

# Physical modeling of moisture content and fungal resistance properties of thermally modified timber

*PhD thesis of Wim Willems*

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## Incentive and objective

Thermally modified wood (TMW) is produced in oxygen-free heating processes above 160°C [8]. Its most-valued properties are an increased fungal resistance (durability) and reduced equilibrium moisture content (EMC), obtained via wood chemical changes that are qualitatively well-known [9]. Quantitative structure-property relations remain to be found. It was recently observed [10] that the CHN(O)-elemental composition of TMW correlates very well with the durability and EMC, in a remarkably similar way for all investigated soft- and hardwoods in a broad range of wood bulk densities. For this reason, a causal relation between the elemental composition of TMW and the durability and EMC is hypothesized. This doctoral thesis [1] is aimed at finding comprehensive and quantitative physical models explaining the causality.

## Approach

The loss of polar hydroxyl sites from hemicelluloses, quantified by the change in molar oxygen to carbon ratio (O/C), is taken as the primary cause of the reduced EMC in TMW, based on a literature study. It is considered that the occupancy of the sorption sites for wood moisture is humidity-dependent, for which a new theory is developed.

TMW durability may be obtained by physical barriers for fungi or moisture exclusion in the cell wall. When these protection mechanisms become inadequate, the durability has to rely on intrinsic chemical resistance against bio-oxidation. A recent study [11] found that the activation energy for biodegradation  $E_a$  of natural organic matter decreases linearly with the average carbon oxidation state,  $Z$ , of the whole substance, which can be expressed in elemental ratios:  $Z=2(O/C)-(H/C)$ . This is used in the durability model for TMW.

## New contributions to wood science

**Van Krevelen Diagram (VKD).** Wood practically consists of three elements ( $CH_yO_x$ ), specified by just two elemental ratios  $x=O/C$  and  $y=H/C$ . Wood can thus be represented by a point  $(x,y)$  in the VKD (Fig.1). Wood modification results in a trajectory in the VKD,

which can be compared to model chemical reactions, providing information on the type of chemical changes [2,13]. A new feature added to the VKD are lines of constant  $Z$ , providing visual guidance whether wood is being oxidized ( $\Delta Z > 0$ ) or reduced ( $\Delta Z < 0$ ).

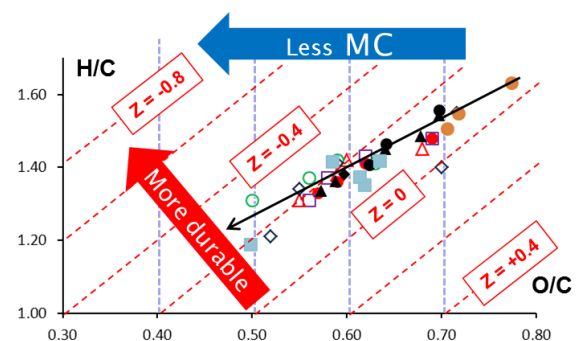


Fig. 1 Van Krevelen Diagram, with data points from 5 different studies, 9 different TMW species, showing a universal trajectory (black arrow pointing in direction of increasing degree of modification)

**Sorption site occupancy (SSO) theory.** This theory is developed from careful analysis of a large number of adsorption and desorption isotherms from various studies [5]. It is found that the moisture content  $u(h,t)$  at humidity  $h$  and time  $t$ , can be factored into  $u(h,t)=c(h,t)\theta(h)$ , where  $c(h,t)$  is directly proportional to the effective number of sorption sites and  $\theta(h)=h^n$  is the (fractional) occupancy of these sites, where  $n \approx 0.73$  at room temperature. Moisture and temperature equalization in the sample is required, but hysteresis, slow relaxation and other time-dependent or non-reversible phenomena are accounted for in  $c(h,t)$ . This makes  $c(h,t)$  an ideal metric for the study of time-dependent hygromechanical cell wall behavior (Fig.2).

**Water chemical potential theory.** Wood moisture can be regarded as a pure water aggregation state, as a result of the very similar but slightly stronger hydrogen bonding interactions in wood compared to bulk water. This renders wood moisture equilibrium directly controlled by the water chemical potential  $\mu=RT \ln 1/h$  [14], exhibited by actual EMC data [4]. This fact greatly simplifies the thermodynamics of wood moisture.

