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ORIGINAL ARTICLE

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Micromorphology and topochemistry of extractives in Scots pine and Norway spruce thermomechanical pulps: a cytochemical approach

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Abstract Due to the increasing demand for Norway spruce as prime raw material for high-yield pulping, recent interest has focused on Scots pine as an alternative. However, the intrinsic properties of Scots pine, particularly the high amounts of extractives and the fiber properties, have been considered a disadvantage for thermomechanical pulping. A study was therefore conducted on the variations in the spatial distribution and redistribution of lipophilic extractives in spruce and pine wood and thermomechanical pulp (TMP) using cytochemical staining methods and chemical analysis. Chemical analyses showed chips from pine thinnings and sawmill slabs to contain three to five and two to three times, respectively, more extractives than found in spruce; in particular, the amount of triglycerides differed significantly. Results from staining techniques on the abundance and distribution of extractives (i.e., fats) between pine and spruce correlated with amounts detected by Fourier transform infrared spectroscopy and gel permeation chromatography. Cytochemical observations revealed information pertaining to species-specific distribution and redistribution of extractives among TMP fines and fibers and indicated the presence of a molecular film of extractives. Results indicate that the high concentrations of extractives in pine ray parenchyma are released during TMP processing and are redistributed onto the surfaces of the pulps, negatively affecting energy usage during primary refining.

Key words Cytochemical staining · Extractives · Norway spruce · Scots pine · Thermomechanical pulp fibers

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Introduction

The most common wood species used for production of thermomechanical pulp (TMP) and chemithermomechanical pulp (CTMP) in Europe is Norway spruce. However, the supply of Norway spruce would soon become limiting if TMP production was significantly increased in Scandinavia. TMP production is considered an environmentally friendly process and TMP has some inherently desirable properties for some applications. Because softwood is mainly used for TMP and the other predominant softwood in Northern Europe is Scots pine, any significant increase in TMP production in Northern Europe using domestic resources would naturally increase the use of Scots pine.

However, there are certain well-known drawbacks in using Scots pine as a raw material for TMP production. In particular, Scots pine exhibits higher specific energy consumption (SEC) and has inferior pulp properties when compared with Norway spruce.[1–3] The higher amount of wood extractives (ca 2.5 times higher than in spruce) reported in Scots pine has traditionally been claimed as a reason for these limitations, especially the poor strength properties.[4–9] The major types of lipophilic extractives (i.e., wood resin) found in spruce and pine are triglycerides (TG), fatty acids (FA), resin acids, sterols, and their esters.[10] In native wood, extractives are localized either in parenchyma cells (i.e., both axial and ray parenchyma) or resin canals (both radial and vertical) and associated epithelial cells.[11] While neutral fats (i.e., triglycerides) including fatty acids dominate the sapwood of both Scots pine and Norway spruce, resin acids (found solely within resin canals) and fatty acids (both unsaturated and saturated FA) are higher in the heartwood of pine.[10]

During primary refining in the TMP process, the integrated native wood cell structure is destroyed, allowing release of extractives from both the resin canals and those encapsulated in parenchyma cells.[12] Because most wood components are retained in the TMP process, the liberated extractives are dispersed in the process water and then redistributed over the pulp during subsequent stages. In the

final paper, fiber-to-fiber bonding is influenced by the structure and chemistry of the pulp-fiber surface. Therefore, presence of extractives will indirectly influence the pulp surface property and constitute an important aspect of the production process for paper affecting formation, quality, and pitch problems.[13–15]

In this study we analyzed extractives in different wood raw materials and TMP of Norway spruce and Scots pine and determined their composition, micromorphological distribution and redistribution, and presence on the pulp surfaces. We employed cytochemical staining of extractives and proteins, wet chemical analysis, Fourier transform infrared spectroscopy (FT-IR), and chromatography. Species-specific distribution patterns of the extractives are reported and discussed from the point of view of the potential use of Scots pine in Nordic TMP production.

Materials and methods

Wood and pulp samples

The wood and TMP samples were Norway spruce (*Picea abies* L. Karst.) and Scot pine (*Pinus sylvestris* L.). TMP was produced using the chips from two categories of material from each wood species; sawmill slabs (denoted "sawmill") representing mainly mature sapwood, and thinnings containing mostly juvenile wood.

TMP was produced at a Metso pilot plant in Sundsvall, Sweden. The pulps were produced using a three-stage refining process. Before refining, the chips were subjected to atmospheric presteaming in a chip bin for 15–20 min before primary-stage refining to approximately 450 ml Canadian Standard Freeness (CSF). Primary stage refining was carried out in a pressurized 20-inch single-disk refiner OVP 20. Secondary and tertiary refining were done atmospherically using a 20-inch single-disk refiner ROP 20. All refiners were equipped with 5811 plates and run at a speed of 1500 rpm.

