HEAT TREATMENTS OF HIGH TEMPERATURE DRIED NORWAY SPRUCE BOARDS: SACCHARIDES AND FURFURALS IN SAPWOOD SURFACES

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Carbohydrates that migrate to wood surfaces in sapwood during drying might influence properties such as mould–susceptibility and colour. Sugars on the surface of Norway spruce boards during various heat treatments were studied. Samples (350mmx125mmx25mm) were double-stacked, facing sapwood-side outwards, and dried at 110°C to a target moisture content (MC) of 40%. Dried sub-samples (80 mm x 125 mm x 25 mm) were stacked in a similar way and further heated at 110°C and at 130°C for 12, 24, and 36 hours, respectively. Glucose, fructose, and sucrose as well as 5-hydroxymethylfurfural (HMF) and furfural in the sapwood surface layer of treated wood were analysed using HPLC (RI- and UV-detectors). Carbohydrates degraded to a lower extent at 110°C than at 130°C. Furfural and to a larger extent HMF increased with treatment period and temperature. Heat treatment led to a decrease in lightness and hue of the sapwood surface of sub-samples, while chroma increased somewhat. Furthermore, considerably faster degradation (within a few minutes) of the carbohydrates on the surface of the dried spruce boards was observed when single sub-samples were conductively hot pressed at 200°C. Treatment period and initial MC influenced the presence of the carbohydrates in wood surface as well as colour change (ΔE_{ab}) of the hot pressed sub-samples.

Keywords: High temperature dryíng; Heat treatment; Sapwood; Norway spruce; Glucose; Fructose; Furfural; Colour; Mould

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INTRODUCTION

Increasing temperatures during the industrial drying of wood has been a trend during several decades, resulting in a more efficient production and controlled properties of wooden boards. However, modern drying schedules also accelerate the migration of soluble sugars to the wood surface (Terziev *et al*. 1993; McCurdy 2005) where they could increase the ability for growth of mould (Theander *et al*. 1993; Sehlstedt-Persson 2011). This issue has become more important with a warmer climate and use of more energy efficient houses. Enrichment of water-soluble carbohydrates during industrial drying can also influence other surface properties of wood such as colour by formation of coloured reaction products, often called Kiln Brown Stain (Sehlstedt-Persson 1995; Kreber *et al*. 1998; McDonald *et al*. 2000). In Scots pine, mostly fructose, glucose, and sucrose have been found as well as minor amounts of other oligosaccharides (Theander *et al*. 1993). The presence of soluble carbohydrates may vary within and between single

boards, and a relatively high content of monosaccharides has been found in winter-felled logs (Saranpää and Höll 1989).

We have been studying mould growth on sapwood surfaces of Norway spruce and Scots pine boards that have been double stacked during drying (Sehlstedt-Persson *et al*. 2011). Sapwood surfaces were more infected by mould when drying was performed at 70°C than during air-drying, especially in the case of pine. However, at higher treatment temperatures (that is 110°C) the ability for mould growth was clearly reduced (Sehlstedt-Persson *et al*. 2011). This could be due to the fact that migrated carbohydrates start to degrade during the thermal treatment leading to lower content of nutrients and a more mould resistant surface. 5-hydroxymethylfurfural (HMF) and furfural are common degradation products from monosugars where HMF is formed from hexoses, whereas furfural mainly originates from pentoses (Fengel and Wegener 1989). Furfurals are not so stable during further heat treatment and can polymerise, degrade (Dunlop and Peters 1953; Gandini and Belgacem 1997), or simply evaporate. Furthermore, during the heating of sugars also several other products can be formed, such as caramelans, caramelens, and caramelins, as well as other furans, maltol, biacetyl, esters, and lactones (Miller 1993). In wood, reactions involving other wood components, such as amino acids forming Maillard products that subsequently can lead to colour formation, are possible (Theander *et al*. 1993; McDonald *et al*. 2000). Finally, reactions involving cleavage of glucosidic bonds in oligo- and polysaccharides that can result in formation of monosaccharides may take place. Arabinogalactan is one example of a soluble polysaccharide that has been found in relatively large amounts in green Norway spruce and Scots pine (Willfor and Holmbom 2004).

Soluble carbohydrates enriched at wood surfaces could act as nutrients for bioorganisms such as mould, and it is of interest to study whether the amount of nutrients could be reduced by heat treatments. Thus, in this paper, we wanted to study how two types of heat treatments (convective heating in an laboratory oven at 110°C and 130°C as well as conductive heating using a hot press at 200°C) influence the presence of glucose, fructose, and sucrose as well as degradation products 5-hydroxymethylfurfural and furfural in surfaces of dried spruce boards.

EXPERIMENTAL

Materials

Four winter-felled green side boards A, B, C, and D (4500 x 125 x 25 mm) from Norway spruce were obtained from Kåge saw mill, Skellefteå, Sweden. Saw dust from Norway spruce (MC 7%) was used. D(+)-Glucose, D(-)-fructose, 5-hydroxy-methylfurfural (95%), furfural was from VWR (furfural was distilled to a colourless liquid before use) and sucrose from Danasugar. Silicon paste was from Silibeton A/S.

Treatments

The conditions employed in the drying and heating experiments are set forth in Table 1.

