Bleachability Improvement of Eucalypt Mechanical Pulps Using Hydrogen Peroxide in Ethanol-water Media

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Alkaline darkening has a negative effect on chemimechanical pulps produced from various eucalypt chips. For instance, the pulp's brightness has been found to drop rapidly when alkali addition exceeds its optimum amount. Therefore, to compare the effects of different media on brightness gain, eucalypt mechanical pulps were bleached using a typical peroxide bleaching sequence in a water medium and in an ethanol-water (E/W) medium. Various pulp brightness levels and changes of residue chemicals in the spent bleaching liquors were investigated. Compared to water medium, the net brightness gain notably increased when using the E/W medium at the same chemical dosages. The rate of pulp brightness loss caused by increasing alkali dosage dropped in the E/W medium. Analyses based on ultraviolet-visible diffuse reflectance spectra of bleached pulps, as well as gel permeation chromatography and pyrolysis-gas chromatography-mass spectrometry spectra of the residues in the spent bleaching liquors, indicated that the contributions to brightness improvement from ethanol-water media could be explained by the selective dissolution and removal of phenolic- or guaiacyl-structured lignin fragments that result in the formation of chromophoric groups under alkaline conditions.

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INTRODUCTION

Eucalyptus spp. plantations are one of the major raw material resources for fibers for the modern pulping industry (Jacier *et al.* 2019). These wood species have many advantages, such as fast growth rate, short plantation rotation, high productivity of logs, high adaptability to different soils and climates, and easily managed forest plantation (Kokta and Ahmed 1993; Isabel *et al.* 2018). They are widely distributed in tropical and subtropical zones of the world, which implies that they can effectively alleviate the supply shortage of fibrous raw materials (Yasuo *et al.* 2008).

Alkaline hydrogen peroxide process is the most effective and practical bleaching process available to the chemimechanical pulp (CMP), while most of lignin is retained (Xu *et al.* 1996). An inspection of the alkaline hydrogen peroxide bleach reaction reveals that it is primarily due to nucleophilic reaction, whereas chromophores are deconjugated by hydrogen peroxide and some specific lignin structures are nucleophilic attacked by sodium

hydroxide (Gierer 1985). During the production of eucalypt CMP, there is a positive relationship between pulp strength and alkali dosage, especially in the bleaching process after refining (Area *et al.* 2010; Hietanen *et al.* 2013; Deng *et al.* 2015). However, the concentration of chromophores in the eucalypt lignin appreciably increases as the alkali dosage increases (Hou *et al.* 2010; Fjellström *et al.* 2011). The CMP is sensitive to alkaline environments, and its brightness rapidly drops when excess alkali is applied (Chen *et al.* 2008). Hence, the adjustment of the alkali dosage during bleaching is not practical. In general, the strength of eucalypt CMP is lower than that of poplar CMP when the same pulping process and conditions are used (Shen *et al.* 2002; Deng *et al.* 2016). A contrary relationship between brightness and strength of bleached eucalypt CMP pulps leads to limitations in its application for high quality grade of paper products.

The color of the chemimechanical pulp has been mainly attributed to the chromophoric structures of lignin (He *et al.* 2004; Seo *et al.* 2015). During peroxide bleaching, the initial chromophoric structures of lignin are eliminated by bleaching chemicals, but new chromophores are simultaneously generated (Maria *et al.* 1997; Leary and Giampaolo 1998). To prepare eucalypt CMP of high brightness and good strength, it is necessary to eliminate or remove the chromophoric groups and the alkali-sensitive chromophore precursors to prevent alkaline darkening. Lignin in CMP is attacked by peroxide and converted into derivatives, which are easily dissolved in an ethanol medium *versus* water (Pan 2011). Therefore, to compare the effects of the bleaching solvent on brightness gain, eucalypt mechanical pulps were peroxide-bleached using a traditional process (totally aqueous medium) or using an ethanol-water medium. Various pulp brightness levels and changes to chemical residues in the spent bleaching liquors were investigated.

EXPERIMENTAL

Materials

Eucalypt (*Eucalyptus urophylla* (6 years old), Guangxi Province, China) mechanical pulp with an initial brightness of 39.4% ISO and Canadian standard freeness (CSF) of 350 mL was prepared at the laboratory of the Pulp and Paper R&D Center located at the Institute of Chemical Industry of Forest Products, Chinese Academy of Forestry (Nanjing, China).

