the chelation stage using sulfuric acid or sodium hydroxide.

Peroxide reinforced oxygen (PO)

Pressurised peroxide bleaching was done in a 650 ml stainless steel vessel, which was equipped with a gas inlet and a stirrer. The pulps were mixed with magnesium sulphate (0.5% o.d. pulp basis), sodium hydroxide (2% o.d. pulp basis), hydrogen peroxide (0.2% o.d. pulp basis) and distilled water to give a pulp concentration of 10%. The mixtures were placed in the vessels, which were pressurised with oxygen (100 Psi) and heated at 100 °C for 1 hour (time to temperature: 30–35 min).

Hydrogen peroxide (P)

The last stage in the bleaching sequences was atmospheric hydrogen peroxide, which was carried out in sealable polyethylene bags, where the pulp slurry and reagent mixtures were hand kneaded. The pulps were treated with DTPA (0.2% o.d. pulp basis), sodium silicate (3% o.d. pulp basis), magnesium sulphate (0.5% o.d. pulp basis), sodium hydroxide (3% o.d. pulp basis) and hydrogen peroxide (3% o.d. pulp basis) at pulp concentration of 10% for 2 hours at 80 °C (in water bath).

Pulp and paper properties

The Kappa numbers of the pulps were determined according to TAPPI Useful Method 246 – Micro Kappa Number, which was modified from the standard Kappa number method (T236) in order to make it applicable to very small samples. The determination of viscosity was carried out according to TAPPI Standard Method T 230 om-89. This method determines the viscosity of 0.5% cellulose solution, using 0.5 M cupriethylenediamine (CED) as solvent and a capillary-type viscometer. Handsheets of 80 g m^{-2} were made according to TAPPI Standard Procedure T 205 sp-02 using British handsheet machine. Ten handsheets were chosen and tested for physical properties in terms of burst, tensile and tearing indices as per TAPPI Procedure T 220 sp-01. Handsheets were conditioned at 23 °C and 50% RH for at least four hours and conditioned grammage was used for calculation of strength indices. The brightness (% ISO) of handsheets was measured with a Technibrite (model TB-1) instrument. Yield was calculated based on the difference of the unbleached and fully bleached pulp weight. Selectivity was expressed as a function of both the Kappa number drop and the loss of viscosity:

$$\text{Selectivity} = \frac{1 - K_f / K_i}{1 - \eta_f / \eta_i}$$

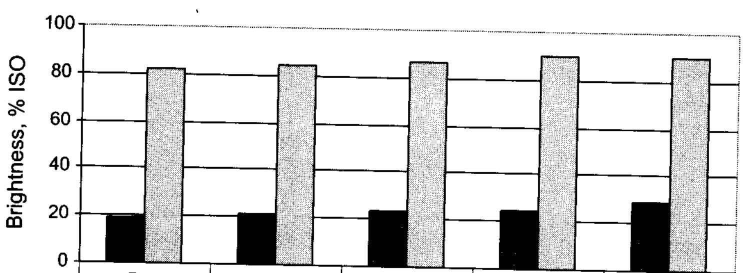
where

K_f = Kappa number after bleaching
K_i = initial Kappa number
η_f = intrinsic viscosity after bleaching
η_i = initial intrinsic viscosity

Results and discussion

Bleaching evaluation

Prior to bleaching, the bast fibres exhibited a brightness of 19.6% ISO, which is 9.2 units lower than that of the core fibres (Figure 2). Although core fibres contain a higher fraction of lignin than bast fibres, the brightness difference is most likely due to the higher amount of extractives and response of bast fibres to kraft pulping. The viscosities of bast and core at 26.72 and 20.39 cP were comparable with the viscosities of softwood and hardwood respectively. Bast fibres consistently demonstrate physical and optical properties that compare with those of softwood fibres, while core fibre properties compare with those of hardwood fibres (Kulger 1988).



	Bast	70:30	50:50	30:70	Core
■ Unbleached	19.6	21.4	23.4	24.2	28.8
▨ Bleached	82.4	84.5	86.1	89.8	90.4

Figure 2 Brightness of unbleached and bleached kenaf pulps

In the bleaching process, one of the most important objectives was to produce pulps with high strength properties along with the required brightness. To achieve this, it is critical to ensure a high selectivity of the process, i.e. to minimise the relative rate of polysaccharide degradation with respect to the rate of delignification or brightening. Table 2 shows that core fibre had the highest selectivity followed by the ratio of 30:70. The least carbohydrate degradation and the most lignin removal occurred in pure core pulp.

