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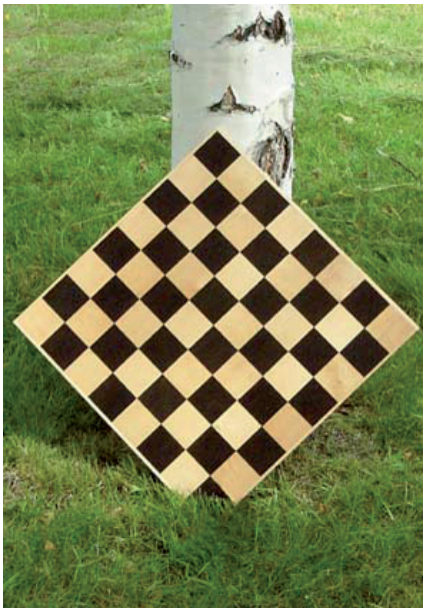
DOCTORAL THESIS

Impact of Drying and Heat Treatment on Physical Properties and Durability of Solid Wood



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Impact of Drying and Heat Treatment on Physical Properties and Durability of Solid Wood

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ABSTRACT

During drying and heat treatment, wood is exposed to a hygrothermal process during which wood properties are chemically and physically affected, resulting in responses on a microscopic as well as on a macroscopic level. The main objective of this thesis is to build knowledge on the interaction between the wood **material properties** and the drying and heat treatment **process** in terms of material **responses**. Hopefully, the benefit of the compiled conclusions in this thesis will contribute to the knowledge base on which decisions are made regarding choice of material and control process parameters in order to attain desired quality in end products.

The results are summarized as follows:
In this study of material properties such as extractive content and its influence on diffusivity, it is shown that density has greater influence than extractive content on diffusivity in pine and spruce. Pine showed lower diffusivity than spruce, but when extractives were removed from pine heartwood, no difference was found in diffusivity compared to pine sapwood or spruce heartwood. The relation between diffusion coefficients in tangential, radial and axial directions in solid pine sapwood was found to be 1:1.8:7 respectively.

Phenomena within the area of process dynamics were also studied. Calculations of thickness of a thin, dry outer shell formed in pine sapwood boards early in the capillary phase of drying were done based on temperature and mass flux measurements. Comparison with dry shell thickness analysed in a computer tomography scanner showed fairly good agreement and was supported by SEM studies of the dark-coloured shell zone in pine sapwood.

The following responses to drying and heat treatment process were studied: strength, sorption/desorption behaviour, dimensional stability, colour changes, capillary water absorption capacity and natural durability.

A decrease of shear strength along grain direction was found for high-temperature dried pine *i.e.* at temperatures exceeding 100°C, compared to boards dried at lower temperatures. No unambiguous decrease of surface hardness, cleavage strength or toughness was found at the same temperature comparison

Noticeable colour-change responses to heat treatment were found when different wood constituents such as pine and spruce sap and extractives from pine heartwood were heat-treated separately. Colour changes increased with time and temperature. An accelerated colour change was found for pine sap and extractives at temperatures exceeding 70°C.

Computer tomography studies of capillary water absorption in heat-treated and dried pine, spruce and birch showed that heat treatment results in a decreased ability to transport free water in the longitudinal direction in all wood types studied except for pine sapwood. The differences in absorption capacity between spruce sapwood, spruce heartwood and pine heartwood were small. SEM studies of the anatomical microstructure were done with focus on the crossfield pits between horizontal ray parenchyma and longitudinal tracheids in pine and spruce. Crossfield pits in heat-treated and dried pine sapwood were found to be considerably more open than those of not artificially dried sapwood, with partly loose or ruptured membranes. No difference in share of open crossfield pits was found between the material dried at 60°C and material heat-treated at 170°C and 200°C. In pine heartwood, the open, ruptured structures found in heat-treated pine sapwood were rare. A hypothesis involving the emptying of the parenchyma cells has been proposed to explain this observation. The open crossfield structures between ray parenchyma and longitudinal tracheids in dried and heat-treated pine sapwood are believed to play an important role in explaining the differences in water absorption between pine and spruce sapwood.

The impact of drying on the natural durability of pine lumber was studied, with mass loss in a rot test as a measure of durability. Air-dried heartwood showed the best durability compared to kiln-dried at 70°C, 90°C and 110°C. Lowest durability was found when drying was performed at 90°C with high material temperature early in the capillary regime of drying with high moisture content. The interpretation is that the duration of high material temperature at high moisture content is a critical state for decay resistance in heartwood. Steam conditioning after drying was found to diminish the durability of sapwood.

The relation between mass loss in rot test and concentration of total phenolics—compounds known to contribute to the natural durability of pine heartwood—showed a weak negative correlation, as did the relation between mass loss and density. Heating of extractive-rich green sawdust caused a reduction of phenolics with temperature and time.

Keywords: *Betula pubescens*, capillary absorption, desorption, diffusivity, dimensional stability, drying, durability, extractives, heat treatment, hygroscopicity, KBS, phenolic content, *Picea abies*, *Pinus sylvestris*, sorption, wood

PREFACE

The work presented in this thesis has been carried out at Luleå University of Technology, Skellefteå Campus, Division of Wood Physics under the supervision of Professor Tom Morén. Many thanks, Tom, for your guidance and encouragement during all this time. Without your tireless support, this thesis would never have been composed!

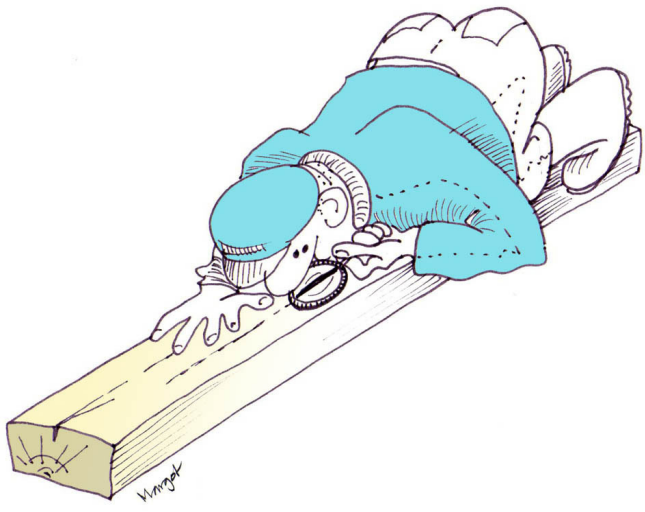
I would like to give my warmest thanks to my colleagues present and prior, especially at the Division of Wood Physics for stimulating discussions and much good laughter: Lena Antti, Dennis Johansson, Lars Hansson, Olov Karlsson, Anna Pantze and Jonas Danvind — Thank you all for your inspiration. Thanks also to all other colleagues and friends at LTU Skellefteå; Olle Hagman and Eva Lövf for helpful statistical discussions. And Thomas Wamming, SP Trätek: cooperation with you has always been a pleasure.

I would like to acknowledge *TCN* (TräCentrum Norr) as well as *Kempe Stiftelsen* and *VINNOVA* (Swedish Agency for Innovation Systems) who through the *SkeWood programme* have funded my work in writing this thesis. I would also like to thank LTU for giving me financial support through the 3-year programme *Forskarskola för Kvinnor* (Research School for Women). My participation in this unit has been of the greatest importance for my decision to complete my PhD studies!

Finally, I turn to my beloved family—Anders, Simon and Nils: thank you for believing in me and for all your love

Skellefteå, September 2008

Margot Sehlstedt-Persson



APPENDED PAPERS

Paper I — S.M.B. Sehlstedt-Persson (1995) High-temperature drying of Scots pine. A comparison between HT- and LT-drying. *Holz als Roh- und Werkstoff* 53: 95–99.

Paper II — M. Sehlstedt-Persson (2000) The effect of drying temperature on subsequent moisture and dimensional change for Scots pine and Norway spruce. *Holz als Roh- und Werkstoff* 58(5): 353. (Brief original)

Paper III — P. Wiberg, S. M. B. Sehlstedt-Persson, T. J. Morén (2000) Heat and Mass Transfer During Sapwood Drying Above the Fibre Saturation Point. *Drying Technology* 18(8): 1647–1664.

Paper IV — Margot Sehlstedt-Persson (2001) The effect of extractive content on moisture diffusion properties for Scots pine and Norway spruce. COST Action E15 Advances in the drying of wood (1999–2003). Proceedings 3rd Workshop on SOFTWOOD DRYING TO SPECIFIC END-USES, 11–13 June, Helsinki.

Paper V — M. Sehlstedt-Persson (2003) Colour responses to heat-treatment of extractives and sap from pine and spruce. Proceedings 8th International IUFRO Wood Drying Conference, Brasov, Romania, 24–29 August.

Paper VI — Dennis Johansson, Margot Sehlstedt-Persson, Tom Morén (2006) Effect of heat treatment on capillary water absorption of heat-treated pine, spruce and birch. Proceedings 5th IUFRO Symposium Wood Structure and Properties ‘06, September 3–6, in Sliač - Sielnica, Slovakia.

Paper VII — Margot Sehlstedt-Persson, Dennis Johansson, Tom Morén (2006) Effect of heat treatment on the microstructure of pine, spruce and birch and the influence on capillary absorption. Proceedings 5th IUFRO Symposium Wood Structure and Properties ‘06, September 3–6, in Sliač - Sielnica, Slovakia. *(Received the “Best Formal Presentation award”)*

Paper VIII — Margot Sehlstedt-Persson, Thomas Wamming (2008) Wood drying process – Impact on Scots pine lumber durability. *(Submitted to Journal of Wood Science)*

Paper IX — Margot Sehlstedt-Persson, Olov Karlsson (2008) Natural durability and phenolic content in dried Scots pine heartwood. *(Submitted to Journal of Wood Science)*

TABLE OF CONTENTS

1 INTRODUCTION

This composite thesis comprises a summary with included articles and conference articles published during the years 1995–2008. Some smaller studies, first published in the summary section of my licentiate thesis, are also included.

The work carried out during these years in various areas of convective drying and heat treatment of wood is described in a fairly extensive and wide-ranging summary section. The articles are not handled in the traditional way, one by one in the summary, since the intention has been to write a continuous summary of a more monographic character.

For guidance while reading the summary section, the following description of the composition hopefully will make reading easier:

The summary section opens with an introduction of the drying process together with explanations of some major terms and expressions, followed by the disposition of the work performed, objectives and limitations.

There follows a chapter with a brief introduction to the major constituents of solid wood and the relation between wood and water, followed by a chapter that introduces the concept of natural durability of wood.

After these introductory sections, the various topics are handled continuously with a background to each subject followed by results from the current thesis.

1.1 Wood drying

Wood as a biological, combustible material is affected and degraded by high temperatures. During drying of wood, a lot of water has to be removed. Thus the artificial drying of wood could be described as a hygrothermal process during which wood properties are chemically and physically affected, resulting in *responses* on a microscopic as well as on a macroscopic level. The extent to which these responses occur is primarily the result of a combination of temperature level, moisture content and time or duration.

Artificial drying of sawn lumber is performed at higher temperatures than a standing tree is normally exposed to in nature. Drying is performed at moderate temperature levels from 40°C–50°C up to temperatures above the boiling point of water; the latter is referred to as high-temperature drying or HT drying. However, heat-treatment processes at temperature levels up to more than 200°C are performed with the main intention not of drying the wood, but rather of achieving

new material properties, such as consistent colour changes, enhanced biological durability and increased dimensional stability.

All work included in this thesis fits into in the following key, Figure 1.1, which describes the process of wood drying and heat treatment.

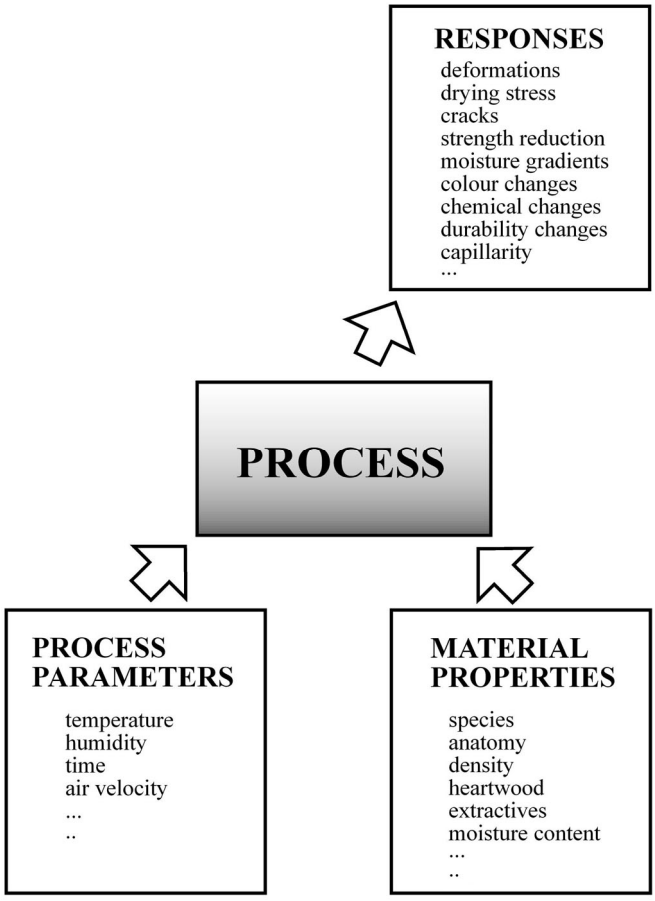


Figure 1.1 Drying and heat treatment of wood—a process in which controllable process parameters and noncontrollable but selectable material properties act together resulting in wood responses or reactions to the drying process.

Drying and heat treatment of wood could be described as follows: the wood material with its sawing pattern and intrinsic **material properties**, such as anatomical structure, density, heartwood content, moisture distribution, reaction

tissue, extractive content and natural biological durability, is subjected to a **process** with controllable **process parameters**, such as temperature, humidity, air velocity, air-reversal interval and time. The result of the process could be expressed as **responses** or reactions to the treatment, responses such as moisture distribution within the load and within individual boards, deformations, drying checks, strength reduction, hygrothermal chemical modifications of wood compounds and changes in colour, natural durability and capillary water absorption ability.

The process parameters during the drying process are controllable, but controlling them to achieve the right quality is a risky task. A good understanding of the wood material and its responses to treatment is fundamental, as well as knowledge of the various critical process stages, in which occur the risk of checking, mould growth, cell collapse, deterioration in durability and unwanted colour changes, together with knowledge of how to take measures to equalize the drying stresses that arise.

It is difficult to control and affect the intrinsic material properties of wood. However, it is possible to make selections and pick the most appropriate material and to reject unsuitable material. A prerequisite for this is a sufficient knowledge of relevant properties.

1.2 Heat treatment of wood

In different heat-treatment processes, such as *ThermoWood* and *PlatoWood* (Sundqvist 2003), when wood is exposed to temperatures between approximately 150°C and 220°C, the main purpose is to achieve new material properties rather than to dry the wood. The objective of such treatment is material responses such as increased biological durability, enhanced dimensional stability and the possibility of controllable colour changes.

The disadvantages that have to be dealt with are reductions in various kinds of mechanical strength and long-term colour stability. The formation of inner cracks in spruce during heat treatment is another problem (Johansson 2005).

1.3 Objectives

Artificial convective drying of wood and heat treatment are hygrothermal processes during which wood properties are chemically and physically affected, resulting in responses on a microscopic as well as on a macroscopic level.

The main objective of this thesis is to build knowledge of the interaction between the wood **material properties** and the drying and heat-treatment **process** in terms of material **responses**. The benefit is hopefully that the compiled conclusions will contribute to the knowledge base on which decisions can be made that will enable

the optimal choice of material and process control to achieve the desired quality in end products.

All work presented in this thesis is based on extensive, experimental laboratory work. The studies are statistically analyzed with random selection of representative test material.

Referring to Figure 1.1, all work included in this thesis has been carried out under the major headings:

- **Responses**
- **Material properties**
- **Process dynamics**

Responses
The following wood **responses** (reactions and changes of properties resulting from a treatment process) are studied:

Strength responses
- Surface hardness
- Shear strength
- Cleavage strength
- Toughness

Moisture-related responses
- Sorption/desorption behaviour and determination of equilibrium moisture content (EMC)
- Dimensional stability
- Capillary absorption in dried and heat-treated wood

Colour changes
- Discoloration beneath the board surface of sapwood in dried boards
- Of various wood components: extractives, sap and extracted wood

Studies in SEM (Scanning Electron Microscopy)
- Studies of the discoloured sapwood zone beneath the board surface
- Studies of crossfield pits and membranes in dried and heat-treated wood

Mould growth
- Impact of drying process

Natural durability
- Impact of drying and conditioning
- Impact of phenolic content

Phenolic content in Scots pine heartwood
- Impact of drying and heating

Material properties
The objective has been to study diffusivity (the ability to transport water vapour within a material), which is of major importance for the drying process in the diffusion-controlled later stages of drying.

Diffusivity
- In different main directions in wood
- In sap- and heartwood as a function of extractive content

Process dynamics
Studies and calculation of the development of a "dry shell" formed in the outer parts of a drying sapwood board early in drying. The study is based on temperature and mass-flux measurement and Computer Tomography (CT) scanning. The phenomenon is confirmed with SEM studies.

1.4 Limitations
The drying technique studied in this work is exclusively convective air circulation drying.

Species included in this work are Scots pine (*Pinus sylvestris*) Norway spruce (*Picea abies*) and European birch (*Betula pubescens*), the prevalent birch species in Northern Sweden

In studies performed at the microscopic level in SEM, phenomena are observed, but not treated statistically; *i.e.*, the occurrences of various phenomena are shown in pictures without any solid statistical appraisal.

2 SOLID WOOD—TREES, WOOD AND WATER

In an evolutionary perspective, trees are ancient organisms that have had a long time to develop ingenious solutions in the art of survival during millions of years. Biological attacks and devastating climate changes are just some of the conditions that have led to biodiversity among the species. Since wood, the material we are interested in as consumers, comes from the trunk of a living, biological organism, there are a lot of characteristics of wood we have to deal with.

The xylem is synthesized from carbohydrates formed in the biochemical photosynthesis process in which the energy of sunlight is harnessed to form glucose and oxygen gas out of water and carbon dioxide gas:

$$12H_2O + 6CO_2 + \text{light} \rightarrow C_6H_{12}O_6 \text{ (glucose)} + 6O_2 + 6H_2O$$

Glucose (or dextrose) is a hexose, a simple monosaccharide containing six carbon atoms. This simple monosaccharide is then composed into different polymers that build up each single cell in the living tree: cellulose, hemicellulose, lignin and extractives.

2.1 Major constituents of wood

Cellulose

Cellulose is the major structural component of wood. Making up approximately one half of both softwoods and hardwoods, it builds the strength of the cell wall (Fengel and Wegener 1984). Cellulose ($C_6H_{10}O_5$) is a long, straight-chain polymer with an average degree of polymerization, DP, of at least 9,000–10,000, possibly as many as 15,000 units of glucose (Rowell 1984). A DP of 10,0000 means that the linear chain is approximately 5 μm long. Bundles of cellulose chains form fibrils, threadlike entities that are “wound” in different layers with different fibril angles in the cell wall.

Crystalline and amorphous portions of the fibrils are present in the cell wall. The crystalline regions of the fibrils are referred to as micelles. These are interrupted by amorphous regions in which cellulose molecules have no fixed arrangements. The micelles are much shorter than the cellulose chains, meaning that an individual cellulose molecule is included in 10 or more such micelles (Haygreen and Bowyer 1982). According to Andersson *et al.* (2004), the crystallinity of cellulose in pine and spruce is 52% ± 3%.

Hemicelluloses (polyoses)
Hemicelluloses (or polyoses) are in close association with cellulose in the cell wall in the construction of fibrils. Hemicelluloses are mixtures of polysaccharides, synthesized almost entirely from 5 different neutral sugars: the hexoses *glucose*, *mannose* and *galactos*e and the pentoses *xylose* and *arabinose* (Rowell 1984; Fengel and Wegener 1984).

Hemicelluloses have a weaker and more differentiated structure than crystalline cellulose. The molecular chains are much shorter compared to cellulose, have side groups and are sometimes branched.

Hardwoods contain more hemicelluloses than softwoods, and the sugar composition is different (Fengel and Wegener 1984).

Lignin
The third major component of wood is lignin, a complex amorphous macromolecule. During cell development, lignin is the last component incorporated into the cell wall, interpenetrating the fibrils and strengthening the cell wall. Lignin is mainly located in the compound middle lamella and in the secondary cell wall. Softwoods contain more lignin than hardwoods, and there are also structural differences between softwood and hardwood lignin (Fengel and Wegener 1984).

Extractives
Wood contains numerous other accessory materials. According to Fengel and Wegener (1984), a simple classification can be made into organic matter, called extractives, and inorganic matter (minerals, *etc*.) summarily obtained as ash. Even if these components normally contribute only a small amount to the wood's mass, they may have a great influence on properties such as colour, odour, durability, sorption/desorption behaviour and permeability. Emissions from wood surfaces derive from extractives.

Extractives of interest in the topic of drying softwood are resin found in resin canals/resin pockets and parenchyma resin, which during the process of heartwood formation "impregnates" the heartwood with transformed substances deriving from dying parenchyma cells.

The composition of extractives varies between species, but also within the tree between sapwood and heartwood.

In pine and spruce, the composition of resin in resin canals differs from parenchyma resin. Canal resin is mainly a mixture of resin acids dissolved in

monoterpenes, while parenchyma resin is composed of fatty acids, fats and waxes (Lindgren and Norin 1969).

It is generally agreed that extractives are "the principal source of decay resistance" in wood (Scheffer and Cowling 1966). The chemical characteristics that separate decay-resistant Scots pine trees from decay-susceptible ones are resin acids, pinosylvins, acetone-soluble extractives and the total amount of phenolics (Harju and Venäläinen 2006). The concentration of total resin acids, which are the major extractive constituent in Scots pine heartwood (Lindgren and Norin 1969; Martínez-Inigo *et al.* 1999), was found to be up to approximately 2 times higher in heartwood in decay-resistant Scots pine trees than in susceptible trees (Harju et al. 2002).

The concentration of pinosylvin and resin acid content in heartwood is shown to vary considerably between individual Scots pine trees, with indications of a strong genetic control of the wide individual variation (Fries *et al.* 2000). The spatial distribution of pinosylvin in pine heartwood was found to decline in inner heartwood, while the concentrations were highest in outer heartwood at the transition between sapwood and heartwood (Bergström 2003).

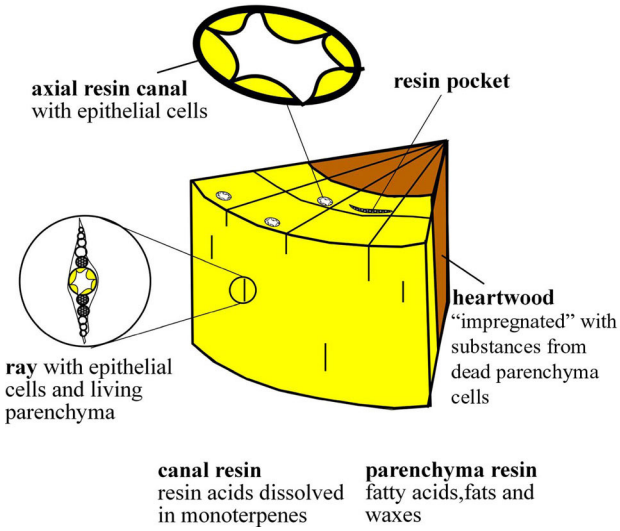


Figure 2.1 Extractives in pine and spruce (from Sehlstedt-Persson 1997).

The amount of extractives differs between pine and spruce. In Table 2.1 some results from different studies are shown.

Table 2.1 Extractive content in percent of dry mass in pine and spruce according to different studies.

Pinus sylvestris		***Picea abies***		**References**
Heartwood	Sapwood	Heartwood	Sapwood	
Up to 8%	2.7%	—	—	Svensson 1989
2.5%–4.8%[1]		1.0%–2.0%[1]		Lindgren and Norin 1969
—	—	0.5%–1.7%[1]	1.4%–4.2%[1]	Pensar 1967
8.6%[1]	2.2%[2]	—	—	Lange *et al.* 1989
3.10%[3]; 2.42% [4]		2.22%[3]; 1.24%[4]		Assarsson and Åkerlund 1966
9.3%[3]	4.5%[3]	0.5%[3]	0.9%[3]	Sehlstedt-Persson 2001 (Paper IV)

[1] Ether soluble
[2] Petroleum ether soluble
[3] Acetone soluble
[4] Ethylic ether soluble

Pine heartwood normally has considerably higher extractive content than pine sapwood, as opposed to spruce, which shows higher values for sapwood than for heartwood. Pine species also have the characteristic of producing rich amounts of resin as a result of injuries. This resin impregnates the wood, creating so-called resinous wood. This property of pine species has been used for industrial extraction of resin by injection of herbicides into living trees. Spruce does not respond to injuries by drenching the tissue with resin (Bergman 1982).

Xylem sap

Even though xylem sap is not a major constituent of wood tissue, a brief description is appropriate, since the drying of wood is a matter of sap removal. Xylem sap moves from the roots up to the leaves in the sapwood of a living tree and consists mainly of water and inorganic ions. One litre of xylem sap contains on average 10–100 mg of inorganic salts; sugars and other organic substances are also present (Fries 1973). The concentration of soluble carbohydrates such as glucose, fructose and sucrose in pine sapwood is greatest in the outer sapwood and decreases gradually towards the innermost sapwood (Saranpää and Höll 1989). The seasonal fluctuation of low-molecular-weight sugars is great, with the highest concentrations occurring during autumn and winter months in pine sapwood (Terziev *et al.* 1996) as well as in spruce sapwood (Höll 1985).

2.2 Water transport in the living tree

The inevitable and never-ending relation between trees, wood and water is of major importance to us as consumers of wood. Starting with a growing tree, a vital

condition for photosynthesis and tree growth to take place is abundant access to water. During the growing season, water is lifted up the tree stem in sapwood by means of capillarity and transpiration from the leaves and needles, with the most intense transpiration from the tree crown during daytime. In some trees, a root overpressure also contributes to sap ascent.

As an example, hundreds of litres of water per 24-hour cycle are emitted from a full-grown beech. A few other examples of transpiration for different species are given in Table 2.2 (Fries 1973).

The path of water up the tree stem is a well-developed internal three-dimensional transport system of hollow cells connected to each other with ingenious pits and pores whose configuration varies from species to species. Hollow tracheids in softwood connected to each other with bordered pits at the ends in the longitudinal direction constitute the main direction of axial water transport. Radial transport takes place in horizontal ray tracheids. Tangential transport takes place via bordered pits connecting the radial walls in neighbouring tracheids.

Table 2.2 Litres of transpiration water/24 hours/kilogram of fresh weight of young trees for some species. (Fries 1973)

Species	Litres of transpiration water/24 hours /kg of fresh weight of young trees
Birch	8—10
Oak	6—8
Beech	3—5
Larch	3—4
Pine	2
Spruce	1—1.5

Figure 2.2 It is striking to realize that huge amounts of water are present in the growing tree. Taking a stroll in a forest containing mainly young trees of pine, for example, in fact means that you are surrounded by more standing mass of water than mass of wood tissue!

2.3 Water in wood

At a macroscopic level, most of the water in a freshly cut trunk is found in the sapwood—the active part of the stem. In a mature tree, the inner parts normally have transformed into heartwood (not all species form heartwood), which contains substantially less water. Moisture content (MC)—mass of water in relation to dry wood mass—in sapwood in a freshly cut pine or spruce (usually called green MC) is approximately 150%, and in heartwood approximately 40%. In birch, which doesn't form heartwood, green MC is approximately 80%–90% in central parts of the stem and approximately 60%–80% in outer parts (Nylinder *et al.* 2001).

At a microscopic level, water is present in the wood structure as free, liquid water in hollow cells, as water vapour in cell cavities and as bound water within the cell wall. Free water is capillary bound in the lumina, while water in the cell wall is bound with hydrogen bonds to the wood structure. In the crystalline regions of the

fibrils, the micelles, it is believed that no free bonding sites to hold water molecules are available; thus water is not held in these crystalline areas. Within the amorphous, disordered regions, however, the hydroxyl groups are accessible for adsorption of water molecules, resulting in lateral swelling (Haygreen and Bowyer 1982; Siau 1971). Bound water, up to fibre saturation point, (FSP), a state in which cell walls are saturated with bound water and no liquid water is present in the lumen, constitutes less than ¼ of the total amount of water in green wood; hence liquid free water makes up the largest portion.

3 NATURAL DURABILITY OF WOOD

The definition of the term durability in the National Encyclopaedia, …"that essential properties are being maintained in spite of external stresses," means that durability depends on what function is being requested. For wood products it might be a matter of maintaining such functions as shape, dimension, colour, strength and decay resistance during their feasible life cycle.

In this thesis, durability is taken as comprising the ability of wood to withstand biological degradation by wood destroying fungi. Mould growth on dried wood surfaces is included as well.

The term natural durability of wood means "the inherent resistance of wood to attack by wood destroying organisms" according to the definition in European Standard EN 350-2. In this standard, wood species are classified in a five class system: 1) very durable, 2) durable, 3) moderately durable, 4) slightly durable and 5) not durable against wood destroying fungi. This ranking of wood species refers to heartwood only, while sapwood should be considered as belonging to durability class 5. The classification system is based on standardized field tests, which are very time consuming, or *in-vitro* short-term laboratory tests using mass loss, expressed as a percentage of the original dry weight, as a measure of durability—the greater the mass loss, the poorer the durability. According to EN 350-2, Scots pine heartwood is classified into class 3–4, Norway spruce heartwood into class 4 and European birch into class 5.

The natural durability of wood has been evaluated by a multitude of methods for many species (Taylor *et al.* 2002). In general, there are difficulties in transforming and comparing results for one species from one test to another. Even though the same standardized decay test was performed at five European test institutes on the same species in a round-robin test, the mass loss was found to vary considerably (Van Acker *et al.* 2003). Furthermore, transferring conclusions from short-term *in-vitro* laboratory tests to the practical service life of wood in outdoor applications is a complicated and unresolved issue.

3.1 Variation in durability

Durability varies considerably between different trees of the same species and also within a single tree. The variation between pine trees from growing stands has been shown to be large in decay tests (Harju and Venäläinen 2006) and a large proportion of this variation is due to genetic differences (Harju and Venäläinen 2002). The variation within a single tree in the radial direction is also large, with higher durability in outer heartwood than in inner heartwood, while tree height, crown limit, wood density, heartwood radius and proportion of latewood have not

explained the variation in durability (Harju and Venäläinen 2006). According to the authors, the most troublesome weakness of Scots pine heartwood is this large variation in durability.

Extractives

It is generally agreed that extractives are "the principal source of decay resistance" in wood (Scheffer and Cowling 1966). The amount of extractives in green Scots pine heartwood varies greatly and can be substantial due to the ability of pine species to produce rich amounts of resin as a result of injuries, forming so called resinous wood (Hillis 1987). Concentrations higher than 30% of the wood mass were found in resinous Scots pine (Lindgren and Norin 1969), but normal concentrations of extractives in pine heartwood are substantially lower.

Extractives have been shown to have an inhibitory effect on fungal degradation in pine heartwood, but considerable differences in tolerance to toxic extractives are also found in various kinds of fungi (Martínez-Inigo *et al.* 1999). Resin acids, which are the major extractive constituent in Scots pine heartwood (Lindgren and Norin 1969; Martínez-Inigo *et al.* 1999), have been reported to cause severe inhibition to wood-inhabiting fungi (Micales *et al.* 1994; Eberhardt *et al.* 1994). Extractive content in heartwood in many species shows an overall pattern with decreasing amounts of extractives towards the pith and higher up the tree (Hillis 1987). This pattern of lower extractive content near the pith may reflect a degradation of extractives over time or an increase in extractive deposits with age (Taylor *et al.* 2002). Lindgren and Norin (1969), however, found an increase in the total amount of extractives towards the pith in Pinus sylvestris.

The chemical characteristics that separate decay-resistant trees from decay-susceptible trees are resin acids, pinosylvins, acetone-soluble extractives and total amount of phenolics (Harju and Venäläinen 2006). The concentration of pinosylvin and resin acid content in heartwood is shown to vary considerably between individual Scots pine trees, with indications of a strong genetic control of the wide individual variation (Fries *et al.* 2000). The spatial distribution of pinosylvin in pine heartwood was found to decline in inner heartwood, while the concentrations were highest in outer heartwood at the transition between sapwood and heartwood (Bergström 2003). The concentration of total resin acids in heartwood in decay-resistant Scots pine trees was found to be 1.6–2.1 times higher than the concentration in susceptible trees (Harju *et al.* 2002).

In decay tests with the brown rot fungus *Coniophora puteana*, Harju and Venäläinen (2006) found a fairly strong negative correlation between mass loss and the concentration of total phenolics measured according to the Folin-Ciocalteau (FC) assay in green Scots pine juvenile heartwood. The FC assay is a chemical,

colorimetric method of determining total amounts of phenolic compounds, thus unspecific, which means that it is not possible to separate different types of phenols from each other. The authors suggest that measurement of total phenolics according to the FC assay could be used for screening the variation in natural durability of Scots pine heartwood and function as an alternative to time-consuming laboratory decay tests.

Density

In some studies, density is also reported to have an impact on natural durability, though with varying results. Chubinsky (2003) found that larch heartwood of high density was more resistant than larch heartwood with low density in decay tests with *Coniophora puteana*. In contradiction to this, Venäläinen *et al.* (2006) found no relationship in larch heartwood between density and mass loss in decay tests with the same fungi. Boutelje and Nilsson (1985) found varying effects of density on mass loss for various fungi in decay tests with pine sapwood. A weak, but significant, negative correlation between mass loss and density was found in tests with the white rot fungus *Phlebiopsis gigantean*, and significant positive correlation in tests with the brown rot fungus *Fomitopsis pinicola*. Sehlstedt-Persson and Karlsson (2008) (Paper IX) found a weak negative correlation between mass loss and density in a 7-week *in-vitro* decay test of dried pine heartwood

A conceivable explanation as to why higher density shows better decay resistance is that denser wood could be expected to have higher resistance to decay simply because of its more solid state and lower porosity during the limited time during which short-term in vitro tests are performed (Sehlstedt-Persson and Karlsson 2008) (Paper IX). High density is also related to higher extractive content, which is known to have an inhibitory effect on fungal degradation (Martínez-Inigo *et al.* 1999). However, no inhibiting effect of density on mass loss was found in long-term exposure outdoors above ground during 9 years for Norway spruce (Bergström *et al.* 2004) or Scots pine lumber (Rydell *et al.* 2005). This exemplifies the difficulties in transferring conclusions from short-term decay tests using one specific fungus to the practical service life of wood in outdoor applications.

3.2 Mould growth

Unlike rot fungi, mould fungi generally grow mainly on the wood surface without penetrating the fibre cell walls. Mould and blue stain fungi are dependent on low-molecular carbohydrates, while rot fungi require nutrients from the cellulose and hemicelluloses and sometimes from the lignin, which leads to degradation and loss of wood mass. Another difference is that mould fungi in general can germinate and grow without access to free water if the RH is high enough, while rot and blue stain fungi require access to free water (Belin *et al.* 1984)

Sapwood, with its poor natural durability, contains high amounts of carbohydrates in the form of free sugars that play an important role as nutrients for, primarily, mould fungi. The concentration of soluble carbohydrates such as glucose, fructose and sucrose in pine sapwood is greatest in the outer sapwood and decreases gradually towards the innermost sapwood (Saranpää and Höll 1989). The seasonal fluctuation of low-molecular-weight sugars is great, with the highest concentrations during autumn and winter months in pine sapwood (Terziev *et al.* 1996) as well as in spruce sapwood (Höll 1985). The surfaces of dried, winter-felled pine sapwood were shown to be more susceptible to mould growth than spring-felled timber (Terziev and Boutelje 1998).

These circumstances in combination with the accumulation of carbohydrates towards the wood surface in sapwood that takes place during drying described in chapter 4.3 are a probable explanation for the growing problem with mouldy and discoloured surfaces of tongued and grooved boards in unheated buildings such as carports (see Figure 3.1).

Figure 3.1 Mouldy and discoloured surfaces of tongued and grooved boards in an unheated outdoor space.
(Photo: Mats Ekevad 2007)

4 DRYING OF WOOD—MOISTURE TRANSPORT IN WOOD

As soon as a tree is cut, the water transport from the soil is interrupted. The trunk is more or less filled with water and stored nutrients that, together with oxygen and suitable temperatures during warm periods, constitute perfect circumstances for attacks of organisms such as fungus, mould and insects. Of greatest concern at this point is to treat the raw wood material in such a way that degradation and injuries are avoided.

Access to oxygen and stored carbohydrates is hard to control, which leaves temperature and water content to deal with in order to make the wood material as unappetizing as possible for the biological attackers. Removal of water to suitable levels through drying is the safest way—but not, in fact, an uncomplicated process.

The drying of wood is a major issue for the subsequent utilization of the wood material—to reduce the weight of the lumber in handling and transport as well as to maintain the right quality of the final wood products in the form of long-term dimensional stability and durability, *etc*.

When wood is dried, enough energy has to be used to break the hydrogen bonds between water and wood (heat of wetting) and furthermore to evaporate the water (heat of evaporation). Much less energy is needed to break the bonds between liquid water that is capillary bound to the saturated cell wall than to break the bonds between water molecules and hydroxyl groups in hemicelluloses/cellulose in the cell wall below FSP. The lower the MC, the more energy is required for each percent of MC to be removed in the diffusion stage of drying below FSP. Thus, since the predominant portion of water in green wood is liquid water, the total amount of energy is larger during drying from green to FSP than from FSP and downwards.

Wood drying on the industrial level has long been based mainly on empirical knowledge. Research within the area of wood drying has led to an increased understanding of the interaction between process and wood material and has contributed to the reduction of many classical drying problems. In Scandinavia, the temperature levels in the kilns have been gradually raised, with many advantages gained in terms of time and energy, decreased mould growth in kilns, decreased crack formation and improved conditioning capacity to equalize stress and moisture gradients.

4.1 Different stages of air-circulation convective drying

After the initial preheating phase, departure of free liquid water is the first stage of drying in the *capillary phase*, in which liquid water moves within the wood in the

transport pathways. During drying below FSP, when all liquid water has disappeared, water is transported as vapour through the wood structure by diffusion; hence this stage is called the *diffusion phase*.

During air-circulation drying, the sawn lumber dries from the outside and inwards. This means that different parts of the board are at different stages simultaneously. The outermost surface layer of a green sapwood board soon dries below FSP and reaches the diffusion phase. At the same time, inner parts contain free water that is transported with low flow resistance in capillary regions within the wood structure. Wiberg and Morén (1999) have studied the distribution of liquid water in the interior of wood using computer tomography or CT scanning. They showed that traditional assumptions about water distribution above FSP with continuous gradients were incorrect. The CT density profiles of a drying board showed uniformly distributed MC profiles with a steep gradient only at the edges.

Early in drying, the drier shell, which is rapidly established, means that all water from the interior has to pass this shell in vapour state. Evaporation of liquid water takes place at a wet evaporation surface, just beneath the dry shell. As drying proceeds, this evaporation surface recedes inwards. The amount of evaporated water at this receding evaporation surface depends on how much heat can be transferred convectively from the air to the wood surface and further via heat conduction, through the dry shell. This means that the early phase of drying is *heat-transfer controlled* (Paper III).

Between the initial heat-transfer controlled capillary phase and the final diffusion phase, a transition phase occurs when the inner continuous “body” of liquid water bursts into subregions. The average MC in sapwood has reached irreducible saturation. Irreducible saturation is well above FSP, since the subregions still contain free water. When irreducible saturation has been reached and the continuous flow of water to the evaporation surface ceases, the evaporation surface rapidly recedes inwards, and the drying goes on to become purely diffusion controlled (Paper III).

4.2 Drying and heat-treatment strategies under study

The drying technique studied in this work is exclusively convective air-circulation drying. In Papers I, II, VIII and IX, responses of wood material to different drying strategies were studied. These drying strategies are:

LT drying	Low temperature drying. No specific temperature range for LT drying is standard, but temperatures are below 100°C.

HT drying — High temperature drying. Drying starts with a rapid increase in temperature up to temperatures above the boiling temperature of water at normal atmospheric pressure. Typical temperatures are between 110°C and 120°C.

LT/HT drying — A combination of low and high temperature drying. Drying starts at conventional low temperatures followed by a final increase in temperature when drying enters the diffusion-controlled regime.

Heat treatment — Papers VI and VII comprise studies of heat-treated wood. Heat treatment of wood is a process in which the main purpose is to achieve new material properties rather than the drying of wood, material responses such as increased durability, dimensional stability and desirable colour changes. Heat treatment of wood to gain higher dimensional stability by reduction of swelling and shrinkage was reported during the 1940s by Stamm *et al.* (1947). Many different heat-treatment methods have been developed since then, such as *StaybWood* and *Staypak* during the early 1950s in the USA, and FWD (Feucht-Wärme-Druck Behandlung) in Germany in the 1970s and 1980s. Today there is a commercial production of heat-treated products in France (*Retified wood*), Germany and Holland (*PlatoWood*) and above all Finland (*ThermoWood*) (Sundqvist 2003), but also on a smaller scale in Sweden.

Heat-treated wood in this thesis is produced according to the Finnish *ThermoWood* concept with superheated steam used as a shielding gas, with temperatures typically between 160°C and 220°C.

4.3 Results from measurements—Process Dynamics and Responses

Dry shell

In Paper III, studies of temperatures and moisture flux from drying pine boards with simultaneous CT scanning are presented. Formation of a dry shell early in the heat-transfer-controlled capillary phase of drying was evaluated in two ways:

- Calculation of the shell thickness by temperature and weight measurements.
- Comparison of dry shell thickness by CT scanning.

A series of tests was run with green pine wood samples, glued and insulated on all but one side and placed on a balance device during drying with the open sapwood side exposed to the circulating air. Temperatures were measured with thermocouples at the board surface under a thin flake of wood, 2 mm below surface and in the centre. Dry- and wet-bulb temperatures and air velocity were measured in the ambient air (see Figure 4.1). By weighing the sample every 30 minutes, the moisture flux and average MC were calculated during drying.

The assumption is made that evaporation initially occurs at the wood surface, which adapts to ambient wet-bulb temperature. As soon as the surface temperature increases above wet-bulb temperature, the evaporation surface is assumed to recede below the surface, forming a thin, dry shell just beneath the surface. This results in the development of a temperature gradient and thus the potential for heat flow inwards from the surface.

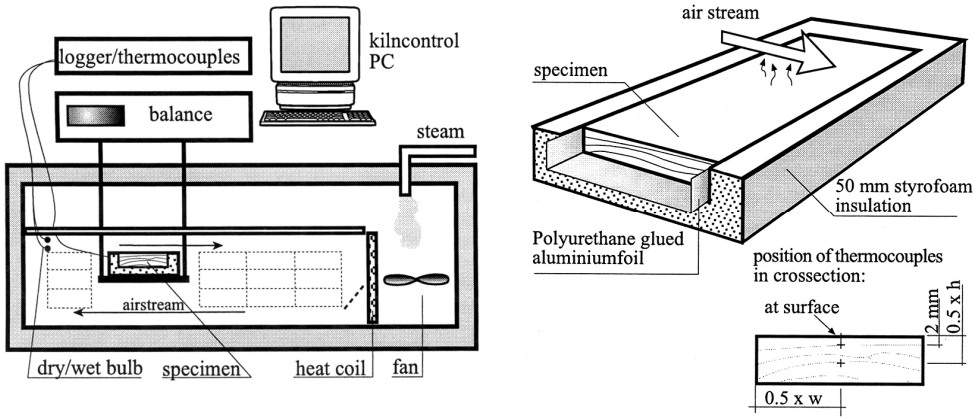


Figure 4.1 Left: Experimental kiln with specimen on a balance. Right: Insulation of and position of thermocouples in specimen. (Paper III)

One test with a pure sapwood board is shown in Figure 4.2, with drying at constant 60°C dry-bulb and 47.5°C wet-bulb temperature. It is evident that the temperature at the wood surface soon diverges from wet-bulb temperature and slowly increases. An abrupt increase is seen after approximately 19 hours. At approximately the same time, average MC reaches FSP, and the mass flux makes a transition from a continuous decrease to a more constant low rate.

Under the simplified assumption that heat of sorption and capillary binding energy are ignored, the measured mass flux G from the board surface is balanced by a corresponding heat of vaporization Q.

This heat is conducted through the thin dry layer to the evaporation surface. According to Fourier's law of conduction, the thickness of the dry shell d can be calculated:

$$d = \lambda \frac{\Delta T}{Gr_T} \quad (m) \qquad [1]$$

where

- λ = heat conductivity (W/m°C)
- ΔT = temperature difference between wood surface and evaporation surface (°C)
- G = mass flux (kg/m^{2}s)
- r_T = latent heat of evaporation (J/kg)

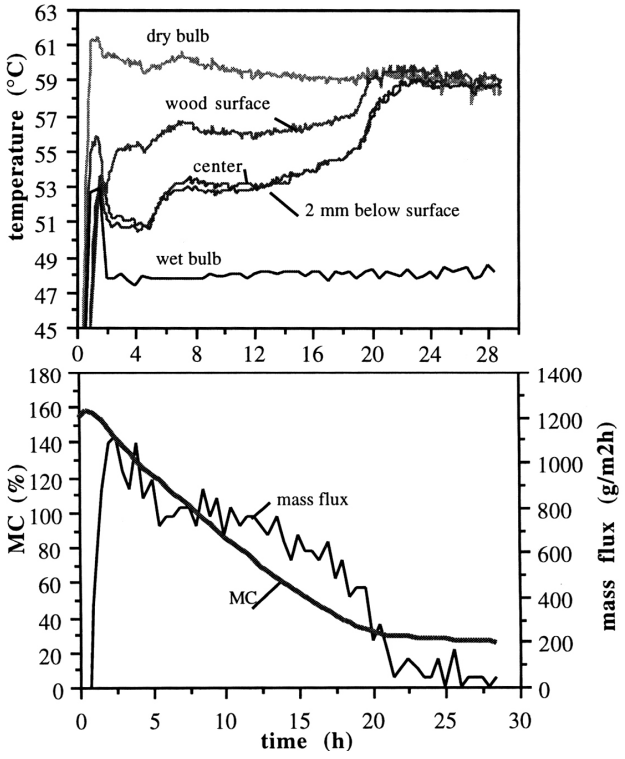


Figure 4.2 Upper: Temperature measurements. Lower: Mass flux and MC (Paper III).

In Figure 4.3 the development of calculated shell thickness is shown for the test series in Paper III.

In practice, measurement of surface temperatures involves difficulties. The method used in these tests, a thermocouple placed under a thin flake of wood, does not ensure an accurate measure of surface temperature and thus also does not ensure the accuracy of calculated shell thickness. However, the phenomenon of an increasing shell thickness—or receding evaporation surface—is clearly demonstrated in these tests.

These findings had not been taken into consideration earlier and were quite controversial when they were reported. Today, the concept of a thin dry layer at the beginning of drying is accepted and has been confirmed by other researchers (Salin 2003; Rémond *et al.* 2005).

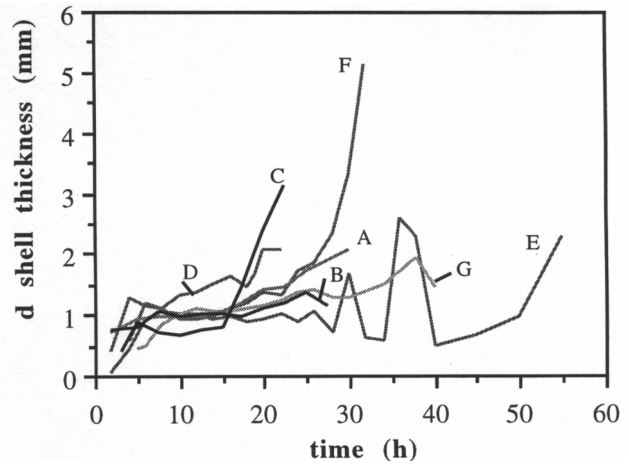


Figure 4.3 Calculated shell thicknesses during drying of pine boards (Paper III).

A comparison of calculated shell thickness between series F in Figure 4.3 and measured shell thickness in a CT-scanned pine board dried under similar conditions shows fairly good agreement (see Figure 4.4).

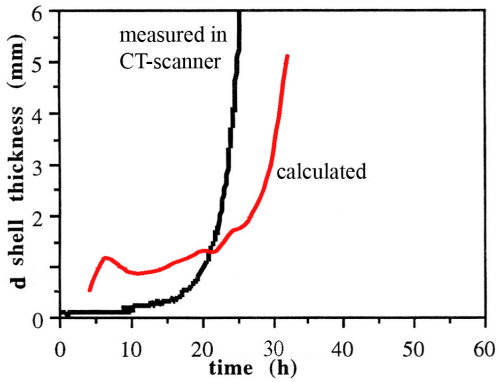


Figure 4.4 Comparison between calculated dry-shell thickness and measured shell thickness in a CT-scanned pine sapwood board dried at 80°C dry-bulb temperature (Paper III).

