Kangas, H. and Kleen, M. (2004). Surface chemical and morphological properties of mechanical pulp fines. Nordic Pulp and Paper Research Journal 19 (2): 191-199.

Surface chemical and morphological properties of mechanical pulp fines

Heli Kangas and **Marjatta Kleen**, KCL, Espoo, Finland

KEYWORDS: Surface chemistry, Surface structure, Mechanical pulp, Fiber, Fines, Fibril, Flake, ESCA, ToF-SIMS, AFM, Chemical composition, Picea abies, Lignin, Extractive, Polysaccharide, TMP

SUMMARY: Different types of fines, i.e. fibrils and flakes, were separated from thermomechanical pulp (TMP) fibers and their surface chemical and morphological properties were studied and compared to those of fibers. Fines contained more extractives and lignin than fibers, both on their surface and in the bulk. Fibrillar fines were especially rich in extractives and lignin, the latter indicating that they originated from primary wall rather than from secondary wall. Flakes had large amounts of lignin on their surfaces. Fibers contained more cellulose than did fines, with 50% of their surface covered with polysaccharides. The most common extractives on the surfaces of fibers and fines were fatty acids, probably present mainly as triglycerides, and sterols and steryl esters.

Fines and fibers differed in their surface morphology. Fibrillar fines were largely covered with two different types of material, interpreted as being lignin and extractives. The surfaces of flake-like fines proved to be mainly covered with granular lignin and cellulose fibrils. On the fiber surfaces, areas with different microfibrillar orientations were found. In some areas the orientation was random as in the primary cell wall layer and in some areas the orientation was parallel to the fiber axis, indicating that S_2 had been exposed during refining.

ADDRESS OF THE AUTHORS: H. Kangas (heli.kangas@kcl.fi), and M. Kleen, KCL Science and Consulting, P.O. Box 70, FIN-02151 Espoo, Finland.

During the mechanical pulping of wood fibers are separated from the wood matrix and a fines fraction is generated. Fines are defined as particles that pass through a round hole 76 µm in diameter or a nominally 200 mesh screen (Tappi Testing method T 261 pm-80). Mechanical pulps contain on average 10-40% of fines, which vary in their shape and chemical composition. Fines may be thin, thread-like particles or bulkier pieces of fiber, cell wall and middle lamella. Ray cells and pores will appear intact or broken among the fines fraction. Fines are traditionally divided into two classes, slime stuff and flour stuff, depending on their physical appearance (Brecht, Klemm 1953). The slime stuff contains swellable fibrillar particles i.e. fibrils and thin lamellae, while flour stuff consists of flake-like fines i.e. pieces of fiber, middle lamella and cell wall. Fibrillar fines are ribbon-like, cellulose-rich particles with good bonding ability, whereas flakes consist of many types of particles with different shapes and sizes. Flakes are usually lignin-rich and enhance the light scattering properties of the paper, while fibrils increase the strength properties.

Mechanical pulping process can be divided into two main stages, fiber separation and fiber development, occurring partly simultaneously (Karnis et al. 1994). In the manufacture of refiner pulps such as thermomechanical pulp (TMP), fiber separation and the release of middle lamella material are followed by delamination and peeling of surface material from the fiber. Flakes are generated during the first stages of refining and thus originate from areas with high lignin contents like the middle lamella or primary wall. Fibrillar fines are generated by peeling of fiber surface from the outer cell wall layers towards the cellulose-rich secondary wall (Karnis 1994). Fines properties such as size and shape depend on the process conditions and their chemistry reflects their origin in the cell wall.

The chemistry of fines has been studied quite extensively. In general, fines contain more lignin than fibers (Chang et al. 1979) while intact ray cells, in particular, have a high extractives content (Westermark, Capretti 1988). The surface chemistry of mechanical pulp fines is known to differ from their bulk chemistry (Koljonen et al. 1997) but less attention has been given to studying the surface chemical properties of different types of fines (Luukko et al. 1999; Kleen et al. 2001; Mosbye et al. 2003).

The surface chemical properties of fines are of great importance for their behavior during pulping and papermaking. The surface chemistry of pulps influences sorption, adhesion, strength and optical properties. Surface chemical composition may also affect the final properties of the paper as well as coating and printing operations. The surface morphology of mechanical pulp fibers and fines may influence the bonding properties of pulps and also affect the roughness of the paper.

The surface chemical properties of mechanical pulps have traditionally been studied with Electron Spectroscopy for Chemical Analysis (ESCA, also called X-ray Photoelectron Spectroscopy or XPS) (Dorris, Gray 1978; Koljonen et al. 1997; Börås, Gatenholm 1999a; Westermark 1999; Mustranta et al. 2000; Mosbye 2003). ESCA gives information about the coverage of lignin and extractives on the pulp surface down to a depth of 5-10 nm. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) can be used to obtain additional information about the surface (Kangas et al. 2002; Kleen et al. 2003). It gives structural information about the surface components present on the outermost surface (1 nm, or one molecular layer). ToF-SIMS may also be used to make some rough quantification of the surface components. In short, with ESCA one may estimate the coverage of lignin and extractives on the surface and with ToF-SIMS one may determine their chemical structures.

The surface morphology of mechanical pulps may be studied by Atomic Force Microscopy (AFM) (Hanley, Gray 1994; Börås, Gatenholm 1999b; Koljonen et al. 2001; Peltonen et al. 2002). In AFM, a raster-type motion

is used to scan the sample surface. By employing phase imaging in AFM different surface components such as lignin and cellulose may be identified based on the degree of phase shift. With AFM a lateral resolution of the order of Ångströms may be achieved and very small details on the surfaces can thus be studied (Moss, Groom 2002).

In this work, the surface chemical properties of fibers and different types of fines, i.e. fibrillar fines and flakes, were studied using ESCA and ToF-SIMS. The surface morphology was studied using AFM. The aim was to obtain basic information about the surface compositions of different types of mechanical pulp fines and fibers by comparing the results obtained from the three different surface-sensitive analytical techniques.

Experimental

Materials
Unbleached spruce (*Picea abies*) thermomechanical pulp (TMP) was taken from a Finnish pulp mill after the second refiner. The Canadian standard freeness (CSF) of the pulp was 124 ml. The weight fraction of long fibers (+14 McNett) was 28.6%, the proportion of middle fraction (48/200) 12.1% and that of fines (-200) 24.7%. The pulp was stored in a freezer until needed.

