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# A molecular model for reversible and irreversible hygroscopicity changes by thermal wood modification

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**Abstract:** Heat treatment (HT) is a well-known means to reduce the equilibrium wood moisture content (EMC) at a specified relative humidity (RH). EMC is profoundly decreased by the loss of accessible hydroxyl groups ( $\text{OH}_{\text{acc}}$ ) in the wood matrix by thermochemical reactions. However, the obtained EMC reduction after HT can be partly reversible, depending on the ability of the wood matrix polymers to fully mechanically relax during HT. We discuss the results of our earlier experimental study on the  $\text{OH}_{\text{acc}}$  content and the associated EMC decrease at 93% RH by a relaxation inhibiting dry-HT vs. a relaxation enabling wet-HT. New experimental results, showing that  $\text{OH}_{\text{acc}}$  does not significantly change during reversible EMC changes, are added to the discussion. This study quantitatively supports a molecular explanation of the reversible EMC, in which wood moisture is principally bound at sorption sites, composed of two functional groups, constituting a hydrogen-donor/acceptor pair, involving at least one  $\text{OH}_{\text{acc}}$  group. The irreversible part of EMC reduction is assigned to the thermochemical removal of  $\text{OH}_{\text{acc}}$  from the wood matrix. The reversible part is attributed to a process of wood polymer conformational rearrangements, bringing an isolated  $\text{OH}_{\text{acc}}$  group in proximity of another free hydrogen-bonding functional group, creating a site for water sorption.

**Keywords:** crosslinks, equilibrium moisture content, heat treatment, mechanical relaxation, sorption sites

## Introduction

The equilibrium moisture content (EMC) of wood can be readily reduced by high-temperature exposure and

drying, although this effect may be partly reversible, as can be verified by the application of consecutive wetting/drying cycles (Obataya and Tomita 2002; Čermák et al. 2015; Altgen and Militz 2016; Obataya and Higashihara 2017; Tarmian and Mastouri 2019). The reversibility has been ascribed by these authors to a non-equilibrium arrangement of wood polymers in the cell wall after the heat treatment (HT). The presence of crosslinks or hydrogen-bonds formed during dry-HT hinders the relaxation of the cell wall polymers toward their thermodynamically most favorable arrangement. This relaxation hindrance in HT-wood may be lifted by a post-treatment of vacuum impregnation with water or by applying consecutive cycles of wetting and drying. In the wet-HT process, polymer relaxation is accomplished during HT, avoiding or reducing the EMC recovery after the HT process (Obataya et al. 2002; Altgen and Militz 2016). The possibility of a (partial) EMC recovery deserves a scientific study, as the EMC is regarded as a key parameter of wood modification (Ringman et al. 2014).

To study the EMC recovery mechanism in more detail, Scots pine sapwood samples were prepared in a wide range of HT severities, obtained by dry heating in atmospheric superheated steam vs. a hydrothermal treatment, both followed by an extraction of the water-soluble degradation products (Altgen et al. 2018b). The accessible hydroxyl group ( $\text{OH}_{\text{acc}}$ ) content was measured by hydrogen-deuterium exchange (HDX) and correlated with  $\text{EMC}_{93\%}$ , the EMC at first exposure to 93% relative humidity (RH). In this way, we could compare the  $\text{EMC}_{93\%}$  at each  $\text{OH}_{\text{acc}}$  content in relatively crosslinked (dry-HT) vs. soft (wet-HT) extractive-free matrices of thermally modified wood. These two extremes were considered to represent the unrelaxed state of as-produced dry heated thermally modified wood and the corresponding final state after full relaxation, without the potentially disturbing effect of residual degradation products in the cell walls.

In the present work, we aim to address some unanswered questions in our previous study: (a) Does the dry-HT sample EMC indeed increase after water leaching? (b) Why is the dry-HT sample not relaxed by the post-HT sample leaching treatment? (c) Does the  $\text{OH}_{\text{acc}}$  content change after relaxation?

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## Materials and methods

### Materials and heat treatment

Scots pine sapwood (*Pinus sylvestris* L.) was cut into blocks of  $20 \times 20 \times 10$  (R  $\times$  T  $\times$  L) mm<sup>3</sup>. The samples were clear of heartwood, knots and macroscopic defects. The samples were oven-dried using a temperature sequence of 40, 60, 80 and finally 105°C, with each temperature being held for 24 h, before the initial dry mass and dimensions were determined. The experimentally investigated sample was heated in an oven at atmospheric pressure with superheated steam to a peak temperature of 225°C, which was held for 180 min, before cooling the oven to room temperature. After production, the sample was dried and stored above silica gel at 25°C for at least 1 week in an exicator.

