Original Article

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Effect of pressurized hot water extraction and esterification on the moisture properties and decay resistance of Scots pine (*Pinus sylvestris* L.) sapwood

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Abstract: Pressurized hot water extraction (HWE) treatment has the benefit of simultaneous extraction of hemicellulose-based carbohydrates and modification of the solid phase, but it does not drastically improve wood durability. However, removing hemicelluloses from the wood by HWE treatment creates water-filled spaces in the cell walls which could be filled with modification agent in order to improve the properties of the wood. Without drying, modification agent can be added into the saturated wood via diffusion. The esterification of wood with citric acid (CA) improves resistance to biological deterioration but increases brittleness. However, combining CA esterification with additional chemicals that form links with CA can mitigate brittleness. This study investigated esterification as a method for modifying HWE treated wood. HWE treatment with CA solution (4% w/v) was applied at 120 °C for 3 h to Scots pine (*Pinus sylvestris* L.) sapwood specimens. The specimens were further modified by diffusion with CA and starch derivatives followed by curing. The applied method changed the moisture properties and chemical composition of the wood. The results showed successful wood bulking. The investigated method slightly improved decay resistance to *Coniophora puteana* and *Trametes versicolor* but did not change resistance to *Rhodonia placenta*.

Keywords: biological durability; citric acid; hygroscopicity; starch; wood modification.

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1 Introduction

Wood modification alters the properties of wood via chemical, thermal or other methods. Typically, the aim of modification is the improvement of wood properties. For wood products intended to withstand variations in environmental conditions, dimensional stability and durability against biological decomposers are key properties (Hill 2006; Thybring 2013; Thybring et al. 2018). Since these properties are strongly affected by changes in wood moisture content (MC), the reduction of hygroscopicity, i.e. wood's ability to absorb and desorb water, is a topic of interest in the field of wood modification (Brischke and Alfredsen 2020).

Pressurized hot water extraction (HWE) is based on treating wood in high temperature water between 100 and 240 °C kept in liquid phase with sufficiently high pressure (Wikberg et al. 2015; Nitsos et al. 2016). As a treatment method pressurized hot water extraction (HWE) of the wood has the benefit of simultaneous extraction of valuable hemicellulose-based compounds and modification of the solid phase. Hemicelluloses with lower molecular mass can be utilized as feedstock for biofuel production, while long-chain compounds can be utilized e.g. in cosmetics, food additives and pharmaceutical products (Amidon and Liu 2009; Mikkonen et al. 2009; Rissanen et al. 2014; Wikberg et al. 2015). However, the benefits of HWE to dimensional stability and durability of the wood are limited (Altgen et al. 2018b, 2020b;

Lillqvist et al. 2019). Even though HWE treatment reduces the amount of accessible hydroxyl groups in the wood (Altgen et al. 2018b; Kyyrö et al. 2021), which has been linked to improved hygroscopicity (Berthold et al. 1996), previous studies suggest that dimensional stability (Altgen et al., 2018b, 2020b; Jo et al. 2020) and durability (Howell et al. 2011; Altgen et al. 2020b) of the modified wood do not considerably improve and may even worsen. The limited effect of HWE treatment on wood properties is partially due to the lack of cross-link formation between wood polymers. During HWE treatment water molecules fill the space previously occupied by degraded wood components, which prevents re-polymerization and formation of additional cross-links between wood cell wall polymers (Altgen et al. 2018a,b, 2020a,b; Lillqvist et al. 2019). HWE treatment mitigates the brittleness caused by thermal treatment when compared to superheated steam treatment, but the enhancement of desirable wood properties, like lower absorption and desorption isotherms is limited (Altgen et al. 2018a, 2020a; Lillqvist et al. 2019). Therefore, previous research regarding HWE treatment has largely focused on extraction of carbohydrates from sawdust or waste wood (Kapu and Trajano 2014; Lillqvist et al. 2019; Altgen et al. 2020b).

HWE treatment causes degradation of wood components, mainly hemicellulose, which dissolve into the extraction liquid (Kapu and Trajano 2014; Nitsos et al. 2016). Recent studies suggest that removing hemicelluloses from the wood by HWE treatment creates water-filled spaces in the cell walls (Altgen et al. 2018b; Lillqvist et al. 2019; Kyyrö et al. 2021). However, when the treated wood is dried, the pores in the cell wall close and some of the cell wall spaces do not re-open upon re-wetting. Presumably, this is due to cellulose microfibril aggregation during drying, which is facilitated by the removal of hemicelluloses as spacers between adjacent cell wall microfibrils. This conclusion was supported by studies on sorption properties and dimensional stability, which showed that moisture content at >93% RH and wet dimensions of HWE treated wood decreased after first drying (Altgen et al. 2018b; Kyyrö et al. 2021). Water-swollen cell wall space is important for modification treatments because the modification agents must diffuse into the cell wall. Without drying and rewetting, penetration of modification agents and other chemicals into saturated wood can be achieved by diffusion (Burr and Stamm 1947; Gregory et al. 2012; Thanh et al. 2018). While several studies have investigated the addition of reagents on heat treated wood to improve e.g. hydrophobic and UV-resistance properties (Miklečić et al. 2017; Shen et al. 2018a,b), these methods primarily focus on surface modification. Since prior to first drying HWE treated wood is fully saturated, the water-swollen cell wall space in wood could potentially be filled with reagents to modify the material thoroughly.

