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Chlorine-Free Bleaching of Kraft Pulp from Oil Palm Empty Fruit Bunches

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Abstract

Chlorine-free bleaching was carried out on kraft pulp from oil palm empty fruit bunches (EFB) with an oxygen (O_2) - acid (H_2SO_4) - ozone (O_3) - hydrogen peroxide (H_2O_2) bleaching sequence. The κ-number (= an indicator of lignin content) of the pulp was reduced considerably after these processes indicating that most of the lignin present in the pulp can be removed using this chlorine-free sequence. Handsheets of both bleached and unbleached EFB pulp were prepared and their paper properties were determined. Brightness, a measure of the whiteness of paper, was achieved to *ca.* 75% for the bleached EFB pulp, showing a possibility of achieving 80% of brightness by chlorine-free bleaching. Paper strengths as indicated by tensile, tear and burst indices as well as stretch did not show significant differences between before and after bleaching. It is notable that these results were obtained despite a large decrease in viscosity by the bleaching process. Moreover, the EFB bleached pulp showed comparable strengths to hardwood pulps, indicating that EFB has the potential as a raw material for chemical pulp production using chlorine-free bleaching sequences.

Discipline: Forestry and forest products
Additional key words: EFB, oxygen, ozone, brightness, paper strengths

Introduction

Oil palm, *Elaeis guineensis*, produces palm oil (PO) and palm kernel oil (PKO), which are widely used in food and other industries such as detergents and cosmetics. Total production of the palm oils is 24.5 million t/y in the world, which accounted for more than 20% of total oil and fats production in 2000[9]. Large producers are Malaysia, Indonesia and Nigeria, which share 47%, 34% and 4.2% of the world production of PO + PKO, respectively.

In Malaysia, the largest producer in the world, total area of oil palm plantation is close to 3.2 million ha, which accounts for almost 50% of the land under cultivation[6]. Although oil from the palm tree is an excellent product for the country, its lignocellulosic residues have not been effectively used. One of the most abundant residues is empty fruit bunches (EFB), which are left behind after removal of oil palm fruits for the oil refining process. Tons of EFB are regularly discharged from palm oil refineries, amounting to 12.4 million t/y (fresh

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weight)[3], some of which are used as fuel, however, most of them are left unused.

To increase the added value of these residues, several investigations have been carried out to produce papermaking pulp from EFB by chemical and mechanical pulping processes[1,2,4,7,12]. It is quite reasonable to produce pulp from the lignocellulosic residues for papermaking. Consumption of paper is increasing dramatically in South East Asian countries including Malaysia, nevertheless a huge amount of EFB are left unused in those palm oil-producing countries.

Although several studies have been carried out on EFB pulping, investigation on pulp bleachability is limited. Due to increased awareness of the danger associated with the usage of chlorine and its derivatives, it is now necessary to utilize elemental chlorine-free (ECF) or totally chlorine-free (TCF) bleaching sequences for pulp. Once this oil palm by-product becomes a raw material for pulp production, it will be essential to have chlorine-free bleaching processes in the future. In this study, kraft pulping was carried out for an EFB sample under several different pulping conditions and chlorine-free bleaching was applied to the EFB kraft pulp.

Materials and Methods

1. Material

The EFB sample used in this study was in the form of fibrous strands. It was supplied by SABUTEK (M) SDN BHD, Malaysia. It had already been manufactured by the company, including the processes of defibrization, washing, cleaning, sorting and drying. The sample strands were used as received. Moisture content of the fibrous strands was determined to be 9.5%.

2. Kraft pulping (KP)

Kraft pulping was carried out using 4-L or 2-L autoclaves manufactured by NAC Autoclave Co., Ltd., Japan. Four pulping conditions were selected as shown in Table 1. After each cooking, the pulp was washed and screened through a 0.2 mm slit (8-cut). Kappa (κ) number and pulp viscosity were determined according to TAPPI Standard T236m-60 and JPRI Standard 3015 (a modified method of TAPPI Standard T230 su-66), respectively.