Kiln Brown Stain (KBS)

Green sapwood is more or less filled with capillary-bound xylem sap and contains stored nutrients/carbohydrates in parenchyma cells in wood rays. Early in drying, when this free water moves towards the evaporation surface beneath the surface, an enrichment of carbohydrates and nitrogen compounds takes place at the surface (Theander *et al.* 1993). The drying rate has a significant effect on this redistribution, with a higher accumulation if the drying rate is high (Terziev *et al.* 1993). At high drying temperatures, a decomposition of the accumulated low-molecular carbohydrates results in visible darkening of the enriched zone typically found just beneath the board surface.

In Paper I this darkening zone was observed in HT-dried pine sapwood (see Figure 4.5).

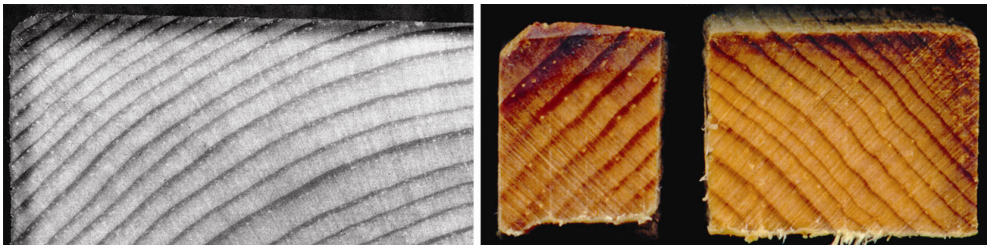


Figure 4.5 Dark-coloured shell in HT-dried pine sapwood just beneath the wood surface (Left photo from Paper I).

The phenomenon of a dark-coloured zone in sapwood beneath the surface is called kiln brown stain (KBS). KBS is a marked problem in HT drying of *Pinus radiata*, since this dark-coloured surface is exposed when the boards are planed after drying. A lot of research, especially in New Zealand, has been conducted since the late 1990s with a view to achieving full understanding and prevention of KBS (Kreber and Haslett 1998; Kreber *et al.* 1998; McDonald *et al.* 2000; McCurdy *et al.* 2005).

This nonenzymatic browning occurs in several ways, of which the following two are most important (Kamuf *et al.* 2003):

1) *Maillard reaction* in which sugars, aldehydes and ketones react with naturally occurring nitrogen-containing compounds to form brown pigments known as melanins. The well-known term Maillard reaction is named after L. C. Maillard (Maillard 1912).

2) *Caramelization* reactions in which sugars are heated in the absence of nitrogen-containing compounds.

The following detailed description of the mechanism for KBS formation (Figure 4.6) is taken from McCurdy *et al.* (2005).

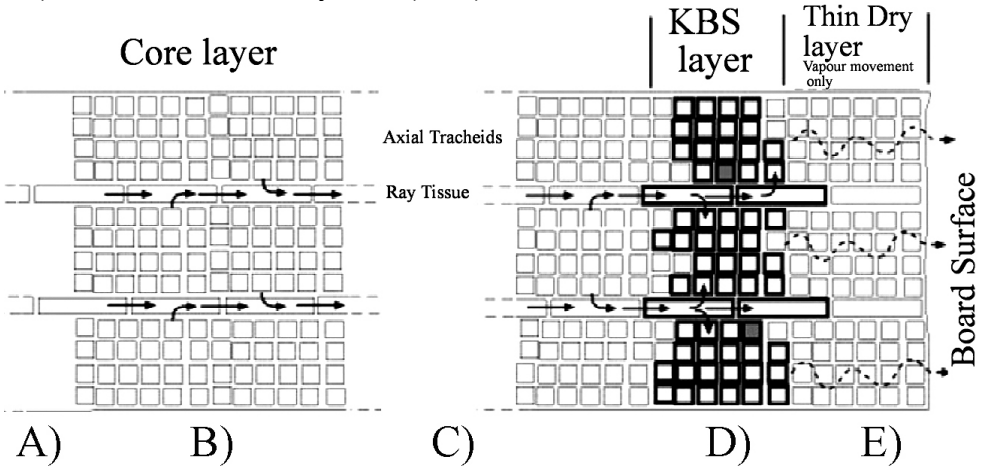


Figure 4.6 *A) Heat causes compounds to be released from the cell walls into the sap. This effect is increased at higher temperatures.*
B) Sap moves into the ray tissue as the axial tracheids cavitate under the water tension. The ray tissue may also cavitate. At certain temperatures the ray parenchyma may also collapse, releasing more compounds into the sap.
C) The sap is transported to the surface by the ray tissue. There may also be some movement of sap through connections between axial tracheids.

D) Sap compounds accumulate in the KBS layer as the water diffuses into the thin dry layer. The heat in the KBS layer causes the compounds to react in the lumens and with the cell walls. This causes the cell walls to darken. Reaction products and resin compounds completely fill some cells.
E) Water and other volatile compounds diffuse through the thin dry layer and disperse into the drying medium.
(Figure and text from McCurdy et al. *2005.)*

4.4 Result from SEM studies of KBS zone

A closer view of the dark-coloured shell zone in pine sapwood using SEM shows cells more or less filled with amorphous substance. In Paper III, SEM pictures of tracheids more or less filled with modified sugar are shown. The fact that this zone with filled lumens is located a few cell rows beneath the surface strengthens the concept of an evaporation surface beneath a thin, dry layer. Further examples from HT-dried pine boards are shown in Figure 4.7.

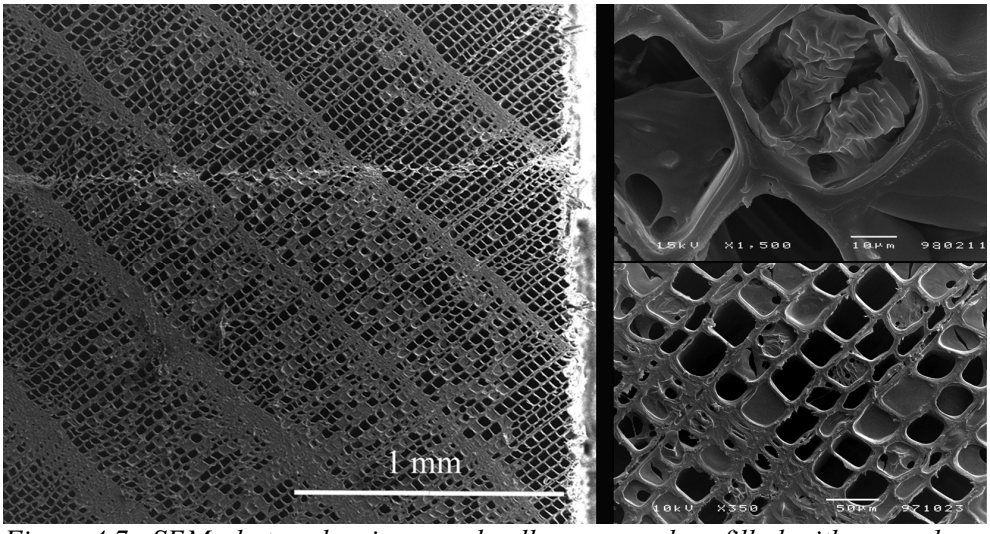


Figure 4.7 SEM photos showing wood cells more or less filled with amorphous substance from KBS zone in pine sapwood HT dried at 115°C. (Sehlstedt-Persson 1998)

4.5 Moisture transport—diffusion in wood

The drying rate of lumber in the later stages of drying is considerably slower than in the initial, heat-transfer controlled stage. In this later stage, the drying rate depends on the ability of wood to transfer water vapour within the wood structure through bound water diffusion when strong hydrogen bonds between water molecules and hydroxyl groups, primarily in hemicelluloses and cellulose, have to be overcome.

Naturally, the more material the vapour has to pass through, the higher is the resistance to vapour transport. Hence, density, porosity, extractive content, moisture content, temperature and accessible anatomical transport passages are all of major importance for diffusion rate in wood.

Cup method

A simple method to investigate diffusion properties of porous material is the "cup method". It is well known that this method contains many critical points, such as sealing of cover, stable climate control and disturbances if the cup has to be removed from the ambient climate during weighing (Nilsson 1988). Also, the moisture-transfer resistance at each surface and in the thin air layer close to the surface must be taken into consideration when calculations of absolute material data are being examined. Still, such a simple method is useful in comparative studies under equivalent conditions to investigate the influence of transport direction or extractive content, as in this thesis.

The cup method is performed with a thin disc of wood used as a carefully sealed cover on a diffusion cup. Different climates on each side of the cover drive the diffusion at a constant ambient temperature. By continuous weighing of the entire cup it is possible to measure the steady-state mass flux when the material has equalized in current climate and to calculate the diffusion coefficient D according to Fick's first law of diffusion at fixed temperature:

$$G = -D\frac{dC}{dx} \qquad \text{(One-dimensional)} \qquad [2]$$

where

G	= mass flux	(kg/m^2s)
D	= vapour diffusion coefficient	(m^2/s)
C	= vapour concentration	(kg/m^3)
x	= distance	(m)

The diffusion coefficient is not constant, but varies with density, MC, temperature, *etc*. It should be noted that the numerical value of the diffusion coefficient varies with the choice of the concentration of potential.

4.6 Results from measurements—Material properties: diffusivity

Diffusivity in different directions for pine wood

A small, unpublished study of diffusion rate in different directions in pine was conducted by the author according to the cup method under stable conditions.

Nine wood samples of conventionally dried pine sapwood, cut with vapour flux in radial, tangential and axial flow direction, were used. The samples (app. 70 x 105 x 3.5 mm) were used as edge-sealed covers on cups containing an aqueous, saturated solution of Potassium carbonate (K_2CO_3, $2H_2O$). The cups were kept in a climate chamber at 31°C, RH 73%, until steady-state vapour flux through the wood samples was confirmed by continuous weighing (after approximately 116 hours).

The RH over a saturated K_2CO_3, $2H_2O$ solution at 31°C is approximately 43% according to Nevander *et al.* (1981).

Calculation of diffusion coefficients, D_w, was done using the difference between EMC in the surrounding air on both sides of the wood cover as potential.

The relation between calculated D_w in tangential, radial and axial direction at 31°C and at an average MC of approximately 10.5% was found to be approximately 1:1.8:7 according to this comparative study (see Figure 4.8).

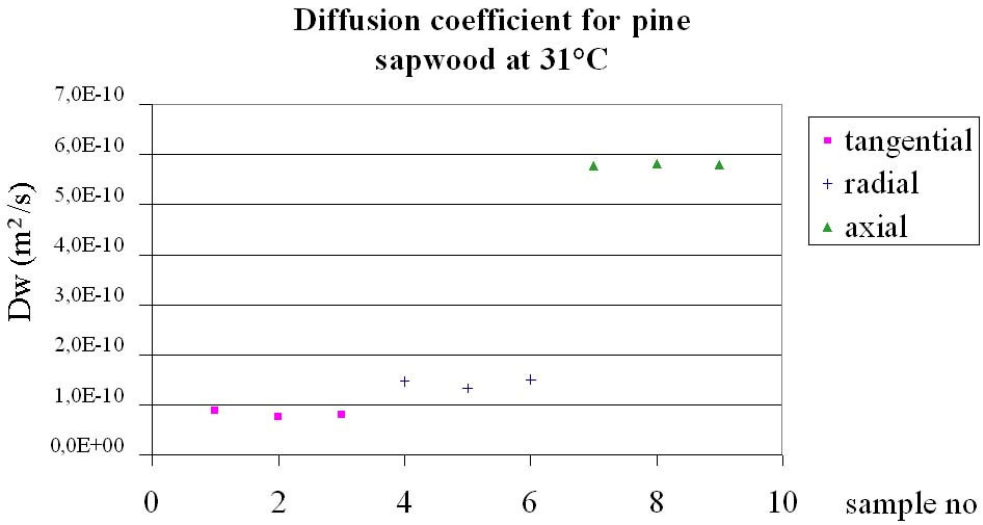


Figure 4.8 Diffusion coefficients in tangential, radial and axial direction for pine sapwood measured with the cup method at 31°C.

This comparative investigation of diffusion rate shows that water-vapour transport, as expected, is highest in the axial direction. Since the main transport of free water or sap in the living tree is in the axial direction, the transport passages are effective, which is also seen for vapour transport—vapour is transported more easily in moist air in the lumina of hollow tracheids than through cell walls and aspirated bordered

pits. The existence of radial wood rays probably explains the higher diffusivity in the radial direction compared to the tangential direction.

Diffusivity in sapwood and heartwood as a function of extractive content

In Paper IV, measurements of the effect of extractive content on moisture-diffusion properties for Scots pine and Norway spruce are presented. The aim was to get a better understanding of the differences in drying rate depending on extractive content in the late, diffusion-controlled regime of drying.

The measurements were performed according to the cup method described earlier, with diffusion cups partly filled with pure water placed in a climate chamber at 60°C and 85% RH with EMC 15%—a common initial climate for normal LT drying. The diffusion coefficients D_w for tangential mass flux were studied.

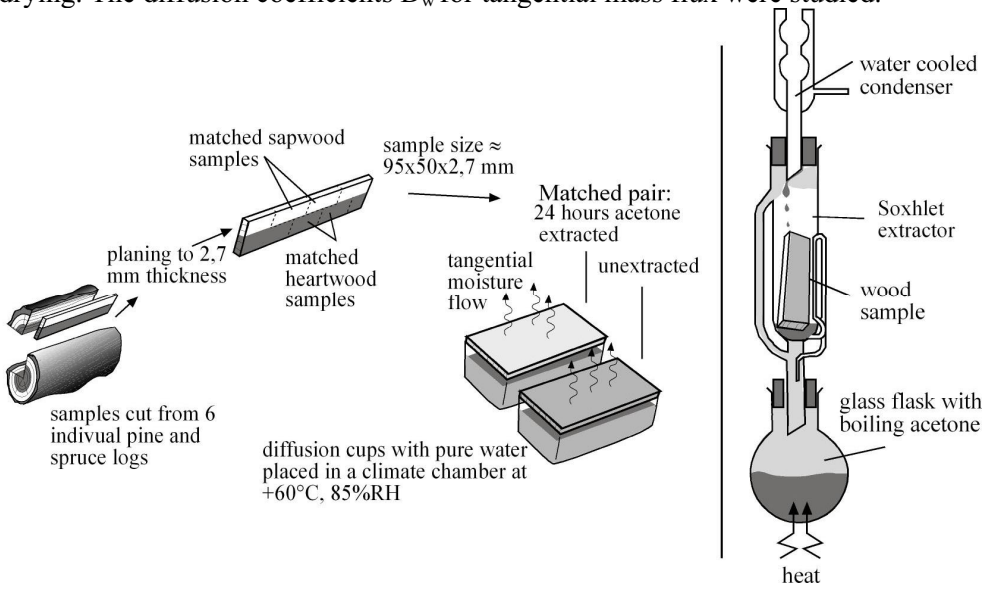


Figure 4.9 Sample preparation and Soxhlet extractor (Paper IV).

A comparative test was performed with matched pairs of sapwood and heartwood samples from both species, where one of the samples in each pair was extracted with acetone (boiling temperature 56.2°C) in solid state in a Soxhlet extractor for 24 hours (see Figure 4.9). The extractive content of the extracted sample was determined, as well as dry density.

The results from the investigation in Paper IV show that:

- Density has a greater effect than extractive content on the diffusion coefficient in pine and spruce at +60°C/85% RH. D_w shows a fairly linear dependency on density for all samples with coefficient of determination R^2 = 0.74 (see Figure 4.10).

- D_w decreases with increased extractive content. A fairly linear dependence between D_w and extractive content is found for pine (R^2 = 0.36) (see Figure 4.11).

- D_w is higher in spruce than in pine in both heartwood and sapwood.

- Density and extractive content are higher in pine than in spruce.

- No difference at 5% significance level is found in D_w between extractive-free pine heartwood and pine sapwood or spruce heartwood.

- Pine heartwood shows a different behaviour than pine sapwood and spruce heart/sapwood. As expected, D_w increases when the extractives are removed. In pine sapwood and spruce sapwood and heartwood, the opposite condition is observed! A more effective aspiration of bordered pits in extracted wood might be an explanation for this. In extracted pine heartwood, however, this phenomenon may be subordinate to the influence of high extractive content.

- The extractives from pine heartwood show variations in colour between samples, from light yellow to brownish yellow (see Figure 4.12). This observation inspired the idea for the study presented in Paper V.

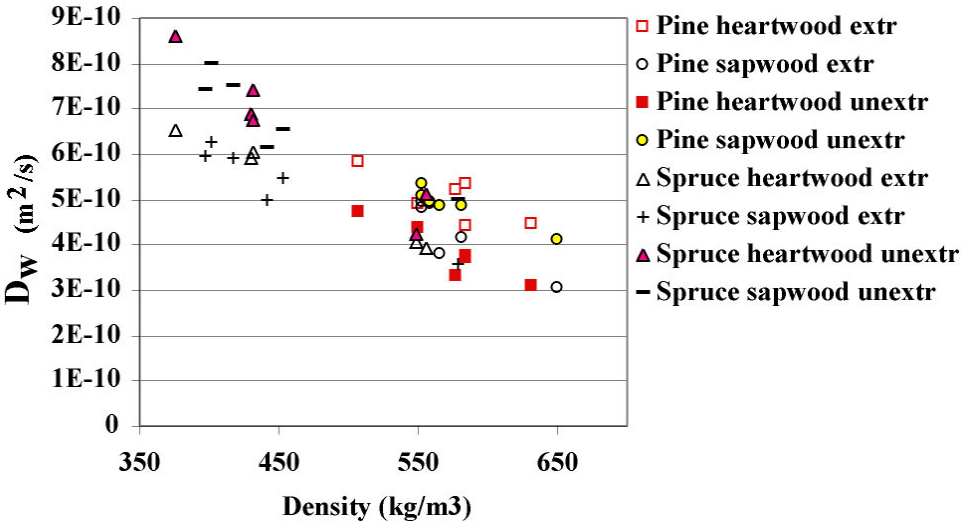


Figure 4.10 Diffusion coefficient as a function of density $\rho_{0,0}$ (Paper IV).

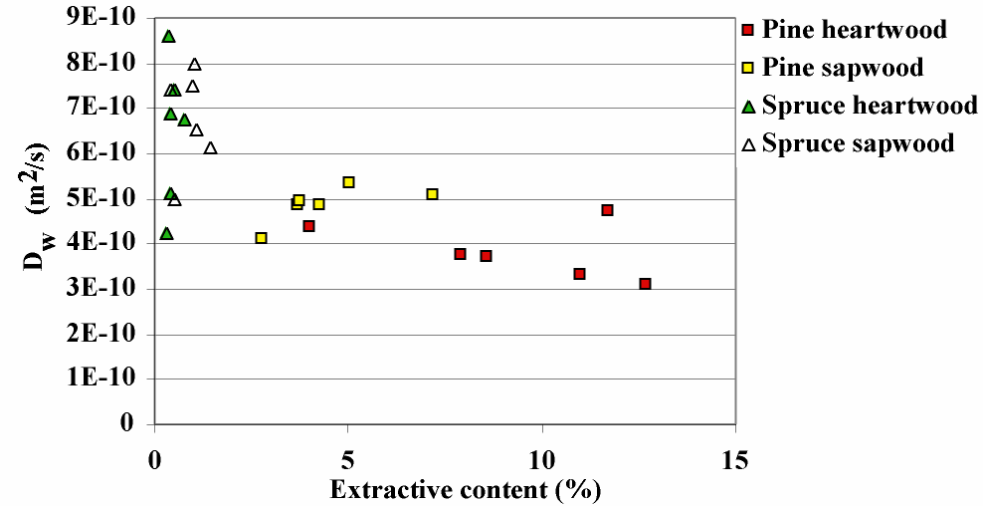


Figure 4.11 Diffusion coefficient in the unextracted samples as a function of extractive content (Paper IV).

Figure 4.12 Variation in colour of collected extractives from pine heartwood from different logs. (Sehlstedt-Persson 2002)

4.7 Wood as a hygroscopic material

Wood dried below FSP is a highly hygroscopic material whose MC depends on environmental factors: temperature and RH. The hydroxyl groups on the cellulose and hemicellulose molecules in the cell wall are mainly responsible for this hygroscopic uptake of water vapour from the surrounding air.

The long-term equilibrium condition between wood and moist climate is expressed as the equilibrium moisture content (EMC). The relation between EMC below FSP and RH is shown in the sorption isotherm. The EMC in a certain climate will not be the same for wood in adsorption (moisture uptake) as for wood in desorption. This is called the hysteresis effect.

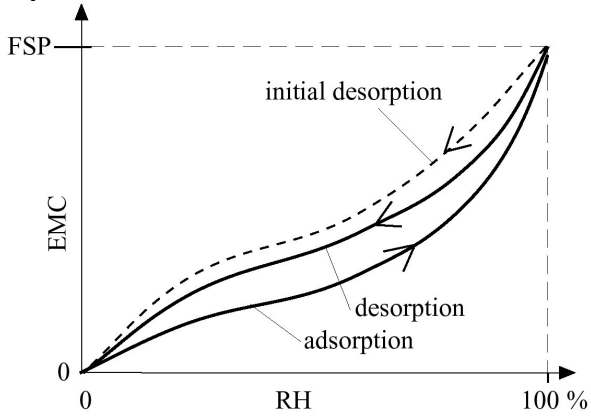


Figure 4.13 The relation between EMC and ambient climate is shown in the sorption isotherm. The deviation between adsorption (moisture uptake) and desorption (drying) is called the hysteresis effect.

The sorption isotherm also depends on factors such as temperature and species, and also on the pretreatment or history of the material. Wood exposed to elevated temperatures, such as during drying, demonstrates a decrease in hygroscopicity compared to unheated wood material. In Chapter 4 this topic is discussed in detail, and results from measurements are presented.

4.8 Moisture-related movement of wood

When MC in wood is below FSP, loss or gain of hygroscopic bound water in the cell wall will result in dimensional changes, namely shrinkage or swelling. Wood is an anisotropic material, which means that these moisture-related dimensional changes vary in different directions. Shrinkage and swelling movements of all wood species are largest in the tangential direction and least in the axial direction, with the radial direction in between.

The shrinkage coefficient β from FSP down to 0% MC in the tangential direction for pine is 7.7% and for spruce 7.8%–8.8%, in the radial direction 4% for pine and 3.6%–4.4% for spruce, and in the axial direction nearly negligible, less than 0.5% for both species (Boutelje and Rydell 1986). If wood contains reaction tissue, the axial shrinkage is larger. The shrinkage of a species also depends on its dry density, which may vary considerably. The higher the dry density, the more hygroscopic bonding sites there are for water molecules and thus greater shrinkage when this water leaves the structure.

The ratio between shrinkage coefficients in the tangential and the radial direction, β_{tan}/β_{rad}, (shrinkage anisotropy) varies between different species and also within species. The larger the ratio is, the more a sawn board will distort and change its cross section after drying, seen, for example, as cupping of a centre board.

Since moisture-related movements in wood depend on the amount of hygroscopic bound water, a decrease of hygroscopicity is expected to diminish these movements and to increase dimensional stability. An increase in dimensional stability is one of the benefits achieved with the heat-treatment process. In Chapter 5 this topic is discussed further, and results from measurements are presented.

5 HEAT AND WOOD—THERMAL DEGRADATION OF WOOD

Wood exposed to elevated temperatures undergoes a thermal degradation process. Kollmann (1960) defined the following three phase points in the exothermic reaction of wood exposed to high temperatures: (1) Flame point 225°C–260°C at which decomposition gases will burn if an ignition source is present; (2) Burning point 260°C–290°C at which burning occurs with a steady flame; and (3) flash point 330°C–470°C, the range of spontaneous ignition.

The extent to which wood is degraded is highly dependent on temperature level, duration of exposure, pressure, MC, *etc*. The influence of water can be also be realized from thermal softening of wood; the higher the MC, the lower the softening temperature (Lenth 1999). Degradation caused by heating of wood in water is predominantly determined by hydrolytic reactions (Fengel and Wegener 1984).

Damage to the wood structure, conversion of components and the occurrence of gaseous degradation products are observed at temperatures higher than 200°C, but under certain conditions, changes in pine wood can be observed even from 100°C (Kollmann and Fengel 1965).

Effects on physical properties caused by heat treatment are decreased hygroscopicity, dry weight reduction by thermal decomposition, colour changes, reduction of mechanical strength, increased dimensional stability and enhanced natural durability in above ground usage.

5.1 Results from measurements—Response: Dry weight reduction

The fact that dry weight reduction occurs during heating of wood is shown in Figure 5.1 from a small unpublished study of long-term dry weights for 5 pine wood samples kept at 103°C for 450 hours, followed by a temperature increase to 120°C, conducted by the author. Compared to the normal dry weight measured after 24 hours of heating at 103°C, a continuous weight reduction of, on average, 0.7% is observed after 450 hours and 1.8% after more than 1800 hours when the temperature is raised to 120°C.

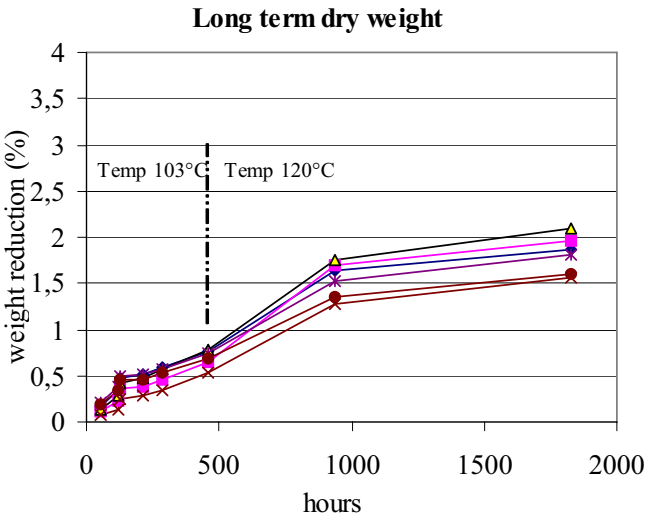


Figure 5.1 Long-term dry weight reduction of small pine wood samples at temperatures 103°C/120°C. Weight reduction in percent of dry weight after 24 hours/103°C; i.e., oven-dry method.

The thermal stability of the different wood constituents varies. In many studies, hemicellulose is reported to be more affected than cellulose (Stamm 1956; Fengel 1966; Kollmann and Fengel 1965; Sivonen *et al.* 2002).

The crystalline structure of cellulose is unchanged, or even improved, at temperatures as high as 200°C, depending on the conditions, according to Fengel and Wegener (1984). Sivonen *et al.* (2002) report an increase of relative crystallinity of cellulose for heat-treated pine together with a decrease in the proportion of amorphous cellulose and a deterioration of hemicelluloses. The changes are most marked at temperatures above 200°C.

Lignin is seen to be the most thermally stable component of wood, even if various changes can be observed below 200°C (Fengel and Wegener 1984).

5.2 Effect of temperature on wood hygroscopicity

Wood that has been exposed to elevated temperatures shows a permanent reduction in hygroscopicity that depends on temperature level and duration of exposure (Skaar 1988). This is mainly associated with a partial decomposition of the most hygroscopic cell wall constituent: the hemicelluloses (Stamm 1964).

As an example, results from Kollmann and Schneider's study (1963) of pine sapwood samples, heat-treated at different temperature levels for durations of 6 h

or 48 h, are shown in Figure 5.2 with desorption/sorption isotherms at 20°C and RH 76%. The effect of treatment temperature on EMC is moderate below 100°C. Above 100°C, hygroscopicity decreases with increasing temperature and duration of treatment seen as a lowering of EMC. The difference between sorption/desorption, *i.e.*, the hysteresis effect, is obvious.

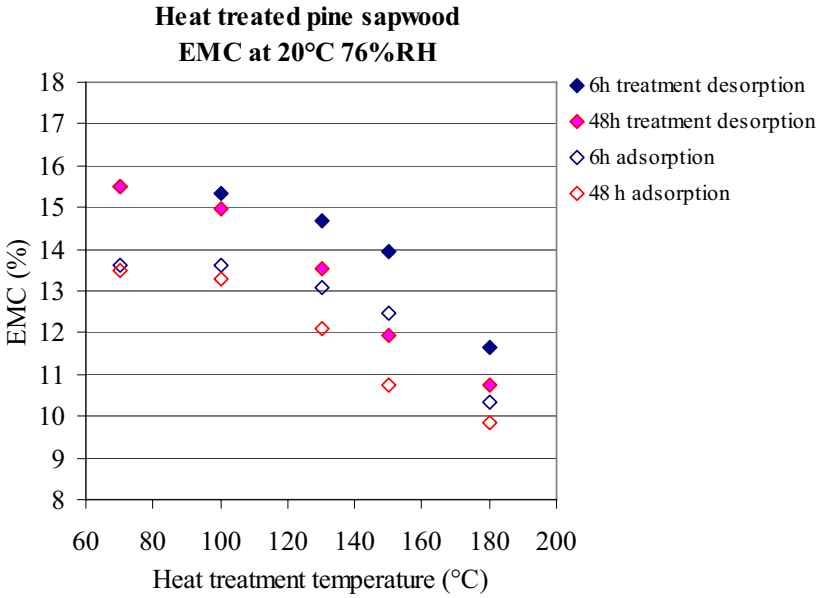


Figure 5.2 Sorption/desorption isotherms for oven-dried pine sapwood samples heat-treated for 6 h and 48 h at different temperatures. (Excerpt of data from table in Kollmann and Schneider 1963)

5.3 Results from measurements—Response: sorption/desorption

In Paper I the sorption/desorption behaviour of pine sapwood dried with three different drying schedules: HT, LT/HT and LT drying below 65°C, are presented. After drying, the lumber was stored for one year indoors at room temperature before sorption/desorption tests were performed at a constant temperature of 47.5°C with stepwise increased RH for the sorption test followed by stepwise decrease in RH for the desorption test.

The results from this study are:

- A difference at 5% significance level exists between all three series in the sorption test. The HT-dried wood has between 1.4% and 2.4% lower EMC than the LT-dried wood, with the LT/HT-dried material somewhere in between.

- The desorption isotherms show a similar relation, but with less pronounced difference between the drying methods.

- A given change in RH results in approximately the same moisture uptake for all three series, though on different levels. The slopes of the isotherms, however, are fairly similar, which means that the change in EMC towards a change of RH is expected to lead to the same moisture-related movement. In the case of oscillating humidity, though, the hysteresis effect is more accentuated in HT-dried material and might decrease moisture-related movement.

- The hysteresis effect was most distinct in the HT-dried wood, up to 2% (see Figure 5.4).

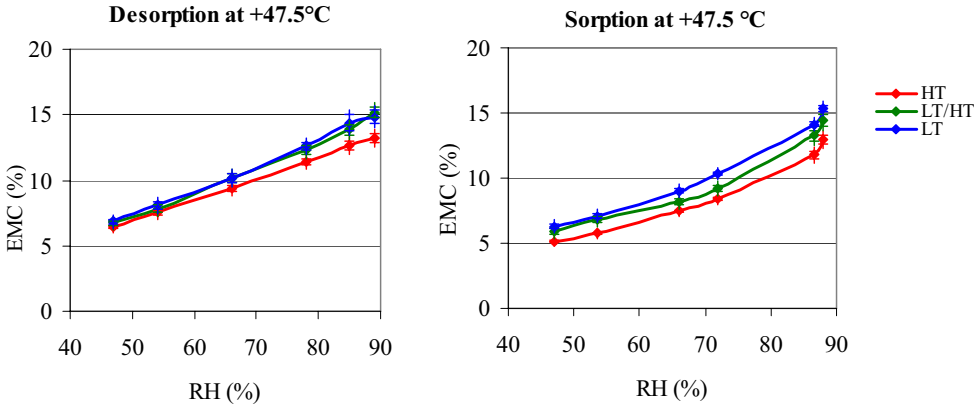


Figure 5.3 Sorption and desorption isotherms at 47.5°C for pine sapwood dried at different temperatures (Paper I).

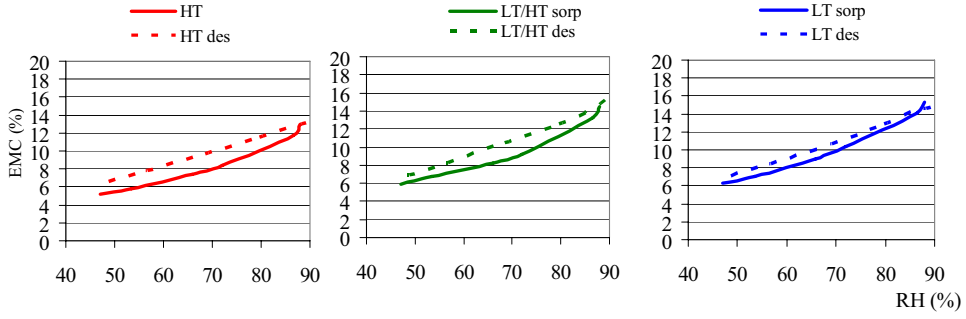


Figure 5.4 Hysteresis effect for different drying temperatures (Paper I).

In order to study the impact of history or former treatment, a comparison between initial desorption isotherm and the isotherms in Paper I was made. Initial desorption isotherms from an earlier study (Morén and Sehlstedt 1984) for pine sapwood during initial drying from green at 20°C and 50°C and desorption isotherms from Paper I at 47.5°C are shown in Figure 5.5. The initial desorption isotherms at 50°C show, in general, some percent higher EMC than the LT-, LT/HT- and HT-dried material, which confirms the statement that prior heat treatment diminishes hygroscopicity. The difference is substantial compared to the initial isotherm at 20°C.

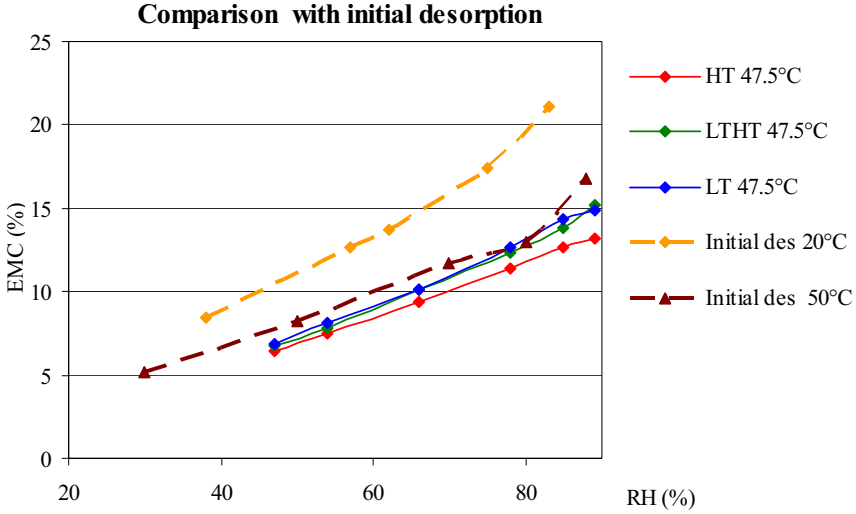


Figure 5.5 Comparison between initial desorption isotherms at 20°C and 50°C from earlier work (Morén and Sehlstedt 1984) and desorption isotherms at 47.5°C for HT-, LT/HT- and LT-dried material (Paper I).

5.4 Effect of remoistening

An interesting question is whether the decreased hygroscopicity for heated wood remains if the wood is remoistened. Results in Morén and Sehlstedt (1984) show that pine sapwood dried to 7% MC at 20°C and then put into water to MC above FSP does not deviate from the initial desorption isotherm for green wood.

Obataya *et al.* (2000) report that if heat-treated hinoki (Japanese cypress) is remoistened to high MC with conditioning at high RH (steaming or boiling) its hygroscopicity recovers almost to its original level.

5.5 Results from measurements—Hygroscopicity of remoistened heat-treated birch

A small unpublished study that investigated this issue was conducted by the author with 2 matched pairs of birch samples, one pair heat-treated at 200°C for 3 hours and one at 200°C for 10 hours. One sample of each pair was put into boiling water for 1 hour and then oven dried to 0% MC together with the matched samples. The two pairs where then put into a constant climate of 35°C, 80% RH, and after 2 weeks, MC was measured. The results in Figure 5.6 show that MC in the remoistened samples was 0.6%, 1.7% higher than in the matched samples. These preliminary results indicate that remoistening seems to lead to regained hygroscopicity for heat-treated birch also.

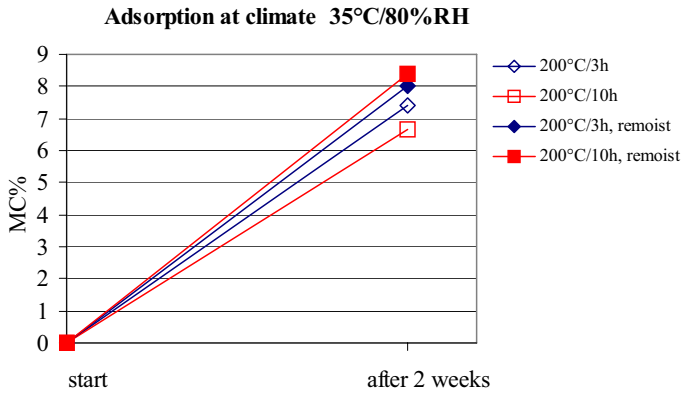


Figure 5.6 Effect of remoistening on regained hygroscopicity for heat-treated birch.

5.6 Effect of temperature on dimensional stability

Enhanced dimensional stability is one of the advantages of heat treatment of wood. Since a decreased hygroscopicity is found also for LT/HT- and HT-dried wood that has been dried at more moderate temperatures, an impact on moisture-related movement in this material is expected.

5.7 Results from measurements—Response: dimensional stability

In Paper II the effect of HT, LT/HT and LT drying on moisture and dimensional changes for Scots pine and Norway spruce during subsequent climate changes was studied. Maximal radial and tangential shrinkage, changes in MC and dimension from green state during cyclic climate changes were calculated and evaluated statistically in order to find differences between drying methods and species.

A summary of the findings in Paper II is:

- No difference was found between pine and spruce in maximal radial or tangential shrinkage in untreated reference material oven-dried from green to 0% MC.

- During cyclic climate changes, the HT-dried material shows a significant reduction of hygroscopicity, with approximately 1% lower MC than the LT and LT/HT series for both pine and spruce.

- LT/HT- and HT-dried pine and spruce material show significantly higher maximum radial and tangential shrinkage after drying to 0% MC than green, untreated reference material, with a greater difference for spruce than for pine. Espenas (1971) also found that shrinkage was greater when drying temperature increased for different hardwoods and softwoods.

- HT-dried spruce shows significantly higher maximum shrinkage than HT-dried pine.

- After some cycles, a radial shrinkage value less than 0.2% per % change in MC was reached for pine and spruce, independent of drying method (see Figure 5.7).

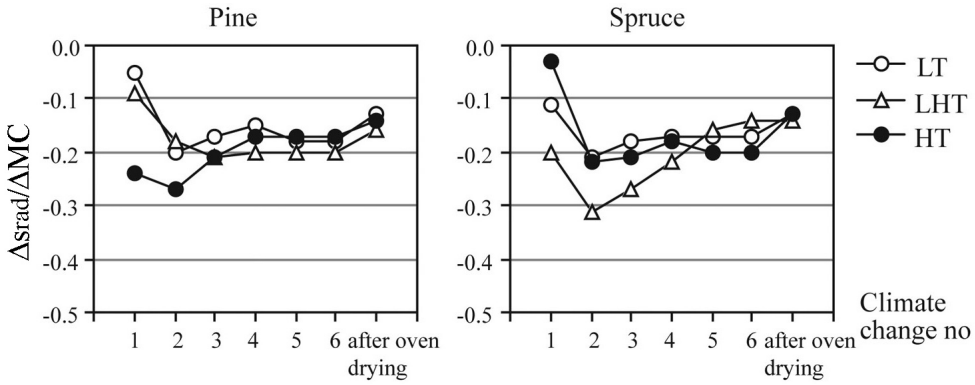


Figure 5.7 Change in radial shrinkage from green state per change in MC (Δs_{rad} /ΔMC) during cycling climate for LT-, LT/HT- and HT-dried material (Paper II).

Therefore, if dimensional stability is expressed as the real movement per change in MC, no difference between drying methods is found.

Kininmonth (1976) reports similar results during moisture uptake and swelling after 24-hour adsorption cycles at 22°C, 95% RH, for radiata pine sapwood dried at different temperatures (air dried, 43°C, 60°C, 77°C and 93°C). Calculation of the ratio of % swelling per % increase in MC of this data shows a fairly constant value of approximately 0.26 (see Figure 5.8).

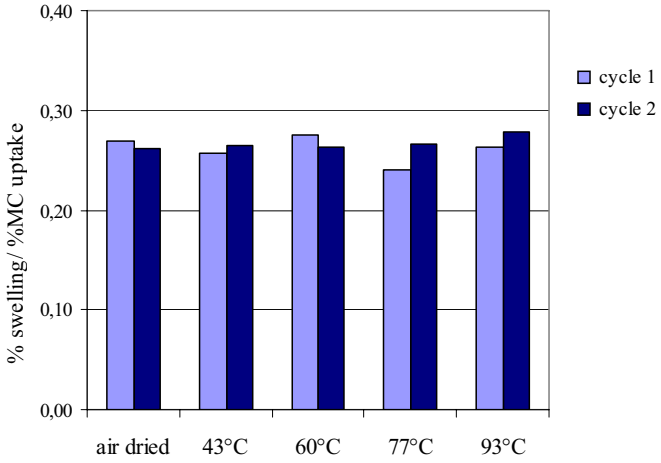


Figure 5.8 Percent swelling per % MC uptake during adsorption cycles for radiata pine sapwood dried at different temperatures. (Excerpt of data from Kininmonth 1976.)

5.8 Effect of temperature on strength properties

Hemicellulose acts as the connecting agent between cellulose and lignin in the cell wall. Since hemicellulose, the most hygroscopic component in wood, is reported to be the least thermally stable wood constituent, thermal decomposition is expected to decrease the strength of wood. Many investigations of strength for different species and the dependency of strength on drying temperatures have been performed. For example, Schneider (1973) showed that maximum crushing strength for pine sapwood dried between 130°C and 180°C was reduced by about 5% and that maximum bending strength was more affected by drying treatment, especially for thicker boards. Teischinger (1992) compared different drying treatments (air drying, LT and HT drying at 110°C) for spruce and the effect on Modulus of Rupture (MOR), Modulus of Elasticity (MOE), bending strength and fracture toughness, where only the latter showed a decrease with increased drying temperature.

Källander *et al.* (2001) showed a reduction of bending and tensile strength measured by a mechanical stress-grading machine for whole planks, for spruce planks dried at 125°C compared to 70°C. MOE showed no reduction.

For heat-treated wood, however, fairly severe reductions of different strength properties are reported. The extent of the reduction depends on how the treatment is performed. Decreased toughness, hardness and strength in bending, compression and tension for *StaybWood* were reported by Stamm *et al.* (1947). Bekhta and Niemtz (2003) show a reduction of bending strength of up to 50% for spruce heat-treated at 200°C compared to 100°C, while the effect on MOE was minor.

5.9 Results from measurements—Response: strength properties

In Paper I a statistical comparison between LT-, LT/HT- and HT-dried pine was made for different strength properties measured in a universal testing machine according to the following descriptions (see Figure 5.9).

Surface hardness: Registration of required force to embed a steel ball with diameter 10 mm to a depth of 4 mm into the wood surface with a test speed of 5 mm/min.

Shear strength at failure along grain direction at different distances from pith.

Cleavage strength at failure perpendicular to grain direction.

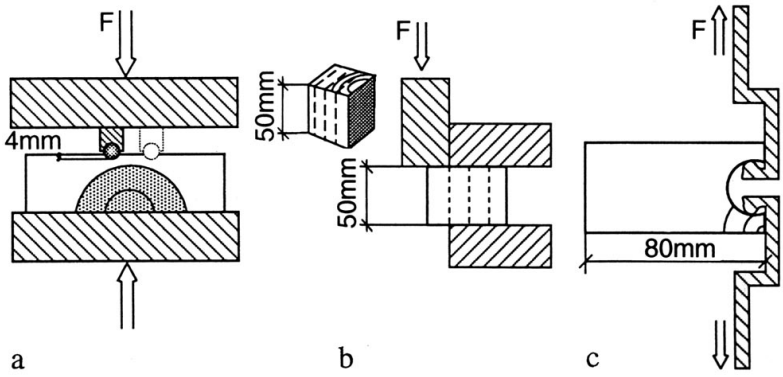


Figure 5.9 Equipment for measuring: A) surface hardness B) shear strength C) cleavage strength (Paper I).

The results in Paper I are:

Surface hardness: No significant difference at 5% significance level was found between the drying methods in spite of a general impression of a hard and brittle material when handling the HT-dried material.

Shear strength: A significant decrease in shear strength along the grain direction was found for HT-dried compared with LT-dried and LT/HT-dried wood and a

tendency toward decrease in shear strength towards the pith in all series. The occurrence of juvenile wood closer to pith might explain the latter.

Cleavage strength: Some indistinct results showing a significantly lower force at failure for HT-dried material than for LT/HT drying, but not compared with the LT series. No difference was found between LT/HT and LT series. Pith position in cross section varied, which might explain the variations.

In another study, the author performed a comparative study of dynamic fracture toughness for small, matched samples of LT- and HT-dried spruce (Wamming *et al.* 1999). LT drying was performed with a maximum temperature of 70°C and HT drying at a maximum of 107°C. The test was done with Charpy equipment, an impact test method with a falling pendulum (see Figure 5.10).

The results from this investigation showed a large variation in toughness in spite of well-matched samples. A tendency toward decreased toughness for HT-dried material compared to LT-dried material was found, but there was no difference at 5% significance level. The influence of material properties such as density and annual ring width was greater than drying method when evaluation was done with multivariate methods. The occurrence of reaction wood as well as larger annual ring width increased the proportion of short, brittle fracture surfaces in HT-dried material.

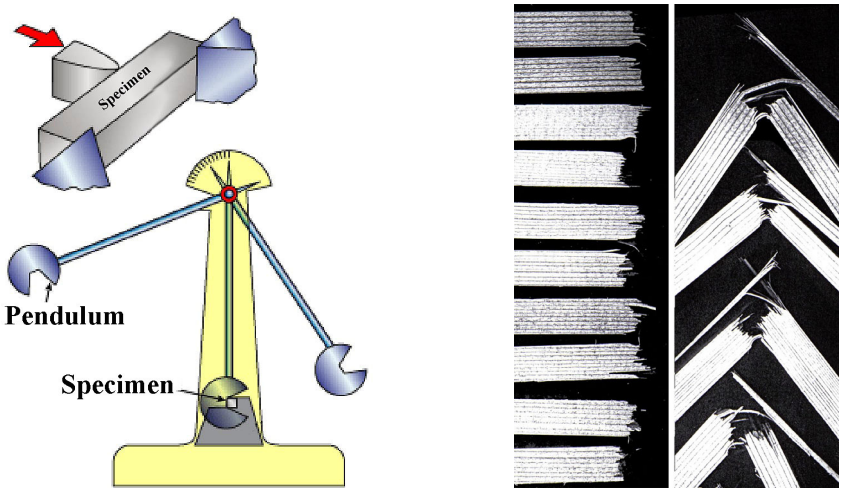


Figure 5.10 Left: Charpy equipment with a falling pendulum for testing dynamic fracture toughness.
Right: Different types of fracture surfaces, with short, brittle fracture surface above. (Wamming et al. *1999)*

6 DRYING AND DURABILITY

The durability of wooden products for outdoor applications is an urgent issue for the future utilization of wood as a competitive construction material. During recent years there has been some indication that the durability of pine heartwood products has declined, such as, for example, high-temperature dried pine poles in playgrounds that have become seriously decomposed after just a few years' usage (Wamming 2005). One hypothesis is that the drying process might negatively affect the natural durability of wood.

The drying process can be seen as a hygrothermal treatment of wood, and the performance of the drying process can be varied infinitely. During this hygrothermal drying process, physical and chemical reactions occur that change the properties of wood and its constituents, including evaporation of volatile compounds, changes in colour, hygroscopicity, consistency of resin and re-distribution of nutrients in sapwood, among other things.

