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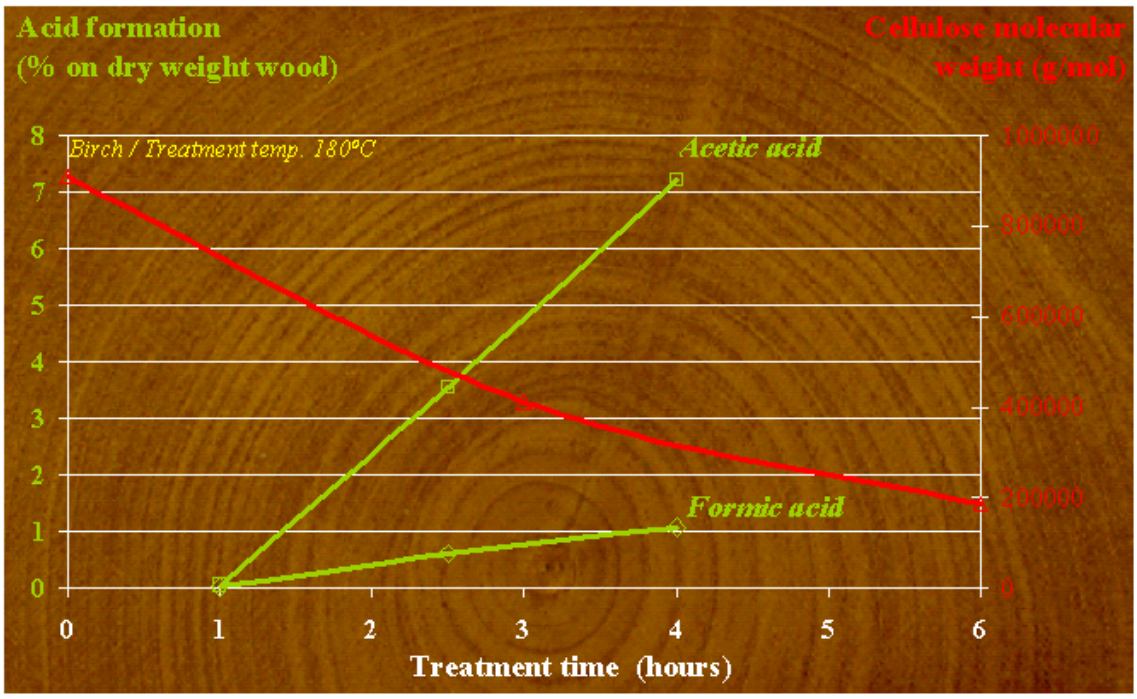
DOCTORAL THESIS

Colour Changes and Acid Formation in Wood During Heating



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Division of Wood Material Science

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Colour Changes and Acid Formation in Wood During Heating

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…….to Erica, Björn and David

Abstract

Heating wood has since ancient times been a method to dry and modify its properties. Nowadays heat is used in industrial processes for the same reasons. Treatment at temperatures above 150ºC can change the colour, improve resistance to biodegradation and enhance dimensional stability. However, losses in the mechanical strength of wood may also occur, and this drawback is a limitation for the use of heat-treated wood in a broad range of products. This thesis suggests that cellulose degradation can contribute to the loss of mechanical strength in wood under high-temperature treatment.

The formation of formic and acetic acid during heat treatment of birch wood has been studied. Substantial amounts of acetic acid (at most 7.2% by weight) and formic acid (at most 1.1% by weight) were found in autoclave experiments at temperatures between 160ºC and 200ºC. It was also found that the average molecular size of both commercially heat-treated birch wood and birch wood treated in laboratory experiments under acidic pH conditions was considerably reduced (42%–53%) in comparison to untreated birch wood. It is reasonable to think that the formation of acid and the accompanying decrease in average cellulose molecular size have a crucial influence on the observed decrease of mechanical strength in heat-treated wood. The thesis suggests that wood can be heat-treated while maintaining mechanical strength through a process design that keeps the wood in neutral to alkaline conditions.

This thesis also describes studies of colour development in birch, Norway spruce and Scots pine wood during hydrothermal treatment, with special reference to treatment at temperatures between 65ºC and 95ºC with high moisture content. The colour responses of wood that had been heat treated or kiln dried have been investigated, and the colour coordinates Lightness (L^*), Chroma (C_{ab}^*), hue (h) and colour difference ΔE_{ab}^* are presented. It is shown that colour changes associated with heat treatment at high temperatures can be obtained by treatment for long periods at temperatures around 100ºC. Such treatments will lead to changes in colour, but presumably no change in dimensional stability or resistance to biodegradation. The origin of colour formation in wood as a result of heating is briefly investigated and discussed. Colour stability during accelerated UV/Visible light exposure of heat-treated samples has been tested and the results are presented in this thesis.

The colour responses of birch, Norway spruce and Scots pine wood were measured after drying in laboratory kiln experiments in the interval of 40º–111ºC, and it was concluded that the average wood colour of a batch can be controlled by regulating time and temperature.

There are some results that show an increase (around 20%) in the mechanical strength of birch wood for heat treatment around 180º–200ºC for approximately 1 hour and that colour measurements may be used as a way to monitor and control the phenomenon. However, further experiments will have to be made to confirm these indications.

Keywords: *Heat treatment, kiln drying, colour, acid formation, cellulose degradation, wood, Norway spruce, Picea abies, Scots pine, Pinus sylvestris, birch, Betula pubescens*

Preface

Theses last few days I have felt like I'm at the brow of a big hill and that to get here have travelled for ages in a hilly landscape on a way with many twists and turns. When I started my Ph. D studies I thought that it would be a more straightforward and easy journey. Nevertheless, these twists, turns and hills have taught me much about the true essence of science and have further developed me as a person. "I have grown from seed to tree."

The thesis has come into existence at Campus Skellefteå during a period from November 1997 to March 2004. The work was principally carried out in two parts–one at the division of Wood Physics until November 2000, and the other at the division of Wood Material Science until now. The purpose of merging these parts into this thesis was to integrate the knowledge from two disciplines, serving as basis for the chemical and physical approach of the work. The thesis is based on many laboratory experiments where the results were intended to be a base for further application in industrial-like processes. It is not advisable that the main conclusions of the thesis be applied directly in industrial processes; they can more usefully be seen as starting points for new experiments that focus on the development of wood-materials and process design.

Gratefully acknowledged is the financing of this thesis provided by Svenskt Trä, SkeWood/VINNOVA and EU må1/Fibernätverket.

I owe my sincere gratitude to Ulla Westermark for supervising me into the complex and exciting world of wood chemistry and for helping me to accomplish this thesis. Thank you Olov K. for all the hours you have shared with me and my problems. Without them I would not have got this far and I would not have had the favour of discussing old but crucial musical genres from the past. I'm also grateful to Tom Morén and Lena Antti for support and guidance during the work at the division of Wood physics. There are many to thank at Campus Skellefteå/Ltu, and I send my best wishes for the future. You have helped me find inspiration, supported me when I needed it, encouraged me to tackle new tasks and helped me into a good mood when I was down. Thank you Brian for revising my English and for showing sincere interest in the contents of the documents.

"We made it," I should say to my beloved family. You have from time to time felt my mental absence, given me space and supported me to carry on this work. You have been waiting with patience for this work to be accomplished these last years. You are fantastic. My love goes to my dear wife Erica and my children Björn and David.

I also send my love to my parents Wolmar and Else-Maj, who really started all this, and to my brothers and sister who have always believed in my work. Many thanks also go to my parents-in-law Sven-Olov and Britta who have been supportive and helpful during the years.

Skellefteå, March 2004

Bror Sundqvist

List of publications

This thesis is based on work reported in the following papers, referred to by their roman numerals in the thesis, and on a technical report.

I **Sundqvist, B. (1999)**. Colour Stability of Capillary Phase Heat-treated Wood Exposed to UV-light. In: Proceedings of the Fourth International Conference on the development of Wood Science, Wood Technology and Forestry (ICWSF), Missenden Abbey, UK, July 14–19. 172–182.

II **Sundqvist, B. (2002).** Colour response of Scots pine (Pinus sylvestris), Norway spruce (Picea abies) and birch (Betula pubescens) subjected to heat treatment in capillary phase. Holz als Roh- un Werkstoff 60:(2) 106–114.

III **Sundqvist, B. (2002).** Wood color control during kiln-drying. Forest Products Journal 52:(2) 30–37.

IV **Sundqvist, B. and Morén, T. (2002).** The influence of wood polymers and extractives on wood colour induced by hydrothermal treatment. Holz als Roh - und Werkstoff 60:(5) 375–376.

V **Sundqvist, B., Westermark, U. and Eriksson, G.** Degradation of cellulose during hydrothermal treatment of birch wood (Betula pubescens Ehrh.). *To be published*.

VI **Sundqvist, B, Karlsson, O. and Westermark, U.** Determination of formic acid and acetic acid concentrations formed during hydrothermal treatment of birch wood and its relation to colour, strength and hardness. *Submitted to Journal of Wood Science, Dec. 2003.*

Sundqvist, B. (2003). Värmebehandling av trä: från ett historiskt perspektiv till kommersiell produktion av idag (Heat treatment of wood: from a historical view to commercial production of today). Technical report 2003:02, Luleå University of Technology, Div. of Wood Material Science. pp 31. ISSN 1402-1536. In Swedish.

Contents

1. Introduction

1.1 From air drying to heat treatment of wood: 20ºC to 200ºC in 100 years.

The xylem of a tree, commonly known as wood, or for an end user often called lumber, has since ancient times been appreciated as a construction material for its strength properties combined with relatively low density and the ease with which it can be cut, carved, bent, etc. However, lumber is seldom used in its green state. Often the wood is dried and modified in some way before use. Green lumber contains nutritive compounds and a lot of water and is therefore prone to be attacked by microorganisms within a quite short time, which often leads to decay. Moreover, green lumber possesses poor dimensional stability if it is used without drying and can give problems when fitted into constructions and can also give unsatisfactory final results.

Since ancient times, air drying or outdoor seasoning of lumber has been the predominant method. This is a slow method and can take from many weeks to years to produce satisfactorily dried lumber for use in construction, and further drying for months indoors may be required for interior use. From ancient times there are examples of accelerating the drying process to make it more efficient by using fumes from fireplaces. In modern times, drying by forced air circulation (artificial drying) was introduced around 1920 (Esping 1992). Nowadays the drying process is often run in batch kilns, i.e., heated chambers, i.e., or progressive kilns with circulating hot humid air in the interval of 40º–90ºC, in order to regulate the process and maintain a high quality of the lumber at low cost.

High temperature (HT) drying at 90º–50ºC in steam atmosphere has been developed for commercial production during the last decades. HT drying gives more dimensionally stable lumber in considerably shorter drying times than does drying at lower temperatures (Kollman and Schneider 1963; Schneider 1973; Hillis 1984; Tarvainen 1995). HT-dried lumber is usually darker and somewhat more reddish (Sehlstedt-Persson 1995).

Thermal treatment or heat treatment is a way of drastically changing the properties of wood and in some sense of producing a "new material". During the last decade heat-treated wood has been commercialized and produced on a larger scale. The treatment is performed in inert surroundings of superheated steam, nitrogen gas or vegetable oil at 150º–250ºC. More information can be found in the technical report "Värmebehandling av trä" (in Swedish) (Appendix I). The background of heat treatment of wood and of its characteristics is also further described in chapter 3.

1.2 Scope of the thesis

The aim of this work can be summarized by the following points:

- To learn more about the origin of the colouration caused by heating and to investigate the possibility of controlling the colour of wood by regulating process parameters. This was done for the range of 40 to 111 degrees Celsius.

- To understand more of the underlying principles that can affect the strength properties of heat-treated wood. This was done for the temperature range of 160 to 200 degrees Celsius.

- To make suggestions for improving heat-treatment processes to obtain a better regulation and better strength and hardness of the heat-treated wood.

The aims of the thesis were sought after by investigations in a broad interval of temperatures (40Cº to 200ºC) with different approaches for lower temperatures compared to higher temperatures. Treating lumber with heat under moist conditions changes the properties of wood in ways that are in some respects unwanted and in other respects intended.

At lower temperatures, up to approximately 100ºC, it is known that only minor changes occur in the mechanical properties of wood. The colour of wood can on the other hand change considerably even at these temperatures, especially for hardwoods, and this was investigated by colour measurements of wood during kiln drying (Paper III) and in laboratory experiments (Papers II and IV). Wood colour can fade when it is exposed to visible and UV light, and this phenomenon was studied in experiments with artificial light exposure (Paper I).

During heat treatment of lumber at temperatures around 200ºC large changes in the wood properties take place. Heat-treated wood exhibits better dimensional stability, better resistance to biodegradation, lower equilibrium moisture content and a brownish colour. Heat-treated wood has been commercialized for outdoor applications such as panelling, garden furniture and decking. However, it is well known that distinct losses in mechanical properties can occur, and this is a drawback when trying to develop and launch heat-treated wood products in the marketplace. If the treatment process can be improved so that loss of strength is diminished or avoided, it might yield wood material suitable for broader utilization in more varied types of products. The underlying reason for the loss of strength is not very well elucidated in the research field of heat-treated wood. Wood strength is explained mainly by the structural components cellulose, hemicellulose and lignin.

The fact that acids can be released from the wood material itself and the effect of the acid conditions in the wood during the heat-treatment process have never been investigated in detail and placed in relation to strength loss. From other technical fields, such as pulp and paper production and bioresource technology, it is well known that cellulose can be

degraded and that organic acids catalyze the degradation of polysaccharides. No focused study for heat treatment of wood has been done concerning the cellulose molecular size and the amount of low molecular organic acids formed. This thesis describes such investigations. The impact on cellulose molecular size and acidity is presented in Paper V, and the formation of low molecular acids and a minor study of mechanical properties is presented in Paper VI.

2. Background

2.1 Wood components and chemical characteristics.

Wood is constituted of a complexity of compounds, from low molecular to polymeric ones. To understand changes in wood under the influence of heat and moist conditions, it is important to know the basic characteristics of the major components that constitute the wood structure. A gross division of the wood components can typically consist of polysaccharides (cellulose, hemicelluloses, starch and pectins), lignin and extractives (Fengel and Wegener 1989; Sjöström 1993).

Hemicelluloses

Wood hemicelluloses are branched amorphous polymers consisting of sugar units of five-carbon-membered rings (pentoses) and six-carbon-membered rings (hexoses) (Figure 1). Some also contain small amounts of sugar acids in the polymers; an example is 4-O-methyl-β-D-glucuronic acid (Figure 1). Deoxy-sugars (Figure 1), such as α-D-rhamnose, can be found in small amounts in some wood species (Fengel and Wegener 1989). The monomer units in the main chain are bonded to each other by ether bonds (-C-O-C-), i.e., glycosidic bonds, between carbon numbers 1 and 4, expressed as β(1→4) (Figure 1). There are also several side groups attached to the main chain as branches (Sjöström 1993).

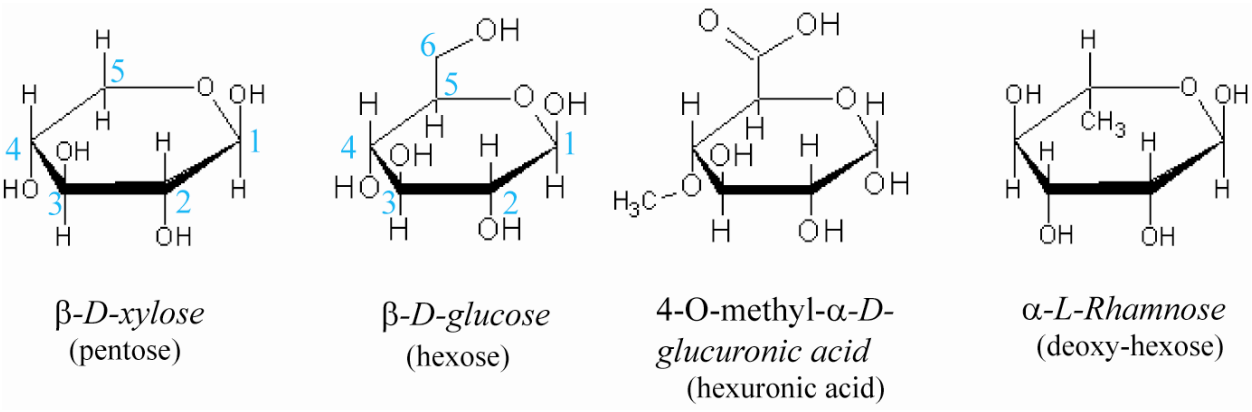

Figure 1: *Examples of common monosugar units found in carbohydrates of wood. The units are shown in pyranose form (ring form with six atoms). Pentoses contain five carbon atoms and hexoses contain six carbon atoms per unit. Carbon numbering in blue. Hexuronic acids include a carboxylic group at carbon number 6 and deoxyhexoses have a hydroxyl group substituted for a methyl group at carbon number 5.*

Hemicellulose average molecular weight varies from 10 000 to 30 000 g/mol, and it is comprised of 20%–30% dry-weight wood. It can be considered the interface between cellulose and lignin in the wood material structure. Hemicelluloses of hardwoods and softwoods generally differ in constitution (Figure 2).

Hemicelluloses of hardwoods consist predominantly of glucuronoxylan (15%–30%) and also to a minor extent of glucomannan (2%–5%). Hemicelluloses of softwoods consist predominantly of galactoglucomannan (20%) as well as smaller amounts of arabinoglucuronoxylan (5%–10%) (Theander and Nelson 1988). There is also galactan in compression wood of softwoods to an amount of approximately 10% (Sjöström 1993).

The glucuronoxylan in hardwoods, with the main chain units of β-D-xylose, has a high incidence of side groups. Approximately 70% of the hydroxyls at carbons 2 and 3 (O2 & O3) are esterified and have acetate groups attached, and approximately 10% of carbon 2 are glucosidically linked with side groups of 4-O-methyl-α-D-glucuronic acids (Sjöström 1993). The glucomannan in hardwoods has a low incidence of side groups.

The arabinoglucuronoxylan in softwoods, with the main chain units of β-D-xylose, has approximately 20% 4-O-metyl-α-D-glucuronic acids glucosidically bonded to carbon 2, and also has approximately 13% α-L-arabinose glucosidically bonded to carbon 3 as side groups (Theander and Nelson 1988). For the galactoglucomannan in softwoods, with the main chain units of β-D-glucose and β-D-mannose, there is 2%–20% of α-D-galactose glucosidically bonded to carbon 6 at the β-D-mannose units (Sjöström 1993) (Figure 2).

Pectins and starch

In wood there are also minor amounts of other polysaccharides. Normal wood contains less than 1% of pectins and even less than that of starch (Fengel and Wegener 1989). Pectins can be found in the middle lamella, primary cell wall and tori of bordered pits and also to a small extent in the fibril structure. Pectins resemble hemicelluloses in structure, and they consist of galacturonans, rhamnogalacturonans, arabinans and galactans (Sjöström 1993). Starch can be found in parenchyma cells serving as storage of nutrition for the living tree, and it consists of amylose and amylopectin.

Cellulose

Cellulose is the most abundant component in wood, 40%–50% of the dry weight, and it plays a major role in wood strength. A cellulose molecule consists of β-D-glucose units bonded with β(1→4) linkages (Figure 1) to a long and linear chain, and the cellulose molecular weight is very large, from several hundred thousand to many million g/mol (Sjöström 1993).

The molecular chains in cellulose appear in the form of elementary fibrils or micelles where the cellulose molecules are aligned in the same direction and tightly packed together. Cellulose elementary fibrils are merged together parallel with hemicelluloses and pectins in between which then form micofibrils. When the microfibrils are aggregated in larger bundles with lignin impregnated in the structure, the fibrils are generated, and they in turn form wood fibres (Sjöström 1993).

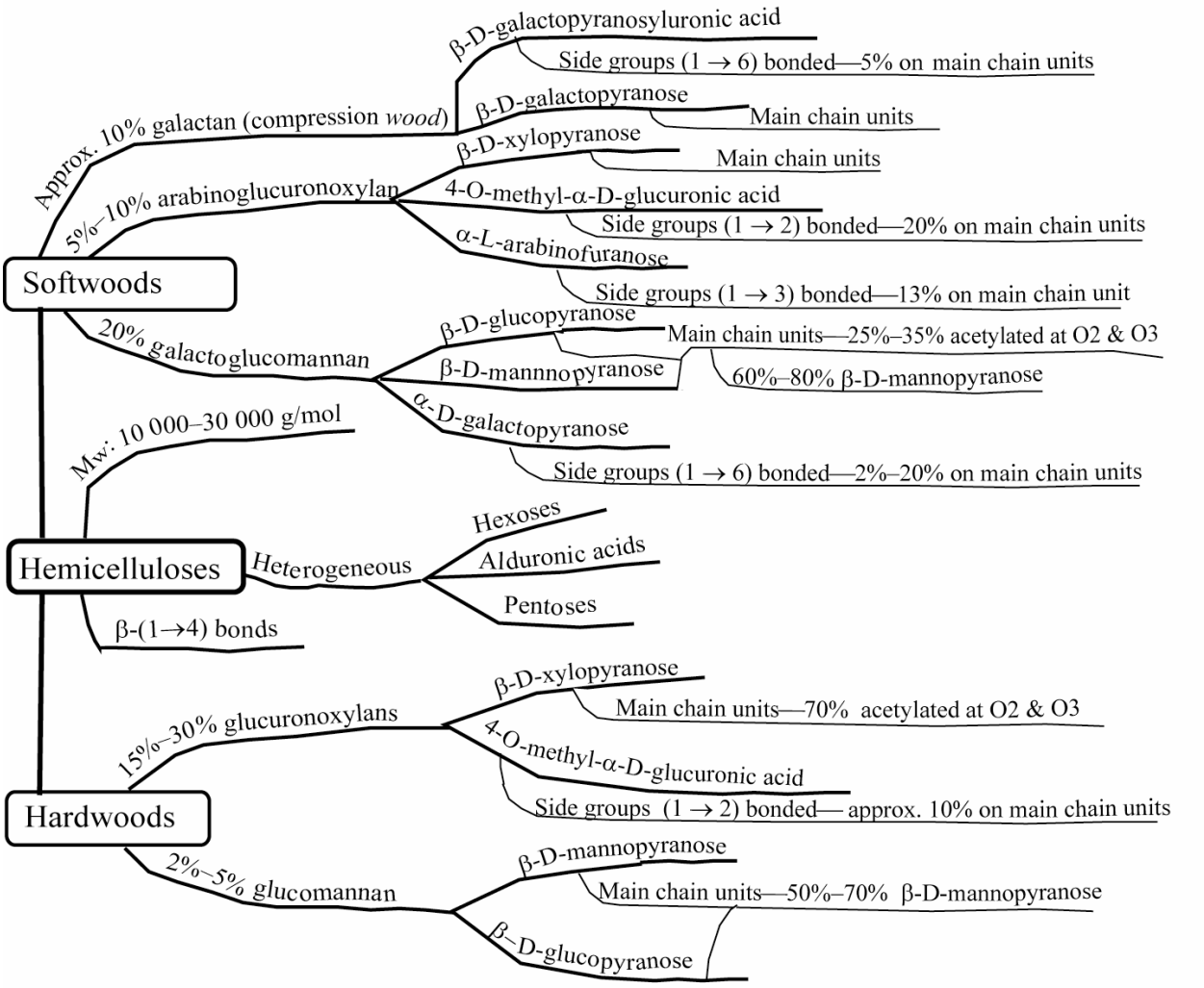

Figure 2:" *The hemicellulose-tree". General morphology of major hemicelluloses in softwoods and hardwoods according to Theander and Nelson 1988, Sjöström 1993.*

The cellulose molecules in the protofibrils are often linked to each other with hydrogen bonds, i.e., between hydroxyls and hydrogens (intermolecular hydrogen bonds). There are also hydrogen bonds within the molecule (intramolecular hydrogen bonds) which give a certain degree of stiffness to the molecular chains (Fengel and Wegener 1989; Sjöström 1993). Between close layers of cellulose molecules, van der Waals forces can also act. A high degree of hydrogen bonds in the fibril structure has a positive effect on wood fibre strength.

Some parts of the cellulose microfibrils are arranged in a regular molecular arrangement, and these parts are therefore crystalline; other parts that are less regularly arranged are amorphous. The crystallinity in wood is difficult to estimate, since most analytical methods alter the cellulose significantly during analysis. For wood pulp the crystalline part is 70%–80% (Fengel and Wegener 1989).

Extractives

Compounds in wood that can be extracted by various solvents and water are called extractives. They are often low molecular, less than 500 g/mol, and can be categorized into many groups according to their chemical constitution. The water-extractable part of wood is often in low concentration compared to the nonpolar substances (Sjöström 1993).

Note that considerable amounts of partly hydrolysed hemicelluloses and pectin can be extracted with water, but they are not considered as extractives. There are other literature that consider water soluble compounds not be included in the definition of extractives. In this thesis the water soluble compounds are included. Wood generally contains 2%–8% extractives based on dry weight (Fengel and Wegener 1989). Some tropical and subtropical species can have even higher values. Heartwood often contains more extractives than sapwood. For instance, Scots pine heartwood typically consists of approximately 12% extractives, while its sapwood consists of only approximately 4% (Sjöström 1993). The extractives are not considered to contribute to the strength properties of wood in any way. Their functions are rather, for instance, to defend against biological attack, to be constituents in biosynthesis, etc. (Table 1). There are also examples of phenolic extractives giving colour (Fengel and Wegener 1989).

Extractives	**General constitution**	**Example of characteristics**
Terpenoids & steroids	Isoprene units. Contain -OH, -C=O, -COOH except terpenes	Odour, flavour, biodegr. resistance (insects)
Fats (and fatty acids)	Esters of higher org. acids with glycerol	Cellular energy source
Waxes	Esters of org. acids with higher alcohols	
Quinones	Cyclic conjugated diketone structure	Colour, biosynthesis const.
Phenolic compounds	Contain benzene ring with -OH	Lignin biosynthesis, colour, biodegradation, resistance, flavour, odour
stilbenes	Diphenylethylene structure	
lignans	Two phenylpropane units coupled	
hydrolyzable tannins	Esters of ellagic or gallic acid with sugars	
flavanoids	Tricyclic structures	
condensed tannins	Polymers of flavanoids	
Inorganic components	Carbonates, silicates, oxalates, phosphates, ions of; Ca, K, Mg, Na, P, Fe, Mn etc.	Biosynthesis constituents (with enzymes)
Various compounds		
hydrocarbons	Alkanes, ethene	Related to biosynthesis
sugars (low mol.)	Sucrose, glucose, fructose, mannose	Cell. energy source, biosynthesis
proteins	Amino acids	Biosynthesis constituents
alkaloids	Cyclic structures containing nitrogen	Toxic, narcotic

Table 1: *Extractives, their difference in constitution and some characteristics (Fengel and Wegener 1989; Sjöström 1993).*

Many groups of extractives often have functional groups that can be quite reactive. Terpenoids, phenolic compounds, quinones, de-esterified waxes and fats can have hydroxyls (-OH), carbonyls (-C=O) and/or carboxylic groups (-COOH) that are considered to be reactive. It can sometimes be difficult to differentiate extractives from other types of compounds. For instance, some phenolic compounds and some quinones can be regarded as both extractives and low-molecular lignin parts (Fengel and Wegener 1989).

Lignin

Lignin is an amorphous polymer with a wide variation in configuration. The average molecular weight is difficult to analyse, and values ranging from a few thousand up to hundreds of thousands have been reported, depending on the analytical methods used (Fengel and Wegener 1989; Lai 1991). The amount of lignin in wood ranges from 20-40% and is often considered to be the glue of the wood structure.

The lignin backbone is based on three types of phenyl propane units: guaiacyl, syringyl and p-hydroxyphenyl propane units (Figure 3). Syringyl units have 2 methoxy groups (-OCH_3) at positions 3 and 5, guaiacyl has one at position 3, and p-hydroxyphenyl propane has none. A free phenolic group (-OH bonded to an aromatic ring) can be found at position 4 for all three units. This phenolic group can be methylated or it can link to other lignin units as an ether bond (Figures 3–5). The existence of free phenolic groups clearly promotes the degradation rate of lignin. 10%–30% of the units in softwood lignin and 9%–15% of the units in hardwood contain phenolic groups (Lai 1991).

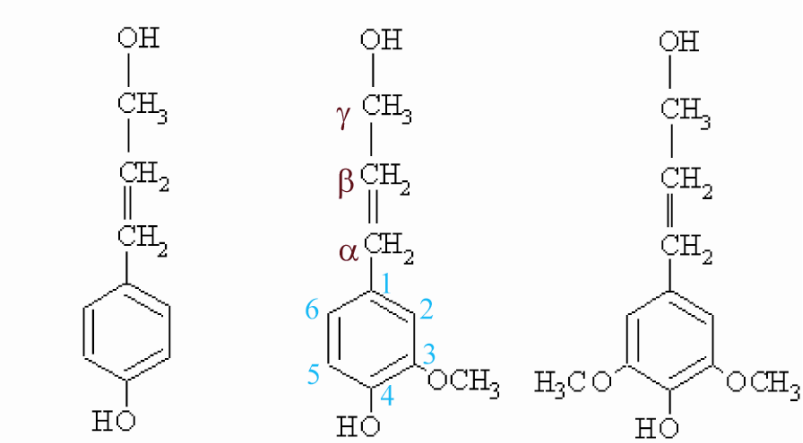

Figure 3: *Examples of the three phenylpropane monomer units of the lignin main structure in wood (p-hydroxyphenyl, guaiacyl and syringyl). Carbon atoms numbered in blue for the aromatic phenyl part. Greek letters in red for the carbon atoms of the propane side chain.*

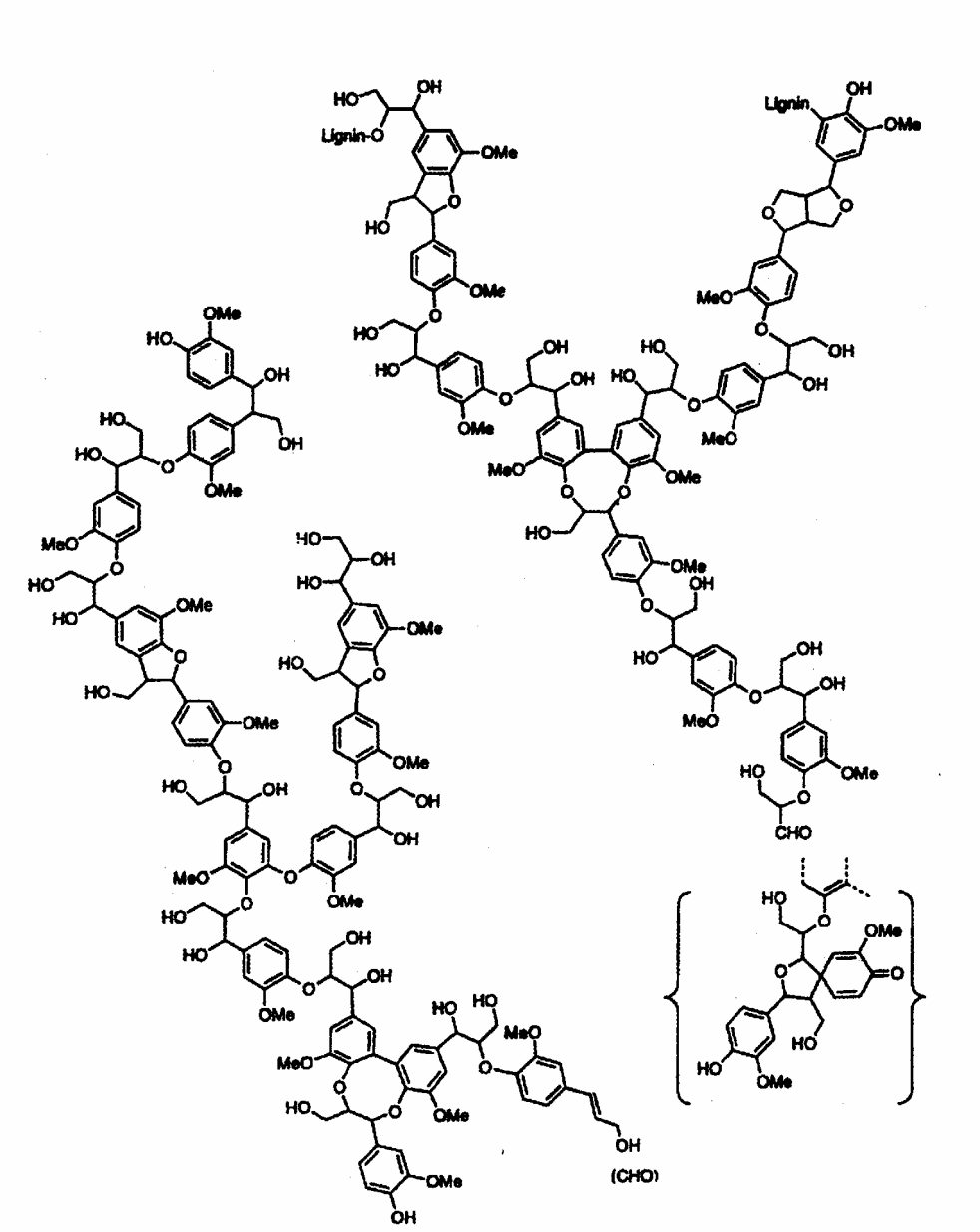

Figure 4: *Softwood lignin according to Brunow et al. 1998.*

Softwoods consists mainly of guaiacyl units and also to some extent of p-hydroxyphenyl units, where the latter is mostly found in compression wood and in the compound middle lamella of softwoods (Fengel and Wegener 1989; Lai 1991). Hardwood lignins consist of syringyl and guaiacyl units (Figure 4). The lignin units are linked together in a variety of chemical bonds (Figures 4 and 5). The predominant types are ether bonds (-C-O-C-) and carbon-carbon bonds. The most common ether bond is the one located between the β-carbon and O4 on an adjacent phenylpropane unit (β–aryl ether) (Figures 3 and 4). To a lesser extent there are also α-aryl-ether and α-O-4 bonds in the lignin structure. Ether bonds are in general much more unstable and susceptible to degradation by heat and chemicals than the carbon-carbon bonds (Lai 1991)

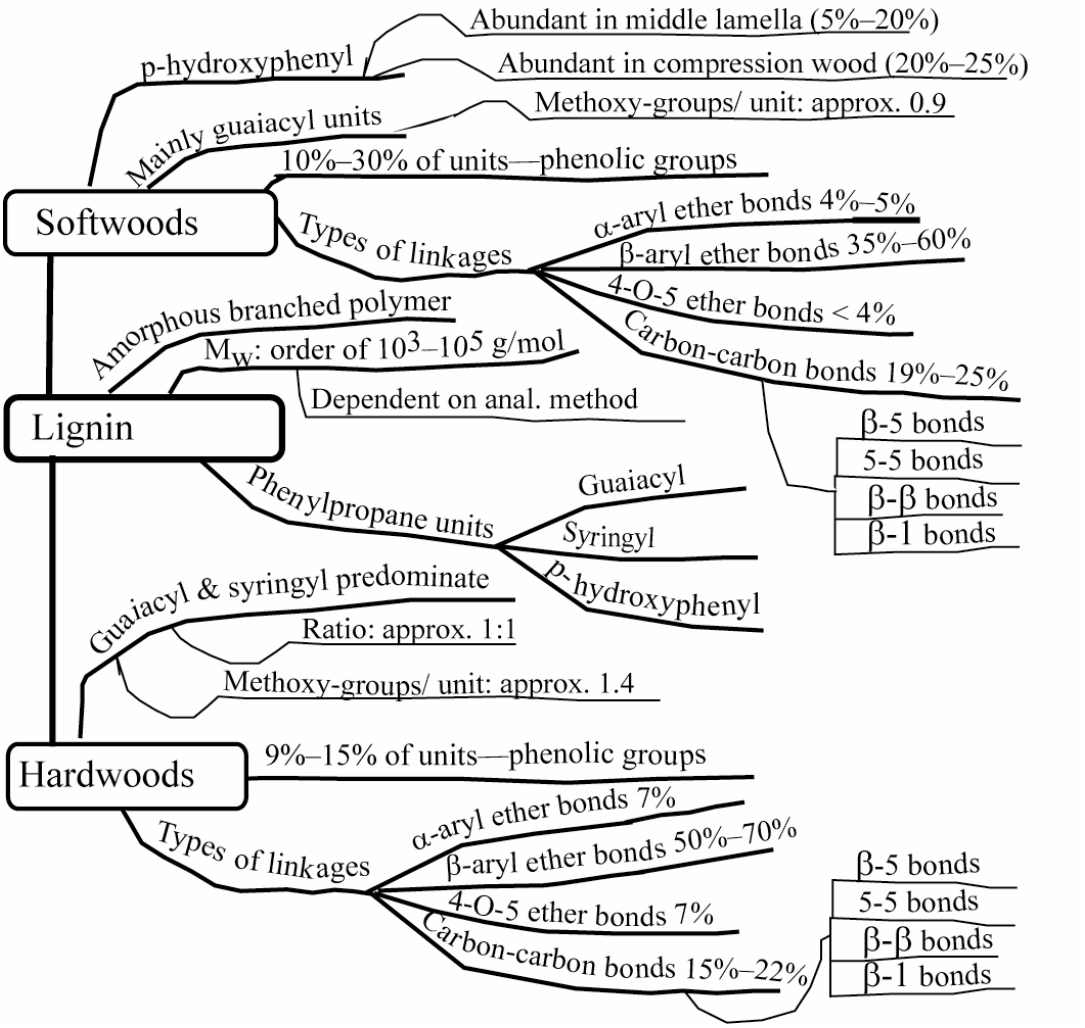

Figure 5: *"The lignin-tree". General morphology of lignin in softwoods and hardwoods according to; Fengel and Wegener 1989; Sjöström 1993.*

2.2 Availability; distribution of the components in wood structure

The most embedded and least available structural component in wood is cellulose, which in other words has a low susceptibility to being affected by solvents, water, etc. The long cellulose molecules are oriented parallel to each other and form long bundles, sometimes called micelles or elementary fibrils. These micelles, oriented in parallel, are merged together to form microfibrils, which in turn are merged together in parallel to form fibrils. The fibrils are the main structural elements of the wood cell wall. Hemicelluloses and pectins are bonded to the surfaces of the cellulose microfibrils and fill out voids between microfibrils. From this arrangement it is clear that hemicelluloses have a higher availability than cellulose and are more susceptible to being affected by solvents and water than is cellulose. For the hemicelluloses and celluloses that are similarly available in the fibre structure, the less regularly ordered amorphous parts are primarily affected, and the highly ordered crystalline parts of cellulose are affected at a later stage.

The fibrils, and to some extent also the microfibrils, based mainly on cellulose and hemicelluloses, are impregnated with lignin and tied together by bonds between lignin units and hemicellulose units. The lignin is considered to be the internal glue of the wood

fibril structure. The lignin is therefore in general as available as the hemicelluloses and is clearly more susceptible than cellulose to being affected by solvents and water.

Extractives are mostly found in and in the vicinity of horizontal and vertical resin canals and tracheid rays and are therefore much more available to solvents and water than the structural components cellulose, lignin and hemicellulose. Some extractives are more evenly distributed in the wood structure, such as phenolic and inorganic compounds (Sjöström 1993). These can be less available, since they can be more or less bonded to the wood structural components.

2.3 Changes of characteristics of wood and its components during heating

The changes that occur in wood at temperatures below 40ºC are mainly attributed to physical changes such as emission of water and volatile extractives such as terpenes (Manninen et al. 2002). However, during storing or seasoning outdoors some chemical changes can occur. The wood can be attacked by rot, mould and bacteria that initiate decay processes, and enzymes may be active. Enzymatic degradation can also produce organic acids that contribute to the decay process. Therefore, keeping the time between felling of timber and further processing short is important if downgrading effects on the wood, for example discoloration, are to be avoided (Kreber and Byrne 1996; Luostarinen et al. 2002).

Some minor chemical changes probably start to occur during drying in the interval 40º–90ºC, most likely predominately by way of certain extractives. In a study of the emission of volatile organic compounds (VOC) from drying of pine and spruce, monoterpenes were found in relatively high concentrations (Englund and Nussbaum 2000). Another positive effect of artificial drying at temperatures around 70°C is the inhibition of biological activity in the tissue of the wood which might otherwise decay the wood. One example is the extermination of a wood destroying nematode by kiln drying (Tomminen and Nuorteva 1992). The colour of wood is somewhat changed in this temperature interval compared to air-dried wood. Softwoods become slightly darker, while hardwoods become considerably darker in general. Softwoods are in general less changed than hardwoods. The level of moisture and the temperature during drying of hardwoods have been found to be the most important factors affecting the darkening (Brauner and Loos 1968; McMillen 1976; Schmidt 1986). Therefore it is reasonable to conclude that a major part of the change in colour is due to compounds emanating from hydrolysis of carbohydrates (Fengel 1966) and extractives (Charrier et al. 1995; Burtin et al. 1998) and their subsequent reactions with other wood components. The effect of kiln drying on wood strength was found to be negligible (Stamm 1956).

A brownish discoloration just beneath the wood surface has been observed for kiln drying (Millet 1952; Theander et al. 1993; McDonald et al. 2000). This discolouration is proposed to be a result of low molecular carbohydrates and nitrogen compounds migrating towards the surface and forming brown reaction products. The reactions are suggested to be of the Amadori-Maillard type (McDonald et al. 2000). This phenomenon is also known as “Kiln Brown Stain” (KBS) for radiata pine (Kreber and Haslett 1998)

For high temperature (HT) drying conditions, 90º–150ºC, the changes for all wood components are more obvious, and losses in wood strength and changes in water sorption have been reported from 100º to 150ºC (Schneider 1971; Schneider 1973). Condensate from HT drying of Radiata pine at 100ºC resulted in considerable amounts of emitted monoterpenes and also minor amounts of emitted formaldehyde, furfural, acetic acid, methanol, diterpenes, etc. (McDonald et al. 1999; McDonald et al. 2002). Carbohydrates of hardwoods and softwoods change similarly during heat treatment. The mass losses of hemicelluloses and cellulose in pine and oak accelerated noticeably when heated above 130ºC for 24 hours (Kollman and Fengel 1965). Spruce wood required heat treatment at temperatures above 100ºC for noticeable amounts of water-extractable products to be obtained, and heat treatments above 150ºC for 24 hours gave a steep rise in the amounts (Fengel 1966). The main part of the extracted products was suggested to be formed by hydrolysis of hemicelluloses.

The lignin of the wood is affected in this interval, and approximately 100ºC for wet conditions is considered to be the plasticization temperature of wood, which is related to changes in the lignin structure. A partial depolymerization has been reported at 135ºC for beech (Košíková et al. 1999). Moreover, splitting of β-aryl ethers and formation of lignin condensation products at 100°–120ºC was found for maple (Kacík et al. 1999), and homolytic cleavage of phenolic β-aryl ether in wood lignin was found around 130ºC (Westermark et al. 1995).

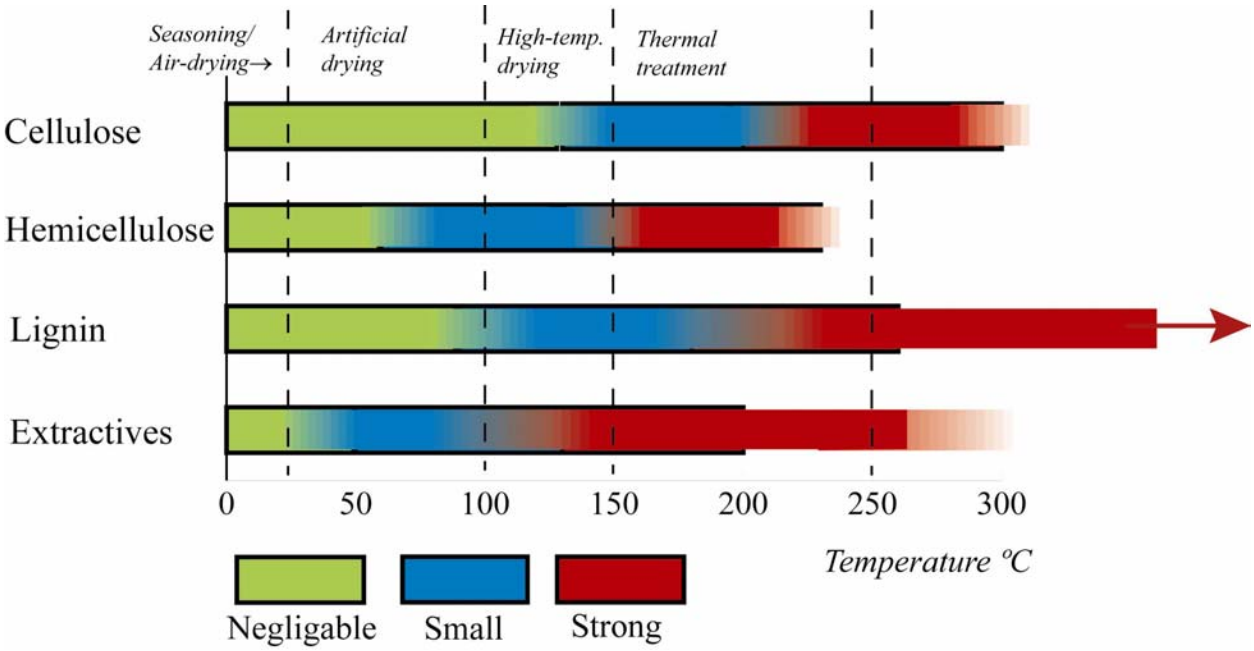

Figure 7: *General changes of wood components due to heat treatment/drying under humid conditions.*

At temperatures of 150º–250ºC, major changes in the wood components occur, both degradation and modification. Earlier studies show that the degradation rate during thermal treatment in model systems was four times higher for hemicellulose than for cellulose and that the degradation rate for lignin was only half of that for cellulose at 150ºC (Stamm 1956). Similar results were obtained for Eucalyptus wood samples at 145º–190ºC (Garrote et al. 1999b). Hemicellulose degradation is predominate at

temperatures below 200ºC. Many investigations have been done on hemicellulose degradation during heat treatment of wood (Stamm 1956; Kollman and Fengel 1965; Fengel 1966; Tjeerdsma et al. 1998b; Sivonen et al. 2002). Many investigations have also been done on the production of saccharides, which further elucidates hemicellulose degradation (Garrote et al. 1999a; Garrote et al. 1999b) and formation of acetic acid (Garrote et al. 2001). The degradation of wood increases in closed treatment systems (Stamm 1956; Sanderman and Augustin 1963b; Burmester 1973). It is suggested that volatile organic acids formed due to heating of wood are trapped in the process and promote the degradation rate (Stamm 1956). The degradation rate of wood is reported to be higher for steaming and in the presence of air during heating than for dry conditions and air-free conditions (Stamm 1956).

More emphasis has been devoted to studies of the change of the structural components in wood due to heat treatment than to studies of the change of extractives initially found in wood. Some extractives, such as hydrolysable tannins in oak and walnut, can be hydrolysed at temperatures above 30ºC (Charrier et al. 1995; Burtin et al. 1998) and can be further degraded at higher temperatures. Initially, volatile extractives in the untreated wood, such as terpenes, are emitted completely during heat treatment up to 200ºC (Manninen et al. 2002). It is also possible that some de-esterfication of fats and waxes occurs, with further degradation as a result. High molecular extractives such as resins have been reported to migrate to the surface of wood with subsequent degradation during heat treatment (Viitaniemi 2001).