Prior to chip pre-steaming at atmospheric pressure (105 °C for 15 min), the eucalypt wood chips were screened to remove pins and over-sizes, washed with tap water at room temperature to remove heavy metals and sand particles, and then dewatered. The pre-steamed chips were compressed with a twin-screw pressurized impregnator (Jiangsu Jinwo Machinery Co., Ltd., Zhenjiang, China), and the impregnated chips were refined in a Kumagai Riki Kogyo (KRK) refiner at atmospheric conditions (KRK No. 2500-II; Kumagai Riki Kogyo Co., Ltd., Tokyo, Japan). The refiner energy input and number of refining passes were set to reach a target freeness of 350 mL CSF. Pulp samples were screened with a vibrating slot screen (Voith Sulzer Paper Technology Inc., Appleton, WI, USA) using 0.2-mm slots. The accepts were thoroughly washed, dewatered using a centrifuge, sealed in plastic bags, and subsequently kept in a refrigerator (4 ℃) until needed.
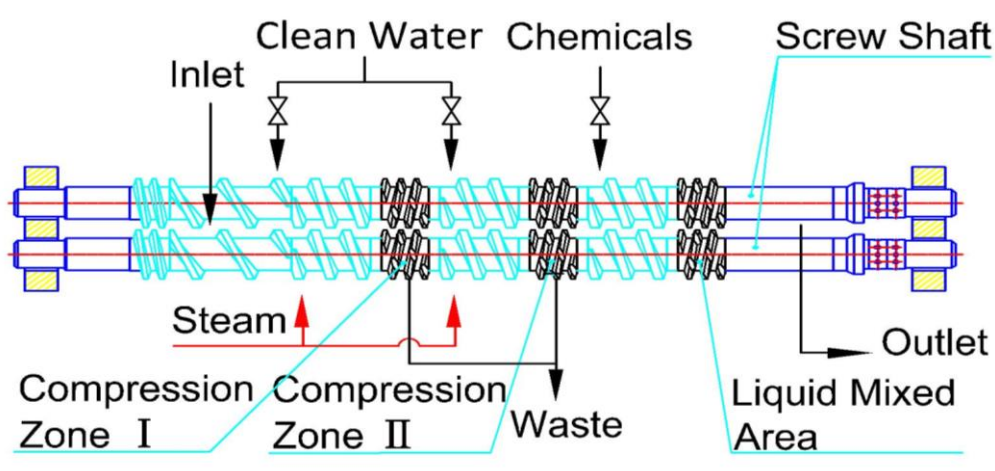
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Fig. 1. Structural diagram of a twin-screw pressurized impregnator

A moderate disruption of wood chips' cellular tissue structures, removal of extractives, and an increment of specific surface area of woodchips are able to facilitate chemical solution penetration in subsequent pulping processes (Tang and Liu 2004). The twin-screw pressurized impregnator (TSPI) was specially designed for crushing and chemical impregnation of wood chips at low cost with high efficiency (Xie *et al.* 2010); a diagram of the TSPI is shown in Fig. 1. The wood chips are compressed at two different compression zones where backward screw bars are installed. When the compression pressure rises up to some level (controlled by compression zone gear's shape and spacing), the fibrous mass is extruded out through chutes opened at the last ring of backward screw bar. Because of the thorough impregnation of the wood chips, chemical solution absorbency of these fibrous materials is three or more times higher than when using a modular screw device (MSD) (Liang *et al.* 2017).

Methods

A conventional peroxide bleaching stage using a totally aqueous medium or an ethanol/water medium was used to brighten the eucalypt mechanical pulp. The bleaching conditions of the peroxide stage are shown in Table 1.

Table 1. Conditions for Peroxide Bleaching Stage

Specifications		Conditions
Chemical Dosage (kg/t o.d. pulp)	H_2O_2	80
	Na_2SiO_3	20
	NaOH*	25 to 75
	DTPA	5
Pulp consistency (%)		20
Temperature (°C)		95
Retention time (h)		2
Note "*": 1- Dosage of NaOH for alkali optimization was at the constant dosage of H_2O_2 of 80 kg/t o.d. pulp; 2- For evaluation of alkaline darkening of eucalypt mechanical pulps, an additional alkali dosage was considered.		