The wood and TMP pulps were used as received and stored frozen in darkness until use. TMP samples were extracted with pure dichloromethane and water respectively and 99% ethanol (2 h × 3) to produce extractive-free TMP. Fully bleached TCF kraft pulp (softwood) provided by Svenska Cellulosa Aktiebolagot (SCA), Sundsvall, Sweden, was used as a negative control for protein and extractives.

Localization of extractives

Cytochemical localization of fats (i.e., triglycerides/free FA) was performed on both wood and TMP samples from Norway spruce and Scots pine to reveal morphological features of their native spatial distribution and subsequent redistribution during TMP refining. Wood disks of mature Norway spruce and Scots pine stored at –20°C were used for localizing lipophilic extractives in their native state. Small wood pieces of ca. 2.0 × 1.0 × 0.5 cm were cut manually from the outer part of the wood disks (i.e., sapwood) of both species and used for sectioning. Samples of never-dried, unbleached spruce and pine TMP produced at the Metso pilot plant, using chips from thinnings as well as sawmill chips that contain mainly sapwood, were used for the localization of triglycerides and fatty acids.

Light microscopy

Radial sections of ca. 7–10 µm thick from both wood species were obtained using a Leitz Wetzlar sliding microtome (Type 1300) and were mounted on glass slides. Small amounts of never-dried TMP pulps were mounted on glass slides and the pulp slurry separated using fine forceps in order to visualize all components including fibers, parenchyma cells, and fines etc. Samples (both wood and pulps) mounted on glass slides were stained using Nile blue for detecting neutral triglycerides and by osmium tetroxide for fats containing unsaturated FAs as described previously for birch wood and kraft pulps.[16] Stained samples were covered with coverslips and examined using a Leica DMLB light microscope and images were recorded digitally with a Leica DC 300 CCD camera and stored using a Leica IM50 Image Manager. The results shown reflect observations on several sections from different staining experiments.

Cytochemical staining of proteins

TMP and extracted TMP of Scots pine and Norway spruce were stained for proteins using the Bio-Rad (Bradford method) protein staining method, according to Hafrén.[17] Cytochemical staining by Coomassie blue was performed using the Bio-Rad Protein Assay (dye reagent concentrate) and bleached kraft pulp was used as negative control. For the spectrophotometric assay of Coomassie dye binding to the pulp, 10.0-mg samples (dry weight) were stained with 1.25 ml Coomassie dye solution (Bio-Rad reagent concentrate/deionized water, 1:4) for 10 min. After brief centrifugation to spin down the pulps, the absorbance (465 nm) of the supernatant was analyzed using a Shimadzu UV-160A spectrophotometer.

Chemical analyses of TMP pulps

Carbohydrate and lignin

The neutral sugar content and composition and lignin content of the pulps were analyzed after hydrolysis by sulfuric acid, according to the standard test method Tappi T-249-cm-85. Klason-lignin was determined as the solid part remaining after filtration of the hydrolysate.

The monomeric carbohydrates were determined in hydrolyzed samples using a Dionex high-performance liquid chromatography (HPLC) system equipped with a pulsed amperometric detector (PAD),[18] and a Dionex PA-1 column using an eluent flow of 1.0 ml/min and postcolumn flow of 0.6 ml/min. Carbohydrates were eluted using the following gradient flow conditions: 90% H_2O, 10% 50 mM NaOH for

Table 1. Analysis of monosaccharides and lignin on thermomechanical pulp (TMP) samples and the total amount of extractives in wood and respective TMPs from third-stage refining

Wood type	Monosaccharide[a] (% dry weight)							Lignin[b]	Total extractive content (% w/w)	
	Galactose	Glucose	Mannose	Arabinose	Xylose	Rhamnose	Total sugar		Wood	Pulps
Spruce thinning	2.0	42.7	13.0	1.1	5.3	0.1	64.1	28.4	0.57	0.70
Pine thinning	1.9	42.8	12.3	1.5	5.8	0.1	64.4	28.3	2.31	2.34
Spruce sawmill	1.7	43.2	13.1	1.0	4.6	0.1	63.7	29.2	0.84	0.86
Pine sawmill	2.0	43.3	14.0	1.3	5.1	0.1	65.8	27.4	3.03	1.81

[a] Anhydrous
[b] Klason lignin (% dry weight)

5 min, 100% H_2O 5–35 min, 100% 50 mM NaOH 35–50 min (column wash), 90% H_2O, 10% 50 mM NaOH for 15 min before the next injection (to establish stable conditions).

Extractives

The total amount of extractives was determined by SCAN-CM 67:03 (content of extractable, lipophilic matter). Extraction was performed with cyclohexane–acetone. The relative composition of the extract was determined by gel permeation chromatography (GPC). The GPC equipment consisted of a modified Waters 600A pump, a Waters U6K injector, and a Waters 2414 refractive index (RI) detector. Analysis was performed with three Waters Ultrastyragel columns (2 × 500 Å + 1 × 100 Å) using tetrahydrofuran (THF) at 1.0 ml/min as the eluent.