Separation of fines
Fines material was separated from fibers using Dynamic Drainage Jar (DDJ) fractionation. DDJ was chosen as the fractionation method because it requires less water than, say, Bauer McNett fractionation, thus reducing the washing effect. The different types of fines were enriched in the fractions using several sedimentation steps. The fractionation procedure is outlined in *Fig 1*. Prior to fractionation, TMP was hot disintegrated (85ºC, 10 min.) and diluted to 0.5% consistency with distilled water. The pulp slurry was passed on to the DDJ apparatus, which was equipped with a 200 mesh (76 μm) wire and propeller stirring, and the valve was opened. The suspension was washed with distilled water until 10 liters of slurry had been collected. The fines fraction passed through the wire while the fibers were retained on the screen. The different types of fines, i.e. fibrillar and flake-like fines, were further separated from each other by sedimentation. The total fines fraction was first allowed to sediment for two days, after which the supernatant enriched in fibrillar fines was collected. Excess water was removed from fibrils by centrifugation (5500 rpm, 15 min). The sediment was again diluted to 10 liters with distilled water. Next morning the clear supernatant was removed and discarded and the volume was again adjusted to 10 liters. This washing of the sediment was repeated three times. The final sediment contained flake-like fines including ray cells and was quite free from fibrillar material. The fractionation results of both fines fractions were evaluated by image analysis, light microscopy and scanning electron microscopy (SEM).
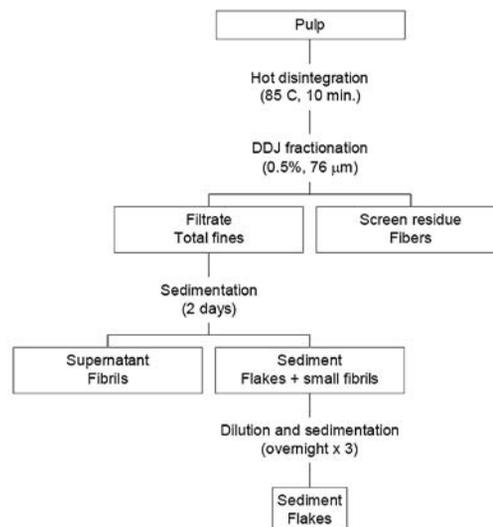

Fig 1. Fractionation procedure used to separate fibers and different types of fines.

Image analysis
The different fines fractions were studied using an image analyzer developed by Luukko (Luukko et al. 1997) and further improved by Metso Corp., Finland. The image analysis program classifies the fines particles into fibrillar and non-fibrillar material and calculates the mass proportion of fibrillar material. The program also identifies particles having rectangular shape, which is typical of ray cells, and computes their mass proportion.

Light microscopy
The flakes fraction was studied visually by light microscopy using an Axioskop 2 instrument from Zeiss. The proportion of intact and broken ray cells and flakes was calculated from a preparation dyed with Graff-C.

SEM analysis
SEM images were taken using JEOL 6335 instrument equipped with a field-emission electron gun. A droplet of the fines suspension was applied to a SEM sample stub. The stub was placed into a vacuum chamber and the pressure reduced to 0.1 Torr. Liquid in the suspension froze and sublimed as the pressure was reduced. The sample was coated with a thin layer of gold-palladium before imaging in the SEM. The voltage used was 5.0 kV and the magnification 200x.

Gross chemical analysis
Carbohydrate composition and Klason and acid-soluble lignin were determined according to TAPPI-T 249 and TAPPI-T 222 modified standards. The amount of acetone extractable material (%) was determined according to standard SCAN-CM 49:93 without prior acidification using a Soxtec apparatus. The extraction time was four hours and the amount of acetone 120 ml.

The chemical compositions of hemicelluloses and pectins were determined by acid methanolysis as described by Sundberg et al. (1996). The reaction time was 3 h. The silylated derivatives were analyzed using GC/MS (Laine et al. 1999). The advantage of acid methanolysis over acid hydrolysis is the simultaneous

determination of all uronic acids with neutral sugars.

The amount of cellulose was calculated from the glucose units given by acid hydrolysis using the factor 0.9 (Hausalo 1995). The amount of hemicelluloses and pectins (galacturonans, arabinogalactans and arabinans) was calculated from the sugar units given by acid methanolysis. Glucomannan was determined as Ac:Gal:Glc:Man 1:0.5:1:4 and converted to polysaccharide using the factor 0.9 and xylan as Ara:4-O-MeGlcA:Xyl 1.3:2:10 and converted to polysaccharide using the factor 0.88 (Sjöström 1993). Arabinogalactan was determined as GlcA:Ara:Gal 0.8:1:3.6 (Willför et al. 2002) and converted to polysaccharide using the factor 0.9. The residual arabinose was calculated as arabinan using the factor 0.88. Rhamnogalacturonan was calculated using the factor 0.9.

Sheet preparation
For surface analyses, small sheets were prepared from the different fractions. The sheets were made in a glass funnel on a 20 μm nylon screen, dried between blotters and stored in a freezer. For ESCA analysis, the sheets were extracted with acetone according to standard SCAN-CM 49:93.

ESCA analysis
The ESCA analyses were performed with an AXIS 165 high-resolution electron spectrometer from Kratos Analytical. Sample sheets were measured before and after extraction using monochromatic Al Kα irradiation (12.5 kV, 8 mA). Both survey scans in the range 0-1100 eV (1 eV step, 80 eV analyzer pass energy) and high-resolution spectra of C 1s and O 1s regions (0.1 eV step, 20 eV pass energy) were recorded, at three different locations for each sample. The area of analysis was about 1 mm^2 and the depth of analysis in the range 2-10 nm. The insulating sample surfaces were neutralized during the measurement with low-energy electrons. The surface coverage (% area) of lignin and extractives was calculated from the averaged C-C percentages in high-resolution C 1s spectra (Kleen et al. 2002). The surface coverage of polysaccharides was calculated as the difference (100 - coverage of lignin - coverage of extractives)%.

ToF-SIMS analysis
The instrument used was a PHI TRIFT II time-of-flight secondary ion mass spectrometer from Physical Electronics. ToF-SIMS spectra in positive and negative ion modes were acquired using a Ga liquid metal ion gun with 15 keV primary ions in bunched mode over the mass range 2-2000 m/z. The primary ion current was 600 pA, time per channel 0.138 ns, analysis area 200x200 μm^2 and acquisition time 5 minutes. Analytical charge compensation was used for insulating pulp samples. The calculated ion dose was $2.7×10^{11}$/cm^2 ensuring static conditions during the acquisition. Three replicate runs were made from each sample. Peak identification in ToF-SIMS spectra was based on model compound analysis. The peaks identified were integrated and normalized to the total intensity of the spectrum.

