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## The role of accessible hydroxyl groups in reversible and irreversible EMC changes by thermal wood modification

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### ABSTRACT

Heat treatment (HT) is a well-known means to reduce the room-temperature equilibrium wood moisture content (EMC) at a specified relative humidity (RH). Already at slightly elevated temperature above room temperature, EMC is decreased in proportion to the exposed temperature. At higher elevated temperature, where wood chemical changes become activated, the EMC is profoundly reduced, mainly caused by the loss of accessible hydroxyl groups ( $\text{OH}_{\text{acc}}$ ) in the wood matrix. However, earlier experiments have shown that 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 present an experimental study on the  $\text{OH}_{\text{acc}}$  content and the associated EMC decrease at 93% RH by a relaxation inhibiting dry-HT versus a relaxation enabling wet-HT. The results of this study quantitatively support a molecular explanation of this phenomenon, in which wood moisture is principally bound by  $\text{OH}_{\text{acc}}$ -pairs, instead of solitary  $\text{OH}_{\text{acc}}$ . The irreversible part of EMC reduction is assigned to the thermochemical removal of  $\text{OH}_{\text{acc}}$  from the wood matrix. The reversible part (EMC recovery), is attributed to a regrouping of solitary  $\text{OH}_{\text{acc}}$  into pairs, thereby restoring moisture sorption sites. Each solitary  $\text{OH}_{\text{acc}}$ , may either be the remaining half of an  $\text{OH}_{\text{acc}}$ -pair after thermal destruction of its partner  $\text{OH}_{\text{acc}}$ , or originate from thermally disrupted  $\text{OH}_{\text{acc}}$ -pairs without  $\text{OH}_{\text{acc}}$  removal. The  $\text{OH}_{\text{acc}}$ -pair recovery mechanism explains the involvement of wood polymer relaxation, necessary to translocate  $\text{OH}_{\text{acc}}$  in the wood matrix.

### 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, Altgen and Militz 2016). 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 towards their thermodynamically most favourable arrangement. This relaxation hinderance 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, since 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 versus a hydrothermal treatment, both followed by an extraction of the water-soluble degradation products (Altgen *et al.* 2018). The  $\text{OH}_{\text{acc}}$  content was measured by hydrogen-deuterium exchange (HDX) and correlated with  $\text{EMC}_{93\%}$ , the EMC at first exposure to 93% RH. In this way, we could compare the  $\text{EMC}_{93\%}$  at each  $\text{OH}_{\text{acc}}$  content in relatively crosslinked (dry-HT) versus soft (wet-HT) extractive-free matrices of thermally modified wood. These two extremes are considered to represent the unrelaxed state of as-produced dry heated thermally wood and the corresponding final state after full relaxation, without the potentially disturbing effect of residual degradation products in the cell walls.

The results in this paper highlight a proposed mechanism for the EMC recovery in thermally modified wood by polymer relaxation. These results are an excerpt from a larger study addressing the changes in elemental chemical composition, dry mass loss and the dimensions in the dry and fully swollen state (Altgen *et al.* 2018).

## EXPERIMENTAL

### *Materials*

Scots pine sapwood (*Pinus sylvestris* L.) was cut to dimensions of 20×20×10 (R×T×L) mm<sup>3</sup>. The samples were clear of heartwood, knots and macroscopic defects. Fifteen replicates per sample group (treatment process and peak temperature) were used. All samples were oven-dried using a temperature sequence of 40, 60, 80 and finally 105 °C, with each temperature being held for 24h, before the initial dry mass and dimensions were determined.

### *Heat treatments and leaching procedure*

For dry-HT, oven-dry samples were heated in an oven at atmospheric pressure with superheated steam to a peak temperature of 180, 195, 210, 225 or 240 °C, which was held for 180 minutes, before cooling the oven to room temperature. For wet-HT, the oven-dried samples were water-impregnated (50 mbar for 1h) first, and then placed in small vessels with addition of deionized water (solid:liquid 1:20 g/g). The filled, closed vessels were heated in a slow rotating air bath digester to a peak temperature of 120, 130, 140, 150, 160 or 170 °C, which was held for 120 min before cooling for 30 min under continuous tap water flow. After HT, all samples, including the reference samples, were leached with deionized water after the treatment. Dry-HT samples and reference samples were vacuum-impregnated (50 mbar for 1 h) with deionized water before leaching. Within the course of two weeks, the water was changed daily to remove the remaining degradation products. The samples were then dried carefully at ambient conditions for a minimum of one week.