The esterification of wood with citric acid (CA) is a non-toxic method for improving resistance to biological degradation. CA molecules are small enough to enter the water-swollen cell wall through micropores. At a sufficiently high temperature and anhydrous state the hydroxyl groups of the wood and CA form ester bonds (Lee et al. 2020). As illustrated by Teacă and Tanasă (2020), these bonds are formed via two-step esterification. Curing CA at a sufficiently high temperature causes the formation of a cyclic anhydride intermediate, which then may react with hydroxyl groups of the wood polymers to form ester bonds. The fixation of a modifying agent like CA into wood causes bulking, which increases anti-swelling efficiency and improves durability against common wood destroying fungi like *Coniophora puteana*, *Rhodonia placenta* and *Trametes versicolor* (Despot et al. 2008; Beck 2020). However, a notable disadvantage of the esterification with CA is increased brittleness in wood, which is likely caused by rigid cross-linking structures between cell wall polymers (Feng et al. 2014; Guo et al. 2019). Therefore, researchers have explored the possibility of combining CA esterification with additional chemicals that form links with CA to mitigate brittleness and further improve the benefits of the modification (L'Hostis et al. 2018; Guo et al. 2019). Starch based chemicals are a potential non-toxic and low-cost source for formation of additional ester links. The utilization of starch and starch-based derivatives with citric acid to form cross-linked structures has previously been extensively studied in the field of food science, but also in the context of wood and paper technology (Kapelko-Żeberska et al. 2022; Watcharakitti et al. 2022).

Apart from wood flour-based composites (e.g. Ou et al. (2016), Bijaisoradat et al. (2021)), previous studies on esterification of wood have been largely limited to modification of untreated wood. The esterification of wood in order to reduce hygroscopicity and improve the durability properties of solid wood while also obtaining hemicellulose-based compounds with HWE treatment has not yet been fully explored. The purpose of the present study was to investigate esterification as a follow-up method for modifying HWE treated wood. Therefore, Scots pine sapwood (*Pinus sylvestris* L.) was modified with HWE treatment followed by diffusion with CA and starch derivatives. Corn starch is the most abundant commercially produced type of starch (Adewale et al. 2022) and was used to prepare the derivatives. The modified solid wood was tested for

mass change, dimensional stability, hydroxyl accessibility, sorption properties and durability against wood decaying fungi. The durability of the modified wood was tested against two brown-rot species, *C. puteana* and *R. placenta*, and one white-rot species, *T. versicolor*.

2 Materials and methods

2.1 Materials

Specimens were cut from kiln-dried Scots pine (*P. sylvestris* L.) sapwood. The specimens for durability, sorption and chemical composition tests were cut according to the standard EN 113-2:2020 (CEN - European Committee for Standardization 2020b) with an end-grain surface of ca. 25 × 15 mm^2 and long-grain dimension of ca. 50 mm. The annual rings were not parallel to the wider faces, but could otherwise run in any direction. Additional virulence control specimens for the durability tests were cut from European beech (*Fagus sylvatica* L.). Separate smaller Scots pine sapwood specimens with different dimensions and annual ring directions (20 × 20 × 10 mm^3 R × T × L) were cut for the determination of dimensional changes. The specimens did not contain heartwood, knots or other visible defects. The average oven-dry density of the specimens was 450 ± 30 kg/m^3 for Scots pine and 610 ± 20 kg/m^3 for beech.

The specimens were distributed between five treatment groups (Table 1). Each treatment group contained 90 large specimens for the fungal resistance test, 10 large specimens for the sorption and chemical composition tests and 20 small specimens for the dimensional stability test. All specimens were oven-dried at 103 °C for 24 h to determine their initial dry mass before HWE treatment. Initial oven-dry dimensions were measured from the dimensional stability test specimens. All mass measurements were done with a precision of 0.001 g.

2.2 Treatment procedure

Figure 1 summarizes the treatment procedure for groups A-E. Group A served as the untreated reference. Specimen groups B-E were HWE treated with CA (4% w/v) solution. The specimens from group B were leached immediately after HWE treatment. Thereby, degradation products and CA were removed from the wood, which allowed the determination of dry mass and volume changes caused by hydrolysis. The specimens from groups C-E were treated in one of three previously prepared treatment liquids: CA, mildly treated starch and CA (S_{mild}), or strongly treated starch and CA (S_{strong}).

2.2.1 Pressurized hot water extraction: Specimens from treatment groups B-E were vacuum-impregnated with citric acid (VWR, CAS no.77-92-9) solution (4% w/v) for 12 h at 5 kPa. These groups were HWE treated at 120 °C and a liquid/solid ratio of 10 (g/g) for 3 h. The HWE treatment of large vacuum-impregnated specimens from groups B-E was performed in an air-bath reactor (Haato Oy, Model 16,140-538, Vantaa, Finland) with space for up to six 2.5 l steel vessels.

The extraction liquid and solid wood residue were separated with 50-µm filtering cloth. A small volume of the extraction liquid was used for the determination of chemical composition. Monocarbohydrates were analyzed from the extraction liquid by HPAEC-PAD without prior hydrolysis. The total amount of carbohydrates was analyzed by first hydrolyzing poly- and oligocarbohydrates in diluted sulfuric acid before HPAEC-PAD analysis according to NREL/TP-510-42,623 (Sluiter et al. 2008), as previously described by Kyyrö et al. (2020). The differences between monocarbohydrate and total carbohydrate contents were used to determine polycarbohydrate content in the extraction liquid. Acid-soluble lignin content was analyzed for the extraction liquid within 6 h after the HWE treatment in a Shimadzu UV-2550 spectrophotometer using a wavelength of 205 nm and an absorptivity constant of 110 g l^{-1} cm^{-1} according to NREL/TP-510-42,618 (Sluiter et al. 2012). Total dissolved solids and ash content in the extraction liquid were determined according to EN 15216:2021 (CEN 2021) and SFS 3008 (Finnish Standards Association 1990), respectively.

The smaller dimensional stability test specimens were put into 225 ml steel vessels and HWE treated in a rotating silicon oil-bath reactor (Haato Oy, Model 43427). After HWE treatment, specimens from group B were immediately water-leached according to EN 84:2020 (CEN - European Committee for Standardization 2020a).

2.2.2 Diffusion liquid preparation and diffusion: After HWE treatment, specimens from treatment groups C-E were diffusion treated in one of the three previously prepared treatment liquids. Citric acid (VWR, CAS no.77-92-9) was used to prepare a solution (4% w/v) that was used as the basis for the preparation of three separate diffusion liquids. The first diffusion liquid consisted only of 4%

Table 1: Treatment methods for five Scots pine sapwood specimen groups A-E and the number of large (25 × 15 × 50 mm^3) and small (20 × 20 × 10 mm^3) specimens.

