

# Effect of Hydroxyl Radical on the Selectivity of Delignification during Oxygen Delignification of Bamboo Pulp

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The main challenge in the oxygen delignification process is the improvement of selectivity. To further understand the effect of the amount of hydroxyl radicals on the selectivity of oxygen delignification, in this work, the hydroxyl radicals were generated by the improved Fenton reaction system and were quantified by UV spectrophotometry. Antioxidants such as ascorbic acid were applied for the scavenging of hydroxyl radicals so that the amount of hydroxyl radicals could be regulated. The bamboo kraft pulps were treated with the Fenton system or the Fenton system combined with ascorbic acid. The results indicated that the improved Fenton reaction system could be used for the determination of hydroxyl radicals by UV spectrophotometry. The amount of hydroxyl radicals could be regulated to a suitable extent by the hydroxyl radical scavengers during oxygen delignification so that the delignification selectivity improvement was achieved.

*Keywords:* Bamboo pulp; Oxygen delignification; Selectivity of delignification; Hydroxyl radical; Radical scavenger

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## INTRODUCTION

At present, oxygen delignification is widely used for lignin removal in pulping and bleaching because of its environmental, technological, and economic benefits. The lower water consumption and effluent discharge is obtained due to the greater recycling potential of oxygen stage effluents. The lower content of chlorinated organics, Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), and color in the bleach plant effluent, as well as lower chemical requirements in subsequent bleaching sequences are obtained by removing much of the lignin in the unbleached pulp in the oxygen stage. Higher yield and brightness of the pulp are finally obtained compared to extending delignification by cooking and bleaching when employing equivalent amounts of chemicals (McDonough 1996; Zou 2002; van Heiningen *et al.* 2003). However, the effectiveness of an oxygen delignification stage is limited because severe cellulose degradation takes place when the delignification is more than 50% with a single stage due to the tendency of secondarily produced active oxygen species to attack carbohydrate as well as lignin, resulting in the deterioration of pulp viscosity and strength properties (McDonough 1996; Violette 2003). Therefore, the lower selectivity is a key obstacle to oxygen delignification. To improve the selectivity of oxygen delignification, many studies have been carried out, such as optimization of process parameters (McDonough

1986; Cao *et al.* 2006), pretreatment of unbleached pulp (Samuelson and Otjeg 1996), reinforcement of oxygen delignification with additives (Pesman *et al.* 2010; Gaspar *et al.* 2009), kinetics of oxygen delignification (Violette 2003; Ji 2007), cellulose protectants (Fu *et al.* 2005; Chen and Lucia 2002), and the reaction mechanism of lignin and carbohydrates (Gierer *et al.* 2001; Reitberger *et al.* 2001; Guay *et al.* 2000; Guay *et al.* 2001). However, our knowledge of oxygen delignification is still far from being complete. High delignification selectivity has not yet been achieved, and therefore oxygen delignification cannot be used more extensively to replace the other means of lignin removal.

In the oxygen delignification process, it is well known that there are several oxygen-containing species, *i.e.*  $\text{HOO}\cdot$ ,  $\text{O}_2\cdot^-$ ,  $\text{HO}\cdot$  and so on, which are mainly generated from reactions between phenolic units in lignin and molecular oxygen during the process (Ericsson *et al.* 1971; Gierer and Imsgard 1977; Gratzl 1992; Yokoyama *et al.* 1996). Studies have shown that these active oxygen species, especially  $\text{HO}\cdot$ , attack not only lignin, but also carbohydrates, resulting in lower pulp strength and yield (Guay *et al.* 2000, 2001). To further understand the underlying fundamental chemistry in oxygen delignification in order to improve the selectivity of delignification, the mechanisms of oxidative degradation of carbohydrates and lignin have been investigated (Konishi *et al.* 2009; Nakagawa *et al.* 2012; Yokoyama *et al.* 2011; Kalliola *et al.* 2011; Rovio *et al.* 2011; Kuitunen *et al.* 2011). Gierer *et al.* (2001) considered oxygen delignification as a free radical process, and it was significant for improving the selectivity of oxygen delignification process to regulate the reaction of oxygen-containing radicals with lignin. Bouchard *et al.* (2010, 2011) regulated reaction behavior of radicals by optimizing the oxygen delignification conditions, such as pH profile, oxygen pressure, procedure for addition of  $\text{MgSO}_4$ , and the retention of hemicelluloses in the pulp. Some studies (Violette and van Heiningen 2002; Colodette and Santos de Campos 1993) showed that the reactivity of oxygen radicals towards the scavengers was higher than that towards the carbohydrates, and the oxygen delignification selectivity could be improved by the scavenging of  $\text{HO}\cdot$  by some radical scavengers such as alcohol, poly-alcohols, aldehydes, organic acid, and polymers during the oxygen process.

