

Advanced Studies on the Topochemistry of Softwood Fibres in Low-Consistency Refining as Analyzed by FE-SEM, XPS, and ToF-SIMS

Hongyan Mou,^{a,b,*} Eduardo Iamazaki,^b Huaiyu Zhan,^a Elina Orblin,^b and Pedro Fardim^{b,*}

The influence of low-consistency refining on the surface chemical and morphological properties of softwood chemical pulp was investigated using a special laboratory refining station and advanced topochemical analyses. Refined pulp was fractionated in order to investigate the refining effect on fibres separately, without fines. The morphological properties of whole pulp and fibre fraction were studied by field-emission-SEM. X-ray photoelectron spectroscopy and time-of-flight secondary ion mass spectrometry (ToF-SIMS) were used to analyze the surface chemistry of the pulp fibres before and after refining. As a result of refining, fibre shape changed from tubular to flat. The surface coverage by extractives increased during refining together with increasing refining energy both in the whole pulp and in the fibre fraction; the increase was more significant in the whole pulp. This is probably due to leakage of hydrophobic components from the pulp fines. In the fibre fraction, surface coverage by lignin increased in the course of refining, but in the whole pulp the trend was the opposite. Similar trends were detected by observing the ToF-SIMS peaks of polysaccharides, lignin, and extractives. Refining modifies the surface chemistry and morphology of fibres, presumably by making structural changes in the fibre cell wall composition. Eventually, these changes induce increased fibre-to-fibre bonding capability and decreased scattering of light.

Keywords: Low-consistency refining; Pine pulp fibres; Surface chemistry; FE-SEM; XPS; ToF-SIMS

Contact information: a: State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, China 510640; b: Laboratory of Fibre and Cellulose Technology, Åbo Akademi, Turku, Finland, 20500; *Corresponding authors: hmou@abo.fi; pfardim@abo.fi

INTRODUCTION

Low-consistency refining of pulp is a mechanical treatment extensively used in stock preparation in papermaking, and the pulp consistency in the refiner is usually between 2% and 6%. In this paper, the term refining refers to the low-consistency process. During refining, mechanical and hydraulic forces are employed to change the fibre characteristics, and this affects both the morphological structure of fibres and the macroscopic properties of paper. It is well known that most of the strength properties of paper increase with pulp refining (Miles and May 1990; Stationwala *et al.* 1991). Different fibre structural changes caused by refining have been reported (Molin and Miller 1992; Molin and Daniel 2004; Page 1989; Laine *et al.* 2004).

There are many theories that explain the refining effects on the fibre cell wall structure and surface morphology (Laine *et al.* 2004), and a classification of primary and secondary effects has been proposed (Page 1989). Fibre straightening is a primary effect

of refining (Molin and Miller 1992; Molin and Daniel 2004). Refining increases the fibre flexibility, resulting in a denser paper; this means that bulk, opacity, and porosity values decrease during the process.

The most significant effects of the mechanical treatment performed at low consistency can be both favourable and detrimental. Effects include, for example, the release of secondary fines, external fibrillation, curling, straightening or shortening of fibres, internal fibrillation, and delamination of cell wall structures (Page 1989). External fibrillation causes delamination of the surface layers, which contributes to the fibre-to-fibre bonding potential and also the retention of filler, pigments, and colloidal particles in papermaking. The fibre shortening also produces fines that fill up the empty spaces in the sheet network and contribute to formation and bonding (Clark 1957). Secondary effects comprise the fibre longitudinal compression, mainly when beating is performed in dispersions with a low solid content, as well as changes in shape and damage to fibre surface and length due to external fibrillation and shortening. Refining also affects the fibre swelling and interaction with water as measured by Schopper-Riegler drainability (SR), freeness, and water retention value (Berthold and Salmén 1997). Bonding and surface specific area increase by refining, but this effect depends on the equipment used and levels-off after a certain time or applied energy load (Baker 2003; Touzinsky *et al.* 1977).

