PROCESS OPTIMIZATION OF TETRA ACETYL ETHYLENE DIAMINE ACTIVATED HYDROGEN PEROXIDE BLEACHING OF *POPULUS NIGRA* CTMP

Qiang Zhao, Junwen Pu,* Shulei Mao, and Guibo Qi

To enhance the bleaching efficiency, the activator of tetra acetyl ethylene diamine (TAED) was used in conventional H_2O_2 bleaching. The H_2O_2/TAED bleaching system can accelerate the reaction rate and shorten bleaching time at relative low temperature, which can reduce the production cost. In this research, the process with hydrogen peroxide activated by TAED bleaching of *Populus nigra* chemi-thermo mechanical pulp was optimized. Suitable bleaching conditions were confirmed as follows: pulp consistency 10%, bleaching temperature 70^oC, bleaching time 60 min when the charge of H_2O_2 was 4%, NaOH charge 2%, and molar ratio of TAED to H_2O_2 0.3. The pulp brightness gain reached 23.6% ISO with the optimized bleaching conditions. FTIR analysis indicated that the H_2O_2/TAED bleaching system can decrease carbonyl group further than that of conventional H_2O_2 bleaching, which contributed to the higher bleaching efficiency and final brightness. The H_2O_2/TAED bleaching had stronger oxidation ability on lignin than that of H_2O_2 bleaching.

Keywords: Populus nigra; H_2O_2; Bleaching; TAED; FTIR

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INTRODUCTION

Hydrogen peroxide has been widely used to bleach high-yield pulp. But the pulp cannot be bleached to a high brightness with hydrogen peroxide only. To increase bleaching efficiency of hydrogen peroxide and the pulp final brightness, conventional hydrogen peroxide bleaching process needs to be modified. There are many methods to achieve this target, such as intensification of pretreatments, bleaching at high temperature, oxygen intensified bleaching, and the use of bleach additives. The method of adding bleach additives was proved as one simple and practical way to improve the bleaching efficiency of hydrogen peroxide.

The hydrogen peroxide/activator bleaching system mainly consists of two chemical agents, hydrogen peroxide and the activator. The activators of tetraacetyl ethylenediamine (TAED) and sodium nonanoyloxy benzene sulfonate (NOBS) have been applied into pulp bleaching successfully in recent years. In the hydrogen peroxide activator bleaching system, peracetic acid is produced, which has a stronger bleaching ability, when activator reacts with hydroperoxyl in alkaline solution (Zhao et al. 2003).

Therefore, the hydrogen peroxide activator bleaching system is essentially that of peracetic acid bleaching.

The use of TAED as an activator of H_2O_2 bleaching has been successfully used in cotton fabric bleaching (Hashem et al. 2003). The application of this process in pulp bleaching also has been studied for its outstanding advantages (Sain and Daneault 2009; Khristova et al. 2003; Hsieh et al. 2006). In this research, the H_2O_2/TAED process was employed in *Populus nigra* CTMP bleaching. The optimum bleaching process was confirmed and the bleaching mechanism was analysed.

EXPERIMENTAL

Materials

Populus nigra (five years) CTMP pulp was obtained from a company in the east of China (Shan Dong Hua Tai Group.). The pulp brightness was 47.2 %ISO. All chemicals used for bleaching were purchased from Beijing Chemical Reagent Company.

Chelation Pretreatment

To reduce the metal ion disturbance, the chelating process was employed before bleaching. Chelation of the pulp was conducted at 10% pulp consistency, pH 5.0, and 70^{o}C for 30 min, with 0.3% EDTA, 3% Na_2SiO_3, and 0.05 % $MgSO_4$ (the contents of all added chemicals are reported based on oven dry pulp).

Bleaching Process

Hydrogen peroxide/activator bleaching was performed in polyethylene bags using the following conditions: 10-20% pulp consistency, 1-5% H_2O_2, 1-4% NaOH, 0-1 molar ratio of TAED to H_2O_2, at 40-80 ^{o}C for 10-120min.

Orthogonal tests were conducted according to Table. 1 [L9(3^4)], as listed.

Table 1. Orthogonal Practice Form

Factor level	A Time (min)	B Temperature(^{o}C)	C H_2O_2 (%)	D T：P (molar ratio)
1	20	50	1	0.1
2	40	70	4	0.5
3	60	90	7	0.7

The bleach liquors were added into the pulp bags in the following order: deionized water, magnesium sulfate, sodium silicate, sodium hydroxide, TAED, and hydrogen peroxide. Then the polyethylene bag was sealed and was placed into a water bath at the design temperature. The spent liquor was filtered with a 200-mesh screen for collecting the fines when the bleaching finished. The filtered spent liquors were collected for residual peroxide and the final pH tests. The bleached pulps were used to make handsheets and the brightness, PC No.(yellowing value), absorption coefficient, and scattering coefficient of handsheets were tested according to methods in the literature (Shi and He 2003). The bleaching efficiency was obtained by the following formula:

$$\text{Bleaching efficiency} = \text{brightness gain}(\%) / H_2O_2 \text{ consumption}(\%)$$