In this study, the  $\text{HO}\cdot$  was generated by the improved Fenton reaction of the  $\text{Co}^{2+}$ - $\text{H}_2\text{O}_2$  system, which can produce more  $\text{HO}\cdot$  than the  $\text{Fe}^{2+}$ - $\text{H}_2\text{O}_2$  system (Ren *et al.* 2000). The relative concentration of  $\text{HO}\cdot$  was determined by UV/VIS spectrophotometry with the change of alizarin violet 3B, a  $\text{HO}\cdot$  scavenger. The  $\text{Co}^{2+}$ - $\text{H}_2\text{O}_2$  system reacted with bamboo kraft pulps to imitate the attack of  $\text{HO}\cdot$  on carbohydrates during oxygen delignification. The  $\text{Co}^{2+}$ - $\text{H}_2\text{O}_2$  system combined with various amounts of  $\text{HO}\cdot$  scavenger was reacted with bamboo kraft pulps to investigate the effect of the amount of  $\text{HO}\cdot$  on the degradation degree of carbohydrates and delignification. We attempted to better understand the effect of the amount of  $\text{HO}\cdot$  on the selectivity of oxygen delignification, which would be highly useful for optimization of the oxygen delignification process by the use of  $\text{HO}\cdot$  scavengers as additives.

## EXPERIMENTAL

### Materials

Bamboos chips were provided by ShaoWu Zhongzhu Pulp & Paper Co., Ltd. (in Fujian Province, China), and included mainly *Bambus Schreber*, *Dendrocalamopsis* (Chia et Fung) Keng f., *Sinobambusa Makino*, and *Phyllostachys Sieb. et Zucc.*

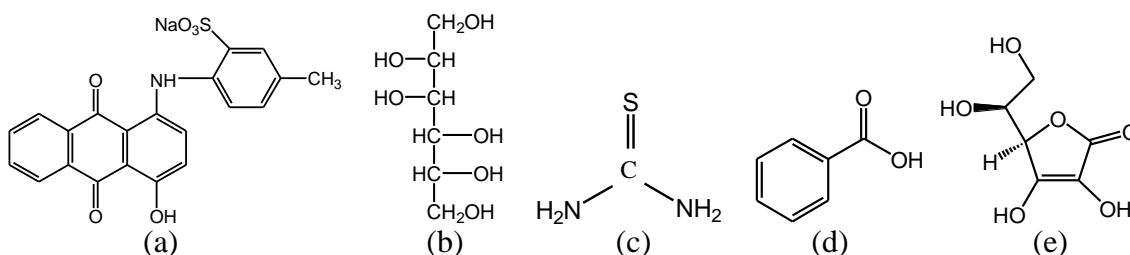
Bamboo pulp was prepared from the chip by the extended modified continuous cooking (EMCC) method with cooking conditions (Cao *et al.* 2006): 14% (expressed as Na<sub>2</sub>O) of active alkali charge at the impregnating zone and the current zone, 30g/L of warm white liquor concentration at the countercurrent zone, 25% of sulfidity, and 160 °C maximum temperature.