Prior to bleaching operation, 20 g (equivalent to o.d. mass) of the pulp was sampled for each bleaching trial, the pulp sample was thoroughly mixed with diethylenetriamine-pentaacetic acid (DTPA), silicate, and bleaching agent solutions alternatively in a high-strength plastic bag, and then transferred into glass bottles. The peroxide bleaching stage was completed in tightly sealed glass bottles with screw caps. Duplicate experiments were performed for each bleaching condition. The bleached pulp was washed and then acidified to an approximate pH of 5 with a diluted sulfuric acid solution prior to brightness pad formation. Paper pad brightness was measured according to TAPPI Standard Method T452 om-98 (1998) using a color and brightness spectrophotometer (Wenzhou Baien Instrument Co., Ltd., Wenzhou, China).

The brightness gain was calculated using Eq. 1,

$$\text{Brightness gain} = \frac{B_1 - B_0}{M_{H_2O_2}} \tag{1}$$

where B_1 is the brightness of the bleached pulp sample (% ISO), B_0 is the brightness of the original pulp (% ISO), and $M_{H_2O_2}$ is the hydrogen peroxide dosage (kg H_2O_2/t o.d. pulp).

The ultraviolet-visible diffuse reflectance (UV-vis DR) spectra of the pulp handsheets were recorded on a Cary 100 spectrophotometer (Agilent Technologies Inc., Santa Clara, CA, USA). A BaSO$_4$ standard was used as the reference background. Pulp handsheets were scanned by incident light with wavelengths that varied from 350 to 600 nm at 5 nm increments; a scanning speed of 200 nm/min was used. The diffuse reflectances were converted to k/s values using the Kubelka-Munk equation Eq. 2,

$$\frac{k}{s} = \frac{(1-R)^2}{2R} \tag{2}$$

where R is the reflectance of the opaque pulp sample (dimensionless), k is the specific absorption coefficient (m^2/kg), and s is the specific scattering coefficient (m^2/kg).

The molecular weight distributions of the residues in the spent bleaching liquor were measured using a Waters 1515-2414 gel permeation chromatograph (GPC) (Waters Corp., Milford, MA, USA). The GPC used three Waters gel columns that were connected series: Ultrahydrogel 500 column (7.8 mm × 300 mm), Ultrahydrogel 250 column (7.8 mm × 300 mm), and Ultrahydrogel 120 column (7.8 mm × 300 mm).

The residual chemical structures from the spent bleaching liquors were characterized by pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS), which consisted of a Shimadzu PY3030 pyrolyzer followed with a Shimadzu QP2010 gas chromatograph and mass-spectrometer (Shimadzu Corp., Tokyo, Japan). Prior to pyrolyzation (pyrolysis conditions: temperature increase from 270 °C to 600 °C with a 20 °C/s heating rate, at the pressure of 100 kPa in a helium atmosphere), the spent bleaching liquor was dried by a LGJ-12 freeze-dryer (Songyuan Huaxin Technology Development Co., Ltd., Beijing, China). The gases of pyrolyzation were transferred into the chromatograph chamber by a gas sample injector that used helium as the carrier gas (1.0 mL/min flow rate) and a 1/50 split ratio. A capillary column, DB-1701 ms (30.0 m × 0.53 mm × 1.50 μm (Agilent Technologies, Santa Clara, CA, USA)) was used in the gas chromatograph. A temperature profile program started at 35 °C for 2 min, increased to 80 °C at a 5 °C/min heating rate, increased to 280 °C at a 15 °C/min heating rate, and held at 280 °C for 5 min. The mass-spectrometer was operated at an electron impact mode (70 eV) with a scanning range from 50 to 400 amu.

