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FT-IR AND UV RAMAN SPECTROSCOPIC STUDIES ON THERMAL MODIFICATION OF SCOTS PINE WOOD AND ITS EXTRACTABLE COMPOUNDS

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FT-IR AND UV RAMAN SPECTROSCOPIC STUDIES ON THERMAL MODIFICATION OF SCOTS PINE WOOD AND ITS EXTRACTABLE COMPOUNDS

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Dissertation for the degree of Doctor of Science in Technology to be presented with due permission of the Department of Forest Products Technology for public examination and debate in Auditorium V1 at Helsinki University of Technology (Espoo, Finland) on the 29th of April, 2005, at 12 noon.

Preface

This study was carried out in the Laboratory of Forest Products Chemistry at Helsinki University of Technology during the years 2000-2003. The research was funded by the National Technology Agency of Finland (TEKES) and a group of Finnish forest cluster companies (Finnforest, Honkarakenne, Metso, M-real, Stora Enso, TekmaWood, UPM-Kymmene, Vapo Timber, and Wood Focus) during 2000-2003. The Foundation of Technology (TES) is thanked for a scholarship.

I wish to express my deepest gratitude to my supervisor, Professor Tapani Vuorinen, for his help, support, and valuable advice during the time of my PhD studies. I am grateful to all my co-authors, Dr. Hanne Wikberg, Professor Sirkka Maunu, Docent Anna-Stiina Jääskeläinen, Professor Pertti Viitanieni, Saila Jämsä, Docents Stefan Willför, and Anna Sundberg, for the fruitful and pleasant collaboration. I want to express special thanks to Hanne for the numerous encouraging and inspiring discussions on the research and other topics. I am also thankful to Drs. Derek Stewart and Gordon McDougall from the Scottish Crop Research Institute for the help and valuable comments.

I want to thank Timo Pääkkönen and Hanna Iitti for the skilful laboratory work included in this thesis and Rita Hatakka, and Mia Löijä for their assistance on the use of spectroscopic equipment. Kati Mäenpää is thanked for providing the literature cited in this thesis. I am grateful to all my friends and colleagues at the Laboratory of Forest Products Chemistry for creating an inspiring atmosphere. It was a privilege to work with you all. Special thanks to Kati, Krista, Minna, Monika, Tiina, and Terhi for the refreshing lunch and coffee break discussions on research and various other topics.

Finally, I want to express warm thanks to my family and friends for love, encouragement, and prayers.

Dundee, Scotland, 14.10.2004

Mari Nuopponen

List of publications

This work is based on the following refereed papers (Appendices I-VI). Papers are referred in the text by Roman numerals.

I Nuopponen, M., Vuorinen, T., Viitaniemi, P., Jämsä, S., Effects of heat treatment on the behaviour of extractives in softwood studied by FTIR spectroscopic methods, Wood Science and Technology, 37 (2003) 109-115.

II Nuopponen, M., Vuorinen, T., Jämsä, S., Viitaniemi, P., Chemical modifications in heat-treated softwood studied by FT-IR and UV resonance Raman (UVRR) spectroscopies, Journal of Wood Chemistry and Technology, 24 (2004) 13-26.

III Nuopponen, M., Wikberg, H., Vuorinen, T., Maunu, S.L., Jämsä, S., Viitaniemi, P., Heat-treated wood exposed to weathering, Journal of Applied Polymer Science, 91 (2004) 2128-2134.

IV Wikberg, H., Nuopponen, M., Maunu, S. L., Sundholm, F., Vuorinen, T., ^{13}C CPMAS NMR and FTIR studies of thermally modified wood exposed to brown and soft rot fungi, Applied Spectroscopy, 57 (2003) 266-273.

V Nuopponen, M., Willför, S., Jääskeläinen, A.-S., Sundberg, A., Vuorinen, T., A UV resonance Raman (UVRR) spectroscopic study on the extractable compounds in Scots pine (*Pinus sylvestris*) wood. Part I Lipophilic compounds, Spectrochimica Acta Part A, 60 (2004) 2953-2961.

VI Nuopponen, M., Willför, S., Jääskeläinen, A.-S., Vuorinen, T., A UV resonance Raman (UVRR) spectroscopic study on the extractable compounds in Scots pine wood (*Pinus sylvestris*). Part II Hydrophilic compounds, Spectrochimica Acta Part A, 60 (2004) 2963-2968.

Contribution of the authors in the preparation of the original manuscripts:

I, II   Mari Nuopponen planned experiments with co-authors, performed spectroscopic analyses, analysed the data and was responsible for writing the manuscripts.

III, IV   Mari Nuopponen planned experiments with co-authors, performed FT-IR and UV Raman spectroscopic work and analysed FT-IR and UV Raman data. In addition, she wrote FT-IR and UVRR spectroscopic parts of the manuscripts as well as introduction part of the Paper III. Hanne Wikberg carried out NMR experiments and wrote parts dealing with NMR results.

V, VI   Mari Nuopponen designed experiments with co-authors, collected UV Raman data and analysed results together with co-authors as well as wrote manuscripts. Stefan Willför was responsible for the gas chromatography part.

Contents

1. Introduction

Properties of heat-treated wood have been studied since 1930. First investigations were conducted in USA and they concentrated on the swelling and shrinkage of thermally treated wood /1/. Since then, much work has been done to clarify changes occurring in thermally modified wood. Over the past two decades, thermally modified wood has drawn a great deal of attention as a durable and environmentally-benign material and new processes to enhance specific material properties of wood were developed. In the mid 1990 Viitaniemi et al. /2-4/ developed a heat treatment process which uses superheated steam at atmospheric pressure. Several studies on alternative heat-treatment processes were conducted in France /5-7/, the Netherlands /8, 9/, Germany /10/, and Japan /11/. In France, wood was heated in an inert atmosphere and products were referred to as "Torrefaction" and "Retifaction". The "Plato Wood" process in the Netherlands involved several heating steps, while the German one took place in vegetable oil.

Thermally treated wood has many technically useful properties. One of the well-known modifications is lower equilibrium moisture content /1, 2, 12, 13/. Treated wood experiences reduced swelling and shrinkage than native wood. In addition, thermal modification of wood at elevated temperatures improves durability against fungi /2, 7, 14/. Furthermore, the darker colour of the heat-treated wood is often desirable and such wood has been proposed as a substitute for some tropical woods. However, the diminished strength of thermally modified wood is deleterious and limits its use under load. The extents of all these modifications depend on the heat treatment conditions: type of the process, duration and temperature of the heat treatment as well as the nature of the wood itself. For example, modifications are normally considerable when the wood is treated at temperatures above 200 °C. Applications of the thermally treated wood are many. It is utilised in interior and exterior claddings, garden furniture, flooring, and sauna furnishing /15/.

Recent developments in spectroscopic equipment and techniques have increased their application in many fields of science and technology. The most important vibration spectroscopic methods in chemical analysis of organic materials are mid infrared (MIR) and Raman spectroscopies. Both of these are rapid and nondestructive means to obtain

qualitative and quantitative structural information. Utilisation of mathematical data processing has improved interpretation and quantification of the spectral data. FT-IR spectroscopy is frequently used in studying lignocellulosic materials, whereas Raman spectroscopy is a fairly new technique in this field.

1.1 Objectives of the research

Many of the properties of thermally modified wood are well-known. However, the mechanisms driving and determining the changes and relationships between physical, morphological, and chemical properties are still not fully understood. For instance, the behaviour of the heat-treated wood under outdoor conditions needs more clarification. Also, a basic knowledge of the chemical and physical modifications is vital for optimisation of processes to produce wood tailored for specific purposes. The main aim of this thesis was to utilise FT-IR and UV resonance Raman (UVRR) spectroscopic techniques to characterise Scots pine wood samples treated by an industrial scale process developed at VTT. In addition, the applicability of UVRR spectroscopy for analysing wood extractives was studied.