Alizarin violet 3B, mannitol, ascorbic acid, CoSO<sub>4</sub>, thiourea, benzoic acid, Na<sub>2</sub>HPO<sub>4</sub>, NaOH, and H<sub>2</sub>O<sub>2</sub> were of reagent grade and used as received. Benzoic acid, thiourea, mannitol, and ascorbic acid solutions were prepared separately at a concentration of 1.0 mmol/L.

## Methods

### Determination of the apparent scavenge rate of HO·

The following solutions were added into a colorimetric tube: 0.6 mL of CoSO<sub>4</sub> solution (0.1 mmol/L), 1.4 mL alizarin violet 3B (see Fig. 1) solution (1.0 mmol/L), 1.0 mL Na<sub>2</sub>HPO<sub>4</sub>-NaOH buffer solution (pH 12), and 1.0 mL H<sub>2</sub>O<sub>2</sub> solution (1%). The solution was diluted to 10 mL with distilled deionized water and shaken well. The final concentrations of CoSO<sub>4</sub>, alizarin violet 3B, and H<sub>2</sub>O<sub>2</sub> were 6.00×10<sup>-3</sup> mmol/L, 0.14 mmol/L, and 29.40 mmol/L, respectively in the colorimetric tube. After 35 min, the absorbance A<sub>1</sub> at 571 nm was measured with a UV spectrophotometer against a blank of deionized water. The reference absorbance A<sub>0</sub> was also measured without 1.0 mL H<sub>2</sub>O<sub>2</sub> solution (1%) while the alizarin violet 3B was not decoloured. The absorbance difference ΔA (ΔA=A<sub>0</sub>-A<sub>1</sub>) is positively related to the amount of HO·.



**Fig. 1.** Chemical structures of alizarin violet 3B (a), mannitol (b), thiourea (c), benzoic acid, (d) and ascorbic acid (e)

Various volumes of mannitol, thiourea, benzoic acid, and ascorbic acid (their chemical structures are shown in Fig. 1) were added into the solution above, and the absorbance was determined at 571 nm after 35 min. The apparent scavenge rate of HO·, *d* was calculated according to the formula,

$$d = \frac{A_2 - A_1}{A_0 - A_1} \times 100\% \quad (1)$$

where A<sub>0</sub> is the absorbance of the solution without H<sub>2</sub>O<sub>2</sub>, A<sub>1</sub> is the absorbance of the solution added with H<sub>2</sub>O<sub>2</sub>, and A<sub>2</sub> is the absorbance of the solution added with H<sub>2</sub>O<sub>2</sub> and a scavenger.

*Reaction of EMCC bamboo pulp and HO·*

Twenty grams of EMCC bamboo pulp (o. d.), 100 mL Na<sub>2</sub>HPO<sub>4</sub>-NaOH buffer solution (pH 12), and specified volumes of 50 g/L H<sub>2</sub>O<sub>2</sub>, 3 mmol/L CoSO<sub>4</sub>, and 50 mmol/L ascorbic acid were added into the plastic bag. In each case the consistency was adjusted to 10% with distilled deionized water (see Table 1). After mixing well, the plastic bag was sealed and immersed under the water (held at 80 °C) with weights for 240 min. The control experiment was performed at the same time. After the reaction, the pulp was completely washed with distilled deionized water, dewatered to a 20% to 30% consistency, dispersed, and equilibrated in a sealed plastic bag (minimum 12 h) for measurement.