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RESULTS AND DISCUSSION

Optimization of Ethanol/Water Ratio for Bleaching Solvent

      The brightness values of bleached eucalypt mechanical pulp using a conventional peroxide bleaching stage at two alkali dosage levels (40 or 50 kg NaOH/t o.d. pulp) with totally aqueous or ethanol-water bleaching media (at various E/W ratios) are shown in Fig. 2. It was observed that the maximum bleached brightness occurred for both alkali levels at an E/W ratio of 0.29:1. Furthermore, as the ethanol content increased, the brightness difference caused by the alkali dosage gradually decreased from 7.55% ISO in the entirely aqueous medium to 1.56% ISO in the 0.6:1 ethanol/water medium. The E/W medium had a pronounced effect on pulp brightness stability against alkaline darkening.
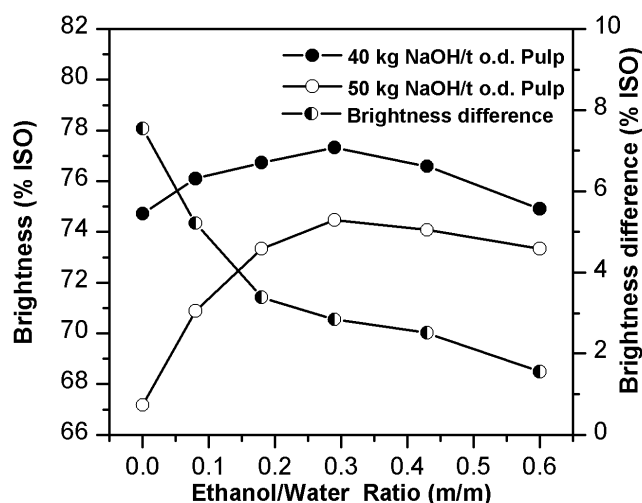

Fig. 2. Effects of E/W bleaching medium composition on peroxide brightness gains at different alkali levels
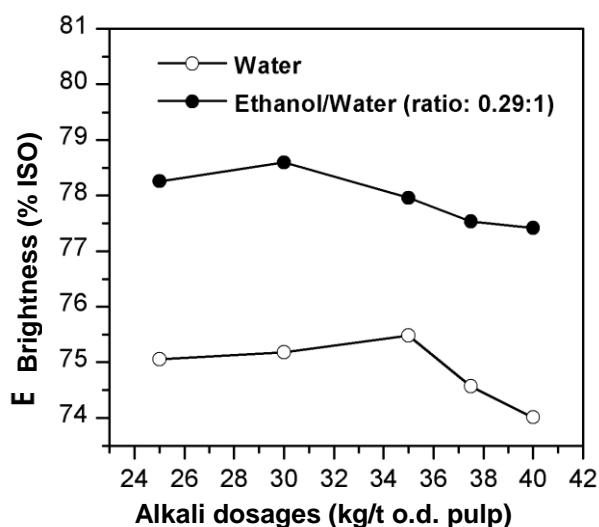

Fig. 3. Bleached pulp brightness at various alkali dosages in peroxide stages conducted in water or 0.29:1 ethanol-water solvent system

Brightness and Strength of Bleached Pulps Effected by Alkali Dosage

To verify alkaline sensitivities to both brightness and strength of bleached eucalypt mechanical pulps, at both water solvent and E/W ratio 0.29:1 ethanol/water solvent systems, the bleaching trials were designed with increasing alkali dosages. Bleached pulp brightness of varying tendencies with increment of alkali dosage are shown in Fig. 3.

It is obvious that at the same peroxide dosage (80 kg H_2O_2/t o.d. pulp), the optimized alkali dosage was 30 kg NaOH/t o.d. pulp for the E/W solvent system and 35 kg NaOH/t o.d. pulp for the entirely aqueous system. The net brightness gain was appreciably higher with the E/W solvent system (0.5 units/kg H_2O_2) *versus* the totally aqueous system (0.45 units/kg H_2O_2); this resulted in a bleaching efficiency increase of 11.1%. It should be noted that the alkaline darkening was decreased with the E/W solvent system *versus* the entirely aqueous system.