Dried extracts were also analyzed by FT-IR for ester and acid components. The IR spectra were collected in the 4000–650 cm^{-1} range using a Nicolet Protege 460 FT-IR instrument with a deuterated triglycine sulfate (DTGS) detector, a KBr beam splitter, with a resolution of 4 cm^{-1} and using 64 scans with a measuring time of 77 s. The IR spectra were normalized against the band for the CH_2 group at 2926 cm^{-1} and also against the strongest carbonyl (C=O) band near 1700 cm^{-1}.

Physical property analysis

CSF was measured according to ISO 5267-2: 2001. Handsheets were made according to SCAN-CM 64:00 and the strength property, tensile index developed was tested under standard conditions according to SCAN-P 67:93 at SCA Graphic Research, Sundsvall, Sweden.

Results and discussion

Pulp and paper properties

In this study, selected pine and spruce trees were cut in the forest and used for thermomechanical pulping in order to obtain well-defined samples for quantitative and comparative studies on the characteristics (e.g., extractives, fiber properties, etc.) of spruce versus pine for TMP production and paper. As expected, there was very little difference between pine and spruce in sugar and lignin content (Table 1) and the data showed normal values for both species,[19] indicating the trees sampled to be representative for average wood of Norway spruce and Scots pine. During processing of the wood chips, the energy consumption was measured at each stage of the three-stage process, but only a few representative data on the electrical energy consumed from the third stage of the pilot plant trial TMP process and the corresponding freeness and tensile strength properties developed in the two species are given in Table 2. As shown previously,[2,3,20] pine wood consumed more electrical energy to a given freeness level (ca. 21% higher SEC in both thinning and sawmill Scots pine compared with spruce, Table 2), but still produced poorer strength properties (ca. 24% less tensile strength by pine thinning and ca. 7% less by pine sawmill, Table 2) compared with spruce using the same TMP process. Possible reasons for such differences have been extensively discussed previously and collapsibility, flexibility, and morphology of fibers are reported to have a strong influence on pulp and paper qualities.[1,2,20] In addition, the surface chemistry of fibers, which is influenced by the presence of extractives, has also been proposed to affect pulp qualities in different ways.[2–9]

Table 2. Representative data on the properties of TMP from third-stage refining of different wood types of Norway spruce and Scots pine

Wood type	SEC (kW h/admt)	Freeness (ml)	Tensile index (kN m/kg)
Spruce thinning	2628	80	45.5
Pine thinning	3326	99	36.6
Spruce sawmill	2866	51	53.3
Pine sawmill	3696	56	49.7

SEC, Specific energy consumption; admt, air dried metric ton

In the present work, the total extractive content was found to be considerably higher in both the pine sawmill and thinnings than for spruce (Table 1). The highest extractive levels were found in the pine sawmill chips and TMP pulp from pine thinnings (Table 1). Thus, the greater amounts of extractives present in Scots pine wood, which are liberated and redistributed over the pulp during refining, may be responsible for some of the differences in prop-

erties and energy consumption exhibited between pine and spruce wood during TMP processing.

Chemistry of wood and pulp extractives

As shown by Garoff[21] and Kokkonen et al.,[8] both the content and composition of extractives is important for their effects on pulp and paper surfaces. The nature of the extractives in the pulp depends on origin and subsequent processing. The total amount of extractives present in the pine raw material under study was more than 3.5 times higher in both the thinnings and in sawmill chips than that present in spruce (Table 1). Triglycerides are the most abundant lipophilic wood resin found in the sapwood of both wood species[10,20,22] and are thought to play a major role in causing pitch problems and increasing SEC.[8,23–25] Cytochemical staining was therefore performed on triglycerides to gain information on both the general spatial distribution of lipophilic extractives and micromorphological features in the native state. Results of staining performed for the relative abundance of lipophilic extractives in native sapwood of both species correlated well with gross chemical analysis. As shown in Fig. 1, Nile blue (stains neutral triglycerides red/pink) stained the contents of almost all ray parenchyma cells in pine (Fig. 1a), while spruce gave a significantly weaker response and the staining of fewer ray parenchyma cells (Fig. 1e) indicating a difference in the relative abundance of triglycerides between the two wood species. A notable distinction between the two species with regard to resin anatomy (i.e., in relation to spatial distribution of fats) of their parenchyma cells was also observed. Fats in spruce were unevenly distributed around the cell lumen of the ray parenchyma cells and preferentially localized along the tangential cell walls (Fig. 1e, inset bottom left in Fig. 1e, and inset top left in Fig. 2b) and seldom observed as globules.