2. Structure of Scots pine wood

2.1 Macroscopic structure

Wood is an anisotropic material which means that it has significantly different properties in longitudinal, tangential, and radial directions (Fig. 1) /16/. This is due to the specific orientation and distribution of cells in wood tissues /17/. The radial surface continues from the cambium across the growth rings to the pith parallel to the stem axis, while the surface tangent to the growth rings and parallel to the stem axis is called the tangential surface. Cross-section or transverse section of wood is the plane perpendicular to the stem axis.

The major cell types of the Scots pine xylems are tracheids and parenchyma cells accounting for approximately 90-94 /18/ and 5-11 % /16/ of the wood volume, respectively. The principal functions of the wood cells are conduction of water, mechanical support, and storage of food reserves. Dead Scots pine tracheids have both

conductive and mechanical properties. They conduct water between tracheids though bordered pits, whereas the ultrastructure and dimensions of the tracheid cell wall has impact on the strength. The living parenchyma cells act as supply of reserve food /19/.
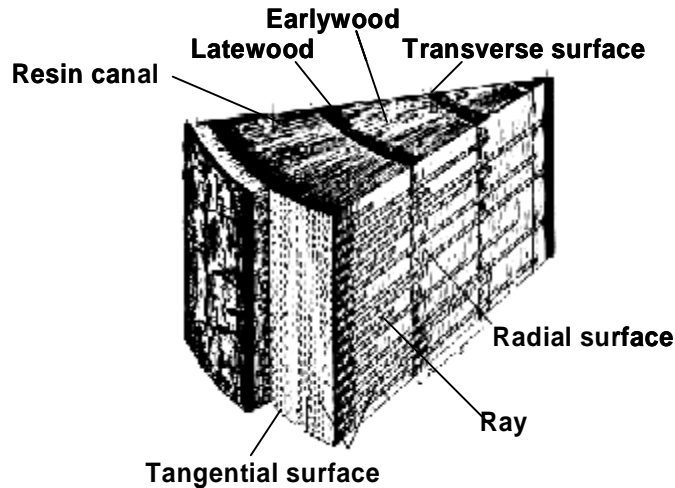
Figure 1. Sections of a Scots pine stem /20/.

Temperate and boreal zone trees have concentric annual growth rings that result from the dissimilarities in the structure, size, and proportions of the various types of cells formed during the different periods of the growing season. Earlywood cells have a large radial diameter, wide lumen and thin walls while those of latewood have thick walls, smaller radial diameter and small lumen. In softwoods, the earlywood cells act as conducting cells while the latewood cells give wood its mechanical strength /16, 18/.

The inner part of the Scots pine tree is often dark-coloured and it is referred as heartwood. The change in colour is derived from resin that is produced by dying parenchyma cells in the transition zone between heartwood and sapwood. Simultaneously, bordered pits of the tracheids become aspirated. As a consequence of this heartwood does not participate in conduction of water /21/.

Lateral displacement, or leaning, of the tree as a result of external forces, such as wind, snow fall, or a landslide, leads to formation of reaction wood. It is formed as a biological response of wood to preserve its original position of the stem and branches. In softwoods the reaction wood is formed on the lower side of the leaning stem or branches and is called compression wood. Compression wood tracheids are shorter and

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thicker than those of normal wood. They also have a round-shaped cross-section instead of angular outline of normal tracheids /16/.

2.2 Chemical composition

Wood is a composite of cellulose, hemicelluloses, lignin, and extractives. Furthermore it contains small amounts of inorganic elements, pectin /22/, proteins, starch, low-molecular weight phenols and oligosaccharides /23/.

The framework component of the wood cell wall is cellulose. The typical cellulose content for Scots pine wood is ~40 % of the dry matter /24/. Cellulose is a linear polymer of 1,4-β-D glucopyranosyl units and exhibits a high degree of polymerization (>10,000). Cellulose molecules tend to form intramolecular and intermolecular hydrogen bonds, whilst clusters of the cellulose molecules are linked together by strong hydrogen bonds. These well-organized units are termed as microfibrils, in which highly ordered (crystalline) and less ordered (amorphous) regions vary in their relative proportions /25/.

Hemicelluloses are surrounding substances between cellulose microfibrils. They are heteropolysaccharides that have a relatively low degree of polymerization (150-200) /25/. Hemicellulose content for Scots pine wood is ~ 25 % of the dry wood /24/. The major hemicellulose in softwoods is O-acetyl-galactoglucomannan accounting for ~ 16 % of the dry wood /24/. The molecule chain is built up of β-D-mannopyranose and β-D-glucopyranose units that are linked with 1,4-glycosidic bonds. Galactoglucomannans are further divided, according to their galactose content, into fractions that are rich and poor in galactose. The molar ratio of galactose:glucose:mannose for the galactose-poor fraction is 0.1:1:4 and that for galactose-rich portion is 1:1:3 /26/. Furthermore, Scots pine contains significant amounts of arabino-(4-*O*-methylglucurono)-xylan (~ 9 %) /24/.

Lignin is a solidifying agent between neighbouring cells and cellulose microfibrils accounting for about 28 % of the dry matter of Scots pine wood /24/. It is a complex high-molecular weight polymer that is built up of phenylpropane units. Phenylpropane structures are linked to each other with ether and carbon-to-carbon bonds. Of the

interunit bonds of lignin, β-O-4 aryl ether type linkages dominate accounting approximately 35 % of all bonds in lignin /27/. Softwood lignin is referred to guaiacyl lignin because its main structural elements originate from coniferyl alcohol precursor. In addition, softwood lignins contain minor amounts of syringyl- and p-hydroxyphenylpropane units /28, 29/. The average amount for the methoxyl groups per 100 phenyl propanoid unit is in the range of 92-97 for softwoods /30/.

Extractives are minor non-structural constituents of wood and they can be removed with neutral solvents such as hexane, acetone, and diethyl ether. Typical non-volatile resin content for Scots pine stemwood is in the range of 1-4.5 % (w/w) /31-33/. The predominant components of the softwood resin are fatty and resin acids, triglycerides, sterols, and steryl esters. Levopimaric acid is the predominant resin acid in Scots pine wood /31/. Of the volatile components of the Scots pine stemwood, α-pinene and Δ3-carene dominate accounting for 88 % of the amount of volatile resin. The total amount of volatiles for Scots pine wood is about 0.6 % (w/w) /34/.

Stemwood of Scots pine wood contains trace amounts (0.5-1 % (w/w)) of low molar mass phenolic compounds (lignans, stilbenes and flavonoids) that are not regarded as wood resin but are co-extracted with wood resin when acetone or other polar solvents are used for extraction /35/.

2.2.1 Location of the wood resin and hydrophilic compounds

Heartwood and sapwood of Scots pine wood have dissimilar extractive distributions and compositions. The major portion of extractives in sapwood is located in axial and radial parenchyma cells. Fatty acid triglycerides are the predominant components comprising ~ 70 % of the hexane extract of sapwood /36/. A typical concentration of triglycerides for Scots pine sapwood is in the range of 0.7-2.3 % (w/w) /37/. Unsaturated oleic, linoleic, and pinolenic acids form the major part of the fatty acids in Scots pine sapwood /31/. Other notable resin substances in parenchyma cells are the steryl esters and free sterols. In addition to the parenchyma resin, sapwood of Scots pine contains small amounts of canal resin, which is mainly composed of resin acids and volatile monoterpenes /38/.