Specimen group	HWE treatment	Diffusion treatment	Curing at 120 °C	Number of large specimens	Number of small specimens
A	No	No	No	100	20
B	Yes	No	No	100	20
C	Yes	Citric acid (4%)	Yes	100	20
D	Yes	Citric acid (4%) and mildly treated starch	Yes	100	20
E	Yes	Citric acid (4%) and strongly treated starch	Yes	100	20

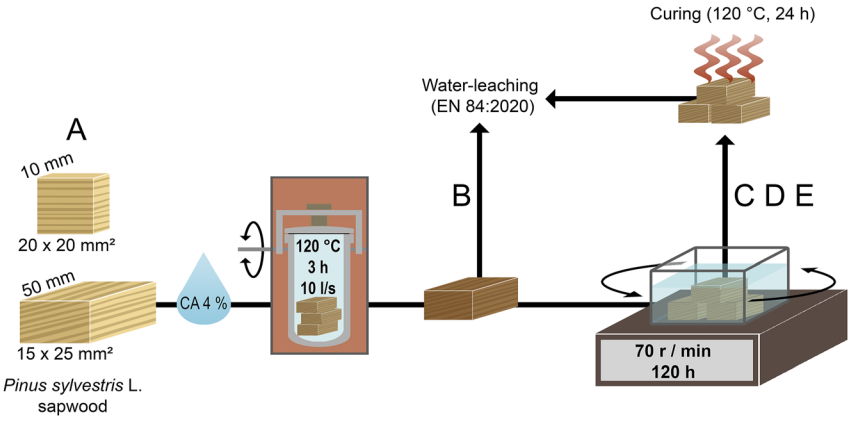

Figure 1: Treatment procedure for five specimen groups A-E.

CA solution. In order to prepare the second and third diffusion liquids, corn starch (Sigma-Aldrich, CAS no. 9005-25-8) was first added to the CA solution to make a starch mixture (20% w/v). The second diffusion liquid (S_{mild}) was prepared with mild treatment: The mixture was stirred continuously at 55 °C for 72 h in order to partially precipitate and partially dissolve the starch. The third diffusion liquid was prepared with strong treatment (S_{strong}): The mixture was put into tightly sealed 225 ml steel vessels and treated at 130 °C for 1 h in a rotating silicon oil-bath reactor (Haato, Model 43427) in order to degrade and dissolve the starch. Right before starting the diffusion treatment, catalyst sodium hypophosphite (Sigma-Aldrich, CAS no. 7681-53-0) was added into the diffusion liquid (0.6% w/v). The HWE treated specimens were put into containers with each of the three diffusion liquids and gently shaken (70 r/min^{-1}) in a flat-bed horizontal shaker for 120 h at room temperature. The containers had approximately 4.7 ml of diffusion liquid per initial oven-dry gram of wood.

2.2.3 Curing and final drying: After diffusion treatment the specimens from groups C-E were removed from diffusion liquid and kept for at least 48 h at 20 °C/65% RH. Next, the specimens were cured in an oven at a temperature sequence of 40, 60, 80, 100 and 120 °C, with each temperature being held for 24 h. Oven-dry masses of the specimens were measured. After treatment procedures all specimen groups A-E were leached according to EN 84:2020 (CEN - European Committee for Standardization 2020a) and afterwards conditioned at 20 °C/65% RH for two weeks and then dried in an oven using a temperature sequence of 40, 60, 80 and 103 °C, with each temperature being held for 24 h. Finally, the oven-dry masses of the specimens were determined.

2.3 Mass change and dimensional stability

Mass change (m/m_0 or m/m_{HWE}) was determined from both large and small specimens by relating the oven-dry mass after treatment procedure and leaching to the initial oven-dry mass (m_0) or oven-dry mass after HWE treatment (m_{HWE}). Since specimen groups C-E were diffusion treated after HWE treatment without intermediate drying, the oven-dry mass after HWE treatment could only be accurately calculated for specimen group B. Therefore, m_{HWE} of specimen groups C-E were calculated based on the average mass loss of specimen group B.

The dimensional stability of the specimens was evaluated by measuring relative dry (V_{dry}/V_0) and wet dimensions (V_{wet}/V_0) from small specimens. Specimens from all treatment groups were oven-dried and their dimensions measured with a precision of 0.01 mm with a calliper both before and after the treatment procedure and leaching. The results were used to calculate initial oven-dry volume (V_0) and oven-dry volume after treatment (V_{dry}). The specimens were vacuum-impregnated with deionized water for 12 h at 5 kPa. The dimensions of fully saturated specimens were measured and used to calculate wet volume (V_{wet}).

2.4 Hydroxyl accessibility and sorption isotherm analysis

To obtain homogenous powder for both OH accessibility and sorption isotherm measurements, two large specimens from each treatment group were ground in a Wiley mill (model 2, manufacturer Arthur H. Thomas Company) to pass through a 30-mesh screen. OH accessibility was gravimetrically measured from the wood powder of each specimen group with an automated sorption balance (DVS Advantage ET, Surface Measurement Systems, UK) to the nearest 0.1 µg. Approximately 15 mg of wood powder were used for each measurement. During the measurements the N_2 flow and the target temperature were kept constant at 200 cm^3 min^{-1} and 25 °C, respectively. The automated sorption balance measurement consisted of a four-step sequence: a) First the specimens were dried using the pre-heater in the automated sorption balance. The temperature was first gradually increased from 25 °C to 60 °C within 1 h, kept at 60 °C for 6 h and finally gradually decreased back to 25 °C within 1 h. After drying, the specimens were kept at 0% target RH for 2 h for temperature stabilization. b) This was followed by specimen deuteration by exposure to D_2O vapor at 95% target RH for 12 h. c) The drying step with the pre-heater was repeated and then the specimens were kept at 0% target RH for 2 h.

The concentration of accessible OH groups (OH_{acc}, in mmol g^{-1}) was determined based on the dry mass difference between the protonated and deuterated state using Equation (1):

$$OH_{acc} = 1000 \times (m_{OD} - m_{OH}) / (\Delta M \times m_{OH}) \quad (1)$$

where m_{OD} is the mass of the deuterated wood specimen (mg) at the end of step c, m_{OH} is the mass of the protonated wood specimen (mg) at the end of step a and ΔM is the atomic mass difference between

deuterium and protium (1.006 g mol^{-1}). OH accessibility measurements were done in triplicate.

