TCF BLEACHING OF *EUCALYPTUS UROPHYLLA×EUCALYPTUS GRANDIS* LH107 OXYGEN-DELIGNIFIED KRAFT PULP – PARTIAL Mg^{2+}/Ca^{2+} SUBSTITUTION FOR CHELANTS IN THE CHELATION STAGE

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Received May 6, 2010

The optimization of bleaching, following the sequence of chelation, peroxyacetic acid and hydrogen peroxide treatments of *E. urophylla* × *E. grandis* LH107 oxygen-delignified kraft pulp, was carried out and the optimal parameters were obtained. In the chelation stage, the effect of partial magnesium acetate and calcium acetate substitution for ethylenediaminetetraacetic acid and diethylenetriaminepentaacetic acid was studied in terms of brightness and polymerization degree of the bleached pulp. It was evidenced that (magnesium acetate + calcium acetate)/ethylenediaminetetraacetic acid was optimal, compared to other treatments in the chelation stage, especially as no washing between (magnesium acetate + calcium acetate) and ethylenediaminetetraacetic acid treatments was necessary. This partial Mg^{2+}/Ca^{2+} substitution for chelants in the chelation stage had a positive impact on totally chlorine-free bleaching, providing pulps with higher brightness and small loss of physical strength.

Keywords: *E. urophylla* × *E. grandis* LH107 kraft pulp, chelation, calcium acetate, magnesium acetate, totally chlorine-free bleaching

INTRODUCTION

The driving force for studying totally chlorine-free (TCF) bleaching of fast-growing wood (such as eucalyptus) has been an ever-increasing concern for the environment and the requirements to lower effluent emissions. In order to reduce the emissions caused by bleaching, efforts have been made to reduce the amount of chlorine-containing chemicals. Replacing these chemicals with oxygen-based chemicals (such as oxygen, hydrogen peroxide, peroxyacid) permits the recovery of a larger part of dissolved organic materials from bleaching, thus reducing the effluent load. Some sequences have been reported in TCF bleaching of eucalyptus pulp, such as $OOL_{HBT}QPoP$, $OL_{HBT}EpP$, OXZP, OQOPQP, OQOp(P+Q), O(Op+Q)(P+Q), (Zq)P, (A(Zq))P, P(Zq)P, QPeracidQPp, QEopQPp, $OA_{(Q)}$PeracidOP, $OA_{(Q)}$ZOP, $OA_{(Q)}$EopP, $OA_{(Q)}$-Po.[1-8] These oxygen-containing chemicals are prone to generate radicals, especially in the presence of transitional metals, contributing not only to the bleaching action, but also to an extensive depolymerization of polysaccharides.[9,10] To remove these cations and, consequently, to reduce subsequent negative effects, chelating agents, such as EDTA and DTPA, most frequently used in the pulp and paper industry, are usually applied in a previous separate stage. However, EDTA and DTPA evidenced a relatively poor biodegradability.[11] For example, EDTA degrades to ethylenediaminetriacetic acid, which then cyclizes to diketopiperizide, a cumulative, persistent, organic environmental pollutant,[12] shown to be both cytotoxic and weakly genotoxic in laboratory animals.[13] Efforts for reducing the amount of needed chelating agents prior to hydrogen peroxide bleaching have been reported.[14] An alternative approach with fewer environmental pollution implications is ion exchange on pulp with cationic ion substitution.

Several authors[15-20] have published reports on the attempts made at modelling the ion exchange between solution and pulp fibers. Thus, Rudie *et al*.[17] found out that Mg^{2+} and Ca^{2+} behaved well in ion exchange over Mn^2, as shown by the selectivity coefficients obtained in metal competition experiments.

The present work aims at verifying the possible reduction of chelants in the conventional Q stage, using partial Mg^{2+} and Ca^{2+} substitution in a TCF bleaching sequence applied to the oxygen-delignified kraft pulp of *E. urophylla* × *E. grandis* LH107, which is a new hybrid wood planted in the Jinggu County of Yunnan Province.[21] The optimization of peracetic acid and hydrogen peroxide bleaching was also carried out. The results were interpreted in terms of the properties of bleached pulp.