Infrared Analysis

A Fourier transform infrared system (FTIR), Tensor 27 spectrometer was used. Lignin samples were prepared using the KBr disc technique. The following conditions were employed after the blank experiments: sample weight was 1.5mg, KBr weight was 150mg, disk thickness was 13mm, and the pressure was 10MPa. The dioxane lignins bleached by H_2O_2/TAED and H_2O_2 were investigated. The infrared red absorption spectra were recorded in the region of 4000-400cm^{-1}.

RESULTS AND DISSCUSSION

Orthogonal Experiments Analysis

Table 2 shows the bleaching conditions according to the experimental design in Table 1, and Table 3 lists the range analysis of four factors on brightness. Figure 1 shows the response curve of the factors relative to brightness.

According to the data listed in Table 3, it can be found that the optimum pulp brightness corresponded to factor A at level 3,factor B at level 2, factor C at level 3, and factor D at level 2.

Figure 1 shows that pulp brightness increased with increasing hydrogen peroxide charge. But the suitable hydrogen peroxide charge needs to be further confirmed.

Bleaching time was an important factor for pulp brightness. According to the curve in Fig. 1, the brightness increased with increasing time. Shen et al. (2008) studied the H_2O_2-TAED bleaching of Chinese fir and found that the bleaching rate of this system was fast. For Chinese fir CTMP, 97% of the bleaching reaction was finished in 30 min. Therefore, the suitable bleaching time was in range of 30 to 120 min for the H_2O_2-TAED system, while 180 to 300 min was needed for conventional H_2O_2 bleaching. Figure 1 shows that brightness gain from 20 min to 40 min was bigger than that from 40 min to 60 min, which indicated that the bleaching reaction was close to completion at 40 min for H_2O_2-TAED bleaching of *Populus nigra* CTMP. Therefore, the bleaching time of H_2O_2-TAED system should be controlled to 60 min.

The pulp brightness first increased and then decreased with the bleaching temperature increasing in H_2O_2-TAED bleaching process according to the curve in Fig. 1. The pulp brightness decreased when the temperature was over 70^{o}C, which indicated that most of H_2O_2-TAED bleaching reaction was completed at lower temperature and the bleaching rate was faster than conventional H_2O_2 bleaching. The elevated temperature increased side effects and decreased the resulting brightness. The optimum bleaching temperature of H_2O_2-TAED bleaching was 70^{o}C.

Table 2. Orthogonal Practice – Brightness

Factors	Time/min	Temperature/^{o}C	Charge of H_2O_2%	T : P
1	20	50	1	0.1
2	20	70	4	0.5
3	20	90	7	0.7
4	40	50	4	0.7
5	40	70	7	0.1
6	40	90	1	0.5
7	60	50	7	0.5
8	60	70	1	0.7
9	60	90	4	0.1

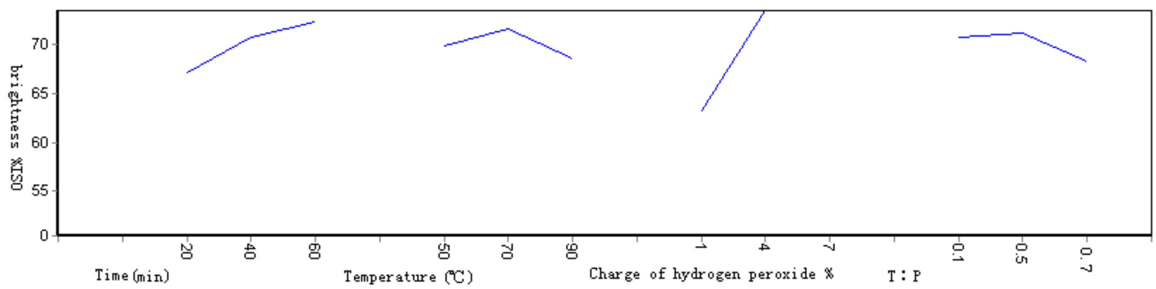

Fig. 1. Response curves

Table 3 and Fig. 1 show that the molar ratio of TAED to H_2O_2 had a significant effect on brightness. Either an excessively low or high charge of activator decreased the brightness.

Zhao et al. (2003) found that the molar ratio of TAED to H_2O_2 was 0.5 in the H_2O_2-TAED bleaching system. But Leduc et al. (1998) concluded that the ratio of 0.3 was suitable for TMP bleaching.

From Fig.1 it can be found that the brightness was best when the ratio was 0.5, but the brightness gain was small when the ratio increased from 0.1 to 0.5. This indicated that further experimentation is needed to confirm the optimum ratio.

