Effect of Microwave-Involved ClO_2 Bleaching on the Characteristics of Lipophilic Extractives of Bleached *Eucalyptus globulus* Pulps

Heng Zhang,[a] Rui Shi,[b] Xin Gao,[a,*] Keli Chen,[a] and Lincai Peng [a]

The preparation of bleached pulp from *Eucalyptus globulus* pulp was evaluated after utilizing chlorine dioxide (ClO_2) with or without microwave irradiation. The three ClO_2-bleaching processes examined were water-bath heating; microwave heating; and microwave pretreatment combined with water-bath heating. These processes were applied to eucalypt pulps that were oxygen-delignified. The effects of the treatments on the levels of lipophilic extractives and properties of the resulting pulps were compared with one another. The microwave-induced treatment had a remarkable effect, leading to an increase in pulp brightness and a decrease in lipophilic extractives when compared with the control (*i.e.*, A). The sample under the condition of microwave pretreatment combined with water-bath heating achieved a higher brightness and reduced lipophilic extractives, which were increased by 45.8% and reduced by 37.4%, respectively. This study demonstrated an effective microwave-pretreated method in ClO_2 bleaching process, which provides a promising route for alleviating pitch deposition problems occurring during pulp manufacture.

Keywords: Lipophilic extractives; Eucalyptus pulp; Microwave treatment; Chlorine dioxide; Bleaching; Pitch deposition

Contact information: a: Faculty of Chemical Engineering, Kunming University of Science and Technology, Kunming 650500, Yunnan, China; b: Zhao Tong University, Zhaotong 657000, Yunnan, China;
** Corresponding author: 1062559315@qq.com*

INTRODUCTION

The lipophilic extractives from chemical wood pulp can lead to many issues in the paper industry. The lipophilic extractives, or "pitch," can be responsible for the formation of sticky deposits on the machinery, which can then result in dark spots in the paper sheet or hinder equipment operations (Allen 2000; Back 2000; Gutiérrez and del Río 2005; Freire and Armando 2006). In the manufacture of alkaline pulps, a large part of the lipophilic extractives in the raw material is removed during the pulping and bleaching operations. However, some chemical species that survive these processes are found as pulp extractives (Bergelin and Holmbom 2003; Freire *et al.* 2005; Freire and Armando 2006; Marques *et al.* 2010a) and dispersed in process waters (Kilulya *et al.* 2012). Particularly, with the current growing pressure for zero discharge and water reclamation, the accumulation of lipophilic compounds in these processes will cause increasing troubles in the papermaking field (Leiviskä *et al.* 2012).

Chlorine dioxide (ClO_2) is an oxidizer commonly used in the bleaching of pulp. It is widely regarded as an ideal bleaching agent in the industry because of its high selectivity in degrading lignin without appreciably oxidizing the carbohydrates. Consequently, the properties of bleached pulp, such as strength and brightness, are usually favorable (Smook 2002).

Eucalyptus is one of the most common hardwoods used for timber and fiber in South China (*e.g*., Guangdong, Guangxi, Hainan, *etc*.). Short-rotation (3 to 15 years) and high yield of dry matter are the main reasons that eucalyptus species are planted so widely (Ouyang *et al.* 2016). It was reported that the eucalyptus plantation area reached 3.68 million ha in China in 2010 (date from the China Eucalyptus Research Centre). *E. globulus* is distributed widely in the areas of Honghe, Baoshan, and Puer in the Yunnan province of China. Most of the eucalyptus found in Puer was cultivated for pulp manufacturing. The pitch, which is worldwide problem in the pulping and paper-making process (Freire and Armando 2006; Silvério *et al.* 2007; van Beek *et al.* 2007), has also plagued local manufacturers, *e.g.*, the Yunnan Yun-Jing Forestry & Pulp mill Co. Ltd., where the manufacturer has to expend nearly 3 million dollars to deal with the problem every year.

Conventional methods for controlling pitch and resin-related problems are extensive wood debarking and seasoning, as well as the application of pitch control additives to the pulp manufacturing process (Kallioinen *et al.* 2003). Different treatment methods work well for specific lipophilic materials after various processes, such as the fatty acid deposits that form after elemental chlorine-free (ECF) bleaching (Silvestre *et al.* 1999; Freire *et al.* 2002). Pitch deposits after totally chlorine-free (TCF) bleaching, on the other hand, consist primarily of fatty acids, sterols, and waxes (del Río *et al.* 2000). In addition, there are significant differences in pitch content and its composition among the variant tree species, as well as different parts of the same tree (Gutiérrez *et al.* 2009).

Microwave heating generates heat inside and outside of materials using microwave radiation; this heating method is more effective than traditional methods because of the improved heat transfer transmission (Pickles 2009). It is known that microwave heating has some important advantages, such as short heating time, simple equipment, and less electrical energy consumption (Issa *et al.* 2015). Microwave treatment has been widely studied for biomass processing to enhance solute dissolution or reactivity in solvents (Verma *et al.* 2011; Xue *et al.* 2012). The use of microwave heating has not been examined for chlorine dioxide bleaching of pulps and may offer a more sustainable and environmentally compatible method for pulp bleaching.

The researchers found that the microwave power could affect morphology on a cellular level by use of electron microscopy techniques in the extraction process. Compared to conventional extraction, microwave power led to more rapid opening of essential oil glands of orange peel (Ferhat *et al.* 2006), sudden rupture in rosemary leaves (Golmakani and Rezai 2008), huge perforations on the cardamom surface (Lucchesi *et al.* 2006), and the destructuration and flattening in the inner parenchyma of the essential oil-containing structures of orange peels (Farhat *et al.* 2010). Furthermore, the microwave power could made much gentler explosive damage during the microwave-water extraction system (Cheng *et al.* 2013). All of these treatments would increase the dissolving of the extractives. Meanwhile, the assistance of microwave treatment during the bleaching process could benefit from the reduction of lipophilic the extractives.

As indicated above, the microwave-water system would have a certain influence on the reduction of plants' extraction contents. This study planned to design a microwave pretreatment bleaching experiment to find out whether it would improve the effect of bleaching and the lipophilic extraction.

The main purpose of this study was to investigate different microwave heating methods during chlorine dioxide bleaching of *E. globulus* kraft pulps, as well as its effects on the lipophilic extractives. This study also compared the methods with one another with respect to pulp properties and fiber morphologies.

EXPERIMENTAL

Materials

Pulp from *Eucalyptus globulus* was selected for this study and supplied by the Yunnan Yun-Jing Forestry & Pulp Mill Co. Ltd. (Pu'er, Yunnan province, China), which produces elemental chlorine free (ECF)-bleached pine and *Eucalyptus globulus* pulps. The oxygen-delignified pulp was chosen as a starting material to perform chlorine dioxide bleaching in this research. The pulp had a kappa number of 11.5, an intrinsic viscosity of 923 mL/g, and a brightness value of 46.1 %ISO.

Sulfuric acid, sodium hypochlorite, sodium thiosulfate, and other chemicals and organic solvents that were used were of laboratory grade (Aladdin, China) and were used as received without further purification. The chlorine dioxide solution was generated in the laboratory prior to performing bleaching reactions. Deionized water was used throughout this work.