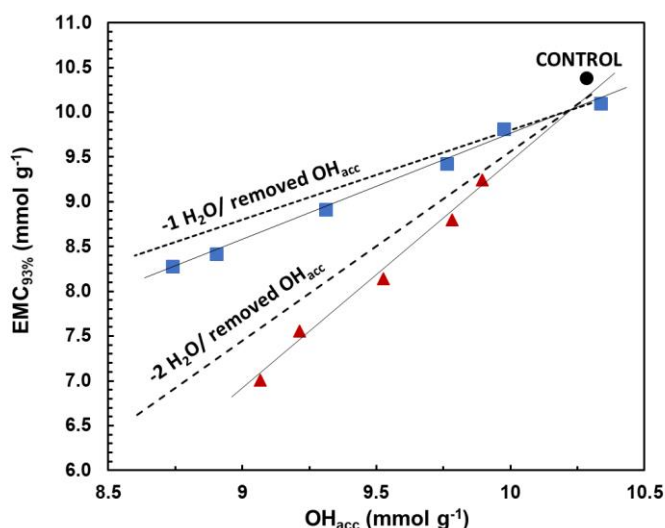
### *Hydrogen-deuterium exchange (HDX) and $\text{EMC}_{93\%}$*

$\text{OH}_{\text{acc}}$  were quantified in a DVS apparatus (DVS Advantage 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. Approx. 15.5 (±0.3) mg of material was taken from the middle of each sample using a razor blade. This material was subjected to the following sequence: (a) a drying step under dry N<sub>2</sub> flow (0% RH) until the mass change per minute was less than 0.0005 % min<sup>-1</sup> over a 10 min period, to determine the initial dry mass; (b) a partial

pressure of 93% using a mixture of dry N<sub>2</sub> and deionized water for 12h, to determine EMC<sub>93%</sub>; (c) a drying step as described above, to remove all water; (d) a partial pressure of 86.5% using a mixture of dry N<sub>2</sub> and deuterium oxide (D<sub>2</sub>O), for HDX; and finally (e) another drying step as described above, to determine the dry mass of the deuterated sample, from which the OH<sub>acc</sub> content can be calculated under the assumption that each accessible OH group exchanges one <sup>1</sup>H atom for a <sup>2</sup>H atom.

## RESULTS AND DISCUSSION

It is generally accepted that thermal wood modification leads to a reduction in EMC. In many textbooks and countless journal articles, the EMC reduction is ascribed to the loss of OH-groups from the wood matrix. However, quantitative experimental studies relating EMC to the content of hydroxyl groups are very scarce. The HDX method has become a major tool in determining the OH-content, since it only counts the relevant OH-groups in moisture sorption that are accessible by water molecules. However, getting reliable results from the adopted gravimetric HDX method requires a sufficient reaction time with D<sub>2</sub>O and very accurate dry mass measurements before and after HDX. The ratio between the determined EMC<sub>93%</sub> and OH<sub>acc</sub> for the pine reference sample gives an occupancy of about 1 mole of water per mole of OH<sub>acc</sub> at 93%RH (Figure 1, closed circle), consistent with independently estimated values for amorphous cellulose by *et al.* (1996) and for wood by Willems (2014). 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 (Thybring *et al.* 2017), 7.5 to 9.5 mmol g<sup>-1</sup> for radiata pine (Popescu *et al.* 2014), 7.5 and 8.1 mmol g<sup>-1</sup> for sesendok and acacia (Rautkari *et al.* 2013) and 6.8 mmol g<sup>-1</sup> for *Styrax tonkinensis* (Phuong *et al.* 2007). On the other hand, similar or slightly higher OH<sub>acc</sub> contents, compared to the value in the present study, have observed for unmodified pine and spruce (Kymäläinen *et al.* 2015, *et al.* 2018).



**Figure 1:** EMC<sub>93%</sub> versus OH<sub>acc</sub> content after dry-HT (triangles) or wet-HT (squares) and leaching. Control sample (circle) is leached, but not exposed to heat.

Our results (Figure 1) confirm that dry-heating causes a much larger EMC-decrease at first 93% RH exposure than hydrothermal treatment at the same modification level, as reported by Obataya *et al.* (2002) on spruce and Altgen and Miltz (2016) on beech. The

differences between the  $EMC_{93\%}$  of dry-HT and wet-HT remain in alternative correlations with the dry mass loss or the oxygen-to-carbon atomic ratio (Altgen *et al.* 2018).

A tentative explanation of the different EMC's at the same  $OH_{acc}$  content is found in the work of Popescu *et al.* (2014) with a cell wall bulking wood modification treatment, where the volume of the incorporated bulking adduct determines the EMC reduction, rather than the associated substitution level of  $OH_{acc}$ . It could be argued that the thermal degradation products of the cell wall become covalently bonded to the cell wall as bulking adducts during dry-HT, whereas they become dissolved in the wet-HT process liquid. Such bulking would implicate a lesser dry mass loss and a larger dry dimension at the same  $OH_{acc}$  content for dry-HT samples. However, at a mass loss of 22%, we observed an equal dry dimension loss and an equal  $OH_{acc}$  content ( $9 \text{ mmol g}^{-1}$ ) for wet-HT and dry-HT (Altgen *et al.* 2018), whereas the  $EMC_{93\%}$  clearly deviate (Figure 1).