AFM analysis
AFM topography and phase images were obtained with a Nanoscope IIIa Multimode instrument from Digital Instruments Inc. in the tapping mode using Pointprobe tips (NCH, Nanosensors) with a resonance frequency of about 260 - 310 kHz. Measurements were performed in air at room temperature using the moderate tapping force (a set-point ratio between 0.4-0.7). No image processing except flattening was carried out. At least five images were taken from each sample.

Results and Discussion

Fractionation efficiency
The fines content of the original TMP varied from 24.7% (measured by Bauer McNett) to 26.7% (by DDJ). The relative amounts of different types of fines in the total fines fraction and in both TMP fines fractions were determined by image analysis. The fines fraction consisted of fibrils (45%), flakes (45%) and ray cells (10%), while the enriched fibrillar fraction contained 85% of fibrillar fines and 15% of other types of fines. The enriched non-fibrillar fraction consisted mostly of flakes (61%) and ray cells (21%), while the rest of the fraction was fibrillar fines (18%). The amount of ray cells in the enriched non-fibrillar fraction was also estimated by studying the fraction under a light microscope and by calculating the amounts of different particles. The content of intact ray cells was found to be 22% and that of broken ray cells 37%. Flakes represented 38%. The proportion of intact ray cells correlates well with the content of ray cells obtained by image analysis. Thus we can conclude that the image analyzer classifies broken ray cells as flake-like fines and the value it gives for the content of ray cells in the fines fraction is underestimated.

SEM images of the fibrillar fraction revealed the fraction to consist of thin, thread-like material (*Fig 2*). The width of one fibril in the fibrillar fraction was estimated to be between 50 nm and 1 μm, indicating that the fibrils seen in the image are bundles of microfibrils, since the diameter of one elementary fibril is on average 3.5 nm (Fengel, Wegener 1984). The material seen in the flake-like material was very heterogeneous, consisting of pieces of cell wall and ray cells as well as intact ray cells and lamellar structures (*Fig 3*). The particles were bigger than in the fibrillar fraction. In conclusion, the enrichment of fibrillar material into one fraction and flake-like material into another seemed to work quite well.

Gross chemical composition
The gross chemical composition of fibers and fines was studied to obtain basic information about their chemistry and to get an idea of the origin of fines. The amounts of mono-saccharides in pulp, fibers and fines are shown in *Table 1*. The contents of lignin, extractives and polysaccharides in pulp and its fractions are shown in *Fig 4*. Many steps are required to obtain all the chemical information shown in this figure, and there are some
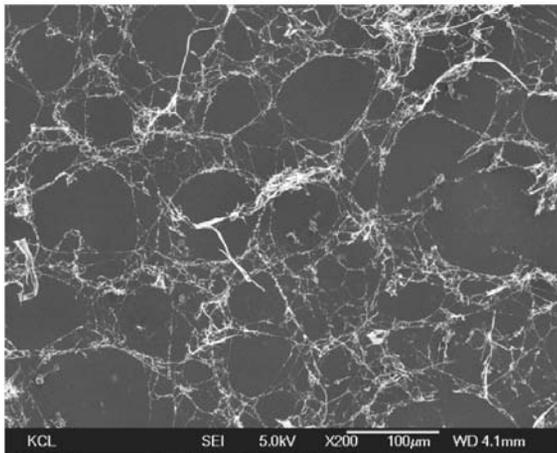
Fig 2. SEM image of TMP fibrillar fraction. Image area 590x440 μm², magnification 200x.
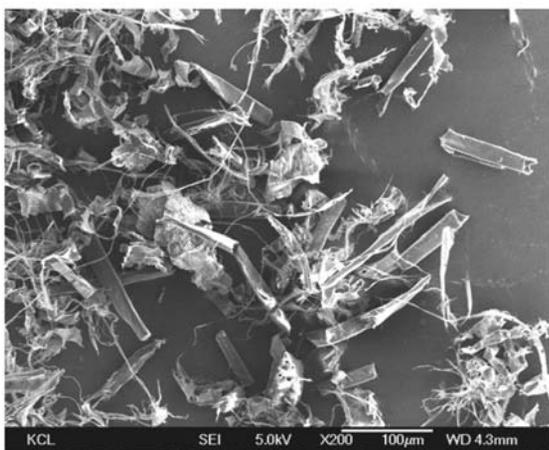

Fig 3. SEM image of TMP flake-like fines. Image area 590x440 μm², magnification 200x.
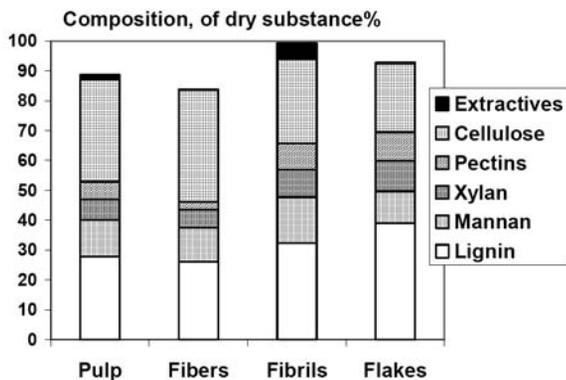

Fig. 4. Gross chemical composition of the TMP and its fractions.

Table 1. The contents of mono-saccharides (mg/100 mg) in TMP, fibers and fines. The glucose content was determined by acid hydrolysis and the contents of other saccharides by acid methanolysis.

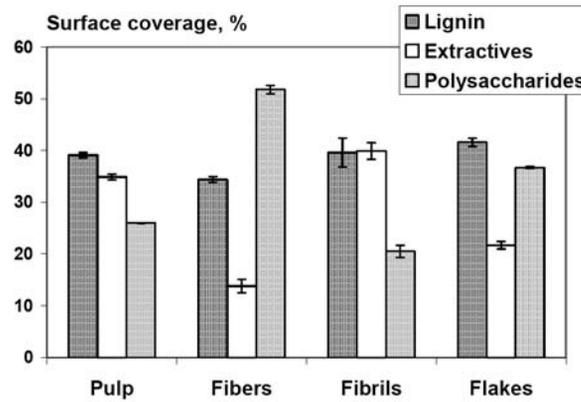|	Pulp	Fibers	Fibrillar fines	Flakes
Arabinose	1.6	1.1	2.9	3.0
Rhamnose	0.3	0.1	0.6	0.6
Xylose	5.8	5.1	7.8	8.7
4-O-Methylglucuronic acid	1.6	1.5	0.7	1.0
Mannose	9.6	8.9	12.0	8.3
Galactose	3.5	2.3	5.4	5.3
Galacturonic acid	2.6	0.9	2.5	2.9
Glucuronic acid	+	+	+	0.1
Glucose	40.4	43.9	34.5	27.6

+ = below detection limit

Fig 5. Surface coverage of lignin, extractives and polysaccharides measured using ESCA.

losses affecting the accuracy of analysis. The total amount shown for each fraction is therefore less than 100%.