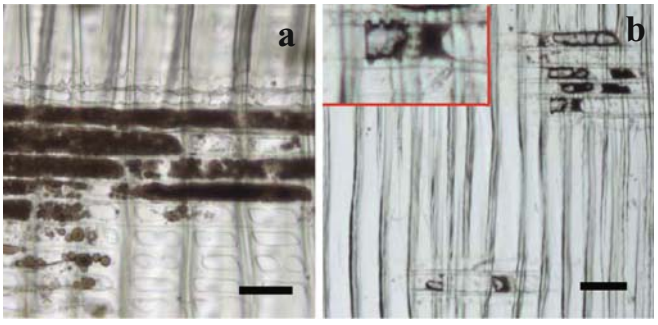

Fig. 2a,b. Radial sections from pine (**a**) and spruce (**b**) sapwood showing the presence and spatial distribution of native fats constituting unsaturated fatty acids stained black by osmium tetroxide. *Inset* (**b**) shows (*top left*) fats in adjacent parenchyma cells (at their corners). *Bars* **a**, 60 µm; **b**, 100 µm

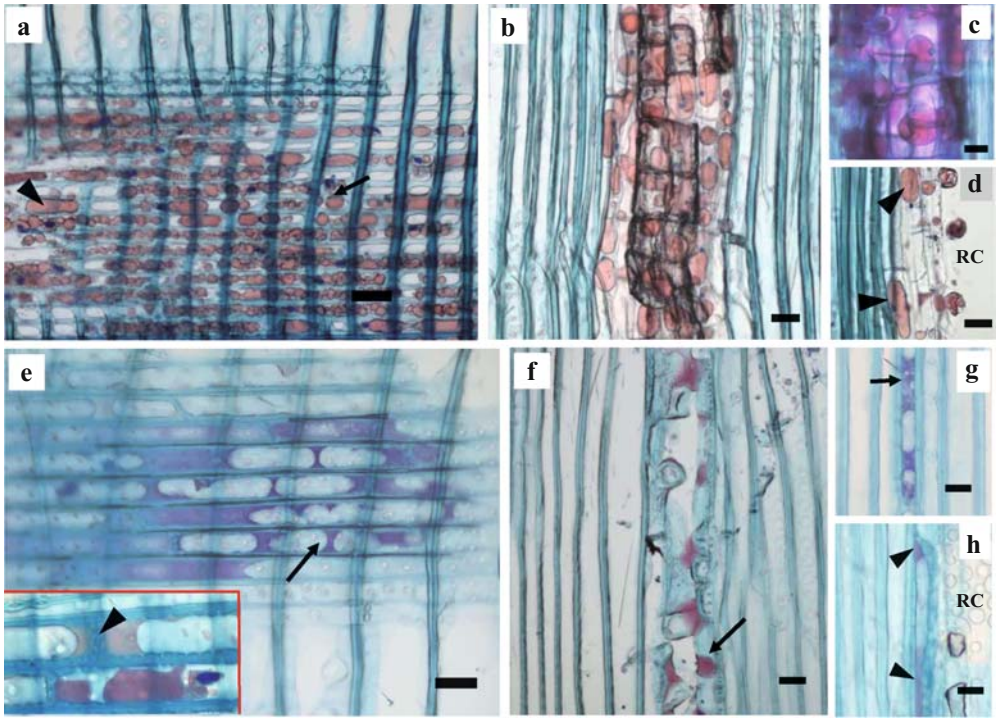

Fig. 1a-h. Localization of native triglycerides in the cell system of Scots pine (**a–d**, *top row*) and Norway spruce (**e–h**, *bottom row*) sapwood using Nile blue, which stains neutral triglycerides red/pink (all radial longitudinal sections). **a** Parenchyma cells in rays, **b** axial resin canal and its surrounding epithelial cells and axial parenchyma adjacent to epithelial cells, **c** closer view of epithelial cells, and **d** strands of axial parenchyma (*arrowheads*) in pine; **e** spruce ray parenchyma containing uneven distribution of fats inside cell lumina preferentially concentrated along the tangential cell walls (*arrow*; inset: *arrowhead* showing tangential double cell wall of two adjacent cells), **f** axial resin canal of spruce and triglycerides associated with epithelial cells (*arrow*), **g** closer view of axial parenchyma dispersed among tracheids containing triglycerides (*arrow*), and **h** axial parenchyma lying next to epithelial cells containing triglycerides (*arrowheads*). *RC*, Resin canal. *Bars* **a**, **b**, **d**, **f–h**, 60 µm; **c**, 100 µm; **e**, 30 µm

Conversely, in pine ray parenchyma cells, fats occupied the majority of cell lumina and were present as several droplets/globules (arrow, Fig. 1a) or less frequently as one very large globule spread over the entire cell lumina (arrowhead, Fig. 1a). Because the average size of the parenchyma cells is much greater in pine than in Norway spruce,[11] there is greater space available inside the cells for storing extractives. Thus, the stronger staining reaction in pine reflected presence of larger quantities rather than differences in chemical reaction to the stain.