Scanning sorption isotherm measurements were performed with an automated sorption balance (DVS Intrinsic, Surface Measurement Systems, UK). During the measurements the N_2 flow and the target temperature were kept constant at 200 cm^3 min^{-1} and 25 °C, respectively. For each measurement, approximately 20 mg of wood powder was placed on the specimen pan of the sorption balance. Absorption isotherms were recorded by applying the following target RH steps: 0-5-15-25-35-45-55-65-75-85-95%. Desorption isotherm were recorded by applying the same RH steps in reverse from 95% target RH to 0% target RH. During each sorption step the target RH was kept until the mass change was 0.001% min^{-1} during a 10 min time window. The final mass at the end of each RH step was used for the MC (in %) calculation according to Equation (2):

$$MC = (m_{RH} - m_{dry})/(m_{dry}) \quad (2)$$

where m_{RH} is the mass of wood specimen at the end of the respective RH step and m_{dry} is the average mass of wood specimen at the end of 0% target RH.

2.5 Durability against wood destroying basidiomycetes

The durability test was done according to the standard EN 113-2:2020 (CEN - European Committee for Standardization 2020b). In total, 90 specimens per treatment group and 30 reference beech specimens were conditioned at 20 °C/65% RH until reaching equilibrium mass. Since one of the treatment groups consisted of unmodified Scots pine sapwood, additional Scots pine reference specimens for virulence control were not prepared. Altogether, 30 replicate specimens from each treatment group were tested against *C. puteana* (Schumach.) P. Karst., strain BAM Ebw 15, *R. placenta* (Fr.) Niemelä, K.H. Larsson & Schigel strain FPRL 280 and *T. versicolor* (L.) Lloyd., strain CTB 863 A. The virulence control beech specimens were tested only against *T. versicolor*. The fungi were maintained at 25 °C on malt agar until inoculation. Kolle flasks with malt agar medium (4%) were inoculated with fungi and used as incubation vessels. After a seven-day incubation period two sterilized wood specimens from the same specimen group were put into each Kolle flask. The sterilization was performed by wrapping the wood specimens in aluminum foil and treating them in an autoclave at 121 °C for 30 min. The specimens were kept inside the inoculated Kolle flasks in a dark culture room at 22 °C/70% RH. After 16 weeks of incubation mycelium was removed from specimen surfaces. The specimens were first kept overnight at 20 °C, then dried in an oven at 40 °C for 72 h and finally at 103 °C for 24 h. The oven-dry masses of the specimens were determined.

The mass loss (ML_F) of each specimen caused by wood destroying basidiomycetes was calculated based on the oven-dry mass of each wood specimen after modification and the dry mass after the 16-week incubation period using Equation (3):

$$ML_F = (m_{mod} - m_F)/m_{mod} \times 100\,\%, \quad (3)$$

where m_{mod} is the oven dry mass before decay (g), and m_F is the dry mass after decay and removal of mycelium (g).

The statistical significance of ML_F was evaluated with Microsoft Excel data analysis tool. The results from untreated specimens were compared with the results from other treatment groups. Statistical significance was evaluated with both p-value 0.05 and 0.01.

2.6 Composition of wood before and after durability test

Chemical composition of all wood specimen groups A-E was determined before and after incubation with *C. puteana* or *R. placenta*. Two specimens from each treatment group were oven-dried at 103 °C and ground into combined powder in a cutting mill (Retsch mill SM 2000) to pass through a 1.0 mm mesh sieve. The specimens used in the composition test were chosen to reflect as accurately as possible the average mass change due to treatment and mass loss due to decay. Moisture content was measured from the powder based on EN 1318-1:2002 (CEN 2002). Extractives were removed from the powder with 150 ml acetone in a Soxhlet apparatus according to TAPPI T 204 cm-97 (TAPPI 2007). Structural carbohydrates and lignin were determined from extracted wood according to NREL/TP-510-42618 (Sluiter et al. 2012). The monosaccharide composition of the hydrolysate was analysed with High-Performance Anion-Exchange Chromatography with Pulsed Amperometric Detection (HPAEC-PAD), as described previously by Lillqvist et al. (2019). Monosaccharide composition was used to calculate cellulose and hemicellulose content, as described previously by Janson (1970). Chemical composition measurements were done in triplicates.

3 Results

3.1 Extraction liquid

Scots pine sapwood specimens were HWE treated with 4% citric acid (CA) solution for 3 h at 120 °C as selected based on pre-test results (Supplementary Figure S.1). Pre-tests using CA solution between 0 and 8% showed that a concentration of 4% resulted in the highest yield of oligo- and polycarbohydrates. The pre-test results also showed that when the CA concentration was ≤4%, the amount of extracted carbohydrates increased linearly with added CA. When the CA concentration was further increased to 4–8%, the overall amount of extracted carbohydates was approximately 10% of reference wood, i.e. over 30% of the hemicellulose content in reference wood. However, oligo- and polycarbohydrate content was highest at 4% CA concentration. Based on the pre-test results, when CA concentration was further increased, dissolved oligo- and polycarbohydrates began to gradually degrade into monocarbohydrates.

Only 2.8 ± 0.3% and 3.7 ± 1.2% of mono- and polycarbohydrates (% of reference wood), respectively, were extracted from the 25 × 15 × 50 mm^3 sapwood specimens. The amount of obtained carbohydrates was over 20% of

the hemicellulose content in reference wood. Lower amounts of the carbohydrates were obtained when compared to pre-test specimens. In line with pre-test results, the ratio between monocarbohydrates and larger carbohydrates was about 50%.

3.2 Wood mass change and dimensional stability

The mass of the wood specimens (Table 2) changed due to degradation caused by HWE treatment as well as by fixation with CA and starch derivatives caused by diffusion and curing. While the mass change of treated specimens (B-E) compared to untreated specimens (A) demonstrated an overall decrease in mass, the change from HWE treated to final specimens highlights the weight gain caused by diffusion and curing.

