CHARACTERIZATION OF BAMBOO SCMP ALKALINE EXTRACTIVES AND THE EFFECTS ON PEROXIDE BLEACHING

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The compositions of alkaline extractives in bamboo sulfonated chemi-mechanical pulps (SCMP) were analyzed by UV spectroscopy and gas chromatography-mass spectrometry (GC-MS), and their effects on peroxide bleaching were studied. The extractives were composed of short-chain aliphatic compounds, phenols, and fatty acids, of which phenols were the major components. The amount of extractives was increased with the dosage of NaOH, and correspondingly, the bleachability of the extracted pulp was improved. When 3.5% NaOH was used, the brightness gain was 5.83%ISO, and the post-color (PC) number was decreased by 55.7%. The phenol compounds, which might easily generate conjugated structures, may play an important role in bleachability of bamboo SCMP and brightness stability of pulp.

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INTRODUCTION

Bamboo is a fast-growing plant widely distributed in the subtropical zone. It is an important raw material in China for manufacturing chemical pulps with high strength properties. Compared with chemical pulps, high yield pulps (HYP) have advantages of lower cost, higher yield, and better optical properties; however, HYP from bamboo is still not commercially available. The difficulty in bleaching is the bottleneck that hinders the industrial production and application of bamboo HYP. It has been reported that the brightness of bamboo sulfonated chemimechanical pulps (SCMP) can hardly reach 75%ISO by hydrogen peroxide bleaching (Huang et al.2006, Li et al. 2009); meanwhile HYP from wood species, such as aspen, can be bleached with peroxide to over 80%ISO (Kong et al. 2003).

Low brightness and poor brightness stability are the major problems for bleached bamboo HYP. The high lignin content in HYP is believed to be the main reason for the problems. Meanwhile, extractives also play an important role in bleaching of HYP, even if present in low amounts. Phenolic constituents in extractives, such as tannins, could react with iron ions and form strongly colored complexes, resulting in decreased brightness of HYP (Friman et al. 2004). The influence of other phenols, such as vanillin, on brightness of bleached HYP has also been reported (Peart and Ni 2001). The condensation of phenols occurred during refining has been considered as a dominant mechanism contributing to the dark coloration of HYP (Johansson et al. 2000; Keating et al. 2006). Therefore, extraction of phenol extractives as a pre-step prior to peroxide

bleaching could be a practical approach for further promoting the brightness and brightness stability of bleached bamboo HYP.

However, until now the compositions of the extractives in bamboo HYP and their effects on pulp bleachability have not yet been fully understood. In this study, the composition of alkaline extractives in bamboo SCMP was analyzed by UV spectroscopy and gas chromatography-mass spectrometry (GC-MS). The effects of extractives, especially phenol components, on peroxide bleaching were also considered.

EXPERIMENTAL

Materials

The bamboo chips cut from 2 or 3-year *Neosinocalamus Affinis* were purchased from a pulp mill in Guangxi, China. The chips with size of $20 \times 20 \times 6$ mm^3 were selected, washed and air-dried before pulping.

SCMP Preparation

Bamboo SCMP was prepared in the lab with sulphonated pretreatment and refining. First, the chips were sulphonated in a laboratory reactor (M/K cooking system) under standard conditions as follows (based on o.d. weight of bamboo chips): Na_2SO_3 15%, NaOH 2%, maximum temperature 130 ºC, resistance time at maximum temperature 120 min, and liquor-to-solid ratio 5. Then, the sulphonated chips were refined on a laboratory single-disc refiner with the following the operating conditions: feedstock consistency 15%, 3-stage refining disc clearance 0.50 mm, 0.15 mm, and 0.15 mm, respectively. The brightness of the pulp was 24.86 %ISO.