Table 1. Drying and Heating Experiments Performed (including untreated control experiments)

Trial	Raw material	Dimensions (mm)	Treatments	Number of samples	Temp (°C)	Time (h)	Analysis type
1	Green spruce samples from side boards A, B, C and D	350x125x25	Double stacked drying (DSD)	32	110	13-17	HPLC, Colour
2	DSD spruce sub-samples	80x125x25	Double stacked oven heating	32	110 130	12, 24, 36	HPLC, Colour
3	DSD spruce sub-samples with MC 7, 18 and 40%	80x125x25	Hot pressing	27	200	0.042 0.083	HPLC, Colour
4	Sawn DSD spruce sub-samples	80x125x23	Arabinose or furfural application and hot pressing	2	200	0.083	Colour
5	Spruce saw dust-water (1:25)		Heating in closed vials	3	110	18, 72	HPLC
6	Spruce sap		Heating in closed vials	4	90 110	18, 72	HPLC

Trial 1: Double stacked drying (DSD) of green spruce samples

Four green sapwood side boards (A, B, C, and D) from Norway spruce were sawn into 4 x 8 samples with dimensions of 350 x 125 x 25 mm. Tangential surface of samples were planed (1 to 2 mm) to diminish influence of pre-drying of surface. Moisture content was measured in short cut-offs from each sample according to the oven dry method, and twenty-four samples were arranged into three new groups containing eight samples each according to decreasing moisture content (130% to 120 %, 120% to 105%, 105% to 85%) without paying attention to which board the samples originated from (low MC was mainly due to that some air-drying took place before cutting into samples). Samples were end-sealed with silicon paste and double stacked with the pith side surfaces facing each other (and sapwood side surfaces facing outwards), as shown in Fig. 1. Eight double-stacked samples were mounted together with clamps into a package, and the package was dried in a laboratory oven at 110^{o}C with air circulation without humidity control. A total of four packages were dried.

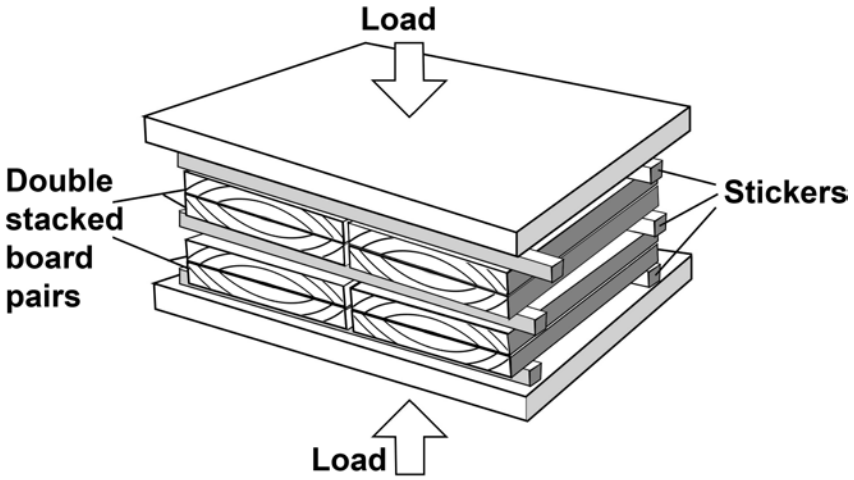

Fig. 1. Double stacked samples during drying to target MC of 40%

During drying of green wood, soluble carbohydrates migrate with capillary water to the wood surface, where water is evaporated but where carbohydrates will remain. When the capillary drying phase in sapwood reaches irreducible saturation (well above the fibre saturation point, FSP), the continuous body of liquid water bursts into sub-regions, and the flow of capillary water, and thus migration of carbohydrates to the wood surfaces, ceases. Because of this, drying was interrupted with the aim of reaching a target MC of 40%, after 13 to 17 hours, depending on the initial MC of samples. Samples were stored in plastic bags in a freezer until further used.

Trial 2: Double stacked heat treatments of dried sub-samples in oven at 110^{o}C and 130^{o}C

Dried samples (350 x 125 x 25 mm) from original board B, C, and D were further sawn into eight series of sub-samples, each comprised of four smaller sub-samples with dimensions of 80 x 125 x 25 mm. The smaller sub-samples were end-sealed, and one sub-sample from each series was used as reference, whereas the other three were used for heat treatment experiments for 12, 24, and 36 hours. Heat treatment was performed by double stacking three sub-samples from each of two series of sub-samples into a package of a total of six sub-samples and heated in oven similar to what was performed during drying (see above). After 12 hours of treatment, one sub-sample from each series was taken out, and the remaining ones were packed again and further heated for 24 hours, and so on. Four replicates were used for each heat treatment temperatures (110^{o}C and 130^{o}C) and treatment periods (12, 24, and 36 h.), as well as for dried reference sub-samples, a total of 32 sub-samples.

Trial 3: Heat treatment of dried sub-samples with hot press plates at 200^{o}C

Three dried samples (350*125*25 mm) from original boards A and C were conditioned outdoors for one month to MC of 18%. Another three samples from original boards B and C were conditioned indoors for two months to MC of 7% and another three samples from original boards C and D were used without conditioning. Each sample was

sawn into three smaller sub-samples (80 x 125 x 25 mm) for a total of 27 (3 x 3 x 3) sub-samples in which one was used as a dried reference and the other two used for heat treatments for 2.5 min and 5 min. Sub-samples were end-sealed and conductive heated using a small press (14 x 14 cm, Fjellman press), as shown in Fig. 2.

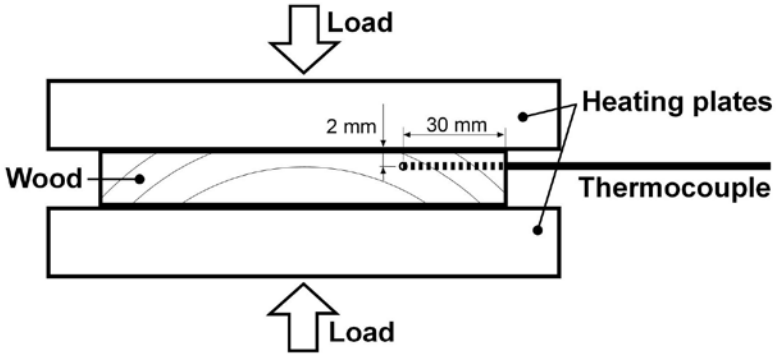

Fig. 2. Conductive heat treatment in a hot press (200°C)

Press plate temperature was set to 200°C and pressing pressure to 1 bar. Compression of wood during heating was small, and the thickness of the sub-samples was similar after and before pressing. Temperature was recorded with thermocouples placed in a drilled small hole at about 2 mm below wood surface and about 3 cm into the wood sub-sample.