### Hydrogen-deuterium exchange (HDX) and EMC<sub>93%</sub>

OH<sub>acc</sub> were quantified in a DVS apparatus (DVS ET, Surface Measurement Systems, London, UK) with a measuring accuracy of 0.1 µg and a gas flow of 200 cm<sup>3</sup> min<sup>-1</sup> at 25°C during the measurement. Samples that were cut from the same slat before HT were used. Approximately 20 mg of material was taken from the middle of each sample using a razor blade.

For HDX the following sequence was applied: (1) determination of oven-dry weight after heating at 60°C for 6 h followed by cooling to 25°C for 2 h; (2) exposure to a set point RH of 95% RH using D<sub>2</sub>O vapor for 12 h; and finally (3) the determination of oven-dry weight as done in step (1). The dry N<sub>2</sub> flow was kept constant at 200 cm<sup>3</sup> min<sup>-1</sup>. OH<sub>acc</sub> was calculated from the relative dry mass increase by HDX, assuming that each accessible OH group exchanges its <sup>1</sup>H atom for a <sup>2</sup>H (D), increasing the initial dry mass m<sub>0</sub> by 1.00616 g per mole of HDX, to a deuterated dry mass m<sub>od</sub>

$$\text{OH}_{\text{acc}} = \frac{m_{\text{od}} - m_0}{1.00616 m_0} \text{ mol g}^{-1}$$

For the determination of the EMC with H<sub>2</sub>O, the same sequence was applied, except that H<sub>2</sub>O vapor was used in step (2) and that step (3) was omitted. When using H<sub>2</sub>O vapor, the measured RH was ca. 93%. However, when using D<sub>2</sub>O vapor, the measured RH was much lower (ca. 87% RH) than the set point RH. It should be noted that the device was not calibrated for D<sub>2</sub>O, but for H<sub>2</sub>O vapor, which results in erratic readings of the humidity probe when using D<sub>2</sub>O. The absolute EMC values for D<sub>2</sub>O and H<sub>2</sub>O vapor should, thus, not be directly compared to one another. The respective EMCs were calculated from the masses m<sub>H<sub>2</sub>O</sub> and m<sub>D<sub>2</sub>O</sub> at the end of the moistening stages

$$\text{EMC}_{\text{H}_2\text{O}} = \frac{m_{\text{H}_2\text{O}} - m_0}{18.0153 m_0} \text{ mol H}_2\text{O g}^{-1}$$

$$\text{EMC}_{\text{D}_2\text{O}} = \frac{m_{\text{D}_2\text{O}} - m_{\text{od}}}{20.0276 m_0} \text{ mol D}_2\text{O g}^{-1}$$

The maximum absolute random errors by DVS are estimated at 0.2% EMC (Glass et al. 2018), corresponding to 0.11 mmol H<sub>2</sub>O g<sup>-1</sup> and 0.10 mmol D<sub>2</sub>O g<sup>-1</sup>, and 0.16 mmol g<sup>-1</sup> in OH<sub>acc</sub> by statistical analysis of data from our previous study (Altgen et al. 2018b).

### H<sub>2</sub>O and DMSO soak procedures

The adopted H<sub>2</sub>O soak treatment procedure consisted of 5 days soaking in deionized water of the wood sample and subsequent drying in an exicator above silica gel. A dimethyl sulfoxide (DMSO) treatment procedure consisted of 5 days soaking in DMSO, 5 days washing in daily changed water and subsequent drying in a desiccator above silica gel. One sample was exposed to the following EMC measurement steps:

- A1. Oven-dry weight and EMC<sub>H<sub>2</sub>O</sub>
- A2. H<sub>2</sub>O soak treatment
- A3. Oven-dry weight and EMC<sub>H<sub>2</sub>O</sub>
- A4. DMSO soak treatment
- A5. Oven-dry weight and EMC<sub>H<sub>2</sub>O</sub>

Another sample was exposed to the following HDX measurement steps:

- B1. HDX with EMC<sub>D<sub>2</sub>O</sub> determination
- B2. H<sub>2</sub>O soak treatment
- B3. HDX with EMC<sub>D<sub>2</sub>O</sub> determination
- B4. DMSO soak treatment
- B5. HDX with EMC<sub>D<sub>2</sub>O</sub> determination.