Other effects such as releasing of colloidal and dissolved substances into the liquid media and abrasion of the surface at a molecular level to produce a gelatinous layer have also been proposed (Laine *et al.* 2004). However, reports regarding the effects of mechanical treatment on the fibre chemistry and the surface structure of fibres are very limited. Usually, it is considered that refining has no effect on fibre chemistry. Moreover, reports regarding the effects of refining on the surface chemistry of fibres are very scarce. Our hypothesis is that during refining, a multitude of surface chemical interactions takes place.

The investigation of fibre surface chemistry and morphology require surface-sensitive techniques. Applications of scanning electron microscopy (SEM) have been performed to evaluate the effects of beating. Fibre fracture and shape flattening (Touzinsky *et al.* 1977), fibre curling (Fardim and Durán 2005), fibrillation (Buchanan and Washburn 1962), delamination of the secondary cell wall S2 (Molin and Daniel 2004), and added swelling (Enomae and Lepoutre 1998) have been reported. X-ray photoelectron spectroscopy (XPS) has been established in pulp and paper research as a tool for detecting the elemental composition and the carbon boundary state in the surface within a range of 3 to 10 nm deep (Brinen 1993; Orblin *et al.* 2011). Also, applications of time-of-flight secondary ion mass spectrometry (ToF-SIMS) have been reported for paper and pulp (Fardim and Durán 2000; Kleen 2000; Fardim *et al.* 2005; Orblin and Fardim 2010).

Combining SEM, XPS, and ToF-SIMS to investigate the refining effects on the surface of eucalyptus kraft pulp samples (Fardim and Durán 2003), the chemical composition of fibre surfaces were modified during refining, and the changes in surface chemical composition with beating were suggested to be included in the refining theories. In this work, to further research the influence of refining, the surface chemistry of the whole pulp as well as separated fibres of softwood pine were investigated before and after refining. A state of the art refining station with controllable refining energy input was used, and the effects were studied with advanced surface analysis by FE-SEM, XPS, and ToF-SIMS.

EXPERIMENTAL

Materials

Bleached pine elemental chlorine free (ECF) pulp from a Finnish pulp mill was used in refining experiments in a ProLab™ laboratory station (Metso Paper, see Fig. 1). Technical details of the refining station can be found in Lundin *et al.* (2008).



Fig. 1. ProLab™ refiner

Methods

The pine pulp was refined at a specific edge load of 2 J/m and a consistency of 5%. The specific energy consumption (SEC) levels were 0, 75, 150, and 250 kWh/t, respectively, with a long medium conical filling. Two series of samples were made: refined whole pulps that included pulp fines, and fibre fraction samples where the pulp fines were removed after refining. The separation was done with a dynamic drainage jar, equipped with a 200-mesh wire and propeller stirring (TAPPI T261cm00). Pulp fines mean the fraction passing a 200-mesh screen. SR was measured after each refining level (ISO5267-1 1999). Fibre length and fines content were measured by Kajaani Fibrelab. Handsheets were prepared in a Rapid Köthen apparatus using deionised water (ISO5269-2 1988), and used for measuring 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 13-P, 19-P, 37-P, and 72-P for the whole pulp sheets, and 13-F, 19-F, 37-F, and 72-F for the fibre fraction sheets, according to the SR values produced by the applied SEC levels (0, 75, 150, and 250 kWh/t, respectively). FE-SEM images were obtained using a JEOL JSMT 300 microscope, operated in secondary electron mode at a beam current of 100 μ A and accelerating voltage of 20 kV. Samples were previously coated with Pt for 20 s with an Agar scientific sputter coating system equipped with a rotating base. Images were obtained in magnifications of 500 \times , 2000 \times , and 20,000 \times .