Trial 4, 5 and 6: Miscellaneous heat treatments

Two experiments were performed in Trial 4, in which a 5% solution of arabinose as well as furfural was applied with brush to a sub-sample, where the enriched surface sheet had been removed. After a few minutes, allowing the liquor to penetrate into the wood surface, the wood sub-sample was heated with a hot press plate at 200°C for 5 min.

In Trial 5, saw dust from dried Norway spruce (MC 7%) was sieved (<1 mm), mixed with water (wood-water 1:25), and heated in small sealed vials at 110°C. The remaining liquor was analysed by HPLC.

In Trial 6 sap was isolated by pressing samples of winter-felled green spruce boards–from Kåge saw mill followed by filtering through a fine filter paper. Heat treatment of sap was performed in small sealed vials in an oven at 90°C and 110°C. Sap was then analysed by HPLC.

Work-up and analysis of water-soluble carbohydrates with HPLC in Trial 1-3 and 5-6

Thin sheets were sawn out (80x125x2 mm) from the enriched sapwood side of surface, milled, and sieved (<1 mm). The content of fructose and glucose at depth more than 2 mm below wood surface was found to be low (Sehlstedt-Persson *et al*. 2011) and was not analysed further. Wood particles were mixed with water (wood-water 1:15) and ultrasound treated for one hour and left over night.

Water extracts from Trial 1-3, liquor from Trial 5 and treated sap from Trial 6 were filtered (50 μm) and analysed by HPLC at 60°C. The HPLC device was equipped with a Water Hi-plex Pb-column (8 μm and 250x7.7 mm) using water as eluent at a flow

of 0.3 mL/min. Furfural and HMF were detected with UV-detector operating at 280 nm, and monosaccharides and sucrose were detected with a RI-detector. A Varian prostar autosampler (model 410), equipped with a 10μL loop, was used and quantitative estimations were made by comparison with calibration curves of individual compounds.

Colour measurement in Trial 1 – Trial 4

Colour measurement was performed with a Minolta Chromameter CR 310 colorimeter on sapwood wood surfaces from heat treatments in oven at 110°C and 130°C (Trial 1 and Trial 2) as well as from treatments with a hot plate at 200°C (Trial 3). The colour system setting was lightness (L^*), chroma (C^*), and hue (h), according to the CIE standard (Hunt 1995). Three measured co-cordinates L^*, C^*, and h were transformed to L^*, a^*, and b^* co-ordinates and ΔE^*_{ab} value, according to the equations below (Hunt 1995).

$$a^* = C \cos h \quad (1)$$

$$b^* = C \sin h \quad (2)$$

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

RESULTS AND DISCUSSION

Double Stacked Drying of Green Spruce Samples – Trial 1

Enrichment of monosaccharides (fructose and glucose) towards the wood surface takes place in situations where moisture can freely evaporate during drying of double stacked boards in a laboratory oven (Sehlstedt-Persson *et al.* 2011). Sugar-enriched wood surfaces from Norway spruce were prepared in a similar way, allowing moisture to freely evaporate from the sapwood-side of the samples until a target MC of 40% was reached (see Fig. 1). Studies on the presence of low molecular weight carbohydrates; fructose, glucose, and sucrose were performed by leaching isolated wood samples of sapwood surface (0 mm to 2 mm) of the dried samples with water, and leachate was analysed with HPLC (Fig. 3).

The content of fructose was found to be higher than glucose, which in turn was higher than sucrose. A considerably larger amount of monsaccharides has been found in the outermost part of wood surfaces where migration is favoured than further into the wood (Sehlstedt-Persson *et al*. 2011). However, in this paper, we wanted to assure that practically all enriched sugars in the wood surface were included in the analysis, and therefore a thicker dimension of isolated surface sheets were chosen, which led to a lower content per dry mass of wood. Distribution of the content of the carbohydrates was fairly narrow in case of fructose and glucose, but much wider for sucrose (Fig. 3). Furthermore, a slight yellowing was observed at the wood surface where migration is favoured; such yellowing is evidence that also other reactions took place.

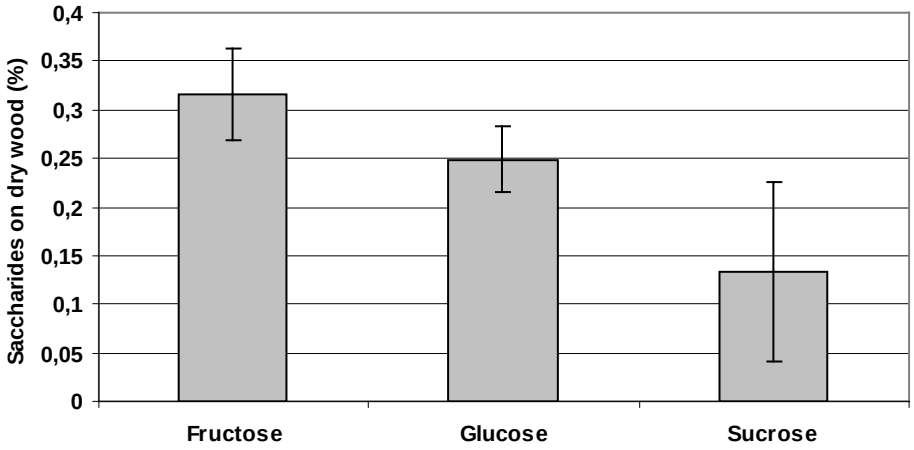

Fig. 3. Average content of fructose, glucose, and sucrose in sapwood surface (0 - 2 mm) of dried spruce samples in Trial 1. Standard deviation based on eight replicates is indicated with brackets

Water-soluble Compounds in Spruce Sub-Sample Surface Heated at 110°C and 130°C

As discussed in the introduction, the heating of monosaccharides will eventually lead to degradation and formation of various degradation products such as furfurals. However, in the case of wood, carbohydrates with higher molecular weight may also contribute to the presence of species having low molecular weight. For example, sucrose, upon hydrolysis of its glucosidic bonds, could form glucose and fructose. Soluble carbohydrates enriched at wood surfaces could act as nutrients for bioorganisms such as mould, and it is of interest to study if the amount could be reduced by various heat treatments (Trials 2 to 4 in Table 1).