Noticeable changes in the lignin structure start at temperatures around 120ºC (Westermark et al. 1995; Kacík et al. 1999), and with rising temperature the changes increase. If oxygen is present during heating of wood, the degradation of lignin clearly increases in comparison to conditions where no oxygen is present (Sanderman and Augustin 1963b). At temperatures around 180ºC the degradation of lignin in heat-treated wood is considerable. Homolytic cleavage of β-ether linkages and formation of radicals in lignin have been found for wood samples (Westermark et al. 1995), and formation of condensation products and possible cross links between lignin and polysaccharides have been reported (Tjeerdsma et al. 1998b; Košíková et al. 1999; Sivonen et al. 2002). Lignin is not changed as much as the hemicelluloses when subjected to hydrolytic conditions below 200ºC (Fengel and Wegener 1989). Mild acidic hydrolysis of lignin is proposed to be the result of the breaking of cyclic α-aryl ether bonds giving various lignin fragments such as lignols (Lai 1991). Above 200ºC the lignin degradation rate and the concentration of radicals that is formed are reported to strongly increase (Sivonen et al. 2001).

2.4 Formation of acids in the wood due to heating

Natural wood is often acidic, with a pH of 3–6. This can be explained by extractives such as fatty acids, acidic phenols, low molecular acids and by carboxylic groups on the structural components (Gray 1958; Ekman 1979; Balaban and Uçar 2001; Jung and Roffael 2002). Emission of acetic acid in low concentrations has been found for dried hardwoods at room temperature, whereas for softwoods acetic acid was not found (Risholm-Sundman et al. 1998).

Upon heating of wood, degradation of hemicelluloses starts with the liberation of acetic acid. It is well known that the hemicelluloses glucuronoxylan in hardwoods and galactoglucomannan in softwoods have O-acetyl side groups attached to the main chain (Figure 2) (Theander and Nelson 1988). These can be split off due to heating of wood. Hydrolytic conditions especially favour the splitting, as compared to dry conditions. Acetic acid and formic acid have been found in emissions from the drying of Radiata pine at 100ºC (McDonald et al. 2002).

The origin of formic acid from wood is not clear and not easy to analyse, since it is of particularly low molecular weight and is volatile. Under harsh conditions, 300ºC and 30 minutes, formic acid was found to mostly originate from carbon 1 (41-45%) (Figure 1) of the glucose units (hexoses) by degradation of glucan as model compound (Ponder and Richards 1995). Similar results were obtained in laboratory experiments at 96ºC up to 72 hours with pentoses, where they concluded that formic acid derived exclusively from terminal carbons, carbon 1 being somewhat more important than carbon 5 (Ahmad et al. 1995). However, since formic acid is detected from wood without raising the temperature (Jung and Roffael 2002), it is reasonable to believe that its origin can be related to the splitting of ester groups of the O-methyl type. However, the existence of such esters in wood has not been investigated, and the origin of formic acid from wood remains obscure.

At temperatures above approximately 150ºC the formation of organic acids in wood is fast, and accelerating concentrations can be found. Acetic acid is the predominant acid found. When wood chips of Eucalyptus were hydrothermally treated at 145°–190ºC for 0.4–7.5 hours, it was found that 40%–50% of the O-acetyl groups in the wood were split off to acetic acid (Garrote et al. 2001). Sivonen et al. (2002) found acetic acid with magnetic resonance studies of Scots pine at 180º–250ºC and also by measuring the emissions from 24 hours of treatment at 230ºC.

2.5 Acidic hydrolysis and heating of wood polysaccharides

The degradation of material that occurs when water or steam is involved is called hydrolysis; i.e., water is one of the reactants. This is the type of reaction that predominates when wood is heated and water is present as wood moisture and/or steam atmosphere. The polysaccharides in wood are more or less prone to being hydrolysed and washed out as mono-, di- and oligosaccharides, while lignin is not prone to being hydrolysed to the same extent (see chapter 2.4).

The hydrolysis rates of polysaccharides are faster in acidic media than in neutral and alkaline media. Most wood species are known to be acidic in the neutral state (Gray 1958; Jung and Roffael 2002), and this condition therefore promotes the hydrolysis of polysaccharides. Furthermore, organics acids such as acetic acid are known to be liberated from wood when it is heated, which will further accelerate the hydrolysis rate (see chapter 2.4).

There are large differences in acidic hydrolysis rates depending on the acidic medium and the characteristics of the polysaccharide. For the acid, the rate depends on characteristics

such as acid strength, hydrolytic activity and the activity coefficient; and for the polysaccharide the rate is dependent on characteristics such as the physical structure, availability, conformation, ring structure and substituents (Fengel and Wegener 1989). Other factors that influence the hydrolysis rate are pH, temperature, time and pressure during the process. The monosaccharide units of the polysaccharides found in wood show the following relative hydrolysis rates: 1, 3, 4–5 and 4–6 for β-D-glucose, β-D-mannose, β-D-galactose and β-D-xylose respectively (Fengel and Wegener 1989). α-L-arabinose shows an even faster relative rate of degradation than β-D-xylose. By choosing conditions, almost complete hydrolysis can be achieved even for cellulose. For instance, wood saccharification is a hydrolytic method of producing mono- and disaccharides from cellulose by using mineral acids that are strong and highly active in high concentrations and at elevated temperatures.

The acidic hydrolysis of hemicellulosic polysaccharides in wood is mainly a matter of breaking the glycosidic bonds (1→4) between monosaccharide units of the chain, the liberation of ester-bonded side groups such O-acetyl and the breaking of other ether-bonded side groups such as α-L-arabinofuranose and α-D-galactopyranose (Figures 1 and 2). This will lower the molecular size, i.e., reduce the degree of polymerisation for the polysaccharide, and fragments of low molecular by-products such as mono- and disaccharides will be solubilized (Fengel and Wegener 1989). Water extracts of untreated and treated spruce wood contained residues of the hemicelluloses galactoglucomannan and arabinoxylan (Fengel 1966; Hinterstoisser et al. 1992). The content of water-soluble products increases with heat-treatment temperature, and a steep increase was noted for temperatures between 150° and 180ºC (Fengel 1966). The water extract content levelled off around 9% at 200ºC. It is reasonable to believe that pectins and starch that has a similar molecular structure as hemicelluloses also become hydrolysed under these conditions.

Splitting of linkages between side groups to polysaccharides and between mono-units of them is typically the initial degradation during hydrolysis. Further hydrolysis of polysaccharides due to more intense heating and prolonged time involve dehydration, abstraction of water (i.e. hydroxyls are split off) and opening of the ring structure of the saccharide units. Dehydration reactions of monosaccharides are known to give hydroxymethylfurfural (HMF) from hexoses and furfural from pentoses (Figure 1) (Theander and Nelson 1988; Fengel and Wegener 1989). HMF and furfural can be further degraded to produce low molecular compounds such as levulinic acid and formic acid from HMF (Fengel and Wegener 1989; Lai 1991). If oxygen is present during the heating of wood, phenolic compounds may be formed from the polysaccharides (Fengel and Wegener 1989).

Cellulose is more resistant to hydrolysis than hemicelluloses, pectins and starch and has generally a more regular and crystalline structure with considerably higher molecular weight. The hydrolysis rate is decided mainly by the degree of crystallinity and the swelling state. Generally, the amorphous parts of the cellulose are hydrolysed first, leaving a residue of cellulose with reduced degree of polymerisation and increased crystallinity (Roffael and Schaller 1971; Fengel and Wegener 1989). In the case of heat-treated wood, the effect on the crystallinity of cellulose is not clear. Increased

crystallinity for the cellulose of heat-treated wood compared to untreated wood has been reported for X-ray diffraction measurements (Bhuiyan et al. 2000).
Furthermore, moist conditions during heating produced a higher crystallinity than the dry conditions. It is suggested that amorphous cellulose and some hemicellulose is converted to crystalline structures. From other investigations using magnetic resonance studies it is suggested that the increase in crystallinity is relative, since the amorphous parts have been degraded (Sivonen et al. 2002). However, from these investigations it is clear that amorphous cellulose and hemicelluloses are much easier to affect than crystalline cellulose. In laboratory hydrothermal treatments of wood below 230ºC, less than 15% cellulose degradation has been found (Garrote et al. 1999a). The residue of mostly crystalline cellulose after hydrolysis and heating of wood is most likely affected, and depolymerization can be expected. From model experiments of cellobiose it was found that the degree of polymerisation (DP) was reduced considerably and levelled of to a DP of 600 to 800 by thermal treatment in the temperature interval from 80ºC to 200ºC (Roffael and Schaller 1971). Investigations concerning the degree of polymerisation of cellulose in heat-treated wood were not found. However, data for processing fibre boards at 170ºC are available and reveal a decrease of average cellulose molecular size (Klauditz and Stegman 1947).

2.6 Colour—the phenomena and appearance of wood

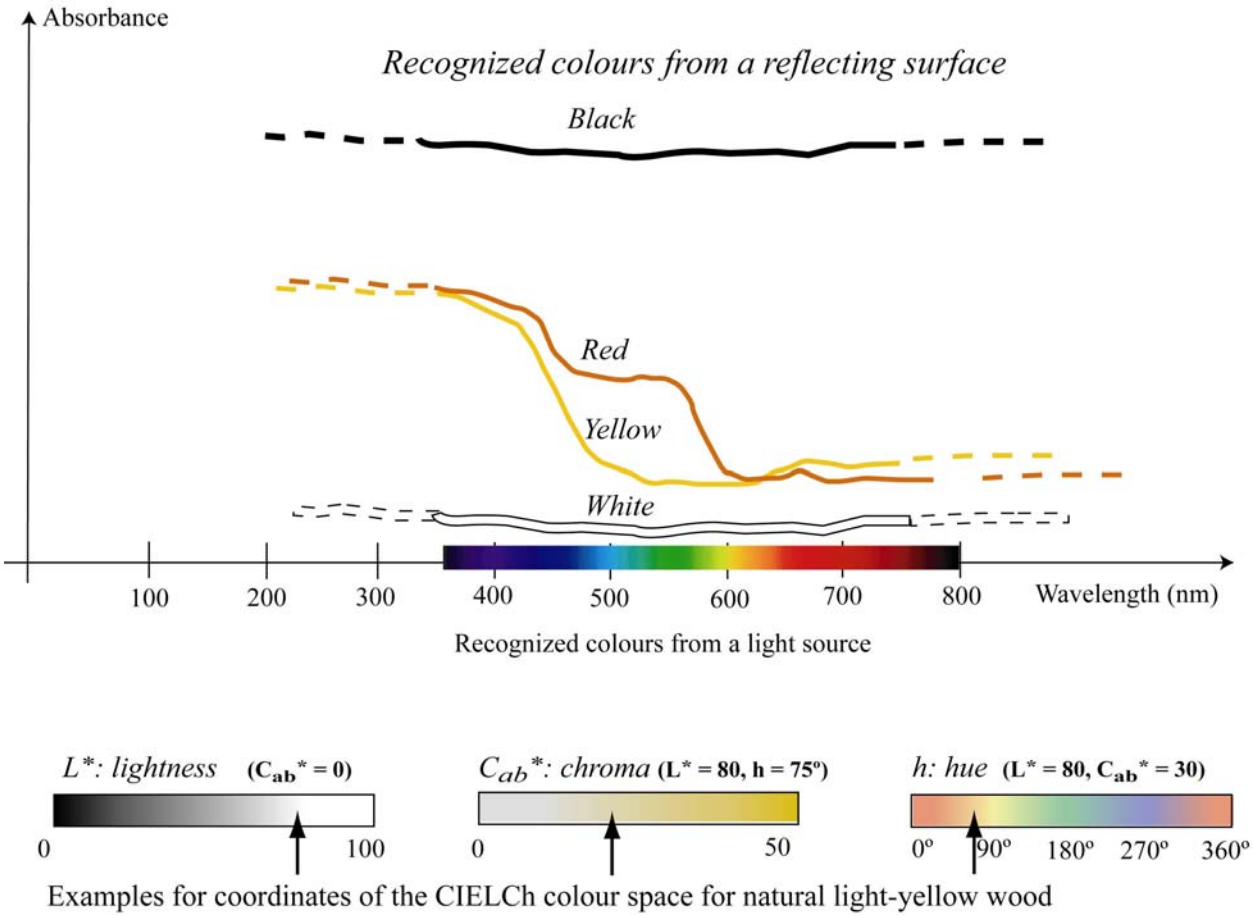

Figure 5*: Examples of absorbance within the interval for visible light (380-800nm) and the colours recognized from the reflecting surface of an observer. Absorbance is given in arbitrary units. A strong absorbance for the whole interval is recognized as a black colour, and a weak absorbance as a white colour. Absorbance of blue and violet colour (380–450 nm) is recognized as a yellow colour, and if also some green colour is absorbed (380–550nm) it is recognized as a red colour. The lower part of the figure is an example of the colour space CIELCh given with examples of its co-ordinates. The arrows point to common values for natural sapwood.*

Visible light consists of electromagnetic radiation in the approximate interval 380–800 nm. When the visible light is reflected and scattered by a surface, it appears to be white. If no scattering occurs it will be recognized as a mirror-like surface. If all visible light is absorbed a completely black surface will be observed.

Colour is recognized when electromagnetic light in some part of the interval 380–800 nm is absorbed, and the rest of the light is reflected and scattered. Scattering of light is a physical phenomenon wherein light hits a surface and reflects in many directions.

For instance, yellow colour of a surface, e.g., the natural colour of light-yellow wood, means that a large portion of the blue and violet colours have been absorbed (380–480 nm) and that considerable scattering has occurred. A more reddish wood, e.g., heat-treated wood, absorbs more the blue and violet light and also some green light at longer wavelengths (480–550 nm) than does natural wood (Figure 5). The scattering is at a

similar level. The colour of a material can be measured and quantified with many standard methods. In this work, the CIE colour space was chosen, and measurements were made with a portable tristimulus colorimeter (see chapter 4.4 for more information). An example of natural light-yellow wood and its approximate values as co-ordinates L^*, C_{ab}^* and h, CIE standard colour space, is given in figure 5.

Cellulose and hemicelluloses are considered to only scatter visible light, and they would alone most likely give a greyish appearance; i.e., no characteristic absorbance in the visible region occurs. This is what can be experienced from greyish wood surfaces exposed to outdoor climate for long periods. Colour is based on chemical phenomena wherein light at certain wavelengths is absorbed by certain molecules or parts of molecules, sometimes called chromophores (i.e., contain chromophoric groups). These molecules have base structures constituted with conjugated double bonds (every second bond is a double bond) and chromophore groups; e.g., carbonyls (Figure 6). The conjugated double bonds enable the existence of delocalised electrons; i.e., loosely bound electrons that can be excited by photons with the energy recognized as visible light. The chromophores can also contain auxochromes, hydroxyls and methoxyls, which further enhance the interaction with electromagnetic radiation (Hon and Minemura 1991). Another type of chromophore is phenolic compounds that are complex bonded to metal ions and form complexes that strongly absorb light (Falkehag et al. 1966). One example is the complex of tannins and iron ions in oak forming a dark discoloration (Hon and Minemura 1991).

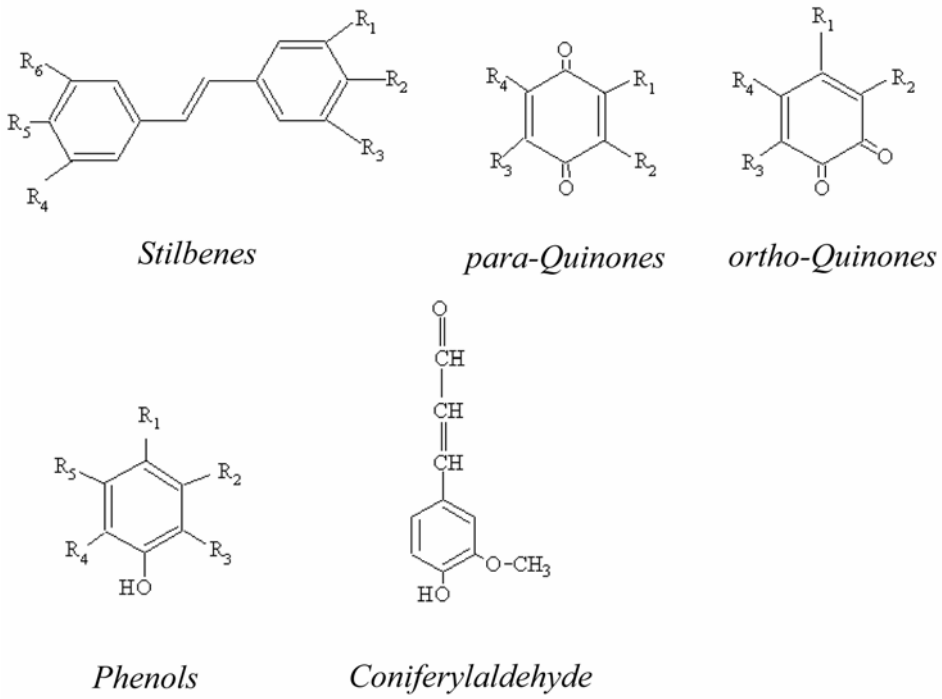

Figure 6: *Examples of chromophoric structures that can be found in wood. R_1 to R_6 denote either hydrogens (H) or continuing organic chains that can be variously constituted.*

The colour of natural light-yellow wood is most likely caused by chromophores in lignin and in extractives, and possibly also sometimes by organometalic complexes in extractives (Falkehag et al. 1966). For lignin in untreated milled wood it is suggested that

there are parts that contain quinonoid and stilbene structures which are the main cause for the yellow appearance (Falkehag et al. 1966; Hon and Minemura 1991).

Colours such as brown, purple, black, red-orange, etc., can be found in the heartwood of many, species and they are explained or suggested to be caused by a variety of phenolic compounds (Figure 6), e.g., tannins, lignans, flavanoids, quinones, etc. (Kondo and Imamura 1985; Charrier et al. 1995; Kawamura et al. 1996; Takahashi 1996; Dellus et al. 1997; Burtin et al. 1998; Chang et al. 1999; Johansson et al. 2000).

During heating and drying of wood, a more intense reddish brownish colour is normally formed but the underlying cause of this is not well understood. Many investigations of the phenomenon have been done, and they suggest a variety of explanations for colour formation resulting from drying and heating. The colour changes due to enzymatic mechanisms are not discussed here, since they are only active below 60º–70ºC. From experiments on heating of Radiata pine and its sap, complemented with experiments on heating of monosaccharides and amino acids, it was concluded that both lignin and hydrolysed carbohydrates participate in the browning (McDonald et al. 1997). The reaction mechanism for the carbohydrates and the amino acids to form coloured compounds was believed to be of the Amadori-Maillard type.

These types of reactions are well known in food processing, and many coloured Maillard reaction products (CMRP) can be formed due to heating (Rizzi 1997). If this type of reaction takes place without amino acids or some other nitrogen-containing compounds, it is called caramelization (Rizzi 1997; Kamuf et al. 2003). Examples of coloured polymeric compounds formed by caramelization are caramelin, caramelan and caramelen (Kamuf et al. 2003).

Sehlstedt-Person (2003) found that heat treatment of sap from Scots pine and Norway spruce at 65º–95ºC generated clear colour changes. It was concluded that compounds in the extractives were the main reason for these changes. In a study on refiner mechanical pulp of white spruce it was found that the colour was up to 75% explained by orthoquinonoid structures in the lignin. Johansson et al. (2002) investigated thermomechanical pulp of spruce, and the discoloration that was observed was suggested to be a result of oxidation of lignin and formation of metal ion complexes.

No literature was found that thoroughly described the chemical reasons for the colour changes in solid wood during heating and drying. However, from the references cited above it can be concluded that these changes cannot solely be explained by a wood component. These colour changes seem to originate from complex changes and degradation of hemicelluloses, lignin and certain extractive compounds.

3. Heat-treated wood—a "new" material

Wood that has been heat treated in the temperature interval 150º–250ºC displays notably changed properties and can therefore in some sense be considered a "new" material. This subchapter describes the general background and the main changes of heat-treated wood. More information can be found in the technical report Värmebehandling av trä (in Swedish), which is appended to this thesis.

3.1 Historical perspective

Since ancient times, the method of heat-treating wooden poles over open fire has been used to enhance its durability in ground contact, and in African countries the tips of wooden spears were hardened by alternately pounding and heating the wood (Rowell et al. 2002).

In the period from 1930 to 1950, mainly in the USA, research and development of heat-treated wood focused on hygroscopicity. Enhancement of swelling and shrinkage were observed (Stamm and Hansen 1937; Thunell and Elken 1948) and a patent was registered as the "Staybwood" process (Stamm et al. 1946). The heat-treated wood of these investigations was never commercialized, probably due to unsatisfactory mechanical properties (Stamm 1956; Stamm 1964).

A lot of work was done, mainly in Germany, during 1950 to 1970 to deepen knowledge about heat treatment of wood and the effects on its properties. Fungal resistance was studied (Buro 1954), the sorption characteristics were investigated (Kollman and Schneider 1963; Schneider and Rusche 1973), wood degradation was studied (Sanderman and Augustin 1963b; Sanderman and Augustin 1963a; Kollman and Fengel 1965; Fengel 1966) and mechanical properties were tested (Schneider 1971; Rusche 1973; Schneider 1973). Furthermore, investigations of heat treatment of wood under high pressure in sealed autoclave systems were also done (Noack 1969; Burmester 1973; Burmester 1975; Burmester and Wille 1976; Giebeler 1983) and a patent was registered for the FWD method "Feuchte Wärme Druck" (Giebeler et al. 1983).

Since the late 1980s interest in finding environmentally friendly wood materials has grown, and heat treatment of wood has been suggested as a possible method to enhance biological resistance without adding harmful additives to the wood. A lot of effort has been made to achieve a good biological resistance. In that context the EU programme "Up-grading of non-durable wood species by appropriate pyrolysis treatment" (Brite-Euram III-programme, BRE-CT- 5006.30.3. 1998) was initiated with a number of different countries participating.

In France, two types of processes were developed, both based on heating in nitrogen gas. Many investigations have been done on the processes called "Torrefaction" and "Retification" (Bourgois and Guyonnet 1988; Bourgois et al. 1991; Dirol and Guyonnet 1993; Troya and Navarrete 1994; Neya et al. 1995; Kamden et al. 1999) and patents have been registered (Guyonnet 1999; Guillin 2000). In Finland, the "Thermowood" process was developed using superheated steam (Viitanen et al. 1994; Viitaniemi and Jämsä 1996; Jämsä et al. 1999) For this process many patents have been registered (Ranta-

Maunus et al. 1995; Viitaniemi et al. 1996; Viitaniemi et al. 2001). Moreover, there has also been a Finnish project called "Wood Wisdom" in which recent contributions to knowledge about the heat treatment of wood were reported (Viitaniemi 2001; Hietala et al. 2002; Sivonen et al. 2002). In the Netherlands, a process called "Plato Wood" has been developed (van Zuylen 1995; Boonstra et al. 1998; Tjeerdsma et al. 1998a) and patented (Rem et al. 1994; Ruyter and Arnoldy 1994). This is a heating process in several steps. In Germany a process has been developed in which the heating of wood takes place in vegetable oils (Sailer et al. 2000; Rapp and Sailer 2001). For these processes developed in various countries, production capacity is many thousands to many tens of thousands of cubic meters per year, but little is known about the global total sales of heat-treated wood.

3.2 Properties of heat-treated wood

Swelling, shrinkage and hygroscopicity

The characteristics of the heat-treated wood from different types of processes vary little in general. Heat treatment of wood produces a material that is less hygroscopic than gently dried wood (Stamm and Hansen 1937; Tjeerdsma et al. 1998a; Obataya et al. 2000). This can be noted as a reduced swelling and shrinkage, up to 50% for treatments at higher temperatures (> 200ºC) and longer times. In that context the sorption and desorption characteristics are also changed. The water uptake in heat-treated wood is slower, and the water release is faster than kiln dried wood (Thunell and Elken 1948; Kollman and Schneider 1963; Schneider 1973; Schneider and Rusche 1973). It is furthermore clear that the equilibrium moisture content (EMC) is reduced by up to 40% compared with untreated wood (Viitanen et al. 1994; Viitaniemi and Jämsä 1996). However, an increase in hygroscopicity has been observed when heat-treated wood was remoistened by water or saturated steam (Stamm and Hansen 1937; Obataya et al. 2000). It is obvious that hydrophilic substances can be formed by remoistening in the cellular structure, but no detailed knowledge about the phenomenon was found in a search of the literature.

Resistance against microbiological attack

Better outdoor durability than untreated wood is known for heat-treated wood. Rot and mould resistance are clearly improved, and a variety of test methods have been used on many species (Buro 1954; Dirol and Guyonnet 1993; Viitanen et al. 1994; Tjeerdsma et al. 1998a; Kamden et al. 1999). Higher treatment temperature and longer times generally result in better rot and mould resistance. This resistance can be related to degradation of the wood material. For instance, a weight loss of at least 3% is recommended for a noticeable effect in a process using superheated steam (Viitaniemi et al. 1997). Many different reasons have been suggested for the enhanced rot and mould resistance, and it is reasonable to believe that it is a combination of many of them. Toxic substances, possibly active against rot and mould, have been found in heat-treated wood (Kamden et al. 2000). Organic acids, especially acetic acid, which is also produced, may cause conditions within the wood to be too acidic for colonization. The consequence of the decrease in hygroscopicity mentioned above is that the heat-treated will have a wood with lower water content than untreated wood exposed to the same environment, and access to water is crucial for many types of rot and mould. When wood is heat treated, a substantial mass

loss is often observed. The substances that are converted (mainly polysaccharides) or leached out (extractives) would otherwise serve as nutrients for rots and moulds (Buro 1954).

Brownish colour

Heat-treated wood is often appreciated for its light brown to dark brown appearance (Noack 1969; Viitanen et al. 1994). Heat-treated wood has therefore been suggested as substitute for some tropical hardwoods. Both treatment time and temperature can be varied to produce a specific brownish colour. Prolonged treatment and/or raised temperature usually give the wood a darker colour. Furthermore, darker heat-treated wood is generally more converted than lighter heat-treated wood, and the colour has therefore been suggested to be an indicator of the degree of conversion (Bourgois et al. 1991) and to be related to losses in mechanical properties (Bekhta and Niemz 2003). However, the brownish colour attained is not stable against light exposure (Jämsä et al. 2000; Ayadi et al. 2003; Mitsui et al. 2003). The coloured substances in the wood are eventually degraded and washed out if the wood is exposed outdoors, leaving a bleached and greyish appearance. No cost-effective and easy method to prevent this fading has been described.

Loss in mechanical properties

A major drawback of heat-treated wood is the loss in mechanical properties. Heat-treated wood has been found to be brittle compared to gently dried wood, especially for treatments over 200ºC. This loss generally increases with increased treatment temperature and time. The impact bending strength, modulus of rupture (MOR) or maximum bending strength and modulus of elasticity (MOE) or similarly flexural modulus can be reduced by up to 50% (Stamm et al. 1946; Schneider 1971; Rusche 1973; Viitaniemi 1997; Kamden et al. 1999; Sailer et al. 2000; Santos 2000; Bekhta and Niemz 2003). Hardness and abrasion resistance are also affected and strong ; reductions have been reported (Stamm et al. 1946; Sanderman and Augustin 1963b; Chang and Keith 1978; Kamden et al. 1999).

Smell of heat-treated wood

During heat treatment a lot of degradation products are produced, and some of them may have an unpleasant smell. Many organic acids and aldehydes such as furfurals are well known to have strong smell, and they can be found as degradation products (Manninen et al. 2002; McDonald et al. 2002). The unpleasant smell of the heat-treated wood is reported to decline noticeably within a few weeks after processing (Syrjänen et al. 2000).

Cellular structure and cracks

Another disadvantage of heat-treated wood is the problems with cracks, both internal and at the surface, and loosening of knots, which varies with species, processing method used, etc. (Schneider 1973; Viitanen et al. 1994; Viitaniemi and Jämsä 1996). Treatment conditions can be of importance to minimize such defects. Carbonization is a method of producing a carbon-based porous material from wood using pyrolysis in an inert atmosphere. If the carbonization is performed with a low rate of heating (5ºC/hour), a wood material with no microcracks and with intact cellular structure and anatomical features can be produced (Byrne and Nagle 1997). From a study of thermally modified

wood was no clear change in the cell dimensions observed when compared to untreated wood (Hietala et al. 2002). So, more knowledge of changes that take place in the microstructure of wood during heat treatment is of interest for developing a material with fewer cracks and defects.

Gluing and painting
Heat-treated wood has been tested for gluing and painting and has generally been approved (Stamm et al. 1946; Chang and Keith 1978; Boonstra et al. 1998). The heat-treated wood surface is more water repellent than untreated wood, and water borne paints and glues can function less well due to a slower penetration into the wood (Viitaniemi and Jämsä 1996). On the other hand, the improved dimensional stability of heat-treated wood can result in better performance of coatings exposed to the elements of outdoor climate (Jämsä et al. 1998).

4. Material and methods

4.1 Wood samples

In this work, Birch (Betula pubescens Ehrh.), Norway spruce (Picea abies L. Karst.) and Scots pine (Pinus sylvestris L.) were investigated (Table 2). Birch is a common species for decorative and furniture applications in Scandinavian countries. Spruce and pine are used in large quantities, especially for construction purposes. The different papers deal with birch wood (Papers I–VI), spruce wood (Papers I–III) and pine wood (Papers I–IV). In Papers I to IV special studies of sapwood and heartwood are presented.

Wood specimens of various types have been used (Table 2). Solid boards for colour measurements (Paper III), small pieces for colour, strength, hardness and mass loss investigations (Papers I, II, IV and VI) and sawdust for cellulose molecular size measurements (Paper V).

The wood material used in all experiments consisted of never-dried-and-frozen wood specimens. This approach was chosen in order to minimize or eliminate differences and uncertainties regarding predrying, storage, ageing, etc.

Table 2: *Summary of material and methods of the thesis.*

Paper	Species	Specimens	Experiments	Equipment	Measurements
I	B, S, P	Small samples (100x60x13) mm^3	UV/Vis.- light exposure, heat treated wood	Metal halide irraditator lamp and glass filter	Colour
II	B, S, P	Small samples (100x60x13) mm^3	Heat treatment, 65-95ºC, high humidity	Glass jars, sealed	Colour
III	B, S, P	Solid boards (800x100x50) and (800x100x38) mm^3	Hot humid air circulation, 40-111ºC	Laboratory kiln drier	Colour
IV	B, P	Small samples (100x60x13) mm^3	Extraction and heating, 95ºC, high humidity	Glass jars, sealed and Soxhlet extractor	Colour
V	B	Sawdust approximate size; (0.5x0.5x 2) mm^3	Heat treatment, aqueuos buffered solution, 180ºC	Teflon vessel, sealed.	Cellulose molecular size
VI	B	Small samples (110x31x4) and (97x27x6) mm	Heat treatment in water, 160-200ºC	Teflon vessel, sealed	Acetic and formic, acid, colour, strength, hardness and mass loss

B: birch/ S: spruce/ P: pine

4.2 Drying and treatment of wood specimens

Two different procedures for heat treatment of wood were performed—in an autoclave (Papers II, V and VI) and in a laboratory kiln dryer (Paper III) (Table 2). The autoclave experiments were performed at 65°–95ºC in sealed glass jars (1000 ml) with approximately 20 ml water added, or at 160°–200ºC in a sealed 120-ml air-free Teflon vessel completely filled with aqueous solution or deionised water. The laboratory kiln uses circulating hot, humid air. The capacity for batches is approximately 0.2 m^3 of lumber.

Colour stability was investigated by UV/visible light exposure of wood samples (Paper I) using a metal halide irradiator (Philips HPA 400) mounted in an electric fitting. A glass filter was used to cut off high-energetic UV light, excluding light with wavelengths shorter than approximately 350 nm. This accelerated light exposure was intended to resemble sunlight that falls on wooden surfaces indoors.

4.3 Chemical analysis

The measurements of the average molecular size of cellulose samples (Paper V) was done by viscosimetric studies of dissolved cellulose samples (SCAN-CM15:99) originating from wood sawdust samples. Preparation of the wood sawdust to enrich the cellulose was done in several steps with repeated procedures of filtration and washing. Extraction of wood samples (Papers IV and V) was done in a Soxhlet extractor with acetone (p. a. quality) as solvent. Removal of lignin (*delignification*) was done by adding portions of sodium chlorite and portions of acetic acid solutions to wood sawdust in an aqueous solution at 70ºC (Paper V). Removal of amorphous polysaccharides, mostly hemicelluloses, leaving predominantly α-cellulose, was done by soaking delignified wood sawdust samples in a 2.5M sodium hydroxide solution in an inert surrounding atmosphere for 16 hours (Paper V).

A Chrompack 9002 gas chromatograph with FID detector was used for organic acid measurements of heat-treated wood (Paper VI) (Table 2). The aqueous samples were first titrated with a tertiary ammonium hydroxide solution and dewatered with a rotary evaporator. Then the samples were dissolved in acetone. Benzyl bromide was added as reagent forming benzyl esters of the organic acids (Bethge and Lindström 1974).

4.4 Physical analysis

Colour measurements (Papers I–IV and VI) were made with a portable tristimulus colorimeter (Minolta CR 310). The colour was characterised by using colour coordinates L^*, a^*, b^*, $C_{ab}{}^*$, h and colour difference ΔE^*_{ab} in standard colour space CIE, Commission Internationale de l'Eclairage (Hunt 1991).

Bending strength and hardness tests were performed on a Hounsfield H25KS UTM (Paper VI). The results of the hardness measurements were mathematically transformed to give Brinell hardness values (EN1534:2000).

Impact bending strength tests (Paper VI) were performed using a Charpy impact tester (VEB Werkstoffprüfmaschinen) (SS161351)

Mass loss due to treatment was measured (Paper VI) by comparing the initial dry weight to the final dry weight. Dry weight estimations were based on the weight of small reference subsamples taken from the samples before and after drying at 105ºC for 16 hours.

4.5 Statistics

Both classical and multivariate statistics were applied in the design of the investigation and in analysis of the results in this thesis. Full factorial designs were applied for experiments (Papers II, V, and VI). Results were evaluated using principal component analysis (PCA) (Paper II), and modelling of colour responses (Paper III) was done using partial least squares (PLS). All statistical calculations were based on 95% confidence level and the assumption of normal distribution of observations, which thus allows application of t-distribution in calculations of confidence intervals (Paper II).

4.6 Laboratory experiments in relation to industrial applications

The experimental setup for heat treatments in this thesis is mainly on a laboratory scale, and the findings can only show the principles at work and the implications and possibilities for industrial application and use. In terms of both the scale of the process and the dimensions of the wood material, large differences from industrial practise are obvious. The industrial process often has a capacity of many cubic meters for solid boards, and it is performed in an air-free atmosphere of superheated steam or nitrogen gas. The heat treatments described in Papers I, II and IV-VI were performed on small specimens on a laboratory scale in sealed vessels. The heat treatment of solid boards (Paper III) was carried out in a laboratory kiln drier. An important aspect of sealed systems is that they retain water/steam and volatile compounds from the wood samples and provide static conditions during treatment, which is an advantage for comparative studies. In practical terms, the experiments are simplified and fewer parameters have to be accounted for when analysing the results.

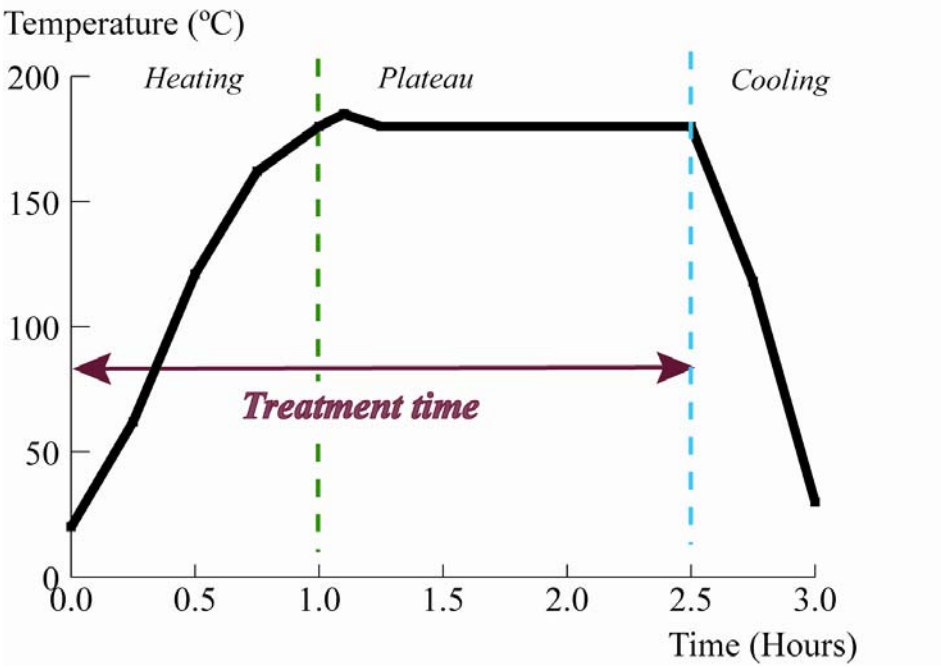

Figure 9: *Tentative temperature profile inside a closed Teflon vessel for a hydrothermal treatment run (Papers V and VI). The curve is constructed from measurements with water heated to 100ºC and measurements with mineral oil heated to 180ºC.*

It is known that heat treatment in water produces different effects than heat treatments in steam on various properties such as sorption, degradation and colour (Noack 1969; Burmester 1973; Schmidt 1986). Deionised water was used for the heat treatments in Papers V and VI, and hot humid air was used in Papers I and II. In industrial processes, superheated steam is often used.

A small comparative study was done to investigate factors such as specimen size, process scale and moisture degree during treatment (Tables 3 and 4). Three methods are presented:

1) Superheated steaming in a pilot plant facility with a capacity of 0.2 m^3 using electric heating and steam generators (superheated steam) to heat-treat wood dimensions of 2000 x 100 x 50 mm.
2) Steaming in an oven, four specimens of the dimensions 100 x 10 x 10 mm were treated in an open Teflon vessel (vent 1.5mm ID) with 5 ml deionised water.
3) Soaking and pressure in an oven, two specimens 110 x 34 x 4 mm and 97 x 27 x 6mm soaked in deionised water and treated in a sealed 120-ml Teflon vessel. The latter method was used in Papers V and VI. All methods used birch wood and a treatment plateau temperature of 200ºC.

The properties measured were colour (CIELCh colour space), material (weight loss) after heat treatment (Table 4), content of water-soluble and total organic acidic content in water extract from leaching (Table 3).

Table 3: *Results from a water extraction of three different heat treatment methods of wood. (3 g wood in 100 ml water). The values presented are based on double tests.*

Heat treatment conditions	**Time** *hours*	**Acids** μ*mol/g*	**pH**
Pilot plant, vented	1.0	6.5	4.5
Superheated steam	4.0	3.8	4.5
Lab. vessel, sealed	2.5	11.6	3.9
Soaking & pressure	4.0	13.0	4.0
Lab. vessel, vented	2.0	3.5	4.6
Steaming	4.0	4.3	4.5

Table 4: *Colour (L^*, C_{ab}^* and h coordinates) and Weight loss results of wood from three different heat treatments. The values presented are based on double tests.*

Heat treatment conditions	**Time** *hours*	**Weight loss** *%*	**Lightness** *L**	**Chroma** C_{ab}*	**Hue** *h*
Pilot plant, vented	1.0	4.2	44	21	60
Superheated steam	4.0	4.3	41	20	59
Lab. vessel, sealed	2.5	5.1	45	20	62
Soaking & pressure	4.0	8.6	37	16	61
Lab. vessel, vented	2.0	2.2	60	23	66
Steaming	4.0	4.5	52	24	64

There is an indication of greater weight loss due to water leaching after heat treatment for wet conditions (soaking) than for drier conditions, with open steaming and superheated steaming falling in between. However, there is an underlying uncertainty with double tests in the results for each method in relation to the different values between the methods, so conclusions cannot be made with certainty.

When it comes to acidic content, it is clear that the soaking method gives a more acidic wood-material than the two other methods. It is possible that a higher degree of hydrolytic conditions (more steam/water) forms more acids and causes more weight loss as a result of wood degradation. However, in the superheated and open process there is an obvious possibility that volatile acids are escaping to the gas phase. It is difficult to say anything definitive about the development of acidity or the escape of volatile acids from the wood in a technical process without proper experiments.

Lightness (L^*) shows the highest numbers for open steaming compared to superheated steaming and soaking conditions. Soaking tends to result in lower values than superheated steaming, at least for 4 hours of treatment. A similar pattern is shown for Chroma (C_{ab}^*), and it is assumed that these two colour coordinates can serves as an

indicator of the degree of wood degradation. Hue (h) shows a somewhat different pattern. Open steaming condition produce a yellower wood with a higher hue than soaking and superheated steaming conditions, which both tend to converge around a value of 60.

On the basis of these results it seems that findings from the laboratory tests can serve as a basis for new ideas to improve industrial production of heat-treated wood. However, new settings for parameters such as temperature and time have to be investigated, since conditions differ greatly. It must, for example, be pointed out that the time/temperature profiles for the pilot-plant treatment and the Teflon vessel treatment are very different (Figure 9). It seems that the degree of interaction of water is an important factor that needs further attention.

5. Results and discussion

5.1 Colour characteristics in the interval 40ºC–111ºC

The results from the studies at lower temperatures, 40º–111ºC, mainly concern the colour response to heating/drying (Papers II and III), colour changes due to artificial UV/visible light exposure of heat-treated wood (Paper I) and the colour response of acetone-extracted wood (Paper IV). These investigations were summarized earlier in a licentiate thesis (Sundqvist 2000).

This temperature interval produces negligible effects on strength properties (Stamm 1956). However, a change in extractive content is expected. Volatile extractive compounds such as low molecular organic acids and terpenes are emitted from wood in this temperature interval (Englund and Nussbaum 2000; Jung and Roffael 2002; Manninen et al. 2002). It is reasonable to believe that some hydrolysis of hemicelluloses and pectin also occur (Fengel 1966; Hinterstoisser et al. 1992).

Colour modification at lower temperatures
The colour responses of birch, Scots pine and Norway spruce to hydrothermal treatment in closed jars at 65º–95ºC for 1–6 days were studied (Paper II). The results show that considerable colour changes can be achieved at temperatures below 100ºC when the wood is in moist conditions and long treatment periods are applied. The colour changes produced by heat treatment occur throughout the depth of the wood material, not just on the surface. Light brown to dark brown colours were generated throughout the range of wood samples. However, it was evident that temperatures above approximately 80ºC were required in order to produce a noticeable colour change, at least for process times shorter than weeks. Similar findings came from a recent study where temperatures above 80ºC were found to be the approximate threshold for accelerating the colour changes for heat treatment of sap from pine and spruce (Sehlstedt-Persson 2003). It has earlier been found that discolouration of oak during drying was found to be most influenced by the degree of moisture in the wood (Schmidt 1986). The colour of wood is dependent on both time and temperature, and a slower colour formation produced at a lower temperature can be balanced by prolonging the treatment time. Hydrothermal treatment was performed in two different systems—one where the wood was immersed in water and the other where

the wood was placed in a moist atmosphere. A comparison of these treatments shows that a similar degree of darkening can be obtained with different conditions. Figure 10 shows that samples treated at 95ºC, 160ºC and 200ºC for different treatment times attain similar values of lightness.

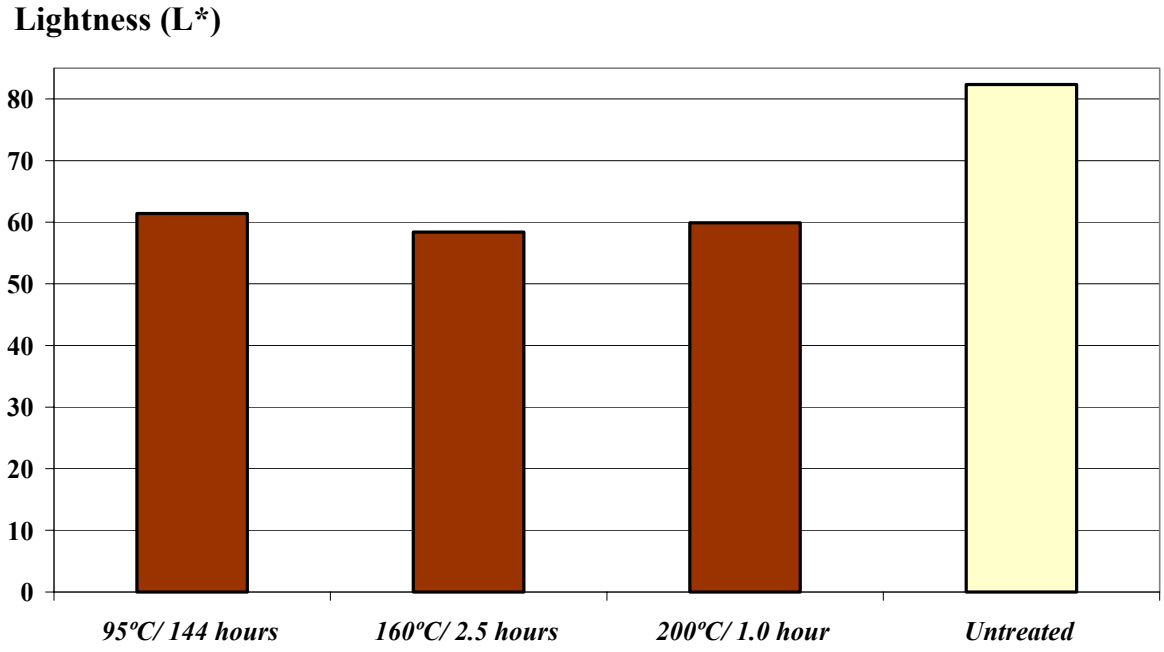

Figure 10: *Comparison of lightness (L^*) of hydrothermally treated birch at different temperatures and times. Treatments were conducted in closed vessels with steam atmosphere (95ºC/144 hours) and water soaking (160ºC/2.5 hours and 200ºC/1.0 hour). The average values for the bars are for 95ºC/144 hours (Paper II), 160ºC/2.5 hours and 200ºC/1.0 hour (Paper VI). Colour measurements of wood samples at moisture content 4%–6% and 3mm planed surfaces (Paper II) or sanded surfaces (Paper VI). Reference samples (untreated birch) were dried at 35ºC for 2 days (Papers II and VI).*

Normal drying of wood can be divided in two principally different phases—above and below the fibre saturation point. The process above fibre saturation with free water present (capillary phase) is mainly driven by the heat transfer into the wood in combination with the influence of capillary forces, and the process below the fibre saturation point (diffusion phase) is limited by the diffusion rate of steam. In between these phase is the transition phase. By modern drying strategies based on the ideas of these phases was the process time shortened considerably, mainly by an increase of heat transfer into the wood during the capillary phase (Morén 2000).