Heartwood resin contains some of the sapwood resin substances as well as additional components, formed during transition of sapwood into heartwood /39/. These components have become distributed throughout the heartwood tissue /40/. Major components in Scots pine heartwood are resin acids. Their total concentration is in the range of 2-9 % /36, 41-43/ of dry wood comprising about 70 % of the total amount of the non-volatile wood resin in Scots pine heartwood. Volatile monoterpenes contribute to the canal resin fluid and they add up to 25-30 % of the total amount of the heartwood resin /34/. Fatty acid esters and most of the steryl esters are hydrolysed in the sapwood/heartwood boundary. Moreover, small amounts of phenolic components are produced during the transition of sapwood to heartwood. The main phenolic compounds in Scots pine stemwood are pinosylvin and its monomethylethers. The content of pinosylvins in the heartwood is about 0.01-1 % (w/w) /35, 41, 43/.
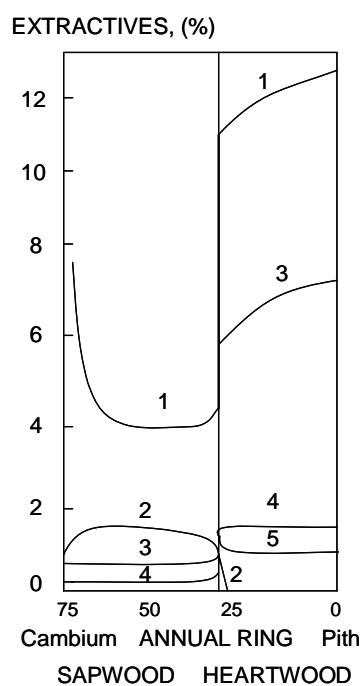
Figure 2. Distribution and composition of wood extractives across the stem of a 75-year-old Scots pine tree according to Lindgren and Norin /35/. Total extractives (1), triglycerides (2), resin acids (3), fatty acids (4), pinosylvins (5).

Wood resin composition and concentration in Scots pine knots and branchwood differs from that of stemwood. Knots and branchwood can contain large amounts of lipophilic extractives, 4.5-32 % (w/w), and these are predominantly resin acids /43/. Recent studies by Willför et al. /43/ revealed that the content of stilbenes and lignans in Scots pine knots can be very high, 1-7 % (w/w) and 0.4-3 % (w/w) respectively. They

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reported that the ratio of pinosylvin monomethyl ether to pinosylvin was higher in knots than in stemwood.

2.3 Modifications in wood structure and its components during heating

2.3.1 Chemical modifications

Some minor changes can be occurred in wood at temperatures above 50 °C, such as elimination of water /44/ and release of volatile components (ie. monoterpenes) /45/. Migration of wood resin onto the surface of wood has been observed at low temperatures 120-160 °C /46, 47/. Of the structural components, hemicelluloses are the most vulnerable to thermal degradation /44, 48/. Degradation rates of hemicelluloses have been reported to be four times higher at 150 °C than that of wood or α-cellulose, whereas lignin deteriorated at about half of the rate of wood /49/. Thermal deterioration of wood and its components is greater under steaming and oxygen than under dry and inert heating conditions /49/. Acetic and formic acids liberated from wood during thermal treatment enhance hydrolysis of hemicelluloses and cellulose /50, 51/. Noticeable decreases in the content of polysaccharides occurs at temperatures above 150 °C /51-53/. Hydrolysed sugars are further dehydrated and great varieties of volatile compounds are formed, such as furfural and hydroxymethyl furfural /54/.

Much work has been conducted on the thermal stability of different lignins /55-58/ and lignin model compounds /59, 60/. The first thermal changes in lignin have been detected at temperatures above 150 °C /61, 62/. Molecular weight of lignin has been reported to decrease extensively at temperatures above ~180 °C in various thermal treatments /55, 57, 63/ as a result of breaking down of aryl-ether interunit linkages. The amount of methoxyl groups in lignin diminished when wood was heated at temperatures above 180 °C /61, 64/. At elevated temperatures (> 200 °C) structure of lignin becomes more condensed /8, 56, 65/.

2.3.2 Physical modifications and fungal resistance

Hygroscopicity and subsequent shrinkage and swelling of wood are reduced by heating above thermal degradation temperatures. Schneider and Rusche /66/ reported that the hygroscopicity of woods heated at temperatures 150-200 °C was diminished up to 35 %. According to Viitaniemi and Jämsä /67/, equilibrium moisture content of wood decreases 40-60 % depending on the heat treatment conditions and wood material.

Diminished strength properties of heat-treated wood are a major drawback limiting its use under load. Bending strength /2, 68/ and modulus of elasticity /69/ have been reported to decrease up to 30-50 % under drastic heat treatment conditions. LeVan et al. /70/ and Winandy /71/ found that the thermal degradation of hemicelluloses was directly related to a strength loss.

Colour of wood darkens as a result of different oxidative and/or hydrolytic discolouring reactions taking place in wood during the heat treatment. Darkening of wood is generally more intensive when heat treatment time is prolonged and temperature raised /72/.

One of the desired properties of the thermally modified wood is better resistance to rot and mould. Several groups /2, 3, 7, 10, 14/ have reported enhanced rot resistance for various wood species as a result of heat treatment. Rot resistance have been associated with degradation of wood constituents /2/, lower equilibrium moisture content /14/, and formation of toxic degradation products /6, 14/.

3. Research methods

3.1 IR spectroscopy

The mid infrared region lies between 2.5-25 μm that corresponds to the wavenumber region of 4000-400 cm^{-1}. A molecule gives a signal in IR spectroscopy if there is a change in a dipole moment during a vibration, which means that molecules having asymmetric bonds are IR active. Complex molecules, such as the wood polymers, have a large number of vibrational modes. Some of the vibrations are localised, while the others are considered as vibrations of the whole molecule /73/. Wavenumber region

between 4000-1500 cm^{-1} in the mid infrared spectrum is referred as a functional group area. Bands in this region are assignable to individual bonds or functional groups of the molecules. Occasionally these bands are useful diagnostically but more often they are supplementary to the spectral region below 1500 cm^{-1} that is called fingerprint region (1500-400 cm^{-1}). IR bands in this region are utilised frequently to confirm the identity of the compound. Also, some bands characteristic for certain functional groups do occur in this region that can be used complimentary to the functional group bands.

Fourier transform spectrometers fitted with modern IR techniques allow rapid analysis of the samples as such without laborious preparation. Also, utilisation of multivariate data analytical techniques has enabled more effective use of the spectral data.

3.1.1 Attenuated total reflectance (ATR) technique

In attenuated total reflectance (ATR) spectroscopy sample is pressed against a crystal of high refractive index (Fig. 3). The incident radiation penetrates into the sample surface through the crystal. The sampling depth depends on the wavelength, the incident angle of the radiation and the refractive indices of the sample and the crystal material (Eq. 1). Usually the analysis depth is in the range of 0.3-3 μm. Commonly used crystal materials are germanium, diamond, KRS-5, and zinc selenide. ATR techniques are referred according to the crystal geometries /74/.
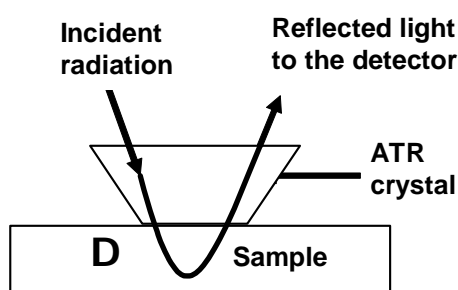

Figure 3. Schematic picture of the microscopic attenuated total reflectance (ATR) spectroscopy. D denotes to the sampling depth.

$$D = \frac{\lambda}{2 \cdot \pi \cdot \left(n_1^2 \cdot \sin^2 \alpha - n_2^2 \right)^{1/2}} \qquad (1)$$

D analysis depth
λ is wavelength
n_1, n_2 are refractive indices of a sample and crystal material, respectively
α is the incident angle of the ATR crystal

3.1.2 Photoacoustic (PA) spectrometry

In photoacoustic (PA) spectroscopy a sample is illuminated with a modulated beam emerging from the interferometer. At wavelengths where a sample absorbs some fraction of incident radiation, a modulated thermal fluctuation will be generated. Modulated heating of the sample causes pressure variation of the gas in the photoacoustic cell and produces a signal, which is detected by a microphone of high sensitivity /75/. All types of materials can be analysed usually as such without preparation.

On the basis of the photoacoustic theory, analysis depth and oversaturation of the strong bands in the spectrum can be controlled by adjusting modulation frequency of the incident radiation. In addition to the modulation frequency, the sample's optical and thermal properties have an impact on the actual analysis depth /76-78/.

