TCF BLEACHING CHARACTER OF SODA-ANTHRAQUINONE PULP FROM OIL PALM FROND

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The OQP, OQP_O, and OLQP bleaching sequences have been applied to oil palm frond soda-anthraquinone pulp. Oxygen delignification resulted in a delignification of approximately half of the kappa number. In comparison between OQP and OQP_O sequences, the OQPO sequence was able to improve brightness from 75.2% ISO to 82.3% ISO. A TCF bleaching sequence involving laccase was also suitable for the frond pulp bleaching. Results indicated that laccase has a good bleaching capability. Short beating in a PFI refiner (about PFI 2000 revolutions) was sufficient to attain good pulp strength of TCF bleached pulp. There was no total organically bound chlorine in the TCF bleaching effluent. The results of this study show that soda-anthraquinone pulping and TCF bleaching is a promising alternative to produce high-quality pulp from oil palm frond for writing and printing paper.

Keywords: Oil palm frond fiber; TCF bleaching; Beating; Bleaching effluent

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INTRODUCTION

Presently, wood is the most widely used raw material for production of pulp and paper in the world. However, increasing demand and potential increases in wood fiber costs have caused the pulp and paper industry to search for the new fiber sources such as non-wood fibers. Tropical plants fibers show great potential as a papermaking raw material. Among those plants, oil palm fiber has attracted particular attention, especially for Southeast Asian countries. Oil palm is an agricultural plant, which is cultivated for its oil-producing fruit. Besides oil, oil palm operations also produce substantial quantities of residues such as trunks, fronds, and the empty fruit bunches (EFB). These residues have been used for biomass and energy generation (Sulaiman et al. 2011). The feasibility of oil palm fibers for papermaking has been known for a long time. Different pulping methods have been used for oil palm trunks and EFB (Law and Jiang 2001; Jiménez et al. 2009; Muthurajah et al. 1977; Aziz et al. 2002; Wan Rosli et al. 1998; Serrano et al. 2008), but with lesser attention directed at the use of fronds (Wan Rosli et al. 2004; Khiari et al. 2010). It is reported in the earlier works that soda-AQ pulping is suitable for oil palm frond fiber and that it is noted for its environmentally friendly character (Jiménez et al. 2009; Wan Rosli et al. 2004).

Totally chlorine free (TCF) bleaching is widely used in the world due to a concern for environmental protection. Biotechnology has rapidly developed in pulping and bleaching processes (Chakar et al. 2004; Fillat et al. 2007; Gamelas et al. 2007; Garcia et al. 2003; Oudia et al. 2007; Roncero et al. 2003). The function of laccase-mediator systems (LMS) has provided to degrade lignin directly. The mediator is typically a compound of low molecular weight capable of diffusing into cellulose fibers. Laccase-mediator systems react with the phenolic and non-phenolic units of lignin to delignify pulp.

Only few references to the bleaching of oil fibers pulp appear to exist. However, most of them are about oil palm EFB. There is no reference to bleaching of oil palm frond fiber pulp. In them, kraft and soda pulp from EFB was bleached with different sequences. EFB pulp was subjected to an OZP (Oxygen-Ozone-Hydrogen Peroxide) sequence with a sulphuric acid treatment between the O and Z steps (Tanaka et al. 2004). Soda, soda-anthraquinone, kraft, and kraft-anthraquinone pulp from EFB were bleached with an OZP sequence in order to assess the effect of the bleaching treatment on viscosity and kappa number; soda-anthraquinone and kraft anthraquinone pulp exhibited 80% brightness while retaining a viscosity above 15 cP (Leh et al. 2005). Leh et al. (2008) optimized oxygen delignification of EFB pulp in TCF pulp production. Ferrer et al. (2011) optimized oxygen pressurized hydrogen peroxide bleaching conditions of soda pulp from EFB fibers.

The aim of this work was to study the bleachability of oil palm frond soda pulp with TCF bleaching sequences. The OQP, OQPO, and OLQP sequences were used. The results of TCF bleaching were also compared with those of CEH (C-chorine, E-alkaline extraction, H-hypochlorite) bleaching. The bleached pulps were beaten with a PFI refiner with different revolutions to make handsheets. The properties of bleaching effluent, such as BOD, COD, TOCl, and SS were also determined.

EXPERIMENTAL

Materials

Oil palm frond fibers were supplied by Ecopalm Paper Sdn Bhd, Malaysia. Fiber was air dried and cut to 5 to 8 cm length with a cutter (Keyang, SC-5, made in China) before cooking.

Analysis of Raw Material

The frond fiber was analyzed as follows: holocellulose by the Wise et al. method (1946); and a-cellulose, lignin, ash, hot water extraction, 1% NaOH extraction and ethanol – benzene extractives according to T0 203 , T 22, T 211, T207, T 212, and TAPPI 204, respectively (TAPPI standards, 2007). The results are shown in Table 1.