## Results and discussion

An EMC recovery after soaking of dry-HT wood, known from the literature (Obataya and Tomita 2002; Altgen and Militz 2016), is observed in the EMC<sub>H<sub>2</sub>O</sub> as well as the EMC<sub>D<sub>2</sub>O</sub> changes (lines 1 and 2 in Table 1). EMC with D<sub>2</sub>O is systematically lower than H<sub>2</sub>O; however, after soaking the relative difference is diminished. This trend is continued after soaking in DMSO, a strongly polar wood-swelling liquid (Mantanis et al. 2009), practically removing all differences between H<sub>2</sub>O and D<sub>2</sub>O (line 3 in Table 1). The soak treatments in H<sub>2</sub>O cause a small dry mass loss (ML), which is further increased by soaking in DMSO and subsequent washing with H<sub>2</sub>O. The progressively swollen wood matrix promotes the release of trapped degradation products that cannot evaporate under dry-HT process conditions, consistent with other studies (Hofmann et al. 2013; Wentzel et al. 2018).

For the first time, OH<sub>acc</sub> has been measured before and after matrix relaxation, during which the EMC is significantly increased. OH<sub>acc</sub> appears slightly decreased, which may be attributed to the loss of dry mass (%ML) from the soak treatments (Altgen et al. 2018b). All measured OH<sub>acc</sub> are larger than  $9.20 \pm 0.16$  mmol g<sup>-1</sup>, the value found in our previous study for the unrelaxed 225°C dry-HT wood sample. This may be attributed either to the sensitivity of the OH<sub>acc</sub> for the new dry weight measurement procedure, or to sample-to-sample variation.

It is generally accepted that thermal wood modification leads to a reduction in EMC, at least in part, ascribed to the loss of OH groups from the wood matrix. However, quantitative experimental studies relating EMC to the

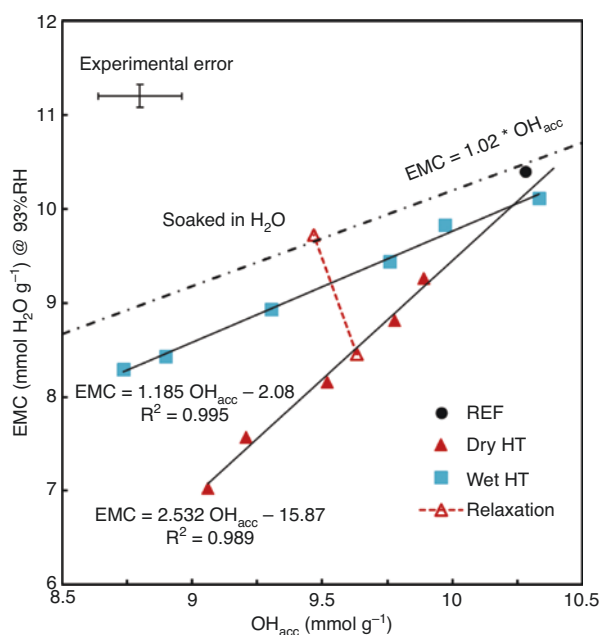
**Table 1:** Effect of water and DMSO soak on 225°C dry-HT.

	H <sub>2</sub> O			D <sub>2</sub> O	
	OH <sub>acc</sub> ± 0.16 (mmol g <sup>-1</sup> )	EMC ± 0.11 (mmol g <sup>-1</sup> )	ML (%)	EMC ± 0.10 (mmol g <sup>-1</sup> )	ML (%)
(1) After dry-HT	9.63	8.45	–	7.20	–
(2) After H <sub>2</sub> O soak	9.47	9.72	1.47	8.79	1.24
(3) After DMSO soak	9.28	11.46	4.30	11.31	4.39

ML (%) is the mass loss measured during the A3 and A5 steps, relative to the A1 step. EMC<sub>H<sub>2</sub>O</sub> are measured in the A1, A3 and A5 steps. OH<sub>acc</sub> and EMC<sub>D<sub>2</sub>O</sub> are measured in the B1, B3 and B5 steps.

content of hydroxyl groups are very scarce. The HDX method has become an important tool in determining the OH content, as it only counts the relevant OH groups in moisture sorption that are accessible by water molecules. However, Lindh et al. (2016) showed experimentally that the OH(3) group, associated with the C3-atom in the pyranose units, of cellulose cannot be deuterated, whereas the molecular dynamics simulation results of these authors indicated a retained hydrogen-bond ability of the OH(3) group with water molecules. On the other hand, quantitative experimental data on the occupancy of water molecules at the OH(3) groups of hydrated cellulose are still lacking. Moreover, hidden OH(3) groups (missed by HDX) in dry-HT wood are not expected to influence the conclusions from our main experiment, the measurement of OH<sub>acc</sub> change by matrix relaxation.

