PRESENCE OF WATER-SOLUBLE COMPOUNDS IN THERMALLY MODIFIED WOOD: CARBOHYDRATES AND FURFURALS

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With thermal modification, changes in properties of wood, such as the presence of VOC and water-soluble carbohydrates, may occur. Thermal modifications under saturated steam conditions (160^{o}C or 170^{o}C) and superheated steam conditions (170, 185, and 212^{o}C) were investigated by analysing the presence of water-soluble 5-(hydroxymethyl)furfural (HMF), furfural, and carbohydrates in heat-treated wood. The influence of thermal modifications on Scots pine, Norway spruce, and silver birch was also studied. Furfurals were analysed using HPLC at 280 nm, while monosaccharides and water-soluble carbohydrates were determined by GC-FID as their acetylated alditiols and, after methanolysis, as their trimethylsilylated methyl-glycosides, respectively. The amount of furfurals was larger in boards thermally modified under saturated steam conditions than those treated under superheated steam conditions. Generally, more of HMF than furfural was found in the thermally modified boards. In process water, in which saturated steam conditions had been used, furfural and only traces of HMF were found. Higher content of water-soluble carbohydrates was found in boards treated in saturated steam rather than in superheated steam. After modification in saturated steam, substantial parts of the water-soluble carbohydrates were due to monosaccharides, but only traces of monosaccharides were found in boards treated under superheated steam conditions.

Keywords: Thermal; Steam; Superheated; Saturated; Birch; Spruce; Pine; Furfural; HMF

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INTRODUCTION

Thermal modification of wood in a semi-closed autoclave under steam conditions has been proposed as a method to more economically produce durable wood products for use above ground when compared to modification under superheated steam conditions. Properties such as durability, colour, and acid content of the material thermally modified under saturated steam conditions has been studied (Ohnesorge *et al.* 2009; Dagbro *et al.* 2010; Torniainen *et al.* 2011).

Wood darkens during thermal modification, and similar colour formation of wood from Scots pine and Norway spruce was found for the two types of processes, even though the treatment under saturated conditions were performed at a treatment temperature that was 40°C lower than used in superheated conditions (Dagbro *et al.* 2010). Moreover, birch gave a darker material than pine and spruce in both treatment processes (Torniainen *et al.* 2011). We have reported that higher acid content could be found in wood thermally modified under saturated steam conditions than under superheated steam conditions, and birch was found to give more acid than pine and spruce (Torniainen *et al.* 2011). It is also striking that the strongest smell was obtained for birch treated under saturated steam conditions. This indicates that degradation reactions of wood components are more prominent under saturated conditions than under superheated conditions and that the extent of degradation is also related to wood species.

Thermal modification of wood leads to a material that is less hygroscopic and more dimensionally stable. This has been attributed to degradation of hemicellulose and to condensation reactions that hinder uptake of moisture by forming new bonds between wood polymers such as lignin (Alén *et al.* 2002; Sivonen *et al.* 2002; Windeisen *et al.* 2007; Tjeerdsma and Militz 2005). Degradation of hemicellulose may take place via formation of soluble carbohydrates, and formation of such products during thermal modification conditions has been presented (Alén *et al.* 2002; Windeisen and Wegener 2009). Further degradation of polyoses without formation of monosaccharides during heat treatment of wood has been proposed (Sandermann and Augustin 1963). Furans can be degradation products from carbohydrates and furfural and 5-(hydroxymethyl)furfural (HMF) have been found during thermal treatments of wood (Fengel and Wegener 1989; Alén *et al.* 2002; Peters *et al.* 2008).

Furfurals have a nutty smell and can, together with other compounds such as maltol, contribute to the odour emitted from heat treated wood (Miller 1998). At room temperature, furfural is in liquid state and is also a relatively volatile compound that contributes to the smell of VOC emitted from thermally modified wood during processing, but also from end products. Furthermore, furfural is also a reactive compound and turns from a colourless liquid to a dark liquid and further on into a dark precipitate on standing in air, probably due to processes involving condensation reactions (Dunlop and Peters 1953; Gandini and Belgacem 1997).

We wanted to study the formation of furfural and HMF in the wood that comes out from thermal modification under superheated and saturated conditions, as it could influence the smell and colour formation of the thermally modified wood products. It is also of interest to characterize and estimate the amount of soluble carbohydrates that could be produced in the processes as well as whether or not hemicelluloses are degraded via formation of monosaccharides. The presence of such compounds could act as nutrients for microorganisms such as mould (Sehlstedt-Persson *et al.* 2011; Karlsson *et al.* 2012).