EXPERIMENTAL

Materials

Fibrous suspensions of the following pulps were used: unbleached kraft pulp (UKP) and oxygen-delignified kraft pulp (OKP) of *E. urophylla* × *E. grandis* LH107 both produced and bleached by OQPaP in the laboratory. Table 1 shows the results of pulping and oxygen delignification. The kappa number of kraft pulp obtained from pulping *E. urophylla* × *E. grandis* LH107 wood has been found as suitable. Typically, the values achieved during eucalyptus wood pulping range between 17 and 15.

Oxygen delignification decreases kappa number to ~12, reaching the optimum level, not beyond ~40%, in kappa number reduction, which may explain that the higher level of ISO brightness (~60%) was obtained at a desirable degree of polymerization (DP) of the O-delignified pulp.

Methods

In the study, suspensions of laboratory oxygen-delignified kraft pulp of *E. urophylla* × *E. grandis* LH107 were treated in double-layer plastic bags, through a QPaP sequence. Chelation with partial Mg^{2+}/Ca^{2+} substitution was performed and compared with other treatments (Table 2).

The charge of Mg and/or Ca in the chelation stage for the ion exchange mechanism was below 0.5%.

Table 1
Results of pulping and oxygen delignification

Pulp	Kappa value	Viscosity (ml/g)	DP	Brightness (% ISO)	Yield (%)
UKP	17.3	1143	1742	34.8	50.29
OKP	11.2	945	1412	59.6	N.D.

N.D.: not determined; Pulping conditions: active alkali charge – 17%, sulfidity – 28%, liquor ratio – 1:4, maximum temperature – 165 °C, time to 165 °C – 2 h, time at 165 °C – 1.5 h; Oxygen delignification conditions: maximum temperature – 100 °C, time at 100 °C – 1 h, O_2 pressure – 0.6 MPa, $MgSO_4$ charge – 0.5%, NaOH charge – 2.5%, pulp consistency – 10%

Table 2
Conditions of chelation with partial Mg^{2+}/Ca^{2+} substitution for chelants and other treatments

Treatment	Water	EDTA	DTPA	(Mg+Ca)	(Mg+Ca)/EDTA or DTPA
Time (h)	1.0	1.0	1.0	1.0	0.5h (Mg+Ca)+0.5h EDTA or DTPA
Charge (%)	-	0.5	0.5	0.5	0.3 (Mg+Ca) +0.2 EDTA or DTPA

60 °C, pulp consistency – 5.0%; Mg:Ca = 8:1 (m:m); Mg:$MgAc_2$, Ca:$CaAc_2$

The pulp obtained at the desired time of chelation was washed with distilled water and subjected to PaP bleaching at 10% pulp consistency. The chemicals used in the trials were calculated for oven dry pulp (o.d. p.).

The content of metallic ions (Fe, Cu, Mn, Zn, Mg and Ca) in the pulps obtained in the chelation stage was analyzed by atomic absorption spectroscopy after wet digestion with nitric acid.

The pulp properties were determined according to TAPPI standard methods and DP was calculated from intrinsic viscosity, using the Mark-Houwink equation:[22]

$$DP^{0.905} = 0.75\ [\eta]$$

where [η] – intrinsic viscosity, mL/g

RESULTS AND DISCUSSION

Chelation – Partial Mg^{2+}/Ca^{2+} substitution for chelants versus other treatments

Chelation was performed under the following conditions of Pa and P bleaching: Pa – 70 °C, 2 h, 2% peroxyacetic acid, 0.3% DTPA, 10% pulp

consistency; P – 90 °C, 2 h, 2% NaOH, 0.1% $MgSO_4$, 1.5% Na_2SiO_3, 0.3% DTPA, 2.0% H_2O_2, 10% pulp consistency.