XPS spectra of the whole pulp and the fibre fraction sample surfaces were obtained with a Physical Electronics PHI2000 ESCA instrument equipped with a monochromatic Al K α X-ray source, operated at 200 W, and charge compensation. The analysis area was 1 mm², 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 done using the pass energy of 187 eV in 3 min, and the high resolution C1s scanning was

conducted using the 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 C1s signal carrying information about the chemical binding state of carbon. The following binding energies, relative to C-C (or C-H) position were employed for the respective groups: (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 C1, and the other states are denoted C₂, C₃, and C₄, in the order of the increasing binding energies.

Surface coverage by lignin (S_{lig}) and extractives (S_{ext}) were determined using the O/C ratio of the untreated and acetone-extracted (Soxhlet, over-night) samples using the equations by Ström and Carlsson (1992), where the O/C ratio of the sample is compared to the theoretical O/C ratios of pure cellulose (0.83) and of a model extractive (0.11).

Secondary ion mass spectra were obtained using a Phi Trift II ToF-SIMS instrument (Physical Electronics, USA) using a primary beam of ⁶⁹Ga 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 hexosans (cellulose and glucomannans), pentosans (xylan), lignin, and various wood extractives in the samples were compared. The characteristic fragments were chosen according to previously published literature (Fardim and Durán 2000; Kleen 2000; Kangas 2007). In order to discount analytical variations, the peak counts were first normalised, dividing by the total counts of the spectrum being interpreted.

RESULTS AND DISCUSSION

Effects of Refining on Pulp and Fibre Properties

The effect of refining on the optical properties of the pulp and the fibre samples was investigated. The whiteness, the brightness, the light scattering coefficient (s), and the light absorption coefficient (k) in relation to SEC are shown in Table 1. As can be seen, both for the whole pulp samples and the fibre fraction samples, the whiteness, the brightness, opacity, and the light scattering coefficient were decreased at high refining power, while the light absorption coefficient slightly increased. Decrease of brightness after refining has also been reported for hardwood of eucalyptus (Fardim and Durán 2000).

It is well known that pulp drainage is reduced by refining due to creation of fines, fibre fibrillation, and delamination, as shown by a fibre length reduction and a pulp fines weight percentage increase in Table 1. This reduction in the drainage rate is one major drawback of the refining process.

The optical properties of the whole pulp sheets did not obviously differ from those of the fibre fraction sheets at the same SEC level, but the fibre fraction maintained the optical properties in harsh refining (high SEC level) better than the whole pulp. The brightness of the fibre fraction was not reduced as much as that of the whole pulp.

The role of the fine material in the optical properties of paper is known to be related to the high specific surface area as well as the eventual lignin content (Asikainen *et al.* 2010), whereas the fibres' contribution can be speculated to be mainly due to the properties of the fibre cell wall, that is, the light reflecting surfaces of the external cell wall layer.

Table 1. Effects of LC-Refining on the Whole Pulp (P) and Fibre Fraction (F) Properties Refined with Different Specific Energy Consumption (SEC)

	P	F	P	F	P	F	P	F
SEC	0 kwh/t		75 kwh/t		150 kwh/t		250 kwh/t	
SR	13.0	ND	19.3	ND	37.4	ND	72.0	ND
Fibre length (mm)	2.4	ND	2.2	ND	1.9	ND	1.5	ND
Fines wt%	2.1	ND	2.4	ND	3.5	ND	4.4	ND
Whiteness	71.4	69.6	68.0	66.7	63.6	64.6	55.4	57.3
Brightness	85.1	85.8	82.9	83.5	80.8	82.4	75.3	77.2
Opacity	78.5	88.6	74.0	77.9	71.2	73.4	58.7	60.2
s	34.9	35.2	27.3	25.6	22.3	22.4	12.6	12.9
k	0.18	0.11	0.21	0.15	0.22	0.15	0.25	0.20

ND: not determined.

s: light scattering coefficient; k: light scattering coefficient.

All optical properties data reported were the mean of ten readings for each test.