Both types of fines contained more lignin, pectins and xylan and less cellulose than did fibers. Fibrillar fines contained more cellulose and mannan than flakes but less lignin, indicating that they originated from inner layers of the cell wall. Fibrils also contained a large amount of pectins, less cellulose and more lignin than fibers. The secondary wall contains no pectin (Hafrén 1999), suggesting that the collected fibrils did not all originate from the secondary wall layer but rather from the primary (P) wall. In addition, only very small amounts of arabinan and galactan are found in the secondary wall of spruce wood, while the opposite is true for the middle lamella (ML) and P layer (Meier 1964).

Flake-like fines isolated in this work contained about 50% more lignin than did the fibers. This is in good agreement with results published by Boutelje and Eriksson (1984) who reported that flake-like fines originating from the middle lamella contain twice as much lignin as fibrils from the secondary wall. The lignin content is highest in the middle lamella (ML) (Sjöström 1993) while ray cells are also heavily lignified (Hardell et al. 1980). In this study, flake-like fines contained more pectins than did the fibers due to the high pectin contents in ray cells, pit membranes and middle lamella (Hafren 1999). Flake-like fines also had a higher xylan content than either fibers or fibrillar fines. The xylan content is higher in both ray cells and ML than in other parts on the wood, ray cells having the highest concentrations of xylan (Westermark et al. 1986). The present results indicate that flake-like fines mainly consist of unbroken and broken ray cells and partly of middle lamella (ML) pieces. The gross chemical compositions obtained in this work were similar to those published earlier (Sundberg et al. 2003; Kleen et al. 2003).

The extractives content of fibrillar fines was many times greater than that of flake-like fines or fibers. The high extractives content of fibrillar fines is probably attributable to the dissolution and dispersion of wood resin during pulping and its readsorption onto fibrillar fines. As the microscope studies of the fines fraction showed, most of the ray cells were broken during refining, thus releasing wood resin into the suspension.

The dispersed wood resin can adsorb onto pulp components during subsequent process stages as the conditions change. The fractionation procedure may also have influenced the extractives content of fibrils, since at least colloidal extractives should remain in the fibrillar fraction after fractionation. When excess water is removed from the fraction by centrifugation, the colloidal particles may either be removed with the water or stay in the sediment with fibrils. In the latter case, extractives would also be retained in the sheet prepared from fibrils. The effect of the experimental conditions on the results will be considered under a separate heading.

Surface chemical properties by ESCA

The ESCA results showed that both types of fines had a greater coverage of lignin and extractives than fibers (*Fig 5*). The fraction with the largest coverage of lignin and extractives was the fibrillar fines fraction. About 80% of its surface was covered with lignin and extractives and only 20% by polysaccharides. Flake-like fines were also largely covered with lignin, but the coverage of extractives was lower on the surfaces of flakes than on fibrillar fines, leaving nearly 40% of the surface covered with polysaccharides. The surface of fibers was the most polysaccharide-rich, surface coverage being over 50%.

Comparing the total lignin content of the fractions to their surface coverage of lignin shows that lignin was somewhat enriched on the surfaces of pulp fractions. For example, on the surface of fibers and fibrillar fines, there was about 25-35% more lignin than indicated by the gross chemical content. The enrichment is more obvious for the whole pulp than for the separate fractions, indicating that dissolution of a small amount of surface lignin or lignin-like material (i.e. lignans) was taking place during the fractionation procedure. Comparison of the bulk extractives content and the amount of extractives on the surface shows that the extractives were very much enriched on the surface, especially on the surface of fines. This agrees well with earlier results (Koljonen et al. 1997).

Surface chemical properties by ToF-SIMS

ToF-SIMS has been reported to be a good method for studying extractives and lignin on the surfaces of mechanical pulps (Kleen et al. 2001; Kangas et al. 2002). In this work, ToF-SIMS was used to study surface extractives on different types of TMP fines and TMP fibers. A number of reference compounds representing the most common extractives found in mechanical pulps made from Norway spruce were analyzed using ToF-SIMS to enable the identification of surface extractives. Based on the reference runs, it was concluded that acidic extractives (i.e. fatty and resin acids) can be successfully analyzed in the negative ToF-SIMS ion

Table 2. Extractives identified from ToF-SIMS spectra and their characteristic peaks.

Extractive	Structure	Neg. peaks (m/z)	Pos. peaks (m/z)
Saturated fatty acids			
Palmitic	$C_{16}H_{32}O_2$	**255**	239, 257
Anteisoheptadecanoic	$C_{17}H_{34}O_2$	**269**	253, 271
Stearic	$C_{18}H_{36}O_2$	**283**	267, 285
Arachidic	$C_{20}H_{40}O_2$	**311**	295, 313
Behenic	$C_{22}H_{44}O_2$	**339**	323, 341
Lignoceric	$C_{24}H_{48}O_2$	**367**	351, 369
Unsaturated fatty acids			
Oleic	$C_{18}H_{34}O_2$ (9)	**281**	265, 283
Linoleic	$C_{18}H_{32}O_2$ (9,12)	**279**	263, 281
Pinolenic	$C_{18}H_{30}O_2$ (9,12,15)	**277**	261, 279
Eicosatrienoic	$C_{20}H_{34}O_2$ (5,11,14)	**305**	
Triglycerides			
Tripalmitin	$C_{51}H_{98}O_6$	255	239, 313, 551
Tri(14-methyl)hexadecanin	$C_{54}H_{104}O_6$		253, 327, 579
Tristearin	$C_{57}H_{110}O_6$	283	267, 341, 607
Triolein	$C_{57}H_{104}O_6$	281	265, 339, 603
Trilinolein	$C_{57}H_{98}O_6$	277	263, 337, 599
Tripinolenin	$C_{57}H_{98}O_6$		261, 335, 595
Resin acids			
Dehydroabietic	$C_{20}H_{28}O_2$	**299**	301
Abietic acid and isomers	$C_{20}H_{30}O_2$	**301**	302
Triterpenoids and steroids			
Sitosterol	$C_{29}H_{50}O$	413	**397**, 414, 429
Campesterol	$C_{28}H_{48}O$		**383**
Steryl esters	-	281, 411, 425	**383, 397, 411, 429**

mode and neutral extractives such as sterols, steryl esters and fatty acid esters in the positive ion mode. Fatty and resin acids can be identified by peaks originating from their molecular ion, which has lost one hydrogen atom and acquired a negative charge ([M-H]$^-$ -ion). Peaks in the positive ToF-SIMS spectra originate either from the protonated molecular ion ([M+H]$^+$) or the molecular ion, which has lost one hydroxyl group ([M-OH]$^+$). The extractives identified based on the reference compound analyses are listed in *Table 2*.