In Paper III, laboratory kiln drying experiments both above and below the fibre saturation point were reported. Colour change was evaluated by multivariate statistics, and factors of importance were evaluated. It was found that the two phases were of similar importance. The mechanisms of colour formation are complex, but it is assumed that oxidative changes predominate, rather than hydrolysis, in the diffusion phase. Oxidation of polysaccharides and lignin may produce phenolic compounds that can induce colour

change (Fengel and Wegener 1989; Lai 1991). Both hydrolytic and oxidative mechanisms have been suggested as the basis for colour formation during steaming in walnut (Burtin et al. 1998). It should also be pointed out that laboratory kiln experiments produced smaller colour changes than experiments in closed vessels.

General colour responses

Birch changes more in colour due to heating than Scots pine and Norway spruce. That hardwoods change more than softwoods is known previously (Hon and Minemura 1991). The colour change (ΔE^*_{ab}) in birch was approximately twice the magnitude of colour change in pine and spruce under treatment at 80ºC and 95ºC for 6 days (Paper II). ΔE^*_{ab} for birch was 20.4 and for pine sapwood 11.7. The characteristic colour changes for birch were decreasing lightness (L^*) and decreasing hue (h), i.e., more reddish colour, with increasing treatment temperature and time (Papers II and III). The chroma (C^*_{ab}), i.e., colour saturation, changed only slightly, indicating possible local maxima with increasing treatment time at temperatures of 65ºC and 80ºC (Paper II).

The characteristics of the colour change for Norway spruce and Scots pine are generally decreasing lightness (L^*) and increasing Chroma (C_{ab}^*) with increasing treatment time and temperature (Papers II and III). Changes in the hue of these two species are small and irregular (Paper II). For instance, spruce sapwood and pine sapwood displayed red-yellow-red shifts, while pine heartwood displayed possible yellow-red-yellow shifts over time at 80ºC (Figure 11).

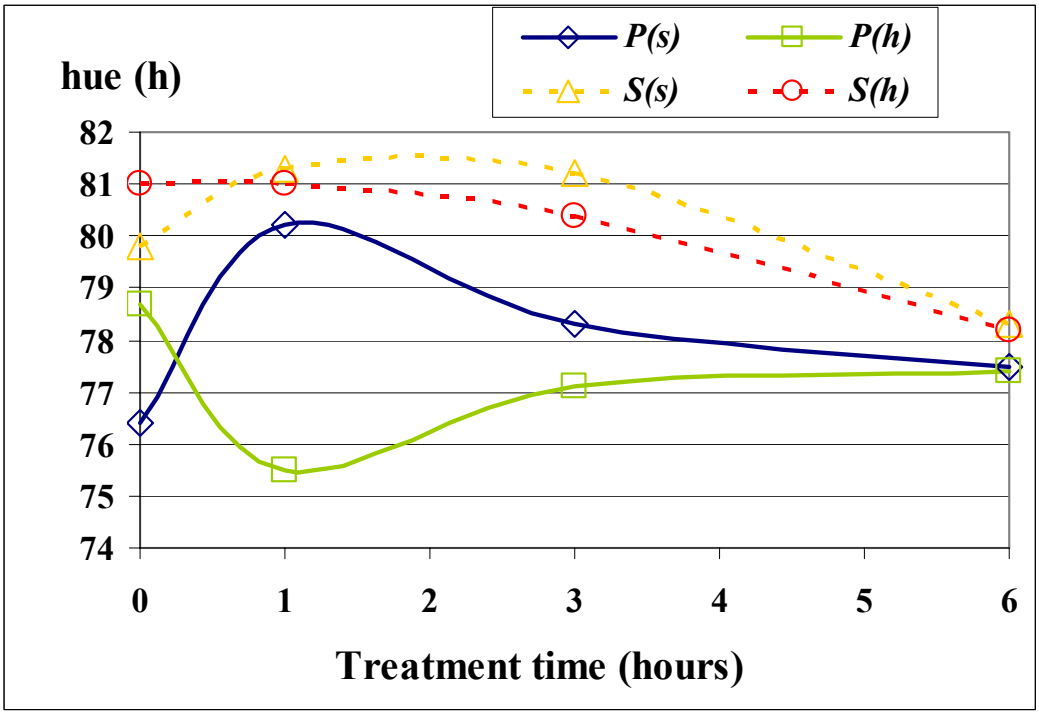

Figure 11: *Hue (h) of hydrothermally treated wood at 80ºC in closed vessel. P(s): Pine sapwood. P(h): Pine heartwood. S(s): Spruce sapwood. S(h): Spruce heartwood.*

The changes in hue indicate that a change of chromophores occurs. It is reasonable to suppose that some types of molecules with chromophoric functions diminish in content

and others increase, or that polymerisation takes place. There is a general rule that states: "the greater the number of conjugated multiple bonds a compound contains, the longer will be the wavelength at which the compounds absorbs light" (Solomons 1986). That means that substances that produce red colour may have more conjugated bonds than those that produce yellow colour.

Colour difference of sapwood and heartwood

In an attempt to distinguish between sapwood and heartwood colour responses to drying, measurements were done on either the side facing the bark (sapwood) or the side facing the pith (heartwood) (Figure 12). Measurements were further restricted by visual selection and the exclusion of measurements based on defects and mixtures of sap/heartwood (Paper III). The results show that consistent differences in colour for the different sides of the boards were found. These differences are assumed to be based on measurement of sapwood and heartwood.

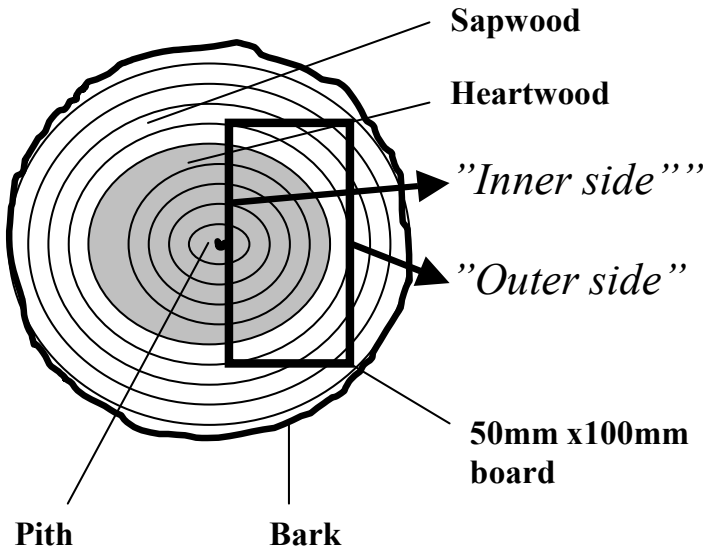

Figure 12: *Schematic view of position of a 50- x 100-mm board in cross-section taken from a small diameter log. Two sides of the board are defined, "outer side" and " inner side". (From Paper III)*

The results of the analysis in this thesis point to an actual difference in average colour for sapwood and heartwood (Table 5). However, the differences in these characteristics are small and seem to depend on the conditions under which the wood has been dried or heat-treated. In the natural wood there are differences in the extractive and lignin composition and content for sapwood and heartwood that are probably the main reason for different colours (Falkehag et al. 1966; Fengel and Wegener 1989). Furthermore, it is reasonable to suppose that factors such as the concentration of oxygen, moisture content and organic acid concentrations in the wood affect the colour of sapwood and heartwood differently during drying and heating.

Table 5: *Colour characteristics of sapwood and heartwood dried at 35ºC for 2 days. Colour coordinates L*, Cab* and h (CIE standard colour space) are presented. Values are taken from Paper II. Measured colour on 3-mm planed surfaces at moisture content 6%–8%.*

Species	Colour co-ordinates	Sapwood	Heartwood	Heartwood is significantly... ....than sapwood
Pine	L^*	84.2	84.1	-
	C_{ab}^*	21.3	22.8	more colour saturated
	h	76.7	80.3	more yellow
Spruce	L*	83.7	84.9	brighter
	C_{ab}*	19.1	18.9	-
	h	79.3	81.0	more yellow
Birch	L^*	82.7	-	-
	C_{ab}^*	18.5	-	-
	h	79.5	-	-

Pine heartwood gently dried at 35ºC for 2 days and planed 3 mm displayed a somewhat more yellowish and somewhat more saturated colour than sapwood did (Table 5). Spruce heartwood had a somewhat brighter and yellower colour than sapwood.

Hue seems to converge to the same yellow-red value at higher temperatures and longer treatment times (6 days) (Paper II) for sapwood and heartwood of both pine and spruce by heating in closed vessels under moist conditions at 80º– 5ºC (Figure 11). The colour change of sapwood and heartwood during heating/drying is not easy to characterize. The changes seem to depend on the conditions used in the treatment/drying process. Table 6 presents the colour responses of sapwood and heartwood for kiln drying or hydrothermal treatment (Papers III and II). No general conclusion can be drawn about the colour changes of sapwood and heartwood due to drying or hydrothermal treatment and their internal colour differences. These average colour differences are small, around 1–3 units, and are difficult to distinguish by the naked eye. A colour difference, ΔE^*_{ab}, of more than approximately 3 units is considered the lower limit for detection (Hon and Minemura 1991).

Colour variance of heat-treated wood

The colour variance of sapwood and heartwood in a batch of boards belonging to a species was estimated (Paper III). The standard deviation was around 1–2 units for the colour coordinates L^*, C_{ab}^* and h of Scots pine, Norway spruce and birch in three different batches treated with different drying schedules. For more moist conditions, such as the hydrothermal treatments in Paper II, the colours were less homogeneous. Standard deviations of around 2–4 units were found for pine heartwood and birch (not divided into sapwood and heartwood). There were also indications that the colour variance increased with longer treatment times and increased temperatures.

Table 6: *Colour characteristics of sapwood and heartwood after hydrothermal treatment or kiln drying. Colour coordinates L*, C_{ab}* and h (CIE standard colour space) are presented. MC is moisture content of the wood during drying. Values are taken from Papers II and III. Measured colour on 3-mm planed surfaces at moisture content 4%–6%.*

Species	Treatment	Colour co-ordinates	Sapwood	Heartwood	Heartwood is significantly... ....than sapwood
Pine	Hydrothermal:	L^*	81.0	78.8	darker
	80ºC 6days	C_{ab}^*	25.8	26.6	more colour saturated
		h	80.2	76.9	more red
Pine	Kiln drying:	L^*	79.9	81.5	brighter
	82ºC 51h (MC > 30%)	C_{ab}^*	25.5	26.9	more colour saturated
	103ºC 37h (MC < 30%)	h	79.5	81.3	more yellow
Spruce	Hydrothermal:	L*	79.4	79.1	-
	80ºC 6days	C_{ab}*	23.4	22.9	-
		h	78.3	78.2	-
Spruce	Kiln drying:	L^*	78.7	79.9	brighter
	82ºC 21h (MC > 30%)	C_{ab}^*	24.2	24.8	-
	111ºC 33h (MC < 30%)	h	79.7	81.0	more yellow
Birch	Kiln drying:	L^*	73.6	69.4	darker
	57ºC 40h (MC > 30%)	C_{ab}^*	19.3	19.9	-
	85ºC 54h (MC < 30%)	h	71.5	68.4	more red

Colour stability of heat-treated wood

The generally natural light yellow colour of wood is not stable against light exposure. For instance, it is well known that wood surfaces outdoors become bleached and may end up with a greyish appearance when exposed to sunlight. Heat treatment of wood gives a reddish brown colour that is often appreciated. However, this generated reddish brown colour is not stable when it is exposed to light. Heat-treated samples from the study in Paper II were used in a UV/Visible light exposure test in Paper I, where the colour change was investigated. The results show that the brownish colour fades considerably after 100 hours' exposure, and colour differences (ΔE^*_{ab}) of 4–8 units were measured. The colour of untreated wood fades also. The typical colour differences of 6–11 units are larger than those for heat-treated wood. The larger colour difference for untreated wood compared with heat-treated wood exposed to UV light has since been confirmed (Ayadi et al. 2003). The results in Paper I also show that untreated birch changes less in colour than pine and spruce.

A rapid colour change occurred during the first 20 hours of UV/Visible light exposure (Figures 13 and 14), especially for heat-treated samples of pine, spruce and birch (Paper I). For pine and birch, this change is characterised by an initial decrease in chroma (C_{ab}^*) (Figure 13) and hue (h) for the first 4 hours (i.e., a decline in saturation and a more reddish colour) and thereafter an increase in chroma and hue (i.e., increased saturation and a yellower colour). The chroma and hue of untreated and heat-treated samples seemed to converge to the same values after 100 hours of UV/Visible light exposure. The lightness (L^*) of the samples decreases considerably for the first 4 hours of exposure, and

thereafter the change is different for different samples (Figure 14). Heat-treated birch samples increase in lightness with exposure for more than 4 hours, while untreated birch, untreated pine and heat-treated pine samples continue to decrease in lightness. The lightness values after 100 hours are related to the treatment conditions and species of the samples (Paper I). Birch samples are darker before and after exposure than pine samples undergoing the same treatment. An increase in the treatment time and temperature of both species produces a decrease in lightness after exposure.

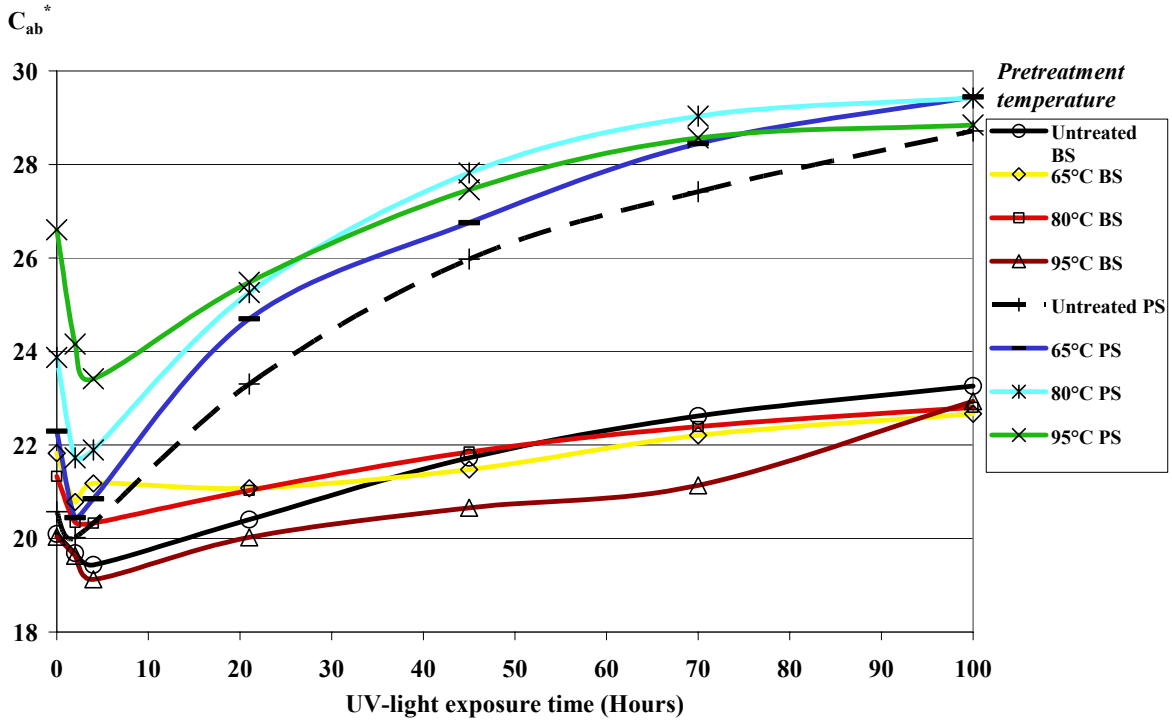

Figure 13: *Chroma (C_{ab}^*) of hydrothermally treated wood exposed to UV light. Pretreatment time was 3 days. Birch sapwood (BS) and Scots pine sapwood (PS). Untreated: drying at 35ºC for 2 days. Colour measurements were made on planed surfaces.*

Thus, after artificial light exposure for longer periods, the colour of untreated and heat-treated samples seem to become similarly yellowish. After approximately 100 hours of UV light exposure, the lightness of samples that had been pretreated at 95ºC seemed to level off at darker values than samples pretreated at 80ºC (Figure 14). Investigations in which UV-absorbing additives were applied to the surfaces of wood report a clear improvement in colour stability (Kai et al. 1985; Grelier et al. 1997). A search of the literature did not yield any research reporting the influence of UV-absorbing additives on heat-treated wood.

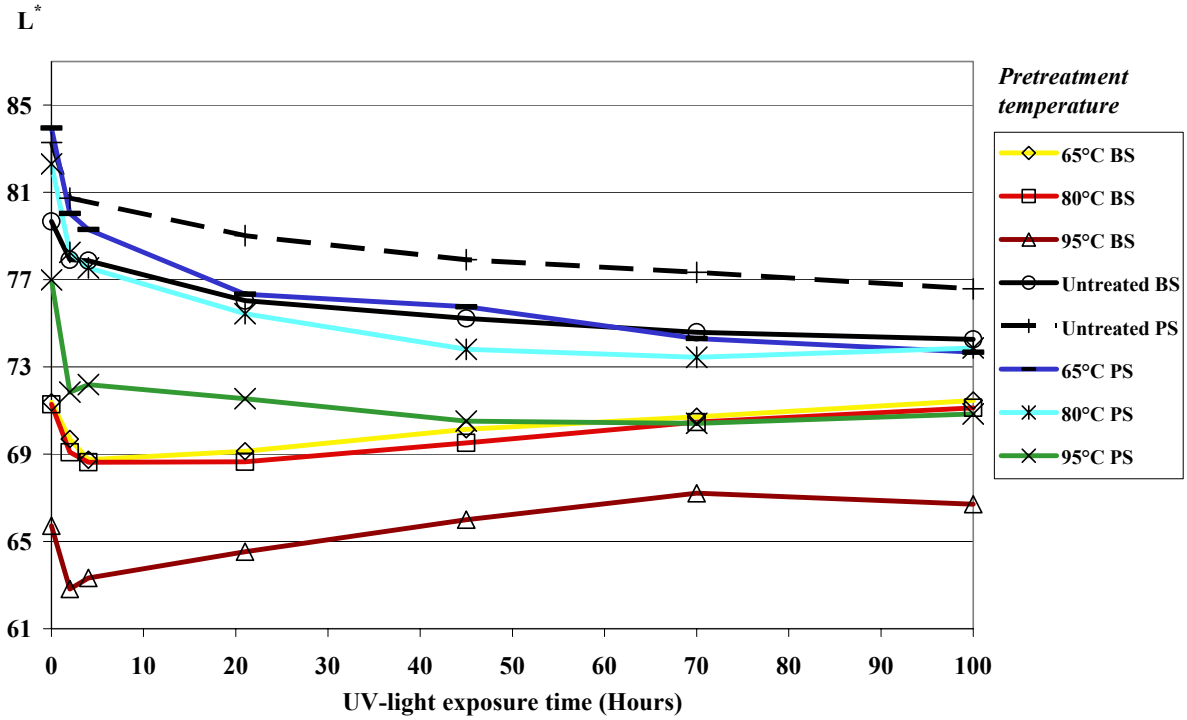

Figure 14: *Lightness (L^*) of hydrothermally treated wood exposed to UV light. Pretreatment time was 3 days. Birch sapwood (BS) and Scots pine sapwood (PS). Untreated: drying at 35ºC for 2 days. Colour measurements were made on planed surfaces.*

Colour and its relation to wood components

The origin of colour in natural wood has been reported to be related to chromophores among extractives (Burtin et al. 1998) as well as chromophoric groups in the lignin (Falkehag et al. 1966). When wood is heat treated, aldehydes and phenols are formed which may result in the formation of coloured compounds after chemical reactions (McDonald et al. 2000). A special problem in the drying of wood is "brown staining". This is a problem related to soluble compounds such as sugar and protein in the sap of wood migrating to the surface during drying. From the field of food process research, Maillard reactions are known to form many coloured compounds from, for example, sugars and sugars/proteins, as a result of heating. This has been presented in model experiments (Rizzi 1997). A small study was done in order to investigate the influence of natural extractives and structural components on the colour change of wood samples as a result of heating (Paper IV). Comparisons were made of the colour of heat-treated samples that had been acetone extracted and samples not extracted before heat treatment. The colour difference presented (ΔE_{ab}^*) was based on the difference between untreated and heat-treated samples (autoclave 3 days, 95ºC). The colour difference between untreated wood samples, not extracted and acetone extracted, was also measured. A clear effect of extraction colour formation was noted. It is concluded that both extractives and structural components (hemicelluloses and/or lignin) take part in the colouring process of wood that results from heating. From a recent investigation on heat treatment of sap and on water-extracted wood samples from pine and spruce (65º–95ºC for 1 to 5 days), it was concluded that mainly extractives were involved in the colouring process (Sehlstedt-Persson 2003). Results concerning the content of acetone-extracted phenolic components investigated by UV/VIS spectroscopy were presented in the Licentiate thesis (Sundqvist

2000). The results indicate that heat treatment altered the composition of phenolic compounds considerably. Heat-treated samples displayed an increase in phenolic compounds absorbing light at wavelengths from 340 to 380 nm.

Modelling of the batch colour of kiln-dried lumber
The average colour of a batch of lumber run in a laboratory kiln dryer was studied, and mathematical models of the colour change due to time and temperature were made (Paper III). The modelling was based on colour measurements on 3-mm planed surfaces, and the model was evaluated with a multivariate statistical method, PLS (Partial Least Squares). The species investigated were birch, Norway spruce and Scots pine. Strong models were obtained, except for Scots pine. The explained variance (R^2_y) was above 0.9 and predicted variance (Q^2) was above 0.8 for the birch and spruce colour models. The weaker model for pine, $R^2_y = 0.66$ and $Q^2 = 0.33$, was mainly explained by difficulty in modelling the colour coordinate hue (h). From the colour measurements it can be seen that the yellow-red hue of pine heartwood shows little variation, and no clear trend related to the drying process was observed.

The results show that it is possible for specific equipment to make a good model for colour formation. It has not been the purpose with this thesis to develop a more general model, as this involves many specific factors in process design. However, the results show that it is possible to govern the average batch colour by regulating the process parameters time and temperature.

5.2 Wood modification in the temperature range from 160ºC to 200ºC

Chapter 5.1 mainly described the change in colour investigated for temperatures below 100ºC. High-temperature drying in the interval of 100º–150ºC is not covered in this thesis. In this interval, minor changes in the lignin structure, some degradation of hemicelluloses and emission of volatile extractives, can be expected. If the treatment temperature is further raised to more than 150ºC, many properties besides the colour of the wood are affected. Swelling and shrinkage are considerably reduced, and fungal resistance is improved, but mechanical strength properties often decline. Heat-treated wood can in some sense be regarded as a “new” environmentally friendly material.

In the technical report “Värmebehandling av trä” (appendix), the historical background, the properties of heat-treated wood and production in different countries up to 2002 are reviewed. The report also contains data on fungal resistance, swelling and shrinkage and mechanical properties as well as background information for these changes occurring during heat treatment with special reference to the analysis of hemicelluloses and lignin. For more information, see also chapters 2.3–2.5 and 3.2.

The effect of heat treatment on cellulose
Studies of cellulose degradation in the heat treatment of wood have hitherto focused on cellulose crystallinity (Košíková et al. 1999; Bhuiyan et al. 2000; Sivonen et al. 2002) and mass loss of cellulose (Stamm 1956; Kollman and Fengel 1965).

These studies show that the cellulose structure is changed and that amorphous parts can be degraded close to and above 200ºC. However, it is difficult to analyse intact cellulose in wood, and if cellulose is isolated from the wood, the structure and configuration are affected by the method used. Cellulose is considered to have a major influence on wood strength, and one of its characteristics that explains this influence is its structure with long parallel and straight molecules packed together. In Paper V, the average molecular size of cellulose from birch heat treated at 180ºC was investigated by chlorite delignification of wood chips and viscosimetric measurements of solubilized cellulose. The results clearly showed that the average molecular size was reduced considerably by treatment for 3 and 6 hours at pH 4 compared with untreated birch (Figure 15). From a complementary study (Paper VI) it was found that the pH of the water phase surrounding the sample was 3 to 4 after heat treatment, which is close to the case of a pH 4 buffer solution. A sample of "Thermowood" of birch was also included in the investigation, and its average molecular size was approximately half that of untreated birch. Undoubtedly, heat treatment at 180ºC in acidic conditions has an impact on cellulose in wood.

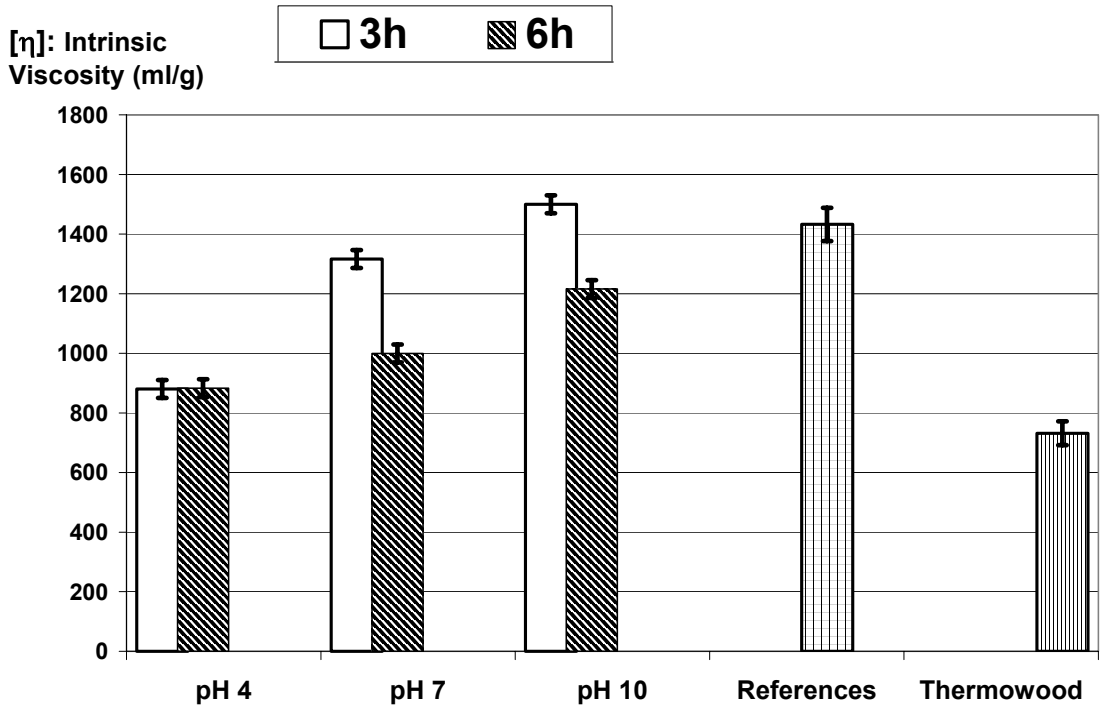

Figure 15: *Average intrinsic viscosity (η): (ml/g) of cellulose from hydrothermally treated birch sawdust. The treatments were done in buffering solutions, pH 4–pH 10 at 180ºC. Reference samples are untreated wood. The Thermowood sample is from commercially produced heat-treated birch wood. The bars show the 95% confidence intervals based on 2–5 measurements. (Paper V)*

Determination of formic acid and acetic acid content in heat-treated wood

It is known that organic acids are formed within wood during heating. Acetic acid was found to be emitted from heat-treated wood (Bourgois and Guyonnet 1988; Manninen et al. 2002). These investigations indicate that the formation and content of these compounds come from the wood itself. The deacetylation and formation of acetic acid by hydrothermal treatment of Eucalyptus wood has been investigated in laboratory experiments (Garrote et al. 2001). The acetic acid content was related to the O-acetyl

content in xylan with different treatments times, and it was found, for example, that 45% of the O-acetyl groups were released as acetic acid during treatment at 175ºC for 1 hour.

Paper VI reports results for formation of both formic and acetic acid during heat treatment of birch studied in a closed and air-free system. The samples were submerged in water, and the acids formed were trapped in the water phase during treatment. Estimations of the acetic acid and formic acid concentration related to birch wood were made by analysing the acid content of the water phase for different treatment conditions. The results show that increase in treatment temperature and time generally increases the concentrations of formic acid and acetic acid (Figure 16). 1.1% (by weight) of formic acid and 7.2% (by weight) of acetic acid in dry wood was found after 4 hours' treatment at 180ºC. The mechanism of O-acetyl groups released from hemicelluloses in wood producing acetic acid is well known. Using the values found in Paper VI for theoretical calculations, the indication is that most of the O-acetyl groups could be released from the xylan. However, the mechanism of forming formic acid from wood is not clear, and the results in Paper VI suggest that formic acid is formed in the same proportion and at the same rate as acetic acid. These facts suggest that the acids are formed by a similar mechanism (Figure 16). Thus it is possible that O-methyl groups also exist in wood hemicelluloses and are released from the wood.

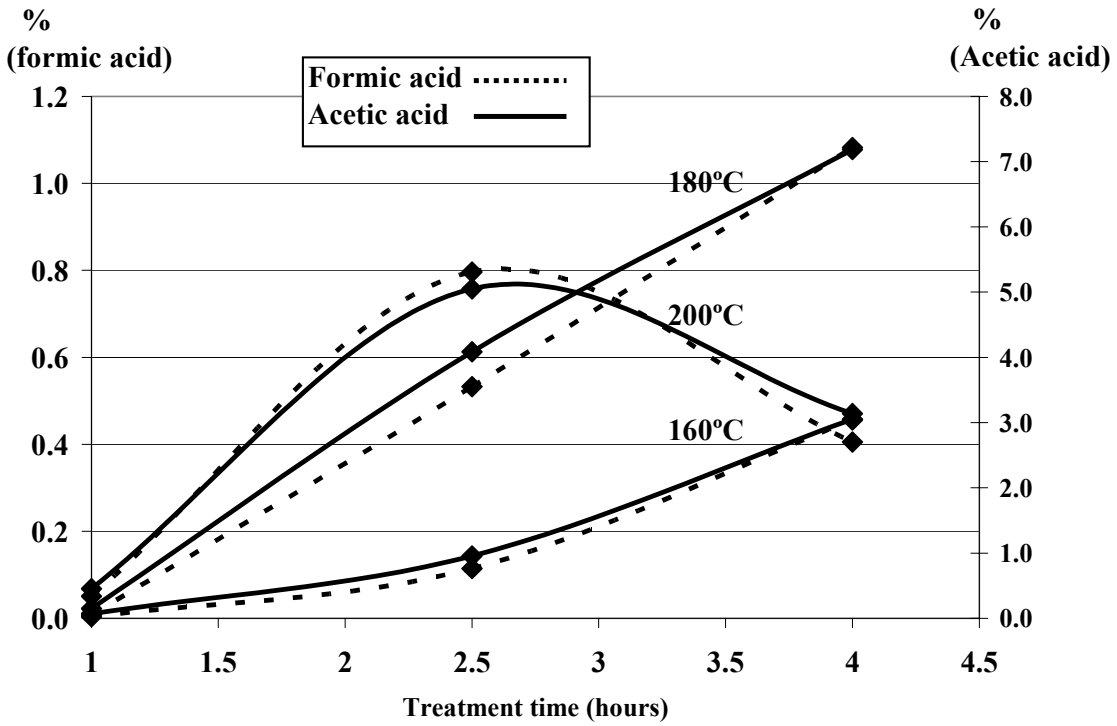

Figure 16: *Hydrothermal treatment of birch wood. Formation of formic and acetic acid (weight acids/weight dry wood). Pooled standard deviations from repetitions for 4.0 hours at 180ºC and for 2.5 hours at 200ºC were calculated to 0.34% (formic acid), 0.50% (acetic acid) (Paper VI).*

Acidity in wood and its relation to cellulose degradation

The degradation of polysaccharides during heating is promoted by humid conditions and accelerated by the influence of acids. Hydrolysis of hemicelluloses has been elucidated in many investigations, but for the hydrolysis of cellulose in wood, little is known, and most investigations have been done with cellulose isolated from wood material before

hydrolysis. Experiments where cellulose of heat-treated birch wood samples has been isolated and analysed are described in Paper V. The influence of acidity during heat treatment at 180ºC was studied by using different pH buffer solutions surrounding the wood samples. The results clearly showed that neutral (pH 7) and alkaline (pH 10) conditions reduce the degree of cellulose degradation in birch (Figure 15). For heat treatment at pH 10 for 3 hours, the effect on cellulose was negligible. The conclusion drawn is that neutral to alkaline conditions within the wood should be maintained in order to minimize cellulose degradation, i.e., decrease of the average molecular size.

Cellulose in wood contributes considerably to its mechanical properties. In a complementary study (Paper VI), large losses in hardness and strength were observed (> 50%) with the same equipment and under similar treatment conditions. For treatments at 180ºC for 1 to 2.5 hours, strength and hardness clearly decrease. These losses in mechanical properties can be linked to the mass loss and increase in formic and acetic acid concentrations found (Paper VI) (Figure 16). It is obvious that it is of great importance to control the formic acid and acetic acid formed in wood during heat treatment, and this can provide an opportunity to avoid or reduce losses in hardness and strength.

The colour response (CIELCh colour system) related to acid concentrations was also studied (Paper VI). Lightness (L^*) decreased with increasing acid concentrations, while Chroma (C_{ab}^*) and hue (h) behaved irregularly with elapsed treatment time for different temperatures.

5.3 Concluding discussion

Heat treatment in humid conditions can be performed over a wide temperature interval when the aim is modification of colour, for example to produce a reddish brown appearance. A low temperature can be compensated for by longer duration in order to achieve the same colouring effect produced at higher temperatures. For instance, hydrothermal treatment for 6 days at 95ºC (Paper II) produces similar light brown colours for birch as 2.5 hours at 160ºC (Paper V) (Figure 10). However, it is reasonable to expect that negative effects on wood strength as a consequence of treatment at higher temperatures (180°–200ºC) can be avoided (Papers V and VI). When considering the longer durations needed for treatment at lower temperatures (Paper II) to resemble treatments at higher temperatures, the economy and energy efficiency of the process will most likely suffer (Table 7). Thus an optimization of the quality of the wood material and productions costs will be important future considerations.

Table 7: *General properties of heat-treated wood based on the findings in the thesis, along with comments.*

Temperatures	Colour change	Loss in mech. properties	Damage in wood structure	Acidic formation	Chain shortening of Cellulose molecules	Increased costs compared to kiln drying
Low:						
95ºC	++	0	0	0	0	+
High:						
160ºC	++	+	+	+	+	
180ºC	+++	++	+	++	++	++
200ºC	+++	+++	++	+++	+++	
0: Negligable +: Small ++: Moderate +++: Strong						

Heat treatment above 200ºC generally produces a wood material with considerable strength, hardness and mass loss (Sanderman and Augustin 1963b; Chang and Keith 1978). Such harsh treatment is often required when fungal resistance for outdoor applications without ground contact is desired. Heat treatments below 200ºC demonstrate the possibility of producing wood material with considerably smaller strength and hardness losses, but with much smaller improvement in fungal resistance than for treatment temperatures exceeding 200ºC (Viitaniemi and Jämsä 1996).

Interestingly, there seems to be some sort of threshold for process time and temperature after which the losses in strength, hardness and mass increase greatly. In this work it has been demonstrated that treatment of birch around 160º–180ºC for approximately 1–2 hours (paper VI) can be tolerated before any severe loss of properties occurs.

Moreover, it also seems possible to enhance strength and hardness slightly in comparison to natural wood within a certain domain of time/temperature of treatment (Kubojima et al. 2000). Small improvements in properties have also been found in this thesis for birch treated in a sealed vessel around 180º–200ºC and for approximately 0–1 hour (Paper VI) (Figure 17).

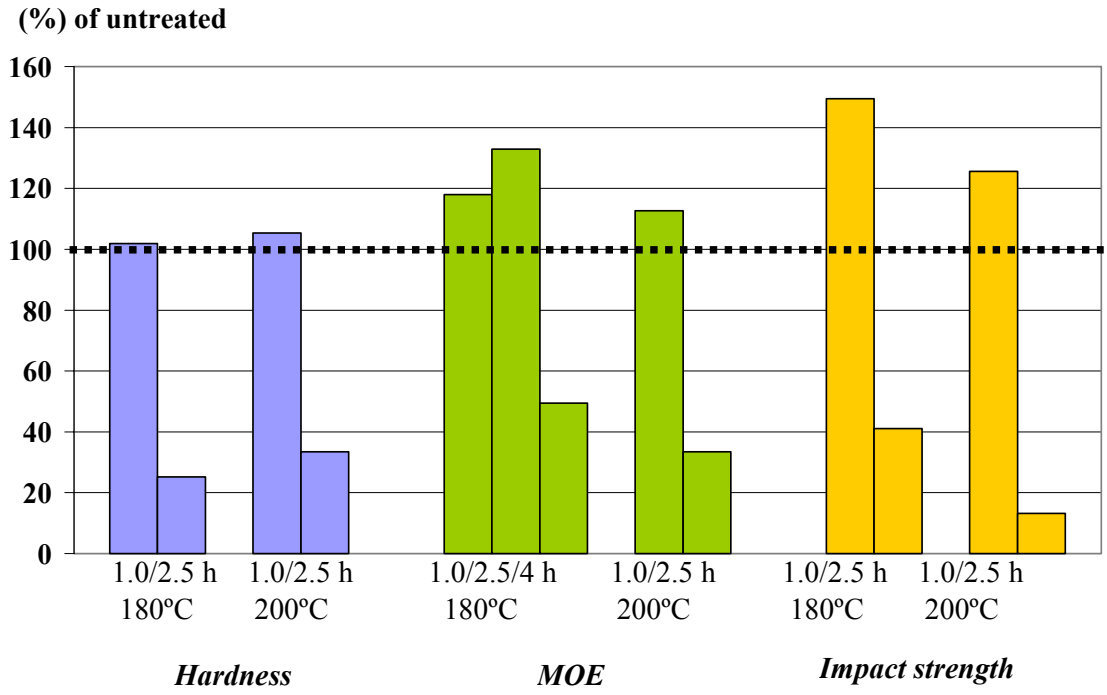

Figure 17: *Relative Brinell hardness, modulus of elasticity (MOE) and impact bending strength for birch wood heat-treated in a sealed autoclave relative to untreated birch. Untreated samples were dried at room temperature (Based on results from Paper VI).*

In practice, some sort of calibration routines will be needed that match the exact layout of each treatment plant. It is obvious that proper optimization and process control are needed in order to avoid considerable strength and hardness loss and also to possibly achieve a small enhancement of the wood strength properties.

A possible way to indirectly monitor the process is colour measurement (Paper VI and (Bourgois et al. 1991). At the treatment temperature and time noted for enhanced strength and hardness, colour coordinate C_{ab}^{*}(chroma) appeared to increase slightly (Figure 18). Chroma seemed also to decrease for conditions when these properties are impaired at prolonged treatment times and even higher temperatures. Colour coordinate h (hue) seems to stabilize around the treatment time and temperature for the enhancements mentioned (Figure 19). Similar results have also been reported in other investigations (Bourgois et al. 1991; Kubojima et al. 2000), where the hue seems to drop again over 200ºC.

A possible explanation for these small enhancements is the condensation reactions and/or cross-linking of degraded compounds from lignin and hemicellulose (Klauditz and Stegman 1947; Tjeerdsma et al. 1998b; Weiland and Guyonnet 2003). Condensation products, called coloured Maillard products, in carbohydrate model systems can have a reddish colour (Rizzi 1997).

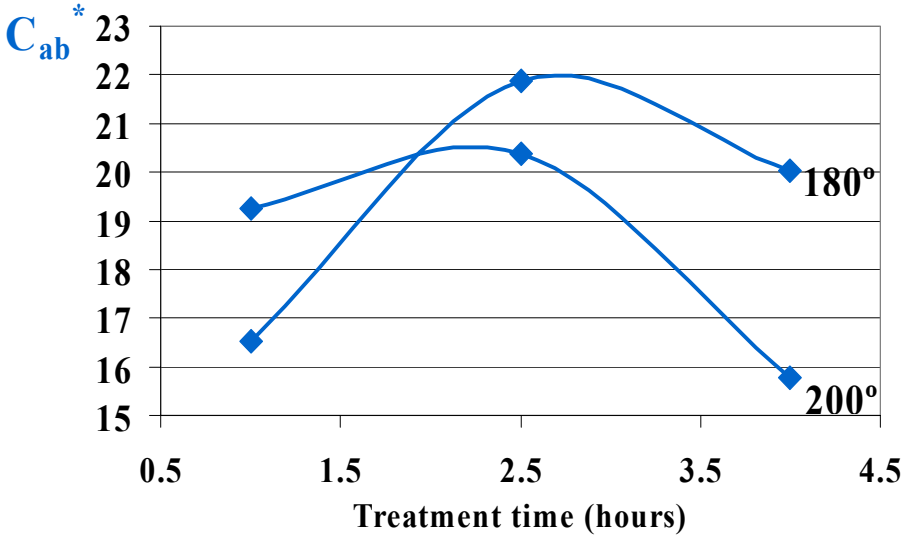

Figure 18: *Colour response Chroma (C_{ab}^*) for birch wood heat treated in a sealed autoclave. (From Paper VI).*

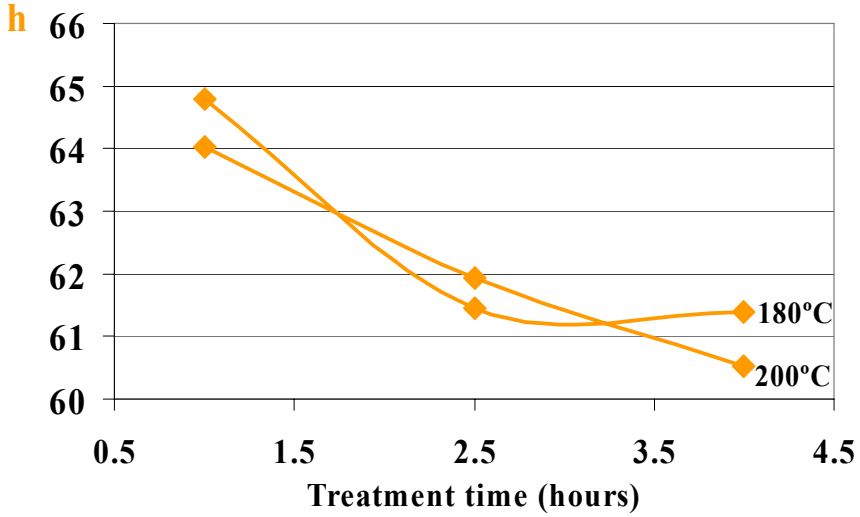

Figure 19: *Colour response hue (h) for birch wood heat treated in a sealed autoclave. (From Paper VI).*

Another possibility for avoiding large strength and hardness losses at temperatures above 180ºC could be a process design that avoids formation and accumulation of acetic acid and formic acid within the wood material (Paper VI). The conditions that favour acidic hydrolysis of carbohydrates are well known (Theander and Nelson 1988).

It is obvious that wood heated around 200ºC, and especially over 200ºC, rapidly decreases in mechanical properties, but also increases in resistance to biodegradation. It is reasonable to presume that the changes in mechanical properties are related to the formation and accumulation of organic acids in the wood which also emit to the surrounding process atmosphere. New processes and process designs that avoid acidic conditions in the wood and maintain the mechanical properties are desirable. Further studies are needed to discover the best conditions for such treatments.

The development of heat-treated wood and the heat treatment process seem to point in different directions depending on which characteristics are in focus and on the price for the final product. For exterior products with good fungal resistance, a process for heat-treating wood in a steam or nitrogen atmosphere over 200ºC for several hours is recommended. This will lead to products with good fungal resistance and a considerable decrease in swelling and shrinkage.

From the end user's perspective it would be interesting to produce heat-treated wood that has good outdoor fungal resistance, improved swelling and shrinkage properties as well as negligible loss in strength and hardness compared to untreated wood. If the wood is kept in mildly alkaline conditions during the heat treatment process, the loss in strength and hardness may be negligible. However, processes designed to meet such requirements are likely to entail higher production costs and more expensive end-user products than the production methods common today. There are probably several ways to avoid acidity during the treatment. The following three possible methods are suggested.

- A process where the wood is soaked in an aqueous buffer solution at pH larger than 7 during heat treatment.

- A process that reduces the concentration of organic acids in the gaseous phase or neutralizes them with ammonia or other alkaline substances.

- Impregnating the wood before heat treatment with additives that have a pH higher than 7.

Another way of maintaining the mechanical properties of wood could be heat treatment around 100ºC, which would involve little formation of organic acids. At this temperature level a distinct colour can change occur, but the improvements in dimensional stability and resistance to biodegradation will probably be negligible.

6. Conclusions

The results in this thesis show the following:

- Neutral to alkaline conditions in the wood during heat treatment can considerably reduce the degradation of cellulose and possibly also minimize losses in strength and hardness of the wood.

- More than 1% formic acid and more than 7% acetic acid (w/w dry wood) can be formed within birch wood due by heat treatment at 180ºC. This can be related to losses in strength and hardness.

- The brownish colour of wood heat treated at temperatures around 200ºC is believed to be attainable by treatment at temperatures below 100ºC for a period of weeks.

- Under certain conditions (approximately 180ºC to 200ºC for a treatment time of 1–2 hours) the heat treatment process seems to produce small enhancements in strength and hardness of the wood.

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Colour stability of capillary phase heat-treated wood exposed to UV-light

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ABSTRACT

Industrial kiln drying of wood at temperatures in the range of 70-100°C changes the colour of the wood. The colour change takes place especially during the capillary phase, above the fibre saturation point. The colour change can be attractive and generates added value. The stability of the colour to light exposure is however an important issue. This study presents results and describes experiments of testing the colour stability of capillary phase heat-treated wood samples. Such heat-treated samples of birch sapwood, spruce and pine sapwood and heartwood were exposed to UV-light (metal halide radiator Philips HPA 400 with a glass filter). In the capillary phase heat-treatment the green samples were kept in the capillary phase, above the fibre saturation point, for several days at higher temperatures and subsequently dried at 35°C for two days. Colour measurements during UV-exposure were made at intervals over a period of 100 hours. This was made with a Minolta chromameter CR-310. The results are presented in ΔE^*_{ab} and L^*C^*h co-ordinates according to the CIE-standard. The experiments show that the colour stability for heat treated wood are generally better during the 100 hours of exposure when compared to untreated wood, except for the first 4 hours. Pine and spruce, heat-treated and untreated materials, show a larger colour change than birch, during exposure. There are indications that higher temperatures and longer times used in the heat-treatment alter the colour response of wood when exposed to UV-light. The chosen method shows promising results for evaluating the colour stability of wood when exposed to UV-light.

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1. INTRODUCTION

The interest for the aesthetic appearance of wood, especially kiln dried, has grown as a consequence of new drying techniques and increased drying temperatures. In this work, a comparison of the UV-light colour stability of capillary phase-heat treated and untreated wood was made. Many investigations have been done concerning the influence of UV and visible light on wood such as e.g. colour, chemical constituents, DRIFT-, UV- and IR-spectroscopy.

The colour change initialised by light is also influenced by additional factors such as temperature, water and atmosphere, especially oxygen (Fengel and Wegener 1989). UV-light penetrates approximately 75 μm and visible light approximately 200 μm.
All wood components are attacked by UV-irradiation and UV-absorption is mainly determined by the lignin content.