Microwave-Assisted ClO_2 Bleaching

The microwave reactor being used in this study is an ultrasonic microwave reaction system (Nanjing Xianou Instruments Manufacture Co., Ltd). The pulps were bleached in polythene bags, meanwhile the polythene bag was putted into a glass breaker for fixation (Fig. 1).

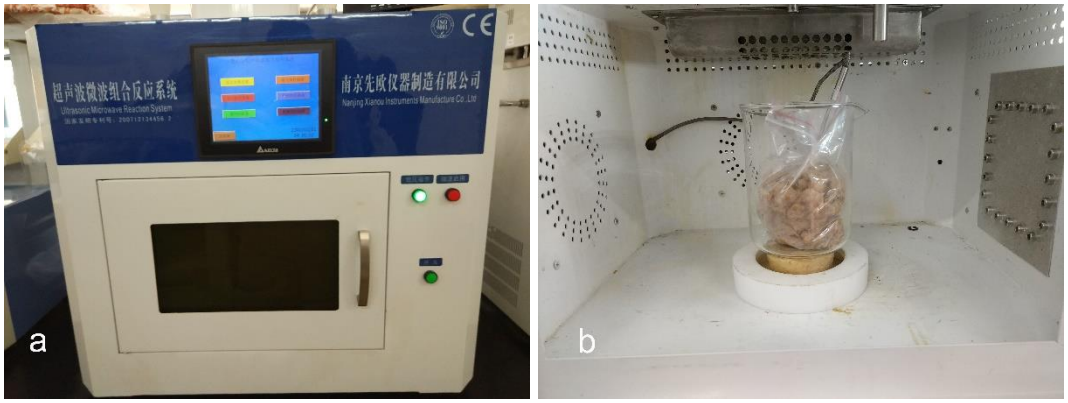

Fig. 1. Microwave apparatus for ClO_2 bleaching: (a) the microwave reaction system, (b) the state of pulp in microwave system.

An orthogonal design of experiments (L_9, 3^3 design) was used to determine the optimum microwave bleaching conditions. Bleaching experiments were performed using 10 g of pulp (oven-dried) that was sealed with bleaching chemicals and water in a polythene bag. Experiments were performed at the following conditions: microwave powers of 250, 300 and 350 W; reaction times of 2, 3, and 4 min; and chlorine dioxide charges of 0.6%, 0.8%, and 1.0% with respect to pulp (as ClO_2). The bleaching experimental design is summarized in Table 1. After the process, the pulp was collected by filtration, thoroughly washed with deionized water until the pH of the pulp was neutral, then disintegrated for further analysis. All the bleaching procedures were performed in duplicate, combined and mixed after the bleaching process.

Table 1. Factors and Factor Levels in Orthogonal Experimental Design

Factors	Levels		
	1	2	3
I: Microwave power (W)	300	250	350
II: Reaction time (min)	4	3	2
III: Chlorine dioxide dosage (%)	0.6	1.0	0.8

The evaluation criterion of microwave heating bleaching effect is based on the maximum brightness in the orthogonal experiments. In this case, the brightness was used as a criterion in this part. After determine the optimum condition of microwave heating bleaching, the three experimental forms, including the water-bath bleaching (A), microwave-heating bleaching (B), and microwave pretreatment bleaching (C), were selected for comparative research (Fig. 2).

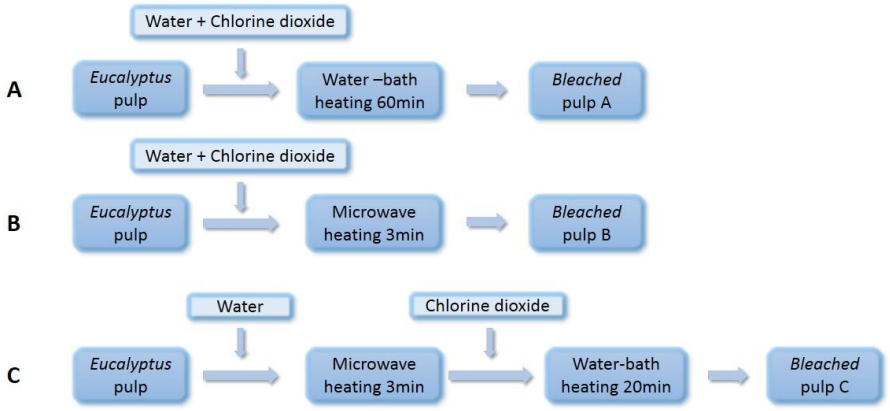

Fig. 2. Sequence of steps for the bleaching treatments in the second experimental phase

All samples were bleached in polythene bags. The bleaching treatment conditions were as follows: (A) 30 g pulp, 10% pulp consistency, 1.0% ClO_2 charge with respect to pulp, and 60 min reaction time in a 70 °C water bath; (B) 30 g pulp, 10% pulp consistency, 1.0% ClO_2 charge with respect to pulp, and 3 min microwave heating at 300 W; and (C) 30 g pulp, 10% pulp consistency, 1.0% ClO_2 charge with respect to pulp, 3 min microwave heating at 300 W, and 20 min reaction time in a 70 °C water bath. After the bleaching treatment, all samples were filtered to remove the bleaching filtrate and washed with deionized water until the wash filtrate had a pH between 7 and 8. The washed pulp was placed into a freezer until needed for further testing.

Pulp Properties

All pulps were characterized using various laboratory test methods from the pulp and paper industry (*e.g.*, Technical Association of Pulp and Paper Industry (TAPPI)). Kappa number (TAPPI T236 om-99), intrinsic viscosity (ASTM D1795-62), and ISO brightness (TAPPI T452 om-02) were determined for pulps in accordance with the respective protocols.

Fiber morphology characteristics of the pulp were evaluated using a fiber quality analyzer (FQA, HiRes Fiber Quality Analyzer LDA02, Software Operation Manual

Version 1.4-BSVCF, Optest Equipment Inc.) following TAPPI standard (TAPPI 271 om-02). The chemical compositions of the bleached pulps were analyzed by various TAPPI laboratory methods: ash (TAPPI T 211 om-93), solvent extractives (TAPPI T204 cm-07), Klason lignin (TAPPI T222 om-83), cellulose (TAPPI T201 wd-76), and pentosans (TAPPI T223 cm-01). Each characterization measurement was duplicated to confirm the repeatability of results.

Acetone Extraction

The bleached pulps were air-dried and milled using an analytical mill (IKA A11 analytical mill). The lipophilic compounds in the resulting pulp flour were extracted using acetone in a Soxhlet apparatus. To a 500-mL Soxhlet thimble was added 10 g of pulp flour (to the nearest 0.0001 g); the thimble was placed into the Soxhlet extractor and extracted for 24 h. The resulting acetone liquor was evaporated using a rotary evaporator until dry. The solids were weighed and re-dissolved in 2 mL of chloroform to isolate the lipophilic extractives from the total acetone extracts (Kilulya 2012) for chromatographic analysis. This extraction procedure was duplicated for each flour sample.

XRD

The overall crystalline phases of samples were determined by XRD measurement on an X'Pert3 powder diffractometer (PANalytical Co. Ltd. Netherlands). The samples were prepared by pressing pulp powder between Si substr and a glass slide into flatten sheets. Radial scans of intensity were recorded at ambient condition over scattering 2θ angles from 3° to 50° (step size=0.01313°, scanning rate = 13.77 s/step) using a Cu Kα radiation (λ=1.5406 Å), an operating voltage of 40KV, and a filament current of 40 mA.

