Impact of Oxygen-Reinforced Alkali Extraction on Eucalyptus Sulfate Pulp for Viscose Fiber Production

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Some pulp mills expect to produce viscose fiber by means of pre-existing pulp production lines as used for conventional kraft pulp having a relatively high content of hemicellulose. In the present study oxygen-reinforced alkali extraction was used to dissolve the oxidized lignin, which increased the content of alpha cellulose and increased the degree of mercerization. This paper considers the influence of alkalinity, time, temperature, oxygen pressure, and borax additive on oxygen-reinforced alkali extraction. According to the experimental results, the optimal oxygen-reinforced alkali treatment conditions were 120 g/L alkali for 30 min at a temperature of 40 °C. Single factor experiment results showed that oxygen pressure was beneficial to the process of alkali extraction, and 0.4 Mpa was selected as the optimal oxygen pressure. Kappa number, alpha cellulose, carboxyl content, and degree of polymerization (DP) were 1.2, 99.18%, 0.00965 mmol/g, and 1505, respectively, under the optimal reaction conditions. Results for the oxygen-alkali treatment showed that borax was important for affecting DP and the amount of cellulose II. DP was decreased to 1282 and the amount of cellulose II was increased to 36% when the borax was added.

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INTRODUCTION

Cellulose, as a linear homopolymeric polysaccharide, is the most abundant biological macromolecule on earth. Native cellulose polymer chains arrange themselves parallel to one another with the same polarity, and such a crystalline arrangement is called cellulose I (Gardner and Blackwell 1974; Sarko and Muggli 1974; Delmer and Amor 1995). A variety of alternative crystalline allomorphs exist in nature. These allomorphs differ in their unit cell dimensions, chain packing schemes, and hydrogen-bonding relationships (Langan *et al.* 1999; Wada *et al.* 2004). Cellulose II is the predominant crystalline allomorph, in which all the cellulose chains are anti-parallel in their arrangement (Kolpak and Blackwell 1976). Compared with cellulose I, cellulose II, with its high reaction activity, is a very important intermediate product.

Cellulose II is easily obtained by the mercerization of native cellulosic materials (Hiroyuki *et al.* 2004). Mercerization of cellulose is an important initial step in the production of many cellulose derivatives. That is because cellulose is activated after the mercerization process (Mansikkaki *et al.* 2007). It has been reported that the enzymatic synthesis of cellulose II with high crystallinity can be achieved from glucose and α-glucose 1-phosphate by use of cellodextrin phosphorylase. Hiraishi *et al.* (2009) have reported the synthesis of highly ordered cellulose II *in vitro* by using cellodextrin

phosphorylase. The methods just mentioned are difficult to implement on an industrial scale by adjusting the original pulp production line. Traditionally, cellulose II is also produced by regeneration from alkali cellulose (*i.e.,* a mercerization process) and utilized on an industrial scale.

The production of viscose fiber is expected to afford pure cellulose that is uncontaminated with other polymers such as hemicellulose and lignin, which are present in common mercerization processing. Thus, the mercerization process to produce viscose cellulose generally takes place after the pulp has been completely bleached. In order to produce the viscose fiber, some pulp mills plan for the production of fibers with high alpha cellulose content by changing the process parameters of an oxygen-alkali bleaching stage. Oxygen-reinforced alkali bleaching is preferred because high alpha-cellulose content can be achieved.

Due to the limits of the oxygen-alkali process, the desired level of mercerization is difficult to achieve. Chemical additives are sometimes necessary to accelerate the permeation of the alkali solution. Borax is a common additive for the preparation process of mechanical pulp. Boric acid and its derivatives, *e.g.* its salts or acids, are in general, suitable for the formation of intermediate derivatives of polysaccharides (Liebert 2010). That is because the electronic ground state of boron is $1s^2 2s^2 2p^1$ and the main oxidation number is 3, which could form either a 4- or 6-coordination compound. Since boron has a small atomic radius, it usually forms a 4-coordination structure. Because of the structure of borax, it can form chemical bonds with the hydroxyl groups of cellulose (Xu *et al.* 2012). In order to produce viscose fiber, process parameters of the original pulp production line should be changed. Thus, this paper investigates the influence of alkalinity, time, temperature, oxygen pressure, and chemical additive on the oxygen-reinforced alkali bleaching process.