Alkaline Extraction and Peroxide Bleaching

Alkaline extraction conditions were selected carefully to minimize the influence of soda-lignin reaction, which were according to the E-stage in the conventional bleaching sequence DEQP. The alkaline extraction was carried out in the polythene bags under the conditions listed in Table 1. After that a filtration was performed to separate pulp from extraction liquor. Then the pulp was thoroughly washed with deionized water at room temperature. The extraction liquid was analyzed as described after the table.

Table 1. Alkaline Extraction Conditions

Sample	Temperature (ºC)	Time (min)	NaOH dosage* (%)	Consistency (%)
1#	50	30	0.5	5
2#	50	60	2.0	10
3#	50	90	3.5	15
4#	70	30	2.0	15
5#	70	60	3.5	5
6#	70	90	0.5	10
7#	90	30	3.5	10
8#	90	60	0.5	15
9#	90	90	2.0	5

* NaOH dosage was based on the o.d. weight of the pulp

The washed pulp was then bleached with chelating (Q) and peroxide bleaching (P). The conditions for chelation were as follows: consistency 10%, EDTA 0.3%, initial pH 3, temperature 60 ºC, and time 60 min (Q). The conditions for bleaching were consistency 15%, NaOH 3%, Na_2SiO_3 3%, H_2O_2 6%, temperature 80 ºC, time 180 min (P). The pulp without alkaline extraction was bleached as a control, following the same conditions as described above.

The brightness and brightness reversion of bleached pulp were determined following the TAPPI Method T452 and UM200. The post-color (PC) number was calculated according TAPPI TIS 017-10.

Content of Alkaline Extractives

The water in the extraction liquid was removed by rotary evaporation and vacuum desiccation, sequentially. Then the extractives were quantified gravimetrically. The results were expressed as percent of the o.d. weight of pulp.

UV Spectroscopy

The alkaline extraction liquor was diluted to an appropriate concentration with deionized water for the UV spectra measurement. Also, the extraction liquor was acidified to pH 2 with sulfuric acid for comparison. UV spectra of extractives were recorded on an Agilent 8453 spectrophotometer using a 1 cm quartz cell. Since the concentration of extractives varies with extraction conditions and dilution times, the UV spectrum for each sample may not be comparable to each other because of the significant difference of absorbance. Therefore, a process of normalization was carried out by assuming that absorbance at 280 nm was 1 for each UV spectrum.

Gas Chromatography-Mass Spectrometry (GC-MS)

Prior to GC-MS analysis, the alkaline extractives samples were silylated by using 99% bis-(trimethylsilyl)-trifluoroacetamide (BSTFA) and 1% trimethyl-chlorosilane (TMS) in the presence of pyridine. 1 mg of dried extractives was weighed accurately, and then dissolved into 1 mL pyridine. The extractives solution was added with 0.2 mg heneicosanoic acid as internal standard and 200 μL silylanization agent (99%BSTFA+1% TMS) to start the reaction. After being kept at room temperature for 60 min, the reaction mixture was directly analyzed by using GC-MS.

GC-MS analysis of the silylated extractives from the bamboo SCMP were performed in an Agilent 7890A/5975C GC-MS system, equipped with a DB-5HT capillary column (25 m × Φ 0.25 mm, 0.11 μm film thickness) from J&W Scientific and an ion-trap detector running in an electron impact (EI) mode. For all extractives, 1 μL of silylated sample was injected by an Agilent auto-sampler with a split of 1:20 and an injector temperature of 280 ºC. The temperature of the capillary column was started at 50 ºC and held for 3 min. Then, it was raised to 200 ºC at a rate of 15 ºC/min and held for 1 min. Finally, the temperature was raised to 360 ºC at a rate of 6 ºC /min. The temperature of the transfer line to the ion trap detector was 280 ºC and the scan range was 50-650 *m/z.*