MATERIALS AND METHODS

Materials

Thermal modification of Norway spruce (S), Scots pine (P), and silver birch (B) were performed under saturated (SA) and superheated (SU) steam conditions (see Dagbro *et al.* 2010; Torniainen *et al.* 2011). Thermal modification under SA conditions was performed at treatment temperatures of 160 and 170°C and under SU conditions at 170, 185, and 212°C. The following materials were analysed: 160BSA, 170BSA, 170SSA, 170PSA, 185BSU, 170BSU, 212PSU, and 212SSU.

Leaching of Thermally Modified Wood

Wood was milled in a Wiley mill and sieved (0.5 mm). 1.00 g of dry wood was mixed with 60 mL of water, treated in an ultrasonic bath for one hour, and left while magnetic stirring over night in a closed vessel. The mixture was filtered and the collected mother liquor was stored in a freezer until further analysis.

Analysis

Evaporating a specified volume leachate and drying it until it reached a constant weight in a desiccator estimated the dry material weight in leachates.

Filtered water solution (50 μm) was analysed by high performance liquid chromatography (HPLC) at 60°C equipped with a Water Hi-plex Pb-column (8 μm and 250 x 7.7 mm) using water as eluent at a flow of 0.3 mL/min. Furfural and HMF were detected with an ultra violet (UV)-detector operating at 280 nm. A Varian Prostar autosampler (model 410), equipped with a 10 μL loop, was used and quantitative estimations were made by comparison with calibration curves of individual compounds.

Gas chromatography (GC) analysis was performed after methanolysis of dried extracts according to Bertaud *et al.* (2002). Separation was performed on a fused silica column CP-SIL 5 CB low bleed (30 m x 0.25 mm x 0.25 μm). The injector was 280°C and the temperature of flame ionisation detector (FID)-detector was 330°C. Helium was used as a carrier gas, flow 1.26 mL/min, split ratio 1:30, and the temperature program was as follows: 50°C for 1 min, the temperature being increased by 10°C/min up to 300°C. Analysis of acetylated alditols without prior hydrolysis was performed using 2-deoxygalactose as an inner standard (Theander and Westerlund 1986).

Methanol extract from spruce thermally modified under saturated conditions at 170°C was analysed by gas chromatography-mass spectrometry (GC-MS) directly without derivatisation. Analysis of dried extract was performed on a fused silica column SLB- 5 ms (25 m x 0.25 mm x 0.25 μm). The injector was 250°C, and the temperature of FID-detector was 280°C. Helium was used as a carrier gas, splitless mode, and the temperature program was as follows: 50°C for 3 min, the temperature being increased by 3°C/min up to 250°C. Electron impact (EI) was used. The mass spectrometer was calibrated with perfluorotributylamine (PFTBA).

HMF was identified by comparison with a reference substance, as well as confirmed by the National Institute of Standards and Technology (NIST) library: m/z 126 (M), as well as fragments M-15, M-29, and M-57. Vanillin was confirmed by the NIST library: m/z 152 (M) and fragments, M-1, M-15, M-29, and M-43.

RESULTS AND DISCUSSION

Furfurals from Leaching of Thermally Modified Wood

Furfural and 5-(hydroxymethyl)furfural (HMF) are volatile degradation compounds that are formed from heat treatment of carbohydrate containing materials such as wood (Fengel and Wegener 1989; Peters *et al.* 2008). HMF and furfural can be dissolved in water and have strong ultra violet (UV)-absorption at 280 nm (in fact, the absorption coefficient is about ten times stronger than for phenols such as lignin). Water-leachate from thermally modified wood samples were analysed using HPLC at 280 nm. In Fig. 1, chromatogram from birch thermally modified at 170°C in saturated steam is presented.