Nile blue also stained epithelial cells surrounding resin canals, in pine (Fig. 1b–d) and in spruce (Fig. 1f), indicating the presence of triglycerides in the living cells even though they are thought to contain primarily resin acids that are normally secreted into adjacent resin canals. A significant difference in the staining reaction shown by the epithelial cells between the two species was also apparent. Like the ray parenchyma, the majority of epithelial cells surrounding pine resin canals stained strongly with Nile blue with presence of large globules (Fig. 1b, c). In contrast, spruce resin canals showed a lesser number of weakly stained epithelial cells. In addition, strands of vertical parenchyma cells (arrowheads in Fig. 1d, h and arrow in Fig. 1g) adjacent to epithelial cells of resin canals also stained indicating the presence of encapsulated fats. These vertical parenchyma cells stained more strongly with Nile blue in pine than in spruce (Fig. 1b, d vs Fig. 1f, h). Staining was also carried out for unsaturated fats, because the majority of native FAs (either free or esterified) in both wood species are unsaturated.[10] Staining was performed using osmium tetroxide that stains unsaturated fats black[26] and a similar result was obtained for both species (Fig. 2). Thus, there was a distinction between the two species with respect to micromorphological features and the spatial distribution of the native dominating lipophilic extractive fats (triglycerides and FA) inside the parenchyma cells (both ray and axial) and epithelial cells in sapwood of Norway spruce and Scots pine.

Scots pine and Norway spruce TMP

Figure 3 shows the composition of the extract content of spruce and pine TMP pulps sampled after a third refining. Comparing the two pulps, it was clear that significant differences existed in both the total amount of lipophilic extractives and the absolute amounts of their different constituents redistributed during TMP processing. The total extractive content was about twice as high in pine pulps than in spruce pulps (Table 1). Although the triglyceride content was the highest among the wood resin constituents in both pulps, pine pulps contained almost double (0.85 mg/kg) the amount present in spruce pulps (0.43 mg/kg). The other major constituents of the lipophilic extractives (i.e., fatty and resin acids) were also greater in pine than in spruce pulps except for steryl esters, which was slightly higher in spruce TMP pulps.

The results obtained from the staining reactions performed for both spruce and pine TMP pulps using Nile blue for triglycerides and osmium tetroxide for unsaturated fats may be discussed in light of the chemical analyses. Neither Nile blue nor osmium tetroxide was sensitive enough to significantly stain fats redistributed on the TMP pulps of both spruce and pine, although it has been successfully shown previously for birch kraft pulps.[16] Even parenchyma cells, which are known to contain considerable extractives within TMP pulps, were poorly stained indicating almost the complete removal of extractives from the cells; an observation consistent with observations of Cisneros and Drummond[12] who used Sudan IV for Norway spruce TMP pulps. Some positive staining reactions were obtained with fines (i.e., fine fibrils; Fig. 4a–c) from pine TMP pulps. However, fines were seldom stained uniformly red/pink over entire fibrils reflecting complete coverage of triglycerides. Interestingly, the staining reaction of fibrils was very pale/light in color in comparison with the staining reaction shown in the native wood, suggesting the existence of triglycerides, presumably in very low concentrations over the surfaces of fibrils. Scots pine is known to produce more fines than Norway spruce during TMP processing[1,3] and that feature of pine TMP was also experienced during the present study (results not shown). Therefore, the greater amounts of fines in pine and their association with wood resin within the pulp may partly explain the problems associated with pine TMP, in particular inferior strength properties. In addition, Fig. 4d–f explained the fate of native fats that originally existed as large globules inside the parenchyma (both ray and axial) and epithelial cells during processing. Due to the mechanical action in refining, these globules were broken down to much smaller droplets allowing for the removal of extractives from the cells through natural openings (i.e., simple pits).[16] It is apparent that the liberated droplets of extractives not only dispersed among the pulp slurry (arrow in Fig. 4f) but also were retained on the outer surfaces of the pulp fibers (Fig. 4d, e).

These observations further indicate that the cytochemical reactions employed were only successful where the surface concentration of fats in pulps was high enough.

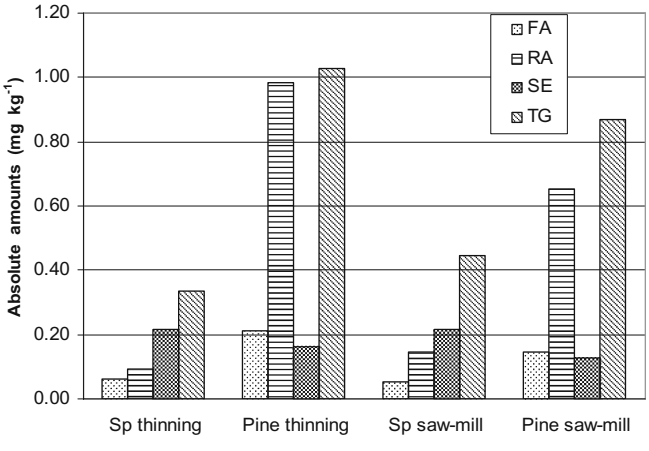

Fig. 3. Weighted absolute composition of the extractive content in spruce and pine thermomechanical pulp (TMP) from the third stage of refining. *FA*, Fatty acids; *RA*, resin acids; *SE*, steryl esters; *TG*, triglycerides