To evaluate the alkaline darkening of the eucalypt mechanical pulp during peroxide bleaching, some additional experiments were conducted in which the alkali dosage was increased further for both water and E/W solvent systems. The results are plotted in Fig. 4.
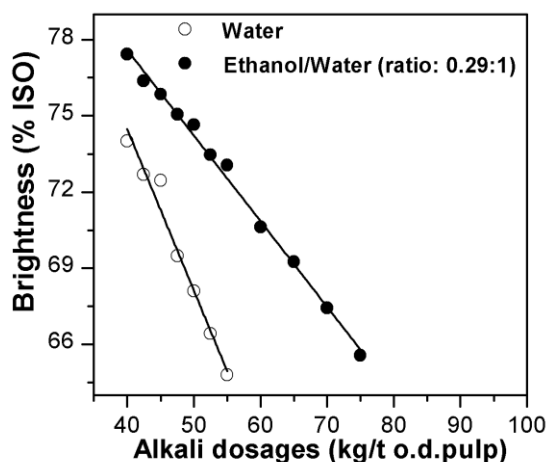

Fig. 4. Alkaline darkening during peroxide bleaching when using water or E/W solvent system at different alkali dosages

Very good linear relationships were observed with the brightness *versus* the alkali dosage for peroxide stages conducted with water or E/W bleaching medium when excess alkali was applied. Linear regressions were performed with the plotted data sets in Fig. 4,

$$y = -0.338x + 91.100, R^2=0.995 \text{ (for E/W bleaching medium)} \qquad (3)$$

$$y = -0.636x + 99.905, R^2=0.972 \text{ (for water bleaching medium)} \qquad (4)$$

where *y* is the peroxide-bleached brightness (% ISO), and *x* is the alkali dosage (kg NaOH/t o.d. pulp).

For the linear equations (Eqs. 3 and 4), the regressed slope (% ISO/(kg NaOH/t o.d. pulp)) can be explained as the brightness loss rate caused by the alkali dosage. For the E/W system, the slope was 0.338, and for the water system, the slope was 0.636. Therefore, the alkaline darkening sensitivity of the bleached brightness was lower by 88.2% when using the E/W solvent system, which provided a wider range for pulp strength improvement by alkali adjustment.

As mentioned earlier, for a fixed peroxide dosage, there is an optimized alkali dosage, especially for the bleaching of eucalypt mechanical pulp. To study the change of

pulp brightness and tensile strength affected by increasing alkali dosage (exceeding its optimum) in both two mediums, the strength properties of bleached pulps are illustrated *versus* pulp brightness in Fig. 5.

The relationships between bleached pulp brightness and tensile strength when using water or E/W medium are illustrated in Fig. 5. The plotted data sets were regressed to yield the following equations,

$$y = k_3x + 88.03, \; k_3 = -1.39, \; R^2 = 0.992 \text{ (for E/W bleaching medium)} \qquad (5)$$

$$y = k_4x + 100.5, \; k_4 = -3.41, \; R^2 = 0.977 \text{ (for water bleaching medium)} \qquad (6)$$

where y is the tensile index (N·m/g), x is the bleached brightness of the pulps (% ISO), and k_3 and k_4 are the slopes (N·m/(g·% ISO)).
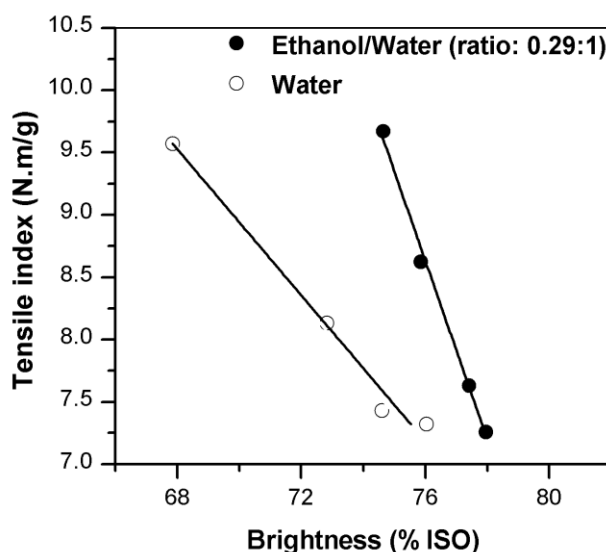

Fig. 5. Alkaline darkening in two bleaching processes *versus* tensile index

With comparison between Eqs. 3 and 4, the absolute value of the slopes (minus means reversed correlationship) indicates that E/W solvent system can weaken brightness sensitivity at the same tensile strength level, and it could provide the opportunity of regulation to gain both higher brightness and better strength of bleached mechanical pulps produced from eucalypt wood chips.

