The Determination of EMC and its Effect on the Analysis of Moisture Sorption in Wood Modified with DMDHEU

Andrés Dieste, Andreas Krause, Carsten Mai, Holger Militz

Wood Biology and Wood Technology Georg-August-Universität Göttingen Büsgenweg 4 37077 Göttingen – Germany

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ABSTRACT

Data obtained from studies on differential heat of adsorption (ΔH_s) and average pore size of beech wood modified with 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) is to elucidate how the equilibrium moisture content (EMC) should be calculated: 1) based on dry modified wood (M); 2) based on dry unmodified wood (M_R). The average pore diameter of the cell wall is reduced because DMDHEU fills the pores, but the modification does not sufficiently change the average pore diameter to affect the condensation of moisture. The chemical composition of the modified cell wall was roughly estimated by stoichiometry, considering the maximal input of OH groups produced by DMDHEU. The molecular weight per adsorption site of a hypothetical wood polymer was calculated by the Hailwood-Horrobin model (W_i) and by stoichiometry (W_c). A ratio between them showed that the number of operative OH groups in modified wood was lower when M was used than when M_R was used. Inasmuch as the results of ΔH_s showed that wood modified with DMDHEU has more OH groups available, M_R was considered a more accurate calculation of EMC. Therefore, it was concluded that M_R should be used for the study of wood/water relations in wood modified with DMDHEU.

INTRODUCTION

On the one hand, adsorption is an exothermic reaction that occurs between an adsorbate and an adsorbent, e.g. water and wood, respectively. The reaction usually involves one layer of water, but it can grow up to ten layers. On the other hand, absorption is the increase in water content as a result of the surface tension forces that operate in the pores (Stamm 1964). The modification of wood with 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) affects both the adsorption behavior and the pore size distribution of wood. The DMDHEU molecule itself, whose molecular weight is composed of up to 39% of OH groups, is not inert to moisture adsorption, but it is even a hygroscopic substance. After the reaction with wood and DMDHEU two alternatives are possible: polycondensation and cross-linking; both produce molecules that are 26% and 24% rich in OH groups, respectively (Petersen 1968). Inasmuch as DMDHEU is a hygroscopic substance, the modification with DMDHEU increases the number of OH groups (Dieste *et al*. 2008).

There are two ways of calculating the EMC of modified wood:

$$M = \frac{m_2 - m_1}{m_1} \times 100 \qquad (1)$$

$$M_R = \frac{m_2 - m_1}{m_0} \times 100 \quad (2)$$

where M is the EMC [%]; m_0 is the oven-dry weight of the specimen before modification [g]; m_1 is the oven-dry weight of the specimen after modification [g]; m_2 is the weight of the specimen after modification in equilibrium with the given relative humidity [g].

On the one hand, M does not take into consideration the increase in weight produced by the chemical. Consequently, the EMC of chemically modified wood is always lower than that of unmodified wood, simply due to the incorporation of the chemical (Hill 2006). Therefore, it is recommended that the calculation of EMC should be based on the dry weight of the wood before the modification, and not on the dry weight of the modified wood (Akitsu *et al.* 1993, Hill 2006). On the other hand, M_R only describes the interaction of water to wood, overseeing the interaction between the chemical and water. The use of M or M_R to calculate EMC can be considered a matter of definition, but it is not a trivial one. The following article will argue that it is a critical issue to understand the wood/water relations in wood modified with DMDHEU.

EXPERIMENTAL

Samples of beech (*F. sylvatica* L.) were modified with DMDHEU as stated in a previous paper (Dieste *et al.* 2008, 2009). The moisture sorption behavior of modified wood was studied using the Hailwood-Horrobin model. The differential heat of adsorption (ΔH_s) was estimated by the Clausius-Clapeyron method and by solution calorimetry (Dieste *et al.* 2008). The average pore diameter of wood after the modification with DMDHEU was obtained by thermoporosimetry using differential scanning calorimetry (Dieste *et al.* 2009). The Hailwood-Horrobin model consists of three elements, namely absorbed water vapor, hydrated wood and dry wood, which form an ideal solid solution. Inasmuch as this heterogeneous system is considered an ideal solution, the activity of the elements equals their mole fractions (Hailwood and Horrobin 1946). The development of these concepts produces the following equation:

$$\frac{H}{M} = A + BH - CH^2 \quad (3)$$

where H is the relative humidity [%]; M is the EMC [%]; and A, B and C are empirical parameters (Skaar 1988).