3.2 Raman spectroscopy

In Raman spectroscopy photons are not absorbed but shifted in frequency below and above the Rayleigh line frequency. Shift of the scattered photons to lower frequencies takes place as a molecule abstracts energy from the exciting photons. A Raman shift to lower frequencies is referred as a Stokes process. Scattered photons can also pick up energy released by a molecule during transitions to the ground state. This phenomenon is referred as an anti-Stokes process and is parallel to the emission /79/. A molecule produces a signal in Raman spectroscopy when there is a change in polarisability. This means that a molecule having a centre of symmetry is Raman active whilst asymmetric

bonds are more active in IR spectroscopy. Consequently, Raman spectroscopy provides complimentary information to IR spectroscopy /74/.
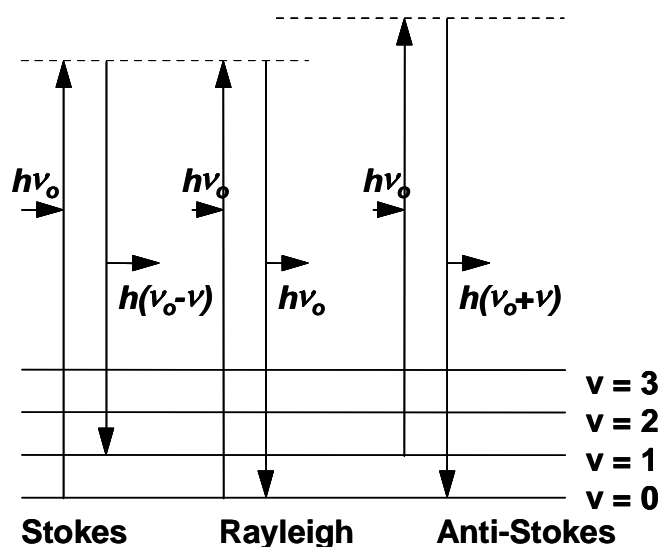
Figure 4. Comparison of the Raman and infrared phenomena: v = vibrational frequency and v_0 =exciting frequency.

Raman spectroscopy has some very useful features over IR spectroscopy. It is possible to detect very low concentrations of substances due to the resonance Raman effect. Resonance enhancement occurs if the excitation wavelength lies close to an electronic absorption of a particular structure within the molecule. The Raman signal can be considerably enhanced, often by several orders of magnitude. The resonance enhancement enables detection of trace amounts of chemical components if the other components in the material do not absorb light at the excitation wavelength /80/.

3.3 Multivariate data analysis methods

Processing of the spectral or other chemical data with multivariate data analytical methods such as, principal component analysis (PCA) and partial least squares (PLS) is referred as chemometrics /81/.

PCA is a powerful method to analyse large amounts of spectral data. Such data are converted into few matrices in PCA, which contain information on the significant similarities/dissimilarities between samples or sample groups. Evaluations of

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similarities/dissimilarities between samples or sample groups are achieved by plotting scores. Loading line plots reveal which variables cause the differences within the samples and with spectral data the loading plot is the subspectrum that shows characteristic vibrations for each samples or sample groups /82, 83/. Loading line plots often facilitate interpretation of the spectral data. For example, baseline variations and spectral noise can be eliminated in many cases as well as the resolution of overlapping bands /84/.

PLS is the most common multivariate data analysis method that is used for establishing quantitative correlations between spectral and chemical data. The whole spectral range can be utilised in PLS calibrations instead of the single band intensities. Spectral data are often pretreated by spectral filters prior to the PLS calibration in order to remove noise and signals that are not related to the wet chemical data /81/.

4. Applications of infrared and Raman spectroscopy in the analyses of wood and its components

Raman and FT-IR spectroscopic methods have been utilised in many investigations into the chemical characterisation of wood and its constituents. In addition, both physical and morphological properties of wood have been studied with IR and Raman spectroscopies. In many studies multivariate data analysis methods have been utilised in combination with spectral data to establish relationship with wet chemical or other data.

FT-IR and UV resonance Raman spectra of softwood (pine) are presented in Fig 5. Functional group vibrations of the softwood IR spectrum include bands due to O-H, C-H, C=O and aromatic ring stretching. The majority of the fingerprint bands in the IR spectrum arises from different vibrations of polysaccharide derived bonds; C-H, C-O, C-O-C, C-OH /85/. Furthermore, guaiacyl lignin contributes to several bands (1420, 1273, 1220, 1140, 1030 cm^{-1}) in the fingerprint region /86, 87/. The UV Raman spectrum of the softwood exhibits vibrations originating mainly from lignin and wood resin, since aromatic lignin and other unsaturated structures are resonance enhanced due to UV excitation /88, 89/. Therefore the most intense Raman signal is at 1605 cm^{-1} resulting from the symmetric aromatic ring vibration. Unsaturated structures derived

from wood resin have UV Raman vibrations at 1650 cm^{-1} /90, 91/. The UVRR spectrum of softwood also contains resonance enhanced bands typical of guaiacyl lignin in the fingerprint region (Fig. 5).
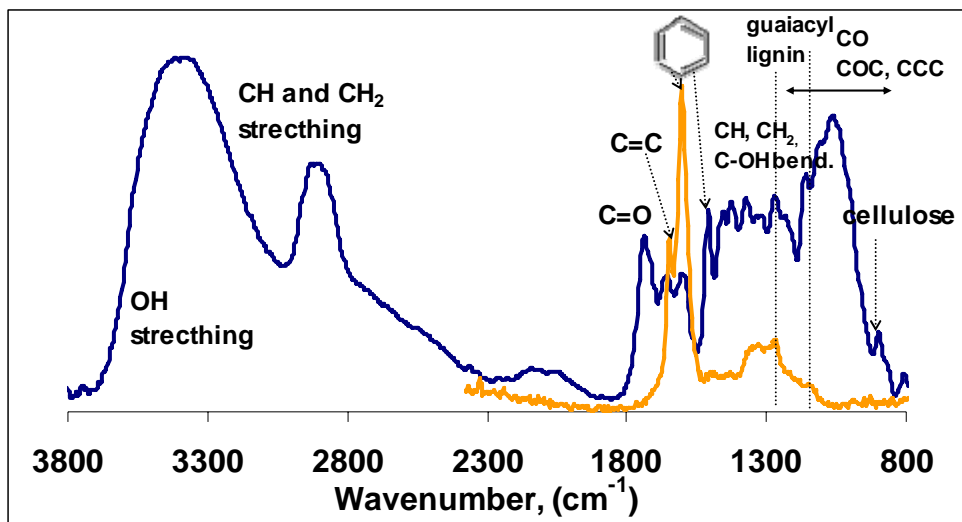
Figure 5. FT-IR photoacoustic (----) and UV resonance Raman (----) spectra of Scots pine wood. UVRR spectrum was collected with excitation wavelength of 244 nm.

4.1 FT-IR spectroscopy

IR spectroscopic methods have been utilised to characterise the molecular structure of wood and its polymers since 1950's.

4.1.1 Polysaccharides

Several research groups have studied band assignments of cellulose with modified celluloses /92, 93/. The degree of cellulose crystallinity was determined using deuterated celluloses in combination with with IR spectroscopy by Mann and Marrinan /94/. Later on (1964) cellulose crystallinity was assessed, by Nelson and O'Connor /95/, from an intensity ratio of IR bands. A more accurate characterisation of the IR spectrum of cellulose was achieved by using mathematical processing, such as deconvolution /96/ and second derivatives /97/. Sugiyama et al. /98/ assigned IR bands for the cellulose allomorphs I$_\alpha$ and I$_\beta$. Thereafter, Kataoka and Kondo /99/ utilised FT-IR spectroscopy to examine the crystalline structure of cellulose during the wood cell formation.