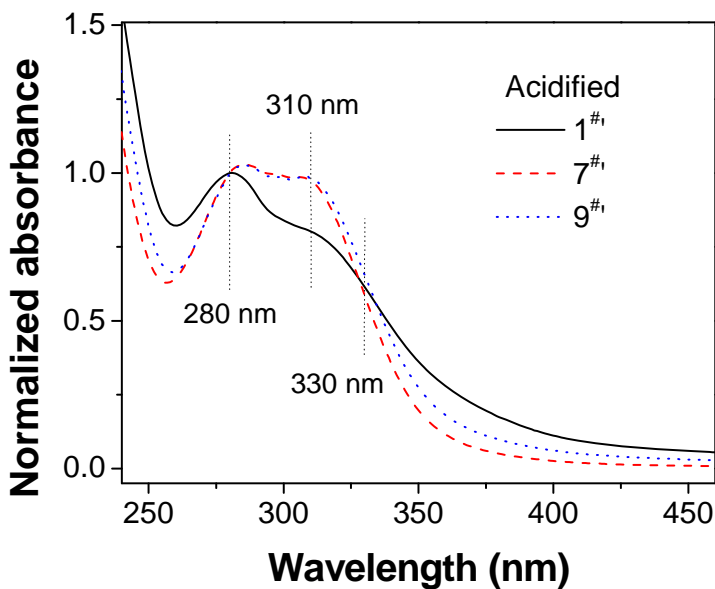The compounds recorded by GC-MS were identified by unequivocal matches with mass spectra of NIST08 libraries.

RESULTS AND DISCUSSION

UV Spectra of Alkaline Extractives

The normalized UV spectra of the extractives in both base and acid media are shown in Fig. 1.
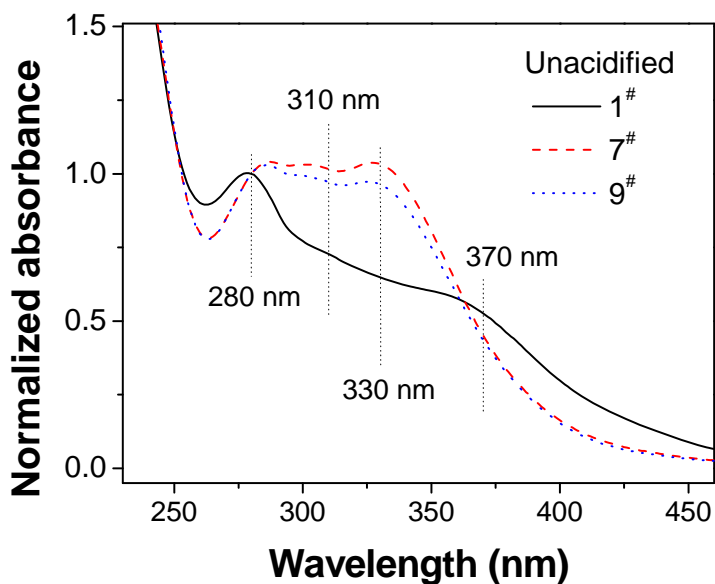
a

b

Fig. 1. UV spectra of extractives before (a) and after (b) acidification

As the spectra of alkaline extractives samples $1^{\#}$, $7^{\#}$ and $9^{\#}$ showed, there was a big difference between samples not only under various extraction conditions but also at different pH for the same extractives. Samples $7^{\#}$ and $9^{\#}$ exhibited higher absorbance between 280 nm and 370 nm, especially around 280 nm and 330 nm, with significant decrease above 330 nm. However, the spectrum of sample $1^{\#}$ was different, exhibiting a peak at 280 nm and lower absorbance at 330 nm than that of $7^{\#}$ or $9^{\#}$. Compared with unacidified samples, the absorption changes of all three acidified extractives were similar. There was a dramatic absorbance decrease around 330 nm and absorption shift to the short wavelength of 280 nm. Meanwhile, only small changes of absorbance occurred near 310 nm.
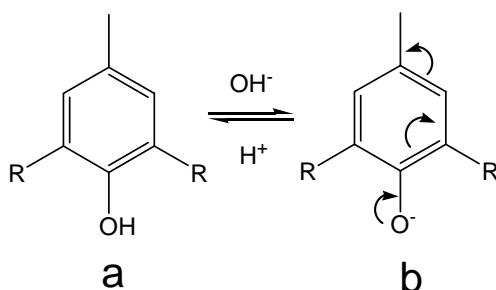