**Table 1.** Reaction Conditions of EMCC Bamboo Pulp and HO·

V <sub>H<sub>2</sub>O<sub>2</sub></sub> (mL)	C <sub>H<sub>2</sub>O<sub>2</sub></sub> (mmol/L)	C' <sub>H<sub>2</sub>O<sub>2</sub></sub> (mmol/L)	V <sub>CoSO<sub>4</sub></sub> (mL)	C <sub>CoSO<sub>4</sub></sub> (mmol/L)	C' <sub>CoSO<sub>4</sub></sub> (mmol/L)	V <sub>VC</sub> (mL)	C <sub>VC</sub> (mmol/L)	C' <sub>VC</sub> (mmol/L)
0	1.47×10 <sup>3</sup>	0	0	3	0	0	50	0
10	1.47×10 <sup>3</sup>	8.17×10 <sup>-2</sup>	1	3	5.56×10 <sup>-3</sup>	0	50	0
20	1.47×10 <sup>3</sup>	1.63×10 <sup>-1</sup>	2	3	1.11×10 <sup>-2</sup>	0	50	0
40	1.47×10 <sup>3</sup>	0.33	4	3	2.22×10 <sup>-2</sup>	0	50	0
40	1.47×10 <sup>3</sup>	0.33	4	3	2.22×10 <sup>-2</sup>	4	50	1.11
40	1.47×10 <sup>3</sup>	0.33	4	3	2.22×10 <sup>-2</sup>	8	50	2.22
40	1.47×10 <sup>3</sup>	0.33	4	3	2.22×10 <sup>-2</sup>	16	50	4.44

V: Volume of additive solution;  
c: Concentration of additive solution;  
c': Concentration of additive in the reaction system with EMCC bamboo pulp.

*Oxygen delignification of EMCC bamboo pulp*

Oxygen delignification was carried out in a Parr reactor (Mode 4843, Parr Instrument Company, Illinois, U.S.). Fifty grams of bamboo kraft pulp mixed with appropriate chemicals and additives was adjusted to 10% consistency with distilled deionized water and then placed into the reactor at 90 °C and oxygen pressure of 0.5 MPa. The NaOH charge (on oven dry pulp) was 3%, and the reaction time was 80 min. The MgSO<sub>4</sub> charge (on oven dry pulp) was 0.5%. The stirring speed was 400 revolutions/min. The concentration of ascorbic acid was varied from 0.5% to 2% based on the weight of bamboo kraft pulp (o.d). After oxygen delignification, the pulp was washed thoroughly with distilled deionized water, dewatered to a 20% to 30% consistency, dispersed, and equilibrated in a sealed plastic bag (minimum 12 h) for measurement.

*Analysis*

The Kappa number and viscosity were determined according to TAPPI T238 and ISO 5351-2010, respectively. The brightness was measured with a Technibrite Micro TB-1C according to ISO 2470-2009. The ratio of delignification, the ratio of viscosity reduction, and the selectivity of delignification were calculated according to the literature (Zou 2002; Violette 2003; Ji 2007),

$$L = \frac{K_0 - K_1}{K_0} \times 100\% \quad V = \frac{V_0 - V_1}{V_0} \times 100\% \quad S = \frac{K_0 - K_1}{V_0 - V_1} \times 100 \quad (2)$$

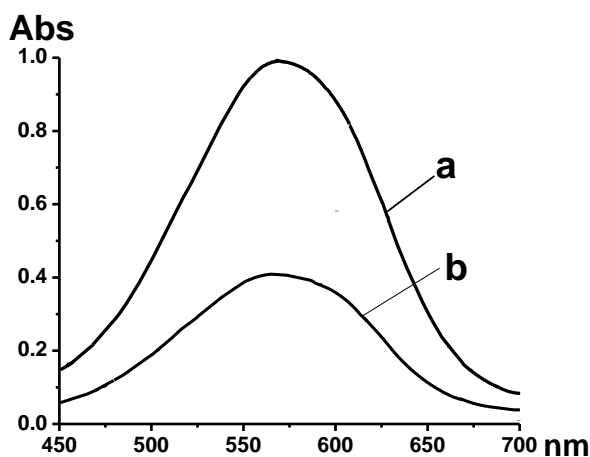
where  $L$  is the ratio of delignification,  $V$  is the ratio of viscosity reduction,  $S$  is the selectivity of delignification,  $K_0$  is the Kappa number before oxygen delignification,  $K_1$  is the Kappa number after oxygen delignification,  $V_0$  is the the viscosity before oxygen delignification, and  $V_1$  is the viscosity after oxygen delignification.