Pulping

Fibers were cooked in an electrically heated rotating digester. The cooking conditions were as follows: liquor-to-wood ratio of 10:1, time to temperature 80 min, time at temperature 120 min, temperature 170^{o}C, NaOH dosage 16% oven-dried pulp(odp), and AQ dosage 0.05% odp. This condition was selected based on the results of previous work (Law and Jiang 2001; Jiménez et al. 2009). The kappa number, brightness, and viscosity of screened pulp were 11.3, 35.2 ISO%, and 1109 mL/g respectively.

Table 1. Chemical Composition of Oil Frond Fiber

Content		Frond fiber
Extraction	Hot water	7.24
	1%NaOH	24.38
	Benzene-ethanol	2.20
Hemicellulose (%)		23.16
Cellulose (%)		42.28
Klason lignin (%)		17.09
Ash (%)		5.95

Oxygen Delignification (O)

Oxygen delignification was done in a 5 L pressure vessel. The condition selected based on previous work (Leh et al. 2008) was as follows: 30 g pulp sample added, adjusted to 10% consistency using distilled water, NaOH charge 2% odp, $MgSO_4$ charge 1% odp, oxygen pressure with 0.6 MPa, temperature at 100^{o}C, and treatment time 1 h.

Laccase Treatment (L)

The pulps were washed with the sodium acetate buffer at pH 4 before L treatment. Laccase was dissolved in the buffer. The mediator HBT (1-hydroxybenzotriazol) and the laccase solution were added into the pulp. Pulp consistency was adjusted with sodium acetate buffer. Then these pulps were transferred into a steel autoclave pressurized with oxygen. The mixing stocks were heated up and kept at a desired temperature with continuous stirring. Laccase treatment was as follows: pulp consistency 5%odp, laccase dosage 20U/g, HBT 1% odp, pH=4.0, temperature 30 ^{o}C, time 3 h, and oxygen pressure 0.6 MPa. This condition was selected based on the work of Garcia et al. (2003).

TCF Bleaching

The pulps were bleached with OQP, OQP_O, OLQP (where O is oxygen delignification, Q a chelating treatment, P hydrogen peroxide stage, P_O oxygen pressurized hydrogen peroxide stage, and L is laccase mediator treatment) sequences, respectively. The conditions selected and modified based on the earlier studies of Moldes et al. (2010) and Ferrer et al. (2011) were as follows: Q stage: DTPA 1.8% odp, pulp consistency 10%, pH value 5 to 6 (adjusted with 1 N H_2SO_4); P_O stage: pulp consistency 5%, H_2O_2 2.0% odp, $MgSO_4$ 0.2% odp, NaOH 1.5% odp, temperature 90^{o}C, time 3.5 h, oxygen pressure 0.6 MPa; P stage pulp consistency 10%, H_2O_2 2.0% odp, $MgSO_4$ 0.2% odp, NaOH 1.5% odp, temperature 85^{o}C, and time 3h.

Pulp Characterization

The bleached pulp samples were characterized by kappa number, brightness, and viscosity according to ISO 302, ISO 3688, and ISO-5351-1, respectively (ISO standard, 2003).

Handsheet Formation and Properties

The bleached pulps were beaten with a PFI refiner to make handsheets. Paper sheets were prepared with an ENJO-F-39.71 sheet machine. The breaking length, burst index, and tear index of paper sheets were determined according to TAPPI methods T-494 om-96, T-494, T-403 om-97, T-414 om-98, respectively (TAPPI standards 2007).

Determination of Bleaching Effluent

BOD_5 (5 day biochemical oxygen demand), CODcr (chemical oxygen demand with dichromate), and suspend solids (ss) of a sample were determined according to the American Public Health Association (APHA) (Greenberg et al. 1995) method. Total organically bound chlorine (TOCl) of the sample was determined by the Schöniger method (Dionex Corp. Sunnyvale, CA, USA).

RESULTS AND DISCUSSION

TCF Bleaching

Oxygen delignification is widely used in pulp bleaching worldwide in accord with stringent environmental regulations, especially in TCF bleaching. So oxygen delignification was employed as the first part of pulp bleaching. The kappa number of the oxygen delignified pulps was 5.9 with 47.1%ISO brightness and 950 mL/g viscosity. Then TCF bleaching sequences of OQP, OQP_O, OLQP, and CEH were compared. The properties of bleached pulps are listed in Table 2.

Table 2. Properties of TCF Bleached Pulps of Frond Fiber

Bleaching sequences	Yield on Unbleached pulp (%)	Kappa number	Brightness (%ISO)	Viscosity (ml/g)
Unbleached	100	11.3	35.2	1106
O	93.1	5.9	47.1	950
OQ	91.4	5.7	50.3	932
OQP	86.2	1.8	75.2	851
OQP_O	82.8	1.0	82.3	825
OL	90.1	4.8	43.6	922
OLQ	89.5	3.71.1	51.4	910
OLQP	83.7	4.8	81.4	838
C	91.6	3.9	54.3	752
CE	89.7	1.2	58.1	703
CEH	85.6		79.1	612

C: consistency 3%, active chlorine 4%, room temp., 1h
E: consistency 10%, NaOH 2%, 60℃, 1h
H: consistency 10%, active chlorine 2%, 40℃, 2h