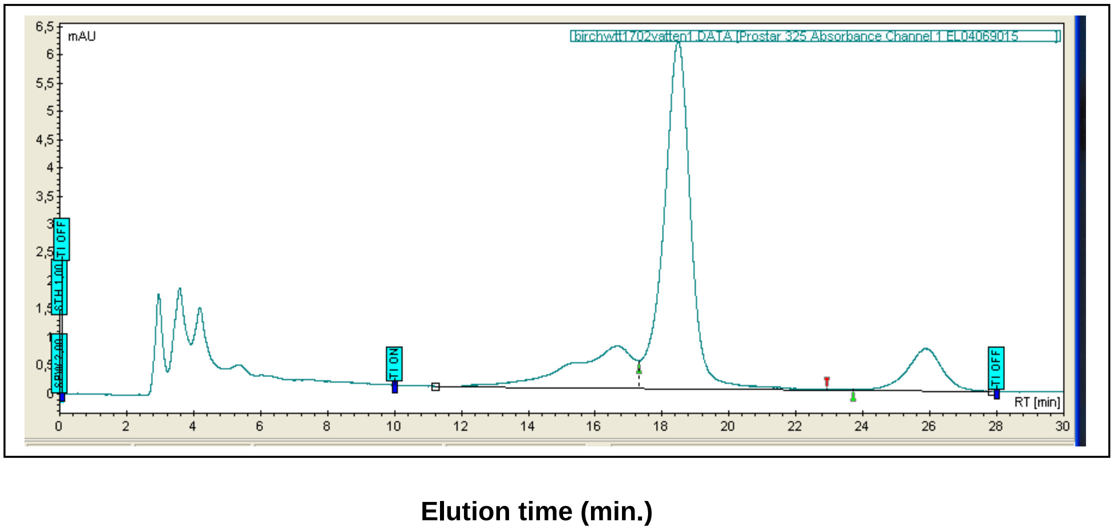

Fig. 1. HPLC (280 nm) of water-extract from birch thermally modified under saturated steam conditions at 170°C (170BSA)

Two fairly symmetric peaks eluting at 18.4 and 25.8 min can be seen. From comparison with reference compounds, the larger peak was attributed to HMF, whereas the smaller one was attributed to furfural. Identification of compounds in minor absorptions at 15.2 min and 16.6 min was not performed (Fig.1). From analysis with HPLC, generally much more furfurals (HMF and furfural) were found in leachates from wood thermally modified under saturated steam (SA) at 170°C than under superheated (SU) steam conditions (Table 1).

HMF is formed from sugars constituted of hexoses such as glucose and mannose, and content of glucomannans is much higher in pine and spruce than in birch. The highest yield of HMF was found in the softwood samples, especially for those modified under SA conditions (Table 1). We have found that colour formation and presence of acid in the wood treated under SA conditions were larger than wood treated under SU conditions (Dagbro *et al.* 2010; Torniainen *et al.* 2011). The presence of acids could catalyse the hydrolytic degradation of wood components to compounds like furfurals. During steam treatment of aspen wood, addition of alkali has been found to decrease the amount of formed furfural (Li *et al.* 2005). However, it could not be ruled out that during modification under SU-conditions, formed furfurals are removed to a higher extent than under SA-conditions; the presence of HMF and furfural in birch treated under SU-conditions seemed to be higher at 170°C than at 185°C (Table 1).

As can be seen in Table 1, furfural was found in much lower amounts than HMF, but was significantly higher in modified birch (170BSA) than in modified spruce and pine (170SSA and 170PSA).

Table 1. Presence of HMF, Furfural in Water Leachate, and Content of Dry Material in Evaporated Water-Leachate from Thermally Modified Wood

Treatment Conditions			Content on Dry Wood (%)*		
Heat transferring media	Wood species	Treatment Temperature (°C)	HMF	Furfural	Dried Leachate
Saturated steam (SA)	Birch	160	0.087	0.031	14.2
SA	Birch	170	0.266	0.071	7.2
SA	Spruce	170	0.792	0.048	6.0
SA	Pine	170	0.586	0.029	6.5
Superheated steam (SU)	Birch	170	0.024	0.022	2.4
SU	Birch	185	0.013	0.010	3.3
SU	Spruce	212	0.059	0.17	2.8
SU	Pine	212	0.035	0.10	2.9
*Duplicate analysis was performed for each data.					

It is rather surprising that much more HMF than furfural was found in treatments with birch, as the content of pentose-rich xylan is much higher than glucomannan in birch. Evaporation, but also degradation or polymerisation to water-insoluble compounds, could be possible explanations. Analysis of process water from thermal modification of mainly pine under SA conditions with HPLC showed, however, the presence of substantial amounts of furfural and only traces of HMF. This suggests that extensive formation of furfural takes place during the thermal treatments under SA conditions and that a considerable amount of formed furfural is evaporated during this thermal treatment. In birch boards treated under superheated steam conditions, the presence of HMF and furfural was rather similar, but relatively more HMF was found in the softwood boards (Table 1).