Crystallinity index (CrI) of each sample was calculated by referring to diffraction intensity of crystalline and amorphous regions using the following empirical equation (Segal *et al.* 1959; Lu and Hsieh 2012),

$$\mathrm{CrI} = \frac{I_{200} - I_{am}}{I_{200}} \times 100 \quad (1)$$

where I_{200} is the peak intensity at plane (200) (2θ=22.6°), and I_{am} is the minimum intensity at the valley between plane (200) and (110) (2θ=18.7°).

GC-MS

The lipophilic fraction of the extractives from the bleached eucalypt pulp was analyzed by GC-MS. An Agilent 6890 GC/5973 MS instrument (Kunming institute of botany CAS, Kunming) was used with a long silica HP-5MS capillary column (30 m x 0.25 mm I.D., 0.25 μm film thickness; J&W), enabling elution of the different lipid classes. The temperature profile of the column was started at 80 °C and raised to 280 °C at a rate of 5 °C /min, and then held at 280 °C for 40 min. The injector and the detector (FID) temperatures were set at 250 °C and 290 °C respectively, the split ratio was set to 10:1. Helium was used as a carrier gas at a flow rate of 1.0 mL/min. The separated compounds from the GC column were identified by mass spectroscopy; the obtained MS spectra were compared with the mass spectra of the Wiley 7n.1 library database to identify individual compounds.

RESULTS AND DISCUSSION

Orthogonal Design of Experiments with Microwave-Assisted ClO_2 Bleaching

Conditions for microwave-heated ClO_2 bleaching of the oxygen-delignified pulp were optimized for producing bleached pulp with favorable brightness. Three experimental factors, I (microwave power), II (reaction time), and III (chlorine dioxide dosage), were examined at three factor levels (Table 1) for their impact on post-treatment brightness. The experimental results and statistical analyses are displayed in Table 2.

Table 2. Results and Analyses from Orthogonal Design of Experiments

Exp. No.	Factor and Factor Values			Blank	Brightness (% ISO)
	I	II	III		
1	I1	II1	III1	1	56.70 ± 0.50
2	I1	II2	III2	2	63.30 ± 0.45
3	I1	II3	III3	3	59.00 ± 0.39
4	I2	II1	III2	3	61.00 ± 0.43
5	I2	II2	III3	1	58.10 ± 0.62
6	I2	II3	III1	2	56.10 ± 0.15
7	I3	II1	III3	2	55.40 ± 0.21
8	I3	II2	III2	3	54.20 ± 0.45
9	I3	II3	III1	1	57.60 ± 0.38
K1	179	173.1	170.4	172.4	
K2	175.2	175.6	178.5	174.8	
K3	167.2	172.7	172.5	174.2	
k1	59.667	57.700	56.800	57.467	
k2	58.400	58.533	59.500	58.267	
k3	55.733	57.567	57.500	58.067	
R	11.8	2.9	8.1	2.4	

Note: k1, k2, and k3, are the average values of the experimental results under different levels of the same factor. By comparing k values, the optimal levels of the factors can be confirmed. R is the difference between the maximum and the minimum average values of the experimental results under different levels of the same factor. High R-values of a factor mean that this factor has a strong effect on the result.

As can be seen in Table 2, the brightness increased for each experimental factor and factor level in comparison to the initial eucalypt pulp brightness (46.1 %ISO). In the present study, three levels were examined for each factor, and the *R*-values were calculated by deducting the lowest brightness from the highest. A higher *R*-value would mean a greater influence of that factor. The *k* and *R*-values of the factors were calculated and listed in Table 2. It can be observed that the influence of these three factors on the brightness, based on the *R*-values, was in the following order: I > III > II. Obviously, the microwave power was the most influential parameter for enhancing pulp brightness, followed by the amount of ClO_2 used, which was followed by the reaction time. Thus, appropriate control of the microwave power is important for preparing bleached pulp with ideal brightness.

In this study, three levels were chosen for each factor. A preferred level would give a higher brightness. Comparing the *k* value of each factor, the optimum conditions for a

favorable brightness of the eucalypt pulp were found to be $I_1II_2III_2$. The corresponding condition for the brightest pulp was at a microwave power of 300 W, a reaction time of 3 min, and a ClO_2 dosage of 1.0%. At these conditions, the intrinsic viscosity (820 mL/g) and kappa number (7.7) values of the treated pulp were much lower than the original oxygen-delignified pulp. Subsequently, the optimal bleaching conditions were $A_1B_2C_2$, which resulted with the highest brightness and lowest lignin level (*i.e.*, kappa no.) in the treated pulp.

Pulp Properties

Before evaluating the lipophilic extractives levels in the bleached pulps, it was necessary to evaluate how microwave irradiation affected the physical and chemical pulp properties. Hence, two comparison experiments involving the tradition water-bath heating (A) and microwave pretreatment heating (C) were carried out (Fig. 1 scheme).

Table 3. Yield, Kappa Number, Brightness, and Viscosity of the Unbleached Pulp and the Three Different ClO_2-bleached Pulps of Fig. 1 Experiments

Pulp	Yield (%)	Kappa number	Brightness (% ISO)	Intrinsic viscosity (mL/g)
A	93.53 ± 0.35	9.16 ± 0.03	51.8 ± 0.85	798 ± 12
B	93.32 ± 0.37	7.87 ± 0.02	63.4 ± 0.70	822 ± 20
C	93.27 ± 0.41	5.43 ± 0.02	67.2 ± 0.35	781 ± 15
Unbleached pulp		11.47 ± 0.02	46.1 ± 0.15	923 ± 25

As shown in Table 3, the bleaching treatments afforded nearly identical pulp yields; the intrinsic viscosity values of these pulps were also very similar (781 to 822 mL/g) and were 101 to 142 mL/g units lower than the unbleached pulp (923 mL/g). The data in Table 3 demonstrate that the carbohydrate damage during bleaching with these three processes was not obvious.

The kappa number is an indirect measure of the residual lignin content in the pulp and is an important quality index of the pulp itself. As exhibited in Table 3, the greatest reduction of the oxygen-delignified kappa number was treatment C (Fig. 1); the kappa number was reduced by more than 50%. On the other hand, treatment A with the water-bath heating had a higher kappa number (9.16). On the other hand, with the residual lignin content declined, the brightness of ClO_2-processed pulps showed the opposite trend to the kappa number. In other words, the brightness of treatment C (67.2% ISO) was higher than other treatments of Fig. 1, particularly treatment A (51.8% ISO).

Hu *et al.* (2012) and Boonsombuti *et al.* (2013) reported that microwave irradiation heating lowered the cellulose crystallinity index (CrI) when compared with conventional heating. These literature observations suggest that, without any chemicals, heating by microwave could break down the crystalline structure of cellulose to a certain extent. A decrease in CrI could increase the accessibility and reactivity of the cellulose. In this case, the ClO_2 more easily penetrated the fibers because of improved diffusion, which improved pulp delignification and brightening. As discussed above, one could conclude that the microwave heating had a remarkable effect on pulp delignification and brightening during ClO_2 bleaching. Compared with microwave-assisted bleaching only (treatment B of Fig. 1), it could be illustrated that the microwave pretreatment would take a better influence on removing lignin and thereby increasing brightness.