Early in the capillary regime of the drying process, when free water in sapwood moves towards the evaporation surface beneath the surface, an enrichment of carbohydrates and nitrogen compounds takes place at the surface (Theander *et al.* 1993). The drying rate has a significant effect on this redistribution, with a higher accumulation if the drying rate is high (Terziev *et al.* 1993). Air-dried sapwood surfaces were shown to have smaller gradients than kiln-dried lumber (Terziev 1995). Planing of kiln-dried sapwood removes the most enriched zone, while in air-dried sapwood, planing may expose wood with a higher nutrient concentration. This affects susceptibility to mould, and mould growth has been shown to be reduced by planing of kiln-dried lumber, while the mould growth on planed, air-dried surfaces increased compared to unplaned surfaces (Terziev *et al.* 1996)

Studies of the impact of different drying methods on the durability of pine and spruce have been done with various short- and long-term decay methods with varying results. No difference between different drying methods was found concerning mass loss in a rot test when comparing air-dried pine lumber with artificially dried pine lumber at temperature levels not exceeding 54°C (Rydell 1981), temperature levels considered moderate by today's standards.

In a long-term outdoor test above ground, air-dried pine and spruce lumber was compared with kiln-dried lumber of the same species (Bergström *et al.* 2004; Rydell *et al.* 2005). Air-dried spruce showed higher mass loss after 9 years' exposure compared to kiln-dried spruce, but also significantly higher average MC during exposure time, which probably explains the higher mass loss because of

more favourable conditions for wood-destroying fungi. However, the drying process in the study is poorly described, merely as "kiln dried".

In the present thesis, the aim of the studies performed within the scope of drying and durability has been to clarify the impact of the drying process on the durability of Scots pine lumber with focus on the performance of the drying process. The following issues have been studied:

Paper I:
Mould growth in an *in-vitro* test on sapwood surfaces dried at three different low and high temperature schedules. Visual estimation of mould growth level was made.

Paper VIII:
Brown rot decay *in-vitro* test. Mass loss as a percentage of the original dry weight was used as a measure of durability. The study comprised the following variables:

Influence of the performance of the drying process
- temperature level
- wood temperature during different regimes of drying
- steam conditioning after drying

Raw material:
- sapwood and heartwood
- inner and outer heartwood

Paper IX
Studies were done on selected, dried heartwood material from Paper VIII and on heated, green heartwood sawdust. The study comprised the following issues:

- impact of drying on the concentration of total phenolics according to the FC assay in dried heartwood
- the relation between mass loss and concentration of total phenolics in dried heartwood is compared with the fairly strong relation found in green heartwood by Harju and Venäläinen (2006).
- impact of heating temperature and time on the concentration of total phenolics in green heartwood sawdust with different extractive content

6.1 Results from measurements—Response: mould growth

In Paper I, a small study of mould growth was performed on sapwood surfaces from Scots pine lumber dried on three different schedules: one high-temperature

(HT) schedule up to 115°C, one low-temperature (LT) schedule below 65°C and one combined LT/HT schedule. An 8-week *in-vitro* test with the mould fungus *Penicillium brevicompactum* was done with a visually estimated mould growth level in a 5 step grading system from 0 (no mould growth) to 4 (very vigorous growth).

The result indicated an inhibiting effect of HT drying with an average mould growth level of 0.8 compared to the LT/HT schedule with a mould growth level of 2.3 and the LT schedule with a mould growth level of 3.2. This small test was, however, performed only with 6 samples per drying series.

6.2 Results from measurements—Response: mass loss in decay test

In Paper VIII, the impact of the drying process on the durability of dried lumber was studied.

Drying was performed in six different series. Series A, air-dried at 20°C–25°C, Series B–E, kiln dried at maximum temperature levels of 70°C or 90°C, and Series F HT-dried at 110°C. Steam conditioning after drying was done on half of each batch except in Series A. Wood temperature was registered in Series B–F during drying.

For the 70°C and 90°C series B–E, two different regulation principles were used after the initial preheating. Both these principles correspond to kiln-drying schedules used at Swedish sawmills:

I. Dry-bulb temperature (T_{db}) gradually rising to maximum temperature level and wet-bulb temperature (T_{wb}) at one or two constant levels. Series B at 70°C and Series D at 90°C

II. Constant T_{db} at maximum level with initial T_{wb} dropping to a constant level. Series C at 70°C and Series E at 90°C.

The difference between these two regulation principles is how fast the wood temperature reaches maximum temperature level. In regulation principle II, the wood temperature reaches maximum temperature level early in the capillary regime of drying when the MC is high, while the wood temperature in regulation principle I reaches maximum temperature considerably later in the drying process when the MC is lower.

After drying and conditioning, samples for a 7-week *in-vitro* decay test with the brown rot fungus *Coniophora puteana* were sawn from sapwood and inner and

outer heartwood. In Figure 6.1, the results from the decay test for all drying series are shown, and in Figure 6.2, the impact of steam conditioning.

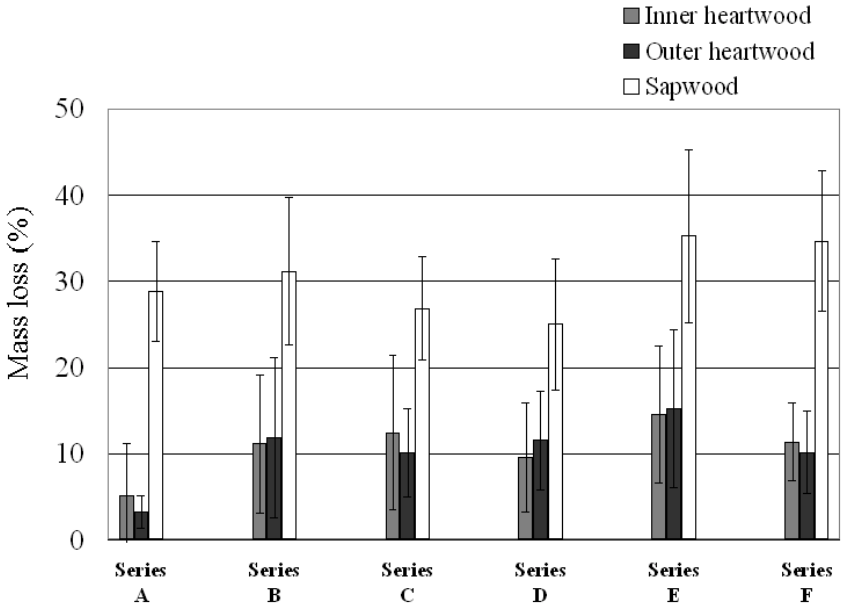


Figure 6.1 Mass losses after 7 weeks' incubation with brown-rot fungus Coniophora puteana for pine lumber dried in series A–F. Data are given as average values with 95% confidence intervals. (n = from 10–16 in each bar) (Paper VIII).

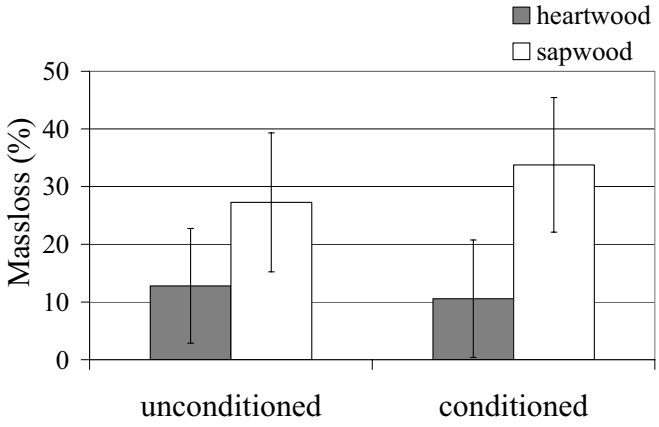


Figure 6.2 Mass loss in pine sapwood and heartwood for unconditioned and conditioned pine lumber as average values for all series except series A. Data are given with 95% confidence intervals. (n = 112 for heartwood and 52 for sapwood) (Paper VIII).

The results can be summarized as follows:

- Air-dried heartwood shows the highest durability compared to the other drying series.

- Drying at 90°C with high material temperature early in drying when MC is high, as in Series E, shows the lowest durability for both sapwood and heartwood. The interpretation is that the duration of high material temperature at high MC is the critical combination for decay resistance in heartwood.

- Steam conditioning after drying lessens the durability of sapwood.

- A large variation in mass loss is seen for all wood types in all series.

- Sapwood shows considerably lower durability—more than two times higher mass loss—than heartwood.

- In contradiction to other studies, no difference is found between the durability of inner heartwood and that of outer heartwood.

6.3 Results from measurements—Response: phenolic content

In Paper IX, the impact of drying and heating on the concentration of total phenolics in heartwood was studied. From the same material reported in Paper VIII, four samples from each drying temperature level, 20°C, 70°C, 90°C and 110°C in series A–F, with the two highest and two lowest mass losses were identified from inner or outer heartwood. From these 16 samples, the concentration of total phenolics was determined as well as density and the concentration of extractives. From drying series E, which on average showed the highest mass loss of all series, ten additional samples were taken randomly for phenolic and extractive analysis to cover the whole range of mass loss. The relation between mass loss and total phenolics in dried heartwood was compared with the fairly strong relation found in green juvenile heartwood by Harju and Venäläinen (2006).

In order to minimize the influence of variation in various wood properties, a study with heating of green mixed and sieved sawdust was also done.

In Figure 6.3, the relation between mass loss and concentrations of total phenolics is shown and compared with the study by Harju and Venäläinen. In Figure 6.4, the results from heating of green sawdust with different extractive content are shown.

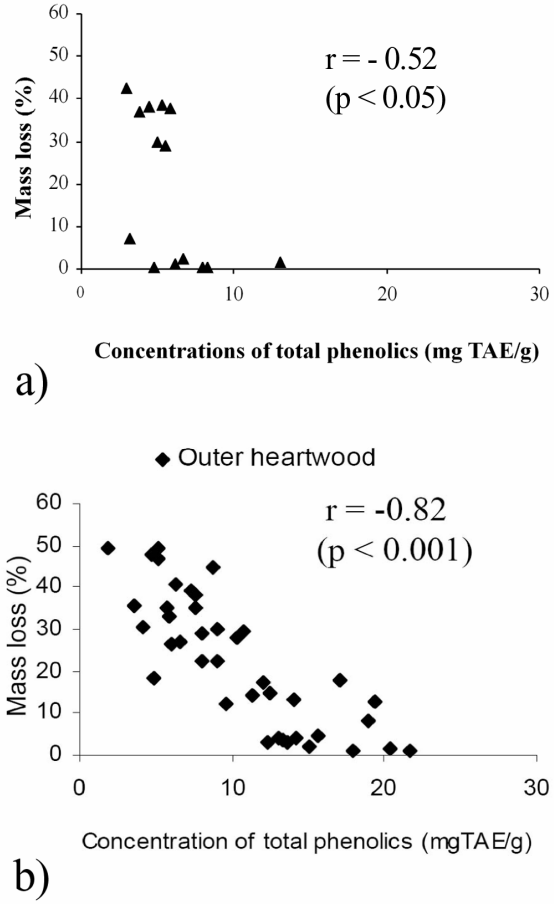


Figure 6.3 Comparison of the relation between mass loss in decay test and concentration of total phenolics according to FC assay in:
a) inner and outer Scots pine heartwood dried at various temperatures. Linear correlation coefficient r = -0.52 (p<0.05)
b) green juvenile pine outer heartwood according to the study by Harju and Venäläinen. Linear correlation coefficient r = -0.82. (Diagram from Harju and Venäläinen). (Paper IX)

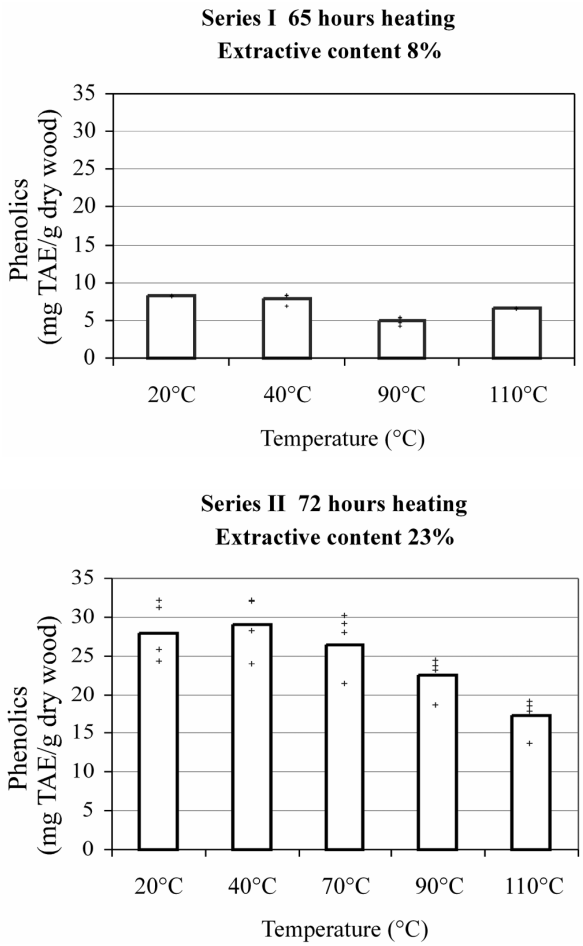


Figure 6.4 Concentration of total phenolics (mg TAE/g dry wood) measured by the FC assay in pine heartwood with normal extractive content (series I) and high extractive content (series II) heated at various temperatures during 65 and 72 hours respectively. Each bar is an average of 4 measurements (Paper IX).

The results can be summarized as follows:

- The study on dried heartwood does not show the same apparent relation between mass loss and concentration of total phenolics as the study by Harju and Venäläinen on green heartwood. A weak negative correlation was found for heartwood dried at various maximum temperatures between 20°C and 110°C with a linear correlation coefficient $r = -0.52$ ($p<0.05$). In

heartwood dried at maximum temperature 90°C, the linear correlation coefficient was $r = -0.42$ ($p<0.2$). These correlation coefficients are weaker than those of the study on green Scots pine heartwood with $r = -0.82$ ($p<0.001$).

- Lower levels of total phenolics were found in dried heartwood than in the study on green heartwood by Harju and Venäläinen.

- A weak negative correlation was found between mass loss and density with a linear correlation coefficient $r = -0.62$ ($p<0.02$), thus somewhat stronger than the correlation between mass loss and phenolics.

- The concentration of total phenolics in heated, mixed, green sawdust was higher in extractive-rich Scots pine heartwood than in heartwood with normal extractive content.

- Heating of green sawdust with high extractive content reduced the concentration of phenolics at temperatures exceeding 70°C up to 110°C during 72 hours of heating, and indications of a reduction were found during 3 hours of heating at temperatures exceeding 160°C up to 180°C. Heating of extractive-rich green sawdust indicated a reduction of phenolics with temperature and time.

7 CAPILLARY WATER ABSORPTION IN HEAT-TREATED WOOD

Heat-treated wood is used in many indoor applications such as furniture, flooring, panelling and interiors of bathrooms and saunas. Heat-treated wood is rot-resistant enough for many outdoor uses, unless there is ground contact, and the market is growing for heat-treated wood also in outdoor applications such as garden furniture, exterior cladding (Metsä-Korteläinen *et al.* 2006) and decking areas. An urgent question in regard to outdoor applications is how absorption of free water in different wood species is affected by the heat-treatment process.

Wood that has been exposed to elevated temperatures shows a permanent reduction in hygroscopicity that is dependent on temperature level and duration of exposure (Skaar1988). Many studies have reported on this subject (Kollmann and Schneider 1963; Espenas 1971; Kinninmonth 1976; Price and Koch 1980; Sehlstedt-Persson 1995 (Paper I). This reduction is mainly associated with a partial decomposition of the most hygroscopic cell wall constituent—the hemicelluloses (Stamm 1964). This reduction of hygroscopicity improves the dimensional stability of heat-treated wood.

The hydrophobic character of wood is also affected by thermal treatment. Hakkou *et al.* (2005) found an abrupt increase in contact angle in heat-treated spruce (*Abies alba*) and pine (*Pinus sylvestris*) at heat-treatment temperatures in the range 100°C–160°C. This decrease of wettability influences the glueability and paintability of wood surfaces, and most likely capillary water absorption in wood as well.

The ability to transport liquid water is shown to be affected by drying and heat treatment. For example, Terziev (2002) found that HT-dried Scots pine increased its ability to transport impregnating liquids as compared to conventionally dried pine.

Metsä-Korteläinen *et al.* (2006) studied radial water absorption in floating tests of dried and heat-treated wood and found significant differences between sapwood and heartwood for both spruce and pine. For pine, the differences were very pronounced, with a rapid absorption in sapwood as compared to heartwood. The effect of heat-treatment temperature upon water absorption in sapwood differed between the two species. In spruce, water absorption decreased in direct proportion to increased temperature, while for pine, the absorption was greatest for 170°C and 190°C. While spruce sapwood samples never reached 30% MC during the whole test, pine sapwood samples approached 30% MC for 170°C and 190°C treatment after only 6 hours' floating. In spruce heartwood, water absorption decreased in direct proportion to increased temperature, while pine heartwood showed a more

complicated pattern. Compared with reference material dried at 70°C, all heat-treated pine heartwood samples absorbed less water, and the highest temperature (230°C) showed the least absorption.

In the present thesis, the studies performed within the scope of capillary water absorption in heat-treated wood, the aim has been to study the impact of heat-treatment temperatures on water absorption in wood using computer tomography (CT) scanning. Studies of the anatomical microstructure have been done in SEM in order to sort out questions arising from the observed differences between species and sapwood/heartwood.

The following issues have been studied:

Paper VI:
Longitudinal water absorption in matched heat-treated and untreated dried boards was studied. CT scanning was used to intermittently monitor the ascent of water.

Species
Scots pine, Norway spruce and European birch. 50- x 125-mm pine and spruce boards containing sapwood and heartwood. 50- x 90-mm birch boards.

Heat treatment and drying
Heat treatment was performed at 170°C and 200°C, and the matched untreated material was dried at a maximum temperature of 60°C.

Absorption test and CT scanning
Longitudinal water absorption in 300-mm-long samples placed in water to a depth of 25 mm. CT scanning was done before test and intermittently over 15 days.

Paper VII:
SEM studies of the anatomical microstructure, pits and pit membranes of material used in Paper VI. Special attention was given to the crossfield pits and the membranes between horizontal ray parenchyma and longitudinal tracheids in pine and spruce sapwood and heartwood.

7.1 Results from measurements—Response: capillary water absorption

In Paper VI, capillary water absorption along the fibres in heat-treated and untreated dried matched boards of pine, spruce and birch was studied during 15 days of absorption (see Figure 7.1). CT scanning was done every 5 millimetres along the samples before testing and after 1, 3, 5, 8, 12 and 15 days of absorption.

In each CT scan, the density value is given as an average density value of wood and water in 0.63- x 0.63- x 5-mm volume-elements or *voxels* in grey-scale images. By subtracting the calculated average dry-wood density value in each voxel in each 5-mm scan, arranged as "slices" on top of each other in an image stack, the distribution of water along the sample is given.

In pine and spruce sapwood, two smaller CT volumes (11 x 11 x 61 voxels) were evaluated and in heartwood, one CT volume (16 x 16 x 61 voxels) as shown in Figure 7.1, right. In birch, which doesn't contain heartwood, one larger, centred CT volume (11 x 104 x 61 voxels) was evaluated. As a simplification, no consideration of swelling was taken into account, and FSP was set to 30% even though FSP is known to decrease in heat-treated wood.

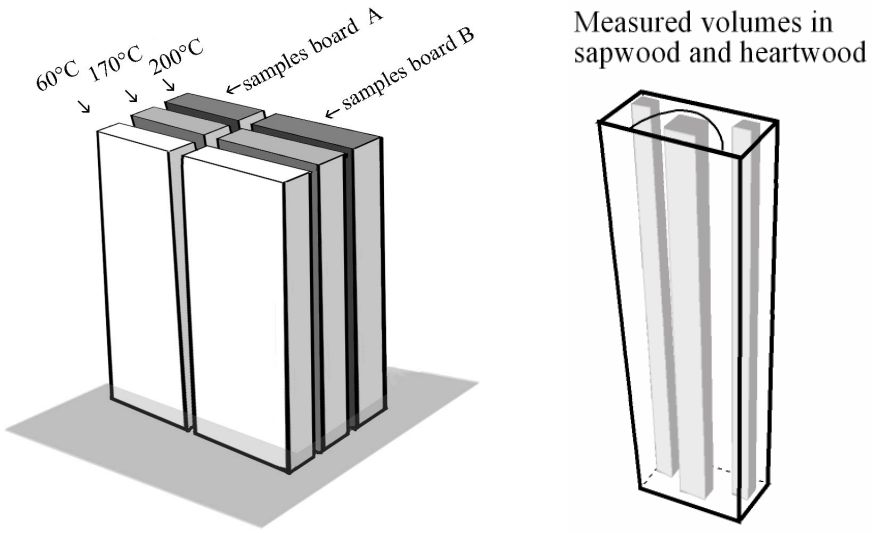


Figure 7.1 Left: Batch with 300-mm-long samples from two boards (out of four for each species) with three treatment temperatures placed in water to a depth of approximately 25 mm for longitudinal water absorption with butt end down (Paper VI).
Right: Measured CT volumes in pine and spruce sapwood and heartwood.

Three different evaluations were done in the CT volumes:

a) average MC of the entire CT volume
b) average MC at every 5 mm along the sample
c) average height to FSP

a) Average MC of the entire CT volume

In Figure 7.2, an example of average MC of the entire CT volumes during 15 days of absorption is shown in birch.

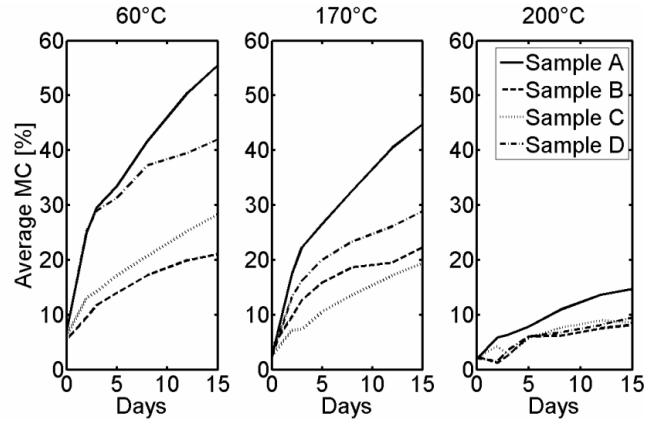


Figure 7.2 The average MC during longitudinal absorption in four birch samples during 15 days (Paper VI).

The results from measurements of average MC of the entire CT volume are summarized as follows:

Birch:

- Great differences between the four samples are found at 60°C (Figure 7.2). This differences decline at higher temperature.

- The increase in average MC after 15 days of absorption is greatest at 60°C and declines with increasing temperature.

Pine and spruce

- Pine sapwood shows a considerably higher increase in average MC at all temperatures after 15 days of absorption compared to pine heartwood and spruce sapwood and heartwood.

- Pine sapwood shows the highest moisture uptake at 170°C while moisture uptake was about the same at 60°C and 200°C.

- The differences between spruce sapwood, spruce heartwood and pine heartwood are small with low moisture uptake, though the biggest increase in samples treated at 170°C.

b) Average MC at every 5 mm along the sample

In Figure 7.3, the average MC along the sample after 5 and 15 days of absorption is shown in a) birch b) pine sapwood and c) spruce sapwood.

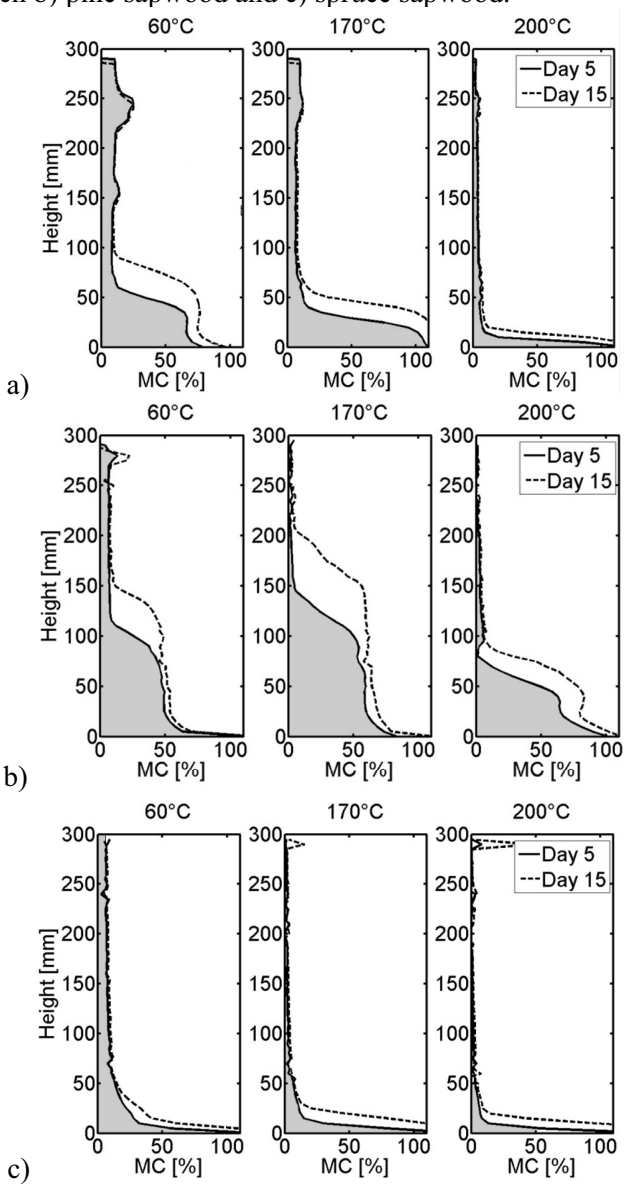


Figure 7.3 The average MC along the sample after 5 and 15 days of water absorption in: a) birch, b) pine sapwood and c) spruce sapwood (Paper VI).

The results can be summarized as follows:

Birch

- The ability to transport free water upwards along the sample decreases with higher temperature. This is clearly illustrated by the shape of the grey-coloured area in Figure 7.3 a). This area corresponds to the increase in average MC in the entire CT volume after 5 days of absorption in sample B in Figure 7.2.

Pine and spruce

- Different absorption behaviour is found in pine and spruce sapwood, Figure 7.3 b) and c)

- The ability to transport free water upwards increases from 60°C to reach maximum at 170°.

- The ability to transport free water upwards is low compared to pine sapwood and declines with increasing temperature.

- The average MC along the sample is almost similar in pine heartwood, spruce sapwood and spruce heartwood, with somewhat higher water uptake in spruce heartwood.

- The ability to transport free water upwards in pine heartwood, spruce sapwood and spruce heartwood is highest at 60°C, but the difference is small between the temperatures.

A correction of the last two sentences in **Conclusions** in Paper VI is as follows:

Heat treatment results in a decreased ability to transport free water upwards in longitudinal direction in all wood types studied except for pine sapwood. In pine sapwood, transport capacity was at a maximum at 170°C treatment temperature.

c) Average height to fibre saturation point (FSP)

In Figure 7.4, the average height to FSP along the 300-mm-long samples after 15 days of absorption is shown. Average height to FSP is calculated as the average length of all connective "voxel bars" with MC of 30% within the CT volume.

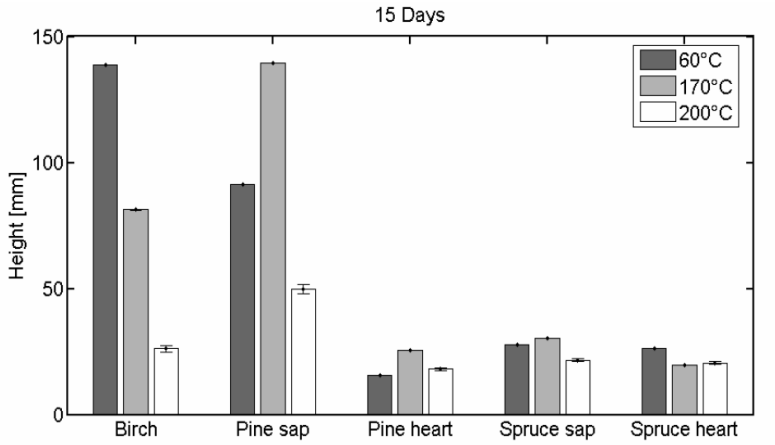


Figure 7.4 Average height to FSP after 15 days' absorption with 95% confidence interval for birch, and sapwood and heartwood of pine and spruce heat-treated at 170°C and 200°C and untreated material dried at 60°C (Paper VI).

The results can be summarized as follows:

- Large differences are found between treatment temperatures for birch and pine sapwood. In birch, the height to FSP decreased with increased temperature. In pine sapwood, the maximum height to FSP was found in the samples treated at 170°C, and the height to FSP at 60°C was significantly higher than the 200°C samples.

- The absorptive behaviour of pine sapwood deviates from all the other softwood types studied.

- The height to FSP in pine heartwood is comparable to spruce sapwood and heartwood. All show small differences between treatment temperatures.

- In pine sapwood, pine heartwood and spruce sapwood, the maximum height to FSP was found in the samples treated at 170°C.

Discussion

As heat treatment of wood has been shown to decrease wettability (Hakkou *et al.* 2005) a decreased capillary absorption capacity is to be expected, since the adhesion between water and the cell walls in the capillaries (lumen) is diminished. In this study, the ability to transport water upwards is also found to decrease with

increasing temperature from 60°C up to 200°C in all wood types except pine sapwood. In pine sapwood, the transport capacity reaches its maximum at 170°C, as illustrated by the shape of the grey-coloured area in Figure 7.3 b). This corresponds to the observations made by Metsä-Kortelainen *et al.* (2006), who found the same pattern in radial water transport in pine sapwood.

This deviating behaviour of pine sapwood is complex. One hypothesis is that formation of small microchecks in the cell walls during the heat-treatment process contributes to the uptake of water due to the increased number of fine capillaries. Then the capillary rise of water in the lumina is promoted by the capillary rise in the more water-saturated cell walls. At temperatures exceeding 170°C, the ability to transport water upwards is found to decline in pine sapwood. The hypothesis is that further decrease of wettability then dominates and lessens the capillary action.

This hypothesis doesn't explain why the same phenomena not are found in pine heart wood or spruce. This is most likely due to differences in anatomical structure. In order to sort out the questions arising from this work, SEM studies of the microstructure of heat-treated and untreated wood were done. These SEM studies are presented in Paper VII.

7.2 Microstructure of pine and spruce

Even if pine and spruce at a first glance seem to have very similar microstructures, the key to the different water absorption behaviour in dried wood will likely be found in differences in anatomical features. In the following section, differences in microstructure will be described that contribute to the different liquid absorption behaviour in the internal three-dimensional transport system.

The most conspicuous anatomical detail is the connection between longitudinal tracheids and horizontal parenchyma cells in rays. In a radial view, a large window-like (*fenestriform*) pit opening is found in pine, with a thin membrane between the neighbouring cells. In spruce, a number of small pits can be seen in the membrane (Figure 7.5).

The frequency of ray tracheids relative to ray parenchyma cells in spruce is much lower than in pine. The average diameter of the simple pits in spruce in the connection between ray parenchyma and vertical tracheids is 2 μm, to be compared to the large fenestriform pits in pine with an average size of 12 x 31 μm. The overall pit area is ten times larger for parenchyma cells in pine than in spruce (Nyrén and Back 1960).

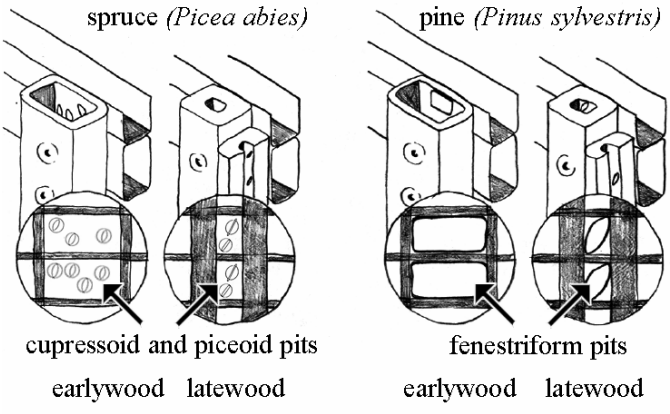


Figure 7.5 Interconnecting pits between ray parenchyma and vertical tracheids in pine and spruce, earlywood and latewood (Paper VII).

Liese and Bauch (1967) studied air-dried pine and spruce and found that all bordered pits in the earlywood zone in sapwood were aspirated in both species. In the latewood zone, however, differences were found between the two species—while between 20% and 25% of the pits were unaspirated in spruce, up to 50% of the pits in pine remained open. Fengel (1970) found that bordered pits in ray tracheids in pine heartwood were predominantly unaspirated, but completely encrusted with heartwood substances, thus closed not by aspiration but by sealing of membranes. This, in combination with pit aspiration in heartwood, probably affects permeability and flow paths in pine heartwood considerably. The overall extractive content in pine is higher than in spruce, especially in the heartwood (Table 2.1), and pine has about twice the average diameter (Back 1969), and four times the volume share (Petric and Scukanec 1973) of axial resin canals compared to spruce.

Olsson *et al.* (2001) studied transverse liquid flow paths in pine and spruce sapwood and heartwood vacuum impregnated with a low-viscous epoxy. They propose a damage hypothesis deriving from the impregnation procedure. For pine sapwood, the liquid flow was enabled through disrupted crossfield pit membranes. For spruce, the thicker ray cell walls in combination with smaller crossfield pits reduced permeability considerably. The reduced permeability in pine heartwood was believed to be the result of deposits of high-molecular-weight substances (extractives) on the cell walls and in the parenchyma ray cells.

de Meijer *et al.* (1998) found a substantially different behaviour of penetration of wood coating liquids into ray parenchyma and ray tracheids in predried pine and spruce. In pine, the major portion of liquid coating flows through the ray

parenchyma cells from cell to cell, while in spruce, the coating flows solely in ray tracheids. While some coatings only penetrated spruce in ray parenchyma into the first cell, the penetration depth in pine parenchyma was as deep as 1000 μm. Coatings were found to flow from the ray parenchyma into longitudinal tracheids through the fenestriform pits in pine. Longitudinal tracheids can be filled by several rays, since on an average each longitudinal tracheid is in contact with 2.4 rays according to a study of Courtois cited in De Meijer *et al.* (1998).

Hayashi *et al.* (1965) found that the leading portion of transverse penetration of water occurred in ray tissue in dried softwood species. In particular, Japanese red pine sapwood showed high penetration between rays and longitudinal latewood tracheids. Like Scots pine, this species has fenestriform pits in the connection between longitudinal tracheids and horizontal ray parenchyma cells.

In order to shed light on questions arising from the study of capillary water absorption (Paper VI), SEM studies of the anatomical microstructure (pits and pit membranes) of heat-treated and dried pine, spruce and birch were done. Special attention was given to the crossfield pits and the membranes between ray parenchyma and longitudinal tracheids in pine and spruce.

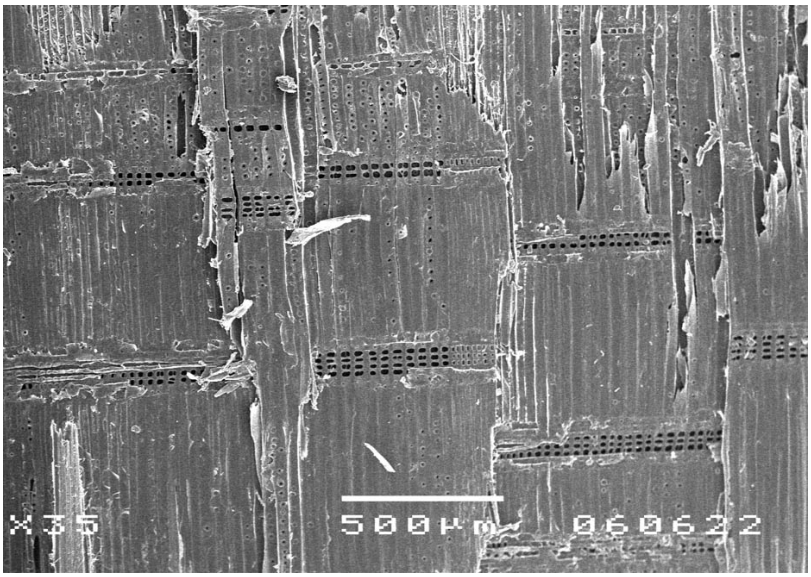
7.3 Results from SEM studies of microstructure of heat treated and untreated wood

In Paper VII, small specimens cut from pine and spruce sapwood and heartwood and from birch wood used in absorption tests (Paper VI) were prepared for SEM studies. Observations were made on radial surfaces carefully split from areas as close as possible to the samples used in the absorption tests. By using split areas for studies, no cutting was done on the observed surfaces in order to minimize manually caused damage. For comparison, observations were also made on newly cut, not artificially dried wood surfaces prepared in the same way. Please note that all specimens put in current SEM microscope are subjected to vacuum and thus are dry. In the following figures, a selection of overviews and details is shown for pine.

Pine sapwood

In Figure 7.6 a) and b), it is shown that a great number of the crossfield pits between horizontal rays and vertical tracheids show an open structure with partly loosened or ruptured pit membranes. No clear difference in share of open crossfield pits is seen between the 60°C and 170°C. A comparison with untreated, fresh pine sapwood in c) shows that these crossfield pits lack the open structures.

a)



b)

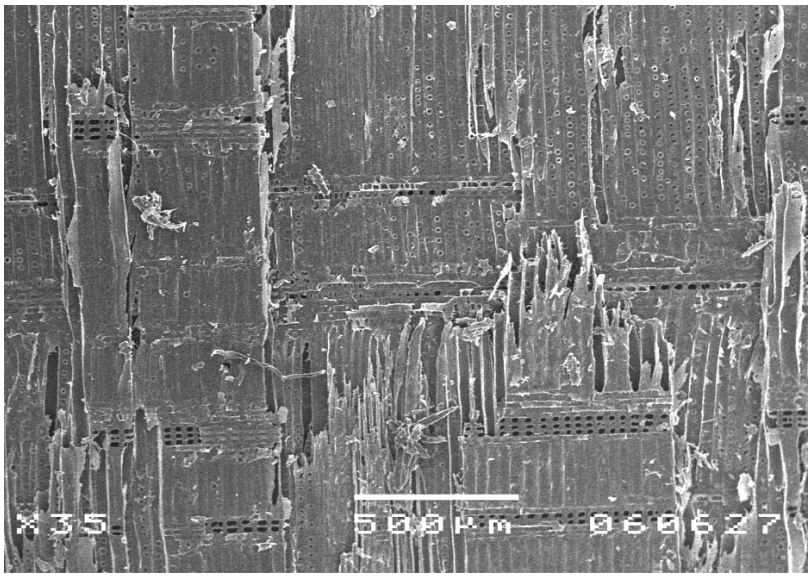


Figure 7.6 a) Radial surface of pine sapwood dried at 60°C.
b) Radial surface of pine sapwood heat-treated at 170°C.

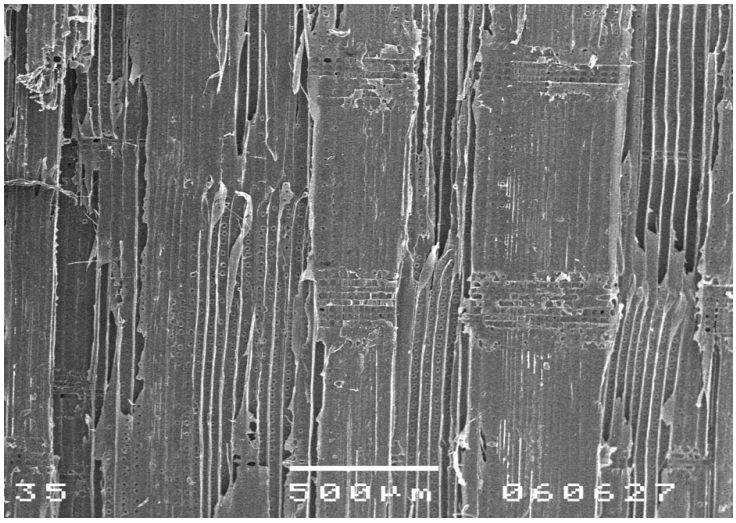
c) 

Figure 7.6 c) Radial surface of fresh, not artificially dried pine sapwood (Paper VII).

Magnifications of the crossfield pits in pine sapwood heat-treated at 170°C seen in Figure 7.7 show an example of crossfield pits with loose or missing membranes (left) and ruptured membranes (right).

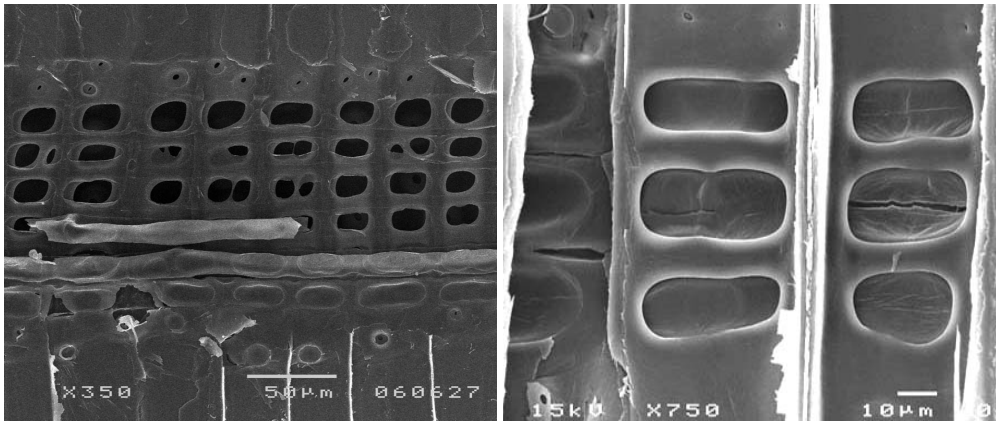


Figure 7.7 Details of crossfield pits in pine sapwood heat-treated at 170°C. Left: Main parts of the pit membrane have come loose. Through the open fenestriform pit opening, it is possible to see the bordered pit in the neighbouring tracheid behind.
Right: Membranes in earlywood partly ruptured. (Paper VII)

Pine heartwood

The crossfield pits in pine heartwood shown in Figure 7.8 appear to lack the occurrence the open, ruptured fields found in heat-treated pine sapwood.

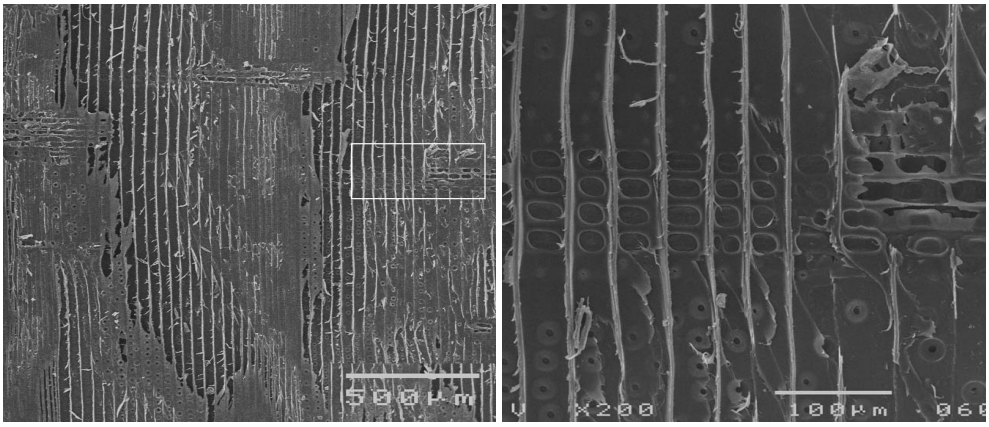


Figure 7.8 Left: Radial surface of pine heartwood heat-treated at 170°C. Right: Detail from figure a) showing crossfield pits with intact membranes. (Paper VII)

Discussion

Judging from the SEM photos, the occurrence of open, partly open and ruptured membranes in the crossfield pits in dried and heat-treated pine sapwood is fairly common. Even if there is a risk that some of this damage was caused when preparing the SEM specimens, there is no doubt that considerably fewer such areas are found on fresh surfaces split in the same way. These open structures in the ray structures of pine sapwood are probably the primary explanation for the effective water uptake in pine sapwood as compared to spruce sapwood reported in Paper VI.

Fewer such open crossfield areas are found in pine heartwood, where water uptake is considerably lower. One hypothesis suggested to explain this is that during heartwood formation in the standing tree, the dying parenchyma cells are slowly emptied of their liquid protoplasm. In green sapwood lumber, however, the living parenchyma cells are emptied much faster during kiln drying. During this fast emptying, the thin membranes in the large fenestriform crossfield pits are subjected to strains that might rupture and damage the membranes. Since no difference in share of open crossfield pits was found between the pine sapwood material treated at 60°C, 170°C and 200°C, the damage probably occurred during the initial, capillary drying stage.

The results from the SEM studies can be summarized as follows:

- Crossfield pits between longitudinal tracheids and radial ray parenchyma cells in heat-treated and dried pine sapwood were found to be considerably more open than those of not artificially dried sapwood. The membranes in the fenestriform pits were found to be partly loose or ruptured. No difference in share of open crossfield pits was found between the 60°C, 170°C and 200°C material.

- Crossfield pits in pine heartwood did not show the same occurrence of open, ruptured fields found in heat-treated pine sapwood. A hypothesis involving the emptying of the parenchyma cells has been suggested to explain this observation.

- In spruce, the crossfield pits seemed to be unaffected by heat treatment and drying as compared to fresh, green spruce sapwood.

- The open crossfield structures between ray parenchyma and longitudinal tracheids in heat-treated pine sapwood are believed to play an important role in explaining the differences in water absorption between pine and spruce sapwood.

- In birch, no visible differences in microstructure that could clarify the observed large difference in capillary water absorption were found when comparing the three different treatment temperatures.

8 WOOD AND COLOUR

The colour of wood is an important aesthetic concern for customers of wood products. Trends favouring blond, light Scandinavian species in furniture vary with periods of darker fashion. Thus, colour changes in wood during drying and heat treatment are a matter of interest. Colour changes might be unwanted and thus be called discolouration on the one hand, or they might be intentional, as in heat treatment, where one objective is to achieve darker hues.

Research on colour development and its dependence on process has been intense during the last decade. Sundqvist, in his thesis (2004), studied the colour stability of wood exposed to UV light and colour development in birch, pine and spruce during hydrothermal treatment, with special reference to treatment at temperatures between 65°C and 95°C with high MC. Colour changes in hardwood, with special reference to beech and birch, during kiln drying were reported by Stenudd (2002) in his thesis.

The colour of natural wood is related to chromophores among extractives in wood (Burtin *et al.* 1998) and in the lignin. When wood is exposed to high temperatures, aldehydes and phenols are formed, which leads to the formation of coloured compounds after chemical reactions (McDonald *et al.* 2000), as seen in the dark-coloured staining of the outer shell of drying sapwood known as KBS, a result of the accumulation of sugars towards the surface during the capillary phase of drying.

8.1 CIE colours and colour spaces

The expression *colour* often means a subjective experience dependent on the available light source, surface properties and the individual viewer's eye. In order to study colour changes, colour has to be measured in an objective way. A method of expressing colour numerically was developed by the Commission Internationale de l'Eclairage (CIE). The method is defined for a "standard observer" based on a large number of individuals' experiences of basic colours whose spectral distributions have been measured with a spectrometer. Numerical values of colour coordinates for a specified light source are then expressed in three-dimensional colour spaces; for example, CIE L*a*b* or CIE L*C*h* according to the CIE standard (Hunt 1995). Coordinates expressed in these two spaces can be translated into each other geometrically, since L*C*h* uses cylindrical coordinates (see Figure 8.1).

For the colour measurements performed in the studies presented here, a photoelectric colorimeter (Minolta Chroma Meter CR310) was used, with chosen colour coordinates expressed in the CIE L*C*h colour space where:

- L* is a measure of lightness from 0 (black) to 100 (white),
- C* is the chroma from 0 (pure grey) to more saturated colour the higher the value,
- h* is the hue angle where 0° is red, 90° is yellow, 180° is green and 270° is blue.

A measure of colour difference ΔE^*_{ab} between two samples can be expressed as the distance between two points in the three-dimensional colour space. ΔE^*_{ab} describes the size of a colour difference, but not the direction in the colour space. A colour difference ΔE^*_{ab} of 1–3 units is the smallest difference that can be discerned by the human eye (Terziev and Boutelje 1998).