Hydrogen Peroxide Charge Effects on H_2O_2/TAED Bleaching

As shown in Figs. 2 to 4, the pulp brightness increased with increasing hydrogen peroxide charges even though the increasing amplitude decreased when the charge was over 4%. This can be explained by saying that the chromophoric groups of lignin decreased due to the oxidation by increasing amounts hydrogen peroxide and made the brightness improve. The bleaching cost is increased if the brightness gain depends merely on increasing peroxide charge as the bleaching efficiency decreased according to Fig. 4.

Consequently, the charge of H_2O_2 cannot be increased without limitation. From the above analysis, it can be concluded that the usage of 4~5% H_2O_2 was suitable for H_2O_2/TAED bleaching.

Table 3. Range Analysis of Brightness

Factors	Bleaching time min	Bleaching temperature °C	Charge of H_2O_2 %	T : P	Brightness
1	20	50	1	0.1	60.9
2	20	70	4	0.5	73.1
3	20	90	7	0.7	67.3
4	40	50	4	0.7	72.3
5	40	70	7	0.1	76.5
6	40	90	1	0.5	63.6
7	60	50	7	0.5	76.7
8	60	70	1	0.7	65.2
9	60	90	4	0.1	75.0
Average value:1	67.1	70.0	63.2	70.8	
Average value:2	70.8	71.6	73.5	71.1	
Average value:3	72.3	68.6	73.5	68.3	
Range value	5.2	3.0	10.3	2.8	

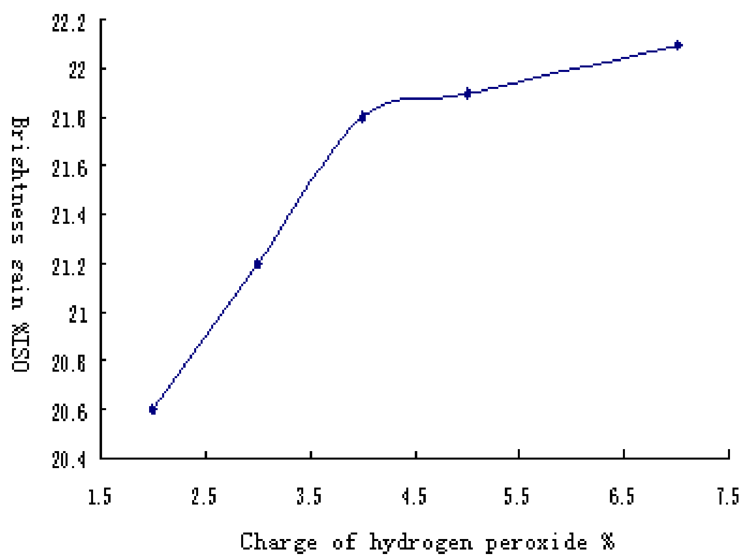

Fig. 2. Effect of H_2O_2 dosage on pulp brightness

The absorption coefficient reflects the ability of light to transform into other energies, which is mainly dependent on the contents of chromophoric groups in pulp and closely relates to bleaching methods and brightness reversion. Table 4 indicates that the absorption coefficient decreased with increasing peroxide level, which mainly is due to the reduced content of the chromophoric groups in lignin. The scattering coefficient mainly correlates with the fiber surface, the density of the pulp sheet, and the interfaces between the fibers and air. Compared to absorption coefficient, the scatter coefficient was less influenced by bleaching.

Table 4. Effects of H_2O_2 Dosages on Bleaching

Charge of H_2O_2 %	Charge of NaOH %	PC No.	Bleaching efficiency	Absorption coefficient $M^2 \cdot kg^{-1}$	Scatter coefficient $M^2 \cdot kg^{-1}$
2	2	3.12	3.75	1.50	52.53
3	2	2.82	3.21	1.30	46.81
4	2	2.72	3.06	1.19	52.49
5	2	2.18	2.81	1.14	53.89
7	2	2.04	2.77	0.93	55.11

Other bleaching conditions: bleaching time 60min, temperature 70^oC,T:P=0.5.

The Charge of NaOH Effects on H_2O_2/TAED Bleaching

Alkali is needed to activate hydrogen peroxide by forming hydroperoxide anion, which was reacted with TAED to generate the stronger bleaching chemical of peracetic acid. On the other hand, too high concentration of the hydroperoxide anions causes decomposition of hydrogen peroxide and brightness reversion (Zeinaly et al. 2009). Therefore, the optimum NaOH charge should be confirmed in H_2O_2/TAED bleaching.