More recently, dynamic FT-IR spectroscopy has been applied to study the structure of cellulose by Hinterstoisser /100, 101/. They demonstrated that it was possible to correlate specific OH-bands with the structure of cellulose. The main bands in the dynamic spectra of native cellulose were derived from the C-O-C bridge connecting adjacent rings and intramolecular hydrogen bonds. Furthermore, interactions between cellulose and other wood polysaccharides were examined with dynamic FT-IR by Åkerholm et al. /102, 103/ while Kacurácova et al. /104/ studied interactions of cellulose/pectin and cellulose/xyloglugan composites.

4.1.2 Lignin and wood extractives

IR band assignments of the lignin model compounds and milled wood lignins have been investigated by numerous groups in the past /86/. More recently, Faix /87/ undertook a detailed study on the differences between lignins of different biological origins. Additionally the studies of Collier et al. /105, 106/ provided new band assignments for lignin. The oriented structure of lignin and its viscoelastic properties have also been examined by dynamic FT-IR spectroscopy /107/. These studies suggested that lignin had a different time dependent behaviour than wood polysaccharides and that lignin was oriented along the fibre axis.

The quantification /108-110/ and chemical heterogeneity /111, 112/ of lignins have been examined by FT-IR techniques linked with multivariate data analytical methods. Moreover, lignin distributions in pulps /113/ and wood chips following impregnation of cooking liquor /114/ were studied with FT-IR microscopic reflection techniques.

Wood resin components can be identified from solid wood /46, 115/ and different extracts of wood /116, 117/ since many of them have strong IR signals due predominantly to their carbonyl structures. FT-IR spectroscopy is also commonly utilised to analyse pitch deposits in pulping and papermaking processes and wood resin in paper and pulp samples /118, 119/.

4.1.3 Structure and modification of wood and its components

Numerous FT-IR spectroscopic studies on the structure of wood have been conducted during the past 50 years. The most current ones deal mostly with the structure of wood

after various modifications. Chemical changes in the molecular structure of wood exposed to natural and/or artificial weathering have been monitored by different FT-IR techniques /120-124/. In addition, depth profiling of the photochemical changes in the exposed wood surface was carried out with FT-IR microspectroscopy /125/. All these studies revealed that the structure of lignin had deteriorated and various new carbonyl containing moieties were formed on the wood surfaces. In addition, IR spectroscopy was applied to detect thermal modifications in wood /115, 126/ and lignin /56/ and changes occurring in wood following fungal decay /127, 128/.

4.2 Raman spectroscopy

Raman spectroscopy is a fairly new technique in the field of wood and lignocellulosic chemistry. In conventional Raman spectroscopy, the light induced fluorescence (LIF) arising from the lignocellulosic samples has limited the number of the applications, because the intensity of the fluorescence often overwhelms the Raman signal. This problem was partly solved earlier by water immersion or oxygen flushing techniques. In many applications LIF has been overcome by the development of the near-infrared (NIR) FT spectrometers. Also, use of UV excitation has shown to be a way to collect good quality Raman spectra from all lignocellulosic materials /88, 89/. Saariaho et al. /129/ used an optical Kerr gate to suppress fluorescence originating from lignin containing pulps.

4.2.1 Wood components

Raman band assignments of guaiacyl and syringyl lignins were examined with NIR FT-Raman by Takayama et al. /130/ while Saariaho et al. /88/ studied the Raman band characteristics of lignin model compounds using UV excitation wavelengths. The lignin contents of unbleached and partially bleached pulps were assessed with NIR FT-Raman technique by Agarwal et al. /131/.

Wood resin was characterised using FT-Raman spectroscopy by Holmgren et al. /132/. They reported a characteristic band of pinosylvin monomethyl ether from the solid wood and its extract. Shen and Rosenholm /133/ examined FT-Raman spectral differences between extracted and exuded wood resin.

4.2.2 Structure and modification of wood

Agarwal and Ralph /134/ applied near infrared FT-Raman spectroscopy for characterisation of Black spruce whereas Yamauchi et al. /135/ recorded typical Raman bands for an Asian hardwood species abundant in flavonoid-like compounds. FT-Raman spectroscopy was also utilised to detect changes in the relative proportions of the crystalline cellulose in wood after (bio)chemical treatments /136/.

Raman spectroscopy has been shown to be a useful tool to detect chromophores in photoyellowed thermomechanical pulps /137, 138/ and bleached chemical pulps /129/. Contributions from chromophores can easily be detected in the region 1500-1750 cm^{-1} because, with the exception of the lignin band at 1600 cm^{-1}, wood components have only weak signals in that region.

Ona et al. /139/ established relationships between FT-Raman data and monosaccharide content of the *Eucalyptus* wood. They also assessed the chemical composition of wood by employing with FT-Raman data and multivariate data analytical approaches /140/. Furthermore, these approaches were used to determine the morphological /141/ characteristics and density /142/ of wood samples.

5. Materials and methods

5.1 Wood samples

5.1.1 Thermal modification

Industrially kiln-dried Scots pine (*Pinus sylvestris*) wood was used as raw material in the heat treatments. Scots pine planks (50×200 mm in cross section) were kiln-dried to a moisture content of 11-16 % (~ 70 °C drying temperature) in the Stora Enso Honkalahti sawmill in south eastern Finland. Prior to the heat treatments planks were cut to a length of 1.5 m and cleaved into two battens (Fig. 6). One batten was used as untreated reference material and the other was heat-treated under steam with a method developed at VTT /3, 4/. The total time for the heat treatment was 3 days and the effective temperatures were 100, 120, 140, 160, 180, 200, 220 or 240 °C. Details of the heat treatments are described in papers I-IV.
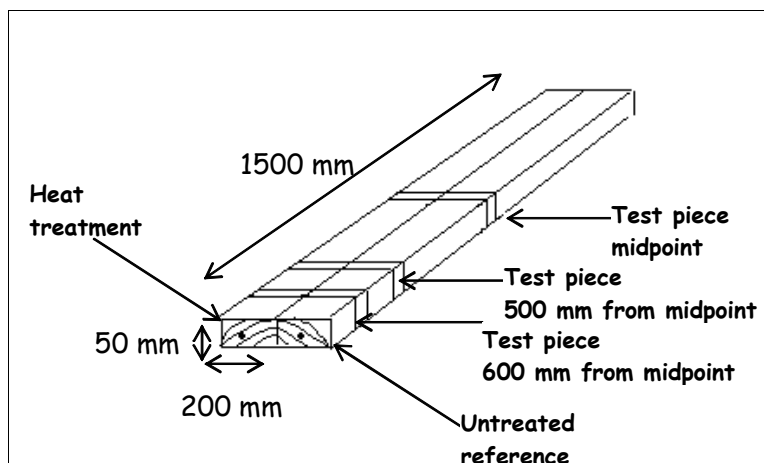
Figure 6. Picture of the kiln-dried pine planks used in the heat treatments, cross-section area of 50 mm * 200 mm and length of 1500 mm.

5.1.2 Weathering experiments of thermally modified wood

Thermally modified panels were weathered, vertically heartwood side up, on racks in Espoo, Finland for seven years (1994-2001). The racks were facing south /143, 144/. Sample preparation for spectroscopic analyses is explained in Paper III.

5.1.3 Brown and soft rot tests of thermally modified wood

The biological durability of pine against brown rot (*Poria placenta*) and soft rot fungus were performed at VTT according to the standards EN 113 and EN 807, respectively. A more detailed description of the tests is given in Paper IV.

5.1.4 Scots pine wood samples for UVRR study

A stemwood disc from a fresh Scots pine tree was sawn. Sapwood and heartwood parts of the disc were sampled and cut into sticks, freeze-dried, and ground in a Wiley mill. In addition, dead branch wood and fresh knotwood Scots pine samples were taken and cut into sticks prior to the UVRR study (Papers V and VI).

5.2 Model compounds

The resin acids, sandaracopimaric, isopimaric, abietic, palustric, neoabietic, and dehydroabietic acids were obtained from KCL (Espoo, Finland). Fatty acid ester (methyl oleate), oleic, linoleic, and linolenic acids were all commercial products (Fluka). Sitosterol acetate and sitosterol were commercial products from Sigma-Aldrich and Merck, respectively. Pinosylvin (3,5-stilbenediol) and chrysin (5,7-dihydroxyflavone) were products from Oy Separation Research Ab and Apin

Chemicals, respectively. The model compounds (5-10 mg) were mixed with KBr (100 mg) and pressed to pellets.