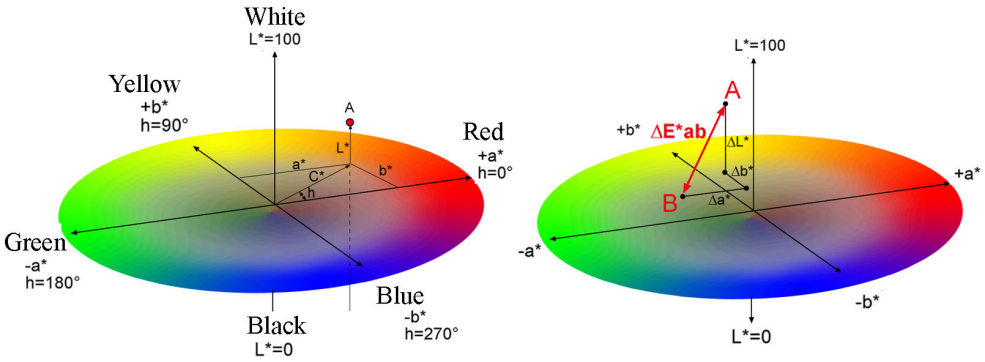


*Figure 8.1 CIE L*C*h*and CIE L*a*b* colour space with colour coordinates and colour difference ΔE^*_{ab}. (Figure from Sehlstedt-Persson 2002).*

8.2 Results from measurements—Response: colour changes upon heat treatment

In Paper IV, extraction of heartwood and sapwood of pine and spruce was done in the study of diffusivity and its dependence on extractive content. One notation from this work was that extractives collected in glass beakers varied in colour between individual samples (see Figure 3.12). Out of curiosity, I heated the glass beakers with collected extractives in an oven at different temperatures. The result of this was an obvious response to heating, with a marked change in colour, increasing with temperature. This lead to the idea of heating different wood constituents separately, work presented in Paper V, in order to investigate colour responses of xylem sap and extractives. Some preliminary tests of extractive-free wood were also done.

Samples from winter-felled pine and spruce timber were used. Xylem sap from sapwood was extruded by mechanical compression, filtered and put into 30 ml glass bottles. A TLC (Thin Layer Chromatography) test of the sap ensured that no extractive remainders were present in the extruded sap. Heat treatment was performed at 60°C, 70°C, 80°C, 90°C and 95°C for 1, 2, 3, 4 and 5 days. Since direct colour measurements in liquid were impossible to perform with the colorimeter, a relative method was used with colour measurements on filter papers soaked with the heat-treated sap.

Results from measurements of heated sap show a clear influence of temperature and time on colour coordinates L* C* h*. The sap became darker and more reddish. Pine sap showed significantly greater change at 5% level of significance than spruce sap. This difference might be explained by the fact that the dry content in pine sap was higher (pine sap 0.32%, spruce sap 0.17%), which indicates a higher carbohydrate content. In pine sap, an accelerated colour change was noted at temperatures exceeding 70°C (see Figure 8.2).

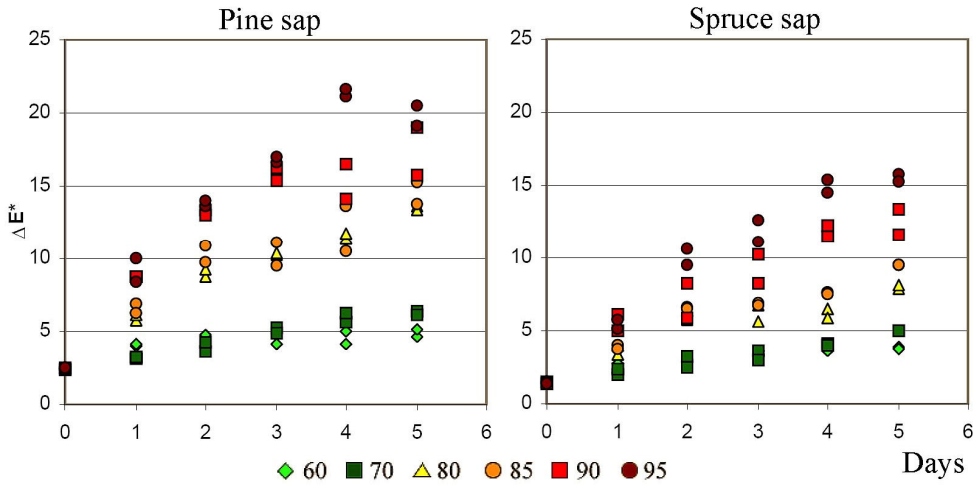


Figure 8.2 Colour difference ΔE^*_{ab} of filter paper before and after soaking with heated sap. The colour difference is caused by heat treatment of sap at different temperatures and durations (Paper V).

For practical reasons, only extractives from pine heartwood were investigated. Extractives were collected by acetone extraction in a Soxhlet extractor. After filtration, the dissolved extractives were distributed in Petri dishes which were heat-treated in the same way as the sap. Colour measurements were made through

the bottom of the glass dishes towards a reference panel in a screen box before and after heat treatment.

For heated extractives, the colour response was considerable, as seen in Figure 8.3. The colour difference ΔE^*_{ab} between unheated and heated extractives shown in Figure 8.4 clearly demonstrates the impact of temperature and time on colour response. An accelerated colour difference was found at temperatures exceeding 70°C.

Multiple linear regression models, with the colour difference ΔE^*_{ab} as a function of time and temperature, show r^2 values of approximately 0.9 for both sap and extractives.

Some preliminary tests with heat treatment of extractive-free wood in wet and dry state showed that heating in wet state causes a notable change of colour, as seen in Figure 8.5. Formation of coloured degradation products deriving from hydrolysis of hemicelluloses may explain the phenomenon.

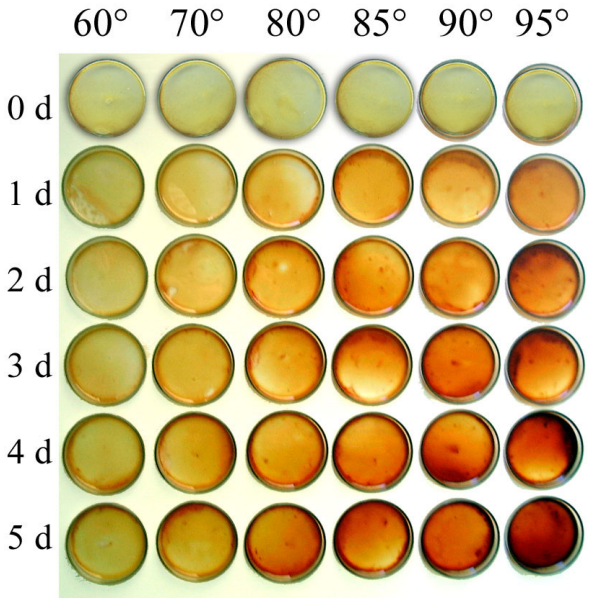


Figure 8.3 Collected pine heartwood extractives heat-treated at different temperatures and durations. (Paper V)

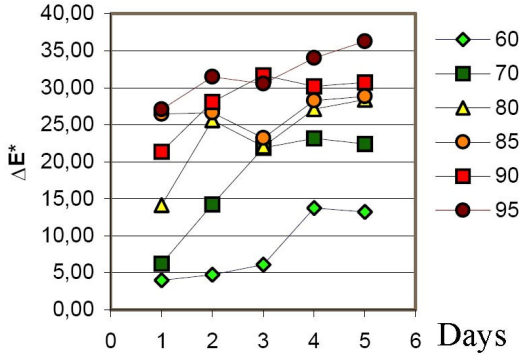


Figure 8.4 Colour difference ΔE^*_{ab} of pine heartwood extractives before and after heating at different temperatures and durations (Paper V).

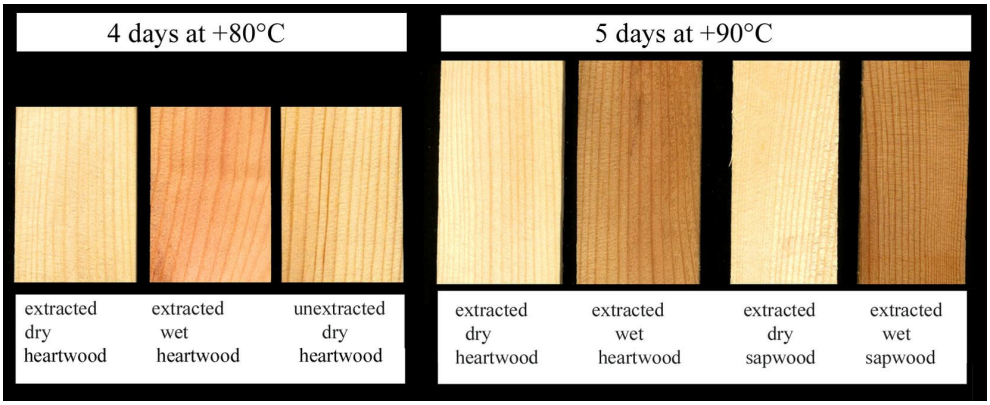


Figure 8.5 Preliminary tests with extracted and unextracted pine wood, heat-treated in dry and wet state (Paper V).

The results from Paper V show that heating causes clearly noticeable colour changes in sap as well as in extractives. The preliminary tests with heating of extractive-free wood indicate that heating in wet state also causes perceptible colour changes in the wood tissue.

9 CONCLUSIONS

During drying and heat treatment, wood is exposed to a hygrothermal process during which wood properties are chemically and physically affected, resulting in responses on a microscopic as well as on a macroscopic level.

A brief summary of the main results in this thesis, with the main object to study the interaction between the wood material properties and the drying and heat-treatment process in terms of material responses, are presented in the following three areas:

- **Responses**
- **Material properties**
- **Process dynamics**

Responses

Strength responses

The hypothesis that a decrease of various strength properties occurs in wood exposed to hygrothermal processes was tested. The following results were found:

Surface hardness

No difference was found between LT-, LT/HT- or HT-dried pine wood.

Shear strength

A decrease in shear strength along grain direction was found for HT-dried pine as compared to LT- and LT/HT-dried pine.

Cleavage strength

No unambiguous decrease in cleavage strength was found for HT-dried pine wood as compared to LT- or LT/HT-dried material.

Toughness

Density and annual-ring width had a greater impact than drying temperature in comparisons of HT-dried spruce to LT-dried spruce. A tendency toward decreased toughness for HT-dried spruce was found, but not at a significant level.

Moisture-related responses

The hypothesis that wood exposed to hygrothermal processes decreases in hygroscopicity, increases in dimensional stability and undergoes changes in its ability to transport capillary water was tested. In order to shed light on questions arising from the study of capillary water absorption SEM studies of the anatomical microstructure were done. The following results were found:

Sorption/desorption
HT-dried pine showed 1.4%–2.4% lower EMC than LT- and LT/HT-dried pine in sorption tests at 47.5°C. Smaller differences were found in desorption tests, 0.5%–1.7%.

The hysteresis effect was more pronounced for HT-dried pine than for LT/HT- and LT-dried pine, with up to 2% EMC difference between sorption and desorption isotherms.

Compared to initial desorption for green, undried pine, the desorption isotherm showed lower EMC for HT-, LT/HT- and LT-dried pine.

Remoistening of heat-treated birch up to MC above FSP seems to lead to regained hygroscopicity.

Dimensional stability
After exposure to a number of cyclic climate changes, LT-, LT/HT- and HT-dried pine and spruce reached a fairly constant value of less than 0.2% radial movement per change in MC. Thus no difference between drying methods was found.

Maximum shrinkage down to 0% MC was higher for LT/HT- and HT-dried pine and spruce than for fresh wood oven-dried from green state to 0% MC.

Capillary absorption in dried and heat-treated birch, pine and spruce
Heat treatment results in a decreased ability to transport free water in the longitudinal direction in all wood types studied except for pine sapwood. In pine sapwood, transport capacity was at a maximum at 170°C treatment temperature.

Pine sapwood shows a considerably higher increase in average MC at all treatment temperatures after 15 days of absorption than pine heartwood and spruce sapwood and heartwood. The differences between spruce sapwood, spruce heartwood and pine heartwood are small. All show approximately the same behaviour with low moisture uptake, though the biggest increase in samples treated at 170°C.

Anatomical SEM studies
SEM studies of pits and membranes showed that crossfield pits between longitudinal tracheids and radial ray parenchyma cells in heat-treated and dried pine sapwood were considerably more open than those of not artificially dried sapwood. No difference in share of open crossfield pits was found between the

artificially dried wood at 60°C and heat-treated wood at 170°C and 200°C. In spruce, the crossfield pits seemed to be unaffected by heat treatment and drying as compared to fresh, green spruce sapwood. The open crossfield structures between ray parenchyma and longitudinal tracheids in dried and heat-treated pine sapwood are believed to play an important role in explaining the differences in water absorption between pine and spruce sapwood.

Colour responses

The hypothesis that wood exposed to hygrothermal processes exhibits colour changes was tested. The following results were found:

Pine sapwood exposed to high temperature exhibits KBS discoloration in a zone just beneath the board surface. SEM studies of this zone showed tracheids more or less filled with amorphous substances deriving from the accumulation of sugars towards the evaporation surface early in the drying process.

Heating of separate wood constituents caused obvious colour changes for sap and extractives as well as for extractive-free wood. Colour changes increased with time and temperature. An accelerated colour change was found for pine sap and pine extractives at temperatures exceeding 70°C.

Mould growth

The hypothesis that wood exposed to hygrothermal processes changes in its susceptibility to mould growth was tested. The following results were found:

A small study in an 8-week mould growth test on dried pine sapwood surfaces showed less mould growth on high-temperature dried wood compared to low/high-temperature dried and low-temperature dried wood.

Natural durability and phenolic content

The hypothesis that wood exposed to hygrothermal processes changes in its decay resistance was tested. The following results were found:

Mass loss in a 7-week brown rot test as a measure of durability showed that air-dried Scots pine heartwood showed better durability compared to kiln drying at 70°C, 90°C and 110°C.

The lowest durability was found when drying was performed at 90°C with high material temperature early in the capillary regime of drying when MC was high. The interpretation is that the duration of high material temperature at high MC is the critical combination for decay resistance in heartwood.

Steam conditioning after drying decreased the durability of sapwood.

In contradiction to other studies, no difference was found between the durability of inner heartwood and that of outer heartwood.

The relation between mass loss in rot tests and concentration of total phenolics in pine heartwood showed a weak negative correlation, as did the relation between mass loss and density. Heating of extractive-rich green sawdust indicated a reduction of phenolics with temperature and time.

Material properties

The objective has been to study wood diffusivity (the ability to transport water vapour), which is of major importance for the drying process in the diffusion-controlled later stages of drying.

Diffusivity as a function of extractive content

The hypothesis that diffusivity in pine and spruce is affected by extractive content was tested. The following results were found:

Density had a greater effect than extractive content on diffusivity for pine and spruce.

Pine heartwood, with its fairly high extractive content, behaved differently from pine sapwood and spruce. As expected, diffusivity decreased with increased extractive content.

Pine exhibited lower diffusivity than spruce, but when extractives were removed from pine heartwood, no difference was found in diffusivity between extractive-free pine heartwood and pine sapwood or spruce heartwood when comparing unpaired groups on average level.

Diffusivity in different directions

The hypothesis that diffusivity in pine sapwood varies in different main directions was tested. The following results were found:

The relation between diffusion coefficients in tangential, radial and axial directions for pine sapwood were found to be 1:1.8:7 respectively.

Process dynamics

The objective has been to study the development of a dry shell formed in the outer parts of a drying sapwood board early in the drying process. The following results were found:

The establishment of a thin dry shell in drying pine sapwood boards early in the drying process was demonstrated, based on temperature and mass-flux measurements. A fairly good agreement was found between calculated dry-shell thickness based on temperature measurements and dry-shell thickness analysed by CT scanning. SEM studies of the dark-coloured shell zone in pine sapwood supported the findings.

Concluding remarks

The main objective of this thesis is to build knowledge about the interaction between wood material properties and the drying and heat-treatment process in terms of material responses.

One example of gained knowledge is the phenomenon of formation of a receding evaporation surface in sapwood early in drying. This is supported by studies in the CT scanner, by temperature and flux measurements and by SEM studies of the dark coloured shell beneath the surface, which was first observed in the work presented in Paper I.

Another example is the hypothesis suggested to explain the difference in capillary water absorption between pine sapwood and pine heartwood with regard to ray parenchyma. During heartwood formation in a standing tree, the dying parenchyma cells are emptied slowly, while in green sapwood, the living parenchyma cells are emptied much faster during kiln drying, resulting in large capillary strains on the fenestriform pit membranes, which might lead to ruptured membranes and hence more effective water absorption.

Hopefully, the benefit of the compiled conclusions in this thesis will contribute to the knowledge base on which decisions are made regarding choice of material and control process parameters in order to achieve desired quality in end products. For instance:

- Avoid high material temperature early in drying when MC is high in order to maintain the natural durability of Scots pine heartwood

- A suitable choice for wood in outdoor applications in terms of capillary water absorption is pine heartwood, spruce sapwood and spruce heartwood, which all show equivalent low capillary water transport ability. Heat treatment decreases absorption capacity.

- Avoid pine sapwood in outdoor applications in terms of capillary water absorption because of its large water absorption capacity.

10 FUTURE WORK

Research and development within the area of wood drying will hopefully continue in the direction of doing more than just drying the wood. New technologies such as laser, UV-fluorescence and x-ray scanning in combination with image processing enable sorting of lumber on the basis of such varying features as heartwood content, density, moisture content, fibre angle, *etc*. This, in combination with increased knowledge of material responses in the drying process, makes it possible to control the process to attain desired quality in end products. This strategy might contribute to an added value in sawmills and in the woodworking industry.

The growth of mould on dried boards in outdoor applications is an increasing problem. Future work should focus on the natural durability of wood and on the study of how to control the material and the drying process in order to mitigate or prevent mould growth on dried boards in outdoor use.

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Paper I

S.M.B. Sehlstedt-Persson
High-temperature drying of Scots pine. A comparison between HT- and LT-drying
Holz als Roh- und Werkstoff 53, (1995) 95-99

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High-temperature drying of Scots pine. A comparison between HT- and LT-drying

S. M. B. Sehlstedt-Persson

Abstract

In order to study the influence of high temperature on wood properties, boards from Scots pine were dried at three different schedules, two high-temperature-schedules (HT) and one at low temperature (LT). Strength properties as hardness, cleavage- and shear-strength were determined and sorption/desorption behaviour were studied. Material was analysed concerning carbohydrate and extractive content and mould growth test at wooden surfaces. Results showed a significant influence of temperature on decreasing shear strength and equilibrium moisture content (EMC) in sorption/desorption tests. Sorption/desorption tests resulted in up to 2.4 % lower EMC for HT dried material at the same climate compared with LT-dried and the hysteresis effect seems to be more pronounced in HT-dried material. Mould growth test showed an inhibiting effect of HT-drying on mould susceptibility at wooden surfaces. Carbohydrate analysis revealed a lower content of hemicelluloses in HT-dried boards which indicates a decomposition of the hemicelluloses explaining the decrease in shear strength and hygroscopic moisture uptake seen in the HT dried boards.

Hochtemperatur-Trocknung von Kiefernholz. Vergleich zwischen Hoch- und Niedrigtemperatur-Trocknung

Um den Einfluß erhöhter Temperatur auf die Holzeigenschaften zu bestimmen, wurden Bretter aus nordischer Kiefer nach verschiedenen Trocknungsplänen, zwei bei hoher Temperatur, einer bei niedriger Temperatur, getrocknet. Härte, Bruch- und Scherfestigkeit wurden bestimmt, sowie das Sorptions- und Desorptionsverhalten untersucht. Zuckeranalysen, Bestimmung des Extraktstoffgehalts und des Pilzwachstums an der Oberfläche wurden an den Proben durchgeführt. Die Temperatur hatte einen signifikanten Einfluß auf die Scherfestigkeit und die Gleichgewichtsfeuchte. Die Sorptions-/Desorptionsversuche führten bei gleichem Konditionierungsklima zu einer um 2.4 % niedrigeren Endfeuchte der HT-getrockneten Proben, bei denen auch der Hysterese-Effekt stärker ausgeprägt erschien. Pilzwachstumstests zeigten eine Hemmung der Pilzentwicklung an der Oberfläche der HT-getrockneten Proben. Bei diesem Proben ließen die Zuckeranalysen auch einen Abbau der Hemicellulosen erkennen, wodurch die Abnahme der Scherfestigkeit und der Feuchteaufnahme der HT-getrockneten Proben erklärt werden kann.

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1 Introduction

Drying of timber at temperatures above the boiling point of water, i.e. high-temperature drying, was used in Sweden for pine and spruce timber until the fifties but was then abandoned. Today this time-saving technique witness a renaissance when knowledge about the advantages of raised temperatures on checking and mould susceptibility has been obtained.

However, HT-drying of wood leads to visible changes of the timber such as discolouration and severe resin flow. Some of these changes are only linked to the surface so planing of the timber removes these effects. Experiences from earlier work (Morén, Sehlstedt-Persson 1990) show that HT-dried Scots pine wood gives a hard and brittle impression and that considerable discolouration appears at the surface and in some cases throughout the timber. The wood also has a characteristic odour of burnt wood. Since we know that wood, as a biological material is subjected to a degradation process during exposition to high temperatures, the need for investigation of different properties as strength and moisture behaviour arises.

Temperature effects on different wood properties for different species has been performed and reviewed by, among others, Hillis (1984) and more recently by Teischinger (1991). In general, different strength properties as shear and crushing strength are reduced at high temperatures compared with LT-drying, to what extent is strongly dependent on species but also on time for exposure to high temperature. Generally, this reduction of strength properties is assigned to a loss or change of the hemi cellulose fraction which is considered to act as a connecting agent between cellulose and lignin.

Wood that has been exposed to high temperatures is less hygroscopic (Espenas 1971, Kininmonth 1976, Price and Koch 1980 e.g.). This effect is obviously dependent on exposure time. Espenas found that the effect of temperature on reduction of hygroscopicity was pronounced above 65°C. Price and Koch showed that the reduction in moisture uptake for HT-dried Southern pine is permanent after one year of storage. Also here the probable explanation is found in the decomposition of hemicelluloses. Hinterstoisser et al. (1992) found an increase of hot water extractible carbohydrates in HT-dried material which she interprets as a decomposition of the hemicelluloses.

Theander et al.(1993) show an accumulation of low-molecular carbohydrates and nitrogen at the surface during the drying process for Pinus silvestris with higher concentrations in winter felled timber. Hinterstoisser et al. (1992) report higher carbohydrate concentration in sapwood from winter-felled Picea abies and also a tendency to variations within the living tree in direction north/south. Terziev et al. (1993) show that the drying rate has a significant effect on the distribution of sugars towards the surface. Thus, enrichment of nutrition at the surface during the accelerated HT-drying is expected in the sapwood where the nutrition is located in a living tree. Enrichment of nutrition towards the surface provides a good condition for mould germination. Theander et al. (1993) and Terziev

(1994) show that rapid drying at low temperatures increases mould growth at wooden surfaces. A legitim question is if this could be seen as an advantage if this outer part is removed by planing.

The objective of this study was to investigate the influence of drying temperature on different specific properties of timber from Scots pine. Strength properties, sorption/-desorption behaviour, discolouration and mould susceptibility are important properties in common use and of great interest to examine for this commercial species.

2 Materials

Boards, 63x150 mm from Scots pine (*Pinus silvestris*) randomly selected from a local sawmill, were dried at three different drying schedules according to Fig.1. Series A dried from green to 5% MC with a rapid increase in temperature up to 115°C (HT-dried), series B dried from green to 12 % MC, beginning at 50°C and finished at 100°C (LT/HT-dried) and series C with pre-dried boards dried from 20 % MC to 8% at temperatures below 65°C (LT-dried). The boards were then stored more than 1 year at 20°C with a relative humidity (RH) of 25-40 %. During this time the moisture content was equalised to equilibrium.

From each series 30 boards were selected and the density in each board was determined by CT- scanning at approximately 6% MC. Samples were cut from each board to investigate surface hardness, shear strength, cleavage strength and sorption/desorption behaviour.

One noticeable effect of HT-drying on the material used in this study was the presence of a distinct dark coloured shell, about 1 mm thick, just beneath the surface. This indicates a chemical change of the wood material during exposition to high temperatures which might affect the mould susceptibility. From each series a few samples were selected for carbohydrate and extractives analysis and mould growth test at SUAS (The Swedish University of Agricultural Sciences) in Umeå and Uppsala.

Statistical analysis was applied on the results in order to find significant differences at 5 % significance level between the three drying methods, using STAT GRAPHICS Plus, PC-program. Multiple regression analysis was also applied on the results using the same program.

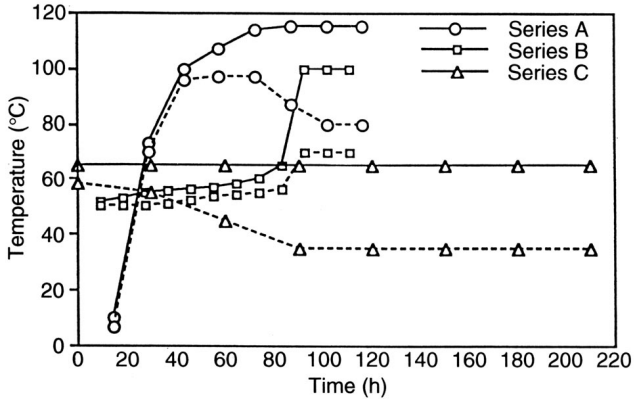

Fig.1. Drying schedules for series A-C. Solid line=dry bulb temperature, dotted line= wet bulb temperature.

Bild 1. Trocknungspläne für die Serien A-C. Durchgezogene Linien: Trockentemperatur; unterbrochene Linie: Feuchttemperatur

3 Test methods

3.1 Surface hardness

Surface hardness test was carried out using an Instron 1185 testing machine where registration was made of the force required to embed a steel ball with 10 mm diameter into the wooden surface opposite the pith to a depth of 4 mm at a speed of 5 mm/minute, Fig.2. Two measurements were made on each sample with notations if the position was in sapwood or heartwood.

3.2 Shear strength

Shear strength along the grain direction was determined at three positions in each sample, 15, 30 and 45 mm from the sapwood side according to Fig. 2 where the force at failure was registered. The distance from the pith was measured at each position since the pith position within cross-sections varied.

3.3 Cleavage strength

Cleavage test was carried out in accordance with ASTM D143 with the exception of shorter length than prescribed because of dimension; 80 mm instead of 95 mm. Registration of the force at failure was made at cleavage perpendicular to the grain direction using an Instron 1185, Fig.2.

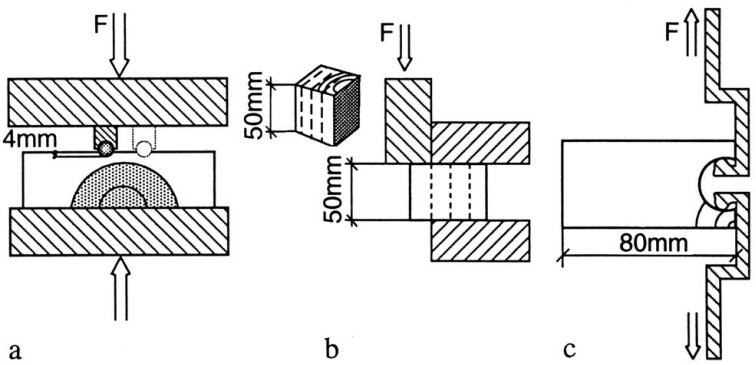

Fig.2. Equipment for measuring: A) surface hardness B) shear - C) cleavage strength. F: Direction of the applied force.

Bild 2. Anordnung zum Messen: A) der Oberflächenhärte B) der Scher- C) der Spaltfestigkeit. F: Richtung der aufgebrachten Kraft.

3.4 Sorption/desorption test

Samples for sorption/desorption test were cut from the board edge with dimension 60 x 50 x 7 mm in order to get mainly sapwood. However, some samples contained both sap and heartwood. Sorption/desorption tests were made in a climate chamber at constant temperature 47.5°C with stepwise increased RH for sorption test: 47, 53.5, 66, 72, 86.5 and 88 % RH, and decreased for desorption test: 89, 85, 78, 66, 54 and 47 % RH. Each climate was held constant until no weight change was noticed and equilibrium was reached. Opening the climate chamber caused disturbances in climate and in moisture content during the weighing procedure, especially at high RH. To minimize the error the weighing order of samples were randomly selected.

Thermocouples connected to a datalogger were registering the climate two times per hour. After finishing the tests all samples were oven-dried at 103°C for determination of oven-dry weight and calculation of moisture content.

3.5 Mould growth

Samples were cut from the board edge and mould growth was tested at SUAS. The samples were inoculated with a spore suspension of *Penicillium brevicompactum* and kept at 23°C and 100 % RH for 8 weeks. Mould growth at the surfaces was examined visually and estimated according to a 5 step grading system from 0-4; 0 means no mould growth and 4 means very vigorous growth. Six parallels of each material were used in the tests.

3.6 Carbohydrate and extractives analysis

Carbohydrate and extractives analysis were made on parts of the material at SUAS. Analysis of the monosaccharide content of arabinos, xylos, mannose, galactose and glucose

using gas-chromatography, was made for series A and C for sapwood and heartwood. Analysis of ethanol soluble extractives content was made for all series.

4 Results and discussion

4.1 Surface hardness

Results from surface hardness tests are presented in Table 1. No significant difference was found between the series or between position in sap or heartwood at 5 % significance level.

Linear regression analysis of the surface hardness dependence on density for all three series gave the equation:

$F = -344 + 4.7\,\rho$, $r^2 = 0.66$ where ρ is the density (kg/m^3) [1] at 6 % MC.

4.2 Shear strength

Shear strength (T) measured along the grain direction at three positions in each sample is presented in Table1. Statistical analysis showed a significant difference at 5 % significance level between series A-B and between A-C at all three positions but not between B-C. Multiple regression analysis showed no clear correlation between shear strength and density or measured distance to pith even if the average results indicate a decrease in shear strength towards the pith in all the three series.

4.3 Cleavage strength

Results from cleavage test perpendicular to the grain are shown in Table 1. Statistical analysis showed a significant difference at 5 % significance level between series A-B but not between A-C and B-C. The position of the pith in the cross sections varied in some samples which probably affects the cleavage strength and the reliability of the analysis. Two types of failures were noticed, both types of the same frequency; failure perpendicular to annual rings along rays and failure along an annual ring, typically following the earlywood zone or the border earlywood-latewood. In samples where the pith was situated within the cross-section, as for 4 samples in series C, the failure ran along the direction to the pith at relatively low load.

4.4 Sorption /desorption

Sorption and desorption isotherms at 47.5°C for series A-C are shown in Fig.3. A significant difference at 5 % significance level exists between all three series in sorption test. The HT dried wood (series A) has between 1.4-2.4 % lower EMC than the LT dried wood (series C) and the LT/HT dried material somewhere in between (series B). As can be seen in fig.3 a given change in RH results in approximately the same moisture uptake for all three series, though on different levels.

[1] Corrected from published version from km/m^3 to kg/m^3)

The desorption isotherm shows a similar relation but with less pronounced difference between the series, 0.5-1.7 % lower EMC for HT-dried material compared with LT dried, the higher value at higher RH.
The difference in EMC between sorption and desorption, that is the hysteresis effect, is greatest in the range of RH between 60-80 %, approximately 2 % for series A and B and 1% for the LT dried material in series C.
Disturbances in climate at high RH during the measuring procedure reveals in a greater standard deviation in EMC because of rapid changes in moisture content.

Table 1 Results as average values of: density, surface hardness, shear strength, cleavage test and mould growth for series A-C. 30 samples in each series except for mould growth test with 6 samples. s= standard deviation

	Series A (HT)	Series B (LT/HT)	Series C (LT)
Density at 6 % MC	452.2	463.6	463.9
s	40.3	29.1	41.3
Surface hardness Fs (N)	1841	1778	1782
s	304	224	254
Shear strength (MPa)			
T_1	8.4	9.8	10.2
s	1.5	1.1	1.0
T_2	8.1	9.3	9.3
s	1.2	1.1	1.0
T_3	7.5	8.7	9.2
s	1.1	0.9	1.3
T_1 - T_3	8.0	9.3	9.6
s	1.3	1.1	1.2
Cleavage F_C (N)	661.7	759.9	718.8
s	134.9	175.6	167.2
Mould growth grading	0.8	2.3	3.2

T_1=15 mm from sapwoodside, T_2=30 mm from sapwoodside, T_3=45 mm from sapwoodside
T_1 - T_3= average for all three positions in each series.

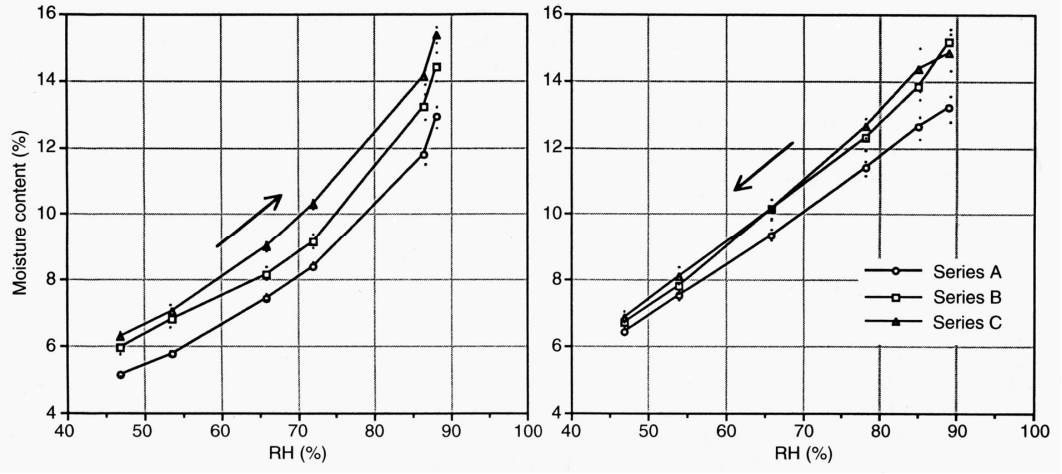

Fig.3. Sorption-(left) and desorption isotherms (right) at 47.5°C for series A-C with standard deviation. 30 samples in each series.

Bild 3. Sorptions-(links) und Desorptionsisotherme (rechts) bei 47.5°C für die Serien A-C mit Standardabweichungen. Jede Serie umfaßt 30 Proben

4.5 Discolouration

The distinct dark-coloured shell just beneath the surface was found in one third of the samples in the LT/HT series and in a majority of the samples in the HT series. This shell, shown in Fig.4, was typically found only in the sapwood and accentuated near the wane. The darkening of this surface-zone at elevated temperatures is probably explained by a decomposition of the nutrition located in the sapwood, which during rapid drying is distributed towards the surface. This thermal degradation of low-molecular carbohydrates, so called *caramelization,* is a process where sugar becomes darker, loses water and becomes more aromatic during heating. The presence of amino acids in combination with sugar during heating is another process that leads to discolouration and yellowing during drying, called Maillard reaction. Theander et al. (1993)

Variations in carbohydrate concentration depending on direction north/south in a living tree and on fell time reported by Hinterstoisser et al. (1992) could explain why some samples had more pronounced shell than others.

The discolouration throughout the cross-section in both sap- and heartwood in HT-dried wood indicates a caramelization-process of the decomposed hemi cellulose.

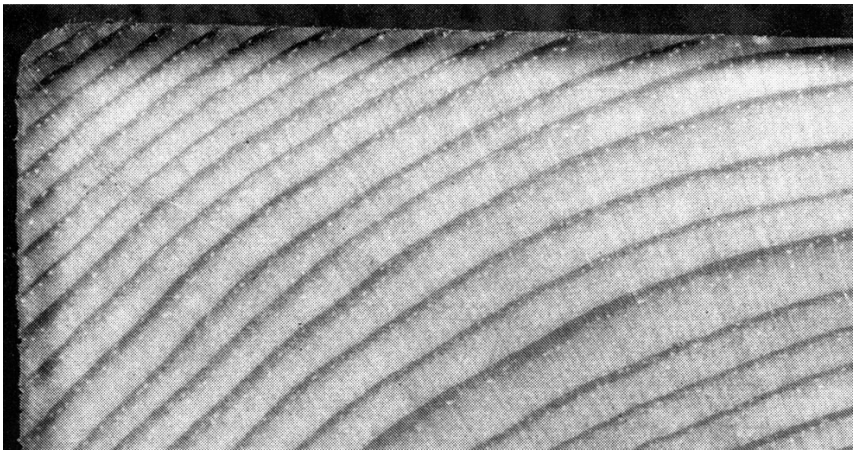

Fig.4. Dark coloured shell near the surface in HT dried sapwood.

Bild 4. Dunkelgefärbte Schicht dicht unter der Oberfläche eines bei hoher Temperatur getrockneten Splintholzes.

4.6 Mould growth

Results from mould susceptibility test performed at SUAS are shown in Table 1 where series A was estimated to have the slightest mould growth and the LT-dried material in series C the most accentuated growth. This test, performed only with a few samples, points at an inhibiting effect of HT-drying on mould susceptibility despite enrichment of sugar at the surface during rapid drying. Caramelization of the carbohydrates at elevated temperatures is probably the explanation.

4.7 Carbohydrate and extractives analysis

Carbohydrate analysis of the monosaccharide content in sapwood and heartwood in series A and C is shown in Table 2 and extractive content in series A-C. Wood that has been HT dried (series A) has a lower content of the monosaccharides from the hemi cellulose (arabinos, xylos, mannos and galactose) compared with LT dried wood (series C). The analysis includes wood taken from the outer parts of the boards with the dark-coloured shell. These preliminary results indicate a decomposition of the hemi cellulose during HT drying.

Extractive content is higher in heartwood than in sapwood in all three series. Series A has the highest total content which probably is explained by natural variations in wood. The difference in extractive content between sapwood and heartwood in each series is though larger in series A (2.2 %) compared with series B (1.4%) and the LT dried series C (1.2%). One explanation could be that HT drying leads to a larger loss of volatile extractive components from sapwood even if notable resin flow visually could be seen at HT dried surfaces.

Table 2 Results from carbohydrate and extractives analysis in percent of weight in the three series.

	Arab+Xyl+Man+Gal (%)	Glucose (%)	Extractives (%)
Series A			
sapwood	17.4	39.2	4.9
heartwood	18.2	35.8	7.1
Series B			
sapwood	-	-	3.7
heartwood	-	-	5.1
Series C			
sapwood	19.1	39.7	3.9
heartwood	19.7	35.4	5.1

5 Conclusions

The main conclusions from this comparison of different properties between boards from Scots pine dried with three different drying schedules are:

- no significant influence of drying method was found on surface hardness despite a general impression of "hard and brittle" HT-dried wood.

- a significant decrease in shear strength along the grain direction was found for HT dried compared with LT dried and LT/HT dried wood and a tendency of decrease in shear strength towards the pith in all series.

- cleavage test gave some indistinct results showing a significant lower force at failure for HT dried material compared with LT/HT drying, but not compared with the LT series. No difference was found between LT/HT and LT series. Pith position in cross-section varied and might explain the variations.

- sorption test at 47.5°C showed 1.4-2.4 % lower EMC for HT dried compared with LT dried wood in the range of 47-89 % RH. A smaller difference was found in desorption test, 0.5-1.7 %.

- the hysteresis effect was most distinct in the HT dried wood, up to 2%. Thus, there seems to be a significant influence of drying temperature on EMC for HT-dried material compared with LT-dried. The slope of the isotherms though are similar which means that

the change in EMC towards a change of RH in the case of pure sorption or desorption are equal in all series, which expects to lead to the same moisture related movement. In the case of oscillating humidity though, the hysteresis effect is more accentuated in HT-dried material and might decrease moisture related movement. [2]

- less mould growth was found at HT-dried wood surfaces.

- carbohydrate analysis showed that HT-dried wood had lower content of the monosaccharides that build up the hemi cellulose fraction compared with LT-dried wood which indicates a decomposition of the hemicelluloses. Hemicelluloses act as the connecting component between cellulose and lignin and are also the most hygroscopic component in wood. A decomposition of the hemicelluloses could therefore explain the decrease in shear strength and in moisture uptake for HT dried wood.

- the typical dark coloured shell found in HT-dried sapwood near the surface is probably explained by a thermal degradation of the carbohydrates which originates from the nutrition in sapwood which during rapid drying have been enriched at timber surface.

- discolouration throughout the timber can be considerable in HT-dried wood as a result of thermal decomposition of the hemicelluloses into low-molecular carbohydrates and other by-products during darkening.

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[2] Correction from published version where half this passage was printed twice

Terziev, N.; Boutelje, J.; Söderström, O.1993: The influence of drying schedules on the redistribution of low-molecular sugars in Pinus sylvestris L. Holzforschung 47(1):3-8
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Paper II

M. Sehlstedt-Persson
The effect of drying temperature on subsequent moisture and dimensional changes for Scots pine and Norway spruce
Holz als Roh- und Werkstoff 58 (5), (2000) 353
(brief original)

Kurz-Originalia · Brief Originals Holz als Roh- und Werkstoff 58 (2000) 353 © Springer-Verlag 2000

The effect of drying temperature on subsequent moisture and dimensional changes for Scots pine and Norway spruce

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Subject The effect of three different drying procedures on moisture and dimensional changes for Scots pine and Norway spruce during subsequent climate changes has been studied.

Material and methods Matched samples of 15 mm thick cross sections from 10 individual green planks (50x100mm^2) of pine and spruce respectively, were dried at three different temperature levels: LT, LHT and HT. In every case during the initial drying phase, the samples were kept in tight glass jars to extend the capillary phase. The drying procedures were performed as follows: LT drying with 48 hours in glass jars at +55°C dry bulb followed by 48 hours at +80°C/ 8%EMC. LHT drying with 48 hours in glass jars at +55°C dry bulb followed by 12 hours at +120°C in dry oven, and finally HT drying with 12 hours in glass jars at +120°C followed by 12 hours at 120°C in dry oven. After drying all samples were equalized in a climate chamber at +30°C/8%EMC for 109 days. After equalization the material was exposed to 6 cyclic climate changes followed by oven drying to 0%MC. In green state, after drying and after every climate change the test series were weighed and dimensional changes were measured on digital scanned grey-scale images. Maximal radial and tangential shrinkage, changes in MC and dimension from green state during cyclic climate changes were calculated and evaluated statistically in order to find if significant differences at 5% level exist between drying methods and species.

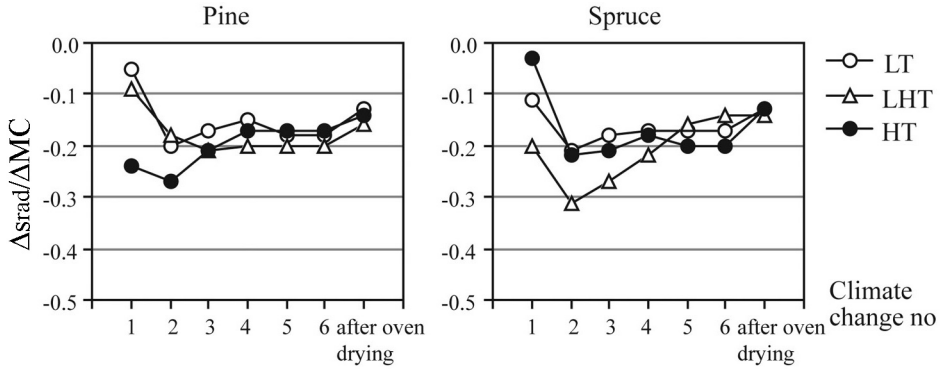

Figure 1 Changes in radial shrinkage from green state per change in MC (Δs_{rad} /ΔMC) during cyclic climate change for pine and spruce dried with three drying procedures.

Results and discussion.

The results are summarized as follows:

- Maximal shrinkage during drying in one step from green to 0%MC at +103°C for 12 hours was measured on a reference material. No difference exists between pine and spruce in maximal radial or tangential shrinkage for this reference material.

- LHT and HT dried material show, for both pine and spruce, significantly higher maximal radial and tangential shrinkage after final oven-drying down 0%MC, compared with reference material.

- HT dried spruce shows significantly higher maximal shrinkage at 0%MC compared with HT dried pine.

- During cyclic climate changes the HT dried material shows significant lower MC compared with LT and LHT series for both pine and spruce.

- The changes in shrinkage from green state (Δs_{rad}) during cyclic climate changes, i.e. the real displacement, show no obvious dependence on drying method. In case of significant differences, the LT dried materials show least changes i.e. are more dimensionally stable contradictory to the results from Sandlands (1999) investigation.

- During climate changes the change in shrinkage from green state /change in MC (Δs_{rad} /ΔMC) show no dependence on drying method or species according to figure 1. After some cycles a radial shrinkage value of < 0.2 %/%MC was reached (Sehlstedt-Persson 2000).

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Paper III

P. Wiberg, S. M. B. Sehlstedt-Persson, T. J. Morén
Heat and Mass Transfer During Sapwood Drying
Above the Fibre Saturation Point
Drying Technology, 18(8), 1647-1664 (2000)

HEAT AND MASS TRANSFER DURING SAPWOOD DRYING ABOVE THE FIBRE SATURATION POINT

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Key Words and Phrases: CT-scanning; dry shell formation; evaporation front; irreducible saturation; kiln brown stain; kiln dimensioning; moisture flux

ABSTRACT

Pine sapwood was dried in an air convection ki1n at temperatures between 60-80 °C. Temperature and weight measurements were used to calculate the position of the evaporation front beneath the surface. It was assumed that the drying during a first regime is controlled by the heat transfer to the evaporation front until irreducible saturation occurs. Comparisons were made with CT-scanned density pictures of the dry shell formation during initial stages of drying of boards.

The results indicate a receding evaporation front behaviour for sapwood above approximately 40-50% MC when the moisture flux is heat transfer controlled. After that we finally reach a period where bound water diffusion is assumed to control the drying rate.

The heat transfer from the circulating air to the evaporation front controls the migration flux. In many industrial kilns the heating coils therefore have too small heat transfer rates for batches of thin boards and boards with high sapwood content.

INTRODUCTION

The wood drying process has been widely studied on an industrial scale as well as in more controlled laboratory experiments. Also, many researchers have been working on models to describe the movement of water through wood during drying in moist air or in steam. Kamke and Vanek (1994) have done an extensive comparison of different wood drying models. Such models are commonly used for the development of drying schedules for batch kilns.

In many cases, modelling of the moisture flux above the fibre saturation point (FSP) is simplified to diffusion equation based models with the moisture content (MC) as the driving force. However, capillary mechanisms also may control the movement of the free water, and such models have been developed taking into account heat flux in the wood as

well as heat and mass transfer analogies at the surface (Luikov 1966 and others). Since such models result in transport coefficients that depend on moisture content and temperature, this raises an experimental problem of separating such independent coefficients in the evaluation of practical experiments.

Plumb et al. (1985) developed a set of governing equations for both capillary and diffusive transport of moisture during wood drying, including heat transfer at the surface. They used gamma ray attenuation to evaluate the moisture content in the wood. They assumed that all evaporation took place at the surface during the early phase of the drying process and that capillary transport of liquid to the surface dominated above the FSP. They concluded that the drying rate is diffusion controlled for low liquid permeability, while the convection mass transfer coefficient dominates at high permeability.

Hunter (1995) suggests very strongly that the gradient in capillary pressure is the driving force between continuous liquid saturation (CLS) and complete saturation. In the range from CLS to FSP, the major resistance to water movement might be evaporation and condensation. The CLS notation corresponds to irreducible saturation, which is defined as a state when the internal free water volume breaks up into regions with no liquid phase contact.

In general, evaporation is assumed to take place at the wood surface during drying in a regime well above the FSP. However, a receding evaporation front has been observed during experimental wood drying at high temperature in superheated steam (Beard et al. 1983-84) as well as the formation of a drier shell during low-temperature drying (Wiberg 1996). Beard et al. also modelled this behaviour and predicted a receding front, where the evaporation takes place as long as capillary forces move water from the interior at a rate corresponding to the evaporation intensity. The position of the evaporation front was determined from temperature measurements. A receding evaporation front has also been observed during drying of hygroscopic materials other than wood. Chou et al. (1997) investigated this experimentally during convective food drying (potatoes) based on temperature measurements.

Several researchers have used the concept of receding evaporation front, and the common way to model this behaviour is to assume that local thermodynamic equilibrium exists in the drier zone between the evaporation front and the surface. Stanish et al. (1986) used fundamental heat and mass transfer equations, which resulted in the prediction of a receding evaporation front. They assumed a water vapour partial pressure driven moisture flux in the dry zone between the evaporation front and the surface, however, with the water molecules in local equilibrium all the time during drying.

Salin (1996) has suggested a non-equilibrium model to account for the deviation from Fickian diffusion behaviour at a surface layer observed by several researchers. Surface emission coefficients deviate considerably from those expected from comparison with classical boundary-layer theory using Lewis's relation for the mass transfer coefficient. A satisfying explanation for this behaviour has not yet been presented.

From experiments in progress using CT-scanning of boards during drying in the low-temperature region (below 100 °C),Wiberg and Morén (1999) have shown that density profiles from interior wood well above the FSP decrease uniformly over the volume for sapwood of Scots pine as long as the drying progresses. (See also Wiberg 1995). This indicates an internal redistribution of free water with little resistance to the internal flux between tracheid cells, since no density gradients developed other than those initially present. The formation of a dry shell was also observed. That is a narrow region from the surface and inwards with a very steep density or moisture gradient. It should be noticed that since the wood shrinks negligibly above the FSP, the density is directly proportional to the moisture content, which simplifies the interpretation of the CT-images.