The effect of various ClO_2 bleaching treatments on the E. *globulus*'s constituents was also investigated, and the results are summarized in Table 4.

Table 4. Constituents of Unbleached and Bleach Eucalypt Pulps of Fig. 1 Experiments

Pulp	Ash (%)	Benzene-ethanol soluble extractives (%)	Klason lignin (%)	Cellulose (%)	Pentosan (%)
A	0.22 ± 0.03	0.47 ± 0.05	0.72 ± 0.01	73.09 ± 0.05	24.54 ± 0.02
B	0.21 ± 0.02	0.37 ± 0.04	0.60 ± 0.02	72.65 ± 0.12	25.19 ±0.03
C	0.29 ± 0.02	0.25 ± 0.05	0.82 ± 0.01	74.12 ± 0.09	23.45 ± 0.01
Unbleached pulp	0.69 ± 0.03	0.62 ± 0.06	9.95 ± 0.01	63.55 ± 0.10	24.50 ± 0.03

In Table 4, the ash contents of all three treated pulps were very similar; the ash content of pulp C was 0.29%, which was just slightly higher than the others. In addition, there was a great reduction of benzene-ethanol soluble extractives content of the bleached pulps *versus* unbleached pulp. Water bath-only bleaching treatment (A) removed 24.6% of benzene-ethanol soluble extractives from the unbleached pulp, while the two microwave-heated treatments, B and C, removed 40.0% and 59.0%, respectively. This result indicated that the microwave heating was beneficial for reducing the benzene-ethanol soluble extractives during ClO_2 bleaching. This feature could have arisen from the unique heating pattern caused by microwave irradiation. Microwave irritation is a rapid and uniform heating process, which directly produces heat throughout the pulp. According to S. Rodríguez-Rojo's research, the plant cell internal mass transport is increased by microwave heating (Rodríguez-Rojo *et al.* 2012). Moreover, the microwave energy would cause internal superheating which lead to liquid vaporization and pressure. The severe thermal, mechanical stress and localized pressures change the physical properties of the cell walls (Golmakani and Rezaei 2008). Above all of these will improved the dissolution of organic extractives in water system (Flórez *et al.* 2014; Nkhili *et al.* 2009), even in the bleaching process. Therefore, the ClO_2-bleached pulp by microwave heating could sustain low benzene-ethanol content. What is more, it was seem that microwave pretreatment bleaching (Method C) had a better effect on dissolving extractives than the directly microwave-heated bleaching (Method B). This finding could be attributed to the longer reaction time in the water bath (23 min) after microwave irradiation than the microwave-heated process alone (3 min).

It was noticed that all these bleaching reactions almost had no effect on the content of pentosan. This observation implied that it did not matter whether the procedure involved water bath heating or the microwave irradiation, with respect to the pulp's pentosan content.

On the basis of the above analyses, it was concluded that the ClO_2 bleaching process involving microwave pretreatment had a positive effect on the pulp delignification, as well as the removal of benzene-ethanol soluble extractives. As a result, this treatment process could facilitate the brightening of the oxygen-delignified pulp to an acceptable extent.

As shown in Table 5, it can be found that the fiber length and fines percent of pulp B and C were higher than pulp A. In addition, both kink angle and kink per mm of fibers obtained from microwave-involved reactions were higher than the bleached pulp heated by water bath. Microwave heating depends on internal dielectric properties of the irradiated material, which is able to create high-frequency vibration at the molecular level (Mishra

and Sharma 2015). The principle of microwave heating were different from water-bath heating. However, the fiber dimensions of all the bleached pulps were very similar. It was implied that microwave heating might not produce severe damage to pulp fibers compared with the water-bath heating in this study.

Table 5. Fiber Quality Analysis (FQA) of Treated Eucalypt Pulps of Fig. 2 Experiments

Sample	Unbleached pulp	A	B	C
Fiber Length Ave., LN (mm)	0.655 ± 0.002	0.651 ± 0.001	0.644 ± 0.002	0.642 ± 0.001
Fines Percent (%)	9.67 ± 0.03	11.92 ± 0.02	12.15 ± 0.02	12.10 ± 0.02
Mean Curl Index	0.136 ± 0.001	0.140 ± 0.001	0.146 ± 0.001	0.143 ± 0.001
Kink Angle Index (°)	35.29 ± 0.01	36.50 ± 0.01	36.87 ± 0.01	36.65 ± 0.01
Kink per mm	1.047 ± 0.002	1.058 ± 0.003	1.097 ± 0.002	1.083 ± 0.002

Analysis of XRD (Wide-angel X-ray diffraction)

Chemical treatment performed on natural fibers can affect the crystallinity of cellulose (Johar *et al.* 2012). Thus, the different bleaching methods would bring various effect to the fibers, and the X-ray diffraction could indicate the effect of the crystallization. XRD measurements for pulp A as well as the pulp B and pulp C showed similar diffraction patterns with three diffraction peaks at 2θ= 15.8°, 22.6°, and 35.0° (Fig. 3), which is characteristic of cellulose I crystals (Li *et al.* 2011; Lu *et al.* 2012).

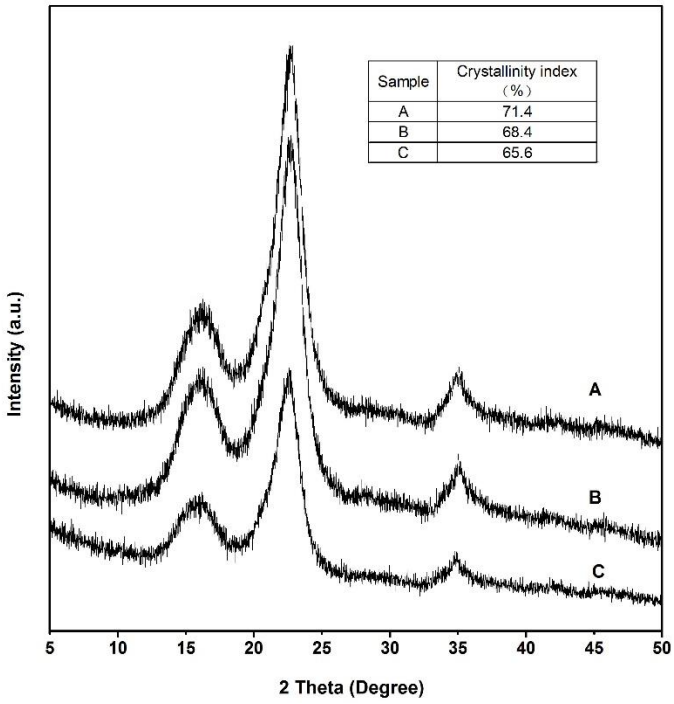

Fig. 3. X-ray diffraction patterns of pulp A, pulp B, and pulp C

All pulps exhibited a sharp high peak at 2θ=22.6°, which is assigned to the lattice plane of cellulose I. Meanwhile there are two overlapped weaker diffractions near the 2θ=15.8° (2θ=14.8° and 2θ=16.3°) were also assigned to the lattice planes of cellulose

I(G.H.D. Tonoli *et al.* 2012). The crystallinity index (CrI) for pulp C was 65.6%, whereas those for the pulp B were 68.4% and 71.4% for pulp A, respectively. The crystallinity index of Pulp B and pulp C were lower than pulp A, which indicated that the microwave heating took damage that was more serious than water-bath heating to the crystalline zone of the cellulose. As reported in the work of Cheng *et al.* (2013), the microwave power could made much gentler explosive damage during the water extraction (Cheng *et al.* 2013). This kind of explosion would took a damage the crystalline zone, and led to the reduced of the crystallinity index. The results of XRD in this experiment confirmed the conclusion of Cheng *et al.* (2013). On the other hand, the decrease of the crystallinity index would took an advantage effect on the dissolving of the extractions, which explained why microwave heating bleached pulp had a lower content of extractives.