Fig. 2. Diagram of structural changes of phenols before (a) and after (b) acidification
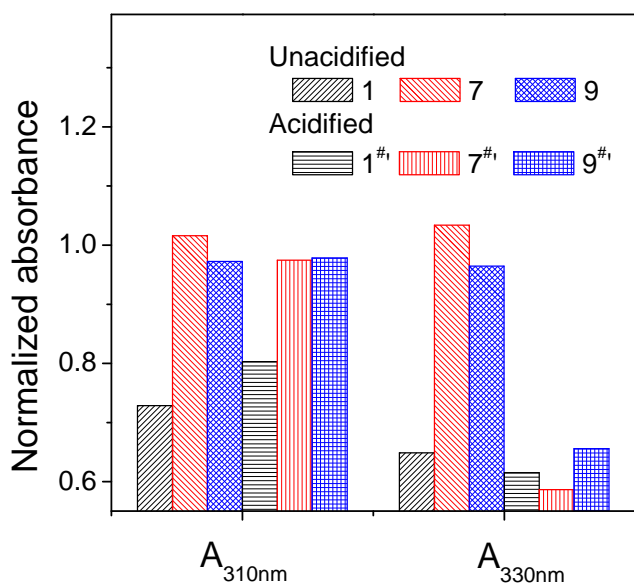

Fig. 3. Normalized absorbance of acidified and unacidified extractives

According to an earlier report (Johansson et al. 2000), the absorption near 280 nm was attributed to some kinds of phenols, and absorptions around 330 nm and 390 nm were from ketones and quinones, respectively. There were less phenols and ketones in samples $1^{\#}$ due to its milder extraction conditions, while $7^{\#}$ and $9^{\#}$ contained more phenols and ketones, which could form conjugated systems and generate darkly colored

structures. After acidification, conjugated systems were changed as shown in Fig. 2, which caused the decrease of absorbance at 330 nm and a red shift of the spectra. Comparing of the normalized absorbance at 310 nm with that at 330 nm after acidification (as shown in Fig. 3), all three samples showed similar trend at 310 nm, but quite different at 330 nm. Decrease of normalized absorbance at 310 nm for sample $7^{\#}$ was the highest (over 50%) followed by sample $9^{\#}$ (about 40%). This indicates that there were large amounts of phenols and ketones, which are sensitive to pH, present in the bamboo SCMP, and phenols were probably the major substances.