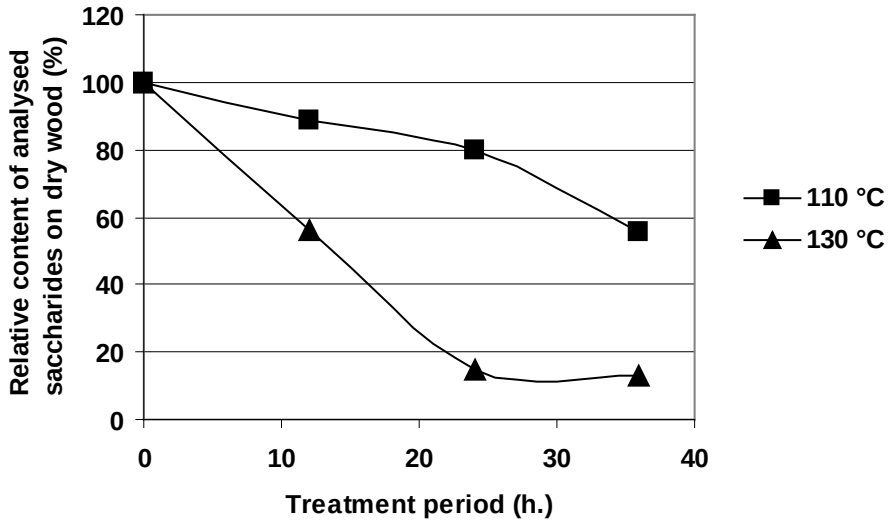

Fig. 4. Relative contents of analysed saccharides (fructose, glucose, and sucrose) in sapwood surface of spruce sub-samples after heat treatment at 110°C and 130°C

Heat treatment in Trial 2 was performed in a laboratory oven with double-stacked sub-samples (with sapwood side facing outwards) to prevent any remaining capillary water from moving deeper into the wood. In Fig. 4, the content of analysed saccharides in sapwood surface of spruce sub-samples after heat treatments at 110°C and 130°C is shown (Trial 2), and a decrease with increasing treatment period could be observed.

A similar decrease in content of each sugar, fructose, glucose, and sucrose, with increased treatment time could be observed at 110°C (Table 2). Standard deviation was, however, relatively large, and a significant decrease could not be deduced at 110°C (Table 2). When heating spruce sub-samples at a treatment temperature of 130°C (Trial 2), a significant degradation of the saccharides could be observed (Fig. 5 and Table 2). Fructose seemed to be more sensitive to heat than glucose and sucrose (Table 2). This could be related to a lower caramellisation temperature for fructose than for glucose and sucrose (Miller 1993). However, after 24 hours of treatment at 130°C, changes in the saccharide content were small and not significant (Fig. 4 and Table 2). It may be explained by formation of monosaccharides by glucosidic cleavage of sucrose and other oligosaccharides (Table 2).

Table 2. Saccharides and Furfurals in Sapwood Surface of Spruce Sub-Samples Heat Treated at 110°C and 130°C. (Standard deviation based on four replicates is written in small figures)

	Content on dry wood (%)				
Treatment	Glucose	Fructose	Sucrose	HMF	HMF
Reference	0.27 0.085	0.30 0.104	0.028 0.0088	0.34×10^{-3} 0.11×10^{-3}	0.092×10^{-3} 0.5×10^{-6}
110°C, 12 h.	0.23 0.092	0.28 0.11	0.017 0.011	0.92×10^{-3} 0.26×10^{-3}	0.34×10^{-3} 1.6×10^{-6}
110°C, 24 h.	0.22 0.073	0.25 0.10	5.4×10^{-3} 3.3×10^{-3}	1.5×10^{-3} 0.63×10^{-3}	0.52×10^{-3} 2.7×10^{-6}
110°C, 36 h.	0.16 0.034	0.17 0.039	5.4×10^{-3} 4.7×10^{-3}	3.4×10^{-3} 0.27×10^{-3}	0.96×10^{-3} 4.1×10^{-6}
Reference	0.22 0.046	0.33 0.095	0.24 0.22	0.42×10^{-3} 0.32×10^{-3}	0.24×10^{-3} 0.20×10^{-3}
130°C, 12 h.	0.12 0.015	0.12 0.025	0.20 0.18	5.9×10^{-3} 1.8×10^{-3}	1.6×10^{-3} 0.44×10^{-3}
130°C, 24 h.	0.058 0.016	0.044 0.0095	0.13 0.14	0.012 1.3×10^{-3}	3.3×10^{-3} 0.37×10^{-3}
130°C, 36 h.	0.064 0.028	0.029 0.020	0.077 0.072	0.020 3.0×10^{-3}	5.0×10^{-3} 0.48×10^{-3}

In Trial 5, sawdust from spruce was heated at 110°C in excess of water, and arabinose was found to be the dominant monosaccharide (0.7% in dry wood after 18 and 72 hours of treatment). This indicates that, under those more extensive conditions, arabinose can be released by hydrolysis of glucosidic bonds in arabinose-containing

carbohydrates (arabinogalactan and softwood xylan). However, in the case of heat treatment of solid wood sub-samples boards, only smaller amounts of galactose and arabinose could be found; this was not quantified further due to over-lap of peaks.