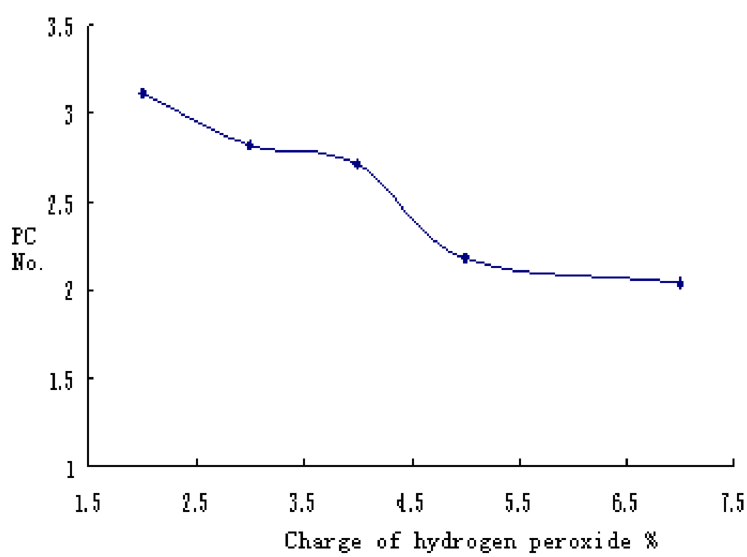

Fig. 3. Effects of H_2O_2 dosages on PC No.

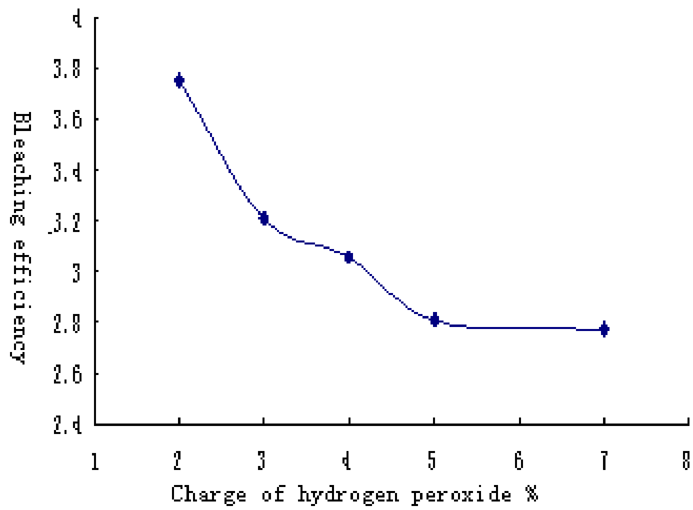

Fig. 4. Effects of H_2O_2 dosages on bleaching efficiency

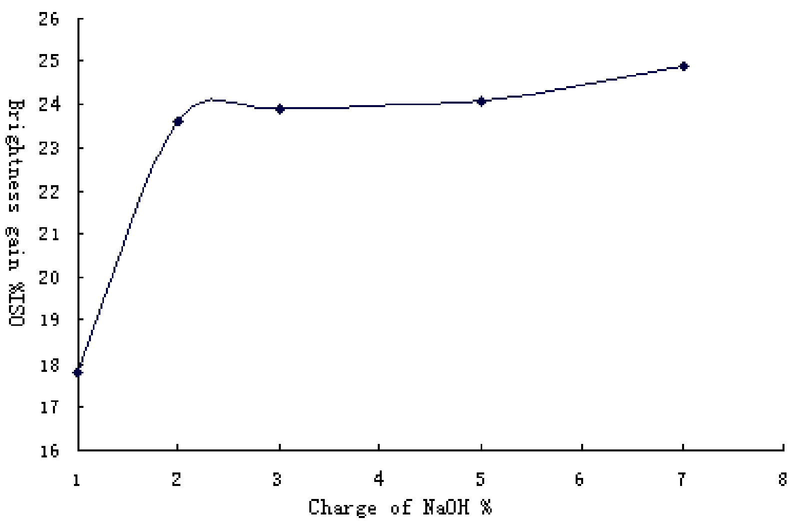

Fig. 5. Effects of NaOH dosages on pulp brightness

As shown in Fig. 5 and Table 5, the pulp brightness increased significantly with increasing NaOH charges. For instance, the brightness value was increased by 5.8 %ISO as the NaOH charge increased from 1% to 2%. But the brightness only increased 1% ISO as the NaOH charge increased from 3% to 7%. The peracetic acid produced in H_2O_2/TAED system contributed to the increase of pulp brightness. On the other hand, the peracetic acid also decomposed according to the following modes (Deng and Feng 2005).

$$R\text{-}COOOH + OH^- \rightarrow R\text{-}COO^- + H_2O_2$$
$$2R\text{-}COOO^- \rightarrow 2R\text{-}COO^- + O_2$$
where R = alkyl group or CH_3.

