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DQP BLEACHING OF *EUCALYPTUS UROPHYLLA* ×*EUCALYPTUS GRANDIS* LH 107 OXYGEN DELIGNIFIED KRAFT PULP

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ABSTRACT

On the basis of optimum variables of parameters was determined that there was operating conditions was achived as follows for DQP bleaching of E. urophylla ×E. grandis LH 107 oxygen delignified kraft pulp: GIF pretreatment stage: 80 ˚C, 5.0 h, 1.2 % NaOH (o.d.p.), 1.4 % H_2O_2 (o.d.p.), 0.06 % $CuSO_4$ (o.d.p.), 2.8 % pyridine (o.d.p.), 0.2 MPa O_2, 5 % pulp consistency; Co-salen pretreatment stage: 70 ˚C, 5.0 h, 3 % NaOH (o.d.p.), 1.5 % H_2O_2 (o.d.p.), 0.03 % Co-salen(o.d.p.), 1:1 pyridine/Co-salen (molar ratio), 0.2 $MPaO_2$, 5 % pulp consistency; D stage: 60 ˚C, 0.5 h, 0.2 % ClO_2 (o.d.p.), 1:3 NaOH/ClO_2 (dosage ratio), 10 % pulp consistency; Q stage: 50 ˚C, 1.0 h, 0.5 % DTPA (o.d.p.), 10 % pulp consistency; P stage: 90 ˚C, 1.5 h, 0.7 % H_2O_2 (o.d.p.), 0.7 % NaOH (o.d.p.), 0.6 % Na_2SiO_3 (o.d.p.), 10 % pulp consistency.

The maximum increase of brightness (2.8 % ISO for GIF pretreatment; 2.2 % ISO for Co-salen pretreatment), tensile index (except for GIF biomimetic pretreatment) and burst index was observed adding GIF and Co-salen biomimetic pretreatment to DQP.

KEY WORDS: eucalyptus(Leizhou No.107), oxygen delignified kraft pulp, DQP bleaching, GIF biomimetic system, Co-salen biomimetic system

INTRODUCTION

In recent years, forest have seen excessive logging and numerous environmental issues. As a results, planting new trees becomes important for the pulp and paper industry. *Eucalyptus* is an appropriate family to evaluate because it has a high growth rate. *E. urophylla*×*E. grandis* LH 107 is a new species planted in Jinggu County in Yunnan Province of China.

Proposed environmental regulations will require kraft pulp producers to eliminate or significantly reduce most types of chlorinated organic discharges. For example, bleach plant process changes that reduce elemental chlorine demand such as chlorine dioxide substitution have been used for many years (Solomon et al. 1996, Huang and Chen 2003). Hydrogen peroxide has been widely used in chemical

pulp bleaching (Basta et al. 2002, Zhan et al. 2002). In this work, the optimization of process parameters was carried out in DQP sequence. Biomimetic pretreatment is a alternative to improve the bleaching efficiency (Huynh 1986, Zhou 2007), the usage of GIF and Co-salen biomimetic system was also explored.

MATERIAL AND METHODS

Raw Material

An *E. urophylla*×*E. grandis* LH 107 oxygen-delignified kraft pulp was used for the bleaching experiments. Characteristics of the pulp are as follows: kappa number 11.70, viscosity 1021 ml•g^{-1}, brightness 58.0 % ISO, degree of polymerization (DP) 1538.

Co-salen complex was synthesized using a typical inorganic synthesis strategy involving condensation reaction to form Schiff base ligand (Scheme 1). Synthesis of salen [N, N-bis(salicylaldehyde)ethylenediimine acid] and Co(salen) {[N, N-bis(salicylaldehyde) ethylenediimino]cobalt(II)} was carried out following the procedure of published literature (Liu et al. 1991, Liu et al. 2002). Chlorine dioxide solution was prepared (Chen et al. 1990) in laboratory.