Terziev et al. (1993) and Terziev (1995) have shown that low-molecular sugars migrate outwards in the capillary region and collect just under the wood surface, causing brownish stain due to chemical modification, e.g. caramelization, showing the position of the evaporating front just below the surface. Kreber and Haslett (1997) attributed the so-called kiln brown stain (KBS) to the same phenomenon in Radiata pine after drying. Since KBS occurs only in sapwood, planing will reveal a dark-coloured surface. It is more or less pronounced depending on species, amount of available nutrients (felling time), drying temperature and time, and is typically developed in the region 0.5 mm under the surface down to a depth of 1.5 - 5 mm. KBS also occurs in Scots pine during drying at elevated temperatures (Sehlstedt-Persson 1995).

This phenomenon indicates a capillary sap migration during a substantial part of the drying period from the interior parts to an evaporation zone positioned in the region of brown stain.

An interesting notation is that the KBS zone occurs at the same depth as the dry shell found in CT-scanning of drying pinewood (Wiberg, Morén 1999). This supports the theory of an evaporation front beneath the surface, enclosing the continuous volume of capillary water, where nutrients are accumulated in the wood structure during evaporation of water.

Similar migration mechanisms are also present in other hygroscopic materials and also in similar systems where there is a more or less fixed edge or evaporation front, such as has recently been explained for a spilled coffee drop (Deegan et al. 1997). In this case, the evaporation flux causes the droplet to shrink by volume, but since the droplet's contact line is fixed, a compensatory liquid flow towards the edge is needed. Otherwise, the droplet's lateral dimensions would decrease, which is not the case.

The objective of the present study was to apply a simplified heat and mass transfer model to predict the observed moisture flux during drying over the FSP. This model was tested against experiments on temperature and weight measurements of samples of clear pine and compared with CT-scanned images of the density distribution of drying wood.

MATERIAL AND METHODS

Weighing during drying

The experiments were conducted in a small laboratory kiln where hot humid air was circulated in a chamber where the temperature and humidity could be controlled. The tested wood specimens were supported on a device connected to a balance and the weights of the specimens were measured every 30 minutes during the drying experiments (Fig. 1). By taking the difference between successive weightings, the moisture flux was calculated as an average for every time interval. During the drying period, the dry and wet bulb temperature was measured with thermocouples every 5 minutes in the circulating air as well as in the wood specimens, at the surface and 2 mm below the surface. The thermocouples were inserted in drilled holes (Fig.2). On the surface the thermocouple was placed under a thin flake of wood.

The specimens, 250-400 mm long boards with varying width and thickness, were freshly cut from logs of pine sapwood and insulated on five sides with glued aluminium foil and Styrofoam. The only open side was exposed to the air stream across the flat side perpendicular to the longitudinal direction of the board (Fig.2).

A number of test runs were performed according to Table 1. The air velocity in all test runs varied between 5.7-6.2 m/s.

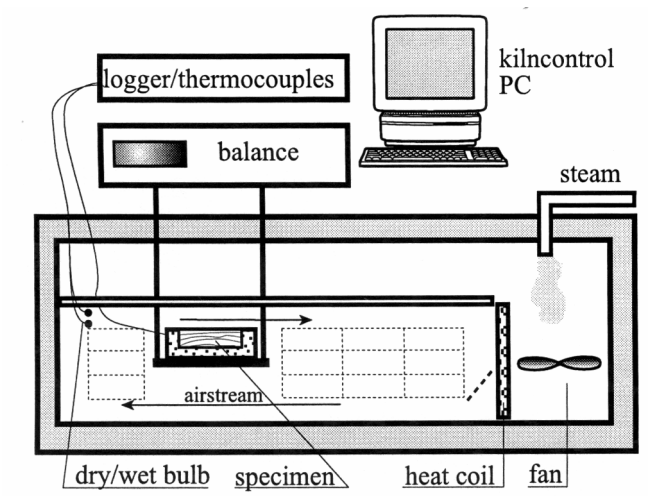

FIGURE 1. Experimental kiln with the specimen supported on a balance.

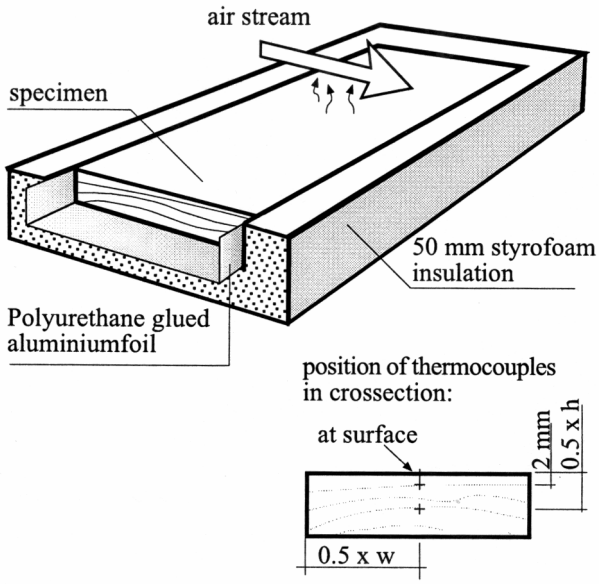

FIGURE 2 Test specimen of pine sapwood board insulated on all sides but one.

TABLE 1. Material and climate for all test runs.
(H = heartwood content of cross section)

Test	Dimension h x w x l (mm)	Density (kg/m^3)	MC start (%)	H[1] (%)	Climate Dry/Wet/EMC (°C /°C/%)
A	50x103x256	484	97	31	60/47.5/≈7
B	50x103x254	472	92	39	60/55/≈12.5
C	51x103x255	430	88	35	80/68/≈7
D	25x121x412	474	154	0	60/47.5/≈7
E	26x121x409	473	148	0	60/55/≈12.5
F	26x123x409	474	131	0	80/68/≈7
G	26x123x407	474	169	0	81/75/≈11

CT -scanning during drying

Specimens of green Scots pine (Pinus sylvestris) were dried in a specially designed drying chamber placed in a CT-scanner. The drying chamber was made of Lexan

[1] Corrected from published version from RH% to H% (heartwood content)

(Plexiglas) and had the form of a tube with a cross section 400 mm in diameter. The tube was connected to a climate chamber and placed in an ordinary Medical X-ray scanner, SIEMENS, SOMATOM AR. T. This experimental arrangement has been reported on earlier (Wiberg 1996).

The wood samples were stored in a freezer and wrapped in plastic bags prior to the test to prevent uncontrolled drying. Before the specimens were put into the drying chamber they were soaked in water in order to thaw and to ensure wetting of the surfaces. Each 100 mm-wide specimen was ripped into two halves approx. 45 mm wide. One half was planed and the other half was sawn on a circular saw to simulate the type of surface produced in a sawmill. By this method, the dry surface layer of the sample was removed and the wet sapwood was exposed.

Dimensions, climate conditions and initial MC of the wood samples are presented in Table 2. All samples in this experiment were 500 mm long and insulated on five sides with glued PVC foil and 50 mm thick Styrofoam.

The samples were continuously scanned every 10 minutes and one drying cycle lasted 17-24 hours depending on species and drying schedule. The scan settings were 110 kV, 100 mA current and 5 seconds scanning time. The scan thickness was 10 mm and the images were reconstructed using the Shepp-Logan reconstruction algorithm available in the CT-scanner.

A preliminary test was additionally made using Medium Density Fibreboard (MDF). The 30 mm thick board was soaked in warm water for about 24 hours in order to get the MC in the board to approximately 120%. The sample swelled and prior to drying the denser surface-layer was ripped off. As to the rest of the test, the previously described methods were used.

TABLE 2. Material and climate for test runs in the CT-scanner.

Test	**Surface treatment**	**Dimension h x w x l (mm)**	**Density (kg/m^3)**	**MC start (%)**	**Air velocity (m/s)**	**Climate Dry/Wet/EMC (°C /°C/%)**
1a	planed	26x47x500	399	147	2	50/29/4
1b	unplaned	27x47x500	420	143	2	50/29/4
2a	planed	26x47x500	430	139	5	50/29/4
2b	unplaned	27x47x500	459	117	5	50/29/47
3a	planed	23x47x500	448	119	2	80/56/4
3b	unplaned	27x47x500	483	127	2	80/56/4

Scanning electron microscopy (SEM)

Pine sapwood, dried at 50, 80 and 115°C, was studied in the region of the dry shell just beneath the surface using a Scanning Electron Microscope (Jeol, JSM-5200). Studies were made on transverse and radial surfaces.

EVALUATION

The evaluation of the experiments follows a stepwise procedure based on the temperature and weight measurements. The assumption is made that the evaporation initially occurs at the wood surface. As soon as the surface temperature increases above wet bulb temperature, the evaporation front is assumed to recede below the surface forming a dry shell layer below the surface. This results in the development of a temperature gradient in the sapwood, shown in Figure 3a, and thus a heat flow inwards from the surface.

The heat flow for a one-dimensional flow is calculated assuming perfect thermal insulation of all sides other than the open one, by conservation of energy in the system. The heat flow Q is calculated on basis of the weighings and mass flux, ignoring the heat of sorption and capillary binding energy:

$$Q = Gr_T \qquad [\mathrm{W/m^2}] \qquad (1)$$

where G is the vapour mass flux and r_T is the latent heat of evaporation at the surface temperature.

Further, if isothermic conditions are assumed, the temperature at the evaporation front is the same as in the wet region above the FSP in the board. This temperature is measured, as well as the surface and air temperature, and since the heat conductivity is assumed to be constant, the distance d from the surface to the evaporation front, or equivalently, the dry shell thickness d, can be calculated according to Fourier's law of conduction:

$$d = \lambda \frac{\Delta T}{Gr_T} \qquad [\mathrm{m}] \qquad (2)$$

where λ is the heat conductivity and ΔT is the temperature difference between the wood surface[2] and the wet inner core of the specimen, taken from measurements.

[2] Corrected from published version from *ambient air* to *wood surface*

Following this procedure, the thickness of the dry shell layer, that is, the distance between the surface and the evaporating front, is determined for every time of weighing and plotted in time.

Flux calculation with density measurements.

The images from the CT -scanner were analysed using an image processing program called SCION Image. It is software originally developed for Macintosh, but now also available to PC users.

At each time step, the density of the sample in every image was determined and the water flux was calculated using the formula:

$$G = \frac{\rho_n - \rho_{n-1}}{t_n - t_{n-1}} h_n \qquad [\mathrm{kg/m^2 s}] \qquad (3)$$

where ρ = density

t = time

h = the height (thickness) of the sample (will shrink slightly during drying).

n = time index

Unplaned and planed samples were then compared with regards to water flux and dry shell development.

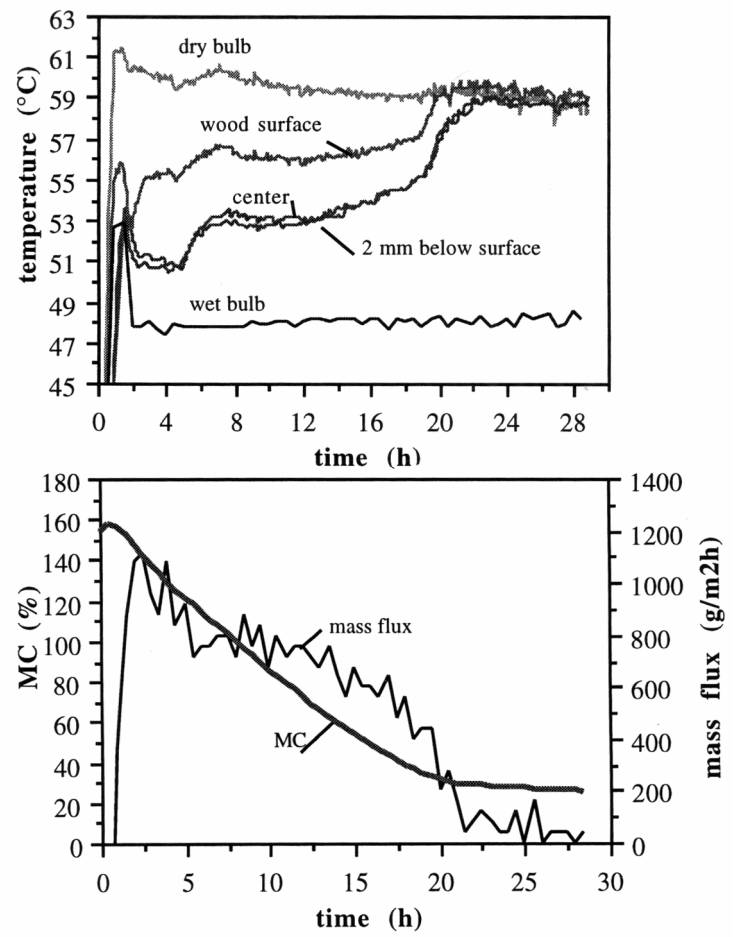

FIGURE 3. Temperature curves for test run D, (3a) and calculated mass flux and moisture content (MC) (3b). Notice the transition period between 18-22 hours when the surface temperature approaches the dry bulb temperature.

RESULTS AND DISCUSSION

The primary set of data can be represented in diagrams where the temperature at different positions in the specimen and MC are plotted in time as in Fig. 3. From such diagrams it is evident that the period with a wet bulb temperature at the surface is very short, if any, when a dry climate is used in the kiln. For more a humid climate, a wet bulb surface temperature can in fact be noticed for a short period.

It should also be observed that there are obvious trends in the shifting of the temperature curves, indicating the existence of different regimes of drying. After recalculation, a plot of the temperature difference between the ambient air and the position 2 mm below the surface, which is proportional to the heat transfer, and a plot of the vapour mass flux are strongly correlated, Fig. 4. This indicates good reliability in the measurements since these results are well in accordance with the energy balance equation (1).

During the heating up period prior to drying, the wood surface is temporarily wetted from condensation of vapour in the moist air, but also because of the expansion of steam bubbles always present in green sapwood, causing a pressure driven water migration from the interior of the specimens. This pressure was in one test measured to be on the order of 1.5 kPa relative to the atmosphere. At this point the temperature of the surface is at wet bulb level.

As the drying starts at constant dry and wet bulb temperatures in the circulating air, the evaporation flux from the surface is at its maximum. Then the evaporation rate decreases successively from a maximum value at the start of the drying, Fig. 4. During this regime of drying, this behaviour is well explained by the increase of the heat resistance in the dry shell between the surface and the evaporation front. The result of the calculation of the thickness of such a dry shell layer coincides fairly with similar CT-scanned measurements for pinewood, Fig. 5.

Wood surface treatment

When comparing the two different treatments of a board surface, the analysis of the CT-images shows that the evaporation front was closer to the surface on the planed samples and that the water flux in the capillary region from the samples was larger. The water flux at different temperatures, air velocities and the two different treatments of the board surface is illustrated in Fig. 6. Overall, the water flux was larger for samples with planed surfaces. The dry shell was thicker in the unplaned samples in two of the three test runs than it was in the planed ones. An other interesting observation was that the water flux at 50 °C and 5 m/s was higher then the water flux at 80 °C and 2 m/s for both unplaned and planed samples. That indicates that air velocity is a more important factor in mass and heat transfer than the temperature, in this case.

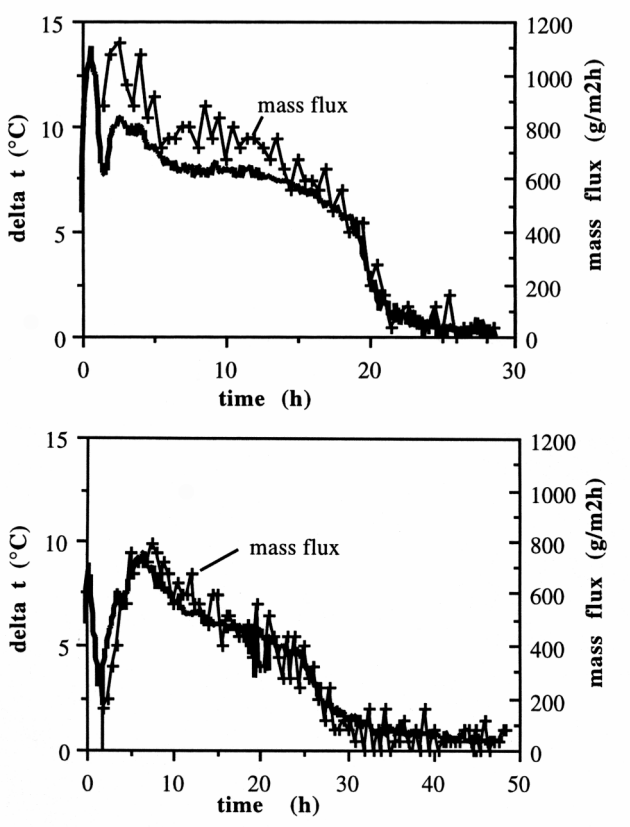

FIGURE 4. Simultaneous mass flux measurements and temperature difference (□T between ambient air and 2 mm position) readings. Test runs D (4a) and F (4b).

Surface and dry shell examination

The analysis of the wood surfaces using SEM showed that the unplaned samples had more loose fibres on the surface than the planed samples, which was to be expected. One can imagine that this will work as insulation and hinder the heat transfer into the wood and result in lower water flux out from the wood. The planed samples seemed to have had a much smoother surface.

In the SEM pictures the KBS was observed closer to the surface on the planed samples than on the unplaned ones. That indicates that the evaporation front was closer to the board surface on the planed samples.

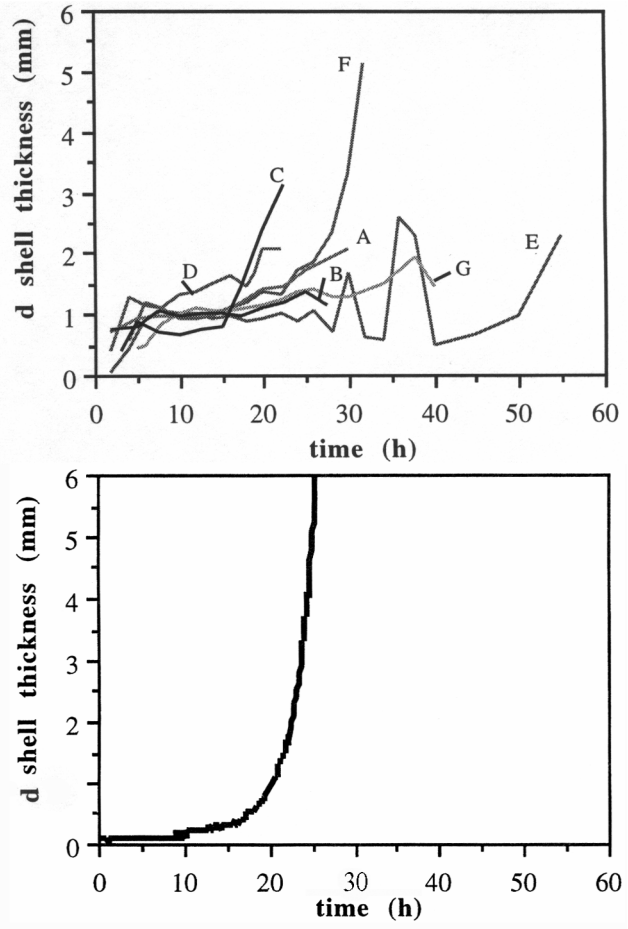

FIGURE 5a) Calculated shell thickness for all test runs. In test E a temperature disturbance occurred, causing irregular behaviour.

b) Comparison with shell thickness according to CT scanning of pine sapwood. The test run is comparable with test F in Fig. 5a.

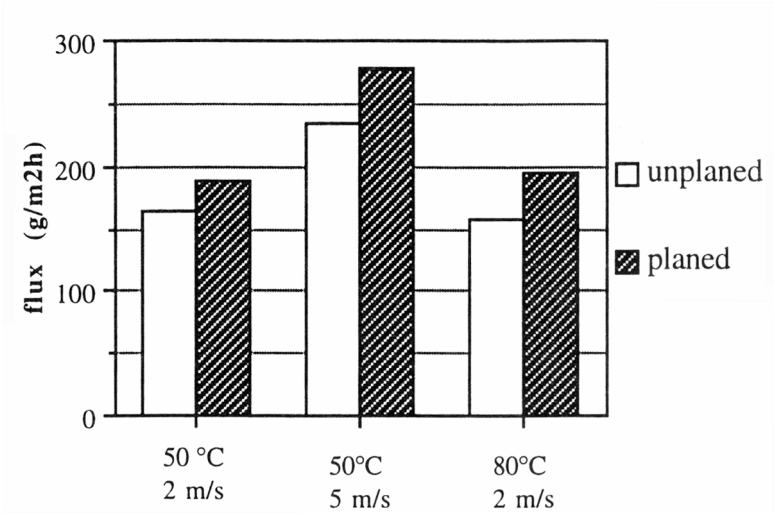

FIGURE 6. Water flux at different climates for planed and unplaned pine. Water flux increases for planed surfaces and higher air velocity.

Fig.7 shows lumens, mainly in earlywood tracheids, partially filled with modified sugars. Note that the lumens in the outermost 7-10 cell rows down to a depth of approximately 0.2 mm are empty.

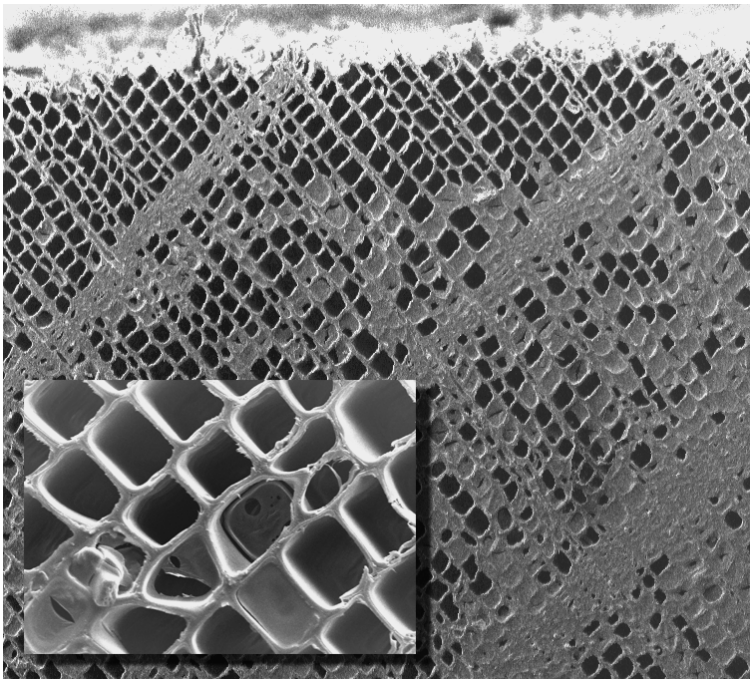

FIGURE 7. Lumen partially filled with modified sugar.

Receding front

Previous results from CT-scanning during drying of pine sapwood showed that free water moves with little resistance in the wet portion of the wood to an evaporation front. Evidently, the conclusion must be that the vapour mass flux during this first regime of drying is controlled by the heat transfer from the air to a receding evaporation front. This is the case as long as the free water migrates within a continuous wet portion of the board well above the FSP.

At approximately 40-50% average MC, a marked transition in the vapour flux occurs in most experiments. This might correspond to a situation where capillary forces no longer play any part in the net migration of free water, where irreducible fibre saturation conditions are reached. The vapour flux decreases rapidly during this period, marking a transition to a regime where bound water diffusion controls the drying rate. This is clearly seen in Fig. 3a, where the surface temperature approaches the dry bulb temperature of the air.

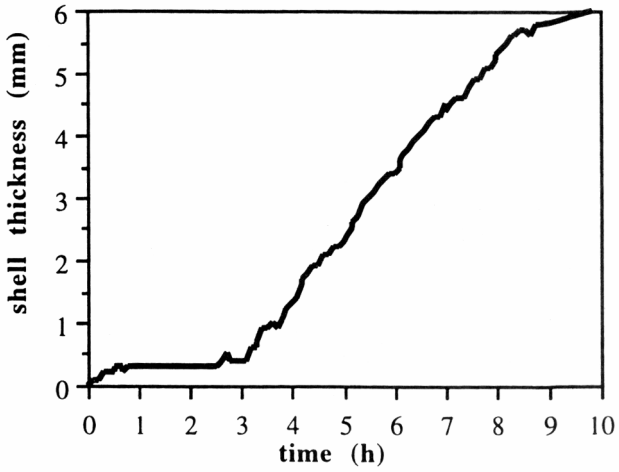

FIGURE 8. Evaporation front in a MDF board. After 3 hours the evaporation front recedes with constant rate into the sample.

A phenomenological explanation of the observed drying development starts with considering the wood sample to be a porous structure allowing water to move between cells, presumably through bordered pit openings between tracheid cells as well as longitudinally in tracheid cell lumens and in wood rays. These transport paths allow flow of free water in the wood structure in transversely to the longitudinal direction as long as the pits are open and not aspirated.

A porous material such as MDF showed similar behaviour to wood. The CT-images of a MDF board showed a very distinct receding front, as illustrated in Fig. 8. During approximately 3 hours the evaporation front was located near the surface or a few tenths of a millimetre beneath the surface. After that the front started to recede into the material at a constant rate. The material in a MDF board has, of course, a different structure from wood without the specific transportation paths, but the example was an indication of how a porous material could behave during drying.

The water permeability in wet pine sapwood is high enough to allow free water migration at a rate that corresponds to the heat transfer from the air to the evaporation front, which controls the drying rate at the air velocity tested in this case.

The receding evaporation front behaviour might be explained by a successive aspiration of pits causing the front to move inwards, until all the wood has lost its free water. Finally, the drying is diffusion controlled below the FSP, with the moisture concentration of bound water as potential for the moisture flux. Now the heat transfer adapts to the evaporation rate as the surface temperature increases and approaches the dry bulb temperature of the air.

In batch kiln drying a marked initial period with high power input is also evident, followed by a final period with much lower input. This agrees well with the concept of receding front and a heat transfer controlled initial regime of drying, followed by the diffusion controlled period.

Since the dry shell forms early during the drying, a considerable moisture transport occurs through this outermost layer. It must be questioned if water molecules in this case are bound to the wood cell material and if so, if local equilibrium exists and if the final evaporation really takes place at the actual wood surface.

An alternative explanation would be that the evaporation beneath the surface creates a pressure driven vapour flux that moves against the temperature gradient. Since the relative humidity of such a steam would decrease below 100 % this could nevertheless allow the formation of a dry shell at equilibrium moisture content, however with little interaction with the vapour flux. The consequence of such a transport mechanism would also be the development of a pressure gradient over the dry shell resulting in a Darcy steam flux. In future work we will extend the measurements to comprise temperature, pressure and density using the CT -scanner.

The observed moisture flux generally results in heat transfer coefficients much higher than expected from established empirical relations for turbulent boundary layers. This cannot be explained on the basis of these experiments and should be further studied.

CONCLUSIONS

Low temperature drying of pine sapwood is controlled by heat transfer during a regime where capillary forces cause free water to migrate from the interior to an evaporation front. This front recedes into the wood until irreducible saturation is reached. Below the FSP, drying is diffusion controlled and the heat transfer adapts to the evaporation rate.

This behaviour is also found for other species than pine, e.g. spruce and birch, but also for a medium density fibreboard soaked in water before drying.

From our experiments at different air temperatures and humidity levels, it appears as if the distance to the evaporation front is initially fairly constant. The front recedes very slowly into the interior of the wood until the average MC is approximately 40-50%, but not until FSP is reached is the drying entirely diffusion controlled.

The capability of water migration in sapwood, which is related to water permeability and capillary pressure, is the critical factor for an optimised drying strategy for sapwood. As long as the heat transfer from the circulating air evaporates less water than the maximum migration flux to the evaporating front, the heat transfer controls the drying. In many industrial kiln constructions the dimensioning of the heating coils is such that this is the case for batches of thin boards or boards with high sapwood content.

Finally, it is concluded that the existence and position of the kiln brown stain in pine sapwood supports the migration drying model based on the receding evaporating front phenomenon.

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Paper IV

Margot Sehlstedt-Persson
The effect of extractive content on moisture diffusion properties for Scots pine and Norway spruce
COST Action E15 Advances in the drying of wood (1999 – 2003). Proceedings 3rd Workshop on SOFTWOOD DRYING TO SPECIFIC END-USES, 11-13 June 2001, Helsinki

THE EFFECT OF EXTRACTIVE CONTENT ON MOISTURE DIFFUSION PROPERTIES FOR SCOTS PINE AND NORWAY SPRUCE

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ABSTRACT

Moisture diffusion coefficients, D_w during steady-state flow were determined at +60°C and 85%RH for matched extracted and unextracted samples of sap- and heartwood from Scots pine and Norway spruce, using diffusion cups. A statistical data analysis shows that pine has significantly lower D_w compared to spruce. D_w decreases with increased density and increased amount of extractives. Pine heartwood shows a different behaviour compared to pine sapwood and spruce sap/heart-wood: as expected D_w increases in the extracted sample compared to the unextracted matched sample. The opposite condition is, a bit surprising, found in the other groups. When all extractives are removed from pine heartwood it acts in the same way as pine sapwood and spruce heartwood.

This study should lead to a better understanding of the differences in drying rate depending on extractive content in the diffusion-controlled regime of kiln drying of softwood.

1 INTRODUCTION

In kiln drying of lumber it's a well-known fact that drying rate seems to differ a lot between individuals of the same species. For example, pine lumber cut from trunk parts close to the root with high heartwood content and density, from experience often dry slower compared to lumber cut from other parts of the tree. Density, sapwood/heartwood portion, extractive content and sawing pattern are some factors that except drying conditions influence the moisture transport in wood.

Extractives in wood cover a large number of different compounds as terpenes, fats, waxes, and fatty acids etc., which can be extracted from wood with solvents. Extractives act as protection against biological attacks but also as nutrition reserve stored in living parenchyma cells. During heartwood formation all living parenchyma cells die and their

content transforms to substances that impregnates the heartwood, which probably obstructs moisture diffusion. The amount and composition of extractives strongly depends on species but also on the position in the tree, growths place etc. Extractive content in heartwood in Scots pine is considerably higher than in sapwood. Pine species have the ability to produce great amounts of extractives (more than 30% of dry weight, Lindgren et al. 1969) which drown the wood if injured. This has been used for industrial production of resin. Spruce does not react in the same way upon injury because of anatomic differences (Back 1969, Hillis 1987). Extractive content in spruce sapwood is higher than in spruce heartwood (Pensar 1967).

Simplified, the kiln drying procedure can be divided into two different regimes; initially one phase ruled by heat transfer when capillary water is abundant followed by a second hygroskopic phase when bound-water diffusion control the drying rate (Wiberg, 2001). When drying down to low moisture content the second diffusion controlled phase normally is the most time consuming part.

The development of new, adaptive kiln drying methods points at the necessity of good knowledge about the material properties of the wood that are to be dried as diffusion properties and its dependent of other material properties.

Fick´s first law of diffusion expresses diffusion at a fixed temperature:

$$G = -D\frac{dc}{dx} \qquad [1]$$

where G = moisture flux, D = vapour diffusion coefficient and dc/dx = the gradient of moisture concentration.

Depending on chosen potential the corresponding vapour diffusion coefficient D varies in unit and value which sometimes could be a bit confusing when reading material data. It should be noted that stating of potential always has to be given when using vapour diffusion coefficients, advisable using an index.

In this work the moisture transfer resistance at each surface is neglected because the ambient conditions are the same for all tests. This means that comparison between specimens depend only on the properties of wood. The potential □M for calculating the diffusion coefficient is thus the equilibrium moisture content in the surrounding air. This leads to the following expression of vapour diffusion coefficient:

$$D_w = \frac{100mx}{tA\rho\Delta M} \qquad [2]$$

where

D_w	= vapour diffusion coefficient	[m^2/s]
m	= mass of water transported in time t	[kg]
x	= sample thickness	[m]
t	= time	[s]
A	= area	[m^2]
ρ	= basic density (dry weight, raw volume)	[kg/m^3]
ΔM	= moisture content difference	[%]

Many researchers have done measurements of diffusion coefficient for different materials, for example Rosenkilde 1996. One stationary method is to use a diffusion cup with the testing material used as a carefully sealed cover. Different climate on each side of the cover drives the diffusion at a constant ambient temperature. By continuous weighing of the cup it is possible to measure the steady-state moisture flux when the material has equalised in current climate (Siau 1995).

However, the method with diffusion cups contains many critical moments as sealing of cover, stable climate control and disturbances if the cup has to be removed from ambient climate during weighing, (Nilsson, 1988).

The aim with this work though, is not to measure the absolute values of diffusion coefficients but to investigate the influence of extractive content on diffusion properties in matched pairs of wood samples in compared studies.

1.1 Work objective

The objective of this work is to investigate the influence of extractive content on moisture diffusion properties for matched extracted/unextracted sapwood/heartwood samples from Scots pine and Norway spruce. Water vapour diffusion coefficient D_w during steady-state flow was measured using diffusion cups.

This study should lead to a better understanding of the differences in drying rate depending on extractive content in the diffusion-controlled regime of kiln drying of softwood.

2 MATERIALS AND METHODS

2.1 Sample preparation

Matched pairs of clear heartwood and sapwood samples from 6 individual green logs from Scots pine (Pinus silvestris) and Norway spruce (Picea abies) were cut according to figure 1. Totally 48 samples were cut from green wood and kept in a refrigerator wrapped in aluminium foil between sample preparation and testing. The sample size was 95x50x2,7 mm^3. Some of the matched pairs from spruce heartwood contained reaction wood. Occurrence of reaction wood is coded in the multivariate analyse of material data.

The samples were cut to minimise cupping when they where mounted as covers on the diffusion cups, which leads to a tangential moisture flow through the samples according to figure 1.

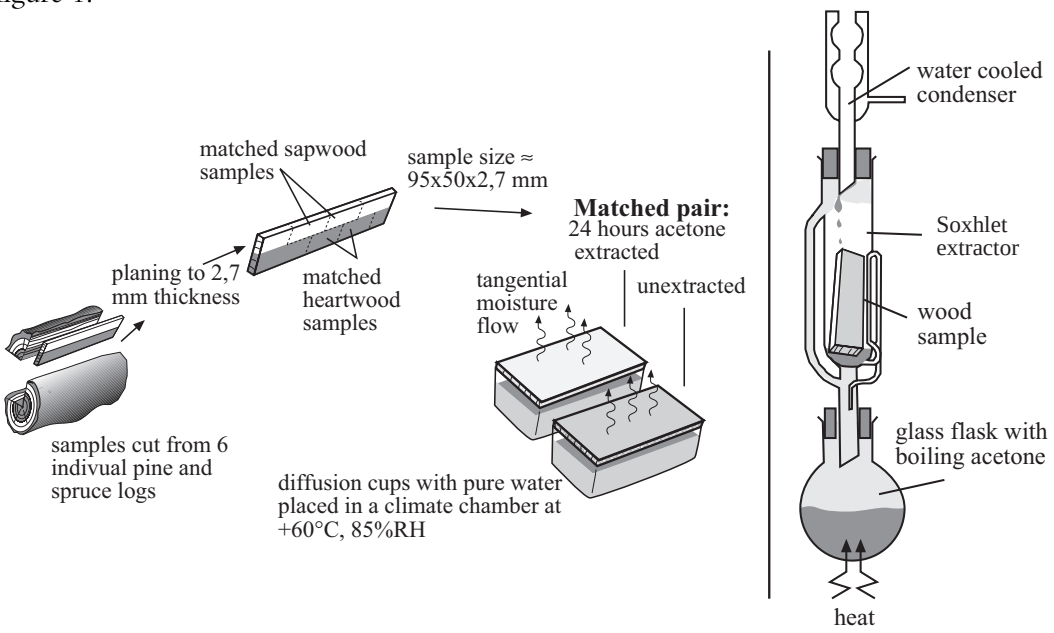

Figure 1 Sample preparation and Soxhlet extractor

2.2 Extraction and testing

One sample of the matched pair was extracted in solid state for 24 hours in a Soxhlet extractor with four extraction cycles per hour. Acetone *99,5% pro analysi* was used as solvent with the boiling temperature +56,2°C. The width of the samples (50 mm) was limited of the inner diameter of the Soxhlet extractor.

After the extraction was completed the extract was filtered through a Munktell Analytical filter paper 00H to remove any loose wood fragment. In a rotary evaporator the solvent was evaporated from the extract and collected in a condenser, leaving the extractives inside a glass flask. The amount of extractives was obtained as the difference in weight of the glass flask including extractives and without extractives after careful cleaning, using a balance with an accuracy of 0,001 gram.

The matched pairs where placed together in a climate chamber at +60°C/85%RH, which corresponds to Equilibrium Moisture Content, EMC 15%, for equalisation during 2 weeks. The samples were then mounted as edge coated covers, carefully sealed with silicon between the sample and the cup, on the diffusion cups 2/3 filled with pure water. EMC within the cup at saturated 100%RH corresponds to 26,5% (Siau 1995). The cups were then kept in the climate chamber during the test, between 14-25 days after the sealing of cups were stated to be tight. Calculated values of D_w are given as the average value from the three last readings for each sample. An example of D_w during time is shown in figure 2. A PC-logger registered dry and wet bulb temperature in the climate chamber. The climate control during test was stable.

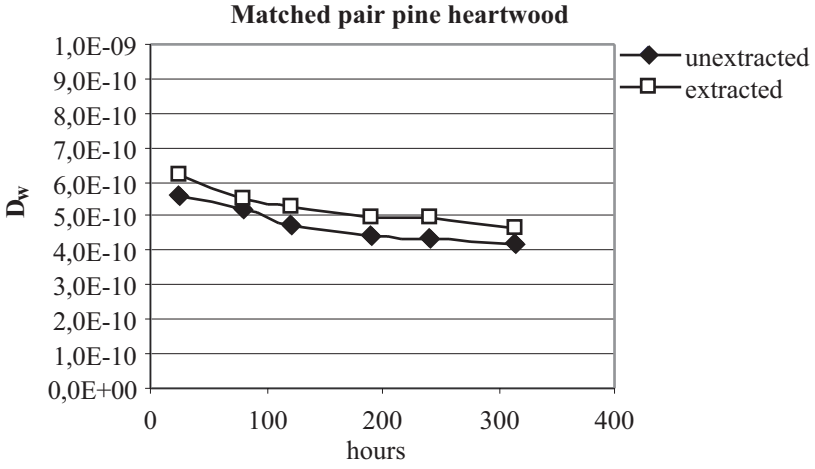

Figure 2 Example of diffusion coefficient D_w during time.

By periodic weighing of the entire assembly after steady-state conditions had been established (seen as a linear relationship between weight and time) the moisture flux was calculated as the rate of weight change divided by the open area for moisture movement. This open area was measured individually for each sample on a digitally scanned image of the underside of the cover facing the water.

Finally, the dry density $\rho_{0,0}$ was calculated by measuring the oven dry weight and dry volume of each samples by lowering in mercury.

Diffusion coefficient D_w was calculated according to equation [2].
In order to evaluate the differences in D_w between paired and unpaired groups, significance test was done at 1% and 5% significance level (Box et al. 1978).

A multivariate principal component analysis of all data was done using the software SIMCA P8.

3 RESULTS

Density, $\rho_{0,0}$ and extractive content for the test material are presented in table 1 as average and standard deviation s.

Table 1 Density of unextracted wood and extractive content as average and standard deviation s of 6 samples in each group.

	Scots pine		**Norway spruce**	
	Heartwood	Sapwood	Heartwood	Sapwood
Density $\rho_{0,0}$ (kg/m^3)	572 s 41	577 s 37	462 s 73	448 s 67
Extractive content (% of dry weight)	9,3 s 3,2	4,5 s 1,5	0,5 s 0,2	0,9 s 0,4

Notations
Mean values of $\rho_{0,0}$ in Träfakta (Boutelje et al 1986) for Scots pine is 450 -500 kg/m^3 and 370-440 for Norway spruce. Scots pine material used in this study shows somewhat higher density, which might be explained by the fact that the test material was cut from parts near the root where the density in a tree normally is highest.

In table 2 average values and standard deviation s is given for calculated values of diffusion coefficient D_w and figure 3 shows D_w for each matched pair group wise. Extractive content of the extracted sample in each pair is shown below the diagrams. Matched pair no. 1 in pine heartwood is cut from the same log as matched pair no. 1 in pine sapwood etc.

Table 2 Diffusion coefficient D_w as average and standard deviation s for unextracted and extracted material with 6 samples in each group.

	Scots pine				**Norway spruce**			
	Heartwood		Sapwood		Heartwood		Sapwood	
	Unext	Extr	Unext	Extr	Unext	Extr	Unext	Extr
D_w (10^{-10}) (m^2/s)	3,8 s 0,6	5,0 s 0,5	4,9 s 0,4	4,3 s 0,8	6,5 s 1,6	5,4 s 1,1	6,8 s 1,1	5,4 s 1,0

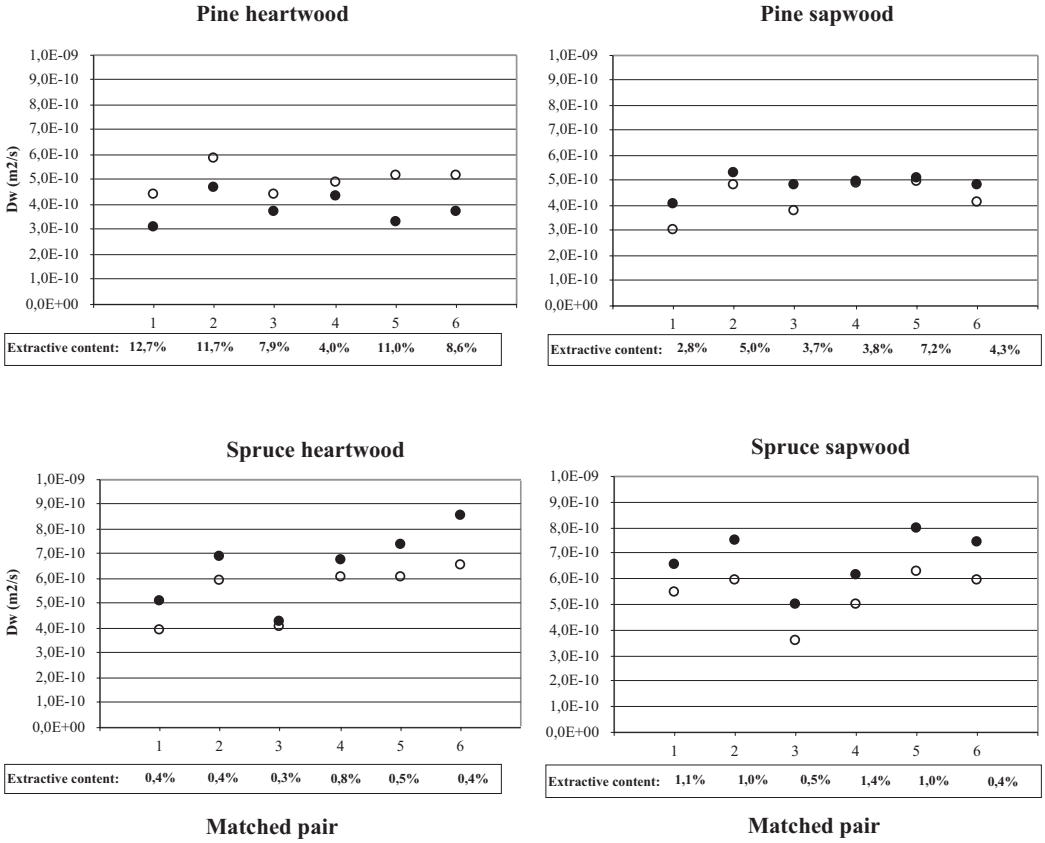

Figure 3 Diffusion coefficient D_w at +60°C/85%RF for extracted/unextracted matched pairs of pine and spruce heartwood/sapwood.
● unextracted ○ extracted

In figure 4 D_w for all samples is plotted as a function of density $\rho_{0,0}$. D_w appears to have an obvious linear relationship on density with a regression coefficient $r^2 = 0,74$

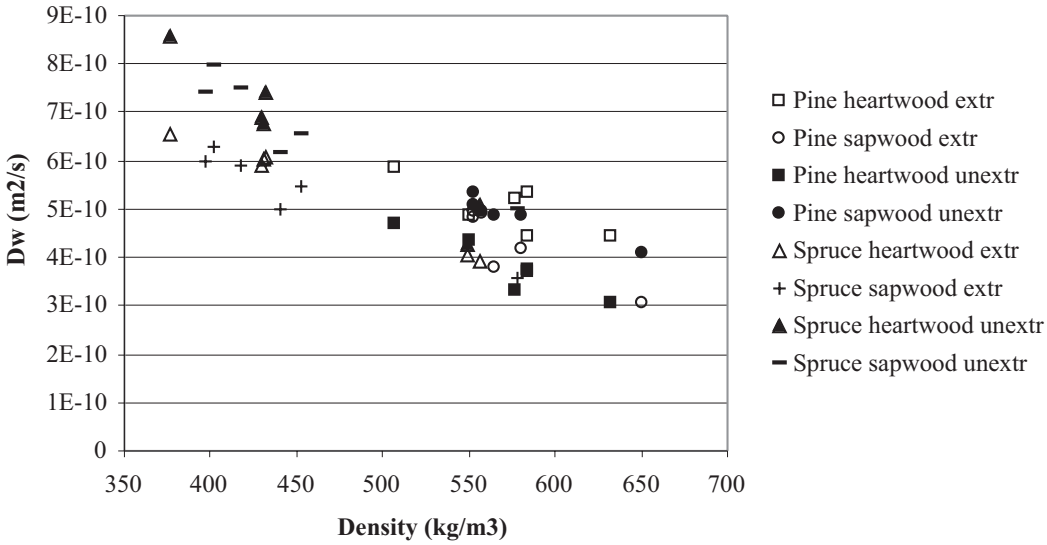

Figure 4 D_w as a function of density $\rho_{0,0}$ for all samples ($r^2 = 0,74$).

In figure 5 D_w in the unextracted samples is plotted as a function of extractive content measured in their matched extracted sample. An increased amount of extractive reduces D_w in pine. Linear regression for pine gives a $r^2 = 0,36$.

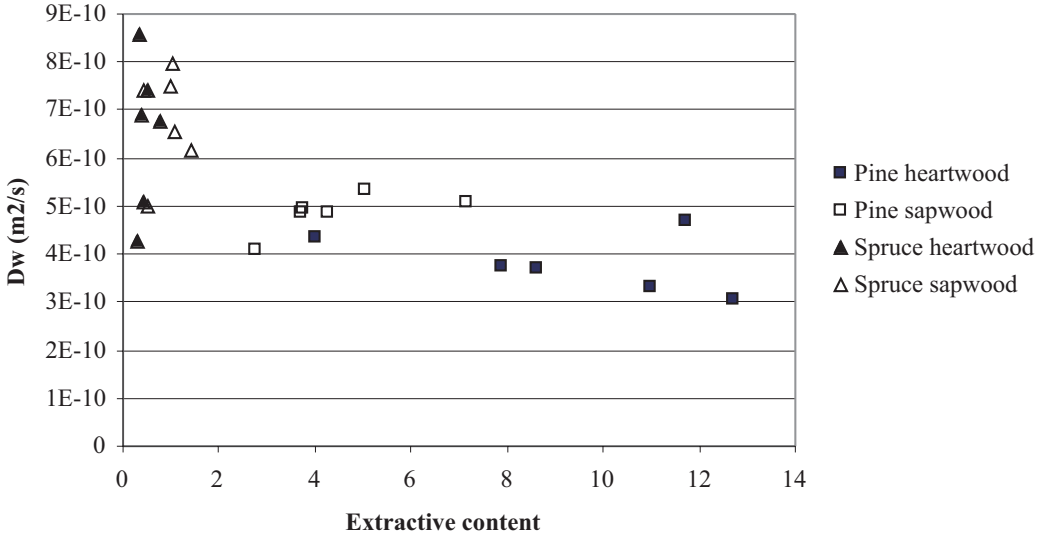

Figure 5 D_w in the unextracted samples as a function of extractive content in their matched extracted samples.

3.1 Statistical analysis

A statistical comparison between D_w in matched pairs of extracted/unextracted wood was done at 1% and 5% significance level, which gave the following results:

- unextracted pine heartwood shows significantly *lower* D_w compared to extracted pine heartwood at 1% significance level
- unextracted pine sapwood shows significantly *higher* D_w compared to extracted pine sapwood at 5% but not at 1% significance level
- unextracted spruce heartwood shows significantly *higher* D_w compared to extracted spruce heartwood at 1% significance level
- unextracted spruce sapwood shows significantly *higher* D_w compared to extracted spruce sapwood at 1% significance level

A statistical comparison between D_w in some selected unpaired groups was done at 1% and 5% significance level, which gave the following results:

- unextracted pine heartwood shows significantly *lower* D_w compared to unextracted pine sapwood at 1% significance level
- unextracted pine heartwood shows significantly *lower* D_w compared to unextracted spruce heartwood at 1% significance level
- unextracted pine sapwood shows significantly *lower* D_w compared to unextracted spruce sapwood at 1% significance level
- extracted pine heartwood show no significant difference compared to pine sapwood or spruce heartwood

Statistical comparison between paired and unpaired groups is summarised in table 3.