5.3 Extractions of the wood samples

Ground, thermally-modified Scots pine samples were extracted with acetone using a Soxhlet apparatus for six hours (Paper II).

Extraction of the ground Scots pine sapwood and heartwood samples was carried out in an ASE (Accelerated Solvent Extractor, Dionex Corp.) apparatus according to Willför et al. /145/. The lipophilic substances were first removed using hexane and thereafter the hydrophilic compounds were extracted with an acetone:water (95:5 v/v) mixture. Knotwood sticks were extracted with acetone for 6 hours using a Soxhlet apparatus (Papers V and VI).

5.4 Gas chromatography

Free fatty acids, resin acids, free diterpenyl aldehydes, and free sterols were analysed as described in papers V and VI and by Ekman and Holmbom /146/. Esterified fatty acids and sterols, as well as oligolignans, were analysed according to Örså and Holmbom /147/.

5.5 FT-IR spectroscopy

FT-IR spectra of the wood samples and acetone extracts were obtained using a Bio-Rad 6000 spectrometer. Photoacoustic (PA) spectroscopy was used to collect spectra from all heat-treated wood samples and extracts (Papers II-IV). Behaviour of wood resin during the heat treatments was studied by microscopic reflection techniques (Paper I).

5.6 Raman spectroscopy

UVRR spectra of the heat-treated samples, wood sticks, model compound pellets and dried extracts were collected with a Renishaw 1000 UV Raman spectrometer coupled to an Innova 90C FreD frequency-doubled Ar+ ion laser (Coherent Inc., CA) tunable to 229, 244 or 257 nm wavelength. Spectra of the model compounds and native wood extracts were collected using all three excitation wavelengths, while 244 nm excitation

was used to record spectra from the heat-treated samples and their extracts. Details of the sample preparations are described in Papers II-III, and V-VI.

Visible excitation Raman spectra of the resin and fatty acids were recorded using a Kaiser Optical Systems HoloLab Raman spectrometer equipped with an Olympus BX60 microscope. The excitation wavelength was 785 nm (Paper V).

6. Results and discussion

6.1 Thermally modified wood

6.1.1 Behaviour of Scots pine wood resin during heat treatment

Thin dark rings around the sapwood edges were observed when Scots pine samples were heated at 100-140°C. FT-IR ATR difference spectrum of the sapwood edge and heartwood (Fig. 7) shows distinct bands for Scots pine wood resin. Positive bands at 3012, 2928, 2854, and 1744 cm^{-1} in the difference spectrum are related to fatty acid esters /148/. Earlier studies have shown that the lipophilic compounds in wood, such fats, waxes, and steryl esters, migrate to the surface of wood after planning and form a monolayer or a structured multilayer /149, 150/. It is also known that drying wood at high temperatures lowers the surface wettability, partly due to the migration of wood extractives to the surface /47, 151/. Moreover, it has been reported that resin was transported to the timber surface during high temperature drying at >100°C /152/.

Triglycerides were not detected on the sapwood at temperatures above 160 °C. This can be due to decomposition and condensation reactions of fatty acid esters. Previous studies have revealed that unsaturated fatty acids and their esters were partly oxidised during wood drying yielding volatile aldehydes, alcohols, and shorter acids /152/.
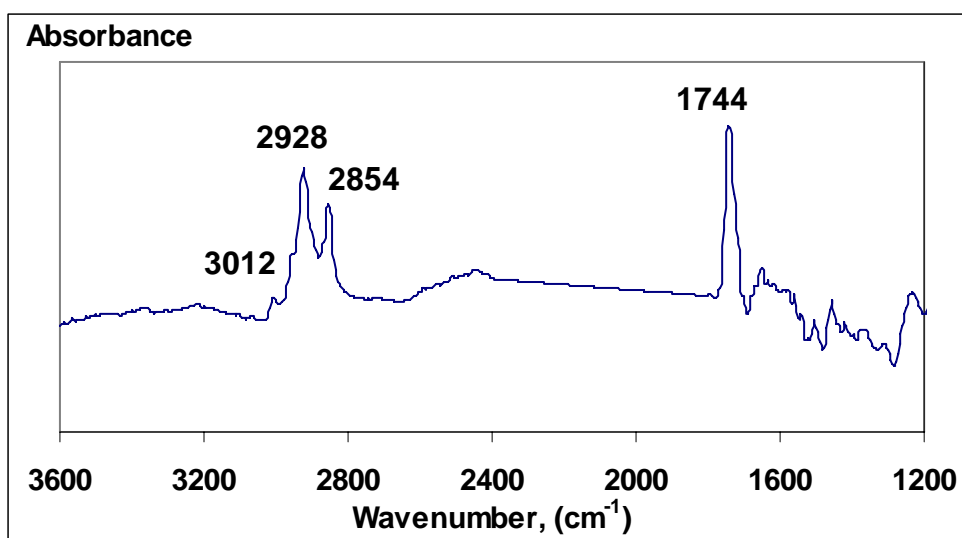
Figure 7. Diamond-ATR difference spectrum of the Scots pine sapwood and heartwood which had been heat-treated at 140°C.

Light microscopy revealed that small resinous spots were observable in the heartwood part of the heat-treated samples. The majority of these spots were detected at the latewood or earlywood/latewood boundary and were clearly distinguished in the samples treated at 100-180 °C. IR spectra acquired from these spots showed absorbance bands typical of resin acids. Following treatments at higher temperatures, the spots were not detected by either light or IR microscopy, in the samples cut from the middle of the heat-treated battens. This observation was confirmed by the IR and UV Raman data collected from acetone extracts of the heat-treated wood samples (Paper II). Both IR and UV Raman spectra from acetone extracts showed characteristic bands for wood resin only when the wood samples had been treated at the lower temperatures (100-180 °C). Moreover, the previously reported band at 992 cm^{-1}, characteristic of pinosylvins, (Paper VI) was detected by UVRR spectroscopy in the samples treated at 100-180 °C.

When the battens were treated at 200 °C, dark resinous areas, that had IR absorbances characteristic of bands for resin acids, were observed in the wood samples taken from the outer parts of the battens. After treatments at higher temperatures (>200 °C) resin acids were no longer detected by IR microscopy, which indicated that the majority of them had been removed from the wood or had been degraded. Kotilainen /153/ demonstrated that the amount of native wood resin in the extracts decreased when wood was heated at high temperatures.

6.1.2 Thermal modification of lignin and polysaccharides

Principal component analysis (PCA) of the FT-IR spectral data showed that the samples treated at the two highest temperatures (220 and 240°C) were separated from those treated at lower temperatures (100-200°C). Positive and negative bands in the loading line plot revealed chemical structures enriched in wood treated at the elevated temperatures and lower temperatures, respectively (Fig. 8). Bands at 1600, 1490, and 1296 cm^{-1} result from vibrations of the aromatic ring which indicated that lignin contents of the wood samples treated at 220 and 240°C were elevated. This was in agreement with the increased Klason lignin contents of the samples (Paper II). A shift of the guaiacyl ring band at 1270 to 1296 cm^{-1} indicated that the structure of lignin was more condensed than that of the wood samples treated below 200 °C /154/. Similar observations have been reported previously by many groups /8, 65, 155, 156/. It has also been suggested that degradation products of hemicelluloses such as, organic acids, and furfural, were involved in the condensation reactions of lignin /157, 158/. Furthermore, Funaoka /56/ et al. identified diphenyl methane type structures in lignin following heating. Many of the negative bands (3452, 1134, and 1083 cm^{-1}) in the loading line plot of the PCA-derived model of the heat-treated Scots pine samples (Fig. 8) arise from the wood polysaccharides and that these are associated with mild heating temperatures; 100-200°C. It is well reported that the wood hemicelluloses begin to degrade at fairly low temperatures /8, 14, 44, 48, 159, 160/. Organic acids such as acetic and formic acid, liberated during the heat-treatment of wood, catalyse chain degradation of cellulose /50, 51/.