The equilibrium between the activities of absorbed water and water vapor is described by the constant K_d, the equilibrium between the activity of hydrated wood over the activity of dry wood and absorbed water is described by the constant K_h, and the molecular weight of a hypothetical polymer capable of reacting with one molecule of water (W_i) were calculated according to (4)-(6) The model does not distinguish between polymolecular adsorbed water molecules and capillary condensed water. The constants are calculated using the empirical parameters A, B and C (Skaar 1988).

$$K_d = \frac{50(-B + \sqrt{B^2 + 4AC})}{A} \quad (4)$$

$$K_h = 1 + \frac{B^2 + B\sqrt{B^2 + 4AC}}{2AC} \tag{5}$$

$$W_i = 1800\sqrt{B^2 + 4AC} \tag{6}$$

RESULTS AND DISCUSSION

Adsorption

The isotherms were obtained by calculating the EMC on a dry modified wood basis *M* and on a dry wood basis (M_R). For the untreated samples all three constants presented indistinct results, independent of the method used to calculate EMC. Similar results were also observed for the constants K_d and K_h. On the contrary, the W_i for the wood modified with DMDHEU showed a clear difference related to the method of calculating EMC. W_i was clearly higher when it was calculated with *M* than when it was calculated with M_R (Table 2). The adsorption phenomenon was also thermodynamically studied. The heat released by the adsorption of water vapor in the surface of a sample at different EMC is called the differential heat of adsorption (ΔH_s). Higher ΔH_s implies higher hygroscopicity. The determination of ΔH_s by empiric isotherms as an input to the Clausius-Clapeyron equation or by solution calorimetry showed that from cero to ~10 % EMC the release of energy due to moisture adsorption was larger in modified samples than in unmodified samples. Two explanations were offered for this phenomenon: 1) more OH groups are available due to the bulking and consequent expansion of the cell wall; 2) DMDHEU has incorporated more OH groups (Dieste *et al*. 2008).

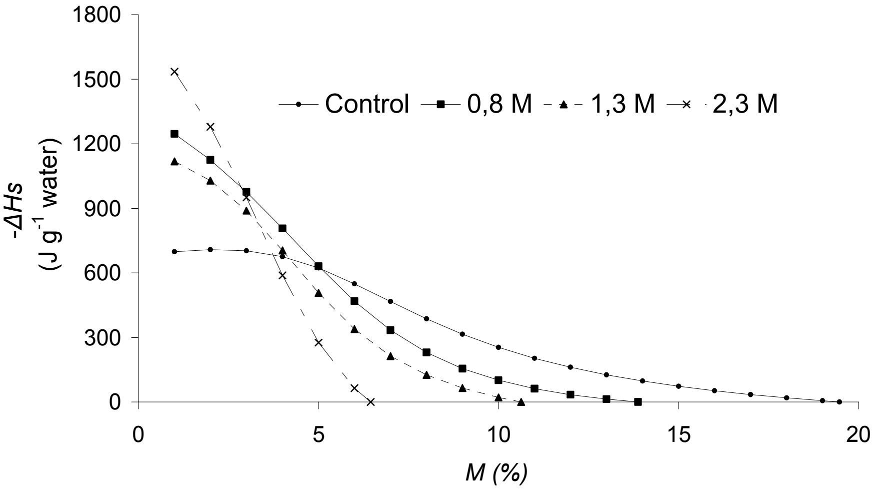

Figure 1: Differential heat of sorption (-ΔHs) calculated from the Clausius-Clapeyron equation as a function of EMC (1)