Analysis of Pitch Deposits

The pitch contents of all bleached pulps were much lower than that of the unbleached one (0.203%), as shown in Fig. 4. Treatment C had a lower content of lipophilic extractives (0.127%) when compared with the other treatments. It was mentioned earlier that the microwave-induced bleaching was advantageous for the removal of low-molecular weight components, which could lead to lower organic extractive levels in the bleached pulps. Additionally, the contents of lipophilic extractives in treatments A and B were nearly identical. This is probably due to the limited reaction time (3 min) of microwave heating during ClO_2 bleaching. Therefore, the resin in the eucalypt pulp might need a longer irradiation period to assist extractives removal.

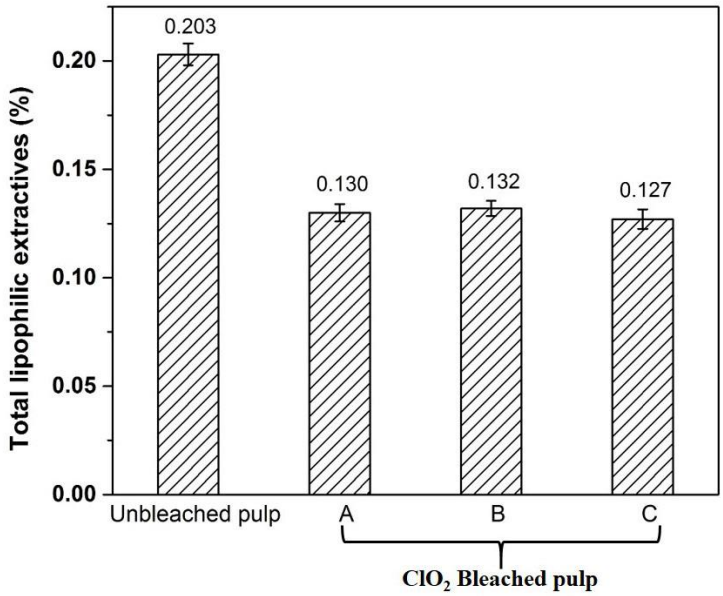

Fig. 4. Total lipophilic extractives of ClO_2-bleached and unbleached eucalypt pulps

With the aim of studying the behavior of the different lipophilic extractives under different bleaching conditions, all the bleached pulps were analyzed. The chemical components of the residual extractives in the bleached pulps were also analyzed. According to the GC-MS analyses, the extractives were identified as (Fig. 5): dibutyl phthalate (**1**), hexadecanol acid (**2**), 1-octadecanol (**3**), 9-octadecenoic acid, (**4**), octadecanoic acid (**5**), hexadecanamide (**6**), 9-octadecenamide (**7**), octadecanamide, hexanoic acid, hexacosane, and erucylamide (**9**).

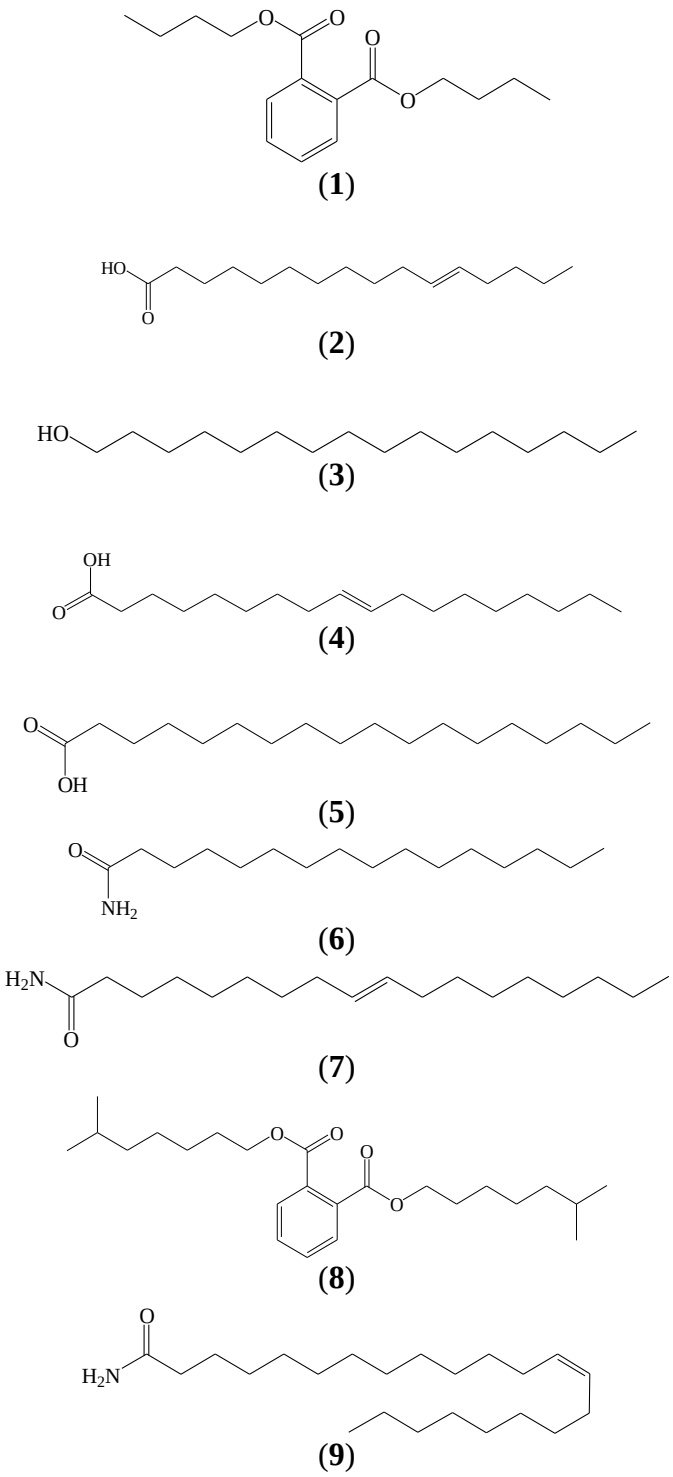

Fig. 5. Chemical structures of compounds representing the main classes of the observed lipophilic extractives: (**1**) dibutyl phthalate; (**2**) hexadecanol acid; (**3**) 1-octadecanol; (**4**) 9-octadecenoic; (**5**) octadecanoic acid; (**6**) hexadecanamide; (**7**) 9-octadecenamide; (**8**) 1,2-benzenedicarbosylic; and (**9**) erucylamide

Table 6. Composition of Lipophilic Extractives (%) in the Bleached Pulps of Fig. 1