When the water-leached material in birch treated under SA conditions at 170°C was further leached with methanol and analysed with HPLC, neither HMF nor furfural could be detected. HMF was found by analysis with GC-MS in amounts in methanol extract from spruce treated under saturated steam conditions (170 SSA) without previous water leaching (Fig. 2). The fragment pattern in MS was similar to the authentic compound of 5-(hydroxymethyl)furfural. Vanillin, which is a common degradation product from lignin but could have a lignan origin as well, was also found. The absorption, tentatively assigned furan-2,5-dicarbaldehyde in Fig. 2 could be one of unknown compounds eluting before HMF in Fig. 1, as it should have rather strong UV-absorption at 280 nm. In Table 1, content of dry material in evaporated water-leachates is reported and it was found to be higher for SA-treated than for SU-treated ones; SA-treated birch at 160°C gave especially large amounts of water-solubles (Table 1). As can be seen from Table 1, furfurals constituted only minor parts of dried material from water leachates.

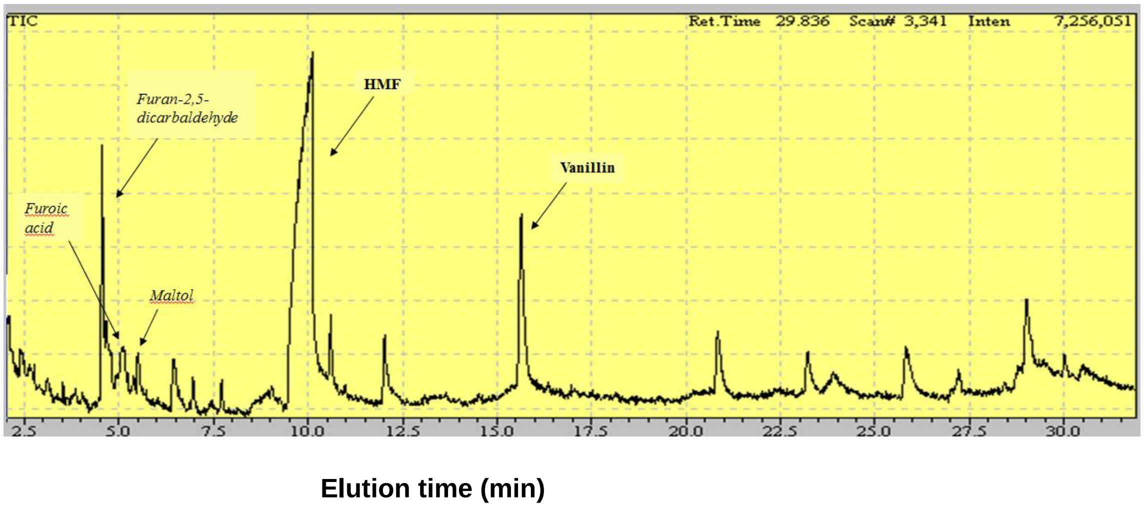

Fig. 2. Leachate from thermal modification in saturated steam conditions at 170°C from spruce (170SSA) analysed by GC-MS. HMF and vanillin was confirmed by comparison with NIST-library while *maltol, furoic acid*, and *furan-2,5-dicarbaldehyde* were tentatively assigned based on molecular peak and dominant fragments.

Soluble Carbohydrates from Water-leaching of Thermally Treated Wood

Furfurals can be formed by heat treatments from carbohydrates in wood, and the rate should be higher for soluble ones with low molecular weight such as monosaccharides. Formation of HMF and furfural is mostly due to carbohydrates based on hexoses and furanoses, respectively. The presence of nutrients such as sugars and fats can increase the rate of mould growth on accessible surfaces, leading to aesthetic disadvantages in, for example, cladding. We have previously found (Sehlstedt-Persson 2011) that high temperature drying can reduce the visible mould growth on surfaces of spruce board to which evaporation of water is directed by a double stacking arrangement. Most of the saccharides that were enriched during the capillary phase were degraded by further heating/drying at 130°C and only slowly at 110°C (Karlsson *et al.* 2012).