Getting reliable results from the adopted gravimetric HDX method requires enough reaction time with D<sub>2</sub>O and very accurate dry mass measurements before and after HDX. The ratio between the determined EMC and OH<sub>acc</sub> for the pine reference sample gives an occupancy of about 1 mol of water per mole of OH<sub>acc</sub> at ca. 93% RH (Figure 1, closed circle), consistent with independently estimated values for amorphous cellulose by Berthold et al. (1996) and for wood by Willems (2014). Note that an occupancy of 1.0 is rather circumstantial, in view of the large slope of the water sorption isotherm between 90% and 100% RH. The found OH<sub>acc</sub> content of 10.3 mmol g<sup>-1</sup> for the leached pine wood control sample is somewhat larger than reported values of 9.0 mmol g<sup>-1</sup> for spruce (*Picea abies* L.) (Thybring et al. 2017), 7.5–9.5 mmol g<sup>-1</sup> for birch (*Betula pendula* L.) (Popescu et al. 2014), 7.5 and 8.1 mmol g<sup>-1</sup> for sesendok (*Endospermum malaccense* Benth. ex Müll.Arg.) and acacia (*Acacia mangium* Willd.) (Rautkari et al. 2013) and 6.8 mmol g<sup>-1</sup> for *Styrax tonkinensis* (Pierre) Craib ex Hartwich (Phuong et al. 2007). On the other hand, OH<sub>acc</sub> contents above 10 mmol g<sup>-1</sup> have been observed for unmodified pine and spruce (Kymäläinen et al. 2015, 2018).



**Figure 1:** EMC<sub>93%</sub> vs. OH<sub>acc</sub> content of dry-HT (triangles), wet-HT (squares) and control sample (circle): data from Altgen et al. (2018b).

The open triangles represent the water soaking relaxation treatment for dry-HT sample (present study).

## Relaxation effect by water soaking dry-HT wood

Our previous results (Figure 1) confirmed that dry-heating causes a much larger EMC decrease at first 93% RH exposure than a hydrothermal treatment at the same modification level, as reported by Obataya et al. (2002) on spruce and Altgen and Militz (2016) on beech. The differences between the EMC of dry-HT and wet-HT remain in alternative correlations with the dry ML or the oxygen-to-carbon atomic ratio (Altgen et al. 2018b). Based on a molecular model of Willems (2018), which will be further elaborated in the present study, and the experimental observations of Obataya et al. (2002) and Altgen and Militz (2016), it was

speculated that the dry-HT line would change after relaxation of the dry-HT material, by an EMC gain of each dry-HT point toward the wet-HT line without change of  $\text{OH}_{\text{acc}}$  (Altgen et al. 2018b). This is reasonably confirmed by our data on EMC and  $\text{OH}_{\text{acc}}$  before and after water soaking the dry-HT 225°C sample, plotted in Figure 1. The expected invariance of  $\text{OH}_{\text{acc}}$  is not perfect, because of the loss of cell wall material by soaking (Table 1, ML values).

While DVS measurements appear to be well-repeatable, resulting in high  $R^2$  coefficients of determination of the regressions (Figure 1), Glass et al. (2018) show that there are systematic errors in the estimated dry masses and EMCs. Most importantly, small deviations in the dry mass before and after HDX influence the calculated  $\text{OH}_{\text{acc}}$  sensitively. As the development of advanced methods for accurate dry mass determination from the DVS curves is still on-going, we adopted an elevated oven-drying temperature at 60°C in the DVS apparatus in our current experiments, instead of 25°C in the earlier studies. This change of drying procedure appears to cause a shift in  $\text{OH}_{\text{acc}}$  by +0.5 mmol g<sup>-1</sup>. Moreover, the lower dry weights achieved by this procedure cause a systematic EMC increase. Hence, the position of the included relaxation data points in Figure 1 may not be accurately aligned with the data points from our previous study. We note that simulations indicate that the ratio between the regression lines for the dry-HT and wet-HT is around 2.0, unaffected by the precise method of dry mass determination.