Part of the negative ToF-SIMS spectrum of TMP fibrillar fines is shown in *Fig 6*. Peaks originating from the most common fatty and resin acids are seen in the mass per charge area (m/z) from 250 to 400. The most intense peaks at 279, 281 and 277 can be assigned to linoleic, oleic and pinolenic acids, respectively, the most abundant fatty acids in Norway spruce (*Picea abies*) (Ekman 1979). These peaks can originate either from esterified or free fatty acids. Smaller peaks at 299 and 301 originate from resin acids, dehydroabietic acid and
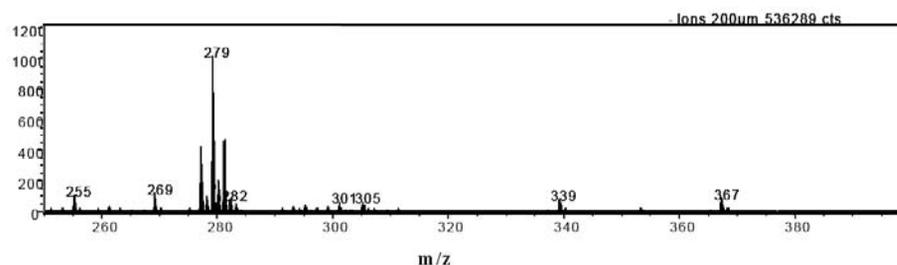

Fig 6. Part of the negative ToF-SIMS spectrum of TMP fibrillar fines.

abietic acid and its several isomers. Peaks originating from resin acids are fairly small compared to the fatty acid peaks. Normally, in the bulk of wood or mechanical pulp, the content of resin acids as compared to the content of free and esterified fatty acids is higher (Ekman 1979; Ekman et al. 1990) than was seen in our samples. The reason for the smaller concentration of resin acids on the pulp surfaces could be that they are washed off more effectively than the free and esterified fatty acids. Käyhkö (2002) analyzed the concentration of water-released wood resin at different process stages in a Finnish TMP mill and found out that nearly half (42-49%) of the wood resin was transferred to the water phase in the pulper after refining. Acidic wood extractives were liberated to lesser extent than neutral extractives such as triglycerides and sterols. Thus we can conclude that more effective washing was probably not the reason for the small intensity obtained for resin acids. Another explanation could be that resin acids are fragmented more extensively in the ToF-SIMS experiment making the method less sensitive for their analysis. This conclusion was supported by the model compound analyses performed.

Peaks originating from sterols, steryl esters, and mono-, di- and triglycerides can be seen in the mass per charge area from about 300 to 600 in the positive ToF-SIMS spectrum (*Fig 7*). The most intense peak at 397 can be identified as originating from sitosterol, the most abundant steroid in wood and higher plants (Sjöström 1993). Triglycerides can fragment to di- and mono-glycerides during the ToF-SIMS experiment and the peaks identified as monoglycerides can be either from di- or triglycerides or to a lesser extent from monoglyce-rides themselves. The monoglyceridic peaks are seen at around m/z 340 and the diglyceridic peaks at around m/z 600. This pattern has been observed in earlier studies (Kleen, Nilvebrandt 2001). Triglycerides are much more common in Norway spruce than either di- or mono-glycerides (Ekman 1979).

The contents of the different extractives on the surfaces of TMP and its fractions were estimated by integrating the characteristic peak for a certain extracti-ves compound in the ToF-SIMS spectra and normalizing the peak intensity to the total intensity of the spectrum. The peaks were assigned to one of the following groups: unsaturated fatty acids, saturated fatty acids, resin acids, sterols and steryl esters and glycerides, and their values were added together. The peaks marked in bold in *Table 2* were used to calculate extractives contents. The method does not give fully quantitative results, but it does allow a
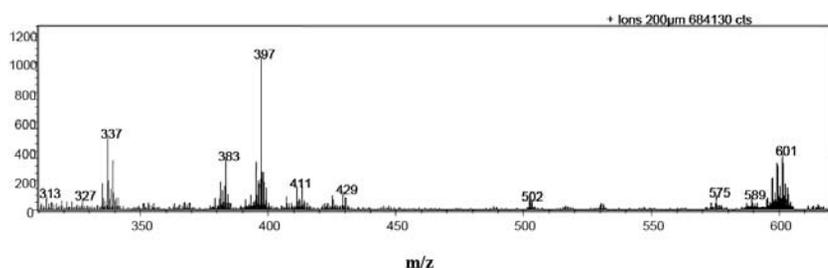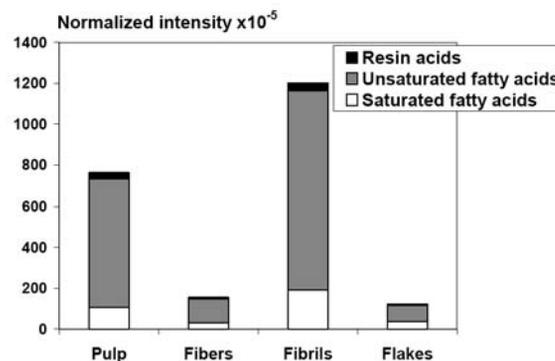

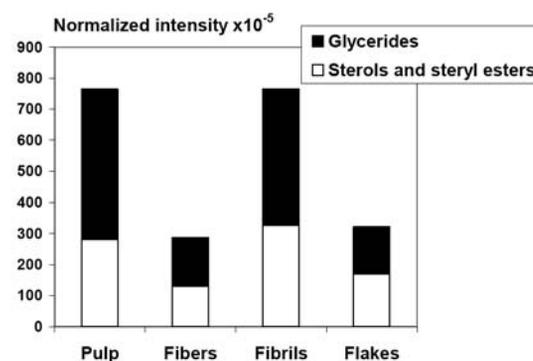Fig 8. Normalized intensities of fatty and resin acid groups as analyzed using ToF-SIMS.