## RESULTS AND DISCUSSION

### Determination of HO·

Among active oxygen species, the HO· radical has a high reactivity that can destroy the cellulose in pulp as well as lignin. Regulation of the HO· radical during the oxygen delignification process should be a good alternative to improve the delignification selectivity. Therefore, it is necessary to determine the concentration of HO· radical during the reaction system. The measurement method was simply done by UV spectrometry with the color change of dye instead of ESR, in which the HO· radical was generated by  $\text{Co}^{2+}$ - $\text{H}_2\text{O}_2$  reaction system.

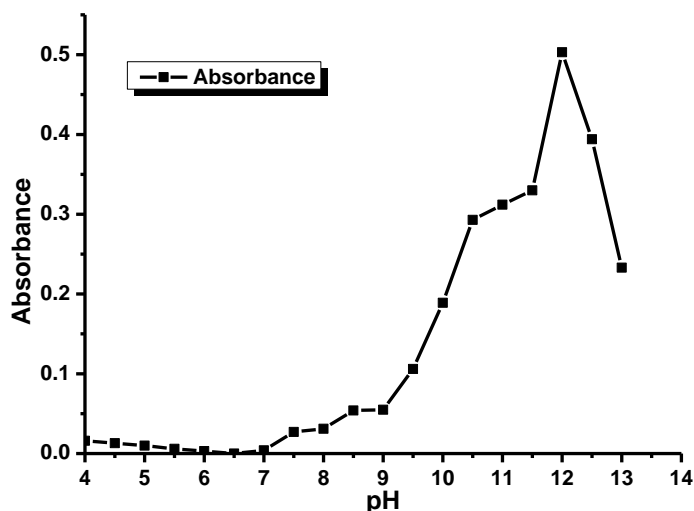
HO· radical generated by  $\text{Co}^{2+}$ - $\text{H}_2\text{O}_2$  system can decolor a dye, alizarin violet 3B. If the absorbance change is related positively to the amount of HO· radical, then the HO· radical can be quantitatively determined by UV/VIS spectrometry. The UV/VIS spectra of alizarin violet 3B from 450 nm to 700 nm were measured by a UV spectrophotometer (UV-2201 SHIMADZU, Japan), and results are shown in Fig. 2. The results showed that there was a peak at about 571 nm for alizarin violet 3B. The HO· radical generated by  $\text{Co}^{2+}$ - $\text{H}_2\text{O}_2$  system can obviously decrease the absorbance of alizarin violet 3B at 571 nm. Therefore, the wavelength of 571 nm was selected for measurement of the HO· radical.



a – no oxidation reaction,  $\text{CoSO}_4$  + alizarin violet 3B + buffer solution (pH=12)  
b – oxidation reaction,  $\text{CoSO}_4$  + alizarin violet 3B + buffer solution (pH=12)+ $\text{H}_2\text{O}_2$

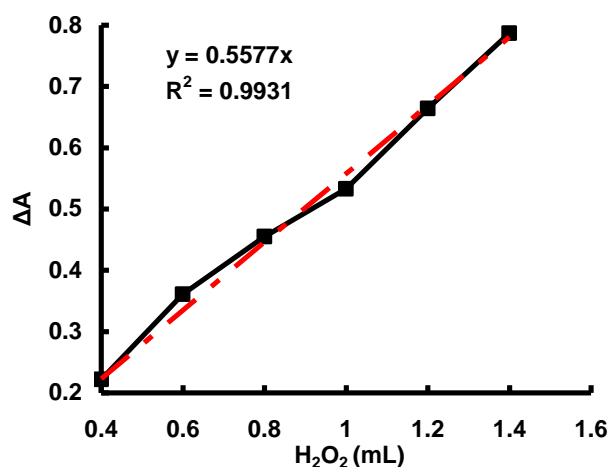
**Fig. 2.** UV-visible absorbance spectra of alizarin violet 3B