In case of thermal modification, the situations were found to be more complicated, and carbohydrates were difficult to analyse quantitatively with the above used HPLC-system as many peaks overlapped. Furthermore, as soluble carbohydrates probably contain those with higher molecular weight, hydrolysis of their glucosidic bonds needs to be undertaken before an analysis of the constituting sugar units can be done. Hydrolysis of xylan has been reported to be more efficient during methanolysis than by hydrolysis in diluted acid (Holmbom and Örså 1993). Total amount of water-soluble carbohydrates in the leachates was therefore analysed as their methyl-glycosides after methanolysis with GC-FID using sorbitol as an internal standard (Table 2).

The content of soluble carbohydrates during treatment under SA conditions was higher than under SU conditions (Table 2). Total amount of methyl-glycosides for pine and spruce was about twice under SA conditions than when under SU conditions. The ratio of methyl-glycosides of glucose to the sum of mannose and galactose were higher after the former than after the latter treatment, which indicates that cellulose could be attacked during SA conditions (Table 2). Such a reaction could lead to a strength decrease of the thermally modified wood.

As could be rationalised from Table 2, much more of methyl-glycosides from galactoglucomannans than from xylans were present in both SA-treated softwoods. In green wood of pine and spruce, the ratio between xylans and glucomannans is about (1:2).

As hydrolysis of glucosidic bond in pentoses during heating is believed to be faster than in hexoses, the results indicate that degradation of xylans leading to formation of products other than soluble carbohydrates takes place to a higher extent than for galacto-glucomannan. Such a suggestion could mean that formation of furfural is favoured rather than formation of HMF, which could be an explanation to the considerable amounts of furfural found in the process water as described above.

Table 2. Carbohydrates from Methanolysis of Water-Leachates from Thermally Modified Wood

Treatment Conditions			Monosaccharide in Water-Leachate on Dry Wood (%)			
Heat transferring media	Wood species	Treatment Temperature (°C)	Xylose	Glucose	Mannose and Galactose	Arabinose
Saturated steam (SA)	Birch	160	9.45	0.60	0.96	0.12
SA	Birch	170	1.54	0.34	0.39	0.02
SA	Spruce	170	0.33	0.78	1.82	0.02
SA	Pine	170	0.24	0.92	1.87	0.01
Superheated steam (SU)	Birch	170	0.22	0.22	0.21	0.04
SU	Birch	185	0.92	0.16	0.22	0.02
SU	Spruce	212	0.17	0.24	0.84	0.01
SU	Pine	212	0.18	0.26	0.94	0.02

Interestingly, the amount of methyl-xyloside was much larger when birch was treated at 160°C under SA conditions than at 170°C (Table 1). This is largely in accordance with the content of evaporated water-solubles that were found to be higher in boards treated at 160°C than at 170°C (Table 1). Analysis of monosaccharides as their acetylated alditols showed that considerably smaller amounts of xylose were present in water-leachate from treatments at 160°C than what could be calculated from the methanolysis treatment (Fig. 3). This indicates that most of the carbohydrates in water-leachate from treatment at 160°C were from soluble xylans.

In the case of treatment at 170°C, the presence of acetylated xylitol and methyl-xyloside from methanolysis were more similar, and thus considerable parts of the soluble products from xylan were due to the presence of xylose. However, it is very likely that at least similar amounts of xylans are released at 170°C, as was observed at 160°C, implicating that further degradation of carbohydrates is accelerated at the higher temperature, such as formation of furfural (Table 1). A higher temperature probably not only favours this process, but also a higher acid content (Torniainen *et al.* 2011), as has been shown during steam treatment of aspen (Li *et al.* 2005). It has been reported that some xylans are less reactive than others (Carrasco and Roy 1992). Xylans with different reactivity could also contribute to the lower content of methyl-xyloside found at higher temperatures.

As could be rationalised from Fig. 3, relatively larger amounts of monosaccharides from galactoglucomannan were also found when birch was treated under SA-conditions at170°C rather than at 160°C.