Leary 1994 gives a review of the recent progress of photoyellowing in lignin. 3 pathways of mechanisms are identified. The formation of free phenoxy radicals, the excitation of carbonyl groups and the most recent which is the major pathway, formation of ketyl radicals producing a phenoxy radical and a ketone.

Acetylated and non-acetylated Radiata pine were exposed to UV and visible light, Xenon irradiator, and subsequently evaluated by colour measurements: CIE L*a*b* colour system, and IR and UV spectroscopy (Dawson and Torr 1992). IR spectroscopy showed that the exposure reduced the lignin aromaticity, caused deacetylation and accumulation of carbonyl and carboxyl containing compounds. The UV/ VIS spectroscopy revealed that the concentration of chromophores around 430 nm increased with time and inversely to the degree of acetylation. Acetylation suppressed the production of chromophores around 530 nm. Colour measurements revealed a fast colour change, ΔE^*_{ab}, for the first 20 hours of non-acetylated and acetylated Radiata pine. L* decreased, a* decreased up to 20 h and thereafter increasing, and b* showed the largest change with increasing behaviour, “a yellowing effect”. The results show that the photodegradation process is active within the first 20 hours of exposure. The photodegradation process involves oxidation of aromatic rings to aliphatic acids, oxidative cleavage of lignin side chains with the formation of aromatic acids and depolymerisation of hemicellulose.

Fir (Abies grandis), MDF-boards (of Maritime pine) and oak wood were treated with antioxidants to achieve a protection against UV/ visible light; in this case a mercury lamp with glass filter was used (Grelier et al. 1997). It was found that ΔE^*_{ab} became around 9 units for Fir at 8 hours of exposure. ΔE^*_{ab} for oak became around 5 units and MDF-board around 3 units for 8 hours exposure. The change for all three materials was noticeably strong for the first hour of exposure.

Spruce (Picea abies), pine (Pinus silvestris), larch (Larix decidua), poplar (Populus Euramericana) and locust (Robinia psudoacacia) were exposed to UV-light, a mercury lamp of 300W, for 200 hours (Tolvaj and Faix 1995). Colour measurements with the CIE L*a*b* colour system and DRIFT spectrometric analysis were made. A rapid change for all species in colour difference ΔE^*_{ab}, around 10 units, for the first 25 to 50 hours of exposure were reported. From 50 to 200 hours the change was comparatively small, ΔE^*_{ab} around 5 units. They all showed yellowing, an increase in a*, with spruce yellowing the most and pine the second most in order, the two softwoods in the investigation. Locust

showed the least yellowing but instead a noticeably shift toward red during exposure, an increase in b*. All species showed a similar pathway in the a* and b* direction except locust during exposure. Since the coloured compounds, produced during exposure, weren't removed to a large extent by water extraction it was assumed that the coloured compounds were oligomeric chromophores, probably originating from leuco chromophores of the lignin moiety. It is also assumed the yellow-reddish colour of locust is due to its extractives.

Five lignans, and one neolignan, extractives, were detected as the main contributor to light induced discoloration in Western hemlock, Tsuga heterophylla (Kawamura et al. 1996). These were: cedrusin, allhydroxymatainresinol, hydroxymatainresinol, oxomatainresinol, α-conidendrin and pinoresinol. Also vanillic acid catechin and vanillin, degradation products of lignin, were detected playing a minor part in the discoloration. In a following study, Kawamura et al. 1998 used the five lignans and vanillin earlier identified in reaction systems to determine reactions and propose mechanisms during the photodiscoloration. It was found that formation of phenoxy radicals in the compounds initiated the photodiscoloration. The formation of quinonemethide intermediates during the progress is also assumed to occur in many of these compounds. It was suggested that phenoxy radicals and quinonemethide intermediates might be converted to quinone derivates and coloured oligomers. The conclusion is that photodiscoloration of Western hemlock do not depend on a few compounds in high concentrations but rather on the co-existence of many compounds.

Photoyellowing of partial acetylation of groundwood pulps (of Picea abies) was used to indicate the mechanisms involved (Ek et al. 1992). Prepared handsheets or thin sheets were irradiated with UV and visible light. Quinones and quinone precursors, such as hydroquinones and catechols are probably important reactants in the yellowing process. Quinones and quinonoid structures absorb light in the wavelengths of the blue-green region, giving a yellow colour appearance.

A pigment causing discoloration in the heartwood of Black walnut, Juglans nigra, was isolated (Kai et al. 1985). Black walnut heartwood has an attractive purple brown colour but light fades this colour to yellow. From the heartwood a purple pigment that was changed to yellow by light, using a mercury lamp for 3 hours or sunlight for 4 hours. Additionally fourteen filters were used with the sunlight to cut off chosen wavelengths under 700 nm to 250 nm. The ethyl acetate insoluble part of the pigment changed for 3 hours of irradiation almost 3 units in ΔE^*_{ab}, L* decreased 3 units, a* increased 1 unit and b* increased almost 4 units. In the ethyl acetate soluble part, the colour changed 3 units in ΔE^*_{ab}, L* decreased 2 units and a* and b* increased 1 unit upon 3 hours irradiation. The large increase in b*, for ethyl acetate insolubles, corresponds well to the change from purple to yellow in the Black walnut heartwood. With sunlight and cut off filters it was demonstrated that UV-light of approximately 350 nm and visible light around 500 nm considerably contribute to the colour change. These results were verified with UV and VIS spectrometric results of the coloured compounds isolated.

Hon 1995 investigated the colour stability of acetylated and unacetylated Southern yellow pine (Pinus spp) by using a mercury lamp of 200 W. For the unacetylated wood ΔE^*_{ab} rapidly reached, approximately 10 days, a change of around 20 units and no big change thereafter up to 56 days of exposure. It was found that acetylation is effective to stabilise wood colour up to 28 hours of exposure and beyond this the effect diminish and

discoloration accelerates.

The yellowing of thermomechanical pulp (TMP) of Black fir was studied when exposed to UV-light in the range 300-400 nm for 65 hours (Roberts et al. 1995). Four chromophores, with peaks around 360 and 425 nm, were suggested to explain yellowing as a result of UV-spectroscopic analysis and photoelectric reflectance measurements. Colour changes were evaluated using the CIE L*a*b* colour system, which showed that UV-exposed unbleached TMP changed from 87.3 to 80.9 in L* units, 0.5 to 3 in a* units and 12.2 to 32.6 in b* units.

Ota et al. 1997, investigated the effect of acetylation on colour stability of kiri veneers (Paulownia tomentosa Steud). Sunlight for 433 hours and a mercury lamp for 720 hours were used as irradiation. Colour measurements were made with a photoelectric reflectance photometer with the CIE L*a*b* colour system. For untreated veneers exposed to sunlight for totally 350 hours. L* did not change throughout the test and stayed at approximately 78 units, a* changed from approximately 2.5 to 1.5 units in 50 hours and thereafter increasing to 2.5 units at 350 hours. b* changed from 18 to 29 units in 170 hours and thereafter stagnating. Corresponding change in ΔE^*_{ab} is approximately 12 units and the change for C* is from 17 to 29 for 170 hours exposure of sunlight and prolonged time causes stagnation for both values. With mercury lamp irradiation L* did not change, approximately 78 units. a* changed from 2 to 1 unit within 20 hours of exposure, then increasing to 2.5 units at 720 hours. b* changed from 17 to 33 units within 200 hours, afterwards decreasing to 30 after 720 hours exposure. Corresponding change in ΔE^*_{ab} is 15 units within 200 hours and then decreasing to 12 units after 720 hours exposure. C* started at 18 and changed to 33 within 200 hours, thereafter decreasing to 30 at 720 hours of exposure.

The aim of this study is to investigate the colour change of capillary phase heat-treated wood compared to untreated wood when irradiated to UV-light. These colour changes are used to evaluate the "colour stability" of the wood samples. The relation of Colour changes induced by exposure and differences in time and temperature in the capillary phase heat-treatment is also investigated. A comparison of the colour stability of the five materials used in the study, Pine sap-and heartwood, Spruce sap- and heartwood and Birch sapwood, is made. Additionally an estimation of the chosen method is made.

2. MATERIAL & METHODS

Green boards of spruce (Picea abies), pine (Pinus silvestris) and birch (Betula pubescens) were taken from local sawmills during winter of 97-98. From these boards samples with dimensions of approximately 13 mm x60 mm x100 mm were sawed. Both sapwood and heartwood samples were produced for spruce and pine whereas for birch only sapwood were produced. The samples have a random mixture of tangential and radial surfaces. The samples were put into sealed glass jars to keep them in capillary phase, approximately above 50% in moisture content, during the heat treatment. At the most the samples showed a weight decrease of approximately 10%, which indicated that treatment occurred only in the capillary phase. From these treatment sets a selection of samples was made for this investigation, Table 1.

Table 1. Capillary phase-heat treated sample sets used for UV irradiation

Materialclass	Temperatures (ºC)/ Times (days)
Pine heartwood	80/ 6
Pine sapwood	65/ 3 ;80/ 3 & 6 ;95/ 3
Spruce heartwood	80/ 6
Spruce sapwood	80/ 6
Birch sapwood	65/ 3 ;80/ 3 & 6 ;95/ 3

After the treatment the samples were dried in a laboratory oven at 35°C for 2 days, reaching moisture content of 4-6%. Also reference sets for each material class, no treatment but drying at 35°C for 2 days, were included in the experiments. Before the UV-exposure the samples were planned approximately 3 mm to remove surface contamination and to resemble surfaces often used for e.g. joineries. For the UV-exposure an armature with a metal-halide irradiator (Philips HPA 400) was used. To cut off wavelengths approximately beneath 350 nm a glass filter was used. The distance from the armature to the samples was approximately 0.5 m during irradiation and the temperature was at the most approximately 40°C at the surface. The weight decrease for the samples was after 100 hours of exposure around 1%. Colour measurements were done using a Minolta Chromameter CR 310 with CIE L*a*b* colour system chosen. The L*a*b* values were transformed into L*C*h and ΔE^*_{ab} values which are presented in this work. ΔE^*_{ab} is the size of the colour difference, L* is lightness, C* is chroma (saturation) and h is hue (shade). The transformations are made by using Equations 1-3. The colour stability of the wood samples is evaluated by examining the colour changes in the colour system presented above.

$$C^* = \sqrt{a^{*2} + b^{*2}} \quad (1)$$

$$h = \arctan(b^*/a^*) \quad (2)$$

$$\Delta E^*_{ab} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (3)$$

3. RESULTS & DISCUSSIONS

The results are presented in diagrams. Each point along the lines in the diagrams is average values of 12 to 15 samples. The corresponding 95% confidence intervals to most average sets are also presented as points around every line point. The sets of samples were the same measured during the whole UV exposure, for each material class.

3.1 Colour stability of material classes

The overall colour stability for all five material classes, untreated and heat treated at 80°C for 6 days, was evaluated by examining the colour difference, ΔE^*_{ab}, Figure 1. All materials have rapid changes for the first 2 hours of exposure. Especially treated materials show a strong colour change during the first 2 hours compared to untreated materials and afterward they change little throughout the 100 hours of exposure. All treated materials show continuos colour changes after 2 hours, during the whole 100 hours of exposure. The final colour changes at 100 hours were clearly stronger for untreated wood compared to treated wood. Birch, treated and untreated, shows the smallest changes of the materials. For treated pine and spruce materials, spruce show smaller changes compared to pine and

for untreated pine and spruce materials is the relationship opposite. From Figure 1 it is concluded that the colour changes, expressed as ΔE^*_{ab} for treated and the untreated wood do not converge to the same final value after 100 hours of exposure. The final content of chromophoric compounds of capillary phase heat-treated wood is different from untreated wood. It is assumed that wood components, mainly hemicellulose, lignin and extractive compounds are degraded by the capillary phase heat-treatment and new chromophoric compounds are produced. The treated materials probably have a content of chromophoric compounds, which interacts faster and ceases earlier with UV-light compared to untreated materials

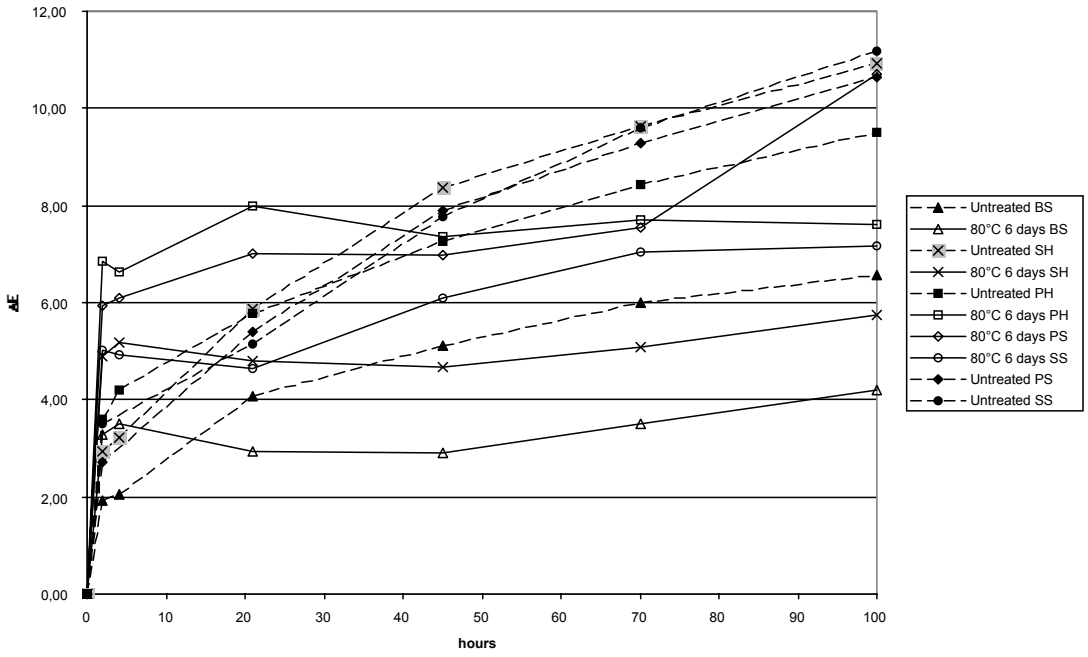

Figure 1. Colour difference, ΔE^*_{ab}, of untreated and capillary phase heat-treated wood exposed to UV-light. Birch sapwood (BS), spruce heartwood (SH) and sapwood (SS), pine heartwood (PH) and sapwood (PS)

3.2 Influence of temperature used in the capillary phase heat-treatment on colour stability

The influence of temperature for capillary phase heat-treatment at 3 days on colour stability was studied for birch and pine sapwood by examining the colour values L*, C* and h . No big differences in Chroma, C*, for pine and birch sapwood, untreated, 65°C, 80°C and 95°C treated was observed, Figure 2. They all have minima around 2-4 hours of exposure and then they increase to finally converge for each species at 100 hours of exposure. All wood materials decrease in lightness; L* during exposure except samples of treated birch sapwood and samples of pine sapwood 95°C-treated, which indicate minima around 2 hours and afterward increase, Figure 3. Both pine and birch sapwood show three different levels of L* according to pre-treatment. The untreated materials are the lightest, 95°C treated are the darkest and in between are 65°C and 80°C materials, showing similar lightness changes during exposure. The hue, h, show the most irregular changes for these materials, Figure 4. Pine sapwood untreated, 80°C- and 95°C-treated converge at 100 hours of exposure while 65°C-treated pine sapwood show a different change in hue during the late stage of exposure. For birch sapwood a rather similar case occurs but now has the 95°C-treated material a different change during the late stage of the exposure, compared

with the other three converging materials. Indications of minima in hue around 2-4 hours are also present in Figure 4 for all treated birch sapwood samples and for 95°C-treated pine sapwood sample. Afterward they all increase in h. These non-converging behaviours in hue may indicate transitions between different photo induced reactions in the materials. Notably, untreated material for both pine and birch sapwood indicates increase in the early stage of the exposure.

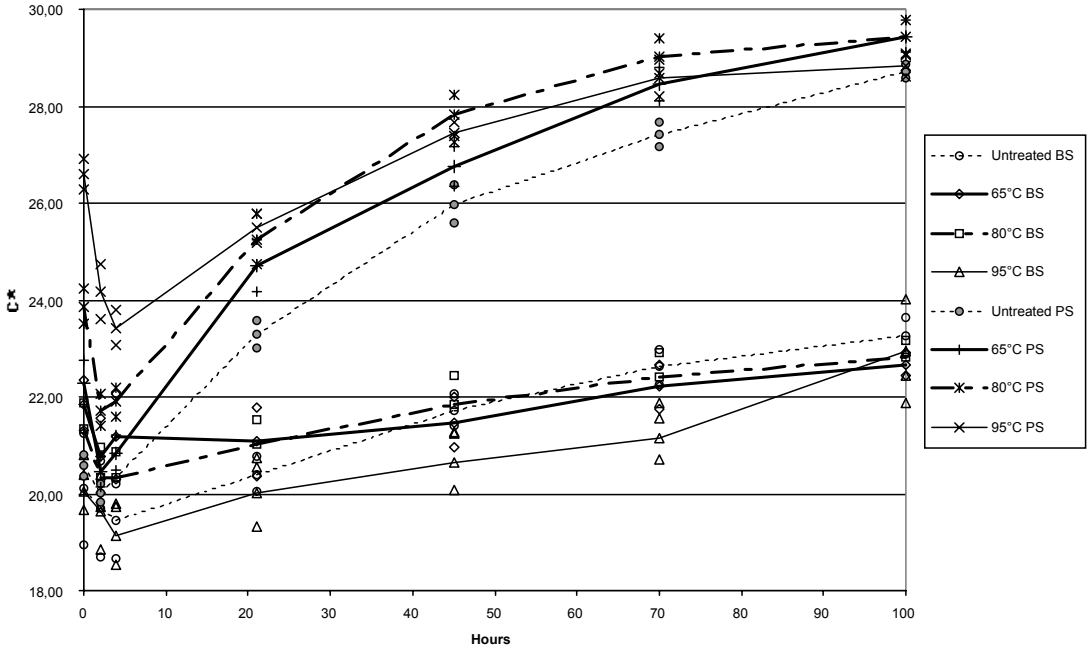

Figure 2. Chroma, C*, of untreated and treated wood exposed to UV-light. 3 different treatment temperatures was used in the capillary phase heat-treatment for 3 days, 65°C, 80°C and 95°C. Birch sapwood (BS) and pine sapwood (PS)

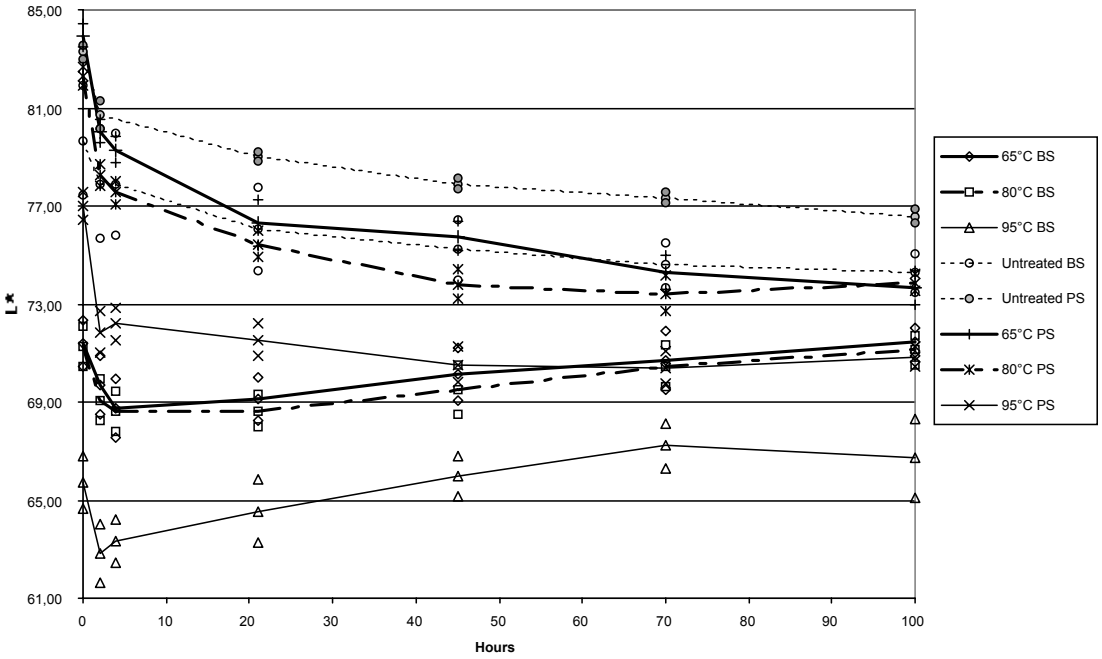

Figure 3. Lightness, L*, of untreated and treated wood exposed to UV-light. 3 different treatment temperatures was used in the capillary phase heat-treatment for 3 days, 65°C, 80°C and 95°C. Birch sapwood (BS) and sapwood (PS)

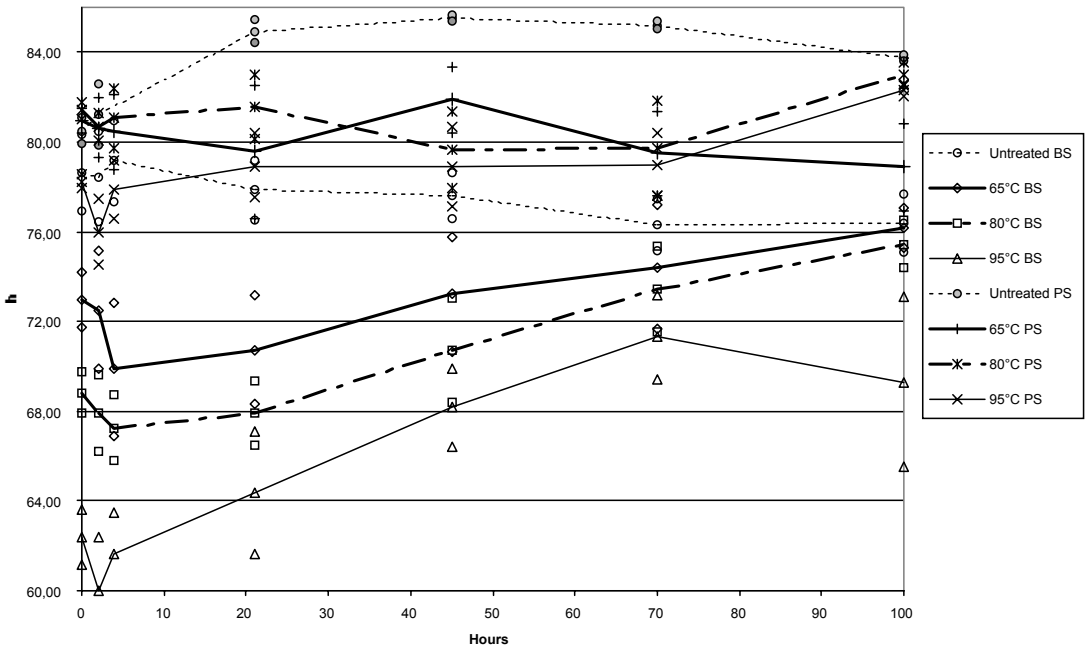

Figure 4. Hue, h, of untreated and treated wood exposed to UV-light. 3 different treatments temperatures was used in the capillary phase heat-treatment for 3 days, 65°C, 80°C and 95°C. Birch sapwood (BS) and pine sapwood (PS)

3.3 Influence of time used in the capillary phase heat-treatment on colour stability

The importance of time used in the capillary phase heat-treatment on colour stability was evaluated by examining colour values L*,C* and h. This was done for untreated and treated pine and birch sapwood exposed to UV-light. For both species materials treated at 80°C for 3 and 6 days were used. For chroma, C*; there are indications of minima around 2-4 hours of exposure for all 6 materials and then they all increase throughout the whole exposure of 100 hours, except birch sapwood treated for 6 days, which shows a irregular change in C*, Figure 5. Pine sapwood materials show larger changes in C* during exposure compared to birch sapwood materials. Pine sapwood materials converge at 100 hours and birch sapwood untreated and 3 day-treated also converge at 100 hours of exposure. Lightness, L*, decreases rapidly for all 6 materials during the 2 first hours of exposure, Figure 6. Pine sapwood, untreated and treated and birch sapwood untreated show continuos decrease in L* during exposure while treated birch sapwood materials indicate minima around 2-4 hours, and then they show an increase. Pine sapwood, 6 day-treated, show a different change in Lightness for the last 30 hours of exposure. Hue, h, for pine and birch sapwood materials, untreated and treated, converge at 100 respectively 70 hours of exposure, except 6 day-treated pine sapwood, Figure 7. During the exposure, birch sapwood, treated, indicates minima around 2-4 hours and show larger changes in hue compared to the 4 other materials. Another interesting change occurs for pine sapwood, 6 day-treated, which decreases in hue for the last 30 hours of exposure.

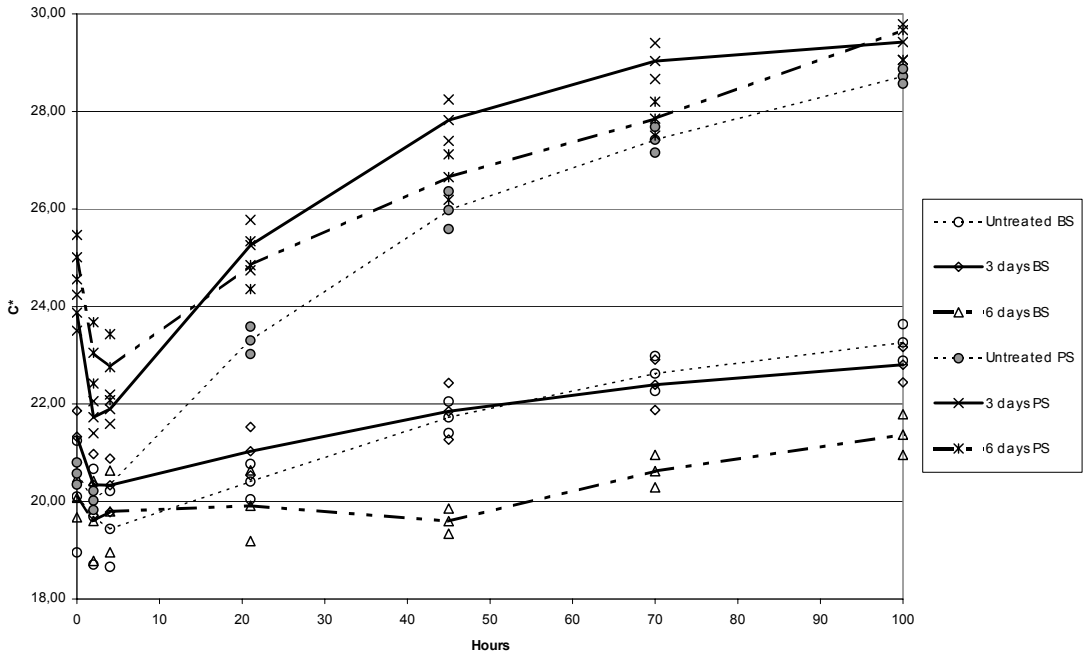

Figure 5. Chroma, C*, of untreated and treated wood exposed to UV-light. 2 different treatment times was used in the capillary phase heat-treatment at 80°C, 3 and 6 days. Birch sapwood (BS) and pine sapwood (PS)

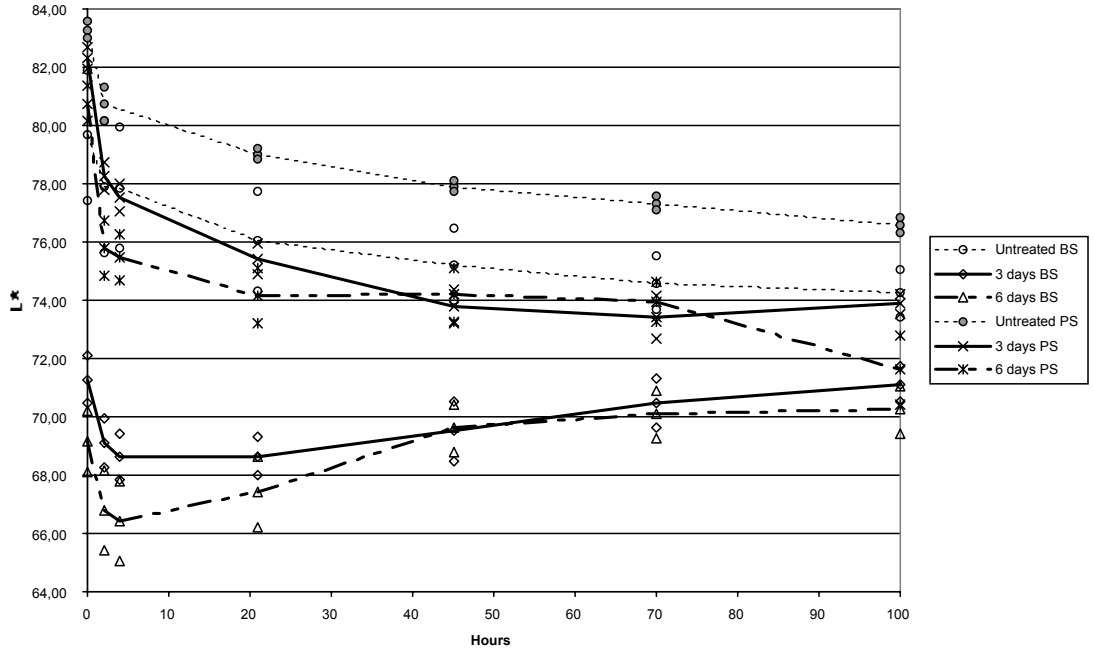

Figure 6. Lightness, L*, of untreated and treated wood exposed to UV-light. 2 different treatment times was used in the capillary phase heat-treatment at 80°C, 3 and 6 days. Birch sapwood (BS) and pine sapwood (PS)

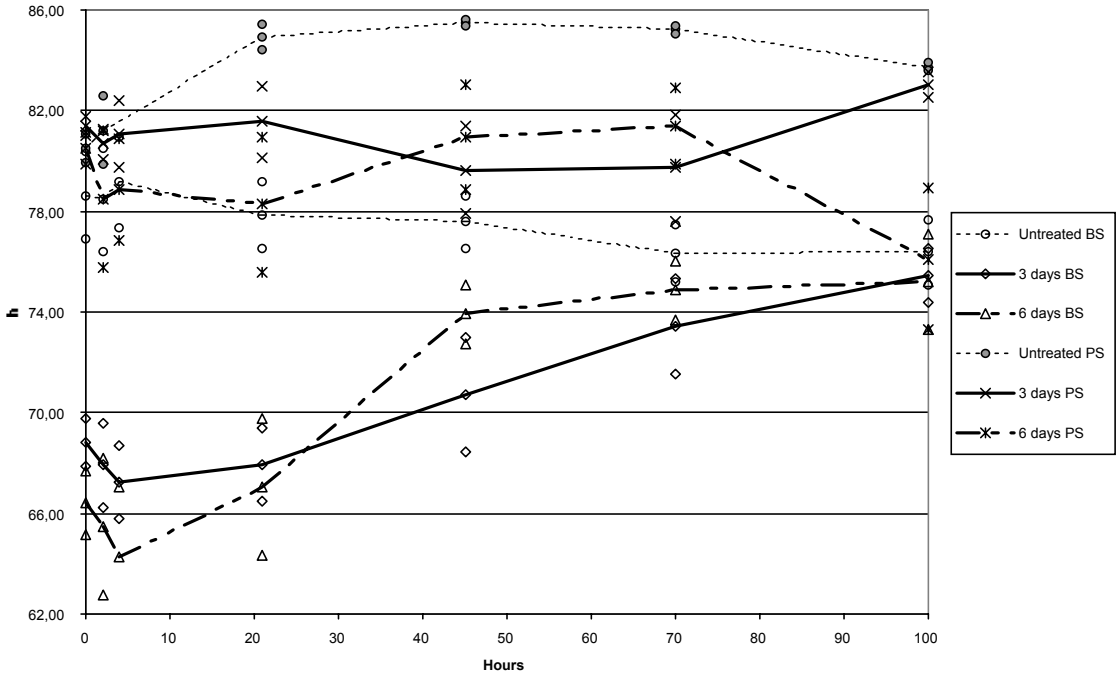

Figure 7. Hue, h, of untreated and treated wood exposed to UV-light. 2 different treatment times was used in the capillary phase heat-treatment at 80°C, 3 and 6 days. Birch sapwood (BS) and sapwood (PS)

4. CONCLUSIONS

- The chosen irradiation method shows promising results for qualitative evaluation of colour stability for wood when exposed to UV-light.

- In general a rapid colour change occurred during the early part of the exposure and especially during the first 4 hours. For many capillary phase heat-treated samples, local maxima or minima for lightness, chroma and hue were indicated around 4 hours of exposure. A more detailed analysis should therefore be done for the first 20 hours in future experiments.

- Untreated and treated pine and spruce samples generally show larger colour changes compared to birch samples during UV-light exposure.

- For each material, capillary phase heat-treated samples showed in general a faster colour change in ΔE^*_{ab} during the first 4 hours of exposure compared to untreated samples. However the final colour change in ΔE^*_{ab} at 100 hours of exposure were in general smaller for capillary phase heat-treated samples than untreated samples.

- Generally a convergent change was indicated for each material in chroma and hue during the UV-light exposure. For lightness no such general convergence was observed and treated samples showed a darker final colour than untreated wood.

- 6 days and 95°C, used in the capillary phase heat-treatment, indicated differences in colour changes compared to the other conditions used in the capillary phase heat-treatment, when exposed in UV-light, especially during the last 30 hours.

- It is assumed that the different colour changes during UV-light exposure between birch sapwood, pine and spruce sap- and heartwood is due to their different contents of lignin, extractives and hemicellulose and their alteration during heat-treatment.

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II

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Color response of Scots pine (*Pinus sylvestris*), Norway spruce (*Picea abies*) and birch (*Betula pubescens*) subjected to heat treatment in capillary phase

B. Sundqvist

Clearwood of Scots pine, Norway spruce, and birch was subjected to heat treatment while capillary water was kept in the wood. The treatments were performed on initially green wood from 65 °C to 95 °C from 0 to 6 days, followed by drying at 35 °C for 2 days. Color measurements, CIEL*C*h color space, were made on dry planed samples using a photoelectric colorimeter. Treatment time was more important than temperature for birch sapwood regarding the color responses, while time and temperature were of similar importance for pine and spruce. Birch sapwood became much redder and darker compared with pine and spruce. The darkening accelerated generally when treatment temperature exceeded approximately 80 °C. Pine and spruce showed generally similar color responses, untreated and treated, except for pine heartwood untreated, which showed a more saturated color. Pine treated at 65 °C and 80 °C showed red-yellow shift and yellow-red shift for sap- and heartwood respectively, as time elapsed. The color homogeneity was less for birch sapwood than for pine and spruce, and the homogeneity was generally indicated to decrease with increasing treatment temperature.

Farbreaktion auf die Hitzebehandlung in kapillarer Phase von Kiefern, Fichten, und Birkenholz

Fehlerfreies Holz von Kiefer, Fichte und Birke wurde einer Hitzebehandlung unterworfen, wobei das Wasser im Holz in kapillarer Phase vorlag. Waldfrisches Holz wurde von 0 bis 6 Tagen bei 65 °C und 95 °C gehalten. Danach erfolgte eine zweitägige Trocknung bei 35 °C. Farbmessungen (CIEL*C*h Farbraum) erfolgten an getrockneten und gehobelten Proben mittels eines photoelektrischen Colorimeters. Die Behandlungsdauer erwies sich als wichtiger als die Temperatur für die Farbreaktion des Birkensplintholzes, während beide für Kiefern- und Fichtenholz gleichbedeutend waren. Birkensplintholz verfärbte sich erheblich röter und dunkler im Vergleich mit Kiefer und Fichte. Dieser Prozeß beschleunigte sich, wenn die Temperatur etwa 80 °C überschritt. Kiefern- und Fichtenholz zeigten allgemein ähnliche Reaktionen (behandelt oder unbehandelt) mit Ausnahme des Kieferkernholzes, welches gesättigtere Farbtöne aufwies. Kiefernholz zeigte nach Behandlung bei 65 °C und 80 °C eine rot-gelb bzw. gelb-rot-Verschiebung in Splint- und Kernholz. Die Homogenität der Verfärbung war in Birkensplinzholz geringer als bei Kiefer und Fichte. Allgemein nahm sie mit steigender Temperatur ab.

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1 Introduction

Color changes often occur when temperatures are raised in industrial kiln drying and its relation to aesthetic appearance is an important issue. It is also of interest to know more about these color changes, since they imply alteration of wood components, which can have an affect on wood properties, such as strength. A kiln-drying process with controlled color change is therefore desired.

The color of a solid material is attributed to the reflection, scattering and absorption of light within the visible range. The absorption of visible light for a material is characteristic and is caused by certain molecules called chromphores (Hon and Shiraishi 1991). In wood light is mainly absorbed by lignin below 500 nm and by phenolic extractives, such as tannins, flavanoids, stilbenes and quinones above 500 nm (Hon and Shiraishi 1991). This author also informs that cellulose and hemicellulose don't absorb light within the visible range.

The phenolic extractives have been widely studied in relation to the natural color of wood. A colored reaction product in walnut is mainly based on hydrojuglone glucoside (Burtin et al. 1997). Ellagitannins in oak cause discoloration (Charrier et al. 1995). Flavanoids in Hazenoki contribute strongly to the color (Kondo and Imamura 1985). A reaction product of dihydroquercetin in Douglas fir is identified as causing discoloration (Dellus et al. 1997).

The natural color of wood is often unevenly distributed. Burtin et al. 1997, investigated the radial distribution of phenolic extractives, some of them strongly influencing the color of wood, at three different heights in three walnut species. The phenolic extractives showed a clear difference in distributions in the radial direction for all three levels. In the longitudinal direction the test specimens at the lowest level contained more phenolic extractives than the other two higher levels.

The natural color of wood is dependent on age, both tree age and wood age (number of annual rings from the pith) for European oaks (Klumper et al. 1993). Younger trees have a lighter and more yellowish color than older trees, which have a reddish-brown color and the color of the wood becomes darker and more reddish towards the pith. Quercus robur was also found to produce a darker and more reddish color when groundwater is abundant in spring.

1.1
Influences of treatment on wood color

Trea usually darken at lower temperatures than softwoods (Hon and Shiraishi 1991). The browning can be characterised as darkening, increased saturation and increased reddish color. This was observed for Norway spruce and Scots pine sapwood during kiln drying, and these changes were stronger for Scots pine (Wiberg 1996). This was also observed for Yellow poplar, Silver maple, and White oak during pressure steam treatment (McGinnes et al. 1984). Besides treatment temperature and time, other factors can be of importance. Accelerated kiln drying without oxygen can prevent discoloration in European oak (Charrier et al. 1992).

In thermally treated wood, phenolic extractives, such as stilbenes in Radiata pine, can contribute to the coloring process (McDonald et al. 1997). Besides phenolic extractives, degradation products from hemicellulose and lignin resulting from thermal treatment, for example, can also be a reason for coloring processes. Increased extractive content is believed to be a result of hemicellulose degradation during pressure steam drying (McGinnes et al. 1984). The presence of arabinose in extraction from kiln dried Radiata pine is believed to be a result of hemicellulose degradation (Kreber et al. 1998). The liberation of acetic acid in thermally treated beech and Scots pine is a result of degradation of hemicellulose, and acetic acid catalyses further lignin degradation (Tjeerdsma et al. 1998).

Furthermore, nutritive compounds such as low molecular sugars and amino acids have been observed to redistribute towards the surface in wood during thermal treatment, accumulating 0.5–1.5 mm below the surface to produce discoloration. This phenomenon has been known for some decades (Millet 1952, King et al. 1976, Theander et al. 1993). The redistribution has been investigated in Scots pine (Terziev 1995) and the discoloration has been investigated in Radiata pine (Kreber et al. 1998, which called the discoloration "kiln brown stain". Kiln brown stain in Radiata pine is proposed to be a result of the Amadori-Maillard reaction of fructose, sucrose, or glucose with glutamatic acid (McDonald et al. 1997).

Oxidative and hydrolytic reactions are mainly considered to be the cause for production of chromophores during thermal treatment of wood, where hydrolytic reactions generally are the dominant process when moisture is present. (Fengel and Wegener 1984).

1.2
Objective

Since hydrolysis was assumed to be the dominant reaction in the coloring process (Fengel and Wegener 1984), the objective of this work was to investigate the color changes for the first part of the drying process when there is capillary water in the wood. This phase is called the capillary phase and referred to as "capillary phase heat treatment" in the following text. The color change in this phase was believed to be dominant when considering the whole drying process. The capillary phase was therefore controlled in the experimental procedure.

The variability of wood color dependent on capillary phase heat treatment was investigated in this work.

The color responses and variables in the investigation were believed to be correlated, and therefore a multivariate approach using principal component analysis was performed, a powerful tool to investigate the structure of multivariate data.

A discussion about the chemical alteration influencing the color change of wood during capillary treatment was also made in conjunction with already known facts.

2
Material and methods

Green pieces of boards, each with the length of 0.5 m, of Norway spruce, Scots pine and birch, were taken from local sawmills in the neighbourhood of Skellefteå, Sweden, during a period from January to March 1998. These pieces of boards originated from separate full-length boards, in order to get a good association with inter-tree color variance for the species Scots pine and Norway spruce. For birch, however, these pieces of boards originated from an unknown distribution of full-length boards. For pine and spruce, the center sawn pieces of board were of dimensions 150 mm × 75 mm and 150 mm × 60 mm in cross section and approximately 200 mm long. The pieces of birch board were approximately 120 mm × 25 mm in cross section and 150 mm long.

From each piece of board of spruce and pine, separated sapwood and heartwood samples dimensioned approximately 60 mm × 13 mm in cross section and 100 mm long were sawn. Only samples of clear wood were selected, avoiding defects, such as knots, rot, juvenile and reaction wood etc. The same procedure was followed for birch, except that no samples with heartwood were produced.

Most of the wood products used for furniture, joinery and panels show a mixture of tangential and radial surfaces. Therefore, samples were randomly produced in terms of tangential or radial surface exposed. The samples produced were immediately marked according to board number and type of material, enclosed in plastic bags and stored in a freezer.

The samples were divided into sets of 30 samples for each material (species and sap- or heartwood) and each treatment time and temperature of the capillary phase heat treatment (see Table 1 below). For each material there were sample sets for the different times at the same temperature in the capillary phase heat treatment originating from the same pieces of boards. This was intended, since the presentation of color responses versus time was the focus of this work. It also made it possible to study the color responses for individual boards if desired. Samples originating from the same board were not perfectly matched; i.e. they did not necessarily contain adjacent wood surfaces. Norway spruce was only investigated at two temperatures (Table 1) since it is not considered as important as pine and birch for joinery, flooring etc. Spruce is also considered less prone to discolor than pine (Wiberg 1996).

In this investigation the green and frozen samples were put into 1000-ml glass jars, 2–4 samples/jar, with metal lids, to ensure that capillary water was present in the wood during the heat treatment. The treatment was performed in a climate chamber, Arctest Arc-1500/0 + 110/RH. When

Table 1. Sets of samples, 30 samples prepared per set, in temperatures and times for capillary phase heat treatment
Tabelle 1. Versuchsgruppen. 30 Proben pro Gruppe je nach Temperatur und Zeit der Hitzebehandlung in kapillarer Phase

Material	Temperatures/°C	Times/days
Pine heartwood	65, 80 and 95	0, 1, 3 and 6
Pine sapwood	65, 80 and 95	0, 1, 3 and 6
Spruce heartwood	65 and 80	0, 1, 3 and 6
Spruce sapwood	65 and 80	0, 1, 3 and 6
Birch sapwood	65, 80 and 95	0, 1, 3 and 6

the treatment was ended, the samples of wood were removed from the glass jars and dried in an another climate chamber, Forma Scientific 39732–011, at 35 °C for 2 days to reach 4.5±1% in moisture content.

It is known that lumber dried at higher temperatures can produce a strongly colored layer 0.5–1 mm thick 0.5–2 mm beneath the surface in sapwood (Millet 1952, King et al. 1976, Theander et al. 1993, Wiberg 1996, Kreber et al. 1997). Furthermore, when wood is used for joinery, furniture or panels, it is often planed 2–3 mm. Therefore all samples in this investigation were planed approximately 3 mm before measuring in order to avoid interference of this colored layer (Hon and Shiraishi 1991). Samples visually observed to expose defects such as mixture of heartwood/sapwood and reaction wood after being dried and planed were removed from the investigation.

Within 1 day after planing, color measurements were made using a tristimulus photoelectric colorimeter, Minolta Chroma Meter CR310, with a measuring head 50 mm in diameter. The color system setting was L*a*b* according to the CIE standard (Hunt 1995). The three measured co-ordinates, L*, a* and b*, were transformed to L*, C* and h co-ordinates and ΔE^*_{ab} values, according to the equations below, (Hunt 1995):

$$C^* = \sqrt{a^{*2} + b^{*2}} \quad (1)$$

$$h = arctan\left(\frac{b^*}{a^*}\right) \quad (2)$$

$$\Delta E^*_{ab}\Delta = \sqrt{(\Delta L^*)^2+(\Delta a^*)^2+(\Delta b^*)^2} \quad (3)$$

L* is the lightness; 0 = black and 100 = white (Fig. 1 below). C* is the chroma or saturation; 0 represents only greyish colors and 60, for instance, represents very vivid colors. h is the hue of a color; 0 or 360 degrees is red, 90 is yellow, 180 is green and 270 is blue (Fig. 1. ΔE^*_{ab} is the color difference between measurements. The L*C*h system was chosen since only one color variable is needed to denote hue, i.e. red, green, blue or yellow, and furthermore, this system is easy to refer to our experience of color characteristics such as lightness, saturation and hue.

Each color parameter, L*, C*, h and ΔE^*_{ab}, was measured for each material, time and temperature. The average color values, standard deviations and 95% confidence intervals (5% significance level), based on t-distribution, were calculated assuming normal distribution.

A multivariate approach was also made using principal component analysis (PCA), software SIMCA P 7.01, Umetrics AB (Wold et al. 1987). In this investigation only average values were chosen for each set in the time-temperature domain for the color variables. PCA is a useful method to evaluate the total structure of the data, or in other words, the relations/correlations between all variables/responses chosen and their importance. PCA also makes it easier to detect statistical outliers and groups of observations. PCA uses transformations to find latent variables, or in other words, orthogonal principal components, which are linear combinations of the original variables. The first principal component (PC) is fitted to explain the greater part of the variance among the observations. The second PC is fitted to explain the second greater part of the variance and so on.