Compound	A	B	C
Fatty acids			
Benzoic acid	-	0.08	0.03
Octanendioic acid	0.05	0.10	-
Dodecanoic acid	0.07	0.05	0.02
3-Hydroxy-4-methoxybenzoic acid	0.19	0.29	0.02
Nonanedioic Acid	0.19	0.24	-
Tridecanoic acid	0.22	0.21	0.10
Tetradecanoic acid	0.07	0.09	0.04
Myristic acid	0.61	0.72	0.39
Syringic acid	0.10	0.18	-
14-Pentadecenoic acid	0.12	0.12	0.08
Pentadecanoic acid	0.45	0.49	0.39
2-Hexadecenoic Acid	0.21	0.13	0.10
Hexadecenoic Acid	0.88	1.13	0.83
Palmitic acid	2.69	3.97	3.00
9-Octadecenoic acid	0.49	0.42	0.37
Heptadecanoic acid	0.90	1.06	0.56
Octadecanoic acid	1.94	2.19	2.11
9-Octadecenoic	2.11	2.48	2.26
Alkanes			
Docosane	-	0.59	0.84
Tricosane	-	0.97	1.13
Tetracosane	0.89	0.86	0.90
9-Tricosene	0.94	0.75	0.96
Pentacosane	0.64	0.58	0.65
Hexacosane	1.15	0.86	1.11
Heptacosane	0.92	1.29	0.96
Erucylamide	2.46	2.29	2.26
Octacosane	0.54	0.46	0.68
Spinacene	0.51	1.19	0.94
Nonacosane	0.57	0.53	1.42
Aldehydes			
Vanillin	0.02	0.11	-
Fatty alcohols			
1-dodecanol	0.03	0.07	0.03
Tetradecanol	0.03	0.05	0.02
1-Hexadecanol	0.19	0.14	0.10
1-Octadecanol	1.79	0.78	1.28
1-Eicosanol	1.01	1.29	0.70
Ester waxes & sterol esters			
Hexanoic acid, 2-ethyl-,cetyl ester	2.32	2.21	2.61
Palmitic acid, *N*-octyl ester	1.29	1.05	1.68
Hexanoic acid, 2-ethyl-,octadecyl ester	1.24	1.40	1.12
9-Hexadecenoic acid, eicosyl ester	0.33	0.44	0.64
Tetradecanoic acid, octadecyl ester	0.15	0.21	0.16
9-Hexadecenoic acid, octadecyl ester	0.19	0.29	0.18
Ethyl-2,4-dihydroxyphenylacetate	0.03	0.05	-
Diisobutyl phthalate	0.81	0.30	0.22
Dibutyl phthalate	2.67	2.10	1.17
γ-18 lactone	-	0.52	-
1, 2-Benzenedicarbosylic	2.32	2.23	2.37
Isopropyl palmitate	0.57	0.46	0.41

Compound	A	B	C
Amines			
N,*N*-Dimethyl dodecanamide	0.08	-	0.02
7,9-Di-*tert*-butyl-1-oxaspiro[4,5]deca-6,9-diene-2,8-dione	0.39	0.41	0.31
Myristamide	0.29	0.40	0.26
Hexadecanamide	2.10	2.47	1.97
9-Octadecenamide	4.20	4.28	3.96
Octadecanamide	1.05	1.13	1.01
Dodecanamide	0.28	0.40	-

"-" Means not detected.

In general terms, the qualitative composition of the lipophilic extractives from bleached pulps was very similar. Fatty alcohols, alkanes, free sterols, and fatty acids were the main lipophilic compounds present in the pulps.

Subsequently, the organic classes and percentages of lipophilic compounds are detailed in Table 6. The lipophilic compounds could be classified into two principal groups, namely organic acids and neutral components. Organic acids include fatty acids, whereas the neutrals include alkanes, fatty alcohols, sterol esters, and sterol glycosides. Generally, the amount of fatty acids was much higher than the neutral components. The major components of these fatty acids were palmitic, octadecanoic, hexadecenoic, and heptadecanoic acids. Noticeably, treatment C had lower fatty-acid levels, which was followed by treatment A and B. At the same time, treatment B had more benzoic, nonanedioic, and syringic acid; these organic acids were not detected in the other treatments. All of the fatty-acid compounds mentioned above in the bleached pulps are closely related to the formation of pitch deposits in ECF bleaching sequences (Silvestre *et al.* 1999; Freire *et al.* 2002; Freire *et al.* 2006; Gutiérrez *et al.* 2008). Thus, it was presumed that microwave pretreatment is a convenient method for fatty-acid removal, which could prevent pitch deposition onto equipment and pitch spots in paper sheets.

It was also observed that the amount of neutral compounds was low in the treated pulps (Table 6). According to the literature, chlorine dioxide has a tendency to react with such unsaturated lipophilic compounds, such as unsaturated sterol esters and alkyl esters; it is likely these substances are easily wash-out of the bleached pulps (Jansson *et al.* 1995; del Río *et al.* 1998; Holmbom 2000; Freire *et al.* 2003). In comparison, treatment C had the lowest amount of esterified compounds relative to the other bleaching treatments.

The removal of lipophilic extractives in the bleaching stage can be achieved by two mechanisms. One can include the dispersion and desorption of pulp lipids followed by removal with water washing. The other mechanism is chemical degradation/modification of the lipids by the bleaching agent, which results in hydrophilic compounds that are more easily solubilized and removed in the washing stage (Holmbom 2000; Marques *et al.* 2010b). It is well known that chlorine dioxide oxidizes such compounds, such as unsaturated steroids, triterpenoids, and unsaturated fatty acids (Holmbom 2000; Marques *et al.* 2010b). Combined with microwave irradiation, the ClO_2 bleaching process could remove more lipophilic extractives, which could relieve or even alleviate pitch problems to some extent.

CONCLUSIONS

1. In this research, oxygen-delignified *Eucalyptus globulus* pulp was bleached with chlorine dioxide (ClO_2) combined with microwave irradiation. This objective was to determine the effect of ClO_2 bleaching treatments on the lipophilic extractives and the resultant pulps. Results indicated that microwave-assisted ClO_2 bleaching was efficient at reducing the lipophilic extractives. Under the conditions of microwave power of 300 W, microwave heating time of 3 min, and ClO_2 charge of 1.0%, the properties of the bleached pulp were kappa number 5.4, ISO brightness 67.2%, and intrinsic viscosity 781 mL/g. This study also revealed that microwave irradiation during ClO_2 bleaching reduced the crystallinity index of the pulp, but it had little effect on the main chemical constituents of the bleached pulp, as well as fiber quality parameters and morphologies.
2. Characterizations of the lipophilic extractives from different chlorine dioxide bleached pulps was performed. The three treatment bleaching, such as water-bath heating, microwave heating, and microwave pretreatment combined with water-bath heating bleaching, led to distinct levels of individual lipophilic extractive compounds. The microwave pretreatment combined with water-bath heating bleaching was more effective at removing lipophilic extractives than the other two treatments. Microwave pretreatment had a positive effect on the removal of residual lignin and lipophilic extractives.

ACKNOWLEDGMENTS

This study was financially supported by the National Natural Science Foundation of China (21276119 and 51363013), Science Research Foundation Project of Yunnan Municipal Education Commission (2016zzx045), and KMUST Scientific Research Foundation for the Introduction of Talent (KKSY201605058).

REFERENCES CITED

Allen, L. H. (2000). "Pitch control in pulp mills," in: *Pitch Control, Wood Resin and Deresination,* E. L. Back and L. H. Allen (eds.), TAPPI Press, Atlanta, GA, pp. 265-288.