Table 2 indicates that the properties of the OQP_o and OLQP bleached pulps were much better than those of CEH bleached pulp, especially with respect to brightness and viscosity. However, the CEH pulp was better than the OQP pulp in terms of kappa number and brightness. But viscosity loss was excessive in the case of CEH pulp. A comparison of OQP and OQP_O sequences showed that a P_O stage could improve brightness from 75.2% ISO to 82.3% ISO. The kappa number of the P_O stage was nearly the half that of the P stage following OQ sequences. Furthermore, the P_O stage led to only small losses in viscosity, but the bleaching yield (82.8%) was lowest in the all bleaching sequences. This indicated that the P_O stage had a good ability to remove lignin, leading to high brightness. At the same time, the P_O stage could retain higher viscosity. The bleaching effect of P_O stage has been proved due to its ability to react with all kinds of coloured carbonyl-containing structures in lignin (Romas et al. 2008). It follows that an oxygen pressurized hydrogen peroxide stage is an effective way to increase pulp brightness.

The pulp brightness after the L stage decreased to 43.6% from 47.1% (O stage). This effect was caused by the lignin fragment degradation by laccase from the pulp. Laccase may affect fiber surface structures and decrease of lipophilic extractives in pulp. So the pulp brightness was 81.4%ISO under OLQP bleaching sequences, which was 6%ISO higher than OQP bleached pulp. The results showed that laccase has a good bleachability for soda-AQ oil frond fiber. OQP bleaching sequences provided the highest yield (86.2%) of all bleaching sequences. The shorter bleaching sequences had higher yields of bleaching.

Beating Character of Pulps

The strength properties of the beaten pulps are listed in Table 3. The results show that TCF bleached pulps were easier to beat to a specified beating degree than CEH bleached pulps.

Table 3. Strength Properties of Beaten Pulps

Bleaching sequences	Beating Degree (ºSR)	CSF (Canadian standard freeness)	Rns	Breaking Length (Km)	Tear Index (mN·m^2/g)	Burst Index (kPa·m^2/g)
OQP	15	710	0	3.1	5.9	2.5
	31	415	1500	5.1	5.6	4.6
	40	309	2000	5.8	5.1	5.0
	55	170	4000	6.7	4.9	5.3
OQP_O	16	680	0	3.2	5.8	2.8
	34	375	1500	5.5	5.5	4.8
	42	280	2000	6.1	5.3	5.4
	60	121	4000	6.9	4.6	6.2
OLQP	15	709	0	3.4	5.8	2.7
	33	380	1500	5.3	5.4	4.5
	40	310	2000	6.2	5.1	5.3
	57	165	4000	6.9	4.6	6.3
CEH	15	711	0	1.7	5.6	2.1
	27	471	1500	4.6	5.2	4.1
	37	334	2000	5.6	4.9	4.9
	51	195	4000	6.1	4.5	5.4

The OQP_O bleached pulps were the easiest to beat. At 2000 revolutions, the beating degree could reach 42°SR. Upon further increasing of the revolutions to 4000, the beating degree reached 60°SR. These effects were most influenced by the O stage and P_O stage. The fiber structure was changed and easier to beat. When the beating degree was about 40°SR, the strength properties of all the TCF bleached pulps were sufficient to make printing and writing papers with other long fiber. To achieve this beating degree, the revolutions of PFI mill was at about 2000. Thus, short beating in a PFI refiner was sufficient to attain good pulp strength. The cost of energy for refining of TCF bleached pulps was lower than that of CEH bleached pulps.

Characteristics of Bleaching Effluent

The characteristics of bleaching effluent of TCF and CEH bleaching sequences of oil palm frond are listed in Table 4. TCF bleaching sequences OQP, OQPO, and OLQP did not generate TOCl. But in the CEH bleaching effluent 545.3 mg/L was detected. TOCl is very toxic towards the environment. In addition, the SS, BOD_5, and COD_{Cr} of TCF bleaching sequences were much lower than those of CEH bleaching sequences (243 mg/L, 143 mg/L, and 2041.4 mg/L). These properties of effluents show that TCF bleaching sequences can be more friendly to the environment.

Table 4. Properties of Bleaching Effluents

Bleaching sequences	TOCl(mg/L)	SS(mg/L)	BOD_5(mg/L)	COD_{Cr}(mg/L)
OQP	---	65	50	167.4
OQP_o	---	81	57	175.5
OLQP	---	58	48	149.2
CEH	545.3	243	143	2041.4

CONCLUSIONS

1. When comparing TCF bleaching sequences (OQP_o and OLQP) and a CEH bleaching sequence, TCF bleached pulps had higher brightness and viscosity. The P_O stage, following oxygen delignification, showed a good bleaching selectivity to remove lignin while preserving high pulp viscosity.
2. Short beating with a PFI refiner was sufficient to attain good pulp strength of TCF bleached pulp.
3. The effluent loadings from TCF bleaching sequences were much less than those from CEH bleaching sequences.
4. The results of this study indicated that soda-anthraquinone pulping and TCF bleaching can produce high-quality pulp from oil palm frond for writing and printing paper.

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