In most cases, the second reaction is the main reaction that causes the decrease of peracetic acid and the bleaching efficiency. From the above analysis, it can be found that the suitable alkali charge can increase the activating effect of TAED and improve the bleaching efficiency, which means the best bleaching results can be obtained. As shown in Table 5 and Fig. 7, a charge of 2% alkali was suitable and the bleaching efficiency was also relatively high at this charge.

Table 5. Effects of NaOH Dosages on Bleaching

Charge of H_2O_2 %	Charge of NaOH %	Brightness gain %ISO	PC No.	Bleaching efficiency
4	1	17.8	1.35	2.83
4	2	23.6	1.87	3.06
4	3	23.9	1.98	3.16
4	5	24.1	2.45	3.10
4	7	24.9	2.46	3.03

Other bleaching conditions: bleaching time 60min, temperature 70 ^{o}C,T:P=0.5

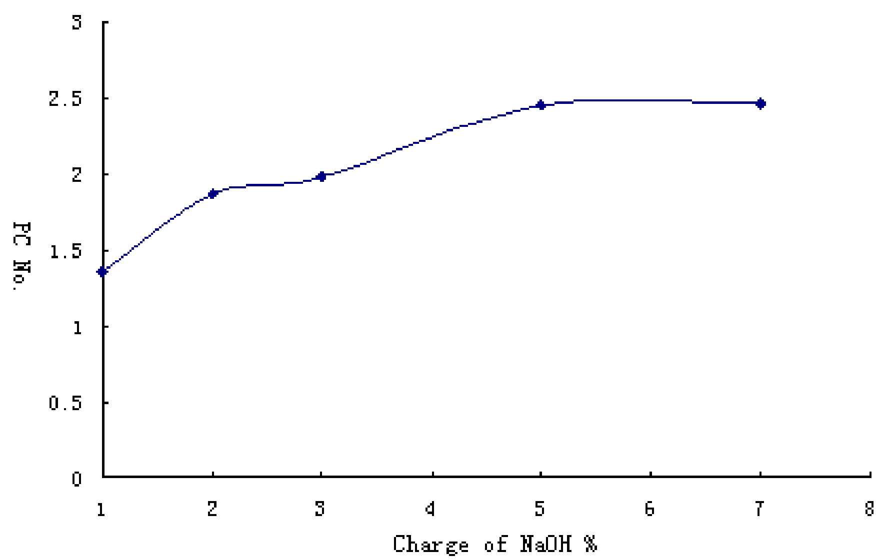

Fig. 6. Effects of NaOH dosages on PC No.

The Molar Ratio of TAED to H_2O_2 Effects on H_2O_2/TAED Bleaching

Theoretically, the molar ratio of TAED to H_2O_2 should be 0.5 according to the reaction mechanism of two chemicals. But researchers have suggested other values for the best ratio under different bleaching conditions (Zhao et al. 2003; Leduc et al. 1998).