ASTM D1795-62 (1984). "Standard test method for intrinsic viscosity of cellulose," American Society for the Testing of Materials, Philadelphia, PA.

Back, E. L. (2000). "Deresination in pulping and washing," in: *Pitch Control, Wood Resin and Deresination*, E. L. Back and L. H. Allen (eds.), TAPPI Press, Atlanta, GA, pp. 205- 230.

Bergelin, E., and Holmbom, B. (2003). "Deresination of birch kraft pulp in bleaching," *J. Pulp Paper Sci.* 29(1), 29-34.

Boonsombuti, A., Luengnaruemitchai, A., and Wongkasemjit, S. (2013). "Enhancement of enzymatic hydrolysis of corncob by microwave-assisted alkali pretreatment and its effect in morphology," *Cellulose* 20(4), 1957-1966. DOI:10.1007/s10570-013-9958-7

Cheng, H. R., Feng, D. L., Jia, X. J., Li., Q. Q., Zhou, Y. H., and Ding, C. B. (2013).

"Structural characterization and antioxidant activities of polysaccharides extracted from *Epimedium Acuminatum*," *Carbohydrate Polymers* 92, 63-68. DOI: 10.1016/j.carbpol.2012.09.051

del Río, J. C., Gutiérrez, A., González-Vila, F. J., Martín, F., and Romero, J. (1998). "Characterization of organic deposits produced in the kraft pulping of *Eucalyptus globulus* wood," *J. Chromatogr. A* 823(1-2), 457- 465. DOI: 10.1016/S0021-9673(98)00179-4

del Río, J. C., Romero, J., and Gutiérrez, A. (2000). "Analysis of pitch deposits produced in Kraft pulp mills using a totally chlorine free bleaching sequence," *J. Chromatogr. A* 847(2), 235-245. DOI: 10.1016/S0021-9673(00)00111-4

Farhat, A., Fabiano-Tixier. A. S., Maataoui, M. E., Maingonnat, J.-F., Romdhane, M., and Chemat, F. (2010). "Microwave steam diffusion for extraction of essential oil from orange peel: Kinetic data, extract's global yield and mechanism," *Food Chemistry* 125, 255-261. DOI: 10.1016/j.foodchem.2010.07.110

Ferhat, M. A., Meklati, B. Y., and Chemat, F. (2007). "Comparison of different isolation methods of essential oil from citrus fruits: cold pressing, hydrodistillation and microwave 'dry' distillation," *Flavour Fragr. J.* 22, 494-504. DOI: 10.1002/ffj.1829

Ferhat, M. A., Meklati, B. Y., Smadja, J., and Chemat, F. (2006). "An improved microwave Clevenger apparatus for distillation of essential oils from orange peel," *Journal of Chromatography A*. 1112(1-2), 121-126. DOI: 10.1016/j.chroma.2005.12.030

Flórez, N., Conde, E., and Domínguez, H. (2014). "Microwave assisted water extraction of plant compounds," *Journal of Chemical Technology and Biotechnology*. 90(4), 590-607. DOI: 10.1002/jctb.4519

Freire, C. S. R., and Armando, J. D. (2006). "Effect of oxygen, ozone and hydrogen peroxide bleaching stages on the contents and composition of extractives of *Eucalyptus globulus* kraft pulps," *Bioresour. Technol.* 97(3), 420-428. DOI: 10.1016/j.biortech.2005.03.006

Freire, C. S. R, Silvestre, A. J. D., Pereira, C. C. L., Pascoal Neto, C., and Cavaleiro, J. A. S. (2002). "New lipophilic components of pitch deposits from a *Eucalyptus globulus* bleached kraft pulp mill," *J. Wood Chem. Technol.* 22(1), 55-66. DOI: 10.1081/WCT-120004434

Freire, C. S. R., Silvestre, A. J. D., and Pascoal Neto, C. (2003). "Oxidized derivatives of lipophilic extractives formed during hardwood kraft pulp bleaching," *Holzforschung* 57(5), 503-517. DOI: 10.1515/HF.2003.075

Freire, C. S. R., Silvestre, A. J. D, and Pascoal Neto, C. (2005). "Lipophilic extractives in *Eucalyptus globulus* kraft pulps. Behavior during ECF bleaching," *J. Wood Chem. Technol.* 25(1-2), 67-80. DOI: 10.1081/WCT-200058241

Golmakani, M. T., and Rezaei, K. (2008). "Comparison of microwave-assisted hydrodistillation with the traditional hydrodistillation method in the extraction of essential oils from *Thymus vulgaris* L," *Food Chemistry*, 109, 925-930. DOI: 10.1016/j.foodchem.2007.12.084

Gutiérrez, A., and del Río, J. C. (2005). "Chemical characterization of pitch deposits produced in the manufacturing of high-quality paper pulps from hemp fibers," *Biotechnol*. 96(13), 1445-1450. DOI: 10.1016/j.biortech.2004.12.008

Gutiérrez, A., Rodríguez, I. M. and del Río, J. C. (2008). "Chemical composition of lipophilic extractives from sisal (*Agave sisalana*) fibers," *Ind. Crop. Prod.* 28(1), 81-87. DOI: 10.1016/j.indcrop.2008.01.008

Gutiérrez, A., del Río, J. C., and Martínez, A. T. (2009). "Microbial and enzymatic control of pitch in pulp and paper industry," *Appl. Microbiol. Biotechnol.* 82(6), 1005-1018. DOI: 10.1007/s00253-009-1905-z

Holmbom, B. (2000). "Resin reactions and deresination in bleaching," in: *Pitch Control, Wood Resin and Deresination*, E. L. Back and L. H. Allen (eds.), TAPPI Press, Atlanta, GA, pp. 231-244.

Hu, Z.-H., and Yu, H.-Q. (2012). "Optimizing and modeling the anaerobic digestion of lignocellulosic wastes by rumen cultures," in: *Biogas Production: Pretreatment Methods in Anaerobic Digestion*, A. Mudhoo (ed.), John Wiley & Sons, Hoboken, NJ, pp. 259-289. DOI: 10.1002/9781118404089.ch10

Issa, A. A., Al-Degs, Y. S., Mashal, K., and Al Bakain, R. Z. (2015). "Fast activation of natural biomasses by microwave heating," *J. Ind. Eng. Chem.* 21, 230-238. DOI: 10.1016/j.jiec.2014.02.029

Jansson, B., Wormald, P., and Dahlman, O. (1995). "Reactions of wood extractives during ECF and TCF bleaching of kraft pulp," *Pulp Paper Can.* 96(4), 42- 45.