HWE treatment followed by leaching (B) resulted in a notable decrease in mass since decomposed wood derivatives were removed prior to drying. The decomposing effect of the HWE treatment was apparent in relation to untreated specimens. The increase in mass caused by the follow-up treatment methods (C-E) was lower than the mass loss caused by the HWE treatment (Table 2, left column). Therefore, the fixation of mass into wood due to the follow-up methods was more evident compared to the HWE treated specimens (Table 2, right column). HWE treatment followed by diffusion with CA (C) increased the mass in comparison to HWE treated specimens. As expected, diffusing HWE treated specimens with a combination of CA and starch derivatives (D and E) further increased mass in relation to HWE treated specimens. There was no significant difference in mass change between treatment groups D and E. Small specimens showed a larger mass change for group D, while the opposite was observed for large specimens. However, these differences between groups D and E were within the standard deviation.

The effect of specimen size on mass change is apparent from the mass loss of HWE treated and leached (B) small and large specimens: 16.3 ± 0.5% and 13.8 ± 0.7%, respectively. However, examining the mass change of treatment groups C and E in relation to HWE treated specimens showed no significant difference in mass fixation between small and large specimens. Unlike other treatment groups, small specimens from treatment group D exhibited more effective mass fixation than large specimens, which could not be explained by random variations.

Relative dry and wet dimensions of each treatment group (Figure 2) show the extent of swelling in the fully saturated wood specimens in relation to dry volume. The relative dry dimensions of the different treatment groups were consistent with the mass change results (Table 2, small specimens). The removal of wood components with HWE treatment followed by leaching (B) both decreased the dry wood volume and increased water uptake. In line with the mass change results, diffusion with CA (C) resulted in relative dry dimensions higher than the HWE treated specimens but lower than the untreated specimens. Also, the water-saturated volume decreased. The diffusion with S_{mild} (D) increased the relative dry dimensions the most and decreased the relative wet dimensions. The overall volume of the fully saturated specimens was nearly identical for groups B and D. The mass change and relative dimension results from specimen groups C and D indicate that the increase in specimen mass increases the relative dry dimensions of the specimens, which simultaneously decreases the water uptake. However, a notable exception to this trend was diffusion with S_{strong} (E), which in addition to increasing dry dimensions also clearly increased relative wet dimensions in relation to group B. In other words, only treatment groups C and D showed improved dimensional stability.

Table 2: Mass change of small (20 × 20 × 10 mm³) and large (25 × 15 × 50 mm³) Scots pine sapwood specimens.

Treatment method	Mass change % (untreated → final)		Mass change % (HWE treated → final)	
	Small specimens (20 × 20 × 10 mm³)	Large specimens (25 × 15 × 50 mm³)	Small specimens (20 × 20 × 10 mm³)	Large specimens (25 × 15 × 50 mm³)
A) Reference	−0.9 (0.2)	−0.7 (0.2)	–	–
B) HWE	−16.3 (0.5)	−13.8 (0.7)	0	0
C) HWE + CA + curing	−9.9 (0.9)	−6.9 (0.6)	7.6 (1.1)	8.0 (0.7)
D) HWE + S_{mild} + curing	−5.7 (1.1)	−5.1 (0.8)	12.6 (1.4)	10.1 (0.9)
E) HWE + S_{stromg} + curing	−6.3 (1.0)	−3.9 (1.5)	12.0 (1.2)	11.5 (1.7)

Includes mass change relative to untreated specimens (m/m_0, left column) and HWE treated specimens (m/m_{HWE}, right column) caused by subsequent treatment procedure. Standard deviations are in parentheses.

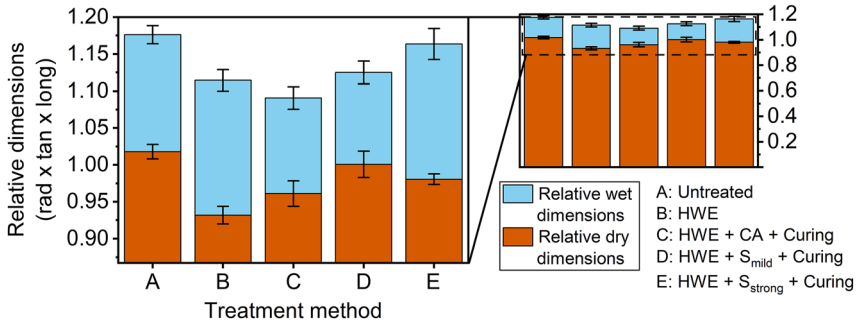

Figure 2: Relative dry (V_{dry}/V_0) and wet dimension (V_{wet}/V_0) of Scots pine sapwood specimens (20 × 20 × 10 mm³) treated with different methods. The error bars indicate the standard deviation.

3.3 Hydroxyl accessibility and sorption properties

HWE treatment (B) decreased the average hydroxyl accessibility of the wood from 9.8 to 9.2 mmol g^{-1} (Supplementary Table S.1). However, the OH_{acc} of all diffusion treated specimens was only 8.6 mmol g^{-1}. The biggest differences in OH_{acc} were between the untreated and HWE treated specimens and all other treatment groups. The mass difference over the final 10 min (dm/dt) at the end of the drying steps (steps a and c, see Equation (1)) did not exceed |0.0002| % min^{-1} (Supplementary Table S.1), which was lower than the threshold of 0.0005% min^{-1} over a 10 min period that was recommended by Uimonen et al. (2020).

Sorption results displayed a clear decrease in absorption and desorption isotherms with HWE treatment (Figure 3). HWE treatment caused a notable decrease in moisture content at all tested RH values, but the differences between specimen groups B-E were more subtle. At ≤35% RH the differences between the moisture contents of all HWE treated specimen groups were small (≤0.36%), regardless of whether the absorption or desorption curve was observed. However, when the RH was higher, the differences between the moisture contents were more notable and the specimen groups could be separated into two categories based on their sorption behaviour: Groups B and E with higher moisture contents in absorption and desorption isotherms, and groups C and D with lower moisture contents in absorption and desorption isotherms at ≥45% RH. The lower sorption isotherms of groups C and D were more pronounced at elevated RH (≥80%).