Effects of Refining on the Surface Morphology

The sheets made from the whole pulp and the fibre fraction samples refined with different SEC levels were analyzed by FE-SEM. The SEC being 0 kWh/t, the samples 13-P and 13-F can be perceived as unrefined. It can be seen from Figs. 2 and 3 that during refining, the fibre shape changed from tubular to flat, meaning that the lumen collapsed as the fibre walls became more flexible. The refining process initially caused a shearing in the fibre wall, followed by an increase in the surface roughness and release of superficial layers. The increased surface fibrillation of the fibres can be distinguished in Fig. 2b, compared to Fig. 2a. It is reasonable to suppose that higher contact areas between the fibres are achieved with flat shapes than with tubular-shaped fibers. The number of reflecting surfaces is thus decreased, affecting the optical properties of the sheet. Similar effects for eucalyptus pulp have also been reported (Fardim and Durán 2003; Mou *et al.* 2010). In addition to the fibre flattening, voids between fibres were filled (Fig. 2b and 3b), supposedly due to external fibrillation and additional fines created, and a film-like connection between fibres was formed (marked by white cycles in Fig. 4). Comparing the fibre fraction and the whole pulp sheets, it can be noted that the fibre fraction sheet structure in Fig. 4 resembled that of the whole pulp sample in Fig. 2a, and after refining (Fig. 2b) the sheet structure was denser in a similar manner as in Fig. 2b. However, the film-like connections were even more prominent in the fibre samples. Perhaps the film was more easily seen because of the lower amount of fine material that would cover it. Another possibility is that in the fibre fraction, more hydrophilic compounds from the cell walls were leaked out during the pulp fines separation stage, contributing to formation of gel-like material, which after drying appears as film. The film was presumably formed of extracellular material including polysaccharides and extractives, as well as very fine cellulosic fibrils produced after high-energy refining. The pulp fines and fibrils were probably generated from the primary wall and outer secondary wall (Li *et al.* 2011a). The increased pulp fines and fibrils can lead to the increase of specific surface area of pulp fibres (Li *et al.* 2011b), thus increasing the bonding potential (*i.e.* the strength properties of the whole pulp sheets). This is also in good agreement with the increased SR value (Table 1) after refining.

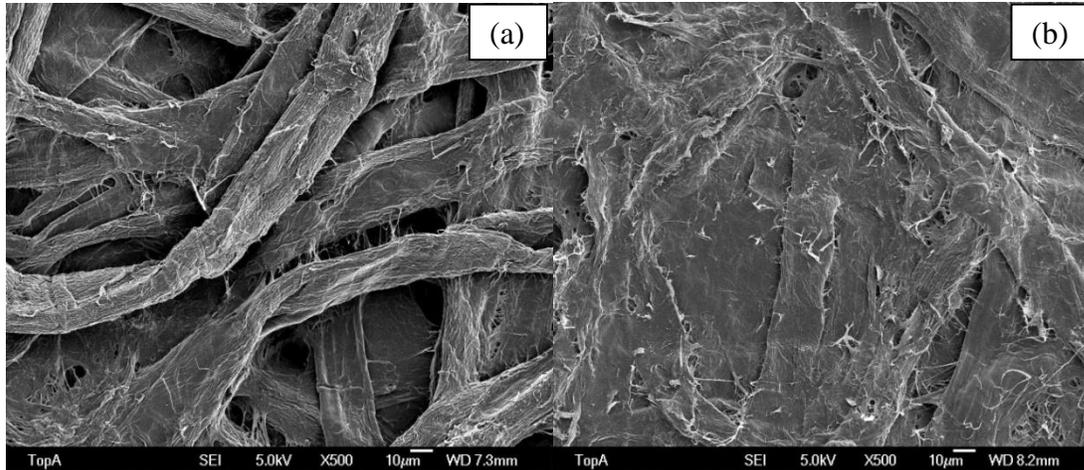


Fig. 2. SEM images of the whole pulp sheets with SEC of 13-P (a) and 37-P (b) at 500x magnification