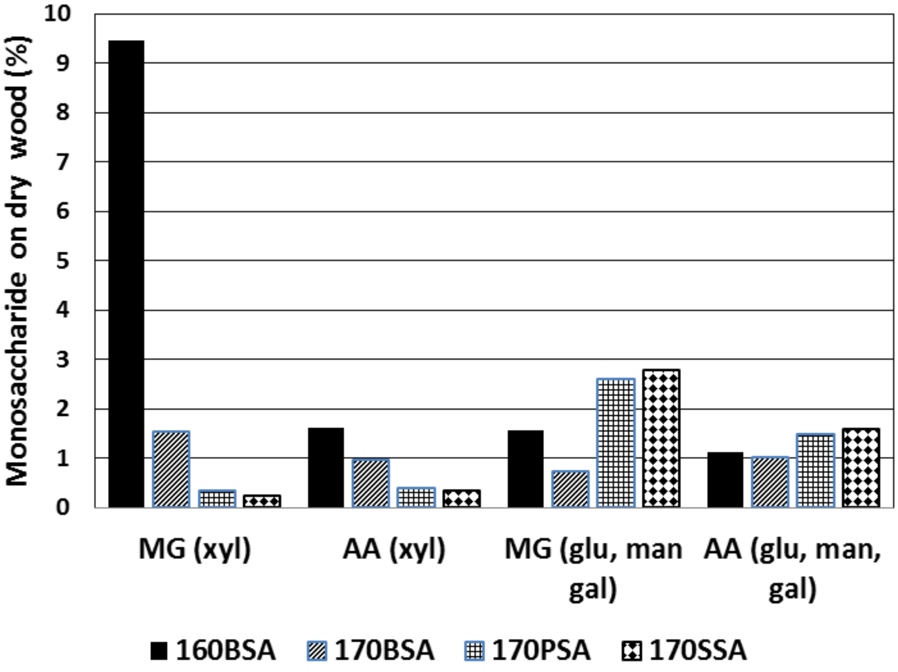

Fig. 3. Content of acetylated alditols (AA) as well as methyl-glycosides (MG) from methanolysis in water leachates from wood thermally modified under saturated steam conditions: Birch heated at 160°C (160BSA) and at 170°C (170BSA), pine heated at 170°C (170PSA), and spruce heated at 170°C (170SSA). Carbohydrates analysed: xylose (xyl), glucose (glu), mannose (man), and galactose (gal).

Soluble galactoglucomannans dominated water-soluble carbohydrates in the leachates from softwood boards treated under superheated conditions (Table 2).

However, only traces of acetylated alditols were found in leachates from those softwoods boards. This is in sharp contrast to what was found for softwoods treated under saturated steam conditions (Fig. 3). This suggests that monosaccharides constituted only small parts of the total released water-soluble carbohydrates under superheated conditions and that methyl-glycosides found in these leachates were mostly from carbohydrates with a degree of polymerization of more than one (Table 2). Since only traces of monosaccharides were found, it is suggested that there was a rapid reaction once monosaccharides are formed or that degradation takes place mainly via other mechanisms. Sandermann and Augustin (1963) suggested that thermal degradation of polyoses takes place not via formation of monosaccharides but via formation of radicals. Furthermore, Li *et al.* (2005) suggested that less hydrolysis and more of homolytic cleavage reactions take place under more neutral conditions during steam treatment of aspen wood. We found considerably less amounts of acid in boards from SU conditions than SA conditions (Torniainen *et al.* 2011). Formation of radicals in wood during thermal modification and that they increased with treatment temperature has been found (Ahajji *et al.* 2009 and Willems *et al.* 2010). Preliminary results indicated that compounds found in the "monosaccharide region" of chromatogram after trimethylsilylation were mostly due to monosaccharides for 170PSA but mostly due to other compounds for 212PSU.

CONCLUSIONS

1. Treatment of Scots pine and Norway spruce under saturated steam (SA) conditions leads to larger formation of furfurals and soluble carbohydrates than treatment under superheated (SU) conditions, even though treatment temperature at SA conditions was about 40 °C lower than at SU-conditions.
2. Despite the fact that the amount of furfurals was lower for softwoods than for birch, it is necessary to reduce the amount of degradation products and soluble carbohydrates to favour use of such wood material in various applications. For example, saccharides in the surface of thermally treated wood should be important in claddings due to higher risk of mould growth.
3. Careful control of the moisture content in the wood during the process is considered to be of large importance as well as to avoid low pH in the wood. A reduction in temperature may seem to be straightforward to reduce the amount of soluble carbohydrates, but treatments with birch showed that such carbohydrates could be present in the material to a larger extent when the temperature was lowered 10 ^{o}C.

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