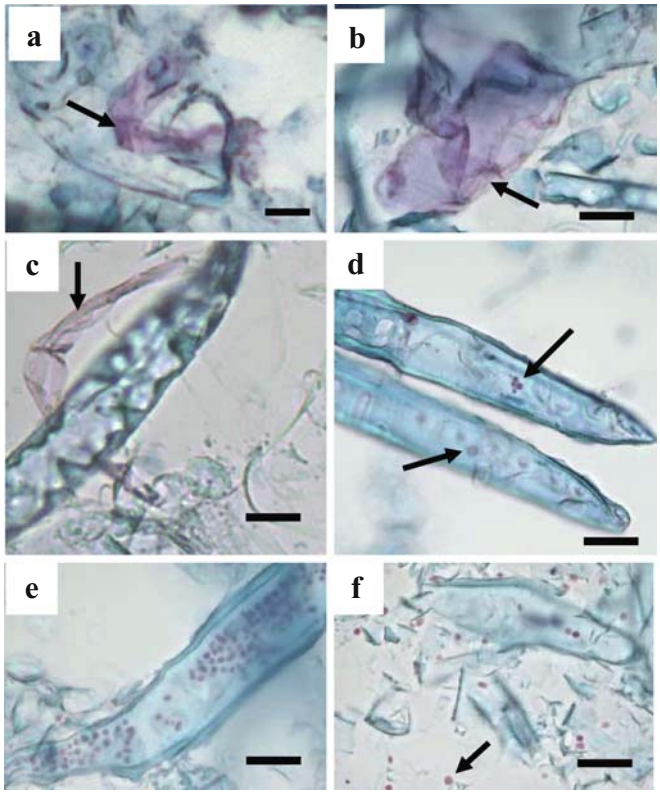

Fig. 4a-f. Staining of triglycerides in pine TMP from the first refining stage using Nile blue. **a–c** Weak staining of primarily fines (i.e., fibrils; *arrows*) in pine TMP; a pale pink/purple color reflects the presence of extractives possibly as a molecular film covering their outer surfaces. **d, e** Many smaller globules of extractives (*arrows*) present in localized areas over fiber surfaces (i.e., retained outer surfaces of pulp fibers) indicating the fate of extractives due to mechanical action during refining. **f** Smaller extractive droplets dispersed among pulp water (*arrow*). *Bars* **a**, 100 µm; **b**, **e**, **f**, 30 µm; **c**, **d**, 60 µm

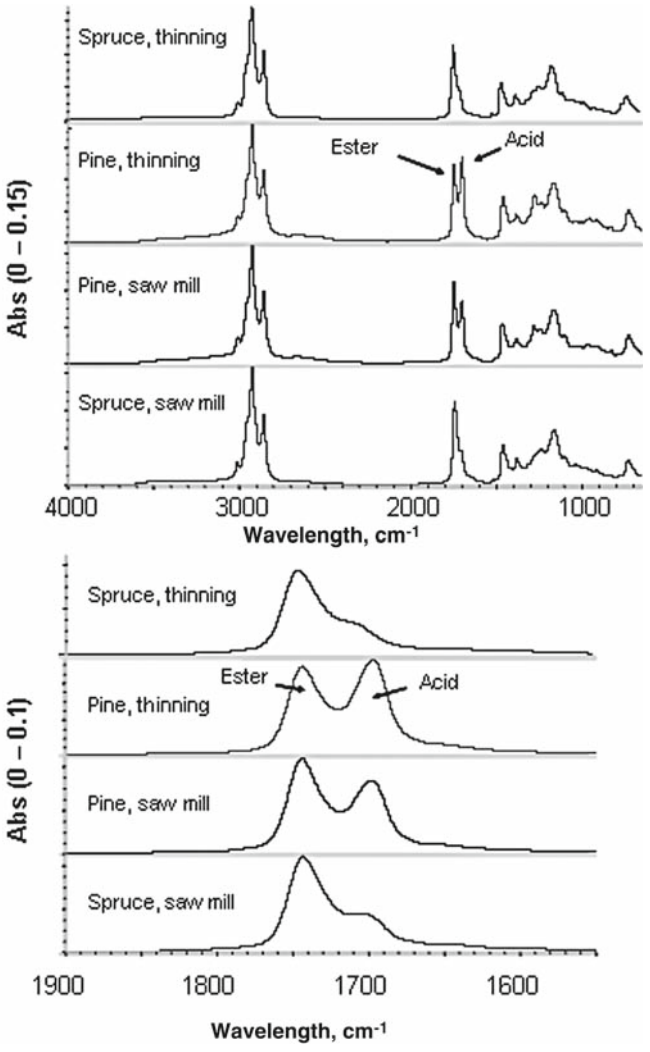

Fig. 5. Fourier transform infrared spectroscopy analyses of extractives from TMP samples. The wavenumber range for free carboxylic acids is 1700–1725 cm^{-1} and for esters is 1735–1750 cm^{-1}.