Various Chromophoric Lignin Structures Contributing to Alkaline Darkening

Chemical structures of lignin in bleached pulps can be characterized by means of UV-vis spectrometry (Halttunen *et al.* 2001; Keating *et al.* 2006). The UV-vis absorbance region for several major chromophore model compounds in lignin are depicted in Fig. 6.
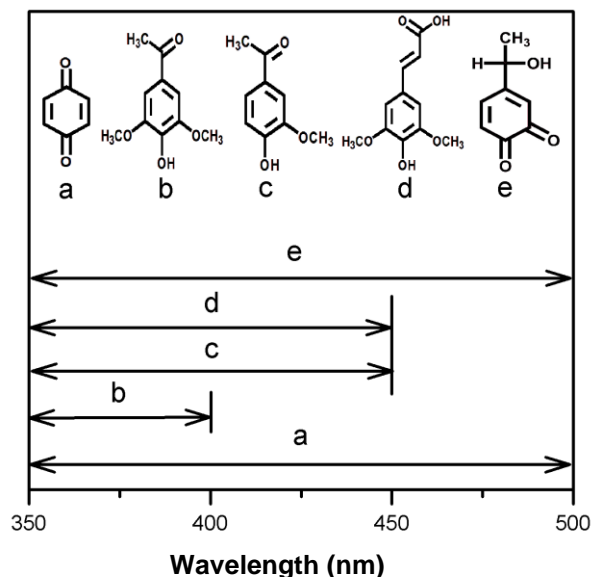
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Fig. 6. UV-vis absorption regions of several major chromophore model compounds for structures in lignin (Loureiro *et al.* 2011); a: p-benzoquinone; b: 3,5-dimethoxy-4-hydroxyacetophenone; c: 4-hydroxy-3-methoxyacetophenone ; d: 3,5-dimethoxy-4-hydroxycinnamic acid; e:o-quinone derivative

The conjugated carbonyl structures at the *α*- and *γ*-position of the aliphatic side chain of syringyl or guaiacyl groups have absorbances around 350 to 450 nm, and the *ortho*- and *para*-quinone groups have absorbances at 350 to 500 nm (Loureiro *et al.* 2010).

Handsheets of 20 g/m^2 grammage were individually prepared using the peroxide bleached pulps that either used water or E/W bleaching media at one of the two alkali dosages (35 kg NaOH/t o.d. pulp or 50 kg NaOH/t o.d. pulp). Their ultraviolet-visible diffuse reflectance (UV-vis DR) spectra were measured. For each solvent system, the $\Delta k/s$ (difference between two sample's k/s values) values calculated from the UV-vis DR spectra of the two alkali dosages are presented in Fig. 7. Clearly, the $\Delta k/s$ values of the bleached pulp in the water system were notably higher than those from the E/W system over the 350 to 600 nm region; a maximum difference appeared near 375 nm. Therefore, it was clear that when the alkali dosage increased from 35 to 50 kg NaOH/t o.d. pulp, the content of carbonyl groups and of *α,β*-double bonds in the aliphatic side-chain increased with the water bleaching medium, while in the E/W bleaching medium, the increase of these structures is rare. In addition, compared to the curve A, at 450 to 500 nm, the $\Delta k/s$ of curve B was close to zero, indicating that structures of *ortho*- and *para*-quinones generated slightly under 50 kg NaOH/t o.d. pulp alkali in the dual-solvents system, which effectively relieves alkaline darkening of eucalypt CMP.
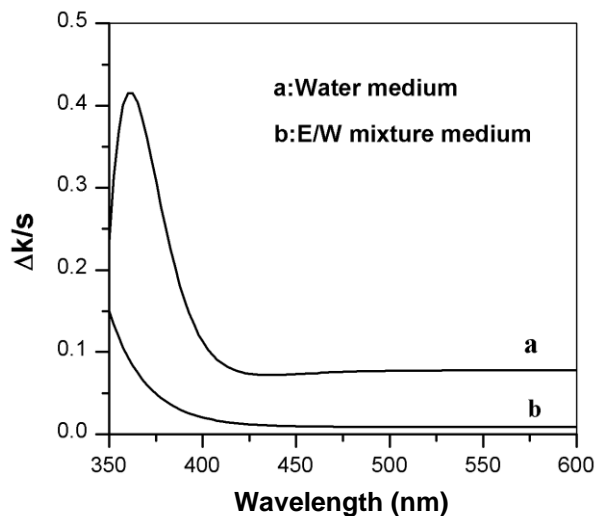
Fig. 7. Comparisons of $\Delta k/s$ spectra for peroxide-bleached pulps using water *versus* E/W solvent systems (bleached pulp with 35 kg NaOH/t o.d. pulp minus bleached pulp with 50 kg NaOH/t o.d. pulp)