PCA of the UV Raman spectral data (Paper II) of the heat-treated wood samples gave a similar result to the model based on the FT-IR data. The loading line plot showed that the guaiacyl structure of lignin was modified at the highest temperatures and new unsaturated and/or carbonyl structures were formed from the degradation products of lignin and amorphous polysaccharides (Paper II).

The acetone extracts of the heat-treated wood samples were examined in Paper II. Both UV Raman and FT-IR spectral data revealed that guaiacyl lignin became partly soluble into acetone when Scots pine wood was treated at 180°C. The amount of substances

derived from lignin in the extracts increased with increasing treatment temperature up to 220 °C. At 240 °C the content of the acetone soluble substances was diminished, which also indicated that lignin was partly condensed. Fengel and Przyklenk /61/ detected increased content of vanillin in methanol:benzene extracts of spruce wood when the samples were heated in the temperature of 150-180 °C. They also found that the amount of vanillin in the extract was decreased at elevated temperatures (200 °C). Westermark et al. /63/ detected homolytic cleavage of β-aryl ether linkages in lignin at temperatures above 130 °C.
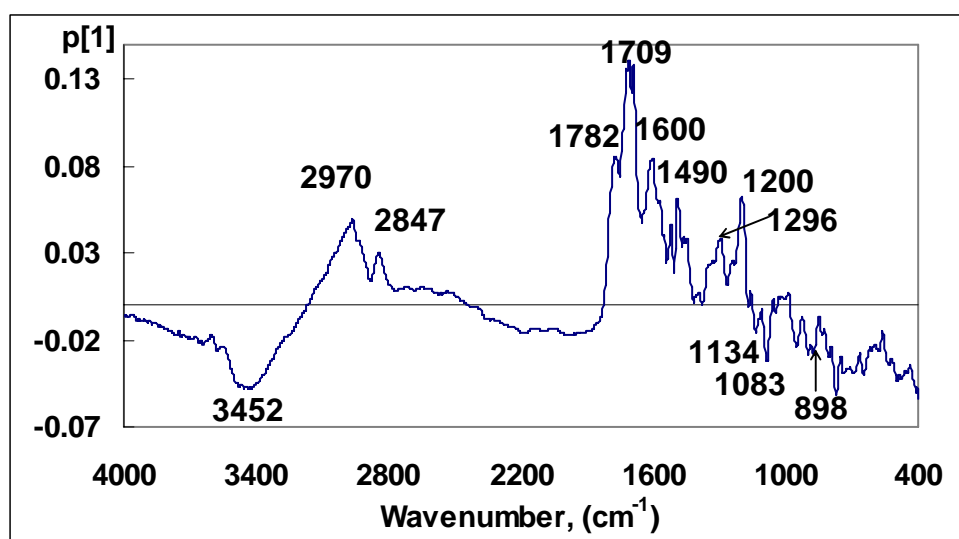
Figure 8. Loading line plot of the PCA model of the heat-treated Scots pine samples based on the FT-IR photoacoustic (PA) spectral data. Positive bands characterise structures typical for the wood samples treated at 220 and 240 °C, while the negative bands reveal structures characteristic for samples heated at 100-200 °C.

6.1.3 Heat-treated wood exposed to weathering

Paper III describes effects of natural weathering on the chemistry of the heat-treated wood. The loading line plot of the FT-IR based PCA model of the weathered and unweathered heat-treated wood (Fig. 9) shows structures degraded and formed on the heat-treated wood surface as a result of weathering. Intensities of the IR absorptions for guaiacyl lignin at 1512, 1269, 1220, 864, and 814 cm^{-1} were reduced and this is in agreement with the findings of previous studies /121-125/. Degradation of lignin was more intense for weathered reference wood than heat-treated wood surfaces according to FT-IR, and UVRR spectral data. It is probable that the condensed structure of lignin

in the heat-treated wood, at least partially, inhibited UV light-induced degradation reactions. Ayadi et al. /161/ suggested that the modified structure of lignin as well as new phenolic moieties were responsible for the improved durability of heat-treated wood exposed to weathering.

The surface of the weathered reference wood was rich in cellulose, whilst that of the heat-treated wood was enriched with conjugated carbonyl structures (bands at 1650 and 1543 cm^{-1}; Fig. 9.) typical of oxidized lignin. Increased content of cellulose /162, 163/ and carbonyl groups /122, 123/ have been reported for the surfaces of weathered native woods. Weathering did not degrade hemicelluloses on the weathered heat-treated wood surfaces to the same degree seen with the reference wood surfaces (Paper III). This most probably results from the decreased content of hemicelluloses in the heat-treated wood.
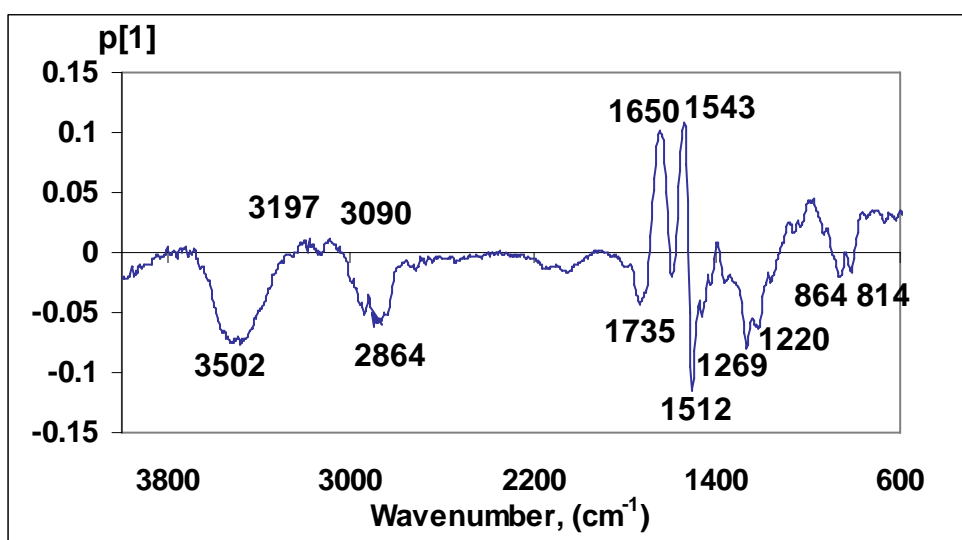
Figure 9. Loading line plot of the PCA model of the weathered and unweathered heat-treated wood based on the FT-IR data. Negative bands show structures degraded during the weathering, while positive bands characterise structures typical for weathered heat-treated wood surface.

6.1.4 Heat-treated wood exposed to fungi

FT-IR and UVRR results of Paper IV showed that both brown and soft rot fungi selectively degraded polysaccharides of the reference wood sample. Brown rot fungus (*Poria placenta*) attacked mainly hemicelluloses, while soft rot fungus depolymerised cellulose as well. Some changes were also seen in the aromatic structure of lignin. Gilardi et al. /164/ observed an extensive degradation of the cell wall polysaccharides as well as slight alterations in the structure of lignin when Scots pine wood was exposed to

brown-rot fungus. It is known that brown-rot fungi primarily attack softwood polysaccharides and, to a lesser degree, modifies lignin, whilst soft-rot fungi degrade both softwood and hardwood polysaccharides /165/.

Weight losses of the wood samples were largest for the reference samples and minor for the wood samples heat treated at >220 °C, which is a sign of increased biological resistance for the heat-treated wood. Only minor chemical changes were observed in the wood samples treated at high temperatures >220 °C. Degradation of the polysaccharides was clearly detected in the FT-IR spectral data of the other samples exposed to fungal decay. Chemical modifications, in particular the reduced hemicellulose contents of the thermally treated wood have been demonstrated to have a significant impact on the biological resistance of wood /14/, since the hemicelluloses are the primary carbon source of such fungi. In addition, the lower equilibrium moisture content probably enhances biological resistance of wood. Kamdem et al. /5/ detected polyaromatic compounds in the extracts of the heat-treated poplar and maritime pine that could contribute to biological resistance of the thermally modified wood. Thus, toxic degradation products of wood polysaccharides, lignin, and extractives can also play a role in fungal resistance of wood following heat treatment. Prolonged heat treatment time /11/ and increased temperature /2, 14/ have been reported to enhance fungal resistance of wood. Moreover, lower pH value of the thermally modified wood can partly contribute to the better durability against fungi /14/.