Fig 9. Normalized intensities of sterol, steryl ester and glyceride groups as analyzed using ToF-SIMS.

comparison between samples.

According to the ToF-SIMS results, both the contents of fatty and resin acids (*Fig 8*) and of sterols, steryl esters and glycerides (*Fig 9*) were highest on the surface of TMP fibrillar fines. The surface contents were very similar for both fibers and flakes. Unsaturated fatty acids were the most common acidic extractives on the surfaces of fibers and fines, as in wood itself (Ekman 1979). The relative proportions of glycerides and sterols/steryl esters were quite similar in the different samples. ToF-SIMS results (*Figs 8* and *9*) on extractives correlate well with ESCA results (*Fig 5*). Both techniques classify the samples in the same order of increasing surface content of extractives.

In wood, the extractives are found in parenchyma cells and in resin canals (Back 2000). During a harsh process like refining, wood cells are broken and some wood resin is dispersed into the water phase. Resin can be adsorbed or deposited back onto the pulp surface as a result of changes in pH, temperature, electrolyte concentration or amount of water (Ekman et al. 1990; Sundberg et al. 1994). The dispersed resin can adsorb onto the fibers and fines either during pulp production or during disinte-gration, fractionation and sheet prepa-ration. Fines have a larger specific sur-face area than fibers, especially fibrillar fines (Wood et al. 1991), indicating their ability to adsorb materials.

However, the adsorption behavior may also depend on the surface chemis-try of materials as suggested by

Fig 7. Part of the positive ToF-SIMS spectrum of TMP fibrillar fines.

Mosbye et al. (2003). They found that the adsorption of colloidal extractives into fines depends on the chemical composition of the fines and that the sterically stabilized colloidal extractives are more easily adsorbed onto lignin-rich flake-like fines than onto the carbohydrate-rich fibrils. In their work, the fines were created by successive refining and the surface chemistry of fines was found to change as more fibrillar fines were created at later refining stages. In our work, the pulp was obtained after the second refining stage i.e. prior to the reject refining, and fibrils were isolated from this pulp. The gross chemical analysis showed that the fibrils originated mainly from the primary wall. Thus the fibrils collected in our work were more similar in chemistry to flakes than they would be if isolated from pulps taken after the reject refining, as our studies have since shown (Kangas et al. 2004). Thus, it can be concluded that fibrillar fines with different surface chemical properties may be found from mechanical pulps, depending on e.g. refining conditions. Pulps from mainline refining may contain fibrils originating from the primary wall, which still have quite high content of pectins and lignin and can readily adsorb extractives on their surface. On the other hand, pulps that have gone through reject refining contain more carbohydrate-rich fibrils from the secondary wall.

Effect of the experimental conditions on the results

All the chemical analysis methods used in this work showed that fibrils were the most extractive-rich pulp fraction, contrary to what has been found earlier (Mosbye 2003). One explanation for the different result was discussed above. However, the question still remained whether the high extractives content was a true result or whether it was due to the experimental conditions, namely the isolation of fibrils from the flake-like fines. Further studies were thus needed to establish this. Our main concern in this respect was the removal of water from the fibrillar fines and whether the centrifugation had been too harsh to retain all the colloidal extractives among the fibrils. A centrifugation speed of 500 g for 30 min has been traditionally used, when removing dissolved and colloidal substances from the pulp (Örså, Holmbom 1994). The speed used in this work was significantly higher, approximately 4700 g, although the centrifugation time was shorter, 15 minutes. The effect of the centrifugation speed on the extractives content of fibrils was therefore tested using three different speeds, namely 500 g, 1500 g and 4700 g. After centrifugation, the supernatant was pipetted off and freeze-dried. The sediment was removed and air-dried on a glass slide. All the materials were analyzed by ToF-SIMS. The results showed that the content of acidic and neutral extractives was higher on the surface of material from the supernatant than on the material from the sediment after centrifugation, i.e. fibrillar fines. The fibrils separated using the highest centrifugation speed had only a slightly higher content of extractives on their surface. Thus it can be concluded that centrifugation had no effect on the extractives content of fibrillar fraction, and that most of the extractives were removed with the water after
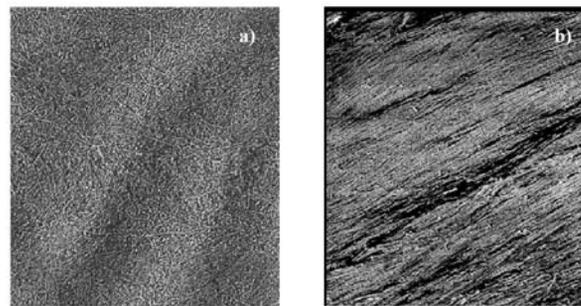

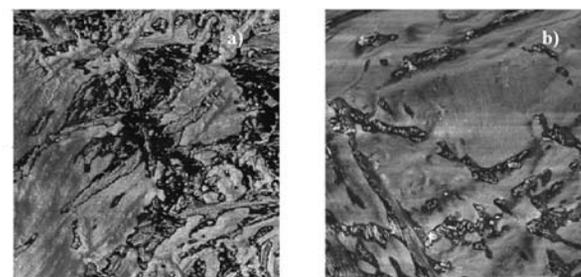Fig 10. AFM phase images of TMP fibers. Image size 3x3 μm^2.

Fig 11. AFM phase images of TMP fibrils. Image size 3x3 μm^2.
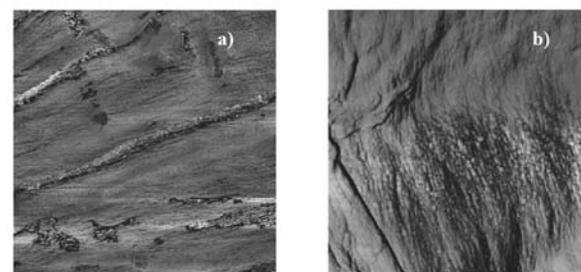

Fig 12. AFM phase images of TMP flakes. Image size 3x3 μm^2.

centrifugation. Therefore, the observed high extractives content on fibrillar surfaces is concluded to be due to the type of fibrils isolated in our work.