However, this does not mean that extractives were not present on the TMP pulps and that complete deresination from the pulp had occurred. Cisneros and Drummond[12] have shown previously that virtually all parenchyma cells are damaged including thin-walled epithelial cells (resin inside cells is squeezed out even during the very early stages of the TMP process during chip compression and fracturing) during TMP refining, causing complete removal of resin from the cells. Obviously, such cell destruction is increased with lower freeness level; that is, there is much more destruction after third-stage refining. These almost completely liberated lipophilic extractives are then dispersed and dissolved into the process water and then redistributed and redeposited on fines and pulp fibers during the subsequent operations, resulting in coatings of extractives.[27,28]

Extractives and TMP fiber surfaces

Extractives from whole pulps were analyzed by FT-IR, which showed the spectra of the four samples to be relatively similar (Fig. 5). However, a distinct difference was shown in the carbonyl band (i.e., esterified and free carboxylic groups), where a higher content of fatty acids and resin acids in pine compared with spruce (Fig. 3) was also indicated. The FT-IR analysis also revealed that about half of the pine (thinnings) fatty acid carboxylic groups and resin carboxylic groups were esterified, whereas the spruce fatty acids and resin acids were mainly esterified. Extractives have previously been shown to affect pulp and paper surface properties, and, as suggested by Garoff,[21] the lubrication ability of the fiber surface by extractives is enhanced by specific chemical structures; for example, a linear hydrocarbon backbone facilitates molecular film formation on the fiber surface and the presence of a hydrophilic group could function as an anchor point onto the fiber surface.

In order to understand the effect of extractives on the fibers of spruce and pine, a newly developed colorimetric method for protein staining on wood fibers was used.[17] Coomassie blue staining of proteins was used as a basis for a spectrophotometric assay. When Coomassie dye binds to

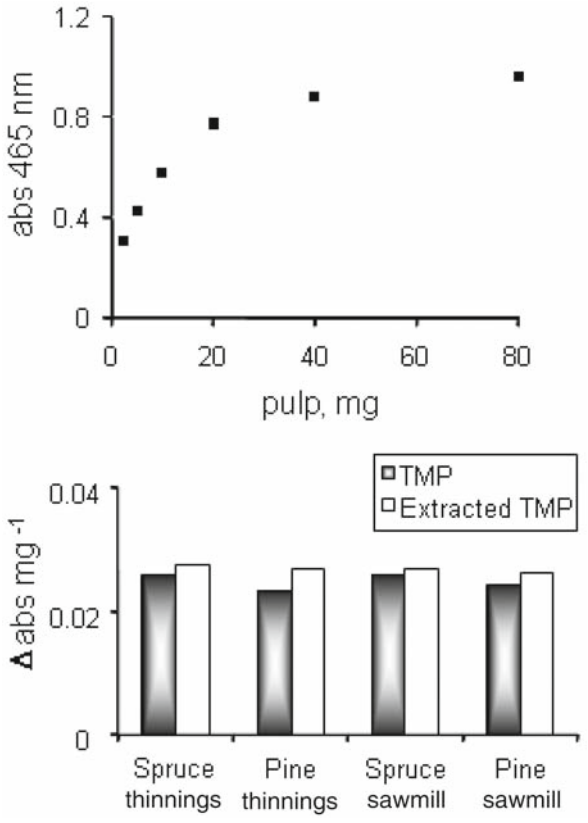

Fig. 6. Colorimetric assay of protein in TMP pulps. Different amounts of representative TMP pulps were stained with Coomassie blue and the reduction of absorbance at 465 nm (shown in positive numbers) increased with increasing amount of pulp (*upper*). *Lower*, different TMP samples labeled for protein (means of duplicates)

proteins in acidic medium, a color change occurs from brown (465 nm) to blue (595 nm); thereby, the removal of unbound dye (i.e., reduction of absorbance at 465 nm) in the presence of fiber-immobilized protein can be measured. In order to optimize the experimental conditions, the amount and concentration of dye and amount of sample were tested in order to produce standard curves. In Fig. 6 (top graph), a known amount of dye (1.25 ml) was added to an increasing amount of pulp and for up to ca. 20 mg of pulp the increasing change in absorbance per unit mass of pulp was basically linear ($R^2 > 0.95$). However, for over 40 mg of pulp, practically all dye was bound to the pulp and the curve leveled off. Thus, the change in absorbance per unit mass of pulp for up to 20 mg (2.5, 5, 10, and 20 mg) was recorded and the slope was used to measure differences of pulp fiber chemistry. In Fig. 6 (lower figure), the TMP samples were stained and the reduction of absorbance at 465 nm was measured as Δabs per milligram. Although not statistically significant, both the pine and spruce samples showed an effect on staining when extracted, possibly indicating that the extractives cover the fiber surface and thereby also some protein, causing the relatively higher staining after extraction for pine because it contains more extractives (Table 1).[8,21] A bleached kraft pulp sample used as negative staining control displayed a reduced staining intensity (Δabs per milligram: $0.0023\,mg^{-1}$). In addition, preliminary results from first-stage refined TMP of high freeness values indicate a negative effect of extraneous extractives on protein stain intensities (Fernando et al. unpublished results).