Remarkably, the applied leaching treatment in the previous study (Altgen et al. 2018b) did not bring about the relaxation effect, in contrast to a similar water soaking procedure in the present study. The main difference between the two cases is that the soaking procedure in the previous study was applied to the sample blocks instead of the much smaller DVS samples.

## Nature of the EMC effect of relaxation in dry-HT wood

Qualitatively, the change in EMC of dry-HT wood after soaking is consistent with a wood polymer relaxation as suggested by earlier authors (Obataya and Tomita 2002; Altgen and Militz 2016). How the relaxation phenomenon physically affects the EMC has not been established yet.

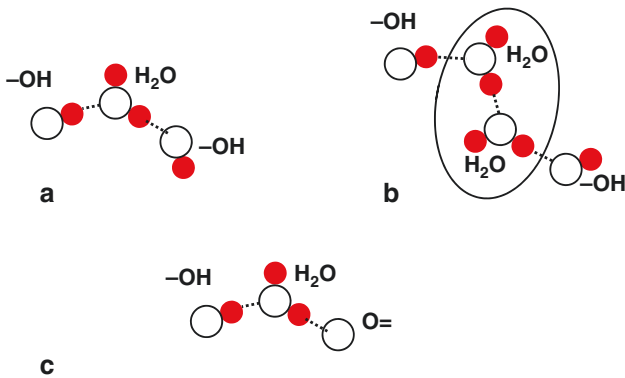
The nearly invariant  $\text{OH}_{\text{acc}}$  with the water and DMSO soaking treatments rules out any explanation of an EMC gain by a correlated increase in  $\text{OH}_{\text{acc}}$ . The observed ML after the water and DMSO soak, from the release of trapped cell wall degradation products, could be considered to play a potential role in water absorption volume

exclusion (cell wall bulking). It is known that bulking of the cell wall by acetylation of  $\text{OH}_{\text{acc}}$  groups does reduce  $\text{OH}_{\text{acc}}$  to a lesser relative extent than the EMC (Popescu et al. 2014). Bulking does not shield nearby OH groups, but it controls the maximum number of  $\text{OH}_{\text{acc}}$  that can be active simultaneously (Willems 2018). This would in principle allow bulking to diminish EMC without changing  $\text{OH}_{\text{acc}}$ , although the attainable EMC reduction by bulking with the observed small ML remains to be quantitatively verified.

Dry-HT provides the most favorable conditions for crosslinking by condensation reactions, compared to wet-HT (Altgen et al. 2018a). This is confirmed by a significantly lower maximum swelling of dry-HT wood by water saturation, compared to wet-HT (Obataya et al. 2002; Altgen et al. 2016, 2018b). Engelund et al. (2013) discussed the function of such crosslinks as swelling restraints controlling the EMC over the entire hygroscopic range (0–95% RH). The thermodynamic interaction of volume expansion (moisture swelling) against stresses imposed by mechanical restraints (matrix rigidity) has been theoretically described by Barkas (1949) and Willems (2014). Using the theory of the latter, relaxation would release a rather high amount (about 7 MPa) of stress to explain the reversible part of the EMC in the 225°C dry-HT sample. It also seems unlikely that the highly non-linear effect of stress on EMC (Willems 2014) and the variability of cell wall stiffness (Wagner et al. 2013) would result in a strictly  $\text{OH}_{\text{acc}}$ -linear EMC deviation between dry-HT and wet-HT (Figure 1).

## A molecular model of the moisture sorption sites in wood

The missing link between EMC and (the relaxation of) mechanical stress might be found in the molecular structure of moisture sorption sites in wood. Willems (2018) considered that the maximum hydrogen-bond enthalpy between H<sub>2</sub>O and an  $\text{OH}_{\text{acc}}$  group (20–25 kJ mol<sup>-1</sup>) is about half the amount needed to explain the wood-water bond enthalpy (>44 kJ mol<sup>-1</sup>). Hence, isolated water molecules or small water clusters were argued to be bound by pairs of  $\text{OH}_{\text{acc}}$  groups, but it is now considered that moisture sorption sites may alternatively be formed by pairing of an  $\text{OH}_{\text{acc}}$  group with any type of hydrogen-accepting oxygen-containing group (Guo et al. 2016) (Figure 2). Relaxation may enter the model as a necessary mechanism to enable the translocation of an isolated  $\text{OH}_{\text{acc}}$  group toward another hydrogen-bonding functional group to form a pair for moisture sorption.