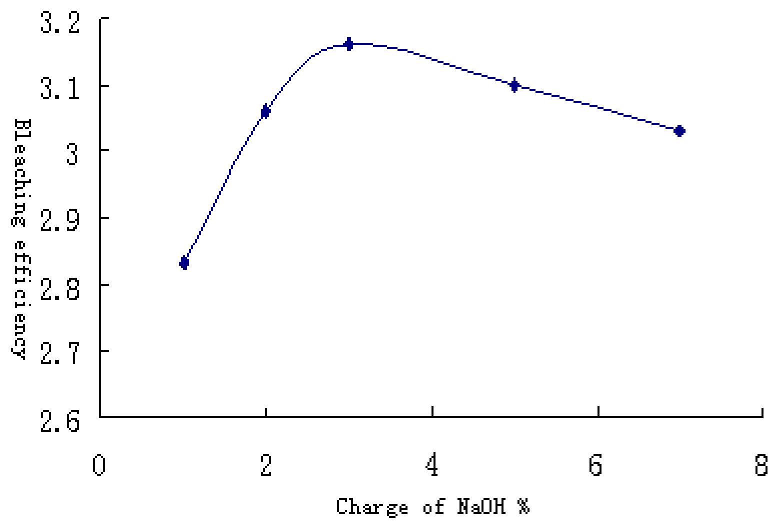

Fig. 7. Effects of NaOH dosages on bleaching efficiency

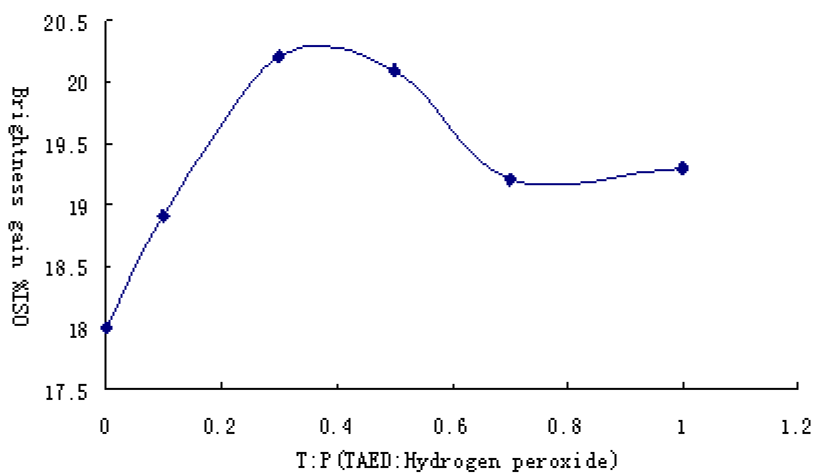

Fig. 8. Effects of TAED dosages on pulp brightness

From the data in Fig. 8 it was found that the best bleaching results were obtained not at the ratio of 0.5, as was indicated by the results of the orthogonal experiments, but at 0.3, which means the highest peracetic acid concentration was achieved at this ratio. Use of an excessively high ratio cannot increase the brightness further, which can be explained as follows: there is a balance between two reactions in the H_2O_2/TAED bleaching system, the production reaction and the decomposition reaction of peracetic acid. The production rate of peracetic acid was accelerated when the TAED charge was large, which made the peracetic acid decompose without reacting with the pulp, and the bleaching efficiency decreased as well.

As shown in Table 6, the absorption coefficient decreased first and then increased, which is mainly caused by changes in the content of chromophoric groups. A suitable ratio made the chromophoric groups decrease, which contributed to the brightness increase, while the too high TAED concentration may have produced new chromophoric groups and caused the observed brightness decrease.

Table 6. Effects of TAED Dosages on Pulp Brightness

T : P	PC No.	Bleaching efficiency	Absorption coefficient $M^2 \cdot kg^{-1}$	Scatter Coefficient $M^2 \cdot kg^{-1}$
0	6.10	2.20	0.89	47.77
0.1	2.12	2.33	0.87	50.38
0.3	2.10	2.96	0.84	51.86
0.5	1.99	3.06	0.90	48.62
0.7	2.05	2.49	0.94	52.39
1.0	2.10	2.38	1.01	47.09

Other bleaching conditions: bleaching time 60 min, temperature 70^{o}C, H_2O_2 4 % and NaOH 2%.

From the analysis above, it can be concluded that the optimum molar ratio of TAED to H_2O_2 in H_2O_2/TAED bleaching system was 0.3, not the ratio of 0.5, as was indicated by the results of the orthogonal experiments.

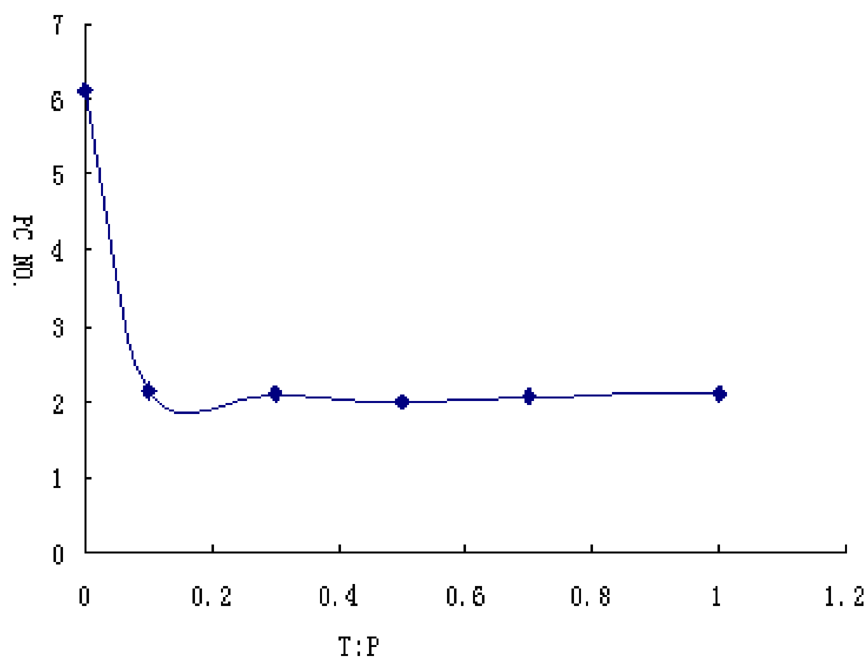

Fig. 9. Effects of TAED dosages on pulp PC No.