Another tentative explanation is a crosslinking between cell wall polymers occurring in dry-HT in contrast to wet-HT. Dry-HT provides the most favourable conditions for crosslinking by condensation reactions. This would implicate that the maximum swelling by liquid water saturation would be significantly less for dry-HT compared to wet-HT, which is indeed confirmed by observations in our study and those of others (Obataya *et al.* 2002, Altgen *et al.* 2016, 2018). A swelling limitation could limit  $EMC_{93\%}$  without effect on the measured  $OH_{acc}$ , since the conversion of  $OH_{acc}$  to  $OD_{acc}$  can proceed sequentially by dynamic occupation of all  $OH_{acc}$  by  $D_2O$ , even if these  $OH_{acc}$  cannot be simultaneously water-occupied, as in the case of cell wall bulking (Popescu *et al.* 2014; Willems 2018). Hence, this study cannot rule-out crosslinks being the reason behind the deviating linear relationship between  $EMC_{93\%}$  and  $OH_{acc}$  for dry- vs. wet-HT. However, based on the observations of Obataya and Tomita (2002) and Altgen and Militz (2016), one can speculate that the  $EMC_{93\%}$  of the dry-HT wood might gradually move towards that of the wet-HT wood. This would implicate that the crosslinks or hydrogen bond interactions are not lasting – which is not verified in this study.

The slope of the linear correlations between  $EMC_{93\%}$  and  $OH_{acc}$  is close to 1.0 mole  $H_2O$  per removed mole of  $OH_{acc}$  for wet-HT and 2.0 for dry-HT, respectively (Figure 1). Statistical linear regression evaluations indicate significant differences from these integer values for the water occupation of the removed  $OH_{acc}$ :  $1.18 \pm 0.04$  for wet-HT and  $2.53 \pm 0.15$  for dry-HT. Interestingly, the ratio between the two measured slopes is an integer, equal to 2 within  $1\sigma$  deviation ( $2.1 \pm 0.2$ ). This points at yet another possible explanation in conjunction with arguments that moisture sorption sites in wood are constituted by *pairs* of  $OH_{acc}$ , binding isolated water molecules as well as small molecular clusters of water, with thermodynamically controlled local occupation statistics (Willems 2018). For each randomly removed  $OH_{acc}$ , a sorption site is lost by the destruction of an  $OH_{acc}$ -pair. However, the remaining halves of each destroyed  $OH_{acc}$ -pair may combine into a new pair, restoring one sorption site from two lost ones. The factor 2 between the slopes of Figure 1 can accordingly be explained by considering that wet-HT provides favourable conditions for wood polymer relaxation by the plasticizing effect of water, enabling the full restoration of sorption sites from isolated  $OH_{acc}$  after thermal destruction of their partner  $OH_{acc}$ . These solitary  $OH_{acc}$  would remain unpaired in dry-HT wood by a lack of relaxation. Dry-HT wood may be subject to stimulated relaxation under service conditions by cycles of wetting and drying, explaining the EMC recovery as observed by Obataya and Tomita (2002) and Altgen and Militz (2016).

The proposed EMC recovery mechanism might be speculated to play a role in the EMC losses by heating at low temperature, below the threshold of any significant wood chemical changes.  $\text{OH}_{\text{acc}}$  pairs might be disrupted without  $\text{OH}_{\text{acc}}$  removal. The EMC loss is fully recoverable by soaking in water (Thybring *et al.* 2017), promoting polymer relaxation. However, Thybring *et al.* (2017) showed that the  $\text{OH}_{\text{acc}}$  content is temporarily reduced after heating, until vacuum impregnation with water restored the original  $\text{OH}_{\text{acc}}$  content, unlike the proposed EMC recovery mechanism where the isolated  $\text{OH}_{\text{acc}}$  remain visible but are inactivated as moisture sorption sites, in absence of a partner  $\text{OH}_{\text{acc}}$ .

## CONCLUSIONS

Pine wood has been thermally modified by dry heating with atmospheric steam and full-liquid hydrothermal treatment. With both heating modes and a subsequent water extraction step to remove residual degradation products, a progressive loss of accessible hydroxyl groups is achieved, responsible for an EMC reduction. The correlation between the EMC after first exposure to 93% RH and the directly measured  $\text{OH}_{\text{acc}}$  content by the gravimetric HDX method is completely different for dry- versus wet-HT.

Confirmed crosslinking in dry-HT wood might be directly responsible for the differences in the initial EMC- $\text{OH}_{\text{acc}}$  relation, compared to wet-HT wood. These crosslinks would limit the EMC by imposing a swelling limit in dry-HT wood, preventing dry-HT wood to take-up the same amount of moisture as wet-HT wood at the same  $\text{OH}_{\text{acc}}$  content. In that case, an EMC recovery in dry-HT wood would be associated with a progressive breaking of these crosslinks, lifting the swelling limit.

Since the ratio of the slopes of the determined EMC -  $\text{OH}_{\text{acc}}$  correlations for dry-HT and wet-HT is very near 2, there is an interesting alternative explanation by taking arguments into account, that require  $\text{OH}_{\text{acc}}$ -pairs for moisture sorption in wood. In this case, the crosslinks in dry-HT wood would have an indirect role, preventing relaxation for the formation of sorption sites by combining solitary  $\text{OH}_{\text{acc}}$  from 2 thermally destructed pairs into 1 new pair. This restoration process is supposed to be fully accomplished during wet-HT, enabling wood polymer relaxation.

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