Characterization of Spent Bleaching Liquor

Using the E/W solvent system during the peroxide bleaching process can lessen the alkaline darkening sensitivity of eucalypt mechanical pulps. Hence, to find out the mechanistic difference between the two bleaching media, the spent bleaching liquors were characterized by gel permeation chromatography (GPC) and the residues in the liquors were characterized by pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS).

The GPC analyses of spent bleaching liquors are shown in Fig. 8. The content in the bleaching residue of sample a was obviously higher than that of sample b. Under alkaline conditions, ethanol ionizes to ethoxylate ions, which are more nucleophilic than hydroxide and can enhance the permeation of the bleaching liquid and strengthen the reaction of the oxidizing agent and lignin. Due to the good solubility of lignin fragments with benzene ring structures in ethanol, more solubles, especially large molecular weight lignin fragments, are dissolved in the residues in spent bleaching liquor in the ethanol-water dual-solvents system compared to the conventional system (region I in Table 2). The region I integral area of the residues in spent bleaching liquor of sample a was 70.2% higher than that of sample b.
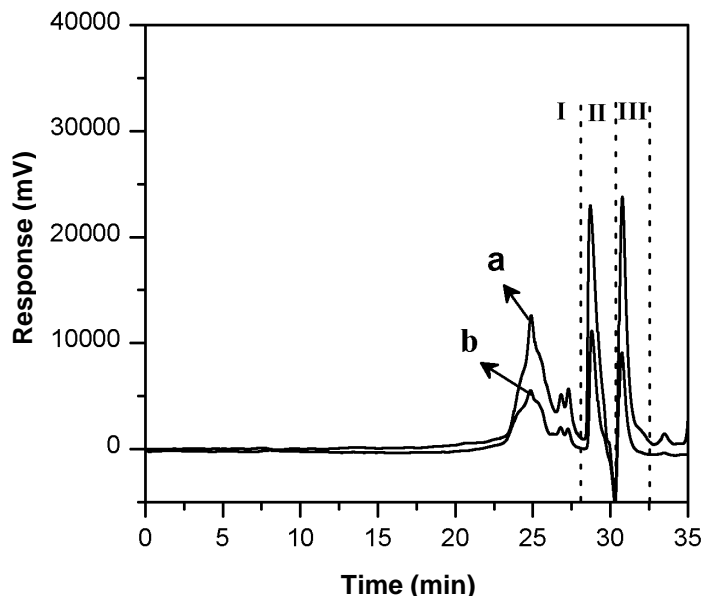
Fig. 8. GPC of residues in spent peroxide bleaching liquors of two pulp samples with similar bleached brightness levels (sample a: bleached in E/W solvent system (75.06% ISO), and sample b: bleached in water solvent system (75.48% ISO))

Table 2. GPC Chromatographic Curve Integral Area (from Fig. 8)

Sample	Region			Total Area
	I	II	III	
a	1.445	0.899	0.833	3.177
b	0.849	0.368	0.286	1.503

The structure of residues in spent bleaching liquors of four samples bleached in two alkali dosages (35 and 50 kg NaOH/t o.d.) and two kinds of solvent systems were characterized by Py-GC/MS, which is an efficient tool to characterize the chemical composition of the macromolecular organic compounds (Ibarra *et al.* 2007; Lima *et al.* 2015). Pyrolysis products in Table 3 were classified as benzene and hydrocarbyl benzene (B), phenol and hydrocarbyl phenol (H), guaiacol and hydrocarbyl guaiacol (G), and syringol and hydrocarbyl syringol (S).