5-Hydroxymethylfurfural (HMF) can be formed during heat treatment via dehydration of hexoses, while furfural can be formed via dehydration of pentoses, but also to some extent from hexoses (Fengel and Wegener 1989). Even though these compounds are neither thermally stable nor non-volatile, they may be used as an indicator of degradation of carbohydrates. From Table 2 and Fig. 5 we can conclude that furfurals in the material after double stacked drying were very low, indicating that degradation of carbohydrates during the drying phase is small. The amount of furfurals was higher but still relatively low in the heat-treated sub-samples compared to the loss of saccharides (Fig. 4 and Fig. 5). Both HMF and furfural increased with treatment time, and HMF was present always in larger amounts than furfural under those conditions (Fig. 5 and Table 2).

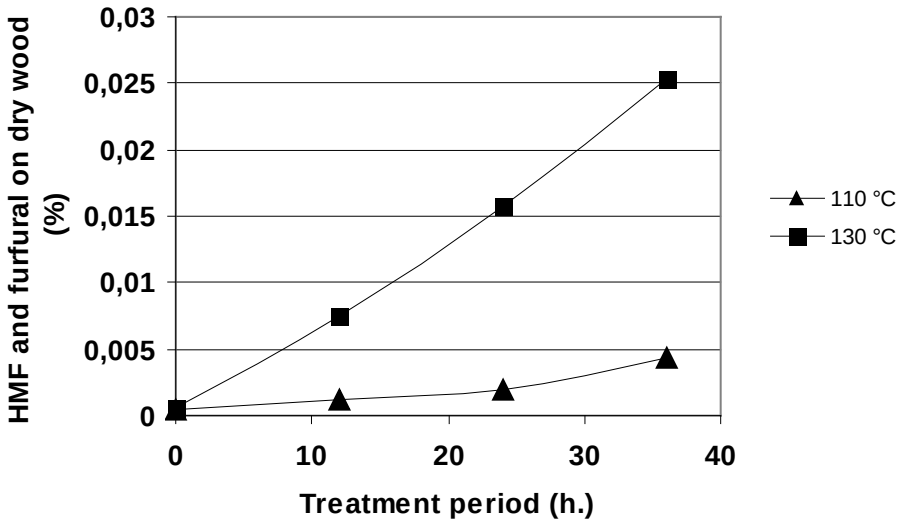

Fig. 5. Content of HMF and furfural in sapwood surface of spruce sub-samples after heat treatment at 110°C and 130°C

Formation of furfurals was more extensive at 130°C than at 110°C, also supporting the fact that sugars are more easily degraded at the higher temperature (Fig. 4). Increase of furfurals at 130°C was fairly linear even after longer treatment periods (>24 h.), which indicates that sugars other than the analysed ones could contribute to formation of furfurals (Figs. 4 and 5). Furfurals are important degradation products when heating saccharides (Miller 1993); however, content of furfurals in the wood after convective heat treatments was considerably lower than what could be expected from degradation of sugars; for example, sum of furfurals and saccharides after heating at 130°C for 36 hours was much lower than starting saccharide content (Table 2). This could be due to emission of degradation products from sugars during heating, but also formation in other products than HMF and furfural as discussed in the introduction. A

thorough investigation of such complicated reactions was considered to not be within the scope of the paper and was not further studied.

The sub-samples after treatment were dry and, therefore, degradation of the sugars may take place at a smaller extent when the heat treatment is finished at shorter treatment periods when aiming at higher target MC (less than 12 hours). Furthermore, as could be expected, the average MC of isolated wood particles from treatments at 130°C was lower (3.8%) than at 110°C (5.3%).

Thermal Stability of Water-soluble Compounds in Spruce Sap

Stability of the sugars and formation of furfurals in liquid state was further studied by heating sap from winter-felled Norway spruce wood (Trial 6). In this way, degradation reactions should be more favoured than when heating solid wood samples (Trial 2 to 4). However, sugars were found to be fairly stable and degradation of glucose and fructose started to be prominent when heated at 110°C for 18 hours, but not when heated at 90°C (Table 3). Also, formation of furfurals was more prominent after 72 hours than after 18 hours of treatment. A minor increase in the presence of arabinose was observed when heated at 110°C (Table 3). Arabinogalactan has been found in relatively large amounts in green Norway spruce and Scots pine (Willfor and Holmbom 2004), and its presence could be a reason for this observation due to hydrolysis of glucosidic bonds in the polysaccharide and release of arabinose during heat treatment. The formation arabinose could also be the main reason for the higher content of furfural observed after heat treatment for 72 hours than for 18 hours, as arabinose could form furfural but not HMF by heat treatment. Thus, formation of arabinose hardly takes place during conventional drying conditions, but it can be formed when wood is dried unter HT-conditions.

Table 3. Content of Monosaccharides and Furfurals in Spruce Sap Heat Treated at 90°C and 110°C for 18 and 72 hours.

	Content (mg/ml)				
Treatments	Glucose	Fructose	Arabinose	HMF	Furfural
Reference	0.22	0.26	0.01	-	-
90°C, 18 h.	0.21	0.24	0.01	-	-
110°C, 18 h.	0.18	0.18	0.03	0.002	0.001
110°C, 72 h.	0.16	0.12	0.05	0.018	0.007

Colour Formation during Heat Treatments of Spruce Sub-Samples at 110°C and 130°C in Trial 2

The thermal treatments lead to a darkening of the surface of wood and were more pronounced at the higher temperature and longer treatment period (Fig. 6). Chroma (C^*) increased with treatment period, pointing to a somewhat more intense colour formation. It can be seen that hue (h) decreased with the treatment period at 130°C (Fig. 5). Furthermore, in Fig.6, a red-yellow-red shift during heat treatment at 110°C is indicated. A similar behaviour was found when spruce sapwood was heated in a closed vessel at 80°C (Sundqvist 2002).