GC-MS Analysis of Alkaline Extractives

Structural analysis of compounds in the extractives by GC-MS was feasible, since this method has been widely used to analyze the extractives in pulps and phenols in water (del Rio et al. 2009). As the total ions chromatogram of alkaline extractives (Fig. 4) showed, many compounds were identified in the alkaline extractives, which could be classified into three types: short chain aliphatic compounds, phenols, and fatty acids. The gas chromatograms indicated there was significant difference between compositions of extractives from experiment $1^{\#}$, $7^{\#}$, and $9^{\#}$. More substances were identified in $7^{\#}$ and $9^{\#}$, suggesting that the more intense conditions were used, the more extracts could be dissolved out.
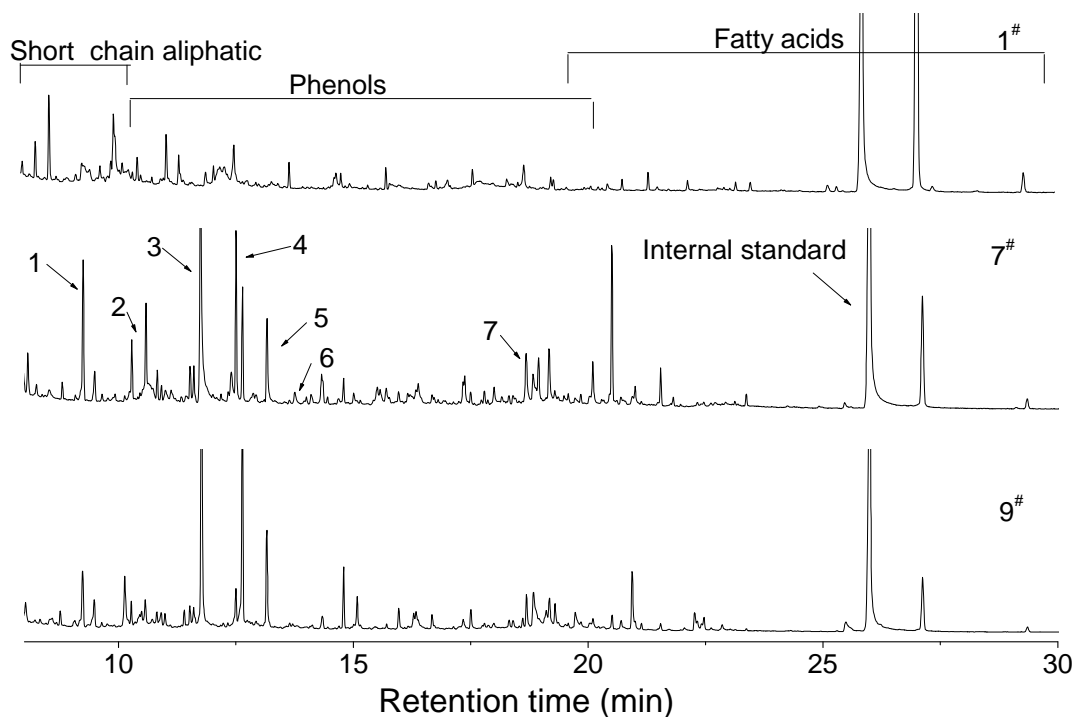

Fig. 4. The total ions chromatogram of alkaline extractives

The major compositions of alkaline extractives obtained from GC-MS are listed in Table 2. Obviously, phenols were the dominant compounds in the alkaline extractives, which was different from those organic solvents extractives containing mainly fatty acids and sterols as reported in the literature (Freire et al. 2006). The major phenols identified