The validation of the PCA is mainly based on cross validation (Wold et al. 1987). Cross validation is a proce-

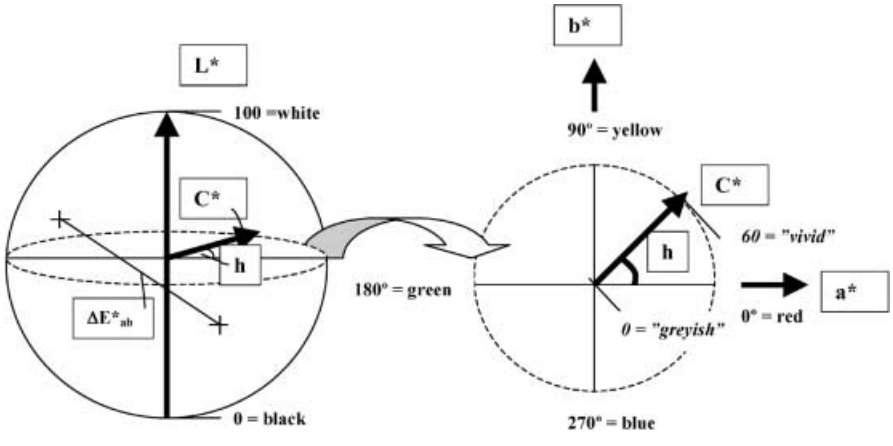

Fig. 1. CIEL*a*b* colour space and the transformation to cylindrical colour space L*C*h. *To the left*: The colour sphere, where the circle of cross section at L* = 50 is denoted. The colour difference (ΔE^*_{ab}) is the distance between two colours (points) within the colour sphere. *To the right*: Cross section at L* = 50 showing the axis from green to red (a*) and from blue to yellow (b*), and the co-ordinates chroma (C*) and hue (h)

Bild 1. CIEL*a*b* Farbraum und seine Transformation in den zylindrischen Farbraum L*C*h. *Links*: Farbkugel mit eingezeichnetem Querschnitt für L* = 50. Die Frabdifferenz (ΔE^*_{ab}) ist der Abstand zweier Farben (Punkte) in der Farbkugel. *Rechts*: Querschnitt für L* = 50 mit der Achse von Grün nach Rot (a*) und von Blau nach Gelb (b*) sowie den Koordinaten Sättigung (C*) und Farbton (h)

dure that stepwise excludes parts of the data and creates modified PCA models. The differences between the modified models and the original PCA model are then summed to produce values used for the validation. A "strong", i.e. reliable, model contains information with good precision, which usually does not change much from the exclusion of data parts. Cross validation is presented as the predicted variance (Q^2). A Q^2 near 100% means a reliable model with good predictability and close to 0% means an uncertain model. The explained variance is expressed as R^2. Close to 100% explains most of the variance in the data and close to 0% almost none.

In order to evaluate the color variation of wood by means of co-ordinates L*, C* and h and ΔE^*_{ab} values, half of the 95% confidence intervals for the average values obtained were examined. Normal distribution, independent and identically distributed observations, was assumed.

3 Results

3.1 Color values

The color responses, color difference (ΔE^*_{ab}), lightness (L*), chroma (C*) and hue (h), for the capillary phase heat treatment were presented as series where color response versus time was focused on for each material and temperature. Tables 2 and 3 are used to present the calculated average values of the color variables as well as half of the corresponding estimated 95% confidence intervals. These confidence intervals were also used to make a study on the color variation for different treatment conditions and materials. A color difference (ΔE^*_{ab}) larger than around 2–3 units is considered to be the limit for the human eye's ability to observe a difference (Hon and Shiraishi 1991).

3.2 Principal component analysis (PCA)

All the results presented in chapter 3.1 (average values, Table 2 and 3) were also used in the principal component analysis (PCA) to evaluate the whole data structure for birch sapwood, pine sap- and heartwood and spruce sap- and heartwood. In the analysis there were four responses: lightness (L*), chroma (C*), hue (h) and color difference (ΔE^*_{ab}), and the variables time and temperature.

The first model in the PCA included all materials and the R^2 was 0.76 and Q^2 was 0.40 with two principal components. Note that the second principal component was weak and not considered significant by SIMCA, but was included to simplify the graphical evaluation, allowing two-dimensional plots.

The score plot, Fig. 2, shows the projected observations, scores, positioned in the transformed space spanned by the two PCs (the two principal components t(1) and t(2)). Capillary phase heat-treated wood was separated from untreated wood by the PCA. Birch sapwood, capillary phase heat treated, forms a separate group with a gradual change toward negative t(1) and t(2) values (Fig. 2). Treated Scots pine and Norway spruce, both sapwood and heartwood, showed a separate group with a common gradual direction upwards to the left, low t(1) and high t(2) values. All the scores related to untreated wood, except untreated pine heartwood, indicate a common group, low and furthest to the right. Untreated pine heartwood scores indicate a separate group above the other untreated wood materials (Fig. 2).

Birch sapwood showed a different gradual change in comparison with that of pine and spruce for capillary phase heat treatment in the first PCA model above (Fig. 2). Consequently, the wood types were then evaluated in separate models for the PCA (Fig. 3a, b, 4a and b). At this stage in the multivariate analysis, it was also interesting to evaluate the relation between variables and responses and also their influence on the scores in loading plots. The loading plots show the strength and the relation of the variables and responses to the principal directions t(1) and t(2). The corresponding score and loading plot can be evaluated complementarily.

The PCA model for birch sapwood alone had an R^2 of 0.86 and Q^2 of 0.53. The second PC was not significant according to SIMCA. This model showed a pattern in the

Table 2. Colour difference (ΔE^*_{ab}) for capillary phase heat-treated wood. Measurements on 3 mm dried planed samples. Average values on top, based on 26–30 samples. Half of the 95% confidence interval below, assuming normal distribution
Tabelle 2. Farbunterschiede (ΔE^*_{ab}) der in kapillarer Phase hitzebehandelten Hölzer. Messungen an 3 mm starken getrocknetzen und gehobelten Proben. Mittelwerte aus 26–30 Proiben und halbes 95% Konfidenz-Intervall unter Annahme einer Normalverteilung

Colour Variable	Species	Wood-type	Temp/ °C	Days			
				0	1	3	6
ΔE^*_{ab}	Pine	Sap	65 °C	0.0	0.8	1.6	2.2
					0.1	0.2	0.1
			80 °C	0.0	1.9	4.0	5.8
					0.2	0.2	0.2
			95 °C	0.0	4.3	8.2	11.7
					0.2	0.6	0.4
		Heart	65 °C	0.0	2.1	3.2	4.5
					0.4	0.5	0.6
			80 °C	0.0	3.4	4.6	6.8
					0.5	0.5	0.6
			95 °C	0.0	6.2	9.6	11.9
					0.9	0.8	0.8
	Spruce	Sap	65 °C	0.0	0.9	1.8	2.6
					0.2	0.3	0.2
			80 °C	0.0	2.3	4.2	6.5
					0.2	0.3	0.3
		Heart	65 °C	0.0	1.3	1.6	2.5
					0.3	0.3	0.5
			80 °C	0.0	2.2	4.2	7.0
					0.4	0.5	0.5
	Birch	Sap	65 °C	0.0	13.1	14.8	15.7
					0.7	0.7	0.7
			80 °C	0.0	8.3	10.6	12.8
					1.3	1.4	1.2
			95 °C	0.0	11.6	16.0	20.4
					1.2	1.4	1.5

Table 3. Colour co-ordinates L*, C* and h for capillary phase heat treated wood. Measurements on 3 mm dried planed samples. Average values on top, based on 26–30 samples. Half of the 95% confidence interval below, assuming normal distribution
Tabelle 3. Farbkoordinaten L*, C* und h für in kapillarer Phase hitzebehandelten Hölzer. Messungen an 3 mm starken getrocknetzen und gehobelten Proben. Mittelwerte aus 26–30 Proben und halbes 95% Konfidenz-Intervall unter Annahme einer Normalverteilung

Colour Variable	Species	Wood type	Temp/ °C	Days			
				0	1	3	6
L*	Pine	Sap	65 °C	84.3 0.3	84.5 0.3	84.4 0.3	84.2 0.2
			80 °C	84.3 0.3	83.9 0.3	82.3 0.3	81.0 0.3
			95 °C	84.0 0.3	81.6 0.4	78.0 0.4	74.8 0.5
		Heart	65 °C	84.3 0.4	82.8 0.4	82.1 0.5	80.9 0.5
			80 °C	84.2 0.4	81.6 0.4	80.6 0.6	78.8 0.6
			95 °C	83.7 0.4	78.6 0.6	75.9 0.6	74.4 0.8
C*		Sap	65 °C	21.2 0.2	21.2 0.3	21.8 0.3	22.3 0.2
			80 °C	21.3 0.2	22.4 0.2	24.3 0.2	25.8 0.3
			95 °C	21.4 0.2	24.6 0.2	27.3 0.2	28.6 0.2
		Heart	65 °C	22.7 0.4	23.3 0.4	23.8 0.4	24.5 0.3
			80 °C	22.7 0.3	24.1 0.2	25.1 0.3	26.6 0.3
			95 °C	23.0 0.4	26.1 0.3	28.3 0.3	30.2 0.4
h		Sap	65 °C	76.7 0.4	77.8 0.4	79.7 0.4	81.0 0.3
			80 °C	76.9 0.4	80.1 0.4	80.6 0.3	80.2 0.3
			95 °C	76.4 0.4	80.2 0.4	78.3 0.2	77.5 0.3
		Heart	65 °C	81.0 0.7	78.2 0.7	76.7 0.9	75.4 0.9
			80 °C	81.1 0.6	77.5 0.9	77.2 1.0	76.9 0.9
			95 °C	78.7 0.6	75.5 0.8	77.1 0.5	77.4 0.6
L*	Spruce	Sap	65 °C	83.4 0.4	83.2 0.4	82.5 0.4	82.2 0.5
			80 °C	84.0 0.2	83.1 0.3	81.7 0.3	79.4 0.4
		Heart	65 °C	84.8 0.4	84.0 0.4	83.9 0.3	83.3 0.4
			80 °C	84.9 0.4	83.5 0.4	81.9 0.5	79.1 0.4
C*		Sap	65 °C	19.1 0.3	19.3 0.2	20.3 0.2	21.1 0.3
			80 °C	19.0 0.3	20.9 0.2	22.2 0.2	23.4 0.3
		Heart	65 °C	18.7 0.4	19.2 0.3	19.8 0.4	20.5 0.4
			80 °C	19.0 0.3	20.7 0.3	21.9 0.3	22.9 0.2
h		Sap	65 °C	78.7 0.5	79.0 0.4	79.0 0.4	79.9 0.5
			80 °C	79.8 0.3	81.3 0.3	81.2 0.3	78.3 0.4
		Heart	65 °C	81.0 0.5	80.7 0.4	81.6 0.3	80.7 0.3
			80 °C	81.0 0.4	81.0 0.4	80.4 0.4	78.2 0.2
L*	Birch	Sap	65 °C	85.6 0.4	73.7 0.7	71.9 0.7	71.0 0.7
			80 °C	81.3 1.1	74.0 0.6	71.8 0.7	69.5 0.7
			95 °C	81.1 1.2	70.3 0.8	66.0 0.7	61.4 0.6
C*		Sap	65 C	16.6 0.4	21.4 0.5	21.0 0.4	21.0 0.4
			80 °C	19.3 0.8	21.3 0.4	21.1 0.5	20.5 0.3
			95 °C	19.5 0.8	20.1 0.4	20.0 0.2	20.6 0.2
h		Sap	65 °C	82.0 0.4	76.2 0.4	73.2 0.5	71.1 0.4
			80 °C	78.9 0.8	73.4 0.5	69.4 0.8	66.4 0.9
			95 °C	77.7 1.0	67.2 0.7	62.6 0.9	63.3 0.5

score plot (Fig. 3a) where treatment time and temperature almost orthogonally span the distribution of the scores (Fig. 3b). In the score plot, 3b, time increases toward low t(1) and t(2), whereas temperature increases toward low t(1) and high t(2) values. The loading plot also showed that C* and ΔE^*_{ab} correlated positively, and L* and h correlated negatively with treatment time. Treatment temperature showed a low influence on the coloring process of treated Birch sapwood. Treatment temperature correlated weakly negatively with L* and h (Fig. 3b).

For the PCA model of Scots pine and Norway spruce, R^2 was 0.82 and Q^2 was 0.52, using two PCs. The second PC was not significant according to SIMCA. The score plot (Fig. 4a) showed no possibility of separating the species into groups. The scores for sap- and heartwood of both pine and spruce interfere, and a common pattern is formed. The corresponding loading plot, Fig. 4b, showed that increased treatment time is in the direction of increasing t(1) and t(2) values and increased treatment temperature is in the direction of increasing t(1) and decreasing t(2) values (Fig. 4a). Treatment time series for some temperatures showed curvilinear shapes in the score plot (Fig. 4a). Heartwood of Scots pine showed curvilinear series with the bow in opposite directions of its sapwood. For Scots pine and Norway spruce, L* and h were negatively correlated, and C* was positively correlated to treatment temperature, as they also were for treatment

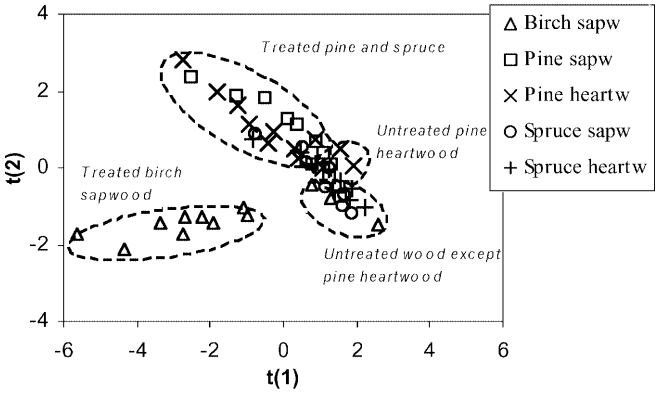

Fig. 2. Score-plot from a Principal Component Analysis (PCA) of capillary phase heat-treated wood. t(1) and t(2): the first and second Principal Component (PC). Six variables were used in the PCA: Treatment time and temperature, Lightness (L*), Chroma (C*), hue (h) and colour difference (ΔE^*_{ab}). 52 observations were used in the PCA, based on the measurement of 5 materials. Capillary phase heat treatment of wood formed separated groups in the PCA from untreated wood. Treated birch (*Betula pubescens*) showed a separate group and treated sapwood and heartwood of both Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*) formed a separate group. Untreated heartwood of Scots pine indicated a separate group

Bild 2. Ergebnisse der PCA (Analyse der Hauptkomponenten) für in kapillarer Phase hitzebehandeltes Holz. t(1) und t(2): die erste und zweite Hauptkomponente. Sechs Variablen wurden für die PCA benutzt: Behandlungsdauer, und Temperatur, Helligkeit (L*), Sättigung (C*), Farbton (h) und Farbdifferenz (ΔE^*_{ab}). 52 Beobachtung aus Messungen an 5 Materialen wurden für die PCA verwendet. Behandeltes Birkenholz bildete eine getrennte Gruppe, außerdem Splint- und Kernholz von Kiefer und Fichte. Auch unbehadeltes Kiefernkernholz deutete eine getzrennte Gruppe an

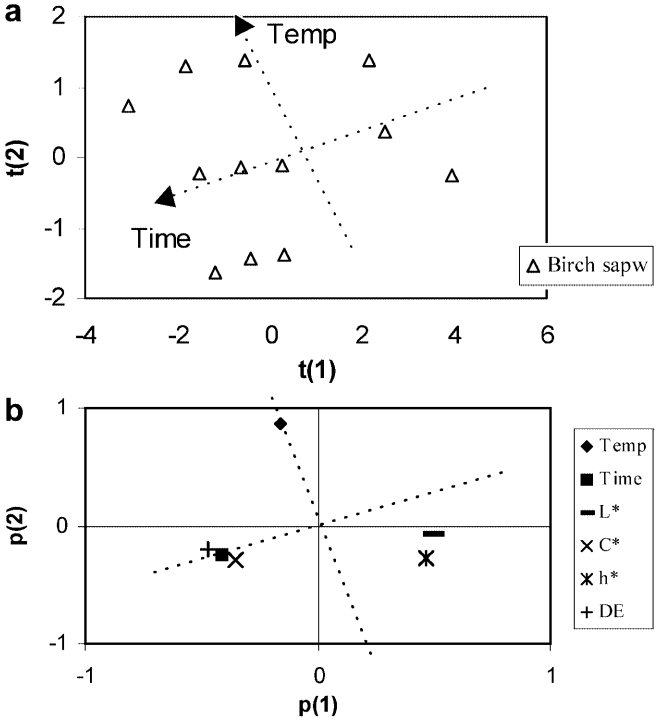

Fig. 3a, b. Score plot and loading plot from a Principal Component Analysis (PCA) of capillary phase heat-treated birch sapwood. t(1) and t(2): the first and second Principal Component (PC). p(1) and p(2) loading components. Six variables were used in the PCA: Treatment time and temperature, Lightness (L*), Chroma (C*), hue (h) and colour difference ($DE = \Delta E^*_{ab}$). 12 observations were used in the PCA. A colour response pattern was present (*a*) with directions for treatment time and temperature. Treatment time showed a stronger influence than temperature on the colour responses, 3b

Bild 3a, b. Ergebnisse und Bewertungs-Grapgh der PCA für in kapillarer Phase hitzebehandeltes Holz. t(1) und t(2): die erste und zweite Hauptkomponente. p(1) und p(2) Bewertungskomponenten. Sechs Variablen wurden für die PCA benutzt: Behandlungsdauer, und Temperatur, Helligkeit (L*), Sättigung (C*), Farbton (h) und Farbdifferenz (ΔE^*_{ab}). 12 Beobachtung wurden für die PCA benutzt. (*3a*) Muster der Farbantwort mit Richtungen für Dauer und Temperatur der Behandlung; (*3b*) die Farbantwort zeigt einen größeren Einfluß der Behandlungsdauer gegenüber der Temperatur

time, except that h correlated weakly for treatment time. Both treatment temperature and time have an influence on the coloring process of Scots pine and Norway spruce sapwood and heartwood.

4 Discussion

The capillary phase heat treatment induced color changes for the species investigated. There was a difference for the color change for birch compared with both Scots pine and Norway spruce (Chapter 3.1) and also the multivariate analysis in Chapter 3.2 and Fig. 2 (PCA). Birch responded faster and more markedly in color difference (ΔE^*_{ab}) than pine and spruce (Chap. 3.1 and Table 2). This difference in color change was believed to be associated with the general difference in hemicellulosic content between softwoods and hardwoods, and the often characteristic composition of phenolic extractives for certain species (Hon and Shiraishi 1991, Fengel and Wegener 1984).

When the color co-ordinates were analysed, different types of responses were found. Birch sapwood decreased in lightness (L*), darkened, for increased treatment time and temperature, and this darkening was large compared with Scots pine and Norway spruce. Birch sapwood showed generally an increase in chroma (C*) (increased saturation) when comparing treated with untreated birch. Despite different treatment time and temperature used, no general difference in chroma was observed for treated birch sapwood. Scots pine and Norway spruce generally increased in chroma with increased treatment time and temperature. Birch decreased considerably in hue (h) (became redder) while pine and spruce showed small changes, both with increased and decreased hue (reddening and yellowing) during treatment (Chapter 3.1 and Table 3).

Interestingly, the multivariate analysis showed that all untreated materials, pine sapwood, spruce sapwood and heartwood and also birch sapwood, formed a separate group in the score plot (Fig. 2). In reality this is also what is found when regarding untreated clearwood of birch, pine and spruce – mostly a similar pale yellow surface. However, pine heartwood, untreated, seemed to form a separate group (Fig. 2) for the untreated materials inves-

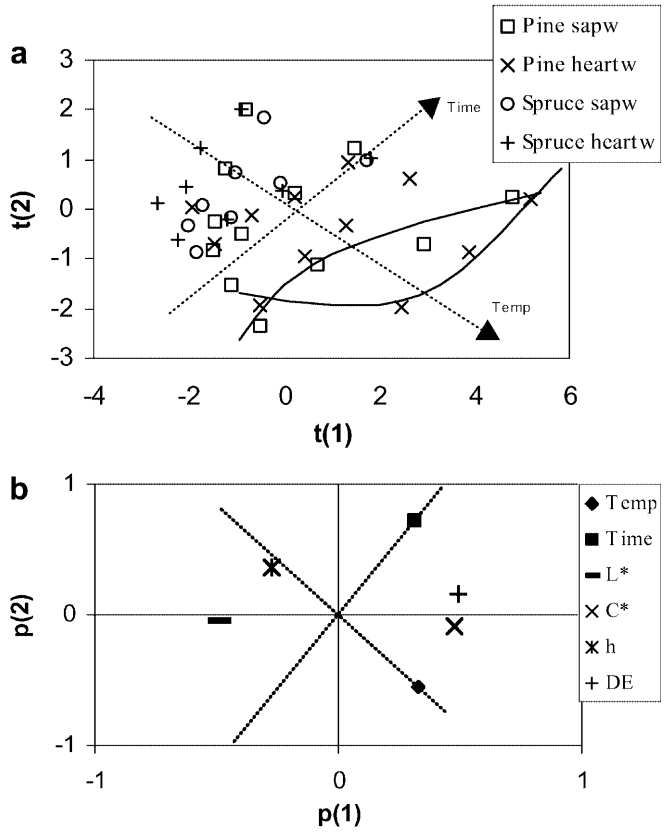

Fig. 4a, b. Score plot and loading plot from a Principal Component Analysis (PCA) of capillary phase heat-treated Scots pine (Pinus sylvestris) and Norway spruce (Picea abies). t(1) and t(2): The first and second Principal Component (PC). p(1) and p(2) loading components. Six variables were used in the PCA: Treatment time and temperature, Lightness (L*), Chroma (C*), hue (h) and colour difference (DE = ΔE^*_{ab}). 40 observations were used in the PCA, based on the measurement of 4 materialclasses. Curvilinear time series for different temperatures were present for the colour responses (*4a*). Scots pine heartwood indicated a subgroup by having curvilinear series with the bow in the opposite direction of sapwood (*4a*). Treatment time and temperature showed an equally strong influence on the colour responses (*4b*)
Bild 4a, b. Ergebnisse und Bewertungs-Grapgh der PCA für in kapillarer Phase hitzebehandeltes Kiefern- und Fichtenholz. t(1) und t(2): die erste und zweite Hauptkomponente. p(1) und p(2) Bewertungskomponenten. Sechs Variablen wurden für die PCA benutzt: Behandlungsdauer, und Temperatur, Helligkeit (L*), Sättigung (C*), Farbton (h) und Farbdifferenz (ΔE^*_{ab}). 40 Beobachtung aus Messungen an 4 Materialgruppen wurden für die PCA benutzt. Gekrümmte Zeitserien ergaben sich für verschiedene Temperaturen (*4a*). Kiefernkernholz zeigt eine Untergruppe zum Splintholz, weil die Krümmung beider Serien entgegengestezt ist. Die Behandlungen Dauer und Temperatur zeigten einen etwa gleich großen Einfluß auf die Farbantwort (*4b*)

tigated. This difference is not easy to discover by visual examination. Pine heartwood is known to have a different composition of phenolic extractives from pine sapwood (Fengel and Wegener 1983), and many species are reported to have higher concentrations of phenolic extractives involved in color appearance in the heartwood than in the sapwood (Dellus et al. 1997, Burtin et al. 1998).

When comparing Scots pine and Norway spruce, generally small differences in color changes were found (Chap. 3.1 and 3.2). In the multivariate score plots (Fig. 2 and 4 (PCA)), treated pine and spruce formed an overlapping group with a common direction upon capillary phase heat treatment.

Scots pine heartwood, untreated, showed higher hue, more yellow, and higher chroma, saturation than pine sapwood (see chapter 3.1 and Table 3). This difference was also found in the PCA (see above). During capillary phase heat treatment at 95 °C, pine heartwood indicated a shift in hue from reddening to yellowing while pine sapwood indicated the opposite shift with increase in time (Table 3). This difference in red-yellow shift for Scots pine sap- and heartwood has not been found reported in any earlier work. The shifts found are probably an indication of stepwise reactions producing altered and degraded colored compounds. Pine heartwood and sapwood treated at 95 °C converge in hue at 6 days (Table 3). It is assumed that the treatment has produced a similar final content of chromophores for this temperature.

For Norway spruce sapwood and heartwood another type of behavior in hue was found. Untreated spruce heartwood showed a more yellowish surface, higher hue, than sapwood for treatments at 65 °C and 80 °C (Table 4). When spruce was treated for 6 days, each treatment temperature seems to have caused convergence in hue for sapwood and heartwood of spruce wood. It is known that sap- and heartwood have different contents of phenolic extractives (Hon and Shiraishi 1991, Fengel and Wegener 1984) and it is assumed that the treatment has produced a similar final content of chromophores in the sap- and heartwood for each treatment temperature. This was the same assumption as for pine, but only when treated at 95 °C.

From the multivariate analysis (PCA), time was found to be the dominating factor for the color change of birch in the capillary phase heat treatment (Fig. 3b). Treatment temperature showed a weak influence compared with time for birch sapwood. For Scots pine and Norway spruce both treatment time and temperature showed influence on the color responses (Fig. 4b) except for hue, which was influenced mostly by temperature. Thus, both time and temperature were found to be important influences on color changes occurring in the capillary phase heat treatment, or in other words during the first part of drying, the capillary phase.

The rate of decrease in lightness (L*), darkening rate, was found to increase in general around 80 °C for Scots pine, Norway spruce and birch sapwood (Table 3). Treatments at 65 °C and 80 °C showed much lighter wood and slower darkening with increasing time than treatments at 95 °C. This indication of a transition in accelerated darkening was believed to be associated mainly with an accelerating degradation of hemicellulose, which can be involved in the production of colored compounds. Since capillary water was present, the degradation was assumed to be mainly hydrolytic (Fengel and Wegener 1984).

The analysis of the color variation revealed that birch has in general more inhomogeneous color than Scots pine and Norway spruce (Table 3). Of the color co-ordinates L*, C* and h, C* showed the smallest color variation while L* and h mostly showed larger and similar color variation for

all materials. However, pine heartwood showed a large color variation of hue in general compared with pine sapwood and spruce sap- and heartwood. The variation for hue of pine heartwood and birch sapwood showed similar results (Table 3).

The color variation for the color difference (ΔE^*_{ab}) was also in general found to be dependent on the temperature used in the capillary phase heat treatment (Table 2). With increasing temperature, a more inhomogeneous color of the wood was generated. This increased inhomogeneous color was assumed to be due to varying concentrations of phenolic extractives involved in the coloring process for a material, acting like a magnifier, when the color change is dependent on temperature. No general influence of treatment time on variation of the color responses was observed. However, Scots pine sap- and heartwood indicated an increase in variation for the color responses with increasing treatment time.

Although the major average color values presented were well fitted in the general trends and patterns, some deviating average color values were observed. For instance, (ΔE^*_{ab}) values for birch sapwood showed larger corresponding values at 65 °C than at 80 °C treatment, which was contrary to the general trend in the data (Table 2). Moreover, untreated sample sets of the same material were found to have separated average 95% confidence intervals despite the fact that they should have overlapped if the intervals were considered reliable. See Table 3 (hue for 0 days treatment of pine heartwood, hue for 0 days treatment of spruce heartwood and lightness, chroma and hue for 0 days treatment of birch sapwood). These deviations were believed to be mainly caused by artefacts of the wood not found in the visual selection, such as infested wood, juvenile wood, reaction wood, mixtures of heart- and sapwood etc. Besides these suspicions, these color deviations can indicate that the obtained 95% confidence average intervals do not represent a reliable color variation for a large population, but merely reflect the color variation for the wood materials used in the investigation. A larger population of boards, i.e. many more trees, would be needed to further investigate these matters.

An acidic smell was noticed from many Scots pine and Norway spruce wood samples during capillary phase heat treatment. This was particularly distinct for pine heartwood and treatment at longer times and higher temperatures. Moreover, corrosion of the metal lids used with the jars occurred and the degree of corrosion seemed to be related to the intensity of the acidic smell. It is known that degradation of hemicellulose can produce acetic acid, sometimes called autohydrolysis (Tjerdsmaa et al. 1998, Hon and Shiraishi 1991). For birch sapwood a sweet and somewhat sour smell was noticed during treatment, and seemed to be more intense for longer times and higher temperatures.

The multivariate approach, using principal component analysis (PCA) was found powerful to investigate complex data sets with correlation among the variables and responses. The PCA complemented and often confirmed the other results in this work.

In future work it would be interesting to test new similar data sets to investigate the reliability of the color response results obtained. May be species and types of wood (sap- and heartwood) are not satisfactory descriptors for dealing with color of wood in a scientific sense. This work has dealt only with the phase of drying where capillary water and unbound water (in the cell walls) were present. Studying the color responses of wood for treatments resembling kiln drying would be interesting, especially in relation to the results obtained in this work as guidance and for comparison. To understand more about the background of the color responses, a chemical analysis could be helpful. An extractive analysis would be suitable. One important issue is the role of degradation of hemicellulose associated with the color change for capillary phase heat treated wood. Degradation of hemicellulose can effect the wood strength.

5 Conclusions

In the capillary phase heat treatment, time was found to be more important than temperature for the color responses for birch. For pine and spruce, treatment time and temperature showed similar importance, except for pine, where hue was mostly influenced by temperature.

Birch sapwood showed a different color change compared with Scots pine and Norway spruce when capillary phase heat-treated. Birch sapwood became much redder and darker while Scots pine and Norway spruce became somewhat darker and more saturated.

An accelerated darkening was observed for all materials investigated when approximately 80 °C was exceeded in the capillary phase heat treatment.

Scots pine and Norway spruce showed, in general, similar color responses, except for the untreated cases where pine heartwood was more saturated in color.

Scots pine, capillary phase-heat treated at 65 °C and 80 °C, showed red-yellow shift and yellow-red shift for sap- and heartwood respectively as time elapsed. Indications of existing local maximal yellow and red appearances were found around 1 day for pine sapwood and heartwood when treated at 95 °C.

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III

WOOD COLOR CONTROL DURING KILN-DRYING

BROR SUNDQVIST

ABSTRACT

The coloration of wood during drying in a laboratory kiln was investigated and modelled using multivariate techniques: principal component analysis and partial least squares (PLS). The wood species included were Scots pine (*Pinus sylvestris* L.), Norway spruce (*Picea abies* [L.] H. Karst), and birch (*Betula pubescens* Ehrh.). Color changes were determined at the unplaned surface and after planing off 1 and 3 mm from the surface using a photoelectric colorimeter. Color parameters presented were lightness, chroma, and hue. PLS models for the color for each species was a useful method and the results indicated possibilities for future batch-color control of kiln-drying. The coloration of the wood was equally intense during the kiln-drying when free water was present (early part) compared to when no free water was present in the wood (late part). The coloration was most intense at the wood surface, however, planing removes the major coloration induced by drying. Color homogeneity was not found to be affected by raised temperatures during drying.

In industrial wood processing, artificial wood drying is often required to achieve a fast and good quality result. Many different drying techniques are used, and the basic principles are circulation with hot air and steam, vacuum, microwaves, etc.

Kiln-drying is a process using heat and steam with air circulation; temperatures have generally increased in recent decades, mainly to speed up the process. This increase has lead to wood with somewhat changed properties, such as lower hygroscopicity, increased brittleness, darker color, etc. (13).

Besides drying, heat treatments in various forms have been used to change the properties of wood, such as rot resistance and color. For example, steaming has been traditionally used to enhance the natural color of walnut (1) and black locust (11). Application of heat and steam has been shown to increase the durability of wood against biodeterioration (4,15,16).

The kiln-drying process of today is often governed by schedules that regulate the kiln parameters needed (19). These traditional schedules are mainly based on the theory of diffusion flow of water. The diffusion is in some models considered to control the drying rate independent of the moisture content (MC) in the wood. However, recent studies on drying have shown that diffusion is not the predominant mechanism when free water (capillary water) is present in the wood structure. In this phase, heat and mass transfer control the drying rate (12,19).

Wood exposed to heat and moisture at the same time often shows color changes (6). The occurrence of free water is thought to cause color changes due to hydrolysis and migration of color precursors (2,8). The influence of free water on color changes that develop during kiln-drying has been recently studied (14). However, in the present work, we report on an attempt to divide the drying process into two phases, when free water is present and when free water is not present (below and above the fiber saturation point). These are expressed as the capillary phase and diffusion phase, respectively, in this work. This was done in order to be able to model the coloration by more easily defining the parameters of the kiln climate and to determine the effect of each individual phase on coloration.

MATERIAL AND METHODS

Green boards of Scots pine (*Pinus silvestris*), Norway spruce (*Picea abies* [L.] H. Karst) and birch (*Betula pubescens* Ehrh.) were taken from small-diameter logs from sawmills near Skellefteå,

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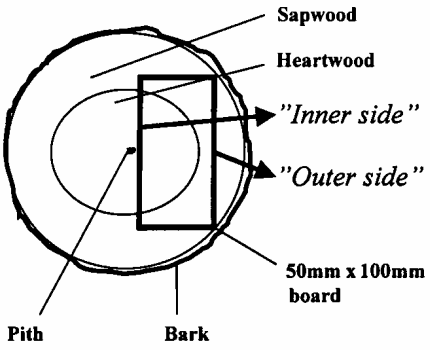

Figure 1. — Schematic view of position in cross section when taken from a small-diameter log, 50 mm by 100 mm board. Two sides of the board are defined: outer side and inner side.

Sweden, in January to April of 2000 (**Fig. 1**). For each species, 21 to 26 boards 4.5 ± 1 m long (50 by 100 mm for spruce and pine and 38 by 100 mm for birch) containing both sapwood and heartwood were selected. Each board was cut into sections of 0.7 to 0.8 m, which were marked according to individual full-length board, section, and species. The board sections were divided into 9 groups of 30 pieces and stored outdoors, covered with snow, to prevent drying.

For each species, the experiments were mainly designed to have drying runs that could be comparative with each other and to emphasize the effect of the two phases (capillary and diffusion) on coloration. This was done by distributing the sections from each board and species to be included in all three drying runs and by drying with chosen temperatures for each phase (**Table 1**). Since the color induced by drying is considered to be strong when free water is present (8,14), lower temperatures were chosen in the capillary phase of drying (**Fig. 2** and **Table 1**). Due to the same consideration, higher temperatures were chosen in the diffusion phase. This drying method is based on novel studies by Morén (12).

The laboratory kiln is based on air circulation, with heating, steaming, and ventilation (**Fig. 3**). The kiln, made of stainless steel, has dimensions of approximately 0.3 m high and 0.8 m wide across the airflow, and 1.4 m long in the direction of airflow. This made it possible to run 30 samples in 3 layers for each drying run. Stickers approximately 20 mm thick were used at the bottom, in be-

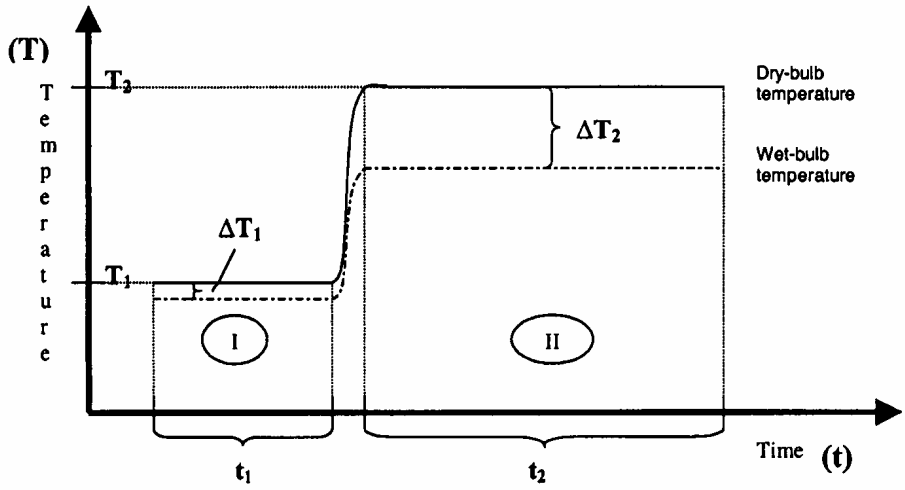

Figure 2. — The drying design. Schematic plot. The capillary phase (I). The diffusion phase (II). T = dry-bulb temperatures; ΔT = wet-bulb depression temperatures; t = times elapsed. Index 1 belongs to the capillary phase and index 2 to the diffusion phase.

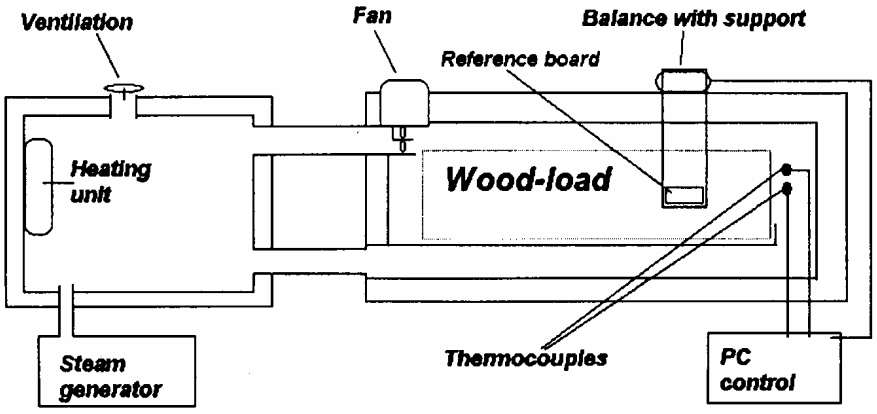

Figure 3. — The laboratory drying kiln. Schematic view. To the left is the climate generator. To the right is the kiln. The principles are circulation of hot and humid air from a heating unit and a steam generator. The airflow is transverse to the direction of the boards. A computer using measurements from thermocouples controls the dryer. The computer also records the climate via thermocouples and the weight of a reference board using a balance with support.

TABLE 1. — Experimental parameters.[a]

Species	Run no.	t_1	T_1	ΔT_1	t_2	T_2	ΔT_2
		(hr.)	------ (°C) ------		(hr.)	------ (°C) ------	
Pine	1	47	48	4	60	84	18
	2	49	65	4	37	82	17
	3	51	82	6	37	103	16
Spruce	4	20	63	3	38	92	17
	5	25	73	4	35	100	16
	6	21	82	4	33	111	19
Birch	7	37	40	4	58	69	17
	8	37	52	4	57	68	15
	9	40	57	3	54	85	17

[a] t_1 = time elapsed in capillary phase; T_1 = dry-bulb temperature in capillary phase; ΔT_1 = wet-bulb temperature in capillary phase; t_2 = time elapsed in diffusion phase; T_2 = dry-bulb temperature in diffusion phase; ΔT_2 = wet-bulb temperature in diffusion phase; nine drying runs.

TABLE 2. — Color results for Scots pine, Norway spruce and birch subjected to kiln drying.[a]

Species	Run no.	Planing depth/mm	Outer side			Inner side		
			L*	C*	h	L*	C*	h
Pine	1	0	80.9 (0.2)	25.8 (0.3)	81.9 (0.2)	78.5 (0.4)	25.9 (0.3)	78.7 (0.4)
	2		**77.4 (0.3)**	**27.8 (0.4)**	**80.6 (0.3)**	**77.7 (0.4)**	**26.6 (0.4)**	**78.4 (0.3)**
	3		**73.0 (0.3)**	**29.6 (0.3)**	**79.3 (0.2)**	**73.4 (0.7)**	**29.4 (0.6)**	**75.7 (0.6)**
	1	1	83.9 (0.3)	21.9 (0.2)	81.8 (0.3)	83.4 (0.2)	22.7 (0.2)	80.6 (0.4)
	2		**81.3 (0.4)**	**24.0 (0.2)**	**80.5 (0.2)**	**82.9 (0.3)**	**23.3 (0.2)**	80.6 (0.4)
	3		**77.4 (0.4)**	**26.3 (0.2)**	**78.7 (0.3)**	**81.1 (0.2)**	**26.1 (0.2)**	80.3 (0.4)
	1	3	83.7 (0.3)	22.3 (0.2)	81.7 (0.3)	83.1 (0.2)	23.5 (0.2)	80.8 (0.4)
	2		**82.4 (0.4)**	**23.3 (0.2)**	**80.6 (0.3)**	82.7 (0.3)	23.5 (0.2)	80.0 (0.4)
	3		**79.9 (0.2)**	**25.5 (0.1)**	**79.5 (0.1)**	**81.5 (0.2)**	**26.9 (0.3)**	**81.3 (0.4)**
Spruce	4	0	78.2 (0.4)	26.6 (0.2)	81.0 (0.2)	80.2 (0.3)	24.1 (0.2)	81.9 (0.3)
	5		**74.0 (1.0)**	26.6 (0.5)	**79.6 (0.3)**	**79.0 (0.3)**	**25.5 (0.2)**	**81.2 (0.2)**
	6		**70.5 (1.1)**	**28.3 (0.4)**	**77.6 (0.3)**	**75.4 (0.3)**	**27.9 (0.2)**	**78.4 (0.2)**
	4	1	82.6 (0.2)	21.6 (0.2)	81.5 (0.2)	83.7 (0.2)	20.4 (0.2)	82.1 (0.2)
	5		**81.0 (0.3)**	**22.2 (0.2)**	**80.3 (0.2)**	**83.2 (0.2)**	**20.9 (0.1)**	81.8 (0.2)
	6		**79.2 (0.2)**	**23.6 (0.2)**	**79.7 (0.2)**	**80.8 (0.2)**	**23.4 (0.2)**	**81.2 (0.2)**
	4	3	82.3 (0.2)	21.5 (0.1)	81.2 (0.2)	83.3 (0.3)	20.9 (0.2)	82.1 (0.2)
	5		**80.8 (0.3)**	**22.1 (0.1)**	**80.2 (0.2)**	**82.6 (0.2)**	**21.6 (0.2)**	81.9 (0.2)
	6		**78.7 (0.2)**	**24.2 (0.2)**	**79.7 (0.2)**	**79.9 (0.2)**	**24.8 (0.3)**	**81.0 (0.2)**
Birch	7	0	74.0 (0.3)	28.0 (0.3)	77.4 (0.3)	70.1 (0.5)	29.5 (0.4)	74.9 (0.4)
	8		**70.1 (0.5)**	27.5 (0.4)	**75.0 (0.4)**	**67.2 (0.5)**	**27.2 (0.4)**	**73.6 (0.3)**
	9		70.5 (0.4)	**26.5 (0.3)**	**76.2 (0.3)**	67.6 (0.4)	27.3 (0.3)	74.2 (0.3)
	7	1	78.7 (0.4)	18.8 (0.3)	75.3 (0.2)	74.5 (0.4)	21.0 (0.2)	73.2 (0.3)
	8		78.6 (0.3)	18.7 (0.2)	75.5 (0.2)	**75.6 (0.3)**	**19.9 (0.2)**	**72.7 (0.2)**
	9		**74.7 (0.3)**	**20.1 (0.2)**	**72.8 (0.3)**	**70.6 (0.4)**	**20.8 (0.2)**	**69.7 (0.3)**
	7	3	75.4 (0.4)	20.2 (0.2)	74.1 (0.2)	72.1 (0.4)	21.3 (0.2)	71.9 (0.2)
	8		76.1 (0.3)	**19.7 (0.1)**	73.8 (0.2)	**73.0 (0.4)**	**20.4 (0.2)**	**71.1 (0.3)**
	9		**73.6 (0.2)**	**19.3 (0.2)**	**71.5 (0.2)**	**69.4 (0.4)**	**19.9 (0.2)**	**68.4 (0.3)**

[a] L* = lightness; C* = chroma; h = hue. Boldface values denote a stepwise significant color change between drying runs. Values in parentheses are confidence intervals. All values are average values based on 70 to 150 measurements from 20 to 30 boards.

tween the layers, and on top, spaced approximately 0.7 m apart. The heating unit has a maximum power of 6 kW and the steam generator has a maximum power of 6 kW. The fan gives an air speed of approximately 2 m/sec. No cooling or dehumidification device is included, only two adjustable vent holes with diameters of 0.1 m. A software program was used to govern the control by using signals from thermocouples. The two signals are dry-bulb temperature and wet-bulb temperature.

For control of MC during drying for the entire charge, the weight of a reference board was recorded continuously (**Fig. 3**). At the start of a drying run, the MC of the reference board was estimated by reference to a slice taken from it, whose MC was calculated by weighing and drying at 103°C for 16 hours. Thus, by using the estimated MC at start and the actual weight of the reference board, the point of time for transition from capillary phase to diffusion phase was decided, as well as the final point of time for the drying run. The transition time point was set when the MC dropped to 30 percent, approximately the fiber saturation point, and the final time point was when the MC dropped to 8 percent. This was, of course, not a precise method for deciding transition and final time since the MC of the reference board represented the whole batch.

The color measurements were done after the kiln-drying with a tristimulus colorimeter, Minolta CR 310, with a measuring head 50 mm in diameter. The color system chosen was $CIEL \times C \times h$, a suitable system for industrial purposes and easy to relate to practical experience of color, lightness, saturation/chroma, and hue (7). Five measurements were performed on each side of each board for unplaned, 1 mm planed, and 3 mm planed. Each batch contained 30 boards. This gives 300 measurements for each planing depth and each batch.

By visual selection, only measurements on clearwood were included in the data, whereas measurements containing knots, dirt, mold, mixture of sapwood and heartwood etc. were excluded. The data were then statistically treated, assuming normal distribution. Average values and the corresponding 95 percent confidence intervals were calculated from the data.

Multivariate analysis, principal component analysis (PCA) and partial least squares (PLS), were done for 3-mm planed boards. The color responses at a planing depth of 3 mm are considered the most important when manufacturing furniture, joinery etc. PCA was done with SIMCA P 7.02 statistical software (Umetrics AB) (20). This is a method that calculates correlation between vari-

ables and responses in a data set, i.e., examines the data structure, using the NIPALS algorithm (9). The program presents different parameters to diagnose the data set and two important ones are R^2 and Q^2. R^2 expresses the explained variance. Close to 0, little variance is explained and close to 1 almost all. Q^2, based on cross-validation (20), expresses the predicted variance, and is often not acceptable below 0.3 and is satisfactory above 0.7. The difference between R^2 and Q^2 should in general be below 0.2 if the analysis is not to be suspected of overfitting the data set and containing unwanted noise. Results are often presented in score and loading plots. The score plots show the observations (i.e., measuring points) projected in two dimensions spanned by the principal components. The first principal component is in the direction were the data has the largest variation, the second in the direction were the second most variation of the data is and so on. The loading plots reveal the relationship between variables and/or responses in two dimensions and they are regarded as complementary to the corresponding score plots (i.e., it is possible to overlap them) (20). In an earlier and similar work, a multivariate analysis PCA was done (14).

Predictive models were made using PLS (3). This method also uses the NIPALS algorithm to investigate correlation. However, PLS in contrast to PCA also makes a linear least square fit between variables and responses and thus generates predictive models. R^2, Q^2, and plots are also used similarly in PLS as in PCA. The importance of each variable in the predictive model is presented in a "variable importance plot" (VIP), where values close to and over 1 are considered important and values less than 0.5 are considered to be of low importance.

RESULTS

In **Table 2**, all color measurements are presented as average values of each drying batch, side of the board, and planing depth. The variation around every average color value can be evaluated by regarding the half of the 95 percent confidence intervals in **Table 2** and moreover a graphic example of the variation is given in **Figure 4**. The multivariate analyses are performed using PCA and PLS, based on average color values. PLS modelling was done separately for each species.