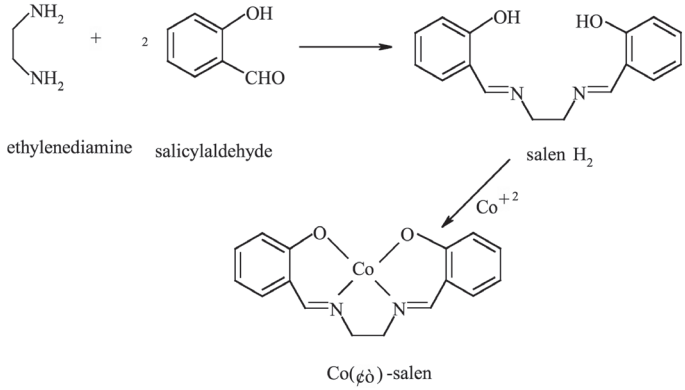


Fig. 1: Synthesis of Co(II)-salen

Conditions of bleaching

Chlorine dioxide bleaching (D), chelation (Q) and hydrogen peroxide bleaching (P) were carried out in the double-layer polyethylene bags, and GIF(Cu) and Co-salen(Co) biomimetic treatment in 1 l stainless steel tank. Reaction tank was tempered on the required temperature by constant-temperature water bath. The oxygen flow was directed into the tank. Cu: 80 °C, 5.0 h, 1.2 % NaOH (o.d.p.), 1.4 % H_2O_2 (o.d.p.), 0.06 % $CuSO_4$ (o.d.p.), 2.8% pyridine (o.d.p.), 0.2 $MPaO_2$, 5 % pulp consistency ; Co: 70 °C, 5.0 h, 3 % NaOH (o.d.p.), 1.5 % H_2O_2 (o.d.p.), 0.03 % Co-salen (o.d.p.), 1:1 pyridine/Co-salen (molar ratio), 0.2 $MPaO_2$, 5 % pulp consistency.

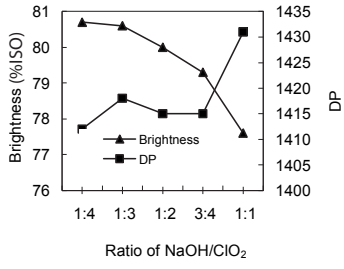
The eucalyptus oxygen delignified kraft pulp and bleached pulp was characterized. The kappa number (TAPPI T236), brightness (TAPPI T452) and viscosity was determined according to TAPPI T230. Handsheets were prepared according to the TAPPI methods. The degree of polymerization(DP) was calculated from intrinsic viscosity using Mark-Houwink equation where ([η]) is the intrinsic viscosity (ml•g^{-1}) of pulp (Rydholm 1965).

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

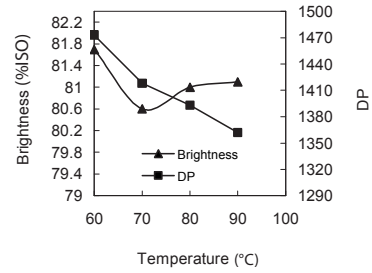
RESULTS AND DISCUSSION

Fig. 1 shows the values obtained for DQP bleaching at different process parameters in D stage. Q: 60 °C, 1.0 h, 0.5 % DTPA (o.d.p.), 10% pulp consistency;. P: 80 °C, 1.5 h, 0.5 % H_2O_2(o.d.p.), 0.5 % NaOH (o.d.p.), 0.4 % Na_2SiO_3 (o.d.p.), 0.5 % $MgSO_4$ (o.d.p.), 10 % pulp consistency.

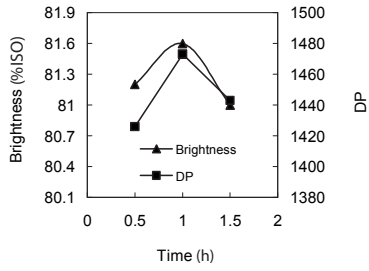
As shown in Fig. 2, there was little change in pulp DP from 1:4 to 3:4 of the ratio of NaOH/ClO_2 (dosage ratio). Higher dosage of NaOH resulted in higher pH value with the ratio of NaOH/ClO_2, this effect on the increase of brightness is negative, especially for the case of 1:3 which corresponding with experience from the field of chlorine dioxide bleaching (Svenson et al. 2002, Ventorim et al. 2005, Svenson et al. 2006). At the higher pH of 1:1, more hemicellulose was possibly dissolved, leaded to somewhat higher pulp DP. On the basis of experimental results was determined that the brightness and DP was acceptable at the ratio of 1:3.



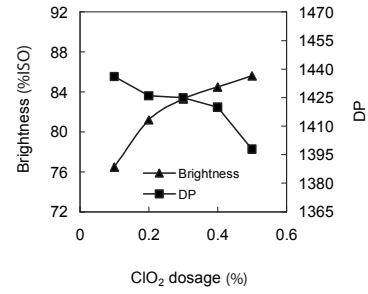
(D: 70 ， , 1.0h, 0.2%ClO_2, 10% pulp consistency)



(D: 1.0h, 0.2%ClO2, 1:3 NaOH/ClO_2, 10% pulp consistency)



(D: 60, ,0.2%ClO_2,1:3 NaOH/ClO_2,10% pulp consistency)



(D: 60, ,0.5h, 1:3NaOH/ClO_2,10%pulp consistency)

Fig. 2: Optimization of process parameters in D stage.

The DP decreased and brightness decreased first and then increased with the temperature, indicating some new chromophores occurred in cellulose degradation. At the temperature of 60 °C, the higher value of brightness and DP was obtained.