Johar, N., Ahmad, I., and Dufresne, A. (2012). "Extraction, preparation and characterization of cellulose fibres and nanocrystals from rice husk," *Industrial Crops and Products* 37, 93-99. DOI: 10.1016/j.indcrop.2011.12.016

Kallioinen, A., Vaari, A., Rättö, M., Konn, J., Siika-aho M., and Viikari, L. (2003). "Effects of bacterial treatments on wood extractives," *J. Biotechnol.* 103(1), 67-76. DOI: 10.1016/S0168-1656(03)00051-8

Kilulya, K. F., Msagati, T. A. M., Mamba, B. B., Ngila, J. C., and Bush, T. (2012). "Controlling the release of wood extractives into water bodies by selecting suitable eucalyptus species," *J. Phys. Chem. Earth* 50-52, 217-223. DOI: 10.1016/j.pce.2012.09.012

Leiviskä, T., Sarpola, A., and Tanskanen, J. (2012). "Removal of lipophilic extractives from debarking wastewater by adsorption on kaolin or enhanced coagulation with chitosan and kaolin," *Applied Clay Science.* 61, 22-28. DOI: 10.1016/j.clay.2012.03.002

Li, Q., and Rnneckar, S. (2011). "Supramolecular structure characterization of molecularly thin cellulose I Nanoparticles," *Biomacromolecules*, 12(3), 650-659. DOI: 10.1021/bm101315y

Lu, P., and Hsieh, Y. L. (2012). "Preparation and characterization of cellulose nanocrystals from rice straw," *Carbohydrate Polymers*. 87, 564-573. DOI: 10.1016/j.carbpol.2011.08.022

Lucchesi, M. E., Smadja, J., Bradshaw, S., Louw, W., and Chemat, F. (2006). "Solvent free microwave extraction of *Elletaria Cardamomum* L.: A multivariate study of a new technique for the extraction of essential oil," *Journal of Food Engineering*, 79(3), 1079-1086. DOI: 10.1016/j.foodeng.2006.03.029

Marques, G., del Río, J. C., and Gutiérrez, A. (2010a). "Lipophilic extractives from several nonwoody lignocellulosic crops (flax, hemp, sisal, abaca) and their fate during alkaline pulping and TCF/ECF bleaching," *Bioresour. Technol.* 101(1), 260-267. DOI: 10.1016/j.biortech.2009.08.036

Marques, G., Rencore, J., Gutiérrez, A.,, and del Río, J. C. (2010b). "Evaluation of the chemical composition of different non-woody plant fibers used for pulp and paper. Manufacturing," *Open Agric. J.* 4(11), 93-101. DOI: 10.2174/1874331501004010093

Mishra, R. R., and Sharma, A. K. (2015). "Microwave-material interaction phenomena: Heating mechanisms, challenges and opportunities in material processing," *J. Compos. Part A*, 81, 78-97. DOI: 10.1016/j.compositesa.2015.10.035

Nkhili, E., Tomao, V., El Hajji, H., El Boustani, E. S., Chemat, F., and Dangles, O. (2009). "Microwave-assisted water extraction of green tea polyphenols," *Phytochem Anal*. 20(5), 408-415. DOI: 10.1002/pca.1141

Ouyang, Y., Xu, D. P., Leininger, T. D., and Zhang, N. N. (2016). "A system dynamic model to estimate hydrological processes and water use in a eucalypt plantation," *Ecological Engineering* 86, 290-299. DOI: 10.1016/j.ecoleng.2015.11.008

Pickles, C. A. (2009). "Microwaves in extractive metallurgy: Part 1 - Review of fundamentals," *Miner .Eng.* 22(13), 1102-1111. DOI: 10.1016/j.mineng.2009.02.015

Rodríguez-Rojo, S., Visentin. A., Maestri, D., Cocero, M. J. (2012). "Assisted extraction of rosemary antioxidants with green solvents," *J Food Eng* 109, 98-103. DOI: 10.1016/j.foodeng.2011.09.029

Segal, L., Greely, J. J., Martin, A. E., and Conrad, C. M. (1959). "An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer," *Textile Research Journal* 29(10), 786-794. DOI: 10.1177/004051755902901003

Silvério, F. O., Barbosa, L. C. A., Maltha, C. R. A., Fidêncio, P. H., Cruz, M. P., Veloso, D. P., and Milanez, A. F. (2007). "Effect of storage time on the composition and content of wood extractives in Eucalyptus cultivated in Brazil," *Bioresour. Technol.* 99(11), 4878-4886. DOI: 10.1016/j.biortech.2007.09.066

Silvestre, A. J. D., Pereira, C. C. L., Pascoal Neto, C., Evtuguin, D. V., Duarte, A. C., Cavaleiro, J. A. S., and Furtado, F. P. (1999). "Chemical composition of pitch deposits from an ECF *Eucalyptus globulus* bleached kraft pulp mill: Its relationship with wood extractives and additives in process streams," *APPITA J*. 52(5), 375-382.

Smook, G. A. (2002). *Handbook for Pulp and Paper Technologists*, 3rd ed., TAPPI Press, Atlanta, GA, pp. 174-175.

TAPPI method T 236 om-99 (1999). "Kappa Number of Pulp," TAPPI Press, Atlanta, GA, USA.

TAPPI method T 452 om-02 (2002). "Brightness of pulp, paperboard," TAPPI Press, Atlanta, GA, USA.

TAPPI method T 271 om-02 (2002). "Fiber length of pulp and paper by automated optical analyzer using polarized light," TAPPI Press, Atlanta, GA, USA.

TAPPI method T 222 om-83 (1999). "Acid-insoluble lignin in wood and pulp," TAPPI Press, Atlanta, USA.

TAPPI method T 201 wd-76 (2004). "Cellulose in Pulp (Cross and Bevan Method)," TAPPI Press, Atlanta, USA.

TAPPI method T 249 cm-85 (1999). "Carbohydrate composition of extractive free wood and wood pulp by gas–liquid chromatography," TAPPI Press, Atlanta, GA, USA.

TAPPI method T211 om-93 (2000). Ash in wood, pulp, paper and paperboard: combustion at 525◦C," TAPPI Press, Atlanta, GA, USA.

TAPPI method T204 cm-07 (2007). "Solvent Extractives of wood and pulp," TAPPI Press, Atlanta, GA, USA.

Tonoli, G. H. D., Teixeira, E. M., Corrêa, A.C., Marconcini, J. M., Caixeta, L. A., Pereira-da-Silva, M. A., and Mattsso, L. H. C. (2012). "Cellulose micro/nanofibres from *Eucalyptus* kraft pulp: Preparation and properties," *Carbohydrate Polymers* 89, 80-88. DOI: 10.1016/j.carbpol.2012.02.052

van Beek, T. A., Kuster, B., Claassen, F. W., Tienvieri, T., Bertaud, F., Lenon, G., Petit-Conil, M., and Sierra-Alvarez., R. (2007). "Fungal bio-treatment of spruce wood with *Trametes versicolor* for pitch control: Influence on extractive contents, pulping process parameters, paper quality and effluent toxicity," *Bioresour. Technol.* 98(2), 302-311. DOI: 10.1016/j.biortech.2006.01.008

Verma, P., Watanabe, T., Honda, Y., and Watanabe, T. (2011). "Microwave-assisted pretreatment of woody biomass with ammonium molybdate activated by H_2O_2," *Bioresour. Technol.* 102(4), 3941-3945. DOI: 10.1016/j.biortech.2010.11.058

Xue, B.-L., Li, M.-F., Xu, F., Sun, R.-C., and Jones, G. (2012). "Microwave-enhanced alkali treatment of *Pinus yunnanensis*: Physiochemical characterization of the dissolved lignins," *Ind. Crop. Prod.* 36(1), 209-216. DOI: 10.1016/j.indcrop.2011.09.008

Article submitted: February 24, 2017; Peer review completed: May 22, 2017; Revised version received and accepted: July 25, 2017; Published: September 6, 2017.
DOI: 10.15376/biores.12.4.7756-7773