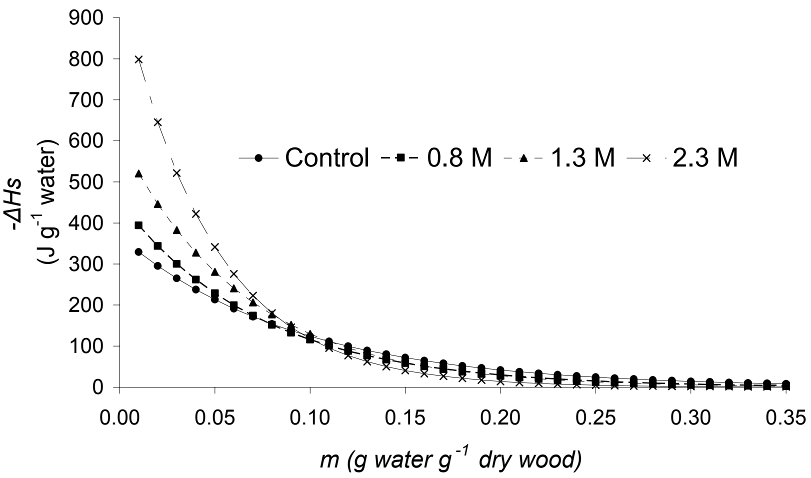

Figure 2: Differential heat of sorption (ΔHs), obtained from solution calorimetry, as a function of EMC (1)

Absorption

Moisture adsorption occurs independently of the pore size of wood. On the contrary, water vapor is condensed in the wood pores depending on pore diameter, temperature and relative humidity (Skaar 1988). It occurs in the macropores of wood, where the thermodynamical properties are similar to that of free water (Stamm 1964). The modification with DMDHEU partially occupies the volume of the macropores. The increase in weight (WPG) is larger than the increase in volume (bulking); thus density is higher.

According to the Kelvin equation, capillary sorption is limited by the diameter of the pores (Stamm 1964). Unmodified cell cavities of wood have a diameter that ranges between $2x10^3$ and $2x10^5$ nm. These calculations are only valid if the number of molecules involved (the hydrodynamic diameter of the water molecule is 0.4 nm) is large enough to permit water tension forces to act (Skaar 1988, Siau 1995). Maloney and Paulapuro (1999) used the change of phase from solid to liquid water to define the limit between micro- and macropores at 1.2×10^2 nm because the properties of water contained in larger pores do not differ greatly from those of free water. Skaar (1988) defined an even higher limit for the change in phase from gas to liquid water, namely 2.1×10^2 nm. Therefore, according to both estimations the modification with DMDHEU affects the diameter of pores that are below the limit of water condensation. The change of phase from vapor to liquid water (condensation) in pores with a diameter larger than 2.0×10^5 nm would be not different from that of free water. Therefore, the diameter of macropores ranges from 1.2×10^2 to 2.0×10^5 nm. The average pore diameter of samples of wood treated with different concentrations of DMDHEU was smaller than 1.2×10^2 nm. The treatment with DMDHEU reduced the proportion of large pores and increased that of small pores (Figure 3) (Dieste *et al*. 2009).

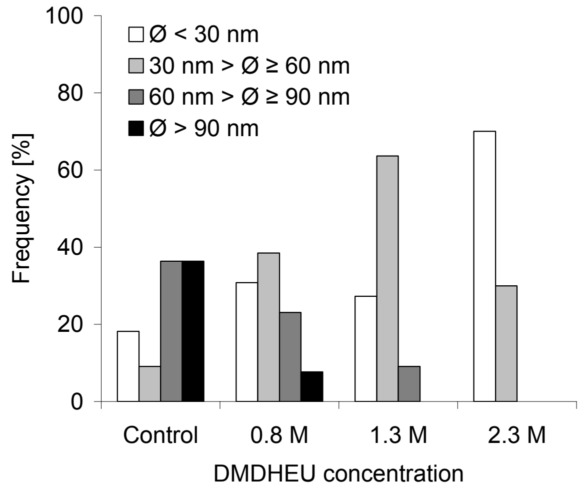

Figure 3: Frequency of pore size distribution at different levels of DMDHEU concentration, determined by differential scanning calorimetry

The deposition of DMDHEU, particularly at high WPG, reduces the larger voids in wood, but not to the extent to affect the capillary condensation. This conclusion is supported by the results of the constant K_d of the Hailwood-Horrobin model, which remains unchanged after the modification (Dieste *et al*. 2008).

The Hailwood-Horrobin constant Wi

The elucidation of which is the more accurate estimation of EMC was done by comparing the Hailwood-Horrobin constant W_i, which was calculated by (6) using EMC on a dry modified wood basis M and EMC on a dry wood basis M_R, with the constant W_c calculated by a stoichiometry approach.