3. Bleaching

The chlorine-free bleaching process studied here includes four sequential steps of oxygen, acid, ozone and hydrogen peroxide bleaching at a pulp consistency of 10% (medium consistency).

Oxygen (O_2) bleaching was carried out using a Mark V High-Intensity Mixer (Quantum Technologies, Inc., U.S.A.) under alkaline conditions by addition of 1% NaOH (w/w) aqueous solution. Magnesium sulfate (0.1%) was also added as a protection reagent for cellulose. Reaction temperature and O_2 pressure were maintained at 95ºC and 5 kg/cm^2, respectively. The total reaction time was 40 min with occasional mixing.

The acid bleaching process was performed in a water bath at 100ºC for 60 min. A heat-resistant plastic bag was used for the reaction. The pulp was treated in a buffer solution of pH 2, adjusted by addition of 4N H_2SO_4. Effluent of the acid bleaching was analyzed by HPLC as described in a previous paper[5].

For ozone (O_3) bleaching, the same mixer for the O_2 bleaching was used, together with an ozone cart. Total amount of O_3 added was 0.5% on pulp. Reaction temperature was maintained at 20ºC for a total reaction time of 2.5 min with occasional mixing.

For hydrogen peroxide (H_2O_2) bleaching, pulp slurry of 10% consistency (adjusted using 0.05N NaOH aqueous solution) was placed in a plastic bag and a corresponding amount of 1% or 2% H_2O_2 was added. Then the reaction was carried out at 80ºC for 120 min in a water bath. A small amount (*ca.* 0.6% on pulp) of a stabilizing agent Dequest 2066 (sodium salt of diethylenetriamine-penta (methylene phosphonic) acid, Monsanto Japan Ltd.) was also added to the pulp.

4. Determination of handsheet properties

From the bleached and unbleached KP, handsheets were prepared and conditioned at 20ºC and 65% relative humidity (RH) according to JIS P8111. Physical and mechanical properties of the handsheets were evaluated according to appropriate JIS standards.

Table 1. Pulping conditions of EFB

Condition	Active alkali (%)	Sulphidity (%)	Liquor to EFB ratio	Cooking temp. (T, ºC)	Time to T (min)	Time at T (min)
I	16	25	10	170	90	90
II	14	25	10	170	90	90
III	16	25	10	160	90	120
IV	16	25	8	170	90	90

Results and Discussion

Yields and properties of EFB kraft pulp prepared in this study are given in Table 2. Referring to Table 1, it is evident that the active alkali concentration is the most effective factor on the yield and properties, compared to liquor/EFB ratio, cooking temperature and cooking time. A reduction of 2% in active alkali substantially increased the κ-number and amount of screenings when the conditions I and II were compared. Liquor to EFB ratio and cooking temperatures did not show any crucial changes except pulp viscosity. When considering κ-number in relation to viscosity, the condition III may be the most desirable one. Overall, the pulps prepared under the given conditions had relatively low κ-numbers with high viscosity values, which indicates that lignin content of each pulp was relatively low and the degree of polymerization (DP) of cellulose remained at an acceptable level. Due to the limited availability of pulps prepared, all pulps prepared under the conditions I, III and IV were mixed together for being used in the bleaching process; the pulp prepared under the condition II was not considered because of its high κ-number. The κ-number and viscosity of the mixed pulp were determined to be 14.9 and 23.9, respectively.

Results for the bleaching process are shown in Table 3. There is a small but gradual decrease in κ-number until the end of the second bleaching stage, i.e. acid bleaching, after which the decrease became more significant by applying the ozone sequence. Pulp viscosity was also reduced in each subsequent sequence with the biggest reduction after O_3 and H_2O_2 bleaching. It is also obvious that the decrease in κ-number after O_2 bleaching is rather small in comparison with O_3 bleaching suggesting the powerful oxidant nature of the latter. This is further confirmed by the viscosity data, which showed a relatively small decrease when using O_2 but a significant reduction with O_3. During ozone bleaching, there is not only a substantial removal of lignin but also an occurrence of attack on cellulose, which is reflected in the viscosity values.