3.2 Multivariate statistical analysis

A multivariate, principal component analysis of all material data using the software SIMCA P8, shows that density has greater influence than extractive content on D_w. It is also shown that occurrence of reaction wood in spruce decreases D_w, which is associated with the higher density in reactionwood compared to normal wood.

3.3 Other observations

The extract from each sample was collected in small beakers. Except different amounts of extractives between samples some other observations were done:

- the extractives from pine heartwood show variation in colour between samples, from light yellow to brownish yellow.

- in consistency, the extractives from pine sapwood have lower viscosity compared to extractives from heartwood.
- an unmistakable scent of vanilla could be distinguished from extract from spruce sapwood. Vanillin is known to form during oxidation of lignin in both basic and acetous conditions (Karlsson 2001).

Table 3 Summary of statistical comparison.

			Scots pine				Norway spruce			
			Heartwood		Sapwood		Heartwood		Sapwood	
			Unext	Extr	Unext	Extr	Unext	Extr	Unext	Extr
Scots pine	Heart wood	Unext		⋆⋆	x x	-	x x	-	x x	-
		Extr			o	o	o	o	x x	o
	Sap wood	Unext				⋆	x	-	x x	-
		Extr					-	-	-	o
Norway spruce	Heart wood	Unext						⋆⋆	o	-
		Extr							o	o
	Sap wood	Unext								⋆⋆
		Extr								

⋆	matched pairs:	significant difference at 5% significance level
⋆⋆	matched pairs:	significant difference at 1% significance level
x	unpaired:	significant difference at 5% significance level
xx	unpaired:	significant difference at 1% significance level
o		no difference at 5% significance level
-		comparison not done

4 CONCLUSIONS

This study shows that density has greater effect than extractive content on the ability of water-vapour diffusion in pine and spruce at +60°/85%RH. Moisture diffusion coefficient, D_w, which expresses the ability of water vapour transport through a material, decreases with increased density and extractive content. D_w shows a fairly linear dependency on density for all samples (figure 4). Occurrence of reaction wood in spruce, which is associated with higher density compared to normal wood, also decreases D_w. A fairly linear dependence on extractive content is also found for pine (figure 5).

A comparison between pine and spruce shows that density and extractive content is higher in pine. Consequently, the water vapour transport capacity is higher in spruce in both heartwood and sapwood.

Pine heartwood shows a different behaviour compared to pine sapwood and spruce heart/sapwood. As expected the water vapour transport capacity significantly increases when the extractives are removed. In pine sapwood and spruce sap- and heartwood, the opposite condition is observed! A more effective aspiration of boarded pits in extracted wood might be an explanation. In extracted pine heartwood however, this phenomena might be subordinated the influence of high extractive content. The observed difference in viscosity between extractives from pine sapwood and pine heartwood might also have an effect.

When extractives are removed from pine heartwood no significant difference is found in the ability to transport water vapour compared to pine sapwood or spruce heartwood in unpaired comparisons of average values.

The extractives from pine heartwood show variations in colour between samples, from light yellow to brownish yellow.

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Paper V

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Colour responses to heat-treatment of extractives and sap from pine and spruce
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Colour responses to heat-treatment of extractives and sap from pine and spruce

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ABSTRACT

Scandinavian sawmills have over the last 20 years adopted ever-higher temperatures in the dry kilns. The reason for this has been improvements in drying quality and kiln capacity. However, some problems relate to this strategy, mainly discolorations and extensive resin flow from knots and heartwood in pine. In this study, underlying factors for changing wood colour were investigated for spruce and pine. From the sapwood portions of wood, sap was extruded by mechanical compression, put in glass bottles and heat-treated at different temperature levels ranging from 60 °C to 95 °C during 1 to 5 days. Then the colour of the sap was measured using a standard colorimeter. Extractives from pine heartwood were also heat-treated and analysed in the same way.

From these experiments it was concluded that much of the colour change in solid wood emanated from colour changes in constituents of the sap and extractives. Pine sap was more susceptible to colour change than sap from spruce. Also, an accelerated colour change was noticed above 70 °C for pine sap. Finally, it was observed that extracted wood that was soaked in water and then heat-treated still underwent some colour change, probably due to secondary hydrolysis of hemicelluloses.

INTRODUCTION

It is a well-known fact that wood changes colour during drying. Artificial air circulation drying of pine and spruce results in a more or less pronounced surface yellowing of sapwood. According to Terziev et al (1993) and Terziev (1995), yellowing of sapwood lumber is explained by the enrichment of sugar and nitrogenous compounds towards the timber surfaces during the initial, capillary phase of drying. Fast drying leads to an increased enrichment towards the surfaces. When this carbohydrate-enriched zone is being heated in the presence of amino acids working as catalysts, a degradation of the carbohydrates takes place at which coloured degradation products are formed. This is called Maillard reaction and is a well-known process within the food industry. Water storage of timber might also lead to a pronounced surface yellowing after drying, (Boutelje 1990, Theander et al 1993).

Paper V: Colour responses to heat-treatment of extractives and sap from pine and spruce

The development of kiln drying schedules for the industrial air-circulation drying of pine- and spruce timber has resulted in general increase of drying temperatures over the last 20 years in Scandinavia with such advantages as shorter drying time, fewer cracks and less deformation. Other consequences of higher drying temperatures are colour changes and darkening of wood but also an increase of resin flow especially around knots in pine.

Drying temperature, time, time in capillary drying phase (i.e. as long as free water is present in the timber) and water content are parameters that influence the colour change (Sundqvist 2000). According to Tarvainen et al (2001) colour change in pine heartwood increases markedly at drying temperatures exceeding 70°C, probably depending on the resin content. The same phenomenon is observed for pine- and spruce sapwood.

Wood properties that affect colour of wood during drying are extractive- and nutrition content. The concentration of soluble nutrition substances varies significantly during the year and reaches maximum levels during winter months (Terziev et al 1997, Hinterstoisser 1994, Höll 1985). According to Terziev et al (1997) the carbohydrate content is more dependent on the time of the year than on growth conditions. Nitrogen content in pine sapwood varies less with the time of the year than does carbohydrate content. In sapwood the carbohydrate content increases towards the cambium.

In the sapwood zone where nutrition has been enriched during drying, a special type of dark discolouration called Kiln Brown Stain (KBS) often occurs at high temperatures with a typical depth of 1-3 mm beneath the surface (Kreber, Haslett 1997). Coloured substances that are formed during chemical reactions when carbohydrates degrade thermally cause KBS. When such timber is planed this dark zone is exposed which is a notable problem. The occurrence of KBS seems to vary in different species, and for Pinus radiata, a pronounced increase of KBS is reported at temperatures exceeding 60°C (Kreber et al 1997, 1998). KBS also appears when pine timber is dried (Sehlstedt-Persson 1995).

Resin flow around knots in pine timber increases markedly at higher temperatures. This appears as substantial dark brownish spots on the surface. However, this crystalline resin disappears after planing and causes no harm.

Aside from colour changes caused by yellowing, KBS and resin flow around knots and pitch pockets, a colour change in the wood substance itself may occur. When wood is heated, a thermal degradation dependent on temperature, time and moisture content takes place. Thermal degradation of wood increases markedly at temperatures over 120°C, but also occur at temperatures beneath 100°C when hemicelluloses are primarily affected. Degradation of the hemicelluloses results in a reduced hygroscopicity, since hemicelluloses foremost absorb water. Degradation substances from hemicelluloses may affect colour of wood.

Collected extractives from acetone-extracted pine and spruce samples also show variation in colour between sap- and heartwood but also between individual samples (Sehlstedt-Persson 2001).

MATERIALS AND METHODS

Timber

1.5 m sections cut from butt- and middle logs of pine and spruce timber felled in January 2002 from a stand near the seaboard of Västerbotten in northern Sweden were used in the tests.

Through careful planing of the trunk surface all remains of bark were removed before the sections were sawed into 4-5 cm thick laminae. The laminae were cut into pure sap- and heartwood sections, which were wrapped into plastic bags and kept in a refrigerator.

Sap

From the sapwood portions of each species, approximately 1.5 l sap was extruded by mechanical compression. The fresh sap was filtered in two steps: first through a roughing filter Munktell no 3 (filtration rate 700 ml/min Herzberg) followed by a second fine filtration through Munktell 00H (40 ml/min Herzberg). The filtered sap was divided into 30 ml glass bottles and stored in a refrigerator.

A TLC-test (Thin-Layer Chromatography) with petroleum ether-ethylic ether 85:15 as solvent showed no occurrence of remainders of extractives in the sap.

Extractives

Small samples cut from pine heartwood were extracted in a Soxhlet-extractor with reflux condenser for 24 hours with acetone 99.5% *pro analysi* (boiling point 56,2°C) as solvent. The extract was filtered through Munktell filter paper 00H to remove wood particles. The filtered extracts from each extraction were mixed in a glass container and kept in darkness.

Since extractions are time-consuming and only small amounts of solid wood samples are possible to use in each extraction, the study was limited to pine heartwood, with its higher extractive content compared to sapwood and spruce heartwood. A total of 15 extractions were done to achieve a sufficient amount of extractives.

The amount of extractives after evaporation of the solvent in a rotary evaporator was 35 gr. This amount was dissolved in 300 cl acetone and then distributed with an injection syringe into Petri dishes (diameter 80 mm, height 15 mm), 10 ml in each. The Petri dishes were kept without cover on a horizontal surface in darkness until the acetone evaporated, leaving the firm extractives evenly distributed on the bottom of the dishes. The Petri dishes were then covered with glass lids.

Heat-treatment

Heat-treatment of sap and extractives was performed in a heating chamber at 60, 70, 80, 85, 90, 95°C for 1, 2, 3, 4 and 5 days. Measurements with thermocouples and a datalogger showed that fluctuation in temperature regulation was ±0.5°C.

Colour measurements

Colour measurements were done using a Minolta CR 310 colorimeter with CIE L★C★h° colour system chosen according to the CIE standard (Hunt 1995). L★ is lightness, C★ is chroma or saturation and h° is hue angle. The light source used was Standard Illuminant D_{65} (average daylight including ultraviolet wavelength region).

The L★C★h° values were transformed to L★a★b★ values in order to calculate the colour difference values $\Delta E^{\star}_{ab}$ according to the following equations:

$$a^* = C\cosh^\circ$$
$$b^* = C\sinh^\circ$$
$$\Delta E^*_{ab} = \sqrt{\left((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2\right)}$$

Note that $\Delta E^{\star}_{ab}$ states the extent of colour difference but not direction. The least colour difference $\Delta E^{\star}_{ab}$ possible for the human eye to distinguish corresponds to 1-3 units (Terziev, Boutelje 1998).

Colour measurements of sap

Using a colorimeter to measure colour in liquids is difficult, for example because of varying reflexion in the liquid surfaces. In order to avoid these difficulties, a relative method was used with colour measurements on filter papers (Munktell 00H, diameter 70 mm) soaked with heat-treated sap. Measurements were performed on both sides of each filter paper, centered on a calibration plate with colour coordinates L★ 96,65, C★ 3,28 and h° 92,2, before they were soaked with sap. Two replicates were used for each treatment. The papers where then placed in plastic bowls (diameter 76 mm) and soaked with 10 ml of heated sap with an injection syringe. The bowls were kept in darkness while the water evaporated and then dried for 1 hour in 30°C, just before colour measurements were performed on each side of the papers.

Colour measurements of extractives

A relative method was used also for measuring the colour of the extractives. The measurements were made before and after heat-treatment through the bottom of the Petri dishes, which was covered with extractives. During measurement, the Petri dish (diameter 80 mm) was centered on the measuring unit of the colorimeter (diameter 53 mm) in a screen box of black cellulose plastic towards a reference panel of white MDF–board with coordinates L★ 92,6, C★ 3,17 h° 94,8 (average values of 10 measurements with standard deviations 0.02, 0.01 and 0.7 respectively).

Heat-treated wood samples

Some preliminary tests with heat-treatment of extractive-free wood samples in wet and dry states were performed. 3 matched samples were cut from green pine heartwood. Two samples were extracted with acetone for 24 hours in a Soxhlet-extractor. One of the extracted samples was soaked in water in a sealed glass bottle. Heat-treatment of the samples took place during 4 days at 80°C: 1 extractive-free in the dry state, 1 extractive-free in the wet state and 1 unextracted in the dry state.

Also, two matched pairs cut from pine sap- and heartwood respectively were extracted and heat-treated at 90°C for 5 days, one from each pair in the wet state and one in the dry state.

RESULTS AND DISCUSSION

Heat-Treated Sap

Results from measurements on filter papers soaked with heat-treated sap are shown in figure 1. The results show a clear influence of temperature and time on $L^\star C^\star h°$ values. $L^\star$ and h° decrease with time and temperature for both spruce and pine, i.e. the sap becomes darker and more reddish. The higher temperature is, the more $L^\star$ and h° decrease with time. The saturation $C^\star$ increases with time and temperature.

Pine sap seems to be more susceptible to heat than spruce sap. Statistical tests of differences between average values between unpaired groups show that:

- At all temperatures spruce sap on the average was lighter than pine sap at a 1% significance level
- At all temperatures saturation $C^\star$ was higher for pine sap than for spruce sap on an average, at a 1% significance level
- Hue angle h° at 60 and 70° was higher (more yellow) but at temperatures ≥80° lower (more reddish) for pine sap compared to spruce sap, at a 5% significance level.

For pine sap, the change of colour coordinates (mainly $L^\star$ and $C^\star$) seems to accelerate at temperatures exceeding 80°. Spruce sap does not show the same behaviour.

Measurements shown in figure 1 include the coordinates of the filter paper itself. Calculation of the colour difference $\Delta E^\star_{ab}$ before and after soaking the papers with sap brings out the effect of the sap only, shown in figure 2. The value at time 0 corresponds to $\Delta E^\star_{ab}$ of fresh, unheated sap.

For both species $\Delta E^\star_{ab}$ increase with time and temperature and are in every case clearly visible for the human eye. On an average $\Delta E^\star_{ab}$ at all temperatures are higher for pine sap at a 5% significance level. An accelerated colour difference seems to occur for pine sap at temperatures >70°C.

Dry content and pH

By evaporating 50 ml of fresh, filtered sap the dry content of sap was found to be 0.32% in pine sap and 0.17 % in spruce sap. The considerably higher dry content of pine sap probably explains the more pronounced colour change, since dry content indicates carbohydrate content.

Measurements of pH in fresh sap at a temperature of 15°C showed that spruce sap had a somewhat higher value of 5.46 compared to 5.10 for pine sap, which agrees well with data given by Fengel, Wegener (1984). According to this reference, the seasonal fluctuations in pH are small.

Multiple regression analysis

Multiple regression analysis of all data (a total of 144 measurements) with $\Delta E^{\star}_{ab}$ for sap as a function of time, temperature and species gives the following linear model within the investigated intervals:

$$\Delta E^*_{ab} = 3{,}59 - 2{,}93^* S + 0{,}048^* T - 4{,}56^* Ti + 0{,}078^* Ti^* T$$

R^2=0,88

where Ti = time, number of 24-hour periods (0-5)

T = temperature, degrees ° (60-95)

S = species, 1 for pine and 2 for spruce

Regression models for each species are:

Pine:

$$\Delta E^*_{ab} = -1{,}43 + 0{,}066 \times T - 5{,}31 \times Ti + 0{,}09 \times Ti \times T$$

R^2=0,90

Spruce:

$$\Delta E^*_{ab} = -0{,}19 + 0{,}03 \times T - 3{,}82 \times Ti + 0{,}066 \times Ti \times T$$

R^2=0,89

Heat-Treated Extractives

The colour coordinates of the pine heartwood extractives, measured through the bottom of the Petri dish, show a marked influence of the heat-treatment; the colour becomes darker, the hue angle decreases (becomes more reddish) and the saturation increases with time and temperature as shown in figures 3 and 4.

The colour difference $\Delta E^{\star}_{ab}$ before (corresponds to the state at time 0 in figure 3) and after heat-treatment is shown in figure 5.

Multiple regression analysis

Multiple regression analysis of the material (a total of 30 measurements) with $\Delta E^{\star}_{ab}$ as a function of time and temperature gave the following linear model within the investigated intervals:

$$\Delta E^{*}_{ab} = -36{,}59 + 2{,}45 \times Ti + 0{,}65 \times T$$

R^2=0,90

where Ti = time, number of 24-hour periods (1-5)

Heat-treatment of wood samples

The preliminary tests with heat-treatment of extractive-free wood samples heated in wet and dry states show that the moisture content in wood during heat-treatment is also of importance for the colour of the wood, figure 6. When extractive-free wood is heated in moist condition, the wood darkens and becomes reddish compared to wood heated in the dry state. The interpretation is that coloured degradation products are formed during hydrolysis of hemicelluloses.

CONCLUSIONS

- Heat-treatment of sap and extractives results in clearly visible colour changes. Lightness $L^{\star}$ decreases, saturation $C^{\star}$ increases and the hue h° moves towards red. The colour changes increase with time and temperature.

- Sap from pine shows significantly greater colour changes compared to sap from spruce at a 5% significance level. This difference is probably explained by the fact that the dry content in pine sap was higher, indicating higher carbohydrate content. Difference in pH values might have an effect as well. Only winter-felled wood was studied, which admits uncertainty since carbohydrate content fluctuates with seasons and species.

- In sap from pine an accelerated colour change is noticed at temperatures exceeding 70°C.

- Multiple linear regression models with the colour difference $\Delta E^{\star}_{ab}$ as a function of time and temperature show R^2 (coefficients of determination) of approximately 90% for both sap and extractives.

- Preliminary tests with heat-treatment of extractive-free wood in dry and wet state show that heating in the wet state causes a notable change of colour. Formation of coloured degradation products deriving from hydrolysis of hemicelluloses might be the explanation.

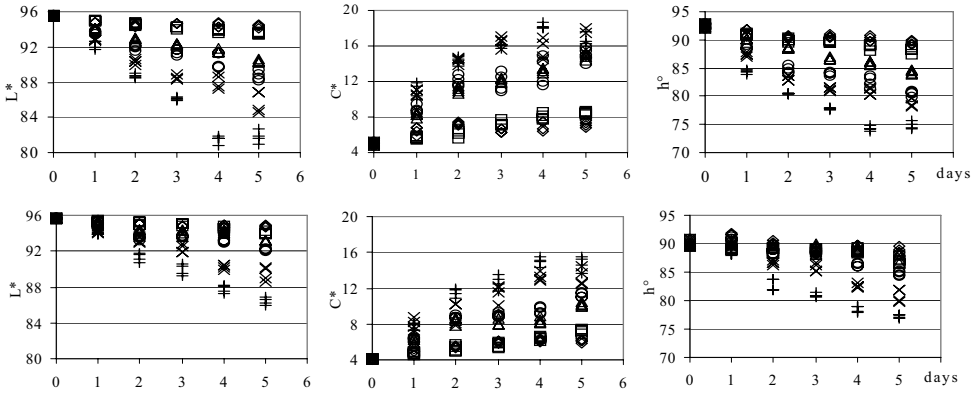

Figure 1 L*C*h° coordinates from colour measurements on filter papers soaked with heat-treated sap. Upper row pine sap, lower row spruce sap
◇60° □70° △80° O85° ×90° +95°

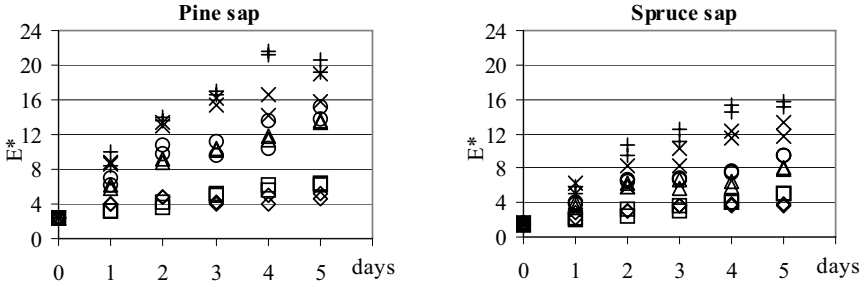

Figure 2 $\Delta E^{\star}_{ab}$ for heat-treated sap at different temperatures.
◇60° □70° △80° O85° ×90° +95°

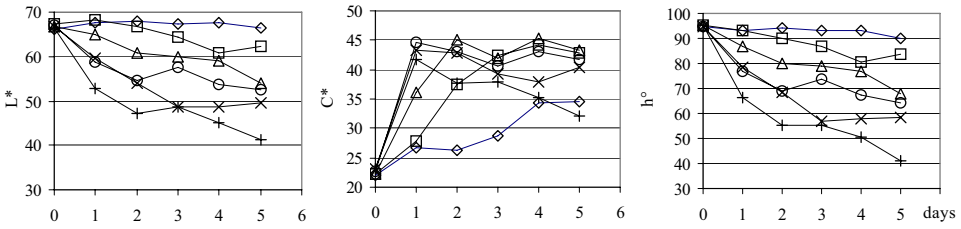

Figure 3 LCh colour coordinates for heat-treated extractives from pine heartwood
◇60° □70° △80° O85° ×90° +95°

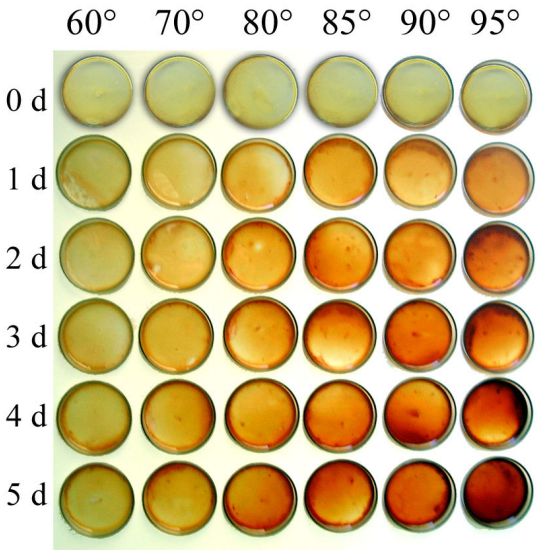

Figure 4 Heat-treated extractives from pine heartwood.

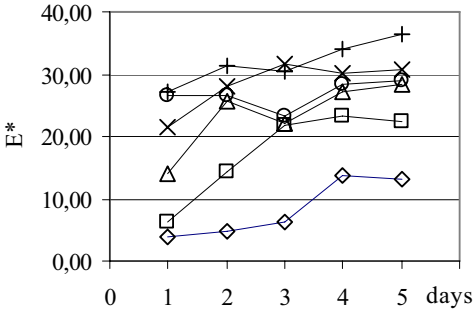

Figure 5 $\Delta E^{\star}_{ab}$ for heat-treated extractives from pine heartwood.
◇60° □70° △80° O85° ×90° +95°

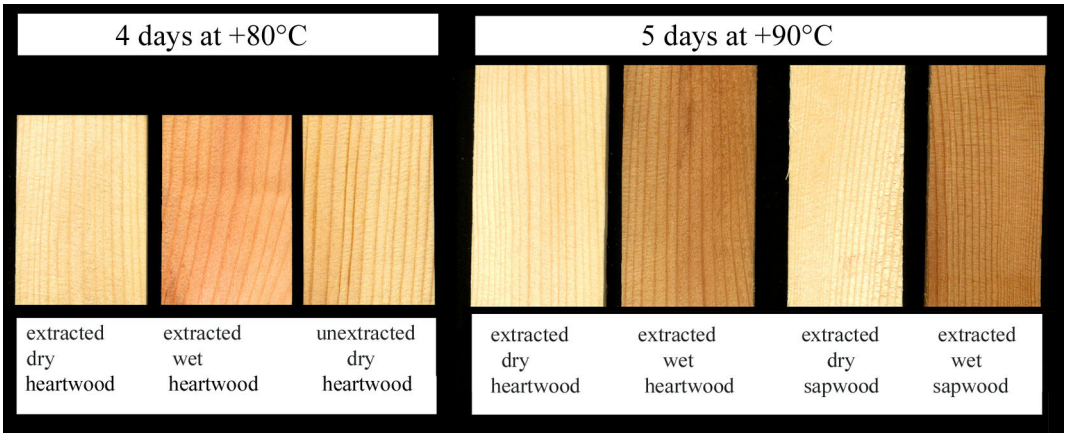

Figure 6 Preliminary tests with extracted and unextracted pinewood, heat-treated in dry and wet states.

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Paper VI

Dennis Johansson, Margot Sehlstedt-Persson, Tom Morén
Effect of heat treatment on capillary water absorption of heat-treated pine, spruce and birch. Proceedings 5th IUFRO Symposium Wood Structure and Properties '06, September 3-6, in Sliač - Sielnica, Slovakia. (2006)

EFFECT OF HEAT TREATMENT ON CAPILLARY WATER ABSORPTION OF HEAT-TREATED PINE, SPRUCE AND BIRCH

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Luleå University of Technology, Division of Wood Science and Technology, Sweden

Abstract

Longitudinal absorption of water in matched heat-treated and untreated boards was studied. The boards are from three different species, Scots pine (*Pinus sylvestris*), Norway spruce (*Picea abies*) and birch (*Betula pubescens*). The heat treatment was performed according to the Thermowood process at two different temperature levels (170°C and 200°C) for all three species. Computer tomography (CT) scanning was used to intermittently monitor the ascent of the water front.

The use of CT scanning enables a study of the liquid water ascent in three dimensions over time. This means that it is possible to determine the influence of different treatment temperatures and species as well as the difference between heartwood and sapwood on capillary action.

The results show that longitudinal water absorption in pine sapwood was substantially larger when heat-treated at 170°C compared to untreated pine sapwood. In pine heartwood, the ascent of water was low in heat-treated as well as in untreated boards. Spruce boards showed low water absorption in sap- and heartwood in heat-treated as well as in untreated boards. Birch showed a decreasing uptake of water with increasing treatment temperature.

Keywords: capillarity, absorption, heat treatment, Scots pine, Norway spruce, birch

INTRODUCTION

Exposing wood to high temperatures induces chemical changes that result in new properties of the wood. Modern industrial heat treatment methods utilize a controlled environment (SUNDQVIST 2003). The purpose of heat treatment is to improve dimensional stability, increase biological durability and, in some cases, control colour changes. Dimensional stability is strongly connected to the hygroscopicity of wood. When wood is exposed to elevated temperatures, the hemicelluloses are partially decomposed, resulting in reduced hygroscopicity (STAMM 1964; KOLLMANN & SCHNEIDER 1963; ESPENAS 1971; KINNINMONTH 1976; PRICE & KOCH 1980; SEHLSTEDT-PERSSON 1995; VIITANIEMI 1997). The reduction of hygroscopicity also influences the wettability of wood (HAKKOU et al. 2005).

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SANDBERG (2002) studied the influence of different wood properties on the absorption of water in spruce. The biggest difference is between sapwood and heartwood. The capillary water height (CWH) in sapwood is approximately 3 times higher than in heartwood. CWH is defined as the average distance to the 40% MC boundary. Growth site influences water absorption; suppressed trees that have grown in areas with good water supply have the highest absorption. Placing the samples with butt end up or down does not influence absorption.

An urgent question for outdoor applications is how absorption of free water in wood is affected by the heat-treatment process. THUNELL & ELKEN (1948) studied swelling and hygroscopicity in 100% relative humidity (RH) and water soaking of pine, spruce, oak, beech and birch after different methods of heat treatment in various environments—air, nitrogen, melted metal (led and tin) and saturated steam at superatmospheric pressures. Hygroscopicity was found to be lower after heat treatment when subjected to 100% RH, but an increase of water uptake when subjected to soaking in free water was found for heat-treated wood**.** This behaviour was most evident when treatment was performed in a steam environment.

In a recent study by METSÄ-KORTELAINEN et al. (2006), radial water absorption of pine and spruce heat-treated at 170°C, 190°C, 210°C and 230°C and a reference material dried at 70°C was studied in floating tests for up to 146 hours. Significant absorption differences between sapwood and heartwood were found for both spruce and pine. For pine, the difference was very pronounced, with a rapid absorption in sapwood compared to heartwood. The effect of heat-treatment temperature upon water absorption in sapwood differed between the two species. In spruce, water absorption decreased directly proportionally to increased temperature, while for pine, absorption was largest for 170°C and 190°C. While spruce sapwood samples never reached 30% average moisture content (MC) during the whole test, after only 6 hours, floating pine sapwood samples approached 30% average MC for 170° and 190°C treatment, and after 146 hours reached approximately 45% average MC. In spruce heartwood, water absorption decreased directly proportionally to increased temperature, while pine heartwood showed a somewhat more complicated pattern during the test. Compared with reference material dried at 70°C, all heat-treated pine heartwood samples absorbed less water, and the highest temperature (230°C) showed the least absorption.

MATERIALS AND METHODS

For this article, longitudinal water absorption for three different species was investigated—birch, spruce and pine. Four industrially predried boards of each species were used in the experiment. Each board was cut into three samples as shown in Figure 1. The industrial predrying down to 18%MC was performed at temperatures below 60°C. The dimensions of the spruce and pine boards were 50 x 125 mm^2, and the birch boards measured 50 x 90 mm^2. The four sample boards were dried further in a climate chamber at 60°C before heat treatment was performed. The sample marked 60°C in Figure 1 was

kept in the climate chamber while the two heat treatments were performed. Heat treatments were performed at 170°C and 200°C as shown in Figure 2.

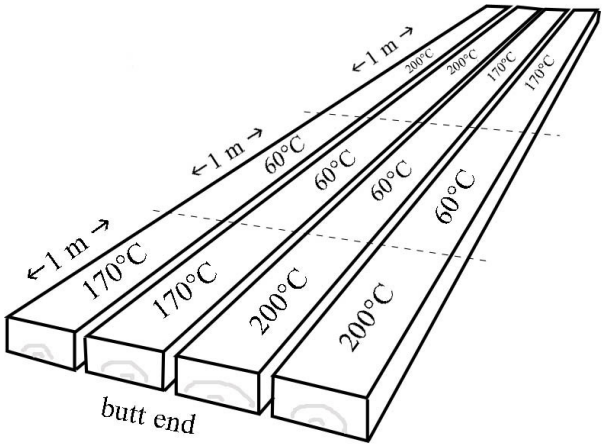

Figure 1 Cutting of the four samples for each species into three matched samples, two for heat treatment at 170°C and 200°C and one as reference dried at 60°C.

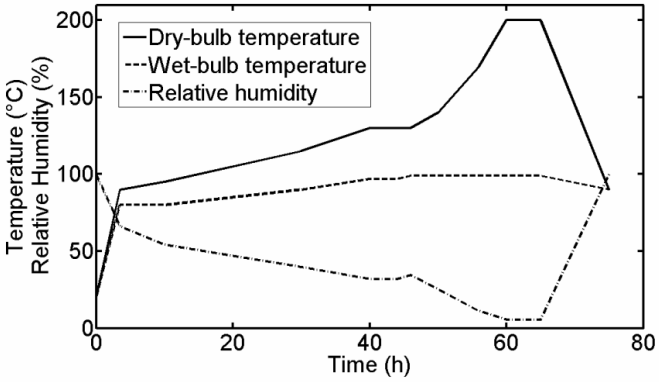

Figure 2 Process schedule for heat treatment at 200°C. The same schedule was used for heat treatment at 170°C, but then the 3-hour-long maximum temperature plateau was held at 170°C.

Each sample was planed and cut into 30-cm-long samples in accordance with Figure 3. From the surplus material, samples were taken for MC control according to the oven-drying method at 103°C for 24 hours. Samples were also taken from the surplus material for SEM studies reported in SEHLSTEDT-PERSSON et al. (2006)

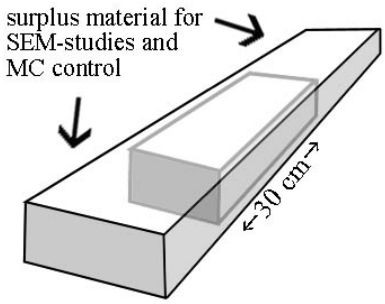

Figure 3 Planing and cutting of samples after heat treatment for absorption test. Samples were chosen with as much clear wood as possible in 30-cm lengths. Material for SEM studies was taken from marked surplus material close to the absorption sample.

During the absorption test in indoor climate, the samples were kept standing in batches of 6 samples in approximately 25-mm-deep water on a metal grid to insure good contact with the water (Figure 4). The samples were always oriented with the butt end down in the water. Intermittently, the batches were placed in the CT scanner, and the movement of water inside the boards was studied by scanning every 5 millimetres along the samples. The size of the voxels in CT volumes was 0.63 x 0.63 mm in the cross-section plane and 5 mm in the longitudinal. Scanning was done before the start of the experiment and then after 1, 3, 5, 8, 12 and 15 days of absorption. Due to technical problems, no scanning was possible for birch after the first day; therefore the first scan for birch was after 2 days of absorption.

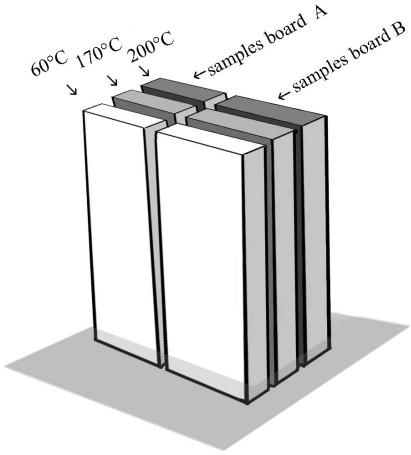

Figure 4 Batch with samples from two boards (out of four for each species) with three treatment temperatures placed in water to a depth of approximately 25 mm for longitudinal water absorption with butt end down. In total, 6 such batches were used in the absorption test with intermittent CT scanning of each batch for pine, spruce and birch over 15 days.

Every voxel in the CT-scanned volume contains the average density for that volume. From this information, the MC can be calculated if the dry density is known. The dry density in this experiment was calculated by using the density from the first CT-scanning sequence by subtracting the MC measured in the surplus material, as presented in Figure 5. In this work, the average density of each board was used in determining the MC during absorption. No consideration of swelling has been taken into account.

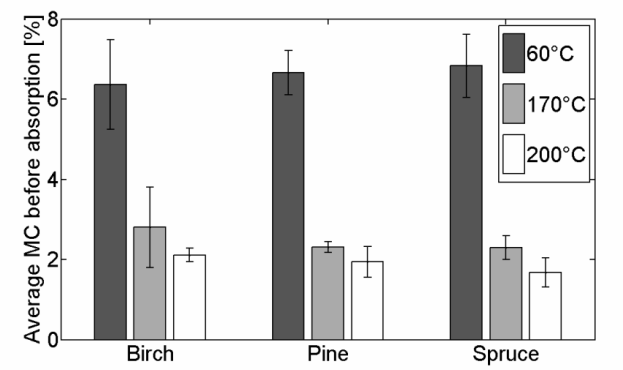

Figure 5 Average MC measured before the samples were placed in water for absorption testing. Measurements were made on the surplus material.

Three different calculations were done within each measured volume in all samples: the average MC at every fifth millimetre, the average MC in the chosen volume and the average height to fibre saturation point (FSP). As a simplification, FSP is set to 30% MC even though FSP is known to decrease with increasing temperature. For spruce and pine, sapwood and heartwood were measured separately in volumes of 11 x 11 x 61 and 16 x 16 x 61 voxels respectively. The measurement in sapwood was done at two different locations in each sample. Since birch only contains sapwood, only one volume of 11 x 104 x 61 voxels in the centre of the board was measured. The height to FSP was calculated by counting all voxels with MC higher than 30% divided by the number of voxels in the cross section of the measured volume.

RESULTS

In birch, the highest average MC after 15 days was found in the untreated 60°C samples (Figure 6). The samples heat-treated at 170°C had somewhat lower average MC, while samples heat-treated at 200°C were found to have a significantly lower average MC.

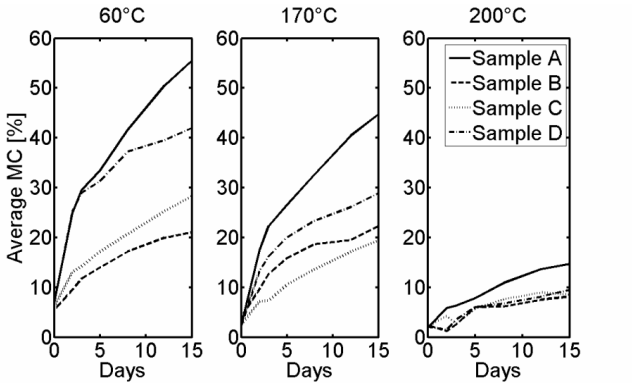

Figure 6 The change in average MC during longitudinal absorption in four birch samples during 15 days.

When looking at the average MC at different heights (shown in Figure 7), it was found that heat treatment seemed to have reduced the heights that the moisture reaches. The curves in 60°C and 170°C have two distinct points of inflexion. The second point of inflexion (marked in Figure 7) shifted towards higher MC values in the samples heat-treated at 170°C. The same pattern was also discernible in the samples treated at 200°C, but due to the low absorption, it can only be seen as a higher maximum MC.

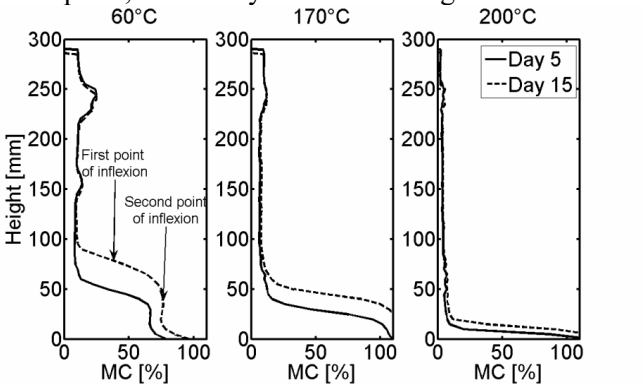

Figure 7 The average MC at different heights of sample B in the longitudinal direction in birch after 5 and 15 days of water absorption. In the 60°C reference sample, the first and the second points of inflexion are marked with arrows. These points are shifted towards higher MC in the heat-treated samples.

In the pine sapwood samples, it was found that the samples heat-treated at 170°C had the highest average MC after 15 days of absorption, while the samples treated at 200°C had absorbed about the same amount as the untreated samples. The untreated samples showed signs of stagnating at about 20% MC, whilst the heat-treated pieces showed no signs of stagnation. The average MC in pine heartwood (shown in Figure 8) was lower than in sapwood. Increase of treatment temperature showed a weak tendency to produce a

decreasing average MC in pine heartwood (Figure 8), but the increase of the average MC was the highest in samples treated at 170°C (Table 1).

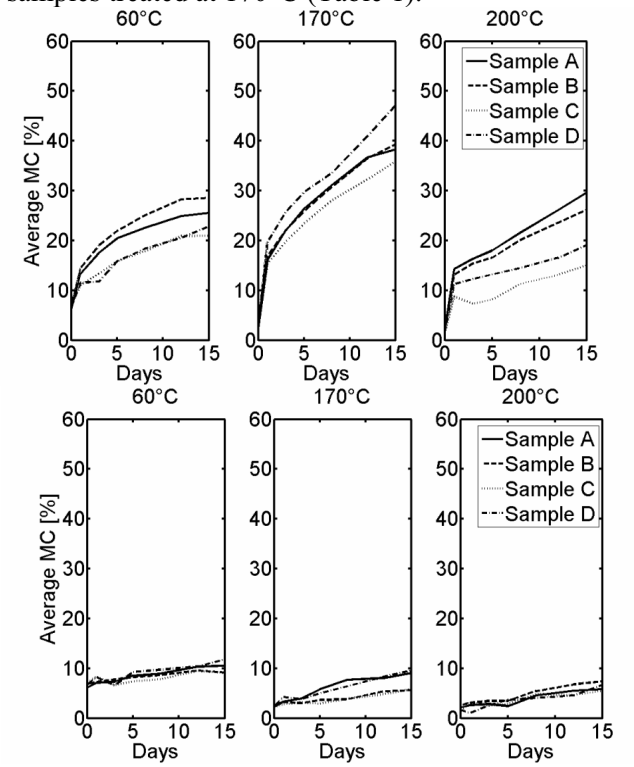

Figure 8 The change in average MC during longitudinal absorption in four pine samples during 15 days. The three upper plots show average MC in pine sapwood, and the three lower show the average MC in pine heartwood.

The height of the absorbed moisture in pine sapwood reached the highest level in samples treated at 170°C, as shown in Figure 9. Pine sapwood showed the same tendency to shift the second point of inflexion towards higher MC in the heat-treated samples. There was no difference found by studying the average moisture content for different heights in pine heartwood.

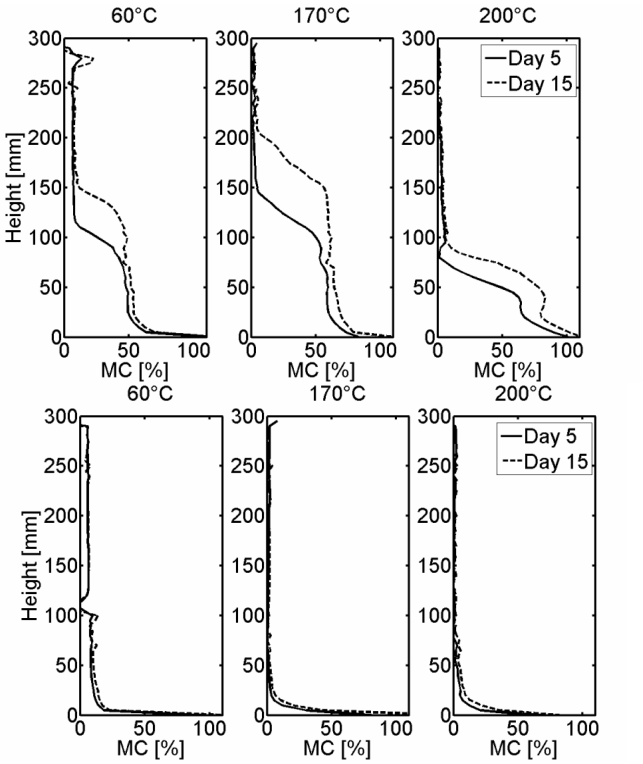

Figure 9 The average MC at different heights of sample B in the longitudinal direction in pine after 5 and 15 days of water absorption. The three upper plots show average MC in pine sapwood, and the three lower show the average MC in pine heartwood.

The average MC of both sapwood and heartwood of spruce after 15 days of absorption shown in Figure 10 are comparable to pine heartwood. Both also showed the same tendency as pine heartwood of increasing treatment temperatures producing a decreasing average MC. As in heartwood of pine, the biggest increase in average MC was found in samples treated at 170°C (Table 1).

Table 1 The increase of average MC from the first to the fifteenth day.

Treatment temperature	Pine heartwood	Spruce sapwood	Spruce heartwood
60°C	3.9%	8.7%	6.5%
170°C	5.7%	10.3%	8.7%
200°C	2.8%	8.8%	6.3%

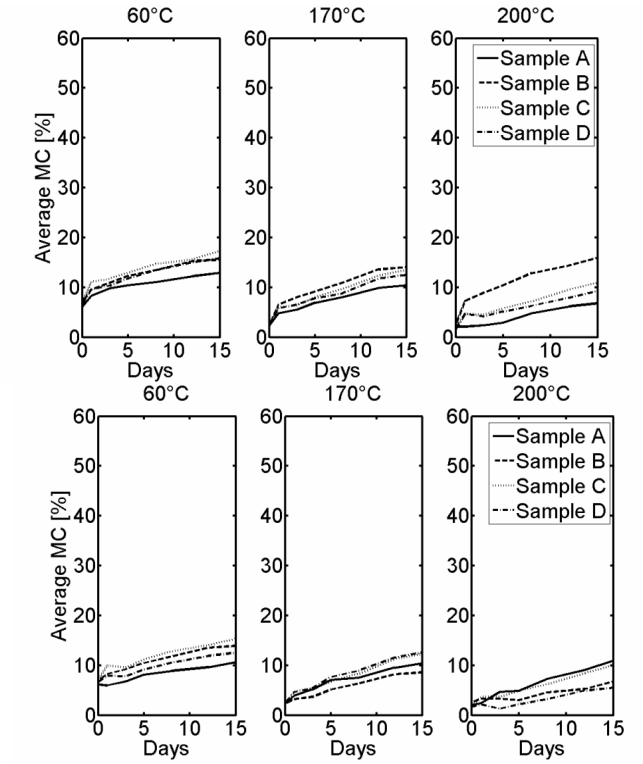

Figure 10 The change in average MC during longitudinal absorption in four spruce samples during 15 days. The three upper plots show average MC in spruce sapwood, and the three lower show the average MC in spruce heartwood.

The height of the moisture in spruce sap- and heartwood (Figure 11) was found to be comparable to that of heartwood in pine. As in pine heartwood, the uptake of water is too low to form a second point of inflexion, but there is a tendency for the heat-treated samples to have higher maximum MC.

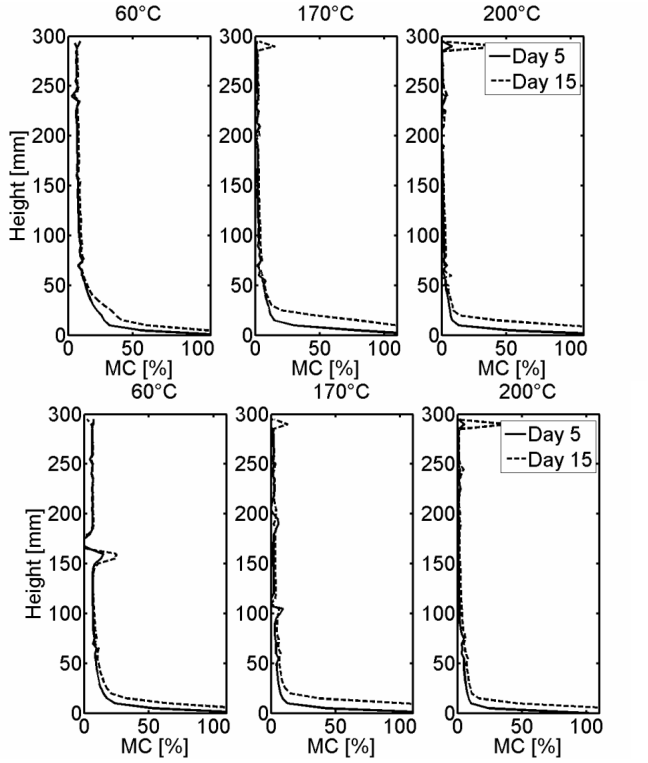

Figure 11 The average MC at different heights of sample C in the longitudinal direction in spruce after 5 and 15 days of water absorption. The three upper plots to show average MC in spruce sapwood, and the three lower show the average MC in spruce heartwood.

The average height to FSP after 5 and 15 days of absorption is shown in Figure 12 with 95% confidence intervals. Large differences are found between different treatment temperatures for birch and pine sapwood, while pine heartwood and spruce show less influence of temperature. For birch, the height to FSP decreased with increased temperature, and this phenomenon was more accentuated after 15 days. In both sapwood and heartwood of pine, the maximum height was found in the samples treated at 170°C. In pine heartwood, the difference is small after five days, but the difference increases after fifteen days. In pine sapwood, the height in the 60°C references was significantly higher than the samples treated at 200°C, while the difference was negligible in heartwood.

After five days, no differences in heights to FSP were established in sapwood of spruce. After fifteen days, the height to FSP in the samples treated at 200°C was lower than in 60°C and 170°C samples. In spruce heartwood, the height to FSP was found to be lower in both groups of heat-treated samples in the untreated 60°C reference material.

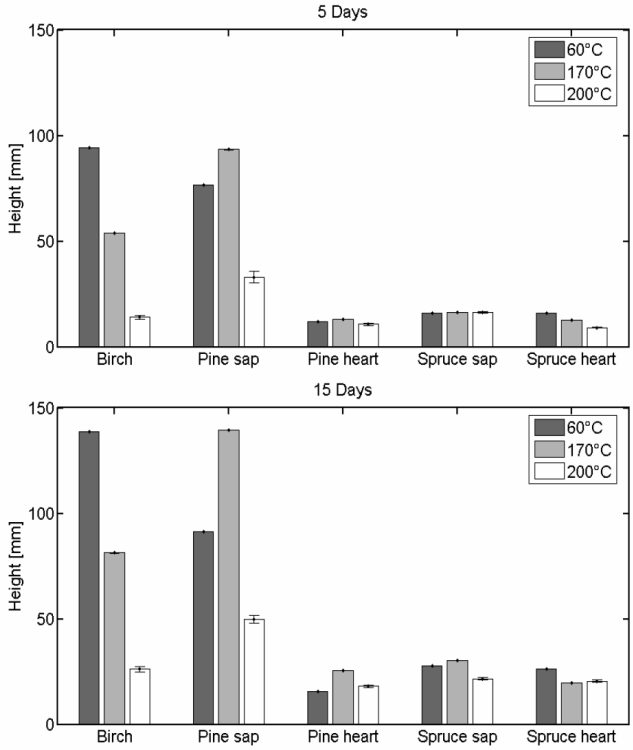

Figure 12 Average height to FSP after 5 days (upper) and 15 days absorption (lower) with 95% confidence interval for birch, and sap- and heartwood of pine and spruce heat treated at 170°C and 200°C and reference material dried at 60°C.