were 2-methoxy-4-vinylphenol (5), 3,5-dimethoxy-4-hydroxy-phenylacetic acid (7), 3-(4-hydroxyphenyl)-2-propenoic acid, 3-(4-hydroxyphenyl)-acrylic acid, and 1,4-benzenedicarboxylic acid. Other phenols present in fewer amounts such as 4-hydroxybenzaldehyde (6) were also detected. In addition, other compounds, such as 2-hydroxypropanoic acid (1), 3-hydroxylpropanoic acid (2), 2,3-dihydrobenzofuran (3), glycerol (4), and so on were identified, as shown in Fig. 5.
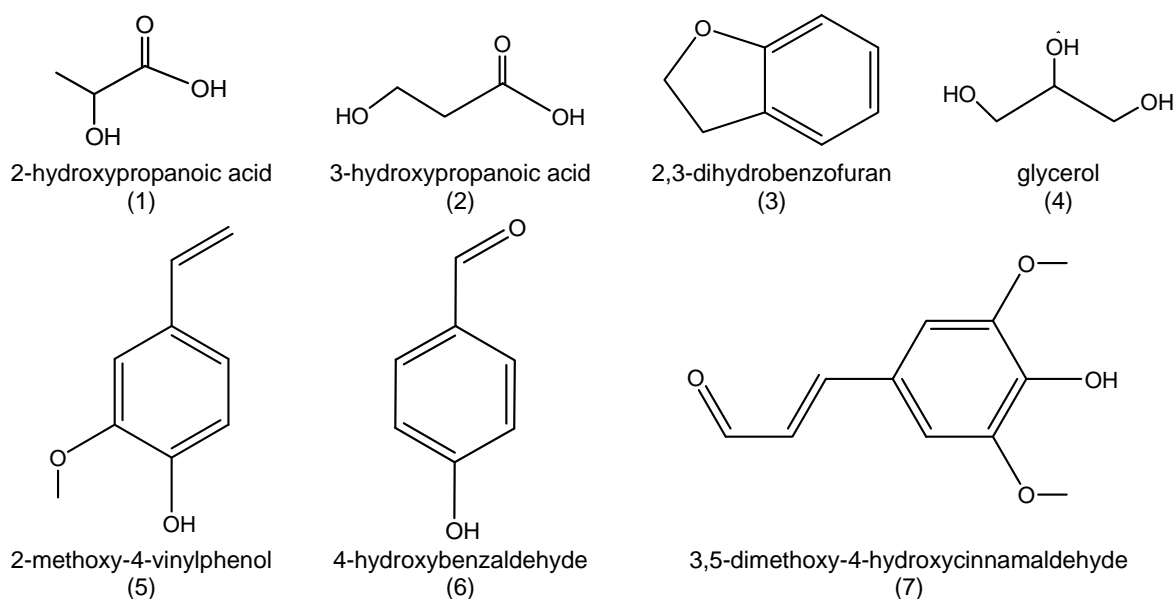
2-hydroxypropanoic acid
(1)

3-hydroxypropanoic acid
(2)

2,3-dihydrobenzofuran
(3)

glycerol
(4)

2-methoxy-4-vinylphenol
(5)

4-hydroxybenzaldehyde
(6)

3,5-dimethoxy-4-hydroxycinnamaldehyde
(7)

Fig. 5. Structures of several compounds identified in alkaline extractives

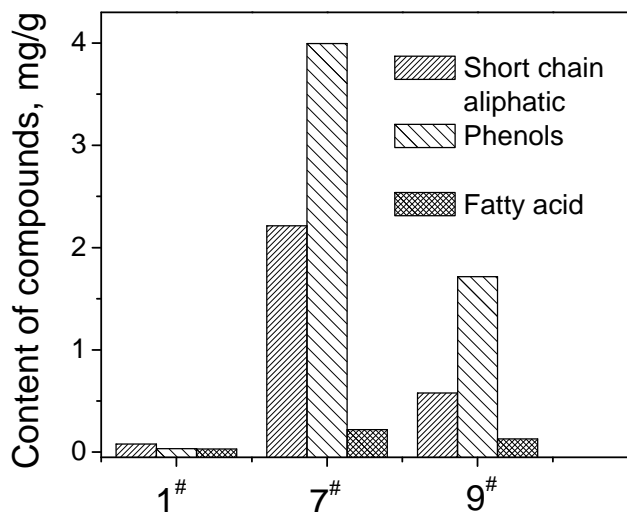The contents of the three components in different extractives were compared, and results are shown in Fig. 6.

Fig. 6. Content of three extractives components in bamboo SCMP

In sample $1^{\#}$, relatively low amounts of phenols were identified compared to the content of short-chain aliphatic compounds (about 55%). But in samples $7^{\#}$ and $9^{\#}$, there were large amounts of phenols, which contributed as the major compounds in extractives (about 62% and 71%, respectively).