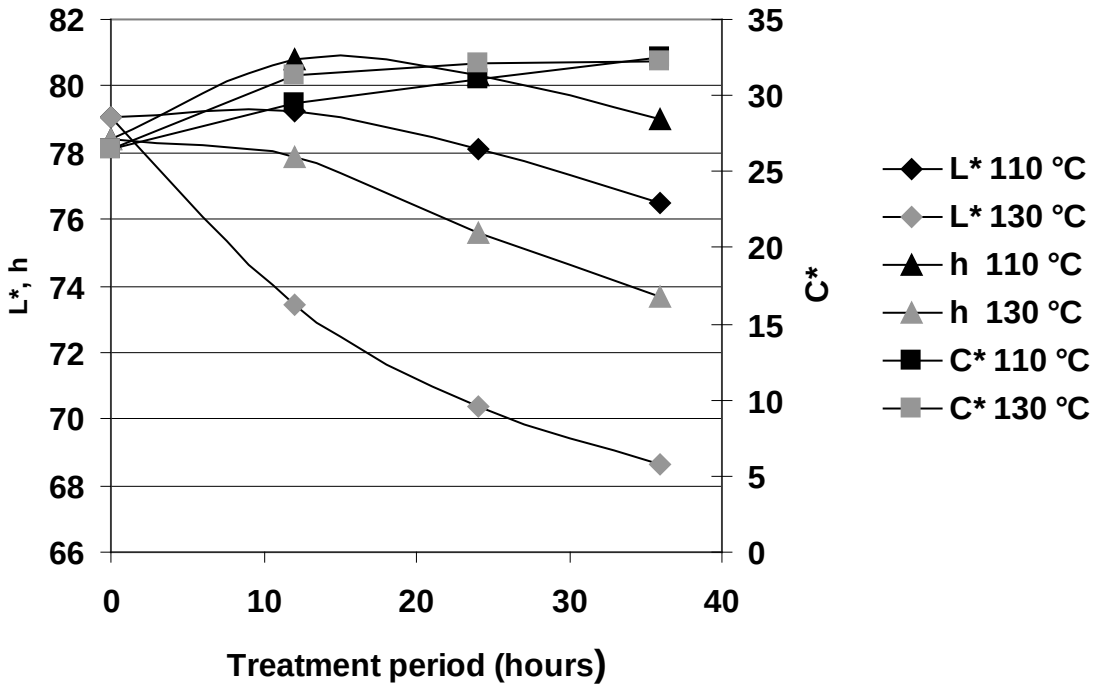

Fig. 6. Colour coordinates for sapwood surface of spruce sub-samples after heating at 110°C and 130°C. Data are based on duplicate measurements.

Water-soluble Compounds in Spruce Sub-Sample Surface Heated at 200°C – Trial 3 and Trial 4

From the results above we suggest that it is possible to degrade low molecular weight carbohydrates in wood surface of Norway spruce by heat treatments at a sufficient temperatures (<130 °C) for a specific heating time (<24 h.). Thus, degradation of saccharides was fairly slow under those conditions.

In order to increase the extent of degradation and concentrate the heat to the wood surface, DSD sub-samples were conductive heated as single pieces by hot press plates at 200°C for short treatment periods with only minimal compression of the wood material (Fig. 2).

Soluble compounds were analysed in the wood surface (0 mm to 2 mm), as above, and data on presence of saccharides and furfurals from the heat treatments can be seen in Table 4. A similar degradation of the saccharides at the higher MC (18% and 40%) was observed (Fig. 7). Although large variation in the data could be observed in Table 4, it is strongly indicated that degradation of carbohydrates of heating was more intense at target MC of 7% than at 18% and 40% (Fig. 7).

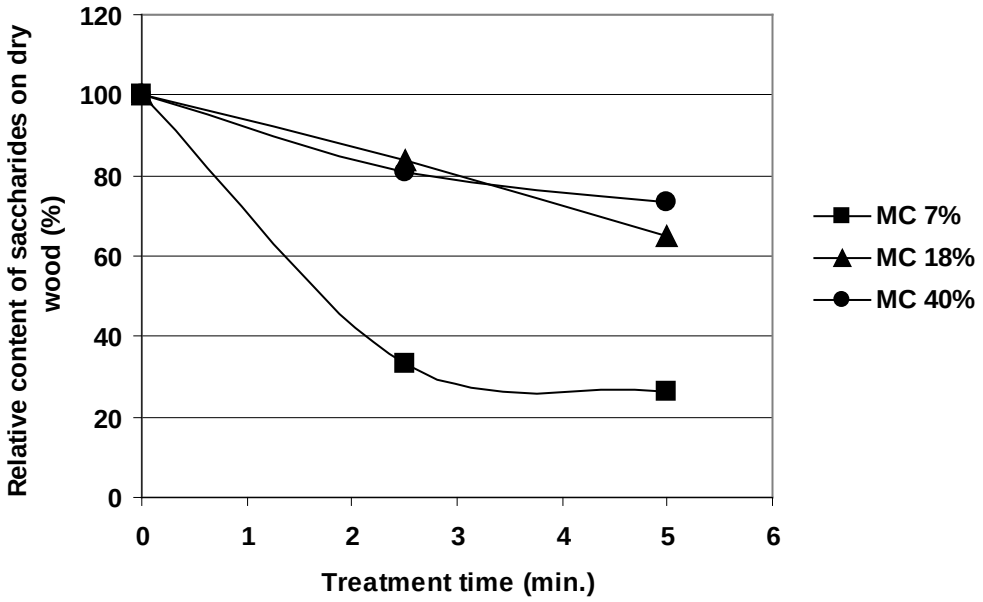

Fig. 7. Influence of initial MC on presence of total analysed saccharides (glucose, fructose and sucrose) in sapwood surface of spruce sub-samples after conductive heating with hot plate at 200°C

After 5 min of heating, the content of furfurals was much higher at MC of 7% than at the higher moisture contents (Fig. 8 and Table 4).