3.4 Resistance to decay by basidiomycetes

C. puteana and *R. placenta* caused mass losses on untreated Scots pine specimens of 27.7 ± 7.0% and 25.9 ± 6.8%, respectively, while *T. versicolor* caused a mass loss of 30.3 ± 6.9% on virulence control beech specimens. Based on the standard EN 113-2:2020 (CEN - European Committee for Standardization 2020b) these results affirm the validity of the durability tests. The results illustrated that the changes to the decay resistance of the tested specimen groups varied greatly depending on the test fungus (Figure 4). HWE treatment (B) did not cause statistically significant changes to decay resistance. However, HWE treatment followed by diffusion (C-E) improved resistance to decay by *C. puteana* and *T. versicolor* (significance level of <0.01). Out of the tested specimen groups, decay resistance to *C. puteana* and *T. versicolor* improved the most when diffusion with CA or S_{mild} (C and D) was implemented into the treatment procedure. Notably diffusion treatment with S_{strong} (E) had lower decay resistance when compared to specimen groups C and D.

While particularly test groups C and D had clearly improved resistance to two of the test fungi, the treatment methods had no effect on resistance to *R. placenta*. *R. placenta* degraded all tested specimen groups strongly and caused mass losses ≥23%. Thus, due to poor resistance to *R. placenta* no specimen group could be assigned into a durability class higher than DC4 according to EN 113-2:2020 (CEN - European Committee for Standardization 2020b).

Figure 5 shows the chemical composition of the wood from different specimen groups (mass %), including mass losses caused by treatments and decay by *C. puteana* or *R. placenta*. The specimens decayed by *C. puteana* and *R. placenta* were chosen for the composition analysis in order to investigate the differences between brown-rot fungi, which caused strong variations in decay results. The most notable change to the chemical composition caused by HWE treatment (B) was the degradation and removal of hemicellulose. Based on the results, HWE treatment or subsequent methods did not cause a notable removal of cellulose or lignin. A proportion of the undecayed wood of groups C-E were not identified by the analytical techniques applied. This proportion is labelled as "other compounds" in Figure 5. Since this mass was present only in specimens treated with diffusion modification (C-E), it is reasonable to conclude that the

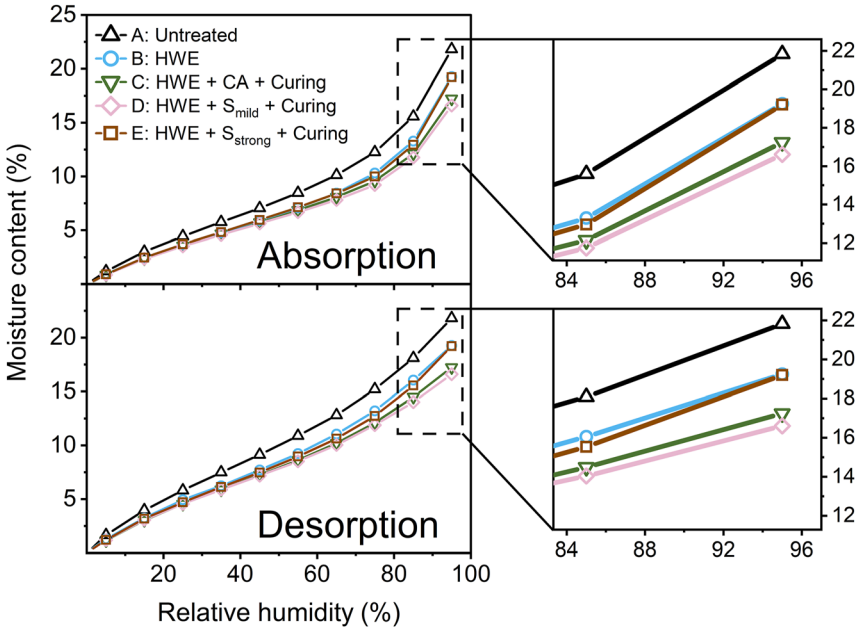

Figure 3: Absorption and desorption isotherms of Scots pine sapwood specimens treated with different methods.

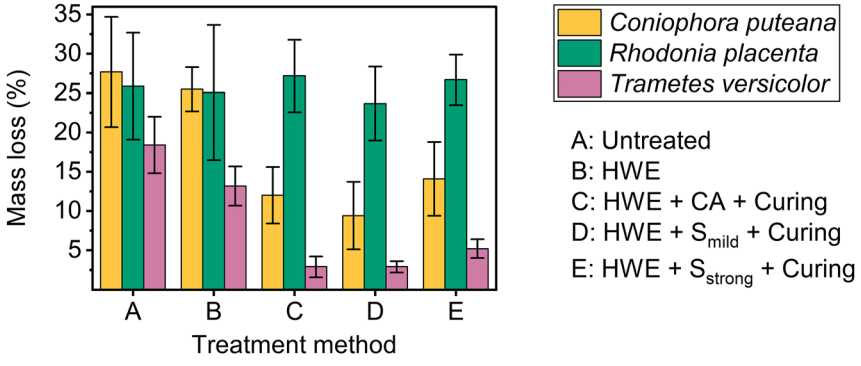

Figure 4: Wood mass loss (%) caused by *Coniophora puteana*, *Rhodonia placenta* and *Trametes versicolor* after 16 weeks of incubation. The error bars indicate the standard deviation.