Table 2. Major Components of Alkaline Extractives, mg/g (o.d. pulp)

Compositions	Peak No.	Content		
		$1^{\#}$	$7^{\#}$	$9^{\#}$
2-methylmalonic acid		0.0410	0.1864	0.0479
2-hydroxypropanoic acid	1	—	0.4819	0.1305
2-hydroxyacetic acid		—	0.1174	0.0718
2-hydroxybutanoic acid		0.0045	0.2407	0.0468
3-hydroxypropanoic acid	2	0.0070	0.4181	0.0731
3-Hydroxybutyric acid		0.0063	0.1052	0.0363
2-Hexenoic acid		—	0.1301	0.0580
2,3-dihydro-Benzofuran	3	—	1.5714	0.6544
Glycerol	4	0.0105	0.5333	0.0987
2-Methoxy-4-vinylphenol	5	—	0.3548	0.2021
2,6-dimethoxy-Phenol		—	—	0.0125
Nonanedioic acid		0.0059	—	0.0129
4-hydroxybenzaldehyde	6	0.0093	0.0255	—
3-hydroxy-4-methoxy- Benzaldehyde		—	0.1656	0.0318
2-methoxy-4-propyl- Phenol		—	—	0.0511
2,4-bis(1,1-dimethylethyl)-Phenol		—	0.0453	0.0119
Ethylhomovanillate		—	0.0444	0.0433
3-Hydroxy-4-methoxybenzoic acid		—	—	0.0383
4-Methyl-2,5-dimethoxybenzaldehyde		—	0.1346	0.0254
2,4'-Dihydroxy-3'-methoxyacetophenone		—	0.0382	0.0306
4-hydroxy-3,5-dimethoxy-Benzaldehyde		—	0.0505	0.0384
2,6-dimethoxy-4-(2-propenyl)-Phenol		0.0070	0.1051	0.0125
1-(4-hydroxy-3,5-dimethoxyphenyl)-Ethanone		—	0.0392	0.0182
4-Hydroxy-2-methoxycinnamaldehyde		—	0.0403	0.0188
Tetradecanoic acid		0.0094	0.0489	0.0307
3,5-Dimethoxy-4-hydroxyphenylacetic acid		—	0.2918	0.0689
3-(4-hydroxyphenyl)-2-Propenoic acid		0.0021	0.2213	0.1847
1,4-Benzenedicarboxylic acid		0.0158	0.2240	—
4-hydroxy-3,5-dimethoxy-Benzoic acid		—	—	0.0635
3-(4-hydroxy-3-methoxyphenyl)-2-Propenoic acid		—	0.0616	0.0584
3-(4-hydroxyphenyl)-acrylic acid		—	0.5417	0.0274
3,5-Dimethoxy-4-hydroxycinnamaldehyde	7	—	0.0396	0.1247
Hexadecanoic acid		0.0110	0.1302	0.0407
Octadecanoic acid		0.0037	0.0398	—
Eicosanoic acid		—	—	0.0448

Effect of Alkaline Extraction on Pulp Bleaching

Alkaline extraction can be an effective method for improving the bleachability of bamboo SCMP. The effects of extraction conditions including temperature, time, NaOH dosage, and pulp consistency on brightness of pulp were investigated by L9 (3×4) orthogonal experiments. The experimental results and influences of four factors are shown in Tables 3 and 4, respectively. About 1.7 to 9.0 g extractives could be removed per 100 g of pulp, depending on the experimental conditions. Correspondingly, a brightness gain of bleached pulps could be achieved ranged from 0.90 %ISO to 5.83 %ISO, and the PC number of bleached pulp could be reduced by up to 55.7%. The F-test of orthogonal designs in Table 4 showed that both the amount of extractives dissolved in alkaline and the brightness of bleached pulp was strongly dependent on the NaOH dosage.