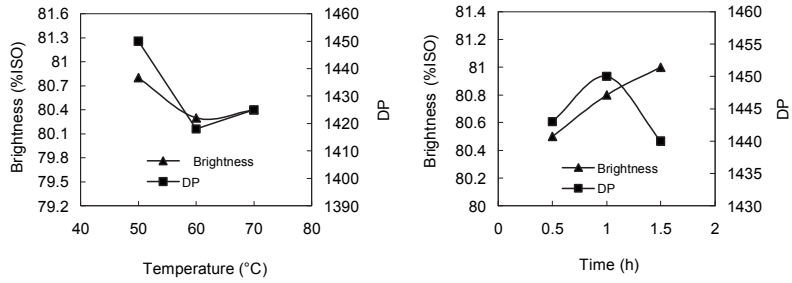
From 0.5 to 1.0 h, more hemicellulose was dissolved while chromophoric structures degraded, the brightness and DP increased. Excessive reaction may lead to chromophoric groups at 1.5 h, the brightness of pulp decreased. Considering the small change of brightness can be said that is

necessary to apply 0.5 h in D-stage in order to achieve of minimum cost.

With the increase of chlorine dioxide dosage, the pulp brightness increased while DP decreased. In the scale of dosage from 0.1 to 0.2 %, a bigger gain of brightness was observed. It is appropriate to employ 0.2 % chlorine dioxide o.d.p..

According to the experimental results, it was decided to adopt the optimal process condition in D-stage as follows: 0.2 % ClO_2 (o.d.p.), 1:3 of NaOH/ClO_2 (charge ratio), 0.5 h, 60 °C, 10 % pulp consistency.

Chelation is usually carried out at or near pH 7. Lower pH solutions are more effective at removing transitional metals, but also remove more of the beneficial metal ions, especially magnesium (Mc Arthur et al. 1986, http://en.wikipedia.org/wiki/Bleaching_of_wood_pulp). So, unadjustment of pH was adopted in Q-stage. Fig. 3 shows the values obtained for DQP bleaching at different temperature and time in Q stage.



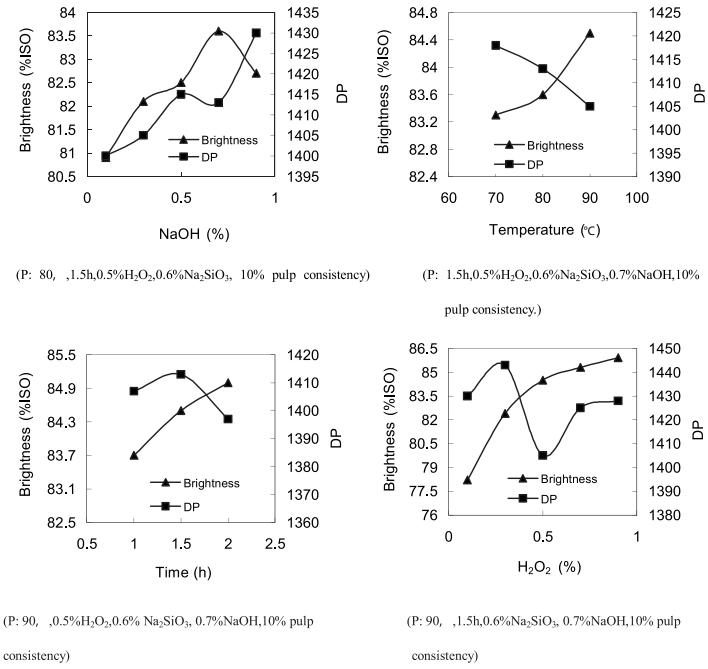
(Q: 1.0h, 0.5%DTPA , 10% pulp consistency.) (Q: 50°C, 0.5%DTPA , 10% pulp consistency.)

Fig. 3: Optimization of process parameters in Q stage

(D:60 °C, 0.5 h, 0.2 % ClO_2, 1:3 NaOH/ ClO 2,10 % pulpconsistency; P:80 °C, 1.5 h, 0.5 % H_2O_2, 0.5 % NaOH, 0.4 % Na_2SiO_3, 0.5 % $MgSO_4$,10 % pulp consistency)

Fig. 3 showed that the bleached pulp with higher brightness and DP could be obtained at 50 °C and 1.0 h. Chelated pulp at optimal Q-condition was then subjected to hydrogen peroxide bleaching.

Fig. 4 shows the values obtained for DQP bleaching at different process parameters in P-stage.



(P: 80, ,1.5h,0.5%H_2O_2,0.6%Na_2SiO_3, 10% pulp consistency)

(P: 1.5h,0.5%H_2O_2,0.6%Na_2SiO_3,0.7%NaOH,10% pulp consistency.)