EXPERIMENTAL

Materials

A typical semi-bleached eucalyptus sulfate pulp (SESP), which was prepared from unbleached kraft pulp (UKP) after single stage oxygen pre-delignification was received from Yunjing Group in Yunnan Province, P. R. China. The bleached hardwood sulfate pulp (BHKP) was prepared by SESP after a ClO_2 bleaching stage in the lab. Approximately 10 g of ESP (o.d. basis) were mixed with 1% ClO_2, and phthalic acid-hydrochloric acid buffer solution (pH 3) was used to maintain the pH at a stable value. The reaction temperature was controlled at 75 ^{o}C, and the reaction time lasted 90 min. BHKP was thoroughly washed with water and stored at 4 °C before further treatment. Sodium hydroxide and borax were purchased from Nanjing Chemical Reagent Co., Ltd. All other chemicals were analytically pure (Shanghai Chemicals Co., Ltd, China) and were used without further purification. Pulp properties are shown in Table 1.

Table 1. Properties of the SESP and BHKP Samples

Types of Pulp	SESP	BHKP
Kappa number	7.9	4.4
Alpha cellulose content (%)	86.90	87.69
Carboxyl content (*μ*mol/g)	41.68	20.24
DP	1460	1460

Methods

Oxygen-alkali treatment of BHKP

Oxygen-reinforced alkali extraction of the ClO_2 treated pulp (BHKP) was carried out in a 1.5 L stainless steel autoclave. Approximately 60 g of BHKP (o.d. basis) were mixed with different ratios of NaOH, water, and $MgSO_4$ (0.03g) in polyethylene plastic bags and then transferred to the stainless steel autoclave completely (Liu and Cao 2012). Oxygen was added to the stainless steel autoclave to create the predetermined pressure (0.4 MPa). Then the 1.5 L rotary electric digester was heated to the target temperature with a water-bath and held the appointed time at the maximum temperature. BHKP after oxygen-alkali pretreatment was thoroughly washed with water and stored at 4 °C before further treatment.

Experimental design

The proposed model used a series of experiments based on a three controllable 3-level factors Taguchi design. For Taguchi analysis, standard L-9 orthogonal array was used, which gives the minimum number of experiments. The further analysis was obtained by MINITAB16.

Pulp properties

The Kappa number of the measured samples were according to TAPPI standard T236 cm-85. The α-cellulose content was according to the reported method of Lawal and Ugheoke (2010). The carboxyl content of samples was determined by an electrical conductivity titration method, according to the reported method of Saito *et al.* (2007). The degree of polymerization (DP) was according to the reported method of Xu *et al.* (2012).

X-ray diffraction

The eucalyptus fiber samples were converted to powder substrates and then subjected to X-ray diffraction analysis from 5° to 40° at 0.05°/min of diffraction angle 2θ using the reflection method by means of a D/Max-3A (Japan) with a Ni-filtered Cu-$K\alpha$ radiation ($\lambda = 0.1548$ nm) at 40 kV and 100 mA. The degree of crystallization of cellulose (X) was determined by Equation 1,

$$X = n \frac{I_k}{I_0}, n = 0.75 \tag{1}$$

where I_0 is the intensity of the maximum diffraction from the baseline, and I_k is obtained by subtracting the base lever from this value (Zhang *et al.* 1993).

The percentage of the cellulose II form in the crystalline aggregation is,

$$C_{II} = \frac{I_{12.0}}{I_{12.0} + 0.5(I_{14.7} + I_{16.1})} \tag{2}$$

where $I_{12.0}$, $I_{14.7}$, and $I_{16.1}$ represent the intensities of diffraction peaks 12.0°, 14.7°, and 16.1° (2θ), respectively (Mansikkaki *et al.* 2007).