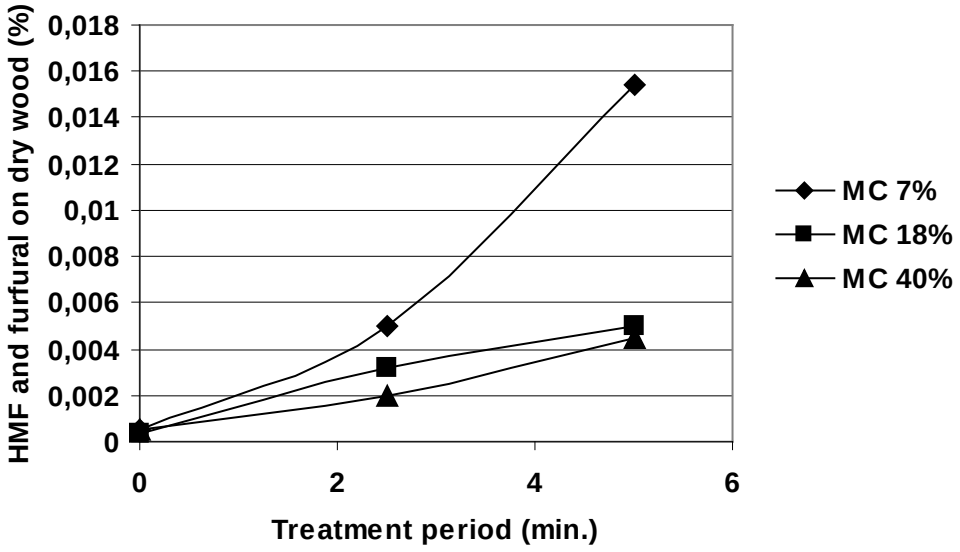

Fig. 8. Content of HMF and furfural in sapwood surface of spruce sub-samples after conductive heating with hot plate at 200°C

This may be related to considerably higher final temperature near the wood surface at the lower than at the higher MC; using thermocouples mounted as described in experimental section a final temperature of 160°C was detected for treatments of sub-samples with MC of 7% and 110°C for treatments of sub-samples with MC of 40%. However, this could not explain why saccharide degradation seemed to be slower after 2.5 min of heat treatment (Fig. 7), and as formation of furfurals did not seem to be reduced, degradation of oligosaccharides and formation of low molecular weight saccharides could be a more probable reason explaining this observation (Table 4).

Table 4. Content of Monosaccharides and Furfurals in Sapwood Surface of Conductive Heat-Treated Spruce Sapwood Sub-Samples using a Hot Press Plate of 200°C. (Standard deviation is written in small figures and was based on three replicates.)

	Content on dry wood (%)				
Treatments	Glucose	Fructose	Sucrose	HMF	Furfural
Reference	0.62	0.90	0.31	0.058×10^{-3}	0.47×10^{-3}
	0.13	0.11	0.24	6.8×10^{-6}	0.049×10^{-3}
Hot pressed	0.22	0.27	0.12	4.3×10^{-3}	0.65×10^{-3}
2.5 min (MC 7%)	0.054	0.093	0.072	2.1×10^{-3}	0.22×10^{-3}
Hot pressed	0.17	0.18	0.13	0.014	1.5×10^{-3}
5 min (MC 7%)	0.052	0.059	0.091	8.5×10^{-3}	1.0×10^{-3}
Reference	0.26	0.31	0.085	0.16×10^{-3}	0.19×10^{-3}
	0.13	0.068	0.068	0.21×10^{-3}	0.089×10^{-3}
Hot pressed	0.11	0.17	0.064	2.9×10^{-3}	0.29×10^{-3}
2.5 min (MC 18%)	0.16	0.19	0.073	6.1×10^{-3}	0.99×10^{-3}
Hot pressed	0.094	0.10	0.038	4.4×10^{-3}	0.57×10^{-3}
5 min (MC 18%)	0.015	0.025	0.18	0.18×10^{-3}	0.44×10^{-3}
Reference	0.27	0.28	0.098	0.23×10^{-3}	0.33×10^{-3}
	0.064	0.083	0.034	0.20×10^{-3}	0.22×10^{-3}
Hot pressed	0.24	0.27	0.046	1.6×10^{-3}	0.40×10^{-3}
2.5 min (MC 40%)	0.068	0.074	0.035	0.15×10^{-3}	0.052×10^{-3}
Hot pressed	0.21	0.24	0.053	4.0×10^{-3}	0.48×10^{-3}
5 min (MC 40%)	0.047	0.044	0.023	0.74×10^{-3}	0.12×10^{-3}

Formation of Colour in Spruce Sub-Sample Heated at 200°C – Trial 3 and Trial 4

Colour formation was studied by calculation of ΔE^*_{ab} of surface from both sides of a single sub-sample board after pressing and comparison with the corresponding reference surface (Fig. 9). Stronger colouring was obtained for surfaces where migration of sugars during double stack drying was not physically hindered. The formation of colour was somewhat more extensive at lower MC than at higher MC. Furthermore, an increase in colour formation with increased treatment period is indicated especially at the lower moisture content (Fig. 8).