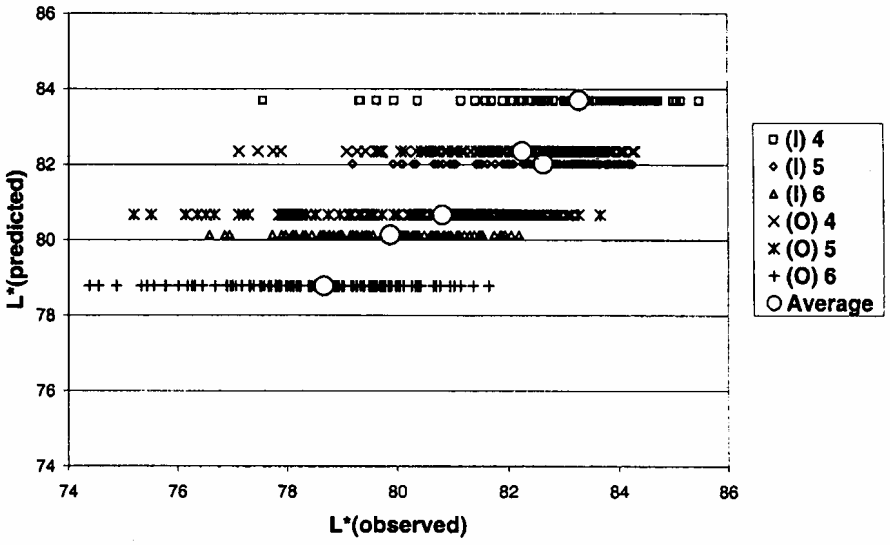

Figure 4.—Observed vs. predicted lightness (L*). Partial least-square model of kiln-dried Norway spruce, planed 3 mm. The observed individual lightness values are presented as well as the average value versus the predicted average value for each drying run and side. The explained variance (R^2) for all measurements and the average values fitted to the linear model are R^2 (all) = 0.54 and R^2 (average) = 0.96.

At first, in order to make an overview, a PCA was done on all three species involved (**Fig. 5**). In the PCA, responses are treated as variables. Eighteen observations (average color values for each species, batch and outer side or inner side) were used, only for 3 mm planed wood. A model with two principal components, $t(1)$ and $t(2)$, was generated for the data with $R^2x = 0.71$ and $Q^2 = 0.49$. From **Figure 5a**, the score plot, Scots pine, Norway spruce, and birch appear as three groups. When the different species show separate clusters, interpretation of the variables in the loading plot shows that there is low reliability and separate models are recommended (20). $w \times c$ is the weighted loading in a direction corresponding to the direction in the score-plot. However, generally pine and spruce are lighter (higher lightness), more saturated (higher chroma), and more yellowish (higher hue) than birch. Birch, as can be expected, exhibited longer drying time in the diffusion phase (higher t_2) than pine and spruce.

As a result of the PCA, predictive PLS models were created for the three species separately. The three species investigated were also treated at different conditions (**Table 1**). For these models, three variables and three responses were used: board side (0 = inner side, 1 = outer side), temperature in the capillary phase, temperature in the diffusion phase, lightness, chroma, and hue. The times for the different drying phases and the wet-bulb depression temperatures showed small variation and low precision and were therefore excluded from PLS modelling (**Table 1**). Six observations for each model/species were used (average color values for each batch and outer side or inner side).

The model for Scots pine was quite weak: $R^2x = 0.94$, $R^2y = 0.66$, and $Q^2 = 0.33$. The model is defined by (L* = lightness, C* = chroma (saturation), h = hue, Side = inner side (= 0) or outer side (= 1) of the board, T_1 = dry-bulb temperature in capillary phase; T_2 = dry-bulb temperature in diffusion phase):

$$L^* = 90.540 - 0.466 \times Side - 0.049 \times T_1 - 0.055 \times T_2$$

$$C^* = 13.458 - 0.919 \times Side + 0.051 \times T_1 + 0.087 \times T_2$$

$$h = 82.602 - 0.177 \times Side - 0.012 \times T_1 - 0.012 \times T_2$$

The variation of hue was large, which gave a bad prediction model (**Fig. 6**), and subsequently the variable Side (**Fig. 7**) for Scots pine was not successfully modelled, which then affected the total model. **Figure 8b** shows that hue is

weak and that Side is of low dependence to the other variables and responses (almost orthogonal). However, for lightness and chroma, the modelling was successful and the importance of the variables is given in **Figure 7**.

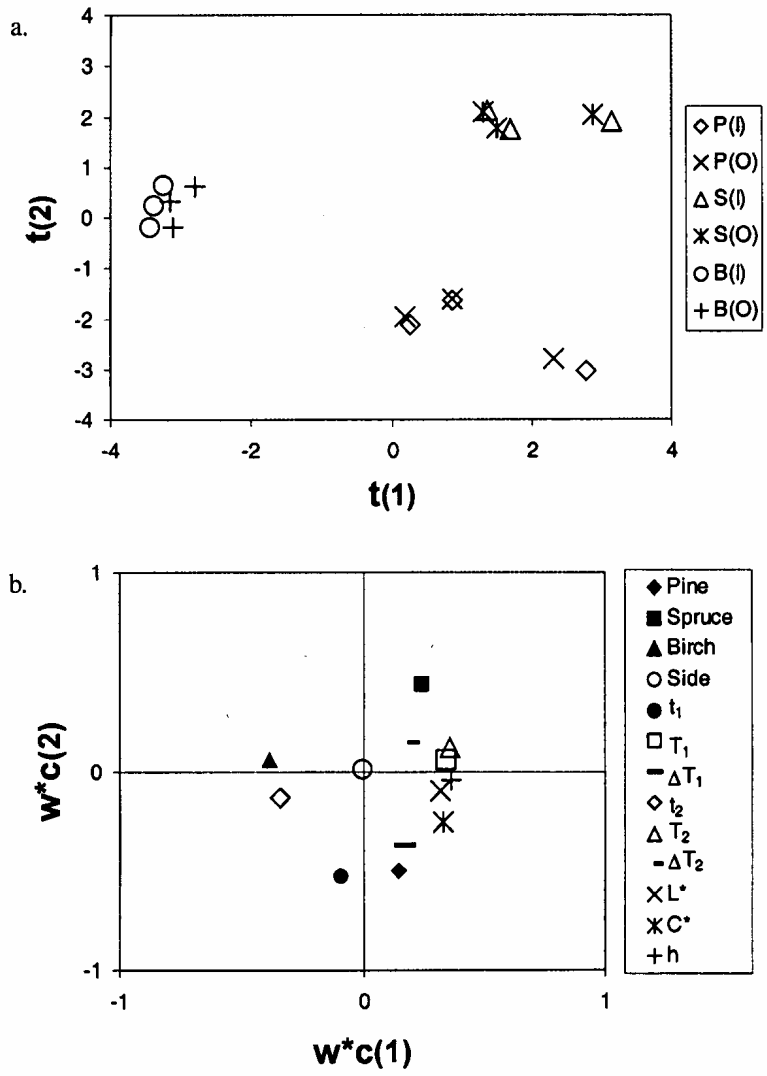

Figure 5. — Principal component analysis. Color of kiln-dried Scots pine (P), Norway spruce (S), and birch (B). 5a: score plot. In parentheses, I is inner side and O is outer side. 5b: corresponding loading plot.

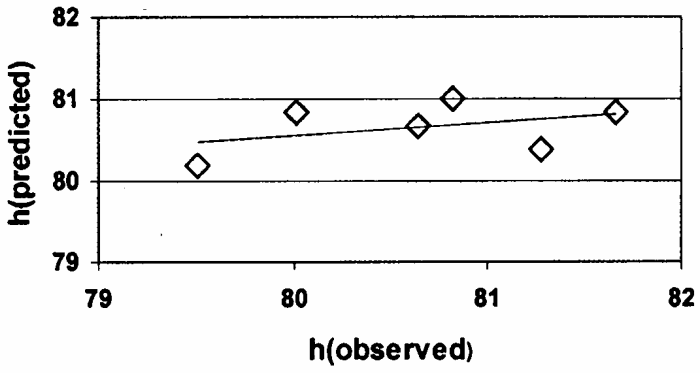

Figure 6. — Observed vs. predicted hue (h). Partial least-square color model of kiln-dried Scots pine, planed 3 mm. $R^2_Y = 0.15$: $Q^2 = 0$

Norway spruce was modelled in the same way as Scots pine, and this generated a strong model with $R^2x = 0.997$, $R^2y = 0.93$, and $Q^2 = 0.85$. The model is defined by:

$$L^* = 98.351 - 1.351 \times Side - 0.091 \times T_1 - 0.097 \times T_2$$

$$C^* = 6.898 - 0.153 \times Side + 0.086 \times T_1 + 0.091 \times T_2$$

$$h = 87.420 - 1.277 \times Side - 0.032 \times T_1 - 0.034 \times T_2$$

The importance of the variables is given in **Figure 7**. All three variables show importance to the model.

Birch was also modelled in the same way as Scots pine, and this also generated a strong model with $R^2x = 0.89$, $R^2y = 0.936$, and $Q^2 = 0.85$. The model is defined by:

$$L^* = 81.511 - 3.654 \times Side - 0.045 \times T_1 - 0.105 \times T_2$$

$$C^* = 24.428 - 0.821 \times Side - 0.043 \times T_1 - 0.023 \times T_2$$

$$h = 82.548 + 2.658 \times Side - 0.074 \times T_1 - 0.113 \times T_2$$

The importance of the variables is given in **Figure 7**.

For all species, the score plots in **Figures 8a, 9a, and 10a** show well-distributed observations according to variables and responses. Side is mainly spread in the vertical direction (outer side downwards) and the three drying batches in the horizontal direction of the plots (higher drying temperatures to the left). The loading plots reveal that Scots pine and Norway spruce become darker, redder, and more saturated when drying temperatures are raised (**Figs. 8b** and **9b**). T_1 and T_2 oppose hue and lightness while they lie close to chroma in the first component. Birch becomes darker, less saturated, and redder when temperatures are increased, T_1 and T_2 oppose lightness, chroma, and hue, mostly in the first component. Furthermore, the loading plot also reveals that color differences between outer side and inner side are distinguishable. Scots pine inner side is lighter, more saturated, and more yellow than outer side, but these loadings are weak in the second component (**Fig. 8b**) and the variable Side is of low importance (**Fig. 7**). Norway spruce inner side is clearly more yellow, lighter,

and indicated less saturated than outer side (**Fig. 9b**). Birch inner side is clearly darker and redder than outer side (**Fig. 10b**). Birch inner side is also somewhat more saturated than outer side.

The color variation within each drying run and side is presented in **Table 2** (as half of the 95% confidence intervals); **Figure 4** shows lightness for Norway spruce as one example. The variation around the average values is large when compared to differences between drying runs. The distribution around the average values were acceptably normal (**Fig. 4**) and similar distributions were obtained for the other color parameters and species.

Discussion

The multivariate methods PCA and PLS were useful for analyzing the data collected and for modelling. The PLS modelling of each species showed stable and strong models, except for pine inner side, which was difficult to model due to the small variation for hue (**Table 2, Fig. 6**). Note that in this work, average color value was used since quite a large variation was expected (5,14,18) and also found in each unique set of measurements (**Fig. 4**). The models indicate that it is possible to govern color on an industrial basis.

Both phases, where free water (capillary phase) is present in the wood and not present (diffusion phase), were similarly important for the color change. This is confirmed when comparing with an earlier color study of kiln-dried Scots pine and Norway spruce (18). Many other investigations have noted strong coloration in treatments by the presence of capillary water (14) and steam (1,11). However, in this investigation, the time for the capillary phase was approximately 1 to 2 days, which are short times for inducing strong color changes. It is therefore reasonable to assume that not only hydrolysis (2) but other mechanisms are important, since free water is not necessary for the production of colored compounds. Coloration of the wood occurs throughout the entire drying procedure.

The two sides of the board, "inner side" and "outer side" (**Fig. 1**), often showed significant color differences (**Table 2**), and this was also indicated in the PLS models by the variable Side. These color differences are similar to those found in an earlier study (14). For inner side, mainly radial surfaces were measured; for outer side, mainly tangential surfaces were measured. An earlier color study on differences between radial and tangential surfaces of Scots pine (5) showed that color differences similar to those found in this study, between inner side and outer side, can increase if compensations are made. It is reasonable to assume that outer side measurements represent sapwood and inner side measurements represent heart-

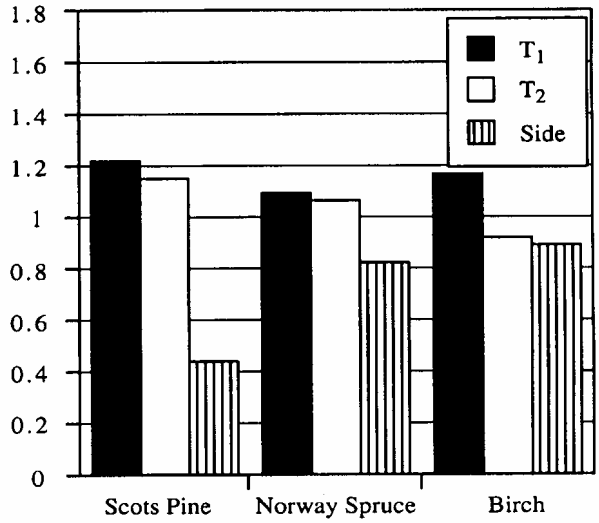

Figure 7.—Variable importance plot. Partial least-square models of kiln-dried Scots pine, Norway spruce, and birch (*Betula pubescens* Ehrh.), planed 3 mm.

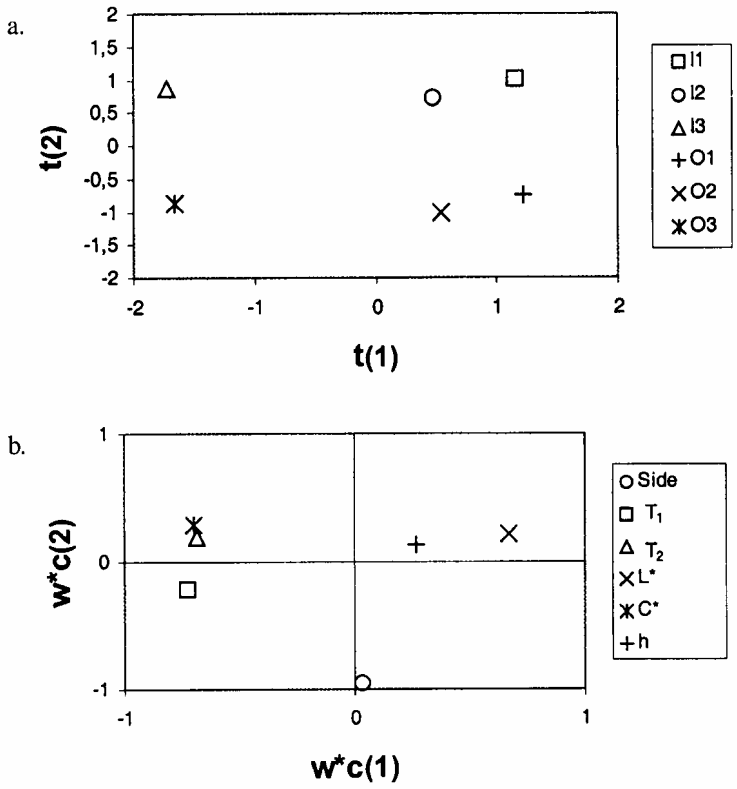

Figure 8.— Partial least-square model. Color of kiln-dried Scots pine planed 3 mm. a: score plot; b: corresponding loading plot. I is inner side and O is outer side. Numbers denote run no (Table 1).

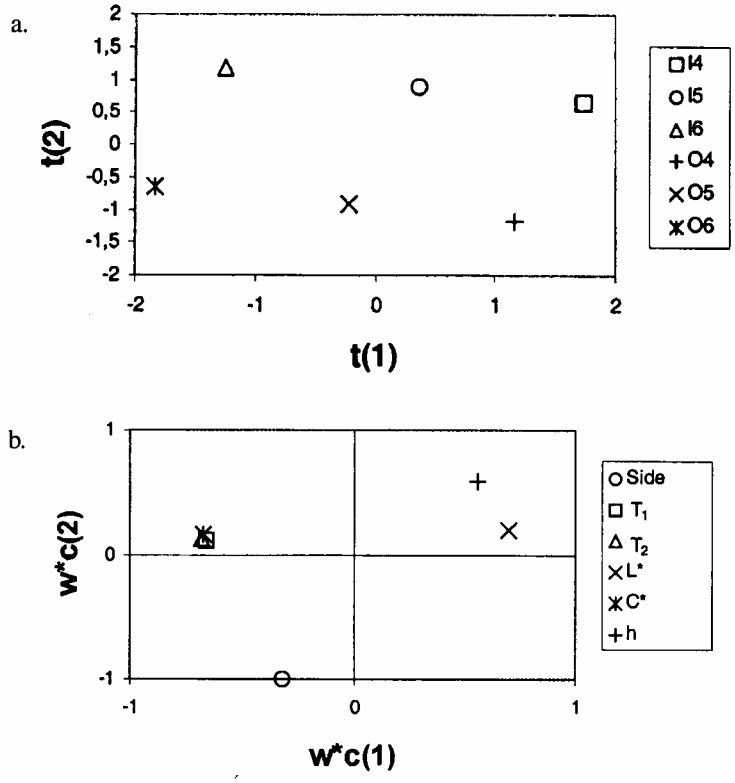

Figure 9. — Partial least-square model. Color of kiln-dried Norway spruce planed 3 mm. a: score plot; b: corresponding loading plot. I is inner side and O is outer side. Numbers denote run no (Table 1).

wood. Further measurements with verified sapwood and heartwood are needed for a final evaluation. If there is truly a difference between sapwood and heartwood, it might be considered in future manufacturing of wood products where there can be strong interest in the color of wood.

In general, the largest color changes were found when comparing unplaned and planed wood (**Table 2**). Comparatively small color changes were found between 1-mm and 3-mm planed wood. The color difference for pine and spruce between unplaned and planed wood increases with increasing dry-bulb temperatures (**Table 2**), but not for birch, studied at lower temperatures. Measurements on planed and sawn Scots pine showed differences in color (5), but these were small in comparison with the differences found in this work. Thus, the surface of dried wood can be noticeably colored, but planing removes the major color change, even when higher temperatures are used in the drying process.

Significant color changes for 1-mm to 3-mm planed wood were observed (**Table 2**). Similar observations have been made previously (18). Sometimes a brownish layer just beneath the surface appears when drying wood (8,10,14,17) but no such layer was observed in this work. This shows that planing depth can be of importance if strong qualitative demands are stated for the color. It also raises the question of whether or not an even deeper planing depth than 3 mm will show distinct color changes.

Color homogeneity, the variation around each average value, was not in general found to be dependent on the temperatures used (**Table 2, Fig. 4**). However, a general dependency of color homogeneity upon temperature was found in an earlier work where the capillary phase was studied (14).

Conclusions

Multivariate PLS modelling is a powerful tool for batch color control of kiln-dried wood. During drying, coloration was found equally strong both when free water and no free water was present in the wood.

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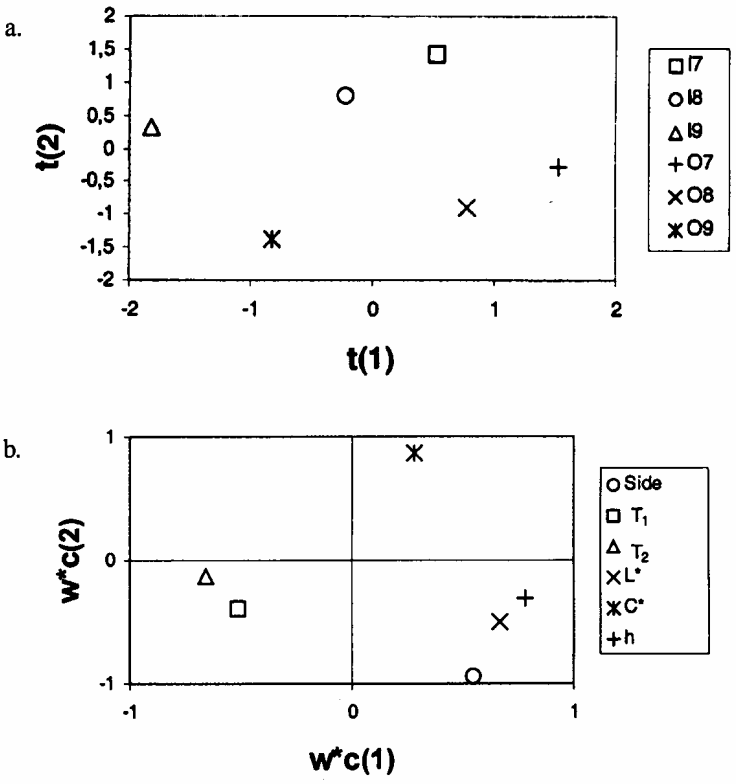

Figure 10.—Partial least-square model. Color of kiln-dried birch (*Betula pubescens* Ehrh.) planed 3 mm. a: score plot; b: corresponding loading plot. I is inner side and O is outer side. Numbers denote run no (Table 1).

IV

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The influence of wood polymers and extractives on wood colour induced by hydrothermal treatment

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Subject

A method to evaluate the influence of wood polymers (hemicellulose and lignin) and extractives on the colour of wood subjected to hydrothermal treatment is proposed. The technique was extraction and colour measurements.

Material and methods

Three matched green-wood samples, 60 mm × 55 mm × 3 mm, each of Scots pine (*Pinus sylvestris* L. *sapwood and heartwood*), both sap- and heartwood, and birch (*Betula pubescens Ehrh.*) were produced (A1, B1 and C1, Fig. 1). One series of samples were then acetone-extracted in a Soxhlet for 24 hours (A2). Acetone is considered a good solvent for most extractives (Sjöström and Alén 1999). Then they were dried at 30°C for 16 hours and colour measurements were made (A3) using a tristimulus photoelectric colorimeter (Minolta chromameter CR 310) with CIELAB colour space (Hunt 1995). This space contains the co-ordinates Lightness (L^*), green-red axis (a^*) and blue-yellow axis (b^*). The next step in the procedure was hydrothermal treatment of wood samples A and B (A4 and B4) at 95°C for 3 days, sealed in glass vessels (1000 ml) with 20 ml added water. Thereafter samples A, B and C (A5, B5 and C5) were dried at 30°C for 16 hours and colour was measured after sanding, 2 mm (Fig. 1).

The difference in colour co-ordinates, ΔL^*, Δa^* and Δb^*, between only hydrothermally treated samples and reference samples was calculated (B5–C5, Fig. 1). Differences in colour co-ordinates between extracted plus hydrothermally treated and reference samples was also calculated (A5–C5). The effect of acetone extraction on colour, of untreated samples, was calculated as the difference in colour co-ordinates compared with the reference (C5–A3). Note the reversed order for the difference since the colour was removed from the sample. From these differences in colour co-ordinates, the colour difference ΔE^*_{ab} is calculated (Eqn 2.1) (Hunt 1995) and presented in the study (Fig. 2).

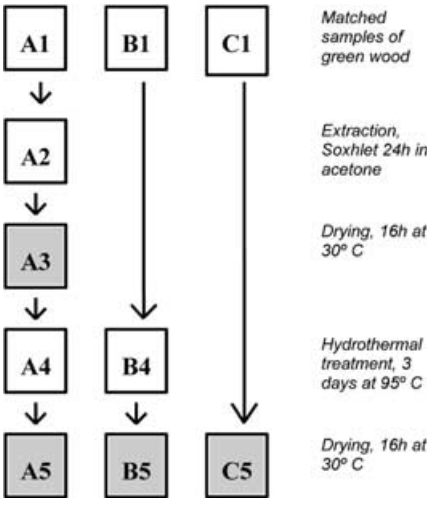

Fig. 1. Flow diagram for experimental procedure. A, B and C: matched samples of wood. Grey-shaded blocks denote colour measurement after operations stated to the right
Bild 1. Flußdiagramm der Versuchsreihe. A, B, C: waldfrische Holzproben; schattierte Blöcke bedeuten Farbmessung nach den rechts bezeichneten Operationen

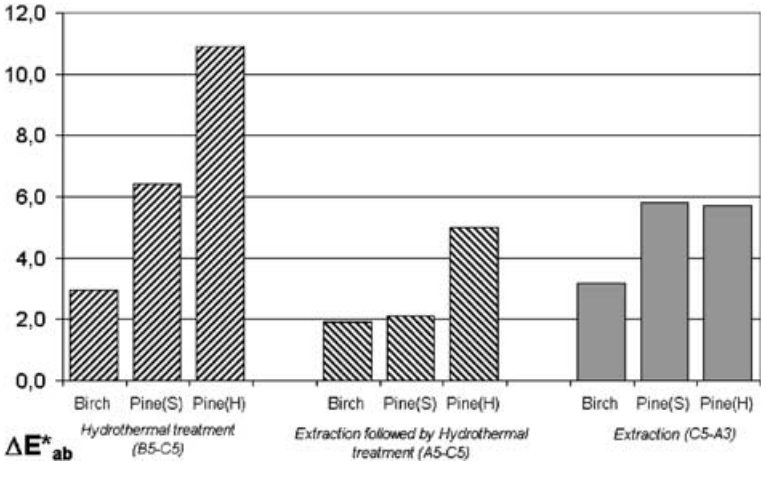

Fig. 2. Colour difference ΔE^*_{ab}, of birch and Scots pine subjected to hydrothermal treatment and extraction. To the left: hydrothermal treatment. In the middle: extraction followed by hydrothermal treatment. To the right: The effect of acetone extraction on colour of untreated samples. S in the figure denotes sapwood and H heartwood. Colour differences are based on measurements for A3, A5, B5 and C5, Fig. 1
Bild 2. Farbunterschiede ΔE^*_{ab} von Birken- und Kiefernholz nach hydropthermaler Behandlung und Extraktion. Links: nur hydrothermale Behandlung. Mitte: Extraktion und hydrothermale Behandlung. Rechts: Extaktion von unbehandeltem Holz. In Klammern: S = Splintholz; H = Kernholz. Farbunterschiede beruhen auf Messungen der Proben A3, A5, B5 und C5 (s. Bild 1)

$$\Delta E^*_{ab} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (2.1)$$

Results and discussion

The results are shown in Fig. 2 as colour difference ΔE^*_{ab} for the differences A5–C5, B5–C5 and C5–A3 (Fig. 1). Both degradation products from wood polymers (hemicellulose and lignin) and extractive compounds were indicated to be participating in the colour formation of wood subjected to hydrothermal treatment. The "standard" group of wood non-extracted and hydrothermally treated, columns to the left, show a quite large colour change (ΔE^*_{ab}) (Fig. 2). The extracted and hydrothermally treated wood, columns in the middle, show smaller but notably colour changes compared to the "standard" group. $\Delta E^*_{ab} = 2$–3 units is approximately the limit for the human eye to recognise a colour change. Thus it is indicated that degradation products of wood polymers participate in the formation of colour during treatment.

The columns to the right, show the difference between extracted and non-extracted untreated wood, mildly dried. This group show that extractives contribute notably to the natural colour and also seem to participate in the colour formation of hydrothermally treated wood. This group can be seen as compensation for the difference between the columns for hydrothermal colour and the columns for extracted plus hydrothermal colour (Fig. 2). However, note that these columns cannot be mathematically added (Eqn 2.1). For qualitative estimations, a further development of the method is needed.

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Degradation of cellulose during hydrothermal treatment of birch wood (Betula pubescens Ehrh.)

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ABSTRACT

Degradation of cellulose during heat treatment of wood has been studied. It was found that the cellulose was heavily degraded both in commercially and laboratory heat treated wood samples probably due to low pH caused by the heat treatment.

An experimental series to investigate the cellulose degradation in Birch wood at different pH levels and times at conditions for heat treatments were performed.
The treatment was done at pH 4, 7 and 10 for 3 and 6 hours at 180°C. The results show that the chosen span of pH and time for the treatment clearly affect the size of the cellulose molecules.

Cellulose degradation was studied using intrinsic viscosity measurements on α-cellulose from the samples. As a result of heat treatment, the viscosity drops from 1430 ml/g (untreated wood) to < 700 ml/g and < 350 ml/g for duration of 3 hours and 6 hours respectively.
Wood buffered in an aqueous solution at pH 4 showed a drop in the intrinsic viscosity to around 880 ml/g. A sample of commercial "Thermowood" yielded an intrinsic viscosity of 732 ml/g.

For neutral and alkaline pH the drop in viscosity is considerably less. At pH 7 and pH 10, treatment for 3 hours showed almost no effect on the degree of polymerisation and treatment for 6 h gave intrinsic viscosities of around 1000 ml/g and 1216 ml/g respectively.
There is a distinct relation between cellulose molecular size and the strength properties of wood. The decrease in cellulose length in unbuffered systems is of an extent that it may affect the strength properties of the treated wood. The experiments show that pH is an important factor to consider.

Keywords: Heat treatment, hydrothermal treatment, birch (Betula pubescens Ehrh.), intrinsic viscosity, cellulose degradation, pH, wood, molecular size

1. INTRODUCTION

Wood is a natural material used and appreciated throughout the world. Durability is a key issue for the increased use of wood in construction and outdoor applications. Heat treatment for increased durability has developed into an industrial process where temperatures in the range of 180–250ºC modify the properties of wood (Millitz and Tjeerdsma 2000; Syrjänen et al. 2000; Vernois 2000; Rapp and Sailer 2001).

These modern industrial thermal methods have clearly shown an improvement in durability, enhancement of the form stability (Thunell and Elken 1948; Buro 1954; Burmester 1973; Viitaniemi 1997; Kamden et al. 1999; Rapp and Sailer 2001) and an appealing brownish coloured wood (Bourgois et al. 1991; Viitaniemi 1997).

Along with improved durability, some negative consequences follow as a result of heat treatment; for example, a wood material that is more brittle, weaker and softer (Stamm 1956; Sanderman and Augustin 1963; Rusche 1973; Schneider 1973; Chang and Keith 1978; Viitaniemi 1997). Heat treatment results in major chemical and structural changes in the wood. Exactly how these changes relate to positive and negative effects on the properties is not well understood. Much work has been done to understand the reasons for changes occurring during heat treatment. Degradation of hemicellulose has been reported and suggested as an important factor in these changes (Sanderman and Augustin 1963; Fengel 1966; Tjeerdsma et al. 1998; Órfão et al. 1999; Zaman et al. 2000; Garrote et al. 2001). Also degradation or modifications of lignin have been reported to occur during heat treatment (Stamm 1956; Burtscher et al. 1987; Bourgois and Guyonnet 1988; Tjeerdsma et al. 1998; Garrote et al. 1999; Órfão et al. 1999).

Changes in the cellulose of wood during thermal treatment have also been reported; namely, an increase in crystallinity (Bhuiyan et al. 2000; Dwianto et al. 2000; Kubojima et al. 2001; Sivonen et al. 2002). Decrease of the average molecular cellulose size has not been reported for heat treated wood but has been found in hardboards (Klauditz and Stegman 1947; Feng et al. 2002). Heat treatment of cellulose resulted in a clear decrease in the average molecular size (Roffael and Schaller 1971).

Not much attention has been paid to the fact that organic acids are released in the process or to what their effect is on the properties of wood. It is well known that formic and acetic acid are liberated from wood during thermal treatment (Alén et al. 1985; Risholm-Sundman et al. 1998; Garrote et al. 2001; Manninen et al. 2002).

The objective of this study was to investigate how different pH levels will affect the average molecular size of cellulose in birch wood (Betula pubescens Ehrh.) during hydrothermal treatment at 180ºC. This was done using chlorite delignification and viscosity measurements on α-cellulose from hydrothermally treated birch wood. A commercial sample of heat-treated wood has also been analysed.

2. MATERIAL AND METHODS

Wood material

Green (never dried) Birch (Betula pubescens Ehrh.) approximately 30 cm in diameter from northern Sweden was used in the experiments. The wood material was stored in a freezer. Wood sawdust (approximate size 0.5 x 0.5 x 2 mm) was manually made using an ordinary handsaw. The direction of sawing was parallel to the grain.

Hydrothermal treatment

The hydrothermal treatment was performed in a 100 ml closed Teflon vessel (HP-500 Plus PFA from CEM, Matthews, NC. USA). Sawdust (6g) was soaked in an 80-ml aqueous buffer solution. The vessel was flushed with nitrogen gas and tightly closed using a support module made of steel. Three different buffer solutions were used: citrate buffer pH 4, phosphate buffer pH 7 (0,4 M) and carbonate buffer pH 10 (0.4 M). Heat treatment was conducted at 180ºC for 3 or 6 hours in a laboratory oven. The treatment time includes a heating period of approximately 60 minutes (heating rate approximately 2.7ºC/min). After the treatment the aqueous solution was filtered off and the treated sawdust was placed in plastic bags and stored in a freezer. As reference samples, sawdust of birch wood without hydrothermal treatment were used.

Procedure for preparation of holocellulose

Holocellulose was made by removal of extractives and lignin. Hydrothermally treated or untreated sawdust was extracted with acetone in a soxhlet apparatus (16 hours) to remove resins. After extraction the wood sample was air-dried at room temperature.

Lignin was removed by sodium chlorite treatment. The delignification time was carefully selected to avoid degradation of the birch sample. The procedure is a modification of previously described methods (Wise et al. 1946; Ahlgren and Goring 1971; Westin 1998).

The following procedure was used: 0.9 g of the wood sample was added to 25 ml of deionised water; 0.31 gram $NaClO_2$ (80%) and finally 80 µl glacial acetic acid was added. The reaction was contained in a 100 ml flask which was sealed and kept at 70ºC and subjected to 45 minutes of magnetic stirring. The addition of $NaClO_2$ and acetic acid was repeated once (total of two additions) and followed by another 45 minutes of treatment with stirring. After delignification the sample was rinsed on a filter with 150 ml deionised water and 30 ml ethanol. Finally, the sample was air-dried at room temperature.

Procedure for preparation of α-cellulose

For preparation of α-cellulose, the holocellulose was extracted by alkali in an inert atmosphere to remove hemicelluloses.

The sample (0.6 g) was placed in a 100-ml beaker, and 50 ml of 2.5 M NaOH was added. The beaker was then placed in a desiccator under nitrogen gas. Extraction was performed for 16 hours at room temperature with gentle stirring. After extraction the sample was rinsed with deionised water until the water reached a pH of 7. The sample was collected on a filter and finally dried at room temperature to a paper-like sheet.

Measurement of cellulose molecular size by viscosimetry
The viscosity average molecular weight of cellulose was measured (SCAN-CM15:99). This is a standard method based on capillary viscosity measurements for pulp and paper dissolved in cupriethylenediamine solution (CED).

The relation between molecular weight of cellulose and viscosity measurements is dependent on calibration, and many relationships have been presented. In this work we have used the relation between intrinsic viscosity [η] and viscosity average degree of polymerisation (P_v); $P_v^{0.90} = 1.65 \times [\eta]$ (Evans and Wallis 1989).

3. RESULTS AND DISCUSSION

The results of the intrinsic viscosity measurements on cellulose are summarized in Fig. 1.. Table 1 gives the degree of polymerisation (viscosity average P_v) calculated as above (Evans and Wallis 1989).

Hydrothermal treatment at acidic pH
The results clearly show the negative effect of hydrothermal treatment in acidic conditions at pH 4 (Fig.1). The viscosity dropped from 1433 ml/g (untreated wood) to 880 ml/g (3 hours) and 883 ml/g (6 hours). The small difference of degradation between 3 and 6 hours at pH 4 may imply convergence when the most easily hydrolysable part of the cellulose is degraded (Bhuiyan et al. 2000; Obataya et al. 2000; Laka et al. 2001; Sivonen et al. 2002). Similar degradation patterns of wood-based samples with a decrease in intrinsic viscosity have been reported (Klauditz and Stegman 1947; Westin 1998; Feng et al. 2002). In a study of thermal treatment of cellulose were the degree of polymerisation reduced and levelled of to values around 600 to 800 (Roffael and Schaller 1971).

The long cellulose molecular chain gives the strength properties to both wood and paper. Viscosity of the pulp is generally used in the pulp and paper industry as a control of paper strength. From measurements on paper it is known that there is dramatic loss in strength when the viscosity value decreases under a certain level (Rydholm 1965). For Kraft pulps this level is around 800–900 ml/g. For wood not much is known about the relation between strength and the degree of polymerisation (P_v), but it can be assumed that strength losses start to occur at similar levels. The data shows such extensive degradation of cellulose already at pH 4 that detrimental effects on the strength properties can be expected.

It is well known that carboxylic acids are liberated during thermal processing of wood (Alén et al. 1985; Risholm-Sundman et al. 1998; Garrote et al. 2001; Manninen et al. 2002).

We have analysed industrially produced Thermowood as a comparison. The average intrinsic viscosity of this sample was 732 ml/g (Fig.1). From the calculation of the viscosity degree of polymerisation (Table 1), the average cellulose chains have been shortened by 42% (pH 4 treatments) and 53% (Thermowood) as compared to untreated wood cellulose.

The acidic conditions that occur during thermal treatment of wood obviously cause shortening of the cellulose molecules (Table 1), which can lead to a loss in wood strength. In this work, the viscosity dropped from 1430 ml/g (untreated wood) to lower than 703 ml/g and lower than 343 ml/g for 3 hours and 6 hours treatment in deionised water respectively. These results suggest that the industrial sample has been subjected to pH values even lower than 4 and that prevailing acidic conditions can be one of the main reasons for the effect on wood strength loss noted as a consequence of the heat-treatment processes.

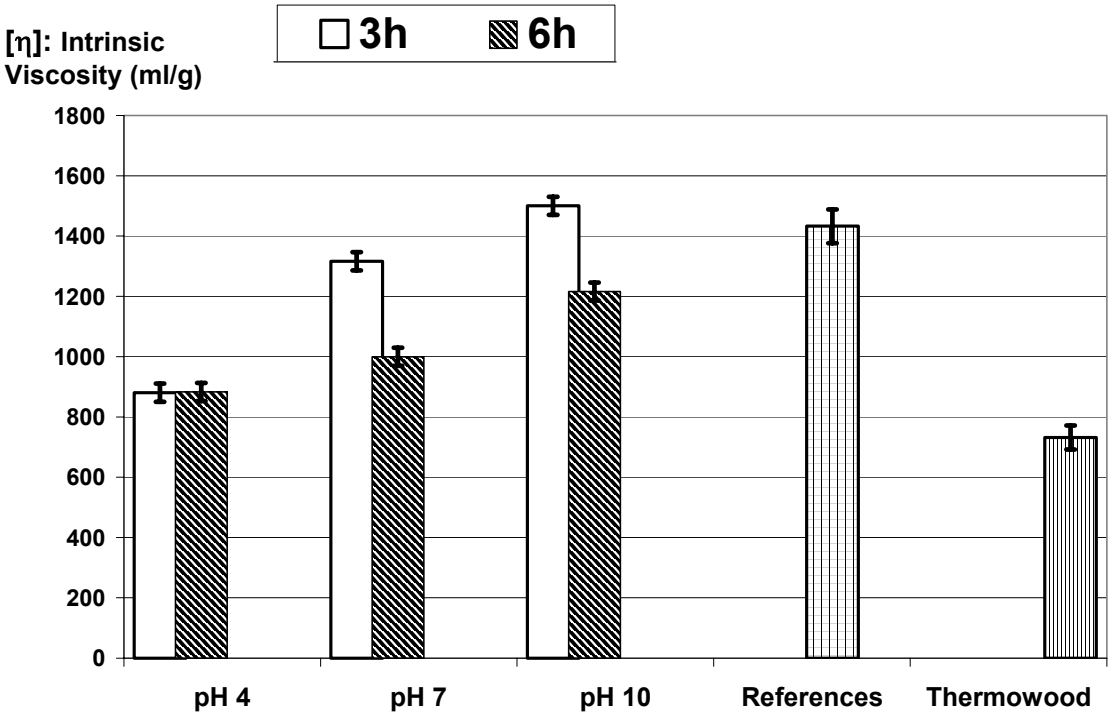

Figure 1: *Average intrinsic viscosity [η]: (ml/g) of cellulose from hydrothermal treated birch sawdust. The treatments were done in buffering solutions, pH 4–pH 10. Reference samples are untreated wood. The thermowood is from commercially produced heat-treated birch wood. The bars show the 95% confidence intervals based on 2–5 measurements*

Hydrothermal treatment at neutral and alkaline pH

At neutral conditions, pH 7, the effect of hydrothermal treatment was less apparent (Fig.1). The intrinsic viscosity dropped to 1316 ml/g (3 hours) and to 1000 ml/g (6 hours). This corresponded to chain shortenings of 9% and 33% respectively (Table 1). This is a considerably better result than in the unbuffered systems. The values are above the limit for extensive strength loss in fibres and only minor wood strength losses can be expected.

The results from the hydrothermal treatment at pH 10 showed that the hydrothermal degradation of the cellulose could almost be avoided (Fig. 1). The intrinsic viscosity was 1500 ml/g (3 hours) and 1216 ml/g (6 hours). The increase in viscosity value of the alkali treated cellulose (3 hours) can imply some type of crosslinking. However, this is not statistically assured (Table 1) and has to be studied in further experiments. For 6 hours' treatment the chain shortening was calculated to17%. The values suggest the possibility of maintaining wood strength during heat treatment processing.

It is also clear that treatment time can be of importance under neutral and alkaline conditions (Fig. 1). A small decrease in intrinsic viscosity was observed on increasing the time from 3 to 6 hours, 316 ml/g (pH 7) and 284 ml/g (pH 10) (Table 1).

Table 1: *Average intrinsic viscosities [η]: (ml/g) and calculated P_v (viscosity degree of polymerisation, (Evans and Wallis 1989)) from hydrothermal treatment of birch sawdust. Cellulose chain shortening are calculated according to (1-P_v[sample]/P_v[Ref.]). Hydrothermal treatments were performed in buffering solutions pH 4–pH 10. Reference samples are untreated wood. The thermowood is from commercially produced heat-treated birch wood. The data is based on 2–5 measurements.*

Sample	[η]	P_v	Chain shortening
References	1433	5604	
Thermowood	732	2657	53%
pH 4/ 3h	880	3261	42%
pH 4/ 6h	883	3273	42%
pH 7/ 3h	1316	5101	9%
pH 7/ 6h	1000	3756	33%
pH 10/ 3h	1500	5897	-5%
pH 10/ 6h	1216	4670	17%

Implications

Carboxylic acids are known to be released during industrial thermal treatment of wood, and marked losses in wood strength have been reported (Viitaniemi 1997; Kamden et al. 1999; Rapp and Sailer 2001). However, by controlling the occurrence of carboxylic acids during thermal treatment of wood, much of the strength loss could be prevented. In this work it has been shown that buffering in alkaline pH prevents the negative effect of cellulose degradation.

Heat treatment causes extensive changes in the wood structure. A considerable part of the hemicellulose is degraded, and lignin is condensed. It is not known exactly which reactions lead to improvement of durability and dimensional stability. It is difficult to speculate what effect an increase in pH will have on the treated wood. Lignin condensation is probably due to homolytic cleavage of ether bonds and subsequent rearrangement reactions (Westermark et al. 1995; Kishimoto and Sano 2002). This type of reaction is not sensitive to pH and should prevail. Hemicellulose degradation, on the other hand, is very sensitive to acid degradation, and hemicelluloses will probably be degraded to a lesser extent at higher pH. The exact effect of heat treatment at higher pH on the mechanical properties of wood will be addressed in further studies.

This paper demonstrates an interesting possibility for maintaining the cellulose structure in wood more or less intact also after extensive thermal treatment. This will probably also prevent wood strength losses. How the thermal process should be designed to maintain more alkaline conditions is an important issue for the future. First, the effect on durability and dimensional stability at high pH treatment has to be verified by future studies in a more industrial-like process, and second, a suitable process layout to minimise or neutralise the acids formed has to be considered.

4. CONCLUSIONS

1. Hydrothermal treatment at low pH results in chain shortening of the cellulose molecules. The decrease in cellulose length in unbuffered systems is of such an extent that it may affect the strength properties of the treated wood.

2. The design of an industrial process should control the acid formation that results from hydrothermal treatment to avoid cellulose degradation in the wood. If possible, the hydrothermal treatment should be performed in neutral to alkaline conditions.

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VI

Determination of formic acid and acetic acid concentrations formed during hydrothermal treatment of birch wood and its relation to colour, strength and hardness

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Abstract
Formation of acetic and formic acid during heat treatment of birch at 160º–200ºC has been studied by gas chromatography as benzyl esters.

High concentrations of formic acid and acetic acid formed by the wood itself during hydrothermal treatment were found. The concentrations of acids increased with both treatment time and temperature. The maximum formic acid and acetic acid concentrations found at 180ºC and 4 hours for the treatment process used in this work were 1.1% and 7.2% based on dry weight wood respectively.

The treated wood material was characterized by mechanical testing (bending tests perpendicular to the grain, modulus of rupture, modulus of elasticity, Brinell hardness, impact bending and colour measurements (CIE colour space).

The experiments where high concentration of acids was formed showed severe losses in mass and mechanical strength. Indications of possible enhanced mechanical properties for the treated, compared to untreated, birch wood were found around 180ºC and 200ºC at short treatment times.

The paper discusses possible degradation reactions coupled to the colour and mechanical properties in relation to acid formation, as well as suggestions for process optimizations.

Keywords: wood, heat, acetic acid, formic acid, birch, degradation, mechanical properties, hardness, colour, mass loss.

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Introduction

Thermally treated wood has been investigated since the middle of the last century and is nowadays produced industrially in many European countries. This has been reviewed in a number of papers (Syrjänen et al.[1], Millitz and Tjeerdsma[2], Vernois[3], Rapp and Sailer[4], Sundqvist[5]). Various types of treatments have been tested, and generally they are performed in an oxygen free environment and at temperatures in an interval between 150ºC and 250ºC.

Heat treatment of wood causes a reduction of hygroscopicity, which gives less swelling, shrinkage, and enhanced fungal resistance compared to untreated wood, thus making it a more durable material and an alternative for wood with added preservatives in exterior applications (Tjeerdsma et al.[6], Kamden et al.[7]).

Along with the improvement in durability, some unwanted effects arise, such as reduction of wood strength (Rusche[8], Kubojima et al.[9], Noack[10]) and reduction of hardness (Sanderman and Augustin[11]). It is therefore of interest to deepen knowledge of and find methods to improve the mechanical properties of heat-treated wood.

Improved durability is often accompanied by reduction in mechanical strength in wood from the industrial processes used today. Heat-treated wood with considerable durability is obtained at temperatures around 250ºC, while mechanical strength drops markedly for treatments at temperatures over 200ºC (Syrjänen et al.[1]). Another feature of heat-treated wood is the change in colour to red-brown. Such material has been suggested as an alternative to the use of dark-coloured wood products from tropical species. It has also been suggested that the colour of wood can serve as an indicator of the degree of its modification (Bourgois et al.[12], Bekhta and Niemz[13]).