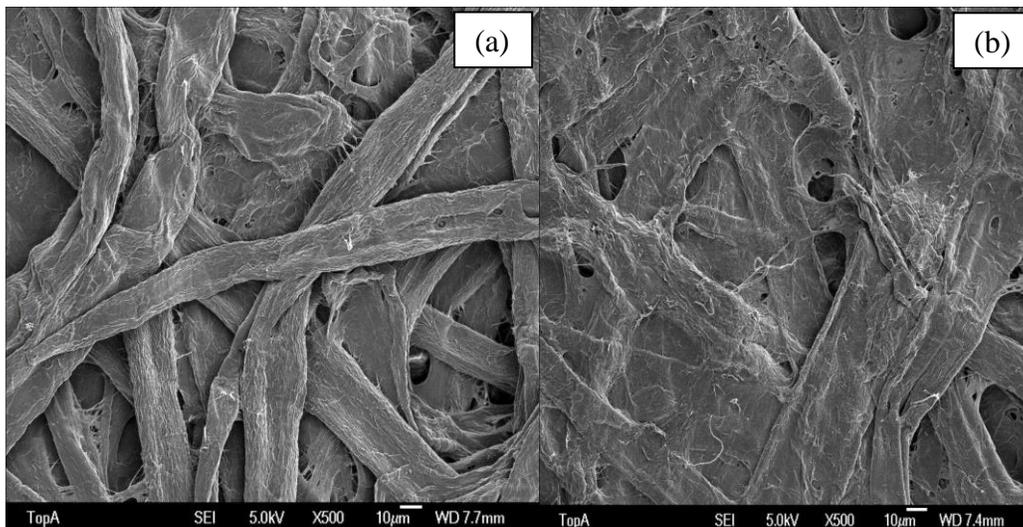


Fig. 3. SEM images of the fibre fraction sheets with SEC of 13-F (a) and 37-F (b) at 500x magnification.

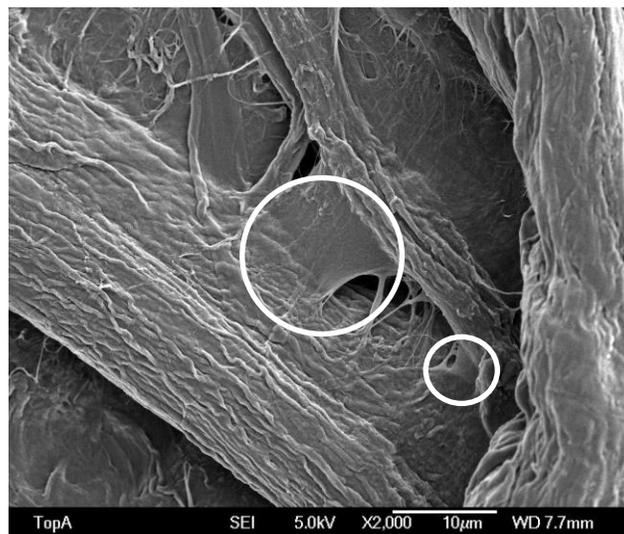


Fig. 4. SEM image of the whole pulp with SEC of 37-P at 2,000x. The parts marked by white circles are gel-like materials.

Larger magnifications of the fibre fraction outer cell wall with the refining energy 0 kWh/t SEC (sample 13-F) and 150 kWh/t SEC (sample 37-F) can be seen in Fig. 5a and 5b, respectively. Using high magnifications, it must be kept in mind that the sample coating can give rise to artefacts regarding the smallest distinguishable details in the images. However, comparison of the different samples showed discernible and characteristic differences. In Fig. 5a, micro-fibril bundles of the thickness of few tens of nanometres can be distinguished. The cell wall had folds with the approximate thickness from 0.3 to 0.6 μm , and on top of them, randomly oriented micro-fibrils of the primary wall were spread. In Fig. 5b, the undulating structures in the cell wall (seen in Fig. 5a) were flattened to a great extent, and the surface was smoothed as it was fully covered with a gel-like material. Presumably, it is deposited on surfaces from material originally present in fibre pores and released by mechanical action during refining. Under the layer, it is possible to discern the highly oriented secondary wall micro-fibrils. The primary wall had been at least partly exfoliated. The flattening of the folds is presumably connected to delaminations taking place in the fibre wall. Considering the wavelengths of white light, these fibre wall structures could be related to the decrease of whiteness and the increase of light absorption, which were detected after refining (Table 1).