By HPLC analysis of the effluent after the acid bleaching, the presence of 2-furancarboxylic acid and 5-formyl-2-furancarboxylic acid was indicated. These two compounds are acid-degraded products of hexeneuronic acid which can be formed from 4-*O*-methylglucuronic acid groups in xylan of softwood and hardwood KPs[5]. The result obtained here may indicate the presence of 4-*O*-methylglucuronic acid groups in xylan of EFB KP. Moreover, the presence of hexeneuronic acid contributes to an increase in κ-number of the pulp. Total amount of the acid-degraded products was calculated to be 0.68 mmol/100 g pulp, which corresponds to 0.58 in κ-number[5]. This is in good agreement with the reduction of κ-number from 11.0 to 10.3 after the acid bleaching as shown in Table 3. It means that the acid bleaching process had only degraded hexeneuronic acid in the EFB KP without the removal of lignin. The degradation does only occur under acidic condition and hexeneuronic acid is assumed to be mostly removed during this process. The above result indicates that the contribution of hexeneuronic acid to κ-number is almost negligible for this EFB

Table 2. Yields and pulp properties of EFB kraft pulps

Condition	Yield (%)	Screened yield (%)	Screenings (%)	κ-number	Viscosity (cp)
I	44.4	43.7	0.65	14.2	19.7
II	45.4	42.0	3.42	25.8	23.2
III	44.6	43.1	1.50	15.8	27.5
IV	44.4	42.6	1.78	18.7	30.2
I,III,IV mix	–	–	–	14.9	23.9

Table 3. Bleaching of EFB kraft pulp

Sequence	κ-number	Viscosity (cp)
unbleached	14.9	23.9
O_2	11.0	22.0
O_2 / acid	10.3	21.2
O_2 / acid / O_3	3.33	16.6
O_2 / acid / O_3 / H_2O_2 1%	–*	11.6
O_2 / acid / O_3 / H_2O_2 2%	–*	11.2

*Not determined.

Table 4. Handsheet properties of EFB kraft pulp

Bleaching sequence	Unbleached	O_2 / Acid / O_3	O_2 / Acid / O_3 / H_2O_2 1%	O_2 / Acid / O_3 / H_2O_2 2%
κ-number	14.9	3.33	–*	–*
Viscosity (cp)	23.9	16.6	11.6	11.2
Freeness (mL)	240	240	230	238
Basis weight (g/m^2)	63.5	59.4	59.6	58.0
Density (g/cm^3)	0.77	0.78	0.82	0.81
Tensile index (N m/g)	67.3	67.5	67.7	63.9
Stretch (%)	4.87	5.88	5.81	4.98
Tear index (mN m^2/g)	12.5	13.0	12.5	11.7
Burst index (kPa m^2/g)	5.33	5.60	5.39	5.05
Folding (MIT, 1 kg)	1,272	1,518	1,160	1,115
Brightness (%)	27.6	55.3	73.2	73.9
Opacity (%)	98.4	85.6	74.4	72.4

*Not determined.