DISCUSSION

The high absorption of water in pine sapwood treated at 170°C supports the results found in METSÄ-KORTELAINEN et al. (2006). This, together with the shifting of the second inflexion point towards higher MC in pine sapwood and birch and the increase of the maximum average MC in spruce sap- and heartwood, confirms the finding in THUNELL & ELKEN (1948) that heat treatment increases the ability to store and transport free water. This can also be seen since birch heat-treated at 170°C has almost the same average MC as the references, but has a lower height to the FSP, which means that there has to be more free water stored in the lower heights of the heat-treated birch. One explanation for this could be that if there is formation of micro cracks of the type discussed in TERZIEV (2002), these could act as new pathways for capillary action of free water. The generated lifting force in a capillary is determined by the contact angle, i.e., the wettability of the material. The wettability of heat-treated wood is decreased with higher treatment temperatures, which would suggest a reduction of the capillary action. However, if the wettability has decreased just slightly while there is a formation of micro

cracks, there could be an increase in the uptake of water due to the increased number of capillaries. When the treatment is performed at higher temperatures it will result in further reduction of the wettability, and thus a reduction of the capillary forces, resulting in less capillary action. This would explain why all samples treated in 170°C have the highest increase of average MC as shown in table 1. It also means that there might be a treatment temperature lower than the ones used in this experiment that would have the same influence on birch. There is little known about how absorption of free water works in wood. If this theory is correct it would mean that the free water is transported through a thin water film on the cell wall inside the vessels rather than through capillary action in the vessels as a whole.

The theory presented gives no explanation as to why pine sapwood has much higher absorption compared to pine heartwood, spruce sapwood and spruce heartwood. This is most likely due to differences in the cell structure. A further study on these differences in structure of the material used in this work is presented in SEHLSTEDT-PERSSON et al. (2006).

The small confidence interval shown in Figure 12 can be misleading, since it is actually smaller than the error of the method used due to the resolution in the longitudinal direction, the placing of the batches in the CT scanner and the fact that swelling has not been taken into consideration.

CONCLUSIONS

Through this study of water absorption using a CT scanner, the following conclusions can be drawn:

- The absorptive behaviour of pine sapwood differs from all the other samples.
- There is a very small difference in absorption between sapwood and heartwood in spruce.
- Absorption in pine heartwood is comparable to the absorption in spruce sapwood and heartwood.
- Heat treatment results in an increased capacity to store and transport free water.
- Heat treatment at 200°C results in lower heights to the FSP in all the groups.

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Paper VII

Margot Sehlstedt-Persson, Dennis Johansson, Tom Morén
Effect of heat treatment on the microstructure of pine, spruce and birch and the influence on capillary absorption.
Proceedings 5th IUFRO Symposium Wood Structure and Properties '06, September 3-6, in Sliač - Sielnica, Slovakia. (2006)

Paper VII: Effect of heat treatment on the microstructure of pine, spruce and birch and the influence on capillary absorption

EFFECT OF HEAT TREATMENT ON THE MICROSTRUCTURE OF PINE, SPRUCE AND BIRCH AND THE INFLUENCE ON CAPILLARY ABSORPTION

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Abstract

Heat-treated and matched boards dried at 60°C of Scots pine (*Pinus sylvestris*), Norway spruce (*Picea abies*) and Birch (*Betula pubescens*) were submerged into water, allowing for water absorption in the longitudinal direction during two weeks in an indoor climate. Heat treatment was performed according to the ThermoWood process at 170°C and 200°C. Boards from pine and spruce contained both sapwood and heartwood. During water absorption, computer tomography scanning (CT scanning) was performed intermittently in order to measure the ascent of capillary water. Longitudinal water absorption in heat-treated pine sapwood was substantially larger than in untreated sapwood. In pine heartwood, the ascent of water was low in heat-treated as well as in untreated boards. Spruce showed low water absorption in sapwood and heartwood in heat-treated as well as in untreated boards. In birch, water absorption was lower in heat-treated wood than in wood dried at 60°.

SEM studies of the anatomical microstructure, the pits and pit membranes, were performed on heat-treated as well as on untreated material. SEM studies revealed damage in heat-treated and dried pine sapwood mainly in pit membranes in the fenestriform crossfield pits connecting longitudinal tracheids with radial ray parenchyma cells. This damage is believed to play an important role in explaining the differences in water absorption between pine and spruce, since the piceoid crossfield pits in spruce seemed to be unaffected by heat treatment. In comparing the three different treatment temperatures in birch, no striking, visible differences were found that could shed light on the observed large differences in capillary water absorption.

Keywords: capillarity, absorption, heat treatment, Scots pine, Norway spruce, birch, SEM, crossfield pit, pit membrane, fenestriform

INTRODUCTION

In various heat treatment processes, such as *ThermoWood* and *PlatoWood*, among other industrial-scale heat treatment processes (SUNDQVIST 2003), wood is exposed to temperatures between approximately 160°C and 230°C. The main purpose of heat treatment is to achieve new material properties, rather than to dry the wood, material properties such as increased biological durability, enhanced dimensional stability and the

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possibility of controllable colour changes. The disadvantages that have to be dealt with are reductions in various kinds of mechanical strength such as increased brittleness and decreased bending and tension strength. Reduced wettability for heat-treated wood also affects its glueability and paintability. The wettability of heat-treated spruce (*Abies alba*) and pine (*Pinus sylvestris*) shows similar behaviour with a sudden decrease in wettability at treatment temperatures in the range between 100°C and 160°C (HAKKOU et al. 2005).

Wood that has been exposed to elevated temperatures shows a permanent reduction in hygroscopicity that is dependent on temperature level and duration of exposure (SKAAR 1988). Many studies have reported on this subject (KOLLMANN & SCHNEIDER 1963, ESPENAS 1971, KINNINMONTH 1976, PRICE & KOCH 1980, SEHLSTEDT-PERSSON 1995, VIITANIEMI 1997). This reduction is mainly associated with a partial decomposition of the most hygroscopic cell wall constituent—the hemicelluloses (STAMM 1964). This reduction of hygroscopicity improves the dimensional stability of heat-treated wood.

Heat-treated wood is used in many indoor applications such as furniture, flooring, panelling and interiors of bathrooms and saunas (VIITANIEMI 2000) but the market is growing for heat-treated wood also in outdoor applications such as garden furniture and exterior cladding (METSÄ-KORTELAINEN et al. 2006).

An urgent question in regard to outdoor applications is how absorption of free water in wood is affected by the heat-treatment process. In a recent study by METSÄ-KORTELAINEN et al. (2006), radial water absorption of pine and spruce heat-treated at 170°C, 190°C, 210°C and 230°C and a reference material dried at 70°C was studied in floating tests for up to 146 hours. Significant absorption differences between sapwood and heartwood were found for both spruce and pine. For pine, the differences very pronounced, with a rapid absorption in sapwood as compared to heartwood. The effect of heat-treatment temperature upon water absorption in sapwood differed between the two species. In spruce, water absorption decreased in direct proportion to increased temperature, while for pine the absorption was largest for 170° and 190°C. While spruce sapwood samples never reached 30% average moisture content (MC) during the whole test, pine sapwood samples approached 30% average MC for 170° and 190°C treatment after only 6 hours' floating, and reached approximately 45% average MC after 146 hours. In spruce heartwood, water absorption decreased directly proportionally to increased temperature, while pine heartwood showed a somewhat more complicated pattern during the test. Compared with reference material dried at 70°C, all heat-treated pine heartwood samples absorbed less water, and the highest temperature (230° C) showed the least absorption.

When free water is absorbed in wood applications, it moves in internal three-dimensional passages in the wood structure deriving from the growth of the tree and which are constructed for the ascent of sap in the living tree. Hollow tracheids in softwood connected to each other with bordered pits at the ends in the longitudinal direction

constitute the main direction of axial water transport. Radial transport takes place in horizontal ray tracheids, and tangential transport via bordered pits connecting the radial walls in neighbouring tracheids. Even if pine and spruce at a first glance seem to have very similar anatomical structures, the key to the different water absorption behaviour in dried wood likely will be found in differences in anatomical structure.

What differentiates spruce and pine wood? Apart from macroscopic differences, such as higher average density for pine, different knot patterns, different extractive content, brighter wood colour in spruce, visible heartwood in pine, but not in spruce, other differences are found at the anatomical level. The most conspicuous anatomical detail that differentiates pine from spruce is the connection between longitudinal tracheids and horizontal parenchyma cells in rays. In a radial view, a large window-like (*fenestriform*) pit opening is found in pine, with a thin membrane between the neighbouring cells. In spruce, a number of small *piceoid* or *cupressoid* pits can be seen in the membrane (Figure 1).

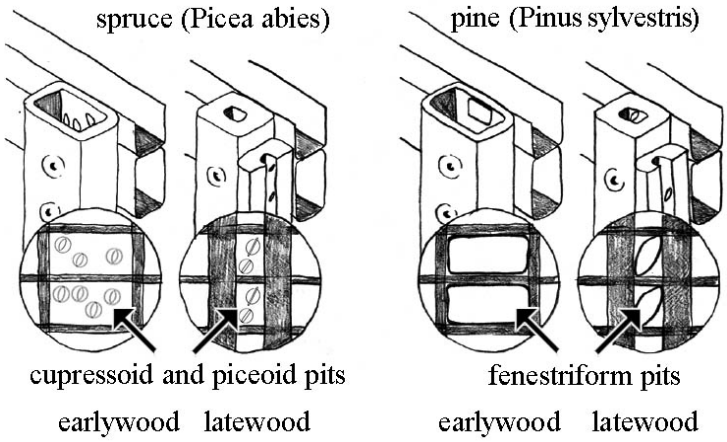


Figure 1 Interconnecting pits between ray parenchyma and vertical tracheids in pine and spruce, earlywood and latewood.

Ray tracheids in spruce (*Picea abies*) are less multishaped in form and appearance than in pine (*Pinus sylvestris*), and their frequency relative to ray parenchyma cells is much lower compared to pine: 1:2.7 and 2.8:1 for spruce and pine respectively. In spruce, only one type of horizontal thick-walled ray parenchyma appears, while in pine, about 15% consists of thin-walled cells. The average diameter of the piceoid or cupressoid simple pits in spruce in the connection between ray parenchyma and vertical tracheids is 2 μm, to be compared to the large fenestriform pits in pine with an average size of 12 x 31 μm. The overall pit area is ten times larger for parenchyma cells in pine than in spruce (NYRÉN & BACK 1960).

LIESE & BAUCH (1967) performed anatomical studies of air-dried softwoods and found that all bordered pits in the earlywood zone in sapwood were aspirated in both pine and spruce. The thin disc-like torus in earlywood pits effectively closes the opening in the pit chamber during withdrawal of capillary water. In the latewood zone, however, where the pit diameter is smaller and the shape of the torus is distinctly thicker and is convex shaped, differences were found between the two species—while between 20% and 25% of the pits were unaspirated in spruce, up to 50% of the pits in pine remained open.

The overall extractive content is higher in pine than in spruce, especially in the heartwood, where the amount is substantially higher in pine. Acetone-soluble extractive content in sapwood was found to be 4.5% and 0.9% and in heartwood 9.3% and 0.5% for pine and spruce respectively (SEHLSTEDT-PERSSON 2001). A great part of the heartwood extractives derives from the content of biologically dead parenchyma cells. In pine, the axial resin canals are active throughout the sapwood, whereas in spruce, only the 3–5 annual rings farthest out are active. Pine also has larger axial resin canals than spruce. The average diameter of resin canals is 200 μm in pine and 100μm in spruce (BACK 1969). The volume share of axial resin canals is 4 times higher in pine than in spruce (PETRIC & SCUKANEC 1973).

FENGEL (1970) observed globular particles of varying size in the living parenchyma cells throughout the sapwood of pine. In the sapwood/heartwood transition zone, where an intense biological activity takes place during the mortification of the parenchyma cells, these globular particles lost their spherical shape and flowed together, and the content was deposited upon the parenchyma cell walls and the membranes of the fenestriform pits. In ray tracheids in heartwood, the bordered pits were found to be predominantly unaspirated, but completely encrusted with heart wood substances, thus closed not by aspiration but by sealing of membranes. This observed encrustation of the membranes with heartwood substances in combination with pit aspiration in heartwood probably affects the permeability and flow paths in pine heartwood considerably.

ULVCRONA et al. (2006) studied linseed oil impregnation of spruce (*Picea abies*), a species known to be difficult to impregnate. A higher average uptake of oil was generally found in earlywood than in latewood even though aspiration of bordered pits is reported to be far higher in earlywood tracheids than in latewood tracheids (LIESE & BAUCH 1967). Exceptional tangential movement of impregnates in latewood bands in white spruce (*Picea glauca*) was observed by KEITH & CHAURET (1988). Similar behaviour occurred in some specimens in the study by ULVCRONA et al. (2006). They also found that oil seemed to stop at the border between latewood and earlywood. Since ray tracheids in spruce often are interrupted by a parenchyma cell at the junction of the annual ring (BAINES et al. 1985), this might explain why penetration often stops abruptly at the annual ring border in the radial direction.

OLSSON et al. (2001) studied transverse liquid flow paths in pine and spruce sapwood and heartwood vacuum impregnated with of a low-viscous epoxy. They propose a

damage hypothesis deriving from the impregnation procedure. For pine sapwood the liquid flow was enabled through disrupted crossfield pit membranes. For spruce the thicker ray cell walls in combination with smaller crossfield pits reduced permeability considerably. The reduced permeability in pine heartwood was believed to be the result of deposits of high-molecular-weight substances (extractives) on the cell walls and in the parenchyma ray cells.

HAYASHI et al. (1965) found from microscopic observation that the leading portion of transverse penetration of water occurred in ray tissue in the dried softwood species Sugi, Hinoki and Akamatsu. Especially sapwood in Akamatsu (Japanese red pine) showed high penetration between rays and longitudinal latewood tracheids. Of the investigated species, Akamatsu was the only species with fenestriform pits in the connection between longitudinal tracheids and horizontal ray parenchyma cells. In fact, the transverse penetration weight of Akamatsu was as large as the longitudinal penetration weight of Sugi and Hinoki. They also observed that intercellular spaces in rays constitute a path of penetration for dyed solution.

In a study of penetration of different wood coatings into predried pine sapwood and spruce, DE MEIJER et al. (1998) found a substantially different behaviour of liquid flow into ray parenchyma and ray tracheids between these two species. In pine, the major part of the coating flows through the ray parenchyma cells from cell to cell, while in spruce, the coating flows in ray tracheids solely. While some coatings only penetrated spruce in ray parenchyma into the first cell, the penetration depth in pine parenchyma was as deep as 1000 μm. Coatings were found to flow from the ray parenchyma into longitudinal tracheids through the fenestriform pits in pine. Longitudinal tracheids can be filled by several rays, since on an average each longitudinal tracheid is in contact with 2.4 rays according to a study of Courtois cited in DE MEIJER et al. (1998). Intercellular spaces in rays were also found to be an effective pathway for liquid flow. A bit surprising is the fact that removal of extractives from the wood samples did not result in any significant differences in penetration (DE MEIJER et al. 1998).

During drying and heat treatment, wood is exposed to a hygrothermal process during which wood properties are chemically and physically affected. The ability to transport liquid water is also affected. TERZIEV (2002) found that high-temperature drying (HT drying) of Scots pine at 115°C significantly increased its permeability to impregnating liquids as compared to pine conventionally dried at temperatures up to 62°C. In a subsequent study of the same material (TERZIEV et al. 2002) it was shown in SEM studies of aspirated bordered pits that pit apertures in HT-dried pine often appeared split and torn, while no such observations were made in conventionally dried material. Also, characteristic microchecks in the S_3 cell wall layer were observed in HT-dried wood, but not in conventionally dried wood. These observations are interpreted as explanations for the increased permeability to impregnating liquids in HT-dried Scots pine wood. Modification of the warty layer in HT-dried wood with a “melted” appearance was also

observed. However, no studies of the cross-pit field between ray parenchyma cells and longitudinal tracheids were done.

The purpose of the present work has been to perform SEM studies of the physical changes of the anatomical microstructure, pits and pit membranes, on heat-treated and dried pine, spruce and birch used in a study of water absorption in the longitudinal direction (JOHANSSON et al. 2006) in order to shed light on questions arising from this study of differences between species and sapwood/heartwood. Special attention was given to the crossfield pits and the membranes between ray parenchyma and longitudinal tracheids in pine and spruce.

MATERIALS AND METHODS

A thorough description of the origin of the wood material and of the drying, heat treatment and absorption tests can be found in the article by JOHANSSON et al. (2006).

Small specimens cut from pine and spruce sapwood and heartwood and from birch wood used in absorption tests were prepared for Scanning Electron Microscope (SEM) studies in a JEOL 5200 scanning electron microscope. All specimens were mounted with carbon paste on metal stubs and sputtered with gold in a Denton Desk II sputter unit before observation. All observations presented in this work were made on radial surfaces carefully split from areas within the planks from surplus material as close as possible to the samples used in the absorption tests. Thus, by using split areas for studies, no cutting was done on the observed surfaces in order to minimize manually caused damage. Areas of interest were chosen from CT-scanned images during the absorption tests. Observed areas had a typical size of 15 x 20 mm. Overviews at quite low magnification, 35 x, were made of all radial surfaces for comparison of general observations.

RESULTS AND DISCUSSION

In the following figures, a variety of overviews and details are shown for pine and spruce.

Pine sapwood

In Figure 2 it is shown that a great number of the crossfield pits in pine sapwood show an open structure with partly loosened or ruptured pit membranes. No clear difference in share of open crossfield pits is seen between the 60°C, 170°C and 200°C samples (Figures 2a, 2b and 2c). A comparison of Figure 2d with untreated, fresh pine sapwood shows that these crossfields lack the open structures. Magnifications of the crossfield pit in pine sapwood heat-treated at 170°C seen in Figure 3 show an example of crossfields with loose or missing membranes (Figure 3a) and ruptured membranes (Figure 3b).

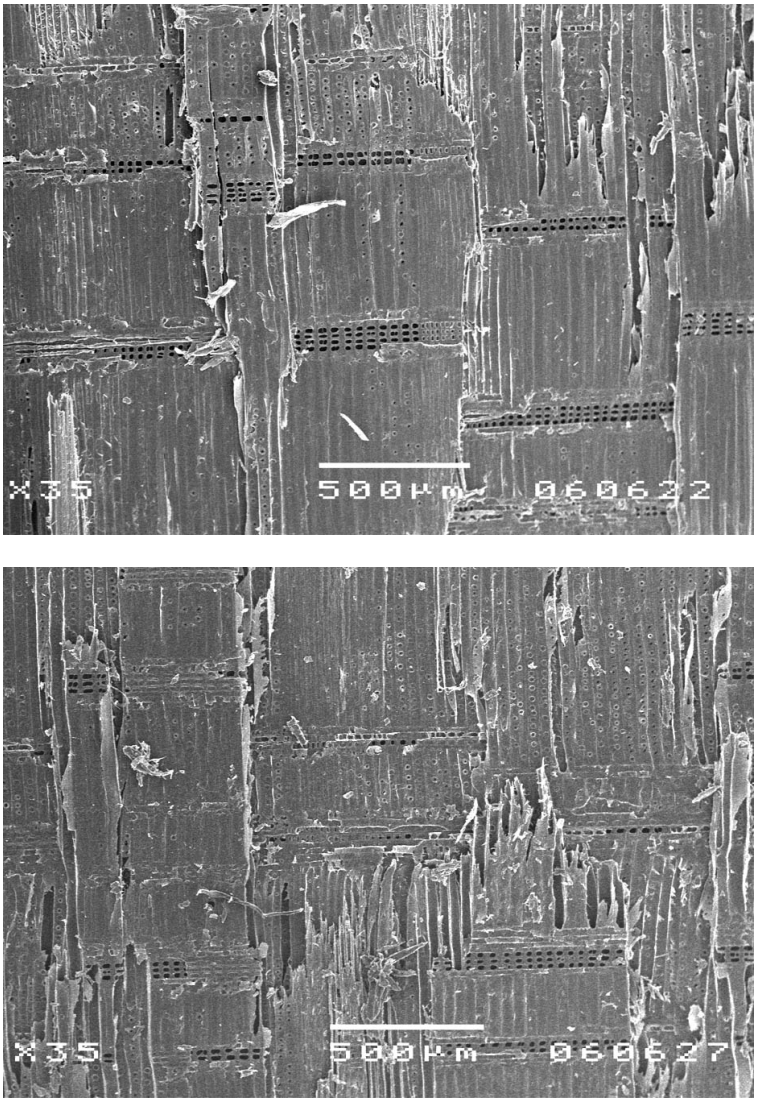


Figure 2 a) upper: Radial surface of pine sapwood dried at 60°C.
b) lower: Radial surface of pine sapwood heat-treated at 170°C.

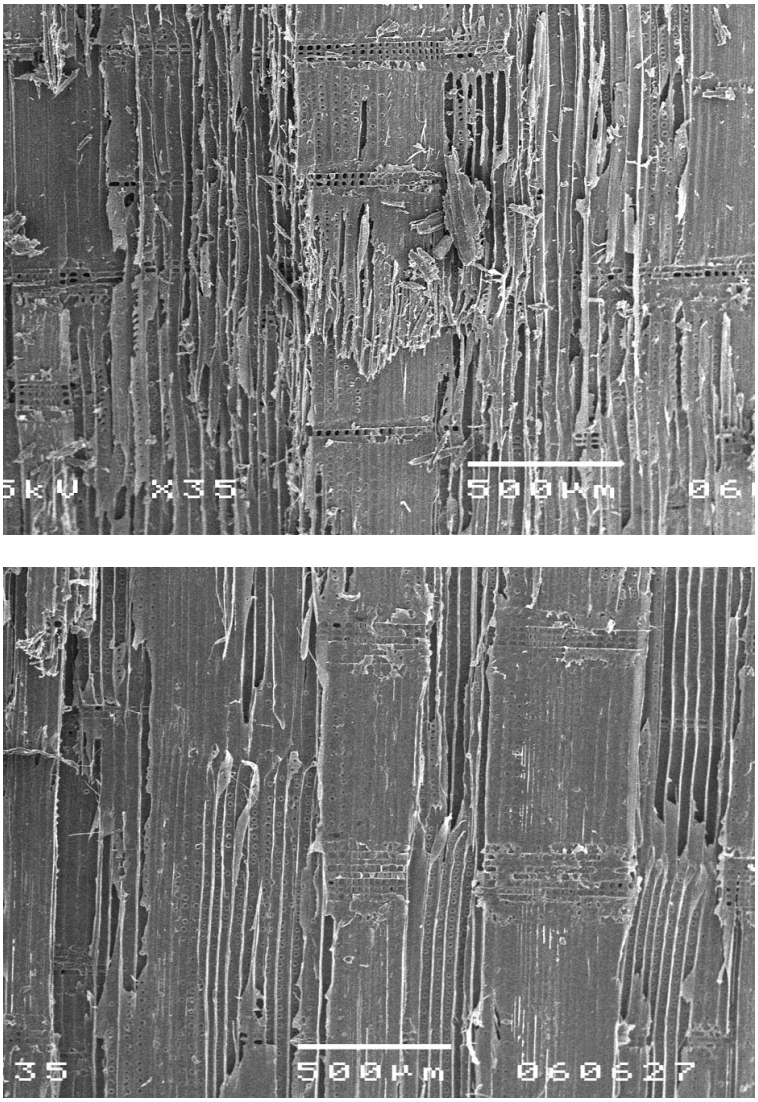


Figure 2 c) upper: Radial surface of pine sapwood heat-treated at 200°C.
d) lower: Radial surface of fresh pine sapwood.

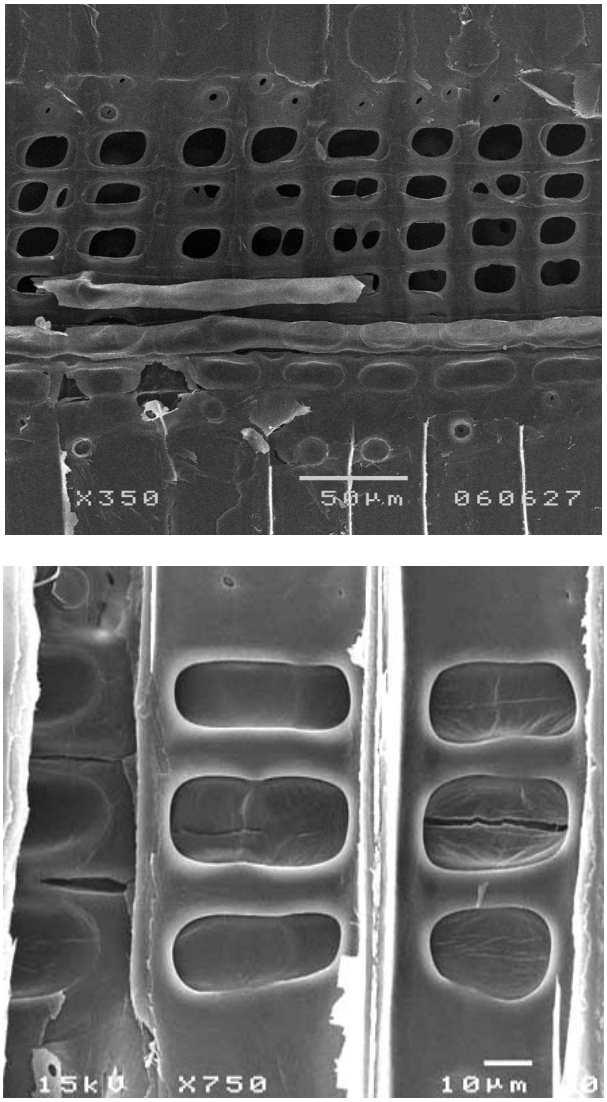


Figure 3 Details from crossfield pit in pine sapwood heat-treated at 170°C.
a) upper Main parts of the pit membrane have come loose. Through the open fenestriform pit opening it is possible to see the bordered pit in the neighbouring tracheid behind.
b) lower: Membranes in earlywood partly ruptured.

Bordered pits in pine sapwood.
Undamaged as well as damaged bordered pits are found in heat-treated pine sapwood. Some examples of ruptured membranes (tori) in aspirated, bordered pits in pine sapwood treated at 200°C are shown in Figure 4.

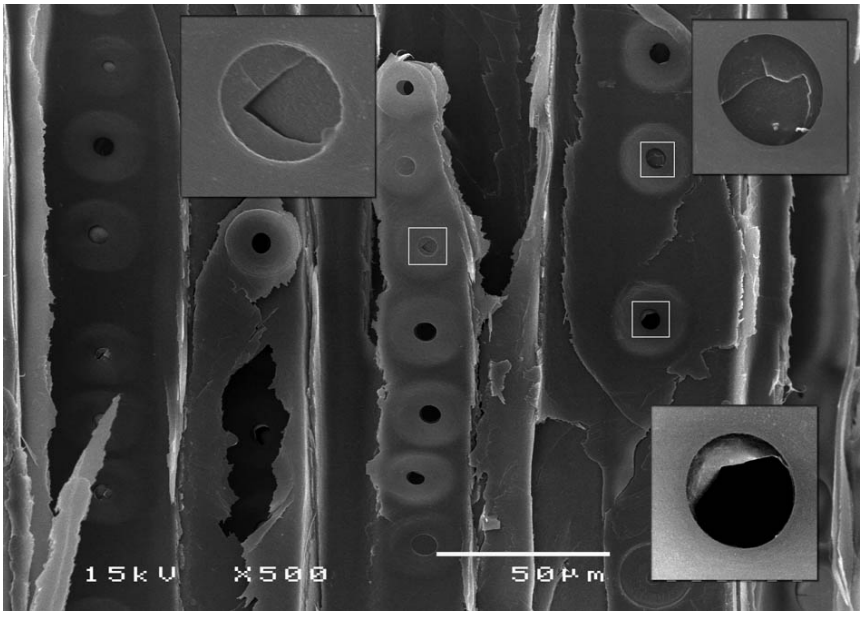
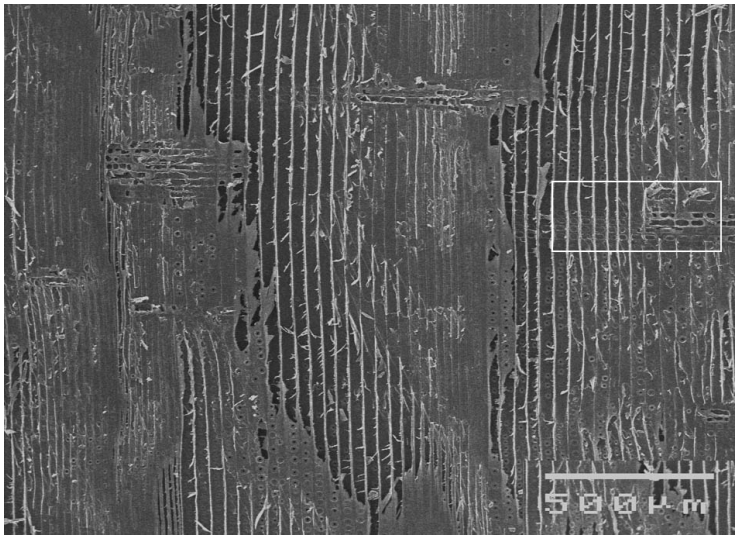


Figure 4 Examples of ruptured membranes (tori) in aspirated, bordered pits in pine sapwood treated at 200°C.

Pine heartwood
The crossfield pits in pine heartwood shown in Figure 5 appear to lack the occurrence the open, ruptured fields found in heat-treated pine sapwood.

Spruce sapwood
When comparing the appearance of the crossfield pits in spruce sapwood, no visual differences are found between wood treated at different temperatures compared to fresh, untreated spruce sapwood (Figure 6).

Birch
No striking, visible differences that could shed light on the large difference in capillary water absorption reported in JOHANSSON et al. (2005) were found in the SEM studies of radial surfaces in birch when comparing the three different treatment temperatures.



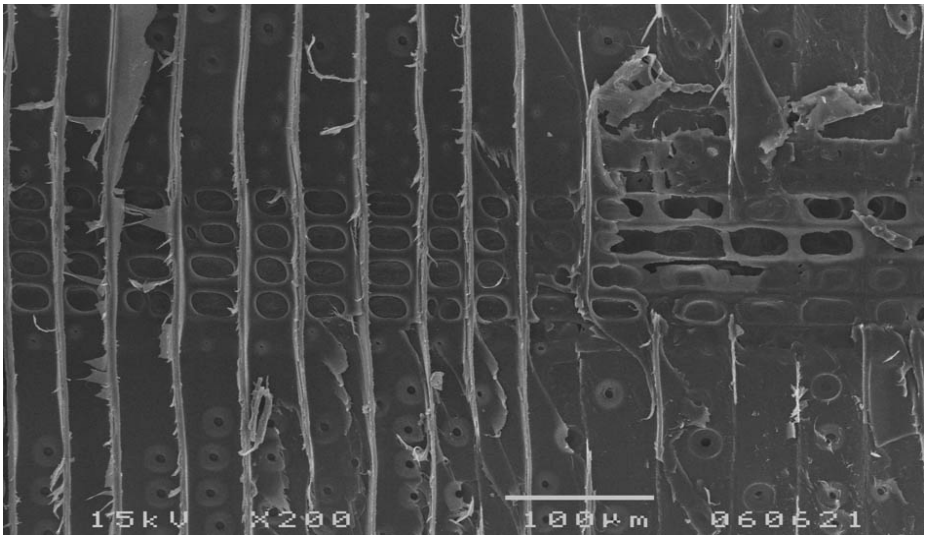


Figure 5 a) upper: Radial surface of pine heartwood heat-treated at 170°C.
b) lower: Detail from figure 5a) showing crossfield pit with whole membranes.

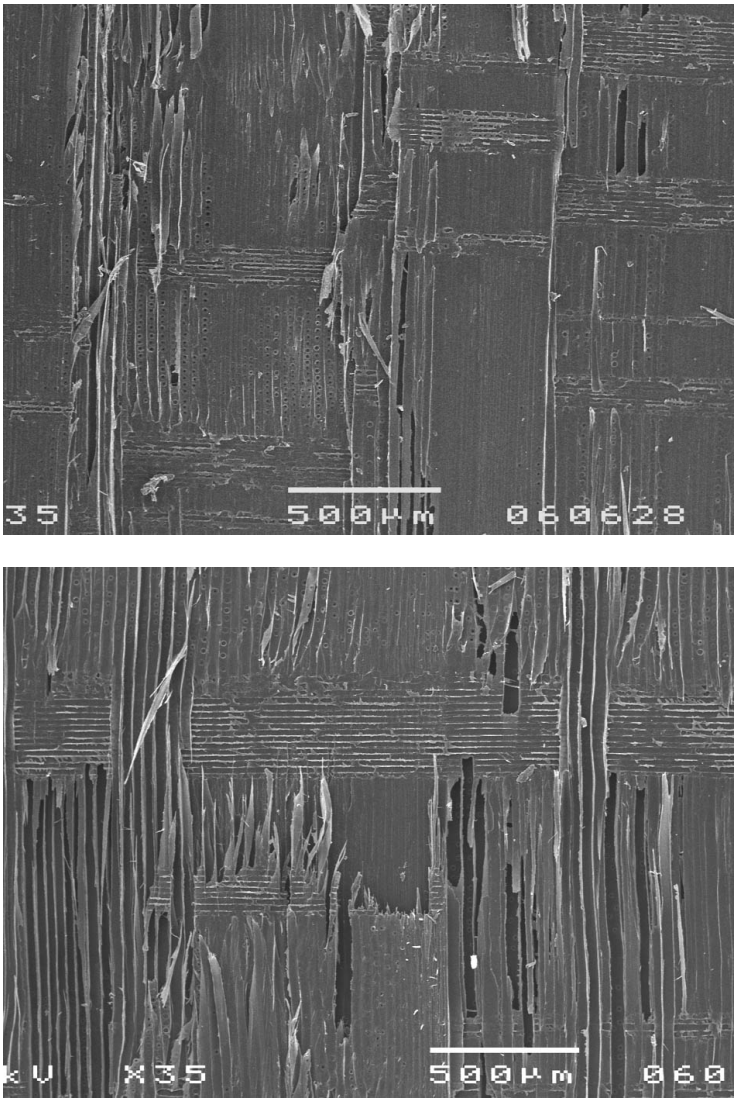


Figure 6 a) upper: Radial surface of spruce sapwood heat-treated at 170°C.
b) lower: Radial surface of fresh spruce sapwood.

DISCUSSION

Judging from the SEM photos, the occurrence of open, partly open and ruptured membranes in the crossfield pits in dried and heat-treated pine sapwood is fairly common. Even if there is a risk that some of this damage was caused during splitting when preparing the SEM specimens, there is no doubt that considerably fewer such areas are

found on fresh surfaces split in the same way. These open structures in the ray structures of pine sapwood are probably the primary explanation of the effective water uptake in pine sapwood as compared to spruce sapwood reported in JOHANSSON et al. (2006).

It is interesting to note that fewer such open crossfield areas are found in pine heartwood where water uptake is considerable lower than in pine sapwood. One hypothesis suggested explaining this is that during heartwood formation in the transition zone between sapwood and heartwood in the living tree, the dying parenchyma cells are slowly emptied of their liquid protoplasm. In green sapwood lumber, however, the living parenchyma cells are emptied much faster during the drying process. During this fast emptying, the thin membranes in the large fenestriform crossfield pits are subjected to strains that might rupture and damage the membranes. Since no difference in share of open crossfield pits was found between the pine sapwood material treated at 60°C, 170°C and 200°C, the damage probably occurred during the initial, capillary drying stage.

High extractive content, aspirated bordered pits, deposition and encrustation of heartwood substances on cell walls and membranes are other factors that diminish water uptake in pine heartwood compared to pine sapwood..

Another question is if resin canals in pine sapwood are paths for water uptake. Compared to spruce, the canals are biologically active throughout the sapwood part of the stem. If these canals are being more or less emptied during the initial, capillary phase of drying at high temperatures, they might contribute to water absorption. Resin flow at lumber surfaces is often seen as small dark spots in pine sapwood areas in dried lumber; the higher the temperature, the more resin that has flowed in the fusiform rays towards the surface.

CONCLUSIONS

During SEM studies of the anatomical microstructure, pits and pit membranes, on radial surfaces of heat-treated and dried pine, spruce and birch wood used in longitudinal absorption tests (JOHANSSON et al. 2006), the following observations were made:

- Crossfield pits between longitudinal tracheids and radial ray parenchyma cells in heat-treated and dried pine sapwood were found to be considerably more open than those of fresh sapwood. The membranes in the fenestriform pits were found to be partly loose or ruptured. No difference in share of open crossfield pits was found between the 60°C, 170° and 200°C material.

- Among undamaged bordered, aspirated pits, damaged bordered pits with ruptured membranes (tori) were also found in heat-treated pine sapwood.

- Crossfield pits in pine heartwood did not show the same occurrence of open, ruptured fields found in heat-treated pine sapwood. A hypothesis involving the emptying of the parenchyma cells has been suggested to explain this observation.

- In spruce, the crossfield pits seemed to be unaffected by heat treatment and drying as compared to fresh, green spruce sapwood.

- The open crossfield structures between ray parenchyma and longitudinal tracheids in heat-treated pine sapwood are believed to play an important role in explaining the differences in water absorption between pine and spruce sapwood.

- In birch, no visible differences that could shed light on the observed large difference in capillary water absorption were found when comparing the three different treatment temperatures.

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Paper VIII

Margot Sehlstedt-Persson, Thomas Wamming
Wood drying process – Impact on Scots pine lumber durability. (2008)
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Wood Drying Process – Impact on Scots pine lumber durability

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Abstract

There are indications that the drying process may affect the natural durability of wood negatively. The impact of various drying processes on the durability of Scots pine lumber has been evaluated with mass loss, in a decay test with brown rot fungus, *Coniophora puteana*, as measure of the decay resistance of sapwood and inner and outer heartwood. Drying with or without steam conditioning was performed in six different series: air drying, kiln drying at temperature ranges commonly used in Swedish sawmills at 70°C and 90°C with two different regulation principles, and one high-temperature drying at 110°C. Durability varied considerably both between and within boards. Sapwood showed considerable less durability than heartwood. No difference in durability was found between inner heartwood and outer heartwood. Air-dried heartwood showed the highest durability compared to other drying series. The lowest durability in sapwood and heartwood was found for series dried at the 90°C temperature level with high material temperature early in drying. The interpretation is that the duration of high material temperature at high MC is the critical combination for decay resistance in heartwood. Steam conditioning after drying decreased durability in sapwood.

Key words Drying, conditioning, durability, Scots pine, heartwood, *Coniophora puteana*

1 Introduction

Durability of wooden products for outdoor applications above ground is an urgent issue for the future utilization of wood as a competitive construction material. During recent years there has been some indication that the durability of pine heartwood products has declined, such as, for example, high-temperature dried pine poles in playgrounds that have become seriously decomposed after just a few years usage[1]. One hypothesis is that the drying process might negatively affect the natural durability of wood. In this study, the main issue is to clarify the impact of the drying process on the durability of Scots pine lumber in above-ground applications.

According to European Standard[2], pine heartwood is classified into class 3–4 (moderately to slightly durable) and pine sapwood into class 5 (not durable) in terms of natural durability to wood-destroying brown rot fungus. Mass loss, expressed as a percentage of

the original dry weight, is commonly used in laboratory tests to assess the natural durability of wood[3]. However, the variation in durability between pine trees from growing stands has been shown to be large in decay tests with the brown rot fungus *Coniophora puteana*[4]. A large proportion of this variation is due to genetic differences[5]. The variation in durability within a single tree in the radial direction is also shown to be large, with higher durability in outer heartwood, compared to inner heartwood, while tree height, crown limit, wood density, heartwood radius and proportion of latewood do not explain the variation[4]. The amount of extractives in heartwood generally increases with distance from pith. The pattern of lower extractive content near the pith may reflect the degradation of extractives over time or an increase in extractive deposits with age. Thus, the age of the tree affects heartwood extractive content[6].

Various heartwood extractives are known to contribute to decay resistance. The chemical characteristics that separate decay-resistant trees from decay-susceptible trees are resin acids, pinosylvins, acetone-soluble extractives and total phenolics measured according to the Folin-Ciocalteau (FC) assay[4]. The spatial distribution of pinosylvin in pine heartwood was found to decline in inner heartwood, while the concentrations were highest in outer heartwood at the transition between sapwood and heartwood[7]. No seasonal trend in the distribution pattern or concentration of pinosylvins was found in pine heartwood[8].

Sapwood, with its low natural durability, contains high amounts of carbohydrates as free sugars that play an important role as nutrients for, primarily, mould fungi. The concentration of soluble carbohydrates such as glucose, fructose and sucrose in pine sapwood is greatest in the outer sapwood and decreases gradually towards the innermost sapwood[9]. The seasonal fluctuation of low-molecular-weight sugars is great, with the highest concentrations during autumn and winter months in pine sapwood[10] as well as in spruce sapwood[11]. The surfaces of dried, winter-felled pine sapwood were shown to be more susceptible to mould growth than spring-felled timber[12].

Early in the capillary regime of the drying process when free water in sapwood moves towards the evaporation front beneath the surface, an enrichment of carbohydrates and nitrogen compounds takes place at the surface[13]. The drying rate has a significant effect on this redistribution, with a higher accumulation if the drying rate is high[14]. Thus, the nitrogen and carbohydrate gradients near the lumber surface in dried sapwood depend on the drying process. Air-dried sapwood surfaces were shown to have smaller gradients than kiln-dried lumber[15].

In mould-growth testing on dried sapwood surfaces, planing was shown to reduce the mould growth on kiln-dried lumber, while the mould growth on planed, air-dried surfaces increased compared to unplaned surfaces[16]. For kiln-dried sapwood, the reduction of mould growth on planed surfaces was higher in fast drying schedules compared to slow drying schedules. Planing of kiln-dried sapwood removes the most enriched zone, while in air-dried sapwood, planing might expose wood with a higher nutrient concentration.

The natural durability of wood has been evaluated by a multitude of methods for many species[6]. In general, there are difficulties in transforming and comparing results from tests on one species to another. Furthermore, even if the same standardized decay test is performed at five European test institutes on the same species in a round-robin test, the mass loss varies considerably[17].

Studies of the impact of different drying methods on the durability of pine and spruce have been done with various short- and long-term decay methods with varying results. No difference between different drying methods was found concerning mass loss in a 10-week rot test when comparing air-dried pine lumber with artificially dried pine lumber at temperature levels not exceeding 54°C[18]—temperature levels considered moderate by today's standards. In a long-term outdoor test above ground, air-dried pine and spruce lumber was compared with kiln-dried lumber of the same species[19, 20]. Air-dried spruce showed higher mass loss after 9 years' exposure compared to kiln-dried spruce[19], but also significantly higher average MC during exposure time, which probably explains the higher mass loss because of more favourable conditions for wood-destroying fungi. However, the drying process in the study[19] is poorly described, merely as "kiln dried". For pine sapwood[20], no difference in mass loss after 9 years' exposure was found between air-dried and kiln-dried material dried at a maximum of 65°C.

Mould growth with *Cladosporium cladosporioides* and *Penicillium commune* has been studied on spruce sapwood and heartwood dried at temperatures between 20°C and 170°C, together with spruce commercially heat-treated at 190°C and 210°C[21]. Mould growth was more pronounced on the original surfaces than on resawn surfaces, and heavier on sapwood than on heartwood. All kiln-dried material exhibited higher mould growth than air-dried material after 20 weeks of exposure, while heat-treated spruce showed very low mould growth levels. An inhibiting effect of higher drying temperatures on mould growth after 8 weeks of exposure with *Penicillium brevicompactum* was found for pine sapwood[22]. In an eight-week rot test with the brown-rot fungus *Fomitopsis palustris* on high-temperature treated Japanese cedar blocks, results show that durability was improved at treatment temperatures higher than 135°C and that longer treatment time resulted in stronger decay resistance[23].

The drying process can in fact be seen as a hygrothermal treatment of wood, and the performance of the drying process can be varied infinitely. The main issue with this study is to investigate if and how the drying processes commonly used at Swedish sawmills affect the durability of pine sapwood and heartwood. The focus is on the performance of the drying process with regard to temperature levels, material temperatures at different stages of drying and the impact of conditioning at the end of the drying process. A short-term *in vitro* test with the brown rot fungus *Coniophora puteana* was chosen as a measure of the durability of sapwood and inner and outer heartwood from winter-felled lumber with a high concentration of nutrients in the sapwood.

2 Materials and methods

Lumber

Centre-sawn boards 50 x125 mm from Scots pine (*Pinus sylvestris L.*) butt logs felled in January 2007 from a stand in Norrbotten in northern Sweden were used in the tests. Each green board was cut into four 1-meter samples (numbered 1–4 from butt to top end) which were end sealed with Sikaflex polyurethane sealant and kept in a climate chamber at 0°C, 95% relative humidity (RH), until the start of drying. Slices from all samples were cut for measurement of moisture content (MC), density and heartwood content. All samples were sorted into six similar series with regard to heartwood content, visually estimated resin content and position along the board. After each drying series, slices for MC control (oven-dry method) were cut from each sample. The samples were then kept in a freezer at -25°C until further cutting of test material.

Drying

Drying was performed in six different series. Series A, considered similar to outdoor air-drying, was, due to the time of year, done indoors at the laboratory on stickers at 20°C–25°C, 38%–45% RH for slightly less than 9 weeks. Series B–F were dried in a small-scale laboratory air-circulation kiln at maximum temperature levels of 70°C, 90°C and 110°C. For the 70°C and 90°C series B–E, two different regulation principles were used after the initial preheating:

I) Dry-bulb temperature (T_{db}) gradually rising to maximum temperature level and wet-bulb temperature (T_{wb}) at one or two constant levels.
II) Constant T_{db} at maximum level with initial T_{wb} dropping to a constant level.

Both these principles correspond to kiln-drying schedules used at Swedish sawmills. Series F was dried with a high-temperature schedule at a maximum temperature of 110°C. During series F, kiln regulation was unfortunately interrupted for 9 hours because of activation of an alarm, which resulted in a temporary temperature drop. The appraisal is, however, that this disturbance had a finite influence on the results in the decay test. The drying series are summarized in table 1 and in figure 1. Schedules for series B–F are presented in detail.

Preheating was performed with saturated steam in series C, E and F and with high pressure water spray in series B and D. Conditioning with saturated steam after drying was done on half of each batch in series B, C, D, E and F, while the other half was removed from the kiln at the end of drying. No conditioning was done on series A.

Wood temperature during drying

The wood temperature in one chosen sample per drying series B–F was registered using a PT100 sensor inserted in a hole drilled from the board edge to half board width at a depth of 5 mm below sapwood surface. No temperature measurements were done in the lumber dried indoors in series A

Decay test

The decay test with the brown rot fungus *Coniophora puteana* (BAM Ebw.15) was performed according to the standardized EN113 decay test, but modified with respect to sample size and incubation time in the same way as described by Harju and Venäläinen[24]. The mass loss of the samples after an incubation time of 7 weeks, expressed as percent of dry mass of wood before decay test, was used as a measure of durability.

Sampling for decay test

Specimens cut into 5- x 15- x 30-mm sized blocks were sawn from dried and planed samples in all six series at three positions: inner heartwood, outer heartwood and sapwood (figure 2). Thus, only planed surfaces were used in the study, with a planing depth of 2–3 mm. For outer heartwood specimens, the distance from pith side was measured. In total, 194 specimens were made; 2 x 66 heartwood and 62 sapwood specimens.

3 Results and discussion

MC and density

The average density, $\rho_{0,raw}$, of all dried boards before drying was 418 kg/m^3, with a standard deviation of 40 kg/m^3. Average MC before and after drying and conditioning (half batches in series B–F) in each series is shown in table 2. In series D, the low final MC after drying was adjusted with an extended two-step conditioning for half the batch.