**Figure 2:** Proposed sorption sites for water, composed of pairs of hydrogen-bonding functional groups, involving at least one OH group: (a) water molecule between two OH groups; (b) water dimer cluster between two OH groups; (c) water molecule between one OH and one carbonyl group (O=).

White disks: oxygen atoms, red disks: hydrogen atoms. Dotted lines: hydrogen bonds.

The model does not only account for the correct magnitude of the binding enthalpy of water to wood, it also explains why some of the  $\text{OH}_{\text{acc}}$  groups in isolation cannot contribute to moisture sorption, despite being accessible. An  $\text{OH}_{\text{acc}}$  group is “inactive” when it is not paired for moisture sorption. The thermally induced disorder and destruction in the wood matrix during HT might be expected to leave some functional groups isolated, requiring a matrix relaxation to re-arrange them into active pairs for moisture sorption (Figure 3).

Figures 2 and 3 show the essence of the proposed moisture sorption model. Single water molecules or small water clusters can bind to sorption sites, constituted by two (H-donor/acceptor pair) functional groups. Such pairs are schematically drawn by ellipses in Figure 3. The pairs can change nearby partners. When HT randomly removes

an active functional group, the remaining free partner can recombine with a nearby functional group, leaving another functional group without partner. This effectively diffuses free hydrogen-bonding functional groups throughout the wood matrix, with minimal conformational polymer movements, until they meet and combine into new pairs.

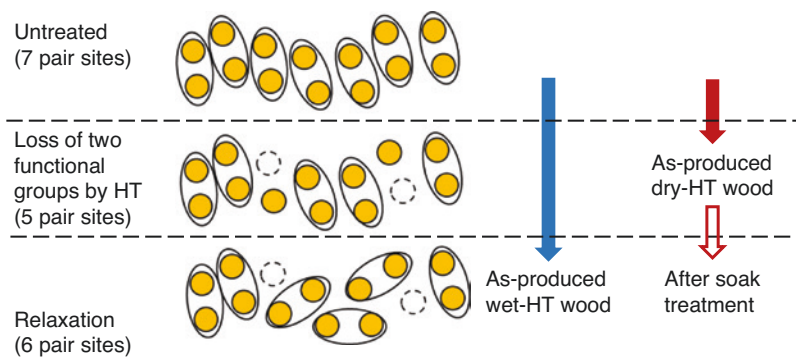
The abundance of crosslinks in dry-HT wood and oven-dry conditions during the dry-HT process are thought to severely hinder the necessary polymer movements for the recombination mechanism. In contrast, the moist conditions and absence of crosslinks in wood in the wet-HT process optimally enable the recombination mechanism. Consequently, wet-HT wood is in the final relaxed state when it leaves the HT reactor, whereas dry-HT wood remains unrelaxed, making the latter susceptible to a post-production relaxation with an associated EMC increase (Figure 3).

Interestingly, the ratio between the two measured slopes of the dry-HT and wet-HT lines in Figure 1 is equal to 2 within  $1\sigma$  deviation ( $2.1 \pm 0.2$ ), which the model of Figure 3 can explain by the recovery of one sorption site pair (wet-HT) for every two lost site pairs in the unrelaxed matrix (dry-HT).

During the proposed relaxation process (Figure 3), the  $\text{OH}_{\text{acc}}$  content is not subject to change, as is reasonably confirmed by comparing the  $\text{OH}_{\text{acc}}$  measurements before and after water soaking.

## Conclusions

The water soak procedure on small as-produced dry-HT wood samples in the present research appears effective in accomplishing relaxation, in contrast to the leach procedure applied to larger as-produced wood blocks in the previous research. The effect of partial recovery of the EMC



**Figure 3:** Schematic representation of the evolution of pair sites after HT.

Re-arrangement during relaxation recovers one pair for every two pairs lost initially by HT. Wet-HT wood completes the relaxation stage during production. Dry-HT wood remains unrelaxed after production, until water soaking.

change by dry-HT was confirmed by water soaking, it did not significantly change  $\text{OH}_{\text{acc}}$ .

The presented molecular model of wood moisture sorption comprehensively explains the different behavior of wet-HT and dry-HT wood, with respect to the reversible and irreversible EMC changes in as-produced thermally modified wood.

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