As to the effect of the partial $MgAc_2$ and $CaAc_2$ substitution for EDTA and DTPA in the Q stage on OQPaP, the results illustrated in Figure 1 permit the conclusion that (Mg+Ca)/EDTA is preferable to (Mg+Ca)/DTPA, in terms of brightness and DP of the bleached pulp, especially when no washing is applied between (Mg+Ca) and EDTA treatments. The fact that the particularly high content of Mn in O-delignified pulp – of 319 ppm – was determined by atomic absorption spectroscopy may explain the experimental results obtained. Of the transitional metals, such as Mn, Fe and Cu, Mn is particularly problematic. However, related to chelation, some researchers indicated that the complexing strength of DTPA to Mn was comparatively poorer under different conditions.[23-25] Meanwhile, the DP of bleached pulp was lower compared to that of (Mg+Ca)/EDTA without washing between (Mg+Ca) and EDTA, at almost the same level of brightness, when $MgAc_2$ was added into the fibrous suspension together with $CaAc_2$, *i.e.* (Mg+Ca), in the chelation stage. In addition, the effect of the (Mg+Ca) charge during the (Mg+Ca)/EDTA treatment (with no washing between (Mg+Ca) and EDTA) was studied, as illustrated in Figure 2. No further increase in the brightness of the resultant bleached pulp was observed when the (Mg+Ca) charge was raised to 0.1%, while the initial DP increased, followed by dropping at a 0.2% (Mg+Ca) charge. The utilization of 0.1% (Mg+Ca) in the (Mg+Ca)/EDTA treatment, without washing between (Mg+Ca) and EDTA, was appropiate.

The removal of the transitional metals present in the pulp was analyzed by atomic absorption spectroscopy during the (Mg+Ca)/EDTA treatment, under optimal conditions. Compared to the control treatment (Table 3), the EDTA or (Mg+Ca)/EDTA treatment in the chelation stage significantly reduced all metallic ions, with the exception of Fe, which was found in significantly high contents in the EDTA-chelated pulp. This explains why the brightness of the resultant bleached pulp increased. (Mg+Ca)/EDTA was found preferable to EDTA in terms of brightness, as a higher value in pulp viscosity was obtained, due to the lower Cu and Fe contents – which agrees with the results of Shen *et al*. – evidencing their intense catalytic effects on H_2O_2 decomposition.[26]

Peroxyacetic acid bleaching

To improve bleaching effectiveness, a peroxyacetic acid stage can be usually employed for prebleaching prior to the peroxide stage.[27] The pulp treated with (Mg+Ca)/EDTA under optimal conditions was subjected to peroxyacetic acid and hydrogen peroxide bleaching. The performance of the Pa stage was studied, as to the effect of temperature, time, peroxyacetic acid charge and chelation.

Effect of temperature on OQPaP bleaching in Pa stage

A turning point was observed at the temperature of 60 °C, for both brightness and DP (Fig. 3), which indicated the presence of more non-reactive chromophore levels and of lower amounts of polymeric hemicellulose.

Effect of time on OQPaP bleaching in Pa stage

As seen in Figure 4, as a result of cellulose degradation, DP decreased with the reaction time. An obvious gain in brightness was obtained at 1.5 h. Unfortunately, after this time interval, brightness decreased.

Table 3
Metallic ions content remaining in pulps after chelation stage

Chelation	Metallic ions content (ppm)						Brightness	Viscosity
	Mg	Ca	Cu	Fe	Mn	Zn	(% ISO)	(ml/g)
Water (Control)	1707	4273	51	89	194	37	82.8	691
EDTA	1378	2291	36	141	48	33	83.8	701
(Mg+Ca)/EDTA*	1421	1608	24	61	99	25	85.2	679

*0.1% (Mg+Ca) + 0.4% EDTA; no washing between (Mg+Ca) and EDTA

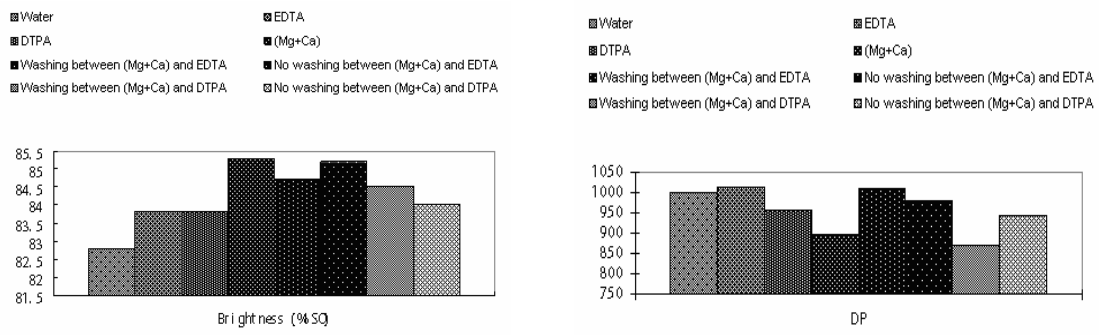

Figure 1: Properties of OQPaP bleached pulp, treated by (Mg+Ca)/chelant, compared to other treatments in Q stage