Viscosity is a measure of the average polymerisation degree of pulp and indicates the degree of carbohydrate degradation during pulping and bleaching (MacLeod *et al.* 1994). As can been seen from Table 2, after bleaching, there was a considerable drop in viscosity for all five pulp samples that coincided with a considerable increase in brightness. Bast viscosity decreased 51.91% down from 26.72 cP to 12.85 cP, while core viscosity decreased 43.40% down to 11.54 cP from a previous 20.39 cP. This most likely is the result of a greater extent of carbohydrate degradation in the bast than in the core. Also, all three blends (in 70:30, 50:50 and 30:70 ratios) have roughly the same condition as bast and core fibres. This reduction in viscosity can cause a decrease in the physical-mechanical paper properties (Roncero *et al.* 2002). Ryynanen *et al.* (1995) demonstrated that with chemical pulps, there was no absolute relationship between viscosity and handsheet strength properties. Although the viscosity results were apparently good for papermaking, there was no guarantee that the mechanical strength of the paper produced from those pulps would be acceptable. Viscosity alone gives no secure information about resultant sheet strength properties. In order to study such paper properties, the handsheet physical-mechanical properties of the bleached pulps were investigated.

The highest and lowest yields were observed in bast and blend of 50:50 respectively (Table 2). The main cause for bleaching yield may be due to the lignin and carbohydrate removal. The yield results were not significantly different.

Determination of paper strength

Pure core fibres had superior tensile (85.06 N m g^{-1}) and burst indices (5.33 kPam^2 g^{-1}) compared with the rest of the samples (Table 3). Furthermore, the blend pulps exhibited strength properties greater than bast along. Paper made from pulps with short fibres is generally stiffer than those made from long fibres. Fibre strength, bonding degree (bonding strength and bonded

Table 3 Strength properties of different fractions and blends of bleached kenaf

Fibre	Tensile index (N m g^{-1})	Burst index (kPam^2 g^{-1})	Tear index (mN m^2 g^{-1})	Bulk (cm^3 g^{-1})
Bast	42.52	3.27	24.27	2.47
70:30	48.51	3.50	21.32	2.09
50:50	57.41	3.69	17.81	1.82
30:70	67.74	4.32	13.09	1.67
Core	85.06	5.33	6.63	1.25

area), fibre curliness and 'weak point' determine the tensile strength of paper sheet. Therefore, tensile strength differences between pulps must arise from fibre strength and/or bonding. When paper is subjected to tensile forces, strong fibres tend to pull out from the network intact, while weak fibres break (Paavilainen 1989).

The principal factor determining the burst strength is fibre density, as measured by either wall thickness or Runkel ratio. The density of the fibre determines its flexibility, which in turn influences the extent of bonding within a sheet (Paavilainen 1989).

Tear index depends on individual fibre strength and on interfibre bonding. Hence, it was expected that pure bast fibre sheets yielded higher tear index (24.27 mN m^2 g^{-1}) than core fibre sheets. Also with increasing bast fibres in mixed pulps, the tensile and burst indices decreased while tear index increased. The tear strength of bast fibres was about four times that of core fibres. This higher tear value is most likely due to the morphological differences in the two fractions.

Conclusions

The following conclusions can be drawn:

(1) As shown in this investigation, in contrast to unbleached kraft wood pulps, different fractions of kraft kenaf pulps can be easily bleached to a high brightness using a four-stage TCF bleaching sequence. This will be a significant advantage for kenaf over wood in many areas.

(2) The TCF $Q_1(PO)Q_2P$ sequence is simple, and only two main stages of bleaching are involved using only one major bleaching chemical, together with two chelation stages.

(3) Final viscosity and brightness values showed that bast, core and blend pulps can be used as substitute for hardwood and softwood fibres.

(4) In general, pure core fibres had the highest burst and tensile indices. It was expected that bast fibres have the strongest tear index compared with the rest of the pulps of kenaf studied.

(5) Bast, core and all blend fibres exhibited great strength characteristics and are viable raw materials for producing quality and inexpensive products.

(6) Fibre strengths of the TCF pulps were suitable for papermaking, although the best mixture of pulps can be chosen to optimise end product requirements.

(7) Different fractions of kenaf pulps and their mixtures could be suitable for a wide range of paper such as printing and packing papers.

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