When compared with recent studies on the surface coverage and depth distribution of lipophilic extractives in mechanical pulps and pulp fiber surfaces using techniques such as X-ray photoelectron spectroscopy (XPS), atomic force microscopy, and time-of-flight secondary ion mass spectrometry, it has been reported that the liberated extractives are capable of forming thin films (i.e., most probably as molecular films) effectively covering TMP fines and pulp fibres.[29–33] According to Kangas and Kleen,[32] TMP fibrillar fines contain most extractives covering almost all surfaces. The above cytochemical results showing a pale/light pink staining of fibrillar fines (Fig. 4a–c) strongly suggest the presence of triglycerides presumably as thin films over fines that was enough to give a staining reaction with Nile blue (i.e., probably as multimolecular films). The greater specific surface area provided by fibrillar fines than by fibers[34] may provide the fibrillar fines with a better ability to adsorb more extractives (presumably up to a few molecular films). However, the majority of the pulps were not stained, and thus together with the results from both the chemical and staining experiments on fats and protein, it was suggested that the lipophilic extractives effectively cover the majority of pulp and pulp fibers most presumably as monomolecular films on the surfaces as previously suggested by Brandal and Lindheim[35] and by recent studies.[36]

Garoff[36] has shown that extractives existing as monomolecular films (monolayers), in particular FAs and resin acids, over paper fiber surfaces are capable in creating boundary lubrication and that this is the type of lubrication by which lipophilic compounds on paper surfaces reduce paper-to-paper friction. It is therefore reasonable to assume that the development of thin extractive films over pulp fibers would have already occurred during primary refining because the conditions in the refiners are favorable. For example, the temperature inside the refiners in general (ca. 120°C) implies that some of the major extractive constituents, in particular triolein and oleic acid (melting points –5°C and 14°C, respectively), would have dissolved and with the mechanical action would evenly distribute allowing coating of pulp fibers and fractions with molecular films (monolayers) as reflected by present staining reactions. Hence, the friction between pulp fibers and the refiner is reduced, which in turn apparently absorbs higher energy for required fiber development. Obviously, this process is more strongly associated with pine TMP pulps (both sawmill and thinnings) containing higher amounts of extractives than spruce pulps as reflected by the chemical analysis on TMP pulps (Table 1, Fig. 3) and the corresponding observed higher energy consumption by pine. This partly explains the observed difference in SEC between the two wood species. The adsorption of extractives onto fiber surfaces and/or covering of fiber surfaces with molecular films may impair the properties of the pulp fiber outer surfaces. This in turn prevents bonding between fibers themselves and pulp fines

and thereby negatively affects the strength properties of handsheets (e.g., tensile strength).[7,8,37] It therefore appears reasonable that the inferior strength properties shown by pine TMP pulps compared with those of spruce may to a certain extent be caused by the presence of higher amounts of extractives in pine pulps, especially over the surfaces of the pulp and pulp fibers.

Cytochemical staining for pulp analyses

To analyze extractives on fibers, pulps, and paper surfaces, different direct chemical and physical methods can be used, although it is also common to measure the indirect effect of extractives on a specific pulp or paper property, such as tensile strength. However, results based on indirect methods often depend on a "compound effect" of different intrinsic and extraneous factors affecting the sample and high resolution and direct chemical analysis, with spatial specificity of a fiber surface not readily performed on a statistically valid part of the whole pulp or paper surface.

Therefore, the use of cytochemical techniques in addressing the problems relating to pitch/wood resin in pulp and paper processing offers an alternate method. While staining may provide a complementary approach to advanced surface analysis techniques like XPS for the analysis of extractives, it also has advantages in that it is relatively easy to use, rapid, and inexpensive. In addition, information can be obtained on the spatial micromorphological distribution/redistribution that can be visualized on single fibers (both internal and external structures) and fractions.

Conclusions

The potential of Scots pine as a supplementary source of raw material to Norway spruce for TMP has over the years initiated research on the differences between the two species. The absolute content and relative composition of extractives has previously been shown to constitute one major difference. In this study, we show there are also additional morphological and spatial differences in the spatial distribution of extractives in Norway spruce and Scots pine, which may further contribute to the effects of extractives on the properties of pulp and paper and on processing.

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