The pH usually is kept at about 12 in the process of oxygen delignification and hydrogen peroxide bleaching. In the present experiments, the absorbance of alizarin violet 3B at 571 nm was recorded over the pH range from 4 to 13. The results (Fig. 3) showed that the optimum pH was 12, which would allow for the determination of the HO· radical under oxygen delignification conditions.



**Fig. 3.** Effect of pH on the absorbance of alizarin violet 3B

Figure 4 shows that the absorbance difference ( $\Delta A$ ) increased linearly with the amount of  $H_2O_2$ . Obviously, there was a near-perfect linear correlation ( $R^2=0.9931$ ) between the amount of  $HO\cdot$  production and that of  $H_2O_2$  employed. Therefore, the amount of  $HO\cdot$  can be regulated by the amount of  $H_2O_2$  addition.



**Fig. 4.** Effect of  $H_2O_2$  on the absorbance difference ( $\Delta A$ )

Figure 5 shows the effect of the amount of  $CoSO_4$  on the absorbance difference ( $\Delta A$ ). The absorbance difference increased slowly with the amount of  $CoSO_4$  and then leveled off when more than 0.6 mL of  $CoSO_4$  was added in the reaction system. In other words, the amount of  $CoSO_4$  was enough for  $HO\cdot$  production when the molar ratio of  $CoSO_4$  and  $H_2O_2$  was 1:15 (see Table 1). Therefore, it can be concluded that  $CoSO_4$  acts as a catalyst and only a little is needed in the reaction system.

The  $HO\cdot$  radical generation by  $Co-H_2O_2$  Fenton reaction was almost completed in 35 min. Table 2 showed that the absorbance change of alizarin violet 3B decreased gradually from the reaction beginning up to 20 min because alizarin violet 3B was decoloured by  $HO\cdot$ ; then the decreasing change slowed down and the absorbance reached a constant level after the reaction time of 35 min. Therefore, the reaction time was chosen as 35 min.

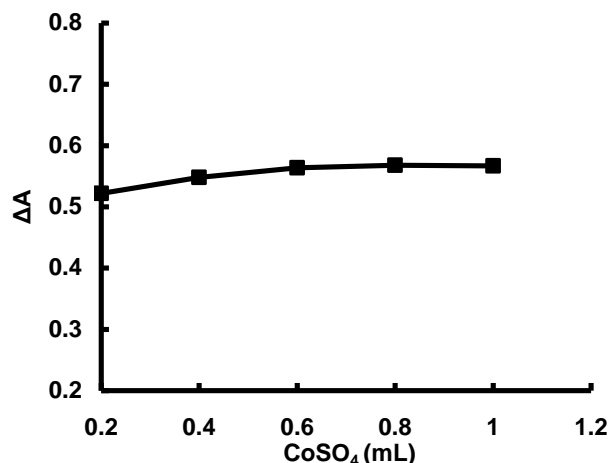


Fig. 5. Effect of CoSO<sub>4</sub> on the absorbance difference ( $\Delta A$ )

Table 2. Absorbance Variation of Alizarin Violet 3B vs. Reaction Time

Reaction time (min)	0	5	10	15	20	25	30	35	40	45
An	0.700	0.640	0.539	0.455	0.393	0.353	0.327	0.319	0.315	0.318
$\delta A^*$		0.060	0.101	0.084	0.062	0.040	0.022	0.008	0.004	-0.003
* $\delta A = A_n - A_{n+1}$										

### Scavenging of HO·

The antioxidants such as ascorbic acid, thiourea, benzoic acid, mannitol, *etc.* were added to the HO· generation system so that they could scavenge hydroxy radicals. The results (Fig. 6) showed that HO· can be quenched to different extents by these scavengers. The scavenging rate of HO· increased with an increase of the amount of antioxidant. Among them, ascorbic acid was the best to quench HO· because a molecule of ascorbic acid quenched HO· more efficiently than a molecule of any other HO· scavenger. The amount of HO· could be regulated by adjusting the HO· scavenger.