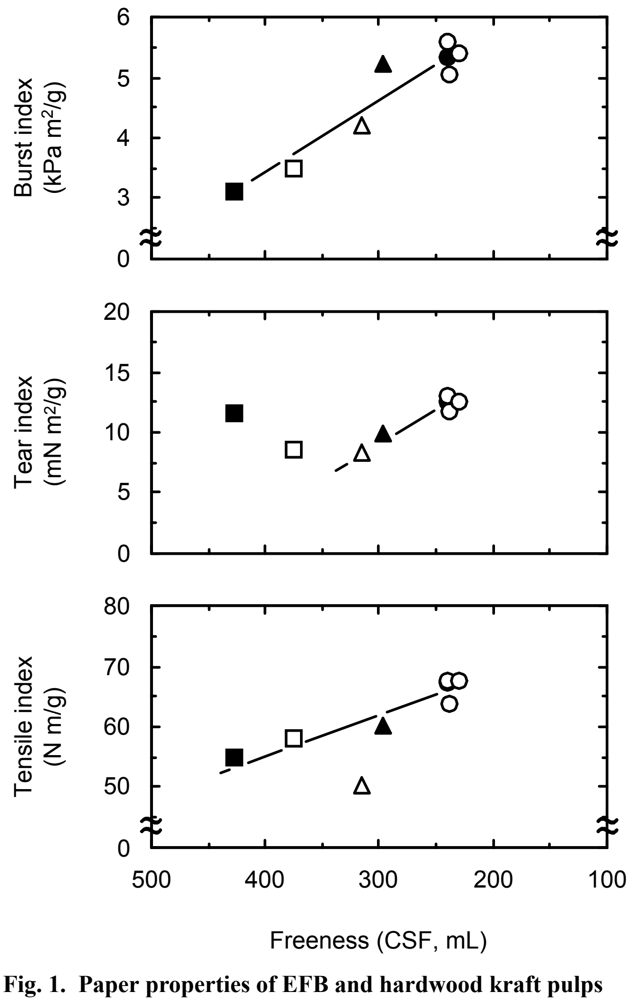

Fig. 1. Paper properties of EFB and hardwood kraft pulps
○ : data from the experiment.
△ : data from the references for EFB KPs[7].
□ : data from the references for hardwood KPs[11].
Open symbols: bleached.
Closed symbols: unbleached.

KP.

Handsheet properties of bleached and unbleached pulp are shown in Table 4. Handsheets of bleached pulp were produced before and after the H_2O_2 bleaching. Compared with the unbleached pulp, there were no significant losses in paper strengths by the bleaching sequences, which are indicated by tensile, tear and burst indices and stretch. A marginal decrease was observed for folding strength of each pulp after the bleaching.

Brightness of the pulp with O_2 / acid / O_3 / H_2O_2 bleaching reached 73–74%. Khoo and Lee achieved the brightness of 80% for an EFB kraft pulp by a chlorine-based bleaching process[7]. Although values of brightness obtained by the chlorine-free bleaching are still lower than that achieved by the chlorine-based bleaching, there is a great potential for the chlorine-free bleaching process to achieve almost the same level in bleachability as chlorine-based bleaching for EFB pulp. It is also interesting to note that after the H_2O_2 sequence, the brightness has been increased drastically whilst maintaining the paper strengths at acceptable levels. Opacity, which is the ability of paper to hide or mask a color or object in back of the sheet, obtained for the bleached handsheet in this study is found to be at a comparable level with that of a hardwood KP, which has almost the same value in brightness[8].

Tensile, tear and burst strengths of EFB handsheets are plotted against freeness (CSF: Canadian Standard Freeness) as shown in Fig. 1. Literature values of EFB KP with chlorine bleaching[7] and hardwood KP[11] are also plotted in this figure for comparison, although there is no comparable pulp data from the references that have almost the same level of freeness as the EFB pulps studied here. In general, tensile and burst indices are dependent on the freeness for the same pulp, i.e. the lower the freeness is, the higher the indices are[7,10]. In contrast, the freeness has less of a contribution to tear index[7], or has an opposed effect to the index[10]. The tensile and burst indices plotted in Fig. 1 exhibited almost linear increases along the decreases of the freeness. For the tear index, the freeness dependence was not observed, which resulted in a similar trend with data of the above-mentioned references[7,10]. These results indicate that the EFB pulps prepared in this study show comparable properties with hardwood kraft pulps. Moreover, the non-chlorine bleaching processes examined in this study may work almost the same as a chlorine-contained process on EFB pulps. It suggests that EFB kraft pulp is able to produce paper sheets with the same strength level as hardwood pulp by using an environmentally friendly method.

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