Effect of peroxyacetic acid charge in Pa stage on OQPaP bleaching

As shown in Figure 5, an increase in the peroxyacetic acid charge enhanced brightness and DP development. However, for a charge above 1.5%, this tendency became weaker, and a brightness ceiling was observed.

Effect of DTPA charge in Pa stage on OQPaP bleaching

DTPA exhibited a positive effect on cellulose in terms of DP. Unfortunately, a negative effect on brightness development was also observed, as shown in Figure 6. This may be related to the decrease in reactivity, because of the retardation on radicals, when DTPA was added to the suspension. However, bleached pulp with acceptable brightness and DP can be obtained at a charge of 0.1% DTPA, in the Pa stage.

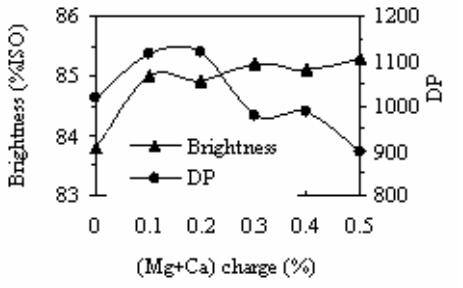

Figure 2: Effect of (Mg+Ca) charge in (Mg+Ca)/EDTA treatment on OQPaP bleaching

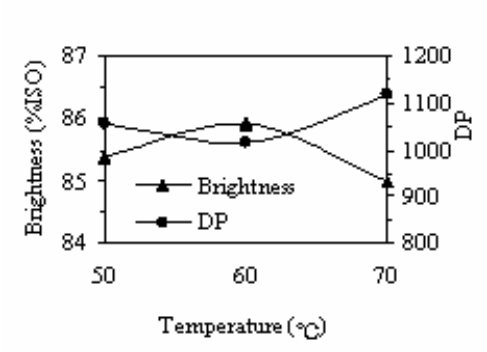

Figure 3: Effect of temperature in Pa stage on OQPaP bleaching (2 h, 2% peroxyacetic acid, 0.3% DTPA)

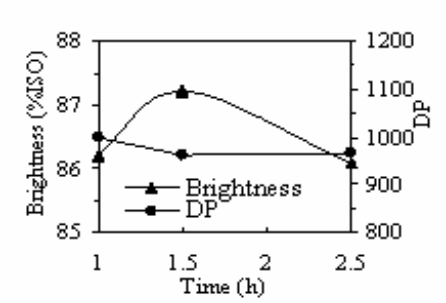

Figure 4: Effect of time in Pa stage on OQPaP bleaching (60 °C, 2% peroxyacetic acid, 0.3% DTPA)

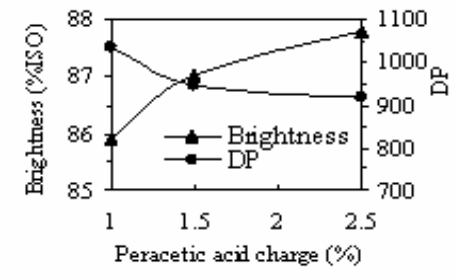

Figure 5 : Effect of peracetic acid charge in Pa stage on OQPaP bleaching (60 °C, 1.5 h, 0.3% DTPA)

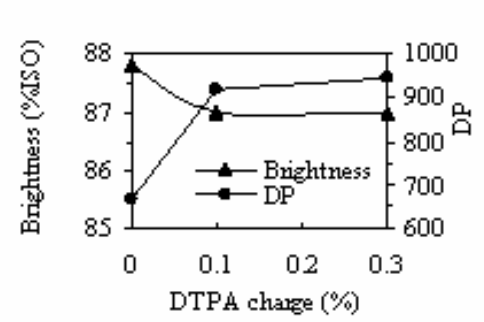

Figure 6: Effect of DTPA charge in Pa stage on OQPaP bleaching
(60 °C, 1.5 h, 1.5% peroxyacetic acid)