As can be observed in Table 3, the residues in the spent bleaching liquors of the E/W systems (M35 and M50) contained more phenol, guaiacol, and syringol compounds, which all have aryl ether bond structures. In particular, guaiacols and syringols both contain aryl ether structures in the *ortho*-position of the aromatic ring, which easily forms the main chromophores at the end of alkaline hydrogen peroxide bleaching. Compared with the water system, the hydroxyl and methoxyl benzene molecules can be well dispersed in the ethanol-water system with low agglomeration because of better solubility in the solvent. Thus, the rearrangement and polycondensation reactions at the end period of bleaching could be avoided to a certain degree. Therefore, in the E/W solvent system, higher brightness is achieved at the same chemical dosage for the totally aqueous system.
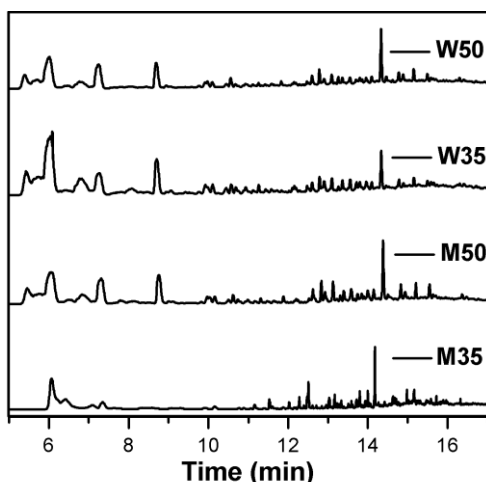
Fig. 9. Py-GC/MS spectra of residues in spent bleaching liquors (M35 is 35 kg NaOH/t o.d. and E/W solvent system, M50 is 50 kg NaOH/t o.d. and E/W solvent system, W35 is 35 kg NaOH/t o.d. and water system, and W50 is 50 kg NaOH/t o.d. and water system)

Table 3. Classification and Relative Content of Residues in Spent Bleaching Liquors in the Four Peroxide Bleaching Processes

	B (%)	H (%)	G (%)	S (%)
M35	4.99	12.90	11.61	10.36
M50	26.56	13.44	5.00	13.66
W35	19.06	6.03	2.50	6.67
W50	27.17	7.70	3.81	5.74

   The rearrangement of lignin fragments containing conjugated carbonyl groups and poly-unsaturated aromatic structures into the *ortho-* and *para-*quinone structures is the main reason for the brightness decrease in the late bleaching stage (Gierer 1990a,b). It was observed that the contents of benzene and guaiacol moieties were similar when comparing the relative intensities of the MS spectra of M50 and W50, whereas in the E/W system, there were more phenolic and syringol moieties. Based on the observations from Fig. 7, the results suggested that more lignin fragments containing phenolic and guaiacol structures were dissolved in the E/W solvent system at the higher alkali levels, which avoided the generation of *ortho-* and *para-*quinone structures that contributed to the alkaline darkening of the eucalypt CMP. Hence, the alkaline darkening of CMP was greatly reduced.

CONCLUSIONS

1. A higher brightness eucalypt mechanical pulp can be achieved by using an ethanol-water bleaching medium at the same chemical consumptions as the traditional peroxide bleaching, and this led to a bleaching efficiency increase of 11.1%.

2. The ethanol-water bleaching medium had a pronounced effect on the alkaline darkening sensitivity of pulps treated with hydrogen peroxide. The alkaline darkening sensitivity of the pulp's brightness was desensitized by 88.2%, and the pulp brightness loss rate caused by increasing alkali dosage dropped 59.2%.

3. It was tentatively suggested that the decrease in alkaline darkening sensitivity was mainly due to the increased dissolution of lignin fragments. These fragments contained phenolic and guaiacol moieties. Their removal avoided the formation of carbonyl groups and the double bond structures in the side-chain conjugated with benzene rings when the system was subjected to increasing alkali amounts.

4. In the alkaline hydrogen peroxide stage, the structural characteristics of the dissolved lignin fragments in the pulp were affected by the dosage of alkali and the bleaching solvent medium used.

ACKNOWLEDGMENTS

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