RESULTS AND DISCUSSION

For the pulp (BHKP) used in this study, under medium consistency conditions (10% pulp consistency), further removal of hemicellulose and transformation of the crystal type were achieved by controlling the oxygen-reinforced alkali extraction conditions. Treatment time, temperature, alkalinity, oxygen pressure, and amount of borax were considered in this study. After oxygen-reinforced alkali extraction, higher alpha cellulose, moderate kappa number, and DP would be desired. Carboxyl content was considered since direct alkaline oxygen degradation of the carbohydrates would generate carboxyl groups. Table 2 lists the results of oxygen-reinforced alkali extraction.

Table 2. Results of Oxygen-Reinforced Alkali Extraction of BHKP

No.	Alkalinity (g/L)	T (°C)	Time (min)	Kappa number	DP	α-cellulose content %	Carboxyl content μmol/g
1	80	40	30	2.1	1481	96.78	19.32
2	80	60	60	2.0	1304	95.29	20.45
3	80	80	90	1.8	865	95.31	26.58
4	120	40	60	1.3	1501	98.39	17.48
5	120	60	90	1.3	1226	98.58	19.46
6	120	80	30	1.3	1037	99.10	18.80
7	160	40	90	1.5	1374	99.74	16.44
8	160	60	30	1.4	1298	99.46	17.89
9	160	80	60	1.2	1029	98.05	18.60

Key Effects of Oxygen-Alkali Treatment on Kappa Number

The kappa number of the eucalyptus sulfate pulp was 4.4 after a single stage of ClO_2 delignification. Table 3 shows the analysis of variance of the kappa number data from the design of experiments utilizing the MINITAB 16 statistical software. The statistical analysis showed that alkalinity and temperature influenced the kappa number; and alkalinity was a significant factor ($p < 0.05$). Alkalinity clearly affected the kappa number. The residual lignin was dissolved in sodium hydroxide.

Table 3. ANOVA Table of Kappa Number for the Selected Parameters and Interactions

Variance	Degrees of Freedom	Seq. SS	Adjusted SS	Adjusted MS	F	*P*
Alkalinity (g/L)	2	0.88580	0.88580	0.44290	66.77	0.015
Temperature (°C)	2	0.08207	0.08207	0.04103	6.19	0.139
Time (min)	2	0.00887	0.00887	0.00443	0.67	0.599
Error	2	0.01327	0.01327	0.00663		
Total	8	0.99000				
	S = 0.0814453	R-Sq = 98.66%	R-Sq（adj.）= 94.64%			

According to Table 2, the increased alkalinity had little influence on delignification when the alkali concentration was more than 120 g/L. Therefore, the optimal alkalinity was 120 g/L. Temperature had a minor effect, compared to alkalinity, and the lowest kappa number was obtained at 80 °C. However, the DP declined severely when the extraction temperature increased. When temperatures were lower, alkaline scission can be minimized; that is because the peeling process would be decreased (Knill and Kennedy 2003). The influence of higher temperature on the decrease of kappa number was limited, but the influence of higher temperature on the decrease of DP was enhanced. Therefore, 40 °C was selected as the optimal temperature.

Key Effects of Oxygen-Alkali Treatment on *α*-cellulose and DP

Table 4 shows the analysis of variance of the DP data utilizing the MINITAB 16 statistical software program. The statistical analysis showed that temperature and time were significant factors at the 95% level ($p < 0.05$). Temperature was the most important factor for DP. More degradation occurred at higher treatment temperatures. Therefore, in order to minimize the DP decrease, 40 °C was selected as the optimal temperature. When treatment time was less than 60 min, treatment time had little impact on DP. However, when the treatment time was more than 60 min, the longer reaction time impacted the DP due to the degradation of cellulose. This delay in DP degradation was due to the slow degradation reaction during the initial phase (Knill and Kennedy 2003). The pulp carbohydrates are composed of two constituents, cellulose and hemicellulose, and these cannot be separated precisely. Alpha-cellulose content is a very important parameter for viscose manufacture and indicates the extent of hemicellulose removal.