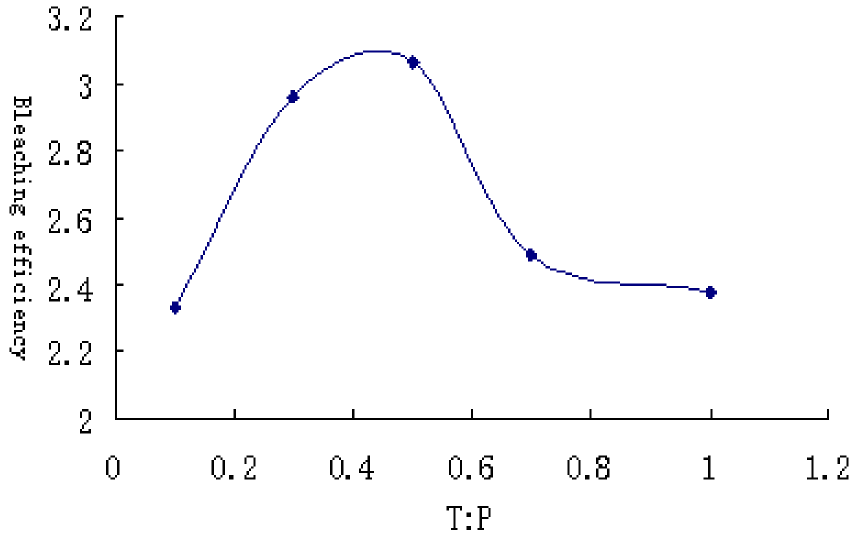

Fig. 10. Effects of TAED dosage on bleaching efficiency

As shown in Table 6 and Fig. 9, the yellowness of pulp with H_2O_2/TAED was lower than that of conventional H_2O_2 bleached pulp, which meant the brightness stabilization was improved by adding the activator.

FTIR Analysis

FTIR spectroscopy was used to demonstrate the bleaching effects in the lignins, comparing the conventional H_2O_2 bleaching and H_2O_2/TAED bleaching processes.

The baseline method was used to quantify the contents of the chromophoric groups in lignins. The absorption peak in 1506 cm^{-1} was taken as the internal standard, and the connection line of 700 cm^{-1} to 1800 cm^{-1} was taken as the baseline. The data are listed in Table 7.

The absorbance peaks in the 1740-1701 cm^{-1} region were attributed to the stretching of C=O stretching of the acetyl group or the ester linkage of carboxylic group of lignins (Sgriccia et al. 2008; Tserki et al. 2005; Alemdar and Sain 2007). As shown in Table 7, the absorption of H_2O_2/TAED bleached lignin at this point was more than that of H_2O_2 bleached lignin. This suggested that the H_2O_2/TAED bleaching system can decrease the content of acetyl group more than conventional H_2O_2 bleaching, which could result in the higher brightness.

The absorption at 1640 cm^{-1} was attributed to the stretching vibration of conjugated carbonyl groups. Compared to the H_2O_2 bleached lignin, a smaller relative absorption was obtained in H_2O_2/TAED bleached lignin, which indicated that the amount of conjugated carbonyl groups was effectively reduced in H_2O_2/TAED bleaching.

The peak at 1595 cm^{-1} was associated to the aromatic skeleton vibration and C=O stretching vibration. The data in Fig. 7 show that the H_2O_2/TAED bleached lignin had a smaller relative absorption value, which indicated that H_2O_2/TAED bleaching can decrease the C=O content further or may decomposed the aromatic ring.

Table 7. Tentative Assignations of the Bands in the Infrared Spectrum Analysis of Bleached Lignins of Populus nigra CTMP

Absorption cm^{-1}	Absorption assignments	Relative absorption in H_2O_2 bleached lignin Ai/A_{1506}	Relative absorption in H_2O_2/TAED bleached lignin Ai/A_{1506}
1705	Non-conjugated carbonyl group	0.30	0.25
1640	Conjugated carbonyl group stretching vibration	0.41	0.39
1595	C=O stretching vibration and aromatic skeleton vibration	0.98	0.85
1506	Aromatic skeleton vibration	1.00	1.00
1462	C-H bending vibration; CH_3, CH_2 bending vibration	1.15	0.86
1330	The bending vibration of C-H and C-O group of the aromatic ring	0.76	0.66
1229	C-O vibration in aromatic ring	1.04	0.97
1123	CH_3 deformation vibration, C-O-C stretching vibration, C-OH stretching vibration(S)	1.54	1.32
1033	Dialkyl ether bond in guaiacyl-type lignin	0.83	0.79

The absorbance peak at 1330 cm^{-1} is attributable to the bending vibration of C-H and C-O group of the aromatic ring (Troedec et al. 2008; Nacos et al. 2006). The relative absorption of H_2O_2/TAED lignin decreased to 0.66 from 0.76 in H_2O_2 lignin, which indicated that the oxidation ability of H_2O_2/TAED bleaching was larger than that of H_2O_2 bleaching.

The peaks at 1123 cm^{-1} and 1033 cm^{-1} were associated to ether-bonds of lignins (Silva et al. 2008). The absorptions of H_2O_2/TAED bleached lignin at these two points were smaller than those of H_2O_2 bleached lignin, which suggested that H_2O_2/TAED bleaching made the ether bonds fracture further.