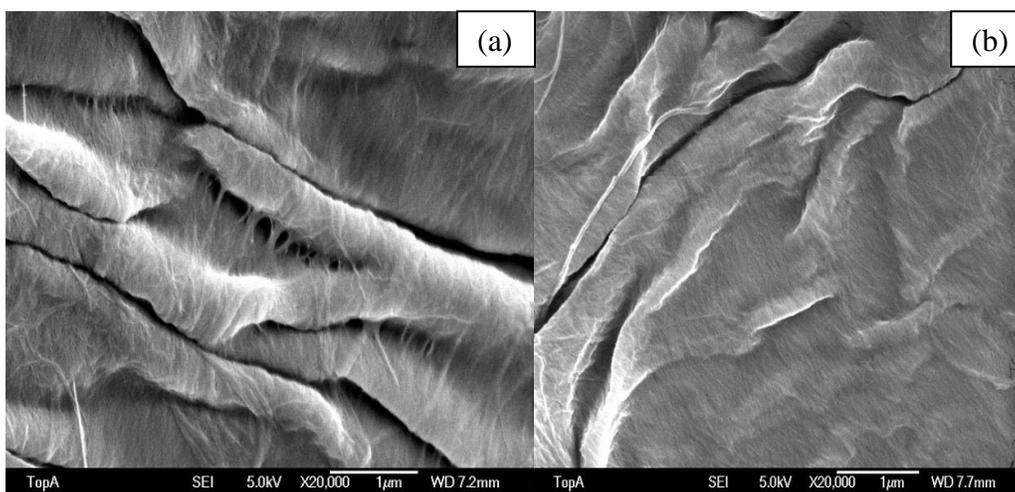


Fig. 5. SEM images of pine fibre with SEC of 13-F (a), and 37-F (b) at 20,000 \times magnification.

Effects of Refining on Surface Chemical Composition

Techniques with different surface sensitivity and specificity were used to study the surface chemical composition before and after refining. An approximate surface depth of 5 to 10 nm can be achieved by XPS, with which the surface coverage by lignin, extractives, and carbohydrates is estimated, while surface depth of 1 to 3 nm can be attained by ToF-SIMS providing more detailed information of chemical composition.

In Table 2, the carbon boundary state (C_1 to C_4) and the O/C ratios of the samples are listed, and the surface coverage by lignin (S_{lig}) and by extractives (S_{ext}) are presented. In general, the whole pulp samples (with pulp fines) had higher C_1 content and lower O/C ratios than the fibre fraction samples (without pulp fines) at the same SEC level. Also, under the SEC level of 0, the fibre fraction samples (13-F) had lower S_{lig} (26.3%) and S_{ext} (2.3%), compared to the whole pulp samples (13-P) with S_{lig} of 31.1% and S_{ext} of 2.4%. This is probably due to the pulp fines, which typically in chemical pulps contain more extractives and lignin than do the long fibres (Bäckström *et al.* 2008; El-Sharkawy *et al.*

2008). Thus, a higher O/C ratio of the fibre fraction samples is probably because of the removal of pulp fines.