Table 4. ANOVA Table of DP for the Selected Parameters and Interactions

Variance	Degrees of Freedom	Seq SS	Adjusted SS	Adjusted MS	F	*P*
Alkalinity (g/L)	2	2174	2174	1087	2.38	0.296
Temperature (°C)	2	346002	346002	173001	389.56	0.003
Time (min)	2	28854	28854	14427	31.57	0.031
Error	2	914	914	457		
Total	8	377944				
S = 21.3776 R-Sq = 99.76% R-Sq (adj) = 99.03%						

Table 5 shows the analysis of variance of the alpha cellulose data. Alkalinity was a significant factor for alpha cellulose; the dissolution of hemicelluloses occurred with a higher alkalinity environment, which yielded higher alpha cellulose content. According to Table 2, alpha cellulose significantly increased when alkali concentration was ≥80 g/L. Moreover, the increased alkalinity had little influence on the dissolution of hemicellulose when the alkali concentration was more than 120 g/L (Table 2). Therefore, the optimum alkali concentration was chosen to be 120 g/L to fully take into account both the kappa number decrease and alpha cellulose increase. The maximum value of alpha cellulose with 120 g/L alkali concentration was obtained in 30 min, operating at the maximum temperature assayed, 80 °C. The minimum value of alpha cellulose using the same alkali concentration was obtained in 60 min when operating at 40 °C. But high temperature greatly influenced DP. Therefore, the optimal conditions of oxygen-reinforced alkali

extraction were selected as follows: 120 g/L alkali; 30 min reaction time; and 40 °C reaction temperature.

Table 5. ANOVA Table of Alpha Cellulose Content for the Selected Parameters and Interactions

Variance	Degrees of Freedom	Seq SS	Adjusted SS	Adjusted MS	F	P
Alkalinity (g/L)	2	19.8187	19.8187	9.9093	115.45	0.006
Temperature (°C)	2	1.0072	1.0072	0.5036	7.90	0.112
Time (min)	2	2.3940	2.3940	1.1970	18.78	0.051
Error	2	0.1275	0.1275	0.0637		
Total	8	23.3474				
S = 0.252477 R-Sq = 99.45% R-Sq（adj）= 97.82%						

Interrelationship between Carboxyl Content, *α*-cellulose and DP

In alkaline hydrolysis, the major loss of insoluble cellulose, in contrast to acidic degradation, is caused by endwise depolymerization reactions (peeling), leading to the formation of soluble carboxylic acid derivatives. Alkali cellulose can be oxidized by oxygen, a reaction that has long been used to reduce the DP of wood pulp (the aging or pre-ripening process) to a level suitable for the manufacture of viscose rayon (Knill and Kennedy 2003). Hemicellulose has a much lower molecular weight than cellulose, in addition to being branched and amphorphous (non-crystalline). The aerobic alkali degradation of hemicellulose is easier than that of cellulose. The first step in this autoxidation process yields carbonyl-containing oxidized celluloses or hemicellulose, which are subsequently degraded by alkali (Knill and Kennedy 2003). Thus, the carboxyl content of cellulose has close ties to DP. Compared to cellulose, hemicellulose, with lower molecular weight, has more reducing terminal groups, which are easily oxidized to carboxyl groups. The carboxyl content increases when the pulp contains more hemicellulose and less alpha cellulose. Therefore, both alpha cellulose and DP are key factors for carboxyl content. According to Table 2, the carboxyl content varied in accordance with both alpha cellulose content and DP. When the *α*-cellulose content was below 96%, the carboxyl content of cellulose was higher than 20 μmol/g. When *α*-cellulose contents were approximately the same as one another, the DP of the cellulose became the key factor for carboxyl content. The carboxyl content was lower when the high DP cellulose had less terminal reducing groups.