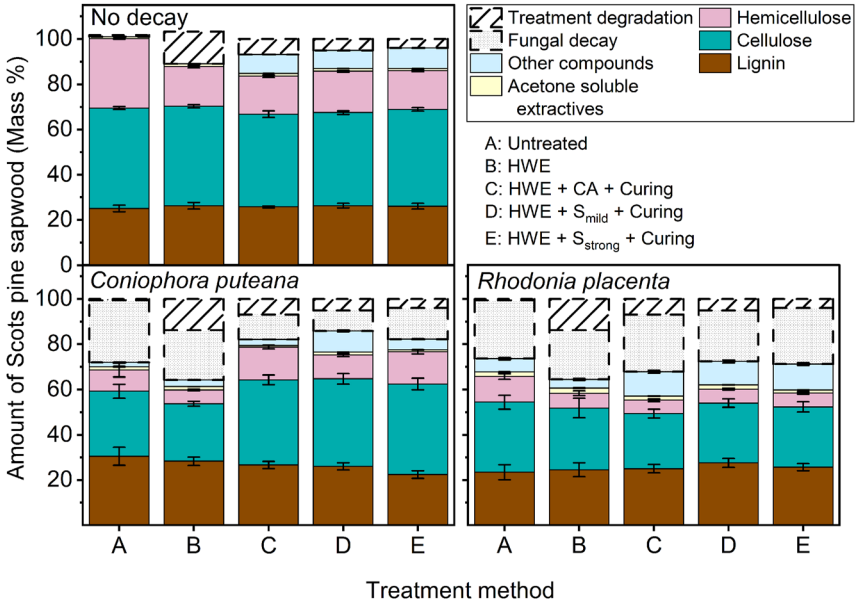

Figure 5: Scots pine sapwood composition (mass %) and changes caused by treatment and decay by *Coniophora puteana* or *Rhodonia placenta*. The error bars indicate the standard deviation.

unexplained mass consisted of added chemicals: CA, starch derivatives and/or sodium hypophosphite.

Decay by *C. puteana* or *R. placenta* caused a decrease in hemicellulose and cellulose content, while the amount of lignin did not change significantly. The decrease in hemicellulose and cellulose content was more drastic for specimens that were more susceptible to decay. Additionally, all specimens degraded by *C. puteana* or *R. placenta* had a small amount of "other compounds".

4 Discussion

The objective of this study was to investigate esterification as a method for modifying HWE treated wood. Since the major advantage of the HWE is the procurement of hemicellulose derivatives, the carbohydrate content of the extraction liquid was evaluated. The results showed that mild CA content (4%) in the extraction liquid enables wood hydrolysis at a temperature of 120 °C. The results also showed that while a relatively low amount of carbohydrates was extracted from the wood in comparison to the pre-test results, HWE treatment resulted in a 50% ratio between monocarbohydrates and larger carbohydrates regardless of specimen size. The consistent carbohydrate ratio is in line with previous research (Kyyrö et al. 2020) and indicates that the overall composition of the extracted compounds is dependent on treatment conditions other than the size of the wood blocks. The reduced extraction of carbohydrates compared to the pre-test results was likely due to decreased treatment efficiency in dependence on increased specimen size (Krogell et al. 2013; Kyyrö et al. 2020; Li et al. 2013). Hemicellulose yields as high as 50–70% have been obtained from softwood powder or chips with HWE treatment (Song et al. 2008; Zhu and Yadama 2016).

To evaluate the moisture properties of the modified wood, analyses were conducted on the mass changes, dimensions, hydroxyl accessibilities and sorption isotherms of the treatment groups. Already the mass change results indicated notable differences between the different treatment methods. In line with previous studies (Nitsos et al. 2016; Wikberg et al. 2015), HWE treatment resulted in mass loss via selective hydrolysis of wood components, mainly hemicellulose, which dissolved into the extraction liquid. The diffusion and curing of HWE treated wood successfully resulted in the fixation of CA and starch derivatives into the wood. These mass change results showed a clear link with relative dry dimensions. A direct correlation could be observed for all treated specimen groups (Supplementary Figure S.2). Mass loss by HWE treatment resulted in a reduction in the dry dimensions of the wood (B). Vice versa the mass increase in diffusion treated and cured specimens was directly proportional to the increase in the dry dimensions (C, D and E). However, the results regarding relative wet dimensions require more complex explanation. There was no direct correlation between the mass change and the relative wet dimensions (Supplementary Figure S.2). HWE treatment decreased the relative dry dimensions but increased the relative wet dimensions of the wood specimens. Thus, the moisture content of water-saturated HWE treated wood was higher when compared to untreated specimens. This phenomenon could be related to the removal of wood extractives, which causes an increase in moisture content at high RH (%) (Jo et al. 2020; Vahtikari et al. 2017). The lack of direct correlation was also observable from the results on diffusion treated specimens. Despite the similar mass changes between treatment groups D and E, the ratio between relative wet and dry dimensions, i.e. the amount of moisture in fully saturated specimens differed. The specimens diffusion treated with CA (C) or S_{mild} (D) had decreased relative wet dimensions, while the specimens diffusion treated with S_{strong} (E) had unexpectedly high relative wet dimensions. Cell wall moisture content correlates with wood dimensions (Ishimaru et al. 2001; Thybring and Fredriksson 2021) and as illustrated by Thybring (2013), increasing the dry dimensions of the wood by fixation of mass should decrease the volumetric margin between the dry and the wet state, while the fully saturated wood volume stays the same. The results from the specimens diffusion treated with CA (C) and S_{mild} (D) fit this model. This indicates successful bulking with added CA and starch derivatives. The specimens diffusion treated with S_{strong} (E) on the other hand were likely affected by other mechanisms in addition to the bulking. The strong starch treatment may have resulted in the formation of derivatives that fixate into the wood but also have high affinity to water or poorer cross-linking properties.

HWE treatment decreased the hydroxyl accessibility of the wood from 9.8 to 9.2 mmol g^{-1}, which can be assigned to the degradation and removal of hemicellulose and a subsequent reduction in the amount of available OH groups (Boonstra and Tjeerdsma 2006; Kyyrö et al. 2021; Lillqvist et al. 2019). The diffusion treated specimens (C-E) had a lower OH_{acc} of 8.6 mmol g^{-1}. In terms of chemical composition, the key difference between HWE treated (B) and diffusion treated specimens (C-E) was the presence of CA during curing. Therefore, the decrease in OH_{acc} density was likely linked to the formation of ester bonds between CA and previously accessible OH groups of the wood. Since the OH_{acc} densities of the specimen groups

C-E were close to equal, the differences in wood moisture properties between these groups were not fully assigned to variations in OH_{acc} content. Previous research showed that mechanisms in addition to the variations in OH_{acc} affect the moisture properties of wood (Altgen et al., 2016, 2018b; Kyyrö et al. 2021; Rautkari et al. 2013; Wentzel et al. 2018). The effect of cellulose microfibril aggregation on the moisture properties of hydrothermally modified wood has been suggested e.g. by Wentzel et al. (2018), Altgen et al. (2018b) and Kyyrö et al. (2021).