Surface morphology by AFM

The different TMP fractions differed in surface morphology. Images of the fiber fraction showed two types of microfibrillar orientation (*Fig 10*). In *Fig 10a* the orientation of fibrils is random, indicating that the primary wall (P) has been exposed during refining. In *Fig 10b* the orientation of fibrils is almost the same as the orientation of the fiber axis, suggesting that the S_2 layer has been revealed. Thus it can be concluded that different cell wall layers were exposed during refining. Cellulose-rich inner cell wall layers contribute to the high coverage of polysaccharides as found by ESCA, and the primary wall increases the surface lignin content of the fraction.

Two types of material were seen on the surface of TMP fibrillar fines (*Fig 11*). Since the ESCA and ToF-SIMS results showed that fibrillar fines were very rich in surface extractives, it is suggested that one of the materials seen in the image is extractives. AFM images of mechanical pulps published earlier have shown lignin as granular structures on the surface (Gustafsson et al. 2001; Koljonen et al. 2003). Although the surface coverage of lignin on fibrillar fines was 40%, only a small amount of granular structures were seen on the surface (*Fig 11b*). It is therefore suggested that lignin may also appear as a non-granular layer on the surface of

mechanical pulp fines. This is supported by earlier findings (Koljonen et al. 2003).

Granular lignin was visible on the surface of flake-like fines (*Fig 12*). Some fibrillar orientation can also be seen on the surfaces of flakes.

Conclusions

Using the fractionation procedure developed here, it was possible to obtain relatively pure fractions of fibers, fibrils and flake-like fines from TMP. The fibrillar fraction consisted almost completely of thin fibrils ranging in width from 50 nm to 1 μm, while flakes contained more heterogeneous material.

Fibers and fines differed in their gross chemical composition. Fines contained more lignin, extractives, pectins and xylan than did fibers. Fibrillar and flake-like fines differed also in their chemistry, fibrillar fines being the most extractives-rich fraction and flakes containing most lignin. It was concluded from the results that fibrillar fines probably originate from the primary cell wall layer, while flake-like fines consist mainly of unbroken and broken ray cells and pieces of middle lamella.

By combining different surface-sensitive techniques, new information was obtained about surface chemical properties. ESCA reveals the surface area covered with lignin, extractives and polysaccharides but gives less information about their chemistry. ToF-SIMS provides structural information about the surface extractives and thus complements the results given by ESCA. For surface extractives, ESCA and ToF-SIMS results correlated well, since both techniques classified the samples in the same order of increasing surface content of extractives. AFM can be used to study fine details on fiber and fines surfaces such as orientation of cellulose microfibrils and the presence of lignin. AFM thus gives additional information about the surface compounds and their morphology.

Both types of fines exhibited more surface extractives and lignin than did fibers. Lignin and extractives covered almost 80% of the surfaces of fibrillar fines. Flakes also had a high surface content of lignin, but the content of surface extractives was lower. The high content of extractives on fibrillar surfaces is probably due to the adsorption of wood resin particles, influenced by the large specific surface are of fibrils and/or their surface chemical composition. According to ToF-SIMS results, the most common surface extractives on fibers and fines were unsaturated fatty acids, probably present mainly as triglycerides, and sterols and steryl esters.

AFM images together with ESCA results revealed that much of the S_2 layer was exposed on fiber surfaces, though remnants of the P wall were also detected. It is suggested that lignin (in both granular and non-granular form) and extractives cover most of the surfaces of fibrillar fines, whereas no clean cellulose fibrils were seen on the fibril surfaces. Flake-like fines were mainly covered with lignin and carbohydrates. The surface lignin on flakes appeared in granular form and some orientated fibrils were also detected on the flake surfaces.

Literature

Back, E.L. (2000): In "Pitch Control, Wood Resin and Deresination". Edited by E.L. Back and L.H. Allen. Tappi Press, Atlanta, pp. 1-35.

Boutelje, J. and Eriksson, I. (1984): Analysis of lignin in fragments from thermo-mechanical spruce pulp by ultraviolet microscopy, Holzforschung 38(5), 249.

Brecht, W. and Klemm, K. (1953): The mixture of structures in a mechanical pulp as a key to the knowledge of its technological properties, Pulp Paper Mag. Can. 54(1), 72.

Börås, L. and Gatenholm, P. (1999a): Surface properties of mechanical pulps prepared under various sulfonation conditions and preheating time, Holzforschung 53(4), 429.

Börås, L. and Gatenholm, P. (1999b): Surface composition and morphology of CTMP fibers, Holzforschung 53(2), 188.

Chang, H.-M., Sinkey, J. D. and Yan, J. F. (1979): Chemical analysis of refiner pulps, Tappi 62(9), 103.

Dorris, G. M. and Gray, D. G. (1978): The surface analysis of paper and wood fibres by ESCA. II. Surface composition of mechanical pulps, Cellul. Chem. Tech 12(6), 721.

Ekman, R. (1979): Analysis of the nonvolatile extractives in Norway spruce sapwood and heartwood, Acta Acad. Aboensis, Ser. B 39(4), 1.

Ekman, R., Eckerman, C. and Holmbom, B. (1990): Studies on the behaviour of extractives in mechanical pulp suspensions, Nordic Pulp Paper Res. J. 5(2), 96.

Fengel, D. and Wegener, G. (1984): "Wood. Chemistry, Ultrastructure, Reactions". Walter de Gruyter, Berlin, p. 95.

Gustafsson, J., Ciovica, L., Lehto, J.H., Tienvieri, T. and Peltonen, J. (2001): The influence of defibration temperature and refining on the surface characteristics of mechanical pulps. Research techniques for tomorrow's papermaking, COST Action E 11 Characterization methods for fibres and paper, Final workshop, 4-5 Oct., Espoo, Finland, pp. 67.

Hafrén, J. (1999): Ultrastructure of wood cell wall, PhD thesis, Royal Institute of Technology, Department of Biotechnology, Stockholm.

Hanley, S. J. and Gray, D. G. (1994): Atomic force microscope images of black spruce wood sections and pulp fibres, Holzforschung 48(1), 29.

Hardell, H.-L., Leary, G. J., Stoll, M. and Westermark, U. (1980): Variations in lignin structure in defined morphological parts of spruce, Svensk Papperstidn. 83(2), 44.

Hausalo, T. (1995): Analysis of wood and pulp carbohydrates by anion exchange chromatography with pulsed amperometric detection. 8th International Symposium on Wood and Pulping Chemistry (ISWPC), June 6-9, Helsinki, Finland, Vol. 3, pp.131.

Kangas, H., Pöhler, T., Heikkurinen, A. and Kleen, M. (2004): Development of mechanical pulp fiber surface as a function of refining energy, Submitted to J. Pulp Paper Sci.