The fact that wood releases various organic acids when it is heated and that acids promote degradation of wood components has been realized in many scientific fields, such as fodder production, biofuel conversion and pulp and paper processing (Dietrichs et al.[14], Fengel and Wegener[15], Garrote et al.[16], Feng et al.[17]). Emission of acetic acids has been reported for heat treatment of wood in steam or nitrogen atmosphere (Manninen et al.[18], McDonald et al.[19], Bourgois and Guyonnet[20]), but not much attention has been paid to the fact that acids catalyse the degradation of carbohydrates (Theander and Nelson[21]) and may cause degradation of lignin (Lai[22]). In our previous study (to be published) it was found that the cellulose average molecular weight was reduced by approximately half both in laboratory samples and in commercial samples of birch wood heat treated at 180ºC. Final pH values of around 3 were recorded for the laboratory experiments. However, for comparable experiments in buffering solution at pH 10 the effect on average molecular weight was negligible. Thus, it is of great importance to understand and to control the formation of acids as well as their effect on wood components and mechanical strength during heat treatment.

Low-molecular organic acids such as acetic and, especially, formic acid are volatile and are difficult to collect and analyse. The total amount of acids found in a specific wood sample can vary due to evaporation and ventilation in heat treatment processes. The predominant low-molecular acids found to be released from wood are generally formic acid and acetic acid, and they are found during wood pulping (Feng et al.[17]) and in cold water extracts of wood chips (Jung and Roffael[23]).

This work analyses the total amounts of acids that can be formed from birch in a closed aqueous system. Analysis of formic and acetic acid was done by gas chromatography as described in an

earlier study (Bethge and Lindström[24]), where the acids are converted to benzyl esters. The resulting effect of acid content on strength, hardness, mass loss and colour was also investigated.

Material and Methods

Wood samples

Birch (Betula pubescens Ehrh.) from north Sweden that had never been dried was cut into specimens of two sizes, 110 x 31 x 4 mm and 97 x 27 x 6 mm, and stored in a freezer.

Hydrothermal treatment

Two pieces of each size of the birch samples (weight 11–12 g) were put in a cylindrical Teflon vessel (HP-500 Plus PFA from CEM, Matthews, NC, USA). The vessel has a volume of 90 ml and an inner diameter of 33 mm. Deionised water (57 ml) was added to fill the vessel. The residual volume in the vessel and the vessel lid were flushed with Argon gas to remove any residual air present. The vessel was closed and sealed using a steel support module. The closed vessel with the specimen was weighed before and after the hydrothermal treatment.

Hydrothermal treatments were performed based on a full factorial design under 9 different conditions; for three different temperatures (160ºC, 180ºC and 200ºC) and for three different times (1.0, 2.5, and 4.0 hours). For 4-hour treatment at 180ºC, two replicates were made, and for 2.5-hour treatment at 200ºC one replicate was made. The Teflon vessel was placed in a laboratory oven for heating. The temperature of the specimen reached the target temperature after approximately 60 minutes, a temperature increase of 2.7ºC/min.

After treatment, the sealed vessel and the support module were cooled in air (15 min) and then in cold water (30 min). The aqueous solution from the hydrothermal treatment was filtered and stored in a closed bottle at 5ºC. The solid part of the specimens was dried and conditioned at room temperature to reach a moisture content of 4–6%. Determination of dry weight: specimens (0.3g) were dried at 105ºC for 16 hours. Mass loss was calculated as the dry weight before and after thermal treatment.

Analysis of formic acid and acetic acid in aqueous solution

Based on the method described earlier (Bethge and Lindström[24]), the following procedure was performed. A sample from the aqueous solution (5.00 ml) was titrated with 0.185 M quaternary ammonium salt solution, n-tetra butyl ammonium hydroxide (Q-salt) to reach neutral pH (7.00). For samples with low acid contents, a 0.046M Q-salt solution was used instead.

The amount of Q-salt in mole needed to neutralise the solution (pH = 7.0) was recorded, which by equivalency gives the total amount of organic acids in the sample. To further stabilise the Q-salt/acid complex, the titration proceeded to approximately pH 8. Hexanoic acid (0.108 M, pH 8 with Q-salt) was used as internal standard. To the titrated sample an equivalent amount (mole) of internal standard to the acid was added.

Water and some solvents from the hydrothermal treatment of birch were evaporated in a rotary evaporator, and dry acetone (5 ml), dried with molecular sieves, was added as a solvent. Finally, benzyl bromide (98%) was added to the sample. The amount of benzyl bromide was calculated from the total amount of acids in the sample to give an excess amount of 30 equimolar %. The sample was then kept in a closed vessel at 40ºC for 1 hour.

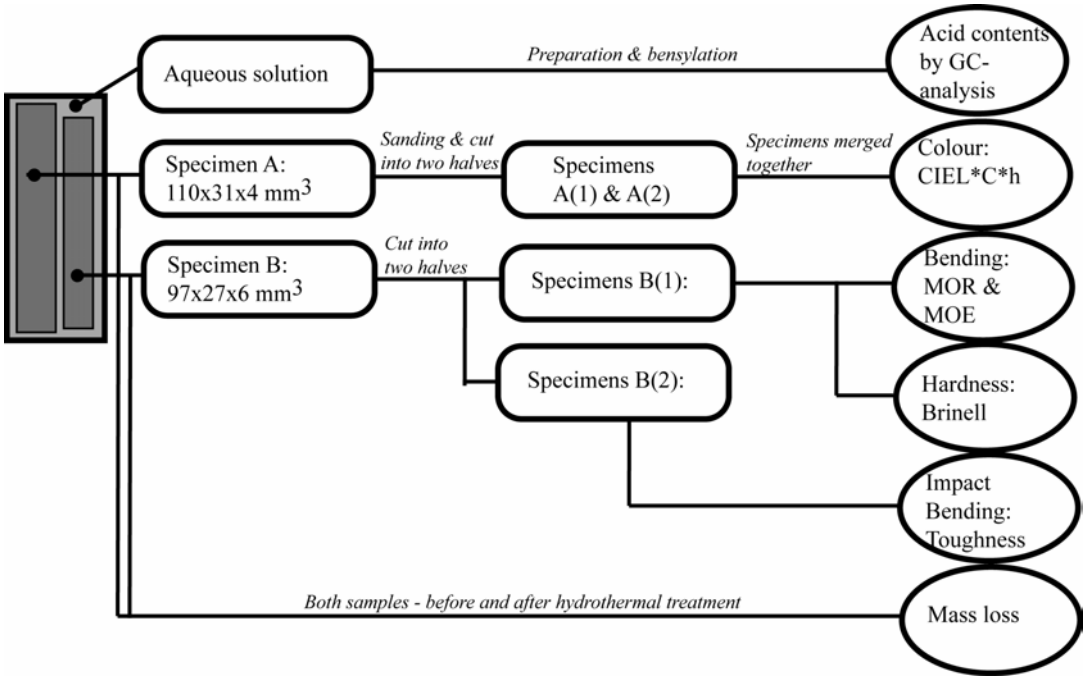


Figure I: *Procedure for characterising the hydrothermally treated birch wood.*

GC determination of formic and acetic acid.

The content of formic and acetic acid in the samples was determined by gas chromatography.

Measurements were made on a Chrompack CP9002 with a flame ionisation detector (FID). Column: DB-5 (J & W Scientific, Folsom, CA, USA) i. d. 0.32 mm (wide bore); film thickness 0.25 mm; length 15 m; carrier gas: helium, 30 ml/min; split 1:116.

An initial temperature of 80ºC for 7 minutes was followed by a temperature increase of 10ºC/minute to reach a final temperature of 250ºC. These settings gave eluation time 4.6 min. for benzyl formate, 5.6 min. for benzyl acetate and 15.2 minutes for benzyl hexanoate (internal standard).

Strength and colour measurements of treated wood specimens

The specimens A were sanded (0.5 mm) and cut into two pieces (Figure I). These two pieces merged together enabled colour measurements with the colorimeter probe inner diameter of 53 mm. The colour measurements were made with a tristimulus colorimeter: Minolta CR310 (CIEL*C$_{ab}^*$h colour system). The effect on colour measurement from the joint between the pieces was less than 0.3 units and was therefore ignored.

The specimens B were cut into two pieces (Figure I). The first one, B(1), was used for three point-bending and hardness tests perpendicular to the grain on a Hounsfield H25KS UTM, and the other, B(2), for impact bending test on a Charpy impact tester; (VEB Werkstoffprüfmaschinen 1972, W = 1.5 kpm, m = 2.035 kg and l = 380 mm)

The span between the supports was 80 mm for the bending tests, and calculations of modulus of elasticity (MOE) and modulus of rupture (MOR) were done (Hodgkinson[25]).

The hardness (H) was a modification of the Brinell method (EN1534:2000[26]). A small steel ball

(5.642 mm) was pressed into the wood specimen, and the deflection, the indentation force and surface mark were recorded.

For the impact bending strength tests, the span between the supports was 40 mm and calculations were done according to (SS161351[27]).

All data were assumed to have normal distribution, and for treatment replicates at 180ºC for 4 hours and at 200ºC for 2.5 hours, pooled standard deviation was estimated and presented.

Results and discussion

Acid formation due to hydrothermal treatment

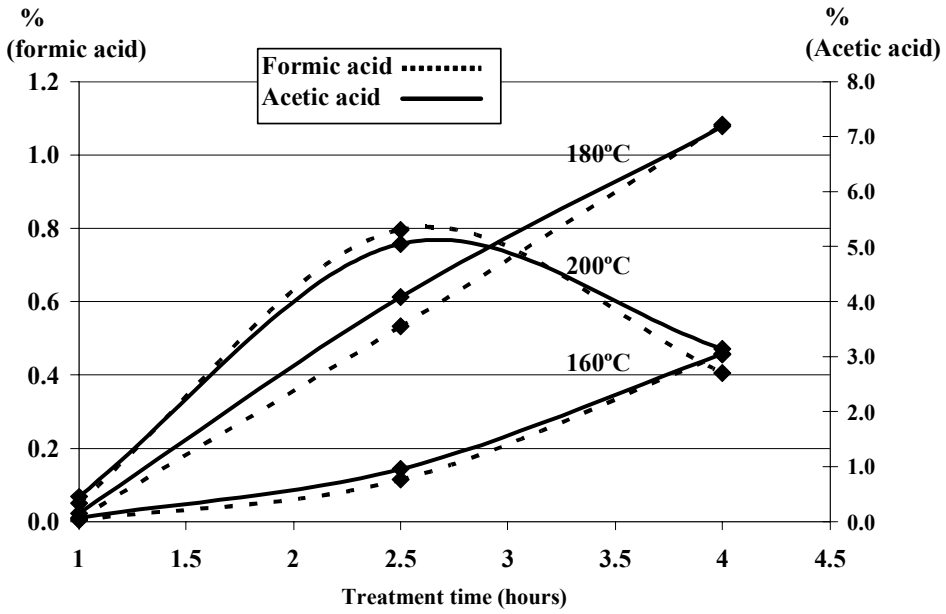
It is known that acidic conditions at elevated temperature can degrade wood by hydrolysis. Acidic conditions can be created by formation of acids from the wood itself. Formic acid and acetic acid are known to be formed during treatment of wood at high temperatures (Feng et al.[17], Manninen et al.[18], Tjeerdsma et al.[28], Alén et al.[29]). Also other organic acids, such as 4-O-methylglucuronic and galacturonic acid, can be formed as a result of hydrolysis of wood. In this work we have studied formation of the low-molecular carboxylic acids (< 150 g/mol) acetic acid and formic acid analysed by gas chromatography.

In hardwoods, acetic acid formation is mainly due to the degradation of the hemicellulose glucuronoxylan, where acetyl groups (at carbon 2 or 3 of the glucuronoxylan backbone) are split off (Theander and Nelson[21]). The origin of formic acid is not clear. It is however known that degradation of hexoses can give formic acid as by products (Lai[22], Ponder and Richards[30]).

Figure IIa shows the formation of acetic acid and formic acid during hydrothermal treatment. Both duration and temperature of treatment affect the concentration of acids. The heating time to reach process temperature is approximately 6o minutes. This heating time is included in all treatment times. That is likely the reason for the small concentrations of acids that have been found after 1 hour (Figure IIa).

The acid concentrations increased with increased treatment time and temperature, except for 4 hours and 200ºC, which may indicate stagnation. If acetic acid is formed exclusively from acetate groups that have been split off in wood, there should be a maximum concentration that could be formed. The maximum concentration obtained in our experiments is 7.2% based on dry weight wood. To investigate if the results in our work may confirm this possible maximum yield of acetic acid, a rough estimation was made. Approximately 33% of birch wood consists of the hemicellulose methylglucuronxylan, which was estimated to have a molecular weight of 181 g/mol per monosugar unit. Furthermore, every unit has on average 0.7 acetate groups attached to it (Theander and Nelson[21]). Calculations from the maximum values of acetic acid in this work suggest that 0.66 acetate groups have been split off. Thus, it is reasonable to believe that the formation of acetic acid comes from acetate groups in the methylglucoronoxylan and that a maximum concentration was indicated for treatment at 180ºC and 2.5 hours. The ratio between acetic acid and formic acid was more or less fixed (5.2 ± 1.2, 95% confidence interval) (Figure IIa). This similar degradation pattern can indicate that the major source of formic acid originate from formate esters in the wood, since the major source of acetic acids seem to originate from acetate esters in the methylglucoronoxylan. By the same calculations for the maximum concentration of 1.1% formic acid found in this work (Figure IIa), every methylglucoronoxylan unit has split off 0.13 formate groups. Formic acid formed as a result of hexose degradation should have shown an increasing trend, not an indication of stagnation as more material gets degraded at longer time periods and at higher temperatures.

The declining concentration at 200ºC can also indicate that acetic acid is consumed in the system, or more likely that the experimental conditions at long treatment times at 200ºC are somewhat uncertain due to the fact that higher temperatures in combination with longer durations sometimes caused leakage from the sealed vessel used in this work (Figure IIa).



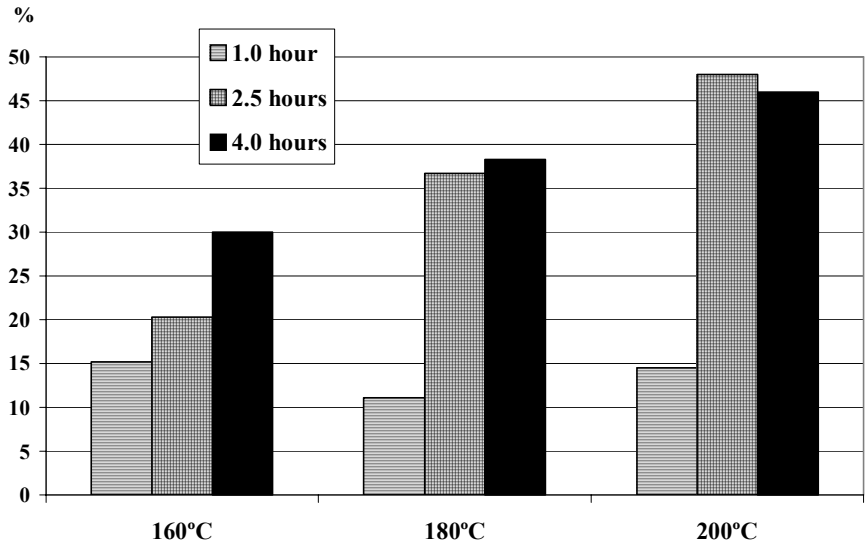


Figure II: *Hydrothermal treatment of birch wood. IIa: Formation of formic acid and acetic acid (weight acids/weight dry wood). IIb: Mass loss related to dry weight wood. Pooled standard deviations from repetitions for 4.0 hours at 180ºC and for 2.5 hours at 200ºC were calculated to; 0.34% (formic acid), 0.50% (acetic acid) and 5.3% (mass loss).*

Industrial relevance and mass loss

In this investigation the hydrothermal treatment has been done with specimens soaked in water at high pressure. A common procedure in industrial production of heat-treated wood is to treat the wood with overheated steam at 1 atmosphere. Figure IIb gives data for weight loss under our research conditions. The weight loss for birch wood for 2.5 and 4.0 hours duration is large 20%–48% (Figure IIb). Typical weight losses in industrial processes using saturated steam are said to be less than 14% (Viitaniemi[31]). In the industrial steam process it is likely that the weight loss is

due to loss of volatile compounds, while in our process the weight loss includes all material that has been degraded and is water soluble during the treatment. It is reasonable to believe that the possibility to form condensations products from degraded lignin and hemicelluloses is better with steaming processes than in our process, since degraded compounds are leached from the wood and diluted by the water. It is difficult to directly compare the two systems. It seems likely that roughly similar amounts of acids are formed in the two systems, but some of the more easily evaporating acids escape during the industrial process. On the other hand, much more water dilutes the acids in our experiments than in the industrial system. This could mean that higher concentrations of acids may occur in the wood in the industrial system.

Birch consists of approximately 40% cellulose, 20% lignin, 33% hemicellulose and 4% extractives (Lai[22]). Degradation of carbohydrates by heat is well known, and it is rapid under acidic conditions. This has been reviewed (Theander and Nelson[21]). A high degradation rate of carbohydrates is promoted by a high degree of availability and low degree of crystallinity, such as for hemicelluloses. The carbohydrate degradation rate also depends on the molecular constitution (Lai[22]). Lignin degradation may also occur, but not to the same extent as for hemicellulose under acidic conditions (Lai[22]). A high degradation rate is known particularly for lignin units containing phenolic groups, which accounts to approximately 10% of all units (Lai[22], Henriksson[32]). Furthermore, α-aryl ether bonds and β-aryl ether bonds linking the lignin units (comprising 50–70% of all bonds) are more easily broken than carbon–carbon bonds (Lai[22], Henriksson[32]). Figure IIb show mass losses of more than 30%, which suggests a considerable degradation of the wood components. It is therefore reasonable to believe that the major part of degradation of the amorphous and relatively readily available hemicelluloses as well as some lignin degradation has occurred by cleavage of the major part of the α-and β-aryl ether bonds for treatments at 180ºC and 200ºC for 2.5 and 4 hours.

The large amount of acids released from the wood can obviously also degrade cellulose. In an accompanying paper we report a reduction of the cellulose average molecular weight by almost half for similar experimental conditions at 180ºC (Sundqvist et al.[33]) (to be published). A much lower extent of degradation occurred at 1.0 hour of duration (Figure IIb), where only extractives and minor parts of the hemicelluloses and lignin seem to be degraded.

Change in mechanical properties of hydrothermally treated birch

The effect on the mechanical properties of wood was in line with the degradation pattern and the formation of organic acids noted above (Figure II).

The treatment time should be at most 2.5 hours for 180ºC and at most 1 hour for 200ºC to avoid significant decreases in modulus of elasticity (MOE), modulus of rupture (MOR) and impact strength compared to references (Figure III and IV). For treatments at 160ºC almost no changes were observed. However, Brinell hardness is affected at temperatures as low as 160ºC, where substantial softening is shown after 4 hours (Figure IV). However, 1 hour treatments at the temperatures examined do not show any softening.

There is an indication of an increase in modulus of elasticity, modulus of rupture and impact strength compared to references for treatment durations of 1 hour at 180ºC and 200ºC. For longer treatment times at 200ºC the mechanical properties declined drastically. In an earlier work, similar effects were observed (Kubojima et al.[9]). An initial increase in strength and hardness can be due to condensation processes in the lignin and hemicellulose as molecules degrade and can form new chemical bonds (Tjeerdsma et al.[28], Sivonen et al.[34], Klauditz and Stegman[35], Li et al.[36]).

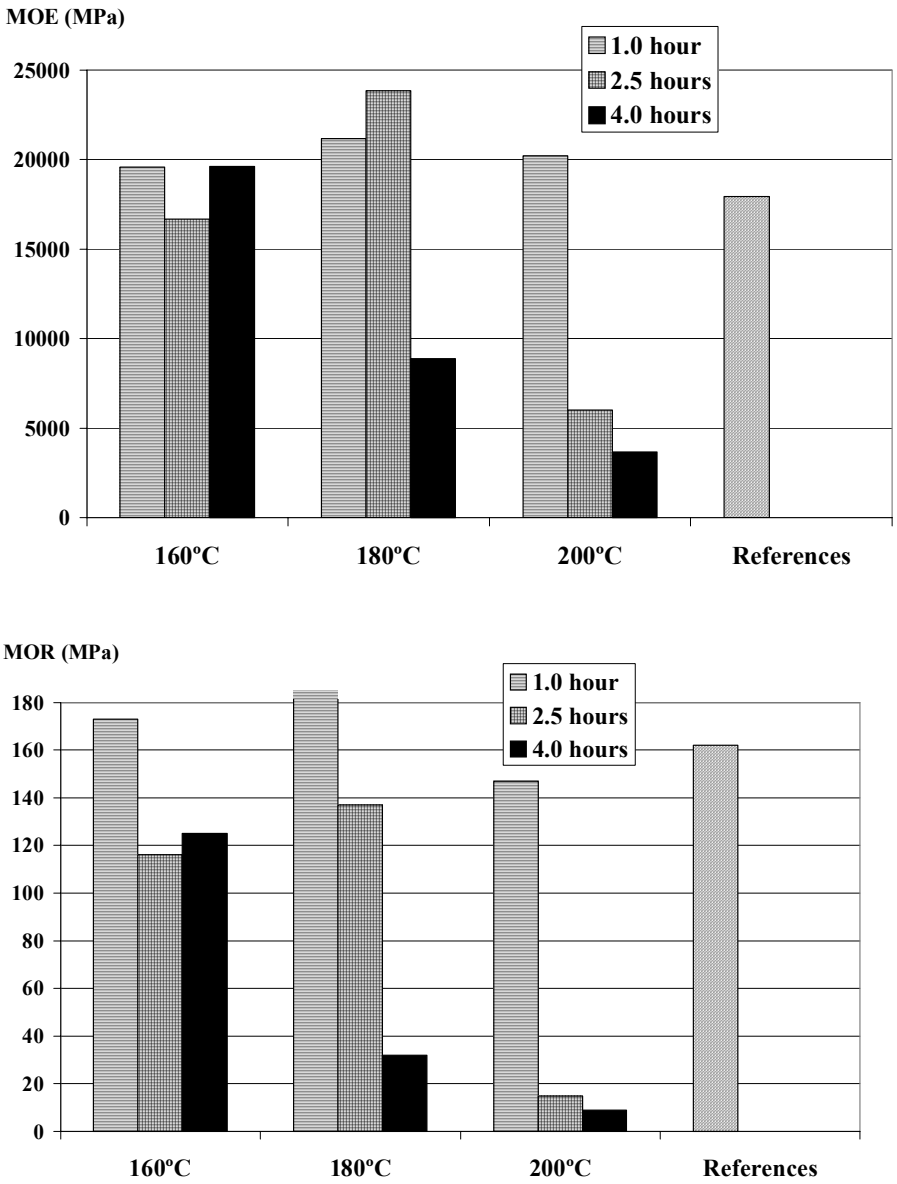


Figure III: *Hydrothermal treatment of birch wood. Bending tests perpendicular to the grain. IIIa: Modulus of elasticity (MOE) in MPa. IIIb: Modulus of rupture (MOR) in MPa. References: Birch dried at room temperature (MC 6%–8%). Pooled standard deviations from repetitions for 4.0 hours at 180ºC and for 2.5 hours at 200ºC were calculated to 2400 MPa (MOE) and 13 MPa (MOR). Standard deviations for references were calculated to 2000 MPa (MOE) and 13 MPa (MOR).*

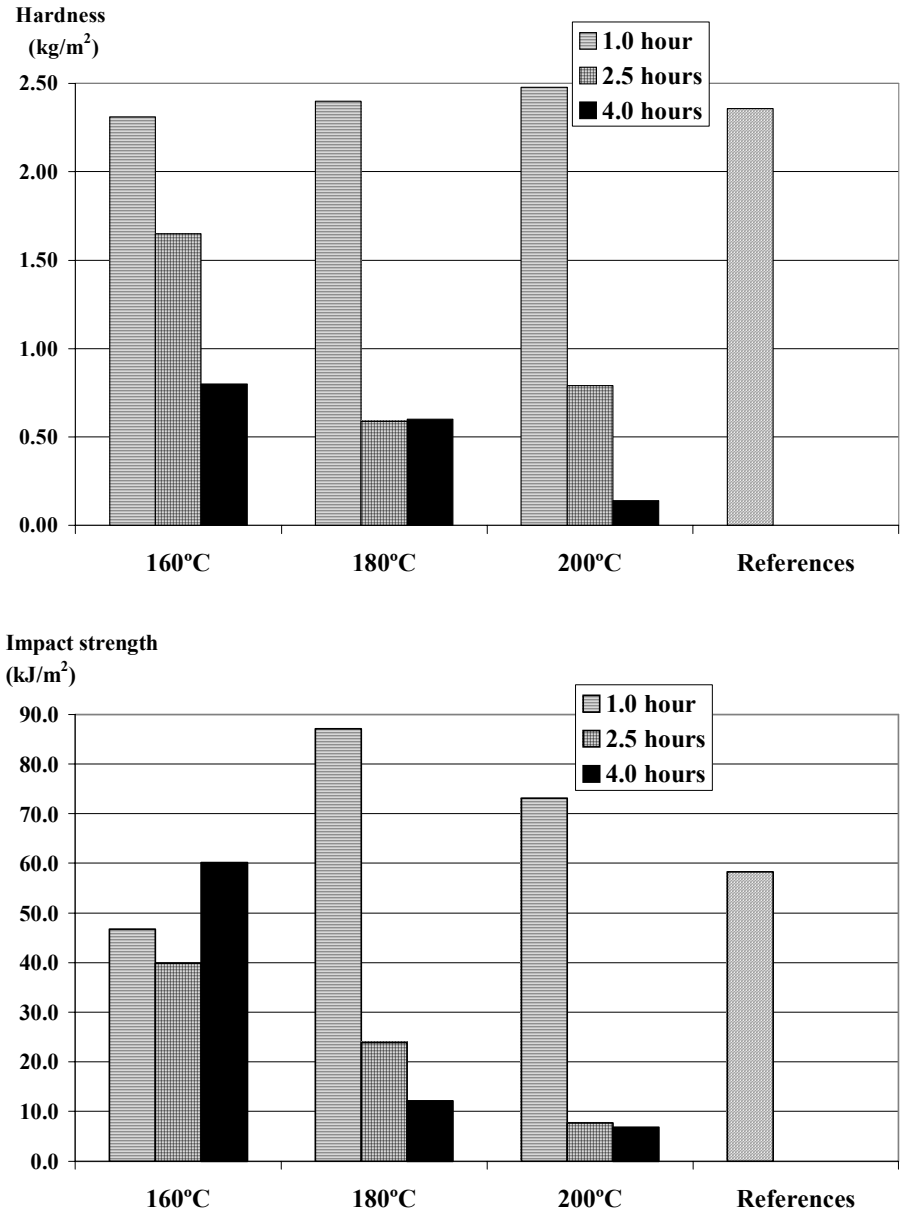


Figure IV: *Hydrothermal treatment of birch wood. Brinell hardness (kg/m^2), IVa, and impact bending strength (kJ/m^2), IVb. References: Birch dried at room temperature (MC 6%–8%). Pooled standard deviations from repetitions for 4.0 hours at 180ºC and for 2.5 hours at 200ºC were calculated to 0.37 kg/m^2 (Hardness) and 2.7 kJ/m^2 (Impact strength). Standard deviations for references were calculated to 0.51 kg/m^2 (Hardness) and 15 kJ/m^2 (Impact strength).*

Colour responses of hydrothermally treated birch

The lightness (L*) of hydrothermally treated wood is suggested to be an indicator of its degree of modification (Bourgois et al.[12]). In the case of birch it decreases both with higher temperature and longer duration (Figure V). A rapid decrease in lightness occurs early in the heat treatment process, where the largest change can be found between 0 and 1 hour treatment despite the fact that the time to reach target temperature was approximately 1 hour. This indicates that much of the decrease in lightness already occurs after a short period of time and at fairly low

temperatures. The decrease in lightness between 160ºC and 180ºC was larger than between 180ºC and 200ºC.

The colour saturation (chroma, C_{ab}^*) shows a more irregular pattern with no pronounced trends (Figure V). An indication of a local maximum for each temperature can be noticed at 4 hours at 160ºC, 2.5 hours at 180ºC and 2.5 hours at 200ºC, but this is not statistically assured.

Similar results for a local maximum of chroma have been reported (Bourgois et al.[12], Bekhta and Niemz[13]). The colour shade (hue) for hydrothermally treated birch seems to converge to a value of around 60 for temperatures around 200ºC and longer durations, (4 hours) (Figure V). Similar results of convergence of hue have been obtained earlier for treatments at 200ºC (Bourgois et al.[12], Bekhta and Niemz[13]). Also for long treatment times, 95ºC and 6 days, a convergence of hue has been found (Sundqvist[37]). For temperatures well over 200ºC the hue decreases again(Bourgois et al.[12]).

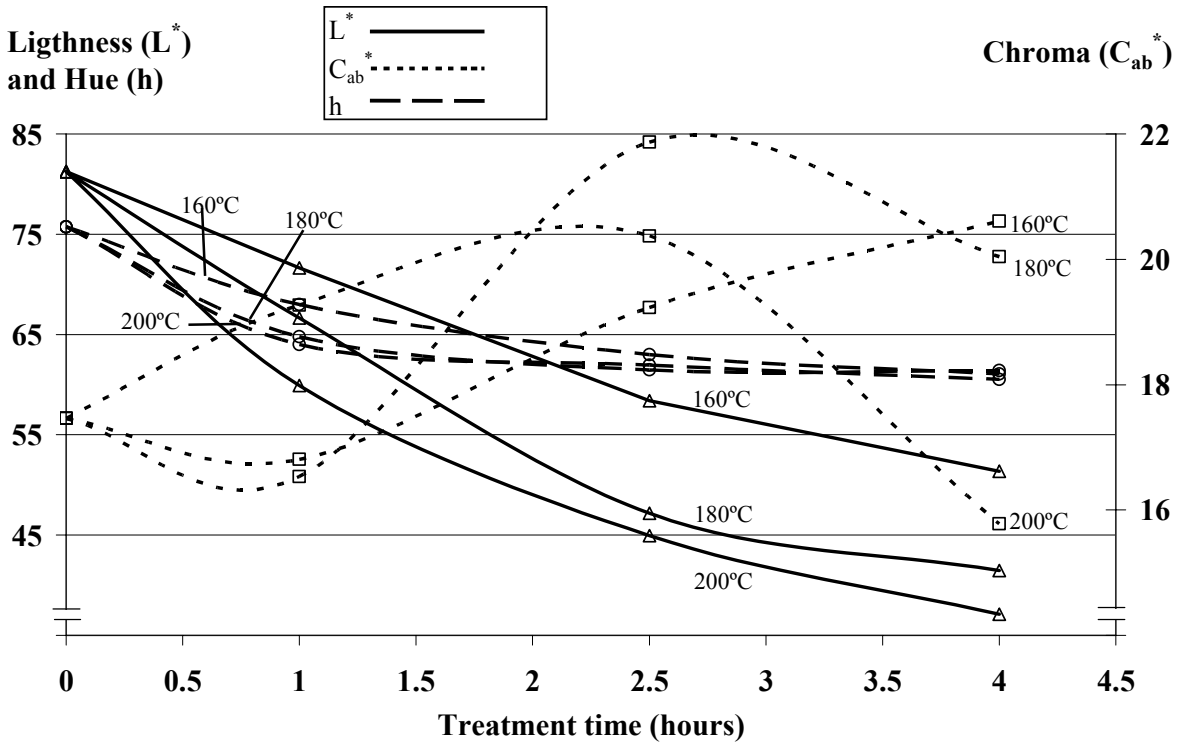


Figure V: *Hydrothermal treatment of birch wood. Colour of sanded specimens, (CIELCh colour space). Lightness (L^*), chroma(C_{ab}^*) and hue (h). References: Birch dried at room temperature (MC 6%–8%). Pooled standard deviations from repetitions for 4.0 hours at 180ºC and for 2.5 hours at 200ºC were calculated to 1.83 (L^*), 1.37 (C_{ab}^*) and 0.20 (h). Standard deviations for references were calculated to 2.37 (L^*), 2.11 (C_{ab}^*) and 2.34 (h).*

The reddish colour and increased colour saturation substantiated as a decrease in hue and increase in chroma can be due to formation of secondary condensation products and/or formation of degradation products of the quinone and quinonemethide types. The reactive compounds can include degradation products from cleavage of α- and β-aryl ether bonds in lignin and degradation products from hemicelluloses. These may produce various condensation products (Lai[22]). Intermediate lignin degradation compounds such as quinones or quinonmethides are known to be strongly coloured (Hon and Minemura[38]).

Conclusions

- This paper shows that during hydrothermal treatment of birch wood considerable amounts of acetic acid and formic acid can be released in the wood material. High concentrations of acetic acid and formic acid were related to high treatment temperatures and long treatment times
- The results indicate that acid formation can be a serious problem in industrial heat treatment processes. Acetic acid and formic acid are volatile, and more experiments are needed to study how the acid formation from wood is affected by different process conditions in industrial plants.
- This paper clearly shows that high concentrations of acids were also related to large mass loss, large loss in mechanical properties, low lightness (L*) and low hue (h).
- For future design of heat treatment processes for wood, it is important to consider the formation of organic acids to avoid unwanted losses in mechanical properties. Control of the acidic concentrations, either through process modifications or some form of impregnation with buffer solutions to prevent low pH, is likely to improve the mechanical properties of heat-treated wood.

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T.R

Värmebehandling av trä:

Från ett historiskt perspektiv
till kommersiell produktion av idag.

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28 oktober, 2002

Värmebehandlat trä; ”Thermowood” (T°W)

Innehåll:

1. Inledning

Trä har i alla tider ruttnat och brutits ned och många olika sätt för att bromsa dessa processer har prövats historiskt. Ett uråldrig sätt att bromsa nedbrytningen är att förkola ytan med hjälp av eld, t.ex. för stolpar till staket och dylikt som skall vara i markkontakt. Detta kan ses som en värmebehandling för att öka beständigheten mot förruttnelse. Idag är impregnering med giftiga kemikalier, s.k. CCA-behandlingar (koppar-krom-arsenik) mycket vanliga. Under 1998 förbrukades ca 6000 ton träbekämpningsmedel i Sverige (Nationalencyklopedin). En mängd olika kemikalier används globalt och internationellt och speciellt inom EU finns starka krafter för att reducera användningen av giftiga kemikalier av miljöskäl. Det är därför angeläget att hitta nya och mera miljövänliga metoder för att öka beständigheten hos trämaterial. Värmebehandling av virke i temperaturer mellan ca 150-250°är en sådan tänkbar utvecklingsmöjlighet.

När man använder trä som byggmaterial uppstår ibland problem med virkets deformation, vridning, kupning, kantkrok etc. Detta har bl.a. lett till att trä som byggnadsmaterial har förlorat marknadsandelar gentemot andra byggmaterial såsom t.ex. stål och betong. Sedan flera decennier tillbaka har man känt till att värmebehandling av virke kan ge ett mer formstabilt material. Detta hänger samman med att träet kan bli mindre känsligt för fukt, mindre hygroskopiskt och sväller och krymper mindre än lufttorkat virke, vilket då ger mindre formförändringar.

Tropiska trädslag är intressanta både av estetiska skäl och att de ofta är naturligt beständiga t.ex. teak , mahogny och merbau. En stark internationell opinion mot rovdrift och skövling av regnskogarna i tropikerna har dock lett till att europeiska alternativ av arter gentemot tropiska arter har blivit intressanta. Värmebehandling av trä har sedan länge visats kunna färgförändra och i viss mån egenskapsförändra virke till att likna vissa tropiska arter såsom teak, mahogny, merbau etc. Uttrycket ”nordens Mahogny” har förekommit om finskt värmebehandlat trä, s.k. ”Thermowood”, se omslagsbilden.

Värmebehandlat trä är alltså intressant ur flera aspekter. Idag finns möjligheter att producera värmebehandlat trä och få ett material som har bättre formstabilitet, har ett exotiskt utseende och har bättre resistens mot röta och mögel mm. Processer för värmebehandling av virke finns idag redan kommersiellt i Finland, Tyskland, Holland och Frankrike. Utvecklingen går vidare mot mer specifika träprodukter med speciella egenskaper.

Intresset för värmebehandlat trä tycks mest vara beroende på den ökade beständigheten mot biologisk nedbrytning som kan fås. Detta syns tydligt genom det EU-projekt som berör detta, ”Upgrading of non durable wood species by appropriate pyrolysis thermal treatment”. EC-Industrial & Material Technologies Program (Brite-EURam 111), EC Bericht BRE-CT-5006 från 1998. Även diskussion om livscykelanalys och hållbara ekologiska material passar för värmebehandlat trä, EU-FAIR Project ”Life Sys Wood” (Robson och Esser 1997). Värmebehandling kan eventuellt också förbättra möjligheten till att kvalitetsmärka trä enligt ISO/EMAS etc. (Ryding 1997).

2. Tillbakablick; vad har gjorts tidigare inom området.

Sedan urminnes tider har värmebehandling av trä över öppen eld varit ett sätt att öka beständigheten. Idéer om att industriellt värmebehandla trä fanns redan på 1910-talet i USA och tidiga patent finns från 1940 talet t.ex. ”Heat-stabilized wood (Staybwood)” (Stamm et. al. 1946) och ”Heat-stabilized compressed wood (Staypak)” (Seeborg et. al. 1948). Även i Sverige fanns det tidigt idéer om att värmebehandla trä (Thunell och Elken 1948). Man var i dessa undersökningar mest inriktad på att förbättra dimensionsstabiliteten. Ingen av dessa processer för värmebehandling av trä ledde inte till någon kommersiell satsning. Nötningsbeständigheten och slagsegheten ansågs för dålig (Stamm 1964)

I Tyskland och USA bedrevs under 50 och 60-talen mycket forskning och utveckling om värmebehandling av trä och under 70 och 80-talet förde man i Tyskland fram idén om FWD-trä (Feuchte-Wärme-Druchbehandlung) (Burmester 1973, Giebeler 1983). Detta ledde inte heller till någon kommersialisering.

Intresset för värmebehandling av trä under 90-talet, mest i Tyskland, Holland, Frankrike och Finland, har lett till kommersialisering i framförallt Finland och Holland. Denna utveckling har mest inriktat sig mot förbättrad rötbeständighet och drivs av de ökande kraven på miljöhänsyn och krav på minskat användandet av träskyddsmedel. Sverige saknar fortfarande forskning om värmebehandlings-processer och anläggningar för värmebehandlat trä men intresset från institutioner och företag är ökande. Utvecklingen inom området går snabbt och en nationell satsning är nödvändig om Sverige skall ha någon chans att kunna följa med i den internationella utvecklingen.

3. Produktion av värmebehandlat trä

Idag finns kommersiell produktion av värmebehandlade träprodukter i Frankrike, Finland, Tyskland och Holland. Av dessa har Holland och Finland den största produktionen för närvarande. I tabell 1 nedan ges en sammanställning av produktionskapaciteten för de aktuella värmebehandlingsmetoderna (från presentation vid temadagen ”Träskydd- Värmebehandlat trä- egenskaper och användningsområden”, 21 november, 2000, Sveriges Provnings- och forskningsinstitut, Stockholm. (Vernois 2000), (Millitz och Tjeerdsma 2000), (Rapp och Sailer 2000), (Syrjänen 2000) och (Jämsä och Viitaneimi 2000). Icke kommersiella processer men historiskt intressanta ”Staybwood” (Stamm et. al. 1946, Stamm 1956, Stamm 1964) och ”FWD” (Feucte-Wärme-Druckbehandlung) (Burmester 1973, Giebeler 1983) tas också upp som jämförelser.

Tabell 1: Produktion och kommersialisering av värmebehandlat trä

Produktnamn	Land	Produktion (m3/år)	Produktionsställen	Träslag, prövade
Thermowood	Finland	35000	8	Tall, gran, björk, asp
Platowood	Holland	50000	1	Tall, bok, gran, Radiatatall och Douglasgran
Retified wood (Förnätat trä)	Frankrike	8000	9	Tall, asp
Le bois perdure (Beständigt trä)	Frankrike	*	*	Tall, asp
Olje-värme trä	Tyskland	2900	1	Tall, gran
Staybwood	USA	-	Har ej kommersialiserats	Sitkagran och tall (W. White)
FWD Fukt-Värme-Tryck trä	Tyskland	-	Har ej kommersialiserats	Björk, asp, tall gran och bok

* Presenteras tillsammans med "Retified wood"

4. Processer för framställning av värmebehandlat trä

Flera principiellt olika processutformningar används kommersiellt**.** I Finland, Holland och Frankrike används värme/kvävgasatmosfär eller mättad vattenånga i kontinuerliga processer. Den holländska metoden som ger s.k. Platowood skiljer sig från de övriga genom att två separata behandlingssteg med torkning emellan används (Tabell 2).

I Tyskland har man valt en annan inriktning vid värmebehandlingen genom att värmeöverföringen sker i olja, se tabell 2. Det är främst vegetabiliska oljor som raps-, solros- och linolja som har prövats och används.

Dessa metoder (Tabell 2) har det gemensamma att de reducerar närvaron av syrgas. Detta var också fallet för ”Staybwood” med metallsmälta och ”FWD” med vattenånga samt kvävgas.

Det är svårt att avgöra med tillgänglig dokumentation huruvida nedtorkat virke, (omkring 10 % fuktkvot) är nödvändigt före uppvärmning och behandling i de olika metoderna. För åtminstone Platowood anges att icke torkat, färskt, virke kan uppvärmas och behandlas direkt om så önskas.

Många olika trädslag har provats och klarar värmebehandling (Tabell 2). Generellt så är barrträ enklare att behandla än lövträ, främst beroende på lägre densitet och högre permeabilitet (Vernois 2000, Syrjänen 2000, Boonstra et. al. 1998). Speciellt intressanta bland lövträden är asp och bok som behåller mekanisk styrka bra och samtidigt som asp visar bra rötbeständighet efter behandling (Vernois 2000, Syrjänen 2000). Bland barrträden är gran och radiatatall (*Pinus radiata*) ansedda som särskilt lämpliga där termobehandling ger särskilt bra rötbeständighet (Syrjänen 2000, Tjeerdsma et. al. 1998). Vissa problem rapporteras från processen. För lågpermeabla trädslag uppstår lättare sprickor och ibland kollaps. Problem kan också uppstå för virke med defekter som reaktionsved, svartkvistar, stora friskkvistar, kådlåpor, vankant etc. (Boonstra et. al. 1998).

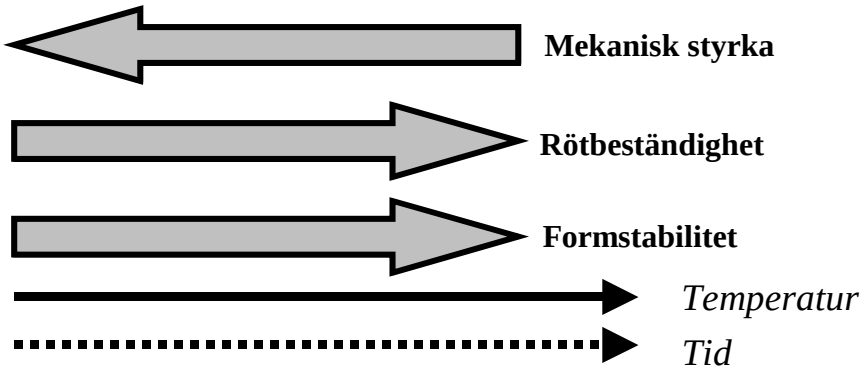
Dimensionen på det behandlade virket har begränsningar. För plank gäller max 50 mm tjockt plank och för rundträ gäller en diameter på max 100 mm för att de ska kunna processas med gott resultat (Boonstra et. al. 1998).

Tabell 2: Värmebehandlingsprocesser.

Produkt-namn	Nedtorkning före behandling	Första steget	Torkning mellan steg	Andra steget	Konditionering avsvalning	Kommentar
Thermwood	Ja, fuktkvot 12-14 %.	Uppvärmning till 150ºC-240ºC, 12-48 timmar.	*Inget, direkt till nästa steg.*	Behandling 150ºC-240ºC, 0.5-4 timmar.	Avsvalning 24 timmar.	
Platowood	Båda färskt och nedtorkat förekommer.	Värme+vattenbad, tryck 8-10 bar, 160ºC-190ºC, 0-4 tim.	3-5 dagar till fuktkvot 10 %.	Behandling i kvävgas, 170ºC-190ºC, 14-16 timmar.	2-3 dagars Konditionering.	
Retified wood (Förnätat trä)	Ja, fuktkvot 10-14 %.	Uppvärmning till 200ºC-260ºC, i kvävgas.	*Inget, direkt till nästa steg.*	Behandling i kvävgas, 220ºC-260ºC, 5-20 timmar.	Ingen uppgift.	Uppvärmning sker med el.
Le bois perdure (Beständigt trä)	(Ja) en artificiell torkning som kan kallas första steg.	Uppvärmning till 200ºC-240ºC, i mättad ånga	*Inget, direkt till nästa steg.*	Behandling i mättad ånga 200ºC-240ºC, 8 -24 timmar.	Ingen uppgift.	Uppvärmning sker med gas (propan).
Olje-värme trä	Ja, fuktkvot 6 %.	Uppvärmning av virke i olja till 180ºC-220ºC, 1-3 tim.	*Inget, direkt till nästa steg.*	Behandling i olja, 180ºC-220ºC, 2-4 timmar.	Avsvalning av oljan.	Eventuell tryck-sättning.
Staybwood	Ingen uppgift.	Uppvärmning till 90ºC-320ºC i luft eller metallsmälta	*Inget, direkt till nästa steg.*	Behandling i metallsmälta eller luft, 90ºC-320ºC, 1 minut-1 vecka.	Ingen uppgift.	
FWD Fukt-Värme-Tryck-trä	Ingen uppgift.	Uppvärmning till 180ºC-200ºC i ånga och kvävgas	*Inget, direkt till nästa steg.*	Behandling i ånga och kvävgas, 180ºC-200ºC, 8-10 bar, 1-4 timmar.	Ingen uppgift.	

5. Egenskapsförändringar för värmebehandlat trä

De flesta undersökningarna visar på samma generella effekter av värmebehandling. Dessa kan illustreras av figur 1 nedan där de mest fokuserade egenskaperna är markerade. Både tid och temperatur anges som viktiga faktorer för egenskapsförändringarna men temperatur är den vanligaste angivna.



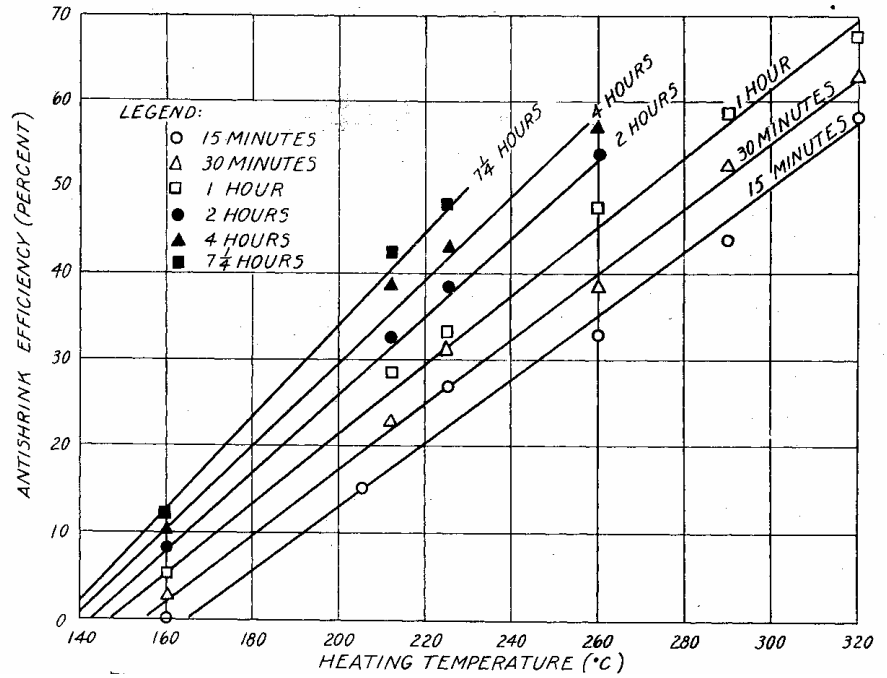
Figur 1: Generella egenskapsförändringar av värmebehandlat trä för förändrad temperatur och tid i behandlingen.