Table 3. Results of L9 (3×4) Orthogonal Experiments

	Dissolved extractives (%)	Brightness (%ISO)	PC number
1	1.8	57.88	2.02
2	4.7	60.85	1.75
3	7.0	61.80	2.43
4	5.3	59.37	1.88
5	5.6	61.19	1.98
6	2.6	59.69	1.96
7	9.0	62.81	1.40
8	1.7	58.41	2.12
9	2.0	60.35	2.88
Control	-	56.98	3.16

Table 4. F-test of Different Factors

	Dissolved extractives	Brightness	PC number
Temp.	0.01	0.44	0.17
Time	0.31	0.59	1.98
NaOH	3.06	3.27	0.24
Cons.	0.62	1.31	1.62

F-test was calculated according to accepted statistical methods
F critical value (0.9) is 3.16 in this case

The relationship between the removal of alkaline extractives and the brightness gain of bleached pulp is shown in Fig. 7. There was an obvious improvement in the brightness of peroxide-bleached pulp increased with the amount of extractives removed from the pulp. The amount of the alkaline-dissolved substances in sample 7[#], as well as brightness gain of bleached pulp was the highest, followed by samples 9[#] and 1[#].
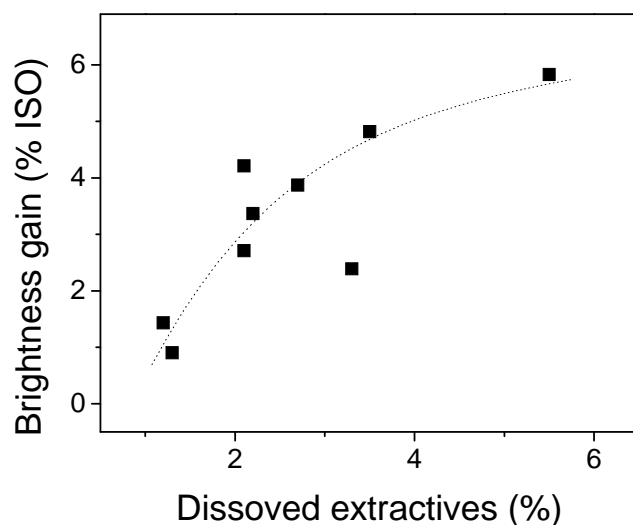
Fig. 7. Relationship between removal of alkaline extractives and brightness gain of peroxide-bleached pulp

The alkaline extraction is known to be an effective method to dissolve phenols (Lozovaya et al. 1999). Combined with the results of GC-MS analysis, the biggest difference between samples $1^{\#}$, $7^{\#}$, and $9^{\#}$ was the content of phenols. The highest content of phenols was found in $7^{\#}$, followed by $9^{\#}$, and $1^{\#}$. The more NaOH dosage was used, the more phenols were dissolved out, and the higher brightness gain of peroxide bleached pulp was obtained. As was noted in the discussion of UV spectroscopic analysis, phenols present in bamboo SCMP can conjugate with ketones and form darkly colored structures (Johansson et al. 2000), decreasing the brightness and stability of peroxide bleached pulp. The close relationship between phenols removed and bleachability of bamboo SCMP suggests that phenols are an important factor that negatively influences the bleachability of bamboo SCMP.

CONCLUSIONS

1. Absorbances around 310 nm and 330 nm in UV spectra of the bamboo SCMP alkaline extractives showed that a large amount of phenols existed in the extractives. GC-MS analysis showed that the alkaline extractives were composed of short-chain aliphatic compounds, phenols, and fatty acids. Phenols were the major compounds in the extractives, and the extraction amounts increased with the dosage of NaOH.
2. Alkaline extractives removed from the pulp provided a significant brightness gain of peroxide bleached bamboo SCMP, which was increased with the dosage of NaOH. As the NaOH dosage of 3.5% was used in extraction prior to peroxide bleaching, the brightness gain reached 5.83%ISO, and the PC number was decreased by 55.7%. The result that the brightness gain was dependent on the dosage of alkali, which was in accordance with the removal of alkaline extractives, especially phenols.

3. Results of UV spectra and GC-MS analysis showed that phenols, which might easily generate conjugated structures, played an important role in bleachability and brightness stability of bamboo SCMP.

ACKNOWLEDGMENTS

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