Table 2. Effects of Refining on Surface Chemical Composition of Pine as Analyzed by XPS

SR-Sample	C ₁ %	C ₂ %	C ₃ %	C ₄ %	O/C	S _{lig} %	S _{ext} %
13-F	18.3	60.4	19.8	1.5	69.6	26.3	2.3
19-F	21.3	58.1	18.1	2.4	67.3	27.4	2.8
37-F	19.8	60.1	18.2	1.9	67.9	28.6	3.3
72-F	19.9	59.8	18.5	1.8	66.1	33.4	5.2
13-P	20.2	66.6	11.3	2.1	67.3	31.1	2.4
19-P	22.4	63.6	11.4	2.7	63.8	27.3	9.2
37-P	20.9	62.4	13.6	3.1	64.1	25.3	10.3
72-P	22.9	62.4	12.2	2.5	65.8	23.5	10.5

13-F, 19-F, 37-F, 72-F of fibre fraction samples, and 13-P, 19-P, 37-P, 72-P of whole pulp samples were with the SEC of 0, 75, 150, and 250 kWh/t, respectively.

Table 2 also shows that S_{lig} of the fibre fraction samples increased with the increase of SEC level, whereas the S_{lig} of the whole pulp samples decreased when the SEC level was increased. A decrease in S_{lig} was also previously reported for eucalyptus kraft pulp during refining (Fardim and Durán 2003). It has also been suggested that hemicelluloses, particularly xylan, arabinan, and galactan, are deposited on fibre surfaces during kraft pulping, as they have been detected clearly enriched in the primary wall of pine kraft pulp, compared to the outer secondary wall (Kibblewhite and Brookes 1976). The pulp fines generated from primary wall with the increase of SEC level presumably contain deposited hemicelluloses. The opposite phenomenon observed in the fibre fraction could be explained by the creation of fibrils, which involves the outer layers of cell walls. Even if the lignin-rich middle lamellae are assumed to be practically all dissolved in a bleached chemical pulp, removal of deposited hemicelluloses in refining and subsequent fractionation stage could reveal lignin remains. Another possibility is that the detected carbon content perceived as lignin with this technique is comprised of fatty acid salts that were not removed in acetone extraction and therefore appear as lignin (Fardim and Durán 2003). In addition, with the increasing of the SEC level, the S_{ext} increased for both of fibre fraction and whole pulp samples. Probably this is due to the fact that hydrophobic compounds that are released from the fibre wall during refining become distributed and re-deposit on the cellulosic surfaces. More extractives may re-deposit on fines, as fines have larger specific surface area. Thus, S_{ext} of pulp samples increased obviously with increasing SEC, as presented in Table 2. However, the S_{ext} increases observed in the case of the fibre fraction samples is possibly due to the deposition of extractives on the surface of fibrils, as pulp fines were already removed after refining.

The ToF-SIMS spectra can give more detailed information on the chemical composition despite the limitations in quantitative application of the technique. In order to compare the relative contents of components on the surfaces, the relative peak intensities were considered. Ratios between the normalised peaks of the whole pulp and the fibre fraction samples with the SEC 0 kWh/t (column 13-P/13-F), as well as ratios between the refined the whole pulp (SEC 150 kWh/t) and fibre fraction samples (column 37-P/37-F) were worked out. Further, the refining effect was studied inspecting the ratios

between refined and "unrefined" samples, both the whole pulp and the fibre fraction (columns 37-P/13-P and 37-F/13-F).

Characteristic peaks of carbohydrates, lignin, and extractives were selected (Table 3). Any value differing from 1 basically signals change in the surface chemical composition in the outmost layer.

Table 3. The Secondary Ions in the Positive ToF-SIMS Spectra, the Relative Intensities of which Were Observed for Pine Whole Pulp (P) and Fibre Fraction (F)