HWE treatment caused a drop in the sorption isotherm curves, which is typical for hydrothermally modified wood (Kymäläinen et al. 2018; Lillqvist et al. 2019). This drop in the moisture contents was observed for all treated wood specimens, throughout the tested RH (%) range (excluding 0%). The differences between the sorption isotherm curves of all treated groups (B-E) were negligible at ≤35% RH. However, the sorption isotherm curves at ≥45% RH were higher for groups B and E and lower for groups C and D. As stated previously, these variations cannot be assigned solely to hydroxyl accessibility. Despite the successful cell wall bulking shown by the results on the relative dry dimensions (C-E), the respective sorption isotherm curves did not display decreased MC values at lower RHs (%). A reduction in moisture content specifically at higher RH values has previously been observed in wood modified by cross-linking, since a more rigid cell wall reduces the uptake of water molecules (Himmel and Mai 2015; Kurkowiak et al. 2021; Xie et al. 2011). Xie et al. (2011) investigated the sorption properties of wood treated with glutaraldehyde and noted that the sigmoidal desorption curve of wood became more linear with increasing weight percent gain (%). They linked this phenomenon to increasing cell wall stiffness. The stiffening effect caused by cross-linking was also shown by Himmel and Mai (2015). Therefore, the lower and more linear desorption curves at higher RH (%) in the specimens diffusion treated with CA (C) and S_{mild} (D) suggest a higher degree of cross-linking. Like relative wet dimensions of the specimens, the changes in the sorption properties of the wood were not directly proportional to the mass change results. Alternatively, differences in the degree of cross-linking could provide an additional explanation to the variations between treatment methods.

The decay resistance of wood is strongly dependent on its moisture properties. The results also showed that the changes to the durability of specimen groups caused by the different treatment methods varied between the tested fungi. Specifically, the results show that the treatment methods affected the decay resistance against *C. puteana* and *T. versicolor* but had minor to no effect on resistance against *R. placenta*. Previous studies on durability of thermally treated wood have also noted the limited effect of thermal treatment on the resistance against *R. placenta* (Lekonogou and Kocaefe 2014; Welzbacher and Rapp 2007). However, the reasons for this phenomenon are not fully understood. When changes to resistance against wood destroying fungi are described throughout this paragraph, this refers specifically to resistance against *C. puteana* and *T. versicolor*. HWE treated wood specimens (B) resulted in a slightly lower mass loss due to fungal decay (ML_F, %) in comparison to untreated specimens (A). Based on the composition analysis, this was likely due to the removal of easily degradable hemicelluloses rather than to an improvement in resistance properties. The wood specimens diffusion treated with CA (C), S_{mild} (D) or S_{strong} (E) had lower ML_F. The remaining holocellulose contents of these specimens were more resistant to removal by fungal decay when compared to untreated or HWE treated wood specimens. Therefore, these groups had improved decay resistance properties. While these results do not challenge the importance of the moisture properties, the improved decay resistance could not be solely assigned to differences in water uptake. As the results on relative dry and wet dimensions and sorption isotherms show, the HWE treated specimens (B) and specimens treated with S_{strong} liquid (E) had similar moisture properties, but group E displayed better resistance to fungal decay. Also, the specimens showed no clear correlation between improved resistance to fungal decay and moisture content after 16 weeks of incubation (Supplementary Table S.2). This suggests that in addition to the relevance of hygroscopicity, the added compounds improve the fungal resistance of the wood via additional mechanisms. It is possible that the fixation of mass in diffusion treated specimens decreased the cell wall porosity. The decrease in porosity might hinder the transportation of the degradation agents (Hunt et al. 2018; Ringman et al. 2014).

Decay by *C. puteana* and *R. placenta* caused ML_F (%) via degradation of hemicellulose and cellulose. *C. puteana* and *R. placenta* did not notably decrease the amount of lignin in the wood, though based on previous knowledge regarding the decay mechanisms of brown-rot fungi, lignin modification or re-arrangement likely occurred (Sista Kameshwar and Qin 2020). Additionally, all specimens degraded by fungi had a small amount of "other compounds", which could be explained by degradation products caused by fungal decay and, in case of specimen groups that were cured prior to leaching (C-E), residues from chemicals added during treatment.

The drastic differences between the ML_F (%) caused by *C. puteana*, *R. placenta* and *T. versicolor* were likely related to the variations in their modes of action. *T. versicolor*'s mode of action is based on simultaneous degradation of cellulose, hemicellulose and lignin using a wide variety of enzymes specialized against each component. The degradation process occurs via thinning, i.e. decay that occurs on the cell wall surface (Bari et al. 2020; Zabel and Morrell 2020). *R. placenta* and *C. puteana* additionally utilize a non-enzymatic degradative mechanism based on the production of hydroxyl radicals through the Fenton reaction for the initial depolymerization of cell wall components in order to access carbohydrates prior to the enzymatic wood decay (Arantes and Goodell 2014; Ringman et al. 2014; Zhang et al. 2016). However, differences between these two brown-rot species have been noted in decay tests against wood (Irbe et al. 2006; Metsä-Kortelainen and Viitanen 2009) and studies regarding the gene expression (Sista Kameshwar and Qin 2020). Metsä-Kortelainen and Viitanen (2009) observed that *R. placenta* caused a relatively high mass loss to thermally treated wood when compared to *C. puteana*. Additionally, Irbe et al. (2006) noted the more rapid formation of new pores by *R. placenta*.

5 Conclusions

Diffusion of HWE treated wood with CA and starch derivatives followed by curing changed the moisture properties of the wood and the resistance against some decay fungi. The obtained results show how the effectiveness of the modification method on changing wood durability varies depending on the test fungi. This research may help in developing methods where the space in the cell walls formed during HWE is utilized for further modification of the wood.

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