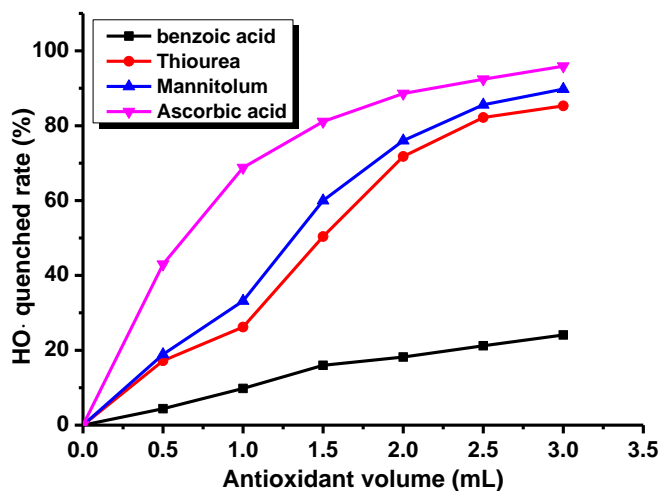


Fig. 6. The relationship between HO· quenched rate and the amount of antioxidants  
Note: The concentrations of antioxidants are all 1.0 mmol/L.

### Reaction of HO· with EMCC Bamboo Pulp

The EMCC bamboo pulps were treated with HO· generated by the Co<sup>2+</sup>-H<sub>2</sub>O<sub>2</sub> system with or without ascorbic acid, a HO· scavenger. The experimental results (Table 3) showed that the delignification rate increased with the increase of the HO· amount by increasing the amount of H<sub>2</sub>O<sub>2</sub> and CoSO<sub>4</sub>. This was because more lignin was degraded by more HO· generated by the Fenton's reaction system. Meanwhile, the rate of viscosity reduction also increased with the amount of HO· because of the poor reaction selectivity of HO·, which could not only react with lignin but also degrade carbohydrates (Gierer *et al.* 2001; Reitberger *et al.* 2001; Guay *et al.* 2000, 2001). The selectivity of delignification was 1.8 when 10 mL of H<sub>2</sub>O<sub>2</sub> were added into the reaction system, but the selectivity of delignification dropped to 1.2 when the amount of H<sub>2</sub>O<sub>2</sub> increased to 40 mL.

**Table 3.** Reaction of HO· with EMCC Bamboo Pulp

H <sub>2</sub> O <sub>2</sub> (mL)	CoSO <sub>4</sub> (mL)	Ascorbic acid (mL)	Bamboo Kraft Pulp After Reaction		Delignification rate (%)	Viscosity reduction rate (%)	Selectivity of delignification
			Kappa number	Viscosity (mL/g)			
0	0	0	12.0	1113	1.6	-1.3	Control
10	1	0	8.8	910	27.9	17.2	1.8
20	2	0	8.1	805	33.6	26.8	1.4
40	4	0	7.0	657	42.6	40.2	1.2
40	4	4	9.5	951	22.1	13.5	1.8
40	4	8	10.2	996	16.4	9.4	1.9
40	4	16	11.1	1047	9.0	4.7	2.1

Note: Original bamboo kraft pulp, Kappa number: 12.2; viscosity, 1099 mL/g; reaction temperature, 80°C; time, 240 min.