Hydrogen peroxide bleaching

Effect of NaOH and H_2O_2 charge in P stage on OQPaP bleaching

Figures 7 and 8 show the results of peroxide bleaching at various NaOH and H_2O_2 charges. Pulp brightness increased with the alkali and peroxide charge. However, when using a NaOH overcharge, alkaline darkening occurred, forming less reactive chromophores towards peroxide bleaching in lignin, and leading to a decrease in brightness (Fig. 7).[28-33] In addition, the DP increased when using 2.5% NaOH in the P stage, as shown in Figure 7, which was possibly due to the overdissolution of hemicellulose from pulp on strong alkality.[34] At optimal alkali and peroxide charges, the maximum brightness obtained was of 87.0% ISO for alkali, while the peroxide charge was of 2.0%.

Effect of temperature and time in P stage on OQPaP bleaching

Brightness development with temperature and time was observed (Figs. 9 and 10). However, an unfavourable brightening effect was observed within a time interval from 120 to 180 min. On the other hand, the DP decreased with temperature and time, due to cellulose degradation.

Physical properties of OQPaP bleached pulp

As the swelling degree was related to the valency of cations present in the pulps, the decrease in multivalent cationic metals generally increased fiber swelling which, in its turn, enhanced bonding, leading to stronger sheets.[35,36] However, despite the decrease in multivalent cationic metals in the pulps after chelation with EDTA or (Mg+Ca)/EDTA (Table 3), a lower tensile index of the bleached pulps was observed, compared to the control sample, as shown in Table 4. The Na^+ level in the pulps, known as affecting fiber swelling, may be one of the reasons.[37] A 5% decrease in tensile index was found when EDTA was replaced with (Mg+Ca)/EDTA, without washing between (Mg+Ca) and EDTA in the Q stage.

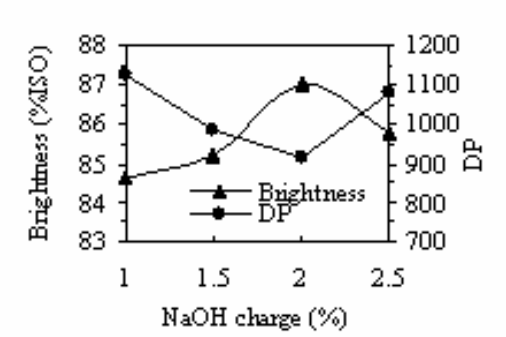

Figure 7: Effect of NaOH charge in P stage on OQPaP bleaching (90 °C, 2 h, 1.5% Na_2SiO_3, 0.1% $MgSO_4$, 0.3% DTPA, 2.0% H_2O_2)

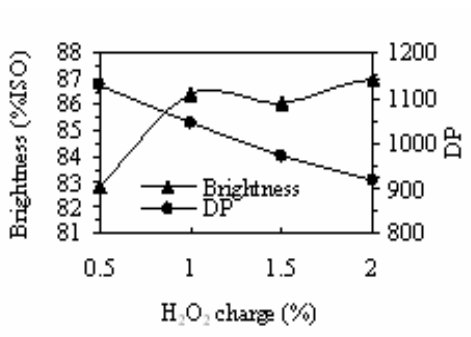

Figure 8: Effect of H_2O_2 charge in P stage on OQPaP bleaching (90 °C, 2 h, 1.5% Na_2SiO_3, 0.1% $MgSO_4$, 0.3% DTPA, 2.0% NaOH)

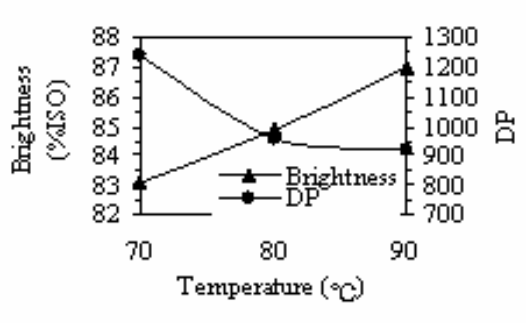

Figure 9: Effect of temperature in P stage on OQPaP bleaching (2 h, 1.5% Na_2SiO_3, 0.1% $MgSO_4$, 0.3% DTPA, 2.0% NaOH, 1.0% H_2O_2)