Table 1: Number of moles of OH groups and molecular weight of wood necessary to adsorb one molecule of water (Wc) estimated for unmodified wood (Fengel and Wegener 2003) and for wood modified with DMDHEU

Component	**Composition [%]**	**OH groups per unit**	**Mol. Wt. of units [gmol^{-1}]**	**Moles OH**	**W_c [gmol^{-1}]**
Lignin	22.9	1	180	0.0013	41
Cellulose	45.9	3	162	0.0085	74
Hexosan	9.9	3	162	0.0018	16
Pentosan	21.3	2	132	0.0032	28
	100.0			0.0148	160
DMDHEU 0.8 M	10.9	3	160	0.0020	17
	110.9			0.0169	177
DMDHEU 1.3 M	18.1	3	160	0.0034	29
	118.1			0.0182	189
DMDHEU 2.3 M	31.0	3	160	0.0058	50
	131.0			0.0206	209

Firstly, the number of moles of OH present in the cell wall of wood modified with DMDHEU was roughly calculated by a stoichiometric approach (Hill and Jones 1996). The fraction of DMDHEU was taken from the WPG values, and it was added to the existent OH moles. In comparison with unmodified wood, wood modified up to 31% WPG increments its OH groups in 35%. This is the main argument to calculate EMC by on a dry modified wood basis: DMDHEU is hygroscopic and therefore should be included in the determination of moisture content. Secondly, the molecular weight of an artificial hypothetical polymer composed of cellulose, lignin, hexosan and pentosan was calculated (W_c). This calculation included the adsorption sites brought in by the modification with DMDHEU. The Hailwood-Horrobin constants W_i and W_c, calculated by the model (6) and by stoichiometry (Table 1), respectively, were used to estimate the number of inoperative OH groups (Spalt 1958) according to the following equation:

$$A_{OH} = \frac{W_i - W_c}{W_i} \times 100 \qquad (7)$$

where A_{OH} is the fraction of inoperative OH groups; W_i is the Hailwood-Horrobin constant calculated by the model; and W_c is the Hailwood-Horrobin constant calculated by stoichiometry.

Table 2: Constants of the Hailwood-Horrobin model (Kd, Kh and Wi) at 20 °C calculated using (M) and (MR); hypothetical molecular dry weight of wood per sorption site (Wc), calculated by stoichiometry; inoperative OH groups (AOH); and differential heat of adsorption calculated by the Clausius-Clapeyron method (-ΔHs*) and by solution calorimetry (-ΔHs**)

WPG [%]	K_d		K_h		W_i [g mol^{-1}]		W_c [g mol^{-1}]	A_{OH} [%]		$-\Delta H_s$ *	$-\Delta H_s$ **
	(M)	(M_R)	(M)	(M_R)	(M)	(M_R)		(M)	(M_R)	[J g water^{-1}]	
–	0.69	0.69	6.77	6.76	246	245	160	35	35	682	329
11	0.67	0.67	7.54	7.61	272	246	177	35	28	1345	359
18	0.71	0.71	9.29	9.11	335	283	189	44	33	1158	453
31	0.69	0.69	11.76	11.92	371	282	209	44	26	1728	627

W_i and W_c would only be equal if all the possible OH groups present in the modified wood were available to adsorb water molecules (Spalt 1958). It was observed that W_i is much higher when EMC is calculated by M than when is calculated by M_R (Table 2). The fraction of inoperative OH groups (A_{OH}) increases when M is used to calculate EMC. The former observation contradicts the results of differential heat of adsorption (ΔH_s), which showed that at EMC below ~10% wood modified with DMDHEU had more adsorption sites than unmodified wood. On the contrary, more OH groups are available when EMC is calculated with M_R.

CONCLUSION

According to a stoichiometric calculation, the modification with DMDHEU increases to 39% the total amount of OH groups in wood modified to 31% WPG, but not all these OH groups are accessible for moisture adsorption. The size of a hypothetical molecule of wood required to adsorb one molecule of water increases as a function of the WPG. When EMC is calculated by M, the inaccessibility of OH groups is high; on the contrary, when EMC is calculated by M_R there is an increase in the number of operative OH groups. EMC is underestimated when it is calculated with M due to two reasons: 1) the EMC is obviously reduced by the weight of the chemical (WPG); 2) W_i is overestimated, because even considering the high possible contribution of OH groups by DMDHEU a large fraction of the adsorption sites appeared inoperative. Therefore, in agreement with Hill (2008), this study recommends that the analysis of moisture sorption for wood modified with DMDHEU should be done using M_R.

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