Kangas, H., Salmi, J. and Kleen, M. (2002): Surface chemistry and morphology of thermomechanical pulp fibers and fines. 7th European Workshop on Lignocellulosics and Pulp (EWLP), August 26-29, Turku, Finland, pp.115.

Karnis, A. (1994): The mechanism of fibre development in mechanical pulping, J. Pulp Paper Sci. 20(10), J280.

Kleen, M., Kangas, H., Laine, C. (2003): Chemical characterization of mechanical pulp fines and fiber surface layers, Nordic Pulp Paper Res. J. 18(4), 361.

Kleen, M. and Nilvebrandt, N.-O. (2001): Simultaneous characterization of free and esterified fatty acids and fatty acid salts using Time-of-flight Secondary Ion Mass Spectrometry. Post-Symposium workshop of the 11th ISWPC, June 18-19, Grenoble, France, pp. 51.

Kleen, M., Räsänen, H., Ohra-aho, T. and Laine, C. (2001): Surface Chemistry of TMP fibers and fines. 11th International Symposium on Wood and Pulping Chemistry (ISWPC), June 11-14, Nice, France, Vol. 1, pp. 255.

Kleen, M., Sjöberg, J., Dahlman, O., Johansson, L.-S., Koljonen, K. and Stenius, P. (2002): The effect of ECF and TCF bleaching on the chemical composition of soda-anthraquinone and kraft pulp surfaces, Nordic Pulp Paper Res. J. 17(3), 357.

Koljonen, K., Stenius, P. and Buchert, J. (1997): The surface chemistry of PGW pulp fibre fractions. International Mechanical Pulping Conference (IMPC), June 9-13, Stockholm, pp. 407.

Koljonen, K., Österberg, M., Johansson, L.-S. and Stenius, P. (2003): Surface chemistry and morphology of different mechanical pulps determined by ESCA and AFM, Colloids Surf. A 228(1-3), 147.

Koljonen, K., Österberg, M. and Stenius, P. (2001): Surface chemistry and morphology of mechanical pulp fibers. 2001 International Mechanical Pulping Conference (IMPC), June 4-8, Helsinki, Finland, Vol. 2, pp. 305.

Käyhkö, J. (2002): The influence of process conditions on the deresination efficiency in mechanical pulp washing, PhD thesis, Lappeenranta University of Technology, Department of Chemical Technology, Lappeenranta.

Laine, C., Haakana, S., Hortling, B. and Tamminen, T. (1999): Application of methylation analysis to samples derived from spruce kraft pulp. 10th International Symposium on Wood and Pulping Chemistry (ISWPC), June 7-10, Yokohama, Japan, Vol.1, pp. 72.

Luukko, K., Kemppainen-Kajola, P. and Paulapuro, H. (1997): Characterization of mechanical pulp fines by image analysis, Appita J. 50 (5), 387.

Luukko, K., Laine, J. and Pere, J. (1999): Chemical characterization of different mechanical pulp fines, Appita J. 52(3), 126.

Meier, H. (1964): In "The formation of wood in forest trees", Edited by M.H. Zimmerman, Academic Press, New York, pp. 137-151.

Mosbye, J. (2003): Colloidal wood resin: Analyses and interactions, PhD thesis, Norwegian University of Science and Technology, Department of Chemical Engineering, Trondheim.

Mosbye, J., Laine, J. and Moe, S. (2003): The effect of dissolved substances on the adsorption of colloidal extractives to fines in mechanical pulp, Nordic Pulp Paper Res. J. 18(1), 63.

Moss, P. and Groom, L. (2002): In "Handbook of physical testing of paper. Vol. 2", Edited by J. Borch, M. B. Lyne, R. E. Mark, C. C. J. Habeger and K. Murakami. Marcel Dekker Inc., New York, pp. 149-265.

Mustranta, A., Koljonen, K., Pere, J., Tenkanen, M., Stenius, P. and Buchert, J. (2000): Characterization of mechanical pulp fibres with enzymatic, chemical and immunochemical methods. 6th European Workshop on Lignocellulosics and Pulp (EWLP), Sept. 3-6, Bordeaux, France, pp. 15.

Peltonen, J., Gustafsson, J., Ciovica, L., Lehto, J. H. and Tienvieri, T. (2002): Morphological, surface chemical and mechanical changes of chemical and mechanical pulp fibers during pulping: an atomic force microscopy study. 2002 International Pulp Bleaching Conference (IPBC), May 21, Portland, OR, USA, pp. 29.

Sjöström, E. (1993): "Wood Chemistry. Fundamentals and Applications". 2. Ed. Academic Press, Inc., San Diego, p. 293.

Sundberg, A., Pranovich, A.V. and Holmbom, B. (2003): Chemical characterization of various types of mechanical pulp fines, J. Pulp Paper Sci. 29(5), 173.

Sundberg, A., Sundberg, K., Lillandt, C. and Holmbom, B. (1996): Determination of hemicelluloses and pectins in wood and pulp fibres by acid methanolysis and gas chromatography, Nordic Pulp Paper Res. J. 11(4), 216.

Sundberg, K., Thornton, J., Ekman, R. and Hombom, B. (1994): Interactions between simple electrolytes and dissolved and colloidal substances in mechanical pulp, Nordic Pulp Paper Res. J. 9(2), 125.

Westermark, U. (1999): The content of lignin on pulp fiber surfaces. 10th International Symposium on Wood and Pulping Chemistry (ISWPC), June 7-10, Yokohama, Japan, Vol. 1, pp. 40.

Westermark, U. and Capretti, G. (1988): Influence of ray cells on the bleachability and properties of CTMP and kraft pulps, Nordic Pulp Paper Res. J. 3(2), 95.

Westermark, U., Hardell, H.-L. and Iversen, T. (1986): The content of protein and pectin in the lignified middle lamella/primary wall from spruce fibers, Holzforschung 40(2), 65.

Willför, S., Sjöholm, R., Laine, C. and Holmbom, B. (2002): Structural features of watersoluble arabinogalactans from Norway spruce and Scots pine heartwood, Wood Sci. Technol. 36(2), 101.

Wood, J. R., Grondin, M. and Karnis, A. (1991): Characterization of mechanical pulp fines with a small hydroclone. Part I: The principle and nature of the separation, J. Pulp Paper Sci.17(1), J1.

Örså, F. and Holmbom, B. (1994): A convenient method for the determination of wood extractives in papermaking process waters and effluents, J. Pulp Pap. Sci. 20(12), J361.