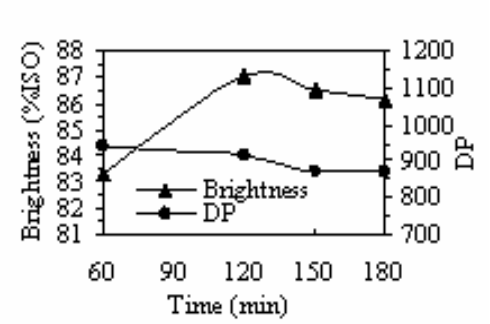

Figure 10: Effect of time in P stage on OQPaP bleaching (90 °C, 1.5% Na_2SiO_3, 0.1% $MgSO_4$, 0.3% DTPA, 2.0% NaOH, 1.0% H_2O_2)

Table 4
Physical properties of the resultant bleached pulp

Chelation	Brightness (%ISO)	Viscosity ($mL \cdot g^{-1}$)	DP	Tensile index ($N \cdot m \cdot g^{-1}$)	Tear index ($mN \cdot m^2 \cdot g^{-1}$)	Burst index ($kPa \cdot m^2 \cdot g^{-1}$)
Water (Control)	79.5	759	1108	61.9	12.3	5.64
EDTA	83.2	838	1236	49.7	13.8	5.03
(Mg+Ca)/EDTA	86.4	719	1044	46.9	12.6	5.55

CONCLUSIONS

The bleaching process of *E. urophylla* × *E. grandis* LH107 oxygen-delignified kraft pulp with OQPaP was optimized using partial Mg^{2+}/Ca^{2+} substitution for chelating agents, compared to other treatments performed in the Q stage. This partial Mg^{2+}/Ca^{2+} substitution had a positive effect on the OQPaP bleaching of *E. urophylla* × *E. grandis* LH107 oxygen-delignified kraft pulp. Bleached pulp can be obtained with the following optimal process parameters: Q – 60 °C, 1.0 h, 0.1% ($MgAc_2$+$CaAc_2$), $MgAc_2$:$CaAc_2$ = 8:1, 0.4% EDTA, no washing between ($MgAc_2$+$CaAc_2$) and EDTA, 5% pulp consistency; Pa – 60 °C, 1.5 h, 0.1% DTPA, 1.5% CH_3COOOH, 10% pulp consistency; P – 90 °C, 2.0 h, 1.0% H_2O_2, 2.0% NaOH, 1.5% Na_2SiO_3, 0.10% $MgSO_4$, 0.3% DTPA, 10% pulp consistency.

ACKNOWLEDGEMENTS: The authors express their gratitude to the National Natural Science Foundation of China (No. 21166011, 20766002) and to the Research Center for Analysis and Measurement (Kunming University of Science and Technology) of China.

LIST OF ABBREVIATIONS

A – Acid stage
$A_{(Q)}$ – Acid stage reinforced with chelant
$CaAc_2$ – Calcium acetate, $Ca(CH_3COO)_2$
DP – Degree of polymerization
DTPA – Diethylenetriaminepentaacetic acid
E – Alkali extraction
Ep – Alkali extraction reinforced with H_2O_2
Eop – Alkali extraction reinforced with O_2 and H_2O_2
EDTA – Ethylenediaminetetraacetic acid
HBT – 1-Hydroxy benzotriazole
L_{HBT} – Laccase stage reinforced with HBT
$MgAc_2$ – Magnesium acetate, $Mg(CH_3COO)_2$
O – Oxygen delignification stage
Op – O_2 stage reinforced with H_2O_2
Op+Q – O_2 stage reinforced with H_2O_2 and DTPMPA
o.d. p. – Oven dry pulp
P – Hydrogen peroxide
Po – Hydrogen peroxide stage reinforced with O_2
Pp – Hydrogen peroxide stage reinforced with positive pressure
P+Q – Hydrogen peroxide stage with DTPMPA
Pa – Peroxyacetic acid stage
Q – Chelation stage
TCF – Totally chlorine-free
X – Xylanase stage
Z – Ozone stage
Zq – Ozone stage reinforced with chelant

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