Table 6. The Effects of Oxygen Pressure on Oxygen-Reinforced Alkali Extraction

No.	Alkalinity (g/L)	T (°C)	Time (Min)	Oxygen Pressure (Mpa)	Kappa number	DP	*α*-cellulose content %
1	120	40	30	0	1.5	1463	98.57
2	120	40	30	0.2	1.4	1490	98.79
3	120	40	30	0.4	1.2	1505	99.18
4	120	40	30	0.6	1.2	1473	99.41
5	120	40	30	0.8	1.2	1490	99.60

Effects of Oxygen Pressure on Oxygen-Alkali Treatment

Experimental results shown in Table 6 demonstrated that oxygen pressure was beneficial to the process of alkali extraction. With the increasing pressure of oxygen, lignin and hemicellulose were more inclined to dissolve in the alkali solution. The pulp after oxygen-reinforced alkali extraction decreased in Kappa number and increased in α-cellulose content. That was because oxygen can further oxidize the residual lignin to promote the dissolution of lignin and hemicellulose. When oxygen pressure was less than or equal to 0.4 MPa, the DP was increased with the dissolution of hemicellulose. The degradation reaction of cellulose increased when oxygen pressure was greater than 0.4 MPa. Thus, the optimal oxygen pressure was 0.4 MPa.

Table 7. The Effect of Borax on BHKP after Oxygen-Reinforced Alkali Extraction

No.	Alkalinity (g/L)	T (°C)	Time (min)	Oxygen pressure (Mpa)	Borax (g/L)	Kappa number	DP	α-cellulose content (%)	X (%)	C II (%)
1	120	40	30	0.4	0	1.2	1505	99.18	45.81	29.47
2	120	40	30	0.4	30	1.3	1283	98.82	45.91	31.58
3	120	40	30	0.4	60	1.3	1282	99.01	46.05	36.00
4	120	40	30	0.4	90	1.3	1256	90.46	46.60	38.44

Effects of Adding Borax on BEK under Optimal Oxygen-Alkali Treatment

Borax was found to be beneficial to the reaction of mercerization. Because the electronic structure of the boron atom is $1s^2 2s^2 2p^1$ and the main oxidation number is 3, boron could form a 4- or 6-coordination compound. Since boron has a small atomic radius, it usually forms a 4-coordination structure. Figure 1 shows the possible boronate structures with carbohydrates (Liebert 2010). Studies were carried out with methyl-α-D-glucopyranoside (Me-α-D-glac) and phenylboronic acid (PBA). Stepwise boronation of Me-α-D-glac with PBA was confirmed, which formed Me-^{4,6}(PhB)-α-D-glac (1) with the OH-6 and the OH-4 in the first step. Secondly, Me-^{2,3}(PhB)$_2$-^{4,6}(PhB)-α-D-glac (2) was formed by the boronation of Me-^{4,6}(PhB)-α-D-glac (1) with PBA (Liebert 2010). Because of the boronation between carbohydrate and borax, it could form chemical bonds with the hydroxyl groups of cellulose (Xu *et al.* 2012). Thus, the reaction solutions were promoted to penetrate into cellulose.

Table 8. The Comparison of BHKP after Oxygen-Reinforced Alkali Extraction

No.	DP	Carboxyl content μmol/g	α-cellulose content %	Kappa number	X %	C II %
1	1460	20.24	87.69	4.4	57.39	0
2	1505	9.650	99.18	1.2	45.81	29.47
3	1282	14.95	99.01	1.3	46.05	36.00

