Low Consistency Refining of Eucalyptus Pulp: Effects on Surface Chemistry and Interaction with FWAs

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The surface chemistry of eucalyptus pulp fibers prior to and after low-consistency (LC) refining was studied using a state-of-the art laboratory refining device and advanced surface analysis techniques. It was found that LC refining could generate fines and fibrillation and change the surface chemical composition of fiber surfaces. Both of these two effects can facilitate the adsorption of fluorescent whitening agents (FWAs) by the combination of increased specific surface area, electrostatic forces, and hydrophobic interactions, thus compensating for the loss of optical properties resulting from LC refining. The mechanical hydraulic force generated by the high refining energy disturbed the FWA retention. Therefore, high refining energy could improve the adsorption of FWAs when they are added after refining, but for better performance, the refining energy should be controlled and lowered. In addition, small amounts of calcium salt added after refining can also ameliorate the adsorption of FWAs.

Keywords: Fluorescent whitening agents; Calcium sulfate; XPS; ToF-SIMS; Low-consistency refining

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INTRODUCTION

Low-consistency refining is commonly used to develop papermaking fiber structures as well as their bonding ability. The structural changes caused by the refining performance include internal fibrillation, fiber shortening, external fibrillation, and fines formation (Mohlin and Miller 1992; 1995; Li *et al*. 2011a). Fibrils containing cellulose are of importance for paper strength properties (Berthold and Salmén 1997; Li *et al*. 2011b). Most of the strength properties of paper are consequently increased by refining, but the opacity is decreased because paper becomes denser. Fluorescent whitening agents (FWAs) are used in paper and board manufacturing to compensate for the loss of whiteness and brightness caused by residual lignin or other color species in paper fibers (Shen 2004; Zhang *et al*. 2010). FWAs absorb light in the near-ultraviolet (UV) region of the spectrum, below about 400 nm, and re-emit the light, as fluorescence, in the violet-blue visible region (Stana *et al*. 1995).

FWAs are based on stilbene derivatives and may be considered chemically similar to anionic direct dyes because they are also quite large linear molecules with extensive delocalized-electron systems and one or more sulfuric acid groups (Roberts 1992). Due to their effectiveness and low cost, the application of FWAs in paper products is economically and environmentally sound because it reduces the use of bleaching chemicals that are usually expensive and toxic to human health (Shen 2004; Shi *et al.* 2012). It has also been reported that chemical additives with cationic and anionic charges that are used to improve the product properties could influence the adsorption efficiency of FWAs (Krässig 1993). For instance, the adsorption efficiency of the brightener is greater for solutions containing cationic surfactants below the critical micelle concentration (*cmc*), while the efficiency is greater for an anionic surfactant above its *cmc* (Iamazaki and Atvars 2007). However, highly charged cationic polyelectrolytes (like retention agents and sizing promoters) can easily reduce the fluorescence effect of an FWA molecule as they interact with each other (Shi *et al*. 2012)

Many studies explaining the refining effects on the fiber cell wall structure and surface morphology have been published (Laine *et al*. 2004, Page *et al*. 1989), but most research focuses on machine parameters (Xian *et al*. 2008; Zhang *et al*. 2010), while there have been no reports on the influence of surface chemistry changes after refining on FWA adsorption.

The surface properties (including surface chemistry) of pulp are of great importance to the downstream processing of paper manufacturing and finishing, such as coating and printing, as they may influence the fiber surface charge, fiber bonding potential, adsorption, and adhesion properties (Mou *et al*. 2013). The surface chemistry of fibers can be analyzed by advanced surface analysis techniques. Scanning electron microscopy (SEM) has been utilized to describe the morphology changes of fibers after mechanical treatment such as beating and refining; changes in fiber shape, fibrillation, swelling, and shrinkage can also be evaluated by SEM (Molin and Miller 1995; Buchanan and Washburn 1962; Touzinsky *et al.* 1977; Mou *et al.* 2013). X-ray photoelectron spectroscopy (XPS) has been applied to analyze the surface chemistry and obtain information about surface lignin, extractives, and carbohydrates (Wang *et al.* 2000; Laine *et al*. 1994, 1996; Fardim and Durán 2000; Mou *et al.* 2013). ToF-SIMS has been used to detect the surface composition and for component imaging of paper, pulp, wood, and deinked pulp (Buchert *et al.* 1996; Brinen 1993; Dalton *et al.* 2002; Fardim and Durán 2000; Fardim *et al.* 2005; Orblin and Fardim 2010). Mou *et al*. (2013) have studied the surface chemistry changes of softwood impacted by LC refining using XPS and ToF-SIMS, but the manner in which surface chemistry influences FWA adsorption onto fibers and the brightening effect is still incompletely understood. The aim of this work was to determine the effects of refining on the surface chemistry changes and on adsorption of the FWAs at given conditions by studying the adsorption of two typical FWAs on eucalyptus pulp before and after LC refining. This will provide a fundamental understanding of the absorption of FWAs in the papermaking processing.

EXPERIMENTAL

Materials

ECF (elemental chlorine-free) bleached eucalyptus pulp board was obtained from a Finnish pulp mill. Pulp samples were refined by a ProLab^{TM} laboratory station under different specific edge load (SEL) and specific energy consumption (SEC) levels with a short fiber (SF) filling (Lundin *et al*. 2008; Mou *et al.* 2013).

Two series of samples were made: refined whole pulps (pulp samples) that included pulp fines, and fiber fractions (fiber samples) where the fines were removed after refining. The separation was done with a dynamic drainage jar equipped with 200-mesh wire (TAPPI T261cm00). The Schopper Riegler drainability value (SR) was measured after each refining step (ISO5267-1 1999). Hand sheets were prepared in a Rapid Köthen apparatus using deionized water (ISO5269-2 1988) for the measurement of optical properties (L&W Elrepho spectrophotometer routine SE070R according to SCAN-CM 27:00) and for surface chemical analyses without any further sample preparation. The samples were identified as 22-Pulp, 37-Pulp, 53-Pulp, 76-Pulp (for pulp samples) and 22-Fiber, 37-Fiber, 53-Fiber, 76-Fiber (for fiber samples) according to the SR values produced by the applied SEC levels (0, 50, 100, and 150 kWh/t, respectively).

Surface Analysis Methods

FE-SEM images were obtained using a JEOL JSMT 300 microscope, operated in secondary electron mode at a beam current of 100 μA and accelerating voltage of 20 kV. Before imaging, samples were coated with Pt for 20 s with an Agar scientific sputter coating system equipped with a rotating base. Images were obtained at magnifications of 5000×.

XPS spectra of the pulp and fiber sample surfaces were obtained with a Physical Electronics PHI 2000 ESCA instrument equipped with a monochromatic Al Kα X-ray source, operated at 200 W, and charge compensation. The analysis area was 1 mm^2, and the take-off angle was 45° relative to the sample surface. At least three different spots were measured on each sample. Low-resolution scanning was performed using a pass energy of 187 eV in 3 min, and high-resolution C_{1s} scanning was conducted using a pass energy of 23 eV in 5 min. A curve-fitting program provided by the instrument manufacturer was used to obtain the oxygen-to-carbon ratios (O/C) of the samples and to interpret the C_{1s} signal, which carried information about the chemical binding state of carbon. The binding energy for aliphatic carbon (C-C or C-H) is 284 eV, and the following energy shifts from that were detected included: (1.7±0.2) eV for C-O, (3.1±0.3) eV for C=O or O-C-O, and (4.6±0.3) eV for O=C-O groups. The aliphatic carbon (C-C or C-H) is denoted C_1, and the other states are denoted C_2, C_3, and C_4, in order of increasing binding energies.