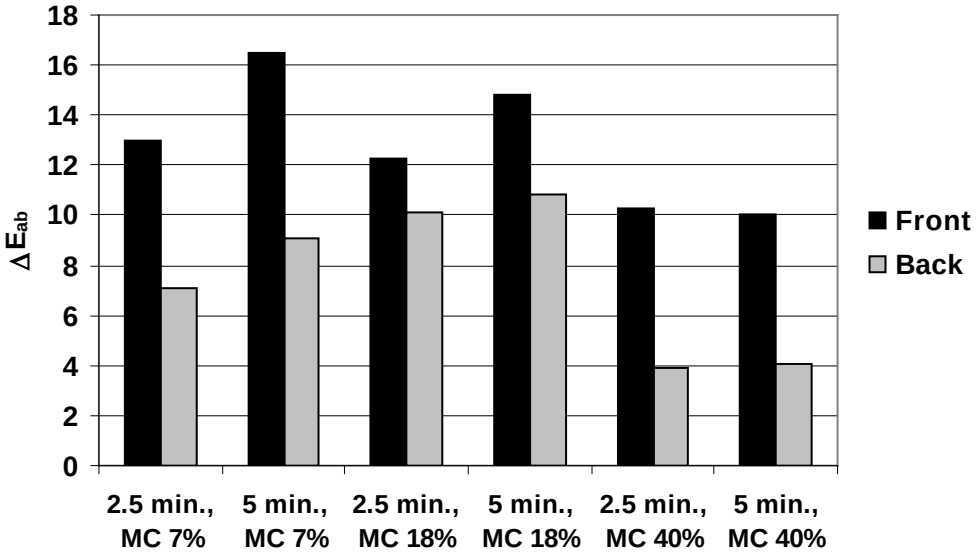

Fig. 8. Colour difference (ΔE^*_{ab}) of surfaces after conductive heating with press plates (200°C). Front: sapwood surface of spruce sub-sample that has been facing outwards during double stacked drying, Back: surface facing pith-side of spruce sub-sample that has been physically blocked during drying. Data is based on duplicate measurements.

As discussed above, degradation of glucose, fructose, and sucrose, as well as formation of furfurals was also more extensive at lower MC than at higher MC (Table 4 and Figs. 7 and 8). In a control experiment (Trial 4 in Table 1), a water solution of arabinose was sprayed over a sawn wood surface and conductively heat-treated at 200°C for 5 min. The treatment gave a coloured surface. In another experiment furfural was applied in similar way but only a small colour formation was observed. This suggests that degradation of migrated monosaccharides play an important part in colour formation of wood surfaces during heat treatments, but probably do not involve furfural degradation product. Although nitrogen content was not analysed it is believed to be low and formation of Maillard products under those conditions should be low.

CONCLUSIONS

Results presented in this paper suggest that it is possible to significantly reduce the amount of water-soluble sugars (glucose, fructose, and sucrose) in wood surface of spruce by heat treatment at 130°C of artificially dried boards. To obtain a considerable degradation, heat treatments at 130°C for longer periods (more than 1 day) needs to be undertaken. Such treatments lead to boards with low moisture content that needs to be reconditioned before use under more humid conditions.

Only a small degradation of saccharides (glucose, fructose, and sucrose) was observed when heated at 110°C. It seems, therefore, not likely that the small degradation of saccharides and thus small reduction in the amounts of nutrients that occurs during HT-drying at 110°C can fully explain the lower mould growth of HT-dried spruce boards

than boards dried at 70°C (Sehlstedt-Persson *et al.* 2011). This could instead involve formation of other compounds during the drying treatments at the higher temperature and will be subject for further studies.

Using a hot plate (200°C) could be an alternative to degrade monosaccharides in wood surface, however, the monosaccharides are not fully degraded and the technique requires rather dry boards to be successful. Colouring can be a drawback but the technique may be used as an indicator for enrichment of carbohydrates in wood surface after drying.

Only small amounts of furfural HMF were found in the sub-samples after heat treatments and any significant odour formation was not recognised.

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REFERENCES CITED

Dunlop, A. P., and Peters, F. N. (1953). *The Furans*, Reinhold Publishing Co., New York.

Fengel, D., and Wegener. (1989). *Wood. Chemistry, Ultrastructure, Reactions*, Walter de Gruyter, Berlin, New York.

Gandini, A., and Belgacem, M. N. (1997). "Furans in polymer chemistry," *Prog. Polym. Sci.* 22, 1203-1379.

Hunt, R. W. G. (1991). "Measuring colour," *Fountain P.*, Surrey, UK.

Kreber, B., Haslett, A. N., and McDonald, A. G. (1998). "Kiln brown stain in radiata pine: A short review on cause and methods for prevention," *Forest Prod. J.* 49(4), 66-70.

McCurdy, M. C. (2005). "Efficient kiln drying of quality softwood timber," *Ph.D thesis*, University of Canterbury, New Zealand.

McDonald, A. G., Fernandez, M., Kreber, B., and Laytner, F. (2000). "The chemical nature of kiln brown stain in *Radiata* pine," *Holzforschung* 54, 12-22.

Miller, D. D. (1998). *Food Chemistry: A Laboratory Manual*, John Wiley and Sons, New York, Chichester, Brisbane, Singapore, Toronto.

Saranpää, P., and Höll, W. (1989). "Soluble carbohydrates of *Pinus sylvestris* L. sapwood and heartwood," *Trees* 3,138-143.

Sehlstedt-Persson, M. (1995). "High temperature drying of Scots pine. A comparison between HT- and LT-drying," *Holz Roh Werkst* 53, 95-99.

Sehlstedt-Persson, M., Karlsson, O., Wamming, T., and Morén, T. (2011). "Mold growth on sapwood boards exposed outdoors: The impacts of wood drying," *Forest Prod. J.* 61(2), 170-179.

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 Roh Werkst* 60, 106-114.

Theander, O., Bjurman, J., and Boutelje, J. B. (1993). "Increase in the content of low-molecular carbohydrates at lumber surfaces during drying and correlations with nitrogen content, yellowing and mould growth," *Wood Sci. Technol.* 27, 381-389.

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

Willfor, S., and Holmbom B. (2004). "Isolation and characterisation of water soluble polysaccharides from Norway spruce and Scots pine," *Wood Sci Technol* 38, 173-179.

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