Dessa egenskapsförändringar för kommersiella värmebehandlade träprodukterna presenteras i tabell 3,6 och 7 och följande avsnitt. Även de icke kommersialiserade ”Staybwood” och ”FWD-trä” tas med för jämförelser.

Generellt så är många egenskaper av värmebehandling för trä kopplade till varandra och i vissa fall kan samband ges mellan dessa. Stamm et.al. 1946, kopplade behandlingstiden och behandlingstemperaturen till krympnings- och svällningsegenskaperna för träet, uttryckt i ASE (Figur 2). Detta står för ”Anti Schrinking Efficiency” (Ekv. 1 nedan).

$$ASE(\%) = \frac{S_R - S_V}{S_R} \qquad (1)$$

S_R: Svällningskoefficienten för referens, obehandlat trä.
S_V: Svällningskoefficienten för värmebehandlat trä.



Figur 2: Anti Schrinking Efficiency (ASE) för värmebehandlad (i flytande metal) tall (Pinus monticola; Western white pine). Prover 13 x 16 tum I tvärsnitt. (Stamm et. al. 1946).

Resistens mot biologisk nedbrytning

Biologisk nedbrytning av trä är ett komplicerat fenomen eftersom många olika typer av svampar, bakterier och insekter kan bryta ned trä. Beroende på i vilken miljö träet skall användas krävs olika kraftig resistens mot biologisk nedbrytning.
I Sverige finns fyra olika skyddsklasser av rötskydd beroende på var materialet skall användas. Tabell 5 ger definition av de olika klasserna och vilka konventionella rötskyddsmedel som används.

Det är noterbart att i den nya lagstiftning som väntas från EU kommer användande av arsenik i rötskyddsbehandling att beläggas med stora restriktioner.
Värmebehandlat virke är idag inte klassat efter detta system och det är svårt att bedöma exakt hur gott rötskydd behandlingen ger speciellt som man haft olika metoder för utvärdering av rötbeständigheten. Tabell 4 ger ett försök till klassning av Thermowood enligt det konventionella systemet.

Tester på hur rötbeständighet utvärderas har gjorts för många olika sätt. Den vanligaste är viktförlust efter inkubering med brunröta och mjukröta (softrot), EN 113, (Tjeerdsma et. al. 1998, Viitanen et. al. 1994, Sailer et. al. 2000, Giebeler 1983, Buro 1954, Kamden et. al. 1999). Även tester för vitröta har gjorts, PrENV 807.

Nedan finns en beskrivning av den rötbeständighet man redovisar i publikationer om temperaturbehandlad ved. I tabell 3 finns dessutom en sammanställning av rötresistens. I denna framgår det att en klar generell förbättring erhålls jämfört obehandlat trä. Vidare så är indikationen att värmebehandlat trä är bra mot brunröta men mindre bra mot vitröta och att värmebehandlat trä inte blir lika rötresistent som CCA-behandlat trä.

Rötbeständigheten ökar för behandling av trä över ca 120°C, och ökar markant över ca 200°C (Buro 1954), (Tabell 3). Generellt gäller då att ökad temperatur ökar beständigheten. Uttryckt i ASE ger ca 40 % ett bra rötskydd (Tabell 3, Figur 2). Detta styrks av ”Thermowood”, behandlad i 200°C, som klarar 4 års utomhusexponering (Jämsä et. al. 1999). Behandlingen gav dock inte skydd mot ytmögel enligt detta test. Tester av trä som behandlats med olje-värme enligt den tyska processen (Rapp och Sailer 2000), pågår och preliminära resultat tyder på att riskklass 4 (A, trä i markkontakt eller vatten) kan nås, med stort oljeupptag och hög behandlingstemperatur, se tabell 3 och 4. Detta har också indikerats för asp och Retified wood Detta är mer krävande än riskklass 3, öppen exponering utan markkontakt, som övriga aktuella behandlingar anges uppnå, Platowood, Thermowood, Retified wood och Le bois perdure (Vernois 2000, Syrjänen 2000, Jämsä et. al. 2000, Millitz och Tjeerdsma 2000). För ”Thermowood” har klassificering gjorts för att relatera till riskklasser enligt EN 335-1, se tabell 4.

I Fig. 3 (Millitz och Tjeerdsma 2000) visas vilka effekter värmebehandling av trä kan ha på rötbeständighet. En klar förbättring för värmebehandlat trä (PLATO) kan noteras. Liknande resultat uppnås generellt i de flesta undersökningarna (Tabell 3). Värmebehandlad radiatatall befanns vara speciellt rötbeständig (Tjeerdsma et. al. 1998). Värmebehandlad asp har också befunnits ha en särskilt bra rötbeständighet (Troya och Navarette 1994). En undersökning där en legeringssmälta bestående av bly, kadmium och tenn, användes för värmebehandlingen av trä, visade att mycket bra rötbeständighet kunde åstadkommas på detta sätt.(Buro 1955)

Inga av dessa aktuella metoder har ännu visat på ett effektivt skydd mot insekter, termiter eller marina skadegörare (Tabell 3), men en något förbättrad resistens mot termiter och marina skadegörare har dock rapporterats (Boonstra et. al. 1998, Vernois 2000), (Tabell 3).

Övermålningsbarhet/ limningsbarhet

Generellt så rapporteras det att lackering och målning av värmebehandlat trä fungerar bra (Jämsä et. al. 1999, Milltitz och Tjeerdsma 2000, Vernois 2000, Rapp och Sailer 2000 och Giebeler 1983). Limningsbarheten är däremot mera osäker och vissa rapporter pekar på att modifierade limtyper kan behövas (Rapp och Sailer 2000).

Tabell 3: Rötresistens och resistens mot insekter etc. för värmebehandlat trä.

Produknamn	Rötresistens (viktförlust)	Rötmetodsbeskrivning	Resistens (insekter etc.)	Kommentar
Thermowood	75 % (180ºC), 1% (230ºC) och referens 1% (CCA). 56 % (180ºC), 20% (230ºC) och referens 10% (CCA)	EN113 (gran), 16 veckors exponering. prENV807 (gran), 24 veckors exponering.	Ingen uppgift.	
Platowood	0-3 % (värmebeh.) och 1-26 % (obehandlat trä). Gran 18% (värmebeh.) och 28% (obeh.). Tall 5% (värmebeh.) och 20% (obeh.).	EN113, 16 veckors exponering. "Soil block", 36 veckors exponering	Prel. ökad resistens mot termiter och marina borrare.	
Retified wood (Förnätat trä)	11-47% (240ºC) och 57-58% (obehandlat trä). 28% (240ºC) och 35% (obehandlat trä).	"Soil block" (tall), brunrötetest. "Soil block" (tall), vitrötetest.	Resistent mot långhornade skalbaggar, ej termiter (prel.).	Asp, föreslagen anv. riskklass 4.
Le bois perdure (Beständigt trä)	*		*	
Olje-värme trä	15 % (180ºC), 2 % (200ºC) och < 2 % (220ºC). 40-48% för referens (obeh. trä) .	EN 113 (tallsplint och gran), 19 veckors exponering.	Ingen uppgift.	Hög temp. och oljeuppt., ev. riskklass 4
Staybwood	4 % (ASE 30 %), 12% (ASE 35 %) och 0 % (ASE > 40%). # 28 % för referens (obehandlat trä).	"Burktest", 2 månader.	Ingen uppgift.	
FWD Fukt-Värme-Tryck trä	2.2 % (värmebehandlat trä) och 17.8 % (obehandlat trä).	Rötkällare (bok).	Ingen uppgift.	

* Presenteras tillsamman med "Retified wood"

ASE: Anti-Schrinking-Efficiency (förändring i krympnings-/svällningstal mellan behandlat och obehandlat trä)

Tabell 4: Värmebehandlingsklasser relaterade till klassning av utomhuspåverkan på trä, EN335-1. (Syrjänen 2000).

Heat treatment classes	Hazard class EN 335-1	Situation in service	Description of exposure to wetting in service	Moisture content of untreated wood	Classification of impregnated timber
1	1	Above ground covered (dry)	permanently dry	permanently under 18 %	
2	2	aboved ground, covered risk of wetting	exposed to occasional wetting	occasionally over 20 %	
3	3	above ground not covered	exposed to frequent wetting	frequently over 20 %	AB (HC3/P8) B (HC3/P5)
	4	in contact with ground or fresh water	permanently exposed to wetting in contact with ground or fresh water	permanently over 20 %	A (HC4/P8)
	5	in salt water	permanently exposed to wetting by salt water	permanently over 20 %	M (HC5/P8)

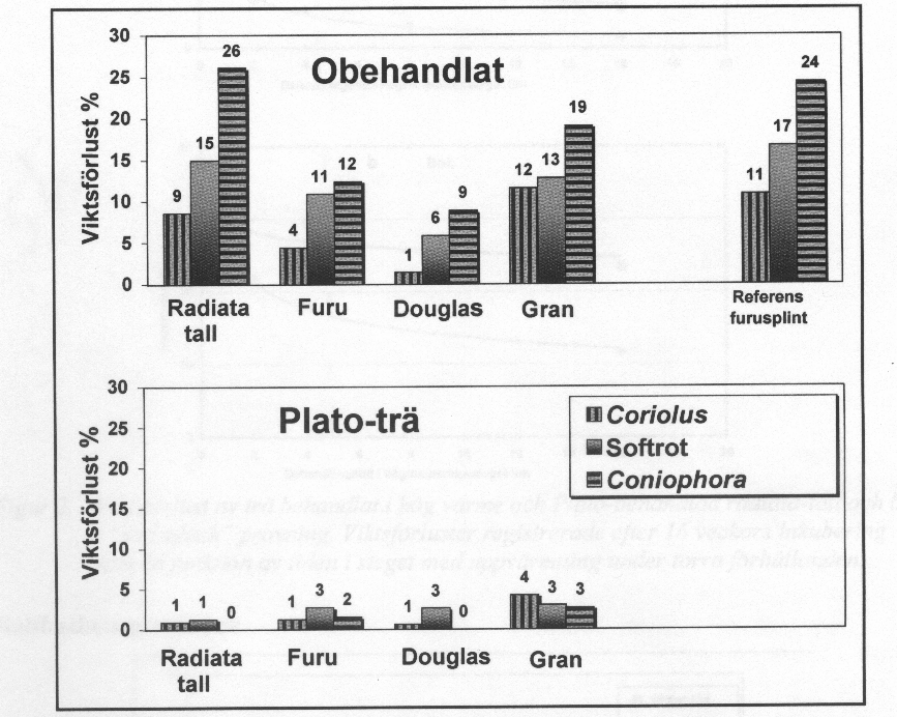
Tabell 5: Enligt träskyddsinstitutet gällande klassning i Sverige och de konventionella kemikalier som idag använts i dessa klasser

Träskyddsklass A Trä i kontakt med mark och (söt) vatten samt trä i konstruktioner ovan mark som kräver speciellt skydd. Krav på impregnering: Full inträngning i splintveden.
Typ av träskyddsmedel CCA* Koppar/krom/arsenik
Kreosot*, Kreosotolja.
CCB, CCP, CC* Koppar/krom/ (bor, fosfor)C, Koppar
Användningsområden
Trä i varaktig kontakt med mark och vatten, i bryggdäck och sötvattensanläggningar
samt trä ovan mark i fasta säkerhetsanordningar och konstruktioner som är svåra att byta ut.
Kreosot endast för yrkesmässig användning. Annan användning endast tillåten först 30 år efter impregnering.
Ej virke till bostadshus. Se CCA klass A.

Träskyddsklass M Full inträngning i splintveden
Typ av träskyddsmedel CCA* Koppar/krom/arsenik Kreosot*, Kreosotolja.
Användningsområden
Trä i varaktig kontakt med havsvatten, som t ex bryggor och hamnanläggningar.

Träskyddsklass AB
Trä ovan mark
Krav på impregnering. Full inträngning i splintveden.
.
Typ av träskyddsmedel
C, Koppar, Organiska utan metaller.
Användningsområden
Trä ovan mark som är utsatt för väder och vind eller kondens och där utbyte av skadade delar eller personsäkerheten inte är av avgörande betydelse.

Träskyddsklass B Färdigbearbetade snickerier ovan mark
Inträngning i splintveden 6 mm från sidan och 50 mm från ändytan.
Typ av träskyddsmedel Organiska utan metaller.
Användningsområden Endast färdigarbetade snickeridetaljer ovan mark t.ex. fönster och dörrar.(Endast vakuumimpregnering)



Figur 3: Röttest på obehandlat och termobehandlat trä. Rötbeständighet mättes som viktförlust för värmebehandlat trä, PLATO och obehandlat trä efter 16 veckors inkubering med ”Soil Block”- och ”miniblock”-metoden. (Millitz och Tjeerdsma 2000).

Orsakerna till den ökade beständigheten har diskuterats och olika tänkbara orsaker har presenterats. Bildning av giftiga ämnen samt organiska syror var en tidig idé (Buro 1954). Detta har senare inte ansetts särskilt viktigt utan att beständigheten beror på förändringar i lignin-kolhydratkomplexet. En hypotes är att hemicellulosa modifieras och bryts ned så mycket att mikroorganismer har svårt att använda den (Viitanen et. al. 1994). En smältning och omflytning av ligninet så att den mikrobiellt åtråvärda hemicellulosan bättre bäddas in eller att hemicellulosan och ligninet förbinds starkare. (Hillis 1984, Tjeerdsma 1998). Urlakning av extraktivämnen befanns också förbättra rötbeständigheten (Kamden et. al. 1999). Mycket återstår dock för att få en samlad bild av hur termobehandlingen ger en rötskyddande effekt för olika träprodukter.

Sorptionsegenskaper

Träets förmåga att ta upp och avge vatten, sorption är en nyckelfaktor för att förstå svällning, krympning och formstabilitet hos materialet. Även rötbeständighet, motverkan mot blånad och ytmögel kan kopplas till sorptionen hos trä. Röta och mögel kräver en viss mängd vatten för att verka, ca 20 % i fuktkvot hos träet. Många resultat har presenterats som visar att värmebehandling minskar träets sorption, se Figur 4 och 5 samt Tabell 6. Generellt så minskar sorptionen med ökad behandlingstid och ökad temperatur (Kollman och Schneider 1963, Schneider och Rusche 1973, Hillis 1984). I temperaturområdet 70-100°C fick man ingen förändring i sorption, vid 100-180°C fick man en gradvis minskning och vid temperaturer mellan 180-200°C fick man en klart minskad sorption (Kollman och Schneider 1963). Men vid lång behandlingstid, 48 timmar, ökade återigen sorptionen efter behandling vid 200°C. Man antar att ligninet förändras (kondenseras). Andra förklaringar är att fler bindningar mellan hemicellulosa och lignin bildas (Hillis 1984). I frånvaro av syrgas (luft) vid värmebehandling blir sorptionen generellt lägre för trä jämfört med värmebehandling då syrgas finns närvarande (Schneider och Rusche 1973, Giebeler 1983).

Värmebehandlat trä indikerar liknande egenskaper beträffande uppfukting och torkning jämfört icke värmebehandlat trä, se Fig. 5 (Jämsä et. al. 1999). Ibland relateras hygroskopiciteten till jämviktsfuktkvoten för ett visst klimat eller förändringen i procent mellan behandlat/obehandlat virke. I tabell 6 och Fig. 4 samt 5 presenteras data som visar en generell sänkning av jämviktsfuktkvoten med ca 40 - 60 % efter värmebehandling (Vernois 2000, Millitz och Tjeerdsma 2000). Jämviktsfuktkvoten blev generellt 4-5 % vid 50 % relativ fuktighet och rumstemperatur för värmebehandlat trä och 10-12 % för obehandlat trä (Tabell 6).

Tabell 6: Sorptionsegenskaper, dimensionsstabilitet och massförändring för värmebehandlat trä.

Produknamn	Sorptionsegenskaper värmebeh. trä	Dimensionsstabilitet	Massförändring (behandling)
Thermowood	Jämviktsfuktkvot minskad med 43-60 %, R.F. 65 %, tall.	Minskad svällning och och krympning (volym) 30-80 %	-5.7 % (205ºC, 4 tim), -11.1 % (230º, 4 tim), tall. -6.4 % (205ºC, 4 tim), -13.5 % (230ºC, 4 tim), björk
Platowood	Jämviktsfuktkvot minskad med ca 40 %, jämviktsfuktkvot ca 6% (värmebeh. trä) och ca 10 % (obeh. trä).	Minskad krympning och svällning; 10 %/13 % (radiellt/tangentiellt) (bok), 11 %/40 % (gran), 33 %/41 % (tall).	Ingen uppgift.
Retified wood ***(Förnätat trä)***	Jämviktsfuktkvot 4-5 % (värmebeh. Trä) och 10-12 % (obeh. trä).	ASE ca 50 % (volym), behandling 230ºC, asp,tall och gran. #	Ingen uppgift.
Le bois perdure ***(Beständigt trä)***	*	*	*
Olje-värme trä	Fibermättnadspunkt 14 % (Värmebehandlat trä), 29% (obehandlat trä), behandling 220ºC.	Minskad krympning och svällning (volym) ca 40 % (behandling 200ºC-220ºC), ca 25 % (behandling 180ºC), tall.	+45 % till +68% i olja (180ºC-200ºC). -2 % till -10 % i luft (180ºC-200ºC).
Staybwood	Ingen uppgift.	Minskad svällning och krympning (volym) ca 15 % (180ºC), ca 25 % (200ºC),ca 40 % (240ºC), tall (W.White).	-1 % (ASE 15 %), -2 % (ASE 23 %), # -8 % (ASE 40 %), granfanér (Sitka).
FWD ***Fukt-Värme-Tryck trä***	Jämviktsfuktkvot 13 % (värmebehandlat trä), 26 % (obehandlat trä), 90 % R. F och 25ºC.	Minskad svällning och krympning (volym) 50-80 %.	-2.5 % till -19.3 % (140ºC- 160ºC), bok. -2.0 % till -8.7 % (140ºC - 160ºC), tallsplint

* Presenteras tillsamman med "Retified wood"

ASE: Anti-Schrinking-Efficiency (förändring i krympnings-/svällningstal mellan behandlat och obehandlat trä)

R.F: relativ luftfuktighet

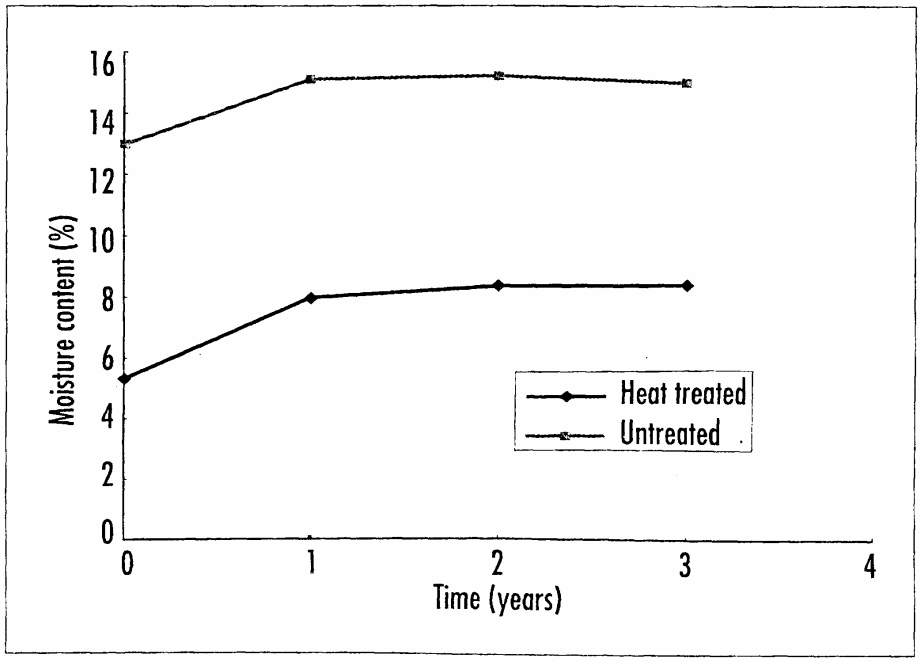
Dimensionsstabilitet

Hygroskopicitets- eller sorptionsförändringar ger förändringar på svällnings- och krympningsegenskaperna för trä (Tabell 6). Rödbok behandlad i autoklav med övertryck och vattenbad vid höga temperaturer (100-180°C) fick en irreversibel svällning tangentiellt och en irreversibel krympning radiellt som ökade då temperatur och/eller behandlingstid ökade (Noack 1969). Med värmebehandling i autoklav och trycksättning 8-10 bar kan 50-80 % minskad svällning och krympning fås (Giebeler 1983).

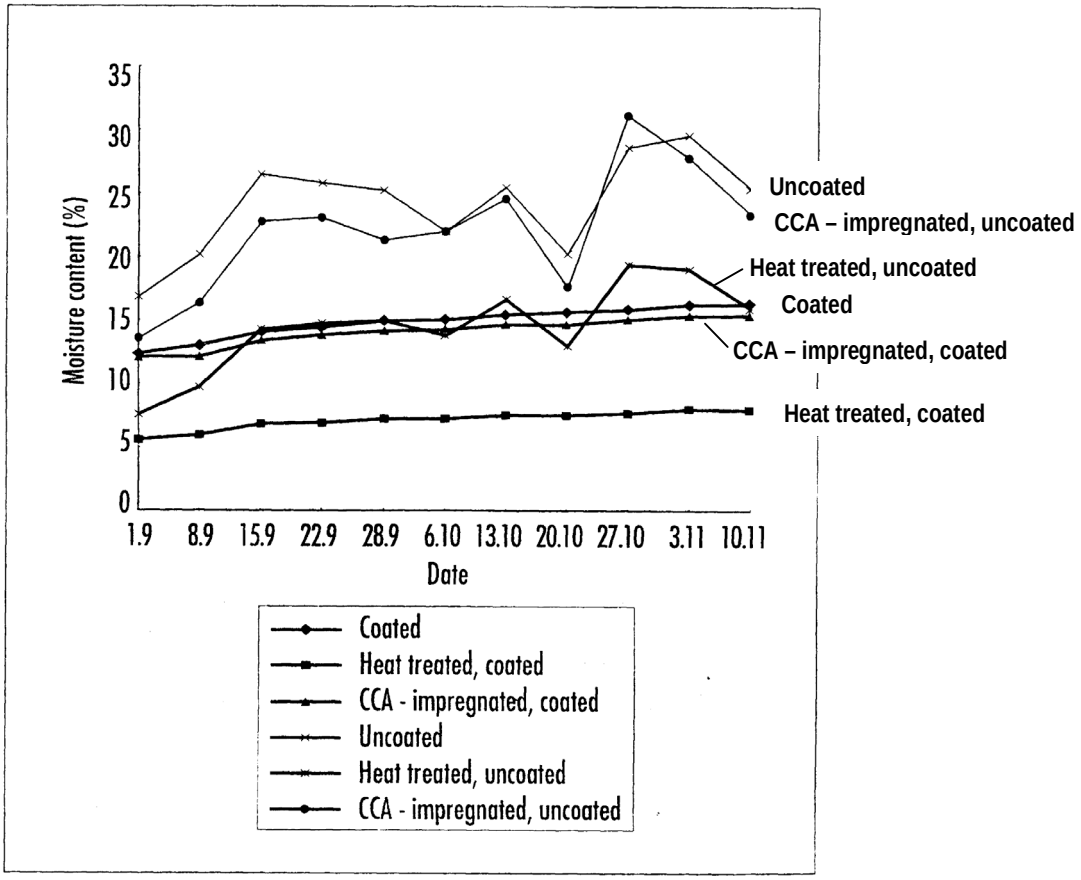
Inoue et. al. 1993, testade komprimering och samtidig värmebehandling av trä för att minimera krympnings- svällningsrörelser. En nästan fullständig fixering av rörelserna kunde uppnås samtidigt som hårdheten ökade och styrkan minskade obetydligt för behandlingar vid 180°C till 200°C i vattenånga. Vid värmebehandling i hetluft under mycket längre tider kunde också en bra fixering av rörelserna erhållas, men hårdhet och styrka minskade då avsevärt.

Dimensionsstabiliteten kan uttryckas ”Anti-Shrink-Efficency” (ASE), ASE visar minskad svällning i jämförelsen mellan obehandlat och behandlat trä (Fig. 2 och Ekv. 1). I allmänhet kan en ASE på 10-50 % fås genom lämpligt val av värmebehandling, se Tabell 6 (Millitz och Tjeerdsma 2000, Stam et. al. 1946, Tjeerdsma et. al. 1998). Generellt ger en ökad behandlingstemperatur en ökad ASE samtidigt som den ger en minskad styrka, se figur 6 och 7.

Värmebehandlat trä tar upp mindre fukt och träet rör sig därför mindre, m.a.o. det är mer formstabilt. Detta visade sig ge förbättrade resultat för ytbehandlade och värmebehandlade prov som exponerades utomhus jämfört med icke värmebehandlade och ytbehandlade prov. Färgskiktet på de värmebehandlade proven hade klart mindre flagning och sprickbildning än ytbehandlade och icke värmebehandlade prov (Jämsä et. al. 1999).



Figur 4: Jämförelse av fuktkvot (moisture content) för sågade och ytbehandlade granpaneler vid utomhusexponering. Ytbehandling med lösningsmedelsburen alkydfärg (Jämsä et al. 1999). Värmebehandlad gran; Heat treated. Icke värmebehandlad gran; Untreated.



Figur 5: Fuktkvot för hyvlade furupaneler ytbehandlade med lösningsmedelsburen syrahärdande snickerifärg vid utomhusexponering (Jämsä et. al. 1999)

Mekaniska egenskaper

De mekaniska egenskaperna försämras oftast när rötbeständighet och dimensionsstabilitet förbättras, se exempel Figur 1, 6,7 och Tabell 7. Slagsegheten (Fig.6) och ythårdheten (Fig. 7) kan bli avsevärt sämre (Stamm 1964, Giebeler 1983), vilket också kan uppfattas som att träet blir sprödare och mindre segt. En något bättre ythårdhet än andra föreslagna värmebehandlingsmetoderna kan noteras för det olje-värmebehandlade träet (Sailer et. al. 2000). Även försämrad böjstyrka, brottstyrka, kompressionsstyrka och dragstyrka kan noteras i varierande grad beroende på hur värmebehandling utförs (Kamden et. al. 1999, Rusche 1973, Schneider 1973, Schneider 1971, Sailer et. al. 2000, Giebeler 1983). Enligt Tjeerdsma et. al. 1998 förlorar PLATO-trä mindre i styrka än många andra värmebehandlingsmetoder p.g.a. ”trestegsprocessen”(Tabell 1).

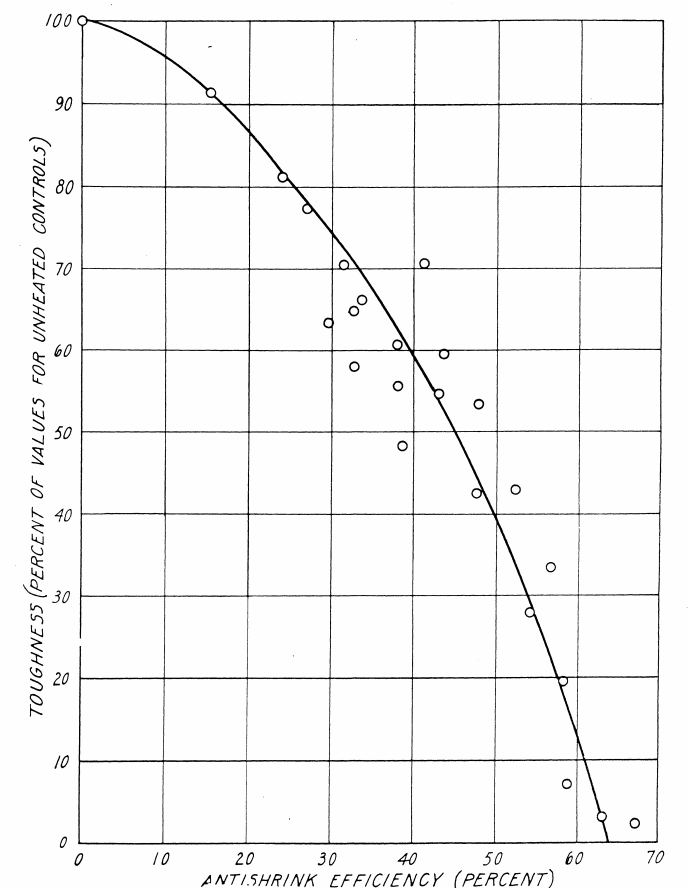
Generellt förlorar barrträ mer i styrka än lövträ (Tjeerdsma et. al. 1998, Schneider 1973). I allmänhet så är styrka korrelerad med nedbrytning räknat i vikt (Rusche 1973, Stamm et. al. 1946). För elasticiteten vid böjning krävs det dock mer än 8 % i viktförlust för att en signifikant förändring ska noteras (Rusche 1973). Behandlingstemperaturen anses som den viktigaste faktorn för förändrade styrkeegenskaper (Tjeerdsma et. al. 1998) och minst 150°C behövs för att styrkenedsättande förändringar skall börja noteras (Schneider 1973). Behandlingstiden är också av betydelse (Schneider 1973, Schneider 1971). Inverkan av syrgas har en starkt negativ inverkan på styrkan (Inoue et. al 1993, Stamm 1956). Närvaro av ättiksyra och andra organiska syror har negativ inverkan (Stamm 1956, Noack 1969). Med trycksättning i behandling rapporteras det att styrkeförluster kan minimeras (Giebeler 1983).

Tabell 7: Brottstyrka (MOR: Modulus Of Rupture) och slagseghet för värmebehandlat trä

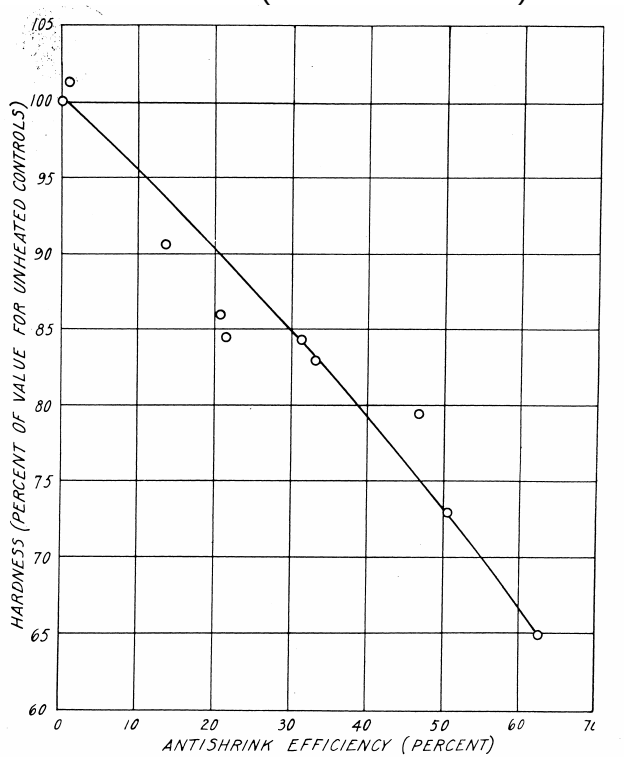
Produknamn	Brottstyrka böjning (MOR)	Slagseghet (pendelhammare)	Kommentar
Thermowood	Minskning 10-30 %.	Ingen förändring (Inga resultat presenterade).	Värmeledningsförmågan minskar med 10-30 %. Ingen förändring i hårdhet (ej pres.)
Platowood	Minskning 3 % (bok), 18 % (tall), beh.temp. 165ºC-185ºC.	Ingen uppgift.	
Retified wood ***(Förnätat trä)***	Minskning 30-40 %, behandlingstemp. 230ºC-240ºC. Minskning 40 % (bok), 8 % (gran), beh.temp ca 200ºC.	Minskning 37%, tall (Maritime), behandlingstemperatur ca 200ºC.	Asp minskar mindre i hållfasthet. Hårdhet: -27 %, Maritime tall, beh.temp.ca 200ºC.
Le bois perdure ***(Beständigt trä)***	*	*	*
Olje-värme trä	Minskning 20 % för beh.temp 180ºC. Minskning 50 % för beh.temp 200ºC.	Minskning 49 %, beh.temp. 220ºC, motsv. exklusive olja, minskning 63 %. Minskning 20 %, beh.temp. 180ºC, motsv. exklusive olja, minskning 40 %.	
Staybwood	Minskning 17 % (ASE 40 %), 5 % (ASE 25 %), beh. i metallbad. # Minskning 50% i luft (motsvarande ASE 40 %). Tall (W.White).	21% minskning, i metallbad (för ASE 40 %), tall (W.White).	Hårdhet: -40 %. Nötning: -90 %, i metallbad, ASE 40 %.
FWD ***Fukt-Värme-Tryck trä***	Minskning ca 10 % (björk), ca 14 % (asp), behandling vid 195ºC och 10 bar under 2.5 timmar.	Ingen uppgift.	

* Presenteras tillsamman med "Retified wood"

ASE: Anti-Schrinking-Efficiency (förändring i krympnings-/svällningstal mellan behandlat och obehandlat trä)



Figur 6: Sambandet mellan seghet (toughness) och dimensionsstabilitet (ASE) för värmebehandlat trä (Stamm et. al. 1964)



Figur 7: Sambandet mellan ythårdhet (hardness) och dimensionsstabilitet (ASE) för värmebehandlat trä (Stamm et. al. 1946)

Ansträngningar att försöka kombinera liten styrkeförlust med ökad rötbeständighet och dimensionsstabilitet är ett genomgående mål i de flesta undersökningar om värmebehandling av trä. Många undersökningar pekar på att optimerad temperatur vid behandling i syrgasfattig/syrgasfri atmosfär är de viktigaste faktorerna för att balansera de önskande egenskaperna. Men många andra faktorer har visats inverka på de mekaniska egenskaperna och relativt lite kunskap finns om vad som sker i trä under värmebehandling ur ett materialtekniskt och materialkemisk perspektiv.

Färg och lukt

Det färska värmebehandlade virket har oftast en karakteristisk röklukt som avtar ganska snabbt (Vernois 2000, Millitz och Tjeerdsma 2000). Virket är generellt homogent ljusbrunt till mörkbrunt beroende på främst temperatur och tid för behandlingen, se omslagsbild, (Boonstra et. al. 1998, Vernois 2000, Syrjänen 2000, Thunell och Elken 1948). För olje-värmebehandlat trä rapporteras en svagare och jämnare färgförändring än de övriga aktuella metoderna (Sailer och Rapp 2000).

Förklaringar till egenskapsförändringar

Förklaringar till vad som händer under värmebehandling pekar på nedbrytning av hemicellulosa som en dominerande orsak till egenskapsförändringarna (Sanderman och Augustin 1963, Fengel 1966, Bobletter och Binder 1980). Det är välkänt att kolhydrater lätt bryts ned vid högre temperaturer och i närvaro av fukt/vatten. Mellan 150 och 180° ökar hemicellulosanedbrytningen starkt (Fengel 1966, Kollman och Fengel 1965). Tall börjar nedbrytas redan vid 100°C medan Ek behöver 150°C (Kollman och Fengel 1965). I närvaro av organisk syra så accelererar nedbrytning av hemicellulosa och cellulosa (Noack 1969). Eftersom hemicellulosa avspaltar organiska syror, främst ättiksyra under värmebehandling (Dietrichs et. al. 1978) så är en snabb nedbrytning ofta förväntad. I naturligt tillstånd så är dessutom trä i de flesta fall något surt, pH 3-6 (Gray 1958).

Huruvida cellulosan i träet förändras är osäkert. Få undersökningar behandlar detta och många anser att ingen förändring sker förrän man överstiger 200°C (Zaman et. al. 2000). Stamm 1956 rapporterar att hemicellulosa bryts ned 4ggr snabbare än cellulosa och lignin hälften så snabbt. Nedbrytning av kolhydrater har i andra sammanhang utnyttjats för att producera melass, försockring (Nationalencyklopedin) och försök till bränsleproduktion såsom t.ex. gengas genom kolhydraterna i träet. (Theander och Nelson 1988, Dietrichs et. al. 1978). Mer detaljerade undersökningar om förändringar i cellulosan, speciellt depolymerisering (kortning av molekylkedjornas längd), är förmodligen av stor vikt för förståelse om träets mekaniska styrka.

Ligninets förändring i samband med värmebehandlingen har diskuterats och undersökts i ett flertal undersökningar (Sarni et. al. 1990, Burtscher et. al. 1987, Hillis 1984, . Ligninet börjar förändras redan vid 120°C och en nedbrytning börjar vid 170-190°C (Sarni et. al. 1990, Sanderman och Augustin 1963). Speciellt närvaro av syrgas betraktas som en mycket viktig faktor vid ligninnedbrytning, oxidation, (Sanderman och Augustin 1963).

En komplex förändring av lignin-kolhydratkomplexet tas också upp i en del undersökningar (Tjeerdsma et. al. 1998, Hillis 1984). Minst 90°C behövs för att plasticera lignin-hemicellulosa och vid temperaturer över glasomvandlingstemperaturen för hemicellulosa anses förbättringar av dimensionsstabiliteten och rötbeständigheten fås för trä genom förnätning (kemiskt) av lignin/hemicellulosa och omfördelning av hemicellulosa.
Li och Lundqvist 2000, undersökte ligninets förändring vid sodablekning (110°C 40 min.) av pappersmassa och fann att radikaler bildas (homolytisk spaltning) vid nedbrytning av ligninet. Möjligheten finns att lignin-radikaler i trä kan vidare reagera med kvarvarande lignin, cellulosa och hemicelullosa och ge förnätning bl.a.

Extraktivämnen såsom fenoler och tanniner etc. diskuteras också ibland att delta eller bidra till egenskaper för värmebehandlat trä (Kamden et. al. 1999, Sarni et. al. 1990), men halterna verkar vara för låga i de flesta fall för att kunna påverka egenskaperna märkbart.

Många undersökningar har gjorts om värmebehandling av trä med en mängd olika metoder och inriktningar. Mera komplexa undersökningar på en mer grundläggande kemiskt teknisk nivå är svåra att finna. Detta skulle behövas för att vidare kunna optimera och differentiera värmebehandlingsmetodiken.

5. Framtida möjligheter

- Bättre kunskaper om den kemiskt-tekniska förändringen i trä skulle kunna leda till att minimera styrkeförlusterna och få ett rötbeständigt, formstabilt och estetiskt tilltalande material.

- Bättre anläggningar för värmebehandling av trä skulle kunna ge möjlighet till att styra/kontrollera kvalitén på material och samtidigt få ekonomisk lönsamhet

- Flera processmetoder kan förmodligen utvecklas vilket skulle kunna ge många olika typer av slutprodukter med hög kvalité.

- Värmebehandlat trä har goda utsikter att kunna kvalitetsmärkas och klara livscykelanalyser och därigenom kunna konkurrera med andra typer av material och produkter.

- Värdehöjning av träslag med lågt anseende, t.ex. asp.

- Förbättrad processkontroll m.h.a av nya mätsystem som mäter exempelvis emitterade produkter från trä

6. Patent

Många patent har tagits inom värmebehandlingsområdet. Två tidiga patent från USA är ”Heat stabilized wood (Staybwood)” (Stamm et. al. 1946) och ”Heat stabilized compressed wood (Staypak) (Seborg et. al. 1948). Staybwood är dimensionsstabilisering av trä genom värmebehandling pga. reducering av hygroskopiciteten. Värmebehandlingen kan göras i het luft eller i en metallsmälta. Staypak är trä som pressas under värmebehandling vid sådana förhållanden att komprimeringen inte förloras för en viss fuktkvot efter att det utsatts för varierande klimat.

Ett mera modernt patent är ”Process för the modification of wood” (Giebeler et. al 1983), Reutgerswerke AG, Tyskland, EP0018446. En process för att modifiera trä och träprodukter genom värmebehandling i en sluten behållare där fuktinnehållet i materialet från början kontrolleras att inte innehålla mer än 10 % (vikt). Detta är ett patent för den beskrivna behandlingen FWD, se kap. 3 tabell 1.

Patent som är kopplade till de i dag aktuella metoderna är ganska många. I Holland kom 1994 ”Process for upgrading low-quality wood” (Rem et. al. 1994), EP0612595, Shell Int. Research. Process för elektriskt baserad värmebehandling med ett första steg, mjukgörning, i ett vattenbad med tillsatser och trycksättning som är minst jämviktstrycket för denna vid aktuell processtemperatur. Det andra steget, torkning av det mjukgjorda träet, det tredje steget härdning och slutligen kylning av träet. Detta patent har också en motsvarighet i USA Rem et. al. 1994), US55555642, Shell Oil Co (US). En utveckling av detta patent med samma namn är, (Ruyter et. al. 1994), EP06234433, Shell Int. Research. Tillkommande uppgifter; första mjukgörande steget genomförs i 160-240°C i närvaro av en pH buffert (pH-kontroll) med pH 3.5-8.0. Detta hydrolyserar hemicellulosan och omfördelar ligninet i träet. Ytterligare utveckling av detta patent kom 1995 med samma namn (Ruyter et. al. 1995), EP0622163, Shell Oil Co (US). Detta har en liknande beskrivning för de beskrivna ovan med skillnaden att temperaturen för mjukgörningen är 120-160°C och att önskade måltemperaturen bibehålls tills skillnaden i temperatur mellan yta och centrum för virkesbitarna är mindre än 20°C.

Från Finland kom 1997 ”Method för improving biodegradation resistance and dimensional stability of cellulosic products” (Viitaneimi et. al. 1997 eller Viitaneimi et. al. 1996), Valtion Teknillinen Tutkimuskeskus (VTT). US5678324 eller EP695408A1 respektive. US-patentet finns i bilaga 1. Denna omarbetades senare med en ny titel, ”Method for increasing the resistance of cellulosic products against mould and decay” (Viitaneimi et. al. 2001), Valtion Teknillinen Tutkimuskeskus, EP695408B1. En metod för att förbättra resistansen för cellulosabaserade produkter mot förruttnelse och nedbrytning, och för att förbättra dimensionsstabiliteten. Cellulosaprodukten värmebehandlas i förhöjda temperaturer. Produkten ska ha en fuktkvot lägre än 15 % och behandlas i minst 150°C i 2-10 timmar tills en viktförlust om 3 % har skett. Mer information om detta patent finns i bilaga 1.

Från frankrike kom 1999 ”Method for treating wood at the glass transition temperature thereof” (Guynnet 1999), NOW, US5992043. En behandlingsmetod där virket behandlas för en bestämd temperatur och tid. Virket uppvärms till sin glasomvandlingstemperatur (Tg) och hålls där tills hela virket når denna. Patent för

”Retified wood” finns beskrivet i ”Reactor for wood retification” (Guillin 2000), Fours et Bruleurs Rey, AU4789399A1. En reaktor med tätad kammare som kan operera stegvis. Den är också utformad för att kunna cirkulera atmosfären inne i kammaren. Virket ska kunna belastas kontrollerat och kontinuerligt. Reaktorn medger en industriell metod för att förnäta trästrukturen (kemiskt).

Förmodligen kan ytterligare patent hittas inom värmebehandlingsområdet men dessa belyser en hel del om dagsläget beträffande den industriella utvecklingen.

7. Sammanfattning

- Värmebehandlat trä kan ge märkbart förbättrad rötbeständighet och dimensionstabilitet.

- De mekaniska styrkegenskaperna för värmebehandlat trä minskar tydligt.

- Temperatur, tid, fukt/vatten, tryck, pH, syrgas är viktiga faktorer vid värmebehandling av trä

- Sverige saknar både industriell tillverkning och FoU på värmebehandling av trä medan Tyskland, Holland, Frankrike och Finland sedan länge bedrivit FoU och redan har eller startar upp industriell tillverkning

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US5678324: Method for improving biodegradation resistance and dimensional stability of cellulosic products

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We claim:

1. A method for increasing the resistance of a cellulosic product against mold and decay and for improving the dimensional stability of said product comprising the steps of:
(A) subjecting a wet cellulosic product to a heat treatment so as to reduce the moisture content of the product to less than 15%; and
(B) subjecting the resulting cellulosic product of step (A) to an atmosphere saturated with steam at a temperature above 150° C. so as to reduce the weight of the product at least 3% by decomposition of wood components present in the cellulosic product.

2. The method according to claim 1, wherein during step (A), the difference between the inner temperature of said product and the outer temperature of said product is maintained at about 10° to 30° C. so as to prevent cracking.

3. The method according to claim 2, wherein step (A) is carried out in the presence of steam.

4. The method according to claims 2 or 3, wherein step (A) comprises the steps of:
(i) placing said product in a drying oven, wherein the temperature of said oven is raised to at least 90° C., and wherein said oven is kept at said temperature until said product has at least approximately reached said temperature,
(ii) gradually increasing the temperature of said oven while maintaining the difference between the inner temperature of said product and the temperature of said oven at less than 30° C. until the desired moisture content of the product has been reached, and optionally,
(iii) gradually lowering the temperature of said oven while maintaining the difference between the inner temperature of said product and the temperature of said oven at less than 30° C. until the inner temperature of said product has reached the desired temperature.

5. The method according to claim 4, wherein the temperature of said oven is raised to at least 100° C.

6. The method according to claim 1, wherein step (A) is carried out at 180° to 250° C. for 1 to 20 hours.

7. The method according to claim 6, wherein step (A) is carried out for about 2 to 10 hours.

8. The method according to claim 1, wherein step (A) is carried out essentially under non-pressurized conditions.

9. The method according to claim 1, wherein said cellulosic product is selected from the group consisting of wood pillars, wood logs, sawn wood, wood veneer, plywood, wood chips, saw dust and wood fibers.

10. The method according to claim 9, wherein said cellulosic product is pine wood, and wherein in step (B), said pine wood is subjected to a temperature of 200° to 250° C. for 2 to 8 hours so as protect against decay.

11. The method according to claim 9, wherein said cellulosic product is spruce wood, and wherein in step (B), said spruce wood is subjected to a temperature of 175° to 210° C., for 2 to 8 hours so as to protect against decay.

12. The method according to claim 9, wherein the cellulosic product is birch wood, and wherein in step (B), said birch wood is subjected to a temperature of 200° to 250° C., for 2 to 8 hours so as to protect against decay.

13. The method according to claim 9, wherein the cellulosic product is larch-tree wood, and wherein in step (B), said larch-tree wood is subjected to a temperature of 200° to 250° C., for 2 to 8 hours so as to protect against decay.

14. The method according to claim 1, wherein in step (B), the weight of the product is reduced at least about 5%.