6.2 Characterisation of the Scots pine wood resin with UVRR spectroscopy

6.2.1 Model compounds

UVRR spectra in Papers V and VI showed that all double bonds and aromatic rings of the lipophilic and hydrophilic model compounds were resonance enhanced as a result of UV excitation. Isolated oleophilic structures had strong Raman signals in the region 1660-1630 cm^{-1}, whereas aromatic rings and conjugated double bonds were represented by UV Raman bands in the region 1649–1548 cm^{-1}.

Some model compounds showed characteristic UV Raman bands in the fingerprint part of the spectrum. Pinosylvin had a relatively intense band in the aromatic substitution region at 996 cm^{-1} which can be useful in identification of stilbenes. Of the other model compounds, dehydroabietic, neoabietic and isopimaric acid showed a weak band below 1000 cm^{-1}.

Distinct structures of the model compounds were enhanced depending on the excitation wavelength. Change in the excitation wavelength had a greatest impact on the aromatic model compounds (Fig. 10). Therefore, particular structure/structures in a molecule can be detected by selecting the excitation wavelength.
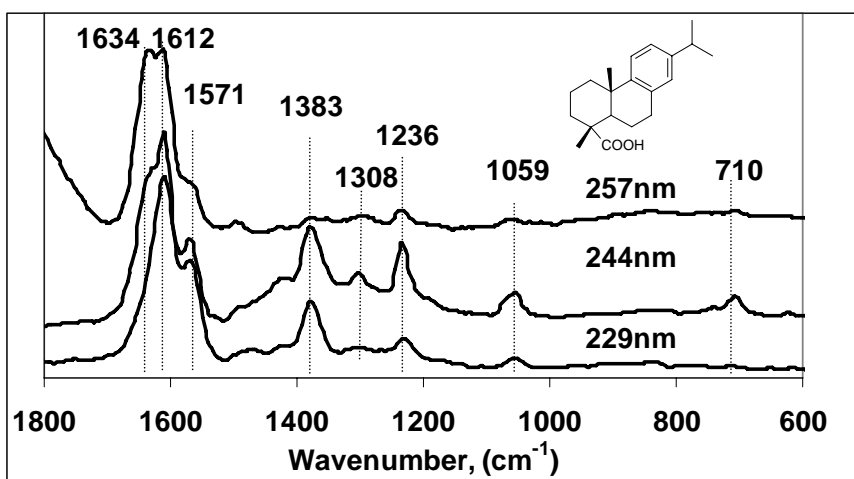
Figure 10. UVRR spectra of dehydroabietic acid collected at the excitation wavelengths of 229, 244, and 257 nm.

6.2.2 Solid wood samples and extracts

UV Raman spectra of the hexane extracts from Scots pine heartwood and sapwood showed characteristic bands for resin and fatty acids in the alkene vibration region (1660-1640 cm^{-1}), which supported the GC analyses (Paper V). It was possible to identify certain resin acids from the spectra and detailed characterisations of the spectra are given in Paper V.

Paper VI includes UV Raman spectra collected from the hydrophilic heartwood and sapwood extracts. Heartwood acetone-water extract had many bands typical of pinosylvin due to its high stilbene content (~ 90 % w/w). In addition, the extract

contained bands distinctive for resin and fatty acids. Sapwood acetone-water extract showed bands due to oleophilic structures at 1655–1650 cm^{-1}.

Wood resin gave UV Raman signals when the spectra were recorded from the unextracted heartwood, knotwood and branchwood samples. UVRR spectra of these samples showed bands in the double bond region at 1660-1650 cm^{-1}. The intensity of the double bond/aromatic ring bands depended on the concentration and location of the wood resin. These bands were most intense for knotwood and branchwood samples abundant in wood resin. In addition, several other bands typical for wood extractives were observed in the spectra of knotwood and branchwood samples (Papers V and VI), which indicated that the wood resin in these samples was resonance enhanced even more than lignin (Fig. 11). A characteristic band of pinosylvin (996 cm^{-1}) was detected in the UVRR spectrum of knotwood (Fig. 11). Holmgren et al. /132/ identified this band in the FT-Raman spectrum of the Scots pine heartwood.
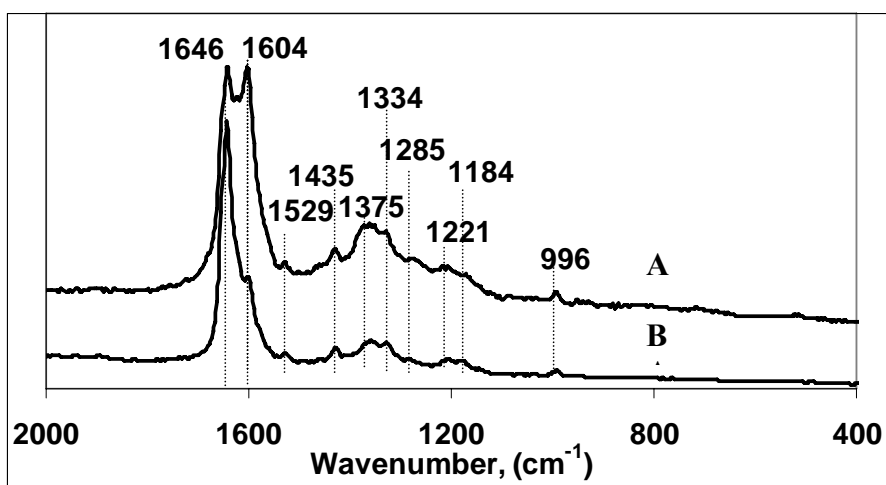

Figure 11. UV Raman spectra of the Scots pine knotwood and its acetone extract. A and B denotes to the spectrum of solid wood and acetone extract, respectively.

7. Conclusions

FT-IR and UVRR spectroscopy provided useful information on modifications at the molecular level in Scots pine wood after thermal treatment. Also, chemical changes in heat-treated wood exposed to natural weathering and fungi were detected by these methods. The main modifications observed in the heat-treated samples (100-240 °C) with UVRR and FT-IR spectroscopy are listed below:

- Fatty acid esters were detected on the sapwood edges at low temperatures (120-160°C).
- Levels of the major native wood resin components decreased in wood at temperatures above 180°C.
- The structure of guaiacyl lignin was increasingly condensed at temperatures above 200°C, especially at 240°C.
- A significant increase in lignin content was detected at temperatures above 180°C, whilst hemicellulose content was diminished.
- Lignin on the surface of thermally modified wood was less vulnerable to natural weathering than that of reference wood.
- Scots pine wood treated at elevated temperatures (220-240 °C) was more resistant to brown and soft rot fungal attack than the untreated wood.

UVRR spectroscopy proved to be a useful tool to detect extractable compounds in native wood samples and their extracts. This was due to the strong resonance enhancement of unsaturated structures of the wood resin components by UV excitation. The UVRR spectra of pinosylvin contained a significantly strong band at 996 cm^{-1} that was detected in the spectra of the solid knotwood samples as well as acetone extracts of stemwood and heat-treated samples.

UVRR spectroscopy can be developed further to determine the content of pinosylvins in solid softwood samples and extracts and as a logical extension of this can be utilised in tree breeding programs to screen out trees rich in pinosylvins. It can also be possible to apply UVRR technique to determine total amount of wood resin in solid wood samples that have even distributions of wood resin. Furthermore, UVRR spectroscopy can be

beneficial in the analysis of pitch deposits in pulping and papermaking processes as well as wood resin in pulp and paper samples.

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