As we know, the amount of HO· can be regulated by ascorbic acid, which is a HO· scavenger. The majority of the added HO· reacts with scavengers when more ascorbic acid is added into the reaction system, while a correspondingly lesser amount of HO· reacts with lignin and carbohydrates. The selectivity of delignification increased with the increase of ascorbic acid amount. The selectivity of delignification was 1.8 when 4 mL of ascorbic acid was added to the reaction system, vs. 2.1 when 16 mL was added. However, the delignification rate decreased with the increase of ascorbic acid amount. The delignification rate was 22.1 when 4 mL of ascorbic acid was added into the reaction system, and the rate decreased to 9.0 when 16 mL was added. Therefore, the addition amount of ascorbic acid could be optimized so that a good delignification rate with a proper selectivity was obtained. Similarly, the amount of HO· can also be regulated to keep a proper concentration by addition of HO· scavengers such as ascorbic acid, thiourea, benzoic acid, and mannitolum in the delignification system of pulp with oxygen-containing bleaching regents, such as oxygen, hydrogen peroxide, and ozone. The loss of pulp viscosity is much less with an increase of delignification selectivity.

### Effect of HO· Scavenger on the Oxygen Delignification of the EMCC Bamboo Pulp

Because HO· resulted in reduction of viscosity of pulp while lignin was removed from the pulp according to the experiments above, the HO· scavenger was added during the oxygen delignification of the EMCC bamboo pulp to investigate the effect of the amount of HO· scavenger on the selectivity of delignification. The experimental results are shown in Table 3.



**Table 4.** Effect of HO· Scavenger on the Oxygen Delignification of EMCC Bamboo Pulp

Ascorbic acid (%)	Bamboo Kraft Pulp After Reaction		Delignification rate (%)	Viscosity reduction rate (%)	Selectivity of delignification	Brightness (%ISO)
	Kappa number	Viscosity (mL/g)				
0	8.1	936	48.4	14.9	4.6	41.1
0.5	9.3	970	40.7	11.8	4.9	35.5
1.0	10.4	1002	33.8	8.9	5.4	31.6
2.0	11.2	1030	28.7	6.4	6.4	30.3

Note: Original bamboo kraft pulp, kappa number: 15.7; viscosity: 1100 mL/g; brightness: 28.1% ISO.

The amount of HO· decreased with the increase of ascorbic acid amount in the EMCC bamboo pulp oxygen delignification system. Therefore, the carbohydrates in EMCC bamboo pulp were less degraded, which led to a viscosity increase and a selectivity improvement. The rate of viscosity decreased from 14.9% to 6.4%, and the selectivity of delignification increased from 4.6 to 6.4 as the charge of ascorbic acid was increased from 0 to 2.0%. Therefore, the amount of HO· played an important role in the delignification process. The selectivity of delignification could be improved by regulation of the HO· charge with the HO· scavengers. However, the reduction of HO· unfortunately resulted in a reduction of delignification during the oxygen delignification process. The process that will increase the rate of delignification with a proper selectivity of delignification or reduce the degradation of carbohydrates at the presence of a large amount of HO· still needs further investigation.

## CONCLUSIONS

1. The improved Fenton reaction of  $\text{Co}^{2+}$ - $\text{H}_2\text{O}_2$  system can be used for the determination of HO· relative quantity. Optimum conditions are as follows: wavelength of 571 nm, pH 12, molar ratio of  $\text{CoSO}_4$  and  $\text{H}_2\text{O}_2$  1:15, and a reaction time of 35 min.
2. HO· has poor selectivity for delignification and degradation of cellulose. The selectivity of delignification can be improved by regulation of the amount of HO·.
3. The amount of HO· can be regulated to keep a proper concentration by addition of HO· scavenger such as ascorbic acid during oxygen delignification of bamboo pulp so that the degradation of carbohydrates is alleviated and the selectivity of delignification is improved.

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