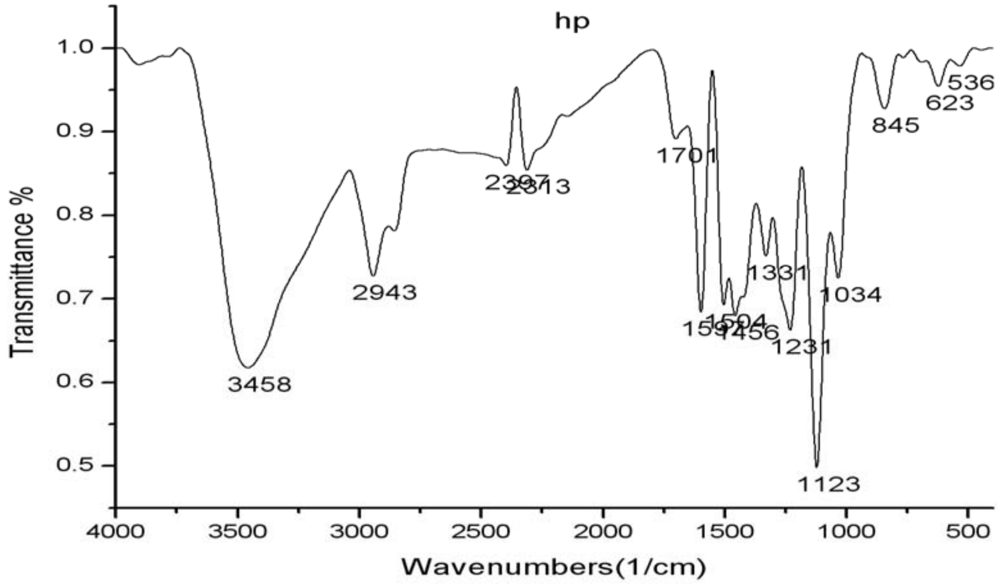

Fig. 11. Infrared Spectrum of H_2O_2 bleached lignin

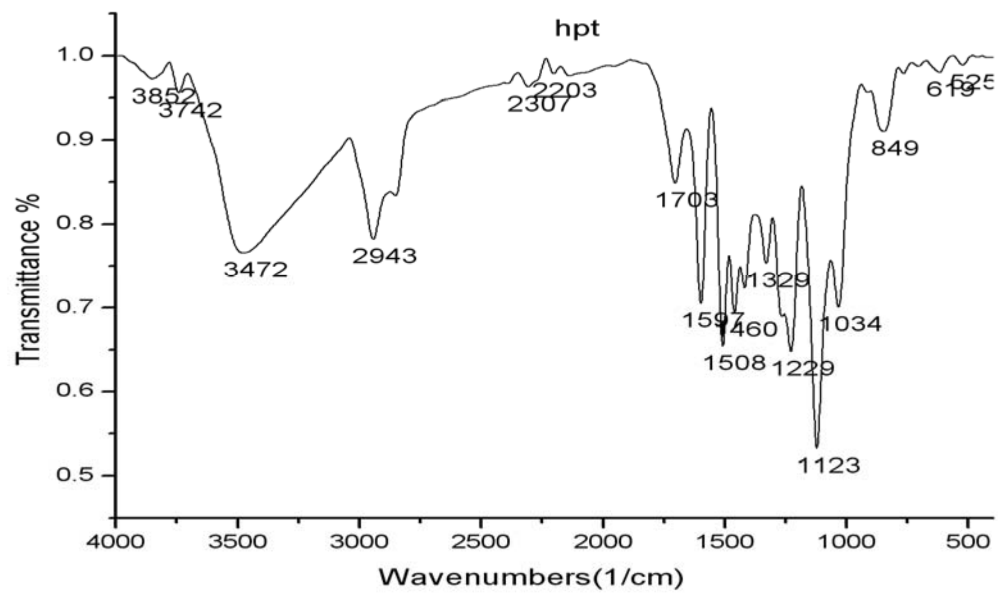

Fig. 12. Infrared spectrum of H_2O_2/TAED bleached lignin

CONCLUSIONS

The optimum bleaching conditions were confirmed as follows: the pulp consistency was 10%, the H_2O_2 charge was 4%, the NaOH charge was 2 %, and the molar ratio of TAED to H_2O_2 was 0.3. The optimum bleaching temperature was 70^{o}C, and the bleaching time was 60 min. A pulp brightness gain of 23.6 % ISO was achieved with the above bleaching conditions.

From the analysis of the FTIR spectrum, it was found that the H_2O_2/TAED bleaching system can decrease carbonyl group further than that of H_2O_2 bleaching, which contributed to the higher pulp brightness. The H_2O_2/TAED bleaching process had stronger oxidation ability on lignin than H_2O_2 bleaching.

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