(P: 90, ,0.5%H_2O_2,0.6% Na_2SiO_3, 0.7%NaOH,10% pulp consistency)

(P: 90, ,1.5h,0.6%Na_2SiO_3, 0.7%NaOH,10% pulp consistency)

Fig. 4: Optimization of process parameters in P stage

(D:60 ˚C, 0.5 h, 0.2 % ClO_2, 1:3 NaOH/ ClO_2, 10 % pulp consistency; Q: 50 ˚C, 1.0 h, 0.5 % DTPA, 10 % pulp consistency)

With the sodium hydroxide charge of 0.1~0.7 % (o.d.p.), an bigger increase in brightness was achieved due to the [HOO^-] (Xie and Zhan 2001). A decrease in brightness was found at 0.9% NaOH (o.d.p.), caused likely by the ineffective loss of hydrogen peroxide at excessive alkalinity (Xie and Zhan 2001). On the other hand, the DP increased, possibly attributable to the dissolve of the low polymeric hemicellulose.

The obvious effect of temperature and time on brightness and DP was observed. The brightness increased and the DP decreased with the temperature and time except for the condition of 1.5h . The bleached pulp obtained at 90˚C and 1.5h was more desirable.

The brightness increased significantly at the charge of 0.1~0.5 % H_2O_2(o.d.p.), and then slowly. In order to ensure the brightness of 85.0 % ISO for industrial application, the charge of 0.7 % H_2O_2 (o.d.p.) was selected optimally. At the same time, the DP was found out to be acceptable.

To improve the bleaching efficiency, the biomimetic system of GIF and Co-salen as a pretreatment prior to DQP was employed in this trial. The effectiveness of the biomimetic systems had been supported by prior studies (Jia and Zhou 2007, 2008a, 2008b, 2009a, 2009b; Qin and Zhou 2008, Deng et al. 2008, Jia et al. 2008, Zhou et al. 2009). Tab. 1,2 shows the values obtained for DQP with biomimetic pretreatment.

Tab. 1: Results obtained at biomimetic pretreatment stage

Biomimetic treatment	Kappa number	Brightness (%ISO)	Viscosity ml.g^{-1}	DP
untreated	11.70	58.0	1021	1538
GIF treated	9.85	67 0	848	1252
Co-salen treated	10.60	67.4	933	1392

Tab. 2: Physical properties of bleached pulp(60±1) °C SR

Sequence	Brightness (%ISO)	Viscosity (ml.g^{-1})	DP	Tensile index (N·m.g^{-1})	Tear index (mN·m^2.g^{-1})	Burst index (kPa·m^2.g^{-1})
OCEH	84.0	726	1055	77.9	11.2	5.75
ODQP	85.3	953	1470	78.2	21.7	6.22
OCuDQP	88.1	804	1181	75.5	13.4	6.35
OCoDQP	87.5	899	1336	83.5	13.9	6.31

Compared to Co-salen, the kappa number of GIF treated pulp was lower, the brightness and DP was also lower indicating that cellulose was degraded more seriously and new chromophores occurred during delignification for GIF system, which supported by the GC-MS detection results (Jia et al. 2008). Tab. 2 showed that the physical properties of pulp bleached by ODQP, OCuDQP and OCoDQP was higher compared with OCEH owe to the selectivity of chlorine dioxide and hydrogen peroxide. The brightness was improved obviously at the acceptable physical properties with the pretreatment of GIF and Co-salen system.

CONCLUSIONS

On the basis of optimum variables of parameters was determined that there was operating conditions as follows: 80 ˚C, 5.0 h, 1.2 % NaOH (o.d.p.), 1.4 % H_2O_2 (o.d.p.), 0.06 % $CuSO_4$ (o.d.p.), 2.8 % pyridine (o.d.p.), 0.2 $MPaO_2$, 5 % pulp consistency in GIF pretreatment stage; 70 ˚C, 5.0 h, 3 % NaOH (o.d.p.), 1.5 % H_2O_2 (o.d.p.), 0.03 % Co-salen (o.d.p.), 1:1 pyridine/ Co-salen (molar ratio), 0.2 $MPaO_2$, 5 % pulp consistency in Co-salen pretreatment stage; 60 ˚C, 0.5 h, 0.2 % ClO_2 (o.d.p.), 1:3 NaOH/ClO_2 (dosage ratio), 10 % pulp consistency in D stage; 50 ˚C, 1.0 h, 0.5 % DTPA(o.d.p.), 10 % pulp consistency in Q stage; 90 ˚C, 1.5 h, 0.7 % H_2O_2 (o.d.p.), 0.7 % NaOH (o.d.p.), 0.6 % Na_2SiO_3 (o.d.p.), 10% pulp consistency in P stage.

The maximum increase of brightness, tensile index (except for GIF biomimetic pretreatment) and burst index was observed adding GIF and Co-salen biomimetic pretreatment to DQP.

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