*The original BHKP (1); BHKP treated under the optimal oxygen-reinforced alkali extraction without adding borax (2); and BHKP under the optimal oxygen-reinforced alkali extraction treatment by adding borax (3)
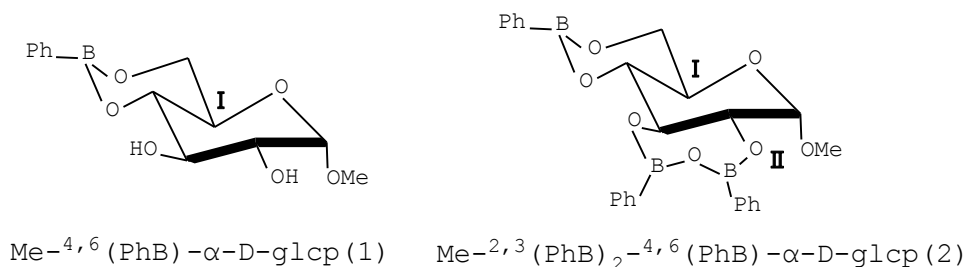
Me-^{4,6}(PhB)-α-D-glcp(1)   Me-^{2,3}(PhB)$_2$-^{4,6}(PhB)-α-D-glcp(2)

Fig. 1. Boronate structures and expected fission processes in MS studies

Experiment results in Table 7 show the effect of borax on BHKP after oxygen-reinforced alkali extraction, and Table 8 compares BHKP after oxygen-reinforced alkali extraction. Results demonstrated that the percentage of C_{II} increased when borax was used. When borax was added, the alpha cellulose and the DP declined remarkably. That was because alkali penetration into the cellulose was promoted and the ratio of mercerization of cellulose increased. But the degradation of cellulose increased severely. Experimental results showed the optimal amount of borax was 60 g/L. Figure 2 shows the X-ray diffraction of the different BHKP treatments under different conditions. According to Table 8, the reaction activity of cellulose was increased after oxygen-alkali treatment because of the decrease of crystallinity. After the oxygen-reinforced alkali extraction, high alpha cellulose content with moderate values of Kappa number and DP were achieved.
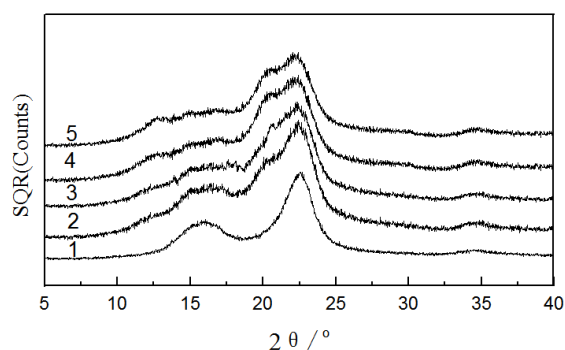

Fig. 2. X-ray diffraction of the original BHKP (1), BHKP under the optimal oxygen-reinforced alkali extraction without adding borax (2), BHKP under the optimal oxygen-reinforced alkali extraction by adding 30 g/L borax (3), BHKP under the optimal oxygen-reinforced alkali extraction by adding 60 g/L borax (4), and BHKP under the optimal oxygen-reinforced alkali extraction by adding 90 g/L borax (5)

CONCLUSIONS

Alkali concentration and oxygen pressure were shown to be the key factors for production of alpha cellulose. Alkali concentration was the most important for affecting Kappa number, while temperature, time, and amount of borax were significant factors for the degree of polymerization (DP) of the cellulose. The maximum value of alpha cellulose with 120 g/L alkali concentration was obtained in 30 min, operating at the maximum temperature assayed, 80 °C. However, high temperature had a big influence on DP. Considering the influence of the various factors, the optimal conditions of oxygen-reinforced alkali extraction were selected as 120 g/L alkali; 30 min reaction time; and

40 °C reaction temperature with 0.4 MPa oxygen pressure. At these optimum conditions, the kappa number, alpha cellulose, and DP were 1.2, 99.18%, and 1505, respectively. Experimental results showed that the reaction solutions were promoted to penetrate into cellulose and Cellulose II increased 36% when the amount of borax additive was used, and the optimal amount of borax was 60 g/L.

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