Surface coverage by lignin (S_{lig}), carbohydrates (S_{car}), and extractives (S_{ext}) was determined using the O/C ratio of the untreated and acetone-extracted (Soxhlet, overnight) samples using the following equations (Ström and Carlsson 1992; Laine *et al.* 1996):

$$S_{ext}= (O/C_{\text{ extracted}}- O/C_{\text{ unextracted}}) / (O/C_{\text{ extracted}}- O/C_{\text{extractives}})*100 \tag{1}$$

$$S_{lig}= (O/C_{\text{ extracted}}- O/ C_{\text{carbohydrate}}) / (O/C_{\text{lignin}}- O/ C_{\text{carbohydrate}})*100 \tag{2}$$

$$S_{car}=1- S_{lig} \tag{3}$$

$$O/C_{\text{carbohydrate}} = 0.83,\ O/C_{\text{lignin}}= 0.33,\ O/C_{\text{extractives}}=0.09$$

ToF-SIMS analysis was done with a Physical Electronics ToF-SIMS TRIFT II spectrometer with a primary beam from a ^{69}Ga liquid metal ion source and charge compensation by electron flood. Spectra were acquired for 3 min using a 25-kV acceleration voltage under static conditions. At least three different spots were analyzed on each sample. The peak intensities of the characteristic peaks from cellulose, hemicellulose (xylan), lignin, and various wood extractives in the samples were compared. The characteristic fragments were chosen according to previously published literature (Fardim *et al*. 2005; Kleen 2000; Kangas 2007). To compensate for analytical variations, the peak counts were first normalized, dividing by the total counts of the spectrum.

FWA Adsorption

The anionic FWAs (DS and P01) and calcium sulfate were supplied by Kemira Company. Both di-sulfonic DS (with a formula of $C_{40}H_{42}N_{12}Na_2O_{12}S_2$) and tetra-sulfonic P01 (with a formula of $C_{40}H_{40}N_{12}Na_4O_{16}S_4$) are stilbene derivatives.

First, 0.3 g $MgSO_4$ was added to a 1% concentration of pulp and then reacted with FWAs for 15 min at pH 6 with magnetic stirring. Paper sheets were formed using a glass funnel. The filtrated solution was examined by fluorescence spectroscopy using a calibration curve (Yamaki *et al.* 2005). Milli-Q purified water was used throughout the paper sheet preparation. FWA sheets were made by glass filter using deionized water for optical properties measurement.

Steady-state fluorescence spectra of FWAs in solution were recorded from λ_{em} = 370 nm to λ_{em} = 600 nm with λ_{exc} = 348 nm using a Lambda 40 UV-Vis spectrofluorometer. All samples were examined two or three times at room temperature, and the average is reported.

RESULTS AND DISCUSSION

Effects of LC Refining on Optical Properties

After refining under various conditions, the optical properties of handsheets made from the pulp and fiber samples were studied, and the results are shown in Table 1. For both pulp and fiber samples, the brightness, whiteness, opacity, and *s* value (light scattering coefficient) decreased with increasing specific energy consumption (SEC), while the yellowness slightly increased. For example, when the SEC increased from 0 to 150 kWh/t, the brightness, whiteness, and *s* value of pulp samples decreased by about 3%, 7.5%, and 42%, respectively. Similar results for the decrease in brightness after refining were also reported for eucalyptus (Fardim and Durán 2000) and for pine (Mou *et al.* 2013).

Table 1 also reveals that both the SR and water retention value (WRV) of pulp samples were raised by refining, meaning that the drainage decreased for pulp samples. This is due to the creation of fines, fiber fibrillation, and delamination effects during refining (Li *et al.* 2011b), and is also consistent with the increase in the fines fraction percentage and the decrease in fiber length (Table 1). This reduction in the drainage rate is one major drawback of the refining process and may cause unwanted issues such as increased sheet shrinkage. The role of fines in the optical properties of paper is known to be associated with high specific surface area and lignin content (Asikainen *et al.* 2010), while the fibers' contribution can be speculated to be a result of the light-reflecting surfaces of the external cell wall layer (Mou *et al.* 2013). Refining has a well-known negative effect on optical properties of pulp. But the brightness and whiteness values of pulp samples were slightly higher compared to fiber samples (Table 1). This is because of the generation of fines, as fines have higher light scattering coefficients which benefit the improvement of optical properties (Li *et al.* 2011a). The somewhat higher opacity of pulp samples compared to fiber samples (Table 1) is also due to the existence of fines in pulp samples.

Table 1. Effect of LC Refining on Fiber Properties of Pulp and Fiber Samples

Fiber Properties	0 kWh/t		50 kWh/t		100 kWh/t		150 kWh/t	
	Pulp	Fiber	Pulp	Fiber	Pulp	Fiber	Pulp	Fiber
SR(^{o})	22.2	ND	37.2	ND	53.4	ND	76	ND
WRV	1.2	ND	1.4	ND	1.6	ND	1.8	ND
Width (μm)	16.9	ND	17.2	ND	17.5	ND	17.6	ND
Fines wt%	1.7	ND	2.6	ND	2.7	ND	3.0	ND
Fiber length (mm)	0.79	ND	0.77	ND	0.75	ND	0.73	ND
Brightness % ISO	87.7	87.4	87.0	86.8	86.4	85.9	85.0	84.2
CIE Whiteness	77.2	76.4	75.2	74.8	73.9	73.5	71.4	70.3
Opacity %	82.8	82.5	81.9	81.9	79.9	79.5	75.4	74.7
Yellowness	5.3	5.6	6.1	6.1	6.3	6.3	6.9	6.8
s m^2/g	48.5	40.1	42.5	38.2	40.1	32.3	28.3	28.3
k m^2/g	0.16	0.15	0.16	0.15	0.17	0.15	0.17	0.15

ND: not determined.
s: light scattering coefficient; *k:* light absorption coefficient.
All optical property data are reported as the mean of ten readings for each test.

Effects of LC Refining on Surface Morphology

The surface morphology and the sheet network can be expected to be related to the paper properties; they could also affect the adsorption of chemical additives and fillers (Alén 2007). Therefore, the surface morphologies of pulp and fiber samples at different SEC levels were analyzed by FE-SEM and the results are shown in Figs. 1 and 2. Samples with a SEC of 0 kWh/t can be considered unrefined.

It has been reported that after refining, the lumen of fibers collapse and the fiber shapes change from tubular to flat (Fardim and Durán 2000; Mou *et al.* 2013). In this study, the surface fibrillation of fibers increased and superficial layers were released after refining. The significant increase in fibrillation after refining can be clearly observed in Fig. 1b, compared to Fig. 1a, and the secondary fibrils are clearly seen in Fig. 2b, after fines were removed. Refining causes a shearing of the fiber wall, usually resulting in internal/external fibrillations and an increase in roughness (Figs. 1 and 2). Similar results have also been reported for pine samples (Mou *et al.* 2013). The fines and fibrils were probably generated from the primary and outer secondary walls, as reported previously (Mou *et al.* 2013). The increase in pulp fines and fibrils can lead to an increase in the specific surface area of pulp fibers, thus increasing the bonding potential (*i.e.*, the strength properties of the whole pulp sheets) and affecting the optical properties of the sheet (Fardim and Duran 2003). This is also in good agreement with the increased SR and WRV values (Table 1) after refining. Severe shrinkage after fiber swelling was detected for both pulp and fiber samples by FE-SEM. After removing fines and fibrils, the compact shrinkage was exposed on fiber samples. The morphology change may influence the chemical agent deposition.

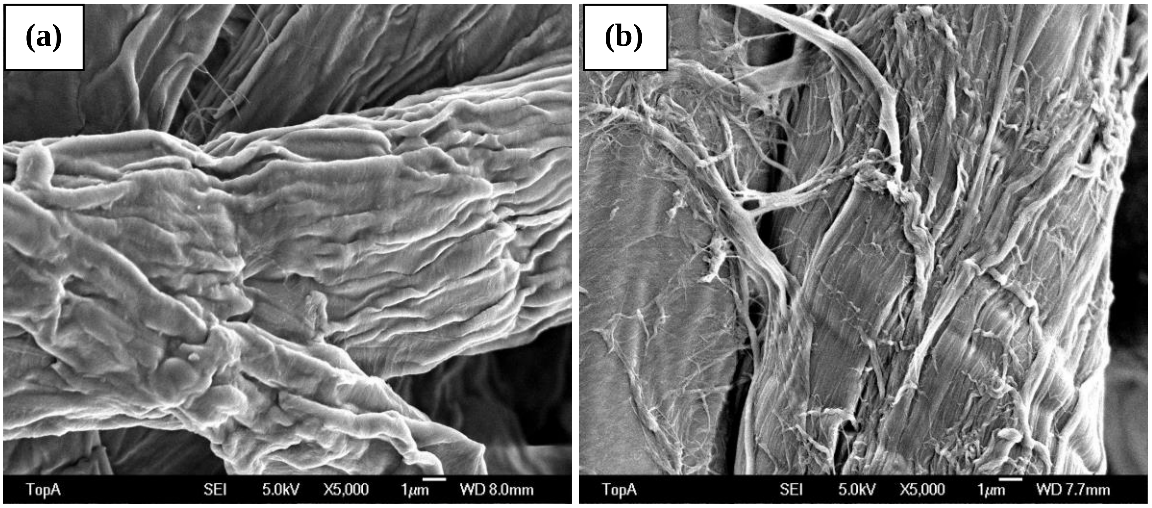

Fig. 1. Pulp samples at an FE-SEM magnification 5,000×, for (a) 0 kWh/t and (b) 100 kWh/t

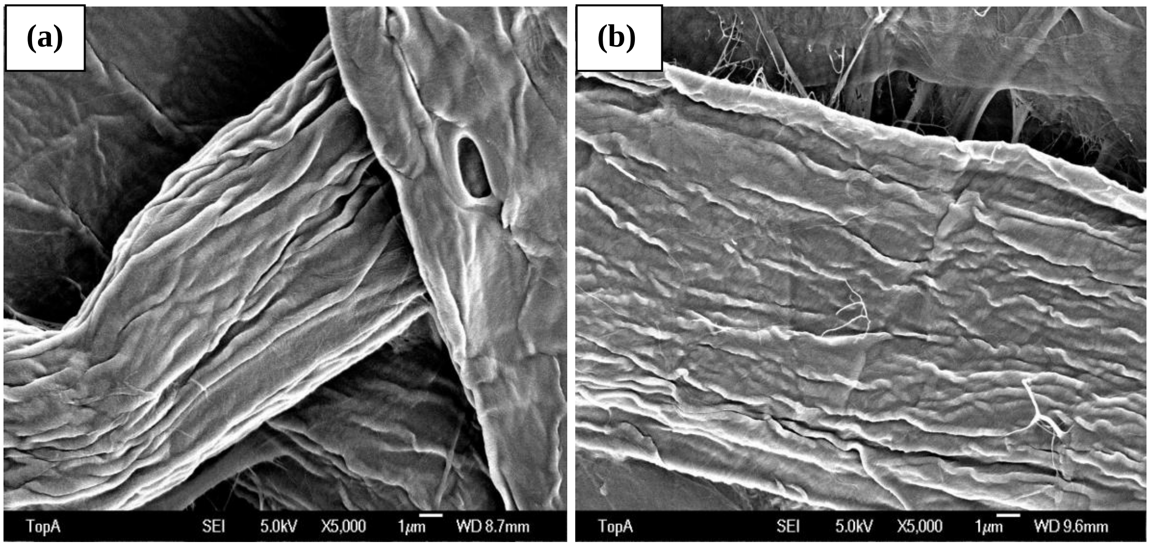

Fig. 2. Fiber samples at an FE-SEM magnification 5,000×, for (a) 0 kWh/t and (b) 100 kWh/t

Effects of LC Refining on Surface Chemical Composition

The surface chemical composition of pulp and fiber samples under different refining levels was analyzed by XPS (Table 2). The content of aliphatic carbon (C_1) was higher in the refined samples than that in the first unrefined samples (*e.g*. 22-Pulp and 22-Fiber). This is due to re-localization of components in the fiber cell wall during refining. Also, the carbon bond C_4, that is, the amount of carboxyl groups, was raised by refining. After removing fines, the C_4 content of the fiber samples was higher than that of the pulp samples. It was assumed that carboxyl groups from fatty acids or xylan were exposed on the surface of fibers after refining and thus can potentially affect the retention of chemical additives. Extraction naturally decreased C_1 and increased C_2 as the carbon-rich extractives were removed. The extraction (the proportional decrease in C_1) was more efficient in the refined pulp samples compared to the unrefined sample (*i.e*. 22-Pulp), which also confirmed that components from the cell wall pores were probably redistributed and spread on the fiber surfaces during the process and were thereafter easily washed away.

The surface coverage by lignin, carbohydrates, and extractives is also shown in Table 2. In pulp and fiber samples, the surface coverage by lignin decreased and carbohydrates increased with added refining energy. The decrease in surface coverage by lignin refers to external fibrillation, where cellulosic fibrils were shredded and opened up, thereby spreading more widely on the surface. Deposition of dissolved hemicelluloses (xylan) is also plausible (Mou *et al.* 2013). The decrease in surface coverage by lignin may enhance the effectiveness of FWAs (Shi *et al.* 2012). The surface coverage by extractives increased, in contrast to the lignin decrease. Table 2 also shows that pulp samples had high lignin and extractive contents compared to fiber samples at the same SEC level. This is probably due to the fact that fines (typically in chemical pulps) contain more extractives and lignin than long fibers (Orblin and Fardim 2010; El-Sharkawy *et al.* 2008; Bäckström *et al.* 2008). The main differences between the pulp and the fiber samples were all due to the different amounts of fines and the composition of the fines. In addition, as shown in Table 2, the C_4 content of pulp and fiber samples was raised with refining. After removing fines, the C_4 proportion in fiber samples was higher than that in pulp samples. The change in surface chemical composition can introduce more negative charges to the fiber surface, and this may affect the retention of cationic chemical additives on fibers in the papermaking process.

Table 2. Effects of LC Refining on Surface Chemical Compositions of Extracted (E) and Un-Extracted Pulp and Fiber Samples

Samples	C_1%	C_2%	C_3%	C_4%	O/C	S_{lig}%	S_{car} %	S_{ext}%
22-Pulp	19.9	47.2	32.2	0.66	0.69	23.1	76.9	4.7
22-E-Pulp	14.9	61.7	22.5	1.01	0.71			
37-Pulp	26.9	50.0	17.4	5.70	0.60	21.7	78.3	18.3
37-E-Pulp	12.1	66.0	22.4	1.01	0.72			
53-Pulp	26.9	50.6	18.9	3.73	0.60	19.2	80.8	20.7
53-E-Pulp	16.2	62.9	17.6	4.25	0.73			
76-Pulp	24.0	52.6	19.6	3.76	0.61	15.7	84.3	21.0
76-E-Pulp	11.9	66.8	18.5	2.87	0.75			
22-Fiber	26.8	45.9	24.7	2.62	0.66	19.0	81	11.6
22-E-Fiber	10.8	68.6	17.6	2.99	0.73			
37-Fiber	28.1	46.3	20.7	4.90	0.66	18.3	81.7	13.4
37-E-Fiber	12.3	66.4	19.7	1.61	0.74			
53-Fiber	25.7	47.8	22.0	4.54	0.63	16.8	83.2	17.4
53-E-Fiber	11.7	65.0	21.8	1.56	0.75			
76-Fiber	24.9	51.5	17.0	6.71	0.62	16.4	83.6	19.9
76-E-Fiber	13.0	63.3	22.4	1.29	0.75			

22-P, 37-P, 53-P, 76-P, pulp samples, and 22-F, 37-F, 53-F, 76-F, fiber samples without fines, correspond to SR values under SECs of 0, 50, 100, and 150 kWh/t, respectively.

The surface compositions of pulp and fiber samples at different SEC levels were investigated by ToF-SIMS spectrometry. The ratios between the peak counts of the characteristic mass peaks from components of interests were studied. Peak intensities were previously normalized by total spectrum counts (Fardim and Durán 2000). Characteristic peaks of cellulose, xylan, lignin, and extractives were selected. The ratios are shown in Table 3. Higher ratios for carbohydrate peaks may be an indication of cellulose and xylan enrichment after refining. Because of the different detection depth between ToF-SIMS (1 nm) and XPS (about 5 nm), ToF-SIMS gives more information about the outermost layer of the fiber surface. The results obtained by the peak intensity ratios of ToF-SIMS spectra showed good agreement with surface coverage results by XPS. The increase in S_{ext} and the decrease in S_{lig} during refining, as estimated by XPS (Table 2), were also observed in the ToF-SIMS peak ratios (Table 3). The xylan ratio value of pulp samples was higher than that of fiber samples with increasing refining energy. According to the ToF-SIMS peak ratio, the increase in the amount of surface extractives on pulp sample (37-Pulp) was due to a release of myristeric, pentadecan, and oleic acids, as well as Ca myristate, pentadecanoate, and palmitate during refining (Fardim and Durán 2000). The exposure of carbohydrates and extractives were probably because of the internal fibrillation of fiber cell walls resulting from the mechanical refining performance. Evidence of xylan deposition and cellulose exposure was observed in the ToF-SIMS peak ratios. Deposition of lignin did not seem to occur for eucalyptus, despite being reported for pine (Laine *et al*. 1996). Polysaccharides contain carboxylic acid side groups, and therefore their exposure probably affects the adsorption of cationic chemical agents. Extractives on fiber surfaces, particularly fatty acid salts, may enhance the hydrophobic interactions with molecules containing hydrophobic portions in their chemical structure.

Effects of LC Refining on FWA Adsorption

FWA adsorption on eucalyptus after refining

The isotherms for anionic DS and P01 adsorption on eucalyptus pulp without refining are shown in Fig. 3, which reveals that DS was more easily adsorbed on eucalyptus than P01. This can be attributed to the different structures of DS and P01. Research work and mill experiences showed that di-FWA (DS) is more effective than tetra-FWA (P01), as di-FWA has stronger adsorption capability than tetra-FWA (Zhang *et al*. 2009).

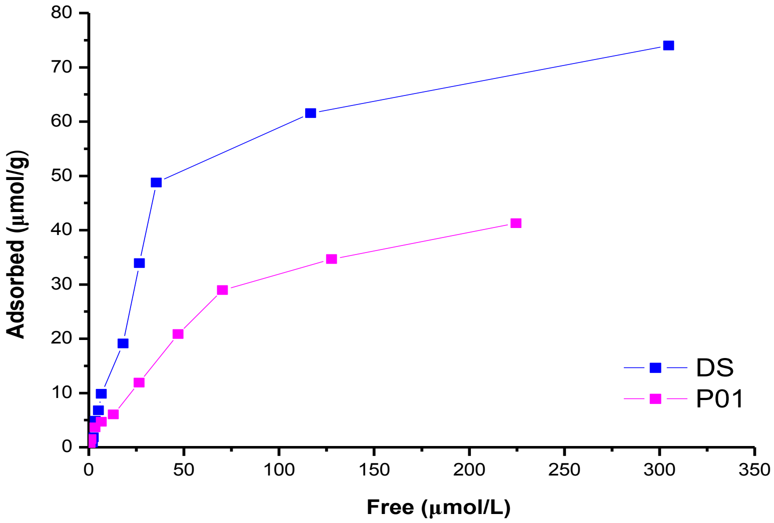

Fig. 3. Adsorption isotherm for FWAs onto reference eucalyptus pulp

Table 3. ToF-SIMS Results for Refined Pulp and Fiber Samples

Component	**Peaks in ToF-SIMS spectra**		**Ratio of peak intensity (normalized)**				
	Peak	Ion	22-Pulp/22-Fiber	37-Pulp/22-Pulp	37-Pulp/37-Fiber	53-Pulp/37-Pulp	53-Pulp/53-Fiber
Carbohydrates							
Cellulose	127+	$C_6H_7O_3^+$	1.0	1.6	1.1	1.6	1.4
	145+	$C_6H_9O_4^+$	0.5	0.8	1.3	1.8	1.4
Xylan	115+	$C_5H_7O_3^+$	2.1	1.4	1.0	1.3	1.2
	133+	$C_6H_9O_4^+$	1.4	1.5	1.1	1.6	1.4
Lignin	137+	$C_8H_9O_2^+$	1.2	1.7	0. 9	0.9	0.7
	151+	$C_8H_7O_3^+$	1.0	0.8	0.9	0.9	0.6
	167+	$C_9H_{11}O_3^+$	1.0	0.6	0.7	0.8	0.7
	181+	$C_9H_9O_4^+$	0.6	0.9	0.7	1.1	1.2
Extractives							
Myristeric	211+	$C_{14}H_{27}O+$	0.7	3.7	0.6	2.1	2.0
	229+	$C_{14}H_{29}O_2+$	0.9	4.3	0.1	1.3	2.6
Pentadecanoic	225+	$C_{15}H_{29}O_2+$	2.3	4.4	1.9	2.1	3.6
	243+	$C_{15}H_{31}O_2+$	0.8	1.5	0.6	1.4	1.9
Palmitic acid	239+	$C_{16}H_{31}O+$	1.2	1.3	1.2	0.6	1.6
	257+	$C_{16}H_{33}O_2+$	1.1	7.3	1.3	1.1	2.8
Oleic acid	283+	$C_{18}H_{36}O_2+$	1.5	3.2	2.9	0.3	1.9
	265+	$C_{18}H_{34}O+$	1.2	1.9	0.5	1.0	3.1
Steric acid	285+	$C_{18}H_{37}O_2+$	1.0	1.2	0.4	1.2	6.6
	267+	$C_{18}H_{35}O+$	1.5	2.4	1.4	0.9	5.4
Lignoceric	369+	$C_{24}H_{49}O_2+$	0	0	0.4	1.8	4.7
	351+	$C_{24}H_{47}O+$	0	0	0	0.6	2.0
	339+	$C_{23}H_{49}O_2+$	2.1	0.3	0.8	1.5	0.7
Pentadecosanic	383+	$C_{25}H_{51}O_2+$	1.0	0.1	0.8	0	0.9
	365+	$C_{25}H_{49}O+$	0.6	0.2	0.3	1.6	3.3
	355+	$C_{24}H_{51}O+$	0	0.2	0.5	0.5	0.4
Calcium	268+	$C_{14}H_{28}O_2Ca+$	0.8	0.3	0	1.0	1.4
Myristate	495+	$C_{28}H_{57}O_4Ca+$	0.5	2.2	0.5	3.8	0.4
Pentadecanate	281+	$C_{15}H_{29}O_2Ca+$	1.2	0.4	0.2	0.2	5.6
	523+	$C_{30}H_{59}O_4Ca+$	0	0	0.7	6.3	3.9
Palmitate	296+	$C_{16}H_{32}O_2Ca+$	0.3	0.2	0.6	2.6	2.9

	Peak	Ion	22-Pulp/22-Fiber	37-Pulp/22-Pulp	37-Pulp/37-Fiber	53-Pulp/37-Pulp	53-Pulp/53-Fiber
	551+	$C_{32}H_{65}O_4Ca+$	0	0	0.6	0	1.5
Stearate	323+	$C_{18}H_{35}O_2Ca+$	1.2	0.2	0.7	0.3	2.6
	324+	$C_{18}H_{36}O_2Ca+$	0	0.2	1.4	1.4	3.5
Sodium Oleate	304+	$C_{18}H_{33}O_2Na+$	0	0	1.1	3.1	1.3
	305+	$C_{18}H_{34}O_2Na+$	0.5	0.3	0.8	0.4	0.9
Eicosenoate	332+	$C_{20}H_{37}O_2Na+$	0	0	1.3	4.2	0.7
	333+	$C_{20}H_{38}O_2Na+$	0.2	0.4	0.5	0	1.5
Lignocerate	391+	$C_{24}H_{47}O_2Na+$	0	0	1.1	0.9	2.6
	413+	$C_{24}H_{48}O_2Na^{2+}$	1.0	0.2	0.6	1.0	10.4
Hexadecanoate	441+	$C_{26}H_{51}O_2Na^{2+}$	1.0	0.1	1.0	1.3	1.3
Sterols							
Sitosterol	415+	$C_{29}H_{51}O+$	0	0	0.8	0	1.0
	414+	$C_{29}H_{50}O+$	0	0	1.0	2.1	1.3
	397+	$C_{29}H_{49}+$	0.5	0.2	1.1	2.5	6.5
Sitostanol	416+	$C_{29}H_{52}O+$	0	0	3.9	2.1	1.3
	398+	$C_{29}H_{50}O+$	0.7	0.1	0.5	1.6	0.5
Oxo-sitosterol	429+	$C_{29}H_{48}O_2+$	0.5	0.1	0.2	2.1	1.5
	411+	$C_{29}H_{47}O+$	1.5	0.1	0.3	2.5	0.5
Metals							
Sodium	23+	Na^+	1.2	1.6	1.9	0.8	1.3
Aluminum	27+	Al^{3+}	0.8	2.1	1.1	0.2	0.2
Silicon	28+	Si^{4+}	1.0	1.8	1.1	2.6	2.4
Calcium	40+	Ca^{2+}	0.9	1.9	1.0	1.2	1.1

After being treated at various refining energy, pulp and fiber samples were treated with fluorescent agents DS and P01 with dosages of 1 kg/ton, 2 kg/ton, 5 kg/ton, 7 kg/ton, and 10 kg/ton, respectively, and the adsorbed amounts are shown in Fig. 4.

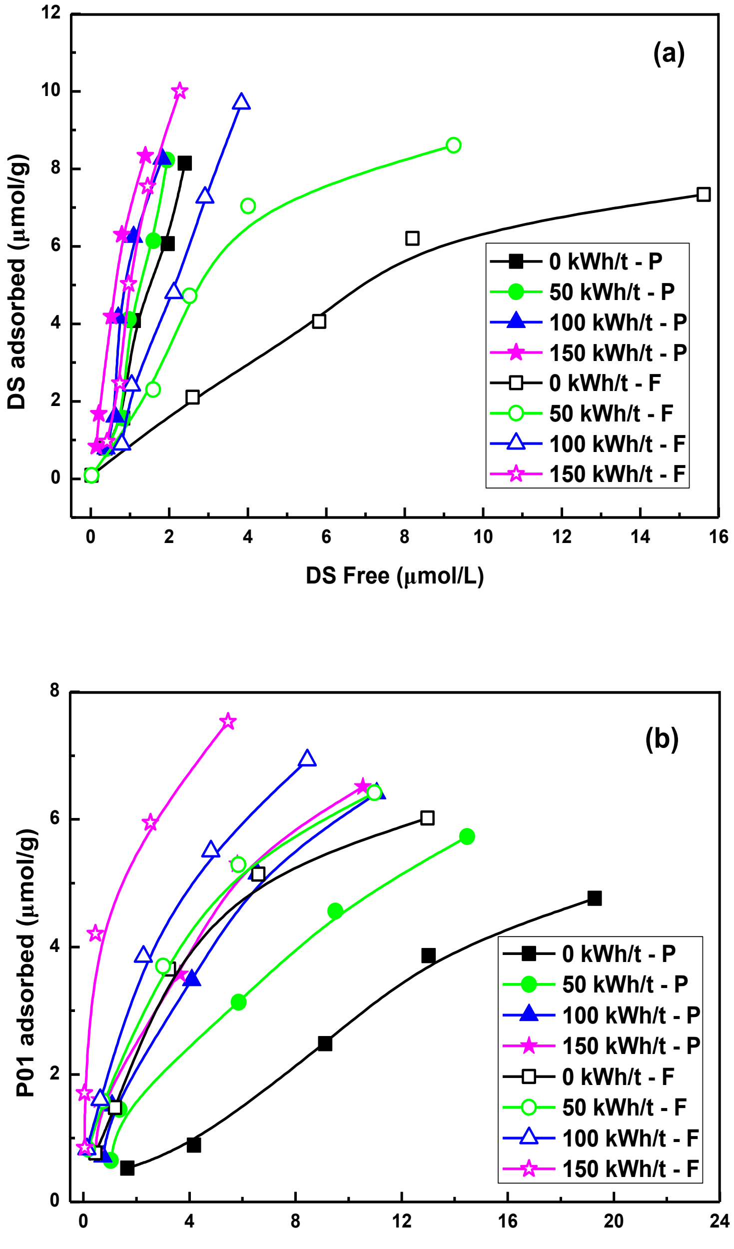

Fig. 4. The adsorption of DS (a) and P01 (b) on refined pulp and fiber samples with different SEC levels

As can be seen from Fig. 4a, at the same refining energy, DS adsorbed more on the pulp samples compared to the fiber samples. This is due to the large specific surface area of fines in pulp samples, as a high specific surface area benefits the adsorption of FWAs (Shi *et al.* 2012). However, for P01, the opposite phenomenon was observed in Fig. 4b, *i.e.*, more P01 could be adsorbed on fiber samples at the same refining energy. This is probably because, compared to fiber samples, pulp samples have stronger anionic charges derived from fines (Hubbe and Rojas 2008; Orblin and Fardim 2011), generating a relatively higher electrostatic repulsion with P01 (which is a tetra-FWA), although fines have large specific surface area. In other words, for the case of P01, the effect of electrostatic forces between pulp samples and P01 is larger than the effect of specific surface area. On the other hand, fines contain more lignin (particularly for the surface coverage by lignin as presented in Table 2), which cover more carbohydrates (*i.e*. cover more binding sites) (Orblin and Fardim 2010). As a result, less P01 was adsorbed on pulp samples. Overall, the adsorption performance of both DS and P01 was improved by refining, as exhibited in Fig. 4. An explanation for this is that hydrophobic extractives trapped in the fiber walls are released to fiber surfaces, as analyzed by XPS (Table 2) and ToF-SIMS (Table 3). The enrichment of hydrophobic extractives promotes hydrophobic interactions with FWAs (Santa *et al*.1995).

Therefore, according to the results in Tables 2 and 3 as well as Fig. 4, it was demonstrated that refining performance could increase the FWAs adsorption through the enhancement of electrostatic forces and specific surface area by creating fines, as well as hydrophobic interactions.

Effects of adding FWAs before LC refining

The addition of DS and P01 before LC refining was also investigated. The FWAs went through the refining process together with fibers, with the adsorption results shown in Tables 4 and 5. Increasing the amount of DS and P01 did not significantly increase the amount adsorbed on the fibers. In addition, the amount of DS (Table 4) and P01 (Table 5) adsorbed did not change with increasing SEC. It is obvious that the mechanical hydraulic force generated by the high refining energy could disturb the FWAs retention.

Table 4. DS Adsorption on Pulp before Refining

Refining Energy (kWh/t)	2 g/ton		7 kg/ton	
	µmol Free /L	µmol adsorbed / g	µmol Free / L	µmol adsorbed / g
0	3.8	1.7	3.0	4.9
50	5.1	1.6	2.9	4.9
100	5.0	1.6	2.3	5.0
150	6.8	1.4	2.9	5.0

Comparing the adsorption amounts in Fig. 4, with dosages of 2 kg/ton and 7 kg/ton, DS was adsorbed less on pulp when it was added before refining compared to its addition after refining. However, for P01, a different tendency was seen. At lower refining energy, P01 added before refining reacted better than that added after refining. Yet, with increasing refining energy, the adsorbed amount of P01 added before refining was less than that when it was added after refining. The mechanical hydraulic force generated by the high refining energy that disturbed the FWA retention behavior could not be neglected. Therefore, the refining performance could enhance FWA adsorption because of the changes in morphology and surface chemical composition and component distribution, as discussed previously. However, if FWAs were added before refining at lower energy, refining was even more beneficial for its adsorption on eucalyptus fiber compared to that if it was added after refining.

Table 5. P01 Adsorption on Pulp before Refining

Refining energy (kWh/t)	2 kg/ton		7 kg/ton	
	µmol Free /L	µmol adsorbed / g	µmol Free / L	µmol adsorbed / g
0	0.9	1.5	6.9	4.7
50	1.2	1.5	7.8	4.5
100	0.7	1.6	7.8	4.5
150	0.9	1.5	6.3	4.8

The Effect of LC Refining on the Optical Properties of Pulp Samples with the Addition of FWAs

Optical properties of pulp samples with FWA addition after LC refining

LC refining had a negative impact on the optical properties of eucalyptus pulp (Table 1). To overcome/minimize the loss of optical properties, different dosages of FWAs were added and the optical properties were determined. The results are shown in Fig. 5.

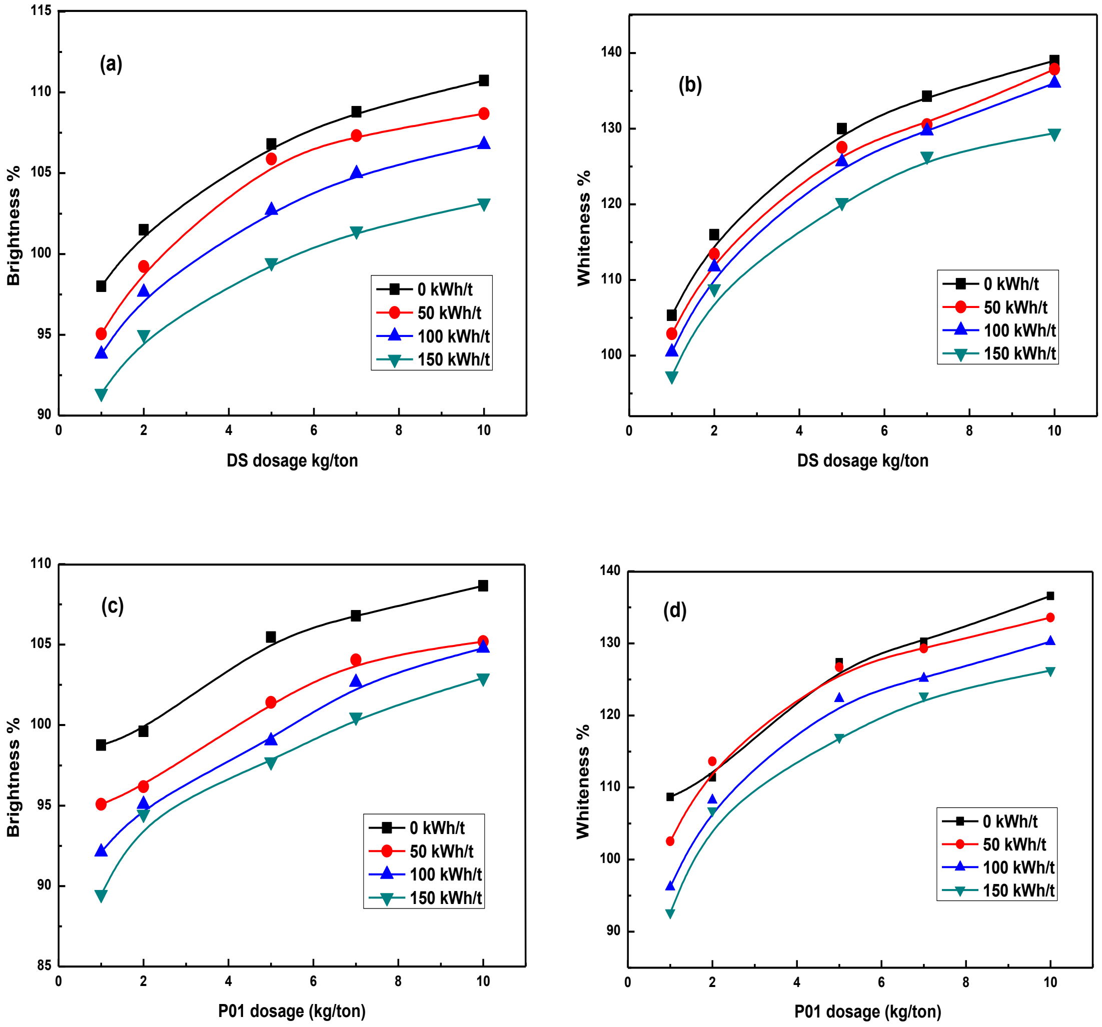

Fig. 5. Effect of DS (a, b) and P01 (c, d) on the brightness and whiteness of pulp samples

Both brightness and whiteness increased dramatically with increasing FWAs dosage. For instance, the brightness increased by about 4% when the DS dosage increased from 1 to 5 kg/ton.

The enhancement of brightness and whiteness obtained from FWAs can compensate for the loss of optical properties resulting from LC refining. In addition, Fig. 5 also shows that DS improved the brightness and whiteness more than P01 did. This is probably because more DS can be adsorbed onto pulp than P01 (Fig. 3). However, there is a clear trend indicating that to obtain the best performance of FWAs, the pulp needs to be refined at SEC levels as low as possible.

Optical properties of eucalyptus with FWA addition before LC refining

The addition of DS and P01 before LC refining significantly improved the brightness and whiteness of P samples as well, as shown in Fig. 6.

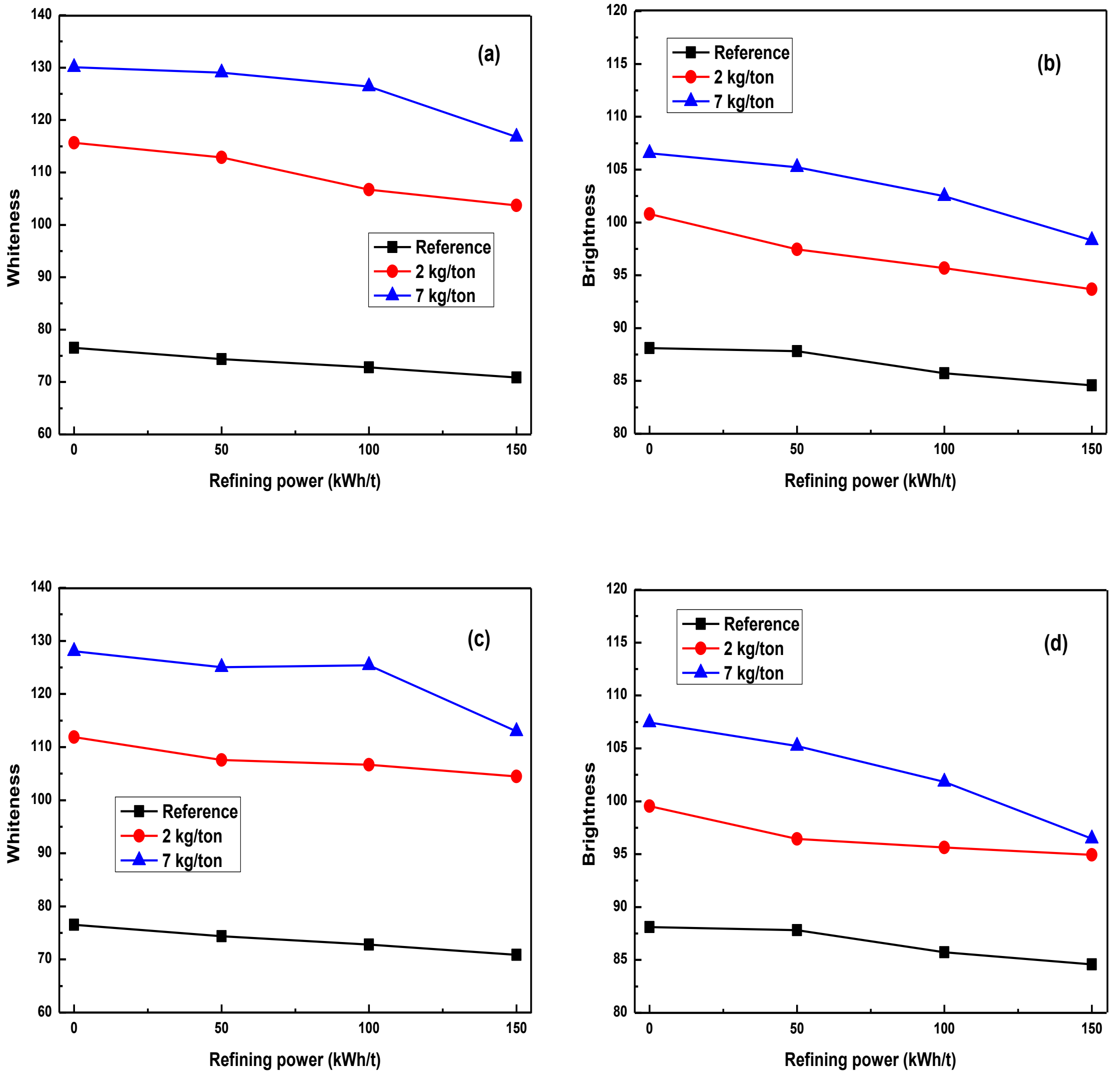

Fig. 6. The effect of DS (a, b) and P01 (c, d) addition before refining on the whiteness and brightness of pulp samples

However, at the same refining energy, both whiteness and brightness with the addition of DS and P01 before refining (Fig. 6) were slightly lower than that with their addition after refining (Fig. 5). For example, under the refining energy of 50 kWh/t with a DS dosage of 2 kg/ton, the brightness and whiteness of pulp samples, where DS was added after refining, are 99 and 114, respectively, while the corresponding brightness and whiteness for the samples where DS was added before refining are 97 and 113, respectively. This may be due to the fact that more FWAs can be adsorbed on fibers after refining, as mentioned previously (Fig. 4, Tables 4 and 5). With a further increase in refining energy, the whiteness and brightness deteriorated (Fig. 6), while further FWA adsorption was not promoted either.

FWAs Adsorption on Eucalyptus with the Addition of $CaSO_4$ Before and After Refining at Low Refining Energy

Calcium sulfate is one kind of filler used in paper coating or filling (Alén 2007) to increase the sheet smoothness, brightness, and printing performance of paper. However, fillers can induce the loss of binding between fibers. The impact of calcium sulfate at two dosages on FWA adsorption under refining was investigated, and the results are shown in Figs. 7 and 8.

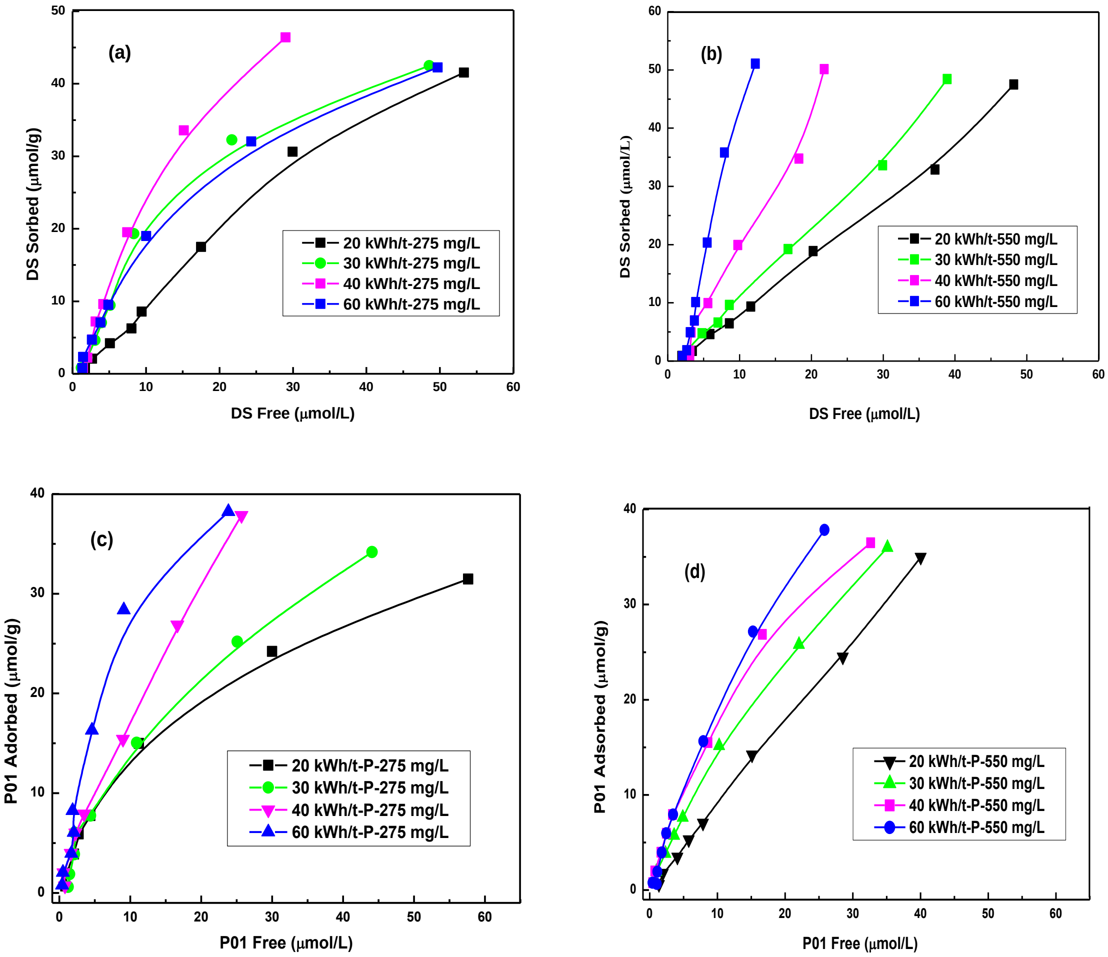

Fig. 7. The adsorption of DS (a, b) and P01 (c, d) on pulp with $CaSO_4$ addition after refining

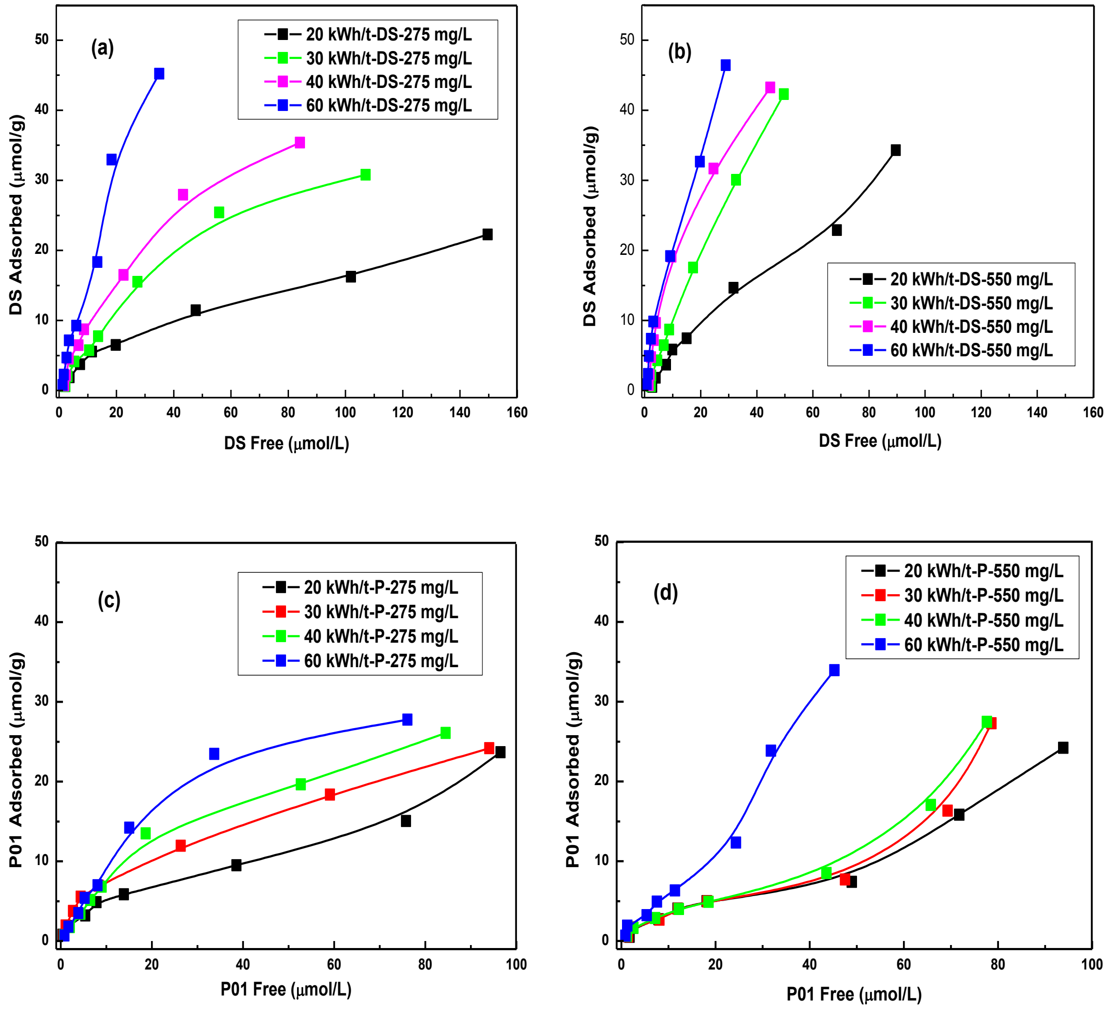

Fig. 8. DS/P01 absorption on eucalyptus pulp with Ca addition before refining

Refining with a low energy input was found to be favorable for FWA adsorption on fibers. After refining, both DS and P01 sorption amounts were increased under energy input levels from 20 to 60 kWh/t with the addition of 275 mg/L calcium sulfate to the pulp, especially in the case of P01. However, the P01 sorption on pulp was not changed when the calcium sulfate dosage was increased to 550 mg/L, although the adsorption of DS did increase a little. The adsorption of Ca^{2+} can reduce the electrical surface charge of anionic materials such as wood pulp by specific cation adsorption. Thus certain amount of Ca^{2+} could improve the retention of FWA (Zhang *et al.* 2009; 2010). Positive effects of cationic surfactants on the sorption of FWAs have been previously reported (Iamazaki and Atvars 2007).

In the cases presented in Fig. 8, calcium sulfate was added to the pulp solution before refining. DS and P01 were reacted with refined calcium sulfate fibers afterwards. For DS, the adsorption value was similar to the value given in Fig. 7. P01 adsorption seemed to be on a lower level with $CaSO_4$ addition before refining compared to that when $CaSO_4$ was added to the fibers after refining. A high calcium amount was unfavorable for P01 adsorption. This may have been because the refining forces affected the calcium sulfate attachment and distribution on the fibers. The improvement of DS and P01 adsorption by calcium sulfate is limited. This will be further studied in future.

CONCLUSIONS

1. The morphology and surface chemical composition of eucalyptus pulp fibers were modified by low consistency (LC) refining, which can improve the adsorption of fluorescent whitening agent (FWAs) by increasing the specific surface area and electrostatic forces (*via* the generation of fines) as well as the binding sites (*via* the enhancement of hydrophobic interactions by the change of surface chemical composition) of fibers. The fines contribute more anionic charges which are beneficial for the adsorption of di-FWA (DS) but not for tetra-FWA(P01).
2. The addition of FWAs can partially compensate for the loss of optical properties resulted from LC refining, but the addition point in the process is important for FWAs adsorption. High refining energy could promote adsorption when FWAs are added after refining, but is not favorable when they are added before refining.

3. Calcium sulfate added in appropriate dosages was retained on the refined fibers and could benefit FWAs adsorption, but with an increased dosage, it supplied a cationic charge to the fibers, which affected FWA adsorption positively.

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