Components	Peaks (m/z)	Unrefined 13-P/13-F	Refined 37-P/37-F	Fibres 37-F/13-F	Pulp 37-P/13-P
<i>Carbohydrates</i>					
Pentosans	115	2.0	1.7	2.1	2.0
	133	5.5	1.7	2.0	1.4
Hexosans	127	2.4	1.7	2.3	1.3
	145	3.1	1.7	2.6	1.4
<i>Lignin</i>	137	1.7	0.7	1.2	0.7
	151	1.2	1.1	1.0	0.8
<i>Extractives</i>					
Resin acid	300	1.2	1.3	0.9	1.2
	301	3.7	0.9	1.1	1.0
	302	1.5	0.9	0.6	0.8
	303	3.5	0.5	0.8	0.7
Fatty acid Palmitic acid	239	1.8	0.6	0.7	0.9
	257	0.3	2.4	1.0	1.0
Stearic acid	267	3.8	1.7	2.8	1.0
	285	1.1	0.9	0.8	1.5
Oleic acid	265	3.7	1.9	3.3	1.0
	283	0.5	2.2	3.8	1.2
Linoleic acid	263	1.8	1.4	1.9	1.2
	281	6.6	2.6	4.5	0.9
Linolenic acid	261	2.4	0.7	0.8	1.3
	279	5.0	2.6	4.7	1.1
Arachidic acid	295	1.9	1.6	1.9	0.7
	313	1.1	0.8	0.8	1.2
Behenic acid	323	3.3	1.9	2.5	0.9
	341	2.1	2.4	2.4	0.9
Tetracosaboic acid	351	1.4	1.5	1.3	1.2
	369	1.6	0.9	2.2	1.0

The refining effect on the surface of the fibre fraction (column 37-F/13-F) was evident. Carbohydrate signals were increased, and most of the extractives were decreased. However, the increase in the lignin signals was not noticeable, which supports the possibility that the detected S_{lig} was due to fatty acid salts. In general, the peak ratios were in agreement with the XPS results. The increase in the S_{ext} detected by XPS could

be due to free fatty acids, mainly oleic, linoleic, and arachidic acid. Also for the whole pulp (column 37 P/13 P), the changes after refining as detected by XPS were in good correspondence with ToF-SIMS peak ratios. However, the remarkable increase of S_{ext} detected by XPS was not accompanied by any clear increase in the extractive peak intensities. The detection depth of ToF-SIMS is restricted on the outmost monolayer, whereas XPS collects information slightly deeper, and a difference in the component distribution is plausible. Further, the signal intensities in ToF-SIMS depend not only on the component content of interest, but also on various electronic, physical, and chemical states during the measurement.

Mechanical action during refining clearly contributes to the release of components entrapped in fibre wall pores to the external liquid phase, as previously suggested (Fardim and Durán 2003). Xylan (pentosan) was likely re-adsorbed rather than exposed on the surface during refining, based on the difference between the surface carbohydrate contents evaluated with ToF-SIMS. It seems reasonable to suppose that cellulose (hexosan) was exposed by a peeling action on the fibre surfaces and that part of the xylan was adsorbed after being released from the cell wall pores in a similar way to the fatty acids. Hydrogen or dispersion bonds are possibly the driving forces for the adhesion of xylan and extractive aggregates onto external fibre surfaces. Fibre chemistry has been shown to affect paper strength properties (Fardim and Duran 2005; Sundberg *et al.* 2000), and thus the chemical changes along with the morphological modifications caused by refining are assumed to be of importance in papermaking.

CONCLUSIONS

1. The effect of low consistency refining on the morphology and the surface chemical composition of pine pulp fibres was investigated, and significant changes were detected. With refining, fibre shape changed from tubular to flat, and external fibrillation was introduced.
2. Refining increased the surface coverage by extractives, mainly fatty acids. The results from XPS and ToF-SIMS were in good agreement with respect to the surface chemical composition. Evidence supporting the release of xylan and its subsequent adherence to the fibre surfaces was found.
3. Refining affects not only the morphology but also the surface chemical composition of the whole pulp in a way that possibly has significance for the final paper properties.

ACKNOWLEDGMENTS

This project was financially supported by Kemira. We would also like to thank Top Analytica Ltd. for providing surface analytical instruments. We thank our colleague Goran Kuzmanovski for his kind help in the work, as well as Dr. Joakim Järnström and Dr. Bin Li for help to improve this manuscript.

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Article submitted: November 22, 2012; Peer review completed: January 11, 2013;
Revised version received and accepted: March 5, 2013; Published: March 21, 2013.