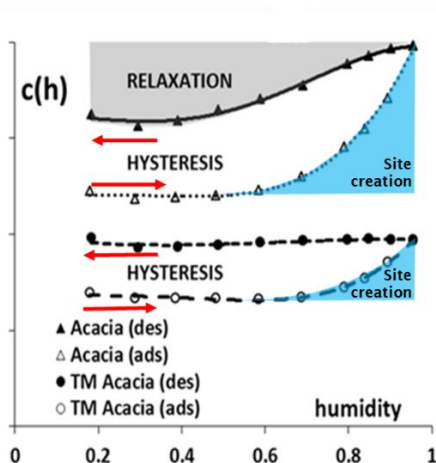


Fig. 2 Sorption site density  $c(h)$  calculated from adsorption (open symbols) and desorption (closed symbols) isotherms of native and TM Acacia mangium. Data from [12].

## Results

VKD-mapping of TMW composition data from various studies and wood species revealed a universal trajectory, suggesting a common wood modification chemistry (Fig.1). Dehydration and decarboxylation reactions appear to be mainly responsible for the decrease in O/C and Z respectively. The VKD is insensitive for deacetylation reactions [2,3].

The X-ratio of European test standard EN113 is chosen as the metric for TMW durability, which is linked to  $E_a(Z)$  by an Arrhenius kinetics model. This leads to  $X \sim \exp(28.5\Delta Z/RT)$ , which is reasonably consistent with durability data of mildly heat-treated wood. Severely heat-treated wood seems to obtain additional resistance from an inhibition of diffusion of fungal degradation agents [3].

Assuming that the loss of one hydroxyl group (one oxygen atom) by heat treatment leads to the loss of one sorption site, the occupancy  $\theta(h)$  is calculated for mildly heat treated wood and found consistent with independent determinations [5]. The glassy state of severely heat-treated wood interferes in the relation between EMC and O/C, but  $\theta(h)=h^n$  is found valid over the entire range of heat treatment intensities for use in SSO-analysis.

## Applicability

The dependency between O/C and H/C (Fig. 1), makes one parameter, O/C, fully specify the elemental composition of TMW, providing an absolute metric for the degree of thermal modification [2,3].

The conversion of EMC data to sorption site density  $c(h)$  enables quantification of hysteresis and relaxation by the involved density of non-equilibrium sorption sites. Fig.2. shows as an example the lack of relaxation in severely heat-treated Acacia, explaining the relatively high hysteresis in TMW at a much lower EMC than native Acacia [5,6].

Since  $\mu$  is a thermodynamic potential,  $EMC(\mu)$  data determined from a room temperature adsorption isotherm, can be transformed to an isotherm at any other temperature and hydrostatic pressure. The in-situ EMC of a wood sample in a high-pressure thermal modification reactor can thus be estimated from the room-temperature adsorption isotherm, as measured after immediate termination of the treatment [4,7].

## PhD Publications (peer-reviewed only)

- [1] Willems W (2015) Physical modeling of moisture content and fungal resistance properties of thermally modified timber. PhD thesis, Göttingen University.
- [2] Willems W, Mai C, Militz H (2013) Thermal wood modification chemistry analysed using van Krevelen's representation. *Int. Wood Prod. J.* 4:166–171
- [3] Willems W, Gérardin P, Militz H (2013) The average carbon oxidation state as a marker for the durability of thermally modified wood. *Polym. Degrad. Stab.* 98:2140–2145.
- [4] Willems W (2014) The hydrostatic pressure and temperature dependence of wood moisture sorption isotherms. *Wood Sci. Technol.* 48:483–498
- [5] Willems W (2014) The mechanism of wood moisture sorption and its hysteresis: the water/void mixture postulate. *Wood Sci. Technol.* 48:499–518
- [6] Willems W (2015) A critical review of the multilayer sorption models and comparison with the sorption site occupancy (SSO) model for wood moisture sorption isotherm analysis. *Holzforschung* 69:67–75
- [7] Willems W, Altgen M, Militz H (2015) Comparison of EMC and durability of heat-treated wood from high versus low water vapour pressure reactor systems. *Int. Wood Prod. J.* 6:21–26

## Other cited literature

- [8] Militz H, Altgen M (2014) Processes and Properties of Thermally Modified Wood Manufactured in Europe. *ACS Symposium Series* 1158, Ch.16, pp. 269–285.
- [9] Hill CAS (2006) *Wood modification – chemical, thermal and other processes.* John Wiley & Sons, Chichester
- [10] Chaouch M, Dumarçay S, Pétrissans A, Pétrissans M, Gérardin P (2013) *Wood Sci. Technol.* 47:663–673
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