Wood temperature during drying

Measurements of the temperature development in the wood material during drying are shown in figure 3 for series B–F. A pronounced difference between the two regulation principles I and II is found in the early stages of drying after the preheating phase. In series C and E with regulation principle II, the wood temperature reaches close to maximum temperature 70°C or 90°C early during the capillary phase of drying when the MC is high with free capillary water present in sapwood and with MC in heartwood close to fibre saturation point. In series B and D with regulation principle I, however, maximum temperature is reached considerably later in the drying process when the MC is

substantially lower. Less temperature difference early in drying between regulation principle I and II can be seen in the 70°C series compared to the 90°C series.

Mass loss in decay test

The mass losses after 7 weeks' incubation time in each series are shown in figure 4 for the three wood type positions inner heartwood, outer heartwood and sapwood. A large variation in mass loss is seen for all positions in all series judging from the confidence intervals. As expected, the mass loss in sapwood in all series is significantly higher (at 5% significance level) than in inner heartwood and outer heartwood.

Series E shows, on average, the largest mass loss compared to all other series for all three wood types. In sapwood, the mass loss in series E is significantly higher only in comparison to sapwood in series D at 10% significance level.

In heartwood, the mass loss, on average, is lowest in series A and highest in series E. Mass loss in outer heartwood in series A is significantly lower than in outer heartwood in all other series (at significance levels between 1 and 10%). Mass loss in inner heartwood in series A is significantly lower compared to series E and F at 10% significance levels.

In contradiction to other studies, no significant difference between mass loss in inner heartwood and mass loss in outer heartwood is found, either in any series or in overall average values. Nor did the mass loss in outer heartwood specimens show any dependence on measured distance from pith side.

Among the various drying strategies, series A, considered equivalent to outdoor air-drying, shows the best decay resistance in heartwood. The average mass loss for heartwood (inner and outer grouped together) in series A is significantly lower compared to all other series (at 5% significance level compared to series B, C, D and F and at 1% compared to series E). Drying with high wood material temperature early in the drying process, such as in series E at 90°C maximum temperature, shows the lowest decay resistance in sapwood and heartwood. The difference for heartwood (inner and outer grouped together) is, however, significantly higher only in comparison to series A.

High material temperature when MC is high, such as in series E is an unsuitable combination for decay resistance in pine heartwood. In fact, these are also the conditions in the high-temperature drying in series F, but since the drying time is short, this combination of high material temperature and high MC doesn't lead to any pronounced decrease in decay resistance compared to the other series.

When comparing the drying time for the two series with maximum temperature 90°C, the total time for material temperature at maximum level is much longer in series D than in series E. Even though this is the case, mass loss is higher in series E. The interpretation of these results is that the duration of high material temperature when MC is high seems to

be the critical combination for decay resistance in heartwood. Duration of high material temperature later in drying when MC is lower, such as in series D, does not show any deterioration of decay resistance compared to series at 70°C

Effect of conditioning on mass loss

At the end of each drying series except series A, steam conditioning was performed on half of each batch. A comparison between mass loss in unconditioned and conditioned sapwood and heartwood is shown in figure 5. No significant effect of conditioning in heartwood is found, but in sapwood, steam-conditioning increases mass loss. The increase is significant at 10% significance level.

In figure 6, the mass loss in conditioned/unconditioned planed sapwood in series B–F is shown. Conditioning has increased mass loss is in all series apart from series C.

A hypothesis is that this increase of mass loss in conditioned sapwood depends on the substantial moistening of the dry lumber surface by condensation water, which redistributes the nutrients that have been accumulated towards the evaporation front beneath the lumber surface during the early stages of drying and makes them more available for decay. In heartwood, it's likely that no such accumulation of soluble nutrients takes place during drying.

Effect of raw material properties on mass loss

The variation in decay resistance is large between different boards, but also within single boards. Investigation of the impact of position along the board showed no dependence on positions 1–4.

One probable explanation to the large variation in mass loss is the natural variability of extractive content between and within individual boards. Extractive content has not been measured.

Linear regression between mass loss and density (of each mass-loss specimen before decay test) indicates a weak negative correlation. The indicated effect of lower mass loss with higher density is probably related to lower extractive content in low density wood.

4 Conclusions

The impact of different drying processes on the durability of Scots pine lumber has been evaluated with mass loss in a 7-week decay test with the brown rot fungus *Coniophora puteana* as a measure of decay resistance. The results are summarized as follows:

- The variation in decay resistance is large between different boards, but also within single boards.

- Sapwood shows considerably lower durability—more than two times higher mass loss—than heartwood.
- In contradiction to other studies, no difference is found between the durability of inner heartwood and that of outer heartwood.
- Air-dried heartwood shows the highest durability compared to the other drying series.
- Steam conditioning after drying lessens the durability of sapwood.
- Drying at 90°C maximum temperature with high material temperature early in drying when MC is high shows the lowest durability for both sapwood and heartwood. The interpretation is that the duration of high material temperature at high MC is the critical combination for decay resistance in heartwood.

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Table 1. Description of drying series A–F.

Series	Maximum temperature	Preheating	Regulation principle	Number of samples	Steam conditioning
A	25°C	-	-	10	-
B	70°C	Water spray	I	10	Half batch 4 hours
C	70°C	Steam	II	10	Half batch 5.5 hours
D	90°C	Water spray	I	10	Half batch 9.7 hours[1)]
E	90°C	Steam	II	10	Half batch 3.7 hours
F	110°C	Steam	-	19	Half batch 3.5 hours

[1)] Extended conditioning to adjust the low final MC after drying

Table 2. Moisture content (MC) before and after drying and conditioning in series A–F.

Series	Average MC before drying (%)	Steam conditioning	Final average MC (%)
A	70	unconditioned	9.0
B	63	unconditioned	10.3
		conditioned	11.4
C	64	unconditioned	7.9
		conditioned	9.9
D	62	unconditioned	6.2
		conditioned	10.9[1)]
E	66	unconditioned	8.9
		conditioned	10.6
F	47[2)]	unconditioned	9.7
		conditioned	11.9

[1)] Low MC after drying was adjusted with an extended conditioning.
[2)] The low average MC before drying in series F is explained by a high fraction of heartwood content.

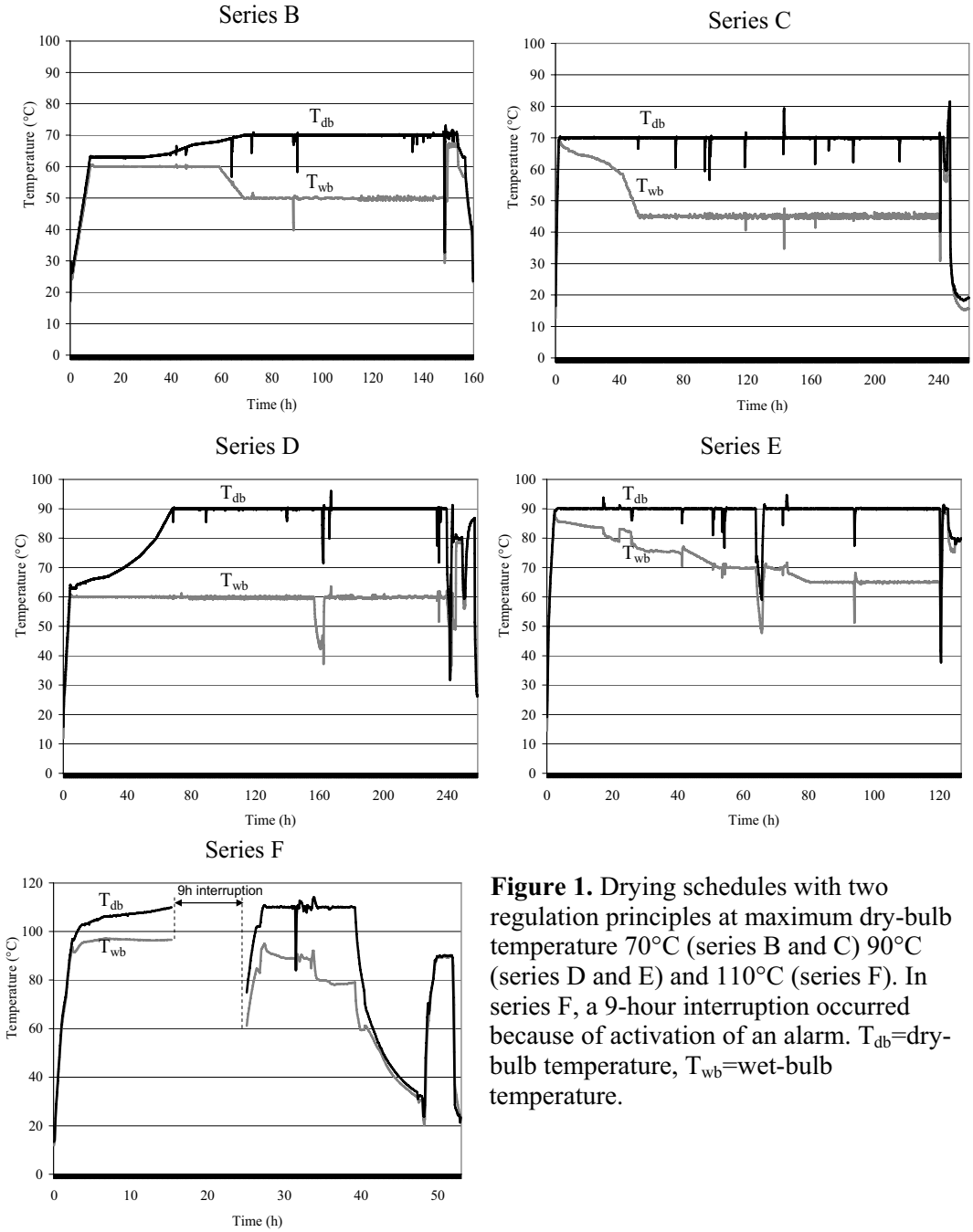

Figure 1. Drying schedules with two regulation principles at maximum dry-bulb temperature 70°C (series B and C) 90°C (series D and E) and 110°C (series F). In series F, a 9-hour interruption occurred because of activation of an alarm. T_{db}=dry-bulb temperature, T_{wb}=wet-bulb temperature.

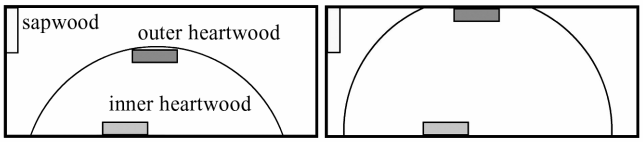

Figure 2. Sampling of specimen for decay test from dried and planed samples in position inner heartwood, outer heartwood and sapwood. For inner heartwood, the pith was avoided. Left: position of outer heartwood specimen in lumber with low heartwood content. Right: with high heartwood content.

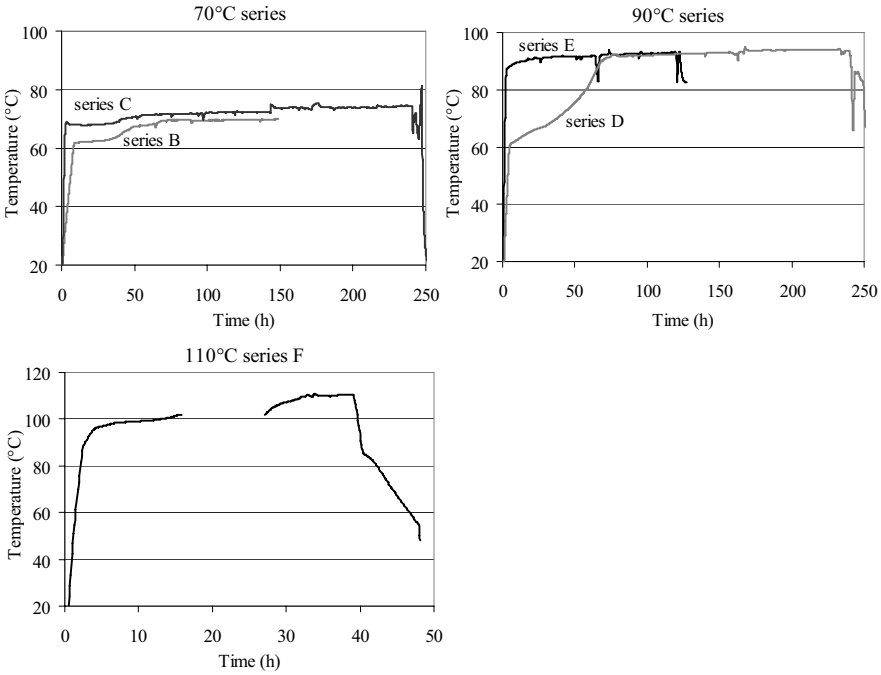

Figure 3. Material temperature during drying in series B and C (left), in series D and E (middle) and in series F (right).

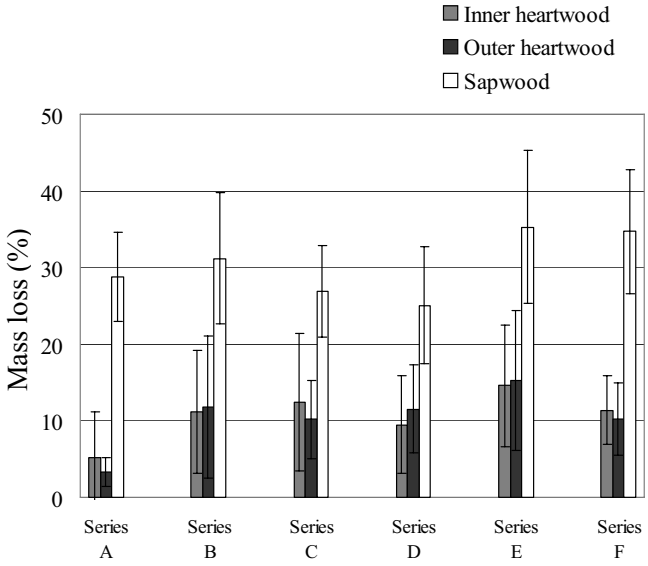

Figure 4. Mass losses after 7 weeks' incubation with brown-rot fungus *Coniophora puteana* for pine lumber dried in series A–F. Data are given as average values with 95% confidence intervals. (n = from 10–16 in each bar).

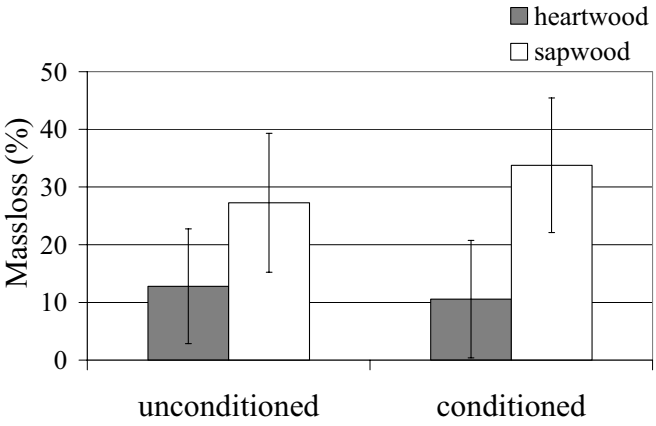

Figure 5. Mass losses in pine sapwood and heartwood after 7 weeks' incubation with brown-rot fungus *Coniophora puteana* for unconditioned and conditioned pine lumber in all series except series A. Data are given as average values with 95% confidence intervals. (n = 112 for heartwood and 52 for sapwood).

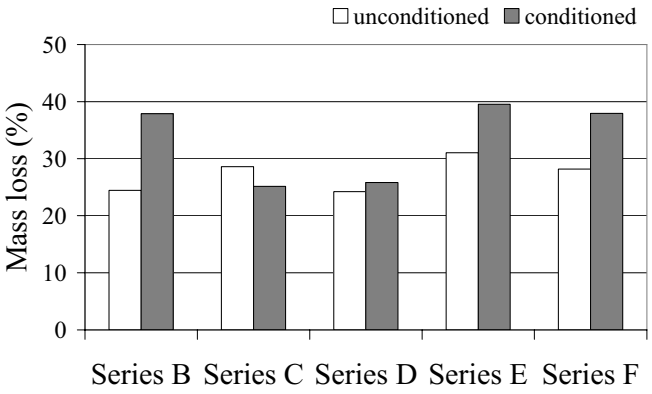

Figure 6. Effect of conditioning on mass loss in pine sapwood in series B–F. Data are given as average values. (n = from 5–8 for each bar)

Paper IX

Margot Sehlstedt-Persson, Olov Karlsson
Natural durability and phenolic content in dried Scots pine heartwood. (2008)
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Natural durability and phenolic content in dried Scots pine heartwood

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Abstract

The impact of drying and heating on the concentration of total phenolics measured according to the Folin-Ciocalteau assay and the durability of Scots pine heartwood were studied by measuring mass loss in a 7 week decay test with the brown rot fungus *Coniophora puteana*. The relation between mass loss and total phenolics in heartwood dried at maximum temperatures (20°C–110°C) showed a weak negative correlation at lower levels of phenolics compared to green heartwood. Mass loss showed a weak negative correlation to density. The concentration of phenolics in heated, green sawdust was higher in extractive-rich Scots pine heartwood than in heartwood with normal extractive content. Heating of green sawdust with high extractive content reduced the concentration of phenolics at temperatures exceeding 70°C up to 110°C during 72 hours of heating, and indications of a reduction was found during 3 hours of heating at temperatures exceeding 160°C up to 180°C. Heating of extractive-rich green sawdust indicated a reduction of phenolics with temperature and time.

Key words Drying, durability, decay resistance, phenolics, Scots pine, heartwood, Folin-Ciocalteau assay, *Coniophora puteana*

1 Introduction

During recent years there has been some indication that the durability of pine heartwood products has declined, and one hypothesis is that the drying process might negatively affect the natural durability of wood. In a recent study, Sehlstedt-Persson and Wamming[1] found that air-dried heartwood showed better durability in decay tests compared to kiln-dried heartwood dried at various temperature levels up to 110°C.

According to European Standard[2], Scots pine heartwood is classified into class 3–4 (moderately to slightly durable) in terms of natural resistance to wood-destroying brown rot fungus. Mass loss, expressed as a percentage of the original dry weight, is commonly used in laboratory tests to assess the natural durability of wood.

The chemical composition of wood varies considerably within any single tree as well as between different trees. This large variability leads to large variations in natural durability. It is generally agreed that extractives are "the principal source of decay resistance" in wood[3]. The amount of extractives in green Scots pine heartwood varies greatly and might be substantial due to the ability of pine species to produce rich amounts of resin as a result of injuries, forming so called resinous wood[4], with extractives in resinous Scots pine reaching concentrations higher than 30%[5] of the wood mass. However, normal concentrations of extractives in pine heartwood are substantially lower: 8.6% ether soluble[6], 9.3% acetone soluble[7] according to various studies.

Extractives have been shown to have an inhibitory effect on fungal degradation in pine heartwood, but considerable differences in tolerance to toxic extractives are also found in various kinds of fungi[8]. Resin acids, which are the major extractive constituent in Scots pine heartwood[5, 8], have been reported to cause severe inhibition to wood-inhabiting fungi[9, 10]. Extractive content in heartwood in many species show an overall pattern with decreasing amounts of extractives towards the pith and higher up the tree[4]. This pattern of lower extractive content near the pith may reflect a degradation of extractives over time or an increase in extractive deposits with age[11]. A study on *Pinus sylvestris*, however, showed an increase in the total amount of extractives towards the pith[5].

The chemical characteristics that separate decay-resistant from decay-susceptible pine heartwood in decay tests with the brown rot fungus *Coniophora puteana* were shown to be resin acids, pinosylvins, acetone-soluble extractives and total phenolics measured according to the Folin-Ciocalteau (FC) assay[12].

The concentration of pinosylvin and resin acid content in heartwood is shown to vary considerably between individual Scots pine trees, with indications of a strong genetic control of the wide individual variation[13]. The concentration of total resin acids in heartwood in decay-resistant Scots pine trees was found to be 1.6–2.1 times higher than the concentration in susceptible trees[14]. The spatial distribution of pinosylvin in pine heartwood was found to decline in inner heartwood, while the concentrations were highest in outer heartwood at the transition between sapwood and heartwood[15].

The variation in durability within a single tree in the radial direction is also shown to be large, with the most decay-resistant parts in the outer part of green Scots pine heartwood in decay tests with the brown rot fungus *Coniophora puteana*[12]. In contrast to these results, no significant difference was found in mass loss in similar decay tests between inner and outer Scots pine heartwood dried at various temperatures[1].

Chubinsky[16] found that larch heartwood of high density was more resistant than larch heartwood with low density in decay tests with *Coniophora puteana*. In contradiction to this, Venäläinen *et al.*[17] found no relationship between density and mass loss in decay tests with *Coniophora puteana* in larch heartwood. Boutelje and Nilsson[18] found varying effects of density on mass loss for various fungi in decay tests with pine sapwood. A

weak but significant negative correlation between mass loss and density was found in tests with the white rot fungus *Phlebiopsis gigantean* and significant positive correlation in tests with the brown rot fungus *Fomitopsis pinicola*[18].

In decay tests with *Coniophora puteana*, Harju and Venäläinen[19] found a fairly strong negative correlation between mass loss and the concentration of total phenolics measured by the FC assay in green Scots pine juvenile heartwood. The authors suggest that measurements of total phenolics according to the FC assay could be used for screening the variation in natural durability of Scots pine heartwood and as an alternative to time-consuming laboratory decay tests.

During drying of wood, a process that in fact can be seen as a hygrothermal treatment of wood, physical and chemical reactions occur that change the properties of wood and its constituents, including evaporation of volatile compounds, changes in colour, hygroscopicity, consistency of resin and re-distribution of nutrients in sapwood among other things. In addition, durability in Scots pine heartwood has been shown to be affected by the drying process[1].

The aim with this study is to investigate how drying and heating of Scots pine heartwood affects the concentration of total phenolics measured according to the FC assay. Furthermore, the aim is to study if the large variation in mass loss in dried heartwood[1] can be explained by the concentration of total phenolics by comparing the relation between mass loss in decay testing and total phenolics in dried heartwood in a similar way as the study done on green Scots pine heartwood performed by Harju and Venäläinen[19]. In order to minimize the influence of variation in various wood properties, a study with heating of green mixed and sieved sawdust was also done.

2 Materials and Methods

Lumber

Centre-sawn boards, 50 x125 mm, from winter-felled Scots pine (*Pinus sylvestris* L.) butt logs from a stand in Norrbotten in northern Sweden, were used in the tests. The green boards were cut into four one-meter-long samples that were then end-sealed. Sixty-six samples from 36 different boards were sorted into six similar batches with regard to heartwood content, visually estimated resin content and position along the board.

Drying

Drying was performed in six different series. Series A, considered similar to outdoors air-drying, was, due to the time of year, dried indoors at the laboratory on stickers at 20–25°C, 38%–45% relative humidity (RH) for just under 9 weeks. Series B–F were dried in a small-scale laboratory air-circulation kiln at maximum temperature levels of 70°C,

90°C and 110°C. For 70°C and 90°C series B–E, two different regulation principles were used after the initial preheating:

I) Dry-bulb temperature (T_{db}) gradually rising to maximum temperature level and wet-bulb temperature (T_{wb}) at one or two constant levels.
II) Constant T_{db} at maximum level with initial T_{wb} dropping to a constant level.

The difference between these two regulation principles is how fast the wood temperature reaches maximum temperature level. In regulation principle II, the wood temperature reaches maximum temperature level early in the capillary regime of drying when the moisture content (MC) is high, while the wood temperature in regulation principle I reaches maximum temperature considerably later in the drying process when the MC is substantially lower.

Series F was dried with a high-temperature schedule at a maximum temperature of 110°C.

A detailed description of the material and drying schedules is found in Sehlstedt-Persson and Wamming[1].

Sampling of the evaluation material

For decay testing, 2 x 66 specimens (5 x 15 x 30 mm) were sawn from dried samples conditioned at equilibrium moisture content (EMC) 10% in all six series from inner and outer heartwood as shown in figure 1. The initial dry weight (m_{dry}) of each specimen before the decay test was measured after drying for 48 hours in a vacuum dessicator with silica gel at 60°C for specimens in series B–F and for specimens in series A, in order not to exceed the maximum drying temperature in series A, after drying for 144 hours in a vacuum dessicator with silica gel at 20°C. The density ($\rho_{dry,10}$) for each specimen was calculated without any volume correction for difference in EMC because of miscellaneous drying in the six series.

Analysis of total phenolics according to the FC assay and of extractive content was done for chosen samples in series A–F on adjacent specimens as shown in figure 1.

Decay test

The decay test with the brown rot fungus *Coniophora puteana* (BAM Ebw.15) was performed according to the standardized EN113 decay test, but modified with respect to sample size and incubation time in the same way as described by Harju and Venäläinen[19] (with the exception of predrying temperature 20°C instead of 60°C for controlling the initial dry weight (m_{dry}) in series A). The mass loss of the samples after an incubation time of 7 weeks, expressed as a percentage of the original dry mass before decay test, was used as a measure of durability.

When the results from the decay test were known, four samples from each drying temperature level, 20°C, 70°C, 90°C and 110°C, in series A–F with the two highest and two lowest mass losses were identified without regard to position in inner or outer heartwood. From these 16 samples, the concentration of total phenolics according to the FC assay was determined as well as the concentration of extractives in specimens cut adjacent to the mass-loss specimen as in figure 1. Furthermore, in series E, dried at maximum temperature 90°C with regulation principle II, which on average showed the highest mass loss of all series as described in Sehlstedt-Persson and Wamming[1], ten additional samples were randomly chosen for phenolic and extractive analysis to cover the whole range of mass loss.

Concentration of total phenolics and extractive content

The specimens cut adjacent to the decay specimens were sawn into small parts using a small band saw carefully cleaned for each sample, and the sawdust was collected and sieved using a mesh grid of 1 mm. For each sample, approximately 1 gram of collected particles, dried in a vacuum dessicator at room temperature, was extracted twice with 15 ml of aqueous acetone solution (acetone-water 8:2) using magnetic stirring for ½–1 hour. After filtering of the extract and washing with 5 ml of solvent, the concentration of total phenolics was determined by the FC assay as described by Harju and Venäläinen[19] in their study on green pine heartwood using Tannic acid as a standard and absorptivity measured at 735 nm. Therefore the results of the total phenolic concentration are expressed as milligrams tannic acid equivalents (TAE) per gram of dry mass of wood.

For determination of extractive content, half of the extract was put into Petri dishes and dried in the lab and in a dessicator. After evaporation of the aqueous acetone solution, the weight of the dry mass of the extract was calculated and expressed in percentage of dry wood weight.

Concentration of total phenolics in heated green sawdust

Since the extractive content varies so much between trees as well as between positions in single trees, and since extractive content has an impact on the concentration of phenolics, a supplementary study was done using mixed sawdust from pine heartwood. Green heartwood sawdust from two trees, one with normal and one with high extractive content, was collected and sieved according to the earlier description. The average extractive content in the mixed sawdust from each tree was measured using a Soxhlet extractor for 24 hours (with four extraction cycles per hour) with Acetone 99.5% *pro analysi* as solvent.

10 grams of sieved, mixed, green sawdust was put into a cylindrical 90 ml Teflon tube vessel and heated. During heating, the vessel was closed and sealed using a steel support module.

In series I, with sawdust from heartwood with normal extractive content, heating was done in an oven at temperatures 20°C, 40°C, 90°C and 110°C during 65 hours respectively.

In series II, with sawdust from heartwood with high extractive content, heating was done at 20°C, 40°C, 70°C, 90°C and 110°C during 72 hours respectively.

In series III, with sawdust from heartwood with high extractive content, heating was done at 110°C, 130°C, 140°C, 150°C, 160°C, 170°C and 180°C during 3 hours respectively.

Approximately 2 grams of sawdust from each heated set was put into glass cups and dried at room temperature in a vacuum dessicator with silica gel for 6 days before performing the FC assay analysis. One gram of dry, heated sawdust from each set was used in FC assay analysis as earlier described.

3 Results and discussions

Mass loss in decay test—impact of concentration of total phenolics

Results from the measurements of total phenolics according to the FC assay, with mass loss after 7 weeks incubation time as a function of total phenolics, are shown in figure 2. Measurements were done on 16 samples with the two highest and two lowest mass losses in inner or outer heartwood from drying series A–F at 20°C, 70°C, 90°C and 110°C.

No clear relation between mass loss and total phenolics is found in the limited samples shown in figure 2. The highest concentration of phenolics is found among the samples with low mass loss. At lower concentrations (in the region 3–6 mg TAE/g dry wood) samples with high as well as low mass loss are found. This indicates that not only concentration of phenolics affects the durability of heartwood. Varying composition of extractives in the samples, such as varying concentrations of resin acids, known to contribute to decay resistance in Scots pine heartwood[14], might be one explanation.

The relation between mass loss and total phenolics in heartwood dried at various maximum temperatures is not as clear as the relation found by Harju and Venäläinen [19] in green heartwood (figure 3). A weaker linear correlation coefficient, r = -0.52, is found in dried heartwood by comparison with r = -0.82 in green heartwood[19], and with lower levels of concentration of total phenolics than in green heartwood. A conceivable explanation for the lower levels of total phenolics might be a hygrothermal degradation of phenolics during drying and/or a lower level of extractive content in dried wood

compared to green wood, since evaporation of extractive compounds takes place during the drying process. However, as the boiling point of most phenols in pine heartwood is considerably higher than the monoterpenes, their volatility will be lower and not especially prone to evaporation during drying. Degradation of phenolics was studied in a separate experiment with heating of sawdust.

In figure 2 and figure 3 left, there is a lack of measurements in the middle region of mass loss, since only samples with the two highest and two lowest mass losses were chosen for FC assay analysis at each temperature level in series A–F. In figure 4, mass loss as a function of total phenolics is shown in drying series E dried at maximum temperature 90°C (which on average showed the lowest durability after drying compared to all other drying series[1]), with ten complementary samples randomly chosen in the middle region of mass loss.

The same pattern is found in series E in figure 4 as in figure 2 (and 3a), with the highest concentrations of phenolics showing low mass loss, and in the region around 5 mg TAE/g high as well as low values of mass loss are found. The linear correlation coefficient was r = -0.42. Thus, the fairly strong linear relation between mass loss and total phenolics found in green, juvenile outer Scots pine heartwood[19] is not found in dried heartwood in this study.

Mass loss in decay test—impact of density

The relation between mass loss and density ($\rho_{dry,10}$) of each decay sample in series E in figure 5 shows a weak negative correlation with a linear correlation coefficient r = -0.62. The linear correlation coefficient between mass loss and density of chosen samples dried at various temperatures in series A–F is r = -0.51. This supports the results found in decay testing with *Coniophora puteana* in larch heartwood by Chubinsky[16] and by Boutelje and Nilsson[18], who found a weak, but significant, negative correlation between mass loss and density in tests with a white rot fungus *Phlebiopsis gigantea* in pine sapwood[18].

A conceivable explanation as to why higher density shows better decay resistance, besides the fact that higher density is related to higher extractive content, which is known to have an inhibitory effect on fungal degradation[8], is also that denser wood could be expected to have higher resistance to decay simply because of its more solid state and lower porosity during the limited time during which short-term *in vitro* tests are performed, in this study during 7 weeks. However, no inhibiting effect of density on mass loss was found in long-term exposure outdoors above ground during 9 years for Norway spruce[20] or Scots pine lumber[21]. This elucidates the difficulties in transferring conclusions from short-term decay tests using one specific fungus to the practical service life of wood in outdoor applications.

Concentration of total phenolics—impact of density and extractive content

The concentration of total phenolics shows a weak positive correlation to wood density, with a linear correlation coefficient r = 0.65 for the 14 samples in series E and r = 0.58 for the 16 samples dried at various temperatures in series A–F. The concentration of phenolics shows a weak positive correlation to extractive content determined in a short-term extraction, with a linear correlation coefficient r = 0.60 in series E and r = 0.46 for samples dried at various temperatures in series A–F. The simplified way of determining extractive content by short-term extraction is not claimed to give the total concentration of extractives, but rather only a relative measure.

Concentration of total phenolics in heated green sawdust

The mass losses in this study show large variations, and the investigated parameters phenolic content, density and extractive content explain only parts of the variation in mass loss in test material deriving from batches of sawn lumber with its normal variation of wood properties. Since one main issue with this work has been to investigate the influence of drying parameters such as temperature level on the phenolic concentration, a supplementary study on heating of mixed wood sawdust was performed in order to minimize the influence of natural variation in various wood properties.

The results from the study on heated, mixed sawdust from pine heartwood with varying extractive content are presented in figure 6. The average extractive content according to the Soxhlet extraction with acetone in series I was 8.2% and in series II–III 23.4%, given in % of dry weight of the extractive-free sawdust.

The concentration of total phenolics was, as expected, found to be substantially higher in heartwood with high extractive content (series II) than in heartwood with normal extractive content (series I). The ratio between phenolics in series I and II is approximately of the same magnitude (≈3) as the ratio between extractive contents. Thus, the concentration of total phenolic content is roughly related to the concentration of extractives. Heartwood with high extractive content, such as in series II with its high concentrations of total phenolics, is expected to show high durability with low mass loss according to figure 3.

The effect of heating temperature was found to be more marked in series II than in series I. In series II, a continuous decrease of the concentration of total phenolics is found at heating temperatures exceeding 70°C.

In figure 7, the results from heating at higher temperatures during 3 hours are presented.

When comparing the concentration of total phenolics in series II (figure 6) and series III (figure 7) at 110°C, it is obvious that the duration of heating has an impact on the content

of total phenolics—heating during 72 hours reduces the phenolics considerably more than heating during 3 hours.

An indication of reduction of phenolic content at heating temperatures exceeding 160°C is found in series III (figure 7). Thus, the concentration of phenolics seems to decrease with a combination of temperature and time during heating in moist conditions. This decrease in concentration of total phenolics in Scots pine heartwood with increasing temperature and duration of heating is expected to lead to a decrease in natural durability. But since heat-treatment of wood performed at temperatures levels far higher than 200°C is shown to increase the durability of wood[22, 23], considerable thermal-dependent chemical modifications of wood components occur during the heat-treatment process, which makes the wood substrate more or less unrecognizable for wood-destroying fungi.

Pinosylvin is a dominant phenol extractive in pine heartwood and has been reported to have antioxidative[24] abilities and to reduce the activity of brown rot fungi[25]. Oxidation of pinosylvin can lead to formation of dark-coloured compounds[26], and condensation with lignin may take place under certain conditions[27, 28]. Furthermore, Julkunen-Titto found that the FC response was dependent on the structure of phenols[29]. Reactions of phenols during heat-treatment can change the FC response of the treated wood and thus explain the lower amount of detected phenols when heating was performed at 90°C and 110°C (figure 6). However, it should be pointed out that during heat-treatment, degradation of lignin results in formation of phenols, and more extensive treatments may lead to an increase of phenols. Analysis of phenols in extracts from heat-treated spruce using the FC method showed that phenols started to increase at temperature higher than 235°C[30].

4 Conclusions

The impact of drying and heating on wood durability and on the concentration of total phenolics measured according to the Folin-Ciocalteau assay in Scots pine heartwood has been studied. Mass loss in an *in vitro* decay test with the brown rot fungus *Coniophora puteana* during 7 weeks has been used as a measure of durability. The relation between mass loss and total phenolics in dried Scots pine heartwood has been studied and compared with a similar study on green Scots pine heartwood[19] in which a fairly strong negative correlation was found. The results are summarized as follows:

- The results in this study on dried heartwood do not show the same apparent relation between mass loss and concentration of total phenolics as the study on green heartwood[19]. A weak negative correlation was found for heartwood dried at various maximum temperatures between 20°C and 110°C with a linear correlation coefficient $r = -0.52$ ($p<0.05$). In heartwood dried at maximum temperature 90°C, the linear correlation coefficient was $r = -0.42$ ($p<0.2$). These correlation coefficients are weaker than those of the study on green scots pine heartwood[19] with $r = -0.82$ ($p<0.001$).

- Lower levels of total phenolics were found in dried heartwood than in the study on green heartwood[19].

- A weak negative correlation was found between mass loss and density with a linear correlation coefficient $r = -0.62$ ($p<0.02$), thus somewhat stronger than the correlation between mass loss and phenolics.

- The concentration of total phenolics in heated, mixed, green sawdust was higher in extractive-rich Scots pine heartwood than in heartwood with normal extractive content.

- Heating of mixed, green sawdust from Scots pine heartwood with high extractive content
    - at 110°C during 72 hours reduced the concentration of total phenolics substantially compared to 3 hours heating.
    - tended to reduce the concentration of total phenolics at temperatures exceeding 70°C during 72 hours of heating.
    - indicated a small reduction of the concentration of total phenolics at temperatures exceeding 160°C up to 180°C during 3 hours of heating.

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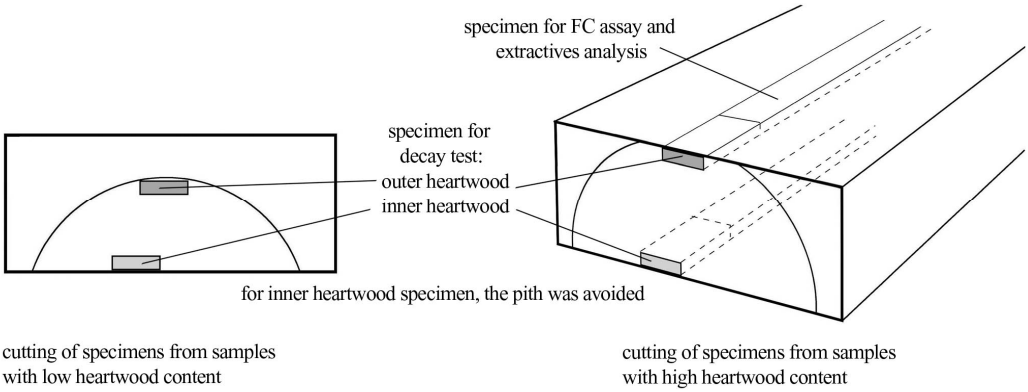


Figure 1. Sampling of the evaluation material for decay test and analysis of concentration of total phenolics and extractives from dried, planed boards.

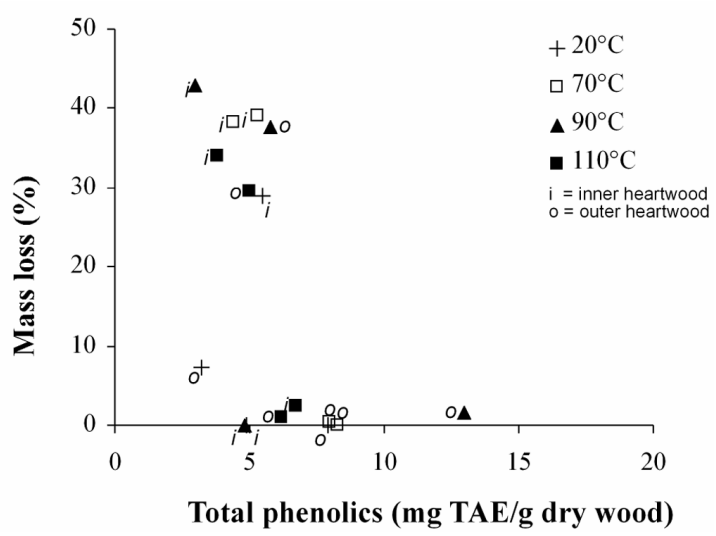
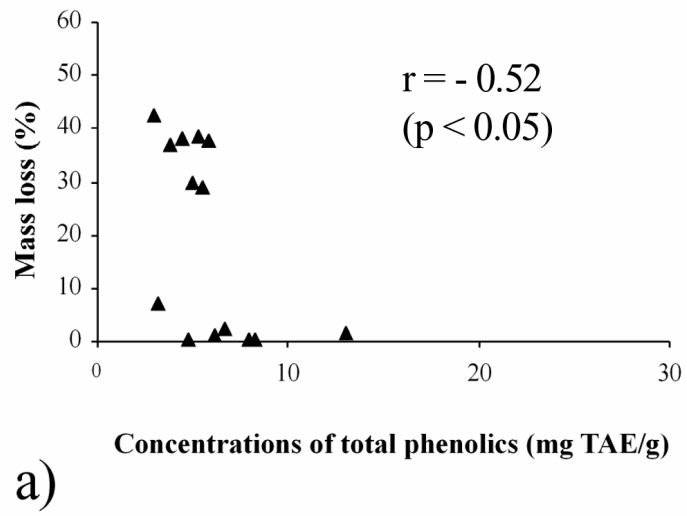


Figure 2. Mass loss in decay test as a function of concentration of total phenolics according to FC assay in pine heartwood dried at various maximum temperature levels. For each temperature level, samples with the two highest and two lowest mass losses were selected from inner or outer heartwood.



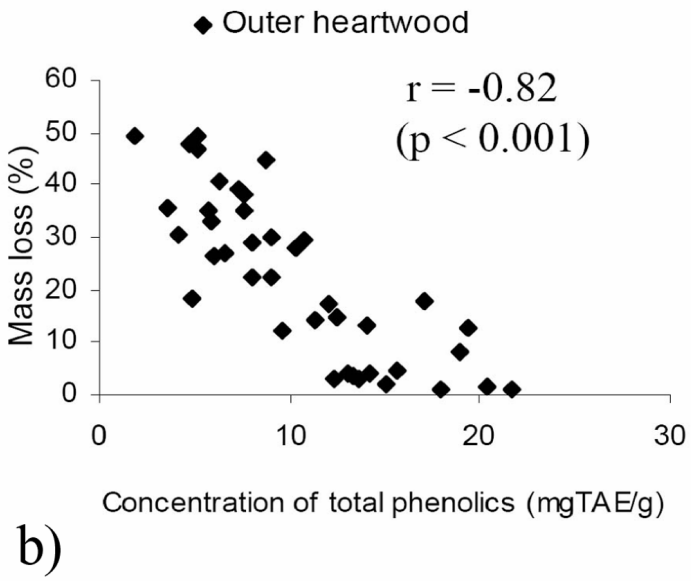


Figure 3. Comparison of the relation between mass loss in decay test and concentration of total phenolics according to FC assay in:

a) inner and outer Scots pine heartwood dried at various temperatures. Linear correlation coefficient r = -0.52 ($p<0.05$)

b) green juvenile pine outer heartwood according to the study by Harju and Venäläinen[19]. Linear correlation coefficient r = -0.82. (Diagram from Harju and Venäläinen[12]).

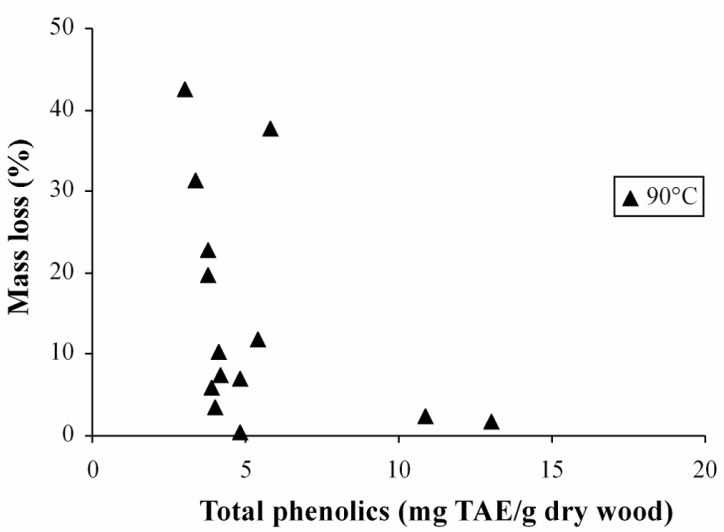


Figure 4. Mass loss in decay test as a function of concentration of total phenolics according to FC assay in pine heartwood in series E dried at 90°C maximum temperature. Linear correlation coefficient r = -0.42 ($p<0.2$).

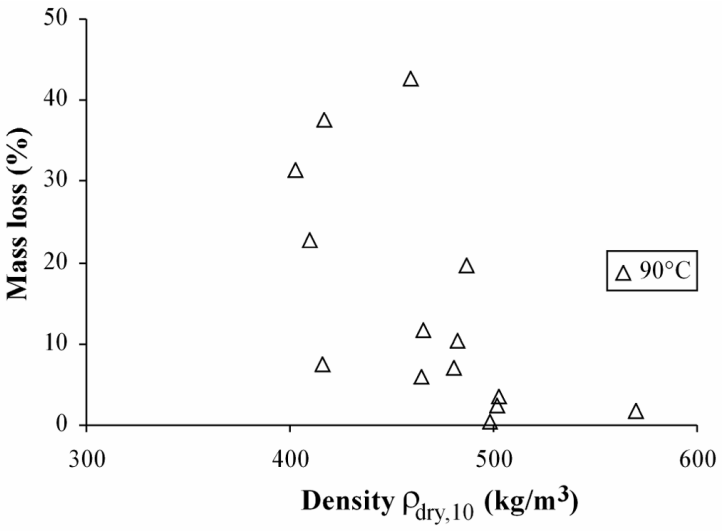


Figure 5. Mass loss in decay test as a function of density ($\rho_{dry,\,10}$) in pine heartwood in series E dried at 90°C maximum temperature. Linear correlation coefficient r = -0.62 ($p<0.02$).

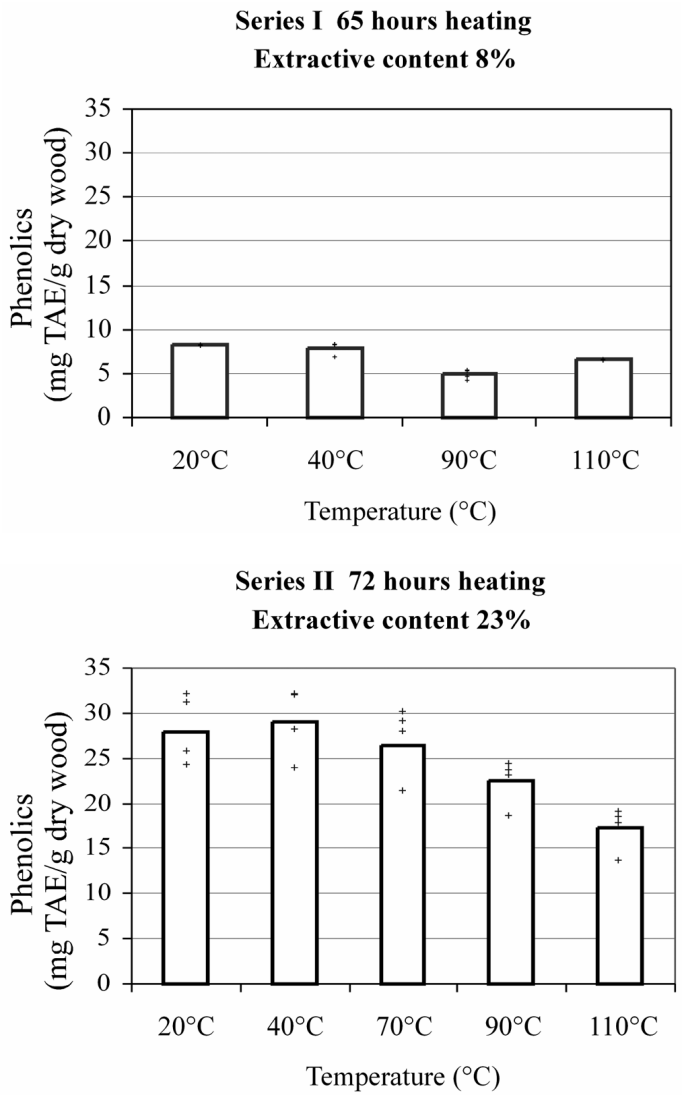


Figure 6. Concentration of total phenolics (mg TAE/g dry wood) measured by the FC assay in pine heartwood with normal extractive content (series I) and high extractive content (series II) heated at various temperatures during 65 and 72 hours respectively. Each bar is an average of 4 measurements.

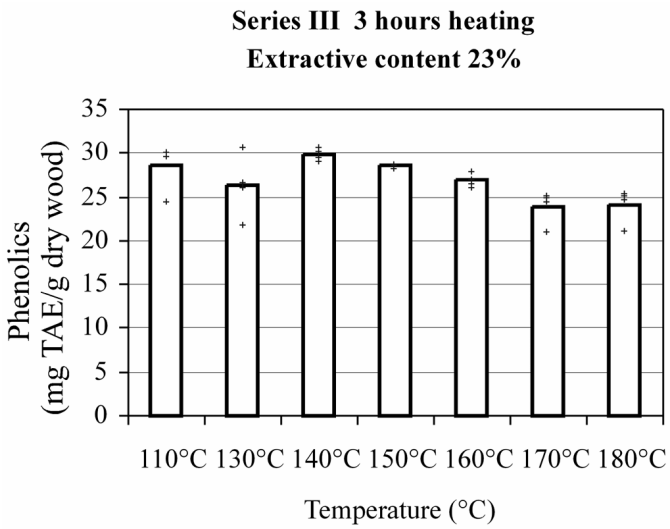


Figure 7. Concentration of total phenolics (mg TAE/g dry wood) measured by the FC assay in pine heartwood with high extractive content heated at various temperatures (series